Supporting information

Polymorphism in the assembly of phase-segregated block molecules: pathway control to 1D and 2D nanostructures

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1. Materials and methods

All chemicals were purchased from commercial sources and used without further purification. The discrete length oligodimethylsiloxanes dihydrides with a length of 8, 16, 24 and 40 repeating units were synthesized according to literature procedures.[1,2] The discrete length oligodimethylsiloxane monohydride with a length of 15 repeating units was synthesized according to literature procedure.[2] Dry solvents were obtained with an MBRAUN solvent purification system (MB-SPS). Oven-dried glassware (120 °C) was used for all reactions carried out under argon atmosphere. Reactions were followed by thin-layer chromatography (TLC) using 60-F254 silica gel plates from Merck and visualized by UV light at 254 nm. Automated column chromatography was conducted on a Biotage Isolera One system using Biotage KP-SIL Silica Flash Cartridges.

NMR spectra were recorded on Varian Mercury Vx 400 MHz, Varian 400MR 400 MHz (400 MHz for 1 H-NMR) spectrometers. Deuterated solvents used are indicated in each case. Chemical shifts (δ) are expressed in ppm, and are referred to the residual peak of the solvent. Peak multiplicity is abbreviated as s: singlet; d: doublet, q: quartet; p: pentet; m: multiplet; dd: double doublet; dt: double triplet; ddt: double doublet of triplets.

Matrix assisted laser absorption/ionization-time of flight mass spectra (MALDI-TOF) were obtained on a PerSeptive Biosystems Voyager DE-PRO spectrometer using α-cyano-4-hydroxycinnamic acid (CHCA) or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCBT) as matrix.

Size exclusion chromatography (SEC) measurements were conducted on a Shimadzu Prominence-i LC-2030C 3D, using eluent flow of 1 mL min^{-1} (chloroform) and solutions were of concentration 1 mg mL^{-1} were filtered through 0.2 μm Whatman Anatop 10 filters before injection. Polarized Optical Microscopy (POM) samples were placed on glass substrates and imaged using Nikon Xfinity1 Lumenera microscope with 5x magnification.

Differential scanning calorimetry (DSC) data were collected on a DSC Q2000 from TA instruments, calibrated with an indium standard. The samples (4-8 mg) were weighed directly into aluminum pans and hermetically sealed. The samples were initially heated to 180 °C and then subjected to two cooling/heating cycles from -50 °C to 180 °C with a rate of 2 K $\min^{-1}$. The data that is presented, represents the second heating and/or cooling cycle.

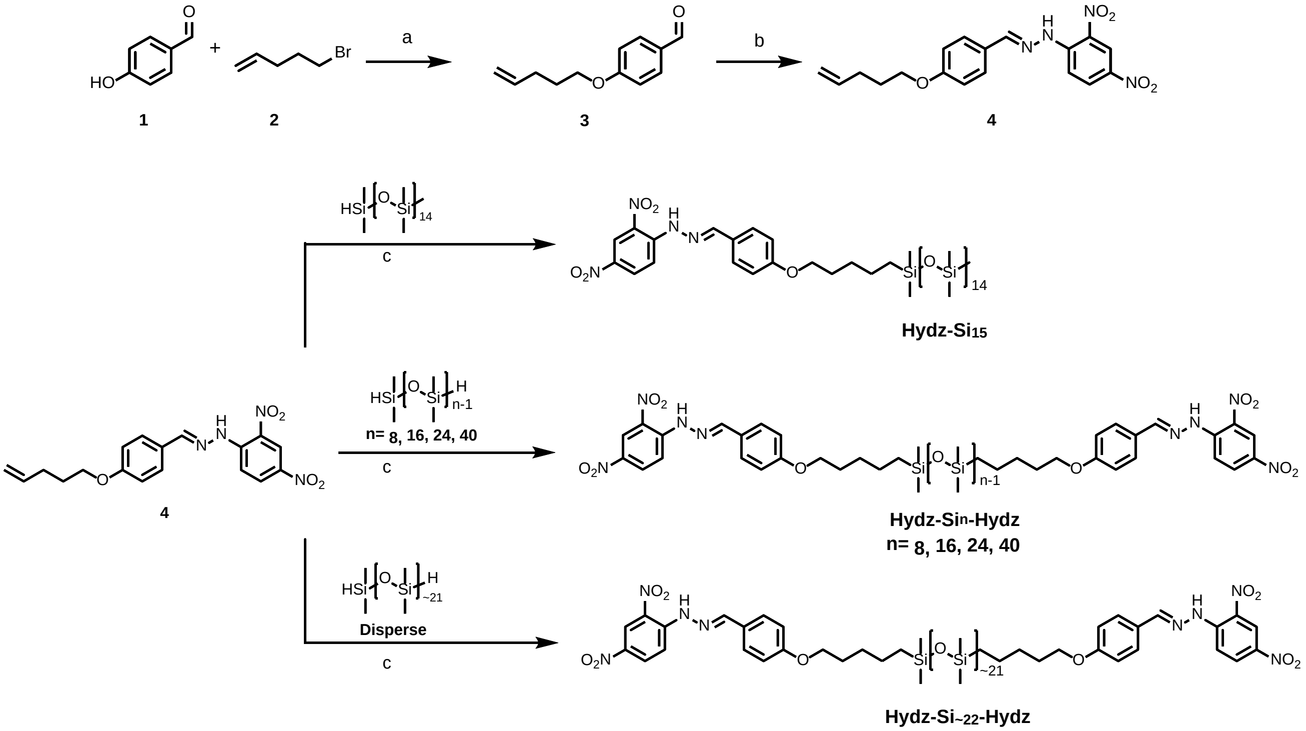
Bulk small angle X-ray scattering (SAXS) was performed on an instrument from Ganesha Lab. The flight tube and sample holder are all under vacuum in a single housing, with a GeniX-Cu ultra low divergence X-ray generator. The source produces X-rays with a wavelength (λ) of 0.154 nm and a flux of 1 × 108 ph s^{-1}. Scattered X-rays were captured on a 2-dimensional Pilatus 300K detector with 487 × 619 pixel resolution. The sample-to-detector distance was 0.084 m (WAXS mode) or 0.48 m (MAXS mode). The instrument was calibrated with diffraction patterns from silver behenate.

The solid state NMR measurements shown in this study have been performed at the Max-Planck-Institute for Polymer Research in Mainz, Germany at an Oxford Instruments 11.7 T superconducting 89mm wide bore magnet (corresponding to 500 MHz 1H Larmor frequency) with a Bruker Avance III console and a commercial double resonance MAS NMR probe supporting zirconia rotors with 2.5 mm outer diameter. If not stated differently, all MAS NMR experiments have been recorded with 25 kHz MAS spinning frequency and 100 kHz rf nutation frequency on both, ^{1}H and ^{13}C, rf channels. ^{1}H MAS and ^{1}H double quantum filtered MAS NMR spectra have been acquired with 16 or 32 transients respectively, applying one rotor period of the Back-to-Back xy16 sequence[3] for double quantum excitation for the DQ filtered MAS NMR spectra. For the CP-MAS NMR spectra a CP contact time of 3 ms was chosen for polarization transfer and swf-TPPM ^{1}H high power decoupling[4] was irradiated during acquisition. 2048 transients with a relaxation delay of 3s have been recorded, in order to obtain a good signal to noise ratio in ^{13}C CP-MAS NMR spectra. The temperature of the spinning samples under fast MAS conditions has been calibrated following the procedure of Bielecki and Burum.[5]

UV-VIS spectra of sheared films were recorded on a PerkinElmer Lambda 750 spectrometer with a rotatable polarizer in front of the beam.

Oscillatory rheology was performed on an Anton Paar MCR 301 rheometer with 10 mm parallel plate tool (Anton Paar PP10) and a gap width of 1 mm. An amplitude sweep was performed to identify the linear viscoelastic region, which occurred below 0.01% strain. All measurements were performed with 10 rad s^{-1} angular frequency.

2. Synthetic procedures



Scheme S1. Synthesis of 2,4-dinitrophenylhydrazone and the corresponding hydrazone-*o*DMS tri- and diblock molecules. Reaction conditions: (a) K_2CO_3, acetone, reflux O/N (88%); (b) *o,p*-dinitrophenylhydrazine, ethanol, reflux 1 h (90%); (c) Karstedt catalyst, DCM, 1-4 h (60-97%).

*4-(Pent-4-en-1-yloxy)benzaldehyde (**3**)*

A solution of 4-hydroxybenzaldehyde (3.0 g, 24.6 mmol, 1 eq) (**1**) and K_2CO_3 (5.1 g, 36.9 mmol, 1.5 eq) in acetone (50 mL) was stirred at room temperature for 1 h. The 5-bromopent-1-ene (4.0 g, 27.0 mmol, 1.1 eq) (**2**) was added dropwise to the solution. Subsequently, the solution was heated to 65 °C and stirred for 18 h under reflux, resulting in full conversion of the starting material. The crude mixture was cooled to room temperature and poured into 50 mL water. The solution was extracted three times with diethylether (3 x 40 mL). The organic layers were collected, combined and dried over $MgSO_4$. The crude mixture was concentrated in vacuo and purified by automated column chromatography using heptane/EtOAc (gradient 90/10 to 60/40) as eluent. The pure product was obtained as a clear solution (4.1 g, 88%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.88 (s, 1H, Ar-C$\underline{H}$=O), 7.83 (d, ^3J = 8.8 Hz, 2H, C$\underline{H}$-C-CHO), 6.99 (d, ^3J = 8.8 Hz, 2H, OC-C$\underline{H}$), 5.85 (ddt, ^3J = 16.9 Hz, ^2J = 10.2 Hz, ^1J = 6.6 Hz, 1H, CH_2=C$\underline{H}$-CH_2), 5.16-4.92 (m, 2H, C$\underline{H}_2$=CH-CH_2), 4.06 (t, ^3J = 6.4 Hz, 2H, C$\underline{H}_2$-O-Ar), 2.25 (q, ^3J = 8 Hz, 2H, CH_2=CH-C$\underline{H}_2$), 1.92 (p, ^3J = 8 Hz, 2H, CH_2-C$\underline{H}_2$-CH_2-O); ^{13}C NMR (100 MHz, $CDCl_3$) δ =190.78, 164.13, 137.41, 131.96, 129.81, 115.47, 114.73, 67.51, 29.96, 28.16 ppm.

*4-(Pent-4-en-1-yloxy)benzaldehyde 2,4-dinitrophenylhydrazone (**4**)*

The 2,4-dinitrohydrazine (contains 50 % water) (1.15 g, 5.8 mmol, 2.2 eq) was dissolved in ethanol (25 mL) and 2 mL of concentrated sulphuric acid was added. The 4-(pent-4-en-1-yloxy)benzaldehyde (0.5 g, 2.6 mmol, 1 eq) (**3**) was added and the reaction was heated to reflux. After stirring for 1 h, full conversion of aldehyde was reached. The solution was cooled to room temperature. The suspension was filtered and the residue was washed with ethanol (20 mL). The product was dried in vacuo yielding an orange powder (0.9 g, 90%).^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.27 (s, 1H, CH-N-N$\underline{\text{H}}$), 9.15 (d, ^3J = 2.6 Hz, 1H, NO_2-C-C$\underline{\text{H}}$-C-NO_2), 8.34 (ddd, ^3J = 9.6 Hz, ^2J = 2.6 Hz, ^1J = 0.8 Hz, 1H, C-CH-C$\underline{\text{H}}$-C-NO_2), 8.07 (d, ^3J = 8 Hz, 1H, C-C$\underline{\text{H}}$-CH-C-NO_2), 8.07 (s, 1H, C$\underline{\text{H}}$-N-NH), 7.71 (d, ^3J = 8.8 Hz, 2H, O-C-CH-C$\underline{\text{H}}$-C), 6.97 (d, ^3J = 8.8 Hz, 2H, O-C-C$\underline{\text{H}}$-CH-C), 5.86 (ddt, ^3J = 16.9 Hz, ^2J = 10.2 Hz, ^1J = 6.7 Hz, 1H, CH_2=C$\underline{\text{H}}$-CH_2), 5.18-4.92 (m, 2H, C$\underline{\text{H}}_2$=CH-CH_2), 4.04 (t, ^3J = 6.4 Hz, 2H, C$\underline{\text{H}}_2$-O-Ar), 2.25 (q, ^3J = 8 Hz, 2H, CH_2=CH-C$\underline{\text{H}}_2$), 1.92 (p, ^3J = 8 Hz, 2H, CH_2-C$\underline{\text{H}}_2$-CH_2-O); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.55, 147.91, 144.83, 137.90, 137.56, 129.97, 129.34, 129.09, 125.62, 123.62, 116.69, 115.42, 115.03, 67.41, 30.04, 28.29 ppm.

General procedure for the coupling of hydrazone to oDMS giving the di- and triblock molecules

The hydrazone **4** (*e.g.*, 1.35 mmol, 2.2 eq) and oligo(dimethylsiloxane)dihydride (*e.g.*, 0.61 mmol, 1 eq) were dissolved in dry DCM (0.25 M) and stirred under argon. One drop of Karstedt's catalyst (soln. in xylene, 2% Pt) was added and the mixture was stirred until full conversion of the hydride. The crude mixture was concentrated in vacuo and purified by automated column chromatography to obtain the pure material.

Hydz-Si$_8$-hydz

Starting with hydrazone **4** (0.25 g, 0.67 mmol, 2.2 eq), *o*DMS_8 dihydride (0.18 g, 0.31 mmol, 1 eq) and Karstedt's catalyst (1 drop) in DCM (1.3 mL), the crude product was obtained after 1.5 h using the general procedure. The material was purified by automated column chromatography using heptane/chloroform (gradient 50/50 to 0/100) as eluent, giving pure material as a red solid (0.29 g, 72%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.26 (s, 2H, CH-N-N$\underline{\text{H}}$), 9.14 (d, ^3J = 2.6 Hz, 2H, NO_2-C-C$\underline{\text{H}}$-C-NO_2), 8.33 (dd, ^3J = 9.5 Hz, ^2J = 2.6 Hz, 2H, C-CH-C$\underline{\text{H}}$-C-NO_2), 8.06 (d, ^3J = 8 Hz, 2H, C-C$\underline{\text{H}}$-CH-C-NO_2), 8.06 (s, 2H, C$\underline{\text{H}}$-N-NH), 7.69 (d, ^3J = 8.8 Hz, 4H, O-C-CH-C$\underline{\text{H}}$-C), 6.95 (d, ^3J = 8.8 Hz, 4H, O-C-C$\underline{\text{H}}$-CH-C), 4.01 (t, ^3J = 6.5 Hz, 4H, C$\underline{\text{H}}_2$-O-Ar), 1.81 (p, ^3J = 8 Hz, 4H, C$\underline{\text{H}}_2$-CH_2-O-Ar), 1.55-1.45 (m, 4H, Si-CH_2-CH_2-C$\underline{\text{H}}_2$), 1.45-1.36 (m, 4H, Si-CH_2-C$\underline{\text{H}}_2$-CH_2), 0.62-0.55 (m, 4H, Si-C$\underline{\text{H}}_2$-CH_2-CH_2), 0.1-0.02 (m, 48H, Si(C$\underline{\text{H}}_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.64, 147.92, 144.80, 137.86, 129.93, 129.30, 129.05, 125.50, 123.59, 116.65, 114.98, 68.24, 29.69, 28.90, 23.07, 18.19, 1.19, 1.09, 0.20 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{52}H_{86}N_8O_{17}Si_8^+$: 1318.43 $[M]^+$; found 1318.42; *m/z* calcd for $C_{52}H_{86}N_8O_{17}Si_8$+$Na^+$: 1341.42 $[M+Na]^+$; found 1341.42.

Hydz-Si$_{16}$-hydz

Starting with hydrazone **4** (0.5 g, 1.35 mmol, 2.2 eq), *o*DMS_{16} dihydride (0.72 g, 0.61 mmol, 1 eq) and Karstedt's catalyst (1 drop) in DCM (2.5 mL), the crude product was obtained after 1.5 h using the general procedure. The material was purified by automated column chromatography using heptane/chloroform (gradient 40/60 to 0/100) as eluent, giving pure material as a red solid (0.81 g, 69%). ^{1}H-NMR (400 MHz, CDCl3): δ = 11.26 (s, 2H, CH-N-N$\underline{\text{H}}$), 9.14 (d, ^3J = 2.5 Hz, 2H, NO_2-C-C$\underline{\text{H}}$-C-NO_2), 8.33 (dd, ^3J = 8 Hz, ^2J = 2.6 Hz, 2H, C-CH-C$\underline{\text{H}}$-C-NO_2), 8.07 (d, ^3J = 8.8 Hz, 2H, C-C$\underline{\text{H}}$-CH-C-NO_2), 8.07 (s, 2H, C$\underline{\text{H}}$-N-NH), 7.7 (d, ^3J = 8.8 Hz, 4H, O-C-CH-C$\underline{\text{H}}$-C), 6.96 (d, ^3J = 8.8 Hz, 4H, O-C-C$\underline{\text{H}}$-CH-C), 4.01 (t, ^3J = 6.6 Hz, 4H, C$\underline{\text{H}}_2$-O-Ar), 1.82 (p, ^3J = 8 Hz, 4H, C$\underline{\text{H}}_2$-CH_2-O-Ar), 1.56-1.47 (m, 4H, Si-CH_2-CH_2-C$\underline{\text{H}}_2$), 1.46-1.37 (m, 4H, Si-CH_2-C$\underline{\text{H}}_2$-CH_2), 0.68-0.52 (m, 4H, Si-C$\underline{\text{H}}_2$-CH_2-CH_2), 0.12-0.01 (m, 96H, Si(C$\underline{\text{H}}_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.84, 148.10, 144.99, 138.08, 130.09, 129.47, 129.26, 125.68, 123.74, 116.83, 115.18, 68.43, 29.86, 29.08, 23.24, 18.37, 1.34, 1.24, 1.22, 1.21, 0.84, 0.36, 0.15 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{68}H_{134}N_8O_{25}Si_{16}$+Na$^+$: 1933.57 [M+Na]$^+$; found 1933.65.

Hydz-Si$_{24}$-hydz

Starting with hydrazone **4** (0.25 g, 0.65 mmol, 2.2 eq), *o*DMS$_{24}$ dihydride (0.54 g, 0.31 mmol, 1 eq) and Karstedt's catalyst (1 drop) in DCM (1 mL), the crude product was obtained after 2 h using the general procedure. The material was purified by automated column chromatography using heptane/DCM (gradient 80/20 to 0/100) as eluent, giving pure material as a red solid (0.65 g, 85%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 11.27 (s, 2H, CH-N-N$\underline{H}$), 9.14 (d, ^3J = 2.6 Hz, 2H, NO$_2$-C-C$\underline{H}$-C-NO$_2$), 8.33 (dd, ^3J = 9.5 Hz, ^3J = 2.5 Hz, 2H, C-CH-C$\underline{H}$-C-NO$_2$), 8.07 (s, 2H, C$\underline{H}$-N-NH), 8.06 (d, ^3J = 9.6 Hz, 2H, C-C$\underline{H}$-CH-C-NO$_2$), 7.7 (d, ^3J = 4 Hz, 4H, O-C-CH-C$\underline{H}$-C), 6.96 (d, ^3J = 8 Hz, 4H, O-C-C$\underline{H}$-CH-C), 4.01 (t, ^3J = 6.6 Hz, 4H, C$\underline{H}_2$-O-Ar), 1.82 (p, ^3J = 8 Hz, 4H, C$\underline{H}_2$-CH$_2$-O-Ar), 1.56-1.47 (m, 4H, Si-CH$_2$-CH$_2$-C$\underline{H}_2$), 1.46-1.37 (m, 4H, Si-CH$_2$-C$\underline{H}_2$-CH$_2$), 0.68-0.52 (m, 4H, Si-C$\underline{H}_2$-CH$_2$-CH$_2$), 0.13-0.03 (m, 144H, Si(C$\underline{H}_3$)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 161.82, 148.11, 144.97, 138.02, 130.09, 129.46, 129.20, 125.65, 123.75, 116.82, 115.15, 68.41, 29.85, 29.06, 23.23, 18.35, 1.57, 1.34, 1.23, 1.22, 1.20, 0.82, 0.35, 0.15 ppm. MS (MALDI-TOF): *m/z* calcd for $C_{84}H_{182}N_8O_{33}Si_{24}$+Na$^+$: 2525.75 [M+Na]$^+$; found 2525.83.

Hydz-Si$_{40}$-hydz

Starting with hydrazone **4** (0.15 g, 0.41 mmol, 2.2 eq), *o*DMS$_{40}$ dihydride (0.54 g, 0.18 mmol, 1 eq) and Karstedt's catalyst (1 drop) in DCM (1 mL), the crude product was obtained after 1.5 h using the general procedure. The material was purified by automated column chromatography using heptane/chloroform (gradient 50/50 to 0/100) as eluent, giving pure material as a red solid (0.41 g, 60%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 11.27 (s, 2H, CH-N-N$\underline{H}$), 9.15 (d, ^3J = 2.5 Hz, 2H, NO$_2$-C-C$\underline{H}$-C-NO$_2$), 8.34 (dd, ^3J = 9.6 Hz, ^3J = 2.6 Hz, 2H, C-CH-C$\underline{H}$-C-NO$_2$), 8.07 (s, 2H, C$\underline{H}$-N-NH), 8.07 (d, ^3J = 9.6 Hz, 2H, C-C$\underline{H}$-CH-C-NO$_2$), 7.7 (d, ^3J = 8.8 Hz, 4H, O-C-CH-C$\underline{H}$-C), 6.96 (d, ^3J = 8.8 Hz, 4H, O-C-C$\underline{H}$-CH-C), 4.01 (t, ^3J = 6.6 Hz, 4H, C$\underline{H}_2$-O-Ar), 1.82 (p, ^3J = 8 Hz, 4H, C$\underline{H}_2$-CH$_2$-O-Ar), 1.53-1.46 (m, 4H, Si-CH$_2$-CH$_2$-C$\underline{H}_2$), 1.46-1.37 (m, 4H, Si-CH$_2$-C$\underline{H}_2$-CH$_2$), 0.64-0.53 (m, 4H, Si-C$\underline{H}_2$-CH$_2$-CH$_2$), 0.14-0.02 (m, 240H, Si(C$\underline{H}_3$)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 161.82, 148.10, 144.98, 138.04, 130.10, 129.47, 129.22, 125.65, 123.76, 116.83, 115.16, 68.41, 29.86, 29.07, 23.23, 18.36, 1.56, 1.34, 1.24, 1.21, 1.19, 0.82, 0.35, 0.15 ppm. MS (MALDI-TOF): *m/z* calcd for $C_{116}H_{278}N_8O_{49}Si_{40}$+Na$^+$: 3710.02 [M+Na]$^+$; found 3710.15.

Hydz-Si$_{\sim 22}$-hydz (disperse)

Starting with hydrazone **4** (0.14 g, 0.39 mmol, 2.5 eq), commercially available *o*DMS$_{\sim 22}$ dihydride (0.26 g, ~0.16 mmol, 1 eq, DP~22) and Karstedt's catalyst (1 drop) in DCM (1 mL), the crude product was obtained after 20 min using the general procedure. The material was purified by automated column chromatography using heptane/chloroform (gradient 70/30 to 0/100) as eluent, giving pure material as a red solid (0.37 g, quant.). ^{1}H-NMR (400 MHz, CDCl$_3$):

δ = 11.27 (s, 2H, CH-N-N$\underline{H}$), 9.14 (d, ^3J = 2.6 Hz, 2H, NO$_2$-C-C$\underline{H}$-C-NO$_2$), 8.33 (dd, ^3J = 9.6 Hz, ^3J = 2.6 Hz, 2H, C-CH-C$\underline{H}$-C-NO$_2$), 8.07 (s, 2H, C$\underline{H}$-N-NH), 8.07 (d, ^3J = 9.7 Hz, 2H, C-C$\underline{H}$-CH-C-NO$_2$), 7.7 (d, ^3J = 8.7 Hz, 4H, O-C-CH-C$\underline{H}$-C), 6.96 (d, ^3J = 8.8 Hz, 4H, O-C-C$\underline{H}$-CH-C), 4.01 (t, ^3J = 6.6 Hz, 4H, C$\underline{H}_2$-O-Ar), 1.82 (p, ^3J = 6.7 Hz, 4H, C$\underline{H}_2$-CH$_2$-O-Ar), 1.54-1.47 (m, 4H, Si-CH$_2$-CH$_2$-C$\underline{H}_2$), 1.46-1.36 (m, 4H, Si-CH$_2$-C$\underline{H}_2$-CH$_2$), 0.62-0.54 (m, 4H, Si-C$\underline{H}_2$-CH$_2$-CH$_2$), 0.11-0.03 (m, 132H, Si(C$\underline{H}_3$)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 161.81, 148.10, 144.97, 138.03, 130.09, 129.47, 129.21, 125.65, 123.75, 116.82, 115.15, 68.41, 29.85, 29.06, 23.23, 18.35, 1.56, 1.34, 1.24, 1.21, 1.19, 0.82, 0.35, 0.15 ppm.

Hydz-Si$_{15}$

The hydrazone **4** (0.3 g, 0.81 mmol, 1.2 eq) and oligo(dimethylsiloxane)monohydride (0.75 g, 0.67 mmol, 1 eq) were dissolved in dry DCM (2 mL) and stirred under argon. One drop of Karstedt's catalyst (soln. in xylene, 2% Pt) was added and the mixture was stirred for 1 h until full conversion of the hydride. The crude mixture was concentrated in vacuo and purified by automated column chromatography using heptane/DCM (gradient 50/50 to 0/100) as eluent, giving pure material as a red solid (0.93 g, 93%). ^{1}H-NMR (400 MHz, CDCl$_3$):

δ = 11.27 (s, 1H, CH-N-N$\underline{H}$), 9.14 (d, ^3J = 2.5 Hz, 1H, NO$_2$-C-C$\underline{H}$-C-NO$_2$), 8.34 (dd, ^3J = 9.6 Hz, ^3J = 2.6 Hz, 1H, C-CH-C$\underline{H}$-C-NO$_2$), 8.07 (s, 1H, C$\underline{H}$-N-NH), 8.07 (d, ^3J = 9.5 Hz, 1H, C-C$\underline{H}$-CH-C-NO$_2$), 7.7 (d, ^3J = 8.6 Hz, 2H, O-C-CH-C$\underline{H}$-C), 6.96 (d, ^3J = 8.6 Hz, 2H, O-C-C$\underline{H}$-CH-C), 4.01 (t, ^3J = 6.5 Hz, 2H, C$\underline{H}_2$-O-Ar), 1.82 (p, ^3J = 8 Hz, 2H, C$\underline{H}_2$-CH$_2$-O-Ar), 1.54-1.47 (m, 2H, Si-CH$_2$-CH$_2$-C$\underline{H}_2$), 1.46-1.36 (m, 2H, Si-CH$_2$-C$\underline{H}_2$-CH$_2$), 0.64-0.53 (m, 2H, Si-C$\underline{H}_2$-CH$_2$-CH$_2$), 0.12-0.01 (m, 93H, Si(C$\underline{H}_3$)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 161.82, 148.11, 144.98, 138.03, 130.10, 129.47, 129.22, 125.65, 123.76, 116.83, 115.15, 68.41, 29.85, 29.06, 23.23, 18.35, 1.94, 1.57, 1.34, 1.29, 1.24, 1.20, 0.83, 0.35, 0.15 ppm. MS (MALDI-TOF): *m/z* calcd for $C_{49}H_{112}N_4O_{19}Si_{15}+Na^+$: 1503.44 [M+Na]$^+$; found 1503.5.

3. NMR spectra of hydz-*o*DMS di- and triblock molecules

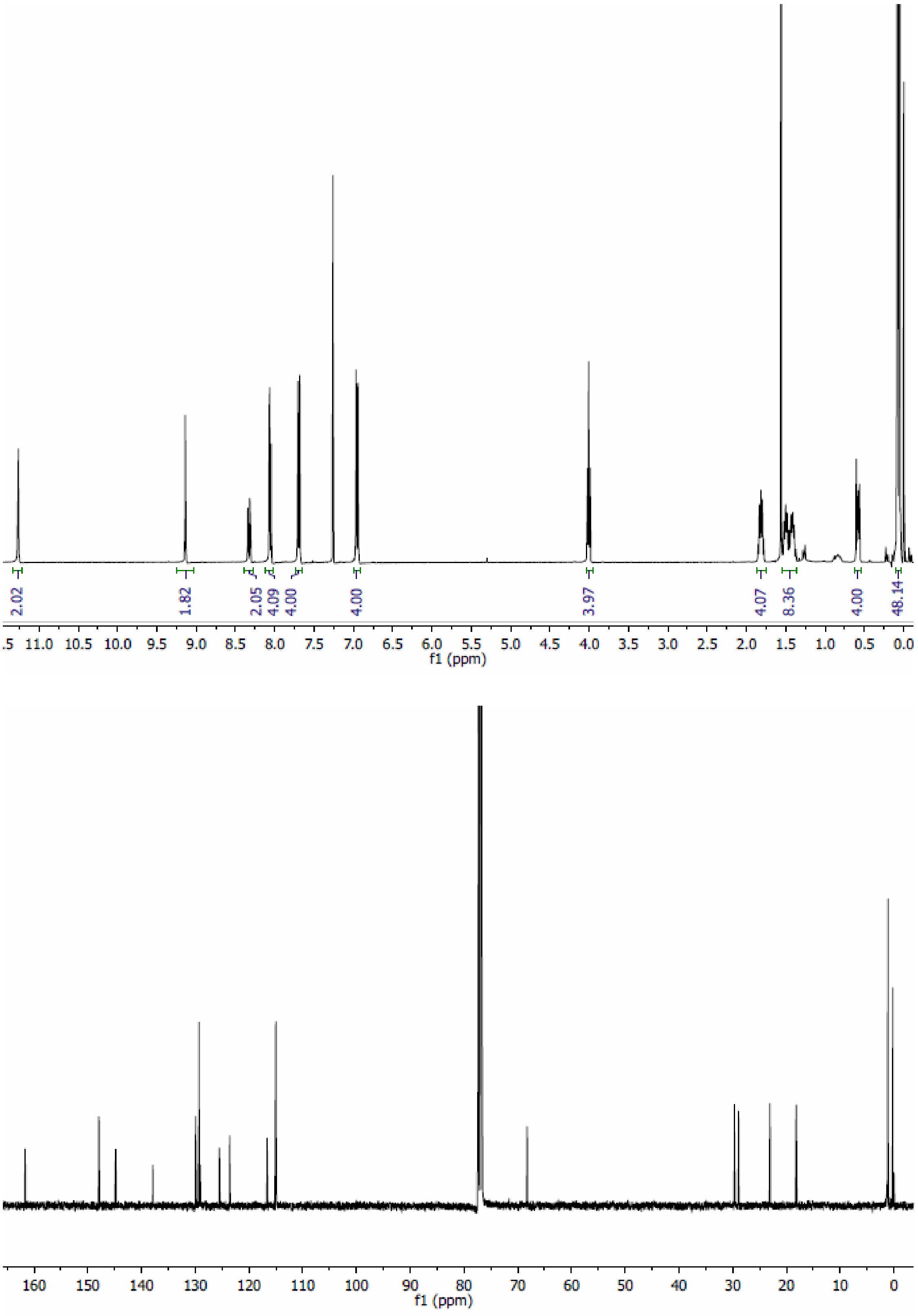


Figure S1. ^{1}H- and ^{13}C NMR of hydz-Si$_8$-hydz

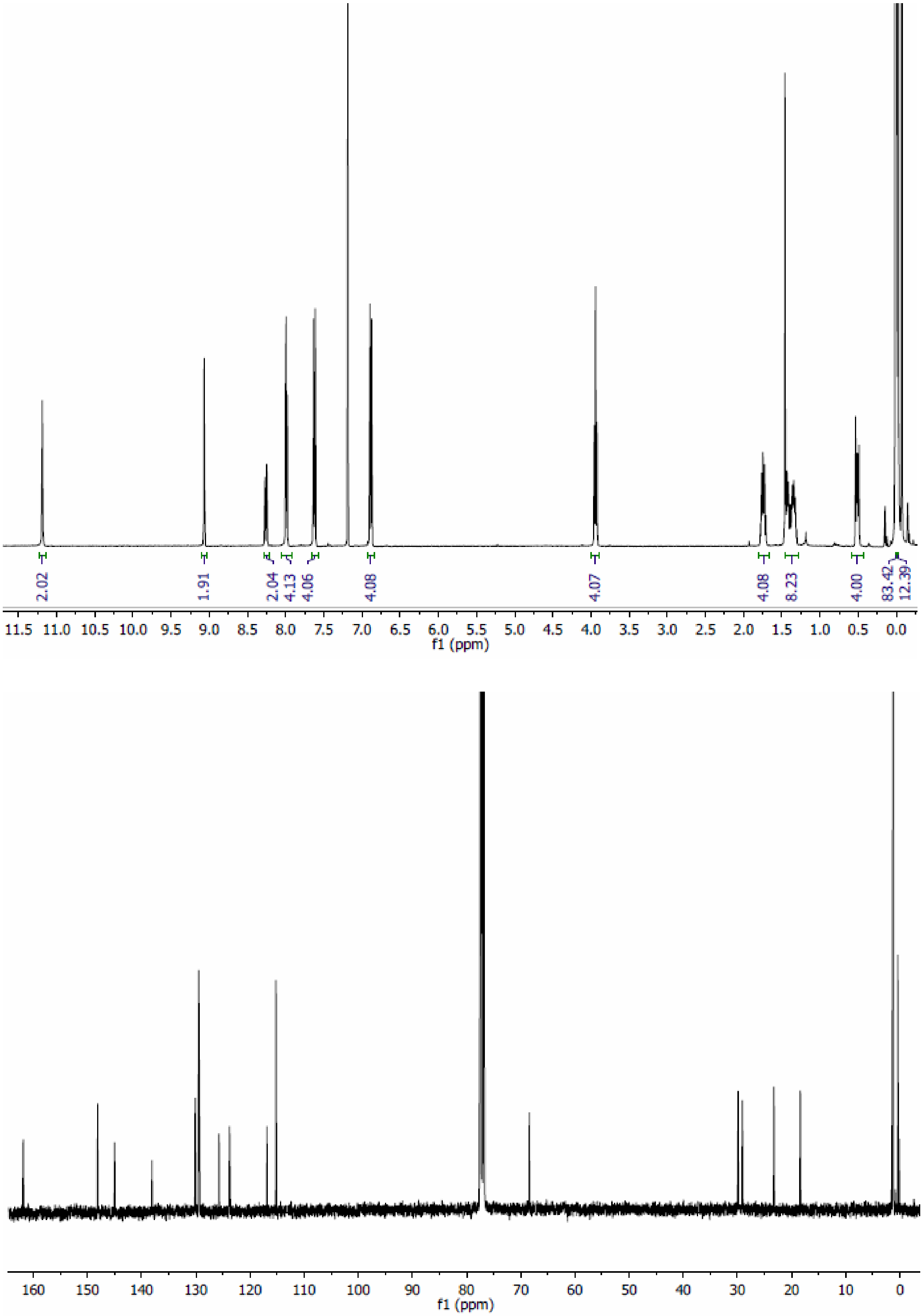
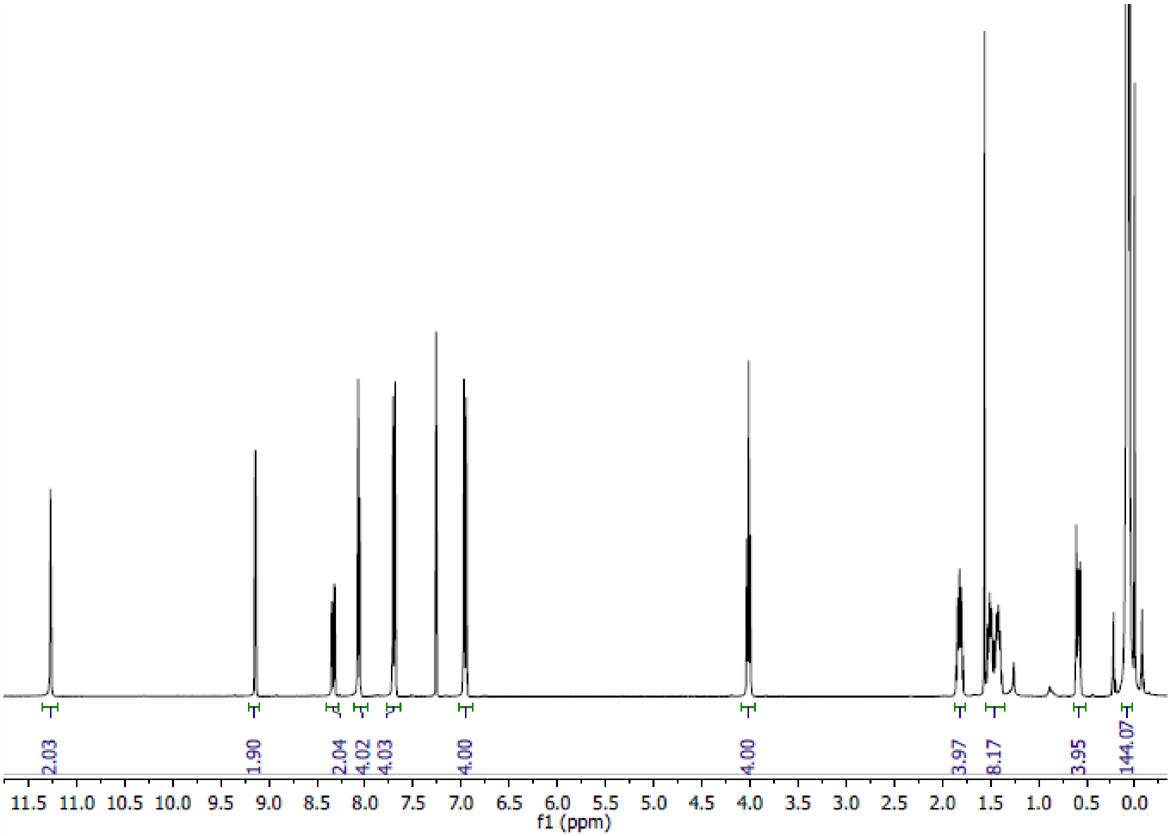


Figure S2. ^{1}H- and ^{13}C NMR of hydz-Si$_{16}$-hydz



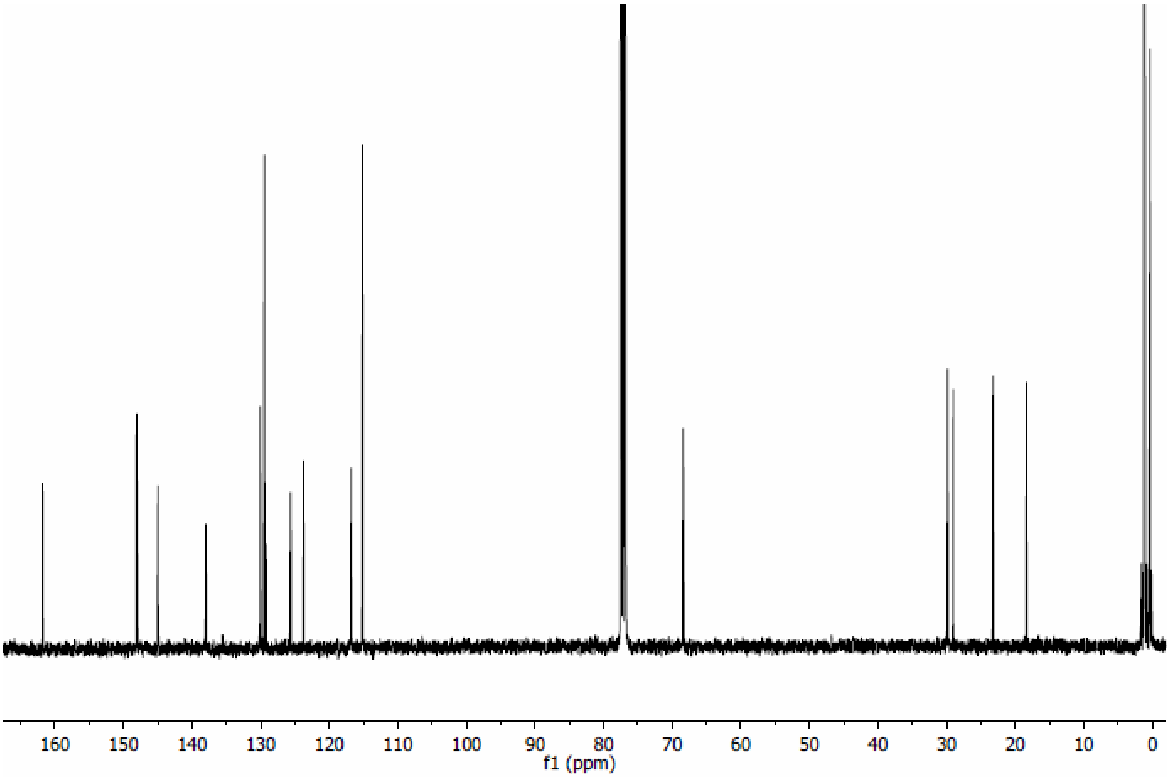


Figure S3. ^{1}H- and ^{13}C NMR of hydz-Si$_{24}$-hydz

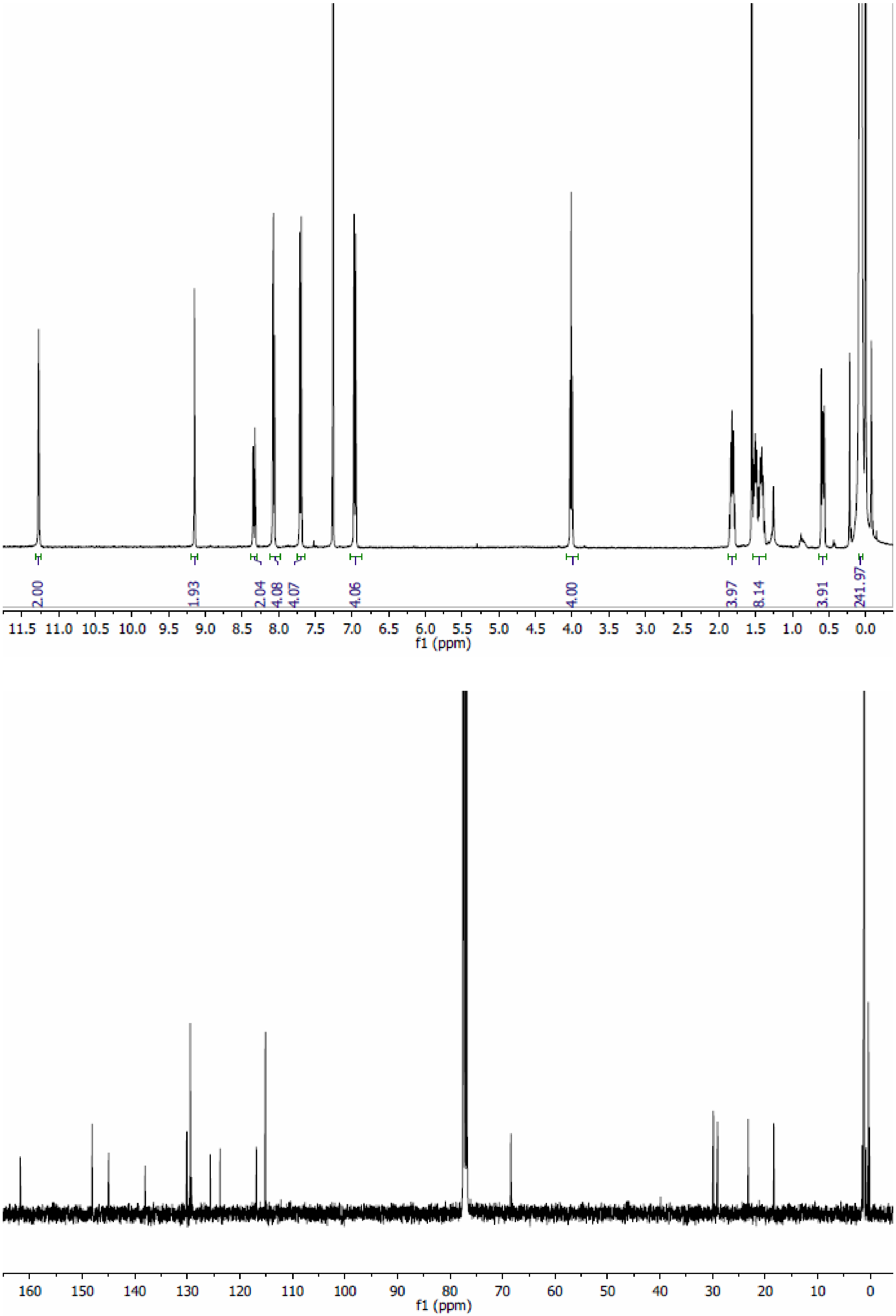


Figure S4. ^{1}H- and ^{13}C NMR of hydz-Si$_{40}$-hydz

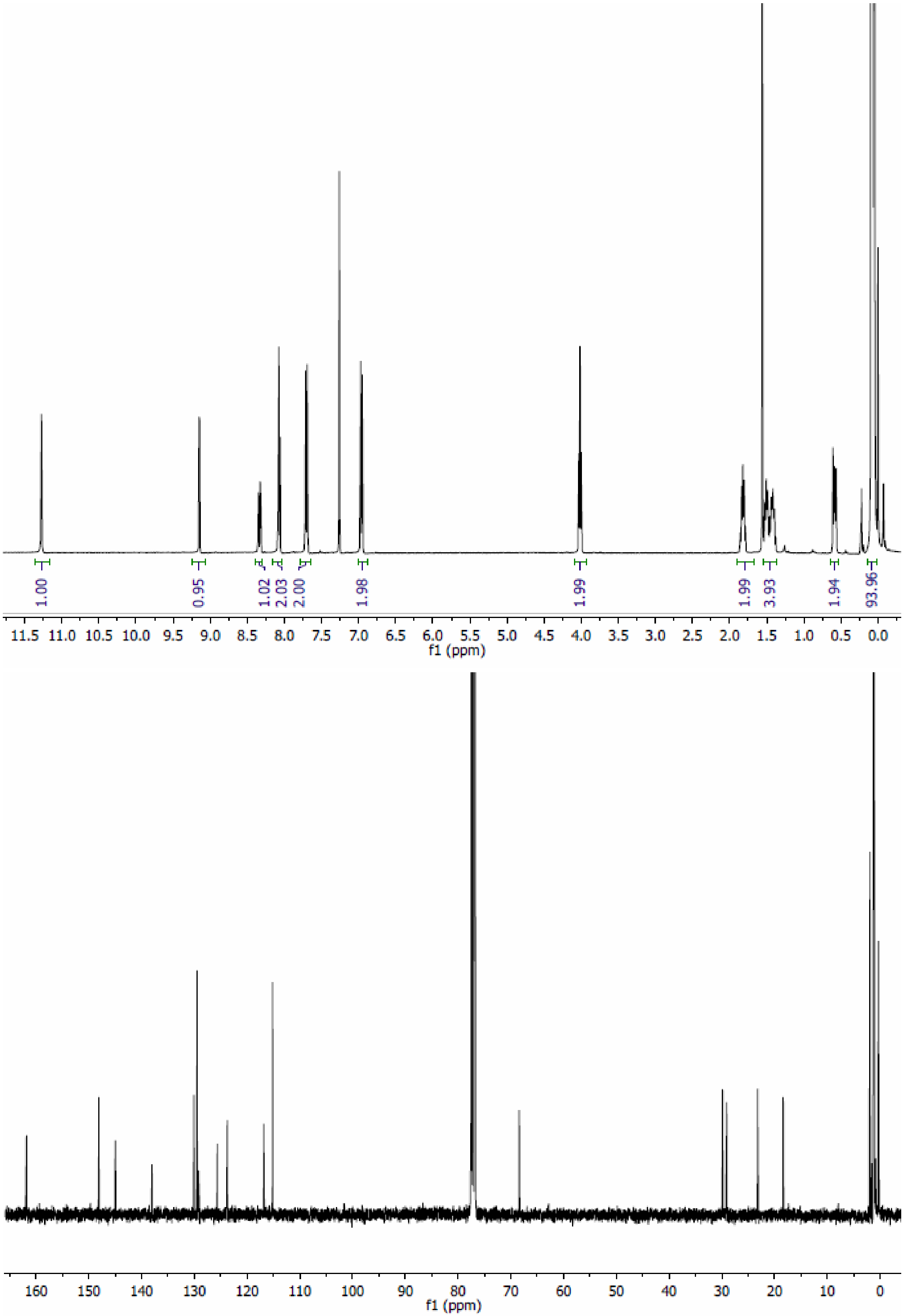


Figure S5. ^{1}H- and ^{13}C NMR of hydz-Si$_{15}$

4. SEC and MALDI-TOF-MS analysis

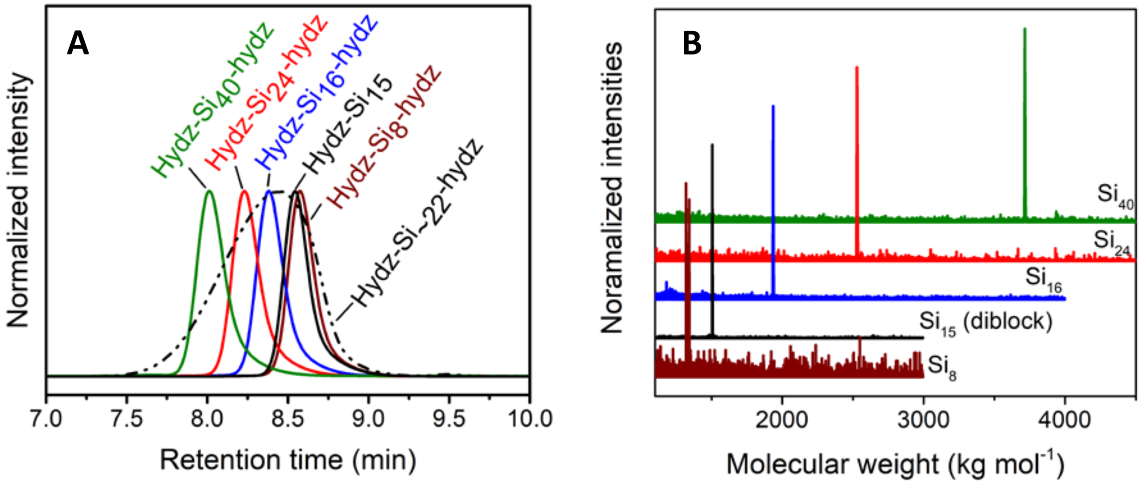


Figure S6. SEC traces (A) and MALDI-TOF-MS (B) spectra of discrete hydz-*o*DMS tri- and diblock molecules.

5. Thermal analysis

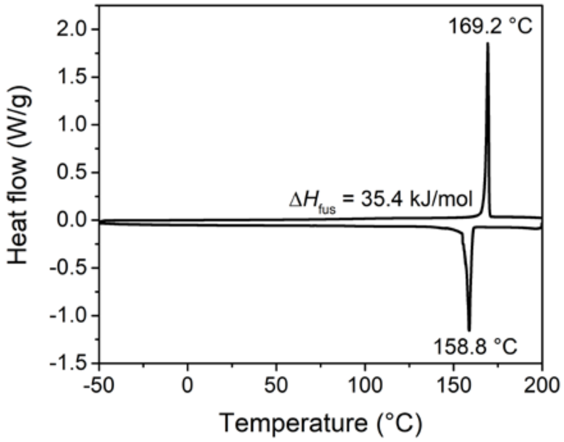


Figure S7: DSC trace of the hydrazone **4**. Second cooling and heating run are shown. Endothermic heat flows have a positive value. A temperature rate of 10 K·min^{-1} was used.

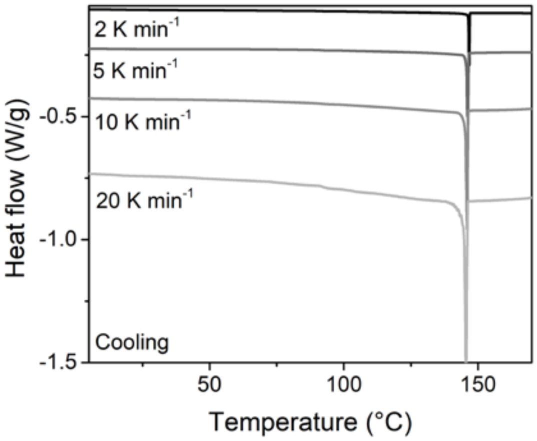


Figure S8: DSC trace of the hydz-Si_{16}-hydz at various cooling rates. Endothermic heat flows have a positive value.

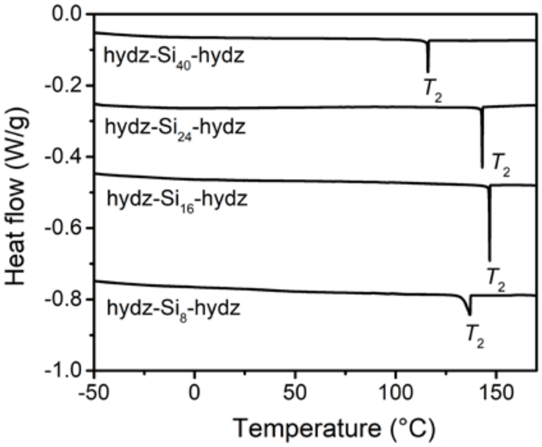


Figure S9: DSC traces (first cooling run) of the discrete hydz-Si_n-hydz block molecules. Endothermic heat flows have a positive value. A temperature rate of 2 K·min^{-1} was used.

6. Variable temperature X-ray scattering measurements

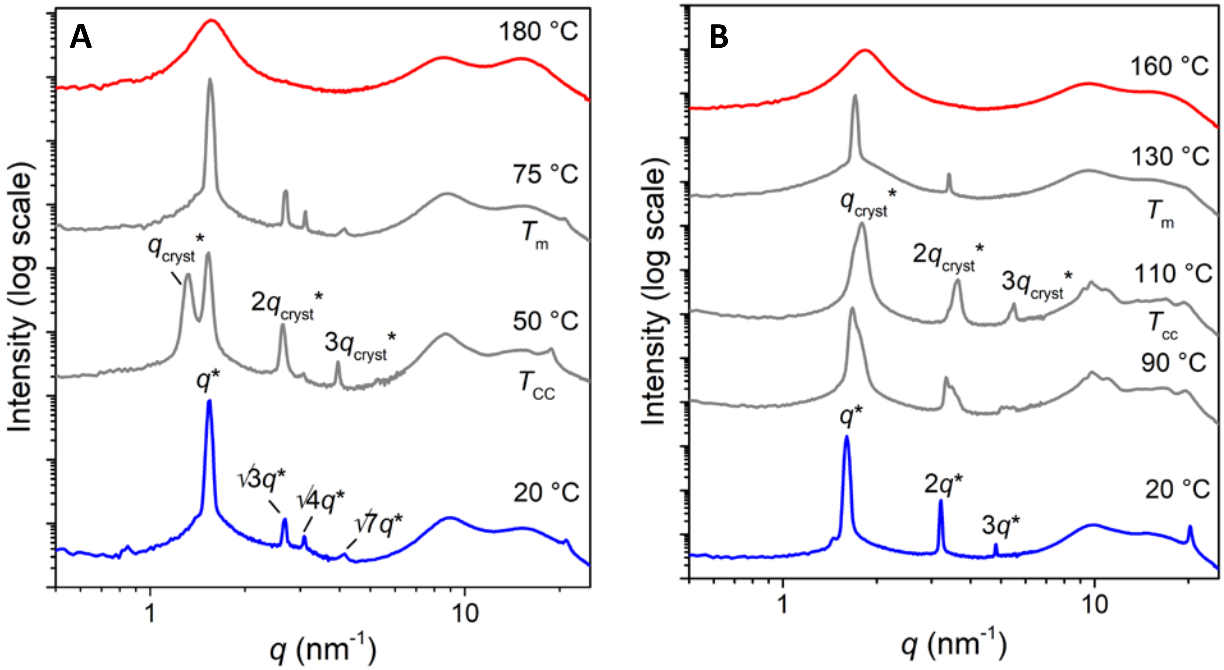


Figure S10. 1-D scattering profiles for hydz-Si$_8$-hydz (A) and hydz-Si$_{16}$-hydz (B) at various temperatures, measured upon heating.

7. Relation between d* and D_{cyl}

$$D_{CYL} = \left(\frac{8 f_{hydz} d^{*2}}{\sqrt{3} \cdot \pi}\right)^{1/2}$$

8. UV-VIS measurements with polarizer

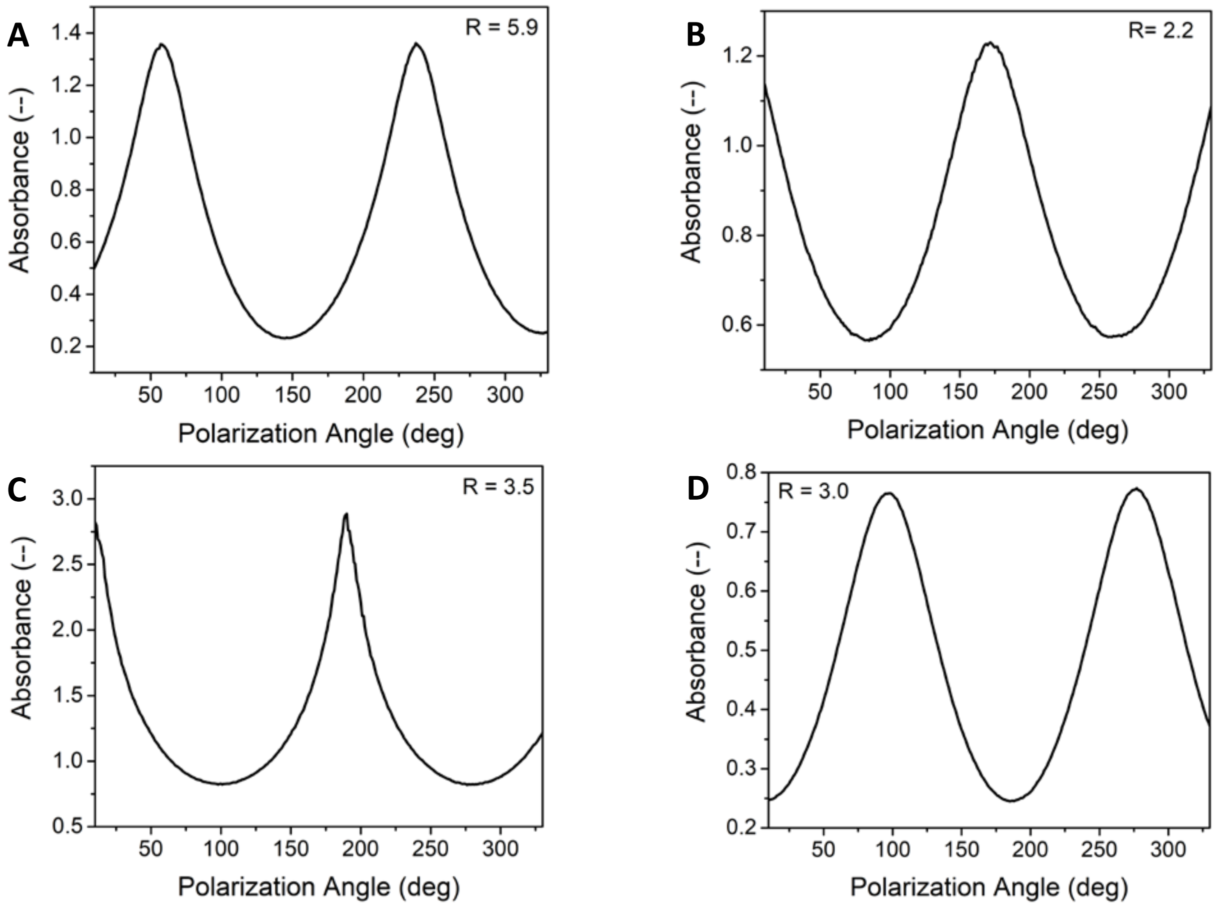


Figure S11. Absorbance dependence on polarization angle of hydz-Si_{16}-hydz (A), hydz-Si_{24}-hydz (B), hydz-Si_{40}-hydz (C) and hydz-Si_{15} (D) measured by UV with rotating polarizer.

Formula for calculation dichroic ratio calculation:

$$R = \frac{A_{\parallel}}{A_{\perp}}$$

In this formula, A is the maximum absorbance and $A_{\perp}$ is the minimum absorbance in above spectra.

9. Variable temperature IR measurements

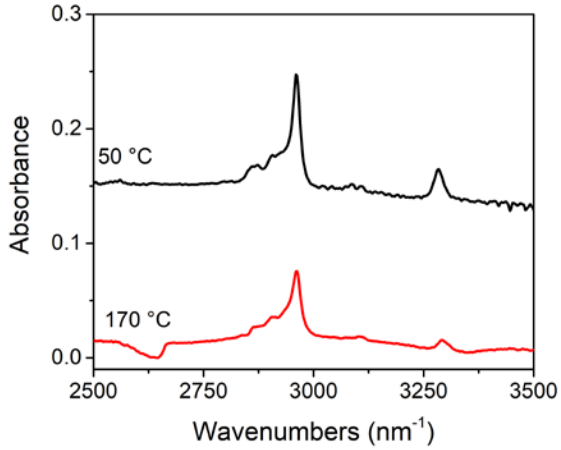


Figure S12. IR spectra of hydz-Si$_{16}$-hydz at 50 °C (black) and 170 °C (red) showing that the band at 3275 nm^{-1} does not disappear upon melting the material.

10. Solid state NMR and FTIR of amorphous and crystalline structures

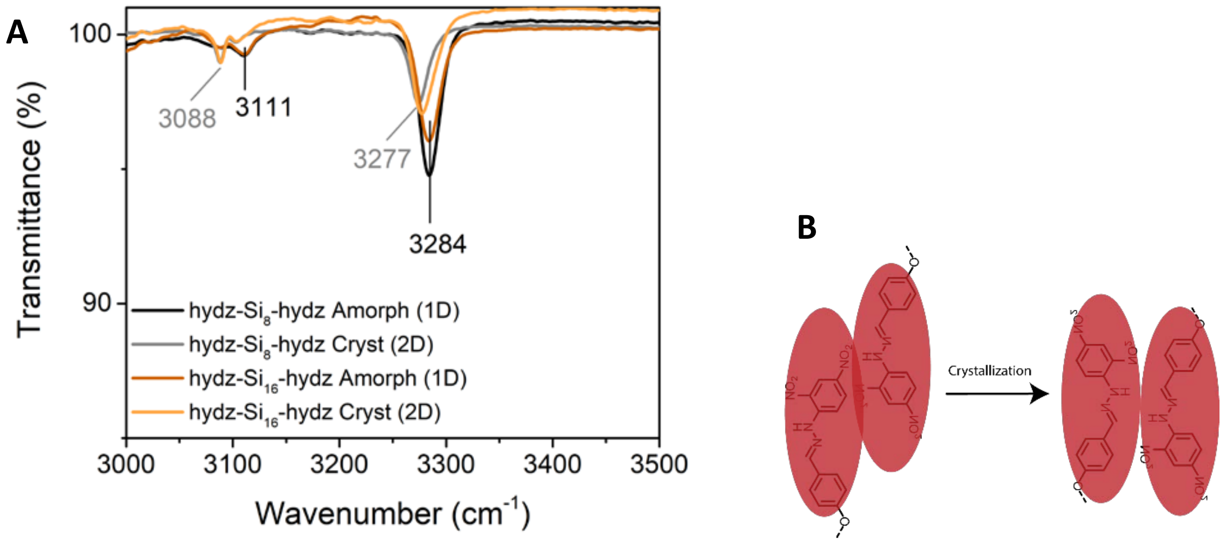


Figure S13. FTIR of amorphous (1D) and crystalline (2D) structures of hydz-Si$_8$-hydz and hydz-Si$_{16}$-hydz showing the shift in C-H and N-H bands (A). Graphic illustration of the shift of the hydrazone rods going from the cylindrical structure to the lamellar structure upon crystallization (B).

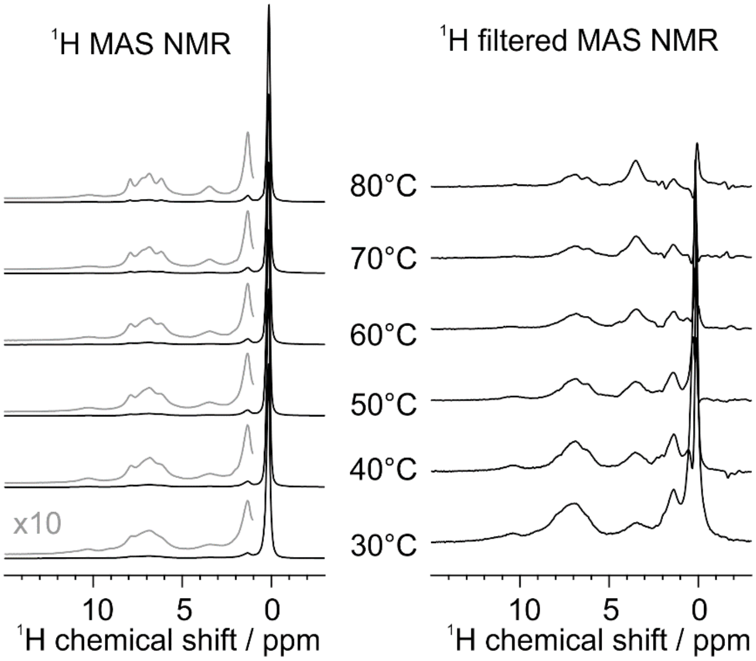


Figure S14. ^{1}H MAS NMR hydz-Si$_{24}$-hydz at various temperatures.

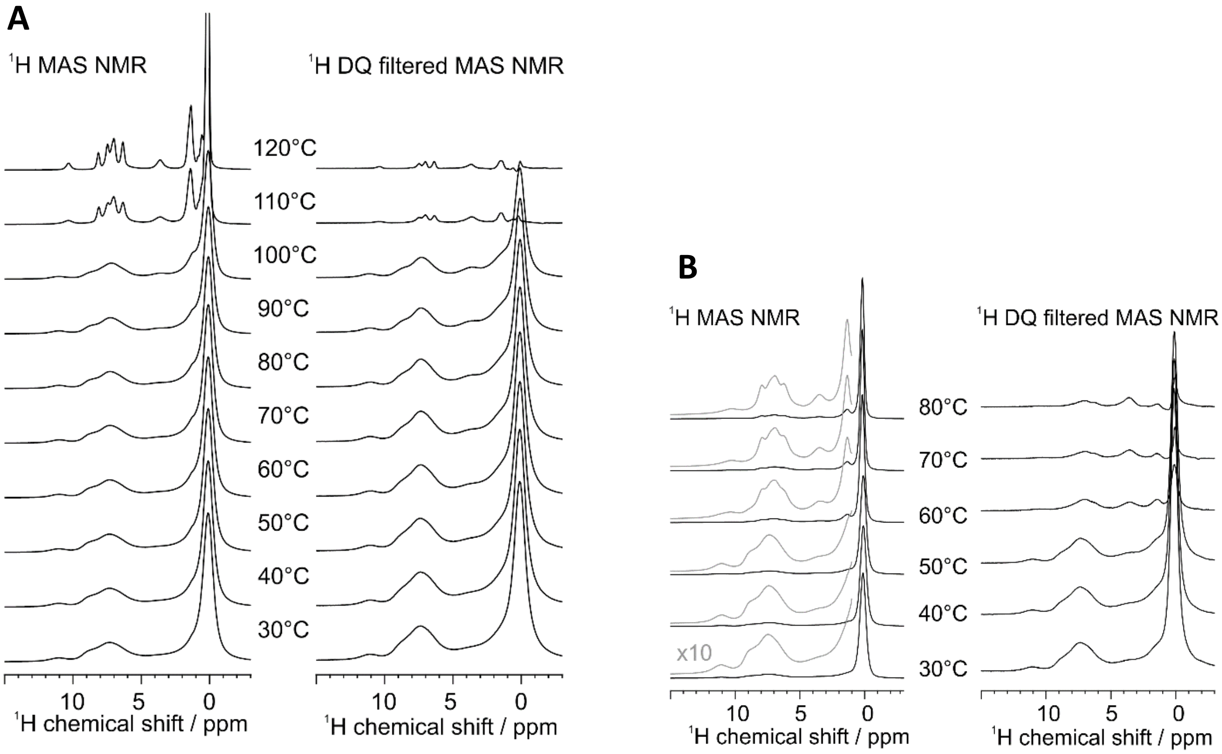


Figure S15. ^{1}H and ^{1}H DQ filtered MAS NMR hydz-Si$_8$-hydz (A) and hydz-Si$_{16}$-hydz (B) at various temperatures.

11. Rheology measurements

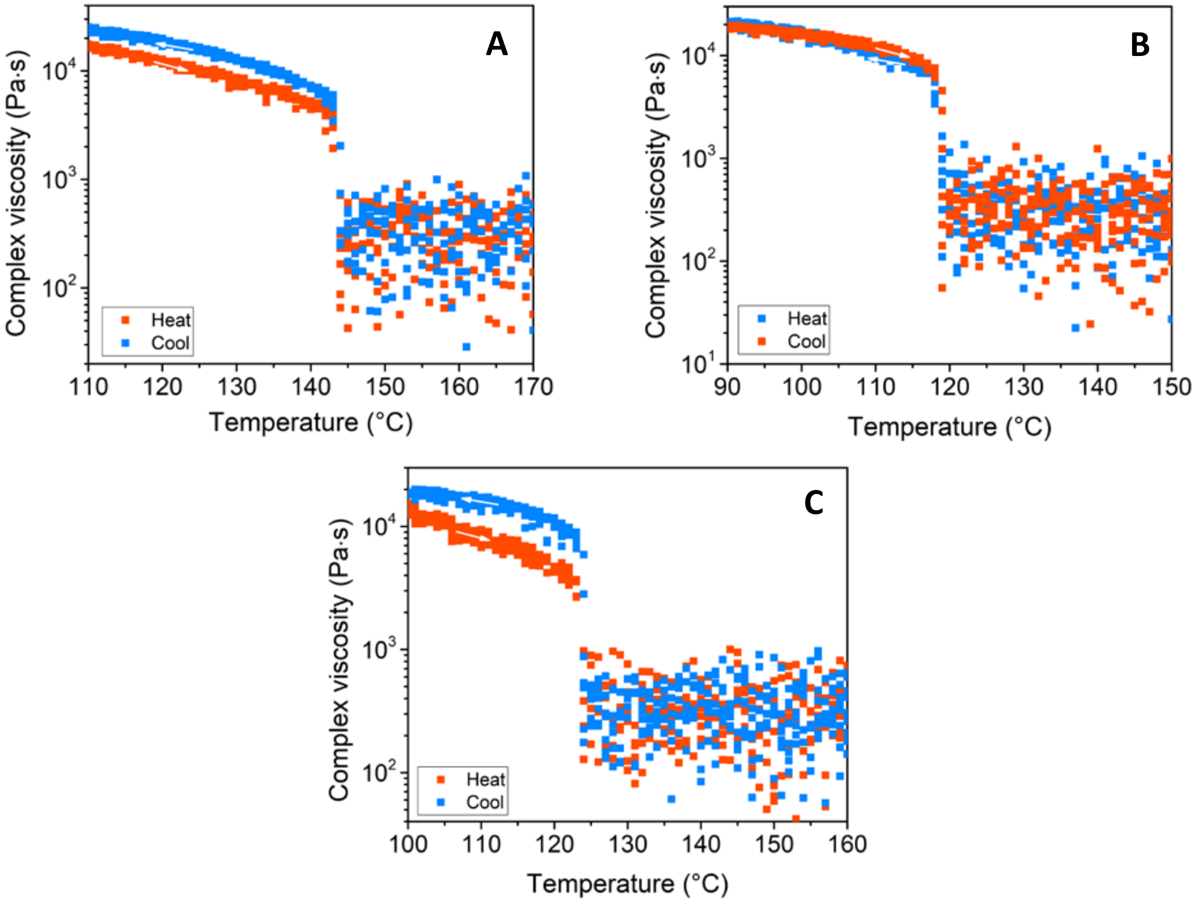


Figure S16. Complex viscosity change of hydz-Si$_{24}$-hydz (A), hydz-Si$_{40}$-hydz (B) and hydz-Si$_{15}$ (C) measured upon heating (red) and cooling (blue) by rheology experiments. A constant strain of 0.01 %, angular frequency of 10 rad·s^{-1} and a heating and cooling rate of 2 K·min^{-1} were used. The viscosity values for the liquid region have a high standard deviation as a result of melting of the block molecules.

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