Revisiting Cyclobutadienemetal Complexes: High-Content Dewar Benzene Polymers and a One-Pot Synthesis of Permethylated Ladderanes

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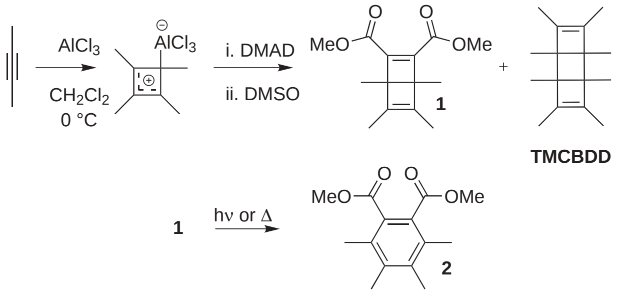
Abstract: High-content Dewar benzene polymers and sterically congested [*n*]-ladderanes have been synthesized from $[4\pi_s+2\pi_s]$ cyclobutadienemetal complex cycloaddition chemistry. In the former case, tetramethylcyclobutadiene–$AlCl_3$ is reacted with an acetylene-containing precursor polymer to yield > 95% Dewar benzene incorporation. In the latter case, [*n*]-ladderanes containing up to thirteen rings are prepared via a one-pot procedure from 2-butyne.

Key words: polymer synthesis, Dewar benzene, [*n*]-ladderanes, cycloadditions, cyclobutadiene

The reaction between anhydrous $AlCl_3$ and an internal alkyne, such as 2-butyne, is a simple and efficient method to produce the corresponding tetraalkylcyclobutadiene-$AlCl_3$ complex (Scheme 1).[1,2] This complex has been utilized extensively in the synthesis of substituted Dewar benzenes and tricyclo[4.2.0.0^{0,0}]oct-3-enes.[2–5] In almost all reported cases, the reacting partners are electron-deficient π-systems, such as acetylene dicarboxylic acid diesters. The accepted mechanism for this reaction is thermal $[4\pi_s+2\pi_s]$ cycloaddition between liberated cyclobutadiene and an electron-deficient 2π component. Yields vary considerably for this reaction, being highly dependant upon the nature of the 2π system. Unsuccessful cycloadditions typically yield cyclobutadiene dimer (octaalkylyl-tricyclo[4.2.0.0^{0,0}]octa-3,7-diene) as the major product (i.e., TMCBDD, Scheme 1).

Having previously reported that Dewar benzene can serve as a photolabile supramolecular protecting group capable of inhibiting solid-state aryl-aryl stacking interactions,[6] we remain interested in translating this concept to polymer chemistry. For example, the ability to photochemically mask and unmask interchain aryl-aryl stacking interactions may influence properties such as polymer solubility and crystallinity. A first step in achieving this goal is the synthesis of high-content Dewar benzene polymers by utilizing the limited repertoire of reactions associated with cyclobutadiene–$AlCl_3$ (CDB–$AlCl_3$) chemistry. Herein we report the chemistry of two organometallic–CBD complexes (Al^{3+} and Fe^{2+}), both capable of yielding polymers of interest. More specifically, both the desired high-content Dewar benzene polymer (synthesized via post-polymerization methods) and permethyleated ladderanes[7] are reported.

To date, our attempts to directly polymerize a Dewar benzene monomer have been unsuccessful. This may be due, at least in part, to the intrinsic reactivity of the Dewar benzene system. Further frustrating our goal is the aforementioned limitations to the synthesis of a large library of Dewar benzene monomers via CBD–$AlCl_3$ synthetic methodology. As such, we focused our attention on post-polymerization methods that employ a CBD–$AlCl_3$-mediated alkyne cyclotrimerization route to Dewar benzenes. This reaction, shown in Scheme 1, is presumed to be a $[4\pi_s+2\pi_s]$ cycloaddition between a transient tetrasubstituted cyclobutadiene and an alkyne dienophile. In our hands, a 1:1 reaction between tetramethylcyclobutadiene (TMCBD) and dimethylacetylene dicarboxylate (DMAD) yields ca. 70% of isolated Dewar benzene **1**, with the remaining side products being unreacted DMAD and octamethyl-tricyclo[4.2.0.0^{0,0}]octa-3,7-diene (tetramethylcyclobutadiene dimer, TMCBDD, Scheme 1). Noting that the only transformation of DMAD in this reaction is to product, we realized the applicability of this synthetic method to post-polymerization conversion of a polymeric DMAD analog [i.e., a poly(dieneophile)] to the corresponding poly(Dewar benzene).



Scheme 1

Polymeric dienophile, poly-**3**, was prepared by the acid-catalyzed esterification of tetraethylene glycol and acetylene dicarboxylic acid (neat, 50 °C, 70 mTorr). The reaction was halted when the mixture became too viscous to be stirred by a magnetic stir bar driven by a magnetic stir-plate. Isolated polymers were subjected to gel permeation chromatography (GPC) analysis and were found to have molecular weights of ca. 2700 (vs polystyrene standards). Given the proof-of-concept nature of these studies, no efforts were made to obtain higher molecular weight polymers.

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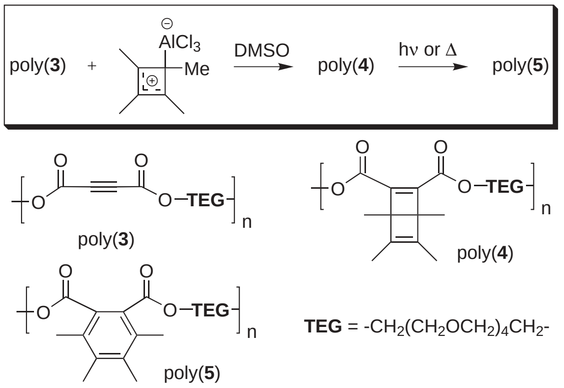
Conversion of poly-**3** to poly-**4** was carried out under conditions similar to the preparation of **2** (Scheme 2). It was found that as the ratio of diene to dienophile increased from 1:1 to 2.5:1, Dewar benzene incorporation increased from ca 60% to >95%. Thus, >95% of acetylene sites in poly-**3** were converted to Dewar benzene moieties via cycloaddition with TMCBD. As before, TMCBDD was the only other major product in the reaction mixture. The isolated crude polymer was washed with pentane to remove TMCBDD impurities. No further purification of poly-**4** was necessary.



Scheme 2

Both the thermal and photochemical isomerization of poly-**4** to poly-**5** were monitored by ^{1}H NMR. For the latter experiment, a solution of poly-**4** in $CDCl_3$ was completely converted to poly-**5** by irradiation with a longwave UV lamp (2.2 W) for ca 60 minutes. For the former experiment, a solution of poly-**4** in toluene-d_8 yielded 50% conversion upon heating at 100 °C for 15 hours. In both cases, ^{1}H NMR peaks associated with the aromatic isomer were identical, with no significant signs of side reactions such as isomerization to prismane. GPC analysis of pre- and post-isomerized polymer (polymers **4** and **5**, respectively) show slightly different retention times (7.69 and 7.84 min, respectively). This difference most likely results from isomerization, as it is not of the magnitude expected if cross-linking via undesirable side reactions had occurred. Note that the longer retention time of poly-**5** may result from increased interaction between aryl moieties of polymer and those present within the GPC stationary phase column packing material (cross-linked divinylbenzene). ^{1}H NMR spectra for polymers **3**–**5** are shown in Figure 1.

Neat samples of compounds **1**–**5** were analyzed by differential scanning calorimetry (DSC). The thermal isomerization of compound **1** to **2** corresponds to an exotherm centered at 147 °C during the heating scan. The ΔH for this process is 60 kcal/mol. This experimental value is in good agreement with the calculated value of 62 kcal/mol (B3LYP/6-31G[d][8]). High purity of the thermal product, compound **2**, can be assessed from the observation of its crystallization at 95 °C during the cooling scan (sharp exothermic peak centered at 95 °C; ΔH = 7.4 kcal/mol). Poly-**3** exhibits one major exotherm centered at 206 °C (ΔH = 35 kcal/mol). We propose this event corresponds to thermal decomposition of the pre-polymer.

Similar to compound **1**, poly-**4** exhibits one major exotherm (62 kcal/mol) during the heating scan. This event is centered at ca. 157 °C. Subsequent heating/cooling scans show no additional exothermic processes corresponding to thermal isomerization. Thermal gravimetric analysis (TGA) reveals that only a slight mass loss (2.4%) takes place over the temperature range corresponding to thermal isomerization.

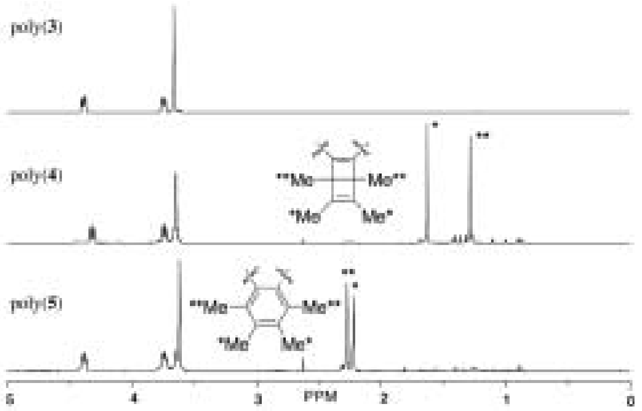
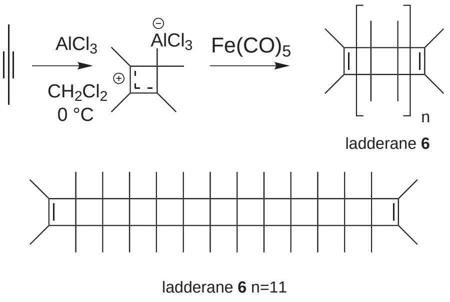


Figure 1 ^{1}H NMR spectra of polymers **3**–**5**

In an effort to screen the chemistry of alternative cyclobutadiene sources, we attempted to prepare and utilize the known tricarbonylcyclobutadiene iron complex $[R_4C_4H_4Fe(CO)_3]$, specifically TMCBD–$Fe(CO)_3$.[1] Our intent was to modify the preparation of this complex by an in situ exchange reaction of TMCBD–$AlCl_3$ with $Fe(CO)_5$ to yield TMCBD–$Fe(CO)_3$ (Scheme 3).



Scheme 3

Under such conditions, the desired iron complex, if formed, underwent rapid decomposition to yield a mixture of hydrocarbons differing by mass units equivalent to C_8H_{12} (FAB$^+$ MS: $C_{16}H_{24}$, $C_{24}H_{36}$, $C_{32}H_{48}$, $C_{40}H_{60}$, $C_{48}H_{72}$, $C_{56}H_{84}$). ^{1}H NMR spectroscopy revealed multiple singlet peaks of differing intensity clustered about the two regions associated with the ^{1}H singlets of TMCBDD (1.44 and 0.95 ppm). The combined analyses, coupled with existing literature precedent of ladderane[9] synthesis via CBD–Fe(CO)$_3$ complexes,[7,10] implicate oligomerization of cyclobutadiene, likely by [4π+2π] cycloaddition, to yield an overall one-pot synthesis of sterically-crowded permethyated ladderanes starting with the C$_4$-building block, 2-butyne. Note that the transformation of $C_4H_6 \rightarrow C_{56}H_{84}$ corresponds to creation of thirteen annulated rings, compound **6** (n = 11, Scheme 3).

The isolated mixture of ladderanes exhibited only moderate stability, with thermal/photochemical decomposition affecting work-up, purification, and isolation. The gradual appearance of hexamethylbenzene along with an increasingly complex ^{1}H NMR spectrum of the mixture corresponds with previously reported degradation pathways.[7] Given the large number of eclipsing butane fragments that can be identified within the framework of compounds **6**, it is not surprising that high (torsional and VDW) strain greatly affects stability in a negative sense. Optimization of reaction conditions and isolation of discrete products are in progress.

This communication has reported preliminary synthetic results leading to two novel polymers: high content Dewar benzene containing polymers and sterically congested permethylated ladderanes. Both utilize cyclobutadiene-metal complexes as key synthetic elements. Further studies are underway and include optimization of reaction conditions and a more comprehensive analysis of the physical properties associated with the aforementioned polymeric materials.

Acknowledgment

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