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Zhenning Yu^a, Eric Fossum^a, David H. Wang^b & Loon-Seng Tan^c

^a Department of Chemistry , Wright State University , Dayton, Ohio, USA

^b University of Dayton Research Institute, Dayton, Ohio, USA

^c Polymer Branch , Materials and Manufacturing Directorate, AFRL/MLBP, Air Force Research Laboratory, Manufacturing Technology Directorate , Dayton, Ohio, USA

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Alternative Approach to an AB₂ Monomer for Hyperbranched Poly(Arylene Ether Ketone Imide)s

Zhenning Yu,¹ Eric Fossum,¹ David H. Wang,² and Loon-Seng Tan³

 ¹Department of Chemistry, Wright State University, Dayton, Ohio, USA
²University of Dayton Research Institute, Dayton, Ohio, USA
³Polymer Branch, Materials and Manufacturing Directorate, AFRL/ MLBP, Air Force Research Laboratory, Manufacturing Technology Directorate, Dayton, Ohio, USA

Abstract: An alternative approach to an AB₂ monomer, N-[3,5-bis(4-hydroxybenzoyl)benzene]-4-fluorophthalimde, **4**, for hyperbranched poly(arylene ether ketone imide)s has been developed. The key steps were a *para*-position selective electrophilic aromatic substitution of fluorobenzene with 5-nitroisophthaloyl dichloride and a subsequent clean conversion of the aryl fluorides to phenol groups using potassium hydroxide as the nucleophile. The overall yield for the synthesis of **4** was 51.6%.

Keywords: branched polymer, monomers, selectivity

INTRODUCTION

The synthesis of branched polymers, in particular hyperbranched systems, has received considerable attention over the past decade because of their unique properties, which include 1) a large number of end groups, 2) low values of intrinsic viscosity, and 3) generally, good solubility characteristics.^[1-6] One such class of hyperbranched polymers is the hyperbranched poly(arylene

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Address correspondence to Eric Fossum, Department of Chemistry, Wright State University, 3640 Colonel Glenn Hwy, Dayton, OH 45435, USA. E-mail: eric. fossum@wright.edu

ether)s, HB PAEs, which are branched analogs of the corresponding engineering plastics.^[7] A wide variety of HB PAEs have been prepared and studied, including HB poly(arylene ether ketone)s,^[7–9] PAEK; poly(arylene ether sulfone)s,^[10–12] PAES; poly(arylene ether phosphine oxide)s,^[13–15] PAEPO; poly(arylene ether quinoxaline)s,^[16,17] PAEQ; poly(arylene ether imide)s,^[18–20] PEI; and poly(arylene ether ketone imide)s,^[21,22] PAEKI.

Typically, the synthesis of an HB PAE is achieved via the nucleophilic aromatic substitution polycondensation reaction of AB_2 -type monomers in which A is either a phenol or aryl fluoride and B is the corresponding reaction partner. One of the limiting factors in the study of HB PAE systems is the synthetic effort required to prepare the appropriate AB_2 monomer. Any practical synthesis of an AB_2 monomer should meet a number of requirements, including 1) high-yielding, facile, and selective reactions; 2) a minimum number of steps; and 3) use of low-cost and readily available reagents.

The most widely studied AB_2 monomer for the synthesis of HB PAEKIs is *N*-[3,5-bis(4-hydroxybenzoyl)benzene]-4-fluorophthalimde, **4**. Two of the reported synthetic routes to **4** are shown in Scheme 1. We now report on an improved synthesis of **1**, which takes advantage of the selectivity shown by fluorobenzene for reaction at the *para*-position during electrophilic aromatic substitution processes. Additionally, the phenol groups are subsequently introduced, via nucleophilic aromatic substitution, using the low-cost reagent potassium hydroxide. Although the current method reverts to a synthesis that involves five steps, the yield and selectivity of several steps is improved significantly, thus providing an efficient, low-cost, and readily scalable approach to the synthesis of **4**. When compared to Method I



(Scheme 1),^[21] the overall yields in the current synthetic route are improved considerably compared to Method II.^[22] The new synthesis represents a considerable cost savings as the imidization reaction, requiring the most expensive reagent (4-fluorophthalic anhydride), is carried out in the final step, limiting expensive material losses.

RESULTS AND DISCUSSION

The previously reported synthetic routes to **4** are shown in Scheme 1. Method I starts by converting 5-nitroisophthalic acid into 5-nitroisophthaloyl dichloride, followed by a Friedel–Crafts reaction with an excess of anisole to provide the corresponding protected bisphenol, **2**. Deprotection of the phenol groups with pyridine hydrochloride and reduction of the nitro group affords the corresponding aniline derivative, **3**. The final product, *N*-[3,5-bis(4-hydroxybenzoyl)benzene]-4-fluorophthalimde, **4**, is provided in an overall yield of 32.3%, by the imidization reaction of **3** with 4-fluorophthalic anhydride. A slightly improved synthesis of **4** has been reported that employs methanesulfonic acid (MSA) and P₂O₅ as the condensing agent, thus eliminating the need to first prepare the diacid chloride.^[23]

Method II begins with the imidization reaction of 5-aminoisophthalic acid, 5, with 4-fluorophthalic anhydride to afford N-(3,5-dicarboxylic acid benzene)-4-fluorophthalimide, $\mathbf{6}$, in 84% yield. The *bis*-phenol moiety of 4 is introduced via the Friedel-Crafts reaction of 6 with an excess of anisole, using methanesulfonic $acid/P_2O_5$ as the condensing agent, to provide N-[3,5-bis(4-methoxybenzoyl)benzene]-4-fluorophthalimide, 7, in 74% yield. The final step involves demethylation of the phenol groups, using BBr₃ in dichlorobenzene at 80°C for 24 h, to afford the desired 4 in an overall yield of 56.6% yield. Method 2 represents a substantial improvement in the overall yield (56.6% versus 32.3%) for the synthesis of 4 with a concurrent increase in efficiency by reducing the number of reaction steps from five to three. However, the reduction in the number of reaction steps comes with a significant increase in the overall cost of the synthesis. For example, 4-fluorophthalic anhydride is a relatively expensive reagent, but it is introduced in the first step of the synthesis. The starting material, 5-aminoisophthalic acid, 5, is considerably more expensive than the corresponding nitro analog. Additionally, demethylation of the phenol groups using BBr₃ often proves to be problematic, especially when a large excess of the reagent is utilized.

Development of a low-cost, efficient synthesis of **4** is vital if the corresponding HB PAEKIs are to be fully studied and exploited on an industrial scale. The current synthetic route to **4**, Method III, shown in Scheme 2, involves five steps, as in method 1; however, the yields and selectivity of the reactions are improved significantly and it takes advantage of low-cost reagents. The fundamental difference, versus the prior two methods, is the

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reaction in which the phenolic moieties are introduced into the molecule. Rather than relying on a demethylation of methoxy protected phenol groups using pyridine hydrochloride or BBr₃, the phenol groups are introduced via a high-yielding nucleophilic aromatic substitution reaction of activated aryl fluorides using low-cost potassium hydroxide as the nucleophile.

Thus, Method III begins with the aluminum chloride-promoted Friedel-Crafts reaction of the diacid chloride of 1 with an excess of fluorobenzene to provide the *bis*-phenol precursor, 3,5-bis(4-fluorobenzoyl)-5-nitrobenzene, 8, in 82% yield. The selectivity of the fluoro group for directing electrophilic aromatic substitution at the *para*-position is typically much greater than that observed for the methoxy group. In fact, for benzoylation, the selectivity is reported to be 100% for the para-position.^[24,25] This may help to explain the significantly improved yield for the Friedel-Crafts reaction in method 3 relative to that for method 1 (82% versus 48%). At this stage, direct conversion of the aryl fluoride groups in 8 to the corresponding phenol groups was unsuccessful, in part, because of a competing substitution reaction of the nitro group. Therefore, the nitro group was first reduced to the amine using hydrogen gas and Pt on carbon under acidic conditions to form the ammonium salt in situ. The free amine was unstable to air, thus the ammonium hydrochloride salt was isolated. Conversion of the aryl fluoride groups to phenols was achieved cleanly in 97% yield by the use of KOH in a mixture of DMSO and water, followed by acidification. The yield of 3, after the first four steps, was 62% versus 45% at the same stage using method 1, representing a significant improvement. In addition, the melting point of 3, prepared via method 3, was 258-259°C compared to 249.5-250.5°C for samples of **3** prepared via method 1, which may be indicative of a slightly higher purity material.

Introduction of the 4-fluorophthalimide was achieved by reaction of **3** and 4-fluorophthalic anhydride, in refluxing acetic acid, to afford the desired AB₂ monomer **4**, in 83% yield. The imidization step required only 2.5 h in refluxing acetic acid, whereas the reaction in NMP (Method I) required heating to 200°C for up to 18 h to reach completion. The structure of **4** was confirmed by comparing its analytical data (¹H and ¹³C NMR spectra) to the reported literature values. Interestingly, the melting point of **4** prepared by method 3 was 296–298°C compared to 274–276°C for samples of **4** prepared by either methods 1 or 2. The overall yield for method 3 was 51.6%, compared to 32.3% (Method I) and 56.6% (Method II).

Although the overall yield for Method III is slightly lower than that for method 2, 51.6 versus 56.6%, it has a number of significant advantages in terms of the ability for scale-up. First, the most expensive reagent, 4-fluorophthalic anhydride, is introduced in the last step of the synthesis, thus representing significant cost savings. Second, the Friedel–Crafts reaction with fluorobenzene provides a more selective method to introduce phenolic precursor groups, in the *para* positions, relative to anisole. Third, starting with the less expensive 5-nitroisophthalic acid rather than 5-aminoisophthalic acid, is more cost effective. Finally, introduction of the phenol groups via nucleophilic aromatic substitution reaction of aryl fluorides with potassium hydroxide affords an extremely low-cost and efficient alternative to demethylation of the methoxy groups using either pyridine hydrochloride or BBr₃.

EXPERIMENTAL

Materials

Fluorobenzene, 5-nitroisophthalic acid, 4-fluorophthalic anhydride, thionyl chloride, DMSO, and aluminum chloride were purchased from Aldrich and used as received. Toluene, ethyl acetate, and ethanol were used as received. Unless otherwise noted, all reactions were performed under a nitrogen atmosphere, and all transfers were done using syringes or cannula as necessary.

Instrumentation

¹H and ¹³C NMR spectra were obtained using a Bruker Avance DMX 300-MHz instrument operating at 300 and 75.5 MHz, respectively. Samples were dissolved in DMSO- d_6 . Elemental analyses were obtained from Midwest Microlabs, Inc., Indianapolis, IN. Melting points were determined using a Mel-Temp capillary melting-point apparatus and are uncorrected.

Procedures

5-Nitroisophthaloyl Dichloride

5-Nitroisophthalic acid (12.67 g, 60 mmol), 35 mL of thionyl chloride, and two drops of DMF were placed in a 250-mL round-bottomed flask, equipped with a stir bar, reflux condenser, and nitrogen inlet. The mixture was heated to and held at a gentle reflux until all solids were dissolved in thionyl chloride. Excess thionyl chloride was removed under reduced pressure to afford 14.43 g (97.0%) of 5-nitroisophthaloyl chloride as a light yellow solid, which was used without any further purification.

3,5-Bis(4'-fluorobenzoyl)nitrobenzene, 8

A solution of 14.88 g (60 mmol) of 5-nitroisophthaloyl dichloride, dissolved in 45 mL of fluorobenzene, was added slowly via an addition funnel, to a stirred suspension of 18.0 g (0.135 mol) of aluminum chloride in 15 mL fluorobenzene. Solids were formed after the addition of 5-nitroisophthaloyl dichloride was completed. The mixture was heated to and kept at reflux for 12 h, at which point it was cooled to room temperature and quenched by pouring into a large excess of cold 10% HCl. Ethyl acetate, 100 mL, was added to the mixture, and the organic layer was separated. The water layer was extracted three times with 50 mL of ethyl acetate. The organic layers were combined and washed with deionized DI water, dilute HCl, then DI water again. The solvents were removed by vacuum to afford a yellow solid. Recrystallization of the crude yellow solid from a mixture of 30 mL of toluene and 150 mL of ethanol provided 18.10 g (82.1%) of yellow crystals with a melting-point of $122-124^{\circ}$ C. ¹H NMR (DMSO- d_6 ; δ in ppm): 7.43-7.48 (t, J 8.8 Hz, 4H); 7.94-7.99 (dd, J₁ 8.8 Hz, J₂ 5.5 Hz, 4H); 8.33–8.34 (t, J 1.4 Hz, 1H); 8.67–8.68 (d, J 1.4 Hz 2H).¹³C NMR (DMSO-d₆; δ in ppm): 115.8 (d, J 22 Hz); 126.9; 132.3 (d, J 2.8 Hz); 133.0 (d, J 10 Hz); 135.5:138.6; 147.8; 165.2 (d, J 253 Hz); 191.7. Anal. calculated for C₂₀H₁₁F₂NO₄: C, 65.40%; H, 3.02%; N, 3.81%. Found: C, 65.01%; H, 2.96%; N, 3.76%.

3,5-Bis(4-fluorobenzoyl)aniline Hydrochloride Salt

A 500-mL high-pressure bottle was charged with 17.90 g (49 mmol) of 3,5bis(4'-fluorobenzoyl) nitrobenzene, 0.9 g of palladium on activated carbon (5% palladium content), 5 mL of 37% HCl, and 300 mL of 95% ethanol. The bottle was placed on the hydrogenation apparatus, and hydrogen gas was charged and discharged five times, followed by agitation at 75–85 psi for 24 h. The reaction mixture was filtered through a cake of Celite[®] 545 to remove the catalyst, and the solvent was removed via rotary evaporation. The solid was slurried in 100 mL of ethyl acetate to afford 13.80 g (80.7%

yield) of ammonium hydrochloride salt as a white solid with a melt point (decomposing) of 195–198°C. ¹H NMR (DMSO- d_6 ; δ in ppm): 7.41–7.47 (t, *J* 8.8 Hz, 4H); 7.65 (t, *J* 1.2 Hz, 1H); 7.79 (d, *J* 1.2 Hz, 2H); 7.90–7.95 (dd, J_1 8.8 Hz, J_2 5.5 Hz, 4H); 8.78 (br, 3H). ¹³C NMR (DMSO- d_6 ; δ in ppm): 115.8 (d, *J* 22 Hz); 124.1; 125.3; 132.7 (d, *J* 10 Hz); 133.0 (d, *J* 2.8 Hz); 138.0; 139.4; 164.9 (d, *J* 252 Hz); 191.7.

3,5-Bis(4'-hydroxybenzoyl)aniline, 3

To a 500-mL round-bottomed flask equipped with a stir bar, 6.75 g (102 mmol) of 85% potassium hydroxide, 25 mL of DI water, and 25 mL of DMSO were charged. The mixture was preheated to 120°C and held at this temperature, at which point 6.38 g (17.1 mmol) of 3,5-bis(4'-fluorobenzoyl)aniline hydrochloride salt, dissolved in 35 mL of DMSO, were added dropwise via an addition funnel. The mixture was held at 120°C for 12 h, cooled to room temperature, and poured into 200 mL of DI water. The mixture was neutralized by adding 10% HCl, until the pH was approximately 8. The resulting yellow solid was isolated by filtration. The solid was dissolved in 90 mL of ethanol and filtered, and the resulting solution was diluted with 360 mL of water. The resulting mixture was heated until it turned into a clear solution, which was allowed to cool to rt to afford 5.51 g (97.0%) of yellow crystals with mp 258–259°C. ¹H NMR (DMSO-*d*₆; δ in ppm): 5.73 (br, 2H); 6.92–6.95 (d, J 8.6 Hz, 4H); 7.02 (t, J 0.9 Hz, 1H); 7.16-7.17 (d, J 0.9 Hz, 2H); 7.72-7.75 (d, J 8.6 Hz, 4H); 10.48 (br, 2H).¹³C NMR (DMSO-d₆; δ in ppm): 115.2; 117.2; 117.6; 128.0; 132.4; 138.6; 148.9; 161.9; 194.3. Anal. calculated for C₂₀H₁₅NO₄: C, 72.06%; H, 4.54%; N, 4.20%. Found: C, 71.46%; H, 4.59%; N, 4.15%.

N-[3,5-Bis(4'-hydroxybenzoyl)benzene]-4-fluorophthalimide, 4

To a 250-mL round-bottomed flask with stir bar, 8.40 g (25.2 mmol) 3,5bis(4'-hydroxybenzoyl) aniline, 4.19 g (25.2 mmol) of 4-fluoro phthalic anhydride, and 75 mL of acetic acid were added. The mixture was heated to and held at reflux for 2.5 h and then allowed to cool to room temperature. The solids were isolated by filtration and washed with acetic acid, and then small quantities of ethanol and ethyl acetate to afford 8.20 g of a light green powder (71.8% yield). An additional 1.25 g (10.9% yield) was recovered from the acetic acid filtrate by precipitating it from water, followed by reslurrying in a small amount (15 mL) of acetic acid and filtering. The melting point of the final product was 296–298°C. ¹H NMR (DMSO- d_6 ; δ in ppm): 6.93– 6.96 (d, *J* 8.7 Hz, 4H); 7.71–7.74 (m, 1H); 7.79–7.81 (d, *J* 8.7 Hz, 4H); 7.89– 7.92 (dd, *J*₁ 7.4 Hz, *J*₂ 2.2 Hz, 1H); 7.97 (t, *J* 1.5 Hz, 1H); 8.05–8.07 (m, 1H); 8.08–8.09 (d, *J* 1.5 Hz, 2H). 105 (br, 2H) ¹³C NMR (DMSO- d_6 ; δ in ppm): 111.3 (d, *J* 25 Hz); 115.4; 121.6 (d, *J* 24 Hz); 126.3 (d, *J* 9.6 Hz); 127.2; 127.8 (d, J.23 Hz) 129.0; 130.5; 132.0; 132.7; 134.6 (d, *J* 10 Hz); 138.5; 162.4; 165.5 (d, J 2.9 Hz); 165.8; 165.9 (d, J 254 Hz); 192.5. Anal. calculated for C₂₈H₁₆FNO₆: C, 69.85%; H, 3.35%; N, 2.91%. Found: C, 69.88%; H, 3.53%; N, 2.82%.

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REFERENCES

- Jikei, M.; Kakimoto, M.-A. Hyperbranched polymers: a promising new class of materials. *Prog. Polym. Sci.* 2001, 26, 1233–1285.
- Sunder, A.; Heinemann, J.; Frey, H. Controlling the growth of polymer trees: concepts and perspectives for hyperbranched polymers. *Chem. Eur. J.* 2000, 6, 2499–2506.
- 3. Inoue, K. Functional dendrimers, hyperbranched and star polymers. *Prog. Polym. Sci.* **2000**, *25*, 453–571.
- Voit, B. New developments in hyperbranched polymers. J. Polym. Sci.: Part A: Polym. Chem. 2000, 38, 2505–2525.
- 5. Kim, Y. H. Hyperbranched polymers 10 years after. J. Polym. Sci.: Part A: Polym. Chem. 1998, 36, 1685–1698.
- Malmstrom, E.; Hult, A. Hyperbranched polymers: a review. J. M. S. Rev. Macromol. Chem. Phys. 1997, C37, 555-579.
- Miller, T. M.; Neenan, T. X.; Kwock, E. E.; Stein, S. M. Dendritic analogues of engineering plastics: a general one-step synthesis of dendritic polyaryl ethers. *J. Am. Chem. Soc.* **1993**, *115*, 356–357.
- Hawker, C. J.; Chu, F. Hyperbranched poly(ether ketone)s: manipulation of structure and physical properties. *Macromolecules* 1996, 29, 4370–4380.
- Baek, J.-B.; Tan, L.-S. Linear-hyperbranched copolymerization as a tool to modulate thermal properties and crystallinity of a para-poly(ether ketone). *Polymer* 2003, 44, 3451–3459.
- Himmelberg, P.; Fossum, E. Development of an efficient synthesis of hyperbranched poly(arylene ether sulfone)s. J. Polym. Sci. Part A: Polym. Chem. 2005, 43, 3178–3187.
- Kricheldorf, H. R.; Fritsch, D.; Vakhtangishvili, L.; Schwarz, G. Multicyclic poly(ether sulfone)s of phloroglucinol forming branched and cross-linked architectures. *Macromolecules* 2003, *36*, 4337–4344.
- Kricheldorf, H. R.; Vakhtangishvili, L.; Fritsch, D. Synthesis and functionalization of poly(ether sulfone)s based on 1,1,1,-tris(4-hydroxyphenyl)ethane. J. Polym. Sci.: Part A: Polym. Chem. 2002, 40, 2967–2978.
- Lin, Q.; Long, T. E. Synthesis and characterization of a novel AB₂ monomer and corresponding hyperbranched poly(arylene ether phosphine oxide)s. *J. Polym. Sci.: Part A: Polym. Chem.* 2000, *38*, 3736–3741.

- Bernal, D. P.; Bankey, N. B.; Cockayne, R. C.; Fossum, E. Fluoride-terminated hyperbranched poly(arylene ether phosphine oxide)s via nucleophilic aromatic substitution. J. Polym. Sci.: Part A: Polym. Chem. 2002, 40, 1456–1467.
- Bernal, D. P.; Bedrossian, L.; Collins, K.; Fossum, E. Effect of core reactivity on the molecular weight, polydispersity, and degree of branching of hyperbranched poly(arylene ether phosphine oxide)s. *Macromolecules* **2003**, *36*, 333–338.
- 16. Baek, J.-B.; Harris, F. W. Synthesis and thermal behavior of phenylethynylterminated linear and hyperbranched poly(phenylquinoxaline)s. J. Polym. Sci.: Part A: Polym. Chem. 2004, 42.
- Baek, J.-B.; Harris, F. W. Fluorine and hydroxyl-terminated hyperbranched poly-(phenylquinoxaline)s (PPQs) from copolymerization of self-polymerizable AB and AB₂, BA, and BA₂ monomers. *Macromolecules* **2005**, *38*, 1131.
- Thompson, D. S.; Markoski, L. J.; Moore, J. S. Rapid synthesis of hyperbranched aromatic polyetherimides. *Macromolecules* 1999, 32, 4764–4768.
- Markoski, L. J.; Thompson, J. L.; Moore, J. S. Synthesis and characterization of linear-dendritic aromatic etherimide copolymers: tuning molecular architecture to optimize properties. *Macromolecules* 2000, *33*, 5315–5317.
- Wu, F.-I.; Shu, C.-F. Hyperbranched aromatic poly(ether imide)s: synthesis, characterization, and modification. J. Polym. Sci.: Part A: Polym. Chem. 2001, 39, 2536–2546.
- Baek, J.-B.; Qin, H.; Mather, P. T.; Tan, L.-S. A new hyperbranched poly(aryleneether-ketone-imide): synthesis, chain-end functionalization, and blending with a bis(maleimide). *Macromolecules* 2002, *35*, 4951–4959.
- Wang, D. H.; Marsh, T.; Yu, Z.; Fossum, E.; Mather, P. T.; Tan, L.-S. Improved monomer synthesis of hyperbranched poly(arylene-ether-ketone-imide)—Part II. ACS Div. Polym. Chem. Poly. Prep. 2007, 48, 428–429.
- Wang, D. H.; Marsh, T.; Mather, P. T.; Tan, L.-S. Improved monomer synthesis for hyperbranched poly(arylene-ether-ketone-imde)—Part I. ACS Div. Polym. Chem. Poly. Prep. 2006, 47, 530–531.
- Rosenthal, J.; Schuster, D. I. The anomalous reactivity of fluorobenzene in electrophilic aromatic substitution and related phenomena. *J. Chem. Ed.* 2003, *89*, 679–690.
- Ingold, C. K. Structure and Mechanism in Organic Chemistry, 2nd edn.; Cornell University Press: Ithaca, NY, 1969.