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Supramolecular AA−BB-Type Linear Polymers with Relatively High Molecular Weights via the Self-Assembly of Bis(*m*-phenylene)-32-Crown-10 Cryptands and a Bisparaquat Derivative

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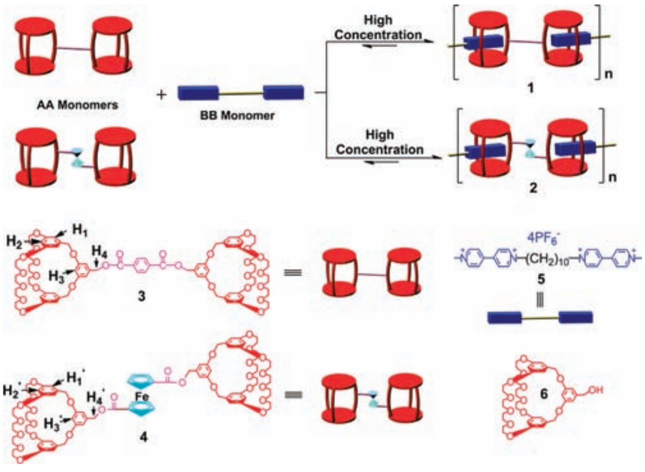
Supporting Information

ABSTRACT: Two novel bis(*m*-phenylene)-32-crown-10-based cryptands, one bearing covalent linkages and the other metal-complex linkages, were designed and prepared. By self-assembly of these biscryptands, which can be viewed as AA monomers, and a bisparaquat, which can be viewed as a BB monomer, AA−BB-type linear supramolecular polymers with relatively high molecular weights were successfully prepared.

Because of architectural differences from traditional covalent polymers, supramolecular polymers, in which noncovalent, mechanically interlocked structures play an important role, are expected to have unique properties and potential applications.[1] In the past decade, supramolecular polymers have been widely studied, and a large variety is known.[2−6] Among them, crown ether-based pseudorotaxane-type supramolecular polymers are very attractive and have been used to prepare various architectures, such as linear,[3] branched,[4] star-shaped,[5] and dendronized.[6] However, in order to prepare large supramolecular polymers, monomers with high association constants are required.[3d,e,7] Cryptands have proved to be much better hosts for paraquat derivatives than the corresponding simple crown ethers;[8] for example, the association constant for hydroxyl-functionalized cryptand **6** and dimethyl paraquat ($K_a = 6.3 \times 10^3\ M^{-1}$ in acetone at 22 °C) is ∼13-fold higher than that between bis(*m*-phenylene)-32-crown-10 (BMP32C10) and dimethyl paraquat.[8d] Morover, unlike the complexes between BMP32C10 and paraquat derivatives with folded or "taco" structures,[9] the complexes between cryptands and paraquat derivatives demonstrate only threaded geometries (pseudorotaxanes) in their X-ray crystal structures.[8] Particularly relevant is the X-ray crystal structure of the pseudorotaxane complex of **6** with dimethyl paraquat.[8d]

Here we report the first two examples of novel AA−BB-type noncovalent supramolecular polymers with relatively high molecular weights based on complexation of BMP32C10 cryptands bearing either covalent (terephthalate) or metal-complex (ferrocene ester) linkages with a bisparaquat. The resulting supramolecular polymers are expected to have well-defined threaded (pseudorotaxane) structures, making it possible to convert them to rotaxanes by attaching bulky stoppers to the ends of the paraquat moieties.

Scheme 1. Schematic Illustration of the Formation of Linear Supramolecular Polymers 1 and 2 by Self-Assembly of AA Monomers 3 and 4, Respectively, with BB Monomer 5



Biscryptands **3** and **4** (the AA monomers) were prepared via the 1-(3′-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI)- and 4-dimethylaminopyridine (DMAP)-promoted coupling reactions of hydroxyl-functionalized cryptand **6**[8d] with terephthalic acid and 1,1′-ferrocenedicarboxylic acid, respectively. The linkers were chosen to assess conformational effects, as **4** with its turnstile-like rotational possibilities is much more flexible than **3**, whose rigid linker imposes a rodlike structure. Bisparaquat **5** (the BB monomer) was obtained via the reaction between 1-methyl-4,4′-bipyridinium hexafluorophosphate and 1,10-dibromodecane followed by counterion exchange; the rather long 10-carbon spacer was chosen based on theory[10] and our earlier studies demonstrating that longer spacers lead to more polymerization and less cyclization.[3d,11] As a result of intermolecular complexation between equivalent amounts of AA monomers **3** and **4** and BB monomer **5** in solution, we expected linear, supramolecular, noncovalent polymers **1** and **2**, respectively, to form at high concentrations (Scheme 1).

Equimolar solutions of **3** and **5** in 1:1 (v/v) chloroform/acetonitrile were deep-yellow as a result of the charge-transfer interaction between the electron-rich aromatic rings of biscryptand **3**

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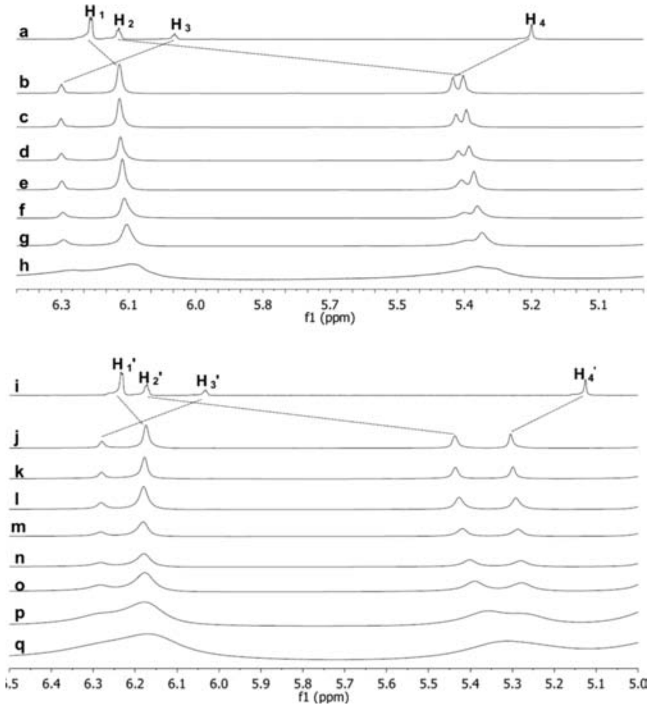

Figure 1. Partial ^{1}H NMR spectra [500 MHz, 1:1 (v/v) $CDCl_3$/CD_3CN, 22 °C]. Upper set of stacked spectra: (a) **3** and (b−h) equimolar solutions of **3** and **5** at concentrations of (b) 87, (c) 135, (d) 164, (e) 212, (f) 247, (g) 290, and (h) 380 mM. Lower set of stacked spectra: (i) **4** and (j−q) equimolar solutions of **4** and **5** at concentrations of (j) 53, (k) 74, (l) 85, (m) 123, (n) 179, (o) 230, (p) 322, and (q) 402 mM.

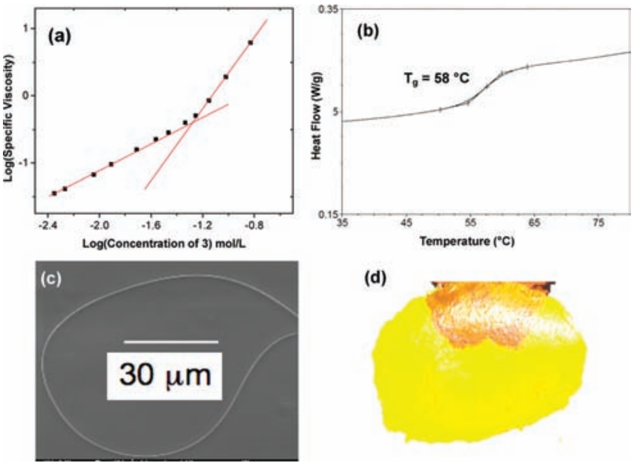

Figure 2. (a) Double-logarithmic plot of specific viscosity of equimolar solutions of **3** and **5** in chloroform/acetonitrile (1/1, v/v) versus concentration. (b) DSC curve of supramolecular polymer **1** (second heating); heating rate 10 °C/min. (c) Scanning electron microscopy (SEM) micrograph of (gold coated) fiber drawn from a concentrated solution of equimolar **3** and **5**. (d) Yellow film cast from an equimolar solution of **3** and **5**.

and the electron-poor pyridinium rings of bisparaquat **5**, providing good evidence of complexation. The ^{1}H NMR spectra were concentration-dependent (Figure 1), indicating the involvement of fast-exchanging noncovalent interactions in solution. The large chemical shift change (~0.8 ppm) of H_2 of biscryptand **3** demonstrated that the percentage of complexed species was concentration-dependent, and the formation of the supramolecular polymer was favored at high concentrations. In addition, all of the proton signals became broad at high concentrations, which indicated the formation of high-molecular-weight polymeric structures. On the basis of the chemical shift change of H_2 of biscryptand **3**, the fraction of complexed biscryptand **3**[12a] (p) and the degree of polymerization (n) were estimated by employing the Carothers equation (Table SI-1).[12b] As the initial concentrations increased, the size of the aggregates increased to larger values, and a supramolecular noncovalent polymer was formed. For example, at 290 mM, n was estimated to be 93 ± 47,[12c] which corresponds to polymer **1** with a number-average molecular weight (M_n) of 241 kDa; this is much higher than the values for BMP32C10-based systems at similar concentrations.[3a,e−g]

Alternatively, using the K_a value for the model complexation of **6** with dimethyl paraquat[8d] in the equation[3e,7] $n = (K_a[\text{conc}])^{1/2}$ at 290 mM, we calculate $n = 43$, $M_n = 112$ kDa for polymer **1**. This equation implicitly assumes that the process is isodesmic and produces no cyclic species, and therefore, these values are considered to be upper bounds. Note that this n value falls near the range of values estimated by NMR.[12c]

Further direct physical evidence for the formation of a large, supramolecular, noncovalent polymer was obtained from a viscosity study. A double-logarithmic plot of specific viscosity versus the initial concentrations of equimolar solutions of **3** and **5** in 1:1 (v/v) chloroform/acetonitrile (Figure 2a) yielded a curve with slope of 1.02 at low concentrations, indicating the existence of cyclic species,[13] as with crown ether-based systems.[3] At high concentrations, the curve had a slope of 2.64, indicating the formation of linear supramolecular polymers **1** of increasing size. The critical monomer concentration ($[M]_{crit}$), above which the linear species are formed exclusively, was found to be 53 mM.[14]

In the case of the interaction between **4** and **5**, similar large chemical shift changes of H_2' that were dependent on the initial concentrations of **4** and **5** were observed (Figure 1). All of the proton signals were broadened at high concentrations, indicating the formation of large supramolecular species. From the determination of p[12a] followed by use of the Carothers equation,[12b] the degree of polymerization n was estimated (Table SI-2). For example, at 230 mM, the n was estimated to be 22 ± 2,[12c] which corresponds to polymer **2** with M_n = 59 kDa. The plot of log(specific viscosity) versus log(concentration) for solutions of **4** and **5** yielded slopes of 1.27 and 2.77 at low and high concentrations, respectively, and $[M]_{crit}$ = 71 mM; the higher $[M]_{crit}$ value suggests that cyclic species were more abundant in polymer **2** than in polymer **1**. This could be ascribed to the relatively flexible ferrocene linkage, which can rotate in solution and thus favor the formation of cyclic species by reducing the end-to-end distances of linear $(AA{-}BB)_n$ species.[10] Since the n values estimated from the NMR results are based on the assumption that there are no cyclic species,[12] these values are erroneously high.

The $[M]_{crit}$ values for **3**/**5** and **4**/**5** are in the range 10−200 mM reported for ditopic ureidopyrimidone (UPy) systems.[2b,13] However, the slopes above $[M]_{crit}$ are smaller than those of the latter systems (in the range 3−6)[2b,13] and the theoretically predicted value of 3.5−3.7,[15] consistent with the smaller association constant of the present system relative to the UPy systems ($K_a > 10^7\ M^{-1}$). Nonetheless, these slopes are among the highest values reported for pseudorotaxane-based supramolecular polymers. Moreover, at the highest measured concentration, 149 mM, the specific viscosity of an equimolar solution of **3** and **5** was 6.3. This is the highest specific viscosity reported for a supramolecular polymer based on pseudorotaxane formation, reflecting the relatively high association constant in this system in comparison with previously studied crown ether-based systems ($K_a < 10^3$ M^{-1}).

Differential scanning calorimetry (DSC) revealed that the solid from evaporation of solutions of **3** and **5** had a repeatable glass-transition temperature (T_g) of 58 °C (Figure 2b), and the solid obtained from **4** and **5** had a T_g of 47 °C. In contrast, hosts **3** and **4** and guest **5** all are crystalline solids (mp 177−178, 75−76, and 276−278 °C, respectively). No melting transitions were observed in the solid supramolecular polymers, nor was crystallization observed up to 180 °C. Thermogravimetric analysis (TGA) revealed that supramolecular polymers **1** and **2** underwent 5% weight loss up to 241 and 291 °C, respectively.

In addition transparent amorphous films (Figure 2d: the red color in the photo is a part of the paper on which the film was cast) were cast from concentrated equimolar solutions of **3** and **5**. Such films can generally be formed only by entanglement of linearly connected macrosized aggregates. Also, although no fibers could be drawn from the individual highly concentrated solutions of monomers **3**, **4**, and **5**, long thin fibers could easily be drawn from concentrated equimolar solutions of **3** and **5** (Figure 2c); these formed in a manner analogous to dry spinning used for covalently bonded polymers.[16] This provided further direct evidence for the formation of supramolecular polymer **1**. Similarly, a brittle film was cast from a concentrated equimolar solution of **4** and **5**, and thin fibers were drawn from the concentrated equimolar solutions of **4** and **5** (see the Supporting Information). The brittle nature of the films of polymer **2** derived from the flexible monomer **4** was surprising to us; it appears that because of the enhanced possibility of cyclization of **4** with **5**,[10] the degree of polymerization of polymer **2** is significantly less than that of polymer **1**, as also indicated by the NMR results.

In summary, we have demonstrated the first formation of AA—BB-type linear supramolecular polymers based on BMP32C10 cryptands. These supramolecular polymers with well-defined pseudorotaxane structures provide a promising route to irreversibly mechanically linked polymers by attachment of bulky stoppers to the ends of α,ω-difunctional bisparaquat derivatives to form rotaxane units, as has been demonstrated in several ways with small-molecule pseudorotaxanes.[17−20] These extensions will be reported in our future publications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Syntheses of **3**, **4**, and **5**; calculated *p* and *n* values for the two supramolecular polymer systems; viscosity study of supramolecular polymer **2**; and thermal analysis results and SEM images of supramolecular polymers **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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