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Synthesis of Soluble Halogenated Polyphenylenes. Mechanism for the Coupling of Halogenated Lithiobenzenes

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ABSTRACT: A method for the synthesis of soluble polyphenylenes that involves the polymerization of 1-halo-4-lithiobenzenes, 1-halo-3-lithiobenzenes, and 1,3- and 1,4-dilithiobenzenes in ethereal solvents is described. The lithiobenzenes are prepared from the corresponding dihalogenated benzenes using *tert*-butyllithium. By varying the monomers and conditions used, a variety of soluble halogenated polyphenylenes can be obtained with weight average molecular weights (M_w) as high as 6000 with polydispersities (M_w/M_n) equal to ~2.8. The prequenched polymers can exist as multilithiated polymers if 2.0 equiv of *tert*-butyllithium is used to form the aryllithium intermediates. The polymers are usually amorphous and contain significant amounts of phenylated polyphenylene units capped with halogens. The polymers are soluble in organic solvents such as THF, chloroform, and methylene chloride. Several of the polymers exhibited low melting and glass transition temperatures. The brominated polymers are easily dehalogenated upon treatment with *tert*-butyllithium in THF at −78 °C followed by quenching with water. The molecular weights of several of the brominated polymers increased upon debromination with *tert*-butyllithium. When the polymerizations were carried out in the presence of 1,3-diphenylisobenzofuran, *o*-benzyne intermediates were trapped as their Diels–Alder adducts. LiH appears to be present in significant amounts upon completion of the polymerization.

Introduction

Since the 1950s, *p*-polyphenylene (PPP) has attracted much attention as a result of its exceptional thermal, electrical, and chemical properties.[2] Undoped PPP is an excellent electrical insulator while the doped form can have conductivities as high as 500 Ω^{-1} cm^{-1}.[2d-f] These properties have enabled PPP to be used as insulating layers in semiconductors and in the preparation of lightweight batteries.[2g] However, the same structural features, namely rigidity and overall molecular symmetry, which give PPP its desirable physical and chemical properties, also hinder the polymer's ability to be processed. These polymers are insoluble in all common organic solvents and have either no, or extremely high melting or softening temperatures. Thus high temperatures and pressures are needed to fabricate the polymers into usable forms.

While most direct approaches to PPP have led to low molecular weight insoluble material,[3] advances in processibility have been made through the preparation of soluble polymeric PPP precursors which, upon pyrolysis, form high molecular weight PPP.[4] Additional classes of substituted and branched polyphenylenes[5] have also been prepared which, due to a lack of polymer symmetry, are soluble in organic solvents and can exhibit low melting[5h] or glass transition temperatures.[5f,g] These materials should offer attractive alternatives to original methods for PPP preparation.

We became interested in polyphenylenes upon discovering an extremely facile Li/HMPA-promoted polymerization method in 1,4-dioxane for the synthesis of soluble brominated polyphenylenes. The polymers were predominantly *para*-linked by FTIR yet still highly soluble in organic solvents.[6] Recently, we reported a similar polymerization of 1-bromo-4-lithiobenzene (1) in THF without the need for the highly toxic hexamethylphosphoramide (HMPA). This polymerization gave soluble brominated polyphenylenes containing approximately equal amounts of *para*- and *meta*-linkages by FTIR analysis.[7] Here we report the detailed results and mechanistic implications of these polymerizations as well as the polymerizations of other mono- and dilithiated benzenes.

Preparation of Halogenated Polyphenylenes in Dioxane with HMPA

Our initial approach to predominantly *para*-linked brominated polyphenylenes involved the formation of 1-bromo-4-lithiobenzene (1) in ether at −78 °C by the slow addition of 2.0 equiv of *tert*-butyllithium (Scheme I). The first equivalent of *tert*-butyllithium was for the lithium–halogen exchange to form 1 and *tert*-butyl bromide. The second equivalent was needed for the E2 elimination of *tert*-butyl bromide to afford lithium bromide, isobutylene, and isobutane. This conveniently made all the byproducts unreactive, leaving no alkyl halides. While the lithium–halogen exchange reaction can be done with 1.0 equiv of either *n*- or *sec*-butyllithium, the byproducts *n*-butyl bromide and *sec*-butyl bromide, respectively, are reactive and remain in the system. When 1.0 equiv of *n*-butyllithium was used to form intermediate 1, no polymeric products were isolated. The intermediacy of 1 in the *tert*-butyllithium reaction was confirmed in a separate experiment by the addition of chlorotrimethylsilane at −78 °C to form 1-bromo-4-(trimethylsilyl)benzene (2) in 86% isolated yield. Compound 1 was then treated at −78 °C with 1.0 equiv of HMPA.[8] Upon addition of HMPA at −78 °C, the reaction solution immediately turned black and viscous. The solution was rapidly added to water in order to confirm that the polymerization was indeed occurring at these low temperatures. After precipitation from ether, a tan solid was isolated. This material had a strong FTIR absorbance at 809 cm^{-1}, indicative of *para*-linked phenyl rings,[9] and a weight average molecular weight (M_w) of 1060 and a polydispersity (M_w/M_n) of 2.88 relative to polystyrene standards. The solid was soluble in THF, methylene chloride, and chloroform. Intrigued by this result, we optimized the yields and molecular weights of this interesting polymerization. The results are shown in Table I.

Our optimal procedure for forming the highest weight and number average molecular weight polyphenylenes with high concentrations of *para*-linked moieties is shown in Table I, entry 1. It is similar to the procedure described above; however, the solvent used was dioxane, *tert*-butyllithium (2.0 equiv) was added at 0 °C, and infusion

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Scheme I

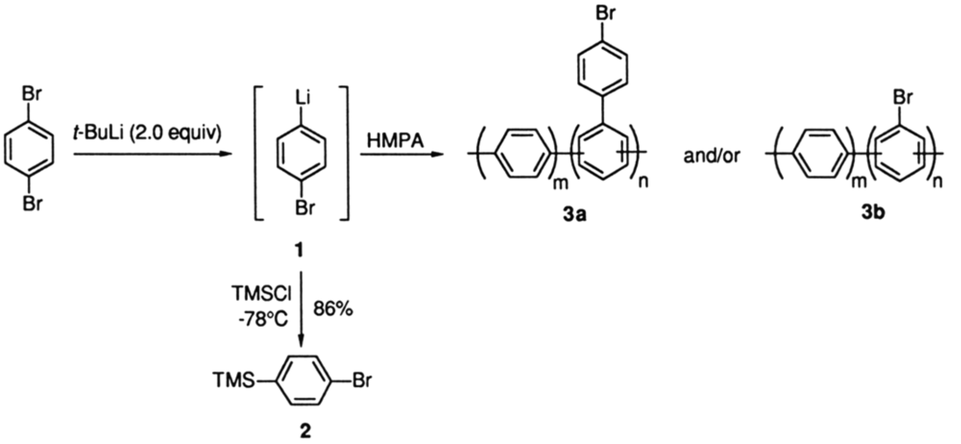


Table I. HMPA-Promoted Polymerization of 1-Bromo-4-lithiobenzene (1)

ent no.	amt of starting material (mmol)	amt of *t*BuLi (equiv)	Li–X exch temp (°C)	Li–X exch. solvent	HMPA infusion temp (°C)	amt of Et_2O insol material (g)	%[a] yield	M_w	M_n	M_w/M_n	FTIR bands (cm^{-1})
1	8.0	2.0	0	dioxane	80	0.25	31	2400	840	2.85	1073.3, 1001.9, 884.7, 809.2, 790.6, 761.6, 698.8
2	4.0	2.0	0	dioxane	22	0.10	25	1950	650	2.98	1074.2, 1003.9, 886.6, 812.2, 790.4, 762.1, 699.7
3	2.0	2.0	−78	Et_2O	−78	0.09	44	1060	370	2.88	1077.2, 1001.2, 885.0, 809.8, 761.2, 697.4, 668.6
4	6.0	2.0	−78	Et_2O	35	0.27	44	1680	440	3.79	1072.7, 1007.3, 889.8, 820.5, 791.0, 758.1, 698.1
5	2.0	2.0	−78	THF	65	0.11	54	2080	590	3.50	1074.0, 1005.8, 821.4, 789.2, 758.9, 698.5
6	4.0	2.0	−78	THF	−78	0.04	10	670	410	1.64	1075.6, 1002.1, 809.8, 788.7, 764.8, 698.5
7	16.0	2.0	0	DME	90	0.19	12	4050	680	5.93	1072.7, 1002.7, 887.9, 808.8, 787.9, 757.9, 696.2

[a] Yields were based on the amount of ether insoluble material collected, elemental data, and the amount of starting dibromide.

of HMPA was done at 70–80 °C. Upon addition of HMPA, the reaction mixture turned black and an exothermic reaction ensued. The polymerization was nearly instantaneous. Quenching with water and isolation of the ether insoluble portion gave a 25–30% yield of polymer **3** (**3** appears to be predominantly **3a** though a mixture of both **3a** and **3b** cannot be ruled out) which by elemental analysis had a 25% bromide content or one bromide group for every three aryl rings. The polymerization yields were based on the elemental data, the amount of ether insoluble material, and the amount of starting dibromide.

Size exclusion chromatography showed that **3**, prepared under our optimized conditions, had $M_w = 2400$ and $M_w/M_n = 2.85$ relative to polystyrene standards.[10] It was apparent from the FTIR analysis that predominantly *para*-linked material was formed by the strong band at 809 cm^{-1}. Weak bands at 885 and 791 cm^{-1} were attributed to *meta*-linkages which destroy the crystallinity of the polymer and impart solubility. Weak branching phenyl stretches were also observed at 762 and 699 cm^{-1}. Bands at 1002 and 1899 cm^{-1} were attributed to *para*-substituted units, and the presence of bromide was confirmed by the C–Br absorbance at 1074 cm^{-1}.[3e,9] Polymer **3** showed a λ_{max} at 274 nm in chloroform. This value was characteristic of mixtures of *para*- and *meta*-linked aryl units when compared to the reported values for oliophenylenes.[11] The λ_{max} values in chloroform for *p*-sexiphenyl and *m*-sexiphenyl are 318 and 248 nm, respectively. Although powder X-ray diffraction (XRD) signals were reported for Kovacic[2a] and Yamamoto PPP,[3e] no diffraction pattern was observed for **3**, consistent with the solubility of the material. Likewise, scanning electron microscopic (SEM) analysis showed the polymer to have a globular morphology pattern (Figure 1).

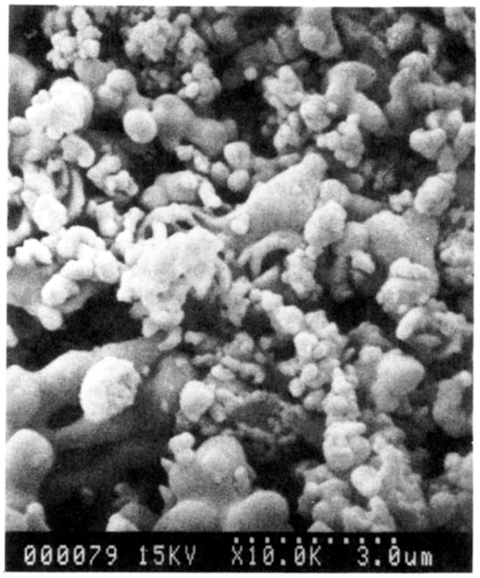
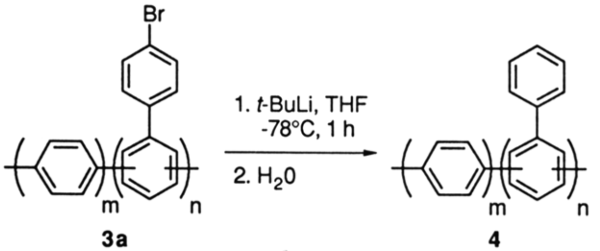


Figure 1. SEM of brominated polyphenylene **3**.



(1)

Since polymer **3** was soluble, debromination was easily achieved by treatment with *tert*-butyllithium in THF at −78 °C (eq 1). After stirring for 1 h at −78 °C, the solution was quenched with water to afford the debrominated polymer **4**. Elemental analysis confirmed that all the bromides had been removed. The UV spectrum of **4** showed a λ_{max} in chloroform of 278 nm, again consistent with mixtures of *para*- and *meta*-linked aryl rings.[11] No powder XRD signals were observed and SEM showed a globular morphology similar to that of polymer **3** (Figure 2). Surprisingly, the M_w of the polymer increased from 2400 ($M_w/M_n = 2.85$) to 3180 ($M_w/M_n = 2.80$) upon

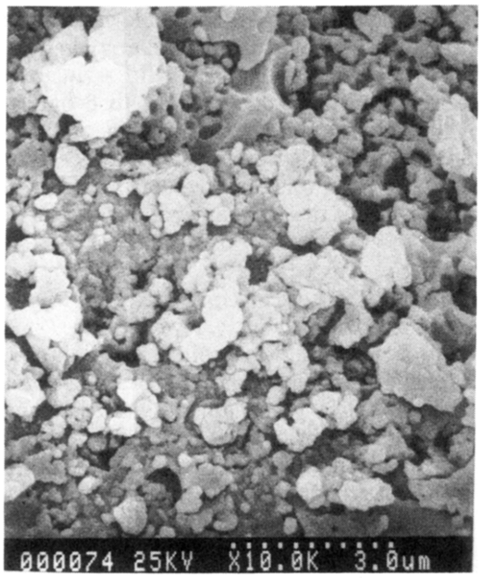


Figure 2. SEM of debrominated polyphenylene **4**.

debromination while the material remained soluble in THF, chloroform, and methylene chloride. This observation may have resulted from the bromides in **3** causing the polymer to be retained more tightly by the SEC columns (cross-linked polystyrene). Another possibility was additional coupling of the polymer chains. The solubility of the material would suggest little or no cross-linking of the polymer chains.

Perhaps the most interesting findings of the debromination came from the FTIR analysis. The C–Br absorbance at 1074 cm^{-1} was absent, further substantiating the removal of the bromide. Also the *para* band shifted from 809 cm^{-1} in **3** to 825 cm^{-1} in **4**. This stretch was still much more intense than the *meta* band; however, the branching phenyl stretches at 760 and 690 cm^{-1} grew in intensity. Substitution along the polyphenylene backbone as well as the incorporation of *meta*-linkages is known to increase the solubility of polyphenylenes.[2b,5,11] These results suggested that some of the rings in the predominantly *para*-linked backbone were possibly substituted with *p*-bromophenyl groups, as in **3a** rather than **3b**.

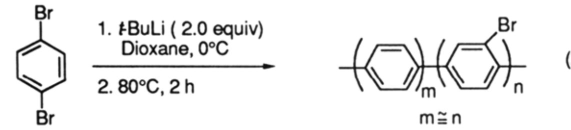
There was little if any aliphatic material present in the ether insoluble portions of **3** or **4** by ^1H NMR. The ^1H NMR (300 MHz, $CDCl_3$) of **3** and **4** showed a broad multiplet from δ 7.0–8.0 ppm presumably due to the presence of various isomeric structural units.[5g] The reported CP/MAS ^{13}C NMR for PPP varies according to the method of preparation. PPP prepared by the Kovacic method shows resonances at δ 139 and 128 ppm, while commercial PPP has shifts at δ 143, 133, 130, and 124 ppm.[12] The ^{13}C NMR (125 MHz, $CDCl_3$) for the brominated polymer **3** showed resonances in the ranges δ 124–130 and 138–142 ppm. For the debrominated polymer **4**, the ^{13}C NMR (125 MHz, $CDCl_3$) chemical shifts were in the ranges δ 124–131 and 138–144 ppm. The proton spin–lattice relaxation times (T_1) of oligophenylenes are known to decrease with increased chain length, and ranges of 910 s for biphenyl to 0.48 s for PPP have been reported.[13] We found that the brominated polymer **3** and the debrominated polymer **4** exhibited T_1 ranges of 0.4–1.6 and 0.9–1.4 s, respectively. This also suggested that reasonable molecular weight material was being formed during the polymerization.

A sample of the debrominated polymer **4** doped with $FeCl_3$ and AsF_5 was subjected to a four-point probe analysis[14] which showed the conductivity of the doped polymer to be in the range 10^{-5} to 10^{-6} Ω^{-1} cm^{-1}. Good pellet formation was difficult and the conductivity was significantly less than the value for PPP prepared by the Kovacic method.[2d,f] The low conductivity is probably due to both the *meta*-linkages and the substituted units which are known to decrease the planarity of adjacent rings thus lowering the extended π-conjugation.[2d] Conductivity studies on solution-cast films were not possible since the material only formed brittle and irregular films presumably due to the low molecular weight and rigid aromatic backbone structure.

Thermogravimetric analysis (TGA; N_2, 20 °C/min, 50–900 °C) of polymers **3** and **4** showed similar char yields of 52% and 54%, respectively. The appearance of the charred material was black and powdery, suggesting that no significant flow had occurred during heating. Differential scanning calorimetry (DSC; N_2, 20 °C/min) of polymers **3** and **4** showed no melting or glass transition points on either the first or second heating runs up to 250 °C.

Cyclic voltammetry studies on **3** and **4** showed both polymers to be electroactive. Studies were carried out both on films and solutions of the polymer. Polymer films were formed on the surface of a platinum electrode by dipping the electrode into THF solutions of the polymer. These studies were carried out in acetonitrile, a solvent which does not dissolve the polymer. The estimated E_{pa} value for *p*-polyphenylene is 1.6 V.[15] Irreversible anodic peak potential (E_{pa}) values for **3** and **4** were 1.44 and 1.45 V, respectively.[16] No corresponding reduction of the polymer films was observed. Solution voltammetry studies of **3** and **4** in methylene chloride showed irreversible oxidations at E_{pa} values of 2.32 and 2.24 V, respectively.[17] The irreversibility is probably due to decomposition of the polymer as well as oxidation of the electrode at these high potentials.

If **1** was heated to reflux at 80 °C for several hours in dioxane without HMPA (eq 2), a small amount (5–7%) of a yellow solid **5** was isolated which was insoluble in common organic solvents. **5** had no *meta*-linkages by FTIR analysis and an intense *para* stretch at 809.7 cm^{-1}. Because of the insolubility, no NMR or SEC data were obtained. Powder XRD showed **5** to be crystalline by the strong transmission bands at 4.20 Å and a weak band at 3.11 Å. Not only did the insolubility and powder XRD confirm the crystallinity of the material, but also the SEM analysis showed **5** to have a flakelike morphology (Figure 3). We thus concluded that **5** was probably a brominated *p*-oligophenylene. By elemental analysis, **5** contained approximately 40% bromide, or one bromide for every two rings. Attempts to relithiate **5** failed to fully debrominate the material though partial debromination could be achieved.



5

(2)

Preparation of Halogenated Polyphenylenes in THF

While conducting our studies on the Li/HMPA-promoted synthesis of halogenated polyphenylenes, we found that polymers with higher concentrations of *meta*-linkages could be obtained when THF was used as the polymerization solvent (Table I, entry 5). Upon further investigation of this reaction, we found that when THF was used, these polymers could be formed without HMPA under a variety of reaction conditions (Table II). Our optimal

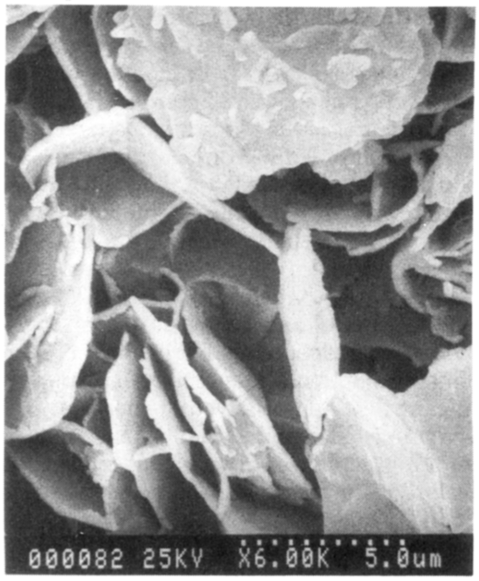
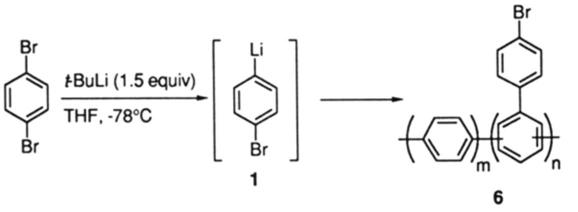


Figure 3. SEM of insoluble brominated polyphenylene **5**.

yields and molecular weights for this system were obtained using 1.5 equiv of *tert*-butyllithium to form **1**. A typical polymerization involved the addition of *tert*-butyllithium (24 mmol, 2.3 M in pentane) to 1,4-dibromobenzene (16 mmol) in THF (16 mL) at −78 °C, thus generating 12 mmol of **1** while 4 mmol of 1,4-dibromobenzene presumably remained unreacted. The reaction was then allowed to warm to room temperature where it turned black. After stirring at room temperature for 2 h, the reaction was quenched with water. Isolation of the ether insoluble portion gave 0.61 g (50%) of polymer **6** as a tan/brown solid (eq 3). SEC showed **6** to have $M_w = 2570$ and $M_w/M_n = 4.06$ relative to polystyrene while the elemental analysis showed 24% bromide or one bromide for every three aryl rings. The yields for the polymers in Table II prepared using 1.8 equiv of *tert*-butyllithium or less were based on this elemental data, the amount of ether insoluble material collected, and the amount of *tert*-butyllithium used to form intermediate **1**.



(3)

Polymer **6** was soluble in THF, chloroform, and methylene chloride. No powder XRD signals were observed, consistent with the solubility of the material. SEM analysis showed a globular morphology pattern. There was no aliphatic material present in the ether insoluble portion of the polymer by ^{1}H NMR (500 MHz, $CDCl_3$) with the aromatic signal at δ 7.2–7.9 ppm. If the polymerization yields were increased by isolation of the hexane insoluble material, aliphatic signals were observed in the ^{1}H NMR. The ^{13}C NMR (125 MHz, $CDCl_3$) of **6** showed peaks in the range δ 124–135 ppm and a smaller set at δ 139–141 ppm.[11] The UV spectrum showed a λ_{max} in chloroform of 284 nm. This was again consistent with mixtures of *para*- and *meta*-linked moieties.[11]

The FTIR spectrum of **6** showed it to contain approximately equal amounts of *para*- (809 cm^{-1}) and *meta*-linkages (787 cm^{-1}). The previous HMPA-promoted method gave a significantly more intense *para*-linked absorbance. Additional bands at 1901 and 1002 cm^{-1} were attributed to *para*-linkages. A weak *meta* band at 889 cm^{-1} was also observable. The branching phenyl stretches at 762 and 698 cm^{-1} were weak while the presence of bromide was confirmed by a C–Br absorbance at 1074 cm^{-1}. Although no clearly distinguishable band corresponding to disubstituted *ortho*-linked units in the 750–755-cm^{-1} region was observed, a shoulder on the low wavenumber side of the 762-cm^{-1} band could be attributed to this type of substitution pattern.[2b,3e,9]

Interestingly, we found that when 2.0 equiv of *tert*-butyllithium were used to convert all of the 1,4-dibromobenzene of **1**, significantly lower yields (25–30%) of ether insoluble material were collected. This could result from the formation of small amounts of 1,4-dilithiobenzene which may act as a chain terminator. Since the low molecular weight material was shown to contain aliphatics, there is the possibility that residual *tert*-butyllithium could be adding to *o*-benzyne intermediates (*vide infra*) which are believed to be formed during the polymerization.[18,19] We noticed that when higher amounts of *tert*-butyllithium were used, the *para* band at 809–812 cm^{-1} would shift to higher wavenumbers, 814–817 cm^{-1}. The branching phenyl stretches at 760 and 690 cm^{-1} also showed small increases in intensity while the C–Br absorption at 1074 cm^{-1} decreased slightly, suggesting that the bromide content in these polymers could be lower. This was confirmed by elemental analysis which showed one of the polymers prepared using 2.0 equiv of *tert*-butyllithium to contain 9% bromide or one bromide for every ten phenyl rings. The yields in Table II for the polymerizations using 2.0 equiv of *tert*-butyllithium were accordingly based on this data. Thus, not only can the conditions of the polymerization be changed to give structurally different polymers, but also the amount of *tert*-butyllithium used can change the degree of bromide content in the material.

To further probe the structure of **6**, the bromides were removed by simple lithium–halogen exchange with *tert*-butyllithium at −78 °C in THF followed by a water quench to form the debrominated polymer **7**. The debromination was confirmed by elemental analysis which showed the material to contain <0.5% bromide. The C–Br band in the FTIR spectrum was absent and the branching phenyl stretches increased substantially. In addition, the *para* stretch at 809 cm^{-1} shifted to 824 cm^{-1}. This again suggested the presence of phenylated polyphenylene previously capped with bromides at the *para* position. Interestingly, the FTIR spectrum of **7** looked remarkably similar to the IR spectrum reported by Stille for phenylated polyphenylene.[2b] The ^{1}H NMR (300 MHz, $CDCl_3$) showed little or no aliphatic material with aromatic signals at δ 7.0–7.9 ppm. ^{13}C NMR (75 MHz, $CDCl_3$) showed signals at δ 126–131 and 139 ppm. The UV spectrum showed a λ_{max} in chloroform at 288 nm, similar to the spectrum of **6**.

When a sample of **6** having $M_w = 1870$ with $M_w/M_n = 2.83$ by SEC was debrominated, the value of M_w increased to 2320 with $M_w/M_n = 2.68$. Recall that this same pattern was observed with the debromination of **3**. The increase in molecular weight could have been an effect of the bromides interacting with the cross-linked polystyrene column. However, the percentage increase in M_w was significantly greater when the debromination was carried out in the presence of HMPA ($M_w = 1970$ with $M_w/M_n = 3.11$ increased to $M_w = 2770$ with $M_w/M_n = 3.41$). This certainly implies that the molecular weight is increasing on debromination and even further on debromination in the presence of HMPA. It is not just an effect of the bromides causing elution rate retardation during SEC.

While the TGA (N_2, 20 °C/min) of the brominated polymer **6** showed a 10% weight loss at 285 °C and a total

Table II. Polymerization of 1-Bromo-4-lithiobenzene (1) in THF

ent no.	amt of starting material (mmol)	amt of *t*BuLi (equiv)	Li–X exch temp (°C)	Li–X exch solvent	polym temp (°C)	polym time	Et_2O insol material (g)	%[a] yield	M_w	M_n	M_w/M_n	IR bands (cm^{-1})
1	16.0	2.0	−78	THF	22	2 h	0.41	31	1890	370	5.12	1074.0, 1004.1, 889.7, 817.0, 788.5, 758.7, 697.3
2	2.0	2.0	−78	THF	65	2 h	0.05	30	2230	610	3.67	1073.4, 1002.7, 884.4, 808.5, 763.7, 699.6
3	16.0	2.0	−78	THF	22	16 h	0.39	30	2240	620	3.63	1074.2, 1004.3, 888.0, 816.9, 788.4, 758.6, 698.6
4	16.0	20	0	DME	95	2 h	0.18	14	1380	770	1.80	1074.5, 1004.3, 890.1, 814.0, 789.6, 761.8, 697.7
5	2.0	2.0	0	dioxane	22	16 h	*b*					
6	2.0	2.0	−78	Et_2O	35	2 h	0.01	6	530	160	3.34	1070.7, 1000.6, 808.4, 780.4, 758.9, 692.5
7	20	2.0	−78	Et_2O	22	16 h	*b*					
8	16.0	25	−78	THF	22	2 h	*b*					
9	8.0	25	−78	THF	22	16 h	0.13	20	2500	630	3.95	1074.5, 1004.8, 880.0, 824.0, 792.4, 758.4, 697.0
10	16.0	1.8	−78	THF	65	2 h	0.65	44	1890	470	3.86	1074.0, 1004.1, 889.7, 817.0, 788.5, 758.7, 697.3
11	16.0	1.8	−78	THF	22	2 h	0.54	37	2000	450	4.49	1073.4, 1002.7, 884.4, 808.5, 763.7, 699.6
12	16.0	1.5	−78	THF	22	2 h	0.60– 0.80	50–65	1360–2570	380–630	3.59–4.06	1073.3, 1002.2, 888.9, 809.4, 787.3, 761.4, 697.9
13	16.0	1.5	−78	THF	65	2 h	0.75	62	1940	500	3.89	1074.2, 1003.5, 890.4, 812.3, 788.7, 763.1, 699.4
14	16.0	1.5	−78	THF	2	16 h	0.55	65	1940	620	3.14	1073.9, 1002.6, 888.6, 810.6, 788.1, 762.4, 698.2
15	16.0	1.5	−78	THF	22	2 d	0.57	47	1890	520	3.64	1074.3, 1003.1, 888.9, 810.9, 787.3, 763.1, 699.7
16	16.0	1.5	−78	THF	65	2 min	0.72	60	1000	190	5.25	1073.7, 1002.8, 888.2, 812.0, 787.8, 759.0, 697.1
17	8.0	1.5	−78	THF	0	2 h	0.29	48	1210	320	3.75	1073.9, 1002.9, 889.8, 810.4, 787.4, 762.9, 698.9
18	16.0	1.5	−78	THF	0	1 h	0.68	44	1120	420	2.68	1073.9, 1002.4, 889.0, 808.9, 786.9, 763.9, 698.2
19	16.0	1.5	−78	Et_2O	22	16 h	*b*					
20	16.0	1.5	0	THF	22	2 h	0.30	25	1800	770	2.33	1074.4, 1003.1, 891.1, 811.8, 787.8, 763.8, 699.0
21	16.0	1.5	−20	THF	22	2 h	0.43	36	1860	770	2.42	1073.7, 1002.8, 889.0, 812.2, 785.6, 761.3, 698.1
22	16.0	1.5	−40	THF	22	2 h	0.54	45	1970	510	3.88	1074.4, 1003.1, 885.4, 811.1, 787.2, 763.9, 698.9
23	10.0	1.3	−78	THF	22	2 h	0.04	23	1230	380	3.29	1073.7, 1003.8, 889.6, 815.5, 788.1, 758.3, 697.4
24	10.0	1.0	−78	THF	22	16 h	*b*					1073.7, 1003.3, 888.9, 815.0, 787.3, 758.3, 697.9

[a] Yields were based on the amount of Et_2O insoluble material collected, elemental data, and the amount of *t*BuLi used. [b] No Et_2O insoluble material obtained.

weight loss of 48% at 900 °C, debrominated polymer **7** showed a 10% weight loss at 429 °C and a total weight loss of 52% at 900 °C. The charred materials were porous and glossy black and appeared to flow during heating.

The DSC (N_2, 20 °C/min) for **6** showed broad endotherms, characteristic of melting events at 152 and 175 °C on the first heating scan. The second heating scan showed possible T_g's at 140 and 210 °C. The DSC thermogram for **7** showed a broad endotherm from 170 to 230 °C on the first heating scan and an apparent T_g at 150 °C on the second heating scan. Since *m*-oligophenylenes have been shown to have lower melting points than the corresponding *p*-oligophenylenes, these events are probably a result of the increased amount of *meta*-linkages and substituted units in **6** and **7** compared to the polymers derived from the Li/HMPA procedure in dioxane.[11,5f–h]

In order to obtain a wider variety of halogenated polyphenylenes, we investigated several additional monomer systems. The results of the polymerization of 1-lithio-3-bromobenzene (**8**) (Scheme II) are summarized in Table III. As before, higher yields were obtained by preparing **8** with 1.5 equiv of *tert*-butyllithium at −78 °C. The intermediacy of **8** was confirmed in a separate experiment by quenching the reaction at −78 °C with chlorotrimethylsilane, which gave a 90% yield of 1-bromo-3-(trimethylsilyl)benzene (**9**). Simply allowing **8** to warm to room temperature and stir 2 h gave a 54% yield of polymer **10**. SEC showed polymer **10** to have higher molecular weights (M_w = 2850) and lower polydispersities (M_w/M_n = 1.89) than the previous polymers derived from 1,4-dibromobenzene. Higher molecular weight material could be obtained if increasing amounts of *tert*-butyllithium were used; however, the yields of ether insoluble material were again reduced. ^1H NMR (300 MHz, $CDCl_3$) showed a broad aromatic signal at δ 6.9–7.9 ppm with no aliphatic material present. If, however, the yields were increased by collecting hexane insoluble fractions, aliphatics were observed in the ^1H NMR. The ^{13}C NMR (75 MHz, $CDCl_3$) of **10** showed

Scheme II

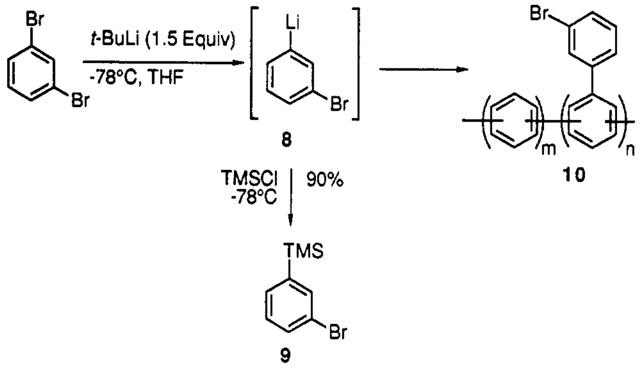


Table III. Polymerization of 1-Bromo-3-lithiobenzene (8) in THF

ent no.	amt of starting material (mmol)	amt of *t*BuLi (equiv)	Li–X exch temp (°C)	Li–X exch solvent	polym temp (°C)	polym time (h)	Et_2O insol material (g)	%^{a} yield	M_w	M_n	M_w/M_n	FTIR bands (cm^{-1})
1	10.0	2.0	−78	THF	22	2	0.37	47	2310	1400	1.65	1073.3, 887.1, 838.9, 782.7, 755.9, 701.1
2	10.0	2.0	−78	THF	22	16	0.35	44	3330	710	4.70	1073.9, 888.1, 839.4, 785.7, 756.0, 701.5
3	10.0	1.8	−78	THF	22	2	0.28–0.30	38–40	2590–4600	1140–1630	2.26–2.83	1074.0, 889.5, 840.0, 785.4, 756.6, 700.4,
4	10.0	1.8	−78	THF	22	16	0.37–0.41	50–54	2810–3030	950–1280	2.37–2.95	1073.9, 889.6, 838.2, 783.8, 755.8, 701.2
5	16.0	1.5	−78	THF	22	2	0.50	54	2850	1524	1.87	1072.0, 883.0, 838.4, 780.8, 755.5, 699.7
6	10.0	1.5	−78	THF	22	16	0.42	67	2660	860	3.08	1073.6, 996.5, 883.4, 835.9, 779.2, 756.6, 701.1
7	16.0	1.5	−78	THF	22	16	0.56	56	2690	1100	2.44	1071.4, 886.0, 838.3, 782.3, 755.4, 700.7
8	16.0	1.5	−78	THF	65	2	0.66	66	2710	1370	1.98	1072.9, 996.2, 839.2, 780.2, 755.7, 700.2
9	10.0	1.5	−78	Et_2O	22	16	*b*					
10	10.0	1.3	−78	THF	22	2	0.04	7	1690	1180	1.43	1073.5, 996.4, 880.6, 838.6, 779.3, 756.8, 696.9
11	10.0	1.0	−78	THF	22	16	*b*					

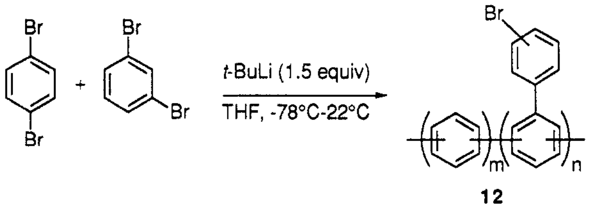
^{a} Yields were based on the amount of Et_2O insoluble material collected, elemental data, and the amount of *t*BuLi used. ^{b} No Et_2O insoluble material obtained.

signals at δ 122–132 and 139–144 ppm. The UV data showed a λ_{max} in chloroform of 256 nm, consistent with predominantly *meta*-linked aryl rings.[10] FTIR analysis of **10** confirmed that the polymer was predominantly *meta*-linked by the intense absorbance at 782 cm^{-1}. The *para*-linked band was weak and had shifted to higher wave numbers at 839 cm^{-1}, confirming that the amount of *para*-linkages in the polymer was low. Branching phenyl stretches at 755 and 700 cm^{-1} were also observed. The C–Br absorption was evident at 1074 cm^{-1}; however, it was noticeably weaker than the previous polymers prepared from 1-bromo-4-lithiobenzene (**1**). The branching phenyl stretches were also much more intense than with earlier systems. All of these factors suggested a lower bromide content. Elemental analysis showed **10** prepared using 1.5 equiv of *tert*-butyllithium to contain 12% bromide or one bromide for every eight phenyl rings. This was significantly lower than the previous polymers prepared from 1,4-dibromobenzene. When increased amounts of *tert*-butyllithium were used to form intermediate **8**, there was a noticeable decrease in the C–Br band at 1074 cm^{-1} and an increase in the branching phenyl stretches at 755 and 700 cm^{-1}. Elemental analysis showed that when 1.8 equiv of *tert*-butyllithium were used, the amount of bromide in these polymers could be reduced to only 8% or one bromide for every eleven aryl rings. When 2.0 equiv of *tert*-butyllithium were used, the bromide content decreased to 2% or one bromide for every 41 aryl rings. The bromide content for the polymers prepared from 1,3-dibromobenzene was therefore considerably less than the polymers prepared from 1,4-dibromobenzene and the effect of the increased *tert*-butyllithium on the bromide content was more pronounced.

Debromination of **10** was achieved upon relithiation with *tert*-butyllithium in THF at −78 °C followed by quenching with water to afford **11**. Again the molecular weight of the polymer increased from M_w = 2360 with M_w/M_n = 2.23 to M_w = 2890 with M_w/M_n = 1.72 suggesting further coupling of the polymer chains. Note the decrease in polydispersity for **11**. Since an increase in the amount of *meta*-linkages is known to improve solubility in polyphenylenes, these predominantly *meta*-linked polymers are more soluble, thereby allowing the lower molecular weight material to be removed during the ether precipitations and, in turn, lower the polydispersities. Elemental analysis confirmed that all the bromide content in **10** had been removed on conversion to **11**. The ^1H NMR (300 MHz, $CDCl_3$) of **11** showed a broad multiplet from δ 6.8 to 8.0 ppm, similar to that of **10**. If hexane insoluble portions were checked by ^1H NMR, small amounts of aliphatic material were observed. The ^{13}C NMR (300 MHz, $CDCl_3$) was also similar with broad peaks at δ 140–142 and 125–132 ppm. The UV spectrum showed λ_{max} at 252 nm, consistent with predominantly *meta*-linked material.[11]

The TGA (N_2, 20 °C/min) of brominated polymer **10** showed 10% weight loss at 434 °C and a char yield of 59% at 900 °C. The debrominated polymer **11** had a 10% weight loss at 468 °C and a char yield of 55% at 900 °C. The DSC (N_2, 20 °C/min) analysis of **10** and **11** showed no melting or glass transition events on either the first or second heating runs up to 250 °C. However, these materials did appear to flow by visual observation of the charred material.

When equal amounts of 1,4- and 1,3-dibromobenzene were treated with 1.5 equiv of *tert*-butyllithium in THF at −78 °C and allowed to warm to room temperature and stir for 2 h, a 62% yield of polymer **12** (M_w = 3340, M_w/M_n = 3.0) was obtained (eq 4). **12** was also predominantly *meta*-linked by FITR analysis, as evidenced by the strong *meta* band at 785 cm^{-1}. The *para* band at 825 cm^{-1} was weak and had shifted to higher wavenumbers compared to the previous polymer prepared using 1,4-dibromobenzene. The UV spectrum showed a λ_{max} in chloroform accordingly at 262 nm, a value between that of **6** at 284 nm and **10** at 252 nm. Elemental analysis showed the material contained approximately 13% bromides or one bromide for every seven aryl rings by elemental analysis.



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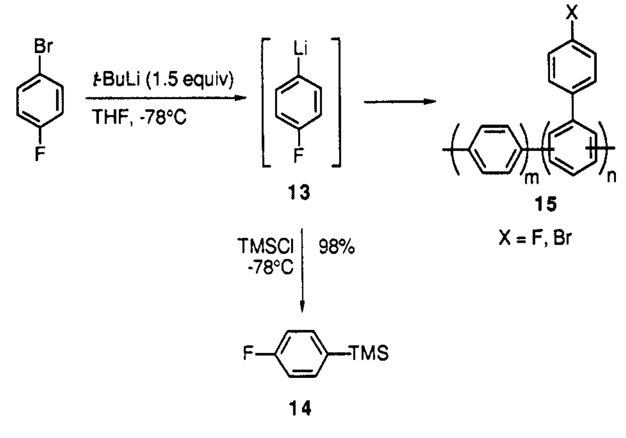
We attempted to make soluble fluorinated and chlorinated polyphenylenes using 1,4-difluorobenzene and 1,4-dichlorobenzene. However, when 1,4-difluorobenzene was

Table IV. Polymerization of 1-Fluoro-4-lithiobenzene (13) in THF

ent no.	amt of starting material (mmol)	amt of *t*BuLi (equiv)	Li–X exch temp (°C)	Li–X exch solvent	polym temp (°C)	polym time (h)	amt of Et_2O insol material (g)	%[a] yield	M_w	M_n	M_w/M_n	FTIR bands (cm^{-1})
1	16.0	2.0	−78	THF	22	2	0.41	31	3100	1000	3.11	1157.6, 1005.1, 888.8, 821.4, 790.3, 758.0, 698.5
2	16.0	2.0	−78	THF	22	16	0.60	45	3250	710	4.57	1074.5, 1005.7, 889.1, 820.4, 789.7, 757.8, 698.5
3	16.0	1.8	−78	THF	22	2	0.51	43	2960	1040	2.60	1157.6, 1004.7, 888.3, 820.0, 789.6, 758.1, 697.8
4	16.0	1.8	−78	THF	22	16	0.40–0.49	34–41	2990–3610	920–1110	3.26–3.25	1158.0, 1005.7, 895.7, 819.0, 788.8, 757.9, 699.5
5	16.0	1.8	−78	THF	0	2	0.14	10	2720	800	3.40	1158.1, 1095.4, 1004.5, 888.3, 816.1, 789.6, 761.8, 698.4
6	5.0	1.5	−78	THF	22	2	0.16	51	6000	2120	2.83	1158.0, 1005.4, 886.3, 818.8, 789.8, 759.1, 699.5
7	16.0	1.5	−78	THF	60	2	0.59	59	5940	2110	2.81	1157.8, 1074.0, 1005.2, 888.6, 819.6, 789.1, 757.9, 699.4
8	16.0	1.5	−78	THF	22	16	0.45	45	4840	1540	3.15	1158.1, 1005.3, 889.9, 818.0, 790.9, 758.3, 699.8
9	16.0	1.5	−78	THF	0	2	0.06	6	940	390	2.41	1160.0, 1003.2, 882.2, 816.2, 791.9, 766.0, 697.2
10	16.0	1.5	−78	Et_2O	22	16	0.10	10	930	430	2.17	1159.5, 1004.2, 893.1, 819.0, 791.8, 765.2, 698.1
11	10.0	1.5	−78	DME	22	16	0.08	13	5690	1560	3.64	1159.0, 1074.3, 1009.6, 876.8, 824.0, 788.1, 757.7, 700.0
12	10.0	1.5	0	1,4-dioxane	22	16	*b*					
13	10.0	1.3	−78	THF	22	2	0.21	39	4050	1920	2.10	1158.0, 1073.9, 1006.7, 882.3, 819.3, 790.2, 759.3, 699.4
14	16.0	1.0	−78	THF	22	16	0.13	20	1820	850	2.10	1120.6, 1073.6, 1009.9, 872.7, 824.0, 784.8, 693.5

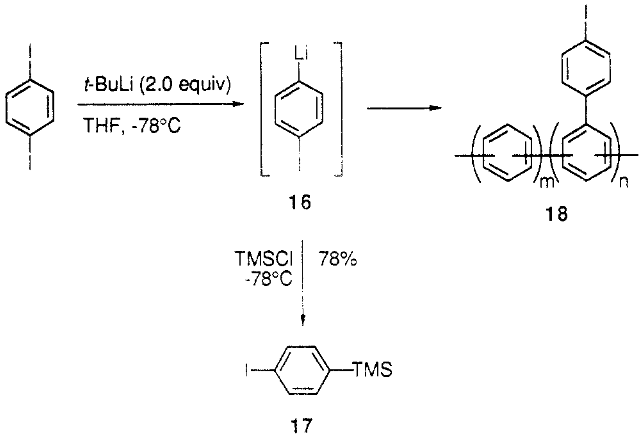
[a] Yields were based on the amount of Et_2O insoluble material collected, elemental data, and the amount of *t*BuLi used. [b] No Et_2O insoluble material obtained.

Scheme III



treated with 2.0 equiv of *tert*-butyllithium at −78 °C in THF and then allowed to warm to room temperature and stir 2 h, a brown insoluble solid containing mixtures of *para* (824 cm^{-1}) and *meta* (874 cm^{-1}) linkages was obtained. When 1,4-dichlorobenzene was treated with 2.0 equiv of *tert*-butyllithium at −78 °C in THF, followed by addition of HMPA at 65 °C, a brown insoluble solid was obtained. This material also contained mixtures of *para* (816.2 cm^{-1}) and *meta* (790.5 cm^{-1}) linkages. These results were not surprising since fluorides and chlorides generally do not undergo facile lithium–halogen exchange reactions.[19] These materials are probably highly cross-linked. Soluble fluorinated polymers could be obtained, however, when the monolithiated substrate of 1-bromo-4-fluorobenzene **13** was stirred at room temperature in THF (Scheme III). The intermediacy of **13** was confirmed in a separate experiment by quenching the reaction solution at −78 °C with chlorotrimethylsilane to give a 98% yield of 1-fluoro-4-(trimethylsilyl)benzene (**14**). The results of the polymerization are shown in Table IV. The optimal results again involved treatment of 1-bromo-4-fluorobenzene with 1.5 equiv of *tert*-butyllithium in THF at −78 °C followed by stirring at room temperature for 2 h. This gave a 51% yield of polymer **15** which had $M_w = 6000$ and $M_w/M_n = 2.83$. Elemental analysis of **15** showed it to contain both bromide (5% or one for every 20 aryl rings) and fluoride (4% or three for every 20 phenyl rings). ^1H NMR (300 MHz, $CDCl_3$) showed no aliphatic material in the ether insoluble portion with aromatic signals at δ 6.8–7.9 ppm. ^{13}C NMR (125 MHz, $CDCl_3$) showed signals at δ 115–116, 126–129, and 139–142 ppm. FTIR analysis showed that the polymer contained mixtures of *para*-linkages at 818 cm^{-1} and *meta*-linkages at 790 cm^{-1}. The *para*/*meta* ratio did appear to favor *para*-linkages, but not as much as the earlier polymers prepared in dioxane. The C–Br absorbance at 1074 cm^{-1} was weak, while a stretch at 1158 cm^{-1} was attributed to the C–F moieties.[20] If increased amounts of *tert*-butyllithium was used, the C–Br absorbance at 1074 cm^{-1} did appear to weaken while the branching phenyl stretches increased in intensity. There was also a no-

Scheme IV

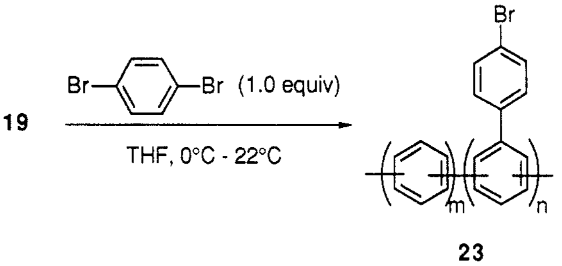


ticeable shift in the *para* band at 818 cm^{-1} to higher wavenumbers (820–821 cm^{-1}). This would again suggest that the halogen content in these polymers was lowered using larger amounts of *tert*-butyllithium. TGA analysis (N_2, 20 °C/min) of **15** showed a 10% weight loss of 449 °C and char yields of 59% at 900 °C. DSC analysis (N_2, 20 °C/min) showed no melting or glass transition events up to 230 °C. However, the charred material was glossy black and did appear to flow on heating.

Soluble iodinated polyphenylenes **18** were also prepared in THF from 1-lithio-4-iodobenzene (**16**) (Scheme IV). The results are shown in Table V. Unlike the previous systems, our optimal conditions for forming polymer **18** involved treatment of 1,4-diiodobenzene with 2.0 equiv of *tert*-butyllithium at −78 °C in THF. The intermediacy of **16** was confirmed in a separate experiment by quenching the reaction solution with chlorotrimethylsilane at −78 °C to give a 78% yield of 1-iodo-4-(trimethylsilyl)benzene (**17**). If the reaction solution was allowed to warm to room temperature and stir for 2 h, yields of up to 65% of polymer **18** and M_w = 4250 and M_w/M_n = 3.05 were obtained. The ^{1}H NMR (300 MHz, $CDCl_3$) showed no aliphatic material in the ether insoluble portion with aromatic signals at δ 6.8–8.0 ppm. The UV spectrum showed a λ_{max} in chloroform at 276 nm. The FTIR spectrum of **18** was similar to the one obtained from the polymerization of 1-bromo-4-lithiobenzene (**1**) in THF. When 1.5 equiv of *tert*-butyllithium was used, the *para* and *meta* bands at 805 and 781 cm^{-1}, respectively, were strong and approximately equal in intensity. Upon moving to 2.0 equiv of *tert*-butyllithium, however, both bands became much weaker and the *para* band shifted to 825 cm^{-1} while the branching phenyl bands at 758 and 697 cm^{-1} increased in intensity. A noticeable decrease in intensity for the C–I absorbance[3e] at 1064 cm^{-1} was also apparent when 2.0 equiv of *tert*-butyllithium was used. Elemental analysis showed that **18** prepared using 2.0 equiv of *tert*-butyllithium contained 10% iodide or approximately one iodide for every 14 phenyl rings. When 1.5 equiv of *tert*-butyllithium was used to form intermediate **16**, the iodide content increased to 36% or one iodide for every three aryl rings. DSC analysis (N_2, 20 °C/min) for **18** showed no transitions on either the first or second heating scans to 230 °C. TGA analysis (N_2, 20 °C/min) showed a 10% weight loss at 322 °C and char yields of 46% at 900 °C. Visual analysis of the charred material did indicate that the material flow during heating.

Dianions of 1,4-dibromobenzene and 1,3-dibromobenzene can also be cleanly generated in ethereal solvents like THF or ether (Scheme V) upon addition to 4.0 equiv of *tert*-butyllithium in THF at −78 °C. The intermediacy of these dianions was confirmed by quenching the reactions at −78 °C with TMSCl to afford excellent yields of the disilylated adducts **20** and **22**.[19b]

Interestingly, when **19** was prepared in THF and allowed to warm to room temperature and stir 16 h, no polymeric products were isolated after quenching the reaction solution with chlorotrimethylsilane. Instead, an 81% isolated yield of **20** was obtained. Thus, without the presence of aryl halides, the polymerization does not occur. When **19** or **21** was treated with 1,4-difluorobenzene, 2,5-dichloropyridine, or 2,6-dichloropyridine, insoluble polymeric products resulted. Soluble brominated polyphenylene **23** was produced from the copolymerization of 1,4-dilithiobenzene (**19**) and 1,4-dibromobenzene (eq 5). The polymerization procedure is similar to the polymerizations discussed earlier but it involves addition of the dilithio species to the dihalogenated aromatic at 0 °C in THF. The reaction is then allowed to warm to room temperature and stir overnight. Isolation of the ether insoluble material gave a 53% yield of polymer **23** which is remarkably similar to the polymers prepared from 1-bromo-4-lithiobenzene (**1**). The yield was based on the amount of dihalogenated aromatics used and the elemental analysis which showed the polymer to contain approximately 11% bromide or one bromide for every nine phenyl rings. **23** had M_w = 3110 with M_w/M_n = 3.6 relative to polystyrene standards. FITR analysis showed approximately equal intensity *para* and *meta* bands at 818 and 789 cm^{-1}, respectively. The ^{1}H NMR (300 MHz, $CDCl_3$) showed a broad aromatic signal at δ 7.0–7.9 with little or no aliphatics. DSC analysis (N_2, 20 °C/min, 50–250 °C) showed a broad endotherm at 165–240 °C on the first heating scan. Apparent T_g's were observed at 150 and 220 °C on the second heating scan. The TGA (N_2, 20 °C/min) showed 10% weight loss at 451 °C and a char yield of 58% at 900 °C. When **23** was debrominated with *tert*-butyllithium in THF at −78 °C, the *para* band shifted to 820 cm^{-1} while the branching phenyl stretches grew in intensity, confirming that the structure was indeed similar to the previous polymer systems. Surprisingly, the molecular weight dropped slightly to M_w = 2950 with M_w/M_n = 3.5. The lower bromide content in this polymer may have hindered additional coupling of the polymer chains.



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Mechanistic Findings

There are several features of these polymerizations which suggest that *o*-benzyne[21] intermediates are involved. The first and most obvious is the presence of both *meta*- and *para*-linkages in all of the polymers. If an *o*-benzyne intermediate as shown below was formed, it could be attacked by an aryllithium species at a position *meta* or *para* to the remaining bromide. Biphenylene and substituted biphenylenes are also known to form during

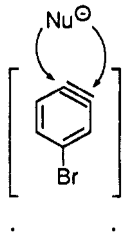
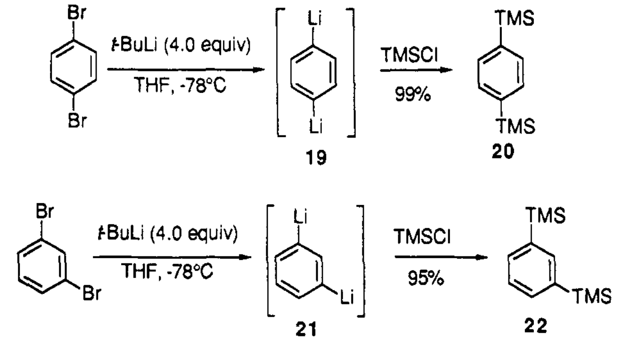


Table V. Polymerization of 1-Iodo-4-lithiobenzene (16) in THF

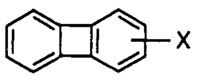
ent no.	amt of starting material (mmol)	amt of *t*BuLi (equiv)	Li–X exch temp (°C)	Li–X exch solvent	polym temp (°C)	polym time (h)	amt of Et_2O insol material (g)	%[a] yield	M_w	M_n	M_w/M_n	FTIR bands (cm^{-1})
1	10.0	2.0	−78	THF	22	16	0.46	53	3530	830	4.23	1063.1, 1005.3, 891.7, 824.5, 790.8, 757.8, 697.1
2	10.0	2.0	−78	THF	22	2	0.57	65	4250	1400	3.05	1056.4, 1005.1, 890.5, 823.8, 790.0, 758.2, 698.5
3	10.0	2.0	0	dioxane	22	16	*b*					
4	10.0	2.0	0	DME	22	16	0.17	20	4130	960	4.29	1063.0, 1002.0, 890.5, 812.1, 786.4, 758.3, 698.6
5	10.0	2.0	−78	Et_2O	22	16	*b*					
6	10.0	1.8	−78	THF	22	2	0.67		2190	550	4.02	1063.3, 1001.4, 887.6, 812.1, 784.7, 758.3, 698.4
7	10.0	1.8	−78	THF	22	16	0.61		2150	630	3.41	1063.6, 1001.6, 887.5, 812.2, 785.1, 758.3, 698.7
8	16.0	1.5	−78	THF	22	2	0.97	68	2000	640	3.13	1063.1, 1001.3, 885.6, 811.6, 784.3, 758.1, 698.7
9	10.0	1.5	−78	THF	22	16	0.55	62	1960	760	2.57	1065.2, 1001.7, 882.2, 812.0, 785.3, 758.2, 700.0
10	10.0	1.5	−78	Et_2O	22	16	*b*					
11	10.0	1.0	−78	THF	22	16	*b*					

[a] Yields were based on the amount of Et_2O insoluble material collected, elemental data, and the amount of *t*BuLi used. [b] No Et_2O insoluble material obtained.

Scheme V



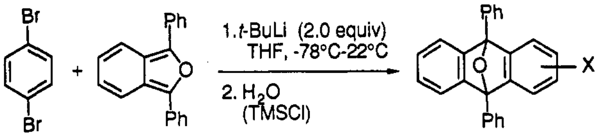
reactions involving *o*-benzyne intermediates.[21a,22] The mass spectrometric (MS) analysis of the ether soluble fractions from polymerizations of 1-bromo-4-lithiobenzene (1) showed M^+ peaks corresponding not only to biphenylene **24a** at 151 amu but also to brominated biphenylene



24a X = H
24b X = Br
24c X = F

24b at 230 and 232 amu. The MS analysis of the ether soluble portions from the polymerization of 1-fluoro-4-lithiobenzene **13** showed fluorinated biphenylene **24c** at 170 amu.

o-Benzyne intermediates can also be trapped as their Diels–Alder adducts.[21a,23] When 1-bromo-4-lithiobenzene (1), prepared using 2.0 equiv of *tert*-butyllithium, was allowed to warm to room temperature for 2 h in the presence of 1,3-diphenylisobenzofuran followed by quenching with water, we searched for the corresponding Diels–Alder adducts (eq 6). Attempts to cleanly isolate and



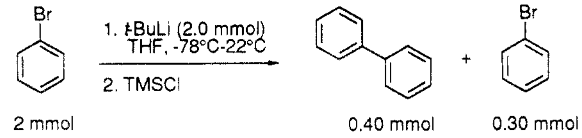
(6)

25a X = H
25b X = Br
25c X = TMS

purify the Diels–Alder adducts by column chromatography [alumina, benzene, ether (1/1)] were unsuccessful since they appeared to decompose on both alumina and silica gel. However, when the partially decomposed yellow materials (R_f = 0.9 in 1:1 benzene/ether) were subjected to MS analysis, M^+ at 346, 424, and 426 amu were observed. These molecular weights did indeed correspond to the Diels–Alder adducts **25a** ($C_{26}H_{18}O$) and **25b** ($C_{26}H_{17}{}^{79}BrO$, $C_{26}H_{17}{}^{81}BrO$). Small amounts of 1,2-dibenzoylbenzene were also obtained from a separate fraction (R_f = 0.6 in 1:1 benzene/ether). A similar *o*-benzyne trapping reaction was then repeated; however, this time, the reaction was quenched with TMSCl. Although ^1H NMR analysis of the crude product did indicate the presence of small amounts of silylated material, purification attempts were again unsuccessful. The peaks in the aromatic region were broadened, suggesting that oligomeric and or polymeric material had been formed. The MS of the crude product did, however, show M^+ at 418 amu corresponding to **25c** ($C_{29}H_{26}OSi$).

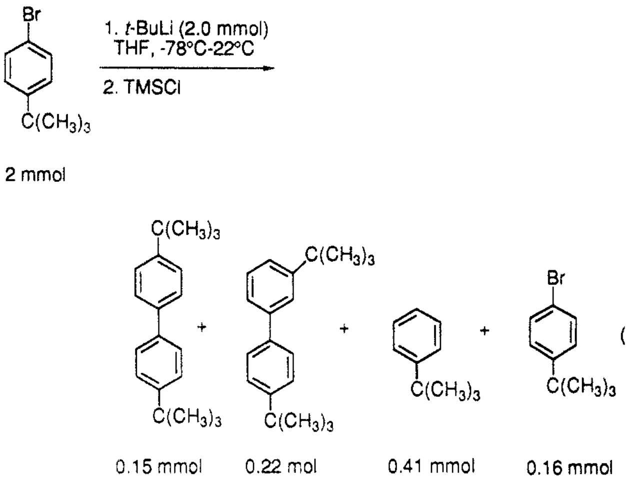
The presence of silylated material was indeed surprising, since many of our higher molecular weight polymers prepared using 1.5 equiv of *tert*-butyllithium were quenched with TMSCl and no silylated material was observed.[7] Thus it is apparent that the polymers prepared using 1.5 equiv of *tert*-butyllithium were not polylithiated. We then polymerized 1-bromo-4-lithiobenzene (1) using 2.0 equiv of *tert*-butyllithium. After stirring at room temperature for 2 h, the reaction was quenched with TMSCl. This time silylated material was observed in the ^1H NMR spectra of both the ether insoluble material and the ether soluble portions. Thus our polymers can exist as lithiated systems if conditions are adjusted. This may enable the polymer to be functionalized *in situ* with a variety of electrophiles. This also explains the lower bromide content in many of the polymers prepared using 2.0 equiv of *tert*-butyllithium.

A mixture of fluorobenzene and phenyllithium in ether and THF at temperatures greater than −25 °C is known to produce 2-lithiobiphenyl *via* an *o*-benzyne intermediate. The process involves abstraction of the proton *ortho* to fluoride by phenyllithium followed by elimination of LiF to give *o*-benzyne. A second equivalent of phenyllithium then adds to the *o*-benzyne giving 2-lithiobiphenyl. If substituted fluorobenzenes are used, isomeric mixtures of lithiobiphenyls are produced.[21a] In order to probe whether similar deprotonations leading to *o*-benzyne intermediates may be occurring in our polymerizations, we generated phenyllithium in the presence of bromobenzene by treating *tert*-butyllithium (2 mmol) with 1 equiv of bromobenzene (2 mmol) in THF at −78 °C to produce a 1:1 mixture of bromobenzene and phenyllithium (recall 4 mmol of *tert*-butyllithium would be necessary for the complete conversion of 2 mmol of the bromobenzene to phenyllithium). The reaction solution was then allowed to warm to room temperature and stir 16 h before quenching with TMSCl (eq 7). This gave 0.40 mmol of biphenyl (GC yield using undecane as an internal standard with the response ratio determined from an authentic sample), while 0.30 mmol of bromobenzene was recovered. No low molecular weight silylated aromatics were detected by GC (comparing



(7)

against authentic silylated aromatics) or by GCMS. Benzene would remain undetected, being in the solvent front. Quaterphenyl species would be beyond the GC range screened. Similar studies were then conducted using 1-bromo-4-*tert*-butylbenzene (2 mmol) (eq 8). 4,4′-Bis(*tert*-butyl)biphenyl (0.15 mmol) and 3,4′-bis(*tert*-butyl)biphenyl (0.22 mol) were obtained along with *tert*-butylbenzene (0.41 mmol) and 1-bromo-4-*tert*-butylbenzene (0.16 mmol). The presence of 3,4′-bis(*tert*-butyl)biphenyl suggests that an *o*-benzyne intermediate was being generated. Again, no silylated material was observed in the GC thermograms. However, if bromobenzene (2 mmol) or 1-bromo-4-*tert*-butylbenzene (2 mmol) were added to *tert*-butyllithium (4 mmol) followed by warming and quenching with TMSCl, the predominant products observed in the GC analysis were, of course, the corresponding (trimethylsilyl)benzene and 1-*tert*-butyl-4-(trimethylsilyl)benzene, respectively. Since no silylated material was obtained in eqs 7 and 8, it implies that the aryllithium species, upon warming, will rapidly deprotonate the existing aryl bromide to form an *o*-benzyne species which is immediately trapped by a second aryllithium.

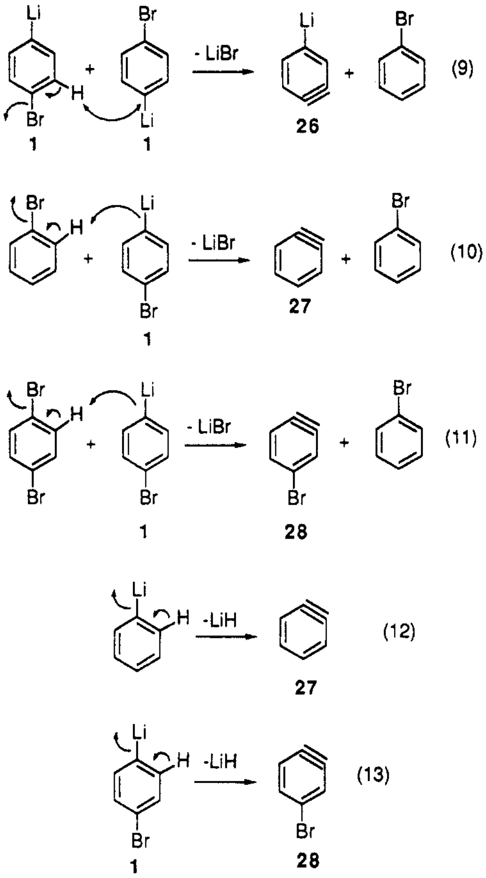


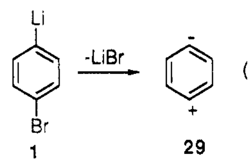
(8)

When we quenched the standard polymerizations (eq 3) with water, we noticed the rapid evolution of a gas. The gas was shown to be H_2 by mass spectrometric analysis. When we quenched the polymerization mixture with D_2O, DH and H_2 were detected. No D_2 was observed, thus no Li(0) forms during the polymerization. Surprisingly, however, on quenching with D_2O, the amount of DH to H_2 formed was 1:1.4. This was checked several times with different sources of D_2O (deuterium content >99%). A large isotope effect appears to be the cause. The H_2 evolution on H_2O quenching is probably caused by the reaction of water with LiH. Therefore, another route to *o*-benzynes could involve the elimination of LiH from an aryllithium species. LiH eliminations are known to occur with heterocyclic aromatics.[24]

Our results suggest that *o*-benzyne intermediates are involved in the polymerization and there are several possible pathways by which they may be generated (Scheme VI). One route is deprotonation of 1-bromo-4-lithiobenzene (1) resulting in the elimination of LiBr to give bromobenzene and a lithiated *o*-benzyne species **26** (eq 9). Presumably, bromobenzene could then undergo deprotonation by a variety of aryllithiums to give *o*-benzyne **27** (eq 10). Deprotonation of unreacted 1,4-dibromobenzene could also occur to give a brominated *o*-benzyne species **28** (eq 11). An additional route, elimination LiH from phenyllithium or 1-bromo-4-lithiobenzene (**1**) may occur as well to give *o*-benzyne intermediates **27** and **28**, respectively (eqs 12 and 13). The formation of LiH and the trapping of the *o*-benzyne intermediates **26**–**28** suggest that all of the routes shown in eqs 9–13 are possible. At this point, however, we can not rule out the participation of an $S_{RN}1$ mechanism.[25] Additionally, the *p*-benzyne intermediate (**29**)[26] is known and it may be forming by the loss of LiBr from 1-bromo-4-lithiobenzene (**1**) (eq 14). However, at this point we have no direct evidence for the intermediacy of **29** in our reaction.

Scheme VI





(14)

In conclusion, it is apparent that this aryl–aryl coupling reaction is well-suited for the rapid preparation of a variety of halogenated polyphenylenes. The mechanism for the polymerization appears to proceed via benzyne intermediates. The solubility and high halogen content in these polymers should offer improvements in both the processing and functionalization of polyphenylenes which may open new avenues for the preparation of functionalized polyphenylene-based materials.[27]

Experimental Section

General Procedures. All operations were carried out under a dry, oxygen-free, nitrogen atmosphere. ^1H NMR spectra were recorded at 300 or 500 MHz on a Brüker AM-300 or Brüker AM-500 spectrometer, respectively. The ^{13}C NMR spectra at 75 or 125 MHz were recorded on a Brüker AM-300 or a Brüker

AM-500 spectrometer, respectively. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS) and ^{13}C resonances (unless otherwise noted) were recorded using the 77.0 ppm $CDCl_3$ resonance of the solvent as an internal reference and are reported in ppm downfield from TMS. Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 Series FTIR. The accurate-mass spectra were determined on a VG Analytical, Ltd., 70SQ high resolution, double-focusing mass spectrometer equipped with a VG 11/250 data system. Molecular weight analyses were performed using two 30- × 75-cm Burdick and Jackson GPC columns (10^5 Å, 10 μm and 500 Å, 5 μm), eluted with THF at 60 °C (flow rate 1.0 mL/min, 700 psi), a Perkin-Elmer LC 250 pump, and a Perkin-Elmer LC-30 RI detector. Molecular weight results were based on five polystyrene standards (M_w = 9200, 7000, 5050, 2950, 2150, 1060, correlation coefficient >0.997) purchased from Polymer Laboratories Ltd. Thermal analyses were performed using a Perkin-Elmer TGA 7 thermogravimetric analyzer (heating rate = 20 °C/min, N_2 atmosphere) and a Perkin-Elmer DSC 7 differential scanning calorimeter (heating rate 20 °C/min, N_2 atmosphere). Combustion analyses were obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091, or Galbraith Laboratories, Inc., P.O. Box 51610, Knoxville, TN 37950-1610. Capillary GC analyses were obtained using a Hewlett Packard Model 5890 gas chromatograph with a Hewlett Packard 3396A integrator. 1,4-Dibromobenzene, 1,3-dibromobenzene, 1-bromo-4-fluorobenzene, 1,4-diiodobenzene, bromobenzene, 1-bromo-4-*tert*-butylbenzene, and 1,3-diphenylisobenzofuran were purchased from Aldrich Chemical Co., Inc. and used without purification. Hexamethylphosphoramide (HMPA) and chlorotrimethylsilane (TMSCl) were purchased from Aldrich Chemical Co., Inc. and distilled from calcium hydride under a nitrogen atmosphere prior to use. Alkyllithiums were purchased from Aldrich Chemical Co., Inc. or Lithium Corp. of America. Reagent grade tetrahydrofuran (THF), diethyl ether, and 1,4-dioxane were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade dichloromethane and toluene were distilled under nitrogen from calcium hydride. Bulk grade hexane was distilled prior to use. Gravity column chromatography and flash chromatography were carried out on silica gel (230–400 mesh from EM Science). In all experimental procedures, unless otherwise noted, flash chromatography refers to chromatography with a nitrogen head pressure.

Trapping of the Intermediate 1-Bromo-4-lithiobenzene (1) To Form 1-Bromo-4-(trimethylsilyl)benzene (2).[28] To a stirring solution of 1,4-dibromobenzene (23.6 g, 100 mmol) in ether (150 mL) was added at −78 °C *tert*-butyllithium (123.5 mL, 210 mmol, 1.7 M in pentane) over 1 h. The solution was stirred for 1 h at −78 °C, and chlorotrimethylsilane (14.0 mL, 110 mmol) was added over 10 min. The solution was allowed to warm to room temperature and stir 30 min. The solution was added to water. The organic layer was washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave 19.6 g (86%) of 2 as a clear colorless oil. FTIR (neat): ν 2955.8, 1573.9, 1479.5, 1375.7, 1250.6, 1106.2, 1066.7, 1012.0, 840.8, 807.2, 754.9, 719.5 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (d, J = 8.3 Hz, 2 H), 7.36 (d, J = 8.3 Hz, 2 H), 0.24 (s, 9 H).

Brominated Polyphenylene 3 Prepared Using HMPA in 1,4-Dioxane. To a 100-mL three-necked round bottom flask equipped with a thermometer, stir bar, and reflux condenser and containing 1,4-dibromobenzene (1.88 g, 8.0 mmol) in dioxane (8 mL) under a nitrogen atmosphere was added at 0 °C *tert*-butyllithium (9.4 mL, 16 mmol, 1.7 M in pentane). The ensuing milky white to yellow reaction mixture was stirred at 0 °C for 30 min. The solution was warmed to reflux (80 °C), and hexamethylphosphoramide (1.4 mL, 8.0 mmol) was added. The ensuing dark black reaction mixture was then allowed to cool to room temperature. The reaction mixture was added to 3 N hydrochloric acid (25 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were washed with 3 N hydrochloric acid (10×) and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave a tan/brown solid. Fractional precipitation with ether gave two fractions of a tan/brown solid. The solid was washed with ether to give 0.25 g (31%) of 3 as a tan/brown solid. FTIR (KBr): ν 3027.9, 2954.0, 1898.8, 1592.1, 1477.8, 1387.9, 1073.3, 1002.0, 884.7, 809.2, 790.6, 761.6, 698.8 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.0–8.0 (m). No aliphatic peaks were detected. T_1 (300 MHz, $CDCl_3$): 0.4–1.6 s. ^{13}C NMR (75 MHz, $CDCl_3$): δ 142–139, 130–124. UV ($CHCl_3$): λ_{max} 274 nm. M_w = 2400; M_n = 840; M_w/M_n = 2.85. Anal. Calcd for $(C_{18}H_{11}Br)_n$: C, 70.36; H, 3.58; Br, 26.06. Found: C, 68.94; H, 4.11; Br, 25.22. Due to difficulties in burning polyphenylene polymers quantitatively, they often do not afford clean combustion analyses.[5d] TGA (N_2, 20 °C/min) showed 10% weight loss at 356 °C and 48% weight loss at 900 °C.

Debromination of 3 To Form 4. To a stirred solution of 3 (0.34 g, M_w = 2400, M_n = 840, M_w/M_n = 2.85) in THF (4 mL) was added at −78 °C *tert*-butyllithium (1.76 mL, 3.0 mmol, 1.7 M in pentane). The ensuing brown black reaction was then stirred at −78 °C for 1 h. To the solution was then added at −78 °C water (15 mL). The solution was then allowed to warm to room temperature. The solution was then poured into 3 N hydrochloric acid. The organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* afforded 0.21 g of 4 as a brown solid. FTIR (KBr): ν 3027.7, 2954.4, 1598.3, 1479.5, 1395.7, 1178.8, 1116.1, 1074.6, 1005.3, 884.3, 825.4, 758.2, 697.7 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4–7.8 (m). T_1 (300 MHz, $CDCl_3$): 0.9–1.4 s. ^{13}C NMR (125 MHz, $CDCl_3$): δ 144–138, 131–124. UV ($CHCl_3$): λ_{max} 278 nm. M_w = 3180; M_n = 1140; M_w/M_n = 2.80. Anal. Calcd for $(C_{18}H_{12})_n$: C, 94.74; H, 5.26. Found: C, 89.96; H, 5.72; Br, 0.0. TGA (N_2, 20 °C/min) showed 10% weight loss at 373 °C and 46% weight loss at 900 °C.

Brominated *p*-Polyphenylene 5 Prepared without HMPA in Refluxing 1,4-Dioxane. To a 100-mL three-necked round bottom flask equipped with a thermometer, stir bar, and reflux condenser and containing 1,4-dibromobenzene (3.78 g, 16.0 mmol) in dioxane (16 mL) under a nitrogen atmosphere was added at 0 °C *tert*-butyllithium (16.0 mL, 32.0 mmol, 2.0 M in pentane). The ensuing milky white to yellow reaction mixture was stirred at 0 °C for 30 min. The reaction mixture was then allowed to warm to reflux (80 °C) for 2 h. The ensuing brown reaction solution was then allowed to cool to room temperature and was added to 3 N hydrochloric acid (25 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave a yellow solid. The solid was washed with ether to give 0.10 g of 5 as a yellow solid (after isolation this solid was insoluble in THF and methylene chloride). FTIR (KBr): ν 1901.7, 1477.9, 1384.2, 1069.9, 1000.5, 809.7, 724.0 cm^{-1}. X-ray diffraction: 4.199, 3.106 Å. Anal. Calcd for $(C_9H_7Br)_n$: C, 55.38; H, 3.59; Br, 41.03. Found: C, 56.02; H, 3.37; Br, 40.54.

Brominated Polyphenylene 6 Prepared Using 1-Bromo-4-lithiobenzene (1) in THF. To a 100-mL round bottom flask equipped with a stir bar and reflux condenser and containing 1,4-dibromobenzene (3.78 g, 16.0 mmol) in THF (16 mL) under a nitrogen atmosphere was added dropwise at −78 °C over 30 min *tert*-butyllithium (10.4 mL, 24 mmol, 2.3 M in pentane). The ensuing milky white to yellow reaction mixture was stirred at −78 °C an additional 15 min. The reaction mixture was then allowed to warm to room temperature and stir for 2 h. The ensuing black reaction solution was then poured into water (25 mL). The organic layer was separated, and the aqueous portion was extracted with methylene chloride (3×). The combined organic layer were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave a tan/brown solid. The solid was washed with ether to give 0.60 g (50%) of 5 as a tan/brown solid. FITR (KBr): ν 3027.0, 1901.1, 1590.6, 1472.4, 1384.0, 1249.1, 1179.6, 1101.5, 1073.3, 1002.2, 967.2, 888.9, 809.4, 787.3, 761.4, 697.9, 506.3 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 7.2–7.9 (m). No aliphatic peaks were detected. ^{13}C NMR (125 MHz, $CDCl_3$): δ 139–141, 124–135. UV ($CHCl_3$): λ_{max} 284 nm. M_w = 2570, M_n = 630, M_w/M_n = 4.06. Anal. Calcd for $(C_{18}H_{11}Br)_n$: C, 70.36; H, 3.58; Br, 26.06. Found: C, 71.49; H, 4.15; Br, 24.33. TGA (N_2, 20 °C/min) showed 10% weight loss at 400 °C and 48% weight loss at 900 °C.

Debromination of 6 To Give 7. To a stirred solution of 5 (0.49 g, M_w = 1870, M_n = 660, M_w/M_n = 2.83) in THF (5 mL) was added at −78 °C *tert*-butyllithium (2.0 mL, 4.5 mmol, 2.3 M in pentane). The ensuing brown black reaction was then stirred at −78 °C for 1 h. The solution was then poured into ice water (15 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* afforded 0.18 g of 7 as a brown ether insoluble solid. FTIR (KBr): ν 3026.4, 1597.7, 1474.2, 1388.5, 1005.4, 890.5, 824.2, 791.5, 758.2, 697.3 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.0–7.9 (m). No aliphatic peaks were detected. ^{13}C NMR (75 MHz, CDCl$_3$): δ 139–142, 126–131. UV (CHCl$_3$): λ_{max} 288 nm. M_w = 2320, M_n = 870, M_w/M_n = 2.68. Anal. Calcd for $(C_{18}H_{12})_n$: C 94.69; H, 5.31. Found: C, 93.12; H, 5.53; Br, 0.0. TGA showed 10% weight loss at 430 °C and 52% weight loss at 900 °C.

Trapping of the Intermediate 1-Bromo-3-lithiobenzene (8) To Form 1-Bromo-3-(trimethylsilyl)benzene (9).[29] To a stirring solution of 1,3-dibromobenzene (0.24 mL, 2.0 mmol) in THF (2 mL) was added at −78 °C *tert*-butyllithium (3.3 mL, 4.1 mmol, 1.2 M in pentane). The ensuing milky white reaction solution was stirred at room temperature for 30 min, and then trimethylsilyl chloride (0.55 mL, 4.3 mmol) was added. The reaction solution was stirred at −78 °C for 5 min and then allowed to warm to room temperature and stir for 2 h. Water (10 mL) was added, and the organic layer was separated. The aqueous portion was extracted with ether (3×). The combined organic layers were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave 0.41 g (90%) of 9 as a tan oil. FTIR (neat): ν 3048.3, 2956.0, 2897.5, 1943.7, 1870.1, 1551.8, 1464.5, 1383.3, 1250.9, 1126.5, 1085.9, 1068.2, 1020.4, 838.9, 779.7, 752.9, 684.5, 654.4 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.58 (br s, 1 H), 7.45 (ddd, J = 7.92, 1.14, 0.96 Hz, 1 H), 7.40 (ddd, J = 7.30, 1.10, 1.10 Hz, 1 H), 7.20 (t, J = 7.40 Hz, 1 H), 0.25 (s, 9 H).

Brominated Poly(phenylene) 10 Prepared Using 1-Bromo-3-lithiobenzene 8 in THF. To a 100-mL round bottom flask equipped with a stir bar and reflux condenser and containing 1,3-dibromobenzene (1.21 mL, 11.0 mmol) in THF (10 mL) under a nitrogen atmosphere was added dropwise at −78 °C over 30 min *tert*-butyllithium (12.0 mL, 24 mmol, 2.0 M in pentane). The ensuing milky white to yellow reaction mixture was stirred at −78 °C an additional 15 min. The reaction mixture was then allowed to warm to room temperature and stir 2 h. The black reaction solution was then poured into water (25 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave a tan/brown solid. The solid was washed with ether to give 0.50 g (54%) of 10 as a tan/brown solid. FTIR (KBr): ν 3027.9, 1595.6, 1466.6, 1072.0, 883.0, 838.4, 780.8, 755.5, 699.7 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.8–7.9 (m). Little or no aliphatic peaks were detected. ^{13}C NMR (125 MHz, CDCl$_3$): δ 139–142, 122–132. UV (CHCl$_3$): λ_{max} 256 nm. M_w = 2850, M_n = 1520, M_w/M_n = 1.87. Anal. Calcd for $(C_{46}H_{33}Br)_n$: C, 83.01; H, 4.96; Br, 12.03. Found: C, 83.28; H, 4.91; Br, 11.80. TGA (N$_2$, 20 °C/min) showed 10% weight loss at 434 °C and 41% weight loss at 900 °C.

Debromination of 10 To Give 11. To a stirring solution of 10 (0.30 g, M_w = 2360, M_n = 1060, M_w/M_n = 2.23) in THF (4 mL) was added at −78 °C *tert*-butyllithium (2.1 mL, 3.5 mmol, 1.7 M in pentane). The ensuing brown reaction solution was stirred at −78 °C for 1 h. The solution was then poured into ice water (15 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* afforded 0.182 g (81.5) of 11 as a brown solid. FTIR (KBr): ν 3056.0, 2956.4, 890.0, 836.8, 790.8, 755.0, 700.0, 669.1 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.8–7.9 (m). Little or no aliphatic peaks were detected. ^{13}C NMR (125 MHz, CDCl$_3$): δ 140–142, 125–132. UV (CHCl$_3$): λ_{max} 252 nm, M_w = 2890, M_n = 1690, M_w/M_n = 1.72. Anal. Calcd for $(C_{46}H_{34})_n$: C, 94.20; H, 5.80. Found: C, 92.44; H, 5.65; Br, 0.0. TGA (N$_2$, 20 °C/min) showed 10% weight loss at 468 °C and 45% weight loss at 900 °C.

Brominated Polyphenylene 12 Prepared Using 1,4-Dibromobenzene and 1,3-Dibromobenzene in THF. To a stirring solution of 1,4-dibromobenzene (1.18 g, 5.0 mmol) and 1,3-dibromobenzene (0.60 mL, 5.0 mmol) in THF (10 mL) was added at −78 °C *tert*-butyllithium (6.5 mL, 15.0 mmol, 2.3 M in pentane). The ensuing reaction solution was stirred at −78 °C an additional 15 min and then allowed to warm to room temperature and stir 2 h. The reaction solution was then poured into water (25 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave a tan/brown solid. The solid was washed with ether to give 0.40 g (62%) of 12 as a tan/brown solid. FTIR (KBr): ν 3026.3, 1596.1, 1470.7, 1388.0, 1073.7, 1005.8, 886.1, 825.1, 784.7, 757.6, 700.0, 616.1 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.8–7.9 (m). Little or no aliphatic peaks were detected. UV (CHCl$_3$): λ_{max} 262 nm. M_w = 3340, M_n = 1110, M_w/M_n = 3.0. Anal. Calcd for $(C_{43}H_{30}Br)_n$: C, 82.43; H, 4.79; Br, 12.78. Found: C, 82.89; H, 4.76; Br, 12.80. TGA (N$_2$, 20 °C/min) showed 10% weight loss at 457 °C and 35% weight loss at 900 °C.

Trapping of the Intermediate 1-Fluoro-4-lithiobenzene (13) To Form 1-Fluoro-4-(trimethylsilyl)benzene (14).[30] To a stirring solution of 1-bromo-4-fluorobenzene (0.11 mL, 1.0 mmol) in THF (1 mL) was added at −78 °C *tert*-butyllithium (0.8 mL, 2.0 mmol, 2.5 M in pentane). The ensuing milky white reaction solution was stirred at room temperature for 30 min, and trimethylsilyl chloride (0.2 mL, 1.5 mmol) was added. The reaction solution was stirred at −78 °C for 5 min and then allowed to warm to room temperature and stir for 2 h. Water (10 mL) was added, and the organic layer was separated. The aqueous portion was extracted with ether (3×). The combined organic layers were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave 0.16 g (98%) of the title compound 14 as a clear oil. FTIR (neat): ν 3031.9, 2956.7, 1893.0, 1591.1, 1499.1, 1458.6, 1249.6, 1232.9, 1162.8, 1105,0, 1080,0, 1026.5, 840.9, 821.5, 756.1, 706.1 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.46 (dd, J = 8.55, 6.30 Hz, 2 H), 7.03 (dd, J = 9.28, 8.67 Hz, 2 H), 0.24 (s, 9 H).

Fluorinated Polyphenylene 15 Prepared Using 1-Fluoro-4-lithiobenzene (13) in THF. To a 50-mL round bottom flask equipped with a stir bar and containing 1-bromo-4-fluorobenzene (0.55 mL, 5.0 mmol) in THF (5 mL) under a nitrogen atmosphere was added dropwise at −78 °C *tert*-butyllithium (3.6 mL, 7.5 mmol, 2.1 M in pentane). The ensuing reaction solution was stirred at −78 °C an additional 15 min and then allowed to warm to room temperature and stir 2 h. The black reaction solution was then poured into water (25 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave a tan/brown solid. The solid was washed with ether to give 0.16 g (51%) of 15 as a tan/brown solid. FTIR (KBr): ν 3027.9, 1598.6, 1475.8, 1387.9, 1227.6, 1158.0, 1005.4, 886.3, 818.8, 789.8, 759.1, 699.5 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.8–7.9 (m). Little or no aliphatic peaks were detected. ^{13}C NMR (CDCl$_3$, 125 MHz): δ 139–142, 126–129, 115–116. UV (CHCl$_3$): λ_{max} 276 nm. M_w = 6000, M_n = 2120, M_w/M_n = 2.83. Anal. Calcd for $(C_{120}H_{84}BrF_3)_n$: C, 86.69; H, 5.06; Br, 4.82; F, 3.43. Found: C, 86.06; H, 5.03; Br, 4.47; F, 3.88. TGA (N$_2$, 20 °C/min) showed 10% weight loss at 449 °C and 41% weight loss at 900 °C.

Trapping of the Intermediate 1-Iodo-4-lithiobenzene (16) To Form 1-Iodo-4-(trimethylsilyl)benzene (17).[31] To a stirring solution of 1,4-diiodobenzene (1.65 g, 5.0 mmol) in THF (5 mL) was added at −78 °C *tert*-butyllithium (4.0 mL, 10.0 mmol, 2.5 M in pentane). The ensuing milky white reaction solution was stirred at room temperature for 30 min, and trimethylsilyl chloride (1.05 mL, 7.0 mmol) was added. The reaction solution was stirred at −78 °C for 5 min and then allowed to warm to room temperature and stir for 2 h. Water (20 mL) was added, and the organic layer was separated. The aqueous portion was extracted with ether (3×). The combined organic layers were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave a brown oil which after purification by column chromatography [silia gel, hexane] gave 1.08 g (78%) of 17 as a clear oil. R_f = 0.80 (hexane). FTIR (neat): ν 3063.2, 2954.8, 1904.3, 1568.9, 1473.8, 1373.9, 1249.4, 1107.0, 1057.4, 1006.0, 840.5, 802.1, 754.2, 710.1 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.68 (d, J = 8.20 Hz, 2 H), 7.23 (d, J = 8.21 Hz, 2 H), 0.25 (s, 9 H).

Iodinated Polyphenylene 18 Prepared Using 1-Iodo-4-lithiobenzene (16) in THF. To a 100-mL round bottom flask equipped with a stir bar and containing 1,4-diiodobenzene (3.30

g, 10.0 mmol) in THF (10 mL) under a nitrogen atmosphere was added dropwise at −78 °C *tert*-butyllithium (8.0 mL, 20.0 mmol, 2.5 M in pentane). The ensuing reaction solution was stirred at −78 °C an additional 15 min and then allowed to warm to room temperature and stir 2 h. The black reaction solution was then poured into water (25 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave a tan/yellow solid. The solid was washed with ether to give 0.58 g (69%) of 18 as a tan/yellow solid. FTIR (KBr): ν 3025.6, 1596.9, 1473.8, 1388.0, 1063.1, 1001.7, 889.3, 819.8, 787.3, 757.4, 696.9 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.8–7.9 (m). Little or no aliphatic peaks were detected. UV ($CHCl_3$): λ_{max} 276 nm. M_w = 4250, M_n = 1400, M_w/M_n = 3.05. Anal. Calcd for $(C_{87}H_{62}I)_n$: C, 84.67; H, 5.03; I, 10.30. Found: C, 83.64; H, 4.99; I, 10.19. TGA (N_2, 20 °C/min) showed 10% weight loss at 322 °C and 54% weight loss at 900 °C.

Trapping of the Intermediate 1,4-Dilithiobenzene (19) To Form 1,4-Bis(trimethylsilyl)benzene (20).[32] To a stirring solution of *tert*-butyllithium (2.0 mL, 4.2 mmol, 2.1 M in pentane) in THF (4 mL) was added at −78 °C *via* cannula 1,4-dibromobenzene (0.24 g, 1.0 mmol) in THF (1 mL). The ensuing reaction solution was stirred at −78 °C for 1 h. Chlorotrimethylsilane (0.3 mL, 2.2 mmol) was added at −78 °C. The reaction solution was stirred at −78 °C for 5 min and allowed to warm to room temperature and stir overnight. Water (10 mL) was added, and the organic layer was separated. The aqueous portion was extracted with ether (3×). The combined organic layers were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave 0.22 g (99%) of the title compound as white flakes. Mp = 93–95 °C. FTIR (KBr): ν 3045.9, 2956.6, 1377.1, 1249.8, 1311.8, 837.6, 803.7, 749.9, 693.8, 633.9, 497.5, 457.9 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (s, 4 H), 0.25 (s, 18 H).

Trapping of the Intermediate 1,3-Dilithiobenzene (21) To Form 1,3-Bis(trimethylsilyl)benzene (22).[32] To a stirring solution of *tert*-butyllithium (2.0 mL, 4.2 mmol, 2.1 M in pentane) in THF (4 mL) was added at −78 °C *via* cannula 1,3-dibromobenzene (0.12 mL, 1.0 mmol) in THF (1 mL). The ensuing reaction solution was stirred at −78 °C for 1 h. Chlorotrimethylsilane (0.3 mL, 2.2 mmol) was added at −78 °C. The reaction solution was stirred at −78 °C for 5 min and allowed to warm to room temperature and stir overnight. Water (10 mL) was added, and the organic layer was separated. The aqueous portion was extracted with ether (3×). The combined organic layers were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave 0.21 g (95%) of the title compound as a tan oil. FTIR (KBr): ν 3034.3, 2955.7, 2898.1, 1576.0, 1404.1, 1363.7, 1312.1, 1248.8, 1143.3, 1107.5, 1051.1, 855.3, 836.7, 787.2, 747.3, 690.3, 619.8 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (br s, 1 H), 7.51 (dd, J = 6.37, 1.20 Hz, 2 H), 7.33 (t, J = 7.05 Hz, 1 H), 0.26 (s, 18 H).

Brominated Polyphenylene 23 Prepared Using 1,4-Dilithiobenzene (19) and 1,4-Dibromobenzene in THF. To a stirring solution of *tert*-butyllithium (7.8 mL, 16 mmol, 2.2 M in pentane) in THF (16 mL) was added at −78 °C *via* cannula 1,4-dibromobenzene (0.94 g, 4.0 mmol) in THF (4 mL). The ensuing reaction solution was stirred at −78 °C for 1 h. The reaction solution was then added via cannula into a solution of 1,4-dibromobenzene (0.94 g, 4.0 mmol) in THF (4 mL) at 0 °C. The ensuing black reaction solution was stirred at 0 °C for 15 min and then allowed to warm to room temperature and stir 16 h. The black reaction solution was then poured into water (25 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave a tan/yellow solid. The solid was washed with ether to give 0.32 g (53%) of 23 as a tan solid. FTIR (KBr): ν 3425.6, 3026.7, 2365.1, 1596.9, 1479.9, 1385.4, 1072.7, 1004.2, 889.9, 818.0, 788.7, 759.7, 697.9, 511.7 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.8–8.0 (m). Little or no aliphatic peaks were detected. M_w = 3110, M_n = 870, M_w/M_n = 3.60. Anal. Calcd for $(C_{52}H_{36}Br)_n$: C, 84.32; H, 4.86; Br, 10.81. Found: C, 83.27; H, 4.87; Br, 10.73. TGA (N_2, 20 °C/min) showed 10% weight loss at 431 °C and 58% weight loss at 900 °C.

Trapping of *o*-Benzyne Intermediates 27 and 28 with 1,3-Diphenylisobenzofuran To Form 25a and 25b. To a stirring solution of 1,4-dibromobenzene (0.24 g, 1.0 mmol) and 1,3-diphenylisobenzofuran (0.27 g, 1.0 mmol) in THF (1 mL) was added at −78 °C *tert*-butyllithium (0.91 mL, 2.0 mmol, 2.2 M in pentane). The ensuing dark red/black solution was stirred at −78 °C for 25 min and then allowed to warm to room temperature and stir 2 h. Water (10 mL) was added. The organic layer was separated and the aqueous portion extracted with ether (3×). The combined organic layers were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo gave a yellow oil which after purification by column chromatography [F-20 alumina, benzene/ether (1:1)] gave 0.28 g of a yellow solid. R_f = 0.9 (1:1 benzene/ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, J = 7.10 Hz, 4 H), 7.34 (t, J = 7.64 Hz, 4 H), 7.25 (m, 6 H), 6.77 (m, 4 H). Some identified aliphatic peaks at δ 0.4–1.4 ppm. LRMS calcd for $C_{26}H_{18}O$ (M^+) 346, found 346; calcd for $C_{26}H_{17}{}^{79}BrO$ (M^+) 424, found 424; calcd for $C_{26}H_{17}{}^{81}BrO$ (M^+) 426, found 426. 1,2-Dibenzoylbenzene (0.08 g) was isolated from a second fraction. R_f = 0.6 (1:1 benzene/ether). FTIR (KBr): ν 1660.2, 1594.2, 1447.8, 1315.9, 1274.3, 1153.8, 937.7, 775.3, 704.3, 645.0 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (dd, J = 7.01, 1.56 Hz, 4 H), 7.28 (m, 2 h), 6.97 (m, 4 H), 6.91 (t, J = 1.47 Hz, 4 H). LRMS calcd for $C_{20}H_{14}O_2$ (M^+) 286, found 286.

Trapping of *o*-Benzyne Intermediate 26 as the Silylated Derivative 25c with 1,3-Diphenylisobenzofuran. To a stirring solution of 1,4-dibromobenzene (0.24 g, 1.0 mmol) and 1,3-diphenylisobenzofuran (0.27 g, 1.0 mmol) in THF (1 mL) was added at −78 °C *tert*-butyllithium (0.91 mL, 2.0 mmol, 2.2 M in pentane). The ensuing dark red/black solution was stirred at −78 °C for 25 min and then allowed to warm to room temperature and stir 2 h. Chlorotrimethylsilane (0.17 mL, 1.4 mmol) was added, and the solution was stirred at room temperature overnight. Water (10 mL) was added and the organic layer separated. The aqueous portion was extracted with ether (3×). The combined organic layers were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo gave 0.44 g of a yellow solid. Crude ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.7–8.1 (m), 0.8–1.4 (m), 0.5–1.5 (m). HRMS calcd for $C_{29}H_{26}OSi$ (M^+) 418.1753, found 418.1742.

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Supplementary Material Available: Figures of all NMR, FTIR, SEC, TGA, DSC, and MS spectra for the compounds described in the Experimental Section (91 pages). Ordering information is given on any current masthead page.

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