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Synthesis of Fusible Branched Polyphenylenes*

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Synopsis

Fusible polyphenylenes with molecular weights approaching 3000 have been prepared by the cationic oxidative polymerization of *m*-terphenyl, *o*-terphenyl, 1,3,5-triphenylbenzene, or mixtures of the terphenyls with biphenyl and with benzene. Polymerizations were carried out in the molten state with either aluminum chloride catalyst and cupric chloride as oxidizer or the much less efficient ferric chloride, which served both functions. Fusible polymer fractions were isolated by a series of continuous extractions with hot aromatic solvents. Polymers in the 2000-to-3000 molecular-weight range generally melted between 300 and 400°C. The polymer chains are presumed to have phenyl branches besides some fused ring structures, evidence of the latter being their carbon-to-hydrogen ratios of up to 1.67.

During the course of an investigation on ablative polymers suitable for use in erosive hyperthermal environments a study was made of polyphenylenes (I) and their methods of synthesis. From theoretical considerations it was anticipated that these materials not only would resist degradation up to 500°C but also would produce exceptionally strong chars upon pyrolysis, liberating hydrogen, which because of its high volume-to-weight ratio would efficiently serve to dissipate heat.

The objective of this research was to prepare a thermosetting polyphenylene resin suitable for fabrication of composite structures. To achieve this objective it was essential that the poly-

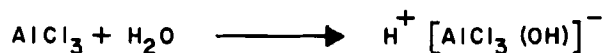
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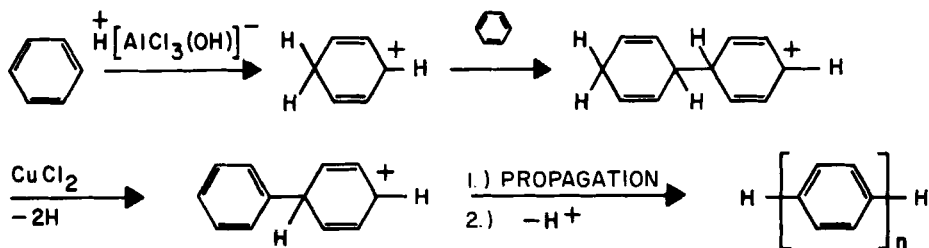
phenylenes be fusible and preferable that they be soluble in appropriate solvents. A principal objective, therefore, was to obtain polymers of high molecular weight without sacrificing fusibility.

BACKGROUND

A number of approaches to the synthesis of polyphenylenes have been described in the literature. Goldfinger (2) prepared polymers from *p*-dichlorobenzene, utilizing the Wurtz-Fittig reaction with sodium or a sodium-potassium alloy. The soluble products had an average molecular weight of 2700 to 2800 but failed to melt at temperatures up to 550°C. Extensive work in our laboratories (3) has revealed that polymers of this type are partially reduced, and their thermal stability never approaches that of a completely aromatic polymer. Polyphenylenes have also been prepared by making the mono-Grignard reagent of dibromoarenes react with cobaltous chloride (4), but in our experience (5) this reaction has afforded soluble products with molecular weights below 1000. The solubility of the polyphenylenes described by Berlin and Parini (6) and by Claesson et al. (7) may also be attributed to nonaromatic moieties.

The highest-molecular-weight polyphenylenes that have been attained, probably in the range of 5000 to 10,000, were reported by Marvel and co-workers (8) and Kovacic and co-workers (9). In the work of Marvel *para* polymers were prepared by the polymerization of 1,3-cyclohexadiene with Ziegler-Natta catalysts followed by halogenation and dehydrohalogenation. Those products which were soluble retained a considerable number of reduced rings, while those which closely approached the polyphenylene structure were insoluble and infusible. In the work of Kovacic polyphenylenes were obtained from the cationic oxidative polymerization of benzene with a Lewis acid as catalyst, water as co-catalyst, and various oxidizing agents. When the catalyst was aluminum chloride and the oxidizing agent was cupric chloride, the polymerization appeared to proceed according to the following reactions:





These polymers were also *para* oriented and, as is typical of the poly-*p*-phenylenes, were infusible and intractable.

The properties of polyphenylenes reported in the literature indicate that irregularities in the molecular structure tend to lower the melting point and enhance solubility. These irregularities include an irregular or random arrangement of *ortho*, *meta*, and *para* linkages within the polymer chain, preferably with a small percentage of *para* linkages. Also effective in reducing melting points is a high degree of branching, especially when the branches have dissimilar lengths and are attached at irregular intervals. Such structural features reduce the crystallinity by preventing close association of the molecules in the solid state and minimize the attractive forces between them. These intermolecular forces consequently can be more readily overcome by heat or solvation.

DISCUSSION

Cationic oxidative polymerizations appeared to be an attractive method of synthesis, because in the polymerization of benzene it yielded fully aromatic polymers with relatively high molecular weights. It was anticipated that this process could be adapted to the preparation of more tractable polyphenylenes by utilizing angular monomers, such as *o*-terphenyl and *m*-terphenyl. These monomers were expected to produce branched polyphenylenes with a low degree of crystallinity.

Soluble and fusible polymers have, indeed, been obtained by such cationic oxidative polymerization, not only from the monomers *o*-terphenyl and *m*-terphenyl, but also from biphenyl, from 1,3,5-triphenylbenzene, and from various mixtures of these monomers, some of which also included benzene. Fractionation by solvent extraction techniques has yielded fusible polymers with molecular weights approaching 3000. Pertinent data for a number of representative preparations are presented in Table 1.

TABLE 1
Data on the Preparation of Polyphenylenes by the Cationic Oxidative Polymerization of Aromatic Hydrocarbons

Run No.	Monomers		Moles AlCl_3	Moles CuCl_2	Other components	Temp. range, $^{\circ}\text{C}$	Total time, hr	Yield, %	Softening or melting point range, $^{\circ}\text{C}$	Extraction solvent pairs ^a		Mol. wt.	Elemental analyses			
	Name	Moles								(-)	(+) .		C	H	Cl	C/(H+Cl)
1	<i>m</i> -Terphenyl	1.00	1.75	2.05	—	100 \pm 5	16	32	—	20BN CB	CB TCB	91.02 89.00	4.78 4.56	0.84 2.07	1.59 1.62	
2	<i>m</i> -Terphenyl	2.0	—	—	3 moles FeCl_3	—	—	8	—	TCB	—	—	—	—	—	
								9	185-210	20BN	BB	—	—	—	—	
								1	305-335	BB	TCB	—	—	—	—	
3	<i>o</i> -Terphenyl	0.87	0.87	1.91	—	147-170	5 1/4	10	—	TCB	—	—	—	—	—	
								13	100-123	M	B	1400	—	—	—	
								32	235-250	B	TCB	—	—	—	—	
								17	> 350	TCB	—	—	—	—	—	
4	Biphenyl	0.97	0.086	2.00	—	102-150	6	12	—	M	B	—	—	—	—	
								14	192-240	B	BB	2900	—	—	—	
								15	310-400	BB	TCB	—	—	—	—	
5	1,3,5-Triphenylbenzene	0.17	0.34	0.333	—	136-182	3	16	—	TCB	—	—	—	—	—	
								15	143-158	M	B	—	—	—	—	
								7	140->375	B	BB	—	—	—	—	
								5	> 375	BB	—	—	—	—	—	
6	<i>o</i> -Terphenyl	1.0	1.5	4.0	—	110 \pm 5	5	18	150-158	10BN	BB	—	—	—	—	
	<i>m</i> -Terphenyl	1.0	—	—	—	—	—	5	282-327	BB	TCB	—	—	—	—	
7	<i>m</i> -Terphenyl	1.0	1.5	4.0	—	85 \pm 5	16	7	—	TCB	—	—	—	—	—	
	Biphenyl	1.0	—	—	—	—	—	26	187-193	20BN	CB	—	—	—	—	
								16	300-330	CB	TCB	—	—	—	—	
8	<i>m</i> -Terphenyl	1.5	2.3	6.0	—	100 \pm 5	16	36	188-208	20BN	BB	—	—	—	—	
	Biphenyl	1.5	—	—	—	—	—	5	274-311	BB	TCB	—	—	—	—	
								6	—	TCB	—	—	—	—	—	

9	<i>m</i> -Terphenyl Biphenyl	2.00 2.00	3.00	8.00	—	130 ± 5	24	11	170-200 BB	20BN BB	B CB	1429					
10	<i>m</i> -Terphenyl Biphenyl	0.25 0.50	0.58	1.25	—	100 ± 5	16	21	— 270-395	20BN CB	B CB		92.97 94.00	4.92 4.75	2.11 1.22	1.57 1.65	
11	<i>m</i> -Terphenyl Biphenyl	0.25 0.75	0.50	1.00	—	100 ± 5	16	21	215-285 275-320	20BN CB	CB TCB		92.88 94.24	4.76 4.88	1.89 0.72	1.62 1.61	
12	<i>m</i> -Terphenyl Biphenyl	0.50 0.50	0.50	1.00	—	123 ± 3	16	22	190-241	20BN CB	CB TCB		92.89	4.76	2.20	1.62	
13	<i>m</i> -Terphenyl Biphenyl	0.50 1.00	0.75	1.50	—	123 ± 3	16	13	170-190	20BN CB	CB TCB		92.96	4.78	1.58	1.62	
14	<i>m</i> -Terphenyl Biphenyl	0.50 1.50	1.00	2.00	—	123 ± 3	16	15	172-204	20BN CB	CB TCB		92.93	4.84	2.54	1.58	
15	<i>o</i> -Terphenyl Biphenyl	0.20 0.20	1.09	0.80	—	135-180	4¼	4.6	—	CH 10BN	10BN						
16	<i>m</i> -Terphenyl Biphenyl Benzene	0.125 0.50	1.125	1.125	0.25 mole water	100-160	4	20	160-175	M T	T BB	1800	94.89	5.25	—	1.52	
17	<i>m</i> -Terphenyl Biphenyl Benzene	0.70 2.08	2.60	5.0	0.55 mole water	100-120	2	5	70-95 160-280	M 15BN	T BB	575 1600	— 94.09	— 4.92	— —	— 1.60	
18	<i>m</i> -Terphenyl Biphenyl Benzene	1.00 0.50 1.50	1.40	6.0	—	165	2¼	14	— 190-220 220-250	BB BB BB	BB BB TCB	1600	— — —	— — —	— — —	— — —	

TABLE 1 (Continued)

Run No.	Monomers		Moles AlCl_3	Moles CuCl_2	Other components	Temp. range, $^{\circ}\text{C}$	Total time, hr	Yield, %	Softening or melting point range, $^{\circ}\text{C}$	Extraction solvent pairs ^a		Elemental analyses				
	Name	Moles								(-)	(+)	Mol. wt.	C	H	Cl	C/(H+Cl)
19	<i>m</i> -Terphenyl Biphenyl Benzene	0.125 0.500 0.500	2.70	2.70	900 ml <i>o</i> -dichlorobenzene (solvent)	<41	7	29 2	215-326	CH	XY					
20	First fraction of product from the preceding preparation ^b	—	0.200	0.200	200 ml <i>o</i> -dichlorobenzene (solvent)	<36	24	32 36 22	180-200 205-225 238-260	M B BB	B BB	600	88.76	4.92	6.13	1.46

^a 15BN 15% benzene in naphtha; 10BN 10% benzene in naphtha; 20BN 20% benzene in naphtha or hexane; CB chlorobenzene; BB bromobenzene; TCB 1,2,4-trichlorobenzene; M methanol; B benzene; T toluene; CH cyclohexane; XY xylene.

^b Monomers were not used in this experiment.

The polymerization procedure was analogous to that utilized by Kovacic for the polymerization of benzene into intractable poly-*p*-phenylene but differed markedly in the work-up in that the fusible polymers of this report had to be isolated by a series of continuous extractions. In nearly all cases aluminum chloride was used as catalyst and cupric chloride was used as oxidant, although in a few experiments both were replaced with ferric chloride, which served as both catalyst and oxidant. Any order of combination of the three reactants was found to be adequate, the reaction being controlled by the rate of addition of the last reactant. The rate of reaction was apparent from the rate of evolution of hydrogen chloride.

Catalytic quantities of aluminum chloride were sufficient to induce extensive polymerization. This observation contrasts with that of Kovacic and Oziomek (9f), who noted that polymerization ceased when the number of moles of cuprous chloride which formed equaled the number of moles of aluminum chloride. The explanation lay in the formation of an unreactive benzene-aluminum chloride-cuprous chloride complex. With the monomers and temperatures employed in the terphenyl-biphenyl polymerizations no such limitation was operative.

Reaction temperatures ranged from near ambient to over 200°. Above 170°, however, chlorination occurs at a significant rate, as evidenced by the evolution of hydrogen chloride at this temperature (without the formation of polymer) from a mixture containing only *m*-terphenyl and cupric chloride.

The reaction was customarily conducted in the molten monomer at temperatures of 100 to 160°C. As the reaction progressed, the viscosity increased, until stirring was virtually impossible, although the reaction continued in the unstirred mass. The imposing problem of mixing makes large-scale preparations extremely difficult and undoubtedly limits both the yields and the molecular weights.

Room-temperature polymerizations were conducted in slurries in *o*-dichlorobenzene; however, the products of these reactions were light yellow in color instead of the usual brown and had rather low molecular weights. The melting ranges, on the other hand, tended to be somewhat higher than that of polymers of comparable solubility obtained from solvent-free polymerizations. Apparently, the slurry polymerization led to the formation of a product with a high degree of crystallinity.

Continuous extraction with methanol, benzene, or benzene-petroleum naphtha mixtures was employed to remove unreacted monomers and polymers with excessively low molecular weights. The desired higher fractions were then extracted with appropriate aromatic solvents, the choice of solvent depending upon the melting range and the molecular weight desired.

The various polymer fractions were characterized by means of their melting ranges, molecular weights, elemental analyses, and thermogravimetric analyses. Molecular weights were determined ebullioscopically in *o*-dichlorobenzene (10).

Although the monomers and the reaction conditions were varied substantially, some general observations can nevertheless be made. Yields of polymers which were extractable with boiling 1,2,4-trichlorobenzene and nonextractable with a mixture of benzene (20%) in petroleum naphtha ranged from about 10 to 50% and averaged about 20 to 35%. Usually 5 to 20% of trichlorobenzene-insoluble polymer was also formed. High reaction temperatures, as might be expected, favored the formation of more intractable products. Low yields of both soluble and insoluble polymer were obtained with ferric chloride.

Although most of the polymerizations were carried out with mixtures, particularly mixtures of biphenyl and terphenyls, individual monomers were studied in many cases. Biphenyl unexpectedly yielded 29% of benzene-insoluble, trichlorobenzene-insoluble polymer. The bromobenzene-soluble, benzene-insoluble fraction of the product had an average molecular weight of 2200. Kovacic and Lange (9g) reported *p*-sexiphenyl as the predominant product of a cationic oxidative polymerization of biphenyl under somewhat different conditions, with only small amounts of *p*-quaterphenyl and higher polymers. The completely *para*-linked nature of their identified products would lead one to believe that *para* linkages also predominated in their unidentified products and that therefore these products would have extremely low solubility. Their results thus appear to differ from the results of our investigation.

Benzene, on the other hand, produced only insoluble polymer, which is in agreement with the observations of Kovacic. To determine whether higher temperatures could induce benzene to polymerize in a more random manner one experiment was carried

out in which the temperature was allowed to rise gradually to 160°C as the reaction progressed. Even under these conditions no significant quantity of soluble polymer was obtained, although a substantial yield of intractable product was produced.

As previously noted, most of the syntheses were carried out with mixtures of *m*-terphenyl and biphenyl as monomers. As can be seen from runs 12, 13, and 14 in Table 1, wide variations in the ratio of these monomers seem to have little effect on the yields. Of this series the 1:1 biphenyl-*m*-terphenyl mixture was polymerized more than twenty-five times.

Several attempts were made to polymerize further the low-molecular-weight products isolated from other reactions by using them as starting materials for subsequent preparations. The yield of polymer with higher molecular weights (as indicated by decreased solubility) was very poor. Apparently, these low-molecular-weight products were relatively unreactive.

As a general rule, the melting range of the extracted material increased with an increase in the boiling point of the extracting aromatic solvent. Figure 1 is a plot of the mean melting points versus the mean boiling points of the solvent pairs used for isolating fractions. The general relationship is apparent, although there

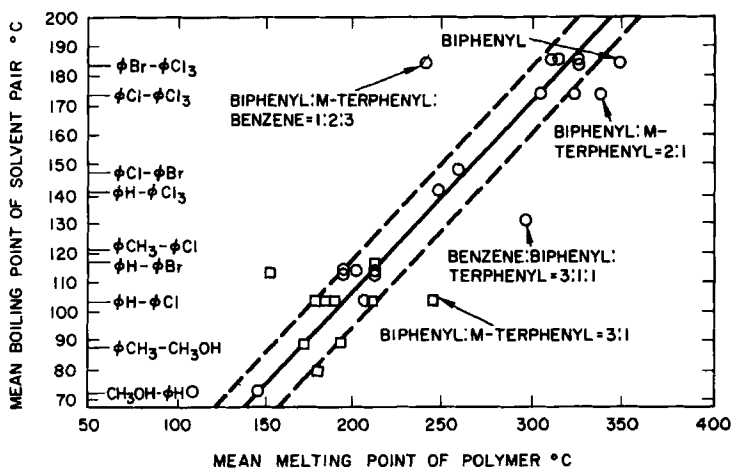


FIG. 1. Relationship of mean melting points to mean boiling points of solvent pair.

are a number of deviations from the trend. It must be remembered, of course, that these data were derived for polymers prepared from a number of different monomers and under widely varying conditions. The quantity of low-melting material present also varied, since the solvent in which the fractions were insoluble was not the same. This low-melting material depressed the upper limit of the melting range to some extent.

Polymer of the desired molecular weight can be extracted from the crude polymerization mixtures by selecting the appropriate solvent pair for its isolation. The molecular weight of the extracted polyphenylene tends to increase with the boiling point of the aromatic solvents used in its isolation. This is illustrated as a general relationship in Fig. 2. The lower boiling of each pair of

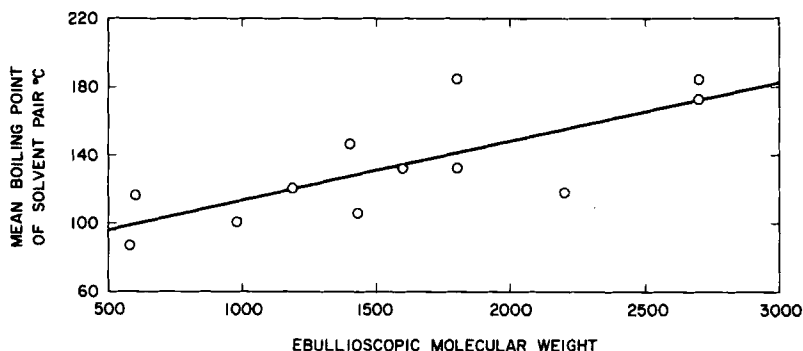


FIG. 2. Relationship of molecular weight to mean boiling point of extraction solvent pair (method of least-squares plot).

solvents is the solvent used for eliminating products with a lower molecular weight; the higher boiling solvent is the one in which the fraction was soluble. Again the deviations from the rule are not unexpected in light of the wide variations in the method of preparation.

Polyphenylenes with a molecular weight of about 2000 or above exhibit a 1-to-2% weight loss at 500° and about a 25% weight loss at 900° when heated in an inert atmosphere at a programmed heating rate of 360° per hour. Typical thermograms are presented in Fig. 3. Polymers with a lower molecular weight can have similar stability

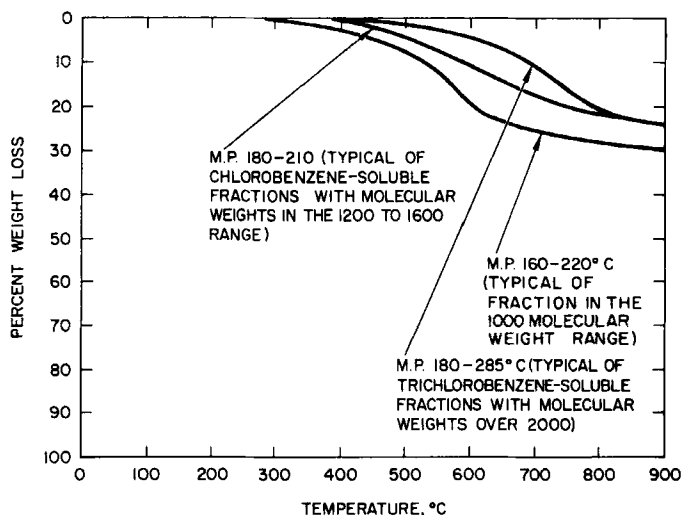
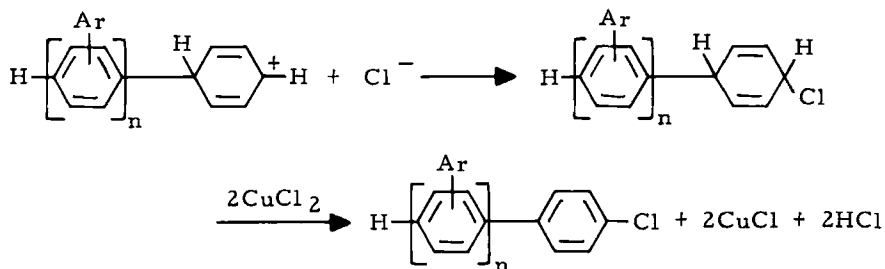


FIG. 3. Thermograms of branched polyphenylenes in nitrogen with a heating rate of 360°/hr.

at 500° but suffer greater weight loss on further heating. The polymers derived from biphenyl alone also were somewhat less stable.

Most of the polymers contained between 1% and 2.5% chlorine, which appeared to be about 1 chlorine atom per molecule. As was noted above, cupric chloride can function as a halogenating agent above 170°, and undoubtedly a small amount of chlorination occurs at lower temperatures as well. Higher percentages of chlorine were introduced when the ratio of aluminum chloride to cupric chloride was kept very low. These conditions would favor chlorination in a competition with polymerization. It is quite possible that the



chain-terminating step is a reaction between the cationic polymer chain and a chloride ion.

Polyphenylenes prepared in *o*-dichlorobenzene also had a higher than usual chlorine content, probably because of reaction of the solvent with the growing polymer chain.

Elemental analyses provided a measure of the extent of cyclization that occurred during polymerization. The C/H ratio, or C/(H + Cl) ratio when chlorine is present, would be 1.50 for a linear polyphenylene of infinite length. Since most of the C/(H + Cl) ratios exceed this value, it is at once apparent that substantial intramolecular cyclization occurs. The extent of cyclization may be calculated from the elemental analysis and the molecular weight by means of the following formulas:

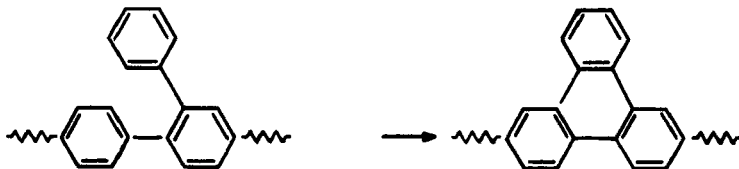
$$\text{Percent of theoretical hydrogen lost due to cyclization} = \frac{100 [(H + Cl)/C]_{\text{theor}} - [(H + Cl)/C]_{\text{exptl}}}{[(H + Cl)/C]_{\text{theor}}}$$

where $[(H + Cl)/C]_{\text{theor}}$ is

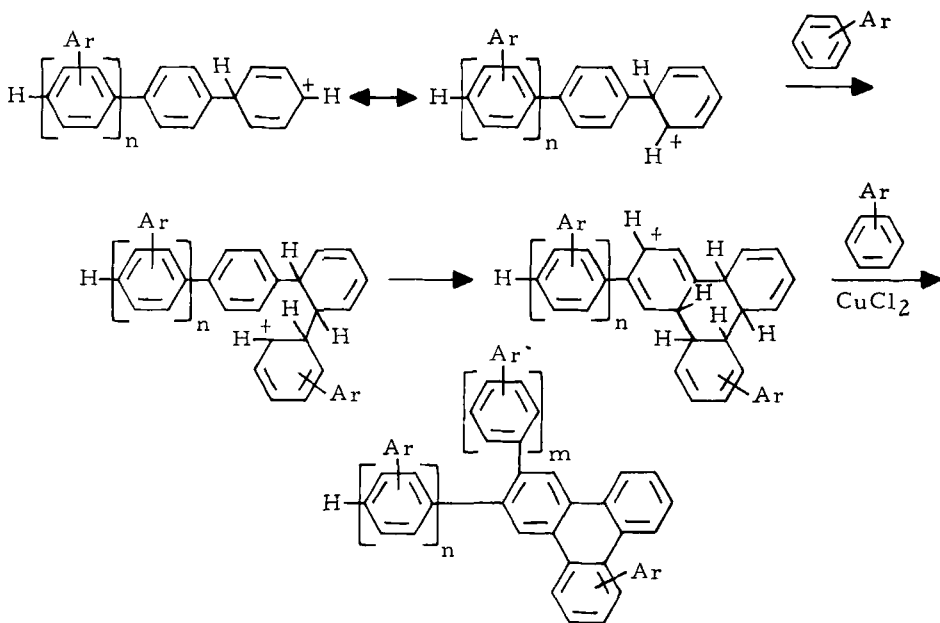
$$\frac{[(\%C) (\text{M.W. of polymer}) (\%)] / [100 (\text{at. wt. of C})] + 2}{[(\%C) (\text{M.W. of polymer})] / [100 (\text{at. wt. of C})]}$$

If one uses the average value for the C/(H + Cl) ratio (1.58) and assumes an average molecular weight of 2000, one can calculate that about 7% of the hydrogen is lost by cyclization.

The most likely form of cyclization would produce triphenylene nuclei in the polymer chain by the same type of reaction mechanism that produces the polymer. This cyclization is illustrated below.



An alternative explanation would be that at elevated temperatures and with the monomers employed chain propagation can proceed through the *ortho* position. This type of propagation was proposed by Kovacic and Wu (9a) for the reaction of benzene with ferric chloride.

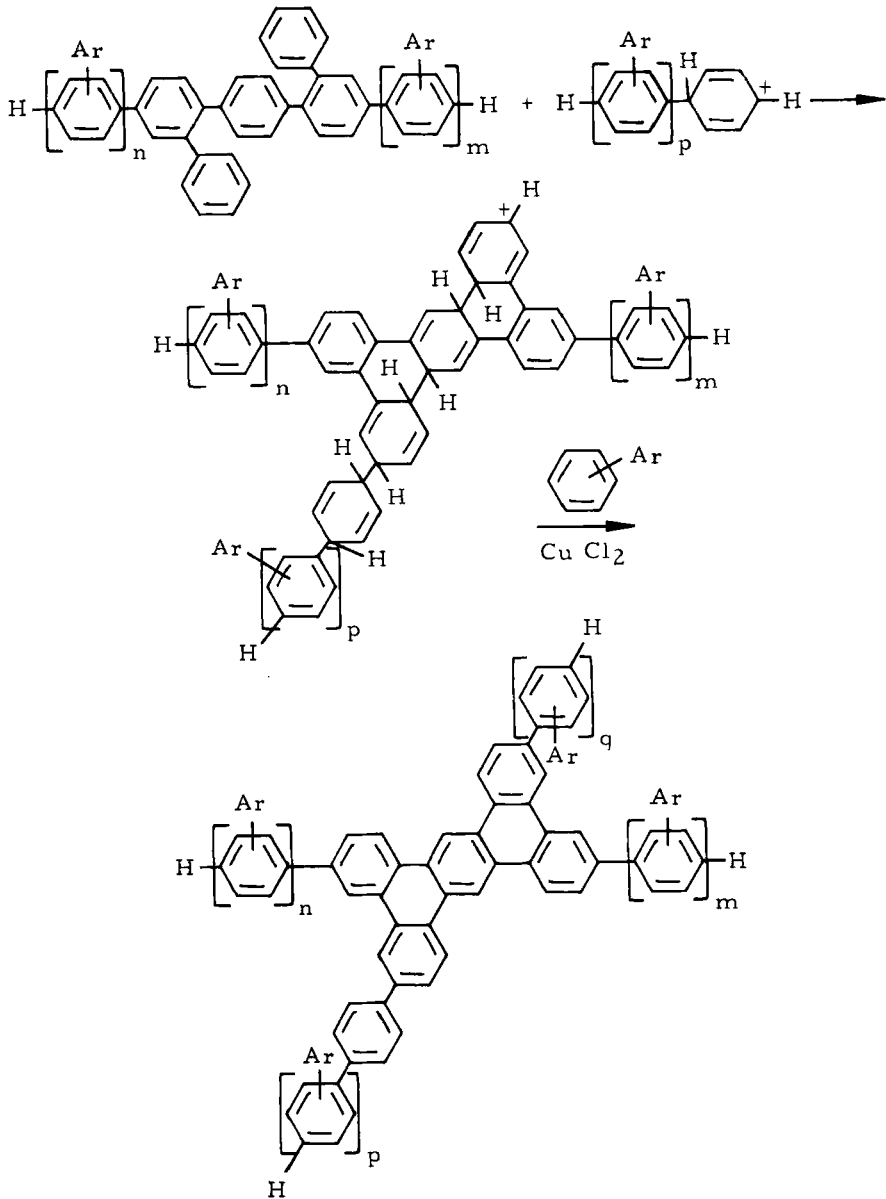


The formation of fused-ring aromatic nuclei may also occur incidentally when a growing polymer chain includes another polymer molecule as part of its structure. This is illustrated on page 196. Whatever the mechanism and structures may be, the products can properly be called polyphenylenes.

Research on procedures for curing these polymers has also been carried out and will be reported in subsequent publications.

Acknowledgment

The authors gratefully acknowledge the valuable technical assistance of Mr. Raymond E. Lawrence.



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1. The term "polyphenylenes" is preferred to "polyphenyls" for the higher polymers where it is desirable to stress the repeating unit rather than a particular molecule with a well-defined structure. This name is in line with current practice in polymer nomenclature. It should also be pointed out that these polymers are not to be confused with polyphenylene oxides, polyphenylene sulfides, etc., which have also been called polyphenylenes in some circles.
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