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NOVEL POLYPHENYLENES CONTAINING ORTHOGONAL PHENYL AND BENZO-CROWN-ETHER GROUPS

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This paper is dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

The synthesis of a new class of polyphenylenes substituted with a large number of phenyl and benzo-crown-ether groups has been described. The polymers, prepared by Suzuki cross-coupling reaction between polyphenylated dibromide and benzene-1,4-diboronic acid, exhibit outstanding solubility in common organic solvents such as THF and chloroform. Preliminary results on molecular weights and thermal analysis of one representative polymer are discussed.

Key Words: Polyphenylenes; Crown-ethers; Conducting polymers; Suzuki coupling; Solid polymer electrolytes; Ionic conductivity

INTRODUCTION

In recent years, polymers containing extended π-conjugation such as polyphenylenes have been attracting increased attention due to their applications

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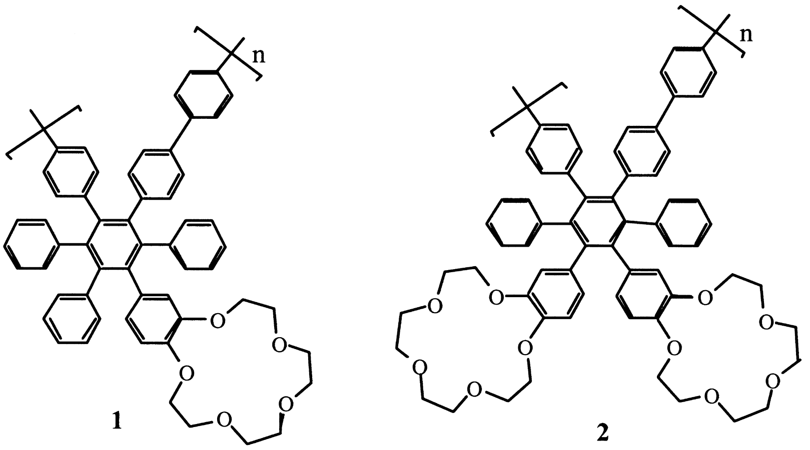
*Corresponding author. E-mail: mandal@iit.edu in the areas of electrically conducting polymers [1-4] and nonlinear optical materials [5-7]. Since unsubstituted polyphenylenes are insoluble in common organic solvents, new synthetic approaches to polyphenylenes that exhibit the combinations of desired properties, such as film-forming capabilities, toughness and thermal properties have been developed [8-10]. The most versatile approach involves Suzuki-type cross coupling reaction of a dihalide and a diboronic acid. This method allows incorporation of pendant aliphatic chains or functional groups (such as CO_2H and SO_3H), which render these polyphenylenes soluble in common organic solvents or aqueous media [8]. While investigating the synthesis and properties of novel polyphenylated derivatives of phthalocyanines [11], porphyrins [12] and carbazoles [13], we noted that these derivatives containing a large number of orthogonal phenyl rings exhibits outstanding solubility in common organic solvents such as THF and chloroform. Müllen *et al.* [14-16]. have reported a variety of polyphenylated benzene derivatives for obtaining planar graphite-like materials. Recently, we reported polyphenylene-based solid polymer electrolyte systems for lithium-ion batteries [17]. These polyphenylenes, which contain pendant oligo-ether chains, were prepared by an oxidative coupling method and displayed high ionic conductivities at room temperature. This observation encouraged us to pursue a new class of polyphenylenes containing crown-ether groups. Polymeric materials containing crown-ethers exhibit excellent ion-sensing and ion-transport properties [18-20]. In this article, we describe the synthesis of two new polyphenylenes **1** and **2** (Figure 1), which contain several orthogonal phenyl and benzo-crown-ether groups prepared by Suzuki coupling.



1

2

Figure 1. Structures of polyphenylenes.

EXPERIMENTAL

4-Iodo-benzo-15-crown-5 (3)

To a 500 mL, round-bottomed flask wrapped with aluminum foil was added 10 g (37.4 mmol) of benzo-15-crown-5, 9.48 g (37.4 mmol) of iodine, and 11.64 g (37.4 mmol) of silver sulfate in 200 mL of methylene chloride at room temperature. The mixture was stirred for 2 days. The solvent was evaporated under reduced pressure. The solid residue was treated with 100 mL of 30% ammonium hydroxide solution to remove the silver salt. After filtration, the solid was washed with water, dried at room temperature and subjected to Soxhlet extraction with n-hexane overnight. The hexane solution, on cooling, gave white crystals of the pure compound. A second crop was obtained by evaporating the filtrate, and recrystallizing the residue from an ether-hexane mixture. Yield: 9.14 g (62%), m.p., 70°-72°C. FTIR (KBr pellet, cm^{-1}): 3077, 2940, 2864, 1258, 1048, 1140. ^1H NMR ($CDCl_3$, ppm) δ: 7.2-6.9 (3H), 4.10 (4H), 3.90 (4H), 3.75 (8H). MS: m/e, 394 (M^+). Anal. Calcd. for $C_{14}H_{19}O_5I$: C, 42.66; H, 4.86. Found: C, 42.43; H, 4.68.

4-(Phenylacetylene) Benzo-15-crown-5 (4)

A three-neck flask, equipped with a reflux condenser, was charged with 2.3 g (5.8 mmol) of **3**, 0.72 g (7 mmol) of phenylacetylene, 30 mL of diethylamine, 17.12 mg of CuI and 84.2 mg of bis(triphenylphosphine)palladium dichloride. The reaction mixture was stirred at 45°C for 8 hours under nitrogen. The solvent was removed in a rotary evaporator. The residue was purified by column chromatography on silica gel, using ethyl acetate as eluent at the beginning, then gradual addition of THF. Yield: 1.52 g (71%), pale yellow solid, m.p., 101°-104°C. FTIR (KBr pellet, cm^{-1}): 2205, 2935, 2865, 1258, 1051, 1129. ^1HNMR ($CDCl_3$, ppm) δ: 7.6-6.8 (8H), 4.2-4.1 (4H), 3.95-3.90 (4H), 3.80-3.75 (8H). MS: m/e, 368 (M^+). Anal. Calcd. for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57. Found: C, 71.49; H, 6.52.

Bis-(4-Benzo-15-crown-5)acetylene (5)

To a solution of **3** (6.22 g, 0.02 mol) in 160 mL diethylamine were added bis(triphenylphosphine)palladium dichloride (55.4 mg, 0.08 mmol) and copper(I) iodide (55.4 mg, 0.16 mmol). The reaction mixture was stirred under nitrogen at room temperature. Acetylene was bubbled into the solution at a very slow rate. The gas was switched on and off alternately about every 10 minutes to let the formed mono-crown-ether acetylene derivative further react with **3** to form the target compound. The progress of the reaction was monitored by tlc (about 3.5 hours required for compound **3** to disappear). The solution was filtered and the crude solid was purified by column chromatography on silica gel using THF as eluent. Yield: 2.47 g (56%), yellow solid, m.p., 154°-156°C. FTIR(KBr pellet, cm^{-1}): 2921, 2862, 1248, 1047, 1135. ^1H NMR ($CDCl_3$, ppm) δ: 7.12-7.02 (4H), 6.85-6.80 (2H), 4.18-4.13 (8H), 3.95-3.90 (8H), 3.80-3.75 (16H). Anal. Calcd. for $C_{30}H_{38}O_{10}$: C, 64.50; H, 6.86. Found: C, 64.45; H, 6.74.

3,4-Bis(4-Bromobenzene)-2,5-diphenylcyclopentadi-2,4-ene-1-one (6)

A solution of 5.89 g (28 mmol) diphenylacetone and 9.2 g (25 mmol) 4,4'-dibromobenzil in 120 mL of absolute ethanol was heated to boiling with stirring, then a solution of 1 g KOH in 30 mL of water was added, and the solution became dark-red. After refluxing for 4 hours, the reaction mixture was hot filtered, the solid was washed with cold ethanol to give a dark red powder. Yield: 11 g (82%), m.p., 239°-240°C. FTIR (KBr pellet, cm^{-1}): 1714, 549. ^1HNMR ($CDCl_3$, ppm) δ: 7.39-7.32 (4H), 7.32-7.23 (6H), 7.23-7.17 (4H), 6.84-6.78 (4H). MS: m/e, 542($M^{+\cdot}$). Anal. Calculated for $C_{29}H_{18}OBr_2$: C, 64.23; H, 3.35. Found: C, 63.99; H, 3.37.

1,2-Bis(4-Bromobenzene)-4-(4-benzo-15-crown-5)-3,5,6-triphenylbenzene (7)

0.70 g (1.92 mmol) of **4** and 1.04 g (1.92 mmol) of **6** were added into a Schlenk tube with 30 drops of cyclohexylbenzene (~0.5 g). The tube was degassed by a series of freeze-pump-thaw cycles, sealed, and placed in a thermoregulated oven at 230°C for 5 hours. The tube was cooled to room temperature, then broken (*caution: contents may be under pressure*). Hexane was added to precipitate the product, then filtered to give a pale gray product. Yield: 1.56 g (92%), m.p., 134°-137°C. FTIR: (KBr pellet, cm^{-1}): 3058, 3026, 2926, 2867, 1258, 1012, 1134. ^1HNMR ($CDCl_3$, ppm) δ: 7.30-6.20 (26H), 4.0-3.6 (16H). Anal. Calcd. for $C_{50}H_{42}O5Br_2$: C, 68.04; H, 4.80; Found: C, 67.93; H, 4.88.

1,2-Bis(4-Bromobenzene)-4,5-bis-(4-benzo-15-crown-5)-3,6-diphenylbenzene (8)

Following the procedure used for **7,** and using 0.84 g (1.5 mmol) of **5** and 0.81 g (1.5 mmol) of **6**, the title compound was obtained as a white solid. Yield: 1.59 g (quant), m.p., 206°-209°C. FTIR (KBr pellet cm^{-1}): 2923, 2862, 1258, 1067, 1133. ^1HNMR ($CDCl_3$, ppm) δ: 7.3-6.3 (24H), 4.0-3.6 (32H). Anal. Calcd. for $C_{58}H_{56}O_{10}Br_2$: C, 64.93; H, 5.26. Found: C, 64.68; H, 5.10.

Polyphenylenes 1 and 2

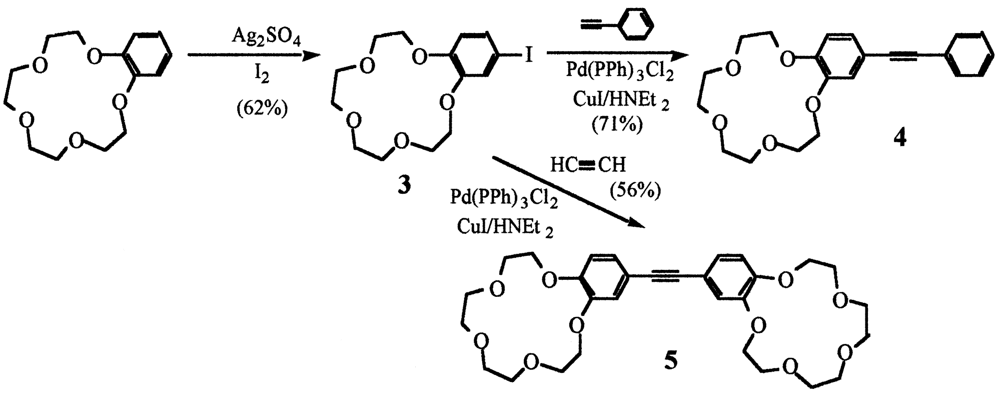
A 50 mL three-neck round-bottomed flask was charged with 0.88 g (1.0 mmol) of compound **7**, 0.17 g (1.0 mmol) of 1,4-benzenediboronic acid, 0.61 g (4 mmol) of CsF and 10 mL of DME and 15 mL of DMSO. Then 0.035 g $Pd(PPh_3)_4$ (0.03 mmol) was added. Under a nitrogen atmosphere, the reaction mixture was heated to ~100°C with stirring for 24 h. The solution was poured into hot water, filtered, extracted with methanol overnight in a Soxhlet extractor, and dried over P_2O_5 in a drying pistol at 80°C, to afford polymer **1** as a pale yellow solid in 66% yield. Following the above procedure, polymer **2** was obtained in 72% yield. Polymer **2**: FTIR (KBr pellet cm^{-1}): 3028, 2910, 2844, 1262. ^{1}HNMR ($CDCl_3$, ppm) δ: 7.48-6.33 (m), 3.56-4.22 (m). Anal. Calcd. for $C_{64}H_{62}O_{10}$: C, 77.55; H, 6.30. Found: C, 76.92; H, 6.38.

RESULTS AND DISCUSSION

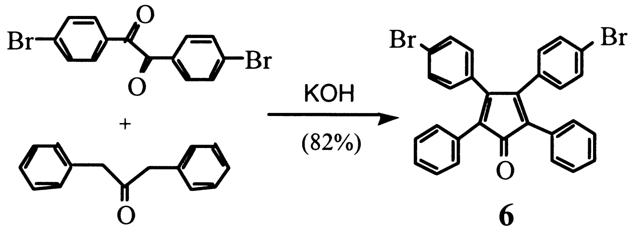
The synthetic sequence commenced with the preparation of two new crown-ethers containing diphenylacetylenes, **4** and **5** (Scheme 1). Compound **4** was obtained in 71% yield by cross-coupling of phenylacetylene and 4-iodo-benzo-15-crown-5 (**3**), which was prepared by silver sulfate-catalyzed iodination of commercially available benzo-15-crown-5.[21] Cross-coupling between two equivalents of **3** and acetylene, using $Pd(PPh)_3Cl_2$ and CuI as catalysts, provided the diphenylacetylene derivative, **5**, in 56% yield.

These diphenylacetylene derivatives were then reacted, in a sealed tube, with a reactive diene, dibromo tetracyclone (**6**, prepared by condensation of 4,4'-dibromobenzil and 1,3-diphenylacetone (Scheme 2)), to produce dibromo polyphenylated monomers, **7** and **8**, in near quantitative yields (Scheme 3) [11].

The polymerization reactions between the polyphenylated monomers and 1,4-benzene diboronic acid [22] were carried out under Suzuki conditions [23], to produce polymers **1** and **2** in high yields (Scheme 3). The polymers were completely soluble in chloroform and THF and form thin films when cast from solution. We attribute the improved solubility to the presence of both orthogonal phenyl rings and crown ether groups in the molecular structure [11-13]. To deter-



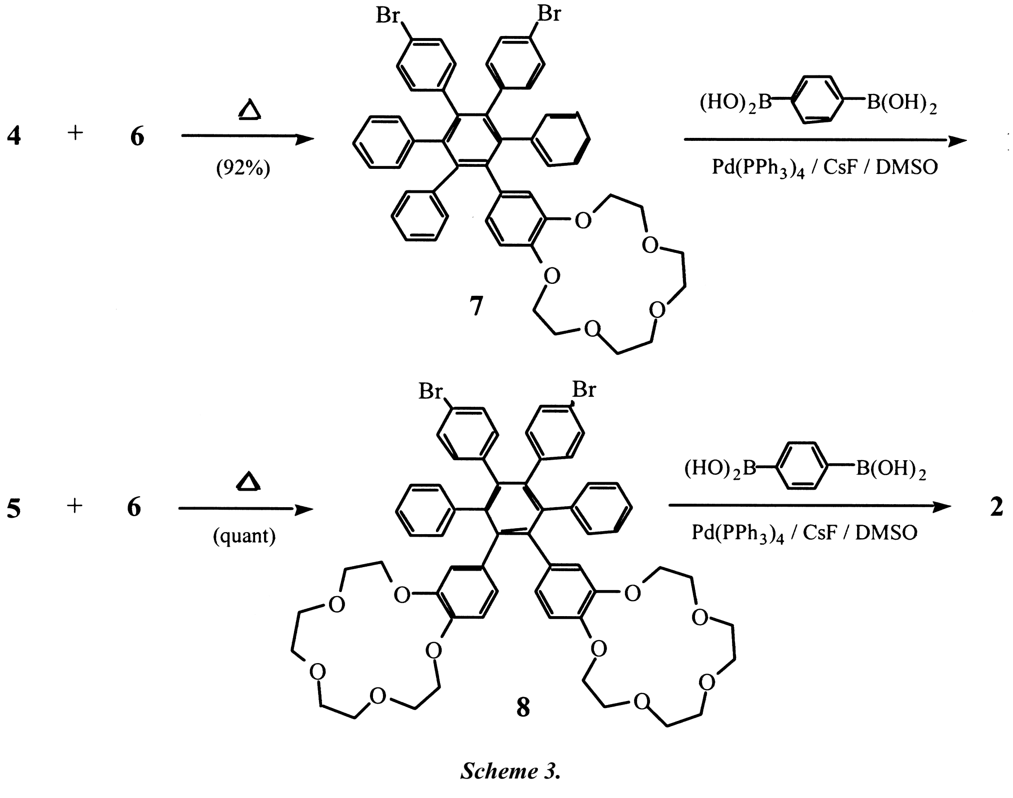
Scheme 1.



Scheme 2.

mine the properties of this class of polymers, we selected **2** as a representative example.

The molecular weights of polymer **2** have been determined using gel permeation chromatography (polystyrene as standard). Using a refractive index detector, **2** gave $M_w = 20{,}440$ and $M_n = 7{,}950$, a polydispersity index of 2.6, and a degree of polymerization of about 21. This value is comparatively lower than those of polyphenylenes prepared by the Suzuki coupling method [8]. Although it has been shown that polystyrene standard gives lower molecular weights (M_n and M_w) than light scattering analyses^{24}, those we obtained are very satisfactory in light of the



Scheme 3.

considerable steric bulk present in the polyphenylated benzene moiety that undergoes polymerization.

Polymer **2** showed complete stability up to 240°C and 10% weight loss did not occur until 435°C in a nitrogen atmosphere. The decomposition after 240°C is attributed to breakdown of the crown-ether groups. The glass transition temperature, T_g, of **2** was observed at 113°C.

Thus, we have prepared a new class of soluble polyphenylenes substituted with multiple phenyl and benzo-crown-ether groups. Experiments involving ion-transport properties, photochemical and chemical planarization studies are in progress and these results, along with properties of polymer **1**, will be presented in the future.

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