Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Tuning polymer properties of non-covalent crosslinked PDMS by varying supramolecular interaction strength

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Materials and methods

All chemicals were purchased from commercial sources and used without further purification. PDMS-co-PHMS precursor polymers were purchased from Gelest (HMS-064, 50,000-60,000 g mol^{-1}, 4-8 % hydride). Polymer PDMS-*g*-BTA and dintro-hydrazone (**1**) were synthesized according to literature procedure.[1,2]

NMR spectra were recorded on Varian Mercury Vx 400 MHz, Varian 400MR 400 MHz (400 MHz for ^1H NMR, and 80 MHz for ^{29}Si 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; q: quartet; p: pentet; m: multiplet. $Cr(acac)_3$ was added to the ^{29}Si NMR samples to reduce signal interference of the NMR sample tube

Liquid chromatography-mass spectrometry (LCMS) was performed on a system consisting of the following components: Shimadzu SCL-10A VP system controller with Shimadzu LC-10AD VP liquid chromatography pumps (with an Alltima C18 3 u (50 × 2.1 mm) reversed-phase column and gradients of water–acetonitrile supplemented with 0.1% formic acid, a Shimadzu DGU 20A3 prominence degasser, a Thermo Finnigan surveyor auto sampler, a Thermo Finnigan surveyor PDA detector and a Thermo Scientific LCQ Fleet. Gradients were run from 5% MeCN to 100% MeCN over a 15-minute period.

All infrared measurements were performed on a Perkin Elmer FT-IR Spectrum Two apparatus.

Size exclusion chromatography (SEC) measurements were conducted on a Shimadzu Prominence-i LC-2030C 3D, using eluent flow of 1 mL min^{-1} (THF) and solutions were of concentration 1 mg mL^{-1} were filtered through 0.2 µm Whatman Anatop 10 filters before injection.

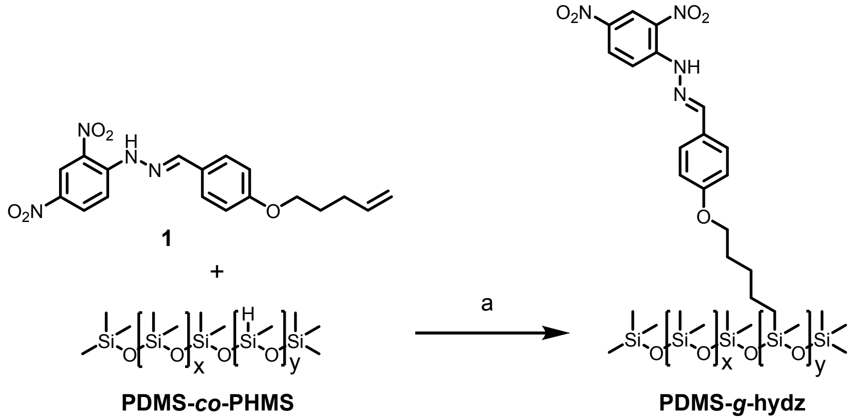
Polarized Optical Microscopy (POM) samples were placed on glass substrates and imaged using Nikon Xfinity1 Lumenera microscope with 5x magnification.

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.

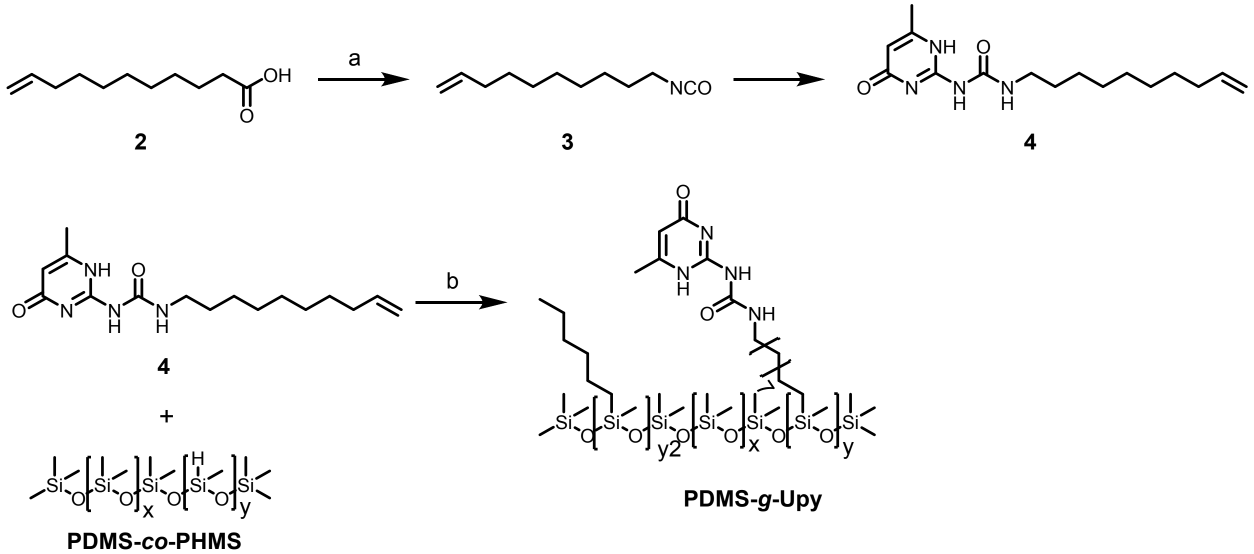
Dynamic mechanical (thermal) analysis (DMTA) is performed on samples with a width of 5.3 mm and thickness of 0.5 – 0.7 mm using a TA instruments Q800 with flat clamps. For the temperature scan measurement, the samples were heated with 3 K min^{-1} from -140 °C to 40 – 160 °C (depending on the polymer), recording the modulus (E', E'') and loss factor (tan (δ)). A frequency of 1 Hz, strain of 0.1% and preload force of 0.01 N were used, which is in the linear viscoelastic regime. For the creep experiments, a stress of 2000 Pa was applied which is in the viscoelastic regime for all polymers. For the stress relaxation experiments, a strain of 1 % was applied which is in the viscoelastic regime for all polymers at all measured temperatures. For PDMS-*g*-hydz and PDMS-*g*-BTA no preload force was used for the creep and stress relaxation experiments. For PDMS-*g*-UPy a preload force of 0.1 N was used.

Tensile tests are performed on dog-bone shaped samples with a width of 1.5 mm, length of 14 mm and thickness of 0.5 – 0.7 mm. Stress-strain curves were measured using a tensile stage equipped with a load cell of 100 N. The tests were performed at room temperature and the load was recorded at a constant strain rate of 0.01 s^{-1}.

Synthetic procedures



Scheme S1: Synthesis of PDMS-*g*-hydz. Reagents and conditions: a) Karstedt's catalyst, DCM, reflux, 4 days (~68%).



Scheme S2: Synthesis of PDMS-*g*-UPy. Reagents and conditions: a) diphenyl phosphoryl azide, Et_3N, DMF 90 °C, 10 minutes; then 6-methylisocytosine, 110 °C, 4 hours (65%); b) 1-hexene, Karstedt's catalyst, chloroform, 45 °C, 4 days (~53%).

PDMS-g-hydz

PDMS-*co*-PHMS (3.8 g, 0.17 mmol) and (2,4-dinitrophenyl)-*p*-(4-pentyloxy)benzylhydrazone **1** (1.3 g, 3.51 mmol, 21 eq) were dissolved in dry DCM (15 mL) and stirred under argon atmosphere. Five drops of Karstedt's catalyst (solution in xylene, 2% Pt) were added. The mixture was heated to reflux temperature and the stirred for four days. After full conversion of the hydride, the crude was concentrated in vacuo. The mixture was dissolved in THF (50 mL), transferred to a dialysis tube (6-8 kDa, RC standard tubing) and dialyzed for two days in 750 mL THF. The product was removed from the dialysis tube and concentrated in vacuo. The product was dissolved in DCM (50 mL) and precipitated in acetonitrile. The product was filtered and the residue was dried in vacuo, yielding the pure product as a red sticky solid (3.3 g, ~68 %).

^{1}H NMR (400 MHz, THF-d_8) δ = 11.22 (s, 1H, N$\underline{H}$), 8.88 (s, 1H, C(NO$_2$)-C$\underline{H}$-C(NO$_2$)), 8.22 (s, 1H, C(NO$_2$)-CH-C$\underline{H}$-C), 8.19 (s, 1H, C(NO$_2$)-C$\underline{H}$-CH-C), 8.00 (s, 1H, N-C$\underline{H}$-Ar), 7.60 (s, 2H, C(CHN)-C$\underline{H}$-CH-C), 6.86 (s, 2H, C(CHN)-CH-C$\underline{H}$-C), 3.90 (s, 2H, O-C$\underline{H}_2$-CH$_2$), 1.70 (s, 2H, O-CH$_2$-C$\underline{H}_2$-CH$_2$), 1.41 (s, 2H, C$\underline{H}_2$-CH$_2$-CH$_2$-Si), 1.41 (s, 2H, CH$_2$-C$\underline{H}_2$-CH$_2$-Si) 0.51 (s, 2H, CH$_2$-CH$_2$-C$\underline{H}_2$-Si), 0.33 – -0.36 (m, 99H, O-Si(C$\underline{H}_3$)$_2$-O).

*1-(Dec-9-en-1-yl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (**4**)*

Undecenoic acid **2** (4.0 g, 21.7 mmol, 1 eq) and triethylamine (2.4 g, 23.9 mmol, 1.1 eq) were dissolved in dry DMF (20 mL) and stirred under argon. Diphenyl phosphoryl azide (7.8 g, 28.2 mmol, 1.3 eq) was added and the mixture was heated to 90 °C. After 10 minutes stirring at 90 °C, intermediate compound **3** was formed and 6-methylisocytosine (4.1 g, 32.6 mmol, 1.5 eq) was added. The mixture was stirred at 110 °C for 4 hours until full conversion was reached. The reaction mixture was diluted with 200 mL MeOH and heated to reflux temperature to obtain a clear solution. The flask was cooled directly into an ice-bath and the product precipitated as a white solid in a yellow solution. The mixture was filtered and the residue was recrystallized in MeOH/DMF (200:10 mL). The product was filtered and dried in vacuo, yielding pure product **4** as a white powder (4.3 g, 65 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 13.13 (s, 1H, C-N$\underline{H}$-C), 11.85 (s, 1H, C-N$\underline{H}$-CO), 10.15 (s, 1H, CO-N$\underline{H}$-CH$_2$), 5.81 (s, 1H, CO-C$\underline{H}$-C), 5.91 – 5.64 (m, 1H, CH$_2$-C$\underline{H}$-CH$_2$), 5.06 – 4.84 (m, 2H, CH$_2$-CH-C$\underline{H}_2$), 3.23 (q, ^3J = 7.6 Hz, 2H, NH-C$\underline{H}_2$-CH$_2$), 2.22 (s, 3H, CH-C-C$\underline{H}_3$), 2.02 (q, ^3J = 7.8, 2H, C$\underline{H}_2$-CH-CH$_2$), 1.60 (p, ^3J = 7.1 Hz, 2H, NH-CH$_2$-C$\underline{H}_2$), 1.49 – 0.94 (m, 10H, (C$\underline{H}_2$)$_5$-CH$_2$-CH); ^{13}C NMR (10 MHz, CDCl$_3$) δ = 173.19, 156.72, 154.88, 148.31, 139.37, 114.24, 106.84, 100.14, 40.23, 33.95, 29.70, 29.54, 29.39, 29.21, 29.05, 27.11, 19.09, 0.15. LC-MS: *m/z* calc for $C_{16}H_{26}N_4O_2^+$: 307.21 Da; found: 307.33 Da.

PDMS-g-UPy

UPy **4** (1.2 g, 3.9 mmol, 13 eq) and PDMS-*co*-PHMS (6g, ~0.3 mmol, 1 eq) were dissolved in dry chloroform (15 mL) and stirred under argon atmosphere. The mixture was heated to 45 °C to dissolve the starting materials. Then, 1-hexene (0.3 g, 3 mmol, 10 eq) and five drops of Karstedt's catalyst were added and the mixture was stirred for four days at 45 °C. After full conversion of the hydride, the mixture was concentrated in vacuo and dissolved in a mixture of 50 mL THF and 15 mL EtOH (needed some heating to dissolve). The dissolved polymer was precipitated in a mixture of acetonitrile (200 mL) and water (pH~10) (50 mL + 1 g K_2CO_3). A gel-like precipitated was formed in a very fine white suspension. The gel-like precipitated was collected and dried in vacuo resulting in the pure product as a brittle solid (3.2 g, ~53%).^{1}H NMR (400 MHz, THF-d_8) δ = 13.27 (s, 1H, C-N$\underline{H}$-C), 12.08 (s, 1H, C-N$\underline{H}$-CO), 10.56 (s, 1H, CO-N$\underline{H}$-CH$_2$), 5.90 (s, 1H, CO-C$\underline{H}$-C), 3.95 (q, ^3J = 6.9 Hz, 2H, NH-C$\underline{H}_2$-CH$_2$), 2.39 (s, 3H, CH-C-C$\underline{H}_3$), 1.75 (s, 8H, NH-CH$_2$-C$\underline{H}_2$ and hexane), 1.69 – 1.39 (m, 95H, (C$\underline{H}_2$)$_5$-CH$_2$-CH and hexane), 0.86 – 0.62 (m, 16H, CH$_2$-CH$_2$-C$\underline{H}_2$-Si), 0.29 (s, 1081H, O-Si(C$\underline{H}_3$)$_2$-O).

Size exclusion chromatography

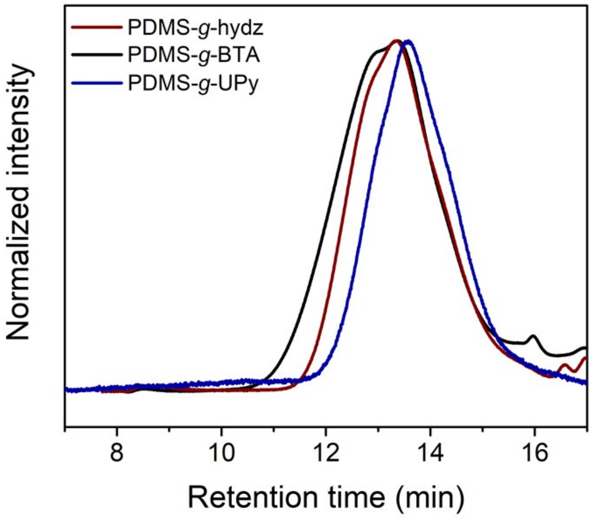


Fig. S1 SEC traces of **PDMS-*g*-hydz** (red), **PDMS-*g*-BTA** (black) and **PDMS-*g*-UPy** (blue).

NMR spectra of polymers

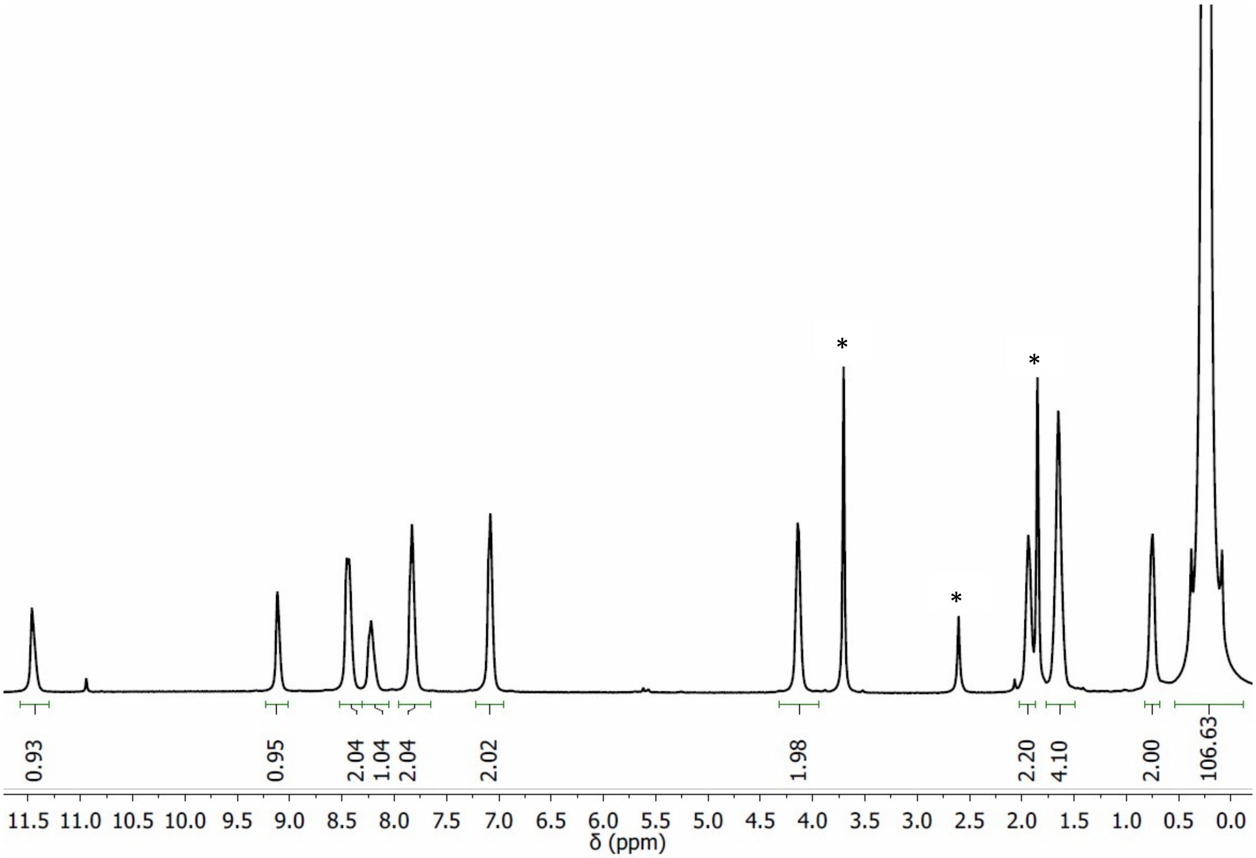


Fig. S2 ^{1}H NMR of **PDMS-*g*-hydz** in *d*-THF. Solvent peaks are indicated by *.

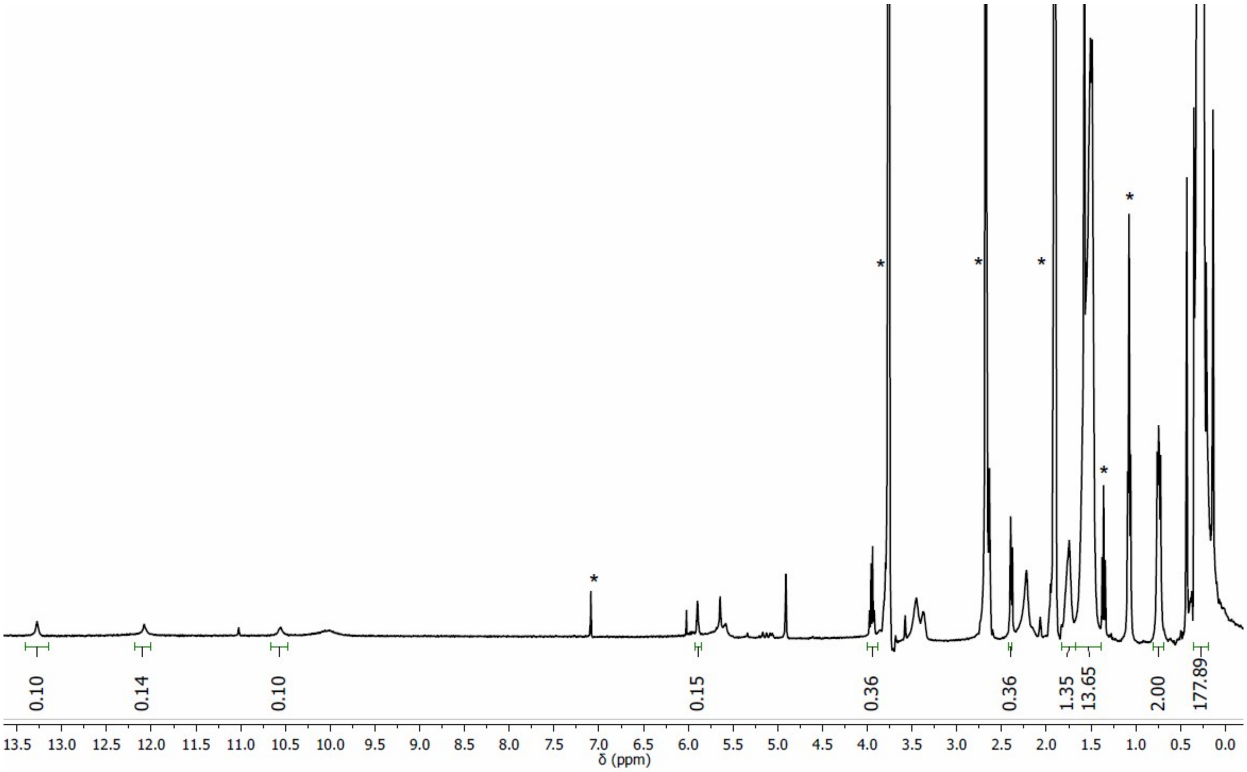


Fig. S3 ^{1}H NMR of **PDMS-*g*-Upy** in *d*-THF. Solvent peaks are indicated by *.

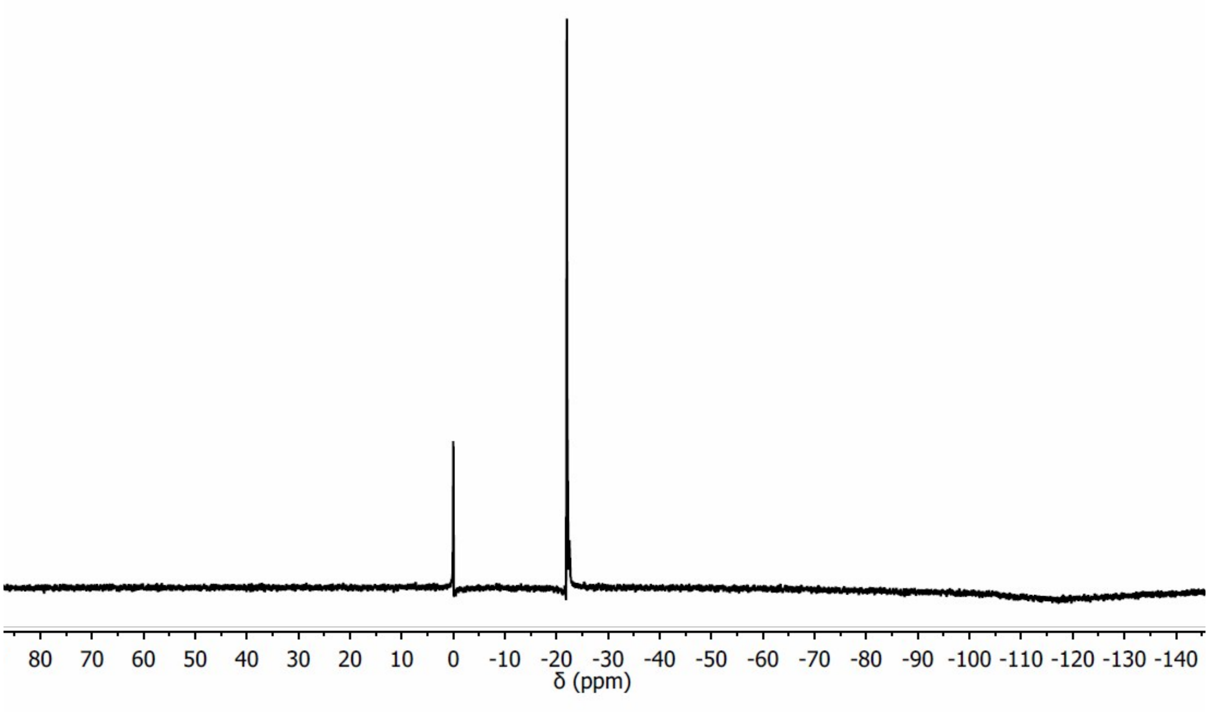


Fig. S4 ^{29}Si NMR of **PDMS-*g*-hydz** in *d*-THF with added TMS as reference.

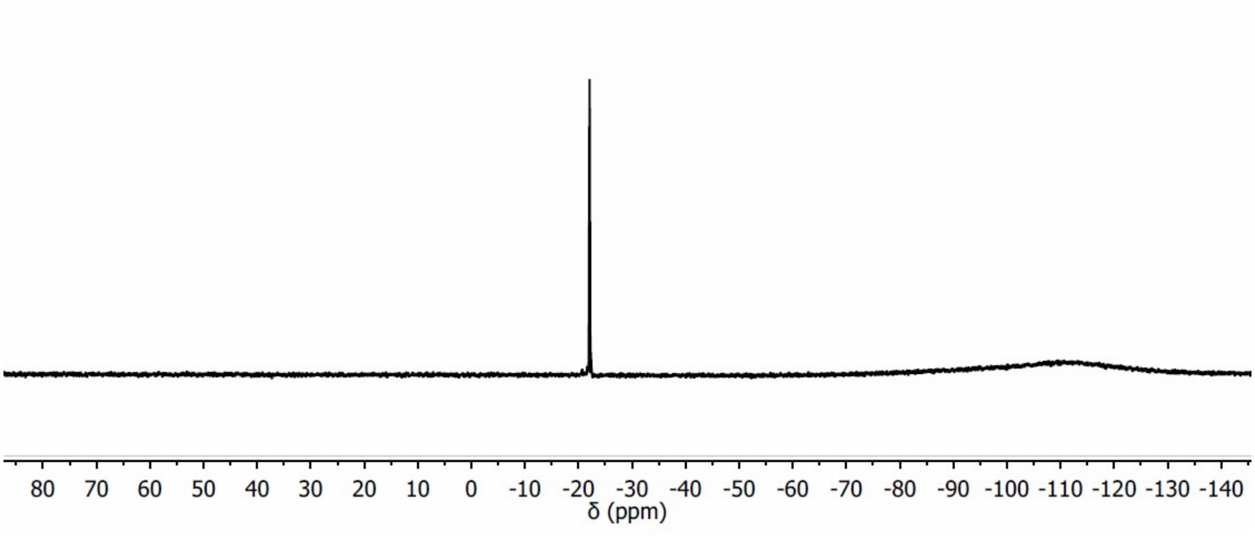


Fig. S5 ^{29}Si NMR of **PDMS-*g*-UPy** in *d*-THF.

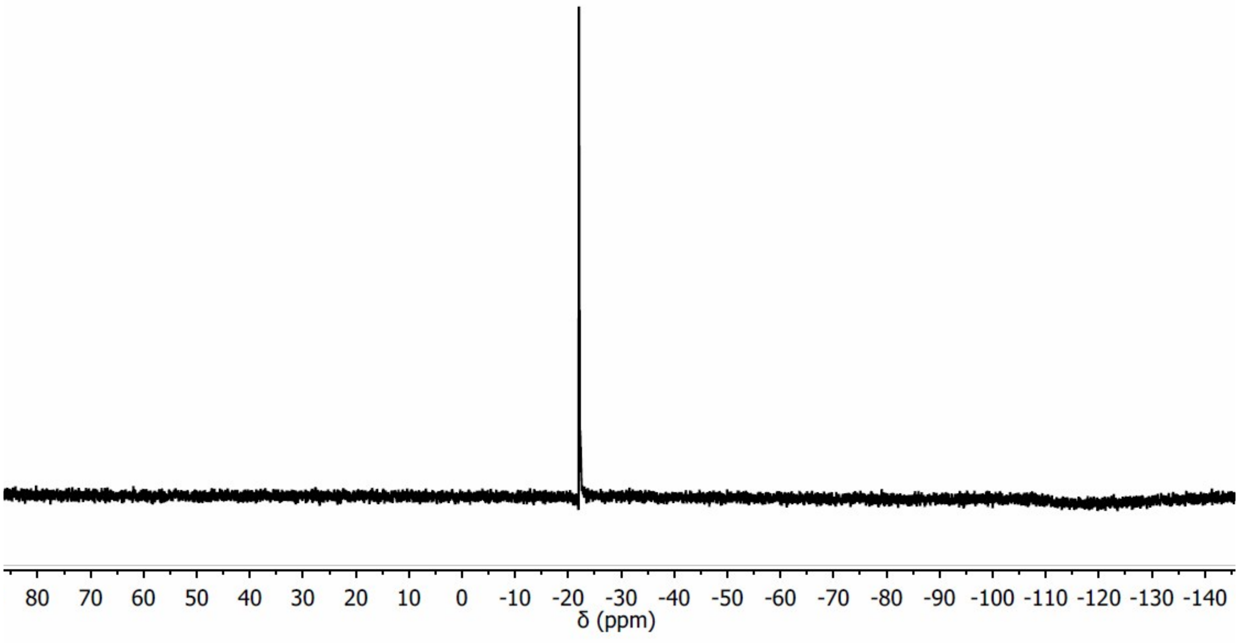


Fig. S6 ^{29}Si NMR of PDMS-*g*-BTA in *d*-THF.

Calculation of mol% graft

The density of grafts was calculated using the following expression:

$$f = \frac{1}{\frac{a}{6} + 1} \times 100\%$$

Where a = total integral of PDMS protons at 0.1 ppm. The spectrum was first normalized to the integral of Si-CH_2 protons at 0.5 ppm (H = 2)

Morphology

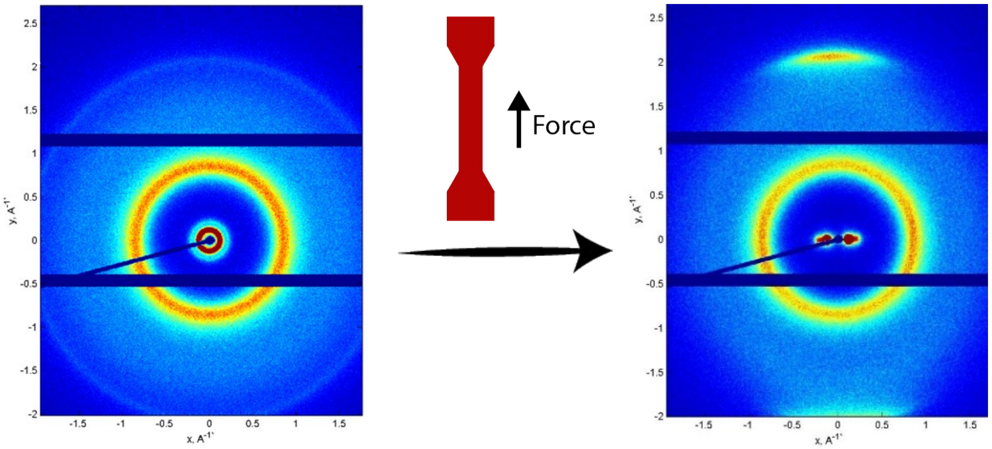


Fig. S7 2D transmission scattering profiles of **PDMS-*g*-hydz** showing the alignment of the hydrazones upon applying a unidirectional force.

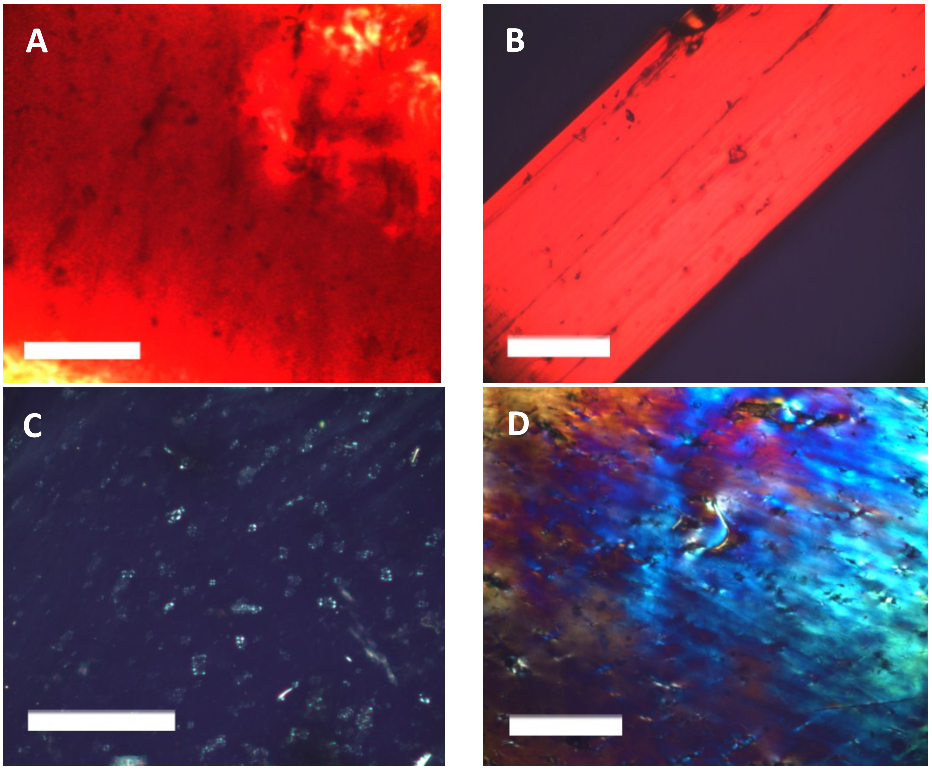


Fig. S8 POM images of **PDMS-*g*-hydz** (A) initial and (B) stretched and **PDMS-*g*-BTA** (C) initial and (D) stretched showing alignment.

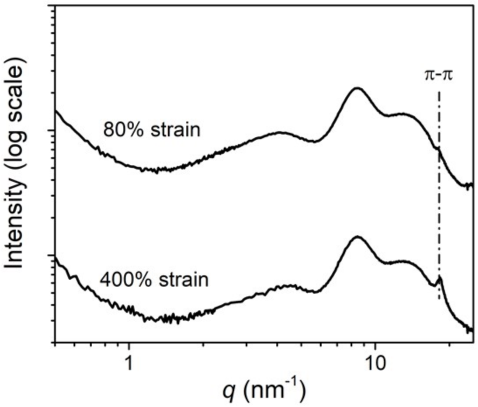
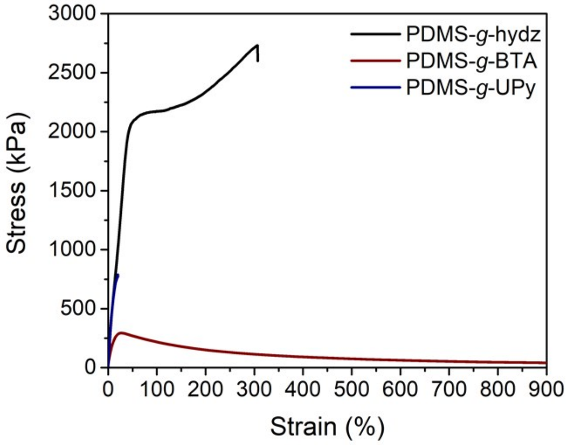


Fig. S9 1-D transmission scattering profiles of **PDMS-*g*-BTA** after applying 80% and 400 % strain.

Stress-strain curves



Polymer	*E* [MPa]
PDMS-*g*-hydz	4.1 ± 0.01
PDMS-*g*-BTA	8.5 ± 0.06
PDMS-*g*-Upy	4.2 ± 0.08

Fig. S10 Engineering stress-strain curve of **PDMS-g-hydz**, **PDMS-g-BTA** and **PDMS-g-UPy**, measured at 0.1 s^{-1}. Average of three measurements. Table includes the Young's modulus which was calculated from the measurements at 0.1 s^{-1}.

Stress relaxation experiments

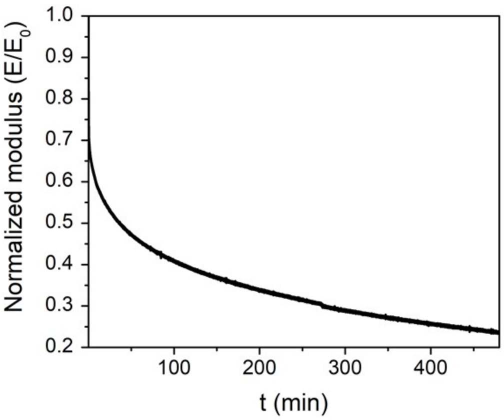


Fig. S11 Stress relaxation of PDMS-*g*-UPy with an applied stress strain of 1% at room temperature.

Calculations for stress relaxation derived activation energy

PDMS-*g*-hydz:

Equation obtained from Arrhenius law: $\ln(\tau^*) = 2.6192\cdot(1000/T) - 9.3746$

The Arrhenius law related to the activation energy: $\tau^* = \tau_0\cdot\exp(E_a/RT)$

Therefore: $\ln(\tau^*) = \ln(\tau_0) + E_a/RT$

$\ln(\tau_0) + E_a/RT = 2.6192\cdot(1000/T) - 9.3746$

$E_a/RT = 2.6192\cdot(1000/T)$

$E_a = 2.6192\cdot1000\cdot R$

$E_a = 2.6192\cdot1000\cdot8.314 = 22\ \mathrm{kJ\ mol^{-1}}$

PDMS-g-BTA:

Equation obtained from Arrhenius law: $\ln(\tau^*) = 4.6389\cdot(1000/T) - 15.9263$

$E_a = 4.6389\cdot1000\cdot8.314 = 39\ \mathrm{kJ\ mol^{-1}}$

PDMS-*g*-UPy:

Equation obtained from Arrhenius law: $\ln(\tau^*) = 8.2618\cdot(1000/T) - 18.4569$

$E_a = 8.2618\cdot1000\cdot8.314 = 69\ \mathrm{kJ\ mol^{-1}}$

Creep experiments

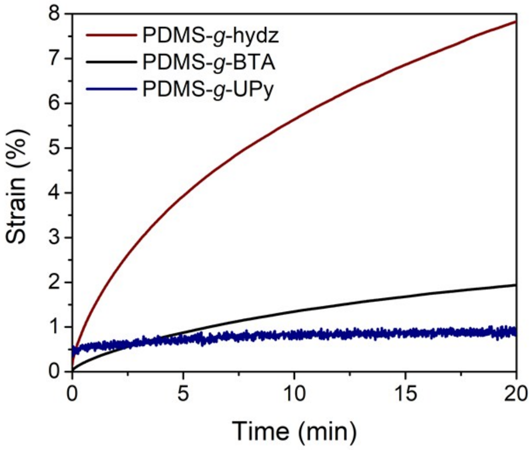


Fig. S12 Creep curves of PDMS-*g*-hydz, PDMS-*g*-BTA and PDMS-*g*-UPy with an applied stress of 2 kPa at room temperature.

References

1 M. L. Ślęczkowski, E. W. Meijer and A. R. A. Palmans, *Macromol. Rapid Commun.*, 2017, **38**, 1–5.

2 B. A. G. Lamers, R. Graf, B. F. M. de Waal, G. Vantomme, A. R. A. Palmans and E. W. Meijer, *J. Am. Chem. Soc.*, 2019, **141**, 15456–15463.