

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

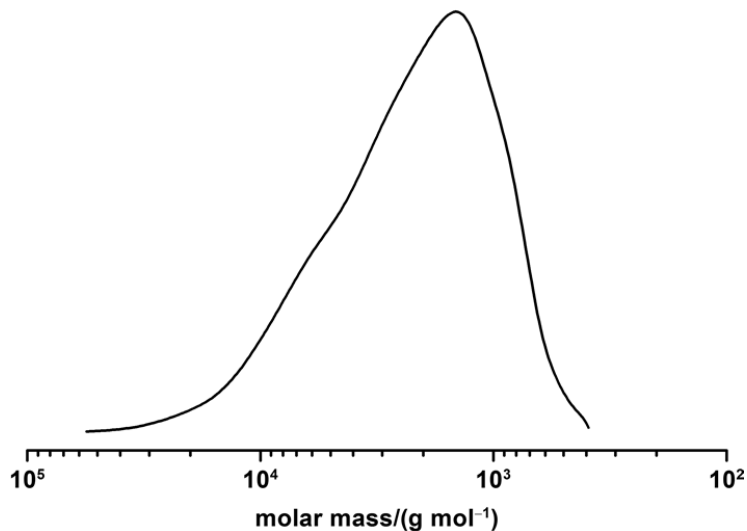


Fig. S1 GPC elution profile of polysilane **PS1-II** after precipitation in MeOH. Molar masses are relative to polystyrene standards.

1.2 NMR Spectroscopy

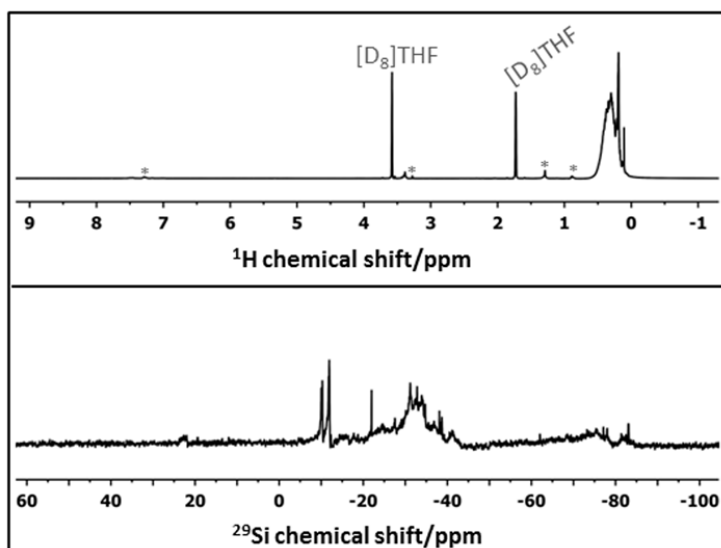


Fig. S2 ^1H NMR (500 MHz) and $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (99 MHz) spectra of polysilane **PS1-II** (solvent: $[\text{D}_8]\text{THF}$). Solvent residues in the powder polysilane are marked with an asterisk (*n*-hexane, methanol and toluene).

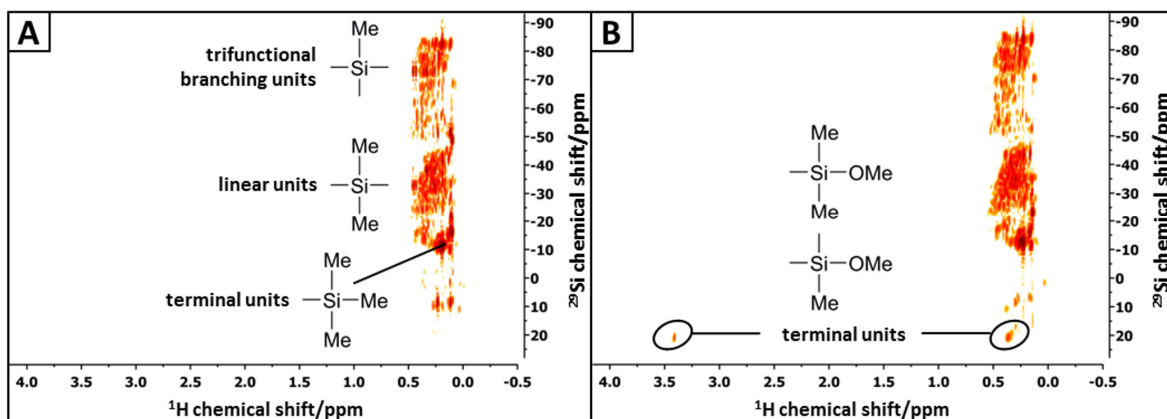


Fig. S3 Colored $^1\text{H}/^{29}\text{Si}\{^1\text{H}\}$ HMBC NMR (^1H : 500 MHz/ ^{29}Si : 99 MHz) spectra of **PS2** (solvent: $[\text{D}_8]\text{THF}$). **A**: NMR spectrum of **PS2-I** recorded after performing work-up procedure I (quenching with MeMgBr and Me_3SiCl). **B**: NMR spectrum of **PS2-II** recorded after precipitation in MeOH (work-up procedure I + II).

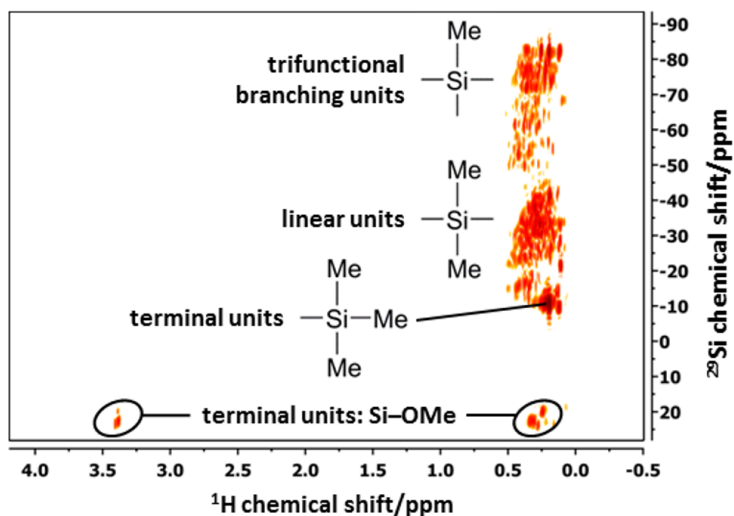


Fig. S4 $^1\text{H}/^{29}\text{Si}\{^1\text{H}\}$ HMBC NMR (^1H : 500 MHz/ ^{29}Si : 99 MHz) spectrum of **PS1-II** (solvent: $[\text{D}_8]\text{THF}$) after performing work-up procedure I (quenching with MeMgBr and Me_3SiCl) and II (precipitation in MeOH).

1.3 ATR-IR, UV/Vis and PL Spectroscopy

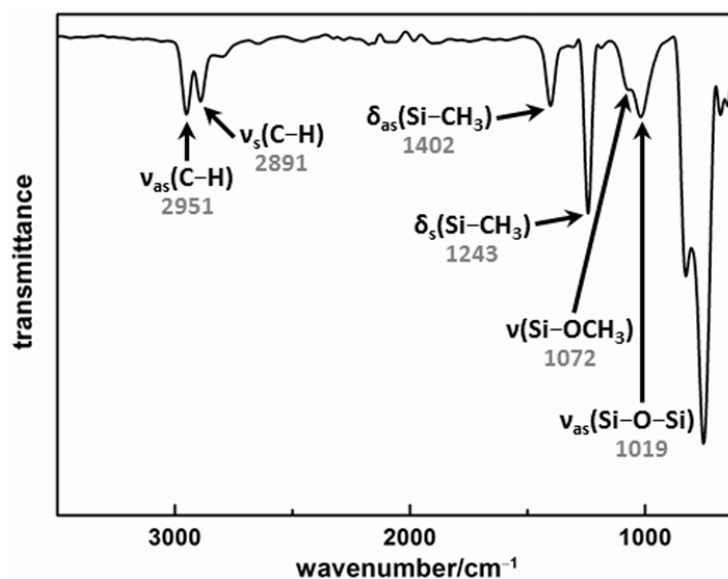


Fig. S5 ATR-IR spectrum of polysilane **PS1-II**. ν – stretching, δ – deformation, as – asymmetric, s – symmetric.

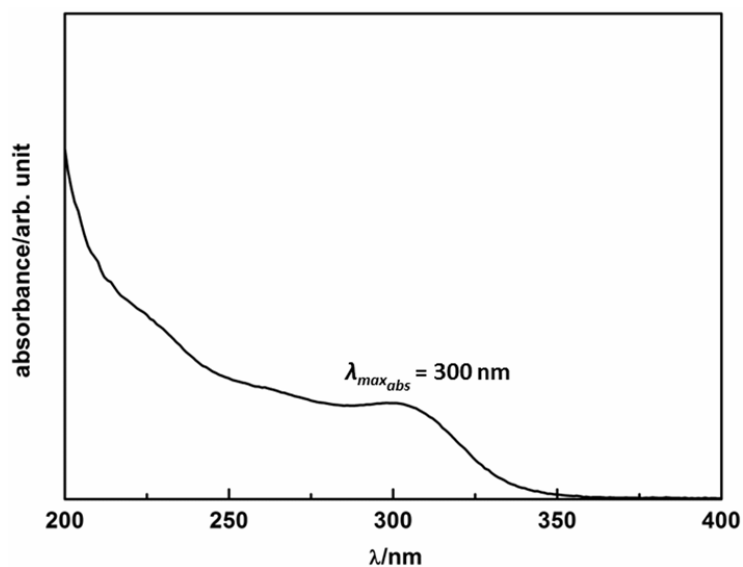


Fig. S6 Solution UV/Vis absorption spectrum of polysilane **PS1-II**.

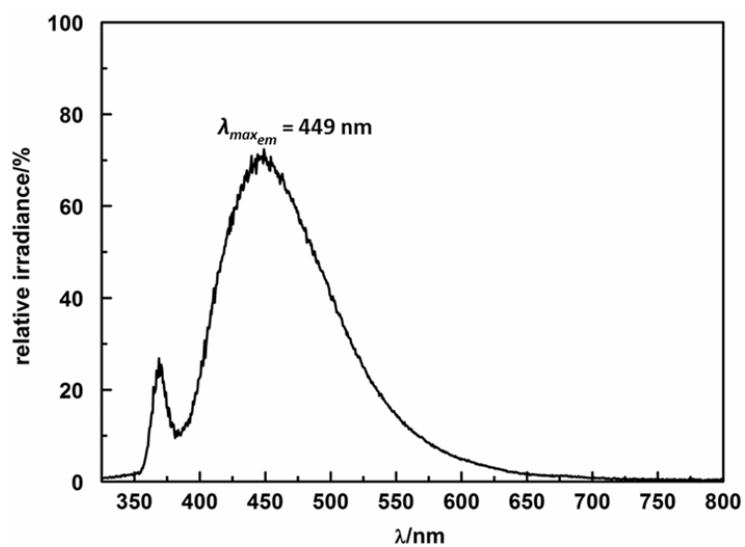


Fig. S7 Emission spectrum of polysilane **PS1-II** ($\lambda_{ex} = 365$ nm). The sharp signal at 365 nm is an artifact as it appears in the emission spectrum of pure THF, too. It can therefore not be assigned to the emission of the linear $\text{Me}_2\text{Si}(\text{Si})_2$ units of polysilane **PS1-II**.¹⁻⁵

1.4 TGA and DSC

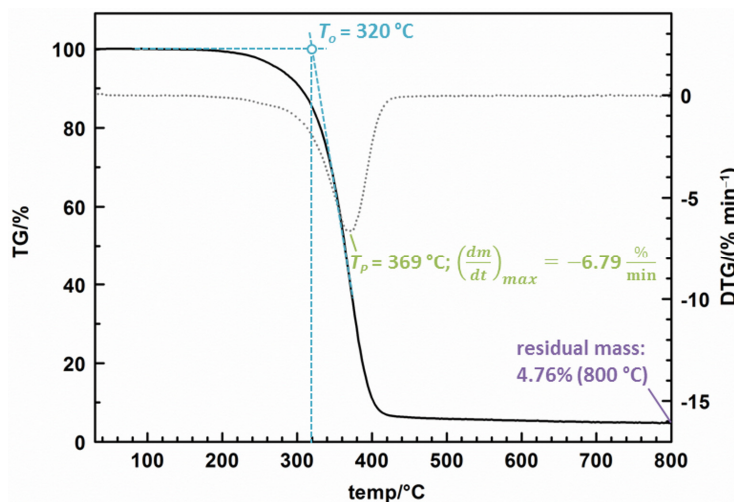


Fig. S8 TG (black solid line) and DTG (gray dotted line) curve of polysilane **PS1-II**, which was heated from 25 °C to 800 °C (heating rate: 5 K min⁻¹) in an argon flow of 20 mL min⁻¹. The DTG curve is the 1st derivative of the TG curve and provides a maximum decomposition rate $\left(\frac{dm}{dt}\right)_{max}$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

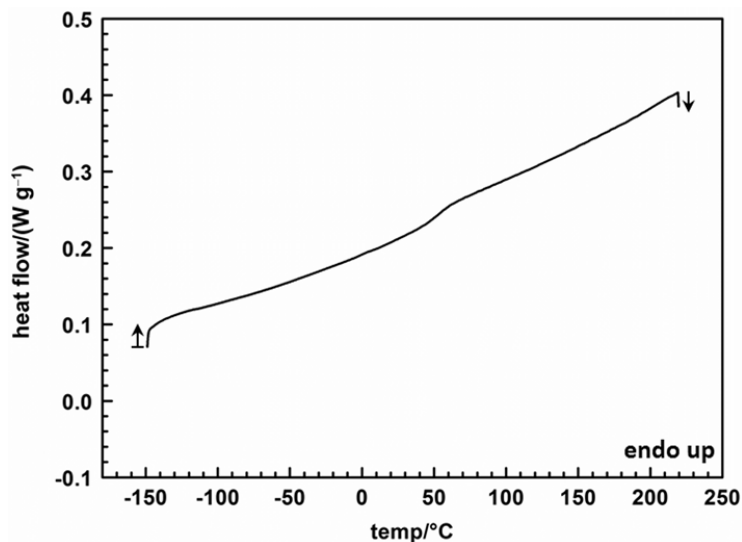


Fig. S9 DSC curve of polysilane **PS1-II**, which was hermetically sealed under argon and was heated from -150 °C to 220 °C using a heating rate of 10 K min⁻¹ (presentation of the 2nd heating cycle).

2. Thermal Rearrangement of PS1-II to PS1-PCS-330 and PS1-PCS-365

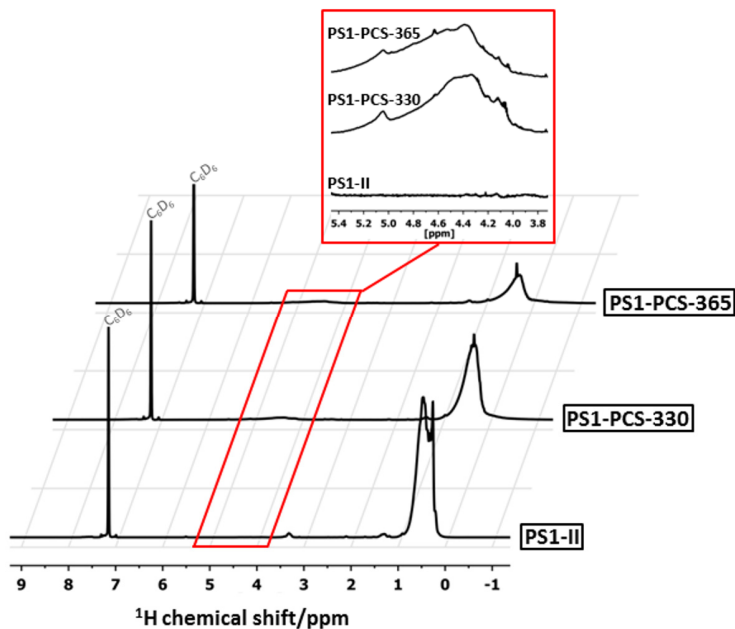


Fig. S10 Comparison of the ^1H NMR spectrum (500 MHz) of polysilane **PS1-II** with the ^1H NMR spectra of the polycarbosilanes **PS1-PCS-330** and **PS1-PCS-365** (solvent: C_6D_6). Inset shows magnified spectra in the range of the 3.8 to 5.4 ppm and the appearance of the proton peak of Si-H.

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

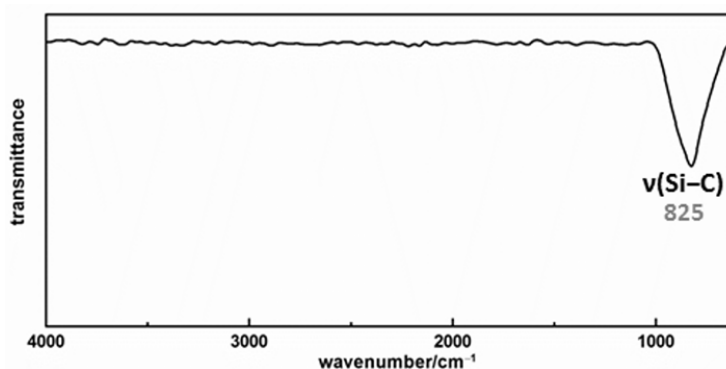


Fig. S11 ATR-IR spectrum of the pyrolysis residue **PS1-SiC-1200**. ν – stretching.

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

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