Supporting Information

Organic-Inorganic Hybrid Nanoparticles *via* Photo-Induced Micellation and Siloxane Core-Crosslinking of Stimuli-Responsive Copolymers

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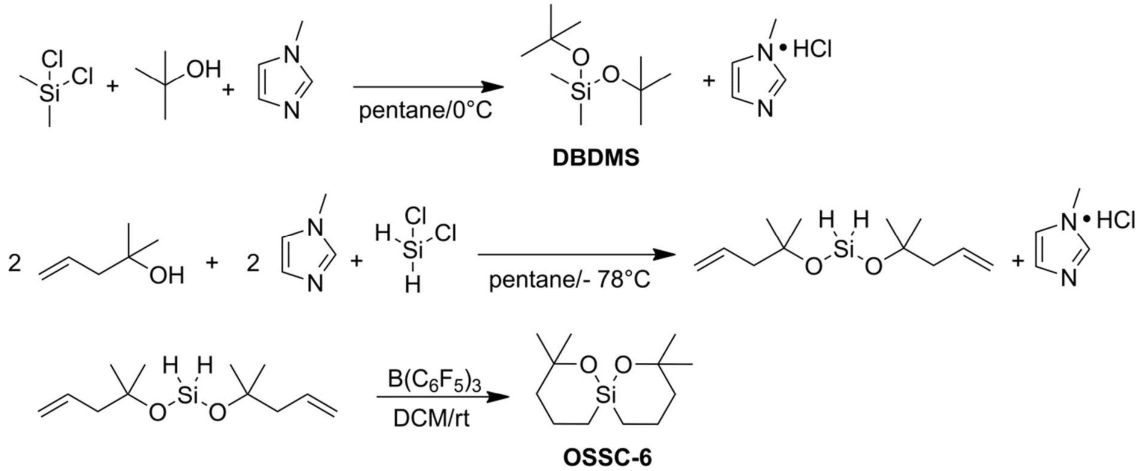
Experimental

General

Unless otherwise stated, all chemicals were purchased from commercial sources and used as received. Diethyl ether, pentane and dichloromethane were dried using a *MBRAUN SPS-800* solvent purification system. 1-Methylimidazole was dried by distillation over sodium and stored over molecular sieve (4 Å). 2-Methylpent-4-en-2-ol and tris(pentafluorophenyl)borane were prepared according to literature procedures.[1-2] All reactions were performed using standard Schlenk techniques.

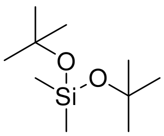
Irradiation was performed with a *MAX-302* from *ASAHI SPECTRA*. Nuclear magnetic resonance was performed on a *Bruker Avance 500 UltraShield* (500 MHz) or a *Bruker Avance 300* (300 MHz). Chemical shifts are reported in ppm relative to tetramethylsilane, the solvent was used as an internal standard (^{1}H: $CHCl_3$ at 7.26 ppm; ^{13}C{1H}: $CDCl_3$ at 77.0 ppm; ^{29}Si are calibrated to the deuterium signal). The coupling constants J are given in Hertz (Hz). Mass and high resolution mass spectra were recorded on a *Thermo Scientific DFS high resolution magnetic sector MS* (electron impact, EI, 70 eV).Static light scattering was performed on a *Wyatt Dawn Heleos-II*, dynamic light scattering on a *Horiba LB-550*. The average hydrodynamic radius is calculated by $\bar{r} = \frac{\sum_1^N r}{N}$. Differential scanning calorimetry (DSC) was carried out on a *TA DSC Q2000* (heating rate: 20K/min). GPC-MALS was carried out on a *Varian LC-920* equipped with two 300 mm analytical *PL Polargel-M* columns and THF as eluent. Absolute molecular weights were determined online by multi angle light scattering (MALS) analysis using a *Wyatt Dawn Heleos II* in combination with a *Wyatt Optilab rEX* as concentration source. Scanning electron microscopy was performed on a *FE-SEM* (*Jeol JSM 7500F*). The micelles were dissolved in dichloromethane (5mg / 1 ml) and one drop of the solution was dropped on a copper grid (*Formvar*/Carbon Films on Cu 300 mesh, diameter 3 mm) and carefully dried *in vacuo* (300 mbar/12 hours). The measurements were performed with 2 to 4.5 kV.

Synthesis of crosslinking agents



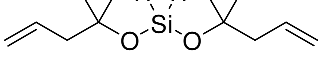
Scheme S1 Synthesis of the silicon-based crosslinkers, di-*tert*-butoxydimethylsilane (DBDMS) and 2,2,8,8-tetramethyl-1,7-dioxa-6-silaspiro[5.5]undecane (OSSC-6)

Di-*tert*-butoxydimethylsilane



A solution of dimethyldichlorosilane (20.0 g; 155 mmol) in 300 mL diethylether was cooled to 0°C and a mixture of tert-butanol (28.7 g; 387 mmol) and 1-methylimidazole (25.5 g; 310 mmol) in 100 mL diethylether was added over a period of 30min. The resulting colorless suspension was stirred for further 12 hours. After filtration and solvent removal *in vacuo*, purification *via* distillation gives pure product in 47% yield (14.91 g; 73 mmol, b.p. 75 °C at 70 mbar). ^{1}H NMR (CDCl$_3$): 0.13 (s, 6 H); 1.31(s, 18 H); **^{13}C-NMR** (CDCl$_{3;}$): 72.3 (s), 32.0 (s), 3.0 (s).

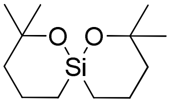
Bis(2-methylpent-4-en-2-yl)oxy)silane



A three-necked Schlenk flask equipped with an addition funnel, a reflux condenser and a valve was charged with 250 mL diethyl ether and one quarter of a mixture of 31.9 g (389 mmol, 2 eq) 1-methylimidazole and 38.9 g (389 mmol, 2 eq) 2-methylpent-4-en-2-ol in 50 mL diethyl ether was added *via* the addition funnel and the resulting mixture cooled to

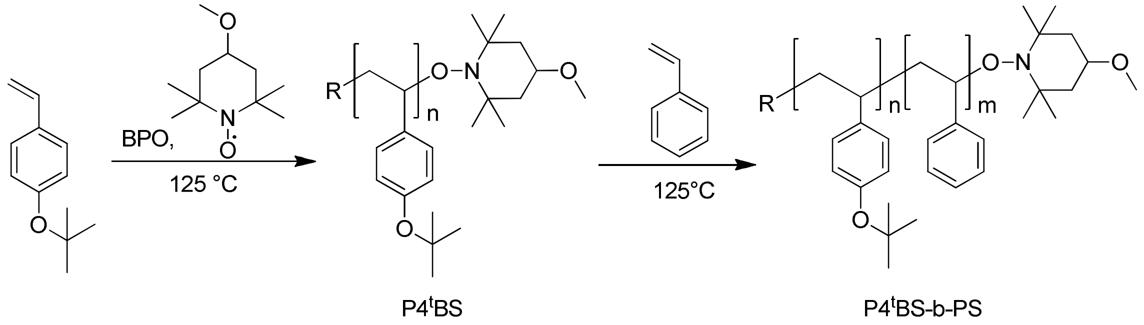
-78 °C. Afterwards, 19.6 g (194 mmol, 1 eq) dichlorosilane, which were previously condensed into a Schlenk flask at -78 °C, were allowed to diffuse slowly into the stirred reaction mixture. Meanwhile, the residual mixture in the addition funnel was slowly added. After complete addition, the resulting mixture is stirred for another 10 h at room temperature. Formed methylimidazole hydrochloride was filtered with a Schlenk frit and the solvent removed from the filtrate under reduced pressure (200 mbar). After fractioned condensation in vacuo (0.3 mbar, 60 °C oil bath temperature), 35.7 g (156 mmol, 81%) bis((2-methylpent-4-en-2-yl)oxy)silane were obtained as a colorless liquid. **^{1}H-NMR** ($CDCl_3$): 5.97–5.76(m, 2H), 5.14–5.00 (H, 4H), 4.67 (s, 2H), 2.29 (d, $^3J = 7.3$ Hz, 2H), 1.3 (s, 12). **^{13}C-NMR** ($CDCl_3$): 134.8 (s), 117.7 (s), 75.5 (s), 49.0 (s), 29.1 (s). **^{29}Si NMR** (60 MHz, C_6D_6) δ (ppm) = -51.05 **MS** (EI), m/z (%): 213.16 (13) [$(M-CH_3)^+$], 187.13 (100), 129.08 (87). [$(M-C_6H_{11}O)^+$]. **HRMS** ($C_{11}H_{21}O_2{}^{28}Si = [(M-CH_3)^+]$): calcd:213.1311, found: 213.1305.

2,2,8,8-Tetramethyl-1,7-dioxa-6-silaspiro[5.5]undecane



To a solution of 23.8 g (104 mmol, 1 eq) of bis(2-methylpent-4-en-2-yl)oxy)silane in 400 mL dry dichloromethane, 1.06 g (2.07 mmol, 2 mol%) $B(C_6F_5)_3$ were added at room temperature. The reaction mixture was stirred for 12 h and the solvent was removed under reduced pressure (200 mbar). Purification of the liquid residue by fractioned condensation (0.3 mbar, oil bath temperature 60 °C) yields 15.5 g (67.6 mmol, 65 %) of the desired product as a colorless liquid. **^{1}H-NMR** ($CDCl_3$): 1.91 – 1.64 (m, 4H), 1.60 – 1.38 (m, 4H), 1.29 (s, 6H), 1.20 (s, 6H), 0.68 – 0.42 (m, 4H). **^{13}C-NMR** ($CDCl_{3;}$): 74.4 (s, 2C), 40.9 (s, 2C), 31.7 (s, 2C), 30.2 (s, 2C), 17.8 (s, 2C), 12.1 (s, 2C). **^{29}Si-NMR** ($CDCl_3$): 14.41 (s). **MS** (EI), m/z (%): 228 (7) [M^+], 213 (100), [$(M-CH_3)^+$], 185 (21), 129 (26), 131 (27), 129 (39), 127 (34), 103 (33), 99 (50). **HRMS** ($C_{12}H_{24}O_2Si$): calcd: 228.1546, found: 228.1542

Polymer synthesis



Scheme S2 P4^{t}BS-*b*-PS by nitroxide-mediated controlled radical polymerization

Poly- *tert*-butoxystyrene (P4^{t}BS)

A mixture of *tert*-butoxystyrene (7.01 g; 39.7 mmol), dibenzoylperoxide (0.109 g; 0.45 mmol) and 4-methoxy-2,2,6,6-tetramethylpiperidin-1-oxyl (0.109 g; 0.58 mmol) (MTEMPO) was degassed and heated *in vacuo* for 60 h at 125 °C. The reaction mixture was frozen in liquid nitrogen, dissolved in a small amount dichloromethane and added to methanol at 0 °C. The precipitate was filtered, dissolved in benzene and freeze dried (Yield: 55%; 3.88g). **GPC-MALS** M_w 18600 g/mol, PDI 1.16. **SLS** M_w 25000. **^{1}H NMR** ($CDCl_3$): 1.10 – 1.50 (br, 11H), 1.60 – 2.15 (br, 1H), 6.10 – 6.55 (br, 2H), 6.55 – 6.90 (br, 2H).

Poly(4-*tert*-butoxystyrene-*block*-styrene) (P4^{t}BS-*b*-PS)

A mixture of Styrene (8.7 g; 83.5 mmol) and poly-*tert*-butoxystyrene (1.95 g) was degassed and heated *in vacuo* for 67 h at 125 °C. The reaction mixture was frozen in liquid nitrogen, dissolved in a small amount dichloromethane and added to methanol at 0 °C. The precipitate polymer was filtered, dissolved in benzene and freeze dried (Yield: 47%; 5.0 g). **GPC-MALS** M_w 220000 g/mol, PDI 1.60. **SLS** M_w 210000. **^{1}H NMR** ($CDCl_3$): 1.10 – 1.35 (br, 3H), 1.35 – 1.65 (br, 2H), 1.65 – 2.25 (br, 1H), 6.10 – 6.90 (br, 3H), 6.90 – 7.25 (br, 3H).

Poly(4-hydroxystyrene-*block*-styrene) (P4HS-*b*-PS)

(4-*tert*-butoxystyrene)-*block*-polystyrene (2.8 g) was dissolved in 100 mL THF, 10 mL conc. hydrochloric acid was added, the resulting mixture refluxed for 3.5 h and added to water at room temperature. The precipitate was filtered, stirred for 1 h in methanol, again filtered and the resulting precipitate (2.2 g) dissolved in benzene and freeze dried. **^{1}H NMR** ($CDCl_3$): 1.10 – 2.30 (br, 4H), 6.10 – 6.90 (br, 2H), 6.90 – 7.25 (br, 3H).

Static light scattering procedure

GPC-MALS was carried out on a *Varian LC-920* equipped with two 300 mm analytical *PL Polargel-M* columns and THF as eluent. Absolute molecular weights were determined online by multi angle light scattering (MALS) analysis using a *Wyatt Dawn Heleos II* in combination with a *Wyatt Optilab rEX* as concentration source.

Table S1 Synthesis and Characterization of P4^{t}BS and P4^{t}BS-*b*-PS.

Polymer	Polymerization time [h]	d_n/d_c [ml/g]	M_w (GPC)^a [g/mol]	M_w (SLS)^b [g/mol]	M_w/M_n^{a}	Yield [%]
P4^{t}BS	60	0.137	18500	25000	1.15	55
P4^{t}BS-*b*-PS	67	0.171	223500	210000	1.6	47

a) determined by GPC-MALS, b) determined by static light scattering (SLS) in batch.

Photo-induced crosslinking of poly(4-hydroxystyrene-*block*-styrene) (P4HS-*b*-PS)

To 82.5 mg poly(4-hydroxystyrene-*block*-styrene) dissolved in 17.5 mL dichloromethane, a solution of 10.5 mg (0.025 mmol) diphenyliodonium hexafluorophosphate in 7.5 mL dichloromethane was added and incubated for 30 min in the dark. After addition of the alkoxysilane and further incubation for 1 hour in the dark, the obtained solution was irradiated for 2 hours with UV-light (200 nm – 300 nm).

Modified procedure for photo-induced crosslinking of poly(4-hydroxystyrene-*block*-styrene) (P4HS-*b*-PS)

To 82.5 mg poly(4-hydroxystyrene-*block*-styrene) dissolved in 17.5 mL dichloromethane, a solution of 10.5 mg (0.025 mmol) diphenyliodonium hexafluorophosphate in 7.5 mL dichloromethane was added and immediately irradiated for 30 min. Afterwards, the alkoxysilane crosslinker is added and the obtained mixture is further irradiated for 2 hours.

One-pot photo-induced micelle formation and crosslinking

To 82.5 mg poly(4-*tert*-butoxystyrene)-*block*-polystyrene dissolved in 17.5 mL dichloromethane, a solution of 10.5 mg (0.025 mmol) diphenyliodonium hexafluorophosphate in 7.5 mL dichloromethane was added and the resulting mixture was irradiated for 1 h with UV light (200 nm - 300 nm). The alkoxysilane was added and the solution was further irradiated for 1 h.

For all crosslinking procedures, DLS measurements were performed directly after irradiation. For further analysis, the formed nanoparticles were dried in vacuum for several hours.

^{1}H NMR Spectroscopy of crosslinked micelles

Figure 1 shows two synthetic steps for the formation of the nanoparticles. The first step employs a cleavage of *tert* butyl groups via the photoacid generator to the hydroxyl substituted P4HS-*b*-PS (**Figure 1; spec. b**) in quantitative conversion. The signals at 1.2 ppm in ^{1}H NMR spectroscopy revealed, in case of OSSC-6, that silane alkoxy substituents remain within the crosslinked micelle (**Figure 1; spec. c**). The intensity of the olefinic proton signals at 4.0 – 5.0 ppm is significantly lower than expected. This indicates partial cationic polymerization inside the micelles of the previously formed isobutylene moieties. Nevertheless, double bonds remain after core-crosslinking providing the possibility of future investigations of post-synthetic functionalization and tailoring of these nanoparticles.

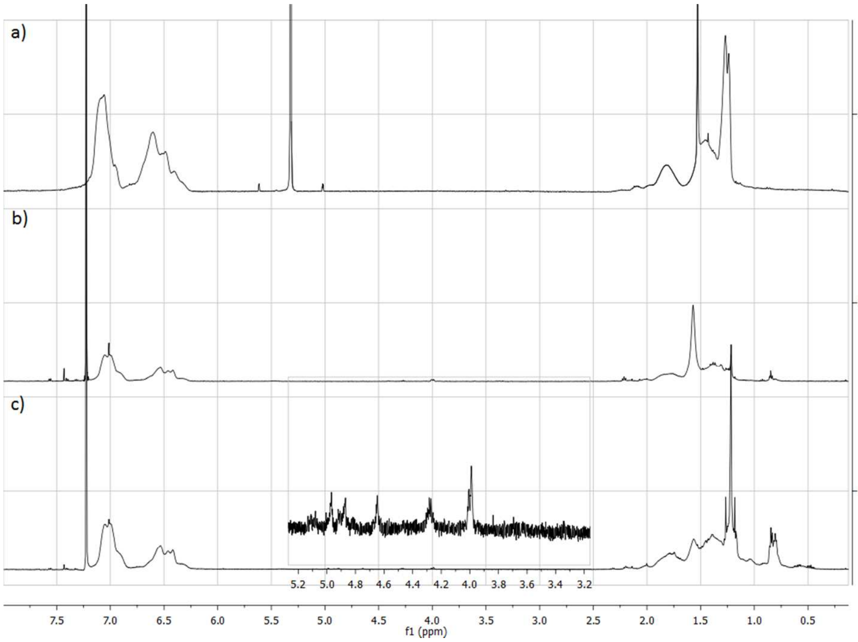


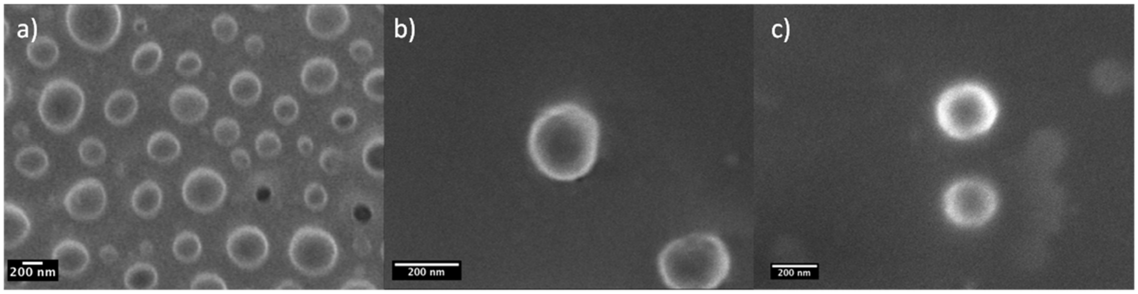
Figure S1 ^{1}H NMR spectra of a) P4^{t}BS-*b*-PS, b) P4HS-*b*-PS micelles after photoacid catalyzed cleavage of the *tert* butyl group and c) P4HS-*b*-PS crosslinked with OSSC-6. Inset: Detail of spectrum c) between 5.2 and 3.2 ppm.

DSC Measurements

Table S2 DSC results of P4HS-*b*-PS and P4^{t}BS-*b*-PS before and after crosslinking with DBDMS and OSSC-6.

Entry	**compound**	**added crosslinker [mmol]**	**multi-step synthesis T_g [°C]**	***one-pot* synthesis T_g [°C]**
1	P4^{t}BS-*b*-PS	-	94	93
2	P4HS-*b*-PS	-	103	103
3	DBDMS-crosslinked P4HS-*b*-PS	0.2	98	97
4	DBDMS-crosslinked P4HS-*b*-PS	0.4	100	101
5	OSSC-6-crosslinked P4HS-*b*-PS	0.2	area	area
6	OSSC-6-crosslinked P4HS-*b*-PS	0.4	area	100

Scanning electron microscopy/DBDMS



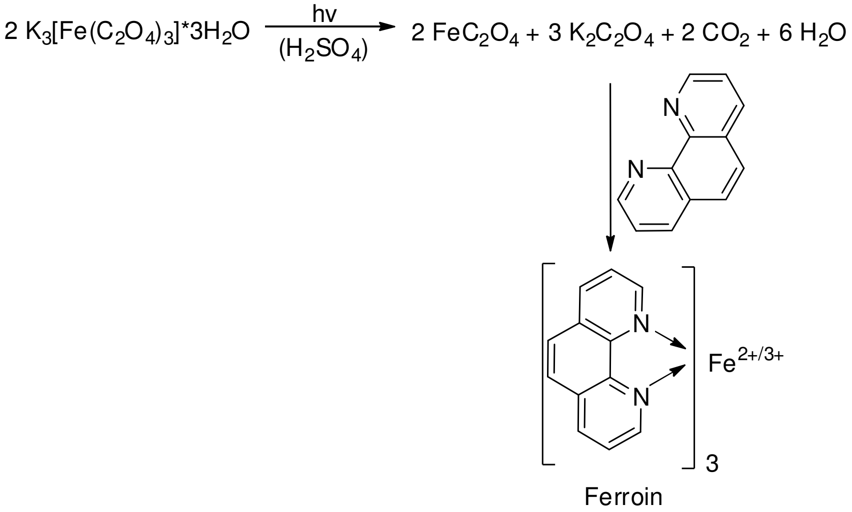
Scheme S3 Representative secondary electron SEM micrographs of a) and b) crosslinked micelle and nanoparticles obtained from the "*one-pot*" crosslinking procedure using 0.2 mmol and c) 0.4 mmol of DBDMS

Energy calibration of the UV-light source

Irradiation was performed with a *MAX-302* from *ASAHI SPECTRA*. The energy of the UV lamp was determined *via* Hatchard-Parker actinometry (**Scheme S$**).[3-5] The energy of the UV lamp in the present study was set to 165 mW (27.5 quanta/sec) and the irradiation was performed by 200 – 250 nm (set with a neutral density filter).

Table S3 Determination of the input energy of the UV light source

Output energy [%]	concentration Fe(II) [µmol/l]	N Fe(II) [µmol]	quanta/sec [10^{16}/s]	Input energy [mW]
50	11,1	0,885	13,1	78
100	23,2	1,858	27,5	165



Scheme S4 Hatchard-Parker actinometry for the determination of the input energy of the light source

Exemplary distribution curves of crosslinking via OSSC-6

The following diagrams show the dynamic light scattering results in the case of 0.2 mmol and 0.4 mmol OSSC-6 in the developed multi-step and one-pot method for the formation of nanoparticles.

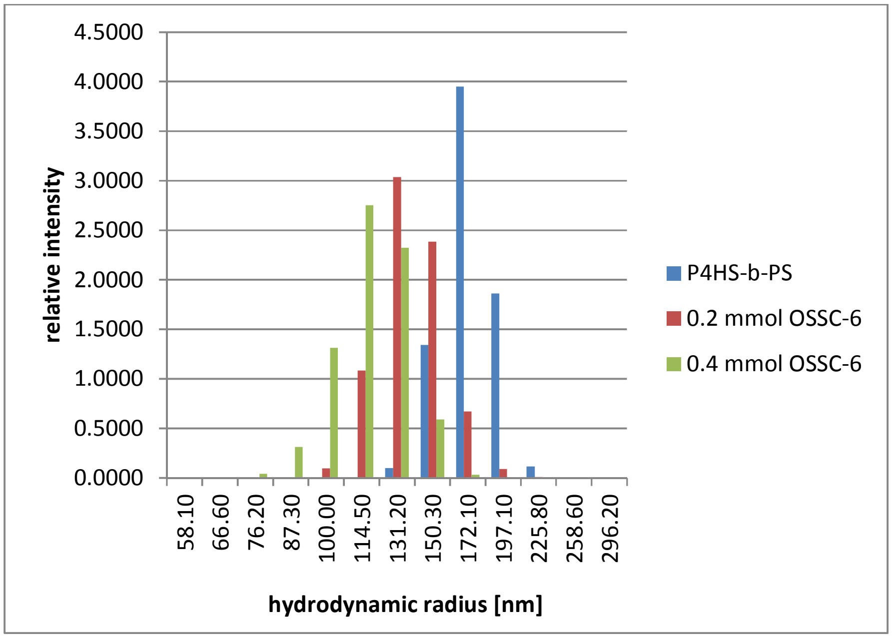


Diagram S1: Crosslinking of P4HS-b-PS with 0.2 mmol and 0.4 mmol OSSC-6 via the one-pot synthesis strategy

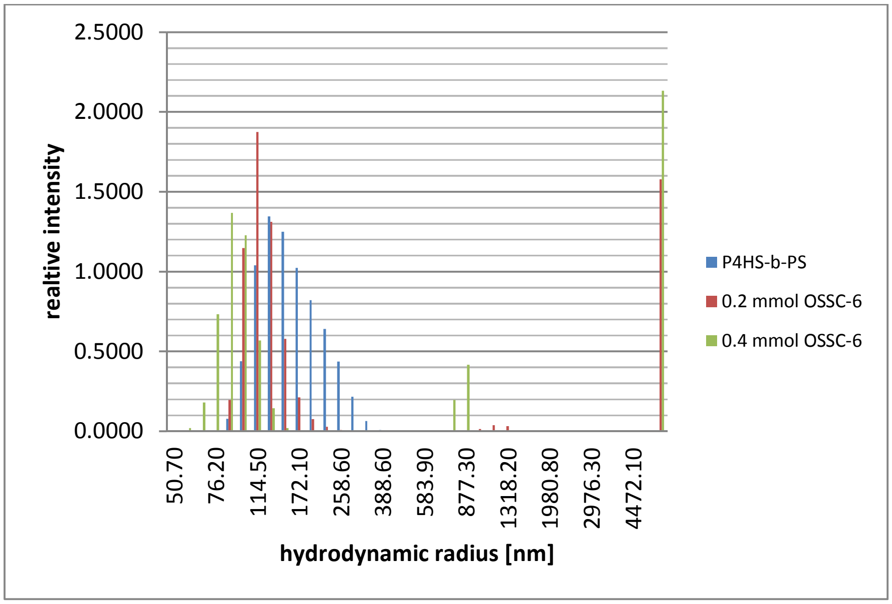
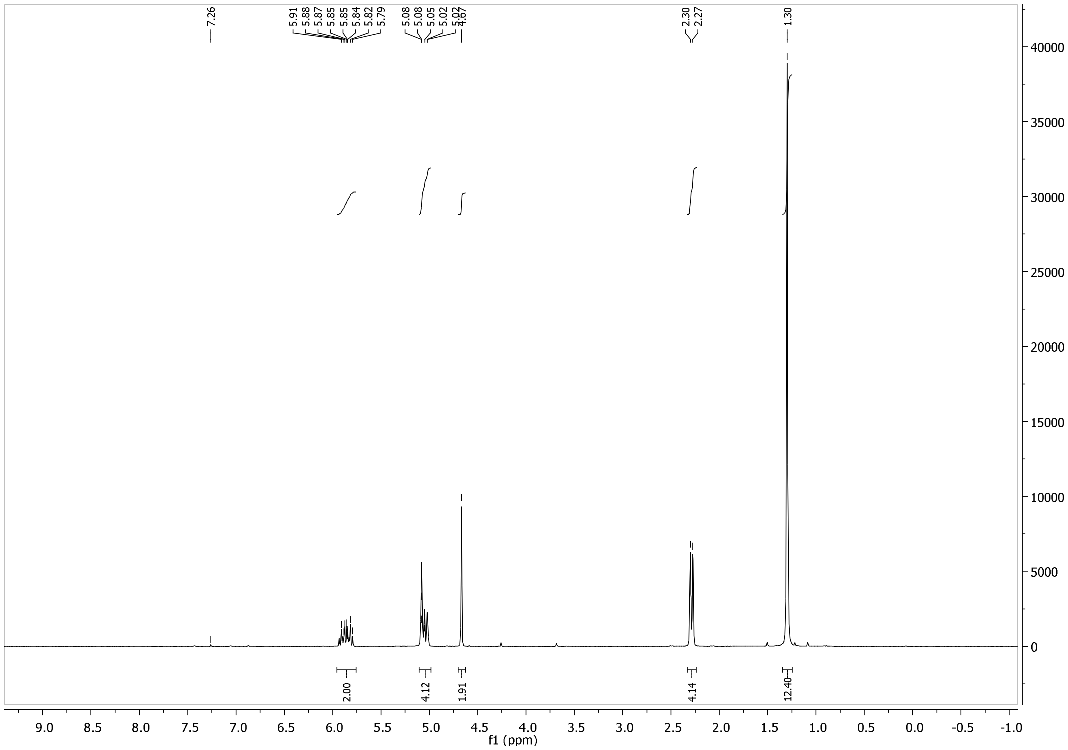


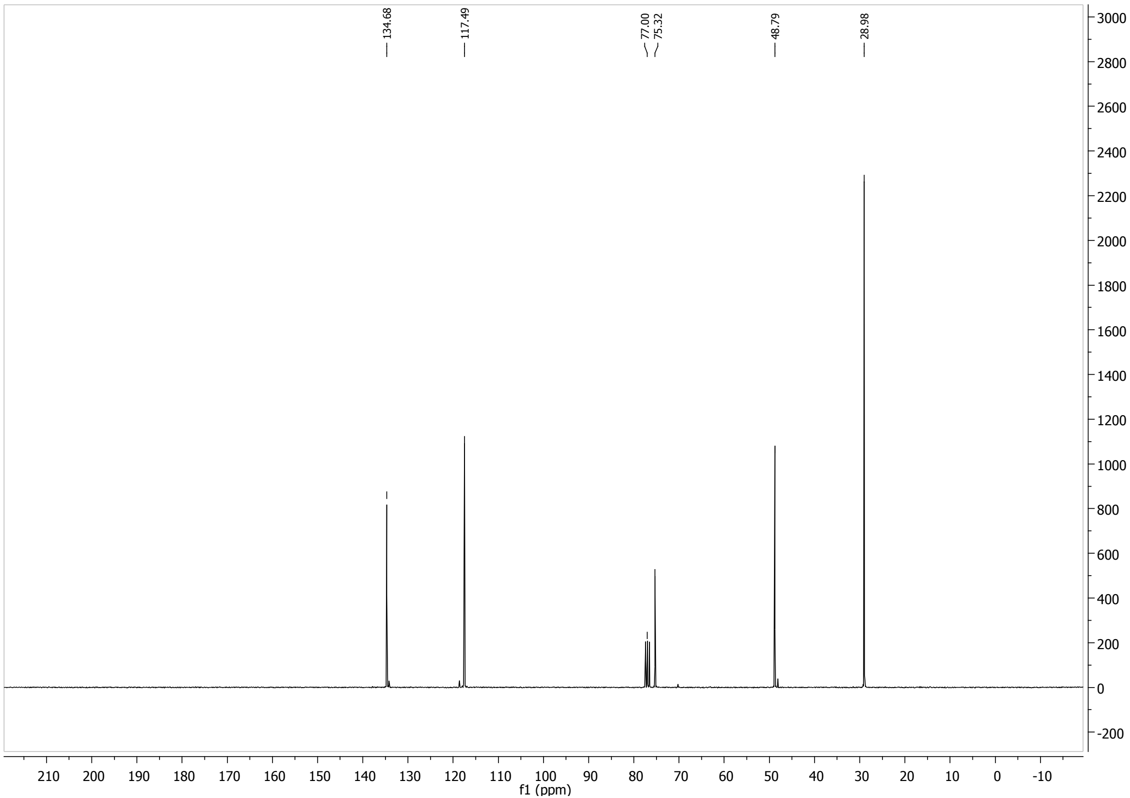
Diagram S2: Crosslinking of P4HS-b-PS with 0.2 mmol and 0.4 mmol OSSC-6 via the multi step synthesis strategy

Spectra

Bis(2-methylpent-4-en-2-yl)oxy)silane

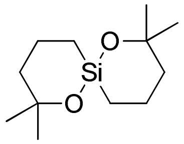


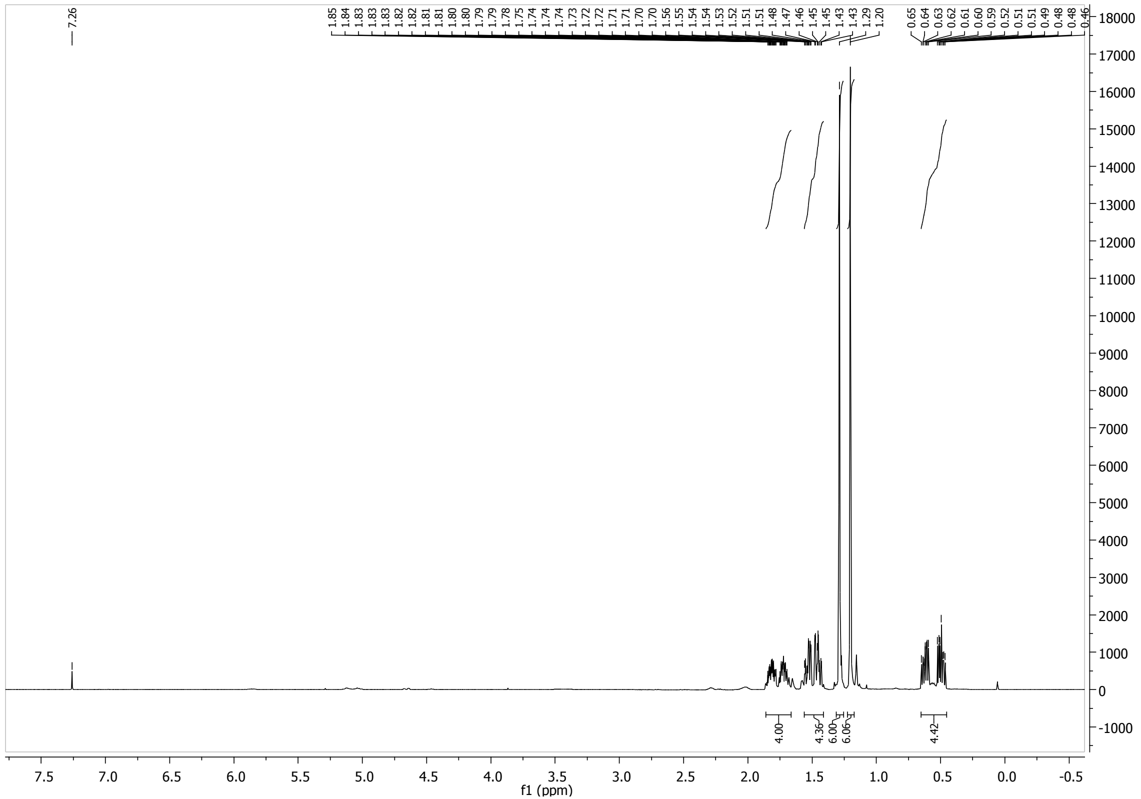
SI Figure S1a. ^{1}H-spectrum of the spiro compound precursor bis(2-methylpent-4-en-2-yl)oxy)silane.



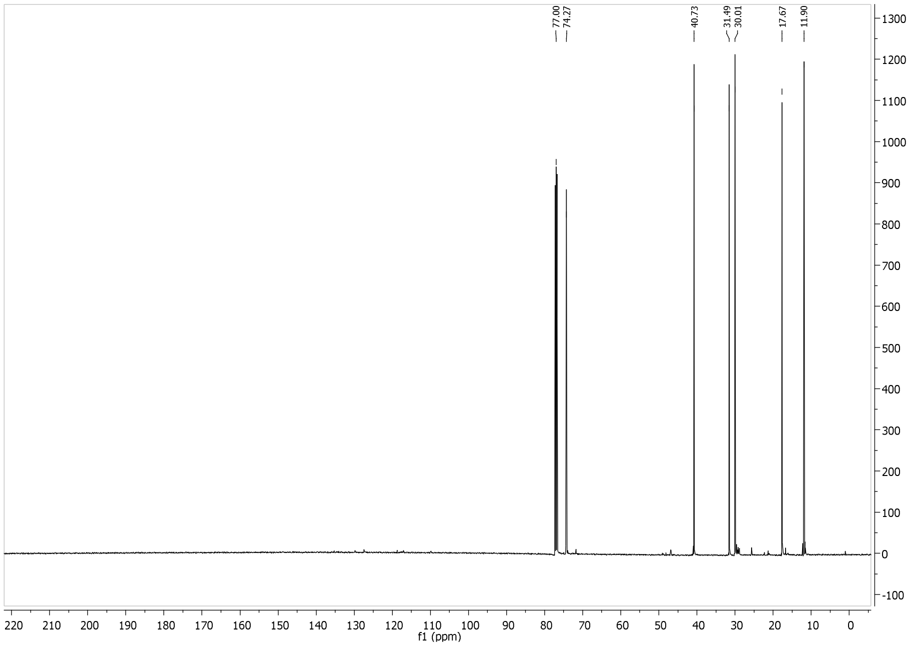
SI Figure S1b. Proton decoupled ^{13}C-spectrum of bis(2-methylpent-4-en-2-yl)oxy)silane.

2,2,8,8-Tetramethyl-1,7-dioxa-6-silaspiro[5.5]undecane (compound 1)

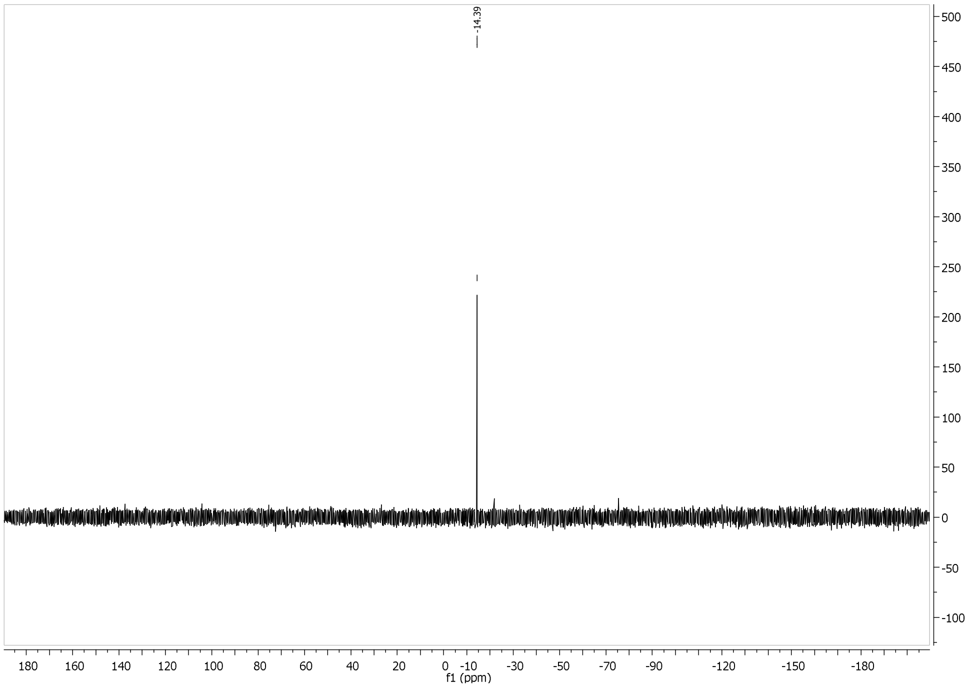




SI Figure S2a. ^{1}H-spectrum of OSSC-6



SI Figure S2b. Proton decoupled ^{13}C-spectrum of OSSC-6



SI Figure S2c. ^{29}Si-NMR of OSSC-6

(1) Lehmann, M.; Schulz, A.; Villinger, A. *Angewandte Chemie International Edition* **2009**, *48*, 7444.

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