# Palladium Catalysis of Ditriflates for the Preparation of Soluble Poly(phenylene) Derivatives†

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ABSTRACT: A new polymerization reaction for the preparation of alkyl-substituted poly(phenylene)s is described based on the coupling of alkyl-substituted aromatic bis(trifluoromethanesulfonate) (triflate) with 1,4-bis(trimethylstannyl)benzene in the presence of a palladium catalyst. Aromatic triflates, readily prepared from the corresponding hydroquinone, were discovered to be excellent substrates in the preparation of soluble poly(phenylene) derivatives with alkyl substituents on alternating aromatic rings. Analysis of the poly(phenylene) derivatives by SEC revealed a near-Gaussian molecular weight distribution curve with degree of polymerization of 11 and polydispersity from 1.3 to 1.7. Analysis by $^{31}$P-NMR revealed the presence of phosphorus, the presence of which limits the catalytic efficiency of palladium leading to a decrease in the degree of polymerization.

## Introduction

Poly(*p*-phenylene) is a rigid-rod polymer[1] that becomes conductive by 14 orders of magnitude upon doping.[2] Numerous methods to synthesize poly(phenylene) have been reported[3] using chemical or electrochemical processes. Direct routes from benzene or biphenyl, first described by Kovacic and co-workers,[4] involved oxidation of benzene on treatment with $AlCl_3$−$CuCl_2$. Alternatively, polycondensation of 1,4-dibromobenzene with magnesium in the presence of nickel catalysts yields poly(phenylene).[5] Indirect methods have gained importance in terms of higher molecular weights.[6] The Stille cross-coupling reaction of vinyl and aryl triflates with organostannanes (Scheme 1)[7] has many of the attractive features of a general carbon−carbon bond formation method including high yields and functional group tolerance. Organostannanes are versatile reagents as they are available from a number of different sources.[8] Aryl triflates are valuable starting materials because of their availability from phenols.[9] Aromatic polyketones have been prepared by palladium-catalyzed coupling of aromatic diacid chlorides with bis(trimethylstannyl) monomers.[10] Other polyaromatic materials from nickel-catalyzed coupling with aryl triflates have been reported.[11] We wish to describe our preliminary efforts preparing alkyl-substituted poly(phenylene)s employing a palladium-catalyzed oligomerization of aryl ditriflates with aryl distannanes.

## Experimental Section

All solvents were distilled prior to use. Tetrahydrofuran (THF) was distilled under nitrogen from molten potassium. Diethyl ether ($Et_2O$) was distilled under nitrogen from sodium metal with benzophenone as an indicator. Dichloromethane ($CH_2Cl_2$) was distilled under nitrogen from calcium hydride ($CaH_2$). 1,4-Dioxane was distilled under nitrogen from lithium aluminum hydride (LAH) and stored over 3-Å molecular sieves. Lithium chloride (LiCl) was dried overnight under vacuum at 140−160 °C. All chemicals were purchased from the Aldrich Chemical Co. or Baxter Scientific Products Co. and used without further purification unless otherwise stated. Mass spectra were obtained using a Finnigan-MAT Model 312 spectrometer with 70-eV EI ionization (source temp = 225 °C) or a VESTEC Laser Tec Research Model mass spectrometer. UV−visible spectra were recorded on a Hewlett-Packard 8450A diode array spectrometer. $^1$H and $^{13}$C spectra were collected on a Varian 300-MHz spectrometer from ≤1% solutions in chloroform-*d* with tetramethylsilane (TMS) as an internal reference. HPLC measurements were carried out on a Shimadzu SCL-10A series system (UV detection, 254 nm) with a Burdick & Jackson SEC column (10 $\mu$, 500 Å, 30 × 0.75 cm). Elemental analyses were obtained from Atlantic Microlab, Inc. Thermal analyses were performed using a Perkin-Elmer DSC-4 system with a heating rate of 10 °C/min under a nitrogen atmosphere.

**5-Bromo-2-hydroxybenzyl Methyl Ether (2).** Into a 100-mL round-bottomed flask was added 5-bromosalicylaldehyde (513.6 mg, 2.55 mmol) which was dissolved in 4 mL of 1 N NaOH, giving a yellow color. Sodium borohydride (0.129 g, 3.40 mmol) was quickly added to the solution. The reaction was stirred at room temperature until TLC analysis showed complete consumption of the starting material (about 1 h). The reaction mixture was poured into a separatory funnel containing water and ethyl acetate. The crude product was extracted twice with ethyl acetate, washed with water and brine, and dried over $MgSO_4$. Filtration and evaporation of the solvent in vacuo left 0.443 g (85.4% yield) of 5-bromo-2-hydroxybenzyl alcohol as a white crystalline solid: mp 108 °C; $R_f$ 0.56 (15% MeOH/$CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 7.21−7.17 (dd, 1H, $J$ = 2.47, 8.64 Hz), 7.15 (br s, 1H), 7.05−7.047 (d, 1H, $J$ = 2.22 Hz), 6.68−6.65 (d, 1H, $J$ = 8.58 Hz), 4.74−4.72 (d, 2H, $J$ = 5.43 Hz), 2.16−2.12 (t, 1H, $J$ = 5.42 Hz); LRMS for $C_7H_7BrO_2$ *m/e* 202 ($M^+$). This material was carried on to the next step. Into a 100-mL round-bottomed flask was placed 430 mg (2.12 mmol) of 4-bromosalicyl alcohol (0.43 g, 2.12 mmol) in 0.60 mL (7.41 mmol) of distilled pyridine and 0.50 mL (5.29 mmol) of acetic anhydride. The reaction mixture was stirred under a nitrogen atmosphere at room temperature until TLC analysis showed complete consumption of the starting material (about 1 h). The reaction was worked up with dilute HCl and ethyl acetate. The organic layer was washed with brine and dried over $Na_2SO_4$. Filtration and evaporation of the solvent in vacuo gave 5-bromo-2-acetoxybenzyl acetate as a yellow oil: 0.591 g (97% yield); $R_f$ 0.33 (25% ethyl acetate/hexane); $^1$H NMR ($CDCl_3$) $\delta$ 7.55−7.54 (d, 1H, $J$ = 2.43 Hz), 7.46−7.42 (dd, 1H, $J$ = 2.41, 8.59 Hz), 6.98−6.97 (d, 1H, $J$ = 8.65 Hz), 5.00 (s, 2H), 2.28 (s, 3H), 2.06 (s, 3H); LRMS for $C_{11}H_{11}BrO_4$ *m/e* 288 ($M^+$). This material was carried on to the next step. Into a 100-mL round-bottomed flask was placed 3.44 g (12.0 mmol) of diacetate, 0.984 g (12.0 mmol) of anhydrous sodium acetate, and 20 mL of distilled MeOH. The reaction was heated to reflux for 1 day. The reaction mixture was cooled and poured into a separatory funnel containing dilute sodium bicarbonate and $CH_2Cl_2$. The aqueous layer was twice extracted with $CH_2Cl_2$. The combined organic layers were washed with brine and dried

† Dedicated to the memory of John and Dee Stille.

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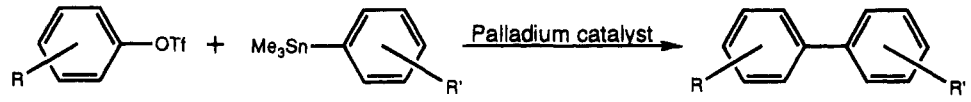
Scheme 1




over $Na_2SO_4$. Filtration and evaporation of the solvent in vacuo followed by column chromatography (50% ethyl acetate/hexane) gave 2.06 g (79% yield) of **2** as a viscous oil: $R_f$ 0.55 (50% ethyl acetate/hexane); $^1$H NMR ($CDCl_3$) $\delta$ 7.51 (s, 1H), 7.29–7.26 (dd, 1H, $J$ = 2.50, 8.61 Hz), 7.12–7.11 (d, 1H, $J$ = 2.60 Hz), 6.76–6.73 (d, 1H, $J$ = 8.64 Hz), 4.59 (s, 2H), 3.42 (s, 3H); LRMS for $C_8H_9BrO_2$ *m/e* (%) 216 ($M^+$, 33), 184 ($M^+ - OCH_3^\bullet$, 84), 156 ($PhBr^+$, 38), 77 ($C_6H_5^+$, 100).

**5-(Tributylstannyl)-2-(*tert*-butyldimethylsiloxy)benzyl Methyl Ether (3).** Into a 250-mL round-bottomed flask were placed 6.59 g (30.4 mmol) of 5-bromo-2-hydroxybenzyl methyl ether, 4.80 g (31.9 mmol) of *tert*-butyldimethylsilyl chloride (TBDMSCl), 3.10 g (45.5 mmol) of imidazole, 20 mL of dimethylformamide (DMF), and a catalytic amount of 4-(dimethylamino)pyridine (DMAP). The reaction mixture was stirred at room temperature until TLC analysis showed complete consumption of the phenol (about 1 day). The reaction mixture was poured into a separatory funnel containing water and ethyl acetate. The aqueous layer was twice extracted with ethyl acetate. The organic layers were combined, washed several times with water and brine, and dried over $Na_2SO_4$. Filtration and evaporation of the solvent in vacuo left an oil which was further purified by column chromatography (12% ethyl acetate/hexane) to give 9.64 g (96% yield) of 5-bromo-2-(*tert*-butyldimethylsiloxy)benzyl methyl ether as a viscous oil: $R_f$ 0.63 (12% ethyl acetate/hexane); $^1$H NMR ($CDCl_3$) $\delta$ 7.47–7.46 (d, 1H, $J$ = 2.64 Hz), 7.24–7.20 (dd, 1H, $J_1$ = 2.58, 8.64 Hz), 6.66–6.63 (d, 1H, $J$ = 8.64 Hz), 4.40 (s, 2H), 3.39 (s, 3H), 0.98 (s, 9H), 0.19 (s, 6H); LRMS for $C_{14}H_{23}BrO_2Si$ *m/e* 332 ($M^+$). This material was carried on to the next step. Into a 100-mL round-bottomed flask was placed 163 mg (0.49 mmol) of the silylated benzyl methyl ether and 20 mL of THF. The solution cooled to −78 °C, and 0.32 mL (0.52 mmol) of *n*-BuLi was carefully added via syringe. The aryllithium was stirred under nitrogen for about 10 min before it was transferred via cannula to a stirred solution of $Bu_3SnCl$ (0.14 mL, 0.50 mmol) in 10 mL of THF at −78 °C. The reaction mixture was stirred for about 40 min at −78 °C and then warmed to room temperature. The reaction was poured into a separatory funnel containing 10% aqueous $NH_4OH$ and ethyl acetate. The organic layer was washed twice more with dilute $NH_4OH$ and once each with water and brine and dried over $Na_2SO_4$. Filtration and evaporation of the solvent in vacuo left a viscous oil which was further purified by column chromatography (4% ethyl acetate/hexane) to give 53 mg (20% yield) of **3** as a colorless oil: $R_f$ 0.50 (4% ethyl acetate/hexane); $^1$H NMR ($CDCl_3$) $\delta$ 7.56–7.55 (d, 1H, $J$ = 1.43 Hz), 7.45–7.42 (dd, 1H, $J$ = 1.44, 7.98 Hz), 7.21–7.19 (d, 1H, $J$ = 7.98 Hz), 4.53 (s, 2H), 3.41 (s, 3H), 1.48–0.84 (m, 27H); LRMS for $C_{26}H_{50}O_2SiSn$ *m/e* 542 ($M^+$).

**5-(Tributylstannyl)-1-(methoxymethyl)phenyl 2-Trifluoromethanesulfonate (4).** Into a 50-mL round-bottomed flask was placed 53 mg (0.098 mmol) of the silyl ether and 10 mL of THF. The solution was cooled to 0 °C under argon. Tetrabutylammonium fluoride (TBAF; 0.10 mL, 0.10 mmol) was added via syringe. The reaction mixture was allowed to stir at 0 °C until TLC analysis showed complete consumption of the starting material (about 20 min). The solvent was removed under reduced pressure, leaving a viscous pale-yellow oil. The crude phenol was dissolved in 10 mL of $CH_2Cl_2$ and slowly cooled to −78 °C under argon. Sodium hydride (80% oil dispersion; 3.8 mg, 0.13 mmol) and *N*-phenyltrifluoromethanesulfonimide ($PhNTf_2$; 39.0 mg, 0.10 mmol) were added to the reaction mixture. The reaction mixture was stirred at −78 °C under argon for 1 h and then warmed to room temperature. TLC analysis showed almost complete consumption of the starting material. The reaction mixture was poured into a separatory funnel containing water and ethyl acetate. The organic layer was washed with water and brine and dried over $Na_2SO_4$. Filtration and evaporation of the solvent in vacuo left an oil which was further purified by column chromatography (12% ethyl acetate/hexane) to give 46 mg (84% both steps) of **4** as a viscous oil: $R_f$ 0.50 (12% ethyl acetate/hexane); $^1$H NMR ($CDCl_3$) $\delta$ 7.56–7.55 (d, 1H, $J$ = 1.43 Hz), 7.45–7.42 (dd, 1H, $J$ = 1.44, 7.98 Hz), 7.21–7.19 (d, 1H, $J$ = 7.98 Hz), 4.53 (s, 2H), 3.41 (s, 3H), 1.55–1.45 (m, 6H), 1.34–1.23 (m, 6H), 1.08–1.02 (m, 6H), 0.89–0.84 (t, 9H, $J$ = 7.25 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 143.78, 138.37, 137.69, 137.48, 130.20, 120.56, 69.07, 58.40, 28.76, 27.09, 13.35, 9.46; LRMS for $C_{21}H_{35}F_3O_4SSn$ *m/e* 560 ($M^+$).

**1,4-Bis(trimethylstannyl)benzene (12).** This compound was prepared according to a literature procedure.[12] From 2.49 g (10.5 mmol) of 1,4-dibromobenzene, 2.13 g (50% yield) of the product was obtained as a crystalline solid: mp 79–80 °C; $R_f$ 0.67 (4% ethyl acetate/hexane); IR (KBr) 3032, 2985, 2914, 1637, 1460, 1369, 1186, 1016, 767 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.46 (s, 4H), 0.35–0.16 (m, 9H, $J_{Sn-H}$ = 26.97 Hz, $J'_{Sn-H}$ = 1.23 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 142.56, 135.83, −10.04; LRMS $C_{12}H_{22}Sn_2$ *m/e* (%) 404 ($M^+$, 2), 389 ($M^+ - CH_3$, 100), 359 ($M^+ - 3CH_3$, 14), 327 ($M^+ - 5CH_3$, 11). Anal. Calcd for $C_{12}H_{22}Sn_2$: C, 35.70; H, 5.49. Found: C, 35.89; H, 5.39.

**2-Hexyl-1,4-hydroquinone (10a).** This compound was prepared according to a literature procedure.[13] The hydroquinone was obtained from the reaction of 1-hexene with $BH_3$–THF, followed by reductive alkylation with 1,4-benzoquinone, 48% yield (two steps): mp 79–80 °C; $R_f$ 0.44 (35% ethyl acetate/hexane); IR (KBr) 3284, 2928, 2856, 1616, 1520, 1460, 1375, 1195, 862, 696 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 6.64–6.59 (m, 2H), 6.54–6.50 (dd, 1H, $J$ = 3.00, 8.43 Hz), 4.39–4.34 (s, 2H), 2.54–2.49 (t, 2H, $J$ = 7.76 Hz), 1.58–1.27 (m, 8H), 0.88–0.84 (t, 3H, $J$ = 6.66 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 149.56, 147.63, 130.29, 116.97, 116.19, 113.41, 32.90, 31.17, 30.96, 30.20, 23.61, 14.29; LRMS for $C_{12}H_{18}O_2$ *m/e* (%) 194 ($M^+$, 84), 123 ($M^+ - 71$, 100). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.22; H, 9.32.

**2-Octyl-1,4-hydroquinone (10b).** This compound was prepared according to a literature procedure.[13] The hydroquinone was obtained from the reaction of 1-octene with $BH_3$–THF, followed by reductive alkylation with 1,4-benzoquinone, 51% yield (two steps): mp 95–96 °C; $R_f$ 0.58 (50% ethyl acetate/hexane); IR (KBr) 3267, 2920, 2850, 1612, 1462, 1381, 1197, 723 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 6.66–6.62 (m, 2H), 6.57–6.53 (dd, 1H, $J$ = 3.00, 8.43 Hz), 4.37 (s, 1H), 4.34 (s, 1H), 2.57–2.51 (t, 2H, $J$ = 7.74 Hz), 1.58–1.27 (m, 12H), 0.90–0.86 (t, 3H, $J$ = 6.75 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 149.57, 147.64, 130.23, 116.94, 116.15, 113.37, 31.68, 29.82, 29.46, 29.28, 29.04, 22.42, 13.82; LRMS for $C_{14}H_{22}O_2$ *m/e* (%) 222 ($M^+$, 40), 123 ($M^+ - 99$, 100). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.52; H, 10.01.

**2-Dodecyl-1,4-hydroquinone (10c).** This compound was prepared according to a literature procedure.[13] The hydroquinone was obtained from the reaction of 1-dodecene with $BH_3$–THF, followed by reductive alkylation with 1,4-benzoquinone, 54% yield (two steps): mp 108–109 °C; $R_f$ 0.64 (50% ethyl acetate/hexane); IR (KBr) 3267, 2920, 2849, 1626, 1462, 1381, 1201, 723 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 6.66–6.62 (m, 2H), 6.59–6.56 (dd, 1H, $J$ = 2.91, 8.34 Hz), 4.35–4.32 (s, 2H), 2.56–2.51 (t, 2H, $J$ = 7.76 Hz), 1.61–1.26 (m, 20H), 0.90–0.86 (t, 3H, $J$ = 5.87 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 151.39, 149.49, 131.73, 117.87, 116.91, 114.11, 32.99, 31.16, 30.97, 30.69, 30.60, 30.51, 30.39, 23.61, 14.28; LRMS for $C_{18}H_{30}O_2$ *m/e* (%) 278 ($M^+$, 100), 123 (75), 91 (32), 57 (16). Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.40; H, 10.93.

**2-[(Ethoxycarbonyl)decyl]-1,4-hydroquinone (10d).** This compound was prepared according to a literature procedure.[13] The hydroquinone was obtained from the reaction of ethyl undecylenate with $BH_3$–THF, followed by reductive alkylation with 1,4-benzoquinone in diethyl ether. The product was

obtained as a tan solid upon standing at 0 °C overnight (62% yield in two steps): mp 56–58 °C; $R_f$ 0.59 (50% ethyl acetate/hexane); $^1$H NMR ($CDCl_3$) $\delta$ 6.63–6.60 (m, 2H), 6.53–6.49 (dd, 1H, $J$ = 2.94, 8.49 Hz), 5.69 (br s, 1H), 5.32 (br s, 1H), 4.15–4.08 (q, 2H, $J$ = 7.14 Hz), 2.53–2.47 (t, 2H, $J$ = 7.71 Hz), 2.30–2.25 (t, 2H, $J$ = 7.50 Hz), 1.61–1.20 (m, 19H); $^{13}$C NMR ($CDCl_3$) $\delta$ 175.23, 149.64, 147.62, 130.32, 116.97, 116.14, 113.34, 60.46, 34.23, 29.74, 29.31, 29.03, 28.93, 28.83, 28.74, 28.69, 24.63, 13.87; LRMS for $C_{19}H_{30}O_4$ *m/e* (%) 322 ($M^+$, 28), 276 ($M^+$ – 46, 68), 123 ($M^+$ – 199, 100). Anal. Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38. Found: C, 70.22; H, 9.47.

**General Procedure for Conversion to Ditriflate: 2-Octylphenyl 1,4-Bis(trifluoromethanesulfonate) (11b).** Into a 100-mL 3 N round-bottomed flask was placed 0.24 g (7.93 mmol) of sodium hydride (80% oil dispersion) and 15 mL of dry THF (or $Et_2O$) under argon. The flask was cooled to 0 °C, and a solution of 0.80 g (3.60 mmol) of **10b** in 20 mL of THF (or $Et_2O$) was transferred via cannula to the NaH suspension, giving a bright-blue color. The reaction mixture was stirred at 0 °C under argon for 5 min before a solution of 2.73 g (7.57 mmol) of *N*-phenyltrifluoromethanesulfonimide ($PhNTf_2$) in 30 mL of THF (or $Et_2O$) was added slowly via cannula to the flask. The reaction mixture was kept at 0 °C for 1 h and then stirred at room temperature for 1 day. The reaction mixture was poured into a separatory funnel containing water and ethyl acetate. The product was extracted with ethyl acetate, and the organic layers were combined, washed sequentially with water and brine, and dried over $Na_2SO_4$. Filtration and evaporation of the solvent in vacuo left a yellow oil. The crude product was purified by column chromatography (12% ethyl acetate/hexane) to afford 1.55 g (89% yield) of **11b** as a viscous oil: $R_f$ 0.54 (12% ethyl acetate/hexane); IR (neat) 2931, 2860, 1620, 1585, 1485, 1377, 1356, 1136, 1350, 1120, 720, 839, 696 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.34–7.31 (d, 1H, $J$ = 8.94 Hz), 7.23–7.22 (d, 1H, $J$ = 2.97 Hz), 7.19–7.15 (dd, 1H, $J$ = 3.03, 8.94 Hz), 2.73–2.68 (t, 2H, $J$ = 7.88 Hz), 1.63–1.24 (m, 12H), 0.88–0.83 (t, 3H, $J$ = 6.75 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 148.51, 147.03, 139.00, 124.05 123.36, 120.61, 125.27, 121.01, 116.73, 112.47 (q, $J_{C-F}$ = 1280.5 Hz, $CF_3$), 125.10, 120.84, 116.57, 112.31 (q, $J'_{C-F}$ = 1278.7 Hz, $CF_3'$), 31.56, 29.83, 29.30, 28.97, 28.89, 22.38, 13.77; LRMS for $C_{16}H_{20}O_6F_6S_2$ *m/e* (%) 486 ($M^+$, 50), 255 (100), 123 (14), 69 ($CF_3^+$, 53), 57 ($C_4H_9^+$, 80). Anal. Calcd for $C_{16}H_{20}O_6F_6S_2$: C, 39.50; H, 4.14. Found: C, 39.62; H, 4.18.

**2-Hexylphenyl 1,4-Bis(trifluoromethanesulfonate) (11a).** The ditriflate was prepared from the corresponding hydroquinone to give the product (98% yield) as a pale-yellow oil: $R_f$ 0.57 (12% ethyl acetate/hexane); IR (neat) 2862, 1620, 1585, 1485, 1215, 1140, 1350, 1120, 839, 696 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.34–7.31 (d, 1H, $J$ = 8.94 Hz), 7.23–7.22 (d, 1H, $J$ = 2.97 Hz), 7.19–7.15 (dd, 1H, $J$ = 3.00, 8.97 Hz), 2.73–2.68 (t, 2H, $J$ = 7.88 Hz), 1.64–1.26 (m, 8H), 0.89–0.84 (t, 3H, $J$ = 6.98 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 148.51, 147.02, 138.98, 124.05, 123.36, 120.61, 125.27, 120.99, 116.73, 112.47 (q, $J_{C-F}$ = 1279.7 Hz, $CF_3$), 125.08, 120.82, 116.57, 112.31 (q, $J'_{C-F}$ = 1277.4 Hz, $CF_3'$), 31.20, 29.83, 29.26, 28.61, 22.22, 13.66; LRMS for $C_{14}H_{16}O_6F_6S_2$ *m/e* (%) 458 ($M^+$, 35), 255 (100), 123 (18), 69 ($CF_3^+$, 81), 57 ($C_4H_9^+$, 28). Anal. Calcd for $C_{14}H_{16}O_6F_6S_2$: C, 36.68; H, 3.52. Found: C, 36.60; H, 3.50.

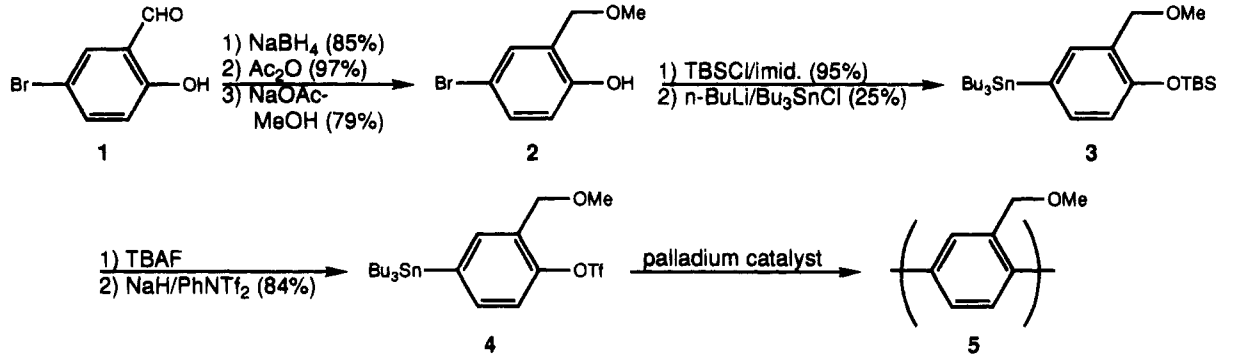
**2-Dodecylphenyl 1,4-Bis(trifluoromethanesulfonate) (11c).** The ditriflate was prepared from the corresponding hydroquinone. After column chromatography (12% ethyl acetate/hexane), 4.46 g (85% yield) of the product was isolated as a white solid upon storing at 0 °C: mp 27.0–27.5 °C; $R_f$ 0.59 (12% ethyl acetate/hexane); IR (KBr) 2928, 1620, 1585, 1356, 1219, 1140, 1350, 1120, 839, 723, 623 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.37–7.34 (d, 1H, $J$ = 8.97 Hz), 7.26–7.25 (d, 1H, $J$ = 3.09 Hz), 7.22–7.18 (dd, 1H, $J$ = 2.96, 9.02 Hz), 2.76–2.70 (t, 2H, $J$ = 7.86 Hz), 1.64–1.27 (m, 20H), 0.90–0.86 (t, 3H, $J$ = 6.66 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 148.59, 147.07, 139.03, 124.07, 123.37, 120.61, 125.32, 121.05, 116.78, 112.52 (q, $J_{C-F}$ = 1280.8 Hz, $CF_3$), 125.14, 120.87, 116.61, 112.35 (q, $J'_{C-F}$ = 1278.2 Hz, $CF_3'$), 31.74, 29.86, 29.44, 29.38, 29.33, 29.27, 29.15, 29.05, 28.98, 22.47, 13.84; LRMS for $C_{20}H_{28}O_6F_6S_2$ *m/e* (%) 542 ($M^+$, 78), 255 (83), 123 (32), 69 ($CF_3^+$, 35), 57 ($C_4H_9^+$, 100). Anal. Calcd for $C_{20}H_{28}O_6F_6S_2$: C, 44.27; H, 5.20. Found: C, 44.26; H, 5.21.

**2-[(Ethoxycarbonyl)decyl]phenyl 1,4-Bis(trifluoromethanesulfonate) (11d).** Into a 100-mL round-bottomed flask was placed 1.60 g (4.96 mmol) of the corresponding hydroquinone in 10 mL of THF. Then the solution was cooled to −65 °C under nitrogen, and sodium hydride (NaH; 305 mg, 10.1 mmol, 80% oil dispersion) was added in two portions. The first portion of NaH was quickly added and the reaction was stirred under nitrogen for 5 min before the second portion of NaH was added and stirred for another 5 min. As the flask was warmed to 0 °C, the color slowly changed to blue–green. The dianion was further stirred for 10 min before a solution of $PhNTf_2$ (3.94 g, 10.9 mmol) in 10 mL of THF was transferred to the dianion solution via cannula. The light-tan reaction mixture was kept at 0 °C for 1 h and then stirred at room temperature for 1 day. The reaction mixture was poured into a separatory funnel containing water and ethyl acetate. The organic layer was washed with water and brine and dried over $Na_2SO_4$. Filtration and evaporation of the solvent in vacuo left a viscous oil, which was purified by column chromatography (toluene) to afford 1.52 g (52% yield) of a pale-yellow viscous oil: $R_f$ 0.44 (1% ethyl acetate/toluene); IR (neat) 2931, 1736, 1427, 1215, 1141, 696, 623 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.37–7.34 (d, 1H, $J$ = 9.03 Hz), 7.26–7.25 (d, 1H, $J$ = 2.88 Hz), 7.22–7.18 (dd, 1H, $J$ = 2.90, 8.96 Hz), 4.16–4.09 (q, 2H, $J$ = 7.14 Hz), 2.75–2.70 (t, 2H, $J$ = 7.86 Hz), 2.31–2.26 (t, 2H, $J$ = 7.53 Hz), 1.64–1.23 (m, 19H); $^{13}$C NMR ($CDCl_3$) $\delta$ 174.26, 148.50, 147.02, 138.94, 124.04, 123.36, 120.61, 125.27, 120.99, 116.73, 112.45 (q, $J_{C-F}$ = 1284.0 Hz, $CF_3$), 125.08, 120.82, 116.55, 112.29 (q, $J'_{C-F}$ = 1279.5 Hz, $CF_3'$), 60.04, 34.20, 29.85, 29.31, 29.14, 29.00, 28.91, 24.75, 13.99; LRMS for $C_{21}H_{28}O_6F_6S_2$ *m/e* (%) 586 ($M^+$, 6), 453 (29), 407 (33), 123 (31). Anal. Calcd for $C_{21}H_{28}O_6F_6S_2$: C, 42.99; H, 4.81. Found: C, 43.07; H, 4.79.

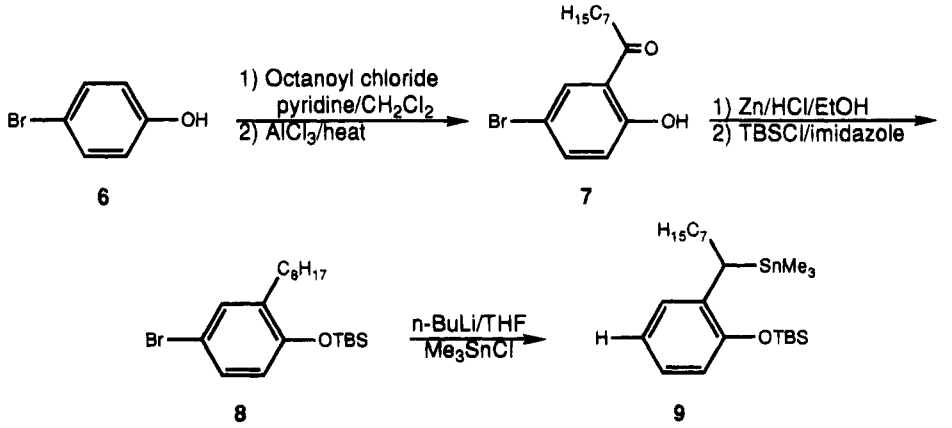
**Polymerizations between Diorganostannanes and *n*-Alkylated Aryl Ditriflates: Polymerization (Slow Addition–High Dilution Method).** A typical polymerization procedure is exemplified by that for polymer **13b**. Into a 100-mL 3 N round-bottomed flask, equipped with a 50-mL addition funnel, reflux condenser, and thermometer, were added the ditriflate **11b** (269 mg, 0.554 mmol), lithium chloride (8.00 equiv), $Pd(PPh_3)_4$ (32 mg, 0.027 mmol), and 10 mL of dry 1,4-dioxane under argon. The addition funnel was charged with 1,4-bis(trimethylstannyl)benzene (**12**; 268 mg, 0.664 mmol) dissolved in 35 mL of dioxane. The stannane solution was slowly added dropwise to the stirred slurry over a period of 1 day at a temperature of 94–98 °C. The color slowly changed from bright-yellow to white. The reaction mixture was heated to reflux until TLC analysis showed complete consumption of the starting material (about 4 days). When exposed to UV–visible light, the TLC of the reaction mixture exhibited a strong fluorescence, indicating the formation of highly conjugated aromatics. The reaction mixture was cooled to room temperature and filtered through a pad of Celite. The reaction mixture was poured into a separatory funnel containing water and dichloromethane. The organic layer was further washed with 5 M HCl (2 × 10 mL) and brine and dried over $Na_2SO_4$. Filtration and precipitation into acetone and collection by a centrifuge afforded a light-yellow solid which was dried in vacuo. The IR and $^1$H NMR data for polymers **13a** and **13c** are similar to those of **13b**: IR (KBr) 3028 ($C_{ar}$–H stretch), 2924, 2854 ($C_{alk}$–H stretch), 1599 ($C_{ar}$–$C_{ar}$ stretch), 1477 ($CH_2$ scissor), 1379 (sym. $CH_3$ bend), 1118 (C–H in-plane bend), 1004 ($C_{ar}$–H in-plane vibration), 810 ($C_{ar}$–H out-of-plane deformation for para-substituted aromatics), 763 ($C_{ar}$–H out-of-plane deformation for monosubstituted aromatics), 696 cm$^{-1}$ (ring puckering deformation for monosubstituted phenyl rings). $^1$H NMR ($CDCl_3$) $\delta$ 7.75–7.33 (br m), 2.70–0.82 (br m).

Polymer **13d** was synthesized similarly as above. Trace amounts of the starting material were removed by column chromatography (toluene). The product was collected with 5% methanol in chloroform and dried in vacuo to give a light brown–yellow thin film: IR (KBr) 2926, 2852 ($C_{alk}$–H stretch), 1736 (C=O stretch), 1475 ($CH_2$ scissor), 1384 (sym. $CH_3$ bend), 1251–1118 (C–O stretch and C–H in-plane bend), 810 ($C_{ar}$–H out-of-plane deformation for para-substituted aromatics), 763 ($C_{ar}$–H out-of-plane deformation for monosubstituted aromat-

**Scheme 2**




**Scheme 3**




ics), 696 $cm^{-1}$ (ring puckering deformation for monosubstituted phenyl rings); $^1H$ NMR ($CDCl_3$) $\delta$ 7.78–7.37 (br m), 4.15–4.08 (br q), 2.73–2.42 (br m), 2.26 (br t), 1.59–1.24 (br m).

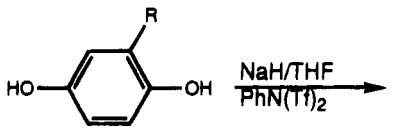
**Polymerization (High Concentration Method).** A typical polymerization procedure is given for polymer **13c**. Into a 25-mL 2 N round-bottomed flask equipped with a reflux condenser and thermometer were added the dodecyl ditriflate **11c** (171 mg, 0.315 mmol), 1,4-bis(trimethylstannyl)benzene (**12**; 153 mg, 0.378 mmol), LiCl (108 mg, 2.52 mmol), $Pd(PPh_3)_4$ (7.3 mg, 0.006 mmol), and 1,4-dioxane (4 mL). The bright-yellow mixture was heated to reflux at 90 °C under argon until TLC analysis showed almost complete consumption of the starting material (about 3 days). The reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite. Filtration and evaporation of the solvent gave a tan solid. The solid was precipitated into methanol, centrifuged, and dried in vacuo to give **13c** as a bronze-tinted thin film, the IR and $^1H$ NMR data of which were the same employing the slow addition method.

The final coupling products were found to be soluble in relatively nonpolar organic solvents such as tetrahydrofuran, chloroform, toluene, and dichloromethane but were insoluble in polar solvents such as acetonitrile and methanol. The $^1H$ NMR spectra displayed two broad sets of lines, an aromatic set from 7.9–7.3 ppm and an aliphatic set from 2.7–0.8 ppm. The aromatic hydrogens were shifted further downfield than those of the monomers (7.4–7.2 ppm). This shift is interpreted in terms of new C–C bonds between the benzene rings. The FT-IR absorption peaks in the 2000–1600 $cm^{-1}$ region indicate the structure of 1,2,4-trisubstituted benzene,[14] implying an *o*- or *p*-phenylene configuration. A number of bands from 900 to 700 $cm^{-1}$ are associated with aromatic C–H out-of-plane bending modes of di- and trisubstituted benzenes.[14] The UV–visible spectra showed a very broad absorption with $\lambda_{max}$ at ca. 310 nm. It is well-known that the absorption band shifts toward higher wavelength when the length of the poly(phenylene) chain increases. Differential scanning calorimetry displayed a relatively low glass transition temperature (second-order transition) as the temperature increased from −25 to +180 °C (scan rate = 10 °C/min). This was interpreted in terms of the existence of the long alkyl chain in the polymer. For polymer **13a**, the $T_g$ showed at −4.32 °C, whereas melting started at about 115.9 °C. For polymer **13d**, the $T_g$ was found to be at 47.9 °C and the melting process started at about 136.7 °C.

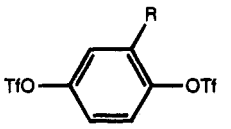
## Results and Discussion

Our initial strategy was based on the preparation of a monomer bearing stannyl and triflate groups para to each other and another substituent as alkyl which should yield alkyl-substituted poly(phenylene) with palladium catalysis. The presence of a side chain increases the solubility of the growing poly(phenylene) during palladium catalysis.[15] Monomer **4** was prepared according to Scheme 2. During the course of the polymerization of **4**, a dark-brown material precipitated out of the solution, and after workup a material was obtained that was insoluble in common solvents. This initial attempt encouraged us to pursue other monomers bearing long alkyl side chains. Acylation of 2-bromophenol with octanoyl chloride followed by Fries rearrangement afforded **7** (Scheme 3). Clemmenson reduction and silylation of **7** afforded **8**. The reduction of the carbonyl group did not affect the bromo substituent. Lithiation of **8** followed by stannylation gave none of the desired monomer. Instead, the stannyl group was found on the benzylic position of the side chain. Performing the reaction at lower temperatures had no effect on the stannylation. Aryl bromides have been transformed to arylstannanes through a palladium-catalyzed reaction with hexaalkylditin.[16] Treatment of **8** with hexamethylditin in the presence of a palladium catalyst afforded the product, however, in low yield (<10%). The failure to prepare a monomer bearing an alkyl chain with both the triflate and stannyl groups in high yield forced a change in our strategy. Our next move was to approach the polymerization through the palladium-

**Scheme 4**




**10 a** R=$(CH_2)_5CH_3$
**b** R=$(CH_2)_7CH_3$
**c** R=$(CH_2)_{11}CH_3$
**d** R=$(CH_2)_{10}COOC_2H_5$




**11 a** R=$(CH_2)_5CH_3$ (98%)
**b** R=$(CH_2)_7CH_3$ (89%)
**c** R=$(CH_2)_{11}CH_3$ (85%)
**d** R=$(CH_2)_{10}COOC_2H_5$ (52%)

**Table 1. GPC Results for Poly(*n*-alkylphenylene)s**

| oligomer | $\bar{M}_w$ | $\bar{M}_n$ | polydispersity | DP |
|---|---|---|---|---|
| **13a** | 3300 | 2000 | 1.67 | 8.5 |
| **13b** | 3300 | 2100 | 1.62 | 8.0 |
| **13c** | 4200 | 3200 | 1.31 | 10.1 |
| **13d** | 6400 | 3800 | 1.70 | 10.4 |
| **13b**[a] | 4500 | 2600 | 1.71 | 9.8 |
| **13c**[a] | 4700 | 3500 | 1.35 | 11.1 |
| **13d**[a] | 3800 | 3400 | 1.14 | 9.3 |

[a] Coupling reaction was performed in a minimum amount of 1,4-dioxane.

catalyzed reaction of two monomers, **11** and **12** (Schemes 4 and 5) which were easily prepared from 1,4-dibromobenzene[12] and benzoquinone,[13] respectively. This approach was discovered to yield the alkylpoly(phenylene)s in good yield (Scheme 5).

The molecular weights of the obtained oligomers were evaluated by SEC analysis calibrated with monodisperse polystyrene standards (MW = 580–22 000) in chloroform.[17] The calibration curve (log MW vs elution time) of the polystyrene standards displayed a linear relationship. A summary of the $\bar{M}_w$ and $\bar{M}_n$ is listed in Table 1. The SEC diagram displayed a near-Gaussian molecular weight distribution curve with polydispersity from 1.3 to 1.7 and degree of polymerization from 8.0 to 11.1. The elemental analyses obtained for the alkylpoly(phenylene)s were close to the theoretical values. For example, for polymer **13d**, the theoretical values of 82.37 (C) and 8.85 (H) compared to the obtained values of 78.82 (C) and 8.62 (H).

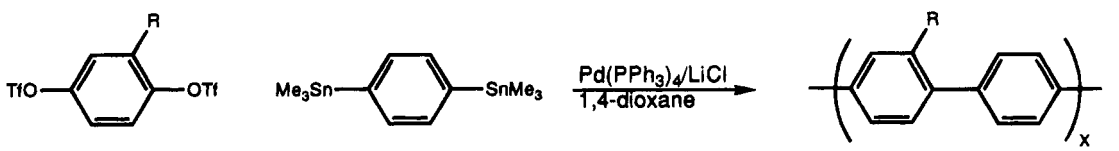
We varied several reaction parameters to maximize the molecular weights of the alkylpoly(phenylene)s: palladium catalyst, solvent, and concentration of the reaction. Several palladium catalysts were surveyed in the coupling reaction and included $Pd(PPh_3)_4$, $Pd_2(dba)_3$/$AsPh_3$, $PdCl_2(P\text{-}o\text{-}tolyl_3)_2$, and $Pd_2(dba)_3$. For the coupling of aryl ditriflates with aryldiorganostannanes, both $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ are efficient catalysts, although faster rates were obtained with the latter one. Performing the reaction in the presence of the $PdCl_2(PPh_3)_2$ gave rise to some transfer of the alkyl groups (methyl) from tin.[18] The best results were obtained using $Pd(PPh_3)_4$ as catalyst in the presence of excess LiCl. During the coupling process there was good evidence of deactivation of the catalyst, with precipitation of palladium black indicating decomposition of the catalyst.[9] Usually a 2–5 mol % palladium catalyst was used; increased amounts of catalyst, however, did not show improvement. Coupling in the presence of DMF accelerated the reaction but also caused a faster decomposition of the palladium catalyst. Using THF as the solvent resulted in the formation of substantial amounts of the cleavage product from the ditriflate monomer, i.e., cleavage of the –OTf to –OH.[18] Dioxane was finally chosen as the solvent as it can moderately solubilize both the LiCl and the product.

The highest molecular weights were obtained employing a minimum amount of solvent. In all polymerizations, the monomer **11d** bearing the ethyl ester chain gave the highest molecular weight average. This could be interpreted as increased solubility of the growing oligomeric product. Changing the organostannane from $Me_3Sn$ to $Bu_3Sn$ resulted in a lower averaged molecular weight, which might be due to the less reactive nature of the $Bu_3Sn$ group. Examination of the oligomers by $^1$H-NMR revealed the absence of the trimethylstannyl group which can be readily seen with distannane **12**. The IR spectra could not be employed due to overlapping bands of any triflate with aromatic bands; $^{13}$C analysis also could not be used as the triflate group is difficult to observe even with pure monomer, such as **11b**. Analysis by $^{31}$P-NMR, however, revealed the presence of phosphorus, possibly as diphenylphosphinyl oxide. It has recently been shown that phosphine ligands normally employed in palladium catalysis, for example, $Pd(PPh_3)_4$, undergo facile aryl–aryl exchange.[19] This exchange process has been shown to limit the catalytic efficiency of palladium, leading to a decrease in degree of polymerization.[20] Recently, a modified catalytic cycle has been proposed that takes into account the aryl scrambling that is sometimes seen in biaryl couplings.[21] A possible chain termination sequence is the formation of diarylphosphinyl adducts which have been observed in other biphenyl couplings.[19,20]

## Conclusions

In summary, our results show that the palladium-catalyzed reaction between a distannane and a ditriflate is a route to alkyl-substituted poly(phenylene)s of regular structure. This synthesis provides access to a new class of processable rigid-rod polymers, and our

**Scheme 5**




**11 a** R=$(CH_2)_5CH_3$
**b** R=$(CH_2)_7CH_3$
**c** R=$(CH_2)_{11}CH_3$
**d** R=$(CH_2)_{10}COOC_2H_5$

**12**

**13 a** R=$(CH_2)_5CH_3$
**b** R=$(CH_2)_7CH_3$
**c** R=$(CH_2)_{11}CH_3$
**d** R=$(CH_2)_{10}COOC_2H_5$

approach is easy in terms of access to monomers. The triflate monomer can be obtained from the corresponding hydroquinone. Other advantages include mild reaction conditions, functional group tolerance, and higher purity of materials. Since the alkyl-substituted poly(phenylene)s show excellent solubility in relatively nonpolar common organic solvents, a series of classical characterization techniques can be applied to analyze the structures and properties of these polymers. Future work will focus on employing phosphine-free catalytic systems in the coupling of ditriflates with distannanes.

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