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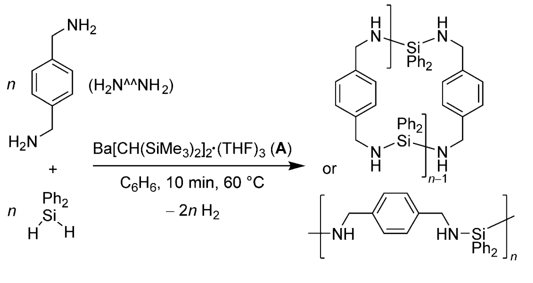
Tailored Cyclic and Linear Polycarbosilazanes by Barium-Catalyzed N−H/H−Si Dehydrocoupling Reactions

Clément Bellini, Clément Orione, Jean-François Carpentier, and Yann Sarazin**

Abstract: *Ba[CH(SiMe$_3$)$_2$]$_2$(THF)$_3$ catalyzes the fast and controlled dehydrogenative polymerization of Ph$_2$SiH$_2$ and p-xylylenediamine to afford polycarbosilazanes. The structure (cyclic versus linear; end-groups) and molecular weight of the macromolecules can be tuned by adjusting the Ph$_2$SiH$_2$/diamine feed ratio. A detailed analysis of the resulting materials (mol. wt up to ca. 10000 g mol^{-1}) is provided.*

Following investigations in the 1980–1990′s,[1] there has been much interest in silicon-containing SiCN preceramic polymers because the resulting amorphous SiCN ceramics offer excellent corrosion resistance, high-temperature stability, and long-term durability for applications as structural materials.[2] Polysilazanes, with their -(Si−N)$_n$- backbone, have enjoyed the most attention.[1,3] They are commonly prepared by ammonolysis or aminolysis of chlorosilanes.[4] The ring-opening polymerization of cyclosilazanes is a cleaner method,[3a,4,5] but it first requires the synthesis of cyclic monomers,[5a,6] and polycondensations by cross-dehydrocoupling of amines and hydrosilanes can be promoted by metal/carbonyl or titanocene precatalysts.[7] In contrast, little is known about polycarbosilazanes, that is, polymers with -(Si−C−N)$_n$- backbones, and this owes much to the lack of synthetic routes and the limited understanding of the microstructures of these polymers.[1] Although it generates ammonium chloride waste, the aminolysis of dichlorosilanes with diamines is the main pathway to accessing polycarbosilazanes.[8] The telechelic oligomers made from H$_2$NCH$_2$CH$_2$NH$_2$ and Me$_2$SiCl$_2$ consist of randomly distributed linear -(Me$_2$SiNHCH$_2$CH$_2$NH)- and cyclic -(Me$_2$Si-cyclo-[NCH$_2$CH$_2$NSiMe$_2$])- units.[8a–c] The dehydropolymerization of 1,4-bis(dimethylsilyl)benzene with ammonia can be catalyzed by [Pd$_2$(dba)$_2$].[9] A strategy based on platinum-catalyzed hydrosilylation of vinyl or allyl silanes yielded hyperbranched and dendrimeric polycarbosilazanes.[10] Elsewhere, we and others have shown that oxophilic, d^0 metal complexes provide competent precatalysts to dehydrocouple hydrosilanes and amines.[11–14] Barium compounds in particular catalyze the coupling of diamines and di(hydrosilanes).[14a,b] We present here an extension of this work to the barium-mediated production of polycarbosilazanes. The rapid and controlled syntheses of either linear or cyclic polymers by dehydropolymerization of *p*-xylylenediamine (represented as H$_2$N^^NH$_2$) and diphenylsilane, together with detailed characterizations, are reported (Scheme 1).

Ba[CH(SiMe$_3$)$_2$]$_2$·(THF)$_3$ (**A**), which was identified as the most efficient of our alkalino-earth precatalysts for N−H/H−Si coupling reactions because of its combination of highly reactive metal and alkyl groups,[14] catalyzes the polycondensation of Ph$_2$SiH$_2$ and H$_2$N^^NH$_2$ upon release of H$_2$ as the sole by-product (Table 1). ^{1}H NMR analysis indicated complete conversion of 100 equivalents of the default monomer per metal within 10 minutes at 60 °C. The resulting polycarbosilazanes featured estimated molecular weights in the



Scheme 1. Dehydropolymerization of Ph$_2$SiH$_2$ and H$_2$N^^NH$_2$ catalyzed by **A**.

Table 1: Dehydropolymerization of Ph$_2$SiH$_2$ and H$_2$N^^NH$_2$ catalyzed by **A**.[a]

[H$_2$N^^NH$_2$]$_0$/[Ph$_2$SiH$_2$]$_0$/[**A**]$_0$	Conv. [%][b]	$X_{n,theo}$[c]	$M_{n,end-group}$ [g mol^{-1}][d]	$M_{n,DOSY}$ [g mol^{-1}][e]	$X_{n,exp}$[f]
P1 20:20:1	>99	n/a[g]	n/a[g]	5600	n/a
P2 100:100:1	>99	n/a[g]	n/a[g]	7100	n/a
P3 125:100:1	>99	8	1500	1900	11
P4 110:100:1	>99	18	5500	6500	38
P5 100:125:1	>99	8	1300	1500	9
P6 100:110:1	>99	18	4600	4400	28
P7 100:105:1	>99	29	9200	10400	61

[a] Reactions in C$_6$H$_6$ at 60 °C for 10 min. [b] Conversion of the default monomer determined by ^{1}H NMR spectroscopy. [c] Theoretical number-average degree of polymerization calculated for 99 % conversion using Carothers' equation: $X_{n,theo} = (1+r)/(1+r-2rp)$ where r is the stoichiometric ratio and p is the extent of the reaction. [d] Number-average molecular weight established by ^{1}H NMR end-group analysis. [e] Number-average molecular weight estimated by ^{1}H DOSY NMR spectroscopy. [f] Experimental degree of polymerization, calculated using the average values of $M_{n,endgroup}$ and $M_{n,DOSY}$. [g] Not applicable for the cyclic polymers recovered under these conditions.

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range from 1400 to 9800 $g\,mol^{-1}$,[15] depending on the N−H/H−Si feed ratio. They were isolated in 75–80 % yield, taking care to use dry, aprotic solvents because of their hydrolytic sensitivity. Reactions at 25 °C for 60 minutes gave similar outcomes.

Although the polycarbosilazanes were soluble in organic solvents, their molecular weights could not be determined by size-exclusion chromatography, owing to their sensitivity under analytical conditions. They were evaluated instead by ^{1}H DOSY NMR spectroscopy in C_6D_6,[16] by using the diffusion coefficient–molecular weight (D_f–m.w.) method described by Grubbs and co-workers.[17] This analysis confirmed the existence of a single main population of polymer chains. Exclusive formation of cyclic polymers was seen for polymerizations performed with equimolar amounts of Ph_2SiH_2 and H_2N^^NH_2 (Table 1, entries 1–2), whereas linear materials were selectively obtained when one of the comonomers was used in excess (entries 3–7). For linear polymers, the D_f–m.w. analyses were corroborated by ^{1}H NMR end-group analysis. In a reasonably good first approximation, the experimental number-average degree of polymerization ($X_{n,exp}$, calculated as the ratio of the experimental molecular weight[15] divided by Flory's mean molecular weight of the Ph_2SiH_2 and H_2N^^NH_2 segments[18]) was commensurate with its theoretical value ($X_{n,theo}$) as given by Carothers' equation.[18,19]

The question of the controlled formation of either cyclic or linear polycarbosilazanes with these systems is both fascinating and important. The macromolecules produced by dehydropolymerizing equimolar amounts of the two comonomers are exclusively cyclic, as revealed by spectroscopic and mass spectrometric analyses. The ^{1}H NMR spectrum of **P2** (Table 1, entry 2) exhibits diagnostic resonances: a doublet centered at $\delta_{1H} = 4.09$ ppm with a relative integration for 4H, assigned to the methylene hydrogen atoms ($^{3}J_{H\text{-}H} = 8.0$ Hz), a triplet at $\delta_{1H} = 1.41$ ppm ($^{3}J_{H\text{-}H} = 8.0$ Hz) integrating to 2H and corresponding to the NH groups, and a broad resonance at $\delta_{1H} = 7.73$ ppm for the 4H which corresponds to the *ortho* hydrogen atoms of the SiC_6H_5 groups (Figure 1). This assignment was confirmed by ^{1}H-^{1}H COSY NMR spectroscopy. No resonance for end-group moieties was detected, and this is fully consistent with a cyclic structure.[20]

Full assignment of all resonances in the ^{1}H and ^{13}C{^{1}H} NMR spectra was straightforward on the basis of the ^{1}H-^{13}C HMBC and HMQC spectra. The resonance for the CH_2 methylene carbon atom appears at $\delta_{13C} = 45.80$ ppm in the ^{13}C{^{1}H} NMR spectrum. The INEPT ^{29}Si spectrum of the polymer features a unique resonance at $\delta_{29Si} = -24.32$ ppm (Figure 1), thus confirming the existence of a single type of silicon atom, as expected for a cyclic structure. The assignment of the key ^{1}H resonances and the absence of a Si−H end-group was further corroborated by ^{29}Si-^{1}H HMQC NMR data. The presence of repetitive -(Ph_2SiNH^^NH)- units (exact mass 316.1395 $g\,mol^{-1}$) was substantiated by ASAP(+) mass spectrometric analysis of the low-molecular-weight component, where the main peak was found at 632.2757 $g\,mol^{-1}$ ($X_n = 4$), and another peak was located at 949.4177 $g\,mol^{-1}$ ($X_n = 6$). In the ATR-FTIR spectrum of the polymer, a single, characteristic absorption band of medium intensity was found for the N−H stretching vibration at ν(N-H) = 3397 cm^{-1}; no band for SiH or NH_2 moieties could be detected. The diffusion coefficient ($1.456 \times 10^{-10}\ m^2\,s^{-1}$) versus molecular weight ($M_{n,DOSY} = 7100\ g\,mol^{-1}$) analysis for the polymer is displayed in Figure 2. The spectroscopic features for the polymer **P1**, also a cyclic polymer, were identical to those of **P2**. Only the diffusion coefficient and hence the value of $M_{n,DOSY}$ for **P1** ($1.776 \times 10^{-10}\ m^2\,s^{-1}$ and 5600 $g\,mol^{-1}$, respectively), differed from those of **P2** (see the Supporting Information).

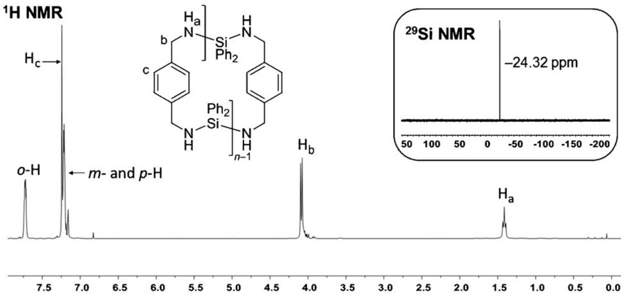

Figure 1. ^{1}H (C_6D_6, 298 K, 400.1 MHz) and ^{29}Si (C_6D_6, 298 K, 79.5 MHz) NMR spectra of the cyclic polycarbosilazane **P2**.

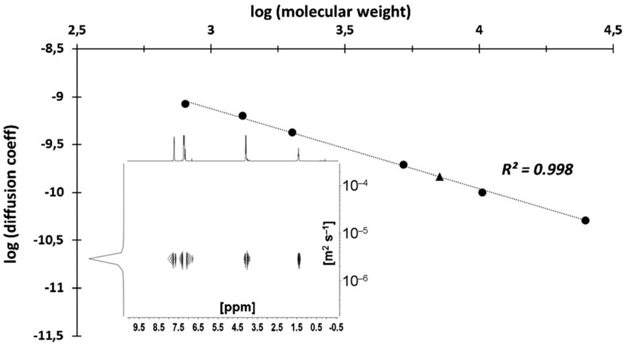

Figure 2. Molecular weight determination by log (diffusion coefficient) versus log (mol. wt) analysis for **P2** (▲). Calibration curve established by ^{1}H DOSY NMR spectroscopy (C_6D_6, 298 K, 400.1 MHz), using four monodisperse PMMAs and two Jeffamines™ (●) as commercial calibrants.[16] The ^{1}H DOSY analysis for **P2** itself (insert) shows the existence of a single main population.

Crucially, with excess H_2N^^NH_2, linear macromolecules having identifiable chain-ends are produced. The polycarbosilazane **P4**, having an estimated molecular weight of ca. 6000 $g\,mol^{-1}$, was obtained with 10 mol % excess of the diamine (Table 1, entry 4), while a 25 mol % initial excess of the diamine yielded the shorter polymer **P3** (entry 3). In agreement with Carothers' theory for a linear polycondensation, $X_{n,exp}$ decreases as the deviation from equimolar contents of the comonomers increases. The two products only differ by their molecular weights, but their main spectroscopic features (NMR, FTIR) are mostly identical, and only those of the shorter **P3** are discussed here. Its ^{1}H NMR spectrum is displayed in Figure 3. In addition to the

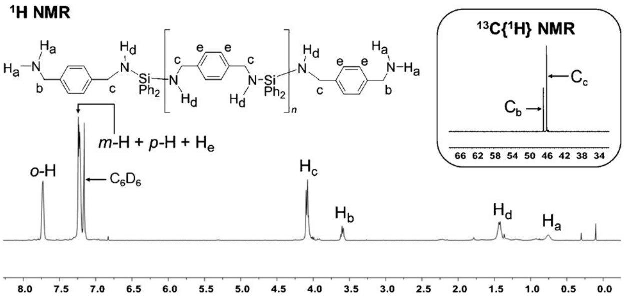

Figure 3. ^{1}H (C_6D_6, 298 K, 400.1 MHz) and of the ^{13}C{^{1}H} (C_6D_6, 298 K, 100.1 MHz) NMR spectra of the linear polycarbosilazane **P3**. Only the aliphatic region from the ^{13}C{^{1}H} NMR spectra is shown.

same resonances as those observed for **P2**, it also contains a quadruplet centred on $\delta_{1H}=3.59$ ppm ($^3J_{H\text{-}H}=8.0$ Hz) and a broad resonance at $\delta_{1H}=0.76$ ppm, which are scalarly coupled to each other according to ^{1}H-^{1}H COSY NMR data. Since the INEPT ^{29}Si spectrum of **P3** exhibits the same, sole sharp singlet as that seen for **P2** ($\delta_{29Si}=-24.32$ ppm), these resonances were respectively attributed to terminal $H_2NC\mathit{H}_2$-methylene and H_2NCH_2- amine residues. This assignment is further corroborated by examination of the ^{13}C{^{1}H} and ^{1}H-^{13}C HMQC NMR spectra (Figure 3), the aliphatic region of which contains only two resonances, a main one at $\delta_{13C}=45.79$ ppm (the same as for **P2**) and a less intense one at $\delta_{13C}=46.58$ ppm, which are assigned to internal (backbone) -HN$\mathit{C}H_2$- and terminal $H_2N\mathit{C}H_2$- groups, respectively. The ^{29}Si-^{1}H HMQC NMR spectrum indicated that the resonances at $\delta_{1H}=3.59$ and 0.76 ppm are not coupled to any silicon atom. In the FTIR spectrum of **P3** (in Nujol), the two absorption bands at $\nu=3400$ (m) and 3308 (m) cm^{-1} were assigned to the stretching modes of N–H bonds in internal -NH- and terminal -NH$_2$ moieties, respectively. These spectroscopic data are congruent with a linear structure, such as that depicted in Figure 3, capped by $-NHCH_2C_6H_4CH_2NH_2$ at each chain-end.

When Ph_2SiH_2 is used in excess compared to H_2N^^NH_2, the dehydropolymerizations catalyzed by **A** also produce linear polycarbosilazanes (Table 1, entries 5–7). With 10% excess, the polymer **P6**, with a molecular weight of about 4500 g mol^{-1}, corresponding to $X_{n,exp}=28$, was obtained (entry 6). With a larger excess (25%), the shorter **P5** was synthesized, with $X_{n,exp}=9$ (entry 5). The polycarbosilazane **P7**, which is of comparatively high molecular weight (ca. 9800 g mol^{-1}), was produced when the excess in Ph_2SiH_2 was reduced to 5% (entry 7). Hence, here again, the observed molecular weight decreases rapidly as the deviation from the 1:1 stoichiometry becomes greater. The spectroscopic features of these three polymers are almost identical. The ^{1}H and ^{29}Si NMR spectra are complicated, and show several new resonances compared to the spectra of the cyclic **P2**. This observed complexity in the spectra is likely due to coupling between reactive NH groups within the polymer chain and the excess Ph_2SiH_2, thus leading to the formation of dangling $NSiPh_2H$ silazanes and perhaps even N_2Si_2 cyclodisilazane (the formation of which can be catalyzed by **A** in coupling reactions between dihydrosilanes, for example, Ph_2SiH_2, and primary amines).[14] Besides, two types of end-groups are also to be expected: $-NHSiPh_2H$ and $-N(SiPh_2H)_2$. These different silicon environments can also be found in **P5**–**P7**, as depicted in Figure 4.[21] The main resonances in the ^{1}H ($\delta=4.09$ and 1.42 ppm), ^{13}C{^{1}H} ($\delta=45.79$ ppm), and ^{29}Si{^{1}H} ($\delta=-24.32$ ppm) NMR spectra of **P5**–**P7** match those for **P2** and **P3**, thus confirming the preponderance of regular repetitive units in the polymer backbone (Figure 4). The data for **P6** are discussed in the followings. In the ^{1}H NMR spectrum there are other identifiable minor resonances: singlets at $\delta_{1H}=5.75$ and 5.74 ppm (SiH atoms of disilazane end-groups), $\delta_{1H}=5.65$ ppm (for the SiH atom of monosilazane end-groups), and $\delta_{1H}=4.38$ ppm ($C\mathit{H}_2N$ atoms of disilazane end-groups), a doublet at $\delta_{1H}=3.91$ ppm ($C\mathit{H}_2N$ atoms of monosilazane end-groups), and a multiplet at $\delta_{1H}=1.04$ ppm ($N\mathit{H}$ atom of monosilazane end-groups). The ratio of monosilazane to disilazane end-groups is about 3:2.

In the ^{29}Si{^{1}H} spectrum, minor resonances at $\delta_{29Si}=-12.92$, -17.10, -24.51 and -29.47 ppm are also visible.[22] They were assigned to the different end-groups and irregular backbone units on the basis of the ^{1}H, ^{29}Si, and HMQC ^{1}H-^{29}Si NMR data (Figure 4). The INEPT ^{29}Si spectrum enhanced the intensities of specific resonances and showed the presence of an otherwise hardly detectable singlet at

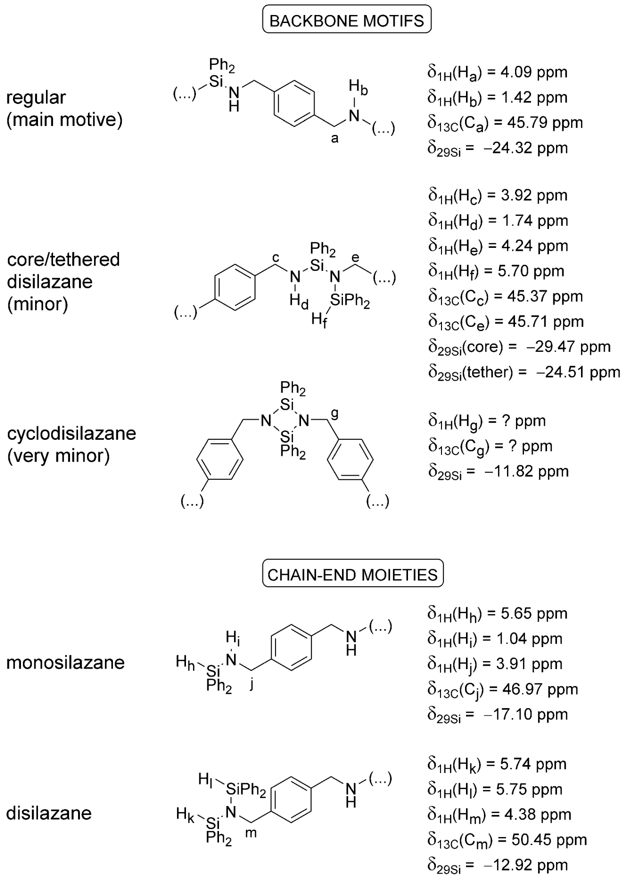

Figure 4. Possible silicon environments, in the polymer backbone and as end-groups, in **P5**–**P7**, which were prepared in barium-promoted dehydropolymerizations with excess Ph_2SiH_2. The assignment of the ^{1}H, ^{13}C and ^{29}Si NMR chemical shifts are given.

$\delta_{29Si} = -11.82$ ppm. Previous knowledge[14] allowed us to assign it to minute amounts of cyclodisilazane units, however, the accompanying resonances for H_g and C_g in the ^{1}H and ^{13}C{^{1}H} spectra were too small to be detected. In the aliphatic region, the ^{13}C{^{1}H} spectra contain the expected main resonance at $\delta_{13C} = 45.79$ ppm, and minor ones at $\delta_{13C} = 50.45$, 46.97, 45.71, and 45.37 ppm; the assignments in Figure 4 were achieved by combining ^{13}C{^{1}H} and ^{13}C-^{1}H HMBC and HMQC NMR data. This analysis suggests a complicated microstructure, wherein the backbone consists mostly of regular motifs with minor inclusions of core/tethered motifs and barely detectable cyclosilazane units, and where the end-groups are distributed between mono- and disilazanes moieties. The identification of the chain-end is corroborated by FTIR analyses. The ATR-FTIR spectrum of **P6** features two key absorption bands of medium intensity at 3393 and 2112 cm^{-1}, the latter being diagnostic of hydrosilanes. They were assigned to the stretching vibration modes of backbone N−H and chain-end Si−H bonds. No band was detected around 3300 cm^{-1}, thus testifying to the absence of NH_2 end-groups as expected from the use of excess dihydrosilane.

Such dehydropolymerizations catalyzed by **A**, without a doubt, follow the mechanistic pathway detailed previously for the barium-catalyzed cross-dehydrocoupling of amines and hydrosilanes.[14] Starting from the barium bis(alkyl) **A**, the key successive steps involve: 1) the formation of the competent barium amide species by protonolysis with H_2N^^NH_2, 2) nucleophilic attack of the N_{amide} atom onto the incoming hydrosilane, thus generating a hypervalent silicate, and 3) a rate-limiting β-hydrogen transfer to barium with concomitant release of the silazane, thus producing a barium hydride species which will then react with another amine to regenerate the catalytically active barium amide compound.

The barium-mediated dehydropolymerization of diamines and dihydrosilanes introduced here is a clean, fast, and versatile route to polycarbosilazanes. Fundamentally, the cyclic or linear microstructures (and, for linear polymers, end-group identity) can be tuned by adjusting the initial comonomer ratio. We are working on improving the productivity figures, and so far we have been able to obtain cyclic polymers by fully converting 500 equivalents of each comonomer (500:500:1) within 2 hours at 60 °C ($M_{n,DOSY} = 6000$ g mol^{-1}). This methodology can a priori be extended to other (co)monomers, for instance aryl-functionalized dihydrosilanes, di(hydrosilane)s, or other diamines (e.g. 1,2-ethylenediamine, piperazine), including functionalized ones. We are for now probing the use of 1) phenylsilane to obtain higher molecular weight and/or reticulated polymers (early attempts seem successful, as insoluble materials have been obtained; this methodology now requires optimization), 2) *N*,*N*′-dimethyl-*p*-xylylenediamine to prevent the formation of backbone cyclodisilazane, and 3) $H_2NCH_2C_6H_4CH_2NHSiPh_2H$, a self-sufficient α,ω-bifunctional monomer, to synthesize polycarbosilazanes with new properties.

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[15] For linear polycarbosilazanes, the values of estimated molecular weights quoted in the text are the average of the values determined by end-group and DOSY NMR analyses; see Table 1.

[16] The calibration curve for the diffusion coefficient–mol. wt. analysis was established using commercially available calibrants: two Jeffamines™ ($M_n = 800$ and $2000\ \mathrm{g\,mol^{-1}}$) and four monodisperse PMMAs in the range 1310–24830 $\mathrm{g\,mol^{-1}}$. It was validated with known monodisperse poly(L-lactide) samples, the molecular weights of which were accurately determined by SEC and ^{1}H NMR end-group analyses.

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[20] With a molecular weight of about 7000 $\mathrm{g\,mol^{-1}}$, the end-groups of a linear structure would be detected easily by NMR spectroscopy, as seen for the polymers corresponding to entries 4 and 7 in Table 1.

[21] The grafting of a side-chain by coupling of H_2N^^NH_2 with a -$SiPh_2H_f$ moiety tethered to the backbone (see Figure 4) cannot be excluded, but no evidence was detected in support of this event. By all accounts, such (…)-NH_2 side-chain residues would inevitably react with excess Ph_2SiH_2 to generate a (…)-$NHSiPh_2$ and perhaps even (…)-$N(SiPh_2)_2$ dangling groups undistinguishable from the main-chain end-groups.

[22] A minor resonance at $\delta_{29\mathrm{Si}} = -7.43$ ppm, assigned to degradation products, was sometimes visible.

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