Synthesis of Poly(silylenemethylene)s Symmetrically Substituted with Alkyl Side Groups Containing 4−6 Carbon Atoms

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ABSTRACT: New poly(silylenemethylene)s with long *n*-alkyl side chains, namely, poly(di-*n*-butylsilylenemethylene) (PDBSM), poly(di-*n*-pentylsilylenemethylene) (PDPeSM), and poly(di-*n*-hexylsilylenemethylene) (PDHSM), have been prepared by means of catalytic ring-opening polymerization of the corresponding tetraalkyl-substituted 1,3-disilacyclobutanes. Polymerization yielded high molecular weight poly(silylenemethylene)s with a strictly alternating SiR_2/CH_2 backbone structure. Longer polymerization times were necessary for 1,3-disilacyclobutanes substituted with longer *n*-alkyl chains than for the polymerization of monomers with methyl groups. High molecular weight fractions of the materials were characterized by calorimetry with respect to their thermal behavior. Considerably higher glass transition temperatures evidenced lower backbone flexibility than for the analogous poly(di-*n*-alkylsiloxane)s. Surprisingly, all homologues including poly(di-*n*-propylsilylenemethylene) (PDPSM) displayed similar phase behavior, showing a small endotherm a few degrees below isotropization, but no broad mesophases as observed in the case of the poly(di-*n*-alkylsiloxane)s.

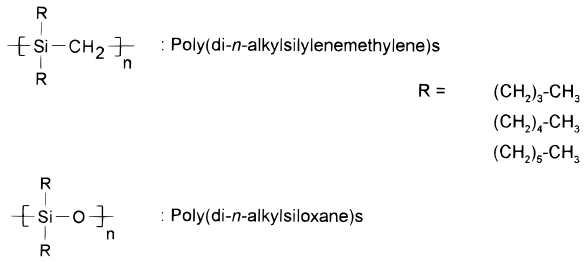
Introduction

Although poly(carbosilane)s belong to an unusual group of polymers consisting of an inorganic backbone substituted with organic side chains, generally designated inorganic/organic hybrid polymers or organometallic polymers,[1] poly(carbosilane)s so far have received less scientific attention than other representatives such as poly(siloxane)s,[2] poly(silylene)s,[3] or poly(phosphazene)s.[4] A considerable variety of backbone structures based on substituted silicon atoms combined with hydrocarbon units have been prepared,[5,6] among which poly(silylenemethylene)s represent a particularly interesting class of polymers.

Poly(silylenemethylene)s, polymers consisting of alternating SiR_2 and methylene units, have mainly been discussed as polymeric precursors for the preparation of SiC so far.[7,8] Only recently has interest shifted to their characteristics as polymeric materials. Poly(silylenemethylene)s can be regarded as carbon analogues of the poly(siloxane)s as well as silicon analogues of the corresponding carbon-based polymers.[6,9] Interrante et al.[10−12] recently described the preparation and characteristics of poly(silaethylene), the silicon analogue of poly(ethylene), revealing considerable differences in thermal behavior compared to poly(ethylene). Poly(silylenemethylene)s with various substituents on silicon, including alkoxy,[13,14] halogeno,[11,15] and aryl groups,[16,17] have been prepared and characterized to some extent.

Surprisingly, there are no reports on poly(silylenemethylene)s substituted symmetrically with *n*-alkyl chains, except for the well-characterized poly(dimethylsilylenemethylene) (PDMSM)[18−20] and poly(di-*n*-propylsilylenemethylene) (PDPSM) prepared in our laboratory recently.[21] Poly(di-*n*-alkylsilylenemethylene)s with side chains longer than methyl are of particular interest as the analogous poly(di-*n*-alkylsiloxane)s (Scheme 1) exhibit unusual mesomorphic properties, i.e., transitions to conformationally disordered, hexagonally packed mesophases.[22−28] It appears that such mesophases are typical for highly flexible inorganic/organic hybrid polymers with longer *n*-alkyl side chains. The existence of a conformationally disordered mesophase was proposed for PDPSM as well; however, the mesomorphic regime was limited to a surprisingly narrow temperature range in contrast to that of poly(di-*n*-propylsiloxane) (PDPS).[21] The synthesis of poly(silylenemethylene)s with *n*-alkyl side chains longer than propyl seemed desirable to us since increases in the length of side groups can have a stabilizing effect on the conformationally disordered state, as observed in the case of the poly(di-*n*-alkylsiloxane)s.[28] In addition, we were interested in studying the effect of larger substituents on the catalytic ring-opening polymerization of 1,3-disilacyclobutanes, which so far is little understood from a mechanistic point of view.

Scheme 1



The current paper describes the synthesis of poly(silylenemethylene)s symmetrically substituted with *n*-butyl, *n*-pentyl, and *n*-hexyl side chains, which is based on the catalytic ring-opening polymerization of the corresponding *n*-alkyl-substituted 1,3-disilacyclobutanes. The results of calorimetric measurements will be presented, giving a first account of the thermal behavior of these interesting inorganic/organic hybrid polymers.

Experimental Section

A. Synthesis. Tetrahydrofuran (THF) was distilled from sodium prior to use; *n*-heptane (Roth) was used as obtained without further purification. Trichloromethylsilane (Fluka) as well as *n*-butyl bromide, *n*-pentyl bromide, and *n*-hexyl

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Table 1. Synthesis of Chloro(chloromethyl)di-*n*-butylsilane (2a), Chloro(chloromethyl)di-*n*-pentylsilane (2b), and Chloro(chloromethyl)di-*n*-hexylsilane (2c)

product	bp [°C (mbar)]	final yield (%)
2a	105−107 (20)	41
2b	101−103 (11)	40
2c	110 (4)	50

Table 2. Synthesis of 1,1,3,3-Tetra-*n*-butyl-1,3-disilacyclobutane (3a), 1,1,3,3-Tetra-*n*-pentyl-1,3-disilacyclobutane (3b), and 1,1,3,3-Tetra-*n*-hexyl-1,3-disilacyclobutane (3c)

product	bp [°C (mbar)]	final yield (%)
3a	129−131 (2)	48
3b	153−155 (2)	42
3c	175−180 ($<10^{-3}$)	29

bromide (Aldrich) were used as received. Magnesium turnings and magnesium powder were dried in vacuo for at least 12 h. $H_2PtCl_6 \cdot 6H_2O$ catalyst was employed as a solution in glyme (1,2-dimethoxyethane) containing 1 wt % of Pt (Wacker). All reactions were carried out under an argon atmosphere; glassware was dried thoroughly prior to use.

1. Trichloro(chloromethyl)silane (1). 1 was prepared according to the method of Schmidbaur et al.[29] A 500 mL two-necked, round-bottomed flask was equipped with stirring bar, thermometer to determine the temperature directly above the surface of the liquid, and a packed column (50 cm). On top of this apparatus was placed a three-necked fillet transition piece containing a second thermometer, the chlorine inlet, and a reflux condenser, which was cooled to 0 °C. The fillet transition piece was illuminated by a 500 W lamp placed outside. The flask was charged with 300 mL (381.9 g, 2.55 mol) of trichloromethylsilane, which was heated to reflux until thermal equilibrium was reached in the reaction zone (∼60 °C). Subsequently, dry chlorine was passed slowly through the reaction zone under irradiation. While the temperature at the upper thermometer remained constant during the reaction, the temperature just above the surface of the liquid rose continuously. After 90 h (102 °C), the reaction was terminated. The yellow liquid obtained was purified by fractional distillation. A total of 45.4 g (0.30 mol) of unreacted trichloromethylsilane was recovered and a main product fraction with a boiling point of 116−118 °C (760 mmHg) was obtained: yield, 270.4 g (1.47 mol, 65%) of **1**; ^{1}H NMR (C_6D_6) δ 2.38 (s, CH_2); ^{13}C NMR (C_6D_6) δ 30.89.

2. Chloro(chloromethyl)di-*n*-butylsilane (2a). A 1000 mL three-necked, round-bottomed flask equipped with stirring bar, addition funnel, and reflux condenser was charged with 34.7 g (1.43 mol) of magnesium turnings in 50 mL of dry THF. *n*-Butyl bromide (143.1 mL, 182.6 g, 1.33 mol) dissolved in 330 mL of dry THF was added slowly within 3 h. After the reaction mixture was stirred at 40 °C for 1 h, the solution of the Grignard reagent was decanted under argon and the remaining magnesium was weighed to determine the conversion (96%).

In a 4000 mL three-necked, round-bottomed flask, 79.7 mL (117.6 g, 0.64 mol) of **1** was dissolved in 2200 mL of *n*-heptane. Butylmagnesium bromide (1.28 mol) was added slowly under strong stirring within 5 h. The exothermic reaction that occurred resulted in the formation of white magnesium salts as byproducts. The reaction mixture was stirred at 50 °C for 1 h. The magnesium salts were removed by filtration and extracted three times with *n*-heptane. Subsequently, the solvents were evaporated and the solution was filtered several times to remove remaining Grignard salts. The remaining yellow liquid was purified by repeated fractional distillation. Apart from dichloro(chloromethyl)-*n*-butylsilane and tri-*n*-butyl(chloromethyl)silane, a central fraction of **2a** was obtained. The boiling point and final yield of **2a** are given in Table 1: ^{1}H NMR ($CDCl_3$) δ 0.93 (m, 10H, SiCH_2CH_2 and CH_3), 1.37 (m, 8H, CH_2CH_3 and SiCH_2CH_2), 2.94 (s, 2H, $ClCH_2Si$); ^{13}C NMR ($CDCl_3$) δ 13.80 (CH_3), 14.30 (SiCH_2CH_2), 24.68 (CH_2CH_3), 25.86 ($SiCH_2CH_2$), 28.40 ($ClCH_2Si$).

3. Chloro(chloromethyl)di-*n*-pentylsilane (2b) and Chloro(chloromethyl)di-*n*-hexylsilane (2c). **2b** and **2c** were prepared in analogy to the synthesis of **2a** described in the preceding section. Boiling points and final yields of **2b** and **2c** are given in Table 1. ^{1}H NMR ($CDCl_3$) of **2b**: δ 0.87 (m, 10H, SiCH_2CH_2 and CH_3), 1.35 (m, 12H, $CH_2CH_2CH_2CH_3$), 2.95 (s, 2H, $ClCH_2Si$). ^{13}C NMR ($CDCl_3$) of **2b**: δ 13.89 (CH_3), 14.24 (SiCH_2CH_2), 22.16 (CH_2CH_3), 22.36 ($SiCH_2CH_2$), 28.43 ($ClCH_2Si$), 35.10 ($CH_2CH_2CH_3$). ^{1}H NMR (C_6D_6) of **2c**: δ 0.90 (m, 10H, SiCH_2CH_2 and CH_3), 1.34 (m, 16H, $CH_2CH_2CH_2CH_2CH_3$), 2.73 (s, 2H, $ClCH_2Si$). ^{13}C NMR (C_6D_6) of **2c**: δ 14.29 (CH_3), 14.56 (SiCH_2CH_2), 22.85 (CH_2CH_3), 22.89 ($SiCH_2CH_2$), 28.42 ($ClCH_2Si$), 31.66 ($CH_2CH_2CH_3$), 32.94 ($SiCH_2CH_2CH_2$).

4. 1,1,3,3-Tetra-*n*-butyl-1,3-disilacyclobutane (3a). 3a was prepared according to the method of Seyferth et al.,[8] which is a modified version of that originally proposed by Kriner.[30] A 500 mL three-necked, round-bottomed flask equipped with stirring bar, addition funnel, reflux condenser, and thermometer was charged with approximately 150 mg of magnesium turnings in 5 mL of dry THF. A few drops of iodomethane and then 1 mL of **2a** were added. The onset of the reaction was evidenced by a sharp exotherm. **2a** (58.8 g, 0.26 mol) and 50 mL of dry THF were added rapidly with continuous stirring. Subsequently, 10.5 g (0.43 mol) of magnesium powder was added portionwise during the course of 4 h, while the reaction temperature was maintained between 35 and 50 °C. Occasional cooling was necessary. After the addition of one-third of the magnesium powder, another 50 mL of THF was added to keep the reaction mixture stirrable. Another 50 mL of THF was added after about two-thirds of the magnesium had been added. The reaction mixture was heated to 50 °C for 2 h and then cooled to 0 °C. After the careful addition of 150 mL of water (0 °C), the organic layer was separated and washed with water. The aqueous fractions were extracted with THF. The combined organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by repeated fractional distillation using a Vigreux column. The boiling point and final yield of **3a** obtained as the central fraction are given in Table 2: ^{1}H NMR ($CDCl_3$) δ −0.13 (s, 4H, $SiCH_2Si$), 0.64 (m, 8H, SiCH_2CH_2), 0.87 (t, 12H, CH_3), 1.31 (m, 16H, $CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$) δ −2.91 ($SiCH_2Si$), 13.84 (CH_3), 16.54 (SiCH_2CH_2), 26.06 (CH_2CH_3), 26.45 ($SiCH_2CH_2$).

5. 1,1,3,3-Tetra-*n*-pentyl-1,3-disilacyclobutane (3b) and 1,1,3,3-Tetra-*n*-hexyl-1,3-disilacyclobutane (3c). 3b and **3c** were prepared in analogy to the synthesis of **3a** described in the preceding section. Monomer **3c** was distilled under high-vacuum conditions. Nevertheless, part of the monomer was lost during fractional distillation due to thermal polymerization. Boiling points and final yields of **3b** and **3c** are given in Table 2. ^{1}H NMR ($CDCl_3$) of **3b**: δ −0.11 (s, 4H, $SiCH_2Si$), 0.65 (m, 8H, SiCH_2CH_2), 0.90 (t, 12H, CH_3), 1.32 (m, 24H, $CH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$) of **3b**: δ −2.87 ($SiCH_2Si$), 14.03 (CH_3), 16.77 (SiCH_2CH_2), 22.39 (CH_2CH_3), 23.46 ($SiCH_2CH_2$), 35.68 ($CH_2CH_2CH_3$). ^{1}H NMR ($CDCl_3$) of **3c**: δ −0.13 (s, 4H, $SiCH_2Si$), 0.62 (t, 8H, SiCH_2CH_2), 0.86 (t, 12H, CH_3), 1.30 (m, 32H, $CH_2CH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$) of **3c**: δ −2.89 ($SiCH_2Si$), 14.17 (CH_3), 16.84 (SiCH_2CH_2), 22.65 (CH_2CH_3), 23.79 ($SiCH_2CH_2$), 31.66 ($CH_2CH_2CH_3$), 33.16 ($SiCH_2CH_2CH_2$).

6. Poly(di-*n*-butylsilylenemethylene) (PDBSM) (4a). A 10 mL flask was charged with 3.0 g (9.6 mmol) of **3a**. A solution of $H_2PtCl_6 \cdot 6H_2O$ catalyst (36 mg) in 1,2-dimethoxyethane (containing 1 wt % of Pt) was added. The mixture was stirred for 96 h at 100 °C under Ar. Subsequently, another 48 mg of the catalyst solution was added as no significant increase in viscosity had been observed. This resulted in a gradual increase in the viscosity of the reaction mixture. After 120 h a gray solid was obtained, which was dissolved in toluene and filtered to remove Pt. Subsequently, the polymer was fractionated by the slow addition of 2-propanol. After a second fractionation using acetone, the resulting high molecular weight fraction of **4a** was dried at 50 °C in vacuo for 12 h; 0.59 g (20%) of a white powder was obtained. Molecular weights obtained by gel permeation chromatography (GPC) are

Table 3. Polymerization of 1,1,3,3-Tetra-*n*-butyl-1,3-disilacyclobutane (3a), 1,1,3,3-Tetra-*n*-pentyl-1,3-disilacyclobutane (3b), and 1,1,3,3-Tetra-*n*-hexyl-1,3-disilacyclobutane (3c)

monomer	$H_2PtCl_6 \cdot 6H_2O$[a] (ppm)	duration of polymerization[b] (h)	yield[c] (%)	yield of high molecular weight fraction (%)	M_n (M_w) of high molecular weight fraction
3a	580	120	44	20	246 000 (349 000)[e]
3b	1000	120	34[d]	19	72 000 (96 000)[e]
3c	260	43	16	11	167 000 (203 000)[f]

[a] Solution in 1,2-dimethoxyethane (containing 1 wt % of Pt). [b] Time needed to achieve solidification of the reaction mixture. [c] Comprising all fractions after the second fractionating precipitation. [d] Molecular weights before fractionation according to GPC (chloroform solution, PS standard): $M_w/M_n = 69\,000/30\,000 = 2.29$, monomodal molecular weight distribution. [e] GPC (chloroform solution, PS standard). [f] GPC (toluene solution, PS standard).

given in Table 3: ^{1}H NMR ($CDCl_3$) δ −0.26 (s, 2H, $SiCH_2Si$), 0.52 (m, 4H, $SiCH_2CH_2$), 0.87 (t, 6H, CH_3), 1.28 (m, 8H, $CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$) δ 0.06 ($SiCH_2Si$), 13.75 (CH_3), 17.33 ($SiCH_2CH_2$), 26.68 (CH_2CH_3), 26.97 ($CH_2CH_2CH_3$).

7. Poly(di-*n*-pentylsilylenemethylene) (PDPeSM) (4b) and Poly(di-*n*-hexylsilylenemethylene) (PDHSM) (4c). 4b and **4c** were prepared in analogy to the synthesis of **4a** described in the preceding section. Amounts of $H_2PtCl_6 \cdot 6H_2O$ catalyst necessary to effect polymerization as well as results of fractionating precipitation using 2-propanol are given in Table 3. ^{1}H NMR ($CDCl_3$) of **4b**: δ −0.29 (s, 2H, $SiCH_2Si$), 0.50 (m, 4H, $SiCH_2CH_2$), 0.87 (t, 6H, CH_3), 1.27 (m, 12H, $CH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$) of **4b**: δ −0.17 ($SiCH_2$-Si), 14.09 (CH_3), 17.53 ($SiCH_2CH_2$), 22.43 (CH_2CH_3), 24.15 ($SiCH_2CH_2$), 36.38 ($CH_2CH_2CH_3$). ^{1}H NMR (C_6D_6) of **4c**: δ 0.24 (s, 2H, $SiCH_2Si$), 1.05 (m, 10H, CH_3 and $SiCH_2CH_2$), 1.61 (m, 16H, $CH_2CH_2CH_2CH_2CH_3$). ^{13}C NMR (C_6D_6) of **4c**: δ 0.64 ($SiCH_2Si$), 14.47 (CH_3), 18.40 ($SiCH_2CH_2$), 23.32 (CH_2CH_3), 25.24 ($SiCH_2CH_2$), 32.34 ($CH_2CH_2CH_3$), 34.58 ($SiCH_2CH_2CH_2$).

B. Methods. 1. Nuclear Magnetic Resonance (NMR). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer. ^{13}C NMR spectra were run with broad-band proton decoupling. Chloroform-*d* and benzene-d_6 were used as solvents, with chloroform and benzene, respectively, utilized as internal standards.

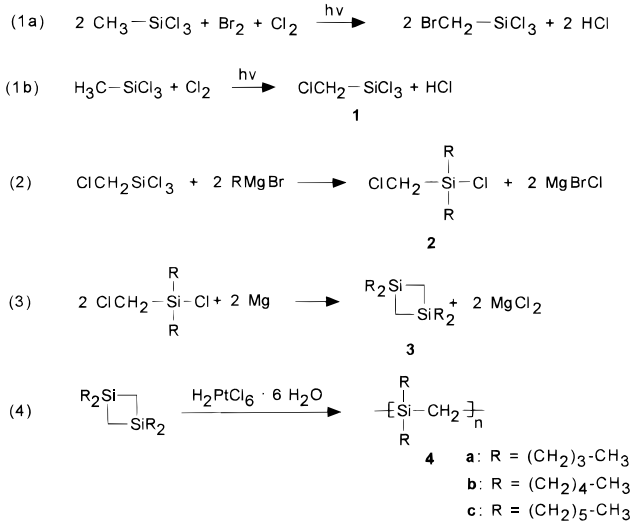
2. Gel Permeation Chromatography (GPC). PL (Polymer-Laboratories) 7.8 mm × 30 cm Ultrastyragel linear columns packed with particles of mixed pore size (10^5, 10^4, 1000, and 100 nm) were utilized for analysis. A differential refractometer was used for detection. The columns were maintained at 20 °C. The eluting solvents were HPLC grade chloroform and toluene at flow rates of 1 mL/min. Retention times were calibrated against known, monodisperse polystyrene standards.

3. Calorimetry. A Perkin-Elmer DSC 7 was used to monitor the thermal transitions at scan rates in the range of 1 to 20 °C/min. All thermograms shown in Figure 3 were obtained after the sample was subjected to a first heating and cooling cycle. The instrument was calibrated with high-purity samples of indium and cyclohexane. Sample weights were typically chosen between 8 and 13 mg. Transition entropies were calculated by assuming equilibrium, i.e., $\Delta H = T\Delta S$.

Results and Discussion

Synthesis. Catalytic ring-opening polymerization of 1,3-disilacyclobutanes known since the pioneering work of Kriner[31] offers the only viable route to high molecular weight poly(silylenemethylene)s with a regularly alternating backbone structure at present. Contrary to the synthesis of poly(siloxane)s,[2] the corresponding cyclic trisilylenemethylenes cannot be employed as monomers since they are strainless.[19] The Wurtz-type coupling reaction of suitably substituted (chloromethyl)chlorosilanes common in the synthesis of poly(silylene)s,[32] on the other hand, leads to backbone randomization.[33] The synthetic route used for the preparation of the *n*-alkyl-substituted 1,3-disilacyclobutane monomers in the current paper (Scheme 2) is analogous to that employed for the synthesis of 1,1,3,3-tetra-*n*-propyl-1,3-disilacyclobutane,[21] roughly comprising the synthetic steps

Scheme 2. Monomer Synthesis and Polymerization



employed by Auner and Grobe[34] for the synthesis of other substituted 1,3-disilacyclobutanes.

Attempts to obtain trichloro(bromomethyl)silane in the first step of monomer synthesis failed. Since bromination of methyl-substituted silanes is known to be difficult,[35] photobromination of methyltrichlorosilane was performed in the presence of chlorine, yielding bromine chloride as an intermediate brominating agent (step 1a, Scheme 2). Contrary to the findings of Speier,[36] perhalogenated species were obtained as the main products by using this procedure. Trichloro(chloromethyl)silane **(1)** could be obtained by gas phase photochlorination of trichloromethylsilane, following the method of Schmidbaur et al.[29] (step 1b, Scheme 2). Reactions of **1** with butyl-, pentyl-, and hexylmagnesium bromide afforded the respective chloro(chloromethyl)-dialkylsilanes **2** in 40−50% yield after repeated distillation, with the C−Cl bond remaining unaffected by the Grignard reagent. The final cyclization step was carried out with Mg according to the procedure given by Kriner.[30] The butyl- and pentyl-substituted 1,3-disilacyclobutanes were obtained in 40−50% yield after repeated distillation, whereas yields of 1,1,3,3-tetra-*n*-hexyl-1,3-disilacyclobutane **(3c)** were considerably lower because a fraction of the monomer was lost because of thermal polymerization due to the rigorous conditions necessary for distillation. The 1,3-disilacyclobutane monomers **3** nevertheless showed excellent thermal stability and could be heated up to 180 °C in vacuo without decomposition or polymerization.

Contrary to monosilacyclobutanes,[37] anionic polymerization of 1,3-disilacyclobutanes does not lead to high molecular weight poly(silylenemethylene)s. Long reaction times are necessary, and transfer reactions limit the molecular weights obtained to 5000.[6,38] Sev-

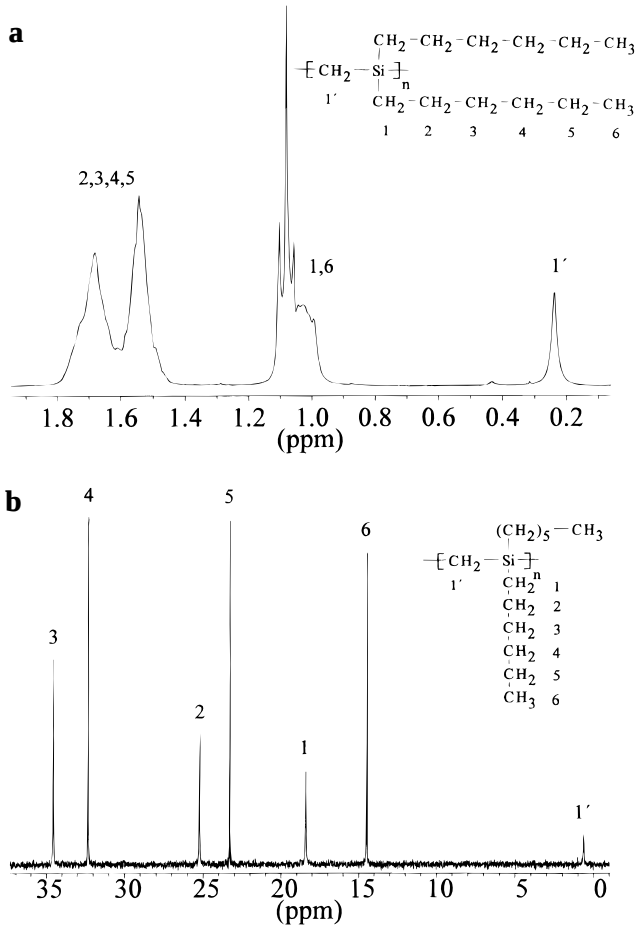


Figure 1. (a) ^{1}H NMR spectrum of a high molecular weight fraction of poly(di-*n*-hexylsilylenemethylene) (PDHSM, **4c**) in C_6D_6. (b) ^{13}C NMR spectrum of a high molecular weight fraction of PDHSM **(4c)** in C_6D_6.

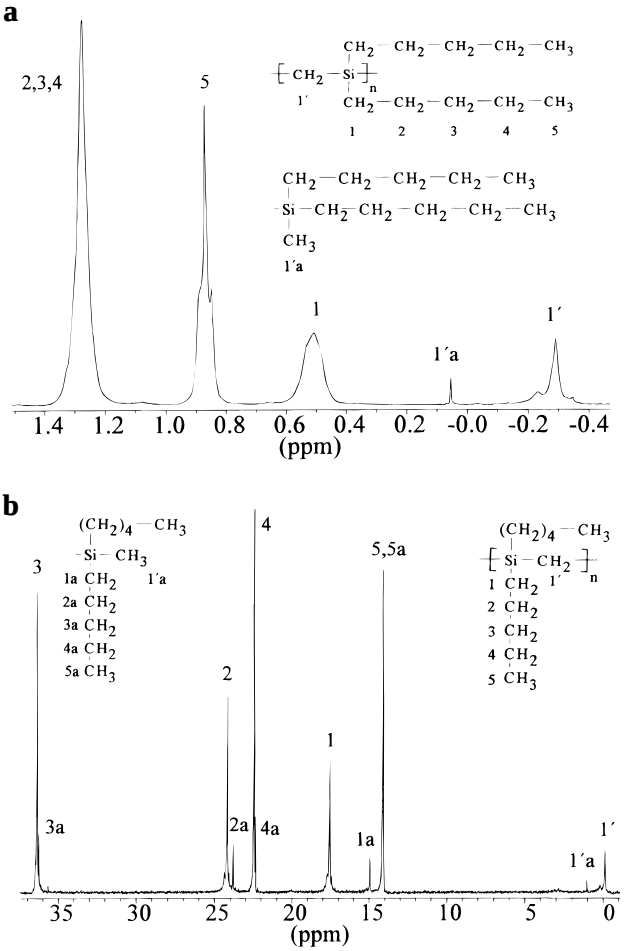


Figure 2. (a) ^{1}H NMR spectrum of a low molecular weight fraction of poly(di-*n*-pentylsilylenemethylene) (PDPeSM, **4b**) in $CDCl_3$. (b) ^{13}C NMR spectrum of a low molecular weight fraction of PDPeSM **(4b)** in $CDCl_3$.

eral efficient transition-metal-based catalysts have been reported, on the other hand.[19,31] 1,3-Disilacyclobutanes with various substituents on silicon have been polymerized in this manner, but often there is little information on the molecular weights of the resulting poly(silylenemethylene), since utility as polymeric precursor for the preparation of SiC was emphasized in most investigations.

Polymerization of the *n*-butyl-, *n*-pentyl-, and *n*-hexyl-substituted 1,3-disilacyclobutanes **3a**−**c** was carried out under Ar atmosphere in bulk at 100 °C by adding a small amount of a solution of H_2PtCl_6 in glyme (1,2-dimethoxyethane). Polymerizations were commonly terminated when the reaction mixture had solidified. Although NMR spectra evidenced the high purity of the 1,3-disilacyclobutane monomers employed, the amount of catalyst required for completion of the polymerizations varied to some extent.

Whereas polymerization of the tetramethyl-substituted 1,3-disilacyclobutane monomer in bulk occurred extremely rapidly within a few seconds, up to 120 h of reaction time were needed under the same conditions for polymerization of the monomers substituted with longer alkyl chains (see Table 3). Samples taken at low conversion during the polymerization of 1,1,3,3-tetra-*n*-hexyl-1,3-disilacyclobutane **(3c)**, on the other hand, already evidenced the presence of high molecular weight material and, thus, clearly a chain growth type of mechanism. Therefore, we conclude that the steric bulk of the substituents affects the rate of propagation less than the initiation step of the ring-opening catalytic polymerization. Polymerization in bulk yielded poly(silylenemethylene)s with a monomodal molecular weight distribution. Fairly narrow (M_w/M_n < 1.4) high molecular weight fractions of the polymers could be obtained as crystalline powders by careful fractionation (see Table 3), which were used for all calorimetric investigations described in the following.

Figure 1a,b gives ^{1}H and ^{13}C NMR spectra of the high molecular weight fraction (M_w = 203 000, PS standard) of poly(di-*n*-hexylsilylenemethylene) (PDHSM, **4c**), obtained by fractionating precipitation. Both spectra were recorded without TMS standard. Only one signal is discernible for the backbone methylene units in each spectrum, clearly demonstrating the regular alternation of SiR_2 and CH_2 units in the polymer backbone. The ^{13}C NMR spectrum was assigned according to the spectrum of the tetrahexyl-substituted 1,3-disilacyclobutane **(3c)**, for which a ^{1}H−^{13}C COSY spectrum has been recorded and in analogy to the spectrum of poly(di-*n*-hexylsilane).[39] The ^{1}H and ^{13}C NMR spectra illustrate that the poly(silylenemethylene)s **4a**−**c** were obtained without low molecular weight impurities after repeated fractionation.

For the transition-metal-catalyzed ring-opening polymerization of monosilacyclobutanes, Eaborn et al. proposed a coordination type of mechanism.[40] A similar mechanism may be suggested for the polymerization of 1,3-disilacyclobutanes. To gain insight into the termination mechanism, identification of end groups seemed desirable to us. Figure 2a,b displays ^{1}H and ^{13}C NMR

Table 4. Thermal Transitions of Poly(di-*n*-alkylsilylenemethylene)s

polymer	M_n (M_w)[a]	T_g[b] (°C)	T_d[c,e] (°C)	ΔH_d (kJ/mol)	ΔS_d (J/K·mol)	T_i[d,e] (°C)	ΔH_i (kJ/mol)	ΔS_i (J/K·mol)
PDMSM	499 000 (721 000)	−87						
PDPSM[21]	88 000 (107 000)	−41	83	0.16	0.44	92	2.70	7.39
PDBSM	246 000 (349 000)	−30	97	0.28	0.75	104	3.55	9.41
PDPeSM	72 000 (96 000)	−55	64	0.18	0.53	71	3.36	9.77
PDHSM	167 000 (203 000)	−56	62	0.30	0.89	67	3.77	11.06

[a] Determined by GPC (PS standard). [b] Heating rate: 20 °C/min. [c] First endotherm in DSC. [d] Transition to isotropic melt. [e] Heating rate: 5 °C/min.

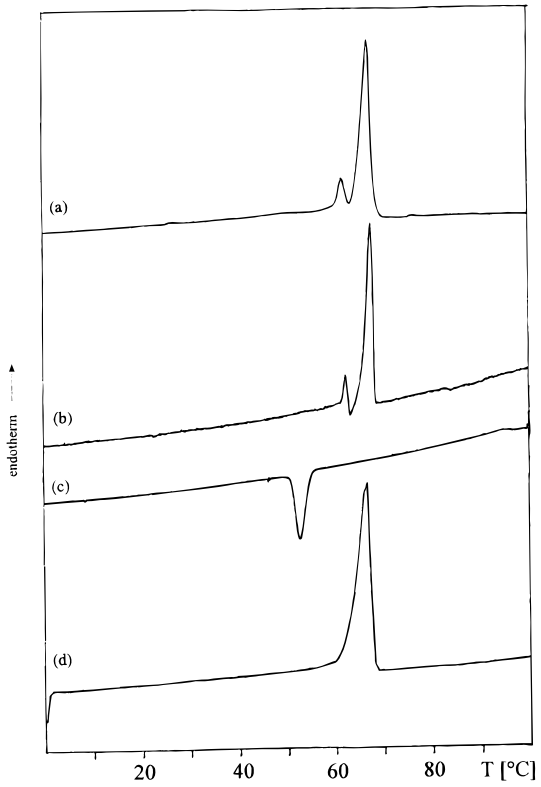


Figure 3. Thermograms of poly(di-*n*-hexylsilylenemethylene) (PDHSM, **4c**) obtained after a first heating and cooling cycle (not shown): (a) heating, rate of 5 °C/min; (b) heating, rate of 1 °C/min; (c) cooling, rate of 1 °C/min; (d) heating of a quenched sample, rate of 5 °C/min.

spectra of the low molecular weight fraction (M_w = 23 000, PS standard) of poly(di-*n*-pentylsilylenemethylene) (PDPeSM, **4b**), again run without TMS standard. Several signals of lower intensity are discernible, which is typical for the spectra of low molecular weight fractions of poly(silylenemethylene)s substituted with other alkyl side chains as well. ^{13}C-DEPT NMR experiments and ^{1}H−^{13}C COSY spectra (not shown here) unambiguously demonstrated that these signals are due to methyldi-*n*-pentylsilyl end groups. The signals at δ 0.05 in the ^{1}H NMR spectrum (Figure 2a) and δ 1.03 in the ^{13}C NMR spectrum (Figure 2b) are due to the methyl groups, whereas the signals at δ 14.94, 22.36, 23.79, and 36.27 in the ^{13}C NMR spectrum can be assigned to the pentyl chains linked to the terminal silicon atoms.

Thermal Behavior. Linear flexible chain molecules like poly(di-*n*-alkylsiloxane)s [$(R_2SiO)_n$], poly(di-*n*-alkylsilylene)s [$(R_2Si)_n$], and poly(di-*n*-alkoxyphosphazene)s [$((RO)_2PN)_n$] show the formation of columnar mesophases despite the absence of rigid mesogenic units in the molecular structure.[22,23] We were interested in determining whether thermotropic columnar mesophases would be observed due to the structural analogy between the poly(siloxane)s and poly(di-*n*-alkylsilylenemethylene)s. Previous studies on poly(di-*n*-propylsilylenemethylene) (PDPSM) evidenced that at least part of the material transformed into a mobile state below isotropization, which may possibly be classified as a conformationally disordered mesophase.[21] To clarify this issue, the corresponding poly(di-*n*-butylsilylenemethylene) (PDBSM, **4a**), poly(di-*n*-pentylsilylenemethylene) (PDPeSM, **4b**), and poly(di-*n*-hexylsilylenemethylene) (PDHSM, **4c**) derivatives were investigated with respect to their thermal behavior. It was assumed that increasing the *n*-alkyl side chain length of the poly(silylenemethylene)s would result in broadening the temperature interval of the disordered state.

The glass transition temperatures of the new poly(silylenemethylene)s, as discerned from DSC measurements, are listed in Table 4 (not shown in Figure 3). The T_g's of PDPSM[21] and PDMSM, which does not show any first-order transitions, are given as well. The glass transition temperatures are considerably higher than those of the analogous poly(siloxane)s,[28] which is a consequence of the reduced backbone flexibility of the poly(silylenemethylene)s. Thus, in terms of their molecular mobility, poly(silylenemethylene)s may be placed between the poly(silylene)s and the highly flexible poly(siloxane)s. The heat capacity changes in the DSC curves at T_g decreased with increasing *n*-alkyl side chain length, demonstrating increasing crystallinity with increasing length of the *n*-alkyl side chains.

Figure 3 shows the DSC thermograms for the PDHSM sample with various thermal treatments upon heating and cooling. All thermograms were obtained after a first heating and cooling cycle (not shown in Figure 3). As in the case of PDPSM,[21] a slight change in the slope of the baseline is noted between 10 and 60 °C, indicating a slow increase in molecular mobility (curves a and b). At 62 °C a small endotherm is observed, which is succeeded by a large endotherm at 67 °C. It could be established by polarizing optical microscopy that the latter reflects the transition to the isotropic melt. In contrast to PDPSM, both transitions remain indistinguishable even upon very slow cooling (curve c). If the sample is quenched by fast cooling from the isotropic state, both transitions become indistinguishable upon heating as well (curve d). Slightly different phase transition temperatures were found for PDBSM and PDPeSM, but, surprisingly, the shape of the DSC curves of PDBSM and PDPeSM proved to be nearly identical to that of PDHSM. Table 4 summarizes the thermal behavior of the different poly(di-*n*-alkylsilylenemethylene)s **4** that have been investigated so far. The *n*-alkyl side chain length does not have a significant influence

on the width of the temperature interval between the two endotherms. The thermal behavior of poly(di-*n*-alkylsilylenemethylene)s thus is different from that of the analogous poly(siloxane)s, which display large mesomorphic regimes that widen with increasing *n*-alkyl side chain length.[28] A detailed investigation of the nature of the small first endothermic transition is in progress.

Conclusions

Three novel poly(di-*n*-alkylsilylenemethylene)s with *n*-butyl, *n*-pentyl, and *n*-hexyl side chains have been synthesized by transition-metal-catalyzed ring-opening polymerization of the corresponding tetraalkyl-substituted 1,3-disilacyclobutanes. Polymerization in bulk yielded high molecular weight polymers with a monomodal molecular weight distribution and a regularly alternating SiR_2/CH_2 backbone structure. Whereas polymerization of the tetramethyl-substituted 1,3-disilacyclobutane was completed extremely rapidly, up to 120 h of reaction time were needed to achieve solidification of the reaction mixture in the case of the monomers substituted with longer alkyl chains. Initiation of ring-opening polymerization seems to be severely complicated by the steric bulk of longer substituents. Like the lower homologue PDPSM, all three compounds exhibited a transition a few degrees below isotropization. Surprisingly, the *n*-alkyl side chain length did not have a significant influence on the width of the temperature interval between the two transitions. Although identification of the phase state in this interval has not yet been achieved, poly(di-*n*-alkylsilylenemethylene)s obviously are completely different from the analogous poly(di-*n*-alkylsiloxane)s with respect to their thermal behavior and do not show significant conformational disorder before melting. The absence of stable hexagonal columnar mesophases in the case of the poly(silylenemethylene)s may be due to the decreased incompatibility of side chains and backbone, as well as to the smaller entropic gain upon formation of the mesophase, compared to the poly(siloxane)s. Further investigations including detailed WAXS analysis of the transitions observed are in progress.

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