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Arylene−Ethynylene Macrocycles via Depolymerization−Macrocyclization

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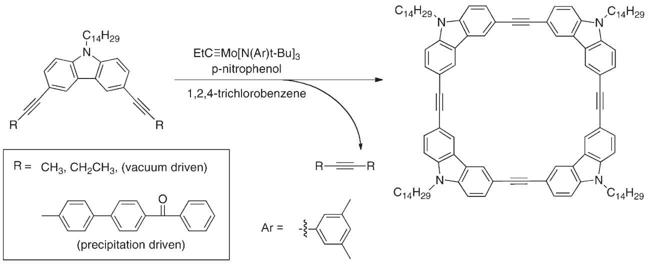
Supporting Information

Arylene−ethynylene macrocycles (AEMs) are an interesting class of molecules due to their ability to self-assemble through aromatic interactions into ordered supramolecular nanostructures.[1] These nanomaterials include 1D nanofibrils, extended tubular channels, discotic liquid crystals, and monolayers.[1] To date, the vast majority of AEMs have been synthesized using kinetically controlled processes, which are typically low-yielding and generally require high-dilution conditions. Recently our group reported thermodynamically controlled macrocyclization using a highly active molybdenum alkylidyne catalyst.[2] Through the use of dynamic covalent chemistry (DCC)[3] it is possible to drive reactions to their thermodynamic products while avoiding the irreversibility of kinetic processes. To drive the equilibrium toward macrocyclic products (see Scheme 1), the monomer's end-group byproduct must be removed by either volatilization or precipitation.[4] A drawback of these approaches is the need for specific difunctionalized monomeric precursors. These include functionalities such as methyl/ethyl or benzoylbiphenyl to yield 2-butyne/3-hexyne or bis(benzoylbiphenyl)acetylene byproducts, which are removed from the reaction mixture by vacuum or precipitation methods, respectively. Additionally, the precipitation driven route is not very efficient from an atom economy perspective, which in some cases the discarded byproducts account for more than two-thirds of the starting mass, and using the sparingly soluble groups can lead to difficult monomer purification, insoluble oligomeric intermediates, as well as difficult product purification. Unfortunately, vacuum-driven methods suffer from scalability due to catalyst pseudopoisoning.[2,4]

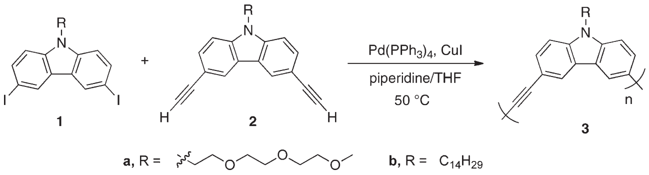
Rarely have macromolecules been considered as synthetic intermediates; nevertheless, here we describe a process in which macrocycles are synthesized under thermodynamic conditions from the alkyne metathesis-enabled depolymerization of arylene−ethynylene polymers.[5,6] The transformation of polymer to macrocycle is an entropically favored process. The requisite arylene−ethynylene or arylene−butadiyne polymers are readily available from palladium- or copper-catalyzed polycondensation reactions of simple starting materials (e.g., aryl halides and/or terminal alkynes).

Carbazolylethynylene homopolymers having *N*-alkyl or triethylene glycol monomethyl ether (Tg) side chains were synthesized from the requisite 3,6-diiodocarbazole (**1**) and 3,6-diethynylcarbazole (**2**) using standard Sonogashira coupling conditions (see Scheme 2).[7] The obtained polymers, requiring no purification, had a polydispersity index of ca. 1.7 and degrees of polymerization near 20 (see Table 1).

Scheme 1. Precipitation and Vacuum-Driven Acyclic Diyne Metathesis Macrocyclization[4]



Scheme 2. Synthesis of Triethylene Glycol (Tg) and Tetradecylcarbazolylethynylene Homopolymers



With polymers in hand, macrocyclic depolymerization was attempted (Scheme 3),[4] using the previously reported molybdenum alkylidyne catalyst.[2] The resulting macrocycles were isolated in good yields: R = Tg (59%); R = $C_{14}H_{29}$ (70%).[8] The process is simple, free of byproducts, and requires only simple monomers to synthesize the precursor polymer.

In part due to the concern of diyne defects in arylene−ethynylene polymers,[9] but also for the ability to generate high-MW material, carbazolylbutadiyne polymers were investigated. To the best of our knowledge, alkyne metathesis of 1,3-butadiynes using molybdenum-based catalysts has not been explored.[10] Access to the desired diyne polymer was accomplished using Hay conditions[11] for the oxidative coupling of terminal

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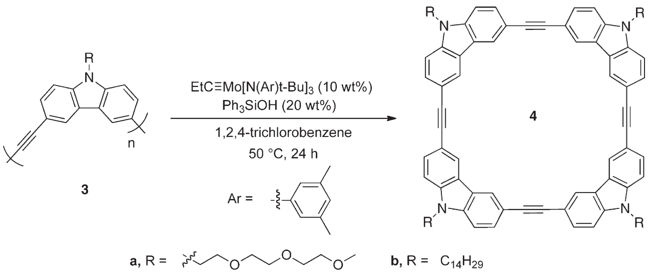
Table 1. Gel Permeation Chromatography Data for Polymers and Macrocycles[a]

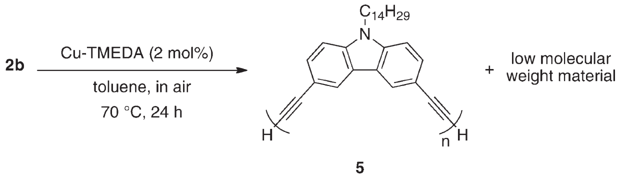
	M_n (kDa)	M_w (kDa)	M_w/M_n	P_n
3a	6.4	11.4	1.8	19
3b	8.5	15.2	1.7	22
4a	1.6	1.6	1.0	
4b	2.4	2.4	1.0	
5[b]	3.7	5.3	1.4	
5[c]	67	164	2.4	165
5[d]	67	145	2.2	165
4b and **6**	2.5	2.6	1.0	

[a] Based on polystyrene standards. [b] Macrocyclic species. [c] Crude polymer. [d] Fractionated polymer.

Scheme 3. Depolymerization−Macrocyclization



Scheme 4. Synthesis of a Carbazolylbutadiyne Polymer 5



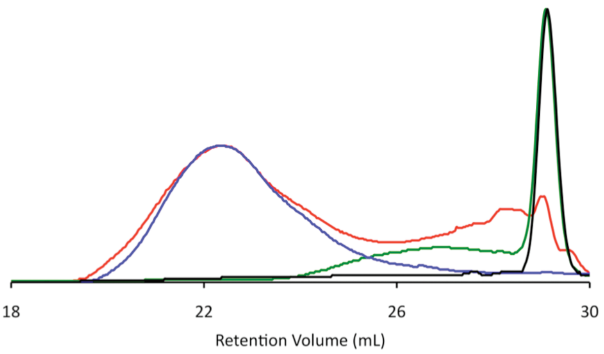
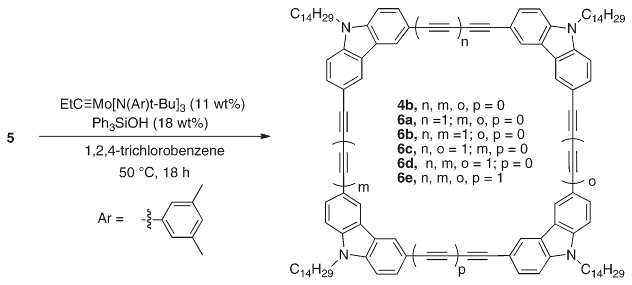


Figure 1. GPC trace of crude diyne polymer mixture (red), fractionated polymer **5** (blue), crude metathesis reaction mixture (green), and purified macrocycles **4b** and **6** (black).

alkynes. Specifically, diethynylcarbazole **2b** was treated with Cu-TMEDA under aerobic conditions (see Scheme 4). The resulting polymer (**5**) had an M_n of 67 kDa and a PDI of 2.4 (see Table 1 and Figure 1). Interestingly, but not unexpected, was the presence of low molecular weight material.[12]

Scheme 5. Synthesis of Macrocycles from Carbazolylbutadiyne Polymer



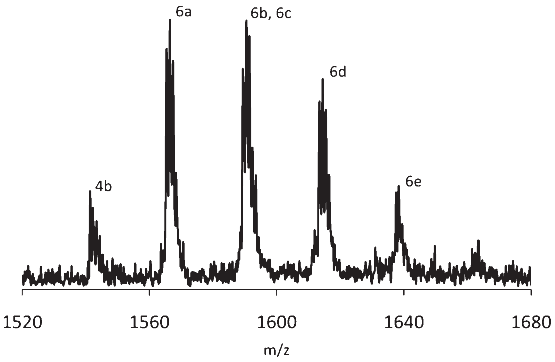


Figure 2. Partial MALDI-TOF mass spectrum of the crude reaction mixture shown in Scheme 5.

Diyne polymer **5** was then subjected to standard alkyne metathesis conditions (see Scheme 5). The GPC trace of the crude reaction mixture shows conversion to lower molecular weight polymer and a monodisperse peak (see Figure 1 and Table 1) eluting near 29 mL. Surprisingly, inspection of the MALDI-MS for the reaction mixture (see Figure 2) showed a statistical distribution of macrocycle products with varying amounts of diyne incorporated in the macrocycle framework (m/z = 1541 (**4b**, no diyne), 1565 (**6a**, 1 diyne), 1589 (**6b** and **6c**, 2 diynes), 1613 (**6d**, 3 diynes), 1637 (**6e**, 4 diynes)). The monodisperse peak in the GPC can be explained by the fact that the size difference between macrocycles is small, two carbon atoms, and therefore the resulting macrocycles are expected to have similar hydrodynamic volumes. The macrocycles were isolated as a mixture by preparatory GPC in a 61% yield (see Figure 1 and Table 1).

In conclusion, we have developed a straightforward method to synthesize AEMs without the generation of byproducts. Additionally, the depolymerization of an arylene−butadiyne polymer results in a mixture of mono- and diyne-containing macrocycles. This depolymerization method is now being applied to macrocycles that were previously unattainable due to the inherently low solubility of precursors and/or oligomers. The method is also currently being explored as a way to obtain quick access to combinatorial libraries of macrocycles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic procedures for polymers and macrocycles, characterization data, and GPC traces.

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(8) To test the extent of the reaction conditions, polymer **3b** (1.8 g, ~300 mM (based on monomer unit) in CCl_4) was subjected to the metathesis catalyst resulting in 850 mg (47% yield) of macrocycle **4b**.

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(12) The low molecular weight material was successfully removed by swelling and washing with dichloromethane. MALDI-MS analysis shows the mixture contains macrocyclic species (m/z = 1229 [3]cycle, 1638 [4]cycle). Similar macrocycles have been reported by: Zhao, T.; Liu, Z.; Song, Y.; Xu, W.; Zhang, D.; Zhu, D. *J. Org. Chem.* **2006**, *71*, 7422–7432.