Communication

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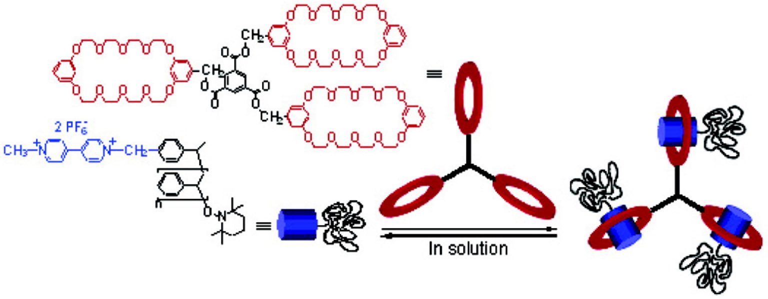

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A Supramolecular Triarm Star Polymer from a Homotritopic Tris(Crown Ether) Host and a Complementary Monotopic Paraquat-Terminated Polystyrene Guest by a Supramolecular Coupling Method

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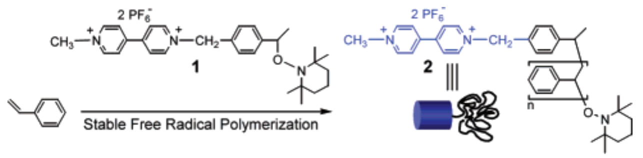
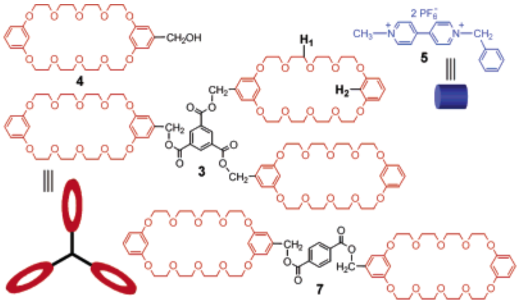
The construction of analogues of traditional macromolecules by supramolecular methods is a topic of great current interest due to not only their topological importance but also their potential functions.[1] Recent examples include dendrimers from cooperative complexation of a homotritopic guest and complementary monotopic dendron hosts,[2] supramolecular modification of dendrimers,[3] a hyperbranched polymer from self-assembly of an AB_2 monomer,[4] and linear polymers from self-organization of well-defined building blocks.[5] Covalent star polymers have been widely studied.[6,7] General methods of preparing them are living polymerizations with multifunctional initiators, coupling reactions of macromolecular chains with multifunctional cores, and polymerizations of difunctional monomers with living polymer precursors as initiators.[6b] Here we report the preparation of the first supramolecular star polymer based on pseudorotaxane complexation.[8] It is from self-assembly of a homotritopic tris(crown ether) host and a complementary monotopic paraquat-terminated polystyrene guest based on the bis(*m*-phyenylene)-32-crown-10/paraquat recognition motif[9] by a supramolecular coupling method, a new method for fabrication of star polymers by using nonconvalent interactions.

The strategy we used to introduce a paraquat moiety at the end of every polystyrene chain is to utilize paraquat-functionalized initiator **1** in the stable free radical polymerization[10] of styrene. The polydispersity from GPC analysis of polymer **2** in 1-methyl-2-pyrrolidinone, 1.37, indicated the living nature of this polymerization. M_n from GPC analysis, 32.3 kg/mol, is close to the value, 35.0 kg/mol, determined from proton NMR integrations of peaks corresponding to pyridinium and aromatic protons. These results demonstrated that every polystyrene chain has a paraquat moiety at one of its two ends.



The homotritopic core molecule, **3**, was prepared by the reaction of monofunctional crown ether **4**[11] and 1,3,5-benzenetricarbonyl trichloride.

Chloroform solutions of host **3** and guest polymer **2** are yellow due to charge-transfer interactions between electron-rich crown ether moieties on **3** and the electron-poor paraquat end unit on **2**. The complex between the homotritopic host **3** and monotopic paraquat-terminated polystyrene guest **2** has a 1:3 stoichiometry as demonstrated by a mole ratio plot (Figure 1a). The model system based on **3** and monotopic guest **5**[5a] also has a 1:3 stoichiometry (Figure 1b). Therefore, supramolecular triarm star polymer **6** forms from tritopic host **3** and monotopic polymeric guest **2** in solution (Scheme 1).



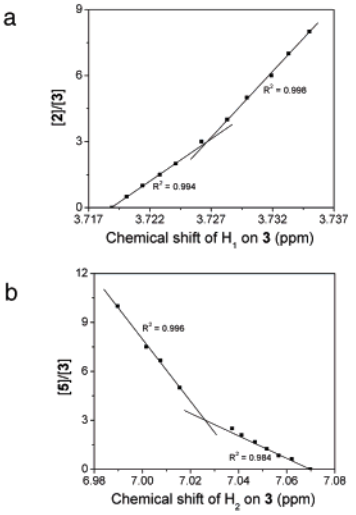
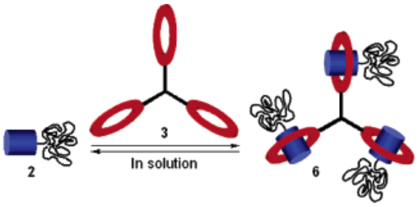


Figure 1. (a) Mole ratio plot for **3** and **2**, indicating 1:3 stoichiometry. The solvent is $CDCl_3$. $[\mathbf{3}]_o = 0.100$ mM. (b) Mole ratio plot for **3** and **5**, indicating 1:3 stoichiometry. The solvent is 2:1 $CD_3COCD_3/CDCl_3$. $[\mathbf{3}]_o = 0.100$ mM.

Scheme 1. Schematic Illustration of the Formation of a Supramolecular Triarm Star Polymer **6** from Homotritopic Host **3** and Monotopic Polymeric Guest **2**



Viscosity studies (Figure 2) provided further evidence for the formation of supramolecular triarm star polymer **6**. As expected, the intrinsic viscosity, [η], did not change from polymer **2** upon addition of monotopic host **4** (0.286 and 0.287 dL/g). However, it increased significantly (~33%) in the solution of ditopic host **7** and polymeric guest **2**, $[\eta] = 0.396$ dL/g; this interaction corresponds to supramolecular chain extension. And finally, the solution

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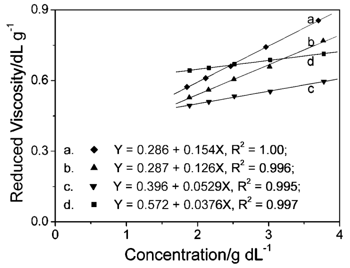

Figure 2. Reduced viscosity as a function of concentration (solutions in chloroform at rt): (a) polymeric guest **2**, (b) monotopic host **4** and polymeric guest **2** (molar ratio 1:1), (c) ditopic host **7** and polymeric guest **2** (molar ratio 1:2), and (d) tritopic host **3** and polymeric guest **2** (molar ratio 1:3).

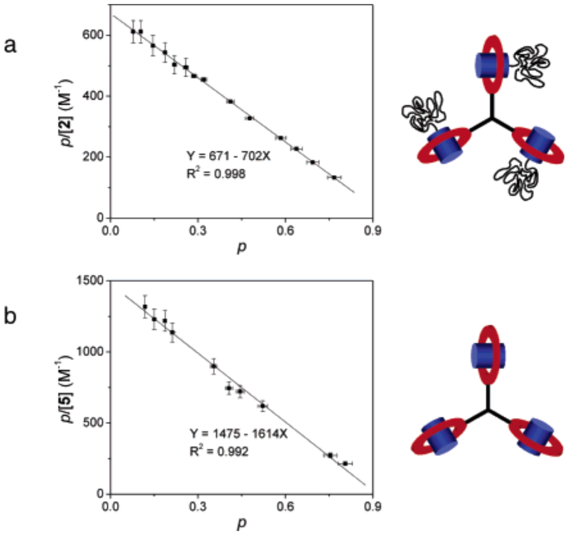

Figure 3. Scatchard plots for the complexations of homotritopic host **3** with (a) monotopic paraquat-terminated polystyrene guest **2** in $CDCl_3$ and (b) model monotopic paraquat guest **5** in 2:1 $CD_3COCD_3/CDCl_3$ at 22 °C. p = complexed fraction of crown ether units. Error bars in p: ±0.03 absolute. Error bars in p/[**2**] and p/[**5**]: ±0.06 relative.

of tritopic host **3** and polymeric guest **2** has an intrinsic viscosity (0.572 dL/g) nearly double that of **2** itself, consistent with formation of the supramolecular triarm star polymer **6**.

To study the relationship among the three crown ether binding sites of **3** during the complexation with polymeric guest **2**, proton NMR characterizations were done on a series of chloroform solutions for which the initial concentration of host **3** was kept constant at 0.100 mM, while the initial concentration of guest **2** was systematically varied. Based on these data, the complexed fraction, p, of crown ether units was determined[12] and a Scatchard plot[13] was made (Figure 3a). The linear nature of this plot demonstrated that the complexation between host **3** and polymeric guest **2** is statistical, i.e., the three crown ether binding sites behave independently. From the intercept and the slope of the plot, the average association constant[14] (K_{av}) is 687 (±82) M^{-1}, which is much smaller than the value, 1550 (±186) M^{-1}, for the model system based on host **3** and model guest **5** in a more polar solvent (Figure 2b),[15] reflecting the steric effect of the polystyryl chains of **2** on host−guest complexation.

In summary, the first supramolecular star polymer based on pseudorotaxane host−guest complexation was prepared. The trapping of the paraquat moieties in this polymer by introducing appropriate blocking groups will produce a mechanically interlocked star polymer. We also provided a new method of preparing guest-terminated macromolecular building blocks, which are very valuable in fabrication of well-defined macromolecular architectures by self-assembly.

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Supporting Information Available: Syntheses of **1**, **2**, **3**, and **7** and an X-ray crystallographic file (CIF) for **BPP34C10•1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Based on these NMR data, Δ_0, the difference in δ values for H_1 of **3** in the uncomplexed and fully complexed species under fast exchange was calculated by extraplotation of a plot of $\Delta = \delta - \delta_u$ vs 1/[**2**]$_0$. Then $p = \Delta/\Delta_0$.

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(14) $K_1 = [\mathbf{3{\cdot}2}]/\{[\mathbf{3}][\mathbf{2}]\}$, $K_2 = [\mathbf{3{\cdot}2_2}]/\{[\mathbf{3{\cdot}2}][\mathbf{2}]\}$, and $K_3 = [\mathbf{3{\cdot}2_3}]/\{[\mathbf{3{\cdot}2_2}][\mathbf{2}]\}$. $K_{av} = (K_1 + K_2 + K_3)/3$. The value of K_{av} is equal to the intercept and the absolute slope of the best fit line in Figure 3. Because K_1:K_2:K_3 = 9:3:1,[13] K_1, K_2, and K_3 were calculated to be 1430, 476, and 159 M^{-1}.

(15) The three association constants corresponding to this model system in 2:1 $CD_3COCD_3/CDCl_3$ were calculated to be 3220, 1070, and 358 M^{-1}.

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