

## Synthesis and characterization of a chlorofunctionalized unsaturated carbosilane oligomer

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### SUMMARY:

Acyclic diene metathesis (ADMET) polymerization offers a viable route for the synthesis of chlorofunctionalized unsaturated carbosilane oligomers. The Si—Cl bond in unsaturated carbosilane monomers remains inert during metathesis and the use of a highly reactive molybdenum-based, Lewis acid-free alkylidene catalyst affords unsaturated chlorofunctionalized carbosilane oligomers with known vinyl end groups. The first synthesis of an unsaturated carbosilane oligomer functionalized with a Si—Cl bond was performed. A chlorofunctionalized silacyclopentene product was also observed, due to a backbiting reaction. This new class of functionalized oligomers has a low glass transition temperature and sites of unsaturation which may be used for further reaction. ADMET chemistry now provides access to a variety of chlorofunctionalized unsaturated carbosilanes which can be used to tailor make hydrolytically stable carbosilane oligomers and polymers via nucleophilic grafting reactions.

### Introduction

A growing interest exists in the synthesis and properties of macromolecules that contain inorganic elements such as phosphorus, nitrogen, and silicon, due to a large demand for materials with properties that conventional organic polymers cannot provide<sup>1)</sup>. Here we report the first synthesis of an unsaturated carbosilane oligomer functionalized with the Si—Cl bond.

One of the first inorganic polymer systems to be described in detail has been polyphosphazene, a backbone of alternating phosphorus and nitrogen atoms<sup>2,3)</sup> (Fig. 1). While the parent backbone, polydichlorophosphazene  $[\text{NPCl}_2]_n$  is an unstable polymer which reacts with air and moisture, hydrolytic stability can be achieved by complete halogen replacement with various nucleophiles<sup>4)</sup>. This elegant research has produced materials spanning from fire resistant elastomers to biocompatible polymers.

Another inorganic polymer system which has found broad technological use, incorporates silicon into the polymer backbone. Silicon based materials have proven interesting due to their electronic, optical, and thermal properties, in addition to their applications as precursors to ceramics. Consequently, the preparation of linear polycarbosilanes (polymers which contain carbon and silicon in the backbone) has received considerable attention for many years<sup>5)</sup>. Recently, a viable synthetic route to linear polycarbosilanes has been established with the advent of acyclic diene metathesis (ADMET) polymerization, chemistry which employs a Lewis acid-free catalyst system<sup>6)</sup>. The catalyst employed for ADMET polymerization is Schrock's Lewis acid-

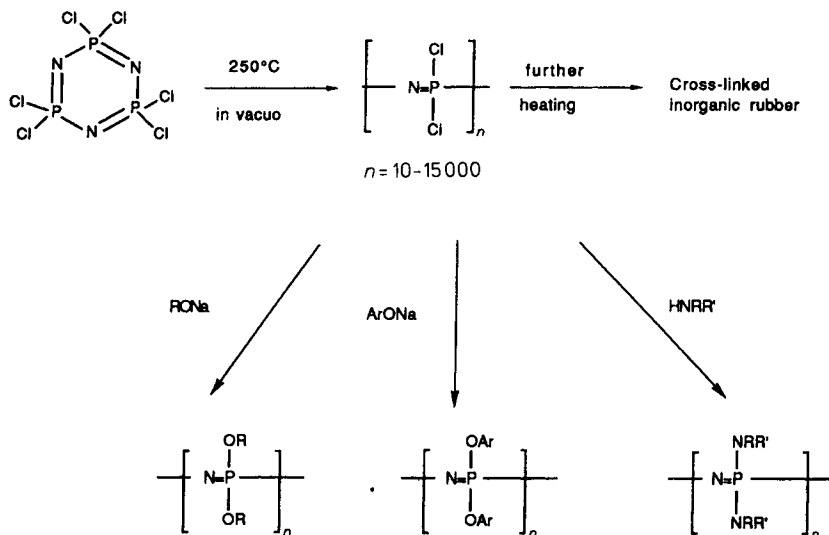


Fig. 1. Classical synthesis of polyphosphazenes. Substitution reactions lead to polymers whose physical behavior is determined by the identity of the nucleophile

free catalyst of the type  $[(\text{CF}_3)_2\text{CH}_2\text{CO}]_2(\text{NAr})\text{M}=\text{CHC}(\text{CH}_3)_2\text{Ph}$ , where  $\text{M} = \text{Mo}$  or  $\text{W}$  and  $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$ <sup>7)</sup> (Fig. 2).

Since the targeted nature of the ADMET reaction permits the inclusion of the Si—Cl bond in the monomer itself, we began to investigate the possibility of forming chlorinated carbosilane backbones. It is now apparent that this bond is completely inert to the metathesis chemistry at hand. This paper reports the first synthesis of a

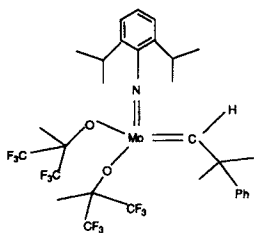


Fig. 2. Schrock's molybdenum based Lewis acid-free alkylidene catalyst used in ADMET reactions

chlorofunctionalized unsaturated carbosilane oligomer which can be reacted with various nucleophiles to vary the physical properties of this oligomer in a manner analogous to the polychlorophosphazenes synthesized by Allcock and coworkers. It is our intention to examine the versatility of chlorocarbosilane polymers in a manner similar to that done for the polyphosphazenes.

## Experimental part

### Materials

Trichloromethylsilane, diethylamine, acetyl chloride, dry air, and allylmagnesium bromide were purchased from Aldrich Chemical Co. and used as received. The molybdenum based Schrock's catalyst was synthesized as described in the literature<sup>7)</sup>. Diethyl ether was purchased from Fisher Scientific and distilled from a dark blue benzophenone ketyl as described in the literature<sup>8)</sup>.

### Polymerization reactions

Monomer **1** was vacuum transferred under an inert atmosphere to a previously dried and evacuated high vacuum flask equipped with a magnetic stirring bar, and the flask was sealed. This monomer was then degassed by three successive freeze, pump, thaw cycles under high vacuum ( $\leq 10^{-5}$  mmHg) prior to reaction. Polymerization was conducted in the bulk on a 1,0–3,0 mL scale. The molybdenum based catalyst was added to the monomer and stirred under inert conditions. The homogeneous, dark brown-colored mixture was stirred at ambient temperature and an immediate evolution of ethylene occurred. Ethylene was removed under full vacuum and an increase in viscosity was observed within 30 min. The viscous mixture was stirred overnight under full vacuum. Polymerization was terminated by exposure to dry air. The viscous oligomer was dissolved in chloroform-*d* and analyzed by NMR and GC/MS. Neat samples were used for all other analyses.

### Characterization

<sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were obtained with a Gemini NMR super conducting spectrometer system. Chloroform-*d* was used as solvent and all chemical shifts are referenced to it. Heteronuclear gated and decoupled quantitative <sup>13</sup>C NMR spectra were run for 10–14 h with a pulse delay of 10–20 s. Infrared analyses were performed on neat oils between NaCl plates using a Bio-Rad FTS/40A infrared spectrometer. Thermal data was obtained with a DSC 2910 differential scanning calorimeter (DSC). DSC samples were analyzed over a temperature range of –120 °C to 40 °C with a scan rate of 10 °C/min and liquid nitrogen as the coolant. Monomer purity was obtained from a Hewlett Packard 5880A gas chromatograph equipped with a methyl silicone column. Molecular weight data were obtained from mass spectral (MS) data, using a Finnigan 4500 gas chromatograph/mass spectrometer employing electron impact (EI) ionization or chemical ionization (CI).

### Diallylchloromethylsilane (**1**)

Diallylchloromethylsilane (**1**) was synthesized as reported in the literature<sup>9)</sup> except acetyl chloride was used instead of hydrogen chloride. Monomer **1** was synthesized 96% pure and had the following spectral properties.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0,41 (s; Si—CH<sub>3</sub>), 1,86 (d; allyl), 4,97 (d; —CH=CH<sub>2</sub>), 5,79 (m; —CH=CH<sub>2</sub>).

<sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = –1,09 (Si—CH<sub>3</sub>), 25,44 (Si—CH<sub>2</sub>—), 116,61 (—CH=CH<sub>2</sub>), 132,70 (—CH=CH<sub>2</sub>).

MS (70 eV, EI): *m/z* 160 (M<sup>+</sup>), 145 (M<sup>+</sup> – CH<sub>3</sub>), 119 (M<sup>+</sup> – allyl).

IR (NaCl): 3081 (m; vinyl), 1631 (s; allyl Si), 1257 (s; SiMe), 473 (s; br SiCl) cm<sup>-1</sup>.

*Poly(1-chloro-1-methyl-1-silapent-3-ene) (2)*

Oligomer (**2**) had the following spectral properties.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 0,41$  (s;  $\text{Si}-\underline{\text{CH}}_3$ ), 1,78 (d;  $\text{Si}-\underline{\text{CH}}_2-$ ), 5,35 (m;  $-\underline{\text{C}}\text{H}=\underline{\text{C}}\text{H}-$ ).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 0,12$  (*trans*  $\text{Si}-\underline{\text{C}}\text{H}_3$ ), 0,26 (*cis*  $\text{Si}-\underline{\text{C}}\text{H}_3$ ), 24,01 (*trans* allyl), 25,66 (*cis* allyl), 123,56 (*cis* vinyl), 125,01 (*trans* vinyl).

MS (70 eV, Cl):  $m/z$  425 ( $\text{M}^+ + 1$ ), 389 ( $\text{M}^+ - \text{Cl}$ ).

IR (NaCl): 3020 (m; C=C), 1216 (s; SiMe), 450 (s, br SiCl)  $\text{cm}^{-1}$ .

**Results and discussion**

Unsaturated polycarbosilanes have been the main focus of several research efforts, due to their intriguing physical properties. For example, Weber and coworkers successfully synthesized poly(allylsilanes) via anionic ring opening polymerization<sup>10</sup>. In addition, Gibson<sup>11</sup>) and Sartori<sup>12</sup>) synthesized similar compounds via ring opening metathesis polymerization of the strained cyclic, silacyclopent-3-ene. More recently, poly(carbosilanes) and poly(carbosiloxanes) have been synthesized via ADMET chemistry<sup>13</sup>), and various polyalkenylenes have been synthesized via this technique<sup>14, 15</sup>). This chemistry is an equilibrium step propagation condensation type polymerization, where the production and removal of ethylene drives the reaction (Fig. 3).

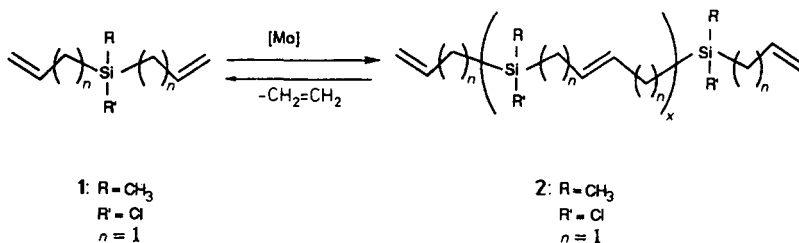


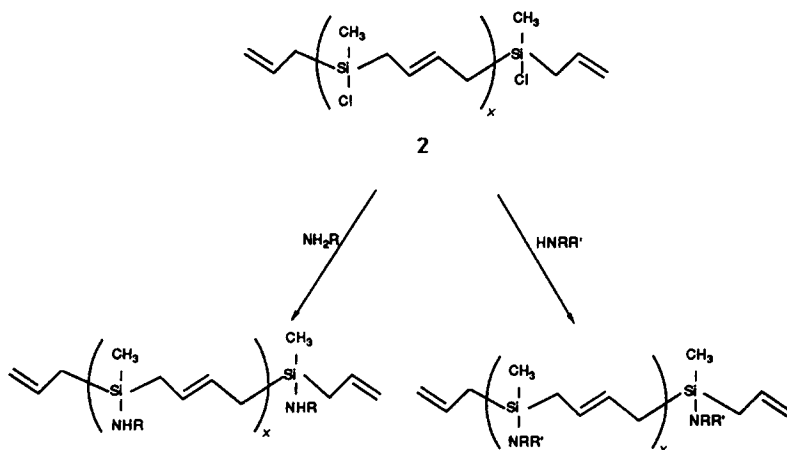
Fig. 3. ADMET reaction of chlorine-functionalized carbosilanes. [Mo] represents Schrock's molybdenum based catalyst

Steric interactions also play a role in this chemistry. Schrock and coworkers demonstrated in model studies with vinyltrimethylsilane that vinylsilanes are inert to metathesis, probably due to steric inhibition which prevents the formation of the intermediate  $\alpha,\beta$ -trimethylsilyl (TMS) metallacyclobutane. This intermediate is required for productive metathesis<sup>16</sup>). Thus, the productive metathesis products (1,2-bis(trimethylsilyl)ethylene) and ethylene are never formed, most likely due to steric interaction between the  $\alpha,\beta$ TMS substituents on the metallacyclobutane ring where the  $\text{C}_\alpha\text{-C}_\beta$  bond is weakened<sup>16</sup>). These findings led to our strategy of separating the sterically hindering methyl group from the terminal olefin with methylene spacers. Thus, diallylsilane monomers exhibit no resistance to productive metathesis and generate clean polymers at low temperatures<sup>6, 13</sup>).

Since the targeted nature of the ADMET reaction permits the inclusion of the Si—Cl bond in the monomer itself, we began to investigate the possibility of forming

chlorinated carbosilane backbones. Thus, a chlorine-functionalized allylic diene has been polymerized by ADMET chemistry to produce a chlorofunctionalized oligomer. This oligomer should be amenable to conversion into either solvent resistant elastomers or high glass transition materials via nucleophilic grafting reactions, as illustrated in *Scheme 1*.

*Scheme 1:*



### Monomer synthesis

Diallylchloromethylsilane (**1**) was synthesized as reported in the literature<sup>9,17)</sup> and, as expected, this monomer is unstable and produces a disiloxane upon hydrolysis. Fig. 4 displays the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for monomer **1**.

The external and internal olefinic protons are shown at 4,97 and 5,79 ppm, respectively, and allylic protons are observed at 1,86 ppm in the <sup>1</sup>H NMR spectrum. The signal for methyl protons is observed at 0,41 ppm. Signals at ca. 0,08, 0,81, and 3,02 are due to the presence of diethylaminomethyldichlorosilane, which was difficult to separate from the monomer by distillation<sup>9)</sup>. Additional signals are due to impurities. The Si—Cl bond stretch is assigned to the band at 473 cm<sup>-1</sup> in the IR spectrum. Mass spectral data indicate the presence of one chlorine atom by having a M+2 peak approximately one-third the intensity of the molecular ion peak. The absence of distinct M+4 or M+6 peaks rules out the presence of two or more chlorine atoms.

### Oligomerization

Several studies have been done to demonstrate the inert nature of the Si—Cl bond. For example, allylchlorodimethylsilane was employed in the ADMET depolymerization of 1,4-polybutadiene<sup>18)</sup> and as a chain transfer agent in the molecular weight control of poly(1-pentenylene)<sup>19)</sup>. Allylchlorodimethylsilane also was reacted under

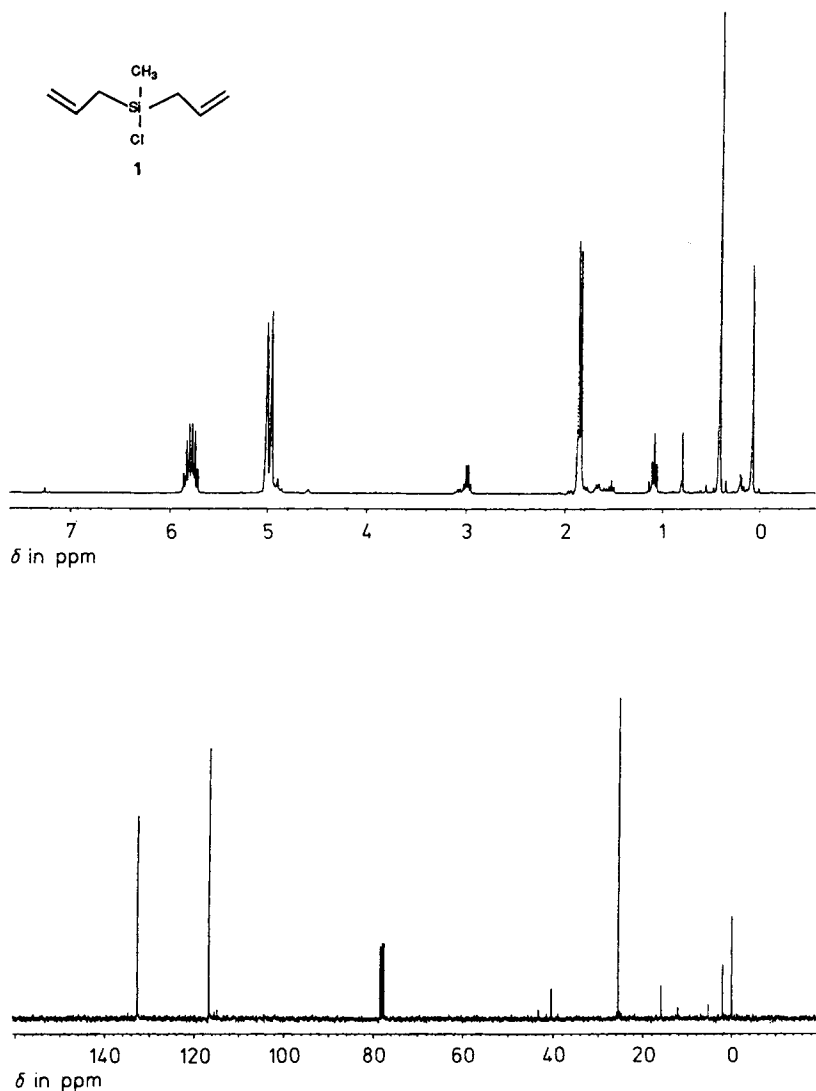


Fig. 4. 300 MHz <sup>1</sup>H NMR (top) and 75 MHz <sup>13</sup>C NMR spectra of diallylchloromethylsilane in chloroform-*d*

metathesis conditions in a model study, and the reactive Si—Cl bond remained inert<sup>13</sup>). These studies show that the labile Si—Cl bond is inert to metathesis in the presence of the alkylidene catalyst which contains various potential nucleophiles (i. e., alkoxy, imido, and alkylidene ligands).

The chemistry of ADMET polymerization is very clean with no side reactions evident except for the formation of trace amounts of cyclic products which result from

backbiting reactions<sup>20</sup>). ADMET polymerizations are performed under bulk conditions, under high vacuum, and with a typical monomer to catalyst ratio of 1000:1. Characteristic manifestations of ADMET polymerization are avid bubbling due to the evolution of ethylene, and the presence of an internal olefin signal in NMR spectroscopy. These manifestations were indeed apparent for the reaction of diallylchloromethylsilane in the presence of Schrock's catalyst, producing the oligomer **2** shown in Fig. 3. The final yield of the condensation reaction is greater than 80%.

Fig. 5 displays the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for the oligomerization product mixture containing ca. 57% oligomer **2**. As anticipated, oligomer **2** is a mixture of *cis* and *trans* isomers and contains a high percent *trans* content (84% by <sup>13</sup>C NMR), which is typical for ADMET chemistry. The oligomer internal olefin protons are shown

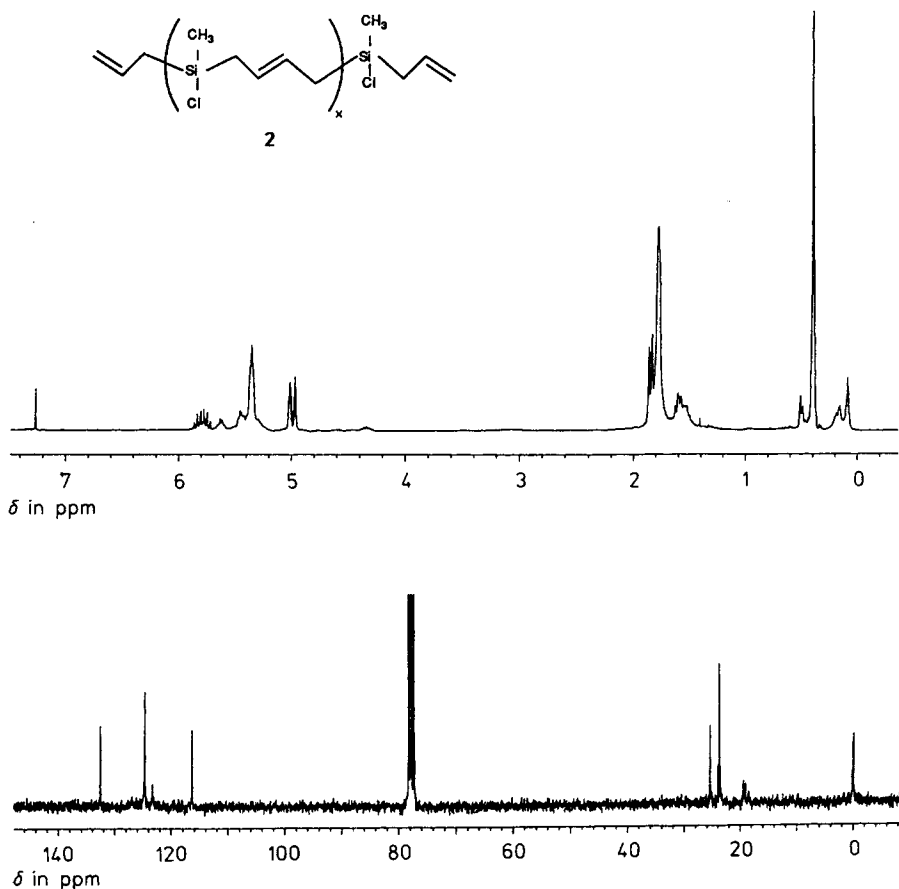


Fig. 5. 300 MHz <sup>1</sup>H NMR (top) and 75 MHz <sup>13</sup>C NMR spectra of poly(1-chloro-1-methyl-1-silapent-3-ene) in chloroform-*d*

at 5,3 ppm in the  $^1\text{H}$  NMR spectrum, and this signal clearly indicates the metathesis occurred. While these *cis* and *trans* internal olefin protons are not completely resolved, the analogous carbon signals are readily distinguished by  $^{13}\text{C}$  NMR at 123 and 125 ppm respectively. Further, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data show terminal vinyl signals (4,97 and 5,79 ppm) which indicate that vinyl groups are the end groups. Integration of internal vs. terminal olefin carbon signals indicates that a low conversion has occurred thus far in our work. Incomplete condensation is most likely due to decomposition of the catalyst by some impurity, and we are striving to increase the purity of the monomer to avoid these catalyst poisoning reactions.

Cyclic compounds also form, for gas chromatography/mass spectrometry data indicate the presence of ca. 38% of the 5-membered cyclic, 1-chloro-1-methyl-1-silacyclopent-3-ene ( $m/z = 132$ ). This cyclic results from a backbiting reaction which probably occurs during polymerization. Cyclic proton signals appear in the  $^1\text{H}$  NMR spectrum (Fig. 5) as follows: 5,62 ppm ( $\text{CH}=\text{CH}$ ), 1,61 ppm ( $\text{Si}-\text{CH}_2$ ), and 0,09 ppm ( $\text{Si}-\text{CH}_3$ ). Other signals are due to impurities.

Further analysis of data support the structure assigned to the chlorofunctionalized oligomer. For example, the *trans* and *cis* allylic peaks are resolved by  $^{13}\text{C}$  NMR and shown at 24 and 25 ppm, respectively. Also, the methyl substituents on silicon are shifted by the *cis/trans* geometry in both carbon and proton spectra. The *trans* signal (0,12 ppm) appears further up field than the *cis* signal (0,26 ppm) in the  $^{13}\text{C}$  NMR spectrum. Moreover, mass spectral data are consistent with the molecular weight values calculated by NMR end group calculation. Specific oligomers can be seen, i. e. mass 424 and 132 for the cyclic formed, however, the molecular weight of the metathesis product has not been determined.

DSC data for oligomer 2 show a glass transition temperature of  $-84^\circ\text{C}$ , which is similar to the value obtained for the polydimethylcarbosilane analogue ( $-67^\circ\text{C}$ )<sup>13</sup>. These values are as anticipated for linear unsaturated polycarbosilanes. A low glass transition indicates flexibility along the polymer backbone, as expected for carbosilane oligomers without bulky substituents. We are confident that the chlorofunctionalized oligomers will lend themselves well to further reactions via grafting chemistry, and we are proceeding in that direction now.

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