Polymers with Linked Macrocyclic Rings in the Main Chain. Zirconocene Coupling of 1,8-Cyclotetradecadiyne

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Inorganic networks with well-defined pore structures have attracted tremendous research attention due to their novel properties and many applications.[1] For example, microporous zeolites are heavily used as catalysts in the petroleum industry.[1b] Recently, there is rapidly growing interest in the construction of porous organic networks,[2] which may be more readily tailored synthetically and therefore offer new applications in catalysis,[3] separations,[4] and chemical sensors.[5] A commonly pursued approach to the synthesis of such materials involves the assembly of molecular organic compounds into hydrogen-bonded networks. However, such materials typically do not have molecular-sieving properties and are unstable at relatively high temperature.[2c,6] An approach that may overcome this problem involves the use of macrocyclic building blocks as "prefabricated nanopores" in the construction of porous networks.[7] In particular, stable structures should result from covalent incorporation of such rings into a network.

Linear polymers incorporating macrocyclic units have been designed for applications in metal ion separation,[8a−c] ion conduction,[8d] and chemical sensing.[8e,f] Previously, macrocycles have been linked into polymeric structures in face-to-face,[9a] face-to-edge,[9b] and edge-to-edge,[9c−f] fashions. Examples of the latter approach involve the Ni-catalyzed coupling of cyclic diynes with carbon dioxide to form ladder polymers.[9d,f] Macrocycles have also been threaded by linear polymers to afford polyrotaxanes[9g,i] and interlocked into chain structures called catenanes.[9h] Recently, we have been investigating the zirconocene coupling of diynes as an efficient route to new polymers and macrocycles (e.g., Scheme 1).[10] This method appears to be generally useful for the synthesis of metal-containing polymers,[11] which are readily converted to other polymers with novel structures. Here we report its application in the synthesis of polymers containing macrocyclic rings in the main chain.

Generation of free zirconocene (by addition of 2 equiv of ^{n}BuLi to a THF solution of zirconocene dichloride at −78 °C, followed by warming to room temperature)[12] in the presence of 1,8-cyclotetradecadiyne (**1**)[13] afforded polymer **2** as an orange, viscous gel (Scheme 2). Polymer **2** is slightly soluble in common organic solvents; therefore a molecular weight analysis by gel permeation chromatography (GPC; polystyrene standards) provided only values for the low molecular weight soluble fraction (M_w/M_n = 4000/2000). No monomeric species from intramolecular coupling of the diyne were observed. Intramolecular coupling would presumably involve the unfavorable formation of a tricyclic compound with 7- and 8-membered rings. After hydrolysis, this polymer is solubilized as the poly(macrocycle) structure **3**, for which M_w/M_n = 29000/6500 (vide infra). Assuming no depolymerization in this step, a molecular weight for the entire sample of **2** can be estimated from the data for **3** as M_w/M_n = 62000/14000. Reduction of zirconocene dichloride by magnesium[14] in the presence of the diyne **1** also gave polymer **2**, but the degree of polymerization from this method is somewhat lower than that from the ^{n}BuLi method.[15]

An apparent limitation to further chain growth in this condensation polymerization is the low solubility of **2**, which results in precipitation of the orange polymer from solution (at low monomer concentrations) or gelation (at high monomer concentrations). Removal of solvent allows isolation of polymer **2** as a moisture-sensitive but relatively air-stable powder. The ^{1}H NMR spectrum of the soluble fraction of this polymer shows broad resonances for the cyclopentadienyl ligands and macrocyclic ring hydrogens, in an integrated ratio which is consistent with the structure shown in Scheme 2.[16] It proved impossible to completely separate **2** from the LiCl byproduct, given the very similar solubility properties for these two components (in hydrocarbon solvents such as toluene and THF). Therefore polymer **2** was used in crude form (as a mixture with LiCl) in further reactions.

Hydrolysis of **2** with hydrochloric acid gave colorless polymer **3**, which has a monomodal molecular weight distribution (M_w/M_n = 29000/6500), in 86% yield along with a quantitative yield of zirconocene dichloride. Separation of **3** from zirconocene dichloride was achieved by methanol-induced precipitation of the polymer from a THF solution. Polymer **3** is stable in air, and soluble in most organic solvents. In its ^{1}H NMR spectrum,[17] two vinylic resonances (at 5.60 and 5.58 ppm) with the same integrated areas suggest an equal number of 1,8- and 1,9-connected macrocycles. A small peak at 5.40 ppm is assigned to the vinyl protons of the end groups. The degree of polymerization estimated from an end group analysis is 42, which is close to the value estimated from GPC analysis (34). The $^{13}C\{^1H\}$ NMR spectrum of **3** also shows two resonances for vinylic CH carbon atoms, along with the expected 11 resonances for the saturated carbons of the ring. Thus, it appears that the zirconocene coupling of 1,8-cyclooctadiyne is completely nonselective, leading to equal numbers of 1,8- and 1,9-substitution patterns.

Reaction of **2** with sulfur monochloride afforded a ladder polymer **4**,[18] along with 1 equiv of sulfur. This polymer is partially soluble in toluene and THF (50%, M_w/M_n = 9100/4000), and the insoluble portion (45%) exhibits an infrared spectrum and a combustion analysis which indicate that it has the same chemical composition as the soluble polymer. Thus, we conclude that the materials isolated from this reaction have the same polymeric structure, with their solubility properties being a function of molecular weight. In the ^{1}H NMR spectrum of **4**, resonances for both the α- and β-CH$_2$ protons on the thiophene ring are shifted to low field (2.5 and 2.7 ppm vs 2.1 and 2.3 ppm for polymer **3**), indicating the presence of aromatic thiophene rings.[19] The UV−vis spectrum of **4** contains a λ_{max} peak at 244 nm, which is also attributed to thiophene functionalities.[19] By elemental analysis and thermal gravimetric analysis (TGA), this polymer contains an additional equivalent of sulfur, and an absorption at 288 nm in the UV−vis spectrum (THF solution) indicates the presence of elemental sulfur. The TGA trace for **4** reveals the quantitative loss of this sulfur (1 equiv) at 280 °C, well before polymer decomposition occurs. Attempts to remove this sulfur by solvent extractions, heating at 150 °C under vacuum, treatment with mercury, or addition of hydrogen peroxide failed. However, the sulfur was removed by heating at 210 °C for

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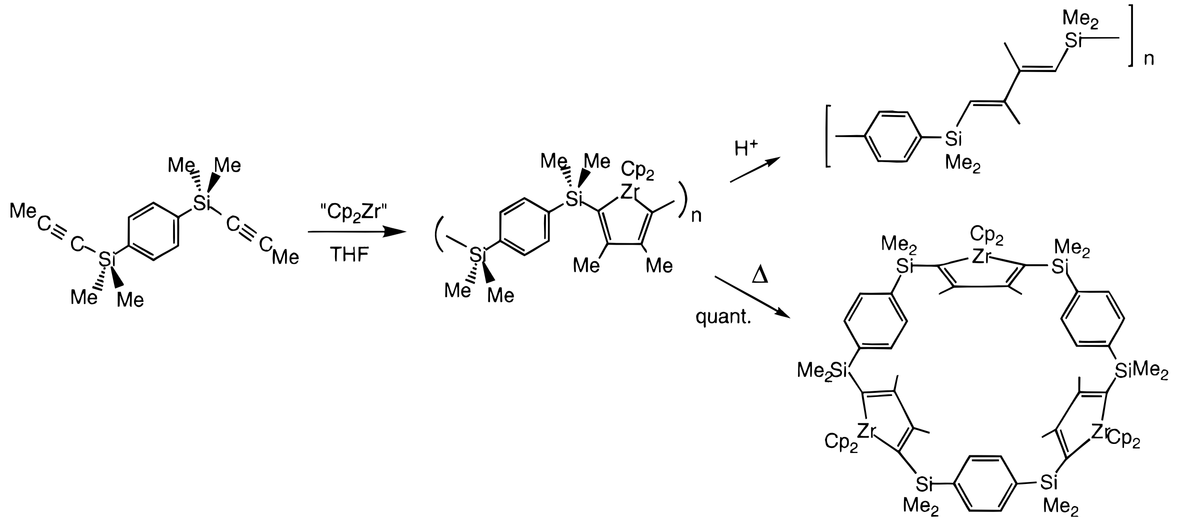
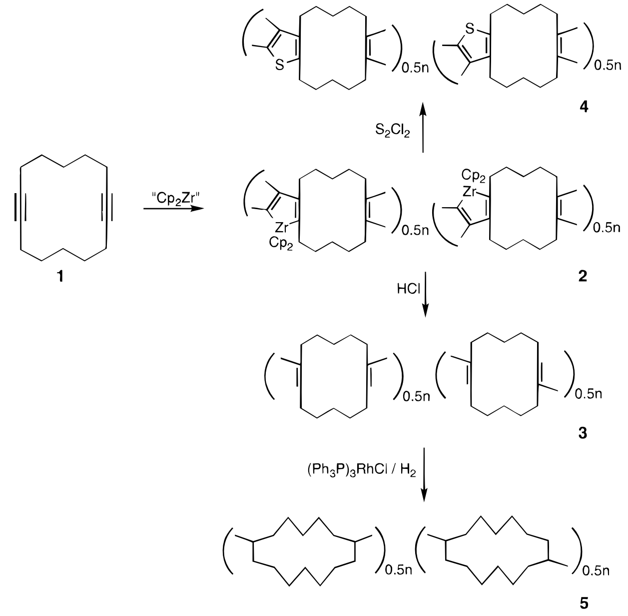
Scheme 1



Scheme 2



72 h under vacuum. Currently, the chemical nature of this additional sulfur has not been determined, but the conditions required for its removal suggest a weak interaction with the polymer chain.

The hydrogenation of polymer **3**, catalyzed by $(Ph_3P)_3RhCl$ in THF solution, afforded the saturated polymer **5** (M_w/M_n = 56000/7400) in high yield (87%, Scheme 2). As expected, the ^1H and $^{13}C\{^1H\}$ NMR spectra for **5** contain only resonances assigned to saturated hydrocarbon chains.[20]

The TGA traces for polymers **3**, **4**, and **5** exhibit onset temperatures for decomposition at 429, 450, and 418 °C, respectively (under nitrogen, Figure 1). The thermal stability of these polymers is therefore close to that of commercial low-density polyethylene (ca. 420 °C).[21] Thus, it appears that the cyclic nature of **5** does not contribute significantly to its stability. The differential scanning calorimetry (DSC) thermogram for monomer **1** displays a phase transition at 33 °C, which is presumably due to a chair → boat conformation change for the macrocycles (Figure 2).[13b] Related phase transitions were observed for all the polymers **2**−**5**, at slightly different temperatures (**2**, −3 °C; **3**, −10 °C; **4**, −2 °C; **5**, −3 °C). The melting temperature of **1** determined by DSC analysis is 98 °C. No glass transitions were observed for polymers **2**, **3**, and **4**; however, polymer **5**, with a more flexible polymer chain, exhibits a glass transition temperature (112 °C) and a melting point of 188 °C.

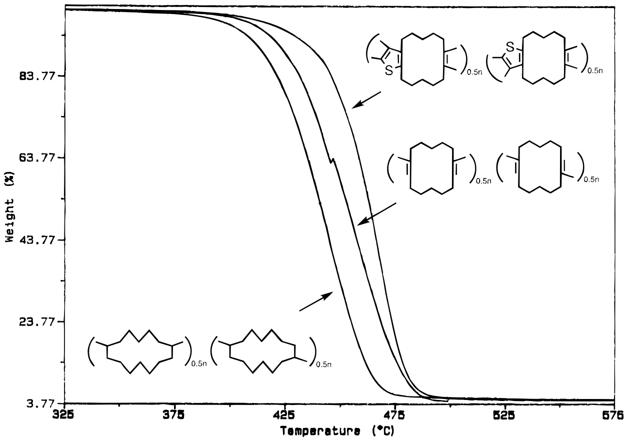


Figure 1. TGA thermograms for **2, 3**, and **4** (5 °C/min, under N_2).

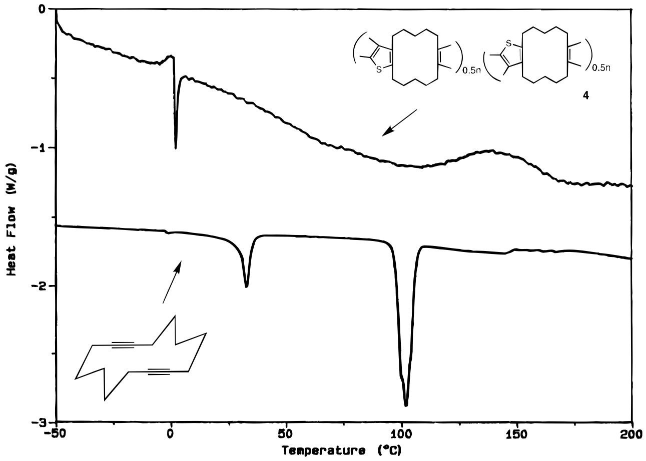


Figure 2. DSC thermograms for **1** and **4** (under N_2, first cycle).

In conclusion, we have demonstrated that zirconocene coupling of a cyclic diyne provides a novel route to ladder polymer structures with zirconacyclopentadiene units in the backbone. This reactive organometallic polymer is readily derivatized to various new structures. Currently, we are examining the conversion of the macrocyclic polymer **3** to functionalized polymers via reactions at the C═C double bonds.

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Supporting Information Available: Experimental procedures and characterization data for compounds (2 pages). Ordering information is given on any current masthead page.

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(15) Because polymer **2** is insoluble, the degree of polymerization for the two samples was compared by examining the molecular weight properties of the hydrolyzed (more soluble) derivatives **3**.

(16) Spectroscopic data for polymer **2**: ^{1}H NMR (benzene-d_6, 400 MHz) δ 6.05 (s, 10 H, C_5H_5), 2.35 (b, 4 H), 1.75 (b, 16 H).

(17) Spectroscopic data for polymer **3**: ^{1}H NMR (benzene-d_6, 400 MHz) δ 5.60 (s, 1 H), 5.58 (s, 1 H), 2.29 (s, 4 H), 2.16 (s, 4 H), 1.44 (s, 12 H). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz) δ C═CH: 142.68, 142.34; *C*═CH: 127.18, 126.90; CH_2: 29.08, 28.71, 28.30, 28.19, 27.98, 27.89, 27.79, 27.73, 27.57, 27.44, 27.21.

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(19) Spectroscopic data for polymer **4**: ^{1}H NMR (benzene-d_6, 400 MHz) δ 2.65 (s, 4 H), 2.50 (s, 4 H), 1.74 (s, 4H), 1.57 (s, 4 H), 1.37 (s, 4 H). For spectroscopic properties for thiophenes, see: *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, W. H., Eds.; Pergamon Press: New York, 1984; Vol. 4, pp 713−740.

(20) Spectroscopic data for polymer **5**: ^{1}H NMR (benzene-d_6, 400 MHz) δ 2.19 (b, 6 H), 1.50 (b, 20 H).

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