

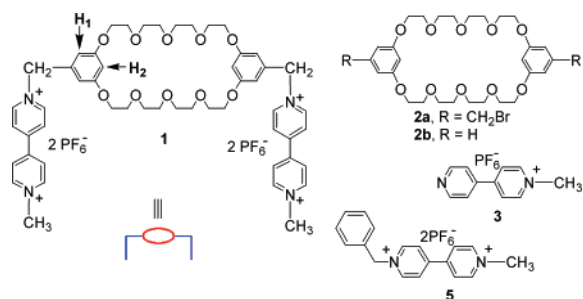
## Formation of a Supramolecular Hyperbranched Polymer from Self-Organization of an AB<sub>2</sub> Monomer Containing a Crown Ether and Two Paraquat Moieties

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Supramolecular chemistry is being widely studied with the aim of developing sophisticated chemical systems from small building blocks by molecular recognition, self-replication, and self-organization based on noncovalent interactions.<sup>1</sup> The combination of supramolecular chemistry and polymer science has led to the appearance of a new field, supramolecular polymers.<sup>2</sup> In the past decade, chemists elegantly fabricated a large variety of supramolecular polymers.<sup>3</sup> However, almost all of these polymers are only one-dimensional.<sup>2,3</sup> Hyperbranched polymers,<sup>4</sup> three-dimensional polymers prepared from polycondensations of AB<sub>m</sub> ( $m \geq 2$ ) monomers, have potential applications as processing modifiers,<sup>5</sup> toughening additives,<sup>6</sup> drug delivery vehicles,<sup>7</sup> synthesis supporting materials,<sup>8</sup> advanced coatings,<sup>9</sup> polymeric electrolytes,<sup>10</sup> and optical waveguide materials.<sup>11</sup> Here, we report the formation of a supramolecular hyperbranched polymer from self-organization of an AB<sub>2</sub> monomer **1** containing complementary recognition sites, a bis(*m*-phenylene)-32-crown-10, and two paraquat moieties.<sup>12</sup>

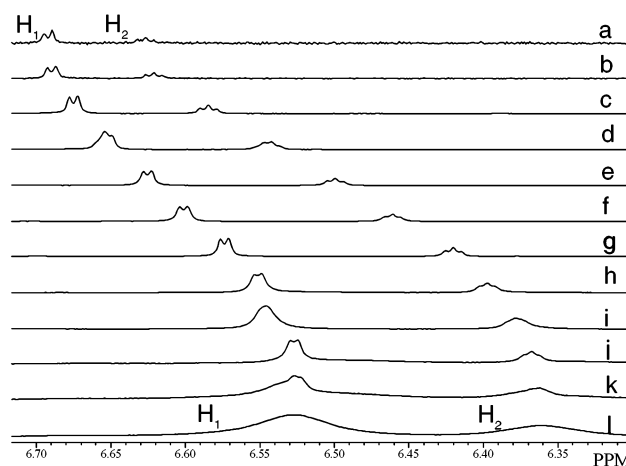


The AB<sub>2</sub> monomer **1** was prepared by the reaction between difunctionalized crown ether **2a**<sup>13</sup> and pyridinium salt **3**<sup>14</sup> followed by ion exchange. At high concentrations, intermolecular complexation of **1** can lead to the formation of hyperbranched supramolecules **4** (Scheme 1). The proton NMR spectra of **1** (Figure 1) are

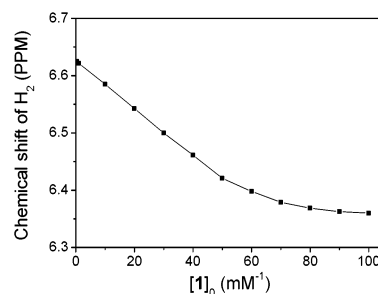
**Scheme 1.** Schematic Illustration of the Formation of the Hyperbranched Supramolecules **4** from the Self-Organization of the AB<sub>2</sub> Monomer **1**



concentration dependent, reflecting the involvement of fast-exchanging noncovalent interactions in solution. The relationship between the chemical shift of H<sub>2</sub> on **1** and its initial concentration is shown in Figure 2. At first, the chemical shift decreased almost linearly with increasing concentration, then slowed, and at 100 mM appeared to level off. These results demonstrated that the percentage of complexed crown ether moieties increased with increasing concentration of **1**, showing the formation of supramolecular hyperbranched polymer **4**. Values of the fraction *p* of complexed crown moieties and the degree *n* of polymerization at different initial



**Figure 1.** Partial proton NMR spectra (400 MHz, CD<sub>3</sub>CN, 22 °C) of **1** at different concentrations: (a) 0.333, (b) 1.00, (c) 10.0, (d) 20.0, (e) 30.0, (f) 40.0, (g) 50.0, (h) 60.0, (i) 70.0, (j) 80.0, (k) 90.0, and (l) 100 mM.



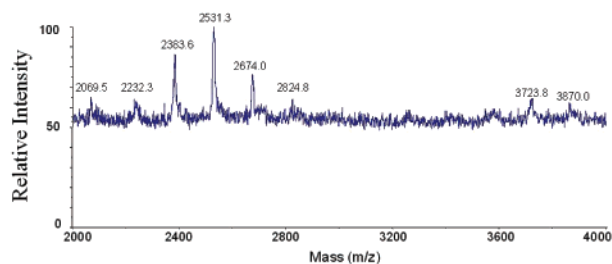
**Figure 2.** Relationship between the chemical shift of H<sub>2</sub> on **1** and the initial concentration of **1**.

**Table 1.** Calculated Values of *p* and *n* at Different Initial Concentrations of **1** Based on  $K_a = 380$  and  $100 \text{ M}^{-1}$  (ref 15)

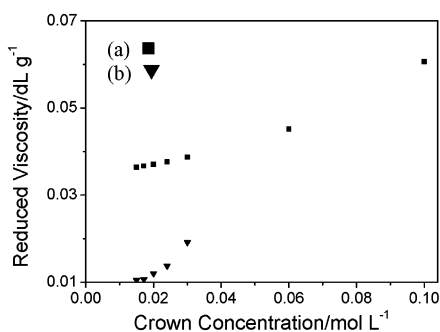
[1] <sub>0</sub> (mM)	<i>p</i> <sup>a</sup>	<i>n</i> <sup>a</sup>
1.00	0.381 (0.156)	1.62 (1.18)
10.0	0.818 (0.586)	5.49 (2.41)
50.0	0.952 (0.852)	20.8 (6.76)
70.0	0.965 (0.886)	28.6 (8.77)
90.0	0.972 (0.908)	35.7 (10.9)
100	0.975 (0.916)	40.0 (11.9)

<sup>a</sup> Values are for  $K_a = 380 \text{ M}^{-1}$ , and values in parentheses are for  $K_a = 100 \text{ M}^{-1}$ .

concentrations of **1** were estimated according to the apparent association constant of the model system based on **2b** and **5** and for a reduced value (Table 1).<sup>15</sup> As the concentration increases, the calculated size of aggregates increases to truly large values, and supramolecular polymers are formed. For example, at  $[1]_0 = 100 \text{ mM}$ ,  $n = 40.0$  for  $K_a = 380 \text{ M}^{-1}$ , corresponding to a polymer molar mass of  $5.94 \times 10^4 \text{ g/mol}$ !



**Figure 3.** Partial MALDI-TOF mass spectrum of the supramolecular hyperbranched polymer **4** measured in the positive-ion mode using 2,5-dihydroxybenzoic acid as the matrix and acetone as the solvent.



**Figure 4.** Reduced viscosity as a function of crown concentration (solutions in acetonitrile at 22 °C): (a) **1**, (b) **2b** and **5** (molar ratio 1:2).

The MALDI-TOF mass spectrum (Figure 3) provided support for the formation of the supramolecular hyperbranched polymer **4**. The strongest peak was found at  $m/z$  1049.7 (100%), which corresponds to  $[1 - 3PF_6]^+$ . Three peaks were found for the dimer  $1_2$ :  $m/z$  2824.8  $[1_2 - PF_6 + H]^+$  (0.9%), 2531.3  $[1_2 - PF_6 - 2HPF_6]^+$  (1.5%), 2383.6  $[1_2 - 4HPF_6 - H]^+$  (1.2%). Two peaks correspond to the trimer  $1_3$ :  $m/z$  3870.0  $[1_3 - PF_6 - 3HPF_6]^+$  (0.8%) and 3723.8  $[1_3 - PF_6 - 4HPF_6]^+$  (0.9%). One peak could be attributed to the pentamer  $1_5$ :  $m/z$  2232.3  $[1_5 - 5PF_6]^{3+}$  (0.9%). Two peaks were due to the hexamer  $1_6$ :  $m/z$  2674.0  $[1_6 - 6PF_6 - CH_3]^{3+}$  (1.1%) and 2069.5  $[1_6 - PF_6 - 3HPF_6 - 3CH_3]^{4+}$  (0.9%).

Viscous flow is characteristic of polymer solutions. Therefore, we turned to viscometry for direct physical evidence of the formation of large self-organized noncovalent polymers.<sup>16</sup> The reduced viscosity of solutions of **1** in acetonitrile increased in nonlinear fashion with the concentration (Figure 4), which reflects the increase of the size of supramolecular hyperbranched polymer **4** with the concentration of **1**. Under the same molar concentration of crown ether units, the solutions of **4** have much higher viscosity than the solutions of a model system containing simple crown ether **2b** and paraquat derivative **5** (molar ratio 1:2). The much higher viscosity observed with **4** can be partially attributed to the polyelectrolyte effect.<sup>17</sup>

In summary, we demonstrated that the  $AB_2$  monomer **1** can self-organize to form a supramolecular hyperbranched polymer in solution. A major limitation of this system is the high monomer concentration (100 mM = 150 g/L) required for high degrees of polymerization. This requires design/syntheses of host-guest systems with higher association constants.<sup>18</sup> Nonetheless, the present results provide proof of principle for a new method of construction of reversible<sup>19</sup> (pseudorotaxane) and potentially permanent (rotaxane, by introduction of appropriate blocking groups on the paraquat units) mechanically linked hyperbranched systems. The utilization of noncovalent interactions can potentially be expanded to prepare other three-dimensional dendritic architectures. Currently, we are focusing on these goals.

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**Supporting Information Available:** Synthesis of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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