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# Orthogonal Synthesis of Poly(aryl ether amide) Dendrons

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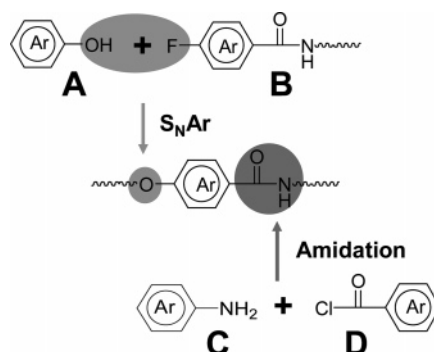
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Dendrimers are monodisperse and perfectly branched macromolecules that are the objects of continuously increasing interests because of their predetermined structures at the nanoscale region and the resulting unique properties.<sup>1</sup> Generally, dendrimers are synthesized by the divergent and the convergent synthetic methods. These synthetic methods inevitably require a repeated deprotection step in addition to the coupling step for the synthesis of the next generation dendron.<sup>2</sup> Several efficient approaches have been proposed to accelerate the dendrimer synthesis. These include the double-stage convergent and double-exponential growth approaches as well as the hypermonomer and orthogonal monomer approaches.<sup>2a</sup> Among these approaches, the orthogonal monomer approach, which excludes the need for activation of peripheral or focal point moieties to continue dendrimer growth, is the most powerful since it gives a new generation at each step.<sup>3</sup> For utilizing the orthogonal monomer approach for a certain dendrimer synthesis, two types of orthogonal AB<sub>2</sub> units, which contain two pairs of complementary coupling functionalities, must be prepared.

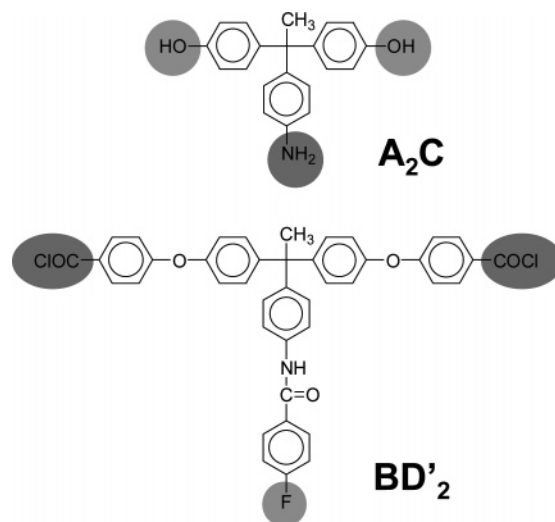
Recently, dendrimers based on the high-performance polymers such as aromatic polyamides and poly(aryl ethers) have been developed by several research groups.<sup>4</sup> For the synthesis of dendritic polyamides, the double-stage convergent approach, the orthogonal monomer approach, and the unprotected AB<sub>2</sub> monomer approach have been successfully exploited.<sup>5</sup> But to the best of our knowledge, such accelerating synthetic strategies have never been attempted for the synthesis of poly(aryl ether) dendrimers.

In this study, we introduce a simple orthogonal convergent methodology for the synthesis of poly(aryl ether amide) dendrons. Nucleophilic aromatic substitution (S<sub>N</sub>Ar) and amidation were chosen as the orthogonal coupling reactions because each coupling reaction does not interfere with the other coupling reaction (Figure 1). Here, both hydroxy nucleophiles and activated halide moieties (A and B) for the S<sub>N</sub>Ar reaction are latent during the amidation reaction. Also, both amine and carboxylic acid moieties (C and D) for the amidation reaction are inert under the conditions of the S<sub>N</sub>Ar reaction. Such orthogonal characteristics of both reactions have been successfully utilized for the synthesis of hydroxy-functionalized linear polyamides and amine-functionalized linear poly(aryl ether ketones).<sup>6</sup>

Alternative stepwise reactions using these two orthogonal monomers can produce poly(aryl ether amide) dendrons. A<sub>2</sub>C (two hydroxy groups (A) and one amine (C)) and BD'<sub>2</sub> (one activated fluorine (B) and two carboxylic acid chlorides (D')) monomers were selected



**Figure 1.** Orthogonal strategy for the synthesis of poly(aryl ether amide) dendrons.



**Figure 2.** Structure of two orthogonal units A<sub>2</sub>C and BD'<sub>2</sub>.

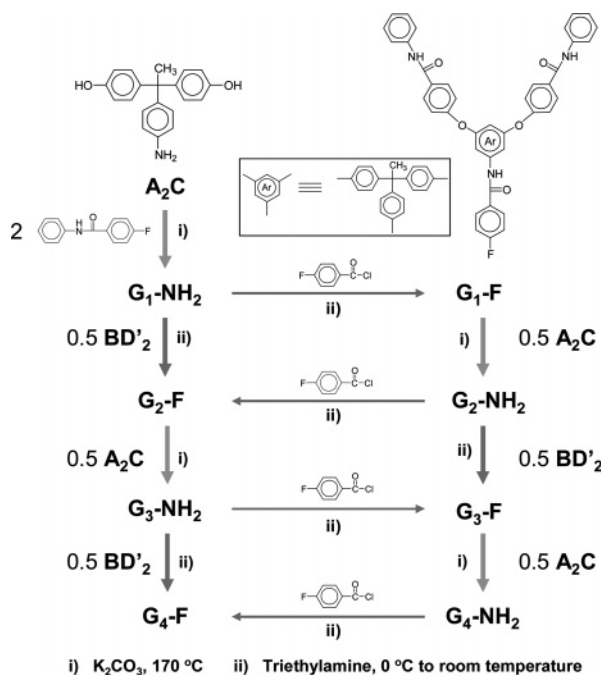
as the orthogonal monomer units for the synthesis of poly(aryl ether amide) dendrons (Figure 2). Instead of BD<sub>2</sub> monomers having two carboxylic acid groups, BD'<sub>2</sub> monomers having two carboxylic acid chloride groups were used for the synthesis of dendrons because direct amidation reaction is possible between A and D' moieties without additional condensation reagents such as DBOP. At first, first-generation dendrons with a focal amine G<sub>1</sub>-NH<sub>2</sub> were effectively synthesized from an A<sub>2</sub>C orthogonal monomer unit via the S<sub>N</sub>Ar reaction. Corresponding G<sub>1</sub>-F dendrons were synthesized by the amidation reaction between G<sub>1</sub>-NH<sub>2</sub> dendrons and *p*-fluorobenzoyl chloride.<sup>7</sup> From these two G<sub>1</sub> dendrons and two orthogonal monomers, A<sub>2</sub>C and BD'<sub>2</sub>, poly(aryl ether amide) dendrons up to fourth generation were successively synthesized as shown in Scheme 1.

After each orthogonal reaction, G<sub>*n*</sub>-NH<sub>2</sub> changes to G<sub>(*n*+1)</sub>-F while G<sub>*n*</sub>-F transforms to G<sub>(*n*+1)</sub>-NH<sub>2</sub>. Because this approach leads to the formation of dendrimers that are not homogeneous in chemical constituents due to the presence of different moieties in the focal point, interconversion reactions between G<sub>*n*</sub>-NH<sub>2</sub> and G<sub>*n*</sub>-F were attempted. Amidation of G<sub>*n*</sub>-NH<sub>2</sub> with *p*-fluorobenzoyl chloride quantitatively produced G<sub>*n*</sub>-F.<sup>7</sup> All the dendrons were purified by just simple reprecipitation of their tetrahydrofuran solution into methanol.

<sup>1</sup>H NMR spectra well matched with the assigned structures of these dendrons. All dendrons showed

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### Scheme 1. Orthogonal Synthesis of Poly(aryl ether amide) Dendrons



characteristic amide proton peaks at 10.2 ppm. The amine protons at the focal point of  $\text{G}_1\text{-NH}_2$  or  $\text{G}_2\text{-NH}_2$  were well observed near 5.0 ppm, but the presence of focal groups in  $\text{G}_3\text{-NH}_2$  or  $\text{G}_4\text{-NH}_2$  were difficult to be identified because these focal groups contribute too much small portion compared with these large dendron structures. FTIR spectra of all dendrons showed the characteristic absorption peaks of amide groups around 3300 and 1660  $\text{cm}^{-1}$ , corresponding to amide N–H stretching and carbonyl C=O stretching, respectively. Also, the absorption peaks of aromatic ether linkages (Ar–O–Ar) were observed at 1240  $\text{cm}^{-1}$  in all cases. All dendrons showed unimodal molecular weight distribution with polydispersity values between 1.1 and 1.2, which shows the effectiveness of this orthogonal synthetic approach of poly(arylene ether amide) dendrons. But the molecular weights of these dendrons might be overestimated in GPC measurement with dimethylformamide with lithium bromide (10 mmol/L) as an eluent,<sup>5b</sup> and therefore, the exact masses of these dendrons were monitored by MALDI-TOF spectroscopy. Up to the  $\text{G}_3$  dendrons, single or quadruple  $\text{Na}^+$  adducts were observed in the MALDI spectrum using the dithranol matrix with sodium iodide as ionizing agents. The multication adducts are not often observed in the MALDI-TOF spectrum of dendritic polymers but may be originated from the high amide contents of these dendrons.<sup>8</sup> In the case of higher generation dendrons, ionization might be so difficult and only fragmented polymer-like species were observed, and the variation of matrix or ionizing agents was not effective in these cases.

All poly(aryl ether amide) dendrons show enhanced solubility resulting from dendritic macromolecular structures compared with the linear or hyperbranched poly(aryl ether amides).<sup>9</sup> These dendrons were easily soluble in common organic solvents such as dichloromethane, chloroform, tetrahydrofuran, and dimethylformamide while the corresponding linear poly(aryl ether amides) often meet solubility problem in chlorinated solvents unlike other linear poly(aryl ethers). Thermal properties of these dendrons were measured by DSC and TGA. All

eight dendrons were amorphous, and any melting transition was not observed in DSC.  $\text{G}_1$  and  $\text{G}_2$  dendrons showed glass transition temperatures between 109 and 181 °C, but higher generation dendrons did not show any thermal transition up to 300 °C. It is not quite certain but seems that higher generation dendrons show higher glass temperatures and that the glass transition temperature difference between  $\text{G}_n\text{-NH}_2$  and  $\text{G}_n\text{-F}$  decreases as the generation number increases. All dendrons were highly thermally stable and showed no weight loss up to 300 °C. In addition,  $\text{G}_3\text{-NH}_2$  and  $\text{G}_4\text{-NH}_2$  showed visible mild fluorescence around 400 nm by excitation with 280 nm light, which the phenyl groups strongly absorbs, but lower generation dendrons showed only weak emission in this wavelength range. This generation-dependent fluorescence may reflect the highly globular geometry of higher generation poly(aryl ether amide) dendrons and the resulting enhanced energy transfer processes within them.<sup>10</sup>

In conclusion, poly(aryl ether amide) dendrons up to fourth generation were efficiently synthesized through an orthogonal convergent approach using both  $\text{S}_\text{N}\text{Ar}$  and amidation reactions. Each single orthogonal reaction produced next generation dendrons with high purity after simple precipitation.

**Supporting Information Available:** A table summarizing the properties of all dendrons, all synthetic procedures,  $^1\text{H}$  NMR, FTIR, DSC, MALDI-TOF mass, ultraviolet, and photoluminescence spectrum of dendrons. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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