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A supramolecularly templated catenane initiator and a controlled ring expansion strategy†

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We report the first synthesis of a catenated polymer *via* a ring-expansion strategy, which is based on a supramolecularly templated initiator. The high yielding synthesis and simple isolation method will enable the investigation and development of this unique polymer system for further applications.

Catenanes are topologically interesting molecules composed of two or more mechanically interlocked rings.[1] Their unconventional geometry is a curiosity, affording novel molecular objects with potential use in nanotechnology. Over the years, various methods have been reported to synthesize low molecular weight catenanes facilitated by inter- and intra-molecular interactions. Such directed approaches include designing molecules based on transition metal-ligand templates[2] or H-bonding precursors.[3] However, synthesis of high molecular weight catenanes remains a formidable synthetic challenge.[4,5]

A few attempts have been reported to demonstrate the synthesis of catenated polymers.[5] Hogen-Esch *et al.* reported the synthesis of catenated polymers by statistical threading of a linear polymer into another cyclic polymer followed by ring closing of the linear polymer.[5c] Takano *et al.* reported the preparation of polystyrene–polyisoprene copolymers with the improved yield of 5%.[5b] Recently, Tezuka *et al.* utilized H-bonding and electrostatic interaction to help their pre-ordering.[5a] However, in all these cases, the very low yield and difficulties in isolation of the products have impeded further physical studies of these interesting macromolecules.[5c,6]

The main challenge in building catenated polymers is then to design a reasonable high yield synthesis strategy. Recently, our group has reported the synthesis of catenated polymers *via* polymerization of styrene from a supramolecularly templated atom transfer radical polymerization (ATRP) initiator followed by intramolecular end-to-end cyclization of the linear polymer chains.[7] The strategy of using a supramolecular template has effectively produced catenated polymer precursors. However, similar to the synthesis of cyclic polymers,[8,9] the ring-closing strategy involves four reactive ends of telechelic precursors under highly dilute conditions. As a result, relatively low yield and difficulties in isolation of the desired product are still unavoidable.[7] Alternatively, another route for fabrication of cyclic polymers is utilizing ring expansion polymerization – a technique whereby insertion of monomer units into a cyclic initiator leads to the growth of polymer chains in a cyclic fashion and the method does not require highly dilute conditions.[9,10] Kricheldorf *et al.* have successfully demonstrated the ring-opening polymerization (ROP) of lactones and lactides by inserting these monomers into the Sn–O bond of cyclic tin dialkoxides.[11] In their study, the macrocycles were prepared under kinetic control with no side reactions observed.[10a] Herein, we report a versatile approach for the preparation of catenated polymers aimed at overcoming the aforementioned difficulties: (1) formation of a catenane initiator through a supramolecular template strategy and ring-closing approach and (2) ring expansion polymerization through the insertion of monomers into the catenane initiator.

Previous reports have shown that a stable conformation in which the reactive groups are positioned closely in space greatly favors the formation of the desired product.[2c] This can be accomplished effectively by sterically restricting the space of the reactive end groups of the ligands or exploiting secondary interactions. Employing rigid ligands, such as a phenyl substituted phenanthroline, could efficiently provide conformational restrictions.[12] Moreover, secondary interactions, specifically aromatic CH···O interactions (and gauche effect) in 2-Cu(I), play a significant role in favoring intra-ligand ring closing to form 3-Cu(I) rather than inter-ligand ring-closing to form the topologically-trivial figure-of-eight isomer.[13] The described synthetic approach substantiates the choice of preparing compound **1** (ESI,† Scheme S2). The supramolecular assembly of compound **1** to complex **2** upon the addition of Cu(I) was confirmed by the UV-Vis analysis, which showed ligand-centered transitions (π–π*) at 283 nm and 321 nm, metal-to-ligand transition (MLCT) at 437 nm and the ligand-to-metal transition (LMCT) at 585 nm (ESI,† Fig. S6).[7] The significant downfield shift observed in the ^{1}H NMR spectrum of the resulting complex was also ascribed to the formation of the phenanthroline copper(I) complex and the electrostatic interactions.[13]

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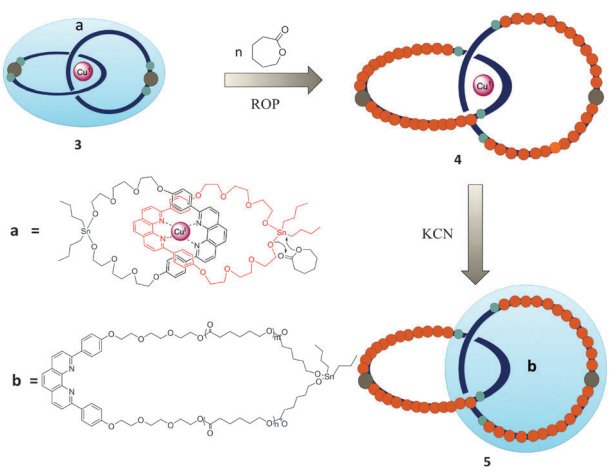
The catenane initiator was obtained by refluxing a dilute chloroform solution of the ligand complex (**2**) with 5% excess of dibutyldimethoxytin overnight. As shown in Fig. S5 (ESI†), the hydrodynamic volume of the catenane initiator (**3**) dramatically increased relative to that of compound **1**, whereas the ring-closing product of compound **1** showed a similar hydrodynamic volume to that of compound **1** itself. Moreover, the isomeric structures of catenane and figure-of-eight can be further distinguished by performing a decomplexation study of the catenane initiator. The disappearance of the peaks lying at 437 nm and 585 nm demonstrated the copper-free catenane initiators after decomplexation by KCN (ESI,† Fig. S8). The figure-of-eight isomer would become a large single ring upon decomplexation and thus, the hydrodynamic volume of resulting species would be larger than that of the interlocked cyclic structures of catenanes.[14] Contrarily, the hydrodynamic volume of the catenane initiator **3** did not change after decomplexation. The smaller GPC traces at larger retention volume were ascribed to the free ligands derived from the unclosed catenane initiators. These results confirmed the interlocked structure of the catenane initiator, giving an overall yield of 80% from the integration of the chromatographic peaks.

Adopting a similar method as reported by Kricheldorf and Schwarz for ring-expansion polymerization,[10a,11] we employed the phenanthroline-based catenane initiator **3** to afford catenated polymers *via* the polymerization of a suitable monomer as shown in Scheme 1. With this design, numerous monomers can be utilized to afford catenated polymers, such as lactones, cyclic diesters, and cyclic aliphatic carbonates.[11a] Recently, creating functionalized monomers, like α-(1-acryloxyethyl)-ε-caprolactone[15] and brominated lactide,[16] has further expanded the variety of monomers that could potentially be utilized. Here, the most commonly used monomer caprolactone (CL) was employed to demonstrate the ring-expansion polymerization. After 18 h of polymerization, 86% monomer conversion was reached (ESI,† Fig. S4). Interestingly, the UV-Vis spectrum of the resulting polymer solution confirmed the continued presence of the phenanthroline copper(I) complex, which featured its stability under this polymerization condition. The significant shift to a lower retention volume compared with that of the catenane initiator **3** suggested the higher molecular weight catenane.



Scheme 1 Synthesis route for a catenated polymer.

To obtain the copper(I) free polymer, a solution of catenated polymer **4** was stirred at 40 °C with 10 equivalents of KCN. The GPC trace of the decomplexation product (Fig. 1A–c) shows no significant shift in retention volume even after removal of copper(I), which indicates a preserved interlocked structure of the catenated polymer. Moreover, peak broadening after removal of copper(I) could be explained by different conformations of the interlocked cyclic polymer chains. The appearance of another peak with lower hydrodynamic volume can be assigned to the free linear polymer chains resulting from the decomplexation of acyclic polymers. The population of the catenated polymer was calculated to be 83% based on the comparative areas of the two peaks assigned to the catenated polymers and free polymer chains. The catenated polymer was obtained in 73% yield by dialysis (Fig. 1A-d, M_n = 4.6 kDa, PDI = 1.89).

It is worth noting that because of the kinetically controlled insertion mechanism with both Sn–O bonds active, two polyester chains grow from one tin atom.[11c] Hence, the average degree of polymerization (DP_n) can be defined as the sum of two polymer chains derived from one tin atom. From the integration of the methylene groups next to the –OOC (l) and methylene groups in the 2,9-diaryl-1,10-phenanthroline diol segment (f + k or g),

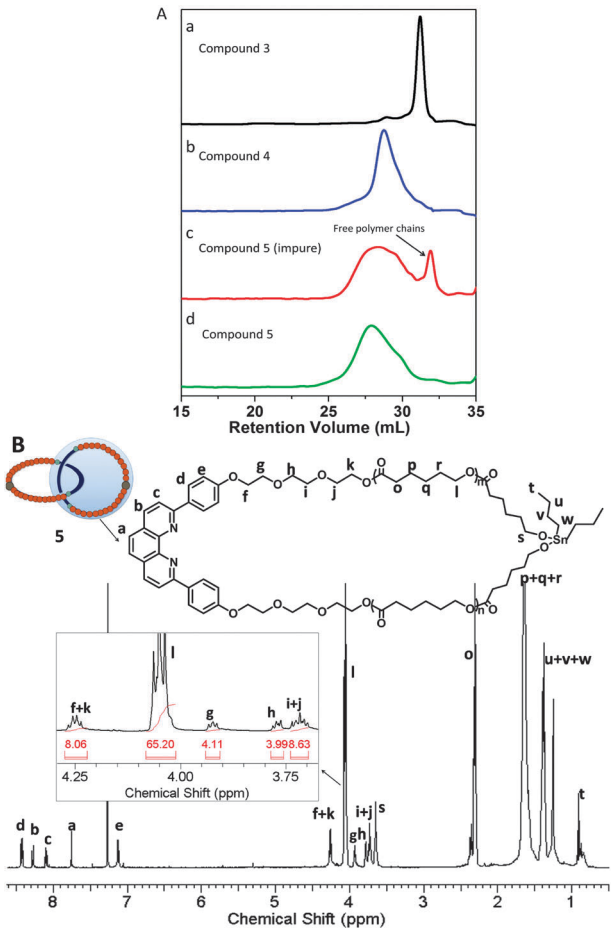


Fig. 1 (A) GPC curves for the (a) catenane initiator **3**, (b) catenated polymer with complex **4**, (c) decomplexation product of catenated polymer **5**, and (d) purified catenated polymer **5**. (B) ^{1}H NMR spectrum of purified catenated polymer **5**.

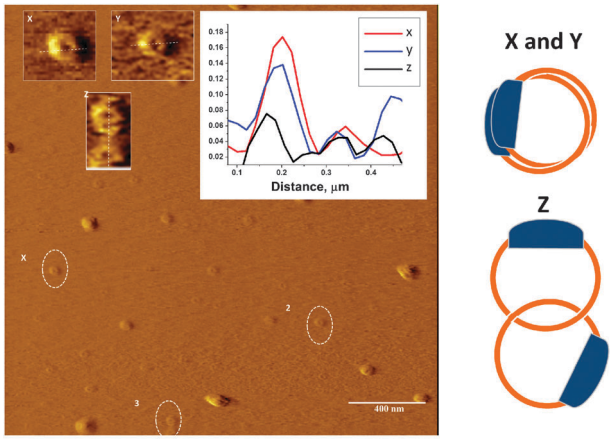


Fig. 2 AFM images of catenated polymer **5**.

the average degree of polymerization (DP_n) for one polymer cycle ($m + n$) is around 33, which translates to 66 monomers per catenated polymer. Thus, the average molecular weight of catenated polymers was calculated to be 9.3 kDa. The large difference in molecular weight determined by ^{1}H NMR (absolute M_n 9.3 kDa) and GPC (apparent M_n 4.6 kDa) reveals the significantly smaller hydrodynamic volume compared to the linear analogue. Moreover, a much smaller intrinsic viscosity value of the catenated polymer compared with the linear analogue further confirmed its compact nature (ESI,† Fig. S16).

Direct imaging techniques offer a unique approach towards the analysis of macromolecules as single nanoobjects. Recently, a few studies using atomic force microscopy (AFM) to investigate neutral macrocyclic polymer chains at the molecular level have been reported.[6,17] Here, we have attempted to directly observe the obtained catenated polymers by AFM. The interlocked cyclic structures of individual polymers (*e.g.* **z** in Fig. 2) were observed on the atomically flat mica substrate. However, most of the structures (*e.g.* **x** and **y**) are overlapped cyclic polymers. This is perhaps due to the strong π–π interactions between the two phenanthroline segments in the catenated polymers. Thus, the measured height for one end of **x** or **y** was suggested to be around twice the height of **z**. To validate our assumption, we have also visualized the catenated polymer with a copper(I) complex where π–π interactions between the two phenanthroline were absent (ESI,† Fig. S13). As expected, more catenated structures were found. This result confirmed the relatively high conformational freedom of the two interlocked cyclic polymers, further elucidating the structural beauty of catenated polymers. More studies on the properties derived from this unique structure are underway.

In conclusion, we have reported a facile approach for the synthesis of catenated polymers *via* a ring-expansion strategy. A catenane initiator was successfully synthesized by the ring closure reaction between the phenanthroline copper(I) complex and dibutyldimethoxytin. Through the insertion of caprolactone monomers, catenated polymers were obtained. Purification of the decomplexed products afforded catenated polymers with a high yield of 73%. The characterization by ^{1}H NMR, GPC, AFM and regioselective ring cleavage study confirmed the target structure.

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