



Acetylenic Poly(aryl ether)s: Preparation of the S_NAr Monomer Bis(4-fluorophenyl)acetylene

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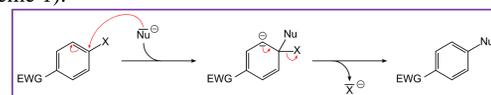


Background

Poly(aryl ether)s (PAEs) are important commercial polymers and are a member of the family of materials known as engineering thermoplastics. A sub-class of the PAEs are the poly(aryl ether ketones) (PAEKs), which are semi-crystalline, thermoplastic polymers, and have high mechanical strength at high temperatures, substantial chemical resistance, low moisture absorption, and good impact strength.^{1,3}

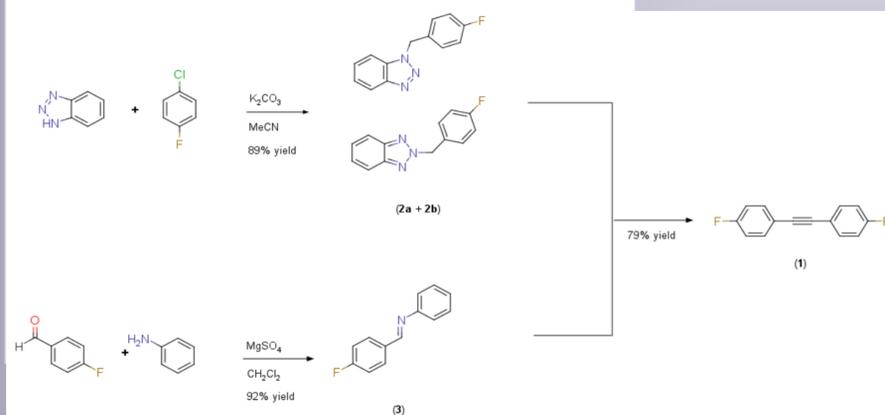
The most ordinarily used synthetic route to PAEs involves creating an ether linkage by nucleophilic aromatic substitution (S_NAr) and requires an electron-withdrawing group to activate the benzene rings. The attached electron-withdrawing group (EWG) is essential to activate the ring and allow the addition of nucleophile.

The addition of nucleophile to an activated benzene ring by an electron-withdrawing group (EWG) forms a resonance-stabilized carbanion and the halogen acts as a leaving group (Scheme 1).



Scheme 1: S_NAr reaction

For this research, a literature method was used to synthesize bis(4-fluorophenyl)acetylene (**1**) with the intent of using the ethynylene bond to activate the phenyl rings for S_NAr polymerization to form PAEs that have alternating alkyne and ether linkages. First, fluorobenzylbenzotriazole (**2**) was synthesized in 89% yield as a mixture of isomers (**2a** and **2b**), by refluxing a mixture of benzotriazole, 4-fluorobenzyl chloride, potassium carbonate, and acetonitrile. Then **2** was reacted with (E)-1-(4-fluorophenyl)-N-phenylmethanimine (**3**), which was prepared by adding a mixture of magnesium sulfate and dichloromethane to 4-fluorobenzaldehyde and aniline (Scheme 2). The formed bis(4-fluorophenyl)acetylene can be used to synthesize poly(oxy-1,4-phenyleneethynylene-1,4-phenylene) using the ethynylene bond to activate bond to activate the phenyl rings for S_NAr reaction (Scheme 3).



Scheme 2. Synthesis of bis(4-fluorophenyl)acetylene (**1**)

RESULTS

Overview - A monomer for the preparation of the acetylenic poly(aryl ether) (POPEP), bis(4-fluorophenyl)acetylene (**1**) was synthesized. The triple bond activates the phenyl rings for S_NAr reactions which can be used for polymerization. The monomer was characterized by ¹H NMR, ¹³C NMR, and APCI-MS and reacted with 2 equiv p-cresol in an attempt to model the polymerization reaction.

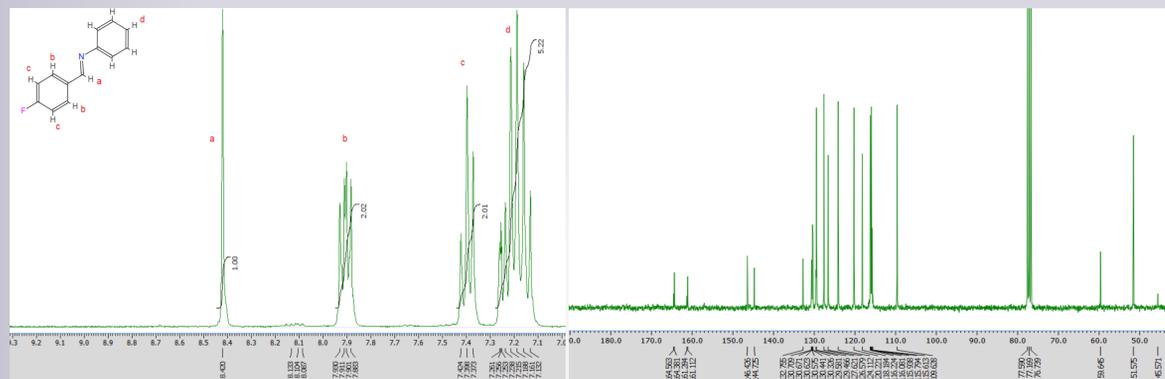


Figure 1: (E)-1-(4-Fluorophenyl)-N-phenylmethanimine (**3**) ¹H NMR in CDCl₃

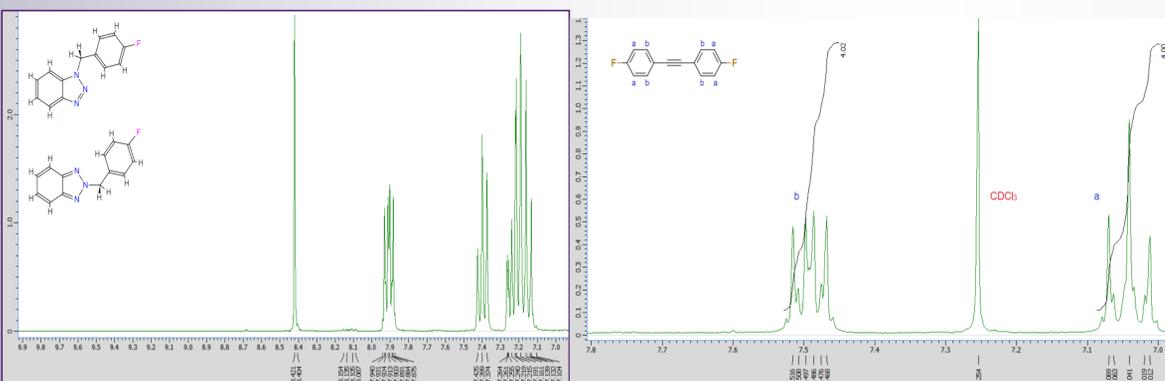
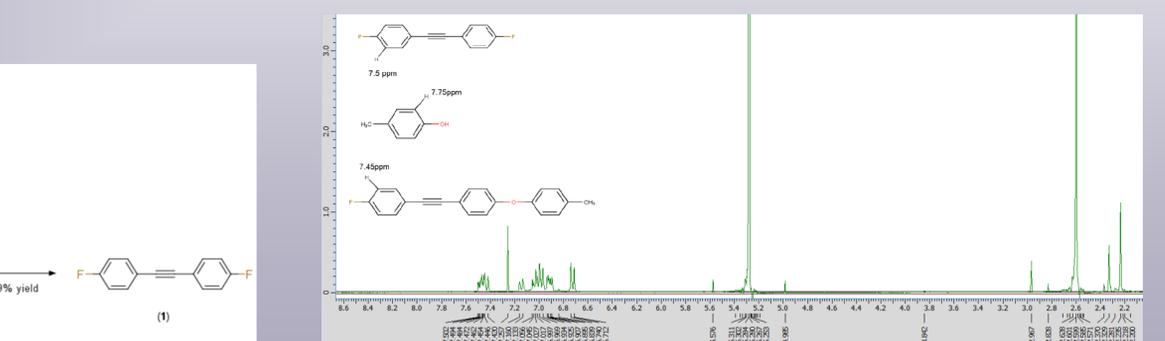


Figure 3. Fluorobenzyl benzotriazole (**2a** and **2b**) ¹H NMR in CDCl₃

Figure 4. ¹H NMR of Bis(4-fluorophenyl)acetylene (**1**)



Scheme 3. Reaction to form model trimer

Experimental

(E)-1-(4-Fluorophenyl)-N-phenylmethanimine (**3**)

To a suspension of **magnesium sulfate** (15.96 g, 132 mmol, 1.10 equiv) in CH₂Cl₂ (150 mL, 0.800 M) was added to **4-fluorobenzaldehyde** (13 mL, 15.04 g, 120 mmol, 1.00 equiv) and **aniline** (11 mL, 11.22 g, 120 mmol, 1.00 equiv) and the reaction mixture was stirred under nitrogen atmosphere at 23 °C for 15 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The crude product was recrystallized from hexanes by cooling the solution in a dry ice/acetone bath. Recrystallization afforded the title compound as a white solid (21.9 g, 110.4 mmol, 60% yield). ¹H NMR (300 MHz, CDCl₃): 8.44 (s, 1H), 7.93 (dd, J = 8.60, 5.59 Hz, 2H), 7.46–7.40 (m, 2H), 7.29–7.25 (m, 1H), 7.24 (d, J = 7.7 Hz, 2H), 7.19 (t, J = 8.6 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): 164.8 (d, J = 250.6 Hz), 159.0, 152.0, 132.7 (d, J = 2.1 Hz), 130.9 (d, J = 8.7 Hz), 129.3, 126.2, 121.0, 116.1 (d, J = 21.7 Hz).

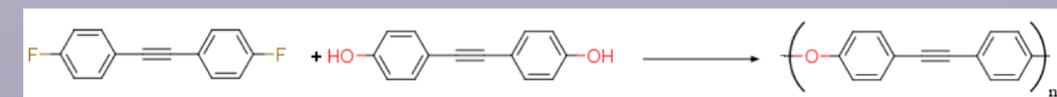
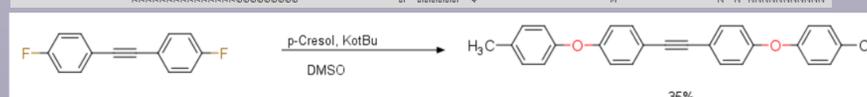
Fluorobenzyl benzotriazole (FBBT) (**2**)

A mixture of **1-H-benzotriazole** (18 g, 150 mmol), **4-fluorobenzyl chloride** (16 mL, 150 mmol) and **potassium carbonate** (70 g, 102 mmol) in **acetonitrile** (300 ml) was refluxed for 1 hour under a positive pressure of nitrogen. After hot filtration, the filtrate was evaporated under reduced pressure. ¹H NMR and C-13 NMR characterized the product as both isomers of the desired product, fluorobenzyl benzotriazole (FBBT) (16.12g, 89%). ¹H NMR (CDCl₃): 8.05 (m, 1.00H), 7.84 (m, 0.76H), 7.37 (m, 5.00H), 7.26 (m, 2.14H), 5.83 (s, 0.83H), 7.79 (s, 2.08H). ¹³C NMR (CDCl₃): Isomer 1: 162.75 (J=247.09), 144.73, 130.60 (J=3.61), 130.38 (J=8.67), 118.18, 115.94 (J=21.67), 59.65. Isomer 2: 162.92 (J=247.81), 146.43, 132.76, 130.69 (J=2.89), 129.53 (J=8.67), 127.62, 124.11, 120.22, 116.08 (J=21.67), 109.63, 45.57.

Bis(4-fluorophenyl)acetylene (1**)**⁵. A mixture of **N-(4-fluorobenzylidene)aniline** (13.15 g, 66 mmol) and **FBBT** (14.995 g, 66 mmol) in **DMF** (80 mL) was added to **t-BuOK** (13. g, 180 mmol) in **DMF** (120 mL) on an oil bath (73 °C), stirred for 1 min and then decanted into ice water. After filtration, the crude product (11.166 g, 95%) was dissolved in pet. ether and DCM prior to column chromatography on alumina, using hexane as the eluant. Evaporation of the solvent in vacuo gave the product as a white powder (7.06 g, 51%). ¹H NMR (CDCl₃, d): 7.49 (m, 3.96H), 7.04 (m, 4.00H).

Bis(4-p-tolxyphenyl)acetylene.

1 (0.214 g, 1.00 mm) was added to a mixture of **p-Cresol** (0.249 g, 2.3 mm), **t-BuOK** (0.26 g, 2.3 mm) and **DMSO** (6 mL, 6mm) on an oil bath (130 °C, stirred for 15 hours under a positive pressure of nitrogen and then extracted with **1M HCl** and washed with **DCM**. Evaporation of the solvent in vacuo gave the product as a tan powder. The resulting product mixture (2.46 g, 35%) was analyzed by ¹H NMR in CDCl₃.



Scheme 4. Reaction to make POPEP

DISCUSSION

Our lab was interested in forming the desired monomer, bis(4-fluorophenyl) acetylene (BFPA) in a large scale, which I accomplished by making 7.10 g. The desired monomer was synthesized in two steps (Scheme 2). Fluorobenzyl benzotriazole (FBBT) was synthesized from 1-H benzotriazole and 4-fluorobenzyl chloride⁵ in good yield (16.123 g, 89%). Purity was checked using ¹H and ¹³C NMR, both of which produced complex spectra due to the presence of two isomers of the desired compound, 1-(4-fluorobenzyl)benzotriazole and 2-(4-fluorobenzyl)benzotriazole (Figure 2,3). ¹³C resonance assignments were assigned on the basis of a ¹³C NMR predictor. The FBBT mixture of isomers was reacted with N-(4-fluorobenzylidene)aniline at 73 °C for 1 min, quenching in ice water. Column chromatography (n-hexane, Activated neutral alumina) afforded a white powder (51%). ¹H and ¹³C NMR characterized the product as BFPA (Figure 4). Yield loss of 49% attributed to inefficient transfers due to the sticky nature of the crude product.

Nalli's lab has used compound **1** in conjunction with the co-monomer bis(hydroxyphenyl)acetylene (BHPA acetylenic to prepare the poly(aryl ether) monomer, poly(oxy-1,4-phenyleneethynylene-1,4-phenylene) (POPEP). (Scheme 4). The conditions employed (NMP, 180 °C) were harsh, however, leading to doubts about the actual polymer structure. One of the goals of my research was to see if the polymerization could be carried out under milder conditions. To test this idea, **1** was reacted with 2 equiv p-cresol to see if a reasonable yield of the trimer (Scheme 3) could be obtained. The 35% yield of dimer obtained was disappointing so we need to find another method in our continuing experiments.

ACKNOWLEDGEMENTS

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