

Synthesis, Isomerization and Ring-Opening Metathesis Polymerization (ROMP) of a Disilanyl Analog of 1,5-Cyclooctadiene Yields Soluble Hybrid Conjugated Polymers

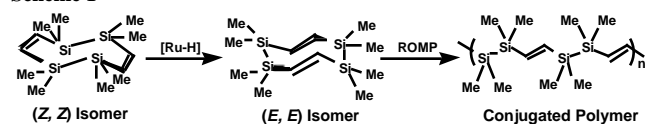
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Introduction

Although polyacetylenes $(-\text{CH}=\text{CH}-)_n$ and polyorganosilanes $(-\text{SiR}_2)_n$ represent structurally distinct classes of polymeric materials, both exhibit extended electron delocalization along the backbone,^{1,2} and become conducting upon doping.^{3,4} The nature of this delocalization is, however, very different in the two materials: polyacetylenes utilize an extended π -network, while polyorganosilanes utilize an extended σ -network. A promising approach to the development of a third class of electron-delocalized polymers that have potentially useful properties involves the synthesis of hybrid polyacetylene-polyorganosilane copolymers with a delocalized π -network. This approach combines the attractive electrical properties of polyacetylenes with the stability and solubility of polyorganosilanes.^{5,6} We wish to develop a new route to this class of materials via the ring opening metathesis polymerization (ROMP) of a disilanyl analog of 1,5-cyclooctadiene: (*E,E*)-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (Scheme 1).^{7,8}

Scheme 1



Results and Discussion

Highly reactive tungsten,^{9,10} molybdenum¹¹ and ruthenium^{12,13} alkylidene complexes are particularly useful for initiating the ROMP of cyclic olefins. Although (*Z,Z*)-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene **1** fails to polymerize in the presence of all three classes of these initiators,⁷ we chose to explore the polymerization of (*E,E*)-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene **2** by exposure to these complexes. The synthesis of **2** was accomplished by the ruthenium hydride catalyzed isomerization of **1** (Scheme 1).⁷

Our studies show that **2** undergoes polymerization in the presence of either $\text{W}(=\text{NPh})(=\text{CHPh}(2\text{-OMe}))(\text{OC}(\text{CF}_3)_2(\text{CH}_3)_2)(\text{THF})$ or $\text{Mo}(=\text{C}(\text{H})\text{CMe}_2\text{Ph})(=\text{NAr})(\text{OCMe}(\text{CF}_3)_2)_2$. When the Mo-based catalyst was used, the molecular weights of the polymers ranged from 1.2×10^5 to 1.4×10^5 , while the polydispersities ranged from 1.6 to 1.8. Preliminary studies showed that the molecular weights could not be controlled by varying the ratio of monomer to catalyst (Figure 1).

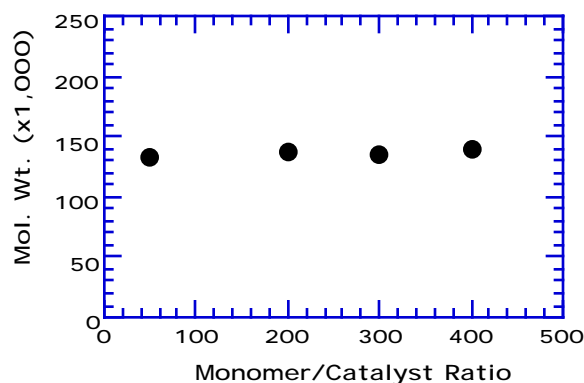


Figure 1. Plot of Molecular Weight versus the Ratio of Monomer to Catalyst for the ROMP of **2** Initiated by the Mo alkylidene.

We examined the solubility of the polymers in variety of solvents. We found that the polymers are readily soluble in benzene, methylene chloride, THF and toluene, but insoluble in DMF and DMSO. Further studies of the polymers are currently in progress.

Conclusions

We have synthesized (*Z,Z*)-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene **1** and isomerized it to (*E,E*)-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene **2**. Exposure of **2** to the active tungsten and molybdenum alkylidene metathesis catalysts generates soluble polymers with hybrid π -conjugation.

Experimental Section

General. All manipulations were carried out under inert atmosphere using Schlenk line and/or glove box techniques. Solvents were dried and purified by passing through columns of activated alumina and Q-5 reagent. The solvents were further degassed using the freeze-pump-thaw methods. The synthesis of (*Z,Z*)-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**1**) and (*E,E*)-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**2**) has been described.⁷

Polymerizations. In a typical polymerization, a Schlenk NMR tube was charged with 20 mg (7.0×10^{-5} mol) of **2** and a minimum amount of C_6D_6 for dissolution of **2**. In a separate vial, a solution of 2.9 mg (3.5×10^{-6} mol) of the molybdenum alkylidene complex $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{NAr})(\text{OC}(\text{CF}_3)_2\text{CH}_3)_2$ in a minimum amount of C_6D_6 was prepared and transferred to the Schlenk NMR tube. The reaction was allowed to proceed for 2 d at rt. The resultant solution was poured into MeOH, and the precipitate was collected. The polymer was purified by re-dissolving in THF and re-precipitating in MeOH. The polymer was dried under vacuum to give 10 mg (50 % yield) of a white solid. ^1H NMR (300 MHz, CDCl_3): 6.55 (s, 4 H), 0.10 (s, 24 H). A similar procedure was used for the ROMP of **2** initiated by the tungsten alkylidene complex $\text{W}(=\text{NPh})(=\text{CHPh}(2\text{-OMe}))(\text{OC}(\text{CF}_3)_2(\text{CH}_3)_2)(\text{THF})$: 20 mg (7.0×10^{-5} mol) of **2** and 2.8 mg (3.5×10^{-6} mol) of tungsten alkylidene complex were used to give 12 mg (60 % yield) of the polymer.

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