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# Tailored Cyclic and Linear Polycarbosilazanes via Barium-catalysed N–H/H–Si Dehydrocoupling Reactions

Clément Bellini,[a] Clément Orione,[b] Jean-François Carpentier,*[a] and Yann Sarazin*[a]

Dedication ((optional))

Abstract: $Ba[CH(SiMe_3)_2]_2(THF)_3$ catalyses the fast and controlled dehydrogenative polymerisation of Ph_2SiH_2 and *p*-xylylenediamine to afford polycarbosilazanes. The structure (cyclic *vs.* linear; end-groups) and molecular weight of the macromolecules can be tuned by adjusting the Ph_2SiH_2/diamine feed ratio. A detailed analysis of the resulting materials (mol. wt. up to *ca.* 10,000 g mol^{-1}) is provided.

Following investigations in the 80-90's,[1] there has been much interest in silicon-containing SiCN preceramic polymers, for 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 polymerisation of cyclosilazanes is a cleaner method,[3a,4,5] but it first requires the synthesis of cyclic monomers;[5a,6] polycondensations by cross-dehydrocoupling of amines and hydrosilanes can be promoted by metal-carbonyl or titanocene precatalysts.[7] By contrast, little is known about polycarbosilazanes, that is, polymers with $-(Si–C–N)_n-$ backbones. This owes much to the lack of synthetic routes and to a limited understanding of the microstructures of these polymers.[1] Although it generates ammonium chloride wastes, the aminolysis of dichlorosilanes with diamines is the main pathway to polycarbosilazanes.[8] The telechelic oligomers made from $H_2NCH_2CH_2NH_2$ and Me_2SiCl_2 consist of randomly distributed linear $-(Me_2SiNHCH_2CH_2NH)-$ and cyclic $-(Me_2Si$-cyclo-$[NCH_2CH_2NSiMe_2])-$ units.[8a-c] The dehydropolymerisation of 1,4-bis(dimethylsilyl)benzene with ammonia can be catalysed by $Pd_2(dba)_2$.[9] A strategy based on Pt-catalysed 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 catalyse the coupling of diamines and di(hydrosilanes).[14a,b] We present here an extension of this work to the Ba-mediated production of polycarbosilazanes. The rapid and controlled syntheses of either linear or cyclic polymers by dehydropolymerisation of *p*-xylylenediamine ($\equiv H_2N^{\wedge\wedge}NH_2$) and

diphenylsilane, together with detailed characterisations, are reported (Scheme 1).
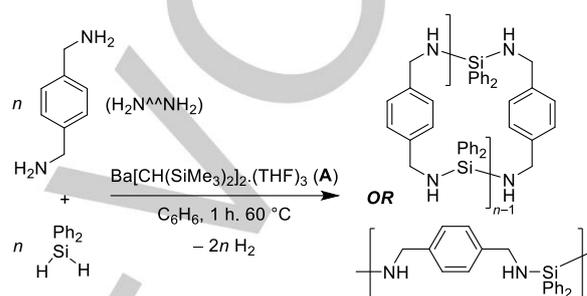
Scheme 1. Dehydropolymerisation of Ph_2SiH_2 and $H_2N^{\wedge\wedge}NH_2$ catalysed by **A**.

$Ba[CH(SiMe_3)_2]_2\cdot(THF)_3$ (**A**), identified as the most efficient of our alkalino-earth precatalysts for N–H/H–Si coupling reactions thanks in particular to its combination of highly reactive metal and alkyl groups,[14] catalyses the polycondensation of Ph_2SiH_2 and $H_2N^{\wedge\wedge}NH_2$ upon release of H_2 as sole by-product (Table 1). ^{1}H NMR indicated complete conversion of 100 equiv of the default monomer *per* metal within 10 min at 60 °C.

Table 1. Dehydropolymerisation of Ph_2SiH_2 and $H_2N^{\wedge\wedge}NH_2$ catalysed by **A**.[a]

	$[H_2N^{\wedge\wedge}NH_2]_0$/ $[Ph_2SiH_2]_0$/$[A]_0$	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]	5,600	n/a
P2	100:100:1	>99	n/a[g]	n/a[g]	7,100	n/a
P3	125:100:1	>99	8	1,500	1,900	11
P4	110:100:1	>99	18	5,500	6,500	38
P5	100:125:1	>99	8	1,300	1,500	9
P6	100:110:1	>99	18	4,600	4,400	28
P7	100:105:1	>99	29	9,200	10,400	61

[a] Reactions in C_6H_6 at 60 °C for 10 min. [b] Conversion of the default monomer determined by ^{1}H NMR. [c] Theoretical number-average degree of polymerisation calculated for 99% conversion using Carothers' equation: $X_{n,theo} = (1 + r) / (1 + r - 2.r.p)$ 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. [f] Experimental degree of polymerisation, 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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        Supporting information for this article is given via a link at the end of
        the document.

The resulting polycarbosilazanes featured estimated molecular weights in the range 1,400-9,800 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 due to their hydrolytic sensitivity. Reactions at 25 °C for 60 min 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$_6$D$_6$,[16] following 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 (*vide infra*) was seen for polymerisations performed with equimolar amounts of Ph$_2$SiH$_2$ and H$_2$N^^NH$_2$ (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 polymerisation ($X_{n,exp}$, calculated as the ratio of the experimental molecular weight[15] divided by Flory's mean molecular weight of the Ph$_2$SiH$_2$ and H$_2$N^^NH$_2$ segments[18]) was commensurate with its theoretical value ($X_{n,theo}$) given by Carothers' equation.[18-19]

The question of the controlled formation of cyclic or linear polycarbosilazanes with these systems is both fascinating and central. The macromolecules produced by dehydropolymerising 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 centred on δ_{1H} = 4.09 ppm with a relative integration for 4H and belonging to the methylene hydrogens ($^3J_{H-H}$ = 8.0 Hz), a triplet at δ_{1H} 1.41 ppm ($^3J_{H-H}$ = 8.0 Hz) integrating for 2H and corresponding to the N*H* groups, and a broad resonance at δ_{1H} 7.73 ppm for the four *o-H* of the C$_6$H$_5$ groups (Fig. 1). This assignment was confirmed by ^{1}H–^{1}H COSY NMR. No resonance for end-group moieties was detected, consistently with a cyclic structure.[20]
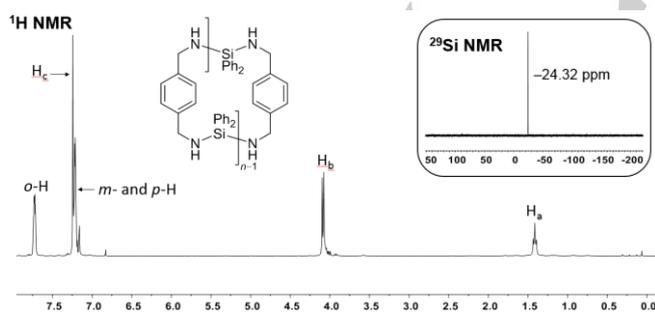

Figure 1. ^{1}H (C$_6$D$_6$, 298 K, 400.1 MHz) and ^{29}Si (C$_6$D$_6$, 298 K, 79.5 MHz) NMR spectra of the cyclic polycarbosilazanes **P2**.

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 C*H*$_2$ methylene carbon atom appears at δ_{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 δ_{29Si} = −24.32 ppm (Fig. 1), confirming the existence of a single type of silicon atoms as expected for a cyclic structure. The assignment of the key ^{1}H resonances and the absence of Si-H end-group was further corroborated by ^{29}Si-^{1}H HMQC NMR data. The presence of –(Ph$_2$SiNH^^NH)– repetitive 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) = 3,383 cm^{-1}; no band for SiH or NH$_2$ moieties could be detected. The diffusion coefficient (1.456×10^{-10} m^2 s^{-1}) *vs.* molecular weight ($M_{n,DOSY}$ = 7,100 g mol^{-1}) analysis for the polymer is displayed in Fig. 2. The spectroscopic features for 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** (1.776×10^{-10} m^2 s^{-1} and 5,600 g mol^{-1}, respectively), differed from those of **P2.** Details are available in the Supporting Information.
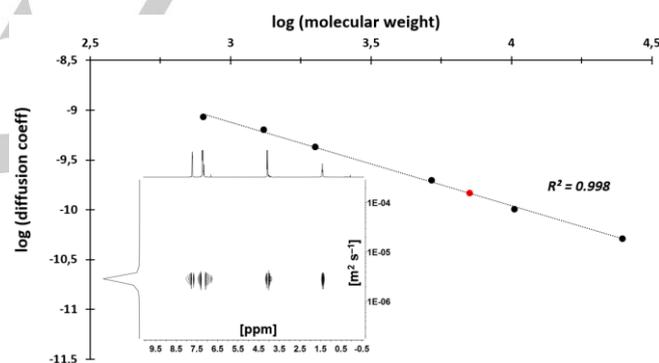

Figure 2. Molecular weight determination by log (diffusion coefficient) *vs.* log (mol. wt.) analysis for **P2** (●). Calibration curve established by ^{1}H DOSY NMR (C$_6$D$_6$, 298 K, 400.1 MHz), using four monodisperse PMMA and two Jeffamines™ (●) as commercial calibrants.[16] The ^{1}H DOSY analysis for **P2** itself (insert) shows the existence of a single main population.

Crucially, with excess H$_2$N^^NH$_2$, *linear* macromolecules having identifiable chain-ends are returned. Polycarbosilazane **P4** of estimated molecular weight *ca.* 6,000 g mol^{-1} was obtained with 10 mol-% excess of the diamine (entry 4), while a 25 mol-% initial excess of the diamine yielded the shorter polymer **P3** (entry 3). In agreement with Carothers' theory for 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 same resonances as those observed for **P2**, it also contains a quadruplet centred on δ_{1H} = 3.59 ppm ($^3J_{H-H}$ = 8.0 Hz) and a broad resonance at δ_{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** (δ_{29Si} = −24.32 ppm), these resonances

were respectively attributed to terminal H$_2$NC*H$_2$*– methylene and *H$_2$*NCH$_2$– amine residues. This assignment is further corroborated by examination of the ^{13}C{^{1}H} (Fig. 3) and ^{1}H-^{13}C HMQC NMR spectra, the aliphatic region of which contains only two resonances, a main one at δ_{13C} = 45.79 ppm (the same as for **P2**) and a less intense one at δ_{13C} 46.58 ppm, assigned to internal (backbone) –HNC*H$_2$*– and terminal H$_2$NC*H$_2$*– groups, respectively. The ^{29}Si-^{1}H HMQC NMR spectrum indicated that the resonances at δ_{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 ν = 3,400 (m) and 3,308 (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 Fig. 3, capped by –NHCH$_2$C$_6$H$_4$CH$_2$NH$_2$ at each chain-end.
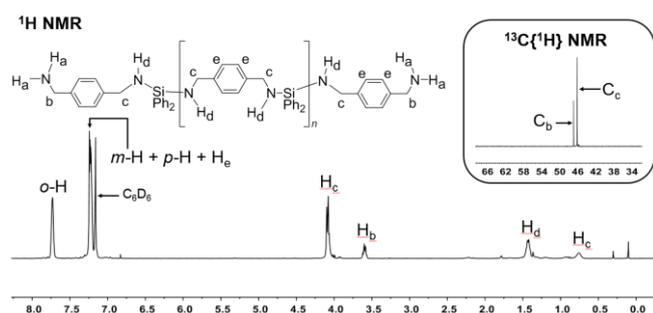

Figure 3. ^{1}H (C$_6$D$_6$, 298 K, 400.1 MHz) and aliphatic region of the ^{13}C{^{1}H} (C$_6$D$_6$, 298 K, 100.1 MHz) NMR spectra of the linear polycarbosilazane **P3**.

When Ph$_2$SiH$_2$ is used in excess compared to H$_2$N^^NH$_2$, the dehydropolymerisations catalysed by **A** also produce linear polycarbosilazanes (Table 1, entries 5-7). With 10% excess, polymer **P6** of molecular weight *ca.* 4,500 g mol^{-1}, corresponding to $X_{n,exp}$ = 28, was obtained (entry 6). With a larger excess (25%), the shorter **P5** was synthesised, with $X_{n,exp}$ = 9 (entry 5). Polycarbosilazane **P7** of comparatively high molecular weight (*ca.* 9,800 g mol^{-1}) was produced when the excess in Ph$_2$SiH$_2$ 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 cyclic **P2**. This is likely due to coupling between reactive NH groups within the polymer chain and the excess Ph$_2$SiH$_2$, leading to the formation of dangling N–SiPh$_2$H silazanes and perhaps even N$_2$Si$_2$ cyclodisilazane (the formation of which can be catalysed by **A** in coupling reactions between dihydrosilanes, *e.g.* Ph$_2$SiH$_2$, and primary amines).[14] Besides, two types of end-groups are also to be expected: –NHSiPh$_2$H and –N(SiPh$_2$H)$_2$. These different silicon environments to be found in **P5-P7** are depicted in Figure 4.[21]

The main resonances in the ^{1}H (δ 4.09 and 1.42 ppm), ^{13}C{^{1}H} (δ 45.79 ppm) and ^{29}Si{^{1}H} (δ −24.32 ppm) NMR spectra of **P5-P7** match those for **P2** and **P3**, confirming the preponderance of regular repetitive units in the polymer backbone (Fig. 4). The data for **P6** are discussed in the followings. In the ^{1}H

NMR spectrum there are other identifiable minor resonances: singlets at δ_{1H} = 5.75 and 5.74 (Si*H* atoms of disilazane end-groups), 5.65 (for the Si*H* atom of monosilazane end-groups) and 4.38 (C*H$_2$*N atoms of disilazane end-groups) ppm, a doublet at 3.91 ppm (C*H$_2$*N atoms of monosilazane end-groups), and a multiplet at 1.04 ppm (N*H* atom of monosilazane end-groups). The ratio of monosilazane to disilazane end-groups is *ca.* 3/2.
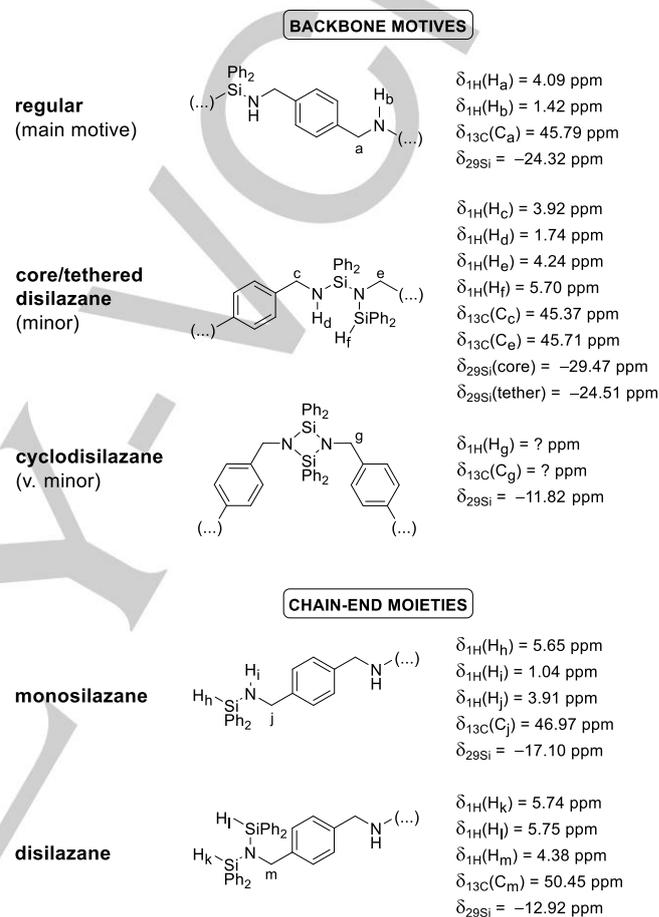

Figure 4. Possible silicon environments, in the polymer backbone and as end-groups, in **P5-P7** prepared in barium-promoted dehydropolymerisations with excess Ph$_2$SiH$_2$, with the assignment of the ^{1}H and ^{29}Si NMR chemical shifts.

In the ^{29}Si{^{1}H} spectrum, minor resonances at δ_{29Si} = −12.92 and −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 (Fig. 4). The INEPT ^{29}Si spectrum enhanced the intensities of specific resonances and showed the presence of an otherwise hardly undetectable singlet at δ_{29Si} = −11.82 ppm. Previous knowledge[14] allowed us to assign it to minute amounts of cyclodisilazane units; the pertaining 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 δ_{13C} = 45.79 ppm, and minor ones at δ_{13C} = 50.45, 46.97, 45.71 and 45.37 ppm; the assignments in Fig. 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, where the backbone consists mostly of regular motives with minor inclusions of core/tethered motives and hardly detectable cyclosilazane units, and where the end-groups are distributed between mono- and disilazanes moieties. The identification of the chain-ends is eased by FTIR analyses. The ATR-FTIR spectrum of **P6** features two key absorption bands of medium intensities at 3,393 and 2,112 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, respectively. No band was detected around 3,300 cm^{-1}, testifying to the absence of NH$_2$ end-groups as expected from the use of excess dihydrosilane.

Such dehydropolymerisations catalysed by **A** without doubt follow the mechanistic pathway detailed previously for the barium-catalysed cross-dehydrocoupling of amines and hydrosilanes.[14] Starting from the barium bis(alkyl) **A**, the key successive steps involve: (*i*) the formation of the competent barium amide species by protonolysis with H$_2$N^^NH$_2$, (*ii*) nucleophilic attack of the N$_{amide}$ atom onto the incoming hydrosilane, thus generating a hypervalent silicate, and (*iii*) a rate-limiting β-H transfer to barium with concomitant release of the silazane, producing a Ba hydride species which will then react with another amine to regenerate the catalytically active Ba amide compound.

The Ba-mediated dehydropolymerisation of diamines and dihydrosilanes introduced here is a clean, fast and versatile route to bespoke 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 endeavouring to improve productivity figures, and so far we are able to obtain cyclic polymers by fully converting 500 equiv of each comonomers (500:500:1) within 2 h at 60 °C ($M_{n,DOSY}$ = 6,000 g mol^{-1}). This methodology can *a priori* be extended to other (co)monomers, for instance aryl-functionalised dihydrosilanes, di(hydrosilane)s, or other diamines (*e.g.* 1,2-ethylenediamine, piperazine) including functionalised ones. We are for now probing the use of phenylsilane to obtain higher molecular weight and/or reticulated polymers (early attempts seem successful, as insoluble materials have been obtained; this methodology now requires optimisation), *N*,*N'*-dimethyl-*p*-xylylenediamine (to prevent the potential formation of backbone cyclodisilazane), and H$_2$NCH$_2$C$_6$H$_4$CH$_2$NHSiPh$_2$H, a self-sufficient α,ω-bifunctional monomer, to synthesise polycarbosilazanes with new properties.
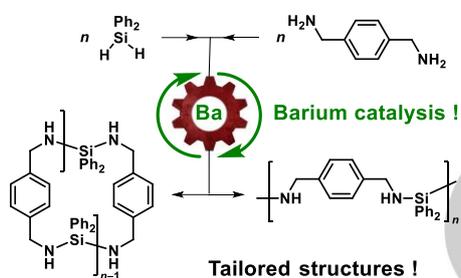
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[15] For linear polycarbosilazanes, the values of estimated molecular weights quoted in the text are the average of the values determined by end-group and DOSY NMR analyses, see Table 1.

[16] The calibration curve for the diffusion coefficient – mol. wt. analysis was established using commercial calibrants, two Jeffamines™ (M_n = 800 and 2,000 g mol^{-1}) and four monodisperse PMMAs in the range 1,310-24,830 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 *ca.* 7,000 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$_2$N^^NH$_2$ with a –SiPh$_2$H$_f$ moiety tethered to the backbone (see Fig. 4) cannot be excluded, but no evidence was detected in support of this event. By all account, such (…)–NH$_2$ side-chain residue would inevitably react with excess Ph$_2$SiH$_2$ 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 δ_{29Si} = −7.43 ppm, assigned to degradation products, was sometimes visible.

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COMMUNICATION

The rapid and controlled barium-catalysed dehydrogenative polymerisation of a diamine with diphenylsilane affords thoroughly characterised polycarbosilazanes with microstructures (cyclic vs. linear), end-groups and molecular weights that can be tailored by selection of the comonomers feed ratio.

Barium catalysis !

Tailored structures !

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