

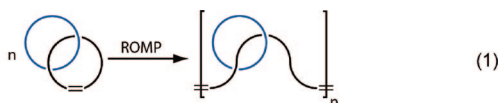
Polypseudorotaxanes via Ring-Opening Metathesis Polymerizations of [2]Catenanes

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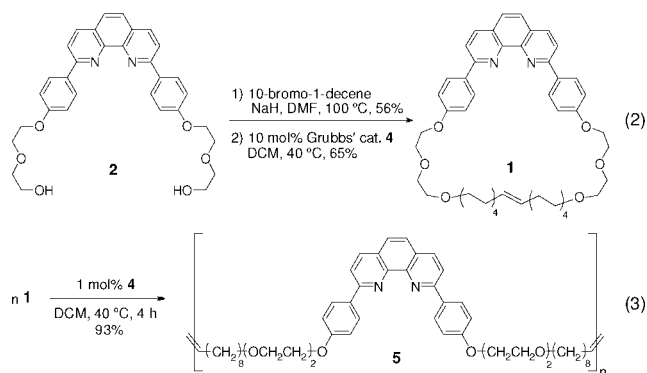
The synthesis of polymers with well-defined mechanical entanglements¹ is a state-of-the-art challenge that is essential to master for greater control over macroscopic materials properties. In our efforts to render such supramolecular polymeric architectures more accessible, we became interested in the novel possibility of preparing polypseudorotaxanes via ring-opening olefin metathesis polymerizations (ROMPs) of olefinic [2]catenanes, eq 1. The realization of this concept is an important advance because, notably, with suitable variation of the starting materials, one may also access daisy-chain polymers as well as rubbery network polymers that feature mobile, slip-link, cross-links—a materials theorist's dream.²



ROMP reactions are typically performed with low molecular weight, strained-ring, olefinic monomers, where ring-opening relieves ring strain, thus driving the process.³ In contrast, macrocyclic olefins are generally uncommon starting materials for these reactions because they are essentially free of ring strain and thus not currently well-suited for living polymerizations and preparation of low polydispersity polymers, block copolymers, etc. ROMP reactions of macrocyclic olefins are not without precedence however as a few examples employing macrocyclic monomers have been recently reported.⁴ In these cases, the olefin metatheses are dynamic processes termed entropy-driven ring-opening metathesis polymerizations (ED-ROMPs);^{4c} they have allowed direct access to polymers with unusual main-chain functionality.^{4a–c} Herein, we communicate the first report of a ROMP of an olefinic [2]catenane to access polypseudorotaxanes.

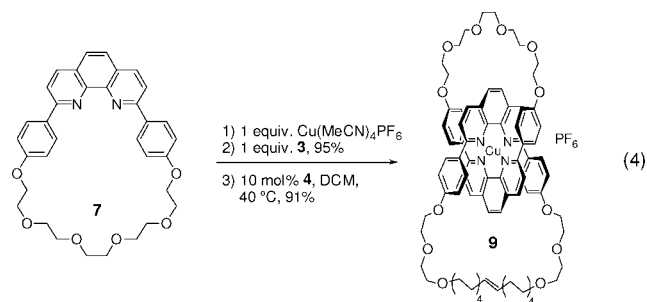
We initially sought to attempt a ROMP of a model, uncatenated, olefinic macrocycle—one, however, that could be readily interlocked with another macrocycle, if desired. An attractive candidate for this test polymerization was the 1,10-phenanthroline-based olefinic macrocycle **1** since catenanes of 1-like compounds have been prepared with very high yields.⁵ Thus 46-membered macrocycle **1** (*E/Z* ratio of 5:1) was synthesized from known diol **2**⁵ via a double etherification to yield intermediary α,ω -diolefin **3** which underwent ring-closing olefin metathesis (RCM) when treated with Grubbs' second-generation catalyst⁶ (**4**) under dilute conditions (10 mM), eq 2.

In a test of the feasibility of ROMP of such a macrocycle, a concentrated DCM solution of olefinic macrocycle **1** (0.5 M) was treated with 1 mol% initiator **4**, eq 3. Over the course of stirring for 4 h at 40 °C, the reaction mixture became significantly more viscous. The reaction was then quenched with ethyl vinyl ether, and a solid residue (**5**) was obtained upon removal of the solvent. The ¹H and ¹³C NMR spectra of **5** appeared similar to the spectra of macrocycle **1** except each signal was somewhat broadened and the *E/Z* ratio of the olefinic signals was found to increase to 12:1.



Macrocycle **1** and product **5** were examined by analytical size exclusion chromatography (SEC), Figure 1. Macrocycle **1** exhibited a single, relatively sharp peak with a retention time of 18.0 min. In contrast product **5** displayed a broad peak (max. at 12.4 min) with a series of small shoulders from 15 to 17 min, indicative of a polydisperse oligomer of **1**. The ratio of the total polymer and oligomer (**5**) to starting material **1** was calculated to be 93:7. Relative to a set of monodisperse polystyrene standards, polymer **5** was estimated to possess a molecular weight (*M_w*) of 116 000 amu, an *M_w*/*M_n* (PDI) of 1.8, and an average degree of polymerization of ca. 83.

With data to support that macrocycle **1** was reasonably amenable to ROMP, we synthesized the Sauvage-type^{5,7} [2]catenane **9** as the key test monomer for our experiments. Using a 1:1 ratio of **3** to **7** (30-membered ring), intermediary [2]pseudorotaxane copper complex **8** was formed and isolated in 95% yield. Complex **8** (3.2 mM) was subsequently treated with 10 mol% **4** to effect RCM; the resulting catenane **9** (*E/Z* ratio of 5:1) was isolated in 91% yield, eq 4. The RCM yield of **9** was significantly higher than the yield of **1**. This result is consistent with previous catenane syntheses via RCM of bis-phenanthroline copper complexes and is presumably due to preorganizational effects of the bis-phenanthroline complex.^{5,8}



To probe and ensure that the bis-phenanthroline copper complex in **9** was sufficiently robust to endure ROMP without dissociation of the two phenanthroline moieties, we treated a dilute DCM

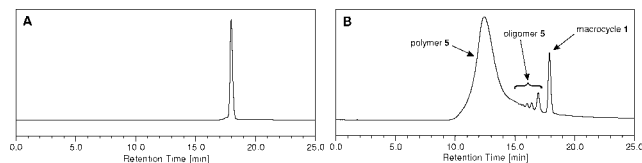
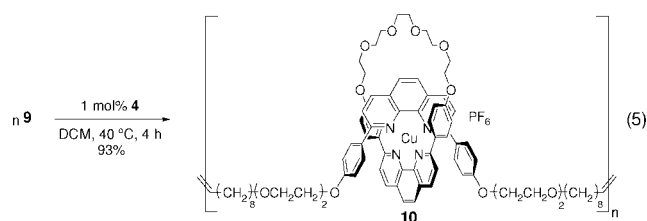


Figure 1. SEC chromatograms of (A) **1** and (B) **5**.

solution of [2]catenane **9** (5 mM) with 5 mol% **4** for 6 h at 40 °C. After quenching the reaction with ethyl vinyl ether, we recovered 96% of [2]catenane **9**. Fortunately, even under dilute ring-opening, ring-closing metathesis (RORM) conditions, the copper(I) ion was able to maintain association of the two phenanthroline ligands of **9**, thus boding well for the synthesis of a polypseudorotaxane with a high, predictable, and controlled density of threaded macrocycles.

For the title reaction, we treated a concentrated DCM solution of olefinic [2]catenane **9** (>0.135 M) with 1 mol% initiator **4**, eq 5. Over the course of stirring for 4 h at 40 °C, the reaction mixture again became significantly more viscous. The reaction was then quenched with ethyl vinyl ether, and a solid product (**10**) was isolated upon removal of the solvent.



The ^1H and ^{13}C NMR spectra of **10** analogously appeared similar to the spectra of [2]catenane **9** except each signal was slightly broadened and the *E/Z* ratio of the olefinic signals was again found to increase.⁹ Importantly, all upfield shifted phenanthroline signals, characteristic of bis-phenanthroline copper complexes, maintained their upfield shift.⁹ This similarity in the NMR spectra of **9** and **10** is strong evidence that the polymer chain produced during the ROMP retained, at least, the vast majority of the threaded macrocycles **7**. For example, in a control experiment, when macrocycle **7**, alone, was treated with 0.5 equiv of Cu(I), the solution did not acquire the dark red color that is characteristic of these bis-phenanthroline copper complexes. Furthermore, the ^1H NMR spectrum of the resultant solution showed negligible upfield shift of the phenanthroline signals,⁹ thus demonstrating little to no formation of $\text{Cu}\cdot\text{7}_2$, as expected,⁷ due to the severe distortion that would be incurred if one macrocycle were to thread another.

Therefore, during the ROMP of **9**, if a fraction of the macrocycles (**7**) had dissociated from polypseudorotaxane **10**, the characteristic upfield signal shift, in the ^1H NMR spectrum, for this fraction of the phenanthroline groups would have ceased and resulted in more complex spectra. From such components, in this case of slow exchange,⁹ the only arrangement in which to achieve clean spectra, where all phenanthroline ligands are involved in bis-phenanthroline copper complexes, is for the macrocycles (**7**) to remain threaded on the polymer backbone of **10**.

Direct examination of catenane **9** and polypseudorotaxane **10** by analytical SEC was complicated due to the ionic nature of these compounds and subtle solubility issues. Instead, the demetallated compounds were studied by SEC. Both **9** and **10** were readily demetallated when treated with aq. KCN in MeCN/DCM,⁹ resulting in near complete loss of color in both cases, while for **10** demetallation additionally resulted in concomitant release of the

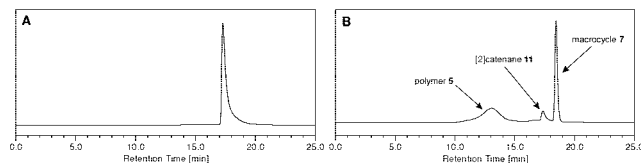


Figure 2. SEC chromatograms of (A) **11** and (B) **12**.

macrocycles (**7**) from the covalent polymer chain (~**5**). Such release demonstrates that the preponderance of ROMP product **10** cannot be cyclic.⁹

The demetallated [2]catenane (**11**) exhibited a single SEC peak, albeit with a tail, with a retention time of 17.3 min, Figure 2a. In contrast the demetallated polypseudorotaxane mixture (**12**) displayed a broad polymer peak (max. at 13.1 min) in addition to two other peaks corresponding to [2]catenane **11** (17.4 min) and macrocycle **7** (18.5 min),⁹ Figure 2b. The bare covalent polymer backbone of **10** (~**5**) was estimated to have a molecular weight (M_w) of 93 000 amu, a PDI of 1.9, and an average degree of polymerization of ca. 63. The ratio of polymer/catenane/macrocycle **7** was calculated to be 47.6:6.6:45.8. Although the measured ratio of polymer to released **7** was near the 1:1 expectation, the experimental bias may be indicative of a minor amount of macrocyclic **7** being mechanically trapped in the polymer, possibly as a result of backbiting during the polymerization process; i.e., a small amount of threaded cyclic polymer may be present. In summary, we have shown that an ED-ROMP reaction of an olefinic Sauvage-type [2]catenane leads to a reasonably high molecular weight main-chain polypseudorotaxane. This approach takes advantage of using a prethreaded monomer to access polymers that are effectively saturated with threaded macrocycles.

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Supporting Information Available: Experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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