Supplementary Information

Synthesis of hydrocarbon-soluble, methyl-substituted highly branched polysilanes via the Wurtz-type reductive coupling of trifunctional trisilanes and their pyrolysis to silicon carbide

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1. Analytical Data of Polysilanes PS1-II, PS2-I and PS2-II

1.1 GPC

![Fig. S1 GPC elution profile of polysilane PS1-II after precipitation in MeOH. Molar masses are relative to polystyrene standards.]

1.2 NMR Spectroscopy

![Fig. S2 ¹H NMR (500 MHz) and ²⁹Si{¹H} INEPT NMR (99 MHz) spectra of polysilane PS1-II (solvent: [D₈]THF). Solvent residues in the powder polysilane are marked with an asterisk (n-hexane, methanol and toluene).]
**Fig. S3** Colored $^1$H/$^{29}$Si{${^1}$H} HMBC NMR ($^1$H: 500 MHz/ $^{29}$Si: 99 MHz) spectra of PS2 (solvent: [D$_8$]THF). A: NMR spectrum of PS2-I recorded after performing work-up procedure I (quenching with MeMgBr and Me$_3$SiCl). B: NMR spectrum of PS2-II recorded after precipitation in MeOH (work-up procedure I + II).

**Fig. S4** $^1$H/$^{29}$Si{${^1}$H} HMBC NMR ($^1$H: 500 MHz/ $^{29}$Si: 99 MHz) spectrum of PS1-II (solvent: [D$_8$]THF) after performing work-up procedure I (quenching with MeMgBr and Me$_3$SiCl) and II (precipitation in MeOH).
1.3 ATR-IR, UV/Vis and PL Spectroscopy

Fig. S5 ATR-IR spectrum of polysilane PS1-II. $\nu$ – stretching, $\delta$ – deformation, as – asymmetric, s – symmetric.

Fig. S6 Solution UV/Vis absorption spectrum of polysilane PS1-II.
**Fig. S7** Emission spectrum of polysilane PS1-II ($\lambda_{ex} = 365$ nm). The sharp signal at 365 nm is an artifact as it appears in the emission spectrum of pure THF, too. It can therefore not be assigned to the emission of the linear Me$_2$Si(Si)$_2$ units of polysilane PS1-II.$^{1-5}$
1.4 TGA and DSC

**Fig. S8** TG (black solid line) and DTG (gray dotted line) curve of polysilane PS1-II, which was heated from 25 °C to 800 °C (heating rate: 5 K min\(^{-1}\)) in an argon flow of 20 mL min\(^{-1}\). The DTG curve is the 1\(^{st}\) derivative of the TG curve and provides a maximum decomposition rate \(\frac{dm}{dt}\)\(_{\text{max}}\) of \(-6.79\ \%\ \text{min}^{-1}\) at 369 °C \(T_p\). \(T_o\) – extrapolated onset decomposition temperature, \(T_p\) – temperature of the DTG peak maximum.

**Fig. S9** DSC curve of polysilane PS1-II, which was hermetically sealed under argon and was heated from –150 °C to 220 °C using a heating rate of 10 K min\(^{-1}\) (presentation of the 2\(^{nd}\) heating cycle).
2. Thermal Rearrangement of PS1-II to PS1-PCS-330 and PS1-PCS-365

![Image of 1H NMR spectra](image)

**Fig. S10** Comparison of the $^1$H NMR spectrum (500 MHz) of polysilane PS1-II with the $^1$H NMR spectra of the polycarbosilanes PS1-PCS-330 and PS1-PCS-365 (solvent: $C_6D_6$). Inset shows magnified spectra in the range of the 3.8 to 5.4 ppm and the appearance of the proton peak of Si–H.

3. Pyrolysis of PS1-II to PS1-SiC-1200

![Image of ATR-IR spectrum](image)

**Fig. S11** ATR-IR spectrum of the pyrolysis residue PS1-SiC-1200. ν – stretching.
4. Abbreviations

ATR-IR, attenuated total reflectance infrared; DRI, differential refractive index; DSC, differential scanning calorimetry; DTG differential thermogravimetric; EDS, energy-dispersive X-ray spectroscopy; GPC, gel permeation chromatography; HMBC, heteronuclear multiple bond correlation; HR-SEM, high resolution scanning electron microscope; INEPT, intensive nuclei enhanced by polarization transfer; $M_n$, number-average molar mass; NMR, nuclear magnetic resonance; PCS, polycarbosilane; PDI, polydispersity index; PL, photoluminescence; PS, polysilane; TGA, thermogravimetric analysis; $T_o$, extrapolated onset decomposition temperature; $T_p$, temperature of the DTG peak maximum; UV, ultraviolet; Vis, visible; XRPD, X-ray powder diffraction.

5. References