Supplementary Information

Synthesis of high molecular weight polymethacrylates with POSS moieties by ATRP

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1. Materials

Copper(I) bromide (CuBr, 99.999%, Aldrich), copper(II) bromide ($CuBr_2$, 99.999%, Aldrich) N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) and ethyl 2-bromoisobutyrate (EBiB, 98%, Aldrich), 1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.1(5,11)]-heptasiloxane-endo-3,7,14-triol - TriSilanolIsobutyl POSS® (Hybrid Plastics), 3-(dimethylchlorosilyl)propyl methacrylate (92%, abcr GmbH & Co. KG), triethylamine (Et_3N, ≥99.5%, Aldrich), phenothiazine (≥98%, Aldrich), DMSO (analytically pure, 99.7%, Avantor Performance Materials Poland S.A.), chloroform-d (99.96 atom% D, Aldrich) were used as received. Toluene (CHROMSOLV PLUS, for HPLC, 99.9%, Aldrich), THF (CHROMSOLV PLUS, for HPLC, ≥99.9%, inhibitor free, Aldrich), hexane (CHROMSOLV PLUS, for HPLC, 97%, Aldrich) were used after purification by MBRAUN Solvent Purification Systems 500.

2. Instrumentation and Characterization

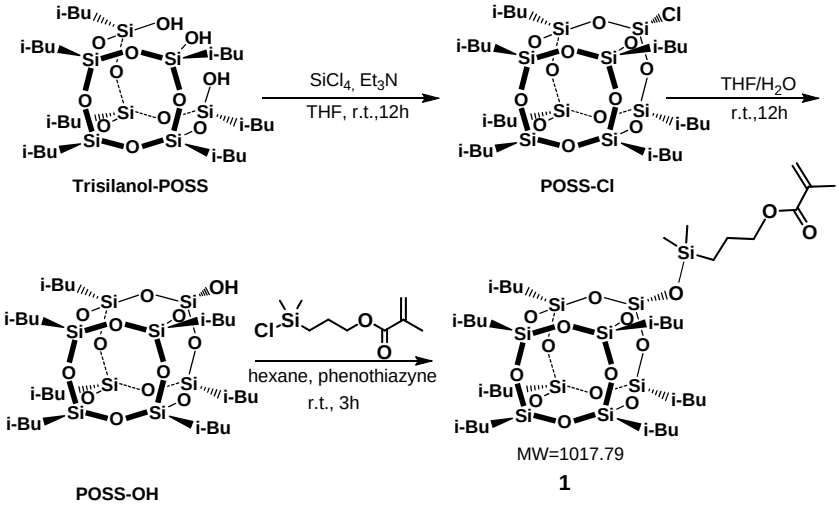
MW and MWD of the formed polymers were measured by gel permeation chromatography using Polymer Standards Services (PSS) columns (guard, 10^5, 10^3, and 10^2 Å), with THF eluent at 35°C, flow rate 1.00 ml/min, and differential refractive index (RI) detector (Waters, 2410). Diphenyl ether was used as the internal standard to correct for any fluctuation of the THF flow rate. The number-average MW ($M_{n\ GPC}$) and MWD (M_w/M_n) were determined with a calibration based on linear poly(methyl methacrylate) (PMMA) standards using WinGPC 6.0 software from PSS.

The detectors employed to measure the absolute MW ($M_{n\ MALLS}$) were a triple detector system containing RI detector (Wyatt Technology, Optilab REX), viscometer detector (Wyatt Technology, ViscoStar), and a multiangle laser light scattering (MALLS) detector (Wyatt Technology, DAWN EOS) with the light wavelength at 690 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology.

^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a Varian Gemini 300 VT spectrometer and Varian Mercury 300 VT in $CDCl_3$.

3. Synthetic procedures

a) Synthesis of (i-Bu)$_7$POSS-OSiMe$_2$-MA (**1**)



Scheme S1. Synthesis of (i-Bu)$_7$POSS-OSiMe$_2$-MA (1).

Compounds $(i\text{-}Bu)_7Si_8O_{12}Cl$ and $(i\text{-}Bu)_7Si_8O_{12}OH$ were synthesized according to the published methods.[1] Next, the portion of $(i\text{-}Bu)_7Si_8O_{12}(OH)$ (30 g, 36.0 mmol) placed in a two-neck flask equipped in stir bar was dissolved in dry hexane (400 ml). To the flask phenothiazine (0.03 g, 0.15 mmol) and Et_3N (5.5 ml, 40.0 mmol) were added. The reaction mixture was cooled down to 0 ^{o}C and subsequently 3-(dimethylchlorosilyl)propyl methacrylate (7.85 ml, 36.0 mmol) was added dropwise. Formation of white suspension of NH_4Cl was observed. The reaction mixture was stirred for 3 h at room temperature. After this time entire mixture was filtered. The residues of NH_4Cl were extracted by water. To the solution in hexane, $MgSO_4$ was added. The suspension was filtrated through silica gel to remove $MgSO_4$ and phenothiazine. Next solvent was evaporated under vacuum. Obtained crude of **1** was washed with cold methanol. Thorough drying gave product with 77% yield (28.2 g). Another synthesis method of **1**was described previously.[2]

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.14 (s, 6H, Si-CH_3), 0.61 (m, 16H, Si-CH_2-), 0.95 (dd, 42H, CH_3), 1.72 (m, 2H, -CH_2-), 1.86 (m, 7H, -CH-), 1.95 (s, 3H, CH_3), 4.08 (t, 2H, H_2C-O), 5.54 (bs, 1H, CH_2=), 6.10 (bs, 1H, CH_2=).

^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): -0.24 (Si-CH_3), 13.85 (Si-CH_2), 18.34 (Si-CH_2, spacer), 22.55 (H_3C-CH), 22.66 (-CH_2-), 24.02 (-CH-), 25.85 (H_3C-C=), 67.10 (H_2C-O), 125.08 (H_2C=), 136.57 (H_3C-C=), 167.59 (C=O).

^{29}Si NMR (79 MHz, $CDCl_3$, δ, ppm): 11.05 (1Si, Q^1), -67.04 (3Si, Q^3), -67.86 (3Si, Q^3), -67.88 (1Si, Q^3) -109,65 (1Si, Q^4).

Elemental Analysis:

$C_{37}H_{80}O_{15}Si_9$ (%): calculated C: 43.66, H: 7.92; found C: 43.38, H: 7.90.

*b) Homopolymerizations **2-10***

To a glass flask with a magnetic stir bar compound **1**, PMDETA and EBiB were added. In a second flask $CuBr_2$ (0.012 g, 0.0054 mmol) with PMDETA (0.0112 ml, 0.0054 mmol) were dissolved in DMSO (0.2 ml) and an appropriate volume of solution was added via syringe to the reaction flask. The reaction mixture was degassed by at least three freeze-pump-thaw cycles and filled with argon (Ar) again. With positive pressure of Ar, CuBr was added to the flask. The flask was evacuated and refilled with Ar and placed in a 50°C oil bath. Samples were taken periodically to measure conversion via ^{1}H NMR and number-average molecular weights via GPC.

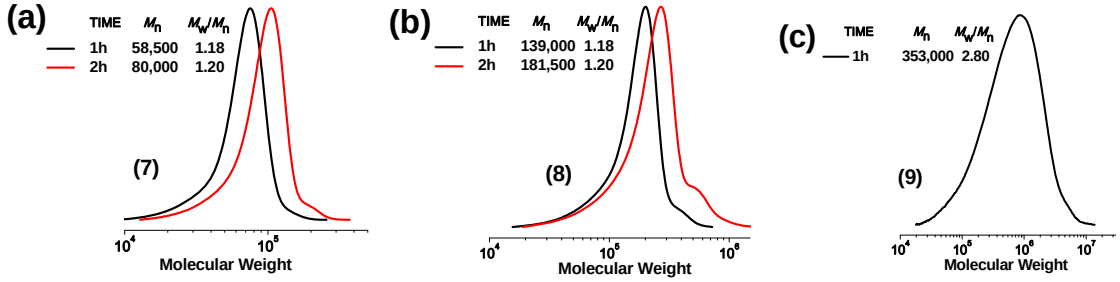


Figure S1. GPC traces of homopolymers **7** (a), **8** (b) and **9** (c) obtained with $[\mathbf{1}]_0/[EBiB]_0$ ratios of 200, 1,000 and 10,000.

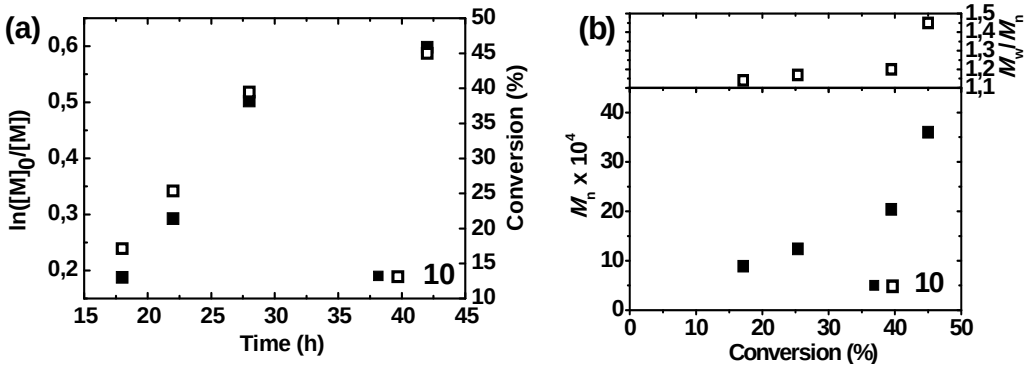


Figure S2. (a) Kinetic plot of $\ln([M]_0/[M])$ vs. time and conversion vs. time. (b) Plot of M_n vs. conversion and M_n vs. M_w/M_n for polymerizations of **10**.

*c) Semi-batch polymerizations **11-12.***

A reaction mixture prepared according to the procedure **2-10**, was placed in a 50°C oil bath. In a second flask **1** was dissolved in toluene (0.5 ml) and the air was removed from the solution by at least three freeze-pump-thaw cycles and refilling atmosphere with argon. The flask was placed in a warm water bath. Formed in this way clear solution was added dropwise via syringe to the reaction mixture.

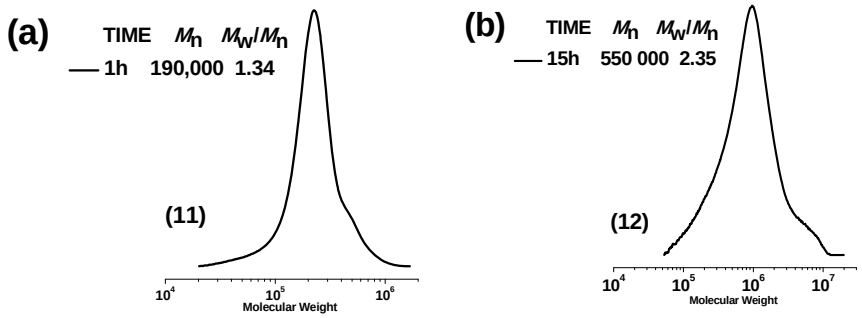


Figure S3. GPC traces of homopolymers with $[1]_0/[EBiB]_0$ ratio of 800 (a) and 3333(b) (polymerizations **11** and **12** respectively).

References

(1) Duchateau, R.; Cremer, U.; Harmsen, R. J.; Mohamud, S. I.; Abbenhuis, H. C. L.; van Santen, R. A.; Meetsma, A.; Thiele, S. K. H.; van Tol, M. F. H.; Kranenburg, M. *Organometallics* **1999,** *18*, 5447-5459.
(2) Mammeri, F.; Bonhomme, C.; Ribot, F. o.; Babonneau, F.; Dirè, S. *Chem. Mater.* **2009,** *21*, 4163-4171.