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New High-T_g, Heat-Resistant, Cross-Linked Polymers. 1. Synthesis and Characterization of Di-*p*-ethynyl-Substituted Benzyl Phenyl Ether Monomers

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ABSTRACT: Six new di-*p*-ethynyl-substituted benzyl phenyl ether monomers were synthesized in high yield by a three-step synthetic route. Dibromo-end-capped compounds of the desired chemical structure were synthesized and oxidatively coupled with 2-methyl-3-butyn-2-ol in the presence of Pd(0)/Cu(I), generating the corresponding bis(butynol) adducts in high yield and purity. The intermediate bis(butynol) adducts were deprotected in a new convenient system, NaOH/1-BuOH. This system could be applied to all the intermediates. Sodium hydroxide has a high solubility in refluxing 1-butanol; the high boiling point of 1-BuOH reduced the reaction time required for deprotection to less than 1 h. The overall yields ranged from 75 to 85%.

Introduction

The objective of this research was to develop new *p*-ethynyl-terminated monomers which could polymerize at moderately elevated temperatures and yield highly cross-linked thermally stable resins suitable as matrices for high-temperature composites. The monomers should also exhibit good solubility in common organic solvents and possess a "processing window" between their melting point and the initiation of polymerization. The highly cross-linked resins should have outstanding heat resistance. This paper concerns itself with the synthesis and characterization of difunctional *p*-ethynylbenzyl phenyl ethers (EBEs). EBEs are expected to have good flexibility and adhesion in the cured state while maintaining ease of processing and high thermal stability. The existence of the benzyl phenyl ether bond between the aromatic rings could reduce brittleness and provide good fiber-matrix bonding in composite applications.

There are several possible synthetic routes to di-*p*-ethynyl-substituted benzyl phenyl ethers. Routes which used *p*-ethynylphenol fail because it self-polymerizes.[1] Therefore, we chose an approach where the ethynyl group is formed in the last step. Many methods have been used to generate aromatic ethynyl compounds.[2–7] The present accepted procedure is the Stephens–Castro coupling reaction[8–10] between an aryl iodide and a protected acetylide. Recent advances[11,12] use a two-step route; an aryl iodide is coupled with (trimethylsilyl)acetylene (TMSA) and the protecting group (trimethylsilyl) is subsequently removed. However, because of the prohibitively high cost of (trimethylsilyl)acetylene, this route has been limited to laboratory preparations.

Since we needed the EBEs in quantity, we applied a procedure which involves coupling of the inexpensive reagent, 2-methyl-3-butyn-2-ol (MEBYNOL), with aryl halides. MEBYNOL has not been widely used for this type of reaction even though it is much less expensive than TMSA because the 2-hydroxypropyl group is not easily removed. Thus, after the formation of the 4-aryl-2-hydroxy-2-methyl-3-butyn-4-yl adduct, the next step, the removal of the protecting group (2-hydroxylpropyl) as acetone, appeared to be complicated. Severe reaction conditions were needed, such as a strong alkaline environment and high temperatures for the deprotection reaction to go to completion. During the deprotection step byproducts appeared or side reactions took place if base-sensitive groups were present in the molecule. MEBYNOL has been used by researchers for the synthesis of other acetylene-terminated aromatic compounds.[13–17] Since an economical, reliable, and high-yield procedure had been developed in our laboratory for the deprotection of other butynol intermediates,[16,17] we wished to extend it to the deprotection of benzyl phenyl ether derivatives.

Results and Discussion

A three-step method (see Figure 1) was used to synthesize six new-*p*-ethynylbenzyl phenyl ether monomers (EBE) (see Figure 2).

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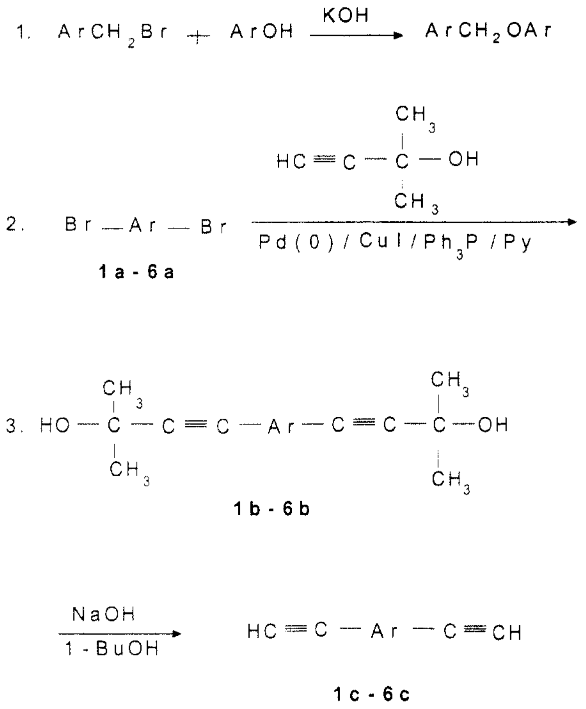
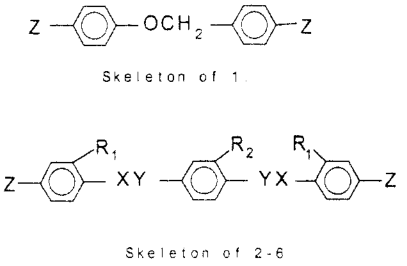


Figure 1. Synthetic route to di-*p*-ethynyl-substituted benzyl phenyl ether monomers, EBEs.



Skeleton	X	Y	R_1	R_2
2	O	CH_2	H	H
3	O	CH_2	Cl	H
4	CH_2	O	H	CH_3
5	CH_2	O	H	Cl
6	CH_2	O	H	H

a: derivatives with Z = —Br

b: derivatives with Z = —C≡C—C(CH3)2—OH

c: derivatives with Z = —C≡CH

Figure 2. Chemical structures of di-*p*-ethynyl-substituted benzyl phenyl ether monomers, EBEs.

Step 1. Dibromo derivatives of the desired chemical structure (Figure 2) were prepared by direct condensation of either *p*-bromophenol with *p*-bromobenzyl bromide (**1a**) and/or α,α'-dibromoxylene (**2a–3a**) or by condensation of *p*-bromobenzyl bromide with the appropriate hydroquinone derivative (**4a–6a**) in the presence of base. (**2a** is included in a Japanese patent[18] concerning its potential use as fungicide and herbicide, but no data are given regarding its physical characteristics.) The physical characteristics for **1a–6a** are listed in Table 1.

Step 2. The second step involves oxidative coupling of **1a–6a** and MEBYNOL in the presence of Pd(0)/Cu(I) and triphenylphosphine. Pd(II) is reduced to Pd(0) in the presence of 2 equiv of triphenylphosphine. Oxidative addition of the aryl bromide to Pd(0) is promoted with Cu(I), followed by substitution of the bromide with acetylide and reductive elimination of the bis(butynol) adduct with regeneration of Pd(0). Base is required to deprotonate the acetylene reagent (MEBYNOL). In the absence of base, coordination of the acetylene reagent to palladium would be through interaction with the triple bond, generating cyclic or linear oligomers of the acetylene reagent. The detailed mechanism of the oxidative addition step between the aryl halide and palladium(0) has been suggested as being nucleophilic aromatic substitution,[19] electron-transfer,[20] or three-center[21] in nature. It should be noted that the nucleophilic nature of the low-valent metals is emphasized in all three proposed mechanisms. Sabourin et al.[13] found that both CuI and Ph_3P enhanced the rate of coupling, and in the absence of Ph_3P the reaction often did not go to completion. They suggested a molar ratio of $Ph_3P/Pd/CuI$ of 15.6/1/4 for optimizing the reaction conditions. In our study it was found that the ratio $Ph_3P/Pd/CuI$ = 10.4/1/3.7 appeared to be the optimum one. Using the procedure described in the Experimental Section, we synthesized the bis(butynol)-substituted benzyl phenyl ethers in high yields (84–99%), though the literature states that aryl bromides[11] are much less reactive than the corresponding aryl iodides toward oxidative addition of Pd(0). Takahashi et al.[11] found that, while aryl iodides could be coupled with (trimethylsilyl)acetylene at room temperature using Pd(0)/Cu(I) catalysis, aryl bromides required substitution with an electron-withdrawing group. Bromobenzene and 4-bromoanisole were found to be inactive. In a previous report,[16] methyl *p*-bromobenzoate (aryl bromide bearing an electron-withdrawing group) was coupled with MEBYNOL in 98% yield and 99% purity by heating the above reagents in Et_3N/Py in the presence of Pd(0)/Cu(I) for only 40 min. Harris et al[22] coupled bis[2-(3-bromophenoxy)ethyl] ether with MEBYNOL in 84% yield after 20 h of refluxing in triethylamine and 57% overall yield after deprotection. The better molar ratio for catalyst/cocatalyst and the use of Py as cosolvent, which increased the reflux temperature, probably helped drive the coupling reaction to completion. The longer reaction time (30 h) is a third factor. The physical data for **1b–6b** (Figure 2) are listed in Table 1.

Table 1. Physical Data for 1a–6a and 1b–6b

code	yield (%)	T_{melting} (°C)	HPLC (t_r) (min)	TLC[a] ($R_f = L_{\text{com}}/L_s$)
1a	97	115–117	3.73	
2a	94	184–186		0.59[b]
3a	98	177–179		0.68[c]
4a	85	175–176		0.65[b]
5a	84	168–170	3.20	
6a	95	187–188	3.45	
1b	89	140–141	2.56	
2b	84	173–175	2.21	
3b	99	155–156	2.83	
4b	92	137–138	2.74	
5b	98	139–140	2.43	
6b	96	184–185	2.6	

[a] TLC was used for the compounds which were insoluble in methanol and the HPLC technique could not be applied. [b] In benzene/hexane = 2/1. [c] In benzene.

Step 3. The next step is the deprotection of the bis(butynol) adduct. Literature procedures[14,23] were attempted, but yields of EBEs were poor. The present approach, excess NaOH in refluxing 1-BuOH, worked well. The monobutynol monoethynyl adduct formed within 4 min (checked by HPLC), but the reaction was complete only after 1 h. The generally accepted mechanism for the

Table 2. Physical Characteristics for 1c–6c

code	yield (%)	T_{melting}[a] (°C)	HPLC, t_r (min)	density (g/cm^3)
1c	90	98	2.80	1.15
2c	99	164	3.06	1.18
3c	92	138	3.37	1.29
4c	96	94	3.34	1.18
5c	92	125	3.00	1.25
6c	94	197	2.87	1.21

[a] Defined by DSC (15 °C/min under N_2).

deprotection reaction is that it initiated by abstraction of the hydroxyl proton of 4-aryl-2-methyl-3-butyn-2-ol (pK_a ≈ 16.5)[24,25] by the base (NaOH), followed by the loss of acetone. The arylacetylide anion, in turn, abstracts a hydroxy proton from another 4-aryl-2-methyl-3-butyn-2-ol which completes the cycle. Although the first step is reversible, it favors the reverse direction due to the pK_a value of water (pK_a = 15.74); the reaction is driven by the loss of acetone. The resulting acetylide anion abstracts a proton from the hydroxyl group of another 4-aryl-2-methyl-3-butyn-2-ol (the pK_a of phenylacetylene is 18.5)[24] since its pK_a is higher than those of water or the alcohol. Also the acetone is distilled off as it is formed. Substitution of the aromatic ring of a 4-aryl-2-methyl-3-butyn-2-ol with an electron-withdrawing substituent drives the first step of the deprotection reaction toward the right. Since the rate-determining step of this reaction is the first one, the reaction goes to completion very rapidly and in high yield. The physical characteristics of EBEs, **1c**–**6c**, shown in Figure 2 are given in Table 2.

Step 3. Overview. Since we wanted to prepare large quantities of the monomers, a general, inexpensive procedure was developed which could be applied to the whole series of bis(butynol)-substituted benzyl phenyl ethers. The best system was NaOH/1-BuOH because (1) it is inexpensive, (2) it could be applied to all bis(butynol) adducts, (3) the high boiling point of the 1-BuOH reduced the reaction time to less than 1 h (much less than procedures previously reported),[14,22] and (4) NaOH has a high solubility in refluxing 1-BuOH. This system is much more effective than others which have been used for the deprotection of monobutynol adducts.[23] Although isopropyl alcohol was successfully used as solvent in the deprotection of an arylbutynol adduct bearing an electron-withdrawing group (4-[4-(methoxycarbonyl)phenyl]-2-methyl-3-butyn-2-ol was deprotected in refluxing NaOH/1-butanol in 98.5% yield and 99% purity within 10 min; the reaction took 2.4 h in refluxing isopropyl alcohol/KOH with the same yield and purity[16]), the deprotection did not go to completion for these materials (90% deprotection) even after refluxing for 3 h. We expect that dry KOH will also be an effective deprotecting agent. It is possible that catalytic amounts of sodium hydride in alcohols will be equally effective.

Purity. The purity of the monomers (**1c**–**6c**) was checked by HPLC and GPC and ranged between 96 and 99.5%. No attempt was made to further purify them by recrystallization or column chromatography. The chemical structure of **1c**–**6c** was confirmed by FTIR, Raman, and ^{1}H-NMR spectroscopies. All IR spectra of the monomers showed intense absorption bands at 3270–3300 and 2100–2108 cm^{-1} due to the C(sp)–H and C(sp)–C(sp) stretch vibrations. Absorption bands at 2873–2920 (C–H) and 1238–1242 cm^{-1} (O–C) were associated with the benzyl ether group. Aromatic bands were seen at 3070 (=CH, stretching), 1602 and 1510 cm^{-1} (C=C, stretching). The presence of the acetylenic group was also confirmed by Raman spectroscopy (Figure 3). The intense singlet at 2102 cm^{-1} in the Raman spectrum of **1c** is correlated with a C(sp)–C(sp) stretching vibration. ^{1}H-NMR spectra of **1c**–**6c** all showed a single peak in the region of 3.25–3.97 ppm attributed to the acetylenic protons. The single peak at 5.02–5.20 ppm was attributed to benzylic protons and the multiple peaks at 6.8–7.55 ppm were associated with the aromatic protons. Figure 4 shows the ^{1}H-NMR spectrum of **2c**, which is representative of this series. The ^{1}H-NMR data for **1c**–**6c** are given in Table 3. All monomers were examined by X-ray and hot-stage cross-polarized microscope and found to be crystalline at room temperature.

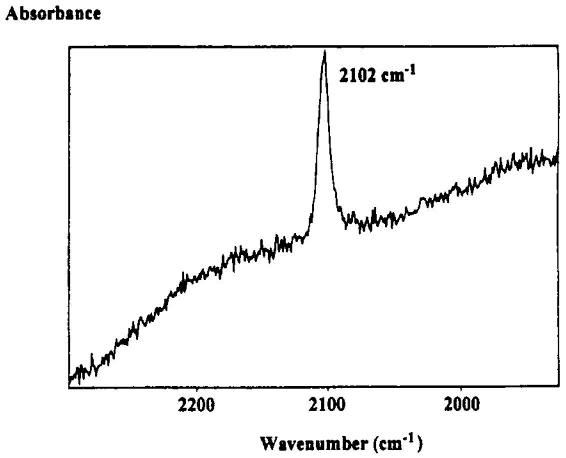


Figure 3. Raman spectrum of **1c**.

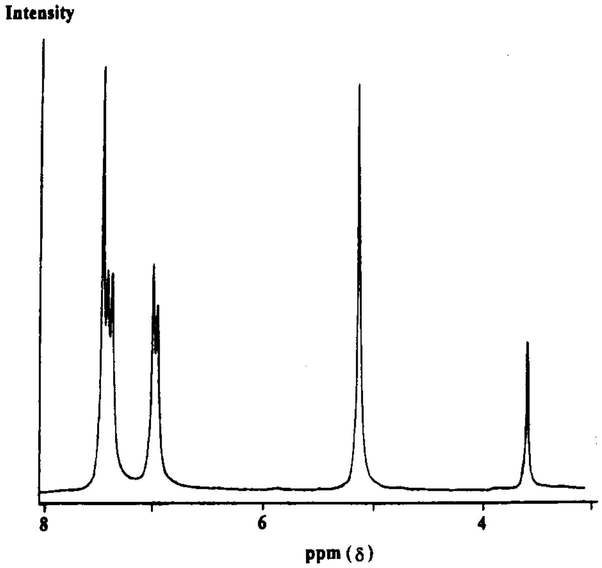


Figure 4. ^{1}H-NMR spectrum of **2c**. (The interpretation is given in Table 3.)

Experimental Section

Materials. Methylhydroquinone and chlorohydroquinone (Aldrich) were recrystallized from toluene. Hydroquinone (Aldrich) was recrystallized from hot water in the presence of sodium sulfite. *p*-Bromophenol, 2-chloro-4-bromophenol, *p*-bromobenzyl bromide, *α*,*α*′-dibromo-*p*-xylene, 2-methyl-3-butyn-2-ol (MEBYNOL), triphenylphosphine, cuprous iodide, and dichlorobis(triphenylphosphine)palladium were used as received from Aldrich. Triethylamine and pyridine (Fisher) were refluxed over KOH pellets and distilled under nitrogen. *N*,*N*-Dimethylacetamide (Aldrich) and 1-BuOH (Fisher) were used as received.

Analytical Methods. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were taken on an XL-200, 200-MHz FT-NMR. Chemical shifts (δ) are given in ppm, with tetramethylsilane as internal standard. Infrared spectra (FTIR) were recorded on a Bio-Rad Digilab FTS-60 spectrometer utilizing KBr pellets. Raman spectra were obtained on a DILOR XY Raman spec-

Table 3. ^{1}H-NMR Spectral Data for 1c–6c

monomer	chemical shifts (δ,[a] ppm) and assignments
1c	3.63[b] (s, 2H, acetylenic), 5.16 (s, 2H, methylenic), 7.10 (d, 2H, $J = 8.5$ Hz, aromatic ortho to oxygen), 7.40–7.52 (m, 6H aromatic ortho to methylenic and ethynyl groups)
2c	3.64[c] (s, 2H, acetylenic), 5.14 (s, 4H, methylenic), 6.95 (d, 4H, $J = 8.4$ Hz, aromatic ortho to oxygen), 7.37–7.45 (m, 8H, aromatic ortho to methylenic and ethynyl groups)
3c	3.25[d] (s, 2H, acetylenic), 5.20 (s, 4H, methylenic), 6.85 (d, 2H, $J = 8.4$ Hz, aromatic ortho to oxygen), 7.30 (s, 4H, aromatic ortho to methylenic groups), 7.43–7.55 (m, 6H, aromatic ortho to ethynyl groups)
4c	2.22[d] (s, 3H, methyl group), 3.28 (s, 2H, acetylenic), 5.05 (s, 4H, methylenic), 6.71–6.80 (m, 3H, aromatic ortho to oxygen), 7.35 (d, 4H, $J = 7.1$ Hz, aromatic ortho to methylenic group), 7.48 (d, 4H, $J = 7.0$ Hz, aromatic ortho to ethynyl group)
5c	3.78[b] (s, 2H, acetylenic), 5.16 (s, 4H, methylenic), 6.83–6.95 (m, 3H, aromatic ortho to oxygen), 7.30 (d, 4H, $J = 7.5$ Hz, aromatic ortho to methylenic group), 7.50 (d, 4H, $J = 7.6$ Hz, aromatic ortho to ethynyl group)
6c	3.97[c] (s, 2H, acetylenic), 5.02 (s, 4H, methylenic), 6.92 (s, 4H, aromatic ortho to oxygen), 7.40 (d, 4H, $J = 7.9$ Hz, aromatic ortho to methylenic group), 7.49 (d, 4H, $J = 8.0$ Hz, aromatic ortho to ethynyl group)

[a] All ^{1}H-NMR spectra were recorded at 45 °C. [b] In acetone-d_6. [c] In DMSO-d_6. [d] In $CDCl_3$.

trometer with CCD detector and laser power 5.85 mW. A Carl Zeiss optical polarizing microscope equipped with a Mettler FP-82 hot stage and a Mettler FP 80 central processor was used to observe the thermal transitions. Twenty-mil-thick pellets were made from the monomers and the polymers by compression molding, and their densities were measured using a density gradient column containing potassium bromide in water. X-ray scans were recorded using a Philips APD 3520 automatic diffractometer with nickel-filtered Cu Kα radiation. Scans were run from 1° to 40° with a goniometer speed of 2°/min. Thin-layer chromatography (TLC) was performed using chromatography sheets of 13 181 silica gel containing fluorescent indicator (Kodak). HPLC was performed using an ISCO-HPLC instrument equipped with a UV detector (254 nm), with methanol as the eluting solvent at a flow rate of 1.0 mL/min. GPC was performed using a Waters GPC I equipped with a differential refractomonitor and a Hewlett Packard UV detector, with one precolumn (Pl gel, 5 μm, 100 Å) and two Pl gel columns (5 μm, 10 and 500 Å) with THF as the eluant at a 1.0 mL/min flow rate.

4-Bromo[1-(4-bromophenyl)methoxy]benzene (1a). To a solution of *p*-bromophenol (8.04 g, 46 mmol) in isopropyl alcohol (110 mL) containing KOH (3.03 g, 46 mmol) was added in parts granular *p*-bromobenzyl bromide (4.59 g, 18 mmol). The resulting solution was stirred at 50 °C. After 20 min, a white precipitate started appearing. The solution was subsequently refluxed overnight. The mixture was refrigerated and filtered, and the resulting white residue was stirred with 200 mL of a saturated sodium carbonate solution (three times) and then with water (200 mL) and finally dried under vacuum. **1a** was obtained in 97% yield and 99% purity and was used without further purification. The physical data of **1a** are listed in Table 1.

4-(2-Hydroxy-2-methyl-3-butyn-4-yl)-1-[[4-(2-hydroxy-2-methyl-3-butyn-4-yl)phenyl]methoxy]benzene (1b). A 500-mL three-necked, round-bottomed flash equipped with a reflux condenser, magnetic stirrer, nitrogen inlet, and calcium chloride guard tube was charged with 100 mL of dry triethylamine, 60 mL of dry pyridine, triphenylphosphine (0.31 g, 1.18 mmol), cuprous iodide (0.08 g, 0.42 mmol), **1a** (99% purity; 12.51 g, 38 mmol), and MEBYNOL (10 g, 114 mmol). Nitrogen was bubbled through this stirred mixture for 20 min. Dichlorobis(triphenylphosphine)-palladium (0.08 g, 0.113 mmol) was then added under a flow of nitrogen. The mixture was refluxed for 30 h. It was cooled to room temperature and filtered to remove the insoluble salt (triethylamine hydrobromide) formed during the reaction. The salt was washed with triethylamine/ethyl ether until the ether washings were clear. The combined filtrates were reduced to dryness. The obtained solid was stirred twice with water, with 200 mL of 3% HCl, and again twice with water. The mixture was filtered, and the residue was dried under vacuum to yield and off-white product (12.96 g) with a melting point of 134–136 °C. Recrystallization from toluene afforded a crystalline solid, **1b** (10.5 g), with 99.5% purity (t_r = 2.56 min by HPLC) and mp 140–141 °C. Its IR and ^{1}H-NMR spectra were consistent with its chemical structure.

4-Ethynyl-1-[(4-ethynylphenyl)methoxy]benzene (1c). (a) To a vigorously stirred solution of **1b** (99.5% purity); 6.78 g, 28.7 mmol) in 1-butanol (110 mL) at reflux was added at once pulverized sodium hydroxide (4.6 g, 117 mmol). The solution was refluxed for 30 min. The solvent was rotoevaporated, and the residue was stirred with 200 mL of water (three times) and filtered. Upon drying under vacuum at 45 °C, a light tan crystalline solid, **1c**, was obtained (5.99 g, 90% yield, and 99% purity by HPLC). Its physical data are listed in Table 2.

(b) A 250-mL flask was charged with t-BuOK (6.78 g, 28.72 mmol) and toluene (65 mL), and the mixture was heated to reflux **1b** (6.78 g, 28.7 mmol) was added at once to the above well-stirred mixture. After 15 min of refluxing the flask was placed in the refrigerator. The cold mixture was filtered, and the filtrate was rotoevaporated under vacuum at about 45 °C. The residue was washed thoroughly with water and dried. **1c** was obtained in 83.5% yield (5.56 g) and 99% purity by HPLC (t_r = 2.80 min).

Synthesis of 2a–6a. (a) **2a** and **3a** were prepared in 94 and 98% yield, respectively, by reacting *p*-bromophenol (8.65 g, 50 mmol) or 2-chloro-4-bromophenol (10.375 g, 50 mmol) with α,α'-dibromoxylene (6.071 g, 23 mmol) in 1-butanol (210 mL) containing potassium hydroxide (2.8 g, 50 mmol). The mixture was refluxed for 25 h. It was refrigerated for 1 h and filtered. The white residue was stirred twice with 70 mL of petroleum ether and dried under vacuum for 4 h. The white crystalline solid was twice stirred with water (150 mL), with 150 mL of a saturated solution of sodium carbonate, and again with water and finally dried under vacuum at 50 °C. The physical data are listed in Table 1.

(b) **4a**, **5a**, and **6a** were prepared in high yield by heating methylhydroquinone (4.39 g, 35 mmol), chlorohydroquinone (5.95 g, 35 mmol), and hydroquinone (3.85 g, 35 mmol), respectively, with *p*-bromobenzyl bromide (17.49 g, 70 mmol) in *N,N*-dimethylacetamide (250 mL) containing potassium hydroxide (3.92 g, 70 mmol), tetrabutylammonium bromide (4.81 g, 14.9 mmol) as phase transfer catalyst, and sodium sulfite (1.5 g) as antioxidant. The mixture was heated at 60 °C for 1 h and then at 135 °C for 35 h and subsequently poured over crushed ice. It was filtered, and the residue was washed twice with water, then with a saturated sodium carbonate solution, and again with water. It was filtered, and the solid was dried at 50 °C under vacuum. The yields were 84–95% with 99% purity (by HPLC). Their physical data are listed in Table 1.

Synthesis of 2b–6b. 2b–6b were prepared by coupling **2a–6a** with MEBYNOL in the presence of palladium(0) complexes using the experimental conditions given for **1b**. These intermediates were obtained in 89–98% yields and 98–99.5% purity after recrystallization from toluene. The physical data are listed in Table 1.

Synthesis of 2c–6c. The deprotection procedure for **2b** is detailed below as representative of the reaction conditions. To a 250-mL single-neck flask equipped with a condenser were added **2b** (5 g, 11 mmol) and 1-butanol (100 mL). The solution was heated to reflux, and sodium hydroxide (1.8 g, 45 mmol) was added at once. The mixture was heated at reflux for 1 h. The solvent was rotoevaporated, and the residue was stirred with 200 mL of H_2O three times and filtered. Upon drying under vacuum at 45 °C, light tan flakes of crystalline solid **2c** were obtained (3.71 g, yield = 99%) with 99.5% purity. The others, **3c–6c**, were obtained in 92–96% yield and 96–99% purity (HPLC and GPC). The physical data for **1c–6c** are listed in Table 2.

Summary and Conclusions

Six new di-*p*-ethynylbenzyl phenyl ether monomers were synthesized in high yield and purity. The coupling step was optimized to the point that we could get complete coupling of aromatic bromo compounds that had an electron-donating substituent para to the bromine. This was because the coupling reaction conditions (2nd step) was optimized by changing the catalyst/cocatalyst molar ratio and raising the reaction temperature.

A new deprotection system (3rd step) was developed. NaOH/1-BuOH appears to be very effective because (1) it is general (it could be applied to all bis(butynol) adducts), (2) NaOH has a high solubility in refluxing 1-BuOH, and (3) the high boiling point of 1-BuOH decreased the reaction time required for deprotection of these very unreactive systems to less than 1 h with little or no byproducts. The deprotection procedure reported here is more effective than those reported in the literature.

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