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One-Pot Synthesis of Polyrotaxanes via Acyclic Diene Metathesis Polymerization of Supramolecular Monomers

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Supporting Information

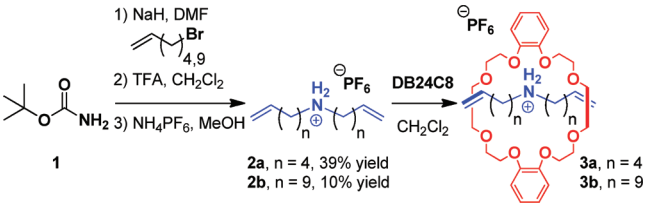
ABSTRACT: A one-pot synthesis of polyrotaxanes has been developed. The method employs a supramolecular monomer comprising a polymerizable ammonium salt and crown ether, in combination with dynamic ADMet polymerization. Ultimately, highly efficient complexation, polymerization, and end-capping were accomplished in a single operation to yield polyrotaxanes with M_w up to 19.3 kDa and >80% of the repeat units being complexed.

Advanced supramolecular and mechanically interlocked polymers such as polyrotaxanes, polycatenanes, and polypseudorotaxanes offer enticing synthetic targets and the promise of unique characteristics.[1] The ability to construct these complicated architectures in an efficient, scalable, and modular fashion is essential to realizing their full potential. A particular challenge in the synthesis of main-chain polyrotaxanes, for example, is achieving a combination of polymerization, threading or "clipping", and end-capping to secure the overall interlocked nature of the ensemble—feats often executed in a stepwise fashion. Inspired by elegant examples that have successfully accomplished these objectives,[2] we sought a system of high efficiency in which polyrotaxanes could be generated in one pot from readily available, modular building blocks via a dynamic polymerization/end-capping strategy. We envisioned that incorporating end-caps during polymerization, while also allowing threading to occur, would benefit from a rapidly equilibrating polymerization such as acyclic diene metathesis (ADMet) polymerization.[3] Herein we describe a method to accomplish a one-pot synthesis of polyrotaxanes via multicomponent ADMet polymerization.

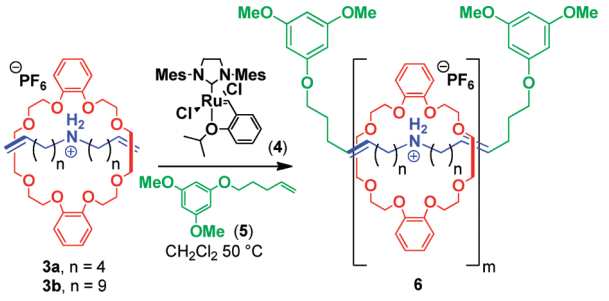
Starting from commercially available *tert*-butyl carbamate **1**, acyclic dienyl ammonium salts **2** were prepared in three steps as depicted in Scheme 1. Specifically, alkylation of **1** using NaH and a bromoolefin in DMF furnished the corresponding dialkyl carbamate intermediates (not shown). Subsequent deprotection using TFA in CH_2Cl_2, followed by anion metathesis with NH_4PF_6, provided the desired dialkenyl ammonium salts bearing 6- or 11-carbon chains (**2a** and **2b**, respectively).

Efficient threading of **2** using dibenzo[24]crown-8 ether (**DB24C8**) was confirmed via ^{1}H NMR spectroscopy of a 1:1 molar ratio of the two species in CD_2Cl_2 (0.01 M in each, initially).[4] The CH_2 protons alpha to the ammonium moiety in **2** displayed resonances at δ = 3.0 ppm and moved downfield to δ = 3.2 ppm in the presence of **DB24C8**, indicating threading to form supramolecular monomers **3** (Scheme 1). Integration of the two signals correlated to ca. 75% threading, and increasing the ratio of **DB24C8**/**2** to 5:1 (0.01 M in **2**, initially) resulted in quantitative threading. The supramolecular complexes (**3a** and **3b**) obtained from 1:1 mixtures of **2** and **DB24C8** were concentrated under vacuum and used directly in subsequent ADMet polymerizations. It is expected that the concentrated mixtures comprising **3** contain a higher composition of the supramolecular complexes than the more dilute solutions used for NMR analysis.

Scheme 1. Synthesis of Dialkenylammonium Salts 2 and Complexation with DB24C8 To Provide Supramolecular Monomers 3



Scheme 2. ADMet Polymerization of Supramolecular Monomers 3 To Form Polyrotaxanes 6 (shown as an idealized, fully threaded polyrotaxane)



Supramolecular monomers **3** (likely as dynamic mixtures with the constituent ammonium salt **2** and **DB24C8**) were found to readily participate in ADMet polymerization (Scheme 2); key results are summarized in Table 1. Initially, a solution containing **3a** was treated with Ru-alkylidene complex **4** and an end-capping chain-transfer agent (CTA) **5**. Using $[\mathbf{3a}/\mathbf{4}]_0$ of 40:1 and $[\mathbf{3a}/\mathbf{5}]_0$ of 2.5:1 (entry 1), the reaction mixture was prepared in dry CH_2Cl_2 (initially 0.5 M in **3a**), sealed under Ar, and vigorously

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Table 1. Data for ADMet Polymerization of 2 To Form Polyrotaxanes 6[a]

entry	monomer	yield (%)[b]	threading (%)[c]	M_w (kDa)[d]	PDI[d]
1	**3a**	85	72	13.2	1.58
2	**3b**	94	82	11.0	1.42
3[e]	**2b**	80	82	19.3	1.18
4[f]	**2b**	50	80	14.9	1.37

[a] Reactions were conducted under Ar atmosphere at 50 °C using $[\mathbf{2}/\mathbf{4}]_0$ or $[\mathbf{3}/\mathbf{4}]_0$ = 40:1 and $[\mathbf{2}/\mathbf{5}]_0$ or $[\mathbf{3}/\mathbf{5}]_0$ = 2.5:1. [b] Isolated yield after precipitation, based on **2** or **3** accordingly. [c] Determined by ^{1}H NMR spectroscopy of the isolated product. [d] Determined by GPC using MALLS. [e] Using $[\mathbf{2b}/\mathbf{DB24C8}]_0$ = 1:1. [f] Using $[\mathbf{2b}/\mathbf{DB24C8}]_0$ = 5:1.

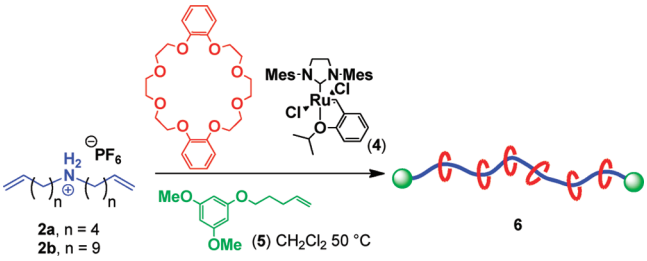
stirred in an oil bath at 50 °C. The viscosity of the solution quickly increased, and after ca. 30 min the mixture was removed from heat and placed under vacuum to remove all volatiles, including ethylene byproduct formed during the polymerization. Fresh CH_2Cl_2 was then added under Ar, and the sealed reaction mixture was again heated at 50 °C. The process of adding CH_2Cl_2 and subsequently removing the solvent under vacuum was repeated after 1, 2, and 12 h intervals. After a total reaction time of ca. 24 h, the mixture was concentrated under vacuum to give a thick tan foam. Analysis of the polyrotaxane via ^{1}H NMR spectroscopy indicated that ca. 72% of the repeat units remained threaded, and gel permeation chromatography (GPC) analysis using multiangle laser light scattering (MALLS) revealed a M_w of 13.2 kDa.

To improve the efficiency of the ADMet polymerization, we next focused on monomer **3b**, bearing longer undecenyl groups in comparison with **3a**. The reduced viscosity of the resulting reaction mixture indeed appeared to facilitate the polymerization, reaching full monomer conversion in ca. 2 h (cf. 90% conversion at 6 h when **3a** was employed). After ca. 12 h and three cycles of solvent removal/addition, the polyrotaxane was concentrated to yield a thick, viscous oil (entry 2). Analysis as before revealed ca. 82% threading and M_w = 11.0 kDa.

Encouraged by the ability to efficiently polymerize the congested supramolecular monomers via ADMet, and the rapid threading observed from ammonium salts **2** and **DB24C8**, we next attempted the polyrotaxane synthesis without discrete preassembly to form **3** (Scheme 3). Accordingly, **2b**, **DB24C8**, and CTA **5** were combined as a heterogeneous mixture, and a solution of catalyst **4** in CH_2Cl_2 was added. The polymerization and solvent cycling were conducted as described above. Analysis of the resulting polyrotaxane revealed similar threading (82%) and an increased M_w of 19.3 kDa (entry 3) in comparison with using the preassembled **3b** monomer (entry 2). Notably, the amount of threading did not benefit from the addition of 5 equiv of **DB24C8** relative to monomer **2b** (entry 4), suggesting that the maximum amount of threading for this particular monomer structure had been reached.

The polydispersity index (PDI) values resulting from the step-growth polymerizations were lower than expected when determined using MALLS analysis (Table 1). It is evident that the polymerizations do not reach full equilibrium, considering the feed ratio of monomer (**2** or **3**) to end-cap (**5**) of 2.5:1 would result in an average degree of polymerization (DP) of 5, and those obtained were greater than 5. The PDI values, however, likely reflect poor resolution of the polyelectrolyte structures during elution on the GPC columns that would manifest in artificially low PDIs. For comparison, we determined the average

Scheme 3. One-Pot ADMet Polymerization To Form Polyrotaxanes



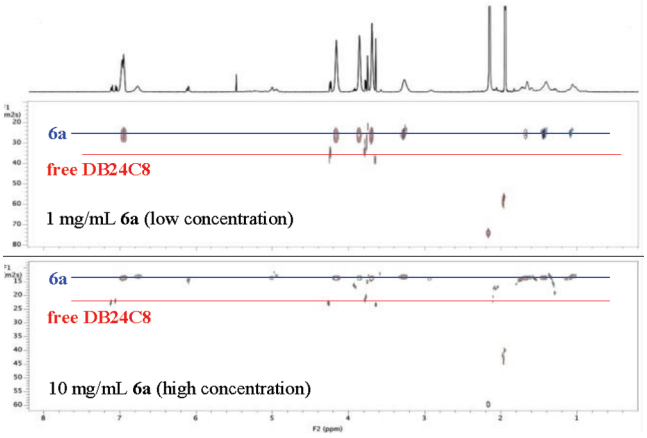


Figure 1. DOSY spectra of polyrotaxane **6a** (blue) and free **DB24C8** (red) at concentrations of 1 mg/mL (top) and 10 mg/mL (bottom).

DP (and corresponding M_n values) via ^{1}H NMR analysis by comparing the integration of the CH_2 protons alpha to the ammonium moiety with that of the dimethoxyarene end-cap. Using the M_w values from MALLS analysis in combination with the M_n values obtained via ^{1}H NMR analysis gives PDIs for entries 1−4 (Table 1) of 1.91, 1.58, 3.55, and 1.65, respectively, that are more consistent with other ADMet polymerizations.

The end-capped, mechanically locked nature of the polyrotaxanes was confirmed via 2-D DOSY NMR experiments.[5,6] As can be seen in Figure 1, the diffusion rates for both the polyammonium backbone of **6a** and the **DB24C8** moieties are correlated to one another, with a diffusion rate value of ca. 2.5×10^{-9} m^2/s. Moreover, this diffusion rate is distinct from that of free **DB24C8**, which displays a faster diffusion rate of ca. 3.5×10^{-9} m^2/s. This supports the successful incorporation of the end-caps but may also have been ascribed to strong ammonium−**DB24C8** interactions. To further support the end-capped nature of **6a**, we compared the DOSY spectrum upon 10-fold dilution, which again revealed consistent diffusion rates of the polymer backbone and the interlocked **DB24C8** moieties.

In conclusion, we have developed a simple strategy for a one-pot, multicomponent synthesis of polyrotaxanes using ADMet polymerization that advances the synthetic capabilities toward advanced macromolecular structures. The efficiency and ease with which these mechanically interlocked macromolecules can be assembled should facilitate rapid modulation to achieve versatile polyrotaxane architectures, and can be readily adapted to incorporate a variety of "metathesis-friendly" substrates.

■ ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures and characterization of all new compounds. This materials is available free of charge via the Internet at http://pubs.acs.org

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