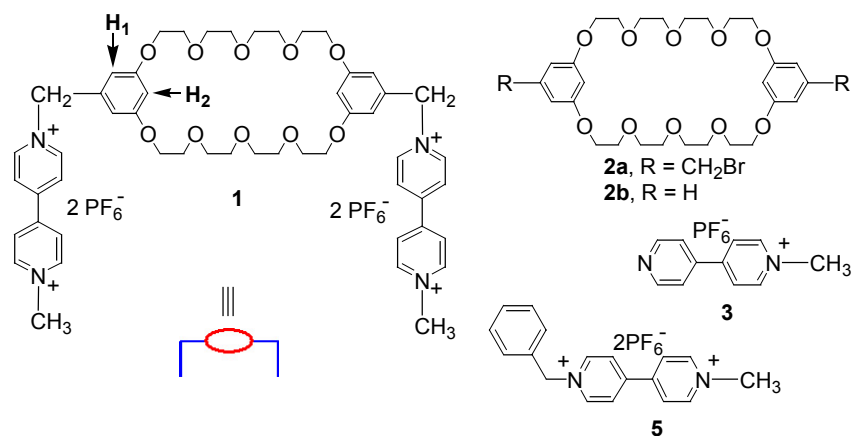


Chapter 20

Formation of a Supramolecular Hyperbranched Polymer from Self-Organization of an AB₂ Monomer Containing a Crown Ether and Two Paraquat Moieties

20.1. INTRODUCTION

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.¹ The combination of supramolecular chemistry and polymer science has led to the appearance of a new field, supramolecular polymers.² In last decade chemists elegantly fabricated a large variety of supramolecular polymers.³ However, almost all of these polymers are only one-dimensional.^{2,3} Hyperbranched polymers,⁴ three-dimensional polymers prepared from polycondensations of AB_m ($m \geq 2$) monomers, have potential applications as processing modifiers,⁵ toughening additives,⁶ drug delivery vehicles,⁷ synthesis supporting materials,⁸ advanced coatings,⁹ polymer electrolytes,¹⁰ and optical waveguide materials.¹¹ Here we report the formation of a supramolecular hyperbranched polymer from self-organization of an AB₂ monomer **1** containing complementary recognition sites, a bis(*m*-phenylene)-32-crown-10 and two paraquat moieties, in solution.¹²



20.2. RESULTS AND DISCUSSION

The AB₂ monomer **1** was prepared by the reaction between difunctionalized crown ether **2a**¹³ and pyridinium salt **3**¹⁴ 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 concentration dependent, reflecting the involvement of fast-exchanging noncovalent interactions in solution. The relationship between the chemical shift of H₂ 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 concentrations of **1** were estimated according to the apparent association constant of the model system based on **2b** and **5** (Table 1)¹⁵ and for a reduced value. 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 $5.94 \times 10^4 \text{ g/mole!}$

Scheme 1. Schematic illustration of the formation of the hyperbranched supramolecules **4** from the self-organization of the AB₂ monomer **1**.

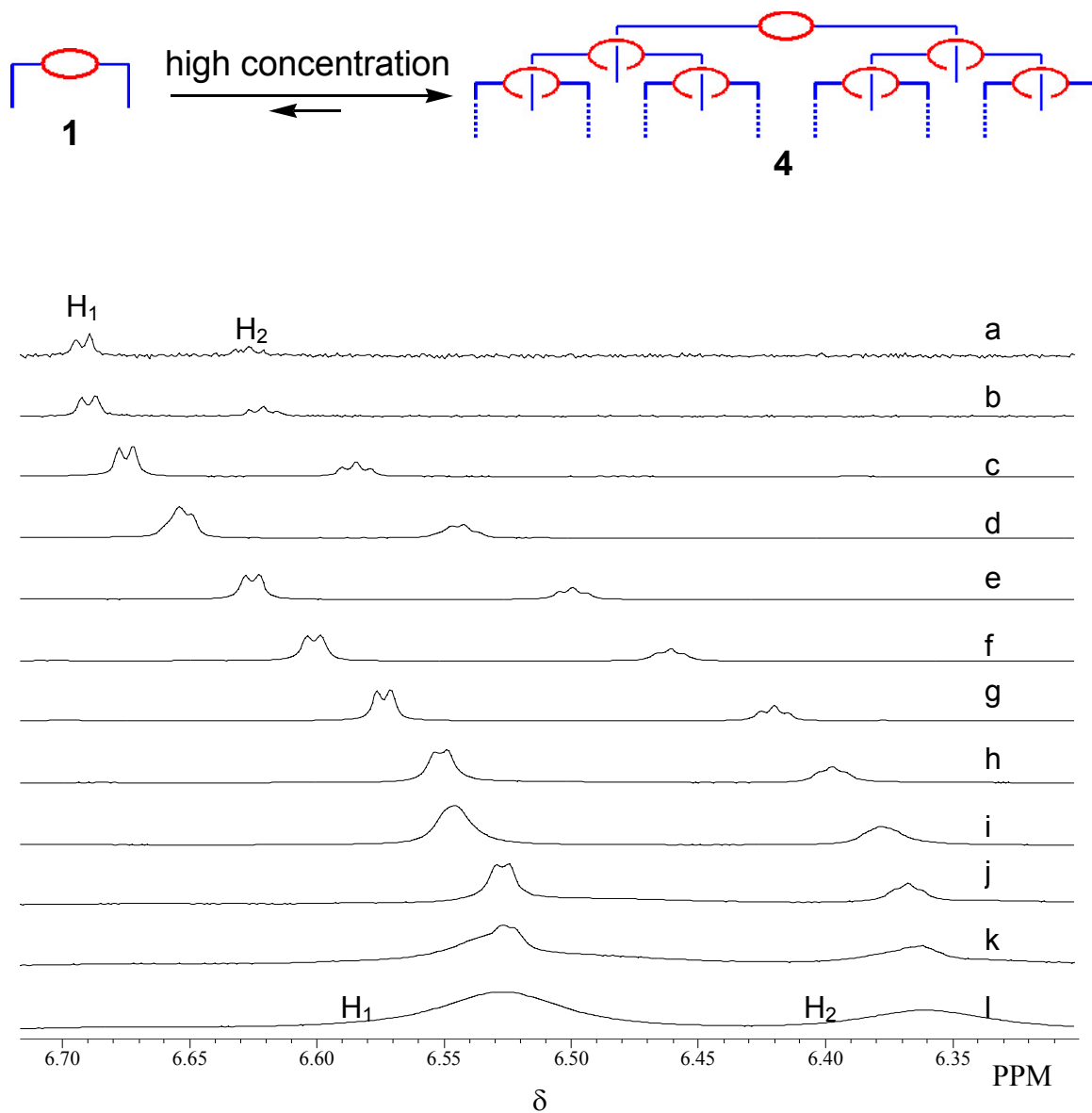


Figure 1. Partial proton NMR spectra (400 MHz, CD₃CN, 22 °C) of **1** at different concentrations: (a) 0.333, (b) 1.00, (c) 10.0, (d) 20.0, (e) 30.0, (f) 40.0, (g) 50.0, (h) 60.0, (i) 70.0, (j) 80.0, (k) 90.0, and (l) 100 mM.

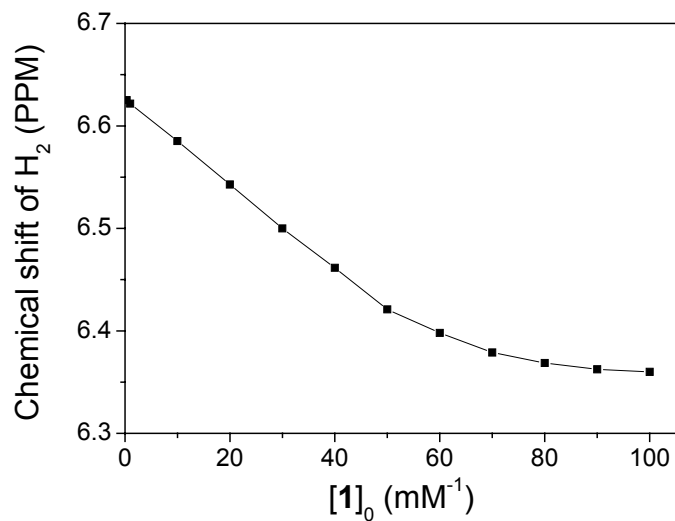


Figure 2. The relationship between the chemical shift of H₂ on **1** and the initial concentration of **1**.

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 $[\mathbf{1} - 3\text{PF}_6]^+$. Three peaks were found for the dimer **1**₂: m/z 2824.8 $[\mathbf{1}_2 - \text{PF}_6 + \text{H}]^+$ (0.9%), 2531.3 $[\mathbf{1}_2 - \text{PF}_6 - 2\text{HPF}_6]^+$ (1.5%), 2383.6 $[\mathbf{1}_2 - 4\text{HPF}_6 - \text{H}]^+$ (1.2%). Two peaks correspond to the trimer **1**₃: m/z 3870.0 $[\mathbf{1}_3 - \text{PF}_6 - 3\text{HPF}_6]^+$ (0.8%) and 3723.8 $[\mathbf{1}_3 - \text{PF}_6 - 4\text{HPF}_6]^+$ (0.9%). One peak could be attributed to the pentamer **1**₅: m/z 2232.3 $[\mathbf{1}_5 - 5\text{PF}_6]^{3+}$ (0.9%). Two peaks were due to the hexamer **1**₆: m/z 2674.0 $[\mathbf{1}_6 - 6\text{PF}_6 - \text{CH}_3]^{3+}$ (1.1%) and 2069.5 $[\mathbf{1}_6 - \text{PF}_6 - 3\text{HPF}_6 - 3\text{CH}_3]^{4+}$ (0.9%).

Table 1. Calculated values of p and n at different initial concentrations of **1** based on $K_a = 380$ and 100 M^{-1} .¹⁵

$[\mathbf{1}]_0$ (mM)	p^*	n^*
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)

* Values outside of brackets are for $K_a = 380 \text{ M}^{-1}$ and in brackets are for $K_a = 100 \text{ M}^{-1}$.

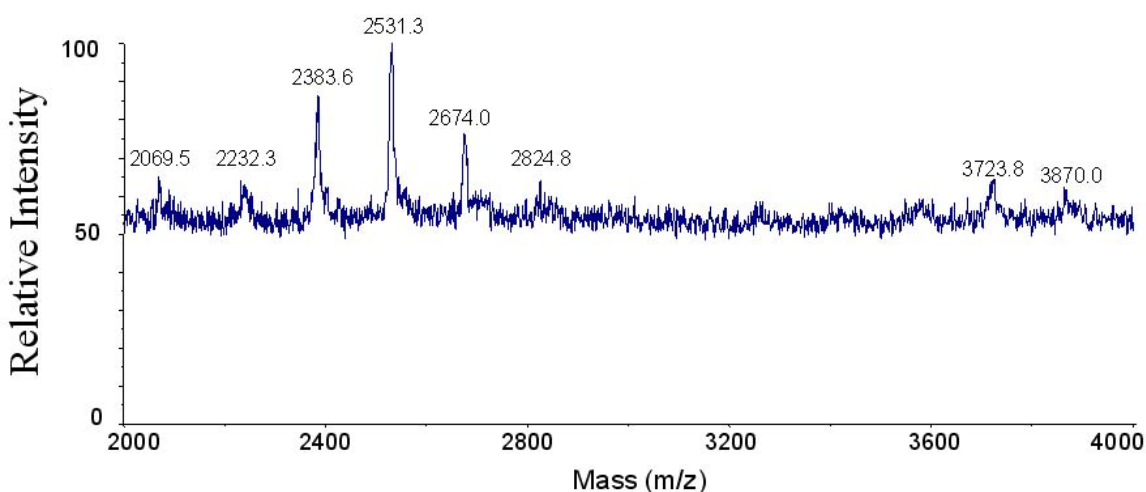


Figure 3. The partial MALDI-TOF mass spectrum of the supramolecular hyperbranched polymer **4**. The spectrum was measured in the positive-ion mode using 2,5-dihydroxybenzoic acid as the matrix and acetone as the solvent.

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.¹⁶ 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.¹⁷

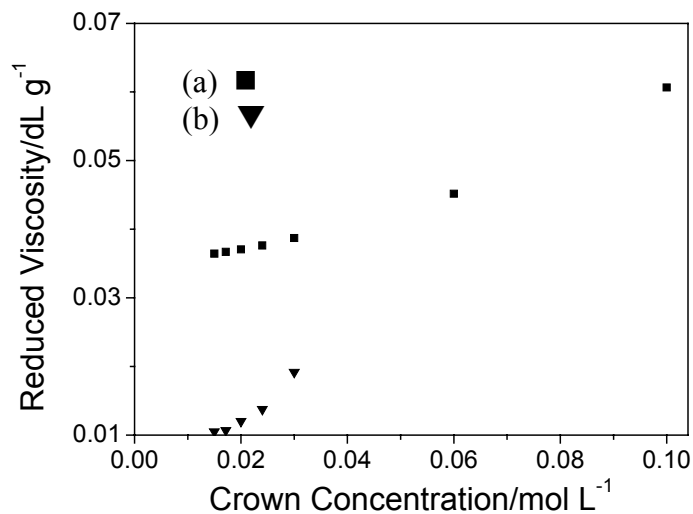


Figure 4. Reduced viscosity as a function of crown concentration (solutions in acetonitrile at 22 °C): (a) **1**, (b) **2b** and **5** (molar ratio 1:2).

20.3. CONCLUSIONS

In summary, we demonstrated that the AB₂ 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.¹⁸ Nonetheless, the present results provide proof of principle for a new method of construction of reversible¹⁹ (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.

20.4. ACKNOWLEDGEMENTS

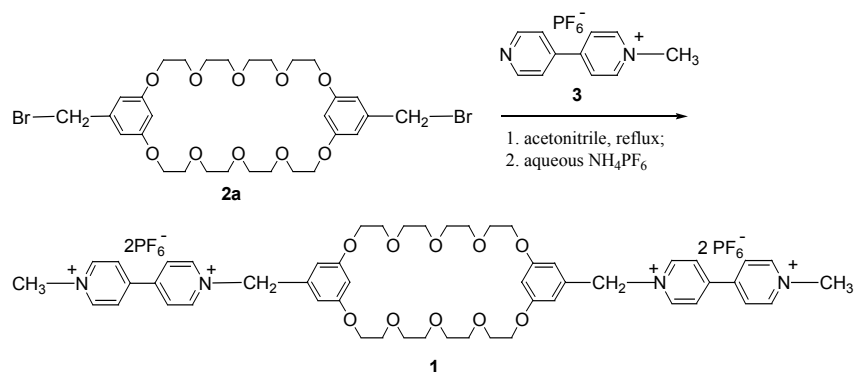
This work was supported by the National Science Foundation (DMR0097126) and the Petroleum Research Fund (40223-AC7). Mass spectra were provided by the Washington University Resource for Biomedical and Bio-organic Mass Spectrometry (NIH P41RR0954).

20.5. SUPPORTING INFORMATION

Experimental Details of Proton NMR Characterizations, Viscosity Measurements and MALDI-TOF Spectrometry

Solutions at different concentrations were prepared independently and characterized on an INOVA 400 proton NMR instrument. The solvent used for all solutions was acetonitrile- d_6 . Reduced viscosities were measured with acetonitrile as the solvent on a Cannon-Ubbelohde semi-micro dilution viscometer with 200 centipoise inner diameter capillary. The association constant (K_a) for the model system based on **2b** and **5** was determined to be $380 (\pm 38) \text{ M}^{-1}$ in acetonitrile by using the Benesi-Hildebrand method (Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703-2707.). A reduced value, 100 M^{-1} , was also used to estimate the values of n and p considering the electron-withdrawing effect of paraquat moieties to aromatic rings of the crown ether unit. **1** was submitted for MALDI-TOF as a solid after dried in vacuum. The sample was dissolved in acetone and mixed 1:2 with the 2,5-dihydroxybenzoic acid matrix in acetone. The spectrum was recorded in positive mode on PerSeptive Voyager RP-DE MALDI-TOF mass spectrometer.

Synthesis of the AB₂ Monomer (**1**)



In a 50-mL round-bottom flask equipped with a magnetic stirrer, **2a** (0.360g, 0.500 mmol), **3** (0.323 g, 1.02 mmol), and acetonitrile (20 mL) were refluxed for 24 hours. The yellow solution was precipitated in diethyl ether to afford a pale yellow solid, which was dissolved in a minimum volume of deionized water and solid NH₄PF₆ was added until no further precipitation was observed. The product was recrystallized from deionized water three times to afford **1** as a pale yellow solid, 0.56 g (76%). mp 236.9-237.7 °C. The proton NMR spectrum of the product is shown in Figure S1. ¹H NMR (400 MHz, CD₃COCD₃, 22 °C) δ(ppm): 9.41 (8H, m), 8.80 (8H, m), 6.74 (4H, m), 6.50 (2H, m), 6.02 (4H, s), 4.78 (6H, s), 4.06 (8H, t, *J* = 4.5 Hz), 3.82 (8H, t, *J* = 4.5 Hz), and 3.66-3.73 (16H, m). HRFABMS (NBA/PEG) *m/z* calcd for [M - PF₆]⁺ C₅₂H₆₄N₄O₁₀P₃F₁₈, 1339.3548, found 1339.3522, error 1.9 ppm. Anal. calcd for C₅₂H₆₄N₄O₁₀P₄F₂₄: C, 42.04; H, 4.35; N, 3.77. Found: C, 41.83, 41.75; H, 4.39, 4.28; N, 3.62, 3.67.

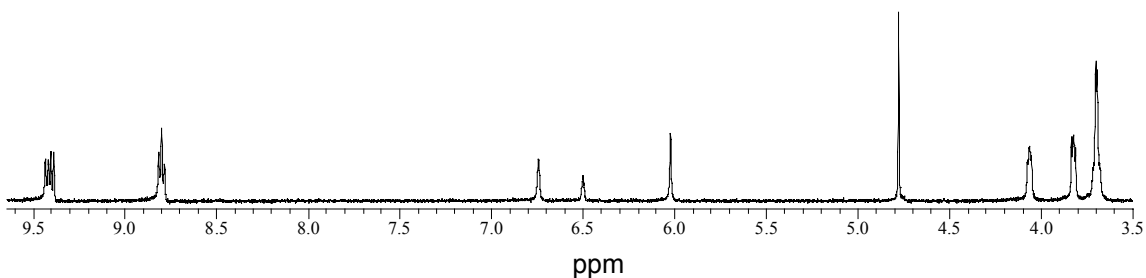


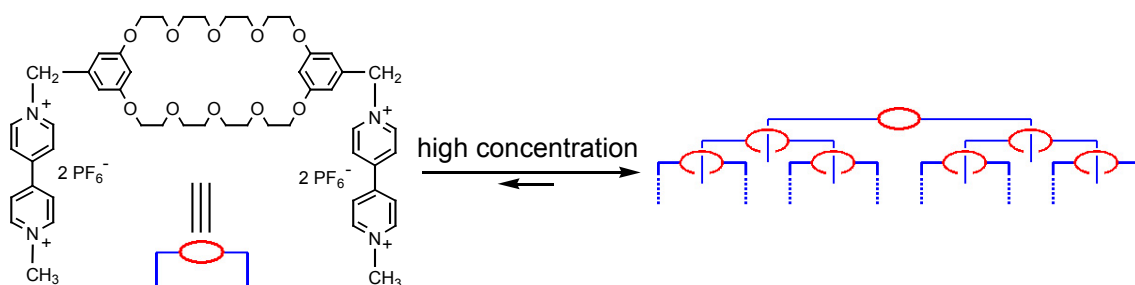
Figure S1. ¹H NMR Spectrum (400 MHz, CD₃COCD₃, 22 °C) of **1**.

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TOC Graphic:

Abstract: An AB₂ monomer containing a bis(*m*-phenylene)-32-crown-10 and two paraquat moieties was designed and prepared. It self-organized to form a supramolecular hyperbranched polymer in solution.
