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Metal-Catalyzed Alkynylation of Brominated Polyphenylenes. Thermoset Precursors of High-Density Monolithic Glassy Carbon

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ABSTRACT: The functionalization of brominated polyphenylenes with several alkynes is described. The bromide groups on the polymer were replaced with terminal alkynes using a Pd/Cu catalyst system. Substitution of nearly all the original bromide locations was achieved. The functionalized polymers, freely soluble in THF, exhibited high char yields of up to 89% on thermolysis to 900 °C under a nitrogen atmosphere. Several of the functionalized polymers, derived from brominated polyphenylenes with approximately equal amounts of meta and para linkages, flowed on heating. The polymer that was functionalized with phenylacetylene exhibited a well-defined melting point at approximately 200 °C and flowed to produce a monolithic disk of glassy carbon. The amount of acetylenic cross-linking units in the polymers functionalized with phenylacetylene appears to be directly related to the char yields of the functionalized polymers. Predominantly meta-linked brominated polyphenylenes were also functionalized with a number of terminal alkynes, and though high char yields of up to 86% were observed, these materials offered no improvements in flow properties. The structure/property relationships and material applications are discussed.

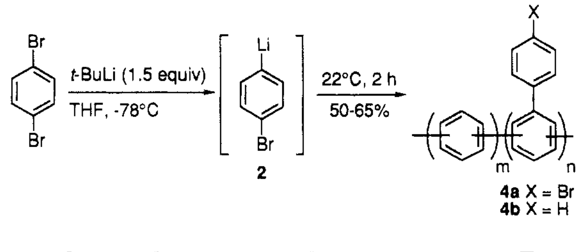
Introduction

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.[1] 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/cm^3.[2] Due to the large weight losses and low density chars exhibited by phenolic resins, multiple impregnation cycles (usually 6 to 7) are required for adequate structural formation. This can greatly raise the cost of the final carbon product. To lower the number of impregnation cycles (the cost-determining step) necessary for high density carbon preparation, the development of high char yielding materials from alkyne-containing organics has been investigated by many.[3] Unfortunately, the difficulty in preparing the alkyne-containing monomers and the explosive nature of the multialkynyl aromatics[3h,4] have retarded the rapid development and commercialization of this process. Likewise, *p*-polyphenylene (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.[5] However, PPP does not flow on thermolysis and it is insoluble in all common organic solvents. This has precluded its use in thermosetting materials.

We recently reported the synthesis of alkyne-containing polyphenylenes possessing several features which make them attractive as thermoset precursors of high-performance, high-density glassy carbon materials.[6] These polymers exhibited 85–90% char yields upon heating in inert atmospheres, while the charred material possessed densities of ≥1.80 g/cm^3 after one heating cycle (50–900 °C). The alkyne-containing polyphenylenes also exhibited a well-defined melting event (~200 °C) prior to conversion to carbon, which may also offer advantages in fabrication processes. Here we report the detailed results of the preparation of these alkyne-containing polyphenylenes as well as the thermal properties of these polymers in nitrogen and air atmospheres.

Results and Discussion

While investigating the thermal properties of predominantly para-linked brominated polyphenylenes **1** prepared in our laboratory using a one-pot HMPA-promoted polymerization of 1-bromo-4-lithiobenzene (**2**) in dioxane[7] (Scheme I), we became interested in using these materials as thermoset precursors to glassy carbon. Although **1** and its debrominated derivative **3** exhibited high carbon-to-hydrogen (C/H) ratios, these predominantly para-linked polymers showed low char yields (approximately 50%) on heating during (TGA) (N_2, 20 °C/min). No melting or softening temperatures were observed by DSC analysis (N_2, 20 °C/min). Visual observation of the charred material after TGA also indicated that no significant flow had occurred on heating. Due to the absence of any significant flow transitions for polymers **1** and **3**, it became apparent that some structural feature of the brominated polyphenylene **1** would need to be changed to obtain processible glassy carbon precursors. During studies of the HMPA-promoted polymerization of **2**, we found that 50–65% yields of ether-insoluble (THF-soluble) brominated polyphenylenes (**4a**) could be prepared using THF as the polymerization solvent (eq 1).[8] Polymer **4a** offered several attractive advantages over **1**. First, the synthesis of **4a** did not require the use of the cancer suspect agent HMPA. Second, **4a** contained higher amounts of meta linkages, which enabled the polymer to melt or flow during thermolysis. The DSC (N_2, 20 °C/min) of **4a** showed broad endotherms, characteristic of melting events at 152 and 175 °C on the first heating scan to 230 °C. While the char yield for **4a** was only 50% by TGA, the charred material was porous and glossy black, which also indicated that the material had flowed during thermolysis. Third, **4a** was shown by elemental analysis to contain up



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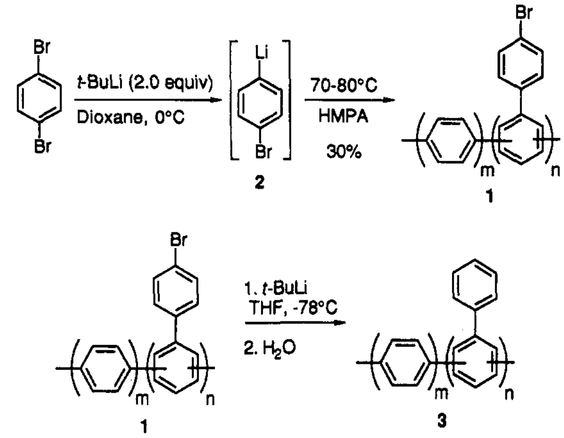
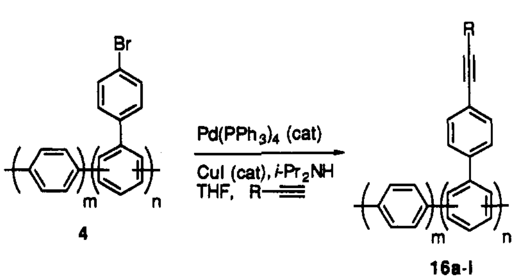
Scheme I



to one bromide for every three aryl rings. Since the material was soluble, the bromide groups in the polymer could be used as functionalization sites. Based on the high char yields of other alkyne-containing aromatics,[3] we decided to functionalize polymer **4a** with a variety of acetylenic groups that would cross-link during thermolysis and reduce the amount of weight loss due to volatilization of the lower molecular weight oligomers. To maintain a processible system, it was important that the acetylenic moiety not cross-link prior to the polymer melt.

Polymer **4a** was functionalized with a number of terminal alkynes using the Stephans/Castro–Sonogashira protocol that employs a Pd/Cu catalyst for cross-coupling of aryl halides and terminal acetylenes.[9] Phenylacetylene, 1-octyne, and (trimethylsilyl)acetylene were obtained commercially. 1-Ethynyl-4-(phenylethynyl)benzene (**7**), 1-ethynyl-3-(phenylethynyl)benzene (**9**), 4-ethynylbiphenyl (**10**), 1-ethynylnaphthalene (**12**), and 2-ethynylbiphenyl (**15**) were prepared using reaction combinations involving the phosphate enolate procedure for acetylene formation,[10] Pd/Cu-catalyzed cross-coupling,[9] and protodesilylation with K_2CO_3 in methanol/ether (Scheme II).

The procedure for coupling the terminal alkynes to polymer **4a** involved treatment of **4a** with the terminal alkyne (3.5 equiv relative to the amount of Br in **4a**) in a THF solution containing diisopropylamine (3.5 equiv relative to the amount of Br in **4a**), CuI catalyst (4.0 mol % relative to the amount of Br in **4a**), and a $Cl_2Pd(PPh_3)_2$ or $Pd(PPh_3)_4$ catalyst (4.5 mol % relative to the amount of bromide in **4a**). The ensuing reaction mixtures were stirred at room temperature for 2 h and then heated (60 °C for 10 h, 100 °C for 5 h) to afford good yields of functionalized polyphenylenes **16b–i** (Figure 1). In most cases, complete bromide substitution was achieved as determined by elemental analysis. All of the functionalized polymers were soluble in THF, methylene chloride, and chloroform. The thermal properties of these polymers are shown in Table I.[6]

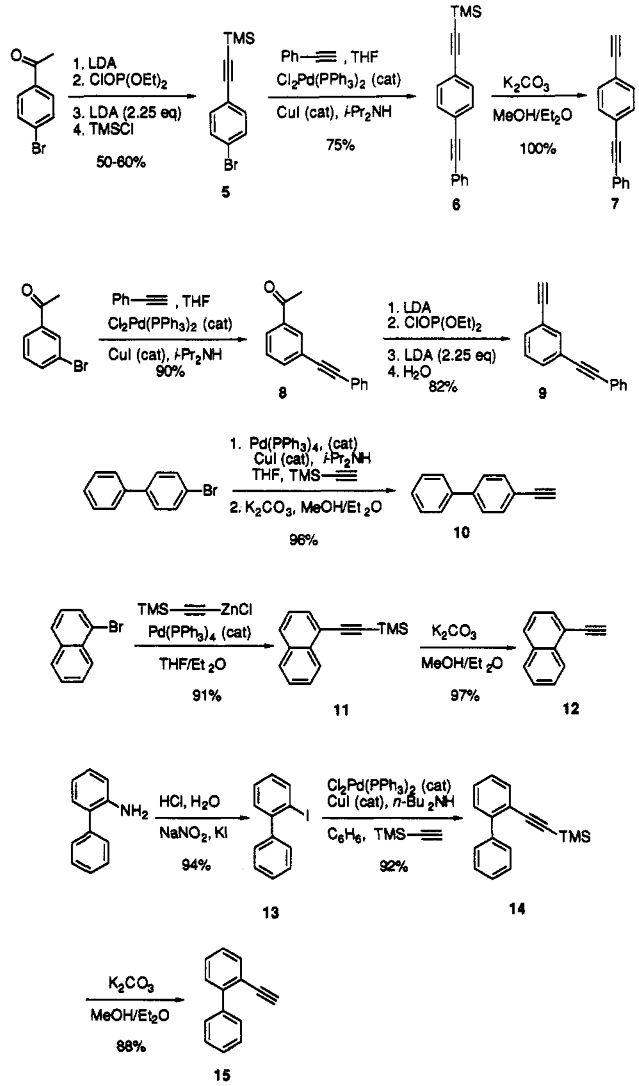


16a, R = H
16b, R = TMS
16c, R = C_6H_{13}-*n*
16d, R = Ph

16e, R = (*p*-C_6H_4)—≡—Ph
16f, R = (*m*-C_6H_4)—≡—Ph
16g, R = (*p*-C_6H_4)—Ph
16h, R = (1-naph)
16i, R = (*o*-C_6H_4)—Ph

Figure 1.

Scheme II



Several structure/property relationships soon became evident and enabled us to rapidly converge on a suitable thermoset precursor to glassy carbon. Polymer **16a** was prepared by addition of tetra-*n*-butylammonium fluoride (TBAF) to **16b** in THF at 0 °C followed by stirring at room temperature for 1 h. Although **16a** exhibited a high char yield (80%), the terminal alkyne was too unhindered and the cross-linking event occurred prior to a well-defined melt or softening point by DSC analysis. The charred material after TGA was also a black powder, again indicating that no flow had occurred. The char had a density of 1.59 g/cm^3.[11] Polymers **16b** and **16c** had internal alkynes and they did exhibit well-defined melts at 140 °C by DSC analysis while the thermolyzed material formed glossy black droplets, which also indicated that a melting event had occurred. However, the introduction of aliphatic groups decreased the char yields to only 69% and 67%, respectively. Remarkably, by functionalizing **4a** (prepared by refluxing 1-bromo-4-lithiobenzene (**2**) in THF for 2 h) with phenylacetylene to produce **16d**, the char yield increased to 86% at 900 °C and the polymer exhibited a well-defined melt at 200 °C. Gravity flow of the melted material occurred to form a glossy black monolithic disk which was amorphous by powder XRD, confirming that the material was indeed glassy carbon.[6] The density of the charred product was 1.83 g/cm^3. Initial data had

Table I. Pd/Cu-Catalyzed Cross-Coupling of Terminal Alkynes with Brominated Polyphenylene 4a

	starting polymer 4a		product								
compd	M_w[a]	M_w/M_n[a]	M_w[a]	M_w/M_n[a]	% Br	% yield	$T_{10\%}$[b] (°C)	% char[c]	T_g[d,e] (°C)	T_m[d,f] (°C)	T_{exo}[d,g] (°C)
16a	3500	3.50	3020	2.32	1.91	56	671	80	180	—	180
16b	1430	4.09	3130	3.58	2.06	55	376	69	—	140	210, 230
16c[h]	1360	3.42	3330	3.32	<0.5	59	430	67	—	140	170
16d[i]	1310	3.29	2590	2.71	<0.5	66	700	86	—	200	220, 320
16e	1890	3.64	4090	3.5	<0.5	78	768	89	206	—	350
16f	1860	2.32	3730	3.2	<0.5	84	810	89	203	—	350
16g	2070	3.76	3610	3.00	<0.5	67	643	85	—	205	220, 310
16h	2330	3.71	3590	2.1	<0.5	58	730	87	—	200	230
16i	1770	4.37	3770	2.06	<0.5	72	511	78	—	150	340

[a] Determined by size exclusion chromatography relative to polystyrene. [b] Temperature at which 10% weight loss occurred by thermogravimetric analysis (TGA) from 50 to 900 °C at 20 °C/min under an N_2 atmosphere. [c] Percent weight of polymer remaining at 900 °C by TGA under the conditions listed in *b*. [d] Determined by DSC from 50 to 500 °C under an N_2 atmosphere. Dashes signify that these values were not clearly discernible by DSC. [e] Polymer glass transition temperature. [f] Polymer melt temperature. [g] Exothermic event characteristic of alkyne couplings. [h] Prepared from the brominated polymer 1 made with HMPA in dioxane as described in ref 7. [i] Prepared from brominated polymer **4a** made by refluxing 1-bromo-4-lithiobenzene (**2**) in THF at 65 °C for 2 h. All other compounds in this table were prepared from **4a** made by stirring **2** in THF at 22 °C for 2 h as described in the Experimental Section.

suggested that no cross-linking events had occurred prior 320 °C; however, at 320 °C a large exotherm was observable by DSC analysis.[6] This cross-linking event was 120 °C higher than the melting temperature. However, upon closer evaluation of the DSC thermograms, a small exotherm at 220 °C was apparent.[12] This would suggest that some cross-linking was occurring soon after the melt. However, the material did indeed flow during the heating process. Interestingly, when we attached phenylacetylene to a predominantly para-linked brominated polyphenylene (prepared using the HMPA procedure[7]), the char yield was high (~82%); however, the flow properties on thermolysis were impaired. The charred material was a black powder; therefore, it had not flowed. Thus the unique flow properties of **16d** are undoubtedly due in part to the higher amount of meta linkages in this polymer system. When a sample of **16d** having $M_w = 2480$ ($M_w/M_n = 3.22$) and a well-defined melt at 180 °C (DSC) was purified further by fractional precipitation from methylene chloride with ether, the flow properties of the polymer were impaired. The thermolyzed material was powdery and it had not flowed. The purified product had a higher molecular weight ($M_w = 3500$) and a lower polydispersity ($M_w/M_n = 2.72$). Thus higher molecular weights and lower polydispersities retard the flow properties of **16d**.

In an effort to further increase the char yields, additional functionalized polymers (**16e**–i) containing high C/H ratios were prepared. From the results in Table I it can be seen that although the char yields were increased to almost 90% for **16e** and **16f**, the flow properties for these two systems were diminished. No T_m was clearly evident by DSC analysis though T_gs were evident. The materials formed dull gray meshes during thermolysis, indicating that some flow had occurred. These meshes were also shown to be amorphous glassy carbon by powder XRD. The densities of the charred products from **16e** and **16f** were 1.95 and 1.39 g/cm^3, respectively. Polymers **16g**, **16h**, and **16i** formed glossy black beads during thermolysis and appeared to have flow properties similar to that of **16d**. However, **16g** and **16i** had char yields of only 84% and 78%, respectively. Polymer **16h** had a slightly better char yield of 87%. The densities of the charred carbon products from **16g** and **16h** were 1.52 and 1.55 g/cm^3, respectively. Thus these polymer systems offer no significant advantages in flow properties or char yields when compared to polymer **16d**; *moreover*, phenylacetylene, the reagent necessary for **16d**, is both inexpensive and commercially available. Furthermore, the density of the charred material derived from **16d** was extremely high (1.83 g/cm^3). This would also lower the cost of fabrication of high-performance carbon materials by limiting the number of impregnation cycles to 1 to 2. Thus **16d** appears to be an extremely attractive thermoset precursor of high-density monolithic glassy carbon.

Table II. FTIR and TGA Data for 16d

FTIR (cm^{-1})[a]	char yield (%)[b]	$T_{10\%}$ (°C)[c]	*t*-BuLi (equiv)[d]
816.8	86.0	670	1.5
817.0	86.0	750	1.5
817.4	86.8	760	1.5
817.6	78.0	544	1.5
818.2	67.0	492	1.8
818.3	69.0	501	1.8
820.0	56.7	425	1.8
820.6	60.0	453	2.0
824.0	50.2	383	2.5

[a] Position of the para band in the FTIR of **16d**. [b] Percent weight of **16d** remaining at 900 °C after TGA from 50 to 900 °C at 20 °C/min under an N_2 atmosphere. [c] Temperature at which 10% weight loss occurred by TGA under the conditions listed in *b*. [d] Equivalents of *t*-BuLi used to prepare polymer **4a**.

Additional studies on the thermal properties of polymer **16d** showed a direct correlation between the carbon char yields, position of the para band stretch in the FTIR of the functionalized polymer, and the amount of *tert*-butyllithium used to prepare the starting brominated polymer **4a** (Table II). As the wavenumber of the para stretch in **16d** decreased, the char yields for **16d** increased. Likewise, as the amount of *tert*-butyllithium used to prepare **4a** increased, the char yield decreased. The polymers with the highest char yields were derived from the brominated polymers (**4a**) prepared using 1.5 equiv of *tert*-butyllithium. Brominated polymers prepared in this manner were shown by elemental analysis to contain 24% bromide or approximately one bromide for every three aryl rings. The position of the para band in the FTIR was approximately 809 cm^{-1}. If higher amounts of *tert*-butyllithium (2.0 equiv) were used to prepare **4a**, the amount of bromide in the polymer was reduced to 9% or approximately one bromide for every ten aryl rings. The wavenumber of the para band in polymer **4a** also increased to 814–817 cm^{-1} if more *tert*-butyllithium was used.[13] Based on these results, it appears that if the amount of acetylenic cross-linking units in **16d** is reduced, the char yields are lowered accordingly.

TGA (20 °C/min) studies in air were also performed on polymer **4a** as well as several of the functionalized polymers derived from **4a**, namely , **4b** (prepared by treatment of **4a** with *tert*-butyllithium and quenching with water) and **16d–h**. The results are shown in Table III. All of the polymers were completely volatilized before 800 °C. While the onset of weight loss for the brominated and debrominated polymers **4a** and **4b** was only 250 °C, polymers

Table III. TGA Data of Polyphenylenes in an Air Atmosphere[a]

polymer	onset of wt loss (°C)	temp of 0% char yield (°C)
4a	250	720
4b	250	760
16d	400	700
16e	400	760
16f	450	780
16g	460	740
16h	480	730

[a] Thermogravimetric analyses in air were performed from 50 to 900 °C at a scan rate of 20 °C/min.

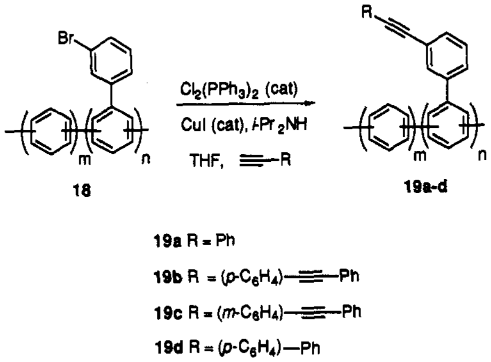
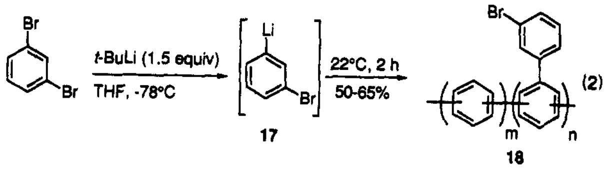


Figure 2.

16d–h, functionalized with acetylenic cross-linking moieties, showed no significant weight loss before 400 °C. Thus the incorporation of acetylenic groups with high carbon/hydrogen ratios improved the thermal properties of the polymers in both nitrogen and air atmospheres. For comparison, the onset of weight loss in air for PPP prepared by the Kovacic method and phenylated polyphenylenes prepared by Stille is reported to be 550 °C. The reported onset of weight loss in air for the Hercules HA-43 resin is 450 °C.[5c]

Predominantly meta-linked brominated polyphenylenes prepared from the polymerization of 1-bromo-3-lithiobenzene (**17**) in THF[13] (eq 2) were also functionalized with a number of thermoactive acetylenic cross-linking groups using Pd/Cu-catalyzed cross-coupling reactions (Figure 2).[10] Surprisingly, these predominantly meta-linked materials offered no improvements in char yields or flow properties. The lower polydispersities ($M_w/M_n = 1.87$) of the starting brominated polymer **18** may be retarding the flow properties of this system. No melting transitions were observed for polymer **18** by DSC (N_2, 20 °C/min) analysis on either the first or second heating runs up to 250 °C. These polymers did, however, appear to flow by visual observation of the charred material after TGA (N_2, 90 °C/min), which showed a 59% char yield for **18**. The results of the thermal analysis of the functionalized polymers **19a–d** are shown in Table IV. A T_g at 180 °C was observable for **19a**, and the charred material appeared as shiny black droplets after TGA. The charred carbon material from **19a** had a density of 1.56 g/cm^3. Polymers **19b** and **19c** appeared as black powders after TGA. The DSC thermogram of **19c** did show an apparent melt at 175 °C. Charred polymer **19d** appeared as a shiny porous bead with a T_g at 190 °C. Carbon materials derived from **19b** and **19c** had densities of 1.57 and 1.61 g/cm^3, respectively.



In conclusion, the ability to functionalize the brominated polyphenylenes using Pd/Cu-catalyzed cross-coupling methodology has provided an overall two-step (polymerization and functionalization) procedure for obtaining thermoset precursors to glassy carbon materials. The low cost of the starting materials, unique flow properties, high char yields of the functionalized polymers, and the high densities of the thermolyzed products make this process attractive for the rapid formation of glassy carbon products requiring high densities.

Experimental Section

General Procedures. All synthetic operations were carried out under a dry, oxygen-free, nitrogen atmosphere. ^{1}H NMR spectra were recorded at 300 or 500 MHz on a Bruker AM-300 or Bruker AM-500 spectrometer, respectively. The ^{13}C NMR spectra at 75 or 125 MHz were recorded on a Bruker AM-300 or Bruker 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 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 preformed using two 30 × 75 cm Burdick and Jackson GPC columns (105 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, 5050, 2950, 2150, and 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. Capillary GC analyses were obtained using a Hewlett-Packard Model 5890 gas chromatograph using a Hewlett-Packard 3396A integrator. 1,4-Dibromobenzene, 1-bromobiphenyl, 4-bromoacetophenone, 3-bromoacetophenone, 1-bromonaphthalene, and 1-octyne were purchased from Aldrich Chemical Co. Inc. and used without further purification. Phenylacetylene was purchased from Farchan Laboratories Inc. and used without further purification. Alkyllithiums were purchased from Aldrich Chemical Co. Inc. or Lithium Corporation 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 as described by Still.[14] Thin-layer chromatography was performed using glass plates precoated with silica gel 60 F_{254} with a layer thickness of 0.25 mm purchased from EM Science.

Brominated Polyphenylene (1). To a 100-mL, three-necked, round-bottom flask equipped with a thermometer, stirbar, 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 1 as a

Table IV. Pd/Cu-Catalyzed Cross-Coupling of Terminal Alkynes with Brominated Polyphenylene 18

	starting polymer 18		product								
compd	M_w[a]	M_w/M_n[a]	M_w[a]	M_w/M_n[a]	% Br	% yield	$T_{10\%}$[b] (°C)	% char[c]	T_g[d,e] (°C)	T_m[e,f] (°C)	T_{exo}[e,g] (°C)
19a[h]	2360	2.00	2870	2.45	1.85	66	638	82.5	180	—	360
19b	2590	2.37	3770	1.85	1.95	78	614	85.5	300	—	150
19c	2690	2.44	3130	2.10	2.14	74	511	81.3	—	175	190
19d	2850	1.87	3330	2.07	1.96	116	480	65.0	190	—	—

[a] Determined by size exclusion chromatography relative to polystyrene. [b] Temperature at which 10% weight loss occurred by TGA from 50 to 900 °C at 20 °C/min under an N_2 atmosphere. [c] Percent weight of polymer remaining at 900 °C by TGA under the conditions listed in *b*. [d] Polymer glass transition temperature. [e] Determined by DSC from 50 to 500 °C under an N_2 atmosphere. Dashes signify that these values were not clearly discernible by DSC. [f] Polymer melt temperature. [g] Exothermic event characteristic of alkyne couplings. [h] Prepared from 18 made by stirring 1-bromo-3-lithiobenzene (17) (prepared from 1.8 equiv of *tert*-butyllithium) in THF at 22 °C for 2 h. All other compounds in this table were prepared from 18 made by stirring 17 (prepared with 1.5 equiv of *tert*-butyllithium) in THF at 22 °C for 2 h.

tan–brown solid. FTIR (KBr) 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 131.91, 128.54, 127.36. 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.[15] TGA (N_2, 20 °C/min) showed 10% weight loss at 356 °C and 48% weight loss at 900 °C.

Debromination of 1 To Form 3. To a stirred solution of 1 (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 3 as a brown solid. FTIR (KBr) 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 140.66, 128.80, 127.26. 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 Polyphenylene 4a. To a 100-mL round-bottom flask equipped with a stirbar 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 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 0.60 g (50%) of **4a** as a tan–brown solid. FTIR (KBr) 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, $CDCl_3$) δ 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 4a To Give 4b. To a stirred solution of **4a** (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 **4b** as a brown ether-insoluble solid. FTIR (KBr) 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.

1-Bromo-4-((trimethylsilyl)ethynyl)benzene (5). The procedure of Negishi[10] was used as follows. To a stirred solution of diisopropylamine (1.54 mL, 11.0 mmol) in THF (11 mL) was added at −78 °C under a nitrogen atmosphere *n*-butyllithium (6.42 mL, 10.4 mmol, 1.62 M). The reaction mixture was stirred at −78 °C for 3 min and then allowed to warm to 0 °C for 5 min. To the reaction mixture was added at −78 °C 4′-bromoacetophenone (1.99 g, 10.0 mmol) in THF (10 mL). The ensuing red reaction mixture was stirred t −78 °C for 1 h before adding diethyl chlorophosphonate (1.53 mL, 10.6 mmol). The reaction mixture was then allowed to warm to room temperature and stir for 30 min. The reaction mixture was then added via cannula into LDA [2.25 equiv; prepared from *n*-butyllithium (13.9 mL, 22.5 mmol) and diisopropylamine (3.22 mL, 23 mmol)] in THF (20 mL) at −78 °C. The ensuing reaction mixture was stirred at −78 °C for 5 min and then warmed to room temperature for 1 h. To the reaction mixture was added trimethylsilyl chloride (1.40 mL, 11.0 mmol) at −78 °C, and the mixture was allowed to stir for 1 h at room temperature. The violet–red solution was poured into water (40 mL) and extracted with ether (3×). The combined ether extracts were dried over magnesium sulfate. Filtration and removal of the solvent in vacuo gave a brown solid which after purification via column chromatography (silica gel, hexane) yielded 1.29 g (51%) of the title compound. R_f = 0.62 (hexane). Mp = 58–60 °C. FTIR (KBr) 2956.9, 2898.1, 2157.6, 1483.9, 1393.2, 1246.2, 1209.5, 1070.7, 1009.5, 865.7, 845.3, 823.0, 757.9, 665.6, 529.3 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.41 (d, *J* = 8.29 Hz, 2 H), 7.30 (d, *J* = 8.29 Hz, 2 H), 0.22 (s, 9 H).

1-(Phenylethynyl)-4-((trimethylsilyl)ethynyl)benzene (6). The procedure of Sonogashira[9] was modified as follows. To a 50-mL round-bottom flask equipped with a stirbar and containing 1-bromo-4-(2′-(trimethylsilyl)ethynyl)benzene (6.74 g, 26.6 mmol), copper(I) iodide (0.15 g, 0.8 mmol), and dichlorobis(triphenylphosphine)palladium(II) (0.56 g, 0.8 mmol) were added at room temperature THF (27 mL), phenylacetylene (4.4 mL, 40.0 mmol), and diisopropylamine (5.6 mL, 40.0 mmol). The ensuing black reaction mixture was stirred at room temperature for 4 days. The reaction mixture was poured into water (30 mL). The organic layer was separated and the aqueous portion extracted with ether (4×). The combined organic layers were washed with aqueous ammonium chloride (3×) and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo gave a brown oil which after purification by column chromatography (silica gel, hexane) gave 5.45 g (75%) of the title compound as glossy white flakes. R_f = 0.45 (hexane). Mp = 114–117 °C. FTIR (KBr) 3053.7, 2957.2, 2898.2, 2152.9, 1601.2, 1508.4, 1440.0, 1405.8, 1248.1, 1105.8, 1070.9, 1017.9, 866.4, 843.8, 755.8, 691.1, 626.7, 545.0, 528.3 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.43 (AB q, *J* = 4.27 Hz, $\Delta\nu$ = 12.44 Hz, 4 H), 7.33 (m 3 H), 0.24 (s, 9 H).

1-Ethynyl-4-(phenylethynyl)benzene (7). To a 50-mL round-bottom flask containing 1-(phenyethynyl)-4-(2′-(trimethylsilyl)ethynyl)benzene (5.37 g, 19.6 mmol) in ether (20 mL) were added at room temperature potassium carbonate (3.59 g, 29.4 mmol) and methanol (45 mL). The ensuing reaction mixture was stirred at room temperature for 3 h. The reaction mixture was poured into water (30 mL). The organic layer was separated and the aqueous portion extracted with ether (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo gave 3.96 g (100%) of the title compound as white flakes. Mp = 86–88 °C. FTIR (KBr) 3291.6, 3052.9, 1499.7, 1441.6, 1247.2, 1103.6, 1069.9, 1023.6, 914.3, 842.1, 757.4, 690.0, 655.2, 625.6, 549.4, 528.2, 458.5 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.46 (s, 4 H), 7.34 (m, 3 H), 3.15 (s, 1 H). HRMS calcd for $C_{16}H_{10}$ (M^+) 202.0783. Found 202.0788.

***m*-(Phenylethynyl)acetophenone (8).** The procedure of Sonogashira[9] was modified as follows. To a 50-mL round-bottom flask equipped with a stirbar and containing 3-bromoacetophenone (1.3 mL, 10.0 mmol), copper(I) iodide (0.048 g, 0.25 mmol), and dichlorobis(triphenylphosphine)palladium(II) (0.18 g, 0.25 mmol) were added at room temperature THF (10 mL), phenylacetylene (1.6 mL, 15.0 mmol), and diisopropylamine (2.1 mL, 15.0 mmol). The black reaction mixture was stirred at room temperature for 1 h and then warmed to 55 °C for 6 h. The reaction mixture was allowed to cool to room temperature and poured into water (25 mL). The organic layer was separated and the aqueous portion extracted with ether (3×). The combined organic layers were washed with aqueous ammonium chloride (3×) and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo gave a brown oil which after purification by column chromatography [silica gel, ether/hexane (1/1)] gave 1.97 g (90%) of the title compound as clear plates. R_f = 0.52 (1:1 ether/hexane). Mp = 74–76 °C. FTIR (KBr) 3080.5, 3003.3, 1679.4, 1600.0, 1570.1, 1490.7, 1421.1, 1351.9, 1312.8, 1279.4, 1241.8, 1136.2, 1081.0, 1019.9, 995.7, 955.6, 914.5, 887.0, 808.1, 757.6, 692.3, 682.8, 602.4, 535.3, 505.8 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (t, J = 1.68 Hz, 1 H), 7.90 (dt, J = 7.86, 1.26 Hz, 1 H), 7.70 (dt, J = 7.80, 1.26 Hz, 1 H), 7.53 (m, 2 H), 7.44 (t, J = 7.74 Hz, 1 H), 7.35 (m, 3 H), 2.62 (s, 3 H).

1-Ethynyl-3-(phenylethynyl)benzene (9). The procedure of Negishi[10] was used as follows. To a stirred solution of diisopropylamine (1.5 mL, 11.0 mmol) in THF (10 mL) was added at −78 °C under nitrogen *n*-butyllithium (6.5 mL, 10.4 mmol, 1.6 M in hexanes). The reaction mixture was stirred at −78 °C for 3 min and then warmed to 0 °C for 5 min. To the reaction solution was added at −78 °C 3-(phenylethynyl)acetophenone (2.2 g, 10.0 mmol) in THF (10 mL). The reaction mixture was stirred at −78 °C for 1 h before adding at the same temperature diethyl chlorophosphonate (1.5 mL, 10.4 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The reaction solution was then cannulated into LDA [2.25 equiv; prepared from *n*-butyllithium (14.1 mL, 22.5 mmol) and diisopropylamine (3.22 mL, 23.0 mmol)] in THF (25 mL) at −78 °C. The ensuing reaction mixture was stirred at −78 °C for 5 min and then allowed to warm to room temperature for 1 h. The solution was poured into water (30 mL) and extracted with ether (3×). The combined ether extracts were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo left a brown oil which after purification by column chromatography (silica gel, hexane) afforded 1.65 g (82%) of the title compound as a clear oil. R_f = 0.47 (hexane). FTIR (neat) 3292.3, 3058.8, 2924.9, 1600.2, 1571.4, 1492.1, 1474.2, 918.7, 895.7, 794.1, 755.2, 687.0 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (t, J = 1.23 Hz, 1 H), 7.50 (m, 4 H), 7.35 (m, 2 H), 7.29 (t, J = 7.74 Hz, 2 H), 3.08 (s, 1 H). HRMS calcd for $C_{16}H_{10}$ (M^+) 202.0783. Found 202.0788.

4-Ethynylbiphenyl[16] (10). The procedure of Sonogashira[9] was modified as follows. To a screw cap tube containing 4-bromobiphenyl (4.66 g, 20.0 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.58 g, 0.5 mmol) in tetrahydrofuran (20 mL) were added at room temperature (trimethylsilyl)acetylene (4.2 mL, 30.0 mmol) and diisopropylamine (3.3 mL, 30.0 mmol). The ensuing black reaction solution was stirred at room temperature for 1 h and then warmed to 40 °C for 36 h. The reaction mixture was allowed to cool to room temperature and poured into water (30 mL). The organic layer was separated and the aqueous portion extracted wth ether (3×). The combined organic layers were washed with aqueous ammonium chloride (3×) and dried over magnesium sulfate. Filtration through a plug of silica gel and removal of the solvent in vacuo gave a brown solid. The crude product was dissolved in ether (20 mL) and treated at room temperature with methanol (20 mL) and potassium carbonate (4.89 g, 40.0 mmol). The reaction mixture was stirred at room temperature for 3 h and poured into water (30 mL). The organic layer was separated and the aqueous portion extracted with ether (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration through a silica gel plug and removal of the solvent in vacuo gave 3.43 g (96%) of the title compound as a yellow solid. Mp = 82–84 °C. FTIR (KBr) 3273.6, 3029.1, 1482.1, 1249.8, 1005.9, 842.1, 769.5, 728.2, 701.3, 665.6, 626.6, 560.2, 503.0 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (m, 2 H), 7.55 (s, 4 H), 7.44 (t, J = 7.12 Hz, 2 H), 7.36 (d, J = 7.29 Hz, 1 H), 3.11 (s, 1 H).

1-((Trimethylsilyl)ethynyl)naphthalene (11). To a stirring solution of (trimethylsilyl)acetylene (1.7 mL, 12.0 mmol) in ether (8 mL) was added at −78 °C *n*-butyllithium (9.1 mL, 12.5 mmol, 1.38 M in hexane). The reaction mixture was stirred at −78 °C for 1 h and added via cannula to flame-dried zinc chloride (2.04 g, 15.0 mmol) in THF (10 mL). The ensuing milky white reaction mixture was stirred at room temperature for 1 h and transferred via cannula to a round-bottom flask containing 1-bromonaphthalene (1.4 mL, 10.0 mL) and tetrakis(triphenylphosphine)palladium(0) (0.23 g, 0.2 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 2.5 h and heated to 55 °C for 24 h. The reaction mixture was allowed to cool to room temperature and poured into water (20 mL). The organic layer was separated and the aqueous portion extracted with ether (3×). The combined organic layers were washed with aqueous ammonium chloride (3×) and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo gave a brown oil which after purification by Kugelrohr distillation (185–200 °C/2.5 mmHg) gave 2.04 g (91%) of the title compound as a yellow oil. FTIR (neat) 3059.0, 2959.4, 2898.5, 2146.9, 1586.4, 1508.0, 1393.3, 1249.7, 1075.7, 1040.5, 1013.2, 882.1, 842.7, 799.0, 772.9, 731.1, 699.2, 645.6 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, J = 8.22 Hz, 1 H), 7.81 (t, J = 7.29 Hz, 1 H), 7.79 (t, J = 6.21 Hz, 1 H), 7.70 (d, J = 7.14 Hz, 1 H), 7.56 (t, J = 6.81 Hz, 1 H), 7.50 (dd, J = 6.87, 9.44 Hz, 1 H), 7.39 (dd, J = 7.17, 8.28 Hz, 1 H), 0.32 (s, 9 H).

1-Ethynylnaphthalene[17] (12). To a 50-mL round-bottom flask containing 1-((trimethylsilyl)ethynyl)naphthalene (3.77 g, 16.8 mmol) in ether (17 mL) were added at room temperature potassium carbonate (4.15 g, 34.0 mmol) and methanol (17 mL). The reaction mixture was stirred at room temperature overnight before being poured into water (30 mL). The organic layer was separated and the aqueous portion extracted with ether (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo gave 2.46 g (97%) of the title compound as a yellow oil. FTIR (neat) 3291.1, 3058.2, 2102.0, 1586.8, 1508.1, 1392.1, 1266.2, 1013.2, 863.5, 799.3, 773.0 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 8.39 Hz, 1 H), 7.85 (d, J = 8.39 Hz, 2 H), 7.73 (dd, J = 6.05, 1.05 Hz, 1 H), 7.58 (ddd, J = 6.94, 6.84, 1.50 Hz, 1 H), 7.52 (ddd, J = 6.84, 6.79, 1.30 Hz, 1 H), 7.42 (t, J = 7.14 Hz, 1 H), 3.47 (s, 1 H).

2-Iodobiphenyl (13). The procedure of Heaney[18] was modified as follows. To a slurry of 2-aminobiphenyl (1.7 g, 10.0 mmol) in concentrated hydrochloric acid (5 mL) and ice was added at 0 °C a solution of sodium nitrite (0.70 g, 10.2 mmol) in water (5 mL). The ensuing reaction solution was stirred at 0 °C for 45 min. The reaction mixture was then poured into a solution of potassium iodide (2.16 g, 13.0 mmol) in water (100 mL) at 0 °C. The reaction solution was allowed to warm to room temperature and stir overnight. Ether 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 2.62 g (94%) of the title compound as a brown oil. FTIR (neat) 3057.2, 1950.4, 1805.3, 1578.6, 1556.5, 1459.9, 1426.8, 1252.9, 1159.4, 1114.3, 1072.6, 1016.8, 1004.1, 945.0, 914.3, 746.6, 699.3, 648.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.92, 0.96 Hz, 1 H), 7.4 (m, 8 H), 7.02 (dt, J = 7.26, 1.86 Hz, 1 H).

2-((Trimethylsilyl)ethynyl)biphenyl (14). The procedure of Sonogashira[9] was modified as follows. To a 50-mL round-bottom flask equipped with a stirbar and containing 2-iodobiphenyl (2.02 g, 7.20 mmol), copper(I) iodide (0.11 g, 0.6 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.25 g, 0.2 mmol) were added at room temperature benzene (8 mL), (trimethylsilyl)acetylene (2.0 mL, 14.4 mmol), and *n*-butylamine (1.4 mL, 14.4 mmol). The ensuing black reaction mixture was stirred at room temperature overnight. The reaction mixture was poured into water (20 mL). The organic layer was separated and the aqueous portion extracted with ether (4×). The combined organic layers were washed with aqueous ammonium chloride and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo gave a brown oil which after purification by column chromatography (silica gel, hexane) gave 1.65 g (92%) of the tital compound as a yellow oil. $R_f = 0.31$ (hexane). FTIR (neat) 3061.0, 3026.1, 2959.1, 2898.1, 2156.5, 1947.9, 1595.1, 1473.8, 1432.1, 1248.8, 1211.1, 1108.7, 1074.0, 1048.9, 1007.8, 950.1, 864.3, 843.3, 757.8, 734.6, 698.1, 643.9 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dt, $J = 8.28, 1.71$ Hz, 3 H), 7.35 (m, 5 H), 7.26 (m, 1 H), 0.11 (s, 9 H).

2-Ethynylbiphenyl (15). To a 50-mL round-bottom flask containing 2-phenyl-1-((trimethylsilyl)ethynyl)benzene (2.9 g, 12.0 mmol) in ether (12 mL) were added at room temperature potassium carbonate (3.5 g, 25.0 mmol) and methanol (12 mL). The reaction mixture was stirred at room temperature overnight before being poured into water (30 mL). The organic layer was separated and the aqueous portion extracted with ether (3×). The combined organic layers were washed with water and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo gave 1.87 g (88%) of the title compound as a tan oil. FTIR (neat) 3286.0, 3061.4, 2954.2, 2105.0, 1595.3, 1474.3, 1432.1, 1249.1, 1074.7, 1008.1, 915.7, 853.9, 757.6, 737.6, 698.9 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (m, 3 H), 7.42 (m, 5 H), 7.30 (m, 1 H), 3.02 (s, 1 H). HRMS calcd for $C_{14}H_{10}$ (M^+) 178.0783. Found 178.0781.

General Procedure for Coupling Terminal Alkynes to Brominated Polyphenylenes. The procedure of Sonogashira[9] was modified as follows. To a screw cap tube containing **4a** (0.29 g, 0.96 mmol), copper(I) iodide (0.04 mmol, 4.0 mol %), dichlorobis(triphenylphosphine)palladium(II), and/or tetrakis(triphenylphosphine)palladium(0) (0.05 mmol, 4.5 mol %) in THF (3 mL) were added at room temperature a terminal acetylene (2.9 mmol, 3.5 equiv) and diisopropylamine (2.9 mmol, 3.5 equiv). The black reaction solution was stirred at room temperature for 1 h and then warmed to 60 °C for 10 h and 100 °C for 5 h. The reaction mixture was allowed to cool to room temperature and poured into water (20 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were washed with aqueous ammonium chloride (3×). Filtration and removal of the solvent in vacuo gave a brown oil which, unless otherwise noted, was stirred with ether, and the ether-insoluble solid was removed by filtration.

Cross-Coupling of (Trimethylsilyl)acetylene with 4a To Form 16b. Fractional precipitation from hexane with ether gave a 55% yield of a gray–brown hexane-insoluble solid. FTIR (KBr) 3029.6, 2956.7, 2896.2, 2155.8, 1599.5, 1474.2, 1249.4, 1004.6, 864.6, 841.9, 790.7, 759.0, 696.8 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.0–8.0 (m, 14 H), 0.26 (br s, 9 H). UV ($CHCl_3$) λ_{max} 290 nm. $M_w = 3130$, $M_n = 880$, $M_w/M_n = 3.58$. Anal. Calcd for $(C_{23}H_{20}Si)_n$: C, 85.13; H, 6.21. Found: C, 83.76; H, 5.84; Br, 2.06. Due to difficulties in burning polyphenylene polymers quantitatively, they often do not afford clean combustion analyses. Mp (DSC) 140 °C. TGA showed 10% weight loss at 376 °C and 30.9% weight loss at 900 °C.

Desilylation of 16b To Form 16a. To a stirring solution of **16b** (0.163 g, 0.50 mmol, $M_w = 3500$, $M_w/M_n = 3.50$) in THF (3 mL) was added at 0 °C tetrabutylammonium fluoride (1.5 mL, 1.5 mmol, 1.5 M in THF). The ensuing reaction mixture was stirred at 0 °C for 30 min and then allowed to warm to room temperature and stir for 1 h. The reaction mixture was 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 (3×), 3 N hydrochloric acid, and sodium bicarbonate and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo gave a tan–brown oil which after fractional precipitation with ether gave 0.074 g (56%) of a tan solid. FTIR (KBr) 3292.4, 3028.5, 2105.8, 1909.6, 1599.3, 1473.8, 1388.5, 1111.3, 1004.8, 892.8, 818.6, 791.1, 762.2, 699.8, 650.9, 614.9, 545.9 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.8–8.0 (m, 27 H), 3.13 (m, 1 H). No aliphatic peaks were detected. UV ($CHCl_3$) λ_{max} 297 nm. $M_w = 3020$, $M_n = 1300$, $M_w/M_n = 2.32$. Anal. Calcd for $(C_{20}H_{12})_n$: C, 95.21; H, 4.79. Found: C, 90.73; H, 5.22; Br, 1.91. TGA showed 10% weight loss at 671 °C and 19.7% weight loss at 900 °C.

Cross-Coupling of 1-Octyne with Brominated Polyphenylene 1 To Form 16c. Fractional precipitation from hexane with ether gave 59% of a brown solid. FTIR (KBr) 3028.1, 2925.7, 2857.2, 2474.4, 2223.1, 1909.5, 1598.1, 1466.0, 1377.8, 1182.1, 1108.2, 1004.0, 886.9, 815.4, 792.6, 760.8, 695.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.0–8.0 (m, 7 H), 2.4 (br t. $J = 8.0$ Hz, 2 H), 1.61 (br pent, $J = 8.0$ Hz, 2 H), 1.5–1.2 (m, 6 H), 0.90 (br t, $J = 7.0$ Hz, 3 H). UV ($CHCl_3$) λ_{max} 288 nm. $M_w = 3330$, $M_n = 1000$, $M_w/M_n = 3.32$. Anal. Calcd for $(C_{26}H_{24})_n$: C, 92.81; H, 7.19. Found: C, 82.24; H, 6.98; Br, <0.5. Mp (DSC) 140 °C. TGA showed 10% weight loss at 430 °C and 33% weight loss at 900 °C.

Cross-Coupling of Phenylacetylene with 4a To Form 16d. Precipitation with ether gave 66% of a gray–brown ether-insoluble solid. FTIR (KBr) 3029.3, 1596.6, 1491.8, 1441.4, 1441.2, 1388.7, 1004.0, 911.1, 817.0, 791.0, 754.0, 689.1, 520.2 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.0–8.0 (m). No aliphatic peaks were detected. UV ($CHCl_3$) λ_{max} 305 nm. $M_w = 2590$, $M_n = 960$, $M_w/M_n = 2.71$. Anal. Calcd for $(C_{26}H_{16})_n$: C, 95.09; H, 4.91. Found: C, 91.06; H, 5.13; Br, <0.5. Mp (DSC, N_2, 20 °C/min) 200 °C. TGA (N_2, 20 °C/min) showed 10% weight loss at 750 °C and 14.0% weight loss at 900 °C.

Cross-Coupling of 1-Ethynyl-4-(phenylethynyl)benzene (7) with 4a To Form 16e. Precipitation with ether gave a 78% yield of a tan–yellow ether-insoluble solid. FTIR (KBr) 3031.5, 2211.9, 1910.7, 1595.6, 1509.1, 1474.0, 1440.7, 1307.2, 1178.1, 1101.1, 1068.7, 1004.1, 911.7, 890.4, 835.1, 789.4, 753.9, 688.6, 547.4, 522.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.0–8.0 (m). No aliphatic peaks were detected. UV ($CHCl_3$) λ_{max} 242, 326 nm. $M_w = 4090$, $M_n = 1160$, $M_w/M_n = 3.53$. Anal. Calcd for $(C_{34}H_{20})_n$: C, 95.30; H, 4.70. Found: C, 90.41; H, 4.81; Br, <0.5. TGA (N_2, 20 °C/min) showed 10% weight loss at 768 °C and 11.5% weight loss at 900 °C.

Cross-Coupling of 1-Ethynyl-3-(phenylethynyl)benzene (9) with 4a To Form 16f. Fractional precipitation from methylene chloride with ether gave an 84% yield of an orange–brown ether-insoluble solid. FTIR (KBr) 3027.6, 1597.9, 1480.5, 1474.5, 1003.9, 890.5, 817.5, 790.2, 753.8, 686.3, 536.0 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.0–8.0 (m). No aliphatic peaks were detected. UV ($CHCl_3$) λ_{max} 288, 304 nm. $M_w = 3730$, $M_n = 1160$, $M_w/M_n = 3.21$. Anal. Calcd for $(C_{34}H_{20})_n$: C, 95.30; H, 4.70. Found: C, 91.13; H, 4.83; Br, <0.5. TGA (N_2, 20 °C/min) showed 10% weight loss at 810 °C and 10.7% weight loss at 900 °C.

Cross-Coupling of 4-Ethynylbiphenyl (10) with 4a To Form 16g. Fractional precipitation from methylene chloride with ether gave 67% of a tan–yellow ether-insoluble solid. FTIR (KBr) 3028.3, 1598.1, 1521.9, 1485.1, 1108.0, 1074.0, 1006.3, 889.8, 838.3, 823.4, 790.2, 762.0, 722.8, 695.9, 556.3, 512.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.0–8.0 (m). No aliphatic peaks were detected. UV ($CHCl_3$) λ_{max} 316 nm. $M_w = 3610$, $M_n = 1200$, $M_w/M_n = 3.02$. Anal. Calcd for $(C_{32}H_{20})_n$: C, 95.02; H, 4.98. Found: C, 91.47; H, 5.24; Br, <0.5. Mp (DSC, N_2, 20 °C/min) 205 °C. TGA (N_2, 20 °C/min) showed 10% weight loss at 643 °C and 15.5% weight loss at 900 °C.

Cross-Coupling of 1-Ethynylnaphthalene (12) with 4a To Form 16h. Fractional precipitation from methylene chloride with ether gave 58% of a gray–brown ether-insoluble solid. FTIR (KBr) 3026.4, 1474.4, 1396.3, 1004.5, 890.5, 818.7, 796.9, 771.6, 699.6, 566.2 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (m, 1 H), 7.0–8.0 (m, 33 H). No aliphatic peaks were detected. UV ($CHCl_3$) λ_{max} 244, 324 nm. $M_w = 3590$, $M_n = 1730$, $M_w/M_n = 2.07$. Anal. Calcd for $(C_{30}H_{18})_n$: C, 95.21; H, 4.79. Found: C, 90.88; H, 5.02; Br, <0.5. Mp (DSC, N_2, 20 °C/min) 200 °C. TGA (N_2, 20 °C/min) showed 10% weight loss at 730 °C and 12.9% weight loss at 900 °C.

Cross-Coupling of 2-Ethynylbiphenyl (15) with 4a To Form 16i. Fractional precipitation from methylene chloride with ether gave a 72% yield of a gray–brown ether-insoluble solid. FTIR (KBr) 3025.8, 1596.6, 1474.0, 1106.2, 1005.2, 888.7, 817.1, 789.9, 754.6, 734.0, 698.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.8–8.0 (m). No aliphatic peaks were detected. UV ($CHCl_3$) λ_{max} 260 nm. $M_w = 3760$, $M_n = 2070$, $M_w/M_n = 1.82$. Anal. Calcd for $(C_{30}H_{20})_n$: C, 94.74; H, 5.26. Found: C, 91.72; H, 5.01; Br, 0.0.

TGA (N_2, 20 °C/min) showed 10% weight loss at 511 °C and 18.7% weight loss at 900 °C. DSC (N_2, 20 °C/min) showed a broad melt at 150–220 °C and a large exotherm at 340 °C.

Brominated Polyphenylene 18. To a 100-mL round-bottom flask equipped with a stirbar 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 for 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 **18** as a tan–brown solid. FTIR (KBr) 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.

Cross-Coupling of Phenylacetylene with 18 To Form 19a. Precipitation with ether gave 66% of a gray–brown ether-insoluble solid. FTIR (KBr) 3053.5, 1597.3, 1467.1, 1441.7, 1175.5, 1069.7, 1026.0, 887.2, 838.0, 786.0, 754.5, 698.2, 616.0, 520.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.8–7.8 (m). No aliphatic peaks were detected. UV ($CHCl_3$) λ_{max} 254 nm. $M_w = 2870$, $M_n = 1170$, $M_w/M_n = 2.45$. TGA (N_2, 20 °C/min) showed 10% weight loss at 482 °C and 17% weight loss at 900 °C.

Cross-Coupling of 1-Ethynyl-4-(phenylethynyl)benzene with 18 To Form 19b. Precipitation with ether gave a 78% yield of a tan–yellow ether-insoluble solid. FTIR (KBr) 3030.0, 1595.3, 1508.4, 1466.6, 1440.9, 1099.6, 1016.3, 888.0, 834.5, 784.1, 753.6, 689.0, 616.4, 545.5, 520.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.8–8.0 (m). No aliphatic peaks were detected. UV ($CHCl_3$) λ_{max} 250, 310 nm. $M_w = 3770$, $M_n = 2030$, $M_w/M_n = 1.85$. Anal. Calcd for $(C_{64}H_{40})_n$: C, 95.05; H, 4.95. Found: C, 90.60; H, 5.09; Br, 1.95. TGA (N_2, 20 °C/min) showed 10% weight loss at 614 °C and 14.5% weight loss at 900 °C.

Cross-Coupling of 1-Ethynyl-3-(phenylethynyl)benzene with 18 To Form 19c. Precipitation with ether gave a 74% yield of a tan–yellow ether-insoluble solid. FTIR (KBr) 3057.4, 1597.2, 1119.9, 888.1, 836.9, 789.0, 755.0, 689.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.5–8.0 (m); unidentified peak at 1.6 ppm. UV ($CHCl_3$) λ_{max} 258 nm. $M_w = 3130$, $M_n = 1490$, $M_w/M_n = 2.10$. TGA (N_2, 20 °C/min) showed 10% weight loss at 511 °C and 18.7% weight loss at 900 °C.

Cross-Coupling of 4-Ethynylbiphenyl with 18 To Form 19d. Precipitation with ether gave 100% of a tan–yellow ether-insoluble solid. FTIR (KBr) 3027.6, 1593.9, 1481.1, 1399.0, 1109.3, 1074.3, 1005.3, 890.2, 837.2, 785.1, 761.2, 696.1, 614.4, 357.5, 509.7 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.6–8.0 (m). Little or no aliphatic peaks were detected. $M_w = 3330$, $M_n = 1610$, $M_w/M_n = 2.07$. Anal. Calcd for $(C_{62}H_{40})_n$: C, 94.90; H, 5.10. Found: C, 91.10; H, 5.35; Br, 1.96. TGA (N_2, 20 °C/min) showed 10% weight loss at 480 °C and 35% weight loss at 900 °C.

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Supplementary Material Available: TGA and DSC thermograms for compounds **1**, **3**, **4a,b**, **16a–i**, **18**, and **19a–d** and the powder XRD of the char for **16d** (43 pages). Ordering information is given on any current masthead page.

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