Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Well-defined 4-arm stars with hydroxy-terminated polyethylene, polyethylene-*b*-polycaprolactone and polyethylene-*b*-(polymethyl methacrylate)$_2$ arms

Zhen Zhang,[a] Yves Gnanou[b] and Nikos Hadjichristidis*[a]

[a]Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, [b]Physical Sciences and Engineering Division
King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Kingdom of Saudi Arabia.

1. General Information

1.1 Materials

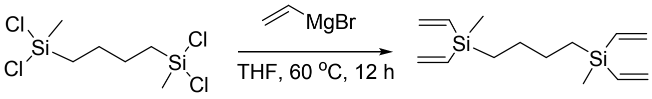
1,4-Bis(dichloromethylsilyl)butane (97%) was purchased from abcr GmbH and used as received. Vinyl magnesium chloride solution (1.6 M in THF), copper(I) bromide (CuBr, 99.999%), trimethylamine *N*-oxide dihydrate (TAO·2H_2O) (≥99%, Aldrich), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) 2,3-dimethylbut-2-ene (≥99%), phosphazene base P2-*t*Bu solution (~2 M in THF, Aldrich), 2,2-dichloroacetyl chloride (98%), borane dimethyl sulfide complex solution (5.0 M in diethyl ether), and pyridine (99.8%) were purchased from Aldrich and used as received. Methyl methacrylate (MMA, 99%) and ε-caprolactone (CL, 97%) were distilled over calcium (I) hydride (CaH). Tetrahydrofuran (THF) and toluene were refluxed over sodium/benzophenone and distilled under a nitrogen atmosphere before use. Dimethylsulfoxonium methylide was prepared according to the Corey's method followed by switching the solvent from THF to toluene.[1] Thexylborane was prepared by reaction of 2,3-dimethylbut-2-ene with borane dimethyl sulfide complex solution according to the literature.[2]

1.2 Instruments

The high temperature gel permeation chromatography (HT-GPC) measurements were carried out at 150 ºC with the Agilent PL-GPC 220 instrument equipped with one PLgel 10 μm MIXED-B column and a differential refractive index (DRI) detector. 1,2,4-Trichlorobenzene (TCB) was the eluent at a flow rate of 1.0 mL/min. The system was calibrated with PS standards. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCE III-500 or 600 spectrometer.

2 Experimental Procedures

2.1 Synthesis of 1,4-Bis(methyldivinylsilyl)butane



1, 90%

Scheme S1. Synthesis of 1,4-bis(methyldivinylsilyl)butane **1**

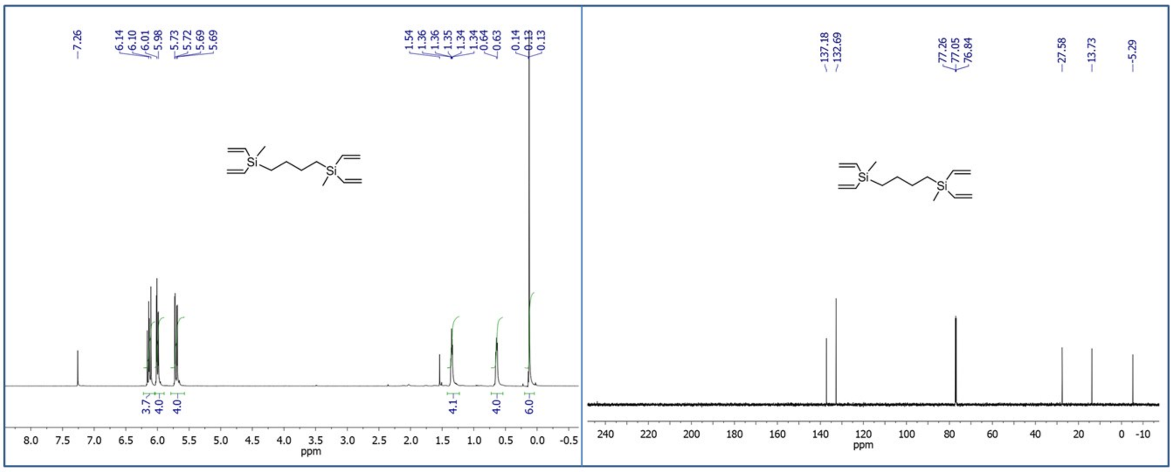
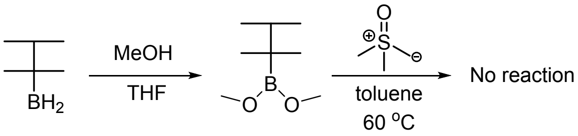


Figure S1. NMR spectra of 1,4-bis(methyldivinylsilyl)butane **1** in $CDCl_3$

To a solution of 1,4-bis(dichloromethylsilyl)butane (1.4 g, 5.0 mmol) in THF (20 mL) vinylmagnisium chloride solution (13 mL, 21 mmol, 1.6 M in THF) was added dropwise at room temperature. The mixture was kept stirring at 60 °C. After 5 h, the reaction was quenched by adding water (50 mL), and the product was extracted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether) and the product was isolated as a colorless oil (1.1 g, 90%). ^1H NMR (Figure S1) ($CDCl_3$, 600 MHz, TMS): δ 0.13 (6H, s), 0.63-0.65 (4H, m), 1.34-1.36 (4H, m), 5.70 (4H, dd, J = 6.0, 24.0 Hz), 6.00 (4H, dd, J = 6.0, 18.0 Hz), 6.13 (4H, dd, J = 18.0, 24.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz, TMS) δ -5.3, 13.7, 27.6, 132.7, 137.2.

2.2 Synthesis of ω-Terminated 4-Arm PE Star Macroinitiator for Polyhomologation of Ylides



Scheme S2. Synthesis of dimethyl thexylboronate and unsuccessful initiation of polyhomologation

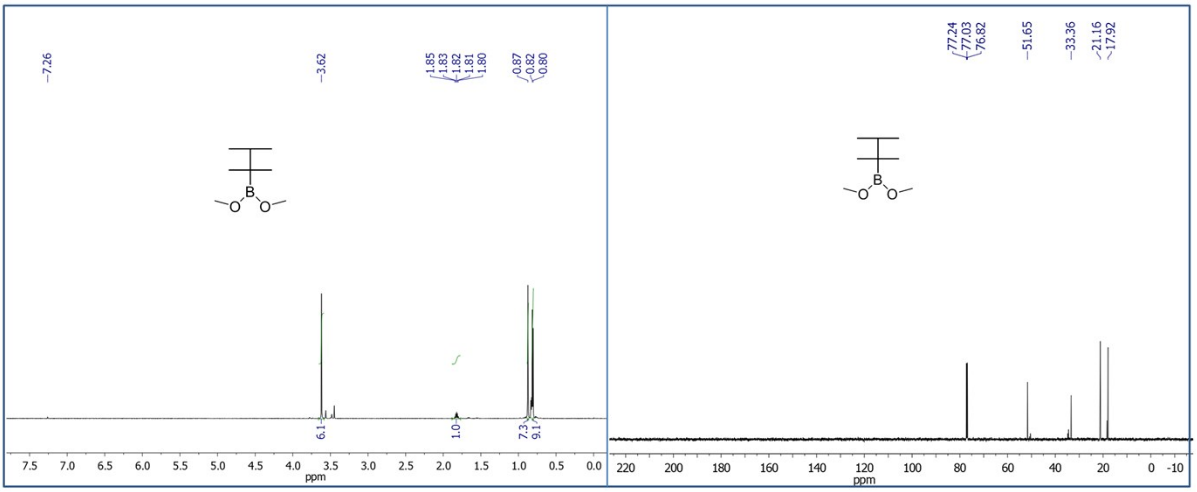
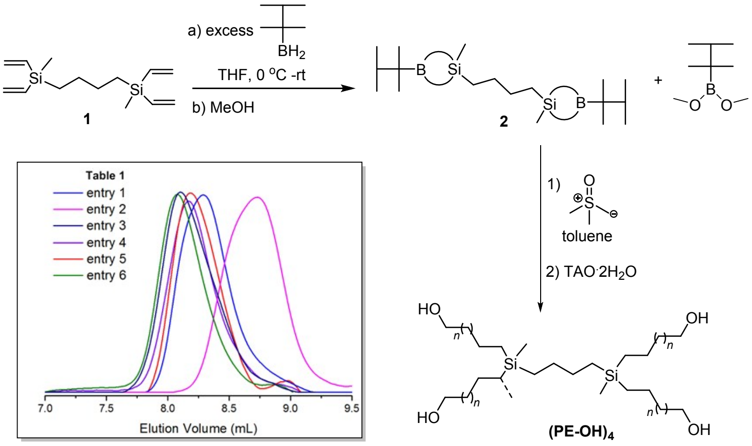


Figure S2. NMR spectra of dimethyl thexylboronate in $CDCl_3$

Dimethyl thexylboronate was prepared according to the reference by adding methanol to the solution of thexylborane in THF.[3] After stirring at room temperature for 30 min, THF and excess of methanol was evaporated under vacuum and then the product was obtained as a colorless oil and characterized by NMR without purification (Scheme S2 and Figure S2).

To a solution of ylide in toluene was added the prepared dimethyl thexylboronate and the mixture was kept stirring at 60 °C for 12 h. Then 0.10 mL of the reaction solution was taken out and added to water containing phenolphthalein (pH indicator). A basic solution indicated the remaining of ylides in the solution. No solid was precipitated when pouring the mixture to methanol, indicating no polymer was formed and dimethyl thexylboronate couldn't initiate polyhomologation of ylides.[4]



Scheme S3. Synthesis of ω-Terminated 4-Arm PE Star 4-arm PEs and the HT-GPC chromatogram

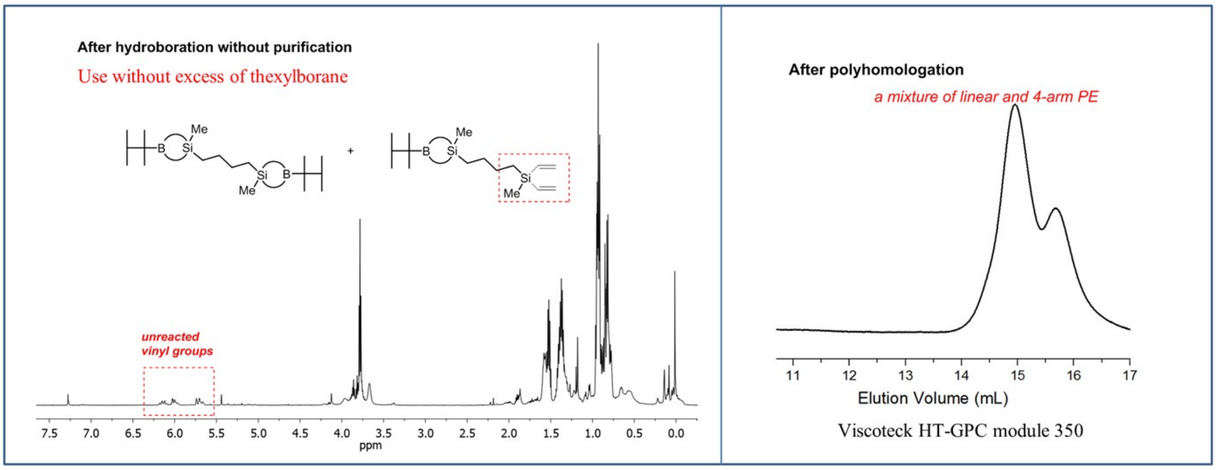


Figure S3. ^{1}H NMR spectrum of prepared crude borane initiators by hydroboration of compound **1** without using excess of thexylborane (left) and HT-GPC measurement of the polymer initiated by the mixture of prepared initiators (right)

To a solution of 1,4-bis(methyldivinylsilyl)butane **1** (0.25 g, 1.0 mmol) in THF (5.0 mL) freshly prepared thexylborane (4.0 mL, ~0.73 M in THF) was added dropwise at 0 °C. Then the mixture was kept stirring at room temperature for 4 h. Methanol (1.0 mL) was added to quench the excess of thexylborane, and then THF and excess of methanol were pumped off at room temperature. THF (5.0 mL) was added to give the borane solution (~0.18 M in THF).

To an ylide solution (14 mL, 0.90 M in toluene) was added the borane solution (0.80 mL, ~0.14 mmol) at room temperature. The reaction was exothermal and became cloudy. After 10 min, the solution was neutral indicating the complete consumption of the ylide. TAO·$2H_2O$ (0.40 g) was added into the solution and the mixture was kept stirring at 80 °C for 4 h. The solution was cooled down, concentrated by rotor evaporator and precipitated in methanol. The white solid was filtered, dried under vacuum and characterized by ^{1}H NMR and HT-GPC (0.16 g, $M_{n,NMR}$ = 3800 g/mol, $PDI_{HT\text{-}GPC}$ = 1.20) (Scheme S3).

2.3 Synthesis of (PE-*b*-PCL)$_4$ Starblock Copolymers

To a solution of $(PE_{58}\text{-}OH)_4$ (0.080 g, 0.091 mmol OH) in 3 mL of dry toluene was added dry ε-caprolactone (CL, 0.60 mL, 5.5 mmol, 60 equiv to OH) and P2-*t*Bu (~2 M in THF, 0.10 mL) under argon. Then the solution was immediately immersed into an oil bath set at 80 °C to activate the polymerization. After 22 h, 0.30 mL of acetic acid was added into the flask to quench the reaction. 0.20 mL of the reaction mixture was taken and characterized by ^{1}H NMR to calculate the monomer conversion (27%, see Figure S3, left). The remaining solution was precipitated in methanol and the resulting white solid was filtered, dried under vacuum, and characterized by ^{1}H NMR and HT-GPC (0.25 g, $M_{n,\ NMR}$ = 8980 g/mol, $PDI_{HT\text{-}GPC}$ = 1.24) (Figure S4, right).

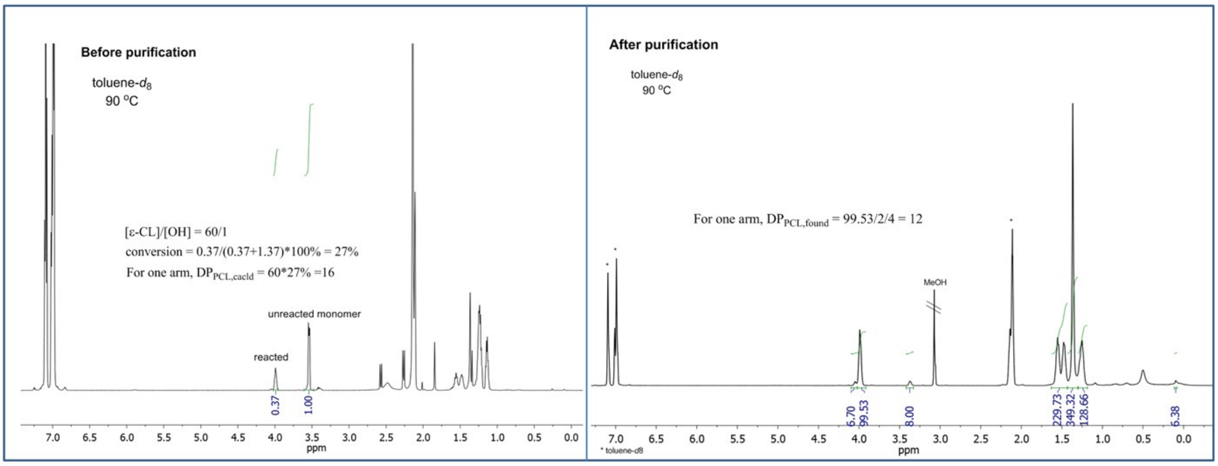


Figure S4. ^{1}H NMR spectra of crude (PE-*b*-PCL)$_4$ (left) and purified (PE-*b*-PCL)$_4$ (right).

2.4 Synthesis of (PE-*b*-PMMA$_2$)$_4$ Dendrimer-Like Star Copolymer

$(PE_{26}\text{-}OH)_4$ (0.10 g, 0.24 mmol of OH) and toluene (5 mL) were placed into a 100 mL Schlenk flask and the mixture was kept under vigorous stirring at 100 °C under Ar. Pyridine (0.10 mL, 1.2 mmol) was added followed by 2,2-dichloroacetyl chloride (0.10 mL, 1.0 mmol). After stirring for 10 h, the reaction mixture was cooled to room temperature and poured into 300 mL of acidic methanol (containing 30 mL of 1 M aqueous HCl). The polymer was filtered, washed successively with methanol (2×20 mL), 1 M aqueous HCl (2×10 mL), and methanol (2×20 mL), and dried at 50 °C for 3 h in vacuum to give an off-white solid.

CuBr (15 mg, 0.10 mmol), MMA (0.77 mL, 7.3 mmol), and toluene (4.0 mL) were placed into a 100 mL Schlenk flask. The mixture was subjected to two freeze-pump-thaw cycles and then PMDETA (43 μL, 0.20 mmol) was added and the mixture was kept stirring at room temperature for 20 min under Ar. Then the macroinitiator $(PE\text{-}Cl_2)_4$ (0.020 g, 0.073 mmol Cl) was added and the mixture was subjected to another two freeze-pump-thaw cycles. The solution was immediately immersed into an oil bath set at 100 °C to start the polymerization under stirring. After 20 h, the polymerization was stopped by cooling in a liquid nitrogen bath. The reaction mixture was poured into cold methanol (300 mL) with stirring. The polymer was filtered, washed with methanol, dried under vacuum, and characterized by ^{1}H NMR and HT-GPC (0.32 g, $M_{n,NMR}$ = 45600 g/mol, PDI = 1.55) (Figure S5).

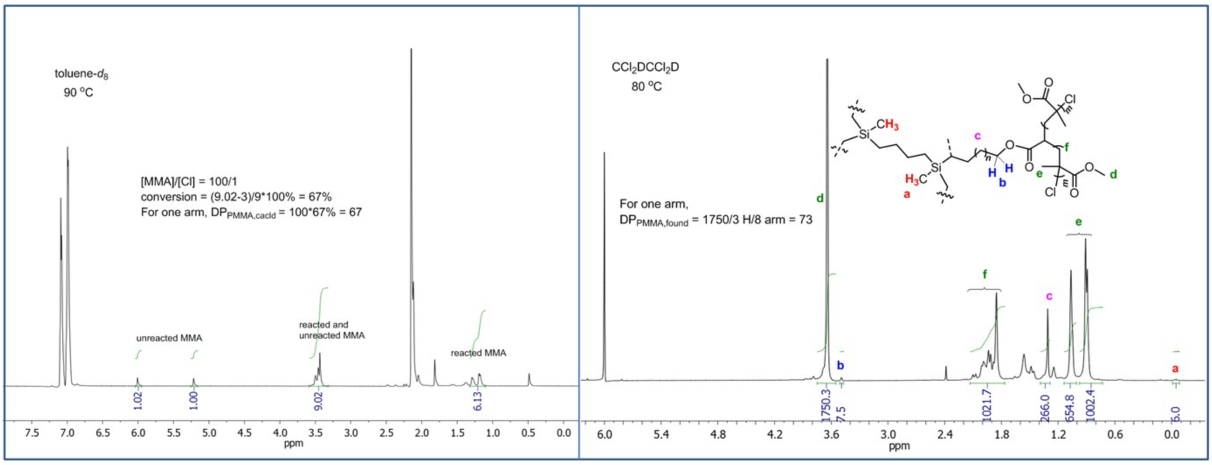


Figure S5. ^{1}H NMR spectra of crude $(PE\text{-}b\text{-}PMMA_2)_4$ (left) and purified $(PE\text{-}b\text{-}PMMA_2)_4$ (right).

3 References

[1] (a) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.* **1965**, *87*, 1353; (b) H. Zhang, N. Alkayal, Y. Gnanou and N. Hadjichristidis, *Chem. Comm.* **2013**, *49*, 8952; (c) H. Zhang, Y. Gnanou and N. Hadjichristidis, *Polym. Chem.* **2014**, *5*, 6431.

[2] E. Negishi and H. C. Brown, *Synthesis* **1974**, 77.

[3] (a) H. C. Brown and J. K. Gerald, *Inorg. Chem.* **1962**, *1*, 204; (b) H. C. Brown, K. M. Arun and U. K. Surendra, *J. Org. Chem.* **1977**, *42*, 1392.

[4] Alkylboronic and alkylborinic esters couldn't initiate polyhomologation, see: J. M. Stoddard and K. J. Shea, *Organometallics* **2003**, *22*, 1124.