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13. ABSTRACT *(Maximum 200 words)*

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Synthesis and Properties of Soluble Oligo- and Polyphenylenes. A Review

by

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Synthesis and Properties of Soluble Oligo- and Polyphenylenes

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Abstract

An overview of the synthetic routes and material properties of soluble oligo- and polyphenylenes is presented with comparisons of the soluble materials to the insoluble poly(*p*-phenylene) (PPP). Covered are main chain phenylene oligomers and polymers; not copolymers that contain non-phenylene units. The specific classes of compounds discussed are poly(*o*-phenylenes), poly(*m*-phenylenes), and substituted polyphenylenes consisting of alkyl-, aryl-, carbonyl-, alkoxy-, nitro-, halo-, fused aromatic-, and ladder-containing moieties.

I. Introduction

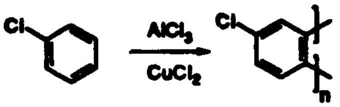
Polyphenylenes have been superbly reviewed by several investigators who have been dedicated to the advancement of this interesting class of compounds.[1-6] Most recent reviews dealt primarily with the *para*-form, poly(*p*-phenylene) (PPP), the most widely investigated constitutional arrangement of the polyphenylene materials. It is easy to appreciate why PPP has been the most widely investigated of the polyphenylenes upon observation of its extremely interesting electronic properties. In its neutral form, PPP is an insulator exhibiting less than $10^{-12}\ \Omega^{-1}\mathrm{cm}^{-1}$ conductivity; however, upon doping with AsF_5, the conductivity can rise beyond the semiconducting and into the metallic region at $500\ \Omega^{-1}\mathrm{cm}^{-1}$.[1,7] Recently, PPP has even been used in the fabrication of a blue light emitting diode.[8] Overshadowing these remarkable properties, however, is the fact that PPP is insoluble and intractable; even hepta(*p*-phenylene) is insoluble in common organic solvents. This intractability problem coupled with the environmental instability of doped PPP has thwarted any serious commercial development of the polymer.

Polyphenylenes often exhibit remarkable thermal stabilities. They have been considered for use in numerous thermally robust organic materials including composites, lubricant additives, hydraulic fluids, heat transfer agents, coolants for nuclear reactors, and thermoset precursors for high performance aerospace materials applications.[2,9] PPP is not the only constitutional form of the polyphenylenes that exhibits these excellent thermal properties. Appropriately substituted polyphenylenes or non-regioselectively linked polyphenylenes are often soluble and can, in some cases, exhibit thermal properties superior to that of PPP. Additionally, efforts to planarize PPP derivatives could lead to uses of these soluble ladder polymers in electronic devices and photonic-based nonlinear optical devices.[10,11]

It is the intent of this non-comprehensive review to survey the synthesis and properties of these less-well-studied soluble oligo- and polyphenylenes. Covered are main chain phenylene polymers and oligomers; not copolymers that contain non-phenylene units. The specific classes of compounds discussed are poly(*o*-phenylene)s, poly(*m*-phenylene)s, and substituted polyphenylenes consisting of alkyl-, aryl-, carbonyl-, alkoxy-, nitro-, halo-, fused aromatic-, and ladder-containing substituents.

II. Poly(*o*-phenylene) Derivatives

Syntheses of chloro-, fluoro-, or bromo-containing poly(*o*-phenylene)s have been achieved using the corresponding monohalobenzene in the presence of an oxidant such as $AlCl_3/CuCl_2$ (eq 1).[2] This oxidant system was extensively investigated by Kovacic to make the parent PPP from benzene.[1,2] The molecular weights of the chloro-containing poly(*o*-phenylene)s corresponded to a degree of polymerization of 10-12 with some polycyclic aromatic moieties being formed. These degrees of polymerization seem quite low with respect to conventional non-rigid rod polymers; however, these molecular weights are within the range of those normally obtained by many standard polyphenylene preparations.



(1)

From a conjugation standpoint that is based on a simple resonance model, one might conclude that poly(*o*-phenylene) should provide a long range π-conjugated pathway. However, there is a large sterically-induced twist angle that prevents the extended π-conjugation. This can best be explained by considering the parent PPP. Even PPP has a 23° twist between the consecutive aryl units due simply to ortho-hydrogen interactions (fig 1).[4] The π-orbital overlap

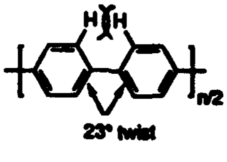


Figure 1. Steric interactions between the ortho hydrogens causing a 23° twist between the consecutive aryl units in PPP.

is a function of the cosine of the twist angle, therefore even at 23°, there is a fair amount of π-orbital overlap remaining. If one simply places substituents along the PPP backbone, the solubility can be enhanced, but the twist angle between the consecutive aryl units widens sufficiently to cause a plummet in the extended π-electronic overlap and a broadening in the band gap with a corresponding diminution in the overall conduction properties (fig 2).

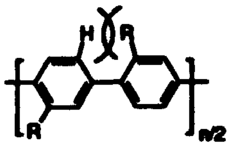


Figure 2. Increase in the twist angle due to more severe steric interactions upon introduction of a substituent onto the polyphenylene backbone.

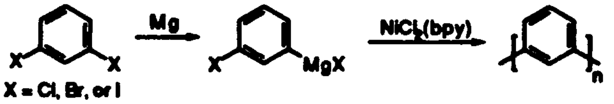
This is in concert with the low overall conductivity of poly(*o*-phenylene)s and substituted PPP derivatives.[4] Similarly, as a result of this decrease in extended π-overlap, standard UV methods can not be used to determine degrees of oligomerization in poly(*o*-phenylene).[2]

Most compounds that display good thermal stability contain a predominance of aromatic moieties. For the oligophenylenes, the *ortho*- and *meta*-fused oligomers have considerably lower melting points than the *para*-fused oligomers. For example, in sexiphenylene, the *ortho*-, *meta*- and *para*-linked compounds have melting points of 216, 147, and 475°C, respectively.[2] While PPP has a polymer decomposition temperature (PDT, based on thermogravimetric analysis (TGA) deflections) in nitrogen of 660-675°C, the mixed *ortho*-, *meta*-, and *para*-system has a PDT of 590°C.[12] Thus the thermal stability is decreased upon the introduction of the non-*para*-linkages while the processability is substantially increased.

III. Poly(*m*-phenylene) Derivatives

Unsubstituted poly(*m*-phenylene) is far more soluble than PPP of a similar molecular weight, however, it eventually becomes insoluble as its molecular weight increases.[13] Extended π-conjugation in poly(*m*-phenylene) is prevented due to the lack of resonance beyond two phenylene units. Therefore, utilization of UV spectra for oligomeric length determination of poly(*m*-phenylene)s is not possible, and one would expect there to be no propensity to generate highly semiconducting systems from these materials. Accordingly, molecular orbital calculations predict a 6.2 eV ionization potential with a narrow bandwidth of 0.2 eV. However, upon doping with AsF_5, a conductivity of $10^{-3}\ \Omega^{-1}cm^{-1}$ was achieved, presumably due to a dopant induced cross-linking that resulted in an intractable PPP-like structure with significantly larger bandwidths.[4]

Poly(*m*-phenylene)s can be conveniently prepared using the Yamamoto procedure (eq 2).[13] Approximately 35% of the polymer formed is soluble in hot toluene. The X-ray diffraction pattern of poly(*m*-phenylene) shows broad peaks which may be attributed to the presence of both *cis-trans* and *trans-trans* conformations (fig 3). The analogous procedure can be used for the synthesis of PPP using a 1,4-substituted benzene. Poly(*o*-phenylene) can not be synthesized by this route since initial Grignard formation leads to elimination with formation of *o*-benzyne.



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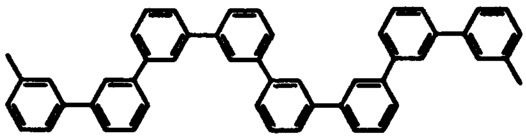
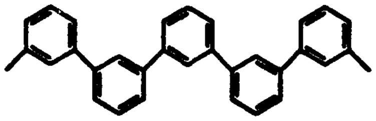


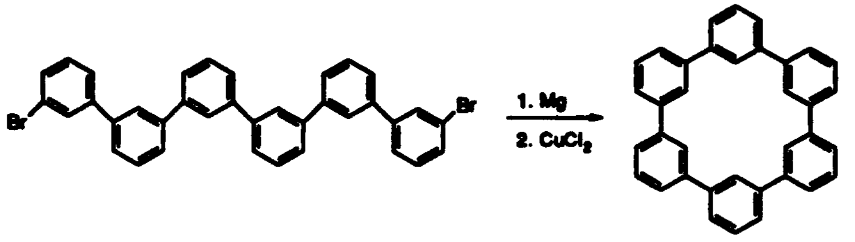
cis-trans



trans-trans

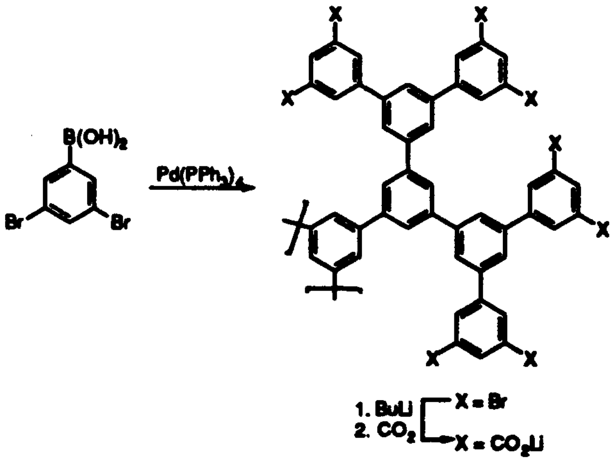
Figure 3. Two possible conformations of poly(*m*-phenylene).

A far less commonly used method has been described involving ethyl acetals of *m*-diacetylbenzene.[14] Some superb early synthetic work has been conducted on the synthesis of well-defined *m*-phenylene oligomers which provided an understanding of how the *meta*-phenylene linkage influences the absorption spectra and thermal properties of the extended phenylene systems.[15] Other studies showed that coupling of *meta*-linked phenylenes afforded cyclic structures (eq 3).[16]



(3)

Recently, the synthesis of a novel hyperbranched *meta*-linked polyphenylene was achieved using a Suzuki coupling in a mixed organic/aqueous medium (eq 4).[17] The polymer had an M_n = 3820 and M_w = 5750. A water-soluble derivative was prepared by lithium-halogen exchange at the bromide locations followed by addition of CO_2 to afford the water soluble lithium carboxylate which is analogous to a "unimolecular micelle".



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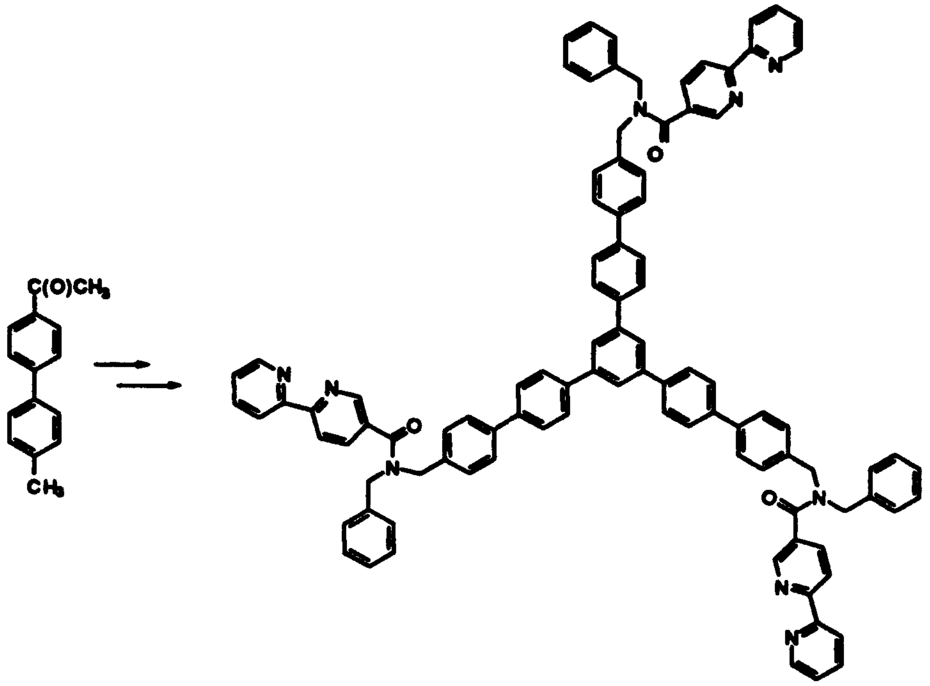
Other interesting 1,3,5-phenylated phenylenes have been prepared with end groups that act as ligands for transition metals (eq 5).[18]



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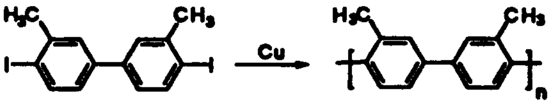
IV. Substituted Polyphenylenes

A. Alkyl Substituents

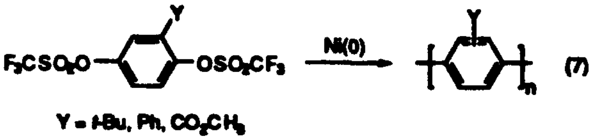
The all *para*-arrangement of a polyphenylene backbone can be made soluble if the phenylene units are appropriately substituted.[19a,b] The Ullman reaction has been used to homocouple 3,3'-dimethyl-4,4'-diiodobiphenyl to form soluble polymers of low molecular weight (eq 6).[2]



(6)

The Ullman coupling sequence is quite general and, in some cases, the molecular weights of the polymers prepared by the Ullman coupling have been reported to be unusually high, over 300,000.

Ni(0) homocouplings of bis(triflate)s have been used to prepare *t*-butyl (M_n = 1000-1500, PD = ~1.2), phenyl (M_n = 700 -2300, PD = 1.1-1.6), and ester-containing (M_n = 2400-6300, DP = 1.5-2.1) poly(*p*-phenylene)s (eq 7).[19c] This method of preparation also appears to be broad in scope.



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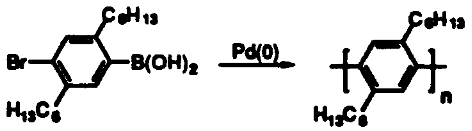
The Suzuki reaction has been used to prepare the soluble poly(*p*-2,5-di-*n*-hexylphenylene) with degrees of polymerization ~30 (eq 8).[20] These have been referred to as "hairy rods" with the rod (phenylene backbone) being the important feature from the electrical, optical, and mechanical viewpoints, while the hairs (alkyl side chains) impart solubility and processability to the material. However, as discussed earlier, the π-conjugation through the chain will be severely passivated by the enhanced twist angle imparted by the alkyl groups. This passivation effect can be clearly observed in the UV spectrum where λ_{max} = 250 nm for these alkylated polymers whereas *p*-sexiphenylene has λ_{max} = 318 nm.[21] Upon differential scanning calorimetric (DSC) analysis of the alkylated polymer shown in eq 8, varying the side chains had a marked effect on the transition into the isotropic melt with a transition from 290-165°C being observed on extension of the alkyl lengths. Thus a tremendous amount of variability in the thermal properties can be realized. This work has also been extended to the synthesis of copolymers containing mixed phenylene and alkylated phenylene units with varying branches (fig 4).[21] This methodology allows one to introduce controlled amounts of the non-substituted units to study the different phase behaviors as one approaches the parent PPP. Other methods



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have employed alkyl groups in conjunction with non-*para* linkages[2] or, most interestingly, introduced

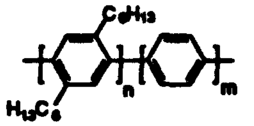
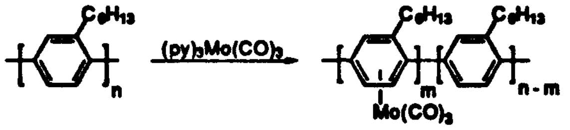


Figure 4. Copolymers containing mixed phenylene and alkylated phenylene units.

π-arene metal complexes to the alkylated polyphenylene to study the electrochemical behavior (eq 9).[22]



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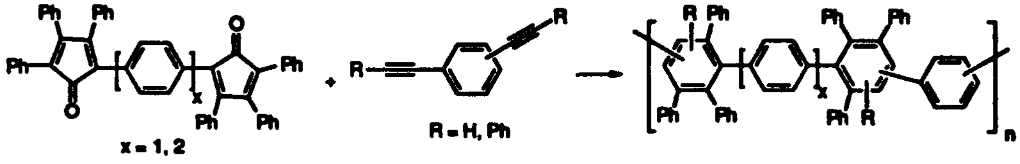
B. Aryl Substituents

A significant amount of work on phenylated polyphenylenes has been conducted using a Diels-Alder approach (eq 10). Molecular weights of 20,000-100,000 have been obtained with



(10)

~15% of the products maintaining their solubility in typical organic solvents. Similarly, pyrone-containing moieties have been used in the Diels-Alder route to these phenylated polyphenylenes.[2] The PDT of poly(phenyl-*p*-phenylene) in nitrogen and air was 575 and 550°C, respectively. Recall the PDT of PPP in nitrogen was 660-675°C, while in air, PPP's PDT is ~550°C.[12] Therefore, while the insoluble PPP is more stable under nitrogen; the soluble phenylated polyphenylenes are comparable in thermal stabilities, in air, to PPP.

Aryl-substituted oligophenylenes have also been synthesized with a high degree of control; the most interesting being the bis(hexaphenylene)benzenes (fig 5).[23]

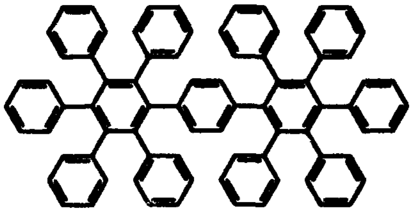
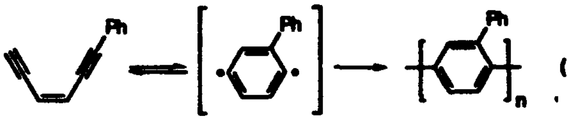


Figure 5. Bis(hexaphenylene)benzene.

Recently, we have been exploring the use of the Bergman cyclization[24] to generate a benzene 1,4-diradical from an enediyne followed by polymerization of the radical species (eq 11).[25] In general, the materials are soluble in typical organic solvents with M_n values ranging from 2,000-10,000 (SEC with PS standards).



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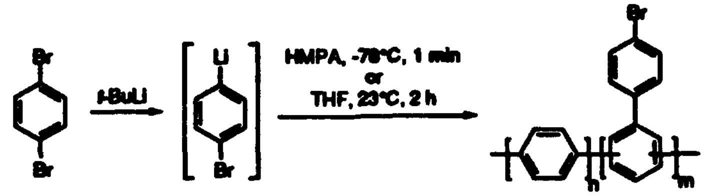
Early work by Goldfinger showed that one could generate soluble polyphenylenes by the Wurtz-Fittig coupling method using 1,4-dichlorobenzene and liquid potassium-sodium alloy.[26] It was later suggested that chlorophenyl polyphenylenes had formed. We discovered an interesting analogous process involving the polymerization of a 1-bromo-4-lithiobenzene intermediate.[27] The intermediate is generated by the mono lithium-halogen exchange on 1,4-dibromobenzene. *t*-Butyllithium is used so that no alkyl bromide species remain in solution; the only by-products are isobutylene, isobutane, and lithium bromide. The polymerization can be nearly instantaneous even at -78°C if we inject hexamethylphosphoramide (HMPA), or it can be carried out in 2 h at room temperature in THF (eq 12). The product is a soluble poly[(*p*-bromophenyl)polyphenylene]. Many of the linkages are non-*para* which arise from a series of orthobenzyne intermediates. The polymers have a globular morphology by SEM analysis and they show no sharp diffraction signals by powder XRD. We also conducted analogous reactions on the 1,3-dibromobenzene as well as the iodo- and fluoro-containing analogs to generate iodo- and fluoro-containing phenylated polyphenylenes. These halophenyl polyphenylenes are particularly useful because they allow further coupling, via the halogenated carbons, to provide new polyphenylene-based materials.



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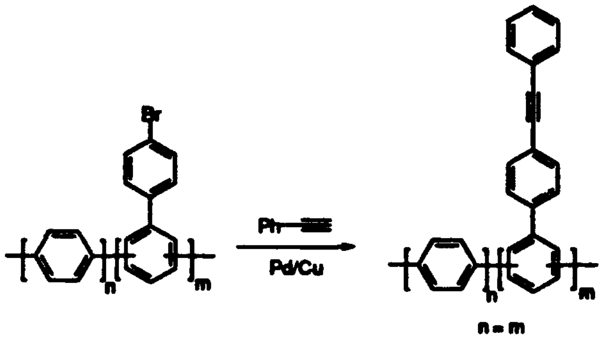
For example, we investigated the use of these high carbon materials in high char yielding thermoset precursors to glassy carbon.[9] Polymeric carbon materials, produced from the thermolysis of organic polymers in inert atmospheres, have seen numerous applications in the aerospace, electrical, medical implant, and automotive industries.[28] While phenolic resins have been used extensively as thermoset precursors of carbon, these resins typically exhibit 35-40% weight loss on thermolysis and densities of the carbon char are approximately 1.3 g/cc.[29] Due to the large weight losses and low density chars exhibited by phenolic resins, multiple impregnation cycles (usually 6-7) are required for adequate structural formation and raising the density to ≥1.8 g/cc (the density necessary for desired rocket booster ablative applications). While the phenolic resins only cost ~$2 per pound, the final carbon monolith for aerospace use often costs $1,200-$1,500 per pound, thus the expense comes from the number of impregnation cycles necessary. As a result, the development of high char yielding materials via few impregnation cycles has become a challenge. PPP has been studied for its applicability as a polymeric carbon precursor because of its high carbon-to-hydrogen ratio and near 80% char yields.[1,2] However, since PPP is insoluble and it can not melt or flow, it can not easily be used in thermosetting materials. Thermolysis (ambient to 900°C, nitrogen atmosphere) of the poly[(*p*-

bromophenyl)polyphenylene] (in eq 12), or the debrominated version, resulted in a 50% weight loss. Remarkably, functionalization of the brominated polymer with phenylacetylene using a Pd/Cu coupling system (eq 13) afforded a polymer that exhibited a 90% char yield while the charred material possessed densities of >1.80 g/cc after just one heating cycle. The alkyne-containing polyphenylene also exhibited a well-defined melting event at ~200°C while the major cross-linking event did not occur until ~310°C. Thus the functionalization of the polyphenylene afforded a material with superb properties for the formation of high density, high char yielding monolithic carbon materials.



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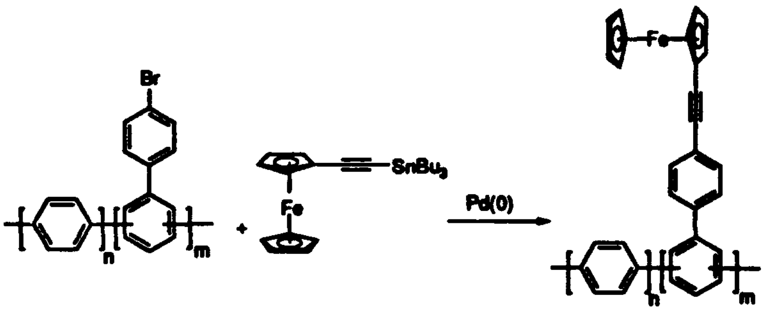
The poly[(*p*-bromophenyl)polyphenylene] was also converted to the alkynylferrocene derivatives (eq 14), but these showed no propensity for hole migration by electrochemical analysis. Two independent oxidation waves were observed, one for the ferrocene unit at E_{pa} = 0.60 V and the other for the polyphenylene at E_{pa} = 2.30 V (Ag/AgNO$_3$ at 0.01 M in CH$_3$CN at 50 mV/s with 0.10 M TEAP and a Pt working electrode).[30]



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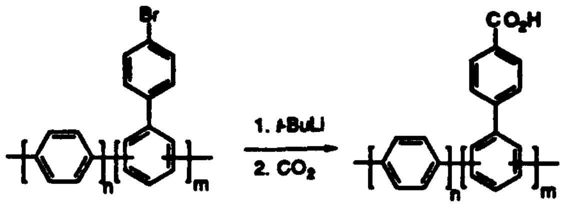
C. Carbonyl Substituents

As mentioned, the poly[(*p*-bromophenyl)polyphenylene] can be further functionalized. For example, lithium halogen exchange followed by quenching with CO_2 and protic work-up afforded the carboxylic acid containing polyphenylene which was soluble in aqueous base (eq 15).[27b]



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A water soluble polyphenylene carboxylate has been prepared in an aqueous medium using the Suzuki coupling process (eq 16).[31] Further work has shown that these polymers

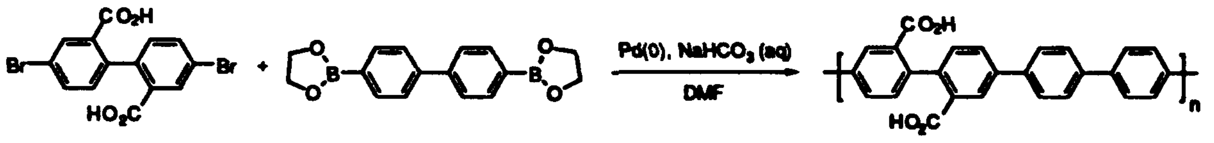

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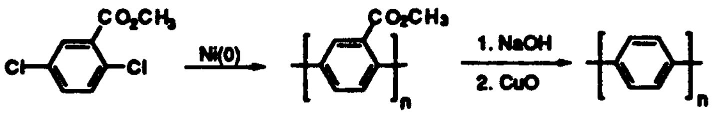
exhibit unusual rheological behavior because of their mixed hydrophobic and hydrophilic units as well as their rigid rod nature. No liquid crystalline phases have been seen and it has been suggested that intermolecular charge repulsions and hydrophobic attractions dominate their unusual solution behaviors.

Ni(0) homocoupling methods have been used to prepare the ester-containing polyphenylenes which can serve as soluble precursor to PPP upon decarboxylation (eq 17).[19,32]



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Other interesting carbonyl-containing soluble polyphenylenes that have received considerable attention are Maxdem Corporation's Poly-X (fig 6). Unfortunately, the synthetic details have not been disclosed though the "route involves relatively inexpensive materials." 33 Poly-X materials are soluble in common organic solvents and they exhibit numerous interesting properties which make them candidates for high performance applications. Poly-X compounds are melt processable even with ~100 phenyl units in the backbone. They are extremely rigid with moduli ranging from 1 million to 2.5 million psi (conventional engineering resins range from 300,000-600,000 psi). They are not highly crystalline and thus reasonably transparent. However, stretch orienting can give anisotropic materials for fiber applications and their processability may afford them important thermoplastic applications.

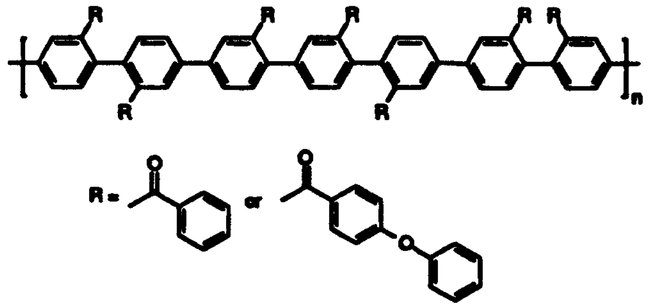
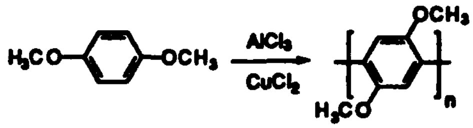


Figure 6. Maxdem Corporation's, Poly-X.

D. Alkoxy and Nitro Substituents.

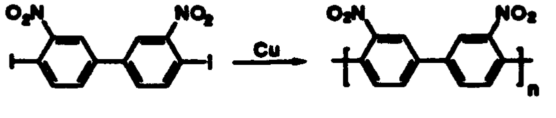
Poly(2,5-dimethoxy-*p*-phenylene) has been prepared by the oxidative coupling of *p*-dimethoxybenzene (eq 18).[34] The polymer was soluble in concentrated sulfuric acid, fusible at



(18)

320°C, and possessed a PDT of ~400°C. Other reports of a similar coupling using $FeCl_3$ on *p*-dimethoxybenzene and *p*-(di-*n*-butoxy)benzene gave polymers that were not cleanly *para*-linked.[35]

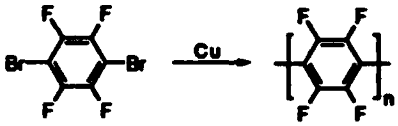
The Ullman coupling has been used to form a nitro-containing PPP with degrees of polymerization ~50 (eq 19). The nitro-containing system was soluble in nitrobenzene and DMF.[2]



(19)

E. Halogen Substituents.

Methods to generate soluble halogen-containing polyphenylenes have been described above in eqs 1, 4, and 12. Similarly, the Ullman reaction has been used to prepare fluorinated polyphenylenes of low molecular weight (eq 20).[2] In general, halogen substituents alone will not be sufficient for inducing solubility of a highly *para*-linked polyphenylene. One needs non-*para* linkages or other substituents to introduce disruptions in the crystallinity of the rigid rod polymer to afford soluble materials. For example, we prepared a brominated oligophenylene that was predominantly *para*-linked. It was insoluble and possessed a plate-like morphology by SEM analysis as opposed to the globular morphology of the randomly linked brominated versions.[27]

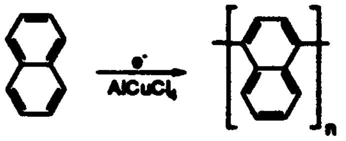


(20)

Halogenated polyphenylenes are generally less thermally stable than the parent PPP. However, the perfluorinated polyphenylenes are an exception. In a nitrogen atmosphere, poly(perfluoro-*p*-phenylene) exhibits a PDT of 720°C; considerably higher than the 660-675°C of PPP. Conversely, in air, PPP shows far more stability than the perfluorinated version.[12]

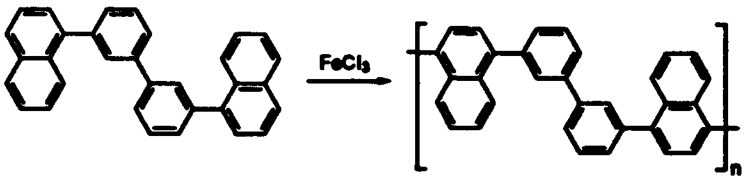
F. Fused Aromatic Substituents

A number of soluble fused aromatic ringed structures have been synthesized which can be viewed as polyphenylene-derived systems. Naphthalene or substituted naphthalenes can be polymerized electrochemically (eq 21) or using $AlCl_3$ or $AlCl_3/CuCl_2$ systems.[1,36] A number of



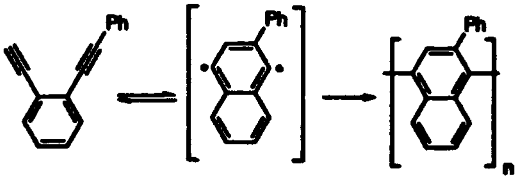
(21)

soluble mixed naphthyl-biphenyl polymers have been prepared using $FeCl_3$ as an oxidant in nitrobenzene (eq 22).[37]



(22)

We have utilized an arenediyne cyclization sequence to make polynaphthalene structures (eq 23) in a Bergman-like cyclization approach similar to that described in eq 11.[25]



(23)

Stoichiometric Ni(0) homocoupling procedures have been used on 1,9-dibromoanthracene for the synthesis of soluble poly(1,9-anthracene) as well as on dibromoquinolines and dibromoquinoxalines to form the three systems shown in fig 7.[38,39]

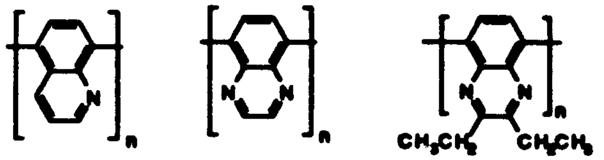
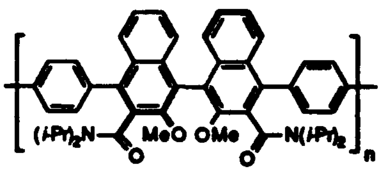


Figure 7. Poly(quinoline-5,8-diyl), poly(quinoxaline-5,8-diyl), and poly(2,3-diethylquinoxaline-5,8-diyl).

Interestingly, these nitrogen containing polymers are sufficiently election deficient so that they can not easily be oxidatively doped, but they can be reductively doped. In general, n-doped polymers are far less environmentally stable than p-doped polymers. However, this study may suggest that by inclusion of enough electronegative atoms (relative to carbon) into a polymer containing 6-membered aromatic rings, one could generate a reasonably stable n-doped conducting polymer by giving sufficient stability to the anionic form.

We have used a Ni(0) coupling to synthesize the chiral binaphthalene-containing polymer (fig 8) to study the degrees of optical rotation caused by a chiral polymer that is forced to remain linear rather than helical along its backbone.[40]



$[\alpha]_D^{24} = -63°$, c = 0.16, THF, (S)

Figure 8. A chiral non-racemic phenylene-derived polymer that is linear along its backbone.

G. Bridging Substituents to form Ladder Polymers with Polyphenylene Backbones

Conjugated ladder polymers are an extremely interesting class of compounds since one can, in principle, tune the twist angle between the consecutive aryl units.[41] For example, as shown in fig 1, there is a 23° twist between the consecutive aryl units of PPP. By placing a substituent on the ring, the twist angle increases and the extended π-conjugation is deterred (fig 2). However, by placing a bridging unit between the consecutive aryl rings (fig 9), one can

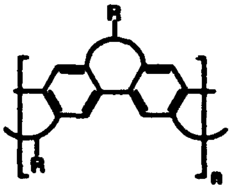


Figure 9. Bridging units permitting the control of the twist angle between the consecutive aryl rings. The R groups permit solubility of the ladder polymers.

maintain a near planar conformation between the consecutive aryl units while introducing the solubilizing handles, R groups, needed for processability. Moreover, by introducing an sp^2-hybridized two-atom bridge (fig 10), the extended π-conjugation will be further increased. The

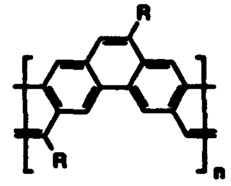
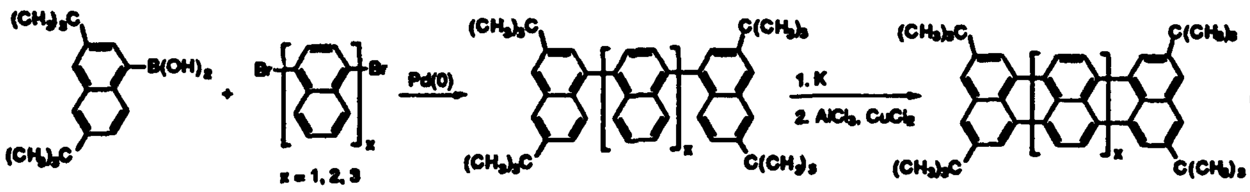


Figure 10. sp^2-Hybridized bridging units which permit a near planar conformation of the polymer while lowering the band gap.

diminution of the twist angle with concomitant increase of the extended π-conjugation can be of considerable importance for boosting the third order nonlinear optical responses; a factor that needs to be exploited for the obtainment of photonic-based devices.[11]

Procedures for the synthesis of substituted oligonaphthalenes and their conversion to the oligorylenes have been developed (eq 24).[42] Suzuki couplings and stoichiometric Ni(0)



(24)

couplings have been used to prepare a number of interesting planar or near planar polyphenylene-like structures (fig 11).[43] We used a similar procedure for the synthesis of planar polyphenylene derivatives wherein an imine formation allowed for the planarization while dodecyl groups permitted the solubility of the polymer and also induced a plasticizing effect to permit the formation of flexible free-standing films (eq 25).[10] There was an enormous bathochromic shift on planarization of the system (λ_{max} = 250 nm to λ_{max} = 490 nm). Infinitely long PPP is predicted to have λ_{max} = 344 nm[28b] while the planar polymer, based on the UV maxima, possesses a far more extended π-conjugation. Optical absorbance maxima that are far greater than that predicted for infinitely long PPP have been similarly observed in other planarized PPP derivatives.[43]

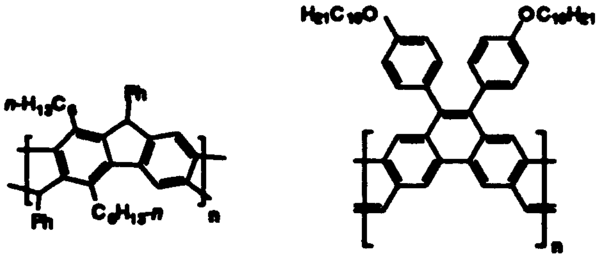
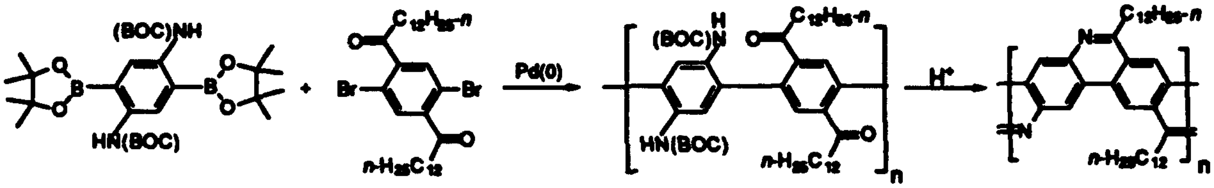


Figure 11. Planarized polyphenylene derivatives that have been synthesized.



(25)

V. Summary

Oligo- and polyphenylenes are an exceeding interesting class of organic compounds. Though the parent PPP is highly insoluble and infusible, soluble versions have been developed which often mimic or surpass PPP in desired high performance material properties. Solubilizing features can include non-*para*-linkages in the main chain as well as substituents along the phenylene backbone. As new synthetic approaches and methodologies are applied to the generation of soluble oligo- and polyphenylenes, important advances in electronics, photonics, and thermally robust polymers are destine to be realized.[44]

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References

[1] P. Kovacic, M. B. Jones,*Chem. Rev.* 1987, *87*, 357. [2] G. K. Noren, J. K. Stille, *Macromol. Rev.* 1971, *5*, 385. [3] J. Economy in *Contemporary Topics in Polymer Science*; (Ed: E. J. Vandenberg), Plenum, New York, 1984. [4] R. L. Elsenbaumer, L. W. Schacklette in *Handbook of Conducting Polymers*; (Ed. T. A. Skotheim), Dekker: New York, 1986. [5] G. Tourillion in reference 4. [6] R. H. Baughman, J. L. Brédas, R. R. Chance, R. L. Elsenbaumer, L. W. Shacklette, *Chem. Rev.* 1982, *82*, 209. [7] D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, R. H. Baughman,*J. Chem. Phys.* 1979, *71*, 1506. [8] G. Grem, L. Günther, B. Ullrich, G. Leising, *Adv. Mater.* 1992, *4*, 36. [9] (a) E. B. Stephens, J. M. Tour, *Macromolecules* 1993, *26*, 2420. (b) E. B. Stephens, J. M. Tour, *Adv. Mater.* 1992, *4*, 570. [10] J. M. Tour, J. J. S. Lamba, *J. Am. Chem. Soc.* 1993, *115*, 4935. [11] H. S. Nalwa, *Adv. Mater.* 1993, *5*, 341. [12] C. Arnold Jr., *Macromolec Rev.* 1979, *14*, 265. [13] T. Yamamoto, Y. Hayashi, A. Yamamoto, *Bull. Chem. Soc. Jpn.* 1978, *51*, 2091. [14] V. V. Korshak, M. M. Teplyakov, D. M. Kakauridze, N. V. Kravchenko, *Dokl. Akad. Nauk. SSSR* 1974, *219*, 117. [15] (a) R. L. Alexander Jr. *J. Org. Chem.* 1956, *21*, 1464. (b) G. F. Woods, A. L. Van Artsdale, F. T. Reed, *J. Am. Chem. Soc.* 1950, *72*, 3221. (c) A. E. Gillam, D. H. Hey, *J. Chem. Soc.* 1939, 1170. [16] H. A. Staab, F. Binnig, *Chem. Ber.* 1967, *100*, 293, 899. [17] (a) Y. H. Kim, O. W.

Webster, *J. Am. Chem. Soc.* 1990, *112*, 4592. (b) For an overview of Pd-catalyzed polyaromatic syntheses, see: A.-D. Schlüter, G. Wegner, *Acta Polymerica* 1993, *44*, 59. [18] P. Belser, A. von Zelewsky, M. Frank, C. Seel, F. Vogtle, L. De Cola, F. Barigelletti, V. Balzani, *J. Am. Chem. Soc.* 1993, *115*, 4076. [19] (a) I. U. Rau, M. Rehahn, *Makromol. Chem.* 1993, *194*, 2225. (b) I. U. Rau, M. Rehahn *Polymer* 1993, *34*, 2889. (c) V. Percec, S. Okita, R. Weiss, *Macromolecules* 1992, *25*, 1816. [20] M. Rehahn, A.-D. Schlüter, G. Wegner, W. J. Feast *Polymer* 1989, *30*, 1060. [21] (a) M. Rehahn, A.-D. Schlüter, G. Wegner *Makromol. Chem.* 1990, *191*, 1991. (b) H. Witteler, G. Lieser, G. Wegner, M. Schulze, *Makromol. Chem., Rapid Commun.* 1993, *14*, 471. [22] H. Funaki, K. Aramaki, H. Nishihara, *Chem. Lett.* 1992, 2065. [23] M. A. Ogliaruso, E. I. Becker, *J. Org. Chem.* 1965, *30*, 3354. [24] (a) T. P. Lockhardt, P. B. Comita, R. G. Bergman, *J. Am. Chem. Soc.* 1981, *103*, 4082. (b) T. P. Lockhardt, R. G. Bergman, *J. Am. Chem. Soc.* 1981, *103*, 4091. [25] J. M. Tour, J. A. John, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1993, *34*(2), 372. [26] (a) G. Goldfinger, *J. Poly. Sci.* 1949, *4*, 93. (b) G. A. Edwards, G. Goldfinger, *J. Poly. Sci.* 1955, *16*, 589. [27] (a) E. B. Stephens, K. E. Kinsey, J. F. Davis, J. M. Tour, *Macromolecules* 1993, *26*, 3519. (b) J. M. Tour, E. B.Stephens, *J. Am. Chem. Soc.* 1991, *113*, 2309. (c) J. M. Tour, E. B.Stephens, J. F. Davis, *Macromolecules* 1992, *25*, 499. [28] (a) E. Fitzer in reference 3. (b) W. Ried, D. Freitag, *Angew. Chem. Internat. Ed. Engl.* 1968, *7*, 835. (c) E. Fitzer, *Pure Appl. Chem.* 1980, *52*, 1865. (d) A. K. Gupta, A. K. Paliwal, P. Bajaj, *J. Macromolec. Sci., Macromolec. Chem. Phys.* 1991, *C31*, 1. [29] (a) J. R. Vinson, T.-W. Chou, *Composite Materials and Their Use in Structures*, Applied Science: London, 1975. (b) M. Molyneux, in *Carbon Fibres in Engineering*, (Ed: M. Langley), McGraw Hill: London, 1973. [30] E. B. Stephens, Ph.D. Dissertation, University of South Carolina, 1992. [31] (a) T. I. Wallow, B. M. Novak, *J. Am. Chem. Soc.* 1991, *113*, 7411. (b) T. Wallow, B. M. Novak, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1992, *33*, 908 and 1218. (c) T. I. Wallow, B. M. Novak, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1993, *34*(1), 1009. (d) T. A. P. Seery, T. I. Wallow, B. M. Novak, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1993, *34*(2), 727. [32] V. Chaturvedi, S. Tanaka, K. Kaeriyama, *Macromolecules* 1993, *26*, 2607. [33]

R. Baum, *Chemical and Engineering News*, February 15, 1993, p 30. [34] M. Katsuya, T. Teshirogi, N. Kuramoto, T. Kitamura, *J. Polym. Sci., Polym. Chem. Ed.* 1985, *23*, 1259. [35] M. Ueda, T. Abe, H. Awano, *Macromolecules* 1992, *25*, 5125. [36] S. Hara, N. Toshima, *Chem. Lett.* 1990, 269. [37] V. Percec, J. Wang, S. Okita, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1992, *33*(1), 225. [38] T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z.-h. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, K. Kubota, *Macromolecules* 1992, *25*, 1214. [39] T. Kanbara, T. Yamamoto *Macromolecules* 1993, *26*, 3464. [40] P. V. Bedworth, Ph.D. Dissertation, University of South Carolina, 1993. [41] For some discussions of aromatic ladder polymers, see: (a) C. G. Overberger, J. A. Moore, *Adv. Polym. Sci.* 1970, *7*, 113. (b) A.-D. Schlüter, *Adv. Mater.* 1991, *3*, 282. (c) L. Yu, M. Chen, L. R. Dalton, *Chem. Mater.* 1990, *2*, 649. (d) S. Y. Hong, M. Kertesz, Y. S. Lee, O.-K. Kim, *Chem. Mater.* 1992, *4*, 378. (e) A. Godt, A.-D. Schlüter, *Adv. Mater.* 1991, *3*, 497. (f) L. Yu, L. R. Dalton, *Macromolecules* 1990, *23*, 3439. (g) C.-S. Wang, *Trends Polym. Sci.* 1993, *1*, 199. [42] (a) U. Anton, A. Bohnen, K.-H. Koch, H. Naarmann, H. J. Rader, K. Müllen, *Adv. Mater.* 1992, *4*, 91. (b) U. Scherf, K. Müllen, *Synthesis* 1992, 23. [43] (a) U. Scherf, K. Müllen, *Polymer* 1992, *33*, 2443. (b) U. Scherf, K. Müllen, *Makromol. Chem., Rapid Commun.* 1991, *12*, 489. (c) U. Scherf, A. Bohnen, K. Müllen, *Makromol. Chem.* 1992, *193*, 1127. (d) U. Scherf, *Synth. Metal.* 1993, *55*, 767. (e) K. Chmil, U. Scherf, *Makromol. Chem., Rapid Commun.* 1993, *14*, 217. (f) U. Scherf, K. Müllen, *Macromolecules* 1992, *25*, 3546.