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# Fluoride-mediated polycondensation for the synthesis of polymers of intrinsic microporosity



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#### ABSTRACT

A fluoride-mediated double S<sub>N</sub>Ar polycondensation method was successfully developed to prepare highmolecular weight polymers of intrinsic microporosity (PIMs). The polymerization was conducted between a *t*-butyldimethylsilyl (TBS)-protected biscatechol monomer (**2**) and a widely used tetrafluoro monomer (**3**) in the presence of fluoride ion with excellent to quantitative yields. Three fluoride ion sources (i.e. KF, TBAF and CsF) were investigated, and all of them were effective as catalysts to give highmolecular weight linear products with good film forming property. Therefore, this method warrants its synthetic utility for PIM synthesis.

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#### 1. Introduction

Since the seminal publication on polymers of intrinsic microporosity (PIMs) by Budd and McKeown in 2004, considerable attention from both academic and industrial community has been drawn to this unique class of polymers [1]. The majority of new PIMs polymers have been prepared following the original protocol [2]. There are few new synthesis methodologies reported in the past decade. As shown in Scheme 1, the classical method undergoes a double nucleophilic aromatic substitution (S<sub>N</sub>Ar) mechanism between biscatechol monomer and tetrafluoro aromatic monomer in the presence of potassium carbonate [3]. Guiver and coworkers further optimized this method with added advantage of dramatically shortened reaction time and significantly increased molecular weight [4]. Most recently, an interesting solid state PIM-1 synthesis by mechanochemistry method was also reported to give highquality PIMs [5]. Most relevant to this work, in 2005, Kricheldorf described a different PIMs synthesis strategy based on trimethylsilyl (TMS)-derived biscatechol (Scheme 1, method B) [6]. According to their findings, the cyclic ladder oligomer and polymers were formed as predominant product. Besides, this "silyl ether

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protocol" still uses the K<sub>2</sub>CO<sub>3</sub> condition.

Pioneered by Kricheldorf et al., fluoride-mediated step growth polymerization was studied as an alternative method to prepare many industrial important high performance thermoplastics (e.g. polyarylethers, polyamide, polyimide, polyester, polybenzoxazoles, polyureas and polysulfates) [7]. For instance, the synthesis of high molecular weight polyarylethers employing trimethylsilyl (TMS) protected bisphenol and activated bisaryl fluoride was successfully achieved at elevated temperature (180-360 °C) catalyzed by CsF or KF [8]. The fluoride-mediated polymerization using silylated monomers has certain utilities in some occasions where the conventional method is unable to be implemented due to poor solubility of phenolate or the acid/base sensitive substrates in the reaction. The fluoride-mediated polymerization enjoys mild reaction condition, neutral condensates byproduct (e.g. alkylsilyl fluoride, alkylsilylacetate, and alkyldisiloxane) and eliminates the use of basic neutralizer [7].

Therefore, we are interested in introducing fluoride-mediated polymerization method to the field of PIMs synthesis. In this work, a new synthetic method for PIMs based on fluoride-mediated polymerization is firstly demonstrated (Scheme 1, **Method C**). <sup>1</sup>H NMR spectra of polymer obtained by this method is identical to traditional one. Three fluoride sources (KF, CsF and TBAF) were investigated, and all of them were effective as catalysts to give high-molecular weight linear products with good film forming property.





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Scheme 1. PIMs synthesis with different dibenzodioxin-forming methods.

#### 2. Experimental

#### 2.1. Materials and methods

All chemicals were purchased from Aldrich and used as received without further treatment, except TFTPN (97%) was purchased from Manchester Organics and recrystallized from ethyl acetate before use. NMR spectra were recorded on a Bruker DRX400 spectrophotometer. Chemical shifts are reported in parts per million (ppm) referenced to  $\delta$  7.26 and 77.0 ppm from chloroform or  $\delta$  2.50 and 39.5 ppm from DMSO for <sup>1</sup>H and <sup>13</sup>C respectively. The multiplicities of <sup>1</sup>H signals are designated by the following abbreviations: s = singlet; m = multiplet; br = broad. All <sup>13</sup>C NMR spectra wereacquired using broadband decoupled mode, and assignments were determined using DEPT sequences. High-resolution mass spectra were obtained by ESI using a Bruker micrOTOF-Q mass spectrometer. Molecular weight and molecular weight distributions were determined by PL GPC-50 instrument equipped with 5 µm PL gel Mixed C columns (heated to 40 °C) arranged in series with chloroform as eluent and a RI detector and the values were calibrated versus polystyrene standard.

#### 2.2. Synthetic procedures

#### 2.2.1. 5,5',6,6'-Tetrahydroxy-3,3,3',3',7,7'-

hexamethylspirobisindane (1) [9].

To a mixture of conc. HBr aq. (36 ml) and acetic acid (33 ml) was added 1,2-dihydroxy-3methylbenzene (16.8 g, 135 mmol) to give a clear solution. Acetone (21 ml, 286 mmol, 2.1eq) was then added dropwisely. After addition, the resulting solution was heated to reflux and kept refluxing for 24 h. The hot mixture was poured into water (360 ml) with vigorous stirring. The precipitate was filtered out. Then the solid was stirred in acetic acid (150 ml) for 1 h, filtered, and washed with acetic acid to give title compound **1** (15 g, 40.7 mmol, 60%) as a white solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  ppm 8.83 (br, 2H), 7.67 (br, 2H), 6.43 (s, 2H), 2.16–2.05 (m, 4H), 1.51 (s, 6H), 1.25 (s, 6H), 1.22 (s, 6H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  ppm 143.95, 142.32, 141.28, 137.46, 119.76, 106.02, 56.96, 56.67, 41.76, 32.54, 29.87, 10.74; HR-MS (ESI) calcd. 391.1880 for C<sub>23</sub>H<sub>28</sub>NaO<sub>4</sub>, found 391.1868 [M + Na]<sup>+</sup>.

#### 2.2.2. 5,5',6,6'-Tetrakis(tert-butyldimethylsilyloxy)-3,3,3',3',7,7'hexamethylspirobisindane(2)

To a suspension of the biscatechol **1** (10.85 g, 29.4 mmol) in anhydrous DMF (135 ml) was added *t*-butyldimethylsilyl chloride (36 g, 239 mmol). The mixture was cooled down in ice-bath and added imidazole (24 g, 353 mmol) slowly within 5 min followed by

addition of DMAP (0.36 g, 2.95 mmol). The mixture was stirred under Ar at room temperature for 3 days. Afterwards, the mixture was poured into methanol (400 ml) slowly and stirred for 1 h. Then, the precipitate was filtered, washed with methanol and dried under vacuum to give the title compound **2** (22.6 g, 27.4 mmol, 93%) as white solid. The crude product was recrystallized from a mixture of THF and MeOH before polymerization. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 6.48 (s, 2H), 2.24–2.17 (m, 4H), 1.62 (s, 6H), 1.29 (s, 6H), 1.27 (s, 6H), 0.97 (s, 18H), 0.96 (s, 18H), 0.22 (s, 6H), 0.19 (s, 6H), 0.14 (s, 6H), 0.05 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 146.21, 144.21, 143.72, 139.96, 125.99, 111.95, 57.90, 56.76, 42.24, 32.69, 29.72, 26.33, 26.27, 18.84, 18.59, 12.73, -3.04, -3.31, -3.68, -3.70; HR-MS (ESI) calcd. 825.5519 for C<sub>47</sub>H<sub>85</sub>O<sub>4</sub>Si<sub>4</sub>, found 825.5540 [M + H]<sup>+</sup>.

#### 2.2.3. General procedure for polymer 4

A mixture of TBS-protected monomer 2 (1 eq.) and Tetrafluoroterephthalonitrile 3 (1 eq.) was suspended in anhydrous DMF or DMAc (solid content ca. 0.125 g total monomer weight in 1 ml solvent). Anhydrous fluoride salt (KF or CsF) was dried in high vacuum at about 120° for 2 h before use (1 M commercial TBAF solution in THF was used directly). After addition of fluoride salt at r.t., the resulting mixture was heated under argon for 72 h in total (Heating procedure I: 70 °C 72 h, II: 70 °C for 6 h, then 120 °C for 66 h). Then, the reaction was cooled down, and poured into water with stirring for 1 h. The mixture was filtered, washed with water thoroughly and dried to give yellow solid as crude product 4 as a yellow solid (crude yield from 74% to quantitative.), which was used directly for GPC measurements. Prior to NMR analysis, polymers were purified via precipitation of polymer solution in CHCl<sub>3</sub> into MeOH. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 6.71 (br s, 2H), 2.25 (br, 4H), 1.74 (br s, 6H), 1.35–1.32 (br m, 12H).

#### 3. Results and discussion

#### 3.1. Synthesis of the silvlated monomer 2

The biscatechol **1** was synthesized via a condensation reaction of 3-methyl catechol and acetone under a harsh acidic condition (Scheme 2). The reaction followed the same procedure in literature recorded by Fritsch [9]. Using trimethylsilyl (TMS) group to protect biscatechol monomers was reported by Kricheldorf aiming at the mechanistic studies of the cyclic PIM formation [6]. Here, instead of TMS group, *tert*-butyl dimethyl silyl (TBS) chloride was employed to give TBS-protected product **2**. Both biscatechol **1** and TBS-protected monomer **2** were characterized by <sup>1</sup>H, <sup>13</sup>C NMR and HR-MS (Fig. S1–S4). All spectra agreed well with the target structures. Additionally, the position of methyl group in benzene ring in

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