BACKGROUND: Polymers represent a ubiquitous class of compounds with diverse and desirable material properties. They are found in plastics, fibers, elastomers, coatings, adhesives, and composites. A major goal of polymer chemistry is to establish the relationship between polymer structure on the molecular level and the macroscale properties these materials exhibit. To this end, synthetic polymer chemists seek to vary the number and types of monomers that are the building blocks of different polymers, as well as the sequence and architecture in which these monomers are linked together. Traditional polymer architectures include linear and branched polymers composed of covalent linkages only. A relatively new polymer architectural class is the main-chain polyrotaxanes/polypseudorotaxanes (Figure 1), a subset of supramolecular polymers. Polyrotaxanes/polypseudorotaxanes incorporate mechanically linked subunits for which the connecting forces are noncovalent interactions\(^1\); typically macrocycles are penetrated by linear polymers. The distinguishing feature of polypseudorotaxanes are the lack of sterically bulky groups that act as stoppers to prevent dethreading of the macrocycles. The unique architectural characteristics of polyrotaxanes/pseudorotaxanes impart these materials with novel properties. However, the correlation between structure and macroscale properties is not well-established due to the synthetic challenge of making such polymers.

![Figure 1. Examples of polyrotaxane and polypseudorotaxane polymer architectures.](image)
# Synthesis of Main-chain Hybrid Polypseudorotaxanes with Controlled Macrocycle Sequence

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The vast majority of polyrotaxanes/polypseudorotaxanes in the literature contain only one type of macrocycle. Polyrotaxanes threaded with two or more different macrocycles are termed hybrid polyrotaxanes.\textsuperscript{2} One example of a hybrid polyrotaxane has been reported in the literature and involves threading of two different crown ethers upon a linear polyester backbone.\textsuperscript{2} No attempt was made to control the macrocycle sequence of the polyrotaxane. A supramolecular polymer utilizing alternating macrocycle sequence based upon \(\alpha\)- and \(\beta\)-cyclodextrins has been developed, however the polymer was not a polyrotaxane but a “daisy-chain” polymer, a supramolecular polymer with noncovalent interactions along the polymer main chain.\textsuperscript{3}

OBJECTIVE: Successful completion of the project described below would represent the first synthesis of a main-chain hybrid polypseudorotaxane where the sequence of the two macrocycles was controlled. Two different hybrid polypseudorotaxanes are proposed (Figure 2), one in which the two macrocycles, \(A\) and \(B\), alternate in sequence \([AB]_n\) and one in which the sequence is \([AAB]_n\). Such materials would allow unprecedented study of the effect of macrocycle sequence on polymer properties.

\[
\begin{align*}
[AB]_n & \\
[AAB]_n
\end{align*}
\]

\textbf{Figure 2.} Polypseudorotaxanes proposed in this study with alternating macrocycle sequence \([AB]_n\) (left) and repeating \([AAB]_n\) (right)

METHOD AND RESULTS: \textbf{I. Synthetic strategy}. The synthesis of hybrid polypseudorotaxanes with alternating macrocycle sequence \([AB]_n\) involves the polymerization of two preformed pseudorotaxane monomers (\(1a\cdot B\) and \(1b\cdot B\)) composed of macrocycle \(B\) and two different difunctional threading components (\(1a\) and \(1b\)) where the ends of \(1a\) and \(1b\) can be covalently joined in a reaction effected by macrocycle \(A\) (Figure 3).
In this proposed study, macrocycle $B$ is cucurbituril[7] (CB[7]), a cyclic oligomer composed of 7 glycouril units linked by methylenes (Figure 4a). Examples of polyrotaxanes/pseudorotaxanes containing CB[7] and other cucurbiturils of different size, namely cucurbituril[6] (CB[6]), are known in the literature. Cucurbiturils are known to bind a variety of small molecules (“guests”) through hydrophobic, ion-dipole and hydrogen-bonding interactions with high affinity. Guests such as $p$-xylenediamine·2HCl ($K_{\text{association}} = 2 \times 10^9$ M$^{-1}$) (Figure 4b) and 1,1′-bis(trimethylammoniomethyl)ferrocene ($K_{\text{association}} = 3 \times 10^{15}$ M$^{-1}$) (Figure 4c) can be used as the CB[7] binding site in the following syntheses.

The ends of $1a$ and $1b$ are proposed to be terminal acetylenes and azides, respectively, (Figure 5) and the identity of macrocycle $A$ is CB[6]. CB[6] is known to catalyze the 1,3-dipolar addition of an acetylene and an azide to form the corresponding 1,2,3-triazole. This reaction has already been elegantly exploited by Steinke in the synthesis of CB[6]-containing polyrotaxanes/polypseudorotaxanes.
A list of molecules for synthesizing hybrid polypseudorotaxanes with alternating [AB]ₙ macrocycle sequence is shown in Figure 6. Four linear targets with two different CB[7] binding sites and either acetylenes or azides at both ends, 1a and 1b (p-xylenediamine binding site), 2a and 2b (bis(amino)ferrocene binding site), would be synthesized and complexed by CB[7] (macrocycle A) to give pseudorotaxane monomers 1a·CB[7] and 1b·CB[7], 2a·CB[7] and 2b·CB[7]. Since CB macrocycles cannot simultaneously bind one ammonium group¹⁰, multiple ammonium moieties must be present with a linker to separate them in order for CB[6]-facilitated polymerization to occur. The polymerization of equimolar amounts of a diacetylene-functionalized pseudorotaxane and a diazide-functionalized pseudorotaxane in the presence of CB[6] (macrocycle A) would then give the desired polypseudorotaxane with alternating [AB]ₙ macrocycle sequence (an example using 2a·CB[7] and 2b·CB[7] is shown in Figure 7). To access hybrid polypseudorotaxanes with [AAB]ₙ macrocycle sequence, complexes 1·CB[7] or 2·CB[7] could be polymerized with uncomplexed 2 or 1, respectively. For example, uncomplexed 2a could be polymerized with 2b·CB[7] resulting in a polymer like the one shown in Fig. 7 except that every other ferrocene unit would not be complexed by CB[7].
Figure 6. Pseudorotaxane monomers 1a·CB[7] and 1b·CB[7], 2a·CB[7] and 2b·CB[7] and their precursors 1a, 1b, 2a, 2b.
II. Synthesis of pseudorotaxane complexes. The syntheses of CB[6] and CB[7] are known. A proposed synthetic scheme for compounds 1a, 1b, 2a, 2b is shown in Scheme 1. The most strategic disconnections are at the C-N bonds. These may be installed using either reductive amination or nucleophilic substitution. Reductive amination is the method of choice for connecting the CB[7] binding site to the linker fragments. The starting materials for either p-xylene-centered compounds (1a and 1b) or ferrocene-centered compounds (2a and 2b), terephthaldicarboxaldehyde and 1,1’-ferrocenecarboxaldehyde, are commercially available or have known syntheses. The appropriate linkers (3, 4) could be made from commercially available 2-bromoethylamine hydrobromide (5) and one equivalent of either commercially available propargyl amine (6) or known 2-azidoethylamine (7).
Scheme 1. Synthesis of diacetylene and diazide compounds.

Once monomers 1a, 1a, 2a, 2b have been synthesized, the polypseudorotaxane assembly would be carried out. Formation of complexes 1a·CB[7], 1b·CB[7], 2a·CB[7] and 2b·CB[7] can be confirmed using $^1$H NMR as the chemical shifts of the protons of the $p$-xylene moiety and ferrocene moiety are shielded in the host-guest complexes relative to free guests. Then equimolar ratios of diacetylenes 1a·CB[7] or 2a·CB[7] would be combined with diazides 1b·CB[7] or 2b·CB[7] in the presence of CB[6] to affect triazole formation under the conditions developed by Steinke$^{10}$ and monitored by $^1$H NMR as the proton of the triazole ring appears at a distinctive chemical shift when complexed by CB[6].
During summer 2007, progress was made on the synthesis outlined above. Procedures for the preparation of molecules 3, 4, and 7 were investigated as well as conditions for the final reductive amination. In addition, other synthetic strategies depending upon SN2 reactions in place of reductive amination were pursued. Finally, the syntheses of alternate monomers to 1 and 2 for the preparation of [AAB]n polypseudorotaxanes, used in reference 10, were also attempted.

REFERENCES


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