



**A Supramolecular Hyperbranched Polymer Based on  
Molecular Recognition Between Benzo-21-Crown-7 and  
Secondary Ammonium Salt**

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## ARTICLE TYPE

## A supramolecular hyperbranched polymer based on molecular recognition between benzo-21-crown-7 and secondary ammonium salt

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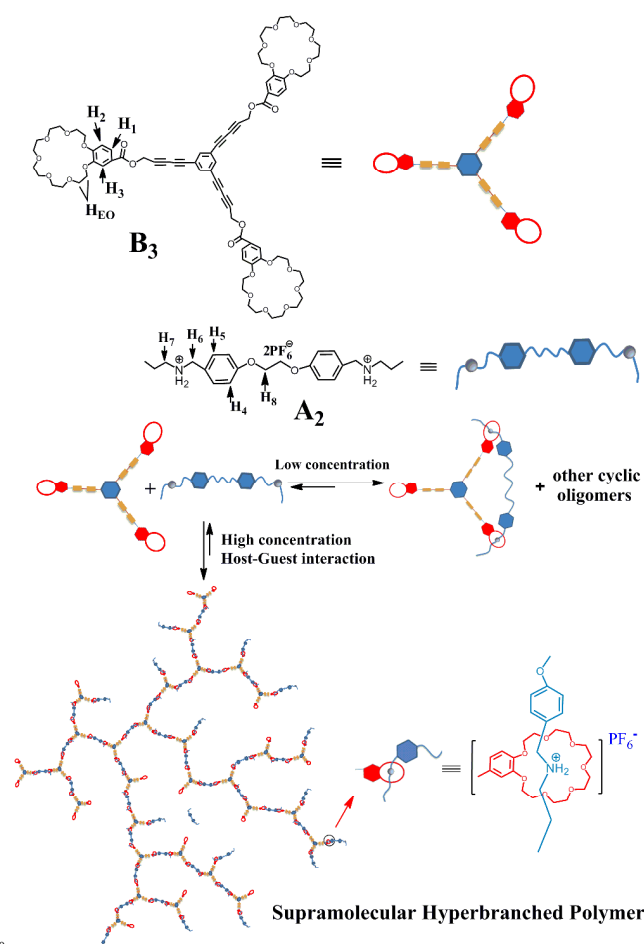
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A novel A<sub>2</sub>-B<sub>3</sub>-type supramolecular hyperbranched polymer was prepared based on the benzo-21-crown-7/secondary ammonium salt recognition motif. The resulting supramolecular polymer exhibited a reversible disassembled-assembled process by adding or removing potassium ion.

Supramolecular polymers are defined as polymeric systems that extend beyond the molecule and utilize noncovalent interactions to control the self-assembly of monomeric units into larger polymeric architectures.<sup>1</sup> Up to now, many kinds of supramolecular polymers employing host-guest interactions,<sup>2</sup> hydrogen bonds,<sup>3</sup> metal coordination,<sup>4</sup> and  $\pi$ - $\pi$  stacks<sup>5</sup> have been reported. Depending on the different numbers and species of host and guest moieties in the monomers, various topologies can be prepared, such as linear,<sup>6</sup> star-shaped,<sup>7</sup> hyperbranched,<sup>8</sup> cross-linked<sup>9</sup> supramolecular polymers. Among these supramolecular polymers, supramolecular hyperbranched polymers (SHPs) have attracted interest due to their unique chemical and physical properties.<sup>8</sup> They can be constructed from unbalanced complementary host and guest unimers, such as AB<sub>2</sub>-type heterotritopic monomers<sup>8a-c</sup> or two-component mixtures of A<sub>2</sub>-B<sub>3</sub>-type heterocomplementary monomers.<sup>8d-e</sup> Huang and Gibson reported a SHP based on AB<sub>2</sub>-type host-guest interaction between BMP32C10 and paraquat units,<sup>8a</sup> as the concentration of monomer increased, the size of aggregates of this system also increased. Alternatively, a novel photoreversible SHP using the host-guest complexation of azobenzene dimer (A<sub>2</sub> monomer) and  $\beta$ -CD trimer (B<sub>3</sub> monomer) was also reported by Zhou and Zhu *et al.*<sup>8d</sup>

Among the hyperbranched structures prepared using A<sub>2</sub>-B<sub>3</sub>-type heterocomplementary monomers, it was found that the same dimer guest molecule can form a bigger supramolecular polymer when polymerized with a more rigid trimer host molecule,<sup>8e</sup> and supramolecular gel was formed instead of hyperbranched polymer if host or guest molecule adopted long flexible alkyl linkers.<sup>10</sup> Based on such observations and previous work on hyperbranched polymers and host-guest supramolecular system,<sup>10b,11</sup> we focused our attention on avoiding the formation of gels and cyclic oligomers to effectively construct the SHPs. Rigid molecules, moderate length of chains, and good solubility of monomers in solution may be important in the preparation of SHP. Benzo-21-crown-7 (B21C7) has been found to strongly bind dialkylammonium salts and secondary dialkylammonium salts are able to thread into the cavity of B21C7 to form threaded

structures.<sup>12</sup> The recognition motif has been extensively utilized to fabricate interlocked structures as well as linear supramolecular polymers.<sup>13</sup> Thus, we found it interesting to construct novel adaptive hyperbranched topologies by self-assembly of crown ether-based recognition building blocks. Herein, we report a novel SHP constructed based on the B21C7/secondary ammonium salt recognition motif (Scheme1). We further demonstrated that the disassembly-assembly of the SHP in solution can be reversibly switched by addition or removal of K<sup>+</sup>.

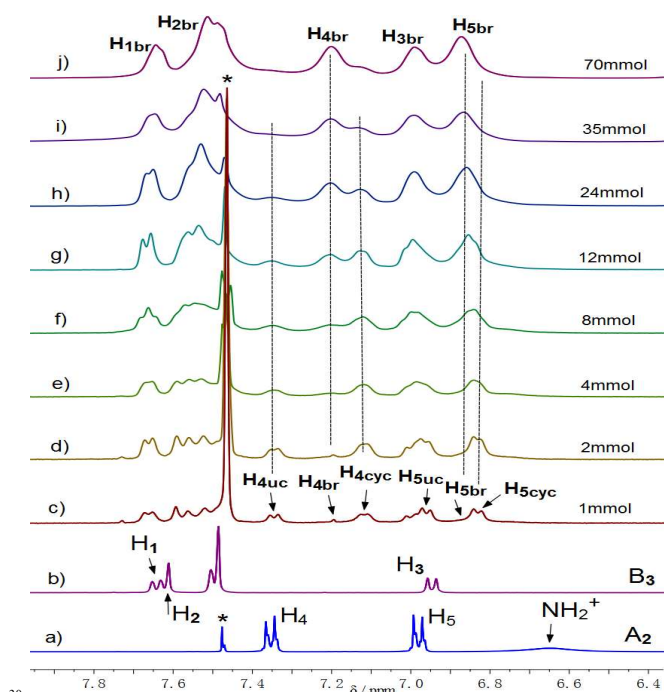


**Scheme 1** Graphical representation of the SHP constructed from monomers A<sub>2</sub> and B<sub>3</sub> by self-assembly.

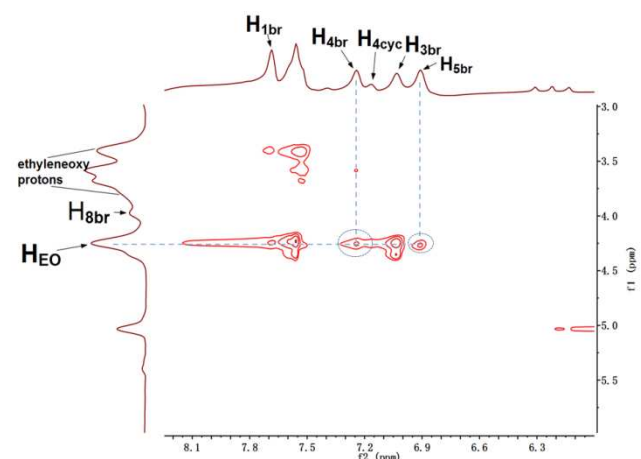
We first designed and synthesized two different monomers: the homoditopic building block  $A_2$ , which contains two symmetrical dialkylammonium units linked by a moderate flexible chain, and the homotripotopic B21C7 monomer  $B_3$ , which consists of three symmetrical B21C7 groups connected by rigid alkynyl chains. The introduction of rigid backbone on the host  $B_3$  may effectively avoid the entanglement of chains leading to the formation of gels, as the moderate length and flexibility of monomer  $A_2$  may allow any appropriate geometry in which the polymer adopted. The synthetic methods and characterization of desired compounds are shown in Supporting Information-8.

The host-guest interaction between  $A_2$  and  $B_3$  is expected to produce cyclic and hyperbranched species (Scheme 1), the ratio of which depends on a number of factors, including the concentration and nature of the linking groups.<sup>14</sup> Proton NMR spectra provided important insights into the host-guest complexation behavior. Upon mixing  $A_2$  and  $B_3$  in  $CDCl_3$ - $CD_3CN$  (1/1, v/v) at  $B_3$  concentrations in the range of 1mM to 70 mM with 1.50 equiv.  $A_2$ , as shown in Fig. 1, complicated and concentration-dependent  $^1H$  NMR spectra were observed, the signals of  $^1H$  NMR spectra were accurately identified by means of  $^1H$ - $^1H$  COSY experiment<sup>12b,13c</sup> (see SI, Figure S2). At low concentration of  $B_3$  (Fig. 1), the signals of protons  $H_4$ ,  $H_5$  of  $A_2$  were all split into two sets of peaks, corresponding to uncomplexed molecules ( $H_{4uc}$ ,  $H_{5uc}$ ) and complexed cyclic oligomers ( $H_{4cyc}$ ,  $H_{5cyc}$ ), which reflected the slow-exchange complexation between B21C7 and secondary ammonium salt moieties on the  $^1H$  NMR time scale. In addition, small sharp peaks ( $H_{4br}$ , 7.23 ppm) corresponding to the hyperbranched

oligomers were also observed, indicating that cyclic oligomers dominate at low concentration. The complexed aromatic protons  $H_4$ ,  $H_5$  on  $A_2$  shifted upfield due to the shielding effect, while the complexed aromatic protons  $H_1$ ,  $H_3$  on  $B_3$  moving downfield supported that the secondary ammonium salt moiety  $NH_2^+$  is located at the center of the B21C7 macrocyclic ring.<sup>9b</sup> As the concentration of the monomers increased, the relative intensity of peaks corresponding to the cyclic oligomers (7.13, 6.83 ppm) and uncomplexed species (7.36, 6.98 ppm) decreased, while the relative intensity of peaks (7.21, 6.87 ppm) corresponding to the hyperbranched assembly increased, indicating that SHPs are predominant at relatively high concentration. The  $^1H$  NMR peaks became broad at high concentration also confirming this conclusion. NOESY NMR spectroscopy was further employed to study the formation of SHP. The experiment was recorded at a relatively high concentration ( $B_3$ , 45 mM), as shown in Fig. 2, the strong correlation between  $H_{4br}$  from  $A_2$  and  $H_{EO}$  from  $B_3$  and between  $H_{5br}$  from  $A_2$  and  $H_{EO}$  from  $B_3$  indicated that the dialkylammonium moiety was complexed tightly with the crown ether moiety in the solution.<sup>9b,13c</sup>



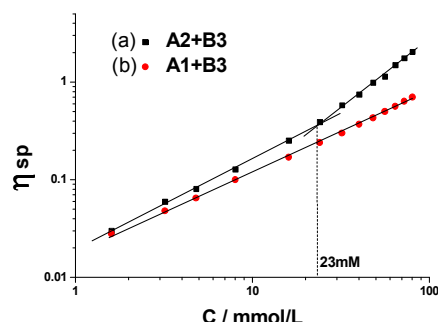
**Fig. 1** Partial  $^1H$  NMR spectra (400 MHz,  $CDCl_3$ - $CD_3CN$  = 1/1, v/v, 298 K) of (a) individual  $A_2$  (b) individual  $B_3$ ; mixtures of  $B_3$  and 1.50 equiv.  $A_2$  at different  $B_3$  concentrations (c) 1mM, (d) 2mM, (e) 4mM, (f) 8mM, (g) 12mM, (h) 24mM, (i) 35mmol, (j) 70mM. Peaks of uncomplexed monomers, cyclic oligomers, and the hyperbranched polymers, are designated as uc, cyc, and br, respectively. Signals affiliated with solvents are denoted by star symbols.



**Fig. 2** Partial NOESY NMR (400 MHz,  $CDCl_3/CD_3CN$  = 1/1, v/v, 298 K) spectrum of a solution of  $B_3$  (45 mM) and 1.5 equiv  $A_2$  (67.5 mM). Peaks of hyperbranched polymers are designated as br.

Viscous flow is a characteristic property of polymer solutions. To further study the self-assembly behavior of  $A_2$  and  $B_3$  in solution, viscosity measurements were performed for this system in  $CHCl_3$ - $CH_3CN$  (1/1, v/v) using a micro-Ubbelohde viscometer (Fig. 3). As a comparison, the specific viscosity of the mixed solution of model compound  $A_1$  and  $B_3$  was also plotted. For the mixed solution of  $A_2$  and  $B_3$ , a double logarithmic representation of specific viscosity versus the concentration of  $B_3$  in chloroform/acetonitrile (1/1, v/v) was obtained. In the low concentration region, the curve has a slope of 1.30, which is a characteristic for non-interacting assemblies of constant size,<sup>15</sup> indicating the predominance of cyclic oligomers in dilute solution. When the concentration was increased above 23 mM (critical polymerization concentration, CPC), a curved slope of 2.15 was obtained, indicating a transition from small cyclic oligomers to bigger hyperbranched polymers. By contrast, specific viscosity changes almost linearly with the concentration of the mixed solution of model compound  $A_1$  and  $B_3$ , indicating that no large sized structures were formed due to only one

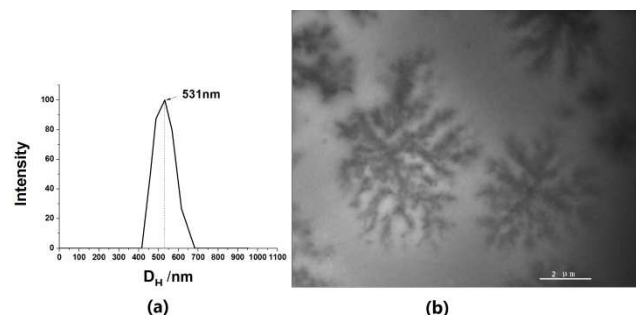
dialkylammonium group on guest A<sub>1</sub>. Furthermore, at the same concentration of crown ether units, the solution of A<sub>2</sub> and B<sub>3</sub> has much higher viscosity than the solution of A<sub>1</sub> and B<sub>3</sub>, the higher viscosity observed in the mixed solution of A<sub>2</sub> and B<sub>3</sub> strongly supported the formation of SHP.



**Fig. 3** Specific viscosity as a function of B<sub>3</sub> concentration (solutions in chloroform/acetonitrile (1: 1, v/v) at 298 K): (a) B<sub>3</sub> with 1.5 equiv. A<sub>2</sub>, (b) B<sub>3</sub> with 3 equiv. A<sub>1</sub>.

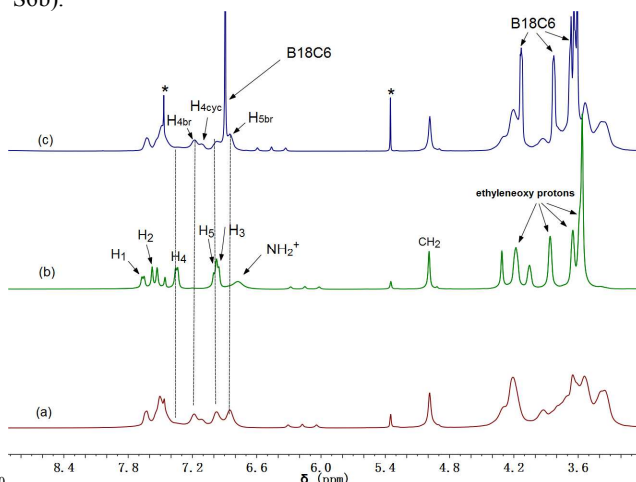
The size and morphology of the obtained SHP were observed using dynamic light scattering (DLS) and transmission electron microscopy (TEM) measurements. DLS can be applied to estimate the size of supramolecular polymer in solution.<sup>16</sup> The solution of B<sub>3</sub> (65 mM, corresponding to 195 mM B21C7 unit concentration) and 1.5 equiv. A<sub>2</sub> in chloroform/acetonitrile (1/1, v/v) has an average hydrodynamic diameter (D<sub>H</sub>) value of 531 nm (Fig. 4a). However, no aggregates were detected for a 10 mM mixed solution of B<sub>3</sub> and A<sub>2</sub> (see SI, Figure S6a), which manifested the formation of SHP depending on the initial concentration of monomers. To observe the real morphology of SHP, TEM was conducted at a high monomer concentration, a drop of sample solution (60 mM B<sub>3</sub> with 90 mM A<sub>2</sub>) was placed on a carbon-coated copper grid. After the solvent evaporated, TEM images were taken. As shown in the representative TEM image (Fig. 4b), large branched aggregates with diameters ranging from 3 μm to 7 μm were observed. The sizes of the aggregates look bigger than those determined using DLS, a close inspection of the aggregates suggests that they are, in fact, a mixture of branches with smaller size. To the best of our knowledge, the average degree of polymerization in supramolecular polymer is dependent on the concentration of the solution and the association constant.<sup>8f</sup> Supramolecular polymer with a larger molecular weight can only be obtained when the system possesses a high monomer concentration. On one hand, during sample preparation, the evaporation of solvent caused the system to have a concentrated state, which can drive further assembly of the supramolecular polymers into larger branched aggregates. On the other hand, branches with smaller size may also superimpose on each other to form macrosized aggregates after the solvent evaporated. The limitations of the TEM technique is difficult to detect the branched structures at a molecular level.<sup>11b</sup> To confirm this, comparative experiments were conducted, where no branches could be observed at the same concentrated solution of individual B<sub>3</sub> or individual A<sub>2</sub>, which eliminates the possibility of large branched structure formed by a sample aggregation of individual B<sub>3</sub> or A<sub>2</sub> in

concentrated solution. XRD was also performed simultaneously to eliminate the possibility of crystallization (see SI, Figure S4).



**Fig. 4** (a) Distribution of the hydrodynamic diameter of a mixture of 65mM B<sub>3</sub> and 97.5mM A<sub>2</sub> in chloroform/ acetonitrile (1 : 1, v/v) at 298 K. (b) Representative TEM image of the supramolecular polymers.

Considering that the B21C7 group can bind K<sup>+</sup> more strongly than the dialkylammonium salt,<sup>12a</sup> we then checked whether the disassembly–assembly of the resulting SHP can be controlled by addition or removal of K<sup>+</sup> in solution (Fig. 5). When 3 equiv. KPF<sub>6</sub> was added to a solution of B<sub>3</sub> (40 mM) with 1.5 equiv. A<sub>2</sub> in CDCl<sub>3</sub>–CD<sub>3</sub>CN (1/1, v/v), the crown ether ring of the B21C7 group of B<sub>3</sub> was occupied by K<sup>+</sup>, driving the NH<sub>2</sub><sup>+</sup> unit to slide out of the cavity of B21C7, a simpler <sup>1</sup>H NMR spectrum was observed due to the disassembly of the SHP (Fig. 5(b)). However, after 3 equiv. benzo-18-crown-6 (B18C6) was subsequently added (Fig. 5(c)), the peaks (H<sub>4</sub>, H<sub>5</sub>) originating from complexed B21C7/secondary ammonium salt units were recovered because K<sup>+</sup> binds B18C6 more tightly, indicating reformation of SHP due to the recovered complexation between B21C7 and secondary ammonium salt. The reversible process was also verified by NOESY and DLS experiments (see SI, Figures S5 and S6b).



**Fig. 5** Partial <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>–CD<sub>3</sub>CN = 1/1, v/v, 298 K) of (a) B<sub>3</sub> (40 mM) with 1.5 equiv. A<sub>2</sub>, (b) after addition of 3 equiv. KPF<sub>6</sub>, and (c) after addition of 3 equiv. B18C6. The asterisk symbols indicate solvent peaks.

In summary, we designed and synthesized a homotritopic monomer containing three Benzo-21-crown-7 units and a complementary homoditopic monomer containing two secondary ammonium salt units. They can self-assemble to form SHP in a concentrated solution. The host–guest interaction between A<sub>2</sub> and B<sub>3</sub> was studied by a combination of various techniques, such as <sup>1</sup>H NMR, COSY NMR, 2D NOESY NMR, viscosity

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