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### New Organosiloxanes Containing Silacycles

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## NEW ORGANOSILOXANES CONTAINING SILACYCLES

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### Abstract

The synthesis of carbon substituted 1,1-dichloro- and 1,1-bis(diethylamino)silacyclobutanes and butenes and their polycondensation reactions with bisphenol A, 1,2-ethanediol and 1,6-hexanediol is described. The monomer silacycles and the organosiloxane polymers are characterized by NMR ( $^1\text{H}$ -,  $^{13}\text{C}$ -,  $^{29}\text{Si}$ -), GPC, DSC and elemental analysis.

### Introduction

Carbon based oligomer and polymer compounds containing different amounts of silacyclic subunits in the polymer backbone are predicted to be materials with useful and promising new properties [1]. The synthetic route to polycarbosilanes starting from silacyclobutanes [2-4] and even from silacyclobutenes [5] with hydrogen substituted ring

carbon atoms is well established. But with respect to the low stability of the four membered rings the polyreaction mostly follows a ring-opening mechanism to form silicon carbon based polymers. There is little known about materials with retention of the silacyclobutane [1] or -butene [1, 6] in the polymer chain. In earlier work we have described the preparatively facile synthesis of silicon dichloro functionalized silacyclobutanes [7] and -butenes [8] of extraordinary stability [9]: Protected by organo groups at the carbon ring moiety and influenced by the dichlorosilyl functionality these cyclic compounds can not be opened by nucleophilic or electrophilic attack and they are thermally stable up to 400°C, even in the presence of transition metals [9, 10]. Furthermore, with transition metal dianions they form quite stable silanediyl complexes which could be characterized by single crystal x-ray diffraction [11]. Both, the silacyclobutane and -butene subunits can be introduced into cyclic  $D_3/D_4$ -analogous silicon oxygen rings [12]. Thus, these compounds are precursors for the syntheses of a new class of silicones, containing different amounts of silacycles (1:2 or 1:3 *rsp*).

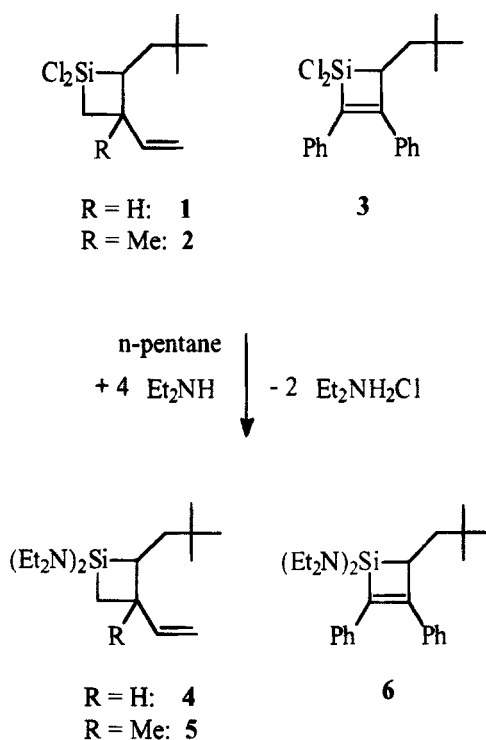
In this paper the polycondensation reactions of dichloro- and bis(diethylamino)silyl functionalized cycles **1** - **6** with different aromatic and aliphatic diols are reported.

### Experimental

All reactions were carried out with exclusion of moisture and oxygen. Solvents were dried by the usual methods. 1,1-Dichloro-1-silacyclobutanes **1**/**2** and -but-2-ene **3** were prepared as described earlier [7, 8].

#### *Synthesis of the bis(diethylamino)functional monomers 4 - 6*

To a solution of 3-15 mmol of the silacyclic compound **1**, **2** or **3** in 50 ml of n-pentane, a mixture of a 6-8molar excess of  $\text{Et}_2\text{NH}$  in 50 ml of n-pentane is added dropwise at room temperature. The precipitated  $\text{Et}_2\text{NH}_2\text{Cl}$  is separated by filtration. The solvent and excess amine are removed under vacuum.



**Scheme 1:** synthesis of 1,1-bis(diethylamino) substituted silacyclobutanes and -butene

*1,1-bis(diethylamino)-3-ethenyl-2-neopentyl-1-silacyclobutane 4*

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, 20°C, ppm): d = 0.92 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.10 (t, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12H, NCH<sub>2</sub>CH<sub>3</sub>), 1.12 (m, 2H, CH<sub>2</sub>), 1.38 (m, 2H, C<sup>4</sup>H<sub>2</sub>), 1.87 (m, 1H, C<sub>3</sub>H), 1.98 (m, 1H, C<sup>2</sup>H), 2.98 (q, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 8H, NCH<sub>2</sub>CH<sub>3</sub>), 4.92 (m, 2H, C<sup>6</sup>H<sub>2</sub>), 5.87 (m, 1H, C<sup>5</sup>H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75.47 MHz, 20°C, ppm): d = 15.34 (NCH<sub>2</sub>CH<sub>3</sub>), 30.01 (C(CH<sub>3</sub>)<sub>3</sub>), 30.14 (C(CH<sub>3</sub>)<sub>3</sub>), 32.35 (C<sup>4</sup>), 38.67 (NCH<sub>2</sub>CH<sub>3</sub>), 44.43 (C<sup>7</sup>H<sub>2</sub>), 110.67 (C<sup>6</sup>), 145.96 (C<sup>5</sup>). <sup>29</sup>Si-NMR (CDCl<sub>3</sub>, 54.4 MHz, 20°C, ppm): d = -8.2. **Anal.** found (calcd) H: 12.56 (12.33); C: 70.02 (69.81); Si: 9.07 (9.04).

*1,1-bis(diethylamino)-3-ethenyl-3-methyl-2-neopentyl-1-silacyclobutane 5*

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, 20°C, ppm): d = 0.93 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.04 (s, 3H, CH<sub>3</sub>), 1.11(t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 12H, NCH<sub>2</sub>CH<sub>3</sub>), 1.12 (m, 2H, CH<sub>2</sub>), 1.30 (m, 2H, C<sup>4</sup>H<sub>2</sub>), 1.83

(m, 1H, C<sup>2</sup>H), 3.03 (q, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 8H, NCH<sub>2</sub>CH<sub>3</sub>), 4.87 (m, 2H, C<sup>6</sup>H<sub>2</sub>), 6.07 (m, 1H, C<sup>5</sup>H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75.47 MHz, 20°C, ppm): δ = 14.97 (NCH<sub>2</sub>CH<sub>3</sub>), 22.35 (CH<sub>3</sub>), 30.07 (C(CH<sub>3</sub>)<sub>3</sub>), 30.76 (C(CH<sub>3</sub>)<sub>3</sub>), 38.56 (NCH<sub>2</sub>CH<sub>3</sub>), 40.43 (C<sup>7</sup>H<sub>2</sub>), 107.15 (C<sup>6</sup>), 147.00 (C<sup>5</sup>). <sup>29</sup>Si-NMR (CDCl<sub>3</sub>, 54.4 MHz, 20°C, ppm): δ = -9.2. **Anal.** found (calcd) H: 12.66 (12.42); C: 70.27 (70.30); Si: 8.48 (8.65).

*1,1-bis(diethylamino)-2,3-diphenyl-4-neopentyl-1-silacyclobut-2-ene 6*

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, 20°C, ppm): δ = 0.78 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.02 (t, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12H, NCH<sub>2</sub>CH<sub>3</sub>), 1.19 (m, 2H, CH<sub>2</sub>), 2.58 (m, 1H, CH), 2.94 (q, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 8H, NCH<sub>2</sub>CH<sub>3</sub>), 7.01 (m, 10H, C<sup>6</sup>H<sub>5</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75.47 MHz, 20°C, ppm): δ = 12.81 (NCH<sub>2</sub>CH<sub>3</sub>), 27.91 (C(CH<sub>3</sub>)<sub>3</sub>), 28.03 (C(CH<sub>3</sub>)<sub>3</sub>), 37.78 (NCH<sub>2</sub>CH<sub>3</sub>), 39.59 (CH<sub>2</sub>), 41.57 (CH), 125.53 - 128.64 (C<sub>arom.</sub>), 136.46 (C<sub>q-arom.</sub>), 136.84 (C<sub>q-arom.</sub>), 144.92 (C<sup>2</sup>), 55.16 (C<sup>3</sup>). <sup>29</sup>Si-NMR (CDCl<sub>3</sub>, 54.4 MHz, 20°C, ppm): δ = -21.8. **Anal.** found (calcd) H: 9.95 (9.74); C: 76.99 (77.38); Si: 6.63 (6.46).

*polycondensation reactions*

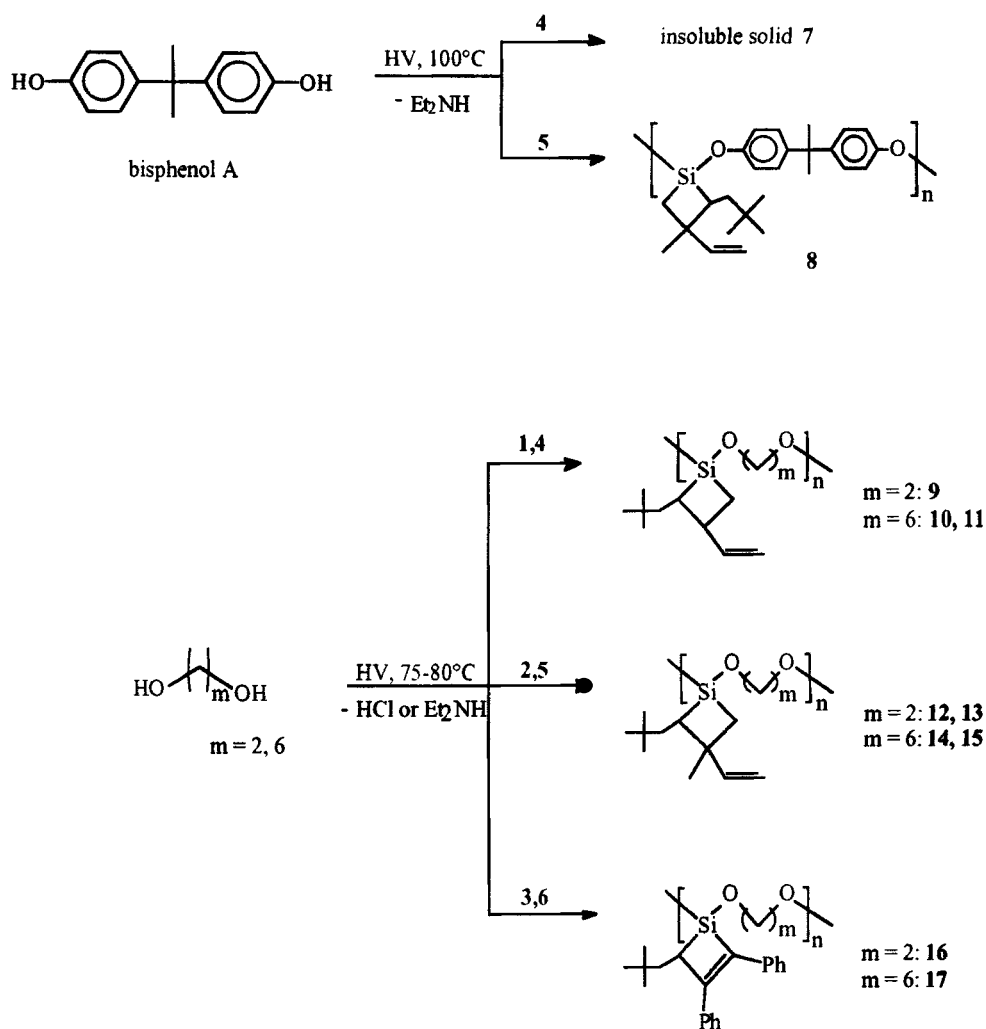
A mixture of an equimolar amount of each of the silacyclic monomers and the diol is stirred for 10 - 18h under vacuum and in a temperature range between 75 and 100°C. The reaction mixture is then dissolved in a small portion of CHCl<sub>3</sub> or THF and the polymer is precipitated in methanol at -5°C.

7

T<sub>G</sub>: 26°C.

8

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, 20°C, ppm): δ = 1.03 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.19 (s, 3H, CH<sub>3</sub>), 1.65 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>), 2.03 (s, 1H, CH), 5.03 (m, 2H, C<sup>6</sup>H<sub>2</sub>), 7.30 - 7.37 (m, 10H, CH<sub>arom.</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75.47 MHz, 20°C, ppm): δ = 29.26 (C(CH<sub>3</sub>)<sub>3</sub>), 30.40



**Scheme 2:** polycondensation reactions of silicon carbon four membered cycles with diols

$(C(CH_3)_3)$ , 40.68 ( $CH_2$ ), 41.44 ( $CH$ ), 63.58 ( $OCH_2$ ), 128.05 - 129.01 ( $C_{arom.}$ ), 144.27 ( $C^2$ ), 158.39 ( $C^3$ ). <sup>29</sup>Si-NMR ( $CDCl_3$ , 54.4 MHz, 20°C, ppm):  $\delta$  = -8.1.  $T_G$ : 32°C.

9

<sup>1</sup>H-NMR ( $CDCl_3$ , 300 MHz, 20°C, ppm):  $\delta$  = 0.87 (s, 9H,  $C(CH_3)_3$ ), 1.29 (m, 2H,  $C^7H_2$ ), 1.46 (m, 2H,  $C^4H_2$ ), 3.94 (s, 4H,  $OCH_2$ ), 4.91 (m, 2H,  $C^6H_2$ ), 5.89 (m, 1H,  $C^5H$ ). <sup>13</sup>C-

**Table 1:** Summary of polycondensation reactions of the silacycles with diols and molecular masses  $M_w/M_n$  of the products

	1	2	3	4	5	6
bisphenol A	no reaction	no reaction	no reaction	insoluble resin 7	rubberlike resin 8 3750/2800	no reaction
1,2- ethanediol	no reaction	rubberlike resin 12 5840/4460	solid 16 2550/1930	rubberlike resin 9 1290/1050	rubberlike resin 13 2800/1950	low oligomer product
1,6- hexanediol	hardly soluble resin 10	rubberlike resin 14 2260/1520	solid 17 2140/1230	rubberlike resin 11 1260/950	rubberlike resin 15 2030/1360	low oligomer product

**NMR** ( $\text{CDCl}_3$ , 75.47 MHz, 20°C, ppm): d = 29.75 ( $\text{C}(\text{CH}_3)_3$ ), 30.52 ( $\text{C}(\text{CH}_3)_3$ ), 38.04 ( $\text{C}^4$ ), 39.67 ( $\text{C}^7\text{H}_2$ ), 41.33 ( $\text{C}^4$ ), 46.24 (CH), 64.31 ( $\text{OCH}_2$ ), 111.58 ( $\text{C}^6$ ), 149.08 ( $\text{C}^5$ ).

**$^{29}\text{Si}$ -NMR** ( $\text{CDCl}_3$ , 54.4 MHz, 20°C, ppm): d = -12.9.  **$T_G$** : -27°C.

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**$^1\text{H}$ -NMR** ( $\text{CDCl}_3$ , 300 MHz, 20°C, ppm): d = 1.03 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 1.38 (s, 4H,  $\text{CH}_2$ ), 1.68 (s, 4H,  $\text{CH}_2$ ), 3.84 (s, 4H,  $\text{OCH}_2$ ), 5.13 (m, 2H,  $\text{C}^6\text{H}_2$ ), 6.19 (m, 1H,  $\text{C}^5\text{H}$ ).  **$^{13}\text{C}$ -NMR** ( $\text{CDCl}_3$ , 75.47 MHz, 20°C, ppm): d = 25.32 (2  $\text{CH}_2$ ), 29.74 ( $\text{C}(\text{CH}_3)_3$ ), 32.39 (2  $\text{CH}_2$ ), 38.58 ( $\text{C}^4$ ), 39.82 ( $\text{C}^7\text{H}_2$ ), 62.97 ( $\text{OCH}_2$ ).  **$T_G$** : -30°C.

**12/13**

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz, 20°C, ppm): d = 0.80 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.03 (m, 3H, CH<sub>3</sub>), 1.21 (m, 2H, C<sup>7</sup>H<sub>2</sub>), 1.42 (m, 2H, C<sup>4</sup>H<sub>2</sub>), 3.87 (s, 4H, OCH<sub>2</sub>), 4.85 (m, 2H, C<sup>6</sup>H<sub>2</sub>), 5.84 (m, 1H, C<sup>5</sup>H). **<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 75.47 MHz, 20°C, ppm): d = 29.68 (C(CH<sub>3</sub>)<sub>3</sub>), 30.16 (C(CH<sub>3</sub>)<sub>3</sub>), 37.98 (C<sup>4</sup>), 39.43 (C<sup>7</sup>H<sub>2</sub>), 41.12 (C<sup>4</sup>), 46.01 (CH), 64.03 (OCH<sub>2</sub>), 111.36 (C<sup>6</sup>), 148.99 (C<sup>5</sup>). **<sup>29</sup>Si-NMR** (CDCl<sub>3</sub>, 54.4 MHz, 20°C, ppm): d = -14.5. **T<sub>G</sub>**: -30°C.

**14/15**

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz, 20°C, ppm): d = 1.07 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.29 (m, 3H, CH<sub>3</sub>), 1.40 (s, 4H, CH<sub>2</sub>), 1.70 (s, 4H, CH<sub>2</sub>), 3.87 (s, 4H, OCH<sub>2</sub>), 5.04 (m, 2H, C<sup>6</sup>H<sub>2</sub>), 6.12 (m, 1H, C<sup>5</sup>H). **<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 75.47 MHz, 20°C, ppm): d = 22.70 (CH<sub>3</sub>), 25.51 (2 CH<sub>2</sub>), 29.94 (C(CH<sub>3</sub>)<sub>3</sub>), 32.95 (2 CH<sub>2</sub>), 38.91 (C<sup>4</sup>), 39.93 (C<sup>7</sup>H<sub>2</sub>), 63.28 (OCH<sub>2</sub>). **<sup>29</sup>Si-NMR** (CDCl<sub>3</sub>, 54.4 MHz, 20°C, ppm): d = -21.1. **T<sub>G</sub>**: -38°C.

**16**

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz, 20°C, ppm): d = 0.86 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.57 (s, 2H, CH<sub>2</sub>), 3.66 (s, 1H, CH), 4.09 (m, 4H, OCH<sub>2</sub>), 7.30 - 7.37 (m, 10H, CH<sub>arom.</sub>). **<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 75.47 MHz, 20°C, ppm): d = 29.26 (C(CH<sub>3</sub>)<sub>3</sub>), 30.40 (C(CH<sub>3</sub>)<sub>3</sub>), 40.68 (CH<sub>2</sub>), 41.44 (CH), 63.58 (OCH<sub>2</sub>), 128.05 - 129.01 (C<sub>arom.</sub>), 144.27 (C<sup>2</sup>), 158.39 (C<sup>3</sup>). **<sup>29</sup>Si-NMR** (CDCl<sub>3</sub>, 54.4 MHz, 20°C, ppm): d = -26.7. **T<sub>G</sub>**: 15°C.

**17**

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz, 20°C, ppm): d = 0.91 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.37 (s, 4H, CH<sub>2</sub>), 1.50 (s, 2H, CH<sub>2</sub>), 1.69 (s, 4H, CH<sub>2</sub>), 3.94 (m, 4H, OCH<sub>2</sub>), 7.28 - 7.35 (m, 10H, CH<sub>arom.</sub>). **<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 75.47 MHz, 20°C, ppm): d = 25.45 (CH<sub>2</sub>), 29.45 (C(CH<sub>3</sub>)<sub>3</sub>), 30.36 (C(CH<sub>3</sub>)<sub>3</sub>), 40.90 (CH<sub>2</sub>), 42.83 (CH), 62.84 (OCH<sub>2</sub>), 127.70 - 128.27 (C<sub>arom.</sub>). **T<sub>G</sub>**: 0°C.



## Results and Discussion

The polycondensation reaction of the silicon carbon four membered cycles **1** - **6** with different diols is a useful method for the preparative facile synthesis of a variety of new organosiloxanes. All products show the intact silacyclic subunits. This fact is proven by the characteristic chemical shifts in the NMR spectra of the silicon and carbon ring atoms and is in good agreement to results published previously [7, 8]. Although the product with the highest molecular weight is obtained from the condensation reaction of silacyclobutane **2** with 1,2-ethanediol, the disadvantage in siloxane formation starting from the dichlorosilyl functionalized monomers **1**, **2** and **3** is the formation of hydrogen chloride, which can not be removed completely. Analysis shows, that about one fourth of the gas evolved remains in the polymer product. To avoid this we investigated the bis(diethylamino)derivatives **4**, **5** and **6** as precursors, and in fact, the polycondensation products contain only traces of nitrogen and do not show any effects of aging after exposure to air. Compared to the dichloro functional silacycles, the aminated derivatives are less reactive towards diols and therefore the molecular weights of the products might be lower. Surprisingly, bisphenol A only reacts with bis(diethylamino) functional silacyclobutanes. As it is known from single crystal x-ray investigations in a whole series of silacyclobutenes [13], this fact may be mainly caused by sterical reasons and/or by the very different solubility of the starting monomers. The steric shielding of the cyclic unit by the organo substituents at the carbon atoms in silacyclobutenes may also be responsible for the fact that the silacyclobutanes are more reactive towards diols and thus, that their polycondensation products are characterized by higher molecular weights.

All the polymers containing silacyclobutane subunits are formed as rubberlike resins with low glass transition temperatures, whereas those built from the silacyclobutene monomers are solids. Some of the polymeric products show only low solubility in common organic solvents; that is why they can not be fully characterized spectroscopically.

### Conclusions

The synthesis of the first organo based siloxanes incorporating four membered silacyclic subunits has been achieved. Thus, we have built up the basis for the preparation and investigation of a new class of compounds which will be enriched by either different silacyclic monomers or by the use of a wide variety of diols.

Furthermore, it might be possible to use these new polymers to form blockcopolymers with siloxanes or organic based polycondensation products. In order to increase the molecular weights we will try to use different crosslinking methods to bind the polymer incorporated silacycles together as well as different catalysts to crosslink the preformed polymers by ring opening polymerization of the silacyclic unit; these experiments are in progress.

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