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Dehydro Coupling of Aromatic Nuclei by Catalyst–Oxidant Systems: Poly(*p*-phenylene)

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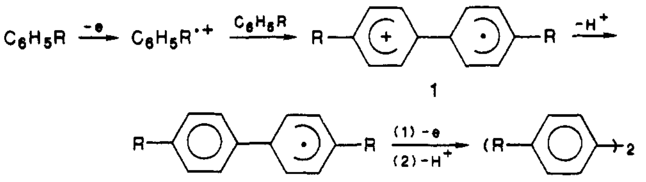
SCHEME I



I. Introduction

The formation of C–C bonds between aromatic rings is an important step in many organic syntheses and may be accomplished by chemical, photochemical, or electrochemical means. General reviews of aryl coupling methods have appeared;[1-3] they have been broad in coverage and have provided brief discussions of the several successful techniques. The present review is much narrower in scope, focusing primarily on the use of chemical catalyst–oxidant combinations to achieve aryl–aryl bond formation by dehydrocoupling.

Poly(*p*-phenylene) (PPP), an insoluble, infusible, low-molecular-weight polymer, can be prepared by direct coupling of benzene nuclei using a Lewis acid catalyst–oxidant combination.[4] PPP has been of recent continuing interest because of its capability of being transformed from an electrical insulator to an electrical conductor.[5] Because of the many developments related to PPP since the substance was last reviewed[1] a thorough discussion of PPP is included in this review.

II. Coupling Systems

A. Introduction

1. Scholl Reaction

An excellent review of the Scholl and related reactions was made available in 1964 by Balaban and Nenitzescu.[6] Although the transformation has been commonly limited by definition to intramolecular dehydrogenation between aromatic nuclei, the reviewers broadened the scope by regarding the process as elimination of two aryl-bound hydrogens accompanied by the formation of an aryl–aryl bond under the influence of Friedel–Crafts catalysts. Since this also encompasses the intermolecular category, the couplings described in the present review, including poly(*p*-phenylene) (PPP) formation, can be considered as generally falling within the domain of the Scholl reaction. The earlier review provided comprehensive coverage with stress on the mechanistic features.

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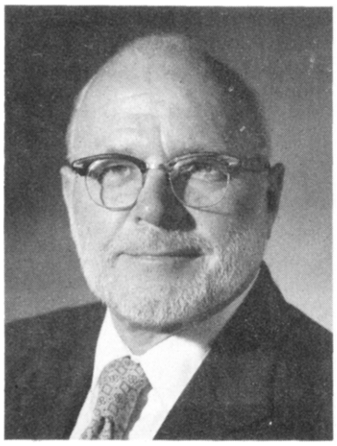

Peter Kovacic was born near Washington, PA. He obtained an A.B. from Hanover College (Indiana) and Ph.D. in organic chemistry from the University of Illinois. After positions as a postdoctorate at the Massachusetts Institute of Technology and instructor at Columbia University, he was a research chemist at the Jackson Laboratory of DuPont. His academic career began at Case Western Reserve University and was continued at the University of Wisconsin-Milwaukee where he is professor of chemistry. He has visited Yugoslavia as a Fulbright Fellow and National Academy of Science Exchange Scholar. Research interests include polymers of the aromatic, conducting, and iminium types, *N*-haloamines, adamantanes, Bredt's rule, bridgehead reactivity, aromatic substitution, and redox metal halides. Recent attention has been centered on unifying mechanisms for the action of drugs, carcinogens, herbicides, and enzymes, involving charge transfer and oxy radicals, with emphasis on iminium ions.

Martin B. Jones was born in Concordia, KS, and received a B.S. in chemistry from Emporia State University in 1974. His graduate work (Ph.D., 1979) was performed at the University of New Mexico with Profs. Ulrich Hollstein and Fritz Allen. Following a postdoctoral appointment with Prof. Kovacic at the University of Wisconsin—Milwaukee, he moved to the University of North Dakota, where he is currently Associate Professor. In 1985, he received the Lydia and Arthur Saiki Prize for Undergraduate Teaching Excellence from the University of North Dakota. Marty's research interests comprise reactions, including polymerization, of aromatic nuclei and the organic chemistry of coal and coal-derived materials.

Two principal pathways have been suggested. The radical cation route is outlined in Scheme I and the σ complex approach in Scheme II. Balaban and Nenitzescu astutely proposed that more than one mechanism may pertain depending upon the substrate and conditions, and this view was reinforced by Clowes who presented a detailed overview in 1968.[7]

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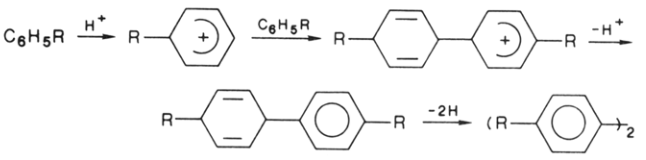

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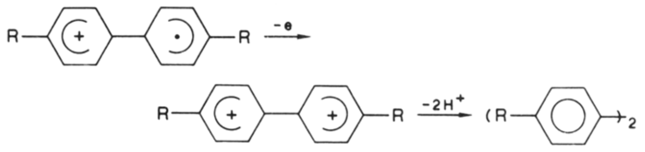

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The radical cation concept was suggested in 1961 by Rooney and Pink[8] who noted that polynuclear hydrocarbons gave rise to these entities on exposure to aluminum halides. Similar observations were made with other reagents which are Scholl promoters. As an example, in the oxidation of 1-ethoxynaphthalene by sulfuric acid,[7] the conclusion was reached from kinetic studies that the rate-determining step entails radical cation formation. With reference to Scheme I, there is considerable support for the existence of monocation radical dimers (**1**) from definitive demonstrations with a variety of systems.[9] It is important to recognize that **1** is an inaccurate oversimplification of the actual structure. Considerable effort has been devoted to the study of the nature of this moiety, mostly involving mass spectrometry and theoretical calculations. The bulk of the attention has been focused on the benzene dimer radical cation. Although earlier proposals concentrated mainly on the sandwich form,[10-15] recent studies indicate that a stair-step structure is equally stable.[16,17] In both cases, the dimer is characterized by a bond distance of 2.6–3.2 Å and a binding energy of 8–17 kcal/mol, with the radical cation delocalized over both nuclei. The theoretical aspects are treated at greater length in section III.C.

Scheme I is inherently more complex mechanistically since steps other than those set forth can lead to the end product. Thus, it is well established that radical cations can dimerize via spin pairing with concomitant disappearance of the ESR signal and formation of a dication, eq 1.[9] From the nature of the molecules which

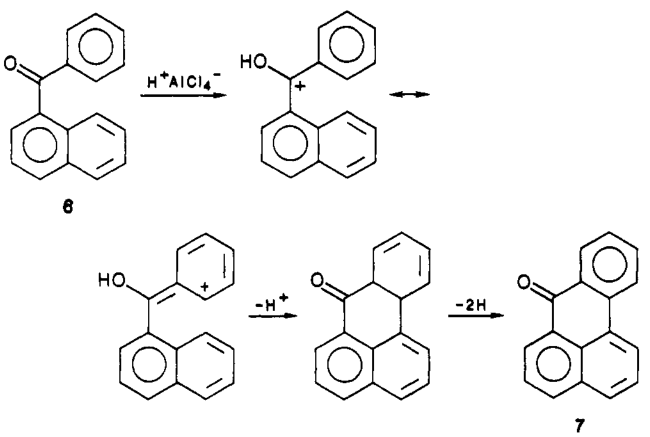
$$2M^{\bullet +} \rightleftarrows M_2^{++} \qquad (1)$$

participate in this manner, the behavior appears to be associated with the more stable species, e.g., those derived from perylene and thianthrene. As expected, the dimerizations are quite solvent dependent. High dielectric constants and strong solvation are desired in order to reduce repulsion between the two positive charges in the dimer.

In addition, theoretically an alternate possibility to step 3 (Scheme I) exists, as illustrated in Scheme III. This comprises another route to the dimer cation (**3**) and should occur only with highly delocalized systems.

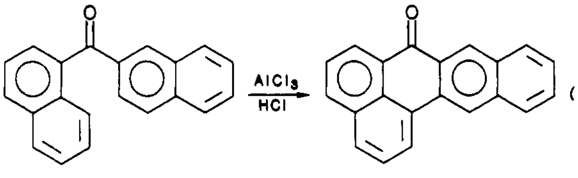
In marked contrast to the σ complex route, there is no dihydro intermediate involved in dimer formation via Scheme I. Hence, isolation of or evidence for the reduced form (**2**) would weigh heavily against a radical cation. However, such reasoning would not apply to oligomerization or polymerization proceeding via this avenue, as apparently pertains in the case of benzene,[17] toluene,[18] chlorobenzene,[18] biphenyl,[19] and naphtha-

SCHEME IV



lene.[18] For formation of the longer chains, mechanistic rationale (section III.C.) and experimental evidence, particularly for naphthalene and benzene, support participation of a dihydro stage.

There are several compelling arguments for the σ complex route (Scheme II) which was formulated initially by Baddeley[20] and subsequently revised by Nenitzescu and Balaban.[21] One important line of evidence comprises the essential role of HCl in certain cases. For example, the protonic acid is required for transformation of 4 to 5 (eq 2).[22] If expelled by a stream of inert



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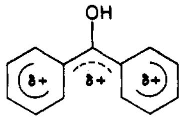
gas, reaction ceases, but is resumed on reintroduction of the promoter. The same behavior was noted for other, related systems. A reasonable interpretation, shown in Scheme IV, involves the ring closure of 6 to benzanthrone 7.[6] The observation that benzophenone is not converted to fluorenone[23] fits the concept since the ring which must undergo electrophilic attack is too highly deactivated in the protonated form (8). Another



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point is that radical cation formation is less likely with electron-withdrawing substituents, such as carbonyl.

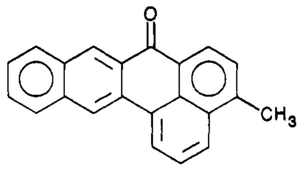
An additional relevant item in this category is the observation that HF yields no ESR signal with aromatic substrates due to its poor oxidizing ability.[24] On the other hand, Scholl reactions are known to proceed in this medium.[25,26]

Compelling evidence is available to support the intermediacy of dihydro 2. It is expected that this type of entity would best survive in extended polynuclear systems and in the absence of a powerful oxidant. These conditions appear to be met when 7,12-diphenyl-1,2-benzanthracene is converted to 1-phenyl-1,3a-dihydro-2,3:4,5-dibenzopyrene by $AlCl_3$ in benzene.[27] Furthermore, the reaction mixture composed of 1-methylnaphthalene, 2-naphthoyl chloride, and aluminum chloride yielded the methylbenzanthrone 9 and an appreciable quantity of molecular hydrogen.[28]

TABLE I. Preparative Methods for Radical Cations

A. Brönsted Acids[a]
  H_2SO_4, CH_3SO_3H, CF_3SO_3H
B. Lewis Acids[a]
  $AlCl_3$, $AlBr_3$, SO_3, SO_3/BF_3, PF_5, CdX_2, HgX_2, PbX_2
C. halogens
  Br_2, I_2, IBr, ICl
D. metal salts
  Co(III), Mn(III), Pb(IV), Ce(IV), Sb(V)
E. via charge transfer complexes
  chloranil, tetracyanoethylene, tetracyanoquinodimethane, tetracyanomuconitrile
F. other chemicals
  O_2, $SO_4^{\bullet -}$
G. irradiation
  photoionization (UV), X-irradiation, γ-irradiation, pulse radiolysis
H. catalyst surfaces[a]
  alumina, silica-alumina, zeolites
I. electrochemical
  anodic oxidation
J. mass spectrometry

[a] Cation radicals are sometimes observed with no added oxidant. In other cases, an oxidant (O_2, KNO_3, $KMnO_4$, $ArNO_2$, RNO_2) is present, either intentionally or unintentionally (O_2).



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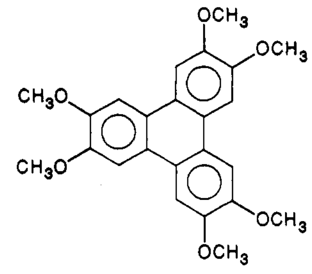
Further support for a duality of mechanism was based upon the divergent behavior of 1,2-dimethoxybenzene.[29] The triphenylene (10) is formed by chloranil



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in sulfuric acid, but not by aluminum chloride in nitrobenzene. However, caution should be exercised in interpretation since various rationalizations are possible.

2. Preparation of Radical Cations

Various reviews deal with formation of radical cations.[9,30-37] The contents of one[9] are summarized in Table I. Many other reagents have been found to induce one-electron oxidation. Since the radical cation topic is a rapidly expanding one which impinges on various areas of research, each year finds an appreciable number of additions to the list. The following tabulation is undoubtedly not exhaustive (Table II).

B. Benzene

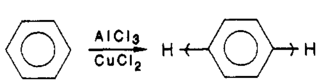
Two decades ago, Kovacic and Kyriakis reported the facile conversion of benzene to poly(*p*-phenylene) (PPP)

TABLE II. Additional Preparative Methods for Radical Cations[a]

A. metal salt
Mg(II) (38), Zn(II) (49), Sn(IV) (40), Hg(II) (41), Ag(II) (42, 43), Fe(III) (44), Tl(II) (43), Ti(III) (45–47), Cu(III) (31), Cu(II) (48, 49), As(V) (50), Cr(II) (31), Co(I) (31), Ir(IV) (31), Mo(V) (51), V(IV) (51)
B. catalyst surfaces
hydrogen zeolon (52), synthetic mordenite (53), alumina (54)
C. other chemicals
OsO_4 (40), NO^+ (55), NO_2^+ (31), $(C_6H_5CO_2)_2$ (56), XeF_2 (57), R^+ (31), peroxydiphosphate (58), HNO_3 (59, 60), NO_2 (55, 61), $S_2Cl_2{\cdot}AlCl_3$ (62), $I_2/AgClO_4$ (63), MnO_2 (64), ferricyanide (64), aminium (31), ClO_2 (31)

[a] References in parentheses.

by treatment with aluminum chloride/cupric chloride at mild temperatures (eq 3).[4] This procedure, which



(3)

involves stirring a heterogeneous mixture of benzene, anhydrous aluminum chloride, and anhydrous cupric chloride for 2 h at 25–35 °C, is probably the most widely used method for the preparation of PPP. Kitajima et al. have reported the synthesis of poly(*p*-phenylene) from exposure of benzene to copper(II) tetrachloroaluminate (prepared by heating a mixture of $CuCl_2$ and $AlCl_3$ at 240 °C for 10 h in a glass ampoule).[65] IR and X-ray analyses of the polymer revealed it to be essentially identical with that obtained via the Kovacic method.

Various other catalyst–oxidant combinations may be employed for this reaction. With aluminum chloride as the Lewis acid catalyst, manganese dioxide,[66] lead dioxide,[66] nitrogen dioxide,[66,67] *p*-benzoquinone,[66] chloranil,[66,68] and air[69,70] have been demonstrated to convert benzene into PPP, although the yields are variable and lower than with $CuCl_2$ as oxidant. Furthermore, structural irregularities are more pronounced with *p*-benzoquinone,[66] chloranil,[66] or air[69,70] as oxidants. Substantial halogen incorporation (>10%) in the polymer is obtained when MnO_2, PbO_2, or chloranil is employed as the oxidant. With NO_2, 1–4% nitrogen is found in the resulting polymer. Aluminum bromide/cupric bromide[66] and antimony pentachloride/cupric chloride[66] are two other combinations which convert benzene to poly(*p*-phenylene). Neither, however, affords yields of product comparable to $AlCl_3/CuCl_2$. Complex arsenic hexafluoride salts ($O_2^+AsF_6^-$ or $C_6F_6^+AsF_6^-$) are capable of oxidizing benzene to a poly(*p*-phenylene)–AsF_6^- salt.[71] The polymer produced in this reaction constituted 20–30 weight percent of the total product. IR spectral data of this polymer closely resembled that of PPP prepared by the Kovacic method.

In some cases, a single reagent can serve as both Lewis acid catalyst and oxidant. Ferric chloride,[72-76] molybdenum pentachloride,[76,77] antimony pentafluoride,[78] and arsenic pentafluoride[79] transform benzene to PPP. The polymer from $FeCl_3$ treatment of benzene is more highly colored, contains more chlorine, and is more amorphous than that from $AlCl_3/CuCl_2$. Molybdenum pentachloride produces a material similar to that obtained from $AlCl_3/CuCl_2$. A low yield of PPP is afforded by exposure of benzene to SbF_5. When a 1:1 mixture of HF:SbF_5 is used in place of neat SbF_5, polymer formation is completely repressed. Treatment of an arsenic trifluoride solution of benzene with arsenic pentafluoride at room or lower temperatures affords a homogeneous solution of PPP.[79] However, structural details of this product have yet to be disclosed.

One of the more novel means of synthesizing poly(*p*-phenylene) involves adsorption of benzene vapors on Cu^{2+} [80,81] or Ru^{3+} [81] ion exchanged montmorillonite. Infrared, resonance Raman, and X-ray spectroscopic data support the *p*-phenylene structure of the product. The polymerization is thought to proceed via cation or radical cation intermediates in the interlamellar space of the clay.

The polymerization of benzene may also be effected via oxidative electrochemical means.[82-95] Anodic oxidation of benzene in liquid sulfur dioxide on a platinum electrode results in the formation of passivating films (quaternary ammonium perchlorate as the electrolyte) or dendrite-like conductive deposits (quaternary ammonium tetrafluoroborate as the electrolyte).[84] Neither product (film or deposit) is pure PPP. Elemental analyses and IR and XPS spectra reveal the polymers to be of the poly(*p*-phenylene) type, but containing variable amounts of oxygen (6–15%), postulated to be present as phenolic –OH. Free-standing polyphenylene films have been prepared by electrochemical oxidation of benzene in a two-phase, HF–benzene, system.[86,87] The mer units in these films are not solely para-linked phenylenes; FT IR spectra reveal the presence of ortho and meta linkages as well as phenolic –OH groups. Electrochemical polymerization of benzene in nitromethane with aluminum chloride and water or an amine yields a black deposit on the platinum anode.[88] Infrared and electron spin resonance spectroscopic data, together with elemental analyses, are suggestive of structural differences between the electrochemically prepared polymer and PPP synthesized via the Kovacic method. Flexible, electrically conductive (100 S/cm) films of poly(*p*-phenylene) have been obtained via electropolymerization of benzene in a nitrobenzene solution containing a composite electrolyte of $CuCl_2$ and $LiAsF_6$.[89] Infrared spectra and elemental analyses of the green film are consistent with similar data for chemically prepared PPP.

Plasma polymerization of benzene yields polyphenylene.[96-98] Depending on the conditions, powders, liquids, or films can be formed.[98] Pyrolysis mass spectrometry of the polymer yields fragments originating from $(C_6H_4)_n$ structures.[99]

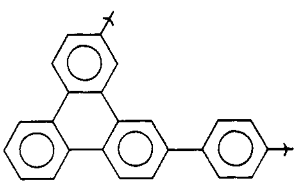
Other coupling systems such as thallium(III) trifluoroacetate/Li_2PdCl_4,[100] thallium(III) trifluoroacetate/$Pd(OAc)_2$,[101] and Pd(II)/heteropoly acids[102] can be gainfully employed for the dimerization of benzene to yield biphenyl. However, none of these reagent combinations has been reported to give polyphenylenes.

C. Lower Oligophenyls

Biphenyl and terphenyl yield mainly sexiphenyl upon treatment with $AlCl_3/CuCl_2$ in *o*-dichlorobenzene at temperatures less than 80 °C.[19,103] At higher temperatures (80–155 °C), processable polymers with meta and para linkages are produced from biphenyl/$AlCl_3$/$CuCl_2$.[19] Likewise, *m*- or *p*-terphenyl or mixtures of the terphenyls with benzene or biphenyl are oxidatively polymerized with $AlCl_3/CuCl_2$ at 85–180 °C to afford fusible polyphenylenes.[104-106] Undoubtedly the presence of meta linkages influences the physical properties because of interrupted regularity in the chain.

As with benzene, $FeCl_3$ and $MoCl_5$ serve dual roles of Lewis acid catalyst and oxidant in the oxidative oligomerization of biphenyl or terphenyl.[103] The major product from treatment of biphenyl with $FeCl_3$ is sexiphenyl; with $MoCl_5$, approximately equivalent amounts of quaterphenyl and sexiphenyl are formed. Neither metal halide is as effective in the nuclear coupling as the combination of $AlCl_3$ and $CuCl_2$. Nuclear coupling of biphenyl in the presence of SbF_5 or SbF_5/HF proceeds to give uncharacterized polymeric material.[78] Presumably radical cations are involved as intermediates.

Recent laser desorption/Fourier transform mass spectrometry (LD/FT MS) studies[107] of the products obtained from treatment of biphenyl with $AlCl_3/CuCl_2$ or $MoCl_5$ revealed the presence of polynuclear species (11) in the sexiphenyl fraction. In contrast, the LD/FT MS of the product from the terphenyl/$AlCl_3/CuCl_2$ system revealed little if any ring-condensed moieties in the sexiphenyl product.



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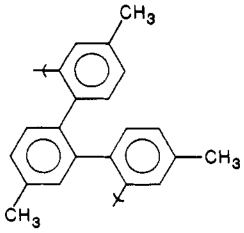
Prolonged exposure of biphenyl, *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl or *p*-sexiphenyl to vapors of AsF_5 causes polymerization to give conductive charge-transfer complexes of poly(*p*-phenylene.[108] Exposure of the complex to moist air or dimethylamine leaves a polymer whose IR spectrum compares favorably to that of PPP prepared from benzene/$AlCl_3/CuCl_2$.

Anodic oxidation of biphenyl on platinum electrodes in liquid SO_2 resulted in formation of passive films when the electrolyte was a quaternary ammonium perchlorate.[84] Under analogous conditions but with a quaternary ammonium tetrafluoroborate as electrolyte, biphenyl formed conductive dendrite-like deposits.[84]

A patent describes the low yield preparation of polyphenylene from biphenyl by treatment with H_2 in the presence of a complex metal oxide catalyst ($10CaO{\cdot}CoO{\cdot}MoO_3{\cdot}8Al_2O_3$) at high temperatures and pressures.[109]

D. Alkylbenzenes

Toluene yields polymer with a poly(*o*-phenylene) backbone (12) upon treatment with $AlCl_3/CuCl_2$.[18,110,111]



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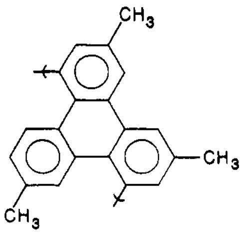

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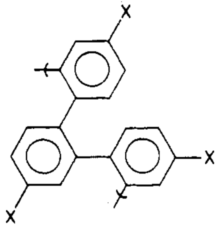
In carbon disulfide solvent, the product is an insoluble, infusible light brown powder. In a neat system, a dark purple-brown solid with a degree of polymerization of ca. 7 is obtained. Because of the observed color[110] and ESR signal,[18] the presence of polynuclear structures (13) has been postulated. Furthermore, the toluene polymer was found to be a complex mixture of oligomers with a lower average molecular weight than the product from benzene/$AlCl_3/CuCl_2$. Uncharacterized polymeric materials were the chief products obtained from $FeCl_3$ oxidation of toluene, ethylbenzene, cumene, and *tert*-butylbenzene.[112] The polymers were postulated to contain structural features arising from both nuclear coupling and side-chain attack on the aromatic ring.

Polymethylbenzenes characteristically produce dehydrodimers (biaryls and diarylmethanes) upon treatment with ferric chloride,[113-116] cobalt(III) trifluoroacetate,[117,118] manganese(III) trifluoroacetate,[117] lead(IV) trifluoroacetate,[117] ferrous chloride/perchloric acid,[119] thallium(III) trifluoroacetate/Li_2PdCl_4,[100] or copper(III) biuret complex,[120] and from anodic oxidation.[121-125] As in the polymerization of benzene (see III.C.), radical cations have been implicated in the coupling mechanism.

E. Halobenzenes

Chlorobenzene[18,126] and fluorobenzene[126] produce polymers with backbones comprised of *o*-phenylene units (14) upon exposure to $AlCl_3/CuCl_2$. The chlorobenzene product was red, with an average degree of polymerization of 10–12. Polymers with varying chlorine content are formed, as determined from LD/FT mass spectra.[127] The coupled product from fluorobenzene was similar in most respects to the chlorobenzene oligomer. However, evidence from oxidative degradation revealed that propagation occurred to some extent by attack ortho to fluorine. Polynuclear regions are presumably present.



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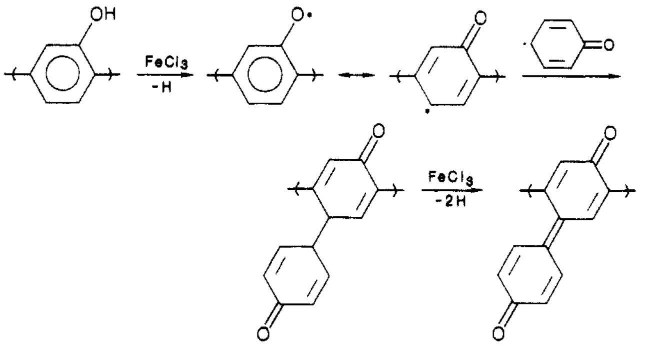
As with benzene, antimony pentafluoride converted fluorobenzene, chlorobenene, and bromobenzene to low yields of polymeric species,[78] presumably of polyphenyl-like structure.

A detailed discussion of the preparation of poly(*p*-phenylene) via organometallic coupling of dihalobenzenes is not within the scope of this review. A previous review describes various methods, such as the Ullmann, Fittig, and Grignard reactions.[1] More recently, two modified Grignard-type reactions have been extensively employed. The method of Yamamoto et al.[128] involves the use of nickel(II) complexes to promote the coupling of aryl Grignards while Taylor et al.[129] utilize 1,4-dichloro-2-butene or 1,4-dichloro-2-butyne as organic coupling promoters.

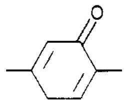
F. Phenols and Phenol Ethers

Phenol is not polymerized by $AlCl_3/CuCl_2$,[130] presumably because of deactivation of $AlCl_3$ by the phe-

SCHEME V



nolic hydroxyl in a manner analogous to retardation by water in the polymerization of benzene.[66] However, $FeCl_3$, which is activated by water,[74] will couple phenol,[130] catechol,[130] or hydroquinone.[130] A detailed study of the phenol polymer was made. Product prepared at 40–90 °C displayed a molecular weight of about 1400; values as high as 10,000 have been reported. The NMR and IR data were consistent with the presence of phenolic structures. However, only about 50% of the oxygen reacts as the phenolic type, and the IR spectrum contained carbonyl absorption which was attributed to **15**. The designation is unlikely since tautomers of this kind generally make a negligible contribution. It seems more plausible that the reactions in Scheme V may be occurring to some extent along the backbone. TGA showed weight loss beginning at 350 °C with a total of 25% at 900 °C. The major decomposition products were CO and CO_2 at the lower temperatures, whereas some H_2O was formed above 450 °C, and H_2 predominated at the upper temperature ranges. β-Naphthol has been coupled under Scholl conditions ($AlCl_3$/CH_3NO_2).[131] The polymer, of narrow molecular weight distribution, was accompanied by dimers and trimers which lowered thermal stability and flow temperature. Oxidative dimerization of β-naphthol and 2,6-dialkylphenols has been accomplished via reaction with manganese(III) acetylacetonate.[132]



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The dehydropolycondensation of thiophenol effected by $MoCl_5$ or WCl_6 led to the formation of a polyphenylene with retention of the SH groups.[133] The powdery product softened at low temperatures and dissolved in organic solvents.

In the aromatic ether category, 2,2′,4,4′-tetramethoxybiphenyl originated in low yield from resorcinol dimethyl ether and aluminum chloride in nitrobenzene.[134] After a report[135] of partial demethylation during polymerization of *p*-dimethoxybenzene by $AlCl_3/CuCl_2$, conditions were subsequently found[136] which yielded a pure linear polymer fusible at 320 °C and possessing an intrinsic viscosity of ca. 0.07 in sulfuric acid. The Scholl review[6] contains various examples of intermolecular coupling of naphthyl ethers, in addition to intramolecular cases with substrates bearing ether or hydroxyl substituents.

G. Nitrogen-Containing Benzenes

Diphenylamine has been converted to a polyamine resin by ferric chloride.[137,138] According to TGA, the product was stable in air up to 465 °C, had a softening point of 80–100 °C, and was soluble in some organic solvents. Darker colored material exhibited decreased thermal stability. Polymer properties were critically dependent on reaction conditions. According to IR data, the aromatic nuclei were involved in coupling, not the NH groups. As a side reaction, nuclear chlorination occurred to the extent of 0.5–6.3% at 35–80 °C. Also investigated were triphenylamine and dibenzylamine.

A similar study was made with product from $(C_6H_5)_2NH/AlCl_3/CuCl_2$.[138] Physical properties were not as critically dependent on reaction temperature as in the $FeCl_3$ case. Polyamines prepared by these methods are converted to Phillips-type resins via cross-linking by *p*-xylene dichloride or *p*-xylylene glycol dimethyl ether in the presence of $SnCl_4$. The end products have become commercially available.

In the Scholl category, dimethylaniline produced tetramethylbenzidine on heating with aluminum chloride in the presence of air.[139] High-temperature oxidative dehydropolycondensation of this monomer provided polyconjugated oligomer.[140]

A patent mentions polymerization of azobenzene by $AlCl_3$–chloranil with no data on product characterization.[141]

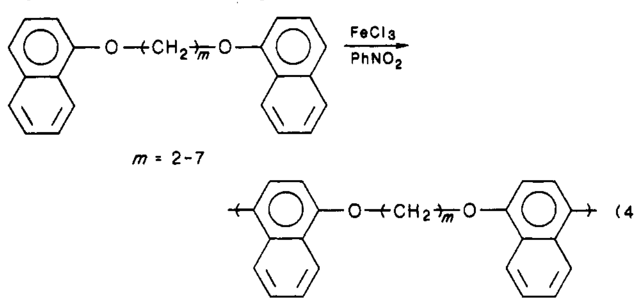
H. Polynuclear Aromatics

The Scholl review[6] lists many cases of dehydrogenative condensation, both inter- and intramolecular. Much work with the former type has been done with naphthalene and its ether derivatives.

Treatment of naphthalene with $FeCl_3/H_2O$ afforded a complex mixture of multiply chlorinated oligomeric material and unsubstituted oligonaphthalenes (e.g. binaphthyls, ternaphthyls, etc.).[18,127,142] With $AlCl_3/CuCl_2$, oligomeric materials which were substantially less chlorinated were obtained.[18,127,142] However, oxidation of the product to totally aromatic oligonaphthalene was not complete, and formation of condensed polynuclear structures was apparent from examination of LD/FT mass spectra.[127] The benzene-soluble fraction from the $AlCl_3/CuCl_2$ product was comprised of 3–6 naphthalene nuclei. The dark purple color and presence of radicals (ESR) were attributed to polynuclear moieties in the chain,[18,142] in agreement with the LD/FT MS results.

Naphthalene may also be oligomerized by the action of $AlCl_3$ alone.[143] The resulting product had an average DP comparable to that of the benzene-soluble fraction from naphthalene/$AlCl_3/CuCl_2$. However, without the oxidant, the oligomers were comprised of 1,4- or 1,2-linked dihydro units. No evidence of condensed ring structures was found.

Substituted naphthalenes undergo nuclear coupling with Lewis acid catalyst/oxidant systems. 1-Chloronaphthalene was converted to oligomeric material with either $FeCl_3/H_2O$ or $AlCl_3/CuCl_2$.[18] Structures for the products were not postulated, although analytical data were in good agreement with a repeating unit of $C_{10}H_5Cl$ for either system. High-molecular-weight linear polymers have been obtained via oxidation of di-1-naphthoxyalkanes with $FeCl_3$ in nitrobenzene[144] (eq 4).



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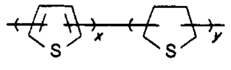
A lesser degree of attention has been paid to higher members. The anthracene/$CuCl_2$/$AlCl_3$ system has been investigated,[145] and there is brief mention of an anthracene/$FeCl_3$ study.[146] In molten Ga_2Cl_6, anthracene forms protonated arenium ion and oligomeric material, principally anthra[2,1-*a*]aceanthrylene in which two bonds join two anthracene rings.[147] Products from the oxidative coupling of phenanthrene or pyrene with $AlCl_3$/$CuCl_2$ included dehydro dimers and trimers, accompanied by higher oligomers.[148] 9,10-Dihydrophenanthrene which behaved similarly, may serve as a precursor of phenanthrene. Pyrene has been oxidatively coupled by periodic acid,[149] molten Ga_2Cl_6,[147] or under Scholl conditions.[150,151] In some cases there was subsequent intramolecular ring closure. Other polynuclear substrates behaved similarly in the Scholl reaction.[150,151] There are numerous examples in the intramolecular category involving formation of five- or six-membered rings.[6] In addition to the hydrocarbon types, the substrates contained a variety of substituents, e.g., carbonyl, hydroxyl, ether, amide, imide, carboxyl, halogen, alkyl, aryl, azo, and cyano.

I. Heterocyclic Aromatics

Relatively few reports describe the direct coupling of heteroaromatic substrates by chemical means. Dehydrocoupling[152,153] of thiophene by $MoCl_5$ or WCl_6 gave products in which the original ring structure was preserved. Chlorinated monomers and dithienyl were also studied. Thiophene and 2,2′-bithienyl are converted to conductive poly(2,5-thiophenediyl) upon treatment with AsF_5[154] or nitrosonium salts ($NOSbF_6$, $NOPF_6$, $NOBF_4$).[155] In a fashion analogous to the synthesis of conductive PPP from biphenyl/AsF_5,[108] the sulfur heterocycles may undergo one-electron oxidation to form a radical cation, which then propagates to give the resulting polymer. Thiophene can be polymerized by $AlCl_3$/$CuCl_2$,[156] but the same result is obtained with $AlCl_3$ alone.[157] The behavior is drastically different from that of benzene. The reaction, designated as disproportionative polymerization, involves conversion to alternating thiophene and tetrahydrothiophene moieties (**16**). Mechanistic features have been addressed. The related monomers, pyrrole[158] and furan,[159] responded similarly on exposure to acid; subsequent ring opening occurred in the furan case. Pyridine is converted to 2,2′-dipyridyl upon treatment with $FeCl_3$ at elevated temperatures.[160,161] Numerous byproducts are also obtained from this reaction.



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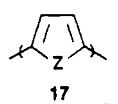
Coupling of benzothiophene was accomplished with molybdenum pentachloride or tungsten chloride.[153,162] A 55–65% yield of oligomer was realized at 343–363 K. The basic structure of the monomer was retained in the repeating units. The product was soluble in organic solvents, softened at 368–393 K, and underwent degradation at 613 K. Oxidation of tetrahydrocarbazole by ferric chloride gave an unsymmetrical dehydrodimer product.[163]

Polymer is formed from dibenzofuran and ferric chloride.[146]

Recently, in connection with an increasing interest in conducting organic polymers, many studies of electrochemical coupling of heteroaromatic nuclei have been reported. For example, pyrrole,[164–167] *N*-alkylpyrroles,[168] thiophene,[167,169,170] and furan[167] all undergo anodic oxidation to yield polymers in which the heteroaromatic nuclei are linked at the 2,5 positions (**17**). Carbazole[169] forms a film of reported poly(3,6-carbazolediyl) structure **18**. Elemental analysis of the polymer reveals it to be rich in hydrogen; thus reduced ring moieties are likely to be present. Isothianaphthene[171] polymerizes to give poly(isothionaphthene) (**19**), provided the electrolyte contains nucleophilic anions such as Cl^- or Br^-. The electrochemical topic has been reviewed.[172]



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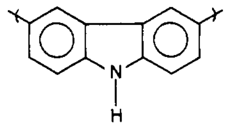
Z = NH, S, O



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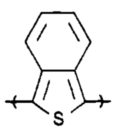

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J. Mixed Coupling of Aromatics

Copolymers have been prepared from combinations of homocyclic aromatic substrates with Lewis acid catalyst–oxidant combinations. For example, mixtures of *m*-terphenyl and naphthalene,[173] benzene,[174] or biphenyl[175,176] afforded soluble, fusible copolymers from reaction with $AlCl_3$/$CuCl_2$[173,175] or $AlCl_3$/O_2.[176] Similarly, soluble copolymers of naphthalene and benzene were obtained via oxidative coupling with $AlCl_3$/$CuCl_2$.[145,177,178] The copolymers generally retain the good thermal stability of PPP, but are more processable. More highly condensed aromatics (anthracene, phenanthrene, pyrene) were also copolymerized with benzene in the presence of $AlCl_3$/$CuCl_2$ to yield tractable products.[179] A novel coupling system comprised of MoO_3/O_2 in liquid HF was employed for the copolymerization of naphthalene with biphenyl or *p*-terphenyl.[180]

Several examples of the synthesis of mixed dimers or trimers are known. Dehydrodimerization results from treatment of naphthalene and mesitylene with $AlCl_3$/$CuCl_2$,[181] $FeCl_3$,[182] Cu(III)-biuret complex in TFA-acetic acid,[120] $Co(OAc)_3$ or $Co(OCOCF_3)_3$,[117] $Mn(OAc)_3$ or $Mn(OCOCF_3)_3$,[117] or anodic oxidation.[183] Biphenyl and mesitylene form a mixed dehydrotrimer (2,4,6,2‴,4‴,6‴-hexamethyl-*p*-quaterphenyl) with $AlCl_3$/$CuCl_2$.[184]

K. Intramolecular Coupling

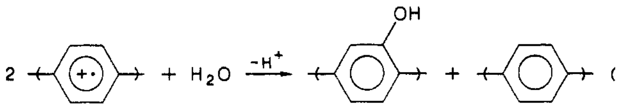
Numerous examples of intramolecular coupling of aromatic nuclei under oxidative conditions are given in earlier reviews.[2,6,185] Commonly employed reagents include $AlCl_3$, $Pd(OAc)_2$, $Tl(OCOCH_3)$, VOF_3, and anodic oxidation.

III. *Poly(p-phenylene)*

A. Structure

An appreciable amount of evidence has accumulated which bears upon the structural nature of PPP. Various lines of data demonstrate that *p*-phenylene moieties predominantly comprise the backbone chain.[4] The C/H ratio from microanalyses is near the theoretical value of 1.5. The principal absorption band in the IR is at 803–805 cm^{-1} characteristic of para substitution. Pyrolysis yielded the lower *p*-phenylene oligomers: terphenyl, quaterphenyl, and quinquephenyl. Gas chromatography of the terphenyl fraction revealed no isomeric material. Chromic acid oxidation produced terephthalic acid and 4,4′-biphenyldicarboxylic acid. The terephthalic acid fraction contained no isomeric dicarboxylic acids. Thus, one can conclude that ortho and meta chain junctures are nonexistent or insignificant. The X-ray diffraction pattern was essentially the same as that reported for polymer prepared from poly(1,3-cyclohexadiene).[186]

Less intense absorption maxima in the IR at 765 and 695 cm^{-1} are assigned to phenyl end groups whose presence is verified by conversion to benzoic acid on oxidation. In addition, there is evidence, with varying degrees of reliability, pointing to the occurrence in minor amounts of a number of structural irregularities. The oxygen, <1% according to elemental analysis, may exist in the form of phenolic hydroxyl introduced during workup by reaction of water with the radical cations present[187] (see section III.D.1.) (eq 5). Aromatic radical cations are known to interact with moisture.[9] There is also 2–4% of chlorine in the product. Some is in the form of *p*-chlorophenyl end groups, according to oxidative degradation, and part is substituted along the chain as evidenced by IR and dechlorination experiments.[188] It is conceivable that chloride functions as the gegen ion for the radical cations present in ordinary PPP. The oligomer exists with a low concentration of radical cations, in stable form, associated with the chains.[187] Uptake of bromine and peroxide supports the proposition that small quantities of cyclohexadiene or *p*-quinoid structures interrupt the normal repeating units, as a consequence of incomplete oxidative rearomatization during polymerization.[70] It is indicative that a greater degree of irregularity pertains when a weak oxidant, such as oxygen, is used in conjunction with $AlCl_3$ during the coupling reaction.[70] Alternatively, polynuclear regions may be generated. For example, when benzene is exposed to $AlCl_3$, a plethora of products results, including some in the polynuclear category, such as naphthalene, phenylnaphthalenes, and acenaphthene.[189] Because of insolubility and of low hydrogen content in some cases, the question of the presence of cross-links has been raised.[190] It is not required to invoke cross-linking since extreme insolubility is reached in the *p*-phenylene series with seven or eight nuclei. The hydrogen deficiency can be rationalized by the generation of polynuclear areas or phenyl side groups. The most convincing evidence against cross-links is the solubilization which results from Friedel–Crafts dialkylation,[191] and the mass spectral findings presented in the next paragraph. Hence, it is appropriate to conclude that cross-links are essentially absent. Various metals in trace quantities have been detected.[192]



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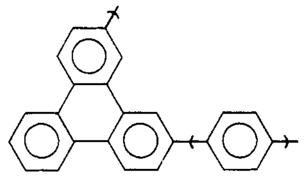
Valuable structural information has been provided based on laser desorption/Fourier transform mass spectrometry.[107,193] Prior assignments have been confirmed in relation to phenylene repeating units, phenyl end groups, and incorporation of either one or two chlorines per chain. Although the existence of polynuclear structures had been previously suggested by several groups, supporting evidence was tenuous. The MS technique demonstrates the presence of oligomer populations in which the phenylene chains are devoid of two hydrogens. Formation of polynuclear regions (**20**) can best account for this observation.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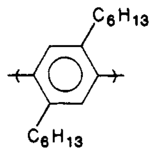
B. Molecular Weight

The extreme insolubility of PPP precludes direct determination of molecular weight by the standard procedures. Fortunately, Friedel–Crafts alkylation yielded a derivative soluble in chloroform.[191] Use of *n*-propyl halide–aluminum chloride provided a dialkylated product which was assigned structure **21** based on the evidence. Data from vapor-phase osmometry indicated a DP of 15.



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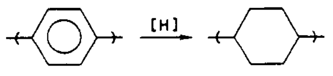
Another indirect approach entailed reduction to the corresponding cyclohexane polymer (**22**). Initially, chemical methods were explored. A product containing an average of nine hydrogens per ring was obtained by reaction with lithium/ethylenediamine.[194] The unexpected insolubility of the reduced material is probably due to some cross-linking. Hydrogenation with rhodium catalyst at high temperature and pressure proved to be more successful.[195] GPC of the soluble derivative demonstrated that the average number of cyclohexane units per chain was 8 with a maximum of 16 and a minimum of 4. The experimental DP is slightly lower than that obtained via the alkylation route. Since only a small



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amount (~5%) of PPP underwent catalytic hydrogenation, the product likely arises from only the lower molecular weight, more soluble fraction. In any case both approaches agree that PPP is a lower molecular weight, oligomeric product.

Additional information on the molecular weight of PPP can be gleaned from infrared spectroscopy. A shift of the infrared para band position to a lower wave number with increasing molecular weight in the phenylene series has been observed.[4,188,191] Since the magnitude of the shift decreases with increasing molecular weight, the method is most applicable to lower molecular weight polymers and for comparison of members which differ widely in molecular weight. The oligo and poly(*p*-phenylene)s exhibit characteristic IR absorptions corresponding to para substitution (from 800–840 cm^{-1}, arising from internal phenylene rings) and mono substitution (from 730–770 cm^{-1} and 690–710 cm^{-1}, arising from the end phenyl units). Quantitative analysis (baseline technique[196]) of the absorption values[188] for the para and mono bands of quaterphenyl, quinquephenyl, and sexiphenyl yielded a linear relationship between the ratio of (Σmono)/para and the number of rings. A regression analysis of the data for the three compounds produced a value of 9 rings for PPP, in good agreement with the average *n* value (8) found from gel permeation chromatography of dehydrogenated PPP[195] and slightly more than one-half the *n* value determined for alkylated PPP.[191] *p*-Terphenyl does not fall on the line, presumably since this homologue does not accurately reflect the typical oligomer makeup, namely, a ratio of internal/terminal rings of ≥ 1. Caution must be exercised in interpreting the IR data. From elemental analysis,[197] chlorine (1–2%) and oxygen (1–2%) are known to be present in PPP prepared in the standard fashion. Substitution along the polymer backbone would alter the infrared spectrum, decreasing the intensity of the para band relative to the mono bands. A small absorption at 850–860 cm^{-1}, characteristic of an isolated hydrogen on an aromatic nucleus, is observed in the spectrum. Treatment with sodium to effect dechlorination causes the disappearance of this band,[188] indicating that chlorine is substituted on internal phenylene units. Attempts to secure pristine polymer by dehalogenation met with obstacles. Furthermore there is evidence for the presence of *p*-chlorophenyl end groups which would increase the para/mono IR ratio. One should also entertain the possible presence of nonaromatic rings in the polymer chain. Structural irregularities, such as *p*-quinoid or cyclohexadiene units, arising from incomplete oxidation have been invoked to rationalize the reactivity toward bromine and peracid.[70] Certainly, interruption of conjugation could have an influence on the spectral results. The value of *n* (9) obtained from IR data should probably be considered at least a lower limit for the degree of polymerization.

The position of the UV absorption maximum could theoretically provide information on the molecular weight. The plot of wave number vs. $1/a^2$ (a = number of benzene rings) shows a good straight-line relationship for the *p*-phenylene series.[4] The accuracy decreases with increasing chain length. The relation between the ultraviolet spectrum and molecular weight has been discussed from the quantum mechanical viewpoint.[198,199] Conjugation results in a bathochromic shift, with λ_{max} increasing asymptotically to a limiting value as the number of aromatic nuclei increases.[200] From calculations based on Davydov's equation[199] and λ_{max} values (in solution) for the lower oligomers, Suzuki[201] reported 339 nm as the peak position when *n* is infinity. In marked contrast, λ_{max} experimental figures as high as 395 nm have been obtained for PPP prepared from neat benzene and in carbon disulfide. Although the correction factor is unknown, it appears unlikely that the discrepancy arises entirely from differences in the method of obtaining the spectra. Perhaps the high experimental values arise from the presence of irregular structures of the *p*-quinoid, polynuclear, or radical cation type.

TABLE III. Properties of PPP from C_6H_6 vs. C_6D_6[a]

monomer	spins/g	C_6H_4 units/spin	color	solubility[b]
C_6H_6	2×10^{18}	3.9×10^{3}	brown	0
C_6D_6	1.3×10^{17}	5.5×10^{4}	light yellow	14

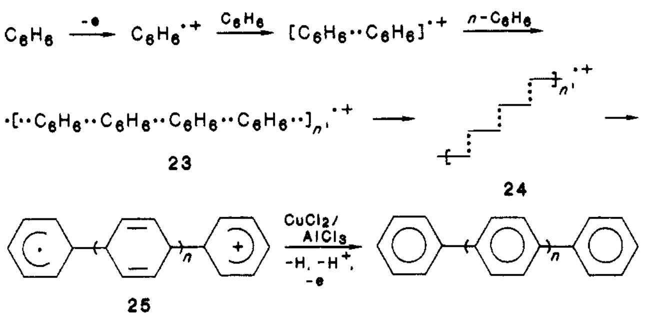
[a] Reaction temperature, 24–28 °C. [b] Percentage of 0.1 g soluble in 100 mL boiling *o*-dichlorobenzene.

Direct measurements have recently been made which provide precise molecular weight data based on laser desorption/Fourier transform mass spectral analysis.[107,193] The average chain was found to contain about 13–14 nuclei in good agreement with the indirect method involving alkylation.[191] A similar value was reported by Froyer et al.[202] Yamamoto PPP exhibited essentially the same chain length by MS, in accord with another report.[203]

Studies have been carried out on the influence of reaction variables on the degree of polymerization. The molecular weight of PPP was influenced by solvent, concentration, and temperature. Relative molecular weights were measured by polymer solubility in chloroform, and positions of the infrared para band and ultraviolet reflectance λ_{max}.[188] The order of effectiveness of the solvents in reducing molecular weight was: *o*-$C_6H_4Cl_2$ > 1,2,4-$C_6H_3Cl_3$ > $SnCl_4$ ~ CS_2 > [C_6H_6]. In general, the molecular weight decreased with increasing temperature and with decreasing concentration.

The situation for the perdeuterated analogue (see section III.C.) was quite surprising. The data for perdeuterated PPP and the alkylated and reduced derivatives indicate a significant decrease in the molecular weight relative to the PPP analogues.[204] Table III summarizes the results in comparison with ordinary PPP prepared at the same reaction temperature. The increased solubility for deuterated PPP is indicative of a lower molecular weight. Furthermore, the lighter color correlates with decreased radical cation content,[187] also suggestive of lower molecular weight. A decrease in spin density (from decreasing radical cation concentration) with decreasing chain length has been noted in the *p*-phenylene (from C_6H_6) series (see section III.D.1.). A diminished ESR signal was observed for the perdeuterated PPP; however, care should be taken in interpreting this result in terms of decreased radical cation content and thus, molecular weight. Substitution of D for H in the polymer results in a narrowing of the ESR trace. Because spin density is directly proportional to the area under the signal, it is conceivable that PPP from C_6D_6 could have a comparable concentration

SCHEME VI



of radical cations yet give a lower calculated spin density than PPP from C_6H_6.

Friedel–Crafts alkylation of perdeuterated PPP[204] with *n*-propyl chloride/$AlCl_3$ yielded product with a weight increase indicating two C_6H_{13} groups per benzene ring (similar to PPP) (see **21**).[191] The solubility of the alkylated polymer made possible the determination of molecular weight by vapor-phase osmometry which provided a value of 1452 for M_n, corresponding to 6 aromatic rings (average) per chain. These figures are significantly lower than those observed for alkylated PPP (M_n = 3755, 15 rings/chain, average).[191] When perdeuterated polymer was catalytically hydrogenated by the method previously reported for PPP,[195] molecular weight determination of the reduced product (see **22**) by vapor-phase osmometry established that M_n = 343, corresponding to DP of 4. The value is less reliable than that obtained for the alkylated polymer. Most of the perdeuterated material remains unchanged, implying that mainly the shorter chains are selectively reduced, thus giving an inaccurate, low DP value. A similar situation in relation to the two methods of indirect molecular weight determination was observed in the PPP case.[191,195] Accurate measurements by LD/FT mass spectral analysis indicated an average length of 10 aromatic rings per chain.[193] Conductivity measurements of the deuterated polymer after being doped with AsF_5 gave a value of 32 S/cm.[204] Following comparable doping, the figure for PPP[5] is 500 S/cm and for *p*-sexiphenyl,[108] 7.4 S/cm. Evidence points to the occurrence of chain extension during doping.[108] This comprises additional evidence for decreased molecular weight in the deuterated case.

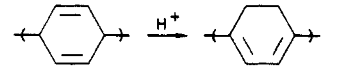
A comprehensive analysis of data dealing with relative molecular weights of PPP prepared by various methods is available.[193,204] Differences in the degree of polymerization between benzene and biphenyl have been addressed.[107]

C. Coupling Mechanism

1. Initiation, Propagation, Oxidation, and Depolymerization

Over the years attention has been devoted to the mechanistic features of the intriguing transformation of benzene on exposure to aluminum chloride/cupric chloride. There is agreement that a benzene radical cation is the initiating species.[205,206] Concerning propagation, one group favored involvement of a radical species,[206] whereas another proposed a carbocation type.[205] The critical deficiencies of both approaches have been pointed out.[205,206] Within the past several years, a novel pathway was suggested for the reaction which has been labeled the stair-step mechanism (Scheme VI).[16,17,204]

It now appears the $C_6H_6{}^{\bullet+}$ serves as the site for coordination with an appreciable number of benzene nuclei in a propagative manner, giving rise to **23**. A side view would appear as stair steps (**24**), ranging from straight to spiral. Apparently, the electrophilic initiator must possess radical character and be completely sp^2 planar. According to the authors' concept of **24**, the nuclei are parallel to each other, but probably not arranged in a highly symmetrical fashion, with the radical cation delocalized throughout the entire system. When chain buildup reaches a certain stage, the radical cation character on the terminal members will be too small to induce further propagation. Evidence indicates that the cationic aspect plays an important role in this phase.[205] Covalent bond formation then leads to **25**. The unlikely feature of σ-complex involvement from the earlier suggestion is nicely obviated. The propagation mechanism is unique in that association, not σ, bonds are formed, and the reactive intermediates are delocalized throughout the growing chain. In contrast, for the classical radical, cation, or anion cases, σ bonds are generated and the reactive intermediate is transmitted unchanged during propagation, leading generally to a comparatively high-molecular-weight polymer. It is reasonable to expect that the 1,4-dihydrobenzene units (**26**) would readily undergo isomerization to the more stable conjugated form in the highly acidic system (eq 7). Oxidative rearomatization of the dihydro structures



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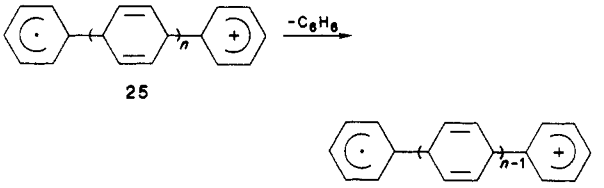
by cupric chloride should be facile, accompanied by formation of cuprous chloride and hydrogen chloride. Furthermore, it appears that **25** can readily undergo unzippering (eq 8), the extent of which partly determines the molecular weight.[16] This path would be in competition with proton loss from **25**, the last step in Scheme VI.



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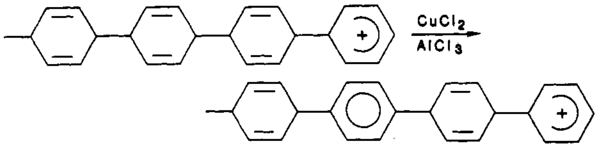
The relatively low molecular weight of PPP (DP = 13–15)[107,191,193] is consistent with the diminution in reactivity of the end groups as chain length increases. Results from polymerization of C_6D_6 can be construed as evidence in support of Scheme VI.[204] Data, based on molecular weight determination, solubility, color, ESR, MS, and conductivity after doping, show that the perdeuterated polymer possesses a lower molecular weight (DP 6).[191,193,204] Both monomers should yield polymers of type **25** with essentially identical molecular weights after propagation via **24** (C_6H_6 or C_6D_6). This is reasonable since the presence of H or D should result in a negligible difference at this stage. Substitution of H by D may well exert a noticeable effect on the fate of **25** with respect to the degree of depolymerization. Based on the primary isotope effect,[191,204] **25** (C_6H_6) should rearomatize more rapidly with loss of H^+, and therefore undergo less unzippering than **25** (C_6D_6). Thus, the slower cleavage rate of C–D vs. C–H increases the extent of dealkylation (eq 8) in the perdeuterated case, giving rise to a polymer of lower molecular weight. Alternatively, the rate determining step may be the rearomatization of dihydrobenzene units by cupric chloride (eq 9). The benzenoid moiety would act as a block to unzippering. Since the oxidation would take place more slowly with the deuterated polymer, there would be a greater opportunity for depolymerization resulting in lower molecular weight.



(9)

Recently, a similar study was made with biphenyl and biphenyl-d_{10} in the $AlCl_3/CuCl_2$ system.[19] The principal product was *p*-sexiphenyl along with some *p*-quaterphenyl and sublimation residue. For both substrates, the yields of *p*-sexiphenyl are fairly similar. However, in the case of $C_{12}D_{10}$, there is a 7-fold increase in the amount of dimer-type product and the quantity of residue was approximately halved. That is, for the various fractions, there is a general, significant shift to lower molecular weight vs. the results from biphenyl. Therefore deuterium substitution brings about the same general effect as for benzene. Hence, a similar type of mechanistic reasoning can be applied in an interpretation of the biphenyl reaction pathway. However, an alternative route should also be considered, at least for the chain forming sequence. Based on oxidation potential, biphenyl is more easily oxidized than benzene to the radical cation.[207] It is known that the more stable radical cations can undergo radical dimerization to dications.[9] In the biphenyl case, subsequent loss of protons would form *p*-quaterphenyl which could continue to propagate in like fashion.

The mechanistic view, particularly in relation to involvement of species **24**, is strengthened by recent work[108] involving solid-state synthesis of PPP from reaction of AsF_5 with the lower oligomers, namely, *p*-terphenyl,[208] *p*-quaterphenyl, *p*-quinquephenyl, and *p*-sexiphenyl. From an inspection of the unit cell of *p*-terphenyl, the authors concluded[108] that reaction between molecules related by the *c*-axis translation provided a likely possibility. The precursor monomers are present in parallel planes with their end carbons in close proximity, as in **24**. It is conceivable that the solution mechanism would also apply to the solid which may be more favorable because of the crystalline structure, thus providing a unifying thesis. By analogy, PPP may undergo further chain extension during doping by AsF_5.[108]

There is highly pertinent prior literature in the domain of mass spectrometry. Benzene dimer radical cations have been the subject of rather extensive investigation by this technique.[10–13] Significantly, small amounts of the trimer species have also been detected.[209] The extent of dissociation (analogous to dealkylation in eq 8) in mass spectrometry is found to increase with increasing deuterium substitution in the reacting ion[13] (compare with the C_6D_6 result). There is some similarity to radiolysis of benzene, which affords gross mixtures containing C_{12} species (biphenyl and reduced biphenyls), C_{18} reduced terphenyls, and uncharacterized higher molecular-weight material.[210–213] An ion–molecule mechanism was advanced to account for the products.[214]

TABLE IV. Bond Distance and Binding Energy for Benzene Dimer Radical Cation

dimer	interring bond distance, Å	binding energy, kcal/mol
stair-step	~2.6	~12
sandwich		
our data[17]	~3.2	~11
lit. data[13]	3.0	8–17

In addition, the mechanistic scheme is supported[16,17] by theoretical calculations on the benzene dimer radical cation which serves as a model for **24**. Prior workers have proposed a sandwich structure for this entity. On the other hand, the "stair step" dimer is equally stable. The data are presented in Table IV.

Ab initio MO calculations were used to characterize coordinations in benzene dimer cation.[16,17] Binding occurs for all arrangements which allow π-overlap between parallel rings. Parity (orbital symmetry) is approximately conserved, and two manifolds which correspond to opposite parities are predicted. Stable species in either manifold exhibit slippery, spongy bonds. In the odd (even) manifold, these are one-coordinatelike (six-coordinatelike) dimers which are bound by 12 (11) kcal/mol at interring distances of ~2.6 (3.2) Å. Analysis of the results suggests that such parity manifolds are generally expected of alternant aromatic dimer cations and also to some extent of their oxidomer analogues. Energy curves were calculated for 20 different coordinations wherein the rings are frozen and constrained to lie one above the other in parallel planes. Lowest energy interring distances and corresponding binding energies were determined for each coordination. It is possible to conclude from the results that several structures may be expected for most aromatic cations. Firstly, the origin of the binding is charge-spin delocalization which preserves aromatic character by moderating the intraring pπ bonds to form interring pσ bonds. That is, the dimeric bonding does not change the monomeric hybridization. Secondly, the monomeric HOMO's are approximately doubly degenerate in alternant systems. Depending on which "degenerate" MO is ionized, there are several different ways to dimerize and achieve interring coordination. The resultant dimers probably exhibit two "parity" manifolds. In relation to the mechanism of polymerization, the benzene dimer radical cation represents a precursor stage leading to **24**.

In summary, the principal supporting evidence for the proposed initiation–propagation is as follows: (1) The species has a relatively low molecular weight, falling in the oligomer region. (2) The molecular weight of perdeuterated PPP is lower than that of ordinary polymer. (3) The $AlCl_3/CuCl_2$ combination is able to produce radical cations, since this dual reactive intermediate is known to be present in the end product. (4) The reagents which effect direct nuclear coupling are generally those which are known to generate aromatic radical cations. (5) The chemical reagents behave in a manner akin to the electrochemistry of aromatic substrates which are initially converted to radical cations at the anode.[31] In both cases the observed transformations include nuclear coupling, nuclear substitution, and side-chain involvement in the α position by alkyl groups.

2. Termination

Structure **25** would be expected to deprotonate at the σ complex end and also at the other terminus after electron loss. Dimerization of **25**, followed by proton ejection, is a possibility. Stable radical cations are known to undergo coupling.[9] Termination exclusively by dimerization would result in a doubling of the molecular weight and the existence of chains comprised of only even numbers of phenylene rings. The mass spectrum of PPP (see section III.B.) reveals the presence of chains with both even and odd numbers of rings. Furthermore, no apparent doubling of molecular weight is evident from the mass spectral pattern. Thus, termination must not be solely by coupling.

In laser desorption/Fourier transform mass spectrometry,[107,193] principal mass peaks corresponded to the phenylene structure. However, an accompanying population of oligomers with two less hydrogens was also observed with $AlCl_3/CuCl_2$. The formation of polynuclear moieties (**20**) provides a plausible rationale. Apparently these arise from chain termination involving the ortho position followed by cyclization. The propagating species could react in this manner either with benzene or another reactive chain.

Evidently chlorination also brings about stoppage of chain extension. The $AlCl_3/CuCl_2$ system results in a low content of chlorine, whereas $FeCl_3$ and $MoCl_5$ yield increased amounts. Incorporation might occur via halogen abstraction from the redox metal halide by the radical portion of **25**. Also redox metal halides are known to effect halogenation of aromatic hydrocarbons. It is indicative that PPP from $FeCl_3$ or $MoCl_5$ gave no evidence for the presence of polynuclear entities according to mass spectral analysis. Apparently termination by halogenation or by polynuclear formation are competing processes.

Similar reasoning can be applied to termination reactions in the case of biphenyl.[107]

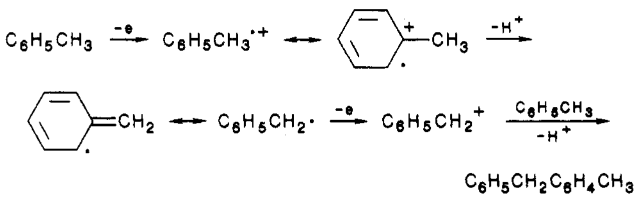
3. Competing Reactions[215]

Ferric chloride serves as a good example to illustrate the competing reactions. With benzene, PPP formation is the principal mode of reaction accompanied by a minor degree of nuclear chlorination.[72-74,216] In sharp contrast, chlorobenzene gives rise to dichlorobenzenes in very high yield with negligible amounts of side reactions.[217,218] Products from the arenes (monoalkylbenzenes,[112,217] xylenes,[114,219] mesitylene,[113] and pentamethylbenzene[113]) include aryl chlorides, biaryls, and diarylmethanes from side-chain participation.

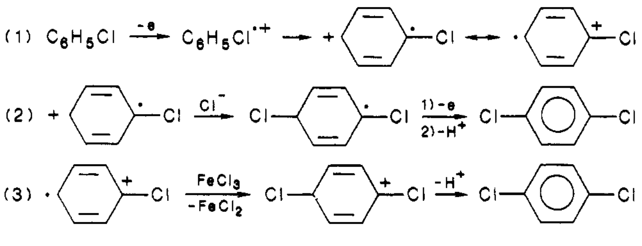
The mechanisms of the reactions which compete with nuclear coupling have been discussed. Radical cations are believed to comprise a common reactive intermediate. The route for the side chain is shown in Scheme VII. Several pathways are conceivable for chlorination (Scheme VIII).

It is evident that, although radical cations appear to be common intermediates in the competing processes, the nature of the aromatic substrate plays an important role in determining the pathway followed. Another crucial variable which influences the preferred route is the catalyst/oxidant system. As an illustration, antimony pentachloride[220] and vanadium tetrachloride[51] attack benzene principally in the chlorinative manner. Whereas ferric chloride prefers to halogenate chlorobenzene,[217,218] nuclear coupling mainly occurs with $AlCl_3/CuCl_2$.[18] In addition, catalytic or cocatalytic effects, e.g., involving water, have been reported for certain of the systems.[73,74]

SCHEME VII



SCHEME VIII



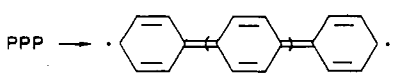
D. Spectroscopy

1. ESR

The ESR characteristics of PPP were first investigated about 20 years ago.[221] Since then a number of investigators have examined this property of the parent material, as well as related polymers.[18,19,187,202,204,222-228] The observed unpaired electrons are highly delocalized and most likely have π-electron character.[224] Since the signal is a singlet which is devoid of fine structure, no detailed information is available. Crude PPP, before acid workup, is dark black in color and exhibits a spin concentration of 1×10^{21} spins/g which corresponds to 8 phenylene units per spin.[187] On the average there are 15 phenylene units per molecule,[191] and hence each chain supports approximately two spins. Purified polymer is light brown and displays a value of 1.5×10^{18} spins/g, corresponding to 5.3×10^3 phenylene units per spin. Various workers are in agreement concerning spin density.[187,222-225] The peak to peak line width is 4–5 G.[225]

Several studies on the nature of the reactive intermediates associated with the chains have been made. The radical species is extremely stable as evidenced by the unreactivity toward nitric oxide[225] and oxygen.[187] Samples at least 10 years old exhibit spin concentrations comparable to those of freshly prepared polymer. Good evidence is available to support the contention that radical cations are formed upon one-electron oxidation of various aromatic substrates.[9] Nucleophilic reactions with model compounds have been demonstrated with a variety of Lewis bases, including water, methanol, cyanide, amines, acetate, chloride, and nitrite.[9] Many of these processes proceed by the half-regeneration mechanism involving two radical cations, one of which undergoes substitution and the other reduction to the parent molecule. Thus, the overall reaction entails reduction of spin concentration and introduction of new groups. As an example, water could conceivably react with PPP radical cations during aqueous workup to reduce the spin concentration and introduce oxygen in the form of hydroxyl groups. Indeed, oxygen is found in small quantities (<5%) by elemental analysis,[197] which indicates that reactions of the type shown in eq 5 may occur. Microanalysis of the polymer reveals the presence of chlorine (1–4%).[197] Data show conclusively that the halogen is introduced during polymerization, apparently from cupric chloride, aluminum chloride, or hydrogen chloride as the source.[187] Chemical and spectral evidence[188] point to the presence of chlorine along the chain and as part of the end groups. Some may serve as counter ions for the radical cations. The behavior of the polymer toward other nucleophiles was also examined.[187] With organic amines, the concentration was reduced from 1×10^{21} spins/g for the pristine polymer to 7×10^{17} spins/g. The end product contained 0.5% nitrogen from the nucleophile. *N,N*-Dimethylaniline occupies a special niche since it has quite a low oxidation potential and generally undergoes electron transfer reactions. From the absence of nitrogen in the polymer, it is evident that no nucleophilic reaction occurs in this case, only electron transfer to reduce the spin concentration (2×10^{17} spins/g). Although thiols produced a lower spin concentration (1×10^{17} spins/g), there was a lesser degree of sulfur incorporation vs. the nucleophilic amines, indicating a greater extent of participation in electron transfer. Therefore, these results can be considered good evidence for designation of the reactive species as a radical cation, at least in part.

It is intriguing that in no case was the spin density reduced below 8×10^{16} spins/g. Several hypotheses have been advanced as rationalizations. It may be that some of the radical cations are buried in the polymer and, since PPP is very insoluble, only the reactive moieties on or near the surface are accessible for attack.[187] A second possibility is that a twisting of the polymer chains renders the radical species sterically inaccessible. Alternatively, more than one type of radical species might be present. Over the years various groups have postulated the presence of polynuclear structures to account for certain properties.[225,227,229] Recently laser desorption/Fourier transform mass spectrometry studies revealed oligomer populations bearing two less hydrogens than the normal PPP chains.[107,193] The most reasonable rationalization comprises polynuclear formation during termination. Therefore it is likely that such entities contribute to the ESR spectrum as had been previously suggested.[202,225,227,229] Consideration should also be given to a purely radical entity of low reactivity. Other investigators have rationalized the existence of unpaired electrons in PPP on the basis of eq 10.[230,231] Apparently, radical stabilization is affected by chain length, steric factors, and formation of charge-transfer complexes. It is conceivable that the residual radical concentration represents the energetically preferred form of the hydrocarbon.



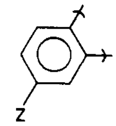
(10)

Similar experiments have been performed with PPP prepared from C_6D_6.[204,224,226] Nechtschein first postulated that the line width of the ESR signal from PPP was principally due to unresolved proton hyperfine splitting.[224] From a comparison of the second moments of the signals obtained from PPP and deuterated PPP, the conclusion was advanced that the unpaired electron is delocalized over 3–5 phenylene units in the chains. However, the equation used to calculate the proton hyperfine contribution to the second moment, taken from Hanna et al.,[232] was subsequently shown to be in error by a factor of 4.[233] More recent measurements based on second moments of ESR signals from PPP and perdeuterated PPP have revealed the extent of delocalization of the unpaired electron to be 2–4 phenylene units.[226] Polynuclear structures appear to be involved as discussed in the previous paragraph.[193]

The ESR signals from PPP synthesized via different routes have been examined.[202,204,227] Comparable spin densities (ca. 10^{18} spins/g) were obtained for PPP prepared from, (1) various catalyst–oxidant combinations;[4,66,73,77] (2) aromatization of poly(1,3-cyclohexadiene) by chloranil[186] or halogen and heat;[234] (3) cycloaddition of a bis(pyrone) with a bis(acetylene);[235] and (4) decomposition of the bis(diazonium) salt of benzidine with Cu(I) as the promotor.[231] However, PPP obtained from the Grignard method of Yamamoto et al.[128] or Taylor et al.[129] exhibited a radical density of only 10^{16} spins/g. Froyer et al.[202] attributed the difference in spin densities between the Yamamoto[128] and Kovacic[4] polymers to the presence of polynuclear structures in the latter material. Similar reasoning was applied to explain the difference between the Taylor and Kovacic polymers.[227]

Biphenyl and terphenyl undergo oxidative nuclear coupling upon treatment with $AlCl_3/CuCl_2$.[103] The predominant product from either starting material was *p*-sexiphenyl, which exhibited a radical density of 3×10^{17} spins/g.[19] This value was essentially unchanged after purification by recrystallization or sublimation. Highly purified *p*-sexiphenyl and commercial *p*-quaterphenyl displayed low concentrations of unpaired electrons (10^{16} and 10^{15} spins/g, respectively), whereas commercial *p*-terphenyl and biphenyl produced no ESR signal. In contrast other investigators observed no signal (less than 10^{14} spins/g) for rigorously purified hexamer.[236] The difference might arise from the presence, in some cases, of polynuclear impurities generated during the coupling reaction. LD/FT mass spectrometry provides evidence for the formation of such structures.[107]

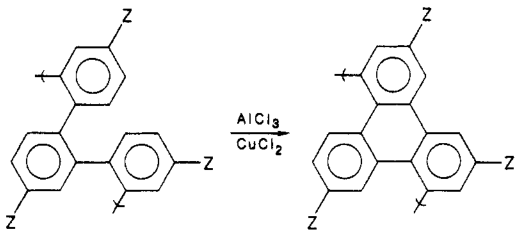
Polymers of chlorobenzene and toluene prepared by treatment with $AlCl_3/CuCl_2$ exhibited radical cation concentrations comparable to that of PPP[18] (~4×10^{18} spins/g). These results were unexpected, since the products appear to contain a poly(*o*-phenylene) backbone (**27**) rather than the poly(*p*-phenylene) type.



27

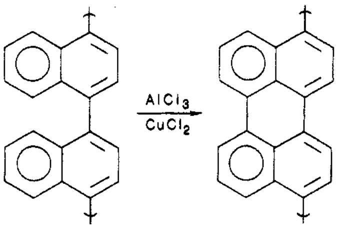
Z = Cl, CH_3

Stabilization of a radical in such a structure is severely curtailed, because steric interference prevents coplanarity of the aromatic rings. The observed ESR data were rationalized on the basis of formation of polynuclear structures (eq 11), which would provide stabilization to the radical cations. Existence of such structures was supported by C/(H + Cl) ratios from elemental analyses.

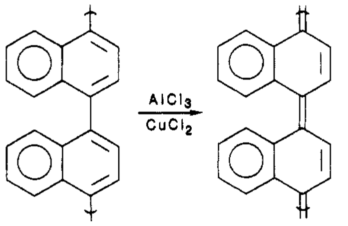


(11)

Likewise naphthalene and 1-chloronaphthalene were polymerized by exposure to $AlCl_3/CuCl_2$ to yield materials with ESR signals which corresponded to 2–5 × 10^{18} spins/g.[18] The lack of coplanarity between adjacent naphthalene nuclei (for example, 1,1′-binaphthyl exists in two enantiomeric forms, with an energy barrier to racemization of 21–23 kcal/mole[237]) was expected to preclude high spin densities in the polymeric products. The observed ESR data were explained in terms of polynuclear (eq 12) and/or quinoidal structures (eq 13), either of which would increase the delocalization of radical cations present.



(12)



(13)

2. IR and Raman

Because of the insolubility of PPP, vibrational spectroscopic techniques have been widely used for its characterization. The strong absorption band at ca. 800 cm^{-1} in the IR spectrum of PPP serves to verify the presence of the para structure (see section III.A.). As mentioned previously, IR spectroscopy has also been employed for approximate molecular-weight determinations (see section III.B.). Infrared absorption band intensities and frequencies have comprised the base for a theoretical study of the electronic structure of PPP.[238] From this work, the polymer was suggested to possess a π-electron system delocalized within individual phenylene rings, but not along the length of the chain. More recently, IR spectra have been used in comparisons of PPP samples prepared by different routes[75,239,240] and for information regarding structural changes in PPP brought about by doping with electron donors or acceptors.[239] As discussed in section III.B., the ratio of mono to para C–H out-of-plane absorption band intensities and the frequency of the para band in the IR can be employed as an indicator of molecular weight.

From photoacoustic[239] or transmission[240] FT IR spectra, PPP prepared via the Kovacic method[66] was found to have a smaller ratio of mono/para absorption intensity and a lower para absorption frequency than PPP prepared via the Yamamoto method.[128] Annealing of Kovacic PPP brought about a diminution of the intensity of the monosubstituted absorptions and a shift of the para band from 809 to 803 cm^{-1}.[239] Both results were consistent with an increase in the degree of polymerization. Similar experiments carried out on Yamamoto PPP resulted in like changes which were smaller in magnitude.

The doping of Kovacic PPP with electron donors (e.g., Na or K) or electron acceptors (e.g., AsF_5 or SbF_5) darkens the polymer drastically, rendering transmission IR spectra of the doped polymers virtually unattainable. However, photoacoustic FT IR measurements have provided valuable information.[239] Donor doping did not cause a shift in the para C–H absorption frequency, whereas a shift of that band from 809 to 805 cm^{-1} was observed for SbF_5-doped PPP. These results were indicative of chain extension during acceptor doping but not during donor doping. This interpretation is supported by the observations that films of biphenyl or terphenyl can be converted to conductive PPP, via simultaneous polymerization and doping upon treatment with AsF_5.[108]

Raman scattering measurements have also been made for Kovacic PPP (native and AsF_5 doped)[241,242] and for native Yamamoto PPP.[241] Both the Kovacic and the Yamamoto polymers exhibit strong fluorescence which masks the Raman signals when excitation in the visible region is used. However, with UV excitation, Raman bands at 1216, 1276, and 1598 cm^{-1} were clearly observed. Similarly, the Raman spectra of Yamamoto PPP had peaks at 1222, 1282, and 1600 cm^{-1}. A Raman study of p-phenylene oligomers from biphenyl to sexiphenyl revealed an increase in the ratio of intensities between the bands at ca. 1220 and 1277 cm^{-1} as the number of phenylene rings in the oligomer increased.

Upon doping, the intense fluorescence of Kovacic PPP disappears from the Raman spectrum.[241,242] Three main bands are observed at 1598, 1320, and 1236 cm^{-1} when the exciting wavelength is 647.1 nm. The former band is independent of exciting wavelength, but the latter two shift to 1275 and 1216 cm^{-1}, respectively, when the exciting wavelength is decreased from 647.1 to 406.7 nm. The latter two modes were proposed to be associated with quinoidal structures in the polymer.

3. NMR

The insolubility of poly(p-phenylene) precluded the use of NMR spectroscopy to characterize the polymer until relatively recently. In 1980, the first NMR spectrum (^{13}C) of PPP was obtained via cross polarization, magic angle spinning (CP/MAS) techniques.[243] Since that time, other ^{13}C NMR[227,236,244,245] and ^{1}H NMR[246] studies have been reported.

PPP exhibits two resonances in the ^{13}C NMR spectrum. The peak at 139 ppm has been assigned to the nonprotonated carbons (i.e., the para-linked carbons) and the peak at 128 ppm to the remaining, equivalent carbons. These assignments were made by comparison to oligo(p-phenylene) models,[236,243,244] by examination of the shifts in resonance positions of alkylated PPP relative to native PPP,[243] and from dipolar dephasing experiments.[236,244] In the two earliest studies, the resonance for the nonprotonated carbons of PPP and model oligomers (139 ppm) was found to be more intense than the resonance for the protonated carbons (128 ppm), even though more of the latter type of carbons are present in each of the samples. This result was explained in terms of a high degree of π-conjugation between rings. However, in a later study[236] of the same oligomers and PPP, the relative peak areas for the protonated vs. nonprotonated carbons were found to agree quite well with predicted values based on molecular structure. The previous anomalous results[243,244] were attributed to instrumental shortcomings.[236]

The proton spin-lattice relaxation times (T_1) of the oligo(p-phenylenes) were found to decrease with increasing chain length,[236,243] ranging from 910 s for biphenyl to 0.48 s for PPP.[236] Two explanations for this result have been advanced—the rate of molecular motion[243] and the presence of paramagnetic centers.[236,243,245,247,248] Molecular motion was proposed to be much slower for the lower oligomers in the series, perhaps attributable to their increased crystallinity relative to PPP.[243] Recent solid-state deuterium NMR studies of PPP reveal that the predominant modes of motion in amorphous regions of the polymer are 180° flips of the phenyl rings.[249] From relaxation experiments, the correlation time (τ_c) of the flips has been determined to be approximately 10^{-7} s at ambient temperature. The concentration of paramagnetic centers (i.e., unpaired electrons) decreased from 10^{18} spin/g for PPP[1,4] to no observed signal for terphenyl or biphenyl,[243] following the trend of increasing T_1 values. When the spin density of PPP was diminished by refluxing with N,N-dimethylaniline,[187,245] the T_1 was increased,[245] in agreement with the previous results.

The chemical shift of protons in PPP has been found to be 7.8 ppm, with a full width at half-height of ca. 14 ppm.[246] The lineshape was approximately Gaussian, and was attributed to relaxation broadening or to heterogeneities in the sample. Doping of the polymer with electron donors resulted in an upfield shift of the resonance (relative to native PPP), whereas a downfield shift was observed for acceptor-doped PPP.[246]

4. Mass Spectrometry

Few studies relating to the use of mass spectrometry for characterization of poly(p-phenylene) have been reported, owing to the nonvolatility and infusibility of the polymer. Pyrolysis mass spectra of plasma polymerized benzene showed fragments originating from phenylene (C_6H_4) structures.[99] From the data, the authors proposed the structure for plasma polymerized benzene to be that of poly(p-phenylene).

More recently, laser desorption/Fourier transform mass spectrometry (LD/FT MS) has been employed for studies of PPP prepared via different routes.[107,193] PPP synthesized from $C_6H_6/AlCl_3/CuCl_2$ was found to have a DP$_n$ of 12–14, in good agreement with previous molecular weight determinations (see section III.B.). Three chemically distinct oligomers were found for each chain length—PPP, which accounted for the majority of the chains, and much smaller amounts of monochlorinated PPP and PPP with polynuclear end moieties (see section III.A.). Each chain length population differed by exactly 76 amu, corresponding to a C_6H_4 unit. Thus, the chlorine of the monochlorinated species was assigned to an end rather than an internal chain. Substantially greater populations of chlorinated oligomers were obtained when benzene was polymerized with $FeCl_3$.[193] Interestingly, oligomers with masses characteristic of the presence of polynuclear moieties were not observed. These data were suggestive of different mechanisms of termination of the growing polymer chain. With $AlCl_3/CuCl_2$, termination appears to involve intramolecular dehydrocoupling to yield polynuclear species, whereas $FeCl_3$ terminates the chain via chlorination of the end ring(s).[193]

Previous investigations attributed the color of PPP at least partially to the presence of polynuclear units.[202,224] LD/FT MS data, although substantiating the existence of oligomers with the requisite condensed ring structure, does not support this hypothesis. PPP prepared from $C_6D_6/AlCl_3/CuCl_2$ is much lighter in color than that synthesized from C_6H_6, but it contains a significantly larger population of oligomers with polynuclear structures.[193] The darker color of regular PPP relative to perdeutero PPP was ascribed to the concentration of free radicals in the final products (2×10^{18} spins/g vs. 8×10^{16} spins/g, respectively).

The chain length of PPP from $C_6H_6/AlCl_3/CuCl_2$, as determined by LD/FT MS, was relatively unaffected by increasing the polymerization temperature from 20 °C to 80 °C. However, the proportion of monochlorinated oligomers at each chain length increased and, as expected, the fraction of material with polynuclear moieties decreased.

Products from oligomerization of biphenyl and terphenyl with Lewis acid catalyst/oxidant systems have been examined by LD/FT mass spectrometry.[107] The sexiphenyl fraction from biphenyl contained significant amounts of polynuclear material, whereas little, if any, condensed moieties were found in the terphenyl product.

5. UV

The use of ultraviolet spectroscopy in studies of the molecular weight of PPP has previously been discussed (see section III.B.).

Thin films of Kovacic PPP exhibit an absorption maximum at 379 nm,[250] in agreement with results from reflectance measurements.[188] In a separate study, the UV–visible absorption threshold was found to be 442 nm, which corresponds to 2.8 eV.[240,251] This value has been suggested to be the minimum optical gap (i.e., band gap) for PPP.[240,251] Previous workers reported a band gap of 3.4 eV, from diffuse reflectance measurement of λ_{max}.[108] The latter value is in good agreement with theoretical calculations (valence effective Hamiltonian technique) for coplanar PPP.[252]

6. Diffraction Techniques

Poly(p-phenylene) prepared by the Kovacic method gives an X-ray diffraction pattern characteristic of a semicrystalline material.[253] Annealing the polymer at 400–500 °C increases the crystallinity and yields a sharp diffraction pattern.[253] A very similar sharp pattern is observed for PPP prepared by the Yamamoto method.[128] The most intense reflection is observed at about 4.53 Å and has been attributed to the lateral packing of PPP chains.[253] Similar results have been obtained from electron diffraction[254-256] and neutron diffraction.[257-259]

Previous X-ray diffraction results were not able to distinguish between monoclinic and orthorhombic unit cells.[251,253] From one electron diffraction study the unit cell was proposed to be monoclinic.[254] Neither the diffraction pattern of the upper layers in a fibril nor the interreticular distance (reflection 002) could be explained on the basis of an orthorhombic system. However, a second investigation, employing oriented, annealed PPP, yielded an electron diffraction pattern attributable to an orthorhombic unit cell.[255]

E. Morphology

Morphology has been investigated in detail by X-ray or electron diffraction for PPP prepared by the $MoCl_5$ or $FeCl_3$ methods.[260] The $MoCl_5$ route produced well-developed fibrillar structures with the molecular axes oriented parallel to the fibril axis. Presumably, these structures arise from propagation involving chain ends aligned on the crystalline surface of the precipitated polymer. Chain distortion may come about through undesirable side reactions and precipitation of lower oligomers. In the case of the $FeCl_3$ polymer, aggregates composed of many crystalline fragments with indefinite shape were formed. The molecular orientation could not be ascertained since electron diffraction gave only broad Debye rings. Presumably, the crystal structure is the same as for the $MoCl_5$ product. The differences are attributed to enhanced participation of side reactions which produce structural irregularity when $FeCl_3$ is used.

A similar study was made with PPP from the $AlCl_3/CuCl_2$ system.[261] From a microscopic examination, the powder was comprised of rods surrounded by unorganized microscopic powder. The rods are made up of fibrils packed in globular structures. Annealing enhanced the crystallinity and microhardness.

F. Mechanical Properties

Variables were examined which influenced the mechanical properties, e.g., tensile strength, of PPP. Good results were obtained by pellet formation at 520 MPa at room temperature followed by sintering at about 600 °C.[192] When the powder itself was sintered or slightly oxidized, fabrication was not possible. High surface area (>35 m^2/g) and low Cl content gave best results. The heating process reduced the amount of Cl present. By addition of inert, nonpolar solvent during the polymerization process, BET surface area was increased. The irregularity or smoothness of the powder structure, as determined by scanning electron microscopy, could be altered substantially by changes in monomer concentration and speed of stirring. There was little or no correlation between fabricated strength and the crystallinity as judged by X-ray diffraction. Under optimum conditions, shaped samples with a tensile strength of 5000 psi could be obtained. The Marvel PPP, prepared by anionic polymerization of 1,3-cyclohexadiene followed by aromatization, exhibited low surface area for the powder and poor strength for the compacted objects.

Mechanical properties of fabricated PPP were compared to those of commercial polyimide and carbon graphite, and were found to fall between the properties of the two.[262] PPP retains toughness over a wide range, but is inherently less tough than polyimide. In high-temperature air-aging studies, property retention was similar to that of polyimide, but the values were lower at the start. It seems that metal-containing impurities, probably mostly copper, accelerate the oxidative degradation of PPP. High-temperature hydrolytic stability of the aromatic polymer was excellent, as would be expected.

A curious, unusual phenomenon was observed in the ablation–compaction of PPP.[263] When a compacted bar drilled with holes was heated at 590 °C under hydrogen pressure, the recovered sample resembled the original very closely except that it was substantially smaller in all dimensions, including the holes. The overall reduction could be as much as 80%. This can be regarded as the chemical counterpart of the aboriginal "shrunken heads". Apparently, as pore volume increases during ablation, surface area increases, in conflict with thermodynamics which requires minimization of surface area. Contraction occurs in order to minimize the energy. No other polymer tested gave a similar result, suggesting that PPP may be unique in this property.

Other mechanical properties are addressed in prior reviews.[1,264]

G. Other Physical Properties

Poly(*p*-phenylene) is a thermally and thermooxidatively stable material. No significant decomposition occurs below 400 °C in air[4,73,77,265,266] and only 7% of the mass is lost when the polymer is heated in N_2 to 900 °C at a rate of 150 °C/h.[266] Thermal loss of H and CH_4 from PPP begins about 400 °C, whereas analogous decomposition of benzene occurs at approximately 600 °C.[267] The decreased thermal stability of PPP relative to benzene was attributed to structural irregularity and presence, in the polymer, of residual impurities such as Cl and O.[267] PPP has been reported to have a greater resistance to thermooxidative degradation than benzene[268] and lower *p*-phenylene oligomers.[268,269] The temperature at which thermal oxidation commenced was determined by defect structures in the polymer.[268] The enhanced stability was attributed to coplanarity of rings,[269] strong intermolecular interactions,[269] and high conjugation energy.[270] Thermal and oxidative degradation of PPP is a complex process which consists of bond cleavage and formation of a crosslinked carbon char.[265,266,271,272] Upon further heating to 2800 °C, the char readily graphitizes.[272]

PPP is also resistant to radiation. The strength of a compressed pellet of the material was essentially unchanged following exposure to 8.95×10^8 rads from a Co^{60} source.[273]

H. Electrical Conductivity on Doping

There has been a large upsurge of activity since the discovery that conjugated polymers are converted to highly conducting materials by doping with either electron acceptors or electron donors. A wide range of electrical conductivities (insulator, semiconductor, metallic), covering 18 orders of magnitude, are obtainable merely by varying dopant concentration. PPP can be classed as one of the top two or three polymers in this domain with regard to the degree of attention and promise of practical application. Considerable effort has been devoted to fundamental and practical investigations of doped PPP,[273] particularly by the Allied group which has recently reviewed this aspect in a broad general manner.[5,274,275] Another fine review is available from Wegner.[190] As a result, this topic will be presented as a brief abstract from the prior coverage.

The parent polymer is a nonconductor ($<10^{-12}$ S/cm). Exposure to AsF_5 produces a dramatic increase to greater than 500 S/cm which is close to the value of 1200 S/cm for polyacetylene. Mechanistically, it appears that hole conductance is involved in the acceptor cases. Evidence has accumulated to support the contention that the best conductivity is associated with polymers having the highest degree of homogeneity. Copolymers generally produce poorer results than the corresponding homopolymers. For example poly(*p*-phenylenevinylene), the copolymer of PPP and polyacetylene, yields a value of 3 S/cm on doping. The decline seems to be the result of carrier localization in the nonhomogeneous systems. Also, theoretical support is provided by ab initio quantum mechanical calculations which demonstrate a correlation between homogeneity and width of the highest occupied π band. In accord is the low conductance (10^{-3}–10^{-2} S/cm) obtained from poly(*m*-phenylene). Evidently, an even lower figure would result except for crosslinking effected by the dopant, which exerts a beneficial effect.

Results have been reported from the AsF_5 doping of various oligomers in the *p*-phenylene series.[108] The conductivities (S/cm) were: terphenyl, 50; quaterphenyl, 6.8; quinquephenyl, 5.8; and sexiphenyl, 7.4. Correlations based on differences in chain length are not possible since the oligomers undergo dopant-induced chain extension. Indeed, PPP (15 monomer units) itself behaves similarly based on end-group analysis and loss of hydrogen.

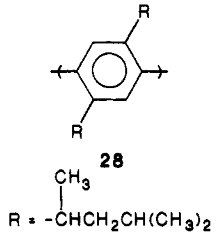
In the electron donor category, conductivity (50 S/cm) can be attained with alkali metals, but the level is an order of magnitude lower than for AsF_5. The electron mode of conductance pertains in contrast to the electron acceptor category. Since chain extension is not apparent with metal doping, the influence of differences in chain length can be determined. For *p*-sexiphenyl and potassium, the value is 0.5 S/cm, slightly lower than the 30 S/cm figure for PPP.[108]

Correlation of structural parameters with conductance has been treated in the prior reviews, and by Froyer et al.[240] It is reasonable to designate molecular weight as a factor. Since chain extension[108,208] evidently occurs during doping by AsF_5, the degree of end group halogenation should have an influence. The presence of polynuclear regions, as indicated by laser desorption/Fourier transform mass spectrometry, might also play a role.[107,193] Solid-state multiple-pulse proton NMR studies of doped PPP have been made.[246]

I. Other Chemical Reactions

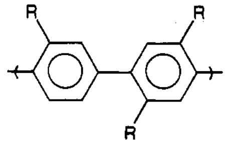
1. Alkylation

Although early attempts to effect Friedel–Crafts alkylation failed with ethyl bromide, isopropyl bromide, *tert*-butyl chloride, and 2,4-dichlorobenzyl chloride,[194] later work met with success,[191] indicating appreciable specificity. Best results were observed with *n*-propyl chloride or bromide and aluminum chloride. Evidence supports assignment of structure **28** to the product. It is apparent that substitution occurs with concomitant dimerization of the alkylating agent. Derivative **28** is of particular interest because of its solubility in chloroform which permits indirect determination of the molecular weight of PPP (see section III.B.). With isopropyl bromide, the weight increase and elemental analysis corresponded to 1.5 C_3 units per phenylene ring. Based on these data and spectral characteristics, structure **29** appears to be a reasonable possibility. The mechanistic subtleties responsible for the difference in results from the various alkyl halides are difficult to rationalize.



28

$R = -CH(CH_3)CH_2CH(CH_3)_2$



29

R = *i*-C_3H_7

2. Halogenation

An appreciable degree of chlorination can occur with $MoCl_5$[77] or $FeCl_3$[73] during benzene polymerization, depending upon the conditions. Perchlorination of PPP has been realized with $Cl_2/AlCl_3/SnCl_4$,[194] and dichlorination with $SbCl_5$.[194] The unreported monochloro derivative was prepared from PPP (10 g), $SbCl_5$ (21 mL), and $SnCl_4$ (76 mL) at 70 °C for 5 h; weight gain and elemental analyses supported the assigned structure. Tribromination is reported.[194] In unpublished work, slightly less than two bromines per ring are introduced when PPP (1 g) is treated with Br_2 (1.7 mL) and $AlBr_3$ (2.6 g) in $SnCl_4$ (20 mL) at 50–55 °C for 2 h (based on weight gain and elemental analyses).

3. Reduction

Reduction with lithium in ethylenediamine yielded material having an average of nine hydrogens per ring.[194] Unfortunately, the product was insoluble, possibly owing to the participation of cross-linking reactions.

In more recent work, hydrogenation was cleanly effected, albeit in low yield, at high temperature and pressure with rhodium catalyst.[195] Structure **22** for the product is consistent with the evidence. Molecular weight data (section III.C.), in comparison with MW from the alkylation approach, may be interpreted on the basis of reduction entailing the shorter chains only.

4. Heat Treatment

Heat treatment of PPP has been carried out with various degrees of severity and for a number of different reasons. Exposure of pellets to temperatures of 400–600 °C was done in connection with studies on X-ray diffraction,[253] conductivity,[276] fabrication,[192] and mechanical properties.[262] In addition to standard annealing effects, the procedure had the desirable result of a drastic reduction in chlorine content.

Degradative pyrolysis, performed as part of polymer characterization, afforded lower oligomers: biphenyl, *p*-terphenyl, *p*-quaterphenyl, and *p*-quinquephenyl.[4] A detailed study of thermolysis was reported with emphasis on ESR, types of radicals produced, and gas-forming processes.[225] Untreated samples possess an unpaired electron which is inert to oxygen and nitric oxide. Pyrolysis gave radicals, presumably formed by chain cleavage, which did interact with nitric oxide. At 250–600 °C, HCl was the principal gas evolved. In the 600–700 °C range, H_2 was the main volatile species, and the residue was shown to be highly crosslinked. Kinetics and activation energies for the gas-forming reactions were determined, and mechanistic features were discussed.

TGA studies have been done by various investigators.[4,73,77,265] The thermogram (inert atmosphere) revealed that breakdown occurred at about 700 °C with a total weight loss of 18% (82% carbonaceous residue) at 900 °C. The most volatile materials formed from PPP on a hot nichrome coil were H_2 and CH_4 (20:1 mole ratio). Char yields, measured at 900 °C, attained a maximum value of 85% at a chlorine content of 6–8%. Samples with higher C/(H + Cl) ratios, presumably due to polynuclear structures, also exhibited increased amounts of char. The ablative characteristics were determined with an oxyacetylene torch at about 2000 °C. Best results (a hard, tightly adhering char layer) were obtained with cured PPP, C/(H + Cl) of 1.8 and 4–5% Cl, mixed with silica or carbon fibers.

In an investigation aimed at the preparation of graphite substitutes,[277] pellets were fired at 650–2500 °C. Mixtures with B, ZrB, Ir, SiC, or graphite were similarly treated. Polymers from toluene and naphthalene were included in the report.

Ablation carried out under H_2 at 590 °C generated CH_4 and C_2H_6.[263] Most of the organic polymer was converted to volatile products. The residue was composed equally of PPP and inorganic materials carried over from the synthesis.

Thermal degradation of PPP prepared from $C_6H_6/FeCl_3/H_2O$ was examined in vacuum at 350–620 °C.[278] Polymer carbon was formed together with H_2 as the major gas and CH_4 as the minor one. TGA (vacuum or under N_2) revealed a moderate, two-step weight loss with the highest volatilization rates between 500–550 °C and at about 700 °C. A similar study was made with material synthesized from $C_6H_5OH/FeCl_3/H_2O$.

5. Oxidation

During microanalysis, vigorous conditions must be used in order to effect complete combustion of the powder. When the pellet is heated with a Bunsen burner in air, the sample glows and slowly decomposes by oxidation/pyrolysis, but there is no self-sustaining flame. TGA data in air have been presented.[1,264] Air aging studies at 316 °C were carried out with fabricated samples.[262] Oxidation is quite likely promoted by trace amounts of metal impurities, e.g., copper salt.[262]

6. Cross-Linking

Fusible, soluble, branched polyphenylenes can be prepared from treatment of a mixture of biphenyl and *m*-terphenyl with $AlCl_3/CuCl_2$.[105] Thermosetting of the resin was accomplished with *p*- or *m*-xylylene glycol and acid catalyst. Cross-linking of diphenylamine polymers is described elsewhere.[138]

7. Others

Other aspects of the chemical properties of PPP are available in a prior review, including sulfonation, nitration, cross-linking, and isomerization.[1] Impure amine was obtained by reduction of the nitro derivative, and the phenolic derivative resulted from caustic fusion of the sulfonic acid.

J. Uses

There is a wide spectrum of potential commercial applications for polyphenylenes. Current attention is focused on their use as electrode materials in electrochemical cells and in light-weight rechargeable batteries of high energy and power densities.[5,190,274,275,279–289] In these applications, PPP is doped to a conductive state, either electrochemically (in situ) or prior to use. PPP has also been employed in the preparation of modified Ti[290] and Pb[291] electrodes, which were subsequently tested for capabilities in the generation of hydrogen and oxygen from aqueous solutions. Nondoped PPP has been claimed to be useful in electrical devices as an insulating layer in semiconductors.[292] Although conductive polymers are being marketed as shielding materials against electromagnetic and radiofrequency interference, alternative technologies, including metallized plastics and conductive plastic composites, are predominant. Wire and cable applications comprise a huge potential outlet. An attractive feature vs. copper and aluminum is the light weight. Also they possess a more uniform level of conductivity than polyethylene composites loaded with carbon black. Another substantial use could be in electric power load leveling stations. Other possible applications include solar cells, semiconductor devices, stabilized electrodes, and low-current circuitry.

PPP has been used as a support material for Co-based catalysts employed in hydroformylation of alkenes[293,294] and for Pt-based catalysts used to synthesize DMF from carbon dioxide, water, and dimethylamine.[295]

Three patents disclose the application of PPP as a solid lubricant.[296–298] Other patents deal with the use of PPP as a lubricant additive[299–302] which bestows the following favorable properties: thermal stability, rust inhibition, low coefficient of friction and wear resistance. PPP can be molded under pressure;[141,273,302–304] subsequent sintering at 500–600 °C produces a toughened material with good thermal and thermooxidative stability.

Various composite materials have employed PPP as a component. Among the other components have been ZrB,[277] SiC,[277] mica,[305] and carbon or graphite fibers.[306-309] The composites possess good mechanical strength and exhibit high thermal and oxidative resistance. Hydroxylated PPP has been used in the preparation of a composite with polymethylenepolyphenylene isocyanate and fiberglass cloth.[310]

Pyrolysis of PPP or partially chlorinated PPP produces a microporous carbon[311,312] with moderately crystalline domains.[312] Carbonization of polymers obtained via Kovacic polymerization of pyrene or 1,3,5-triphenylbenzene yielded carbonaceous material with a high degree of graphitization.[313] Mesophase pitch suitable for formation of highly oriented carbon fiber was obtained from heat treatment of naphthalene or phenanthrene polymers prepared under Kovacic conditions.[314]

Miscellaneous uses claimed for PPP include a filler in rubber stock to increase the heat and thermal aging resistance of the vulcanizate;[315] a thin film optical shutter;[316] and a model for petroleum asphaltenes, in their complexing behavior with titanium tetrachloride.[317] Polynitrophenylene has been claimed to be useful as a binder in 4.7-mm munitions.[318]

K. Comparison of Poly(*p*-phenylene)s Synthesized by Various Routes

In addition to the Kovacic method,[4] the preparation of poly(*p*-phenylene) has been accomplished by dehydrogenation of poly(1,3-cyclohexadiene),[186] by Diels–Alder cycloaddition of 5,5′-*p*-phenylenebis(2-pyrone) with *p*-diethynylbenzene in solution at 200–300 °C,[235] by Grignard coupling of *p*-dibromobenzene employing nickel chloride dipyridyl[128] (Yamamoto method), or 1,4-dichloro-2-butene[129] (Taylor method) as promoters, by nickel(0) complex-catalyzed electropolymerization of *p*-dibromobenzene[319] (Fauvarque method), and by thermal treatment of polymers obtained from radical polymerization of derivatives of 5,6-dihydroxy-1,3-cyclohexadiene.[320] The latter route comprises a novel biotechnological approach to PPP, since the monomer is synthesized via oxidation of benzene with the genetically modified bacteria *Pseudominium putida*. Each of these methods produces colored (yellow to brown), insoluble, infusible powders. The infrared spectrum of each product is dominated by a strong absorption at 800–810 cm^{-1}, characteristic of para disubstitution of a phenyl ring. X-ray[186,235,253] and electron[254-256] diffraction are also quite similar. Thus, the gross structural features of the materials obtained from each preparation are undoubtedly the same.

More detailed examinations of the products from the usually employed methods (Kovacic, Yamamoto, Taylor, Fauvarque) have revealed differences. Analysis of the ratio of absorption values for the mono and para bands in the IR suggest that the Kovacic and Fouvarque polymers possess approximately the same chain length (12 phenyl rings),[319] whereas the Taylor and Yamamoto polymers are somewhat shorter (9 phenyl rings).[227] The IR data, however, are not substantiated by recent LD/FT mass spectral results, which demonstrate that the Kovacic and Yamamoto polymers have the same average degree of polymerization (14 rings).

The UV–visible spectra of the Kovacic and Fauvarque polymers is nearly identical, in absorption threshold, $\lambda_{\max}$ and width of absorption band.[319] This suggests that the two polymers possess similar chain length distribution and average molecular weight, in good agreement with IR data. In contrast, the Yamamoto polymer exhibits the same absorption threshold (2.8 eV) but has a broader absorption band and a $\lambda_{\max}$ that is shifted to higher energy,[240,251,319] indicative of long chains but a larger distribution of chain lengths.

The color of the Kovacic polymer is brown; the other three preparations yield yellow product. Previously, the color of Kovacic PPP had been attributed to the presence of polynuclear regions.[188] LD/FT mass spectral data clearly indicate the presence of such regions in Kovacic PPP and the absence of these moieties in Yamamoto PPP.[193] However, perdeutero PPP prepared by the Kovacic method contains a greater concentration of polynuclear species than normal Kovacic PPP, but is yellow in color.[193] A more reasonable explanation for the observed color differences is the concentration of radical species. Kovacic polymer possesses a spin density two orders of magnitude greater than Yamamoto[202,227,319] or Taylor[227] polymer and 1–2 orders of magnitude greater than Fauvarque polymer.[319]

T_1 relaxation times are shorter for the Kovacic PPP than for the Yamamoto PPP,[202] attributable to a large concentration of paramagnetic defects in the former polymer.

Elemental analysis and LD/FT MS data reveal that the percentage of halogen present in the polymers is smaller for Kovacic and Fauvarque PPPs (2% Cl and 4% Br, respectively)[193,319] and greater for Yamamoto and Taylor PPPs (6–8% Br).[129,193] In the Kovacic preparation, halogenation is postulated to be a competing reaction with formation of polynuclear moieties for termination of polymerization.[193] The presence of bromine in the other three products is attributable to unreacted end groups from the starting material. The lower halogen content of the Fauvarque polymer relative to the Taylor and Yamamoto polymers is suggestive of higher molecular weight for the former material, in accord with IR and UV results.[319]

For similar levels of doping with AsF_5, Kovacic PPP is almost two orders of magnitude more conductive (270 S/cm) than Yamamoto product. Earlier, these results were ascribed to a difference in chain length between the Kovacic and the Yamamoto polymers.[240] However, in view of the more recent findings of similar chain lengths for the Kovacic, Fauvarque and Yamamoto polymers,[193,319] the aforementioned conclusion should perhaps be reexamined. A major structural difference between the Kovacic polymer and the poly(*p*-phenylene)s prepared from *p*-dibromobenzene is the presence of polynuclear-terminated chains in the former case.[193] These moieties possess lower oxidation potentials than a corresponding straight chain and thus should be more readily doped to an electrically conductive state. Chain extension of lower oligophenyls (and presumably PPP) is known to occur upon doping with AsF_5.[108]

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Registry No. PPP, 25190-62-9.

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