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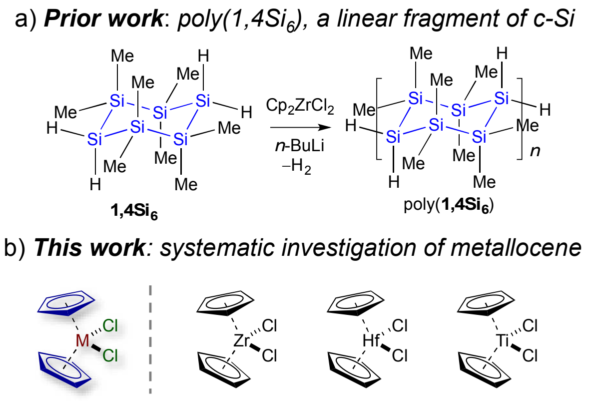
Poly(cyclosilane)s, conjugated polymers inspired by crystalline silicon, are synthesized by group 4 metallocene-promoted dehydrocoupling polymerization. Changes in metallocene structure and reactivity are correlated with changes in poly(cyclosilane) chain length and optical properties. This work demonstrates the ability of target-directed synthesis to afford tunable, complex polymeric architectures.

Multistep strategic synthesis has found minimal application in the preparation of functional polysilanes, despite progress in the synthesis of complex molecular silanes.[1] We recently demonstrated the synthesis of a poly(cyclosilane), a novel inorganic polymer in which the repeat unit is a six-membered ring of silicon atoms, a structure inspired by a one-dimensional fragment of crystalline silicon.[2] Here, we explore the influence of the coordination polymerization catalyst on the structure of the poly(cyclosilane)s. Our results support the existence of a common mechanism between monosilane and cyclosilane coordination polymerization and point to the potential for advanced catalysts to provide fine-control over polysilane properties. This synthetic approach to complex polysilane frameworks complements efforts demonstrating that increasing the complexity of the organic side chains on polysilanes results in novel properties and functions.[3] Such efforts include hybrid σ,π-silane donor-acceptor compounds that are efficient hole transport materials,[4–9] asymmetric systems displaying nonlinear optical behavior,[10–14] and fluorinated side chains controlling the global conformation, autoxidation, and absorbance properties of polysilanes.[15–17] Poly(cyclosilane)s add to the body of work on polymeric main group optoelectronic materials.[18–20]

A key strategic element of our poly(cyclosilane) synthesis is the design of **1,4Si$_6$**, a bifunctional monomer for transition metal-catalyzed dehydrocoupling polymerization (Figure 1a). In prior work, we employed the combination of zirconocene dichloride (Cp_2ZrCl_2) and butyllithium (*n*-BuLi), to initiate step-growth polymerization.[21–23] ^{1}H and ^{29}Si NMR spectroscopy in combination with infrared spectroscopy provided evidence of an unbranched structure. The poly(cyclosilane) backbone is capped with SiMe and SiH groups, while polymer end groups are secondary silanes (Si_2SiH_2).


a) ***Prior work***: *poly(1,4Si$_6$), a linear fragment of c-Si*

b) ***This work***: *systematic investigation of metallocene*

Figure 1. a) Klausen synthesis of poly(**1,4Si$_6$**), a poly(cyclosilane) resembling a linear fragment of crystalline silicon, via dehydrocoupling polymerization. The metallocene is activated in situ by n-butyllithium. b) This work reports a systematic investigation of metallocene-promoted **1,4Si$_6$** dehydrocoupling polymerization.

Herein, we systematically vary the metallocene structure. The identity of the transition metal (Ti, Zr, or Hf), as well as the cyclopentadienyl ligands and alkyl substituents influence the degree of polymerization and backbone structure of the resulting poly(cyclosilane). Structural changes are correlated with changes in dehydrocoupling polymerization rate. The optical properties of these novel conjugated inorganic polymers are sensitive to structural perturbations.

Polymerization studies were initiated with the catalytic system first detailed by J. Corey, the in situ activation of a metallocene dichloride (Cp_2MCl_2, M = Ti, Zr, Hf) with *n*-BuLi.[22] Table 1 summarizes the molecular weight characteristics of poly(**1,4Si$_6$**) samples arising from variations in the group 4 metal center. Standard polymerization conditions are

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Table 1. Variation of poly(**1,4Si$_6$**) molecular weight characteristics with metallocene initiator.

Entry	Metallocene	M_n (Da)[a]	M_w (Da)[a]	Đ[b]	$\overline{DP}$[c]
1	Cp_2ZrCl_2/*n*-BuLi	2670	3580	1.34	9
2	Cp_2HfCl_2/*n*-BuLi	2150	2920	1.36	7
3	Cp_2TiCl_2/*n*-BuLi	1980	3650	1.85	6

[a] Determined by gel permeation chromatography (GPC) with UV detection at 254 nm relative to a polystyrene standard.

[b] Đ = M_w/M_n

[c] The ratio of poly(**1,4Si$_6$**) M_n and **1,4Si$_6$** M_n, as determined by GPC analysis.

Cp_2MCl_2/*n*-BuLi (5.6/11.2 mol%) in toluene at room temperature. A standard 24-hour reaction time was employed to probe both rapid and more sluggish reactions. Poly(**1,4Si$_6$**) slowly oxidizes upon air exposure but is indefinitely stable when stored in a nitrogen atmosphere glove box. All structural characterization was carried out using air-free technique.

The Cp_2ZrCl_2/*n*-BuLi system provided the highest molecular weight polymer (entry 1) and all monomer is consumed within the 24-hour reaction period. Cp_2HfCl_2/*n*-BuLi is slower than Cp_2ZrCl_2/*n*-BuLi (entry 2), with unreacted monomer observed after 24 hours, and somewhat lower poly(**1,4Si$_6$**) molecular weights. Cp_2TiCl_2/*n*-BuLi provides low molecular weigh material that is more disperse than both the Zr- and Hf-derived samples (entry 3).

NMR spectroscopy reveals that significant structural rearrangement accounts for the lower molecular weights and high dispersities observed with Cp_2TiCl_2/*n*-BuLi. ^{29}Si NMR spectroscopy is a sensitive probe of poly(cyclosilane) structure.[2,24–26] Figure 2 shows the ^{29}Si {^1H} DEPT NMR spectra of poly(**1,4Si$_6$**) prepared with different metallocene initiators. Cp_2ZrCl_2/*n*-BuLi and Cp_2HfCl_2/*n*-BuLi provide polymers with the signature resonances of a linear poly(cyclosilane). These signatures include a δ −102 resonance assigned to the secondary silane polymer end groups (labelled *Si*H_2) and the δ −120 resonances assigned to internal tertiary silanes (*Si*H). Consistent with the molecular weight trends and shorter chain lengths documented in Table 1, in Cp_2HfCl_2/*n*-BuLi polymers, the end group resonances are more intense than observed with Cp_2ZrCl_2/*n*-BuLi. Both polymer samples also feature δ −35 resonances assigned to backbone *Si*Me_2, which appear less intense than *Si*H resonances due to weaker two-bond ^1H-^{29}Si polarization transfer.[27]

Poly(**1,4Si$_6$**) arising from Cp_2TiCl_2/*n*-BuLi catalysis has a very different structure. A cluster of resonances between δ −35 and –45 are consistent with backbone *Si*Me_2 resonances while the signature end group and backbone *Si*H_2 and *Si*H resonances diminish in intensity. ^1H NMR also supports significant structural differences, as the Si-H signals for Zr- and Hf-derived polymers are similar in appearance while the Ti-derived polymer exhibits very broad Si-H resonances (Figure S1). Corey et al. reported appx. 10% yield of alkyl redistribution products in the Cp_2TiCl_2/*n*-BuLi polymerization of $PhSiH_3$, while <5% redistribution was observed with a Zr catalyst.[23] Even a small amount of Ti-catalyzed alkyl scrambling in the **1,4Si$_6$** monomer introduces significant amounts of cyclosilanes that can act as chain capping agents or branching points (Figure S2). We note that polymer molecular weights in silane dehydrocoupling are highest for primary silane monomers, while secondary silanes provide short oligomers and tertiary silanes are unreactive. This suggests that alkyl redistribution to more highly substituted species depresses polymerization, consistent with the lower molecular weight species observed by GPC (Table 1).

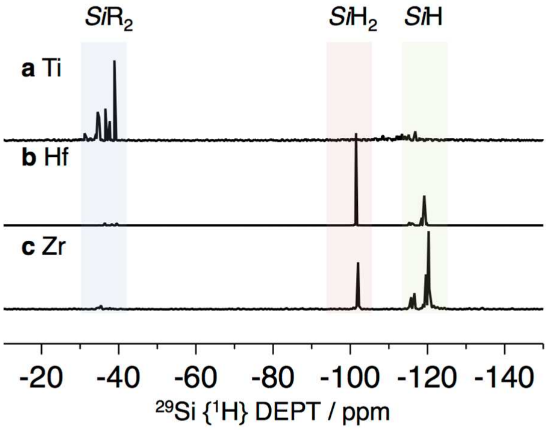

Figure 2. Cropped ^{29}Si {^1H} DEPT NMR spectra of poly(**1,4Si$_6$**) in benzene-*d*$_6$ arising from a) Cp_2TiCl_2/*n*-BuLi, b) Cp_2HfCl_2/*n*-BuLi, and c) Cp_2ZrCl_2/*n*-BuLi promoters. Regions assigned to alkyl- and H-substituted silanes indicated. DEPT = distortionless enhancement by polarization transfer. *J* coupling value for evolution time: $^2J_{Si\text{-}H}$ = 120 Hz.

UV-vis spectroscopy supports the hypothesis that Ti-catalysis provides a unique poly(**1,4Si$_6$**) structure relative to Zr- and Hf-catalysis. All poly(**1,4Si$_6$**) samples, no matter which catalyst system was employed, are red-shifted relative to**1,4Si$_6$**, which strongly absorbs ca. 210 nm ultraviolet light. This red-shift suggests extended σ-conjugation relative to the monomer. Both Zr- and Hf-derived samples of poly(**1,4Si$_6$**) have a pronounced feature around 265 nm, as well as a higher-energy transition at 239 nm. Ti-derived poly(**1,4Si$_6$**) has

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Table 2. Metallocene ligand effects on the molecular weight characteristics of poly(**1,4Si$_6$**).

Entry	Metallocene	M_n (Da)^a	M_w (Da)^a	Đ	$\overline{DP}^b$
1	Cp_2ZrCl_2/*n*-BuLi	2670	3580	1.34	9
2	Cp_2ZrCl_2	346	355	1.03	1
3	Cp_2ZrMe_2	2650	4720	1.78	8
4	$CpCp^*ZrCl_2$/*n*-BuLi	2100	2840	1.36	7
5	$Cp^*_2ZrCl_2$/*n*-BuLi	354	430	1.22	1

[a] Determined by gel permeation chromatography (GPC) with UV detection at 254 nm relative to a polystyrene standard.

[b] The ratio of poly(**1,4Si$_6$**) M_n and **1,4Si$_6$** M_n, as determined by GPC analysis.

a broader and less well-defined absorption profile consistent with a more disperse material.

Our observations suggest that the rate of dehydrocoupling within group 4 follows the trend of Zr > Hf > Ti. We attribute the structural changes observed with Cp_2TiCl_2/*n*-BuLi to alkyl scrambling of the monomer. These results parallel $PhSiH_3$ polymerization with early transition metals. Corey and Tilley have suggested a σ-bond metathesis mechanism for $PhSiH_3$ dehydrocoupling polymerization.[22,28]

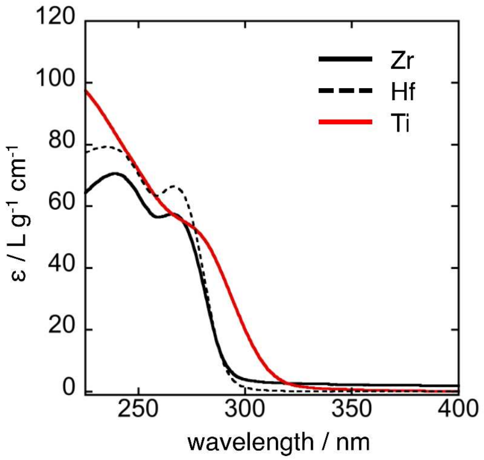

Figure 3. Absorption spectra of poly(**1,4Si$_6$**) samples arising from Zr (solid black), Hf (dashed black) and Ti (solid red) catalysis. Spectra recorded in THF at room temperature.

To further establish the existence of a common mechanism between $PhSiH_3$ and **1,4Si$_6$** dehydrocoupling polymerization, we investigated if ligand effects persist across both monomer types. In the context of Cp_2MX_2 (X = $SiTMS_3$, TMS, H, or Cl) derivatives, Tilley has reported that π donor ligands (e.g. chloride) inhibit dehydrocoupling by stabilizing the electron-deficient d^0 metal center required for σ-bond metathesis.[28–30] Corey reports similar observations with Cp_2ZrCl_2 and notes distinctions between Cp_2ZrMe_2 and the Cp_2ZrCl_2/*n*-BuLi system that suggest Cp_2ZrBu_2 is not the active catalyst.[22]

We find that activation with *n*-BuLi is required for significant polymerization, as Cp_2ZrCl_2 alone provided recovered starting material (Table 2, entry 2). Dimethylzirconocene (Cp_2ZrMe_2) provided poly(**1,4Si$_6$**) with similar molecular weight characteristics as Cp_2ZrCl_2/*n*-BuLi after 24 hours (entry 3), however, a several hour induction period was observed. These results support the Corey hypothesis that coordinatively unsaturated species arising from β-hydride elimination are the active catalysts.[22,31] The slow elimination of methyl groups, which lack β-hydrides, from Cp_2ZrMe_2 contributes to the observed induction period.

Substitution of the cyclopentadienyl ligands has competing steric and electronic effects on the rate of $PhSiH_3$ dehydrocoupling polymerization. While pentamethylcyclopentadiene (Cp*) is more electron-donating than the Cp ligand, the increased steric bulk inhibits the formation of inactive hydride-bridged dimers.[32] Mixed CpCp* complexes have the optimal balance of sterics and electronics and often provide the highest molecular weight polysilanes.[33] However, in our hands, incomplete conversion and a modest decrease in the M_n of poly(**1,4Si$_6$**) was observed with mixed zirconocene $CpCp^*ZrCl_2$/*n*-BuLi (entry 4) while $Cp^*_2ZrCl_2$/*n*-BuLi (entry 5) was unreactive. These data suggest that the factors that inhibit metallocene dimerization also inhibit **1,4Si$_6$** polymerization.

Addition of fresh catalyst to the polymerization did not result in increased polymer molecular weight (Table S1). The lack of further increase in molecular weight suggests depolymerization under extended reaction times (thermodynamic conditions).[28] Poly(**1,4Si$_6$**) is sparingly soluble in toluene and the polymerization becomes heterogeneous over time, potentially implicating polymer precipitation as a factor in the ceiling on poly(**1,4Si$_6$**) molecular weight.

Overall, the similar catalyst structure-activity relationships between $PhSiH_3$ and **1,4Si$_6$** support a common mechanism, despite the greater steric hindrance present in **1,4Si$_6$** which might inhibit σ-bond metathesis. A kinetic isotope effect experiment provides additional support. We synthesized **1,4Si$_6$**-*d$_4$* by dearylation of known **1** and reduction of the intermediate silyl triflate with lithium aluminum deuteride

(LAD, Figure 4). A toluene-d_8 solution of **$1,4Si_6$** or **$1,4Si_6$**-d_4 and pre-activated Cp_2ZrCl_2/*n*-BuLi ([monomer]$_0$:[initiator] = 10:1) was monitored by ^{1}H NMR spectroscopy at 50 °C. The instantaneous concentration of **$1,4Si_6$** was determined relative to a diphenylmethane internal standard. The integrated rate plots of **$1,4Si_6$** and **$1,4Si_6$**-d_4 reveals a primary deuterium kinetic isotope effect of k_H/k_D = 2.41 in **$1,4Si_6$** dehydrocoupling polymerization (Figure S3). A comparable k_H/k_D (2.9) was measured in the thermolysis of $CpCp^*Hf(SiH(D)_2Ph)Cl$ to $CpCp^*HfH(D)Cl$ and $(PhH_2Si)_2$.[29] The mechanistic continuity suggests that the discovery of catalysts able to effect high polymers from $PhSiH_3$ may be viable for cyclosilanes.

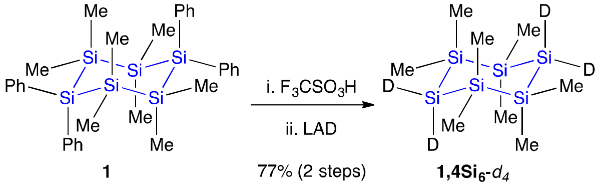

Figure 4. Synthesis of **$1,4Si_6$**-d_4. LAD = lithium aluminium deuteride.

In conclusion, this study reports synthesis-structure-property relationships in a novel class of conjugated inorganic polymers, the poly(cyclosilanes). We demonstrate mechanistic continuity between dehydrocoupling polymerization of a bifunctional cyclosilane monomer and $PhSiH_3$ through catalyst structure-activity relationships and a kinetic isotope effect study. This work demonstrates the ability of target-directed synthesis to afford tunable, complex polymeric architectures.

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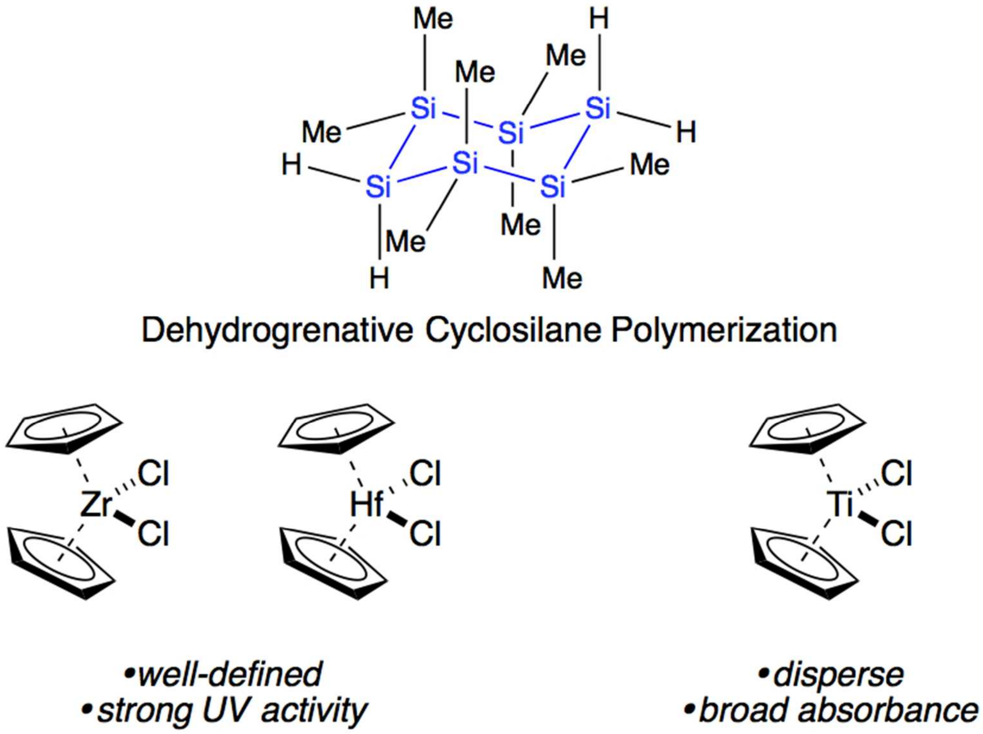

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