

Supporting Information

Polyhomologation based on *in situ* generated Boron-thexyl-silaboracyclic initiating sites: a novel strategy towards the synthesis of polyethylene-based complex architectures

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1. General Information

1.1. Materials

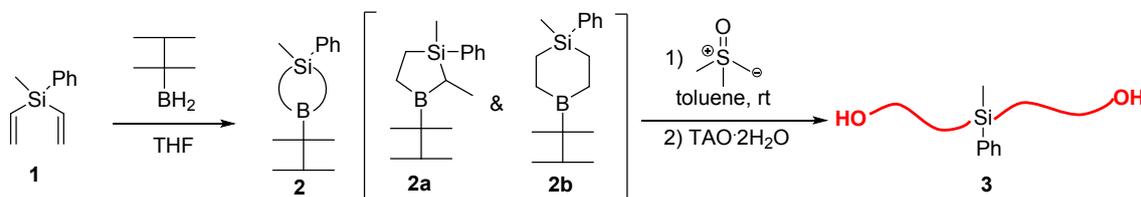
Ethyl 2-bromoisobutyrate (EBiB, 99%), copper(I) bromide (CuBr, 99.999%), vinylmagnesium bromide solution (1.0 M in THF), vinyl magnesium chloride solution (1.6 M in THF), methylmagnesium chloride solution (3.0 M in THF), dichloromethylvinylsilane (97%), 2-hydroxyethyl methacrylate (97%), 2,3-dimethylbut-2-ene ($\geq 99\%$), borane tetrahydrofuran complex solution (1.0 M in THF), ethylene glycol (99.8%), 3-chloro-1-propanol (98%), triethylamine ($\geq 99\%$), 4-(Dimethylamino)pyridine (DMAP, $\geq 99\%$) and pyridine (99.8%) were purchased from Aldrich and used as received. Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) and styrene (St, $\geq 99\%$) were distilled over calcium(I) hydride (CaH) under reduced pressure before use. Tetrahydrofuran (THF) and toluene were refluxed over sodium/benzophenone and distilled under a nitrogen atmosphere just before use. Dimethylsulfoxoniummethylide 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 tetrahydrofuran complex solution (BH₃ THF, 1.0 M in THF) according to the literature.^[2] Polyethylene (PE) standard ($M_p = 119.6 \times 10^3$ g/mol, PDI = 1.20) was a gift from ExxonMobil.

1.2. Instruments

Gel permeation chromatography measurements were carried out with a Viscotek HT-GPC module 350 instrument with two PLgel 10 μ m MIXED-B columns. 1,2,4-Trichlorobenzene (TCB) was used as eluent at a flow rate of 0.8 mL/min at 150 °C. The system was calibrated with PS standards. The ¹H and ¹³C NMR spectra were recorded with a Bruker AVANCE III-400, 500 or 600 spectrometer. Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC1/TC100 system in an inert atmosphere (nitrogen). The samples were heated from room temperature to 160 °C, cooled to -60 °C and finally heated again to 160 °C with a heating/cooling rate of 10 °C/min. The second heating curve was used to determine the glass transition temperature (T_g), melting temperature (T_m) and degree of crystallinity.

2. Experimental Procedures

2.1 Synthesis of α, ω -dihydroxyl PE



Scheme S1. Synthesis of α, ω -dihydroxyl PE **3** from methylphenyldivinylsilane **1**.

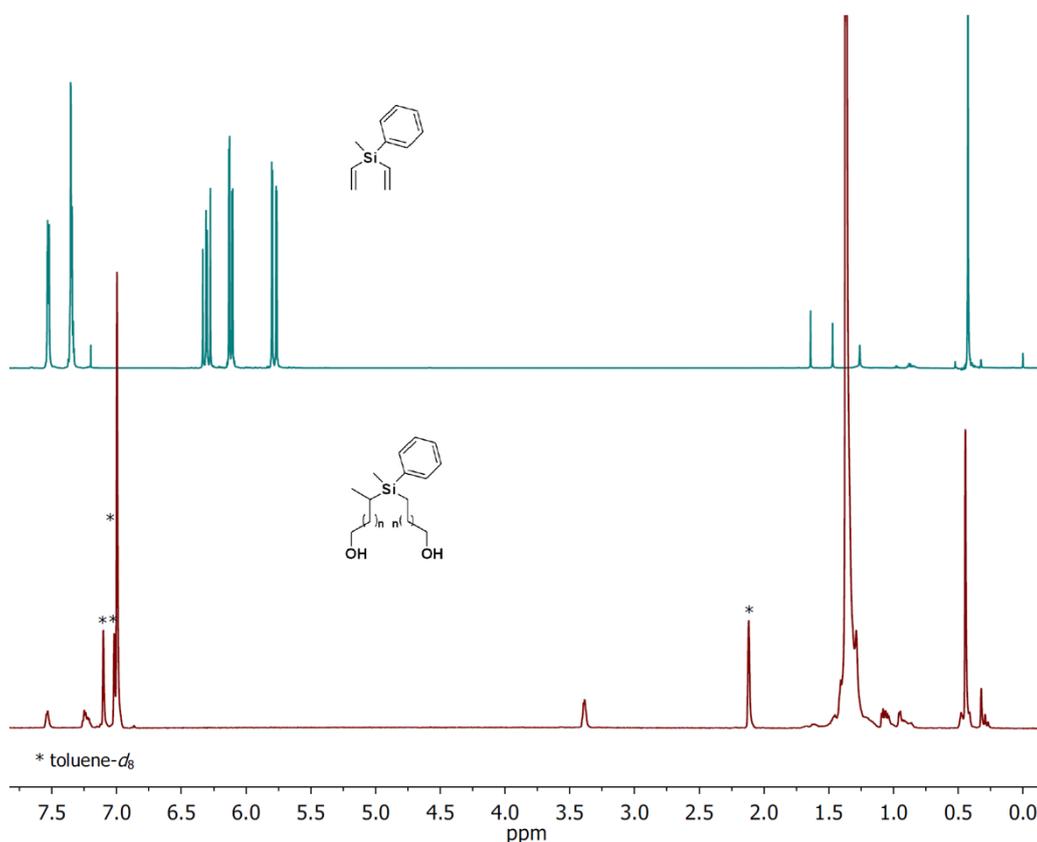


Figure S1. ^1H NMR spectra of methylphenyldivinylsilane **1** and α, ω -dihydroxyl PE **3**.

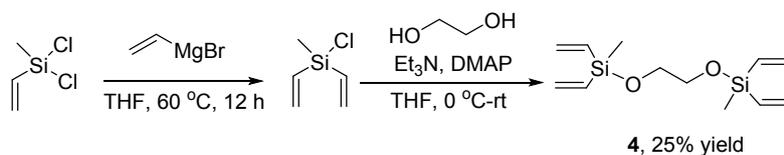
To a solution of methylphenyldivinylsilane **1** (0.87 g, 5.0 mmol) in THF (5 mL) freshly prepared thexylborane (6 mL, 0.89 M in THF) was added dropwise at 0 °C over 20 min. Then the mixture was stirred at room temperature overnight to give a solution of B-thexyl-silaboracycle **2**.

To the solution of B-thexyl-silaboracycle **2** (0.5 mL) degassed methanol (1.0 mL)^[3] was added and then the solvent was evaporated under vacuum. The ylide (6 mL, 1.1 M in toluene) solution was added to this flask and stirred at room temperature. After 20 min, the solution became cloudy and $\text{TAO} \cdot 2\text{H}_2\text{O}$ (200 mg) was added and stirred at 80 °C overnight. The solution was cooled down, concentrated by rotor evaporator and

precipitated in methanol. The white solid was filtered, dried under vacuum and characterized by ^1H NMR and GPC ($M_{n,\text{NMR}} = 1.4 \times 10^3$, $\text{PDI}_{\text{GPC}} = 1.25$).

3 mL of B-thexyl-silaboracycle **2** solution was taken and the solvent was evaporated under vacuum. Then toluene (5 mL) and TAO \cdot 2H $_2$ O (300 mg) was added and the reaction was heated to 100 °C with stirring under Ar overnight. The solvent was removed under vacuum and ethyl acetate (20 mL) was added. After filtration, the filtrate was condensed and purified by preparative TLC (SiO $_2$, petroleum ether/ethyl acetate = 2/1) to give an oily colorless mixture of diols (1,4-diol/1,5-diol = 60/40). 1,5-diol: 2,2'-(methyl(phenyl)silanediy)bis(ethan-1-ol)^[4], ^1H NMR (CDCl $_3$, 500 MHz, TMS): δ 0.35 (3H, s), 1.28 (4H, t, $J = 10.0$ Hz), 1.87 (2H, brs), 3.86 (4H, t, $J = 10.0$ Hz), 7.36-7.41(2H, m), 7.55-7.58 (3H, m); 1,4-diol: 2-((1-hydroxyethyl)(methyl)(phenyl)silyl)ethan-1-ol, ^1H NMR (CDCl $_3$, 500 MHz, TMS): δ 0.37 (3H, s), 1.18-1.22 (1H, m), 1.27 (3H, d, $J = 10.0$ Hz), 1.37-1.43 (1H, m), 3.18 (2H, brs), 3.68-3.73 (1H, m), 3.77-3.92 (2H,m), 7.36-7.41(2H, m), 7.55-7.58 (3H, m).

2.2 Synthesis of 4-arm PE star



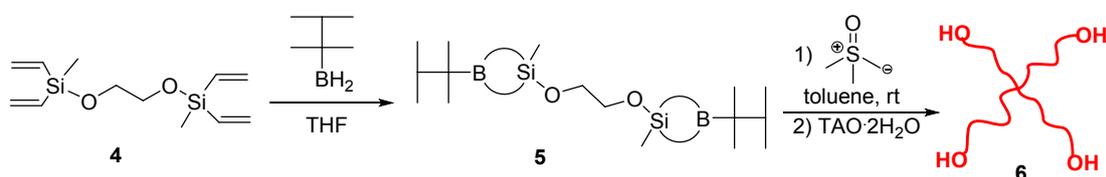
Scheme S2. Synthesis of 3,8-dimethyl-3,8-divinyl-4,7-dioxo-3,8-disiladeca-1,9-diene **4**.

Synthesis of 3,8-dimethyl-3,8-divinyl-4,7-dioxo-3,8-disiladeca-1,9-diene (**4**) (Scheme S2)

To a solution of dichloromethylvinylsilane (4.2 g, 30 mmol) in THF (40 mL) vinylmagnesium bromide solution (30 mL, 30 mmol, 1.0 M in THF) was added by autoinjector during 1 h at room temperature. The reaction mixture was stirred at 60 °C overnight and cooled to room temperature to give a solution containing chloromethyldivinylsilane.

To a solution of ethylene glycol (0.74g, 12 mmol) in THF (20 mL) Et $_3$ N (8.4 mL, 60 mmol) and DMAP (0.15 g, 1.2 mmol) were added. The mixture was cooled to 0 °C, and the solution of crude chloromethyldivinylsilane prepared above was added dropwise. After the addition, the mixture was stirred at room temperature overnight. The reaction was quenched by adding water (50 mL), and the product was extracted with EtOAc. The organic phase was washed with brine, dried over Na $_2$ SO $_4$ and concentrated under vacuum. Distillation under reduced pressure gave the pure product as a colorless oil (0.75 g, 25%

yield). $^1\text{H NMR}$ (CDCl_3 , 400 MHz, TMS): δ 0.26 (6H, s), 3.70 (4H, s), 5.84 (2H, dd, $J = 4.0, 20.0$ Hz), 6.08 (2H, dd, $J = 4.0, 16.0$ Hz), 6.15 (2H, dd, $J = 16.0, 20.0$ Hz); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, TMS) δ -3.7, 64.2, 134.5, 135.5; MS (%) m/z 254.18 (M^+ , 14), 241.16 (93), 203.12 (88), 145.13 (100), 131.15 (32).



Scheme S3. Synthesis of 4-arm PE star **6** from **4**.

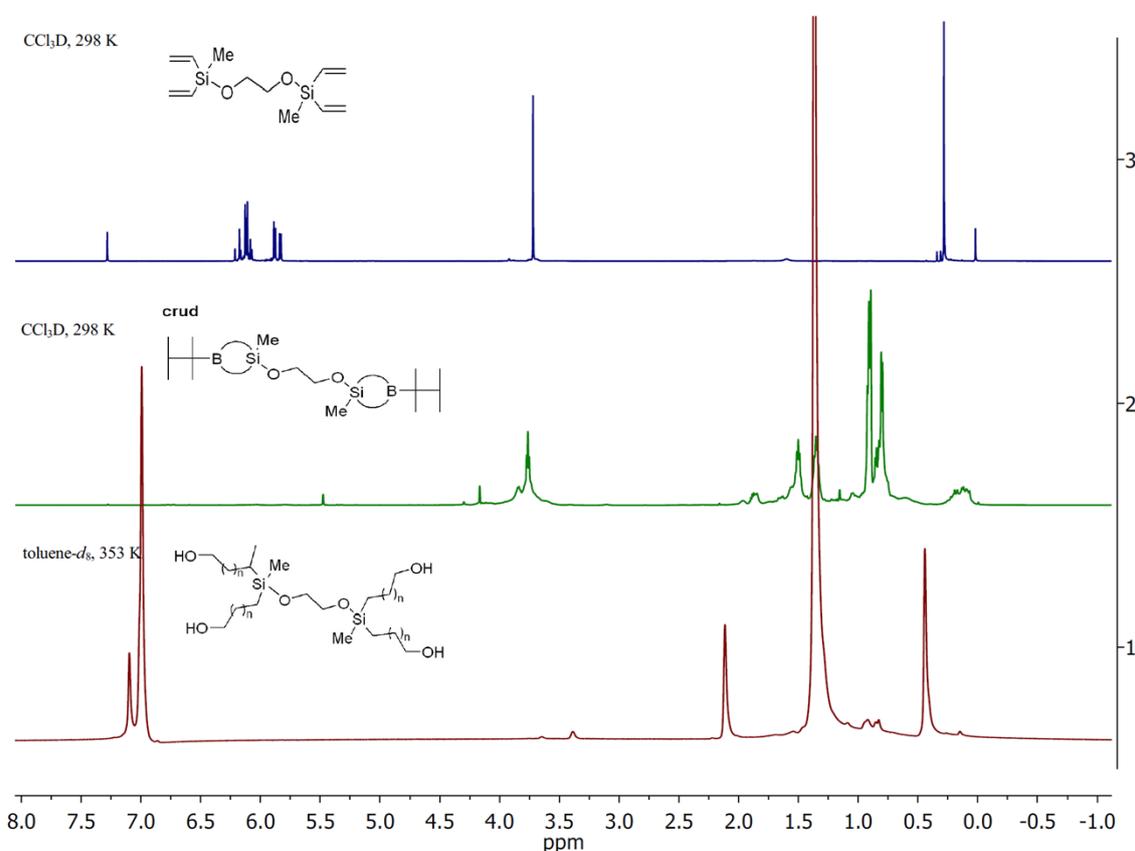


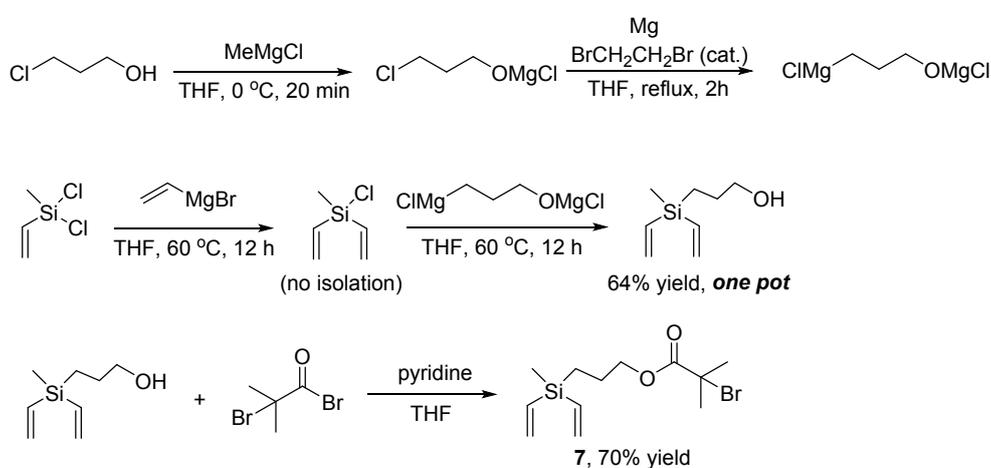
Figure S2. $^1\text{H NMR}$ spectra of initiator precursor **4**, initiator **5** (crude) and 4-arm PE star **6**.

Synthesis of 4-arm PE star (**6**)

To a solution of 3,8-dimethyl-3,8-divinyl-4,7-dioxa-3,8-disiladeca-1,9-diene **4** (64 mg, 0.25 mmol) in THF (5 mL) freshly prepared hexylborane (0.8 mL, 0.89 M in THF) was added dropwise during 30 min. Then the mixture was stirred at room temperature overnight. 0.1 mL of the mixture was taken and the solvent evaporate under vacuum. The $^1\text{H NMR}$ signal of vinyl group was disappeared indicating the completion of

the hydroboration reaction (Figure S2). Methanol (0.3 mL) was added to quench the excess hexylborane and then the solvent was evaporated. THF (5 mL) was added to give the borane solution (0.05 M in THF). The ylide solution (10 mL, 1.0 M in toluene) and then the borane prepared above (0.4 mL, 0.05 M) was added to a flask at room temperature. After 24 h, the solution became cloudy. TAO·2H₂O (200 mg) was added into the solution and stirred 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 ¹H NMR and GPC (36 mg, 26%, $M_{n,NMR} = 3.0 \times 10^3$, $PDI_{GPC} = 1.63$).

2.3 Synthesis of PE-based 3-miktoarm star copolymer



Scheme S4. Synthesis of 3-(methyldivinylsilyl)propyl 2-bromo-2-methylpropanoate **7**.

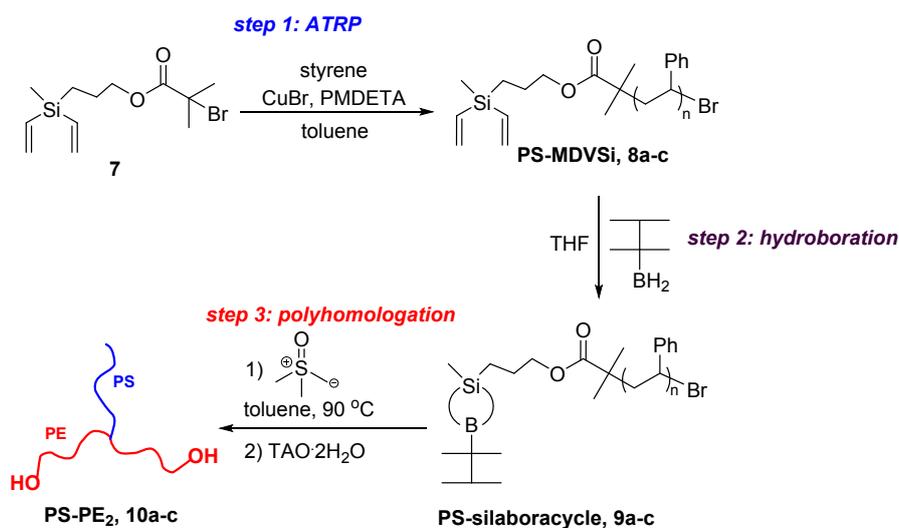
Synthesis of 3-(methyldivinylsilyl)propyl 2-bromo-2-methylpropanoate (**7**) (Scheme S4)

Methylmagnesium chloride solution (13.3 mL, 40 mmol, 3.0 M in THF) was added dropwise and under stirring to a solution of 3-chloro-1-propanol (3.78 g, 40 mmol) in THF (50 mL) at 0 °C. After stirring for further 20 min, magnesium turnings (1.06 g, 44 mmol) and a catalytic amount of 1,2-dibromoethane were added. The reaction mixture was heated under reflux for 3 h and cooled to room temperature to give a gray solution of ClMg(CH₂)₃OMgCl.

To a solution of dichloromethylvinylsilane (5.6 g, 40 mmol) in THF (40 mL) vinylmagnesium bromide solution (40 mL, 40 mmol, 1.0 M in THF) was added by autoinjector during 1 h at room temperature. The reaction mixture was stirred at 40 °C overnight. Then the Normant-Grignard reagent ClMg(CH₂)₃OMgCl, prepared as described above, was added dropwise and the mixture was kept stirring at 40 °C for 5 h. The reaction was quenched with saturated NH₄Cl solution, and the mixture was treated with EtOAc. The combined organic extracts were washed with brine, dried over MgSO₄, filtered and concentrated. The crud

product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1) and the product 3-(methyldivinylsilyl)propan-1-ol was isolated as a colorless oil (3.74 g, 60% yield).

To a solution of 3-(methyldivinylsilyl)propan-1-ol (1.40 g, 9.2 mmol) in THF (15 mL) pyridine (0.88 g, 11.1 mmol) was added and the mixture was cooled to 0 °C, followed by the dropwise addition of 2-bromoisobutyryl bromide (2.56 g, 11.1 mmol). The reaction was stirred overnight at room temperature followed by dilution with hexanes (20 mL) and washing with brine. The organic extracts was dried over MgSO₄, filtered and concentrated. The crud product was purified by flash chromatography on silica gel (eluent: hexanes) and the product 3-(methyldivinylsilyl)propyl 2-bromo-2-methylpropanoate **7** was isolated as a yellow oil (1.97 g, 70% yield). ¹H NMR (CDCl₃, 400 MHz, TMS): δ 0.17 (3H, s), 0.68-0.72 (m, 2H), 1.66-1.74 (2H, m), 1.93 (6H, s), 4.13 (2H, t, *J* = 8.0 Hz), 5.74 (2H, dd, *J* = 4.0, 20.0 Hz), 6.03 (2H, dd, *J* = 4.0, 16.0 Hz), 6.13 (2H, dd, *J* = 16.0, 20.0 Hz); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ -5.4, 9.8, 22.8, 30.8, 56.0, 68.3, 133.4, 136.2, 171.2; MS (%) *m/z* 304.25 (M⁺, 0.02), 199.21 (29), 183.19 (22), 169.17 (49), 157.18 (100).



Scheme S5. Synthesis of 3-miktoarm star copolymer **10** via combination of ATRP with polyhomologation.

Synthesis of 3-miktoarm star copolymer (**10**) (Scheme S5)

As an example the synthesis of PS-MDVSis_{5,2K} **8c** is given. Styrene (2.60 g, 25 mmol), PMDETA (234 mg, 1.35 mmol) and toluene (10 mL) were charged into a dry 50 mL Schlenk flask. The mixture was subjected to three freeze-pump-thaw cycles and then CuBr (2.60 g, 0.675 mmol) and 3-(methyldivinylsilyl)propyl 2-bromo-2-methylpropanoate (152 mg, 0.5 mmol) were added under Ar. The solution was then immediately immersed into an oil bath set at 90 °C to start the polymerization under stirring. After 5 h, the mixture was

diluted with THF and passed through a short silica gel column to remove the copper catalyst. The collected eluent was concentrated and precipitated into excess of methanol twice. The product **8c** was obtained by filtration and dried under vacuum ($M_{n,GPC} = 5,200$, $PDI_{GPC} = 1.18$). 1H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.14 (s, 3H), 0.49 (s, 2H), 0.86 (3H, s), 0.92 (3H, s), 1.20-2.52 (98H, m), 3.30-3.53 (2H, m), 4.36-4.57 (1H, m), 5.67-5.76 (2H, m), 5.96-6.17 (4H, m), 6.28-7.30 (158H, m).

To a solution of PS-MDVS_{i5.2K} **8c** (100 mg) in THF (5 mL) freshly prepared thexylborane (0.30 mL, 0.89 M in THF) was added dropwise at 0 °C and the mixture was stirred at room temperature overnight. 0.1 mL of the mixture was taken and the solvent was evaporated under vacuum. The 1H NMR signal of vinyl group was disappeared indicating the completion of the hydroboration reaction. Methanol (0.3 mL) was added to quench the excess thexylborane and then the solvent was evaporated. The ylide (10 mL, 0.89 M in toluene) solution was added subsequently and the mixture was stirred at 90 °C. After 1h, 0.1 mL of the reaction solution was taken out and added to water containing phenolphthalein. The neutral solution indicated that all ylide was consumed. TAO·2H₂O (200 mg) was added into the solution and stirred at 80 °C overnight. The solution was cooled down and the cloudy solution was concentrated by rotor evaporator and precipitated in methanol. The white solid was filtered, washed with toluene (30 mL), dried under vacuum and characterized by 1H NMR and GPC (78 mg, 35%, **10c**, $M_{w,GPC-LS} = 423 \times 10^3$, $PDI_{GPC-LS} = 1.35$) (Fig S3). Another two 3-miktoarm star copolymers with different molecular weights of $M_{w,GPC-LS} = 506 \times 10^3$ (**10a**, $PDI_{GPC-LS} = 1.32$) and $M_{w,GPC-LS} = 367 \times 10^3$ (**10b**, $PDI_{GPC-LS} = 1.56$) were prepared using the same procedure. In the DSC traces (Fig. S4) of **10b**, the melting temperature at 116 °C was attributed to the PE arms whereas the glass transition temperature of PS-MDVS_i **8b** at 85 °C was completely covered by the melting process of the PE arms.

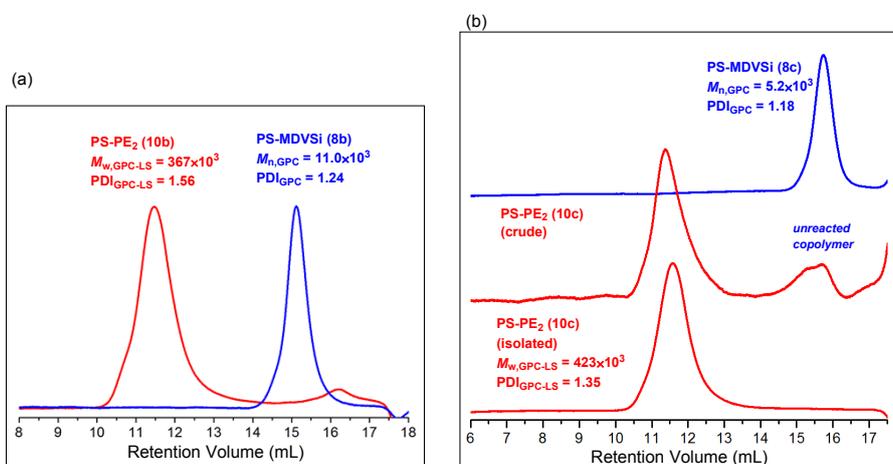


Figure S3. GPC chromatogram of PS-MDVS_i **8b** & **c** and the 3-miktoarm star copolymers PS-PE₂ **10b** & **c**.

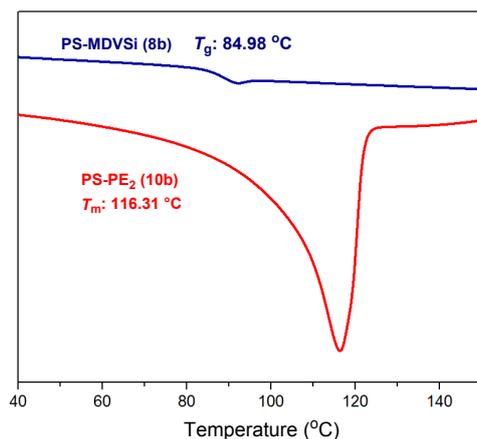
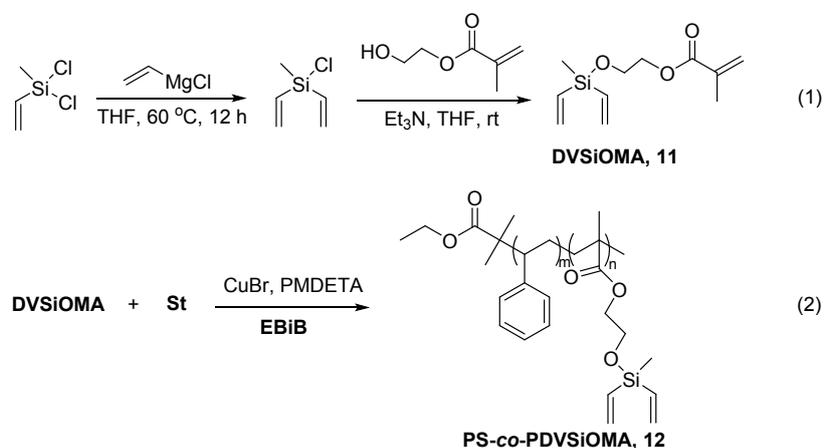


Figure S4. DSC curves of PS-MDVSi **8b** and PS-PE₂ **10b** (nitrogen atmosphere, 10 °C/min, second heat cycle).

2.4 Synthesis of PE-branched double graft copolymer



Scheme S6. Synthesis of 2-((methyldivinylsilyl)oxy)ethyl methacrylate (DVSiOMA) **11** and copolymer PS-*co*-PDVSiOMA **12** by ATRP.

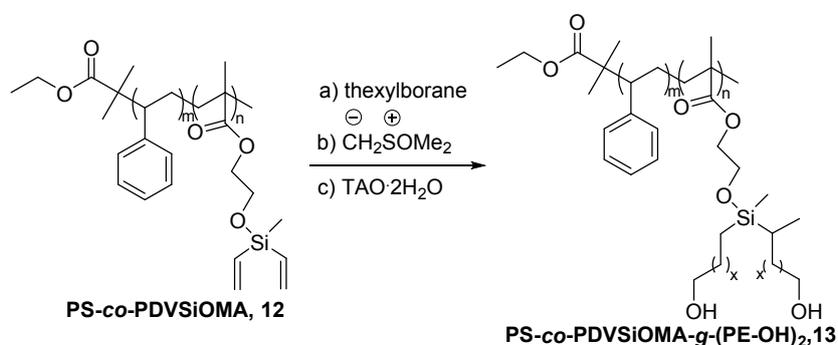
Synthesis of 2-((methyldivinylsilyl)oxy)ethyl methacrylate (DVSiOMA, **11**) (Scheme S6, entry 1)

Dichloromethylvinylsilane (3.9 mL, 30 mmol) in dry THF (50 ml) was cooled to 0 °C using an ice-water bath. Vinyl magnesium chloride solution (18.8 mL, 1.6 M in THF, 30 mmol) was added dropwise and under stirring via syringe during 1 h. The resulting solution was slowly heated to 60 °C and left under stirring overnight. Then the reaction mixture was cooled to 0 °C and 2-hydroxyethyl methacrylate (3.0 mL, 25 mmol) was added in one portion. Triethylamine (10.5 mL, 75 mmol) was added dropwise, a white solid was formed immediately. After stirring at room temperature for 5 h, the reaction was quenched with water (50 ml), and extracted twice with ether. The ether layers were combined and washed with brine, dried with MgSO₄, filtered, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (SiO₂, eluent: petroleum ether/ethyl acetate/triethylamine = 200/10/1) to give the

final product appeared as a colorless oil (2.1 g, 37% yield). ^1H NMR (600 MHz, CDCl_3 , ppm): δ 0.28 (3H, s), 1.95 (3H, s), 3.87 (2H, s), 4.23 (2H, s), 5.58 (1H, s), 5.78-5.90 (2H, m), 6.05-6.18 (5H, m); ^{13}C NMR (CDCl_3 , 120 MHz, TMS): δ -3.8, 18.4, 61.2, 65.8, 125.7, 134.9, 135.2, 136.3, 167.4; MS (%) m/z 199.18 (M^+ -27, 46), 157.17 (18), 155.15 (100), 129.19 (6), 113.14 (20).

Copolymerization of DVSiOMA with styrene by ATRP (Scheme S6, entry 2)

For the synthesis of $\text{PS}_{38}\text{-}co\text{-PDVSiOMA}_3$, styrene (2.60 g, 25 mmol), DVSiOMA (0.51 g, 2.2 mmol), PMDETA (191 mg, 1.1 mmol) and toluene (8 mL) were charged into a dry 50 mL Schlenk flask. The mixture was subjected to three freeze-pump-thaw cycles and then CuBr (79 mg, 0.55 mmol) and EBiB (98 mg, 0.5 mmol) were added under Ar. The solution was then immediately immersed into an oil bath set at 90 °C to start the polymerization under stirring. After 22 h, the mixture was diluted with THF and passed through a short silica gel column to remove the copper catalyst. The collected eluent was concentrated and precipitated into excess of methanol twice. The product was obtained by filtration and dried under vacuum (1.3 g, $M_{n,\text{GPC}} = 6,700$, $\text{PDI}_{\text{GPC}} = 1.31$). ^1H NMR (CDCl_3 , 600 MHz, TMS): δ 0.22 (s, 9H), 0.75-1.06 (m, 18H), 1.14-2.52 (137H, m), 3.00-3.67 (12H, m), 4.19-4.66 (2H, m), 5.67-6.21 (18H, m), 6.28-7.30 (197H, m).



Scheme S7. Synthesis of PE-branched double graft copolymer **13** from PS-co-PDVSiOMA **12** by polyhomologation.

Synthesis of PE-branched double graft copolymer $\text{PS-co-PDVSiOMA-g-(PE-OH)}_2$ (**13**) (Scheme S7)

To a solution of $\text{PS}_{38}\text{-}co\text{-PDVSiOMA}_3$ (400 mg) in THF (5 mL) freshly prepared thexylborane (0.60 mL, 0.89 M in THF) was added dropwise at 0 °C and the mixture was stirred at room temperature overnight. 0.1 mL of the mixture was taken and the solvent was evaporated under vacuum. The ^1H NMR signal of vinyl group was disappeared indicating the completion of hydroboration reaction. Methanol (50 mL) was then added under Ar and the mixture was filtered in a glove box and dried under vacuum to give a white solid.

The excess ylide (12 mL, 0.72 M in toluene) solution was added to above dry solid (120 mg) and the mixture was stirred at 90 °C. After 1.5 h, TAO·2H₂O (200 mg) was added into the solution and stirred at 80 °C overnight. The solution was cooled down and the cloudy solution was concentrated by rotor evaporator and precipitated in methanol. The white solid was filtered, washed with toluene (30 mL), dried under vacuum and characterized by ¹H NMR and GPC ($M_{w,GPC-LS} = 218 \times 10^3$, $PDI_{GPC-LS} = 1.35$) (Figure S5 & 6). The PE-branched double graft copolymer showed much lower intrinsic viscosity than the corresponding linear PE of the Mark–Houwink–Sakurada plots (TCB, 150 °C) (Figure S7).

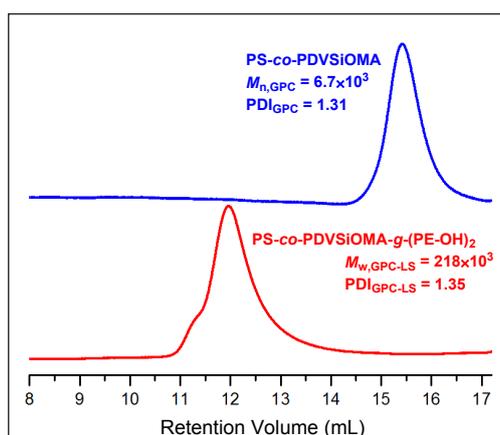


Figure S5. GPC chromatogram of PS-*co*-PDVSIOA and PS-*co*-PDVSIOA-*g*-(PE-OH)₂.

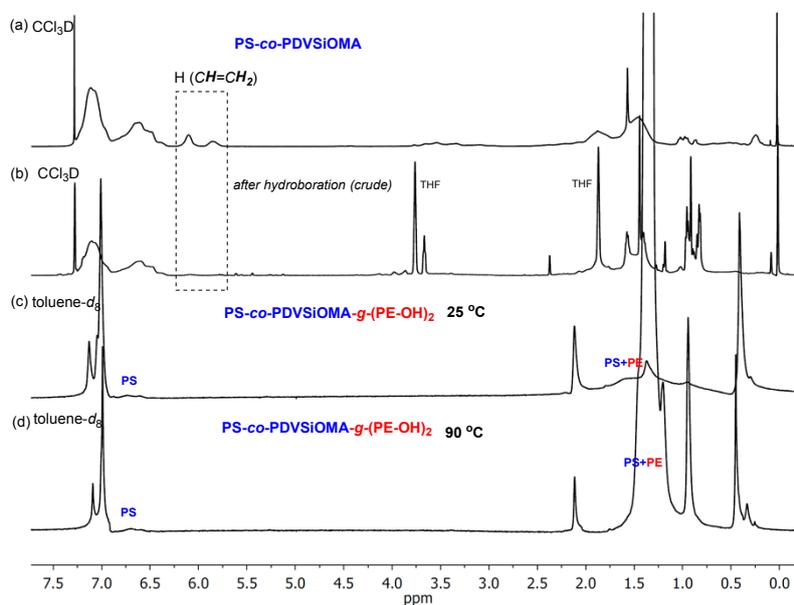


Figure S6. ¹H NMR spectra of (a) PS-*co*-PDVSIOA (chloroform-*d*, 25 °C); (b) after hydroboration of PS-*co*-PDVSIOA with hexylborane (crude, chloroform-*d*, 25 °C); (c) PS-*co*-PDVSIOA-*g*-(PE-OH)₂ (toluene-*d*₈, 25 °C); (d) PS-*co*-PDVSIOA-*g*-(PE-OH)₂ (toluene-*d*₈, 90 °C).

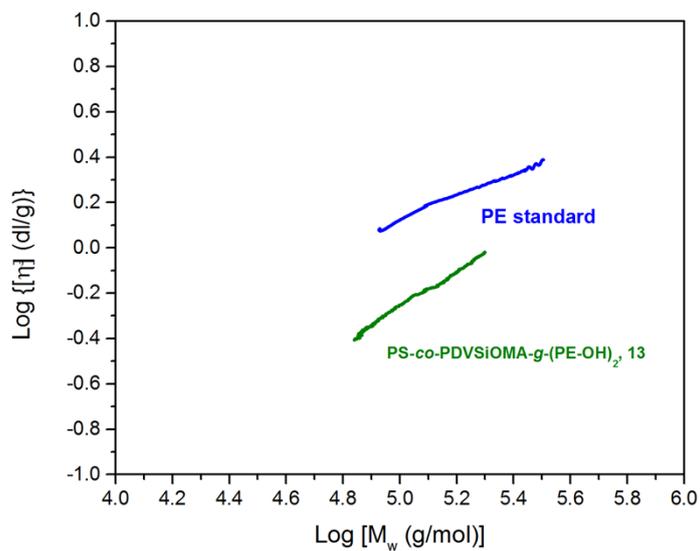
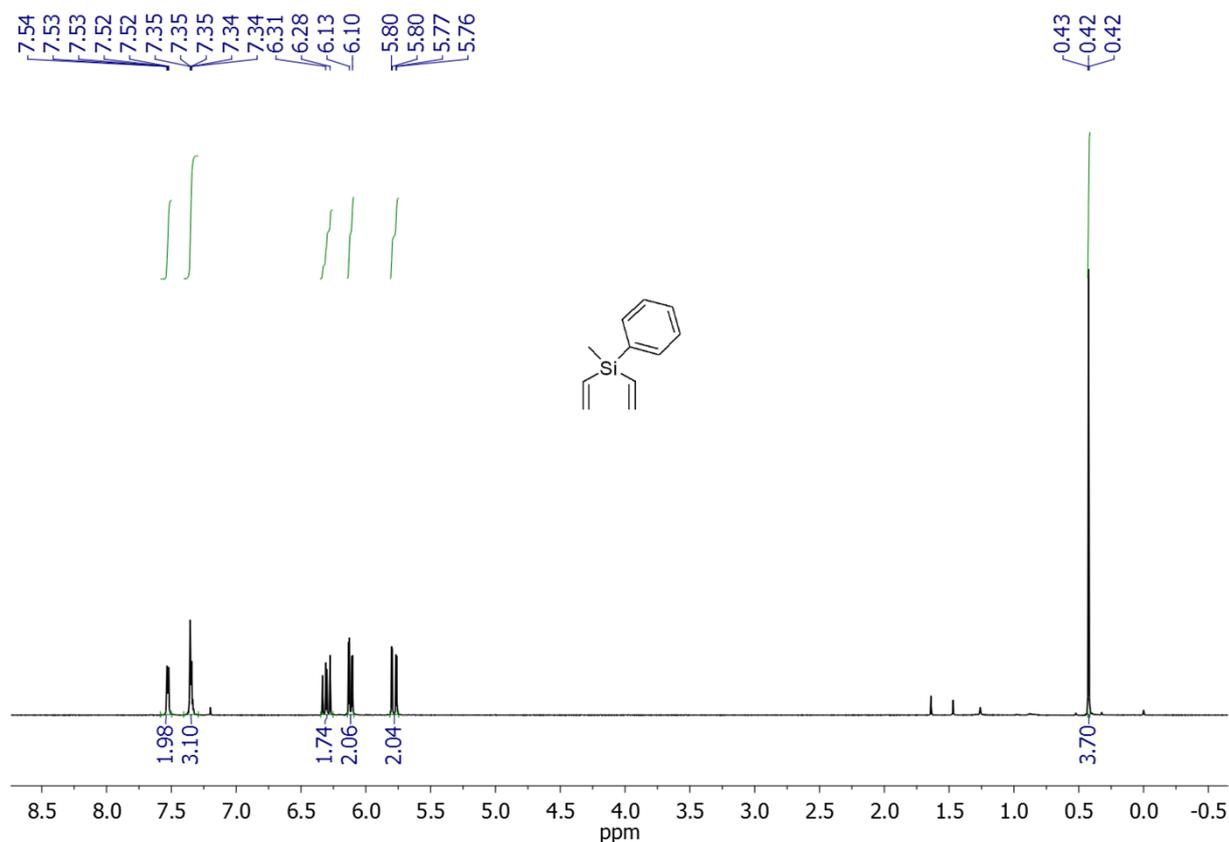
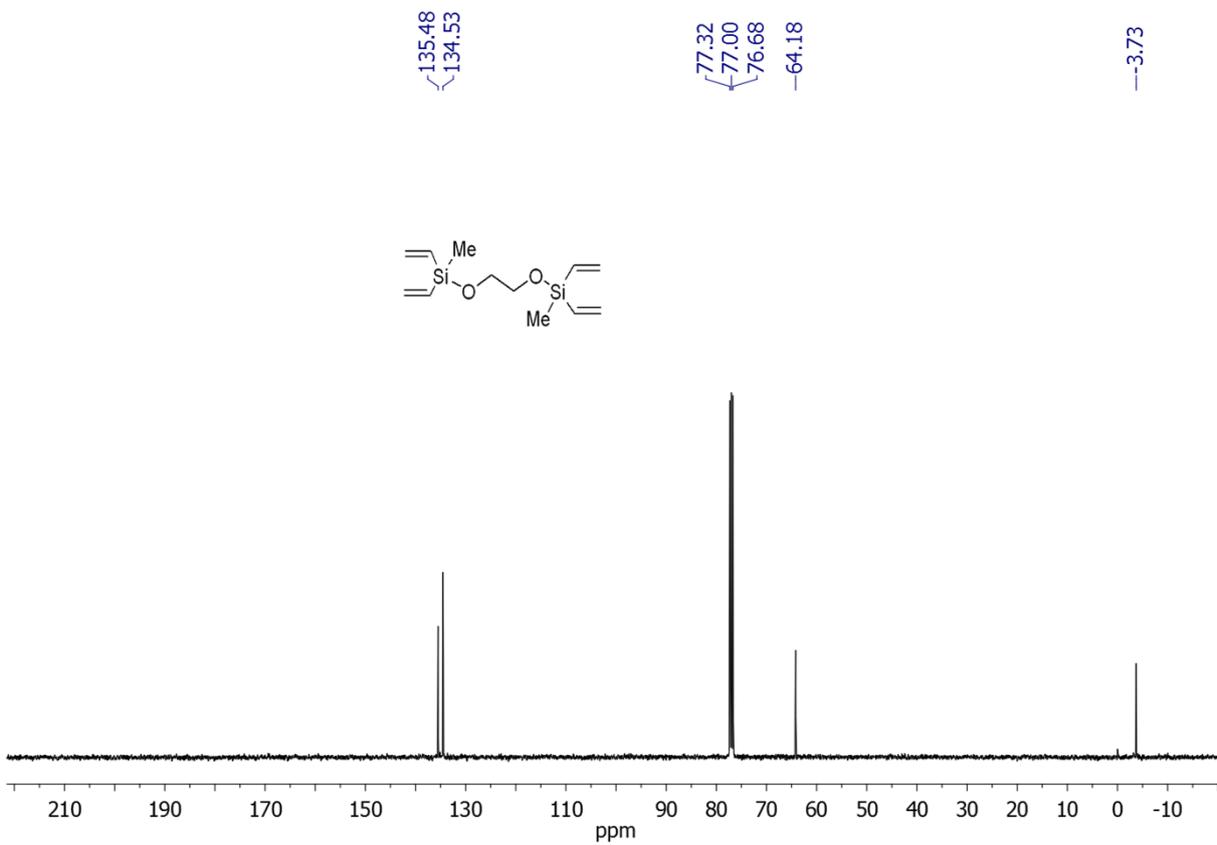
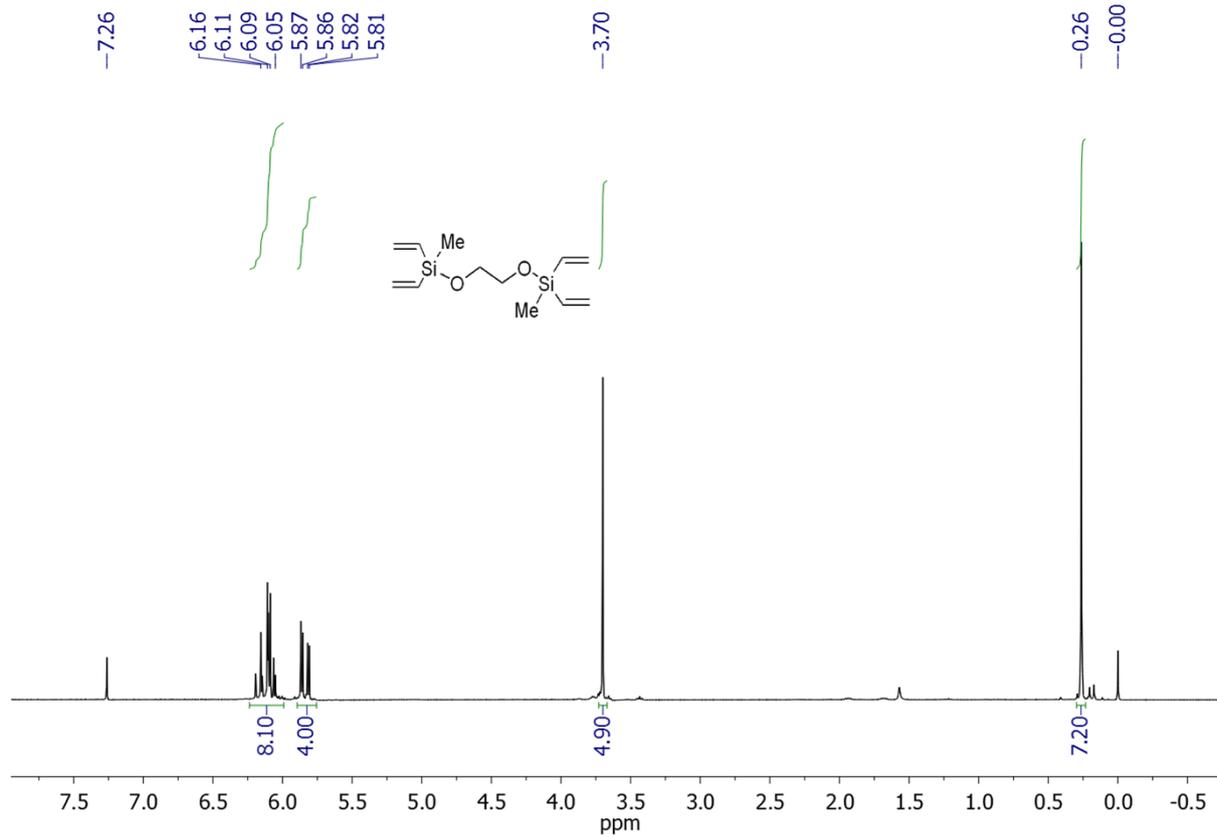
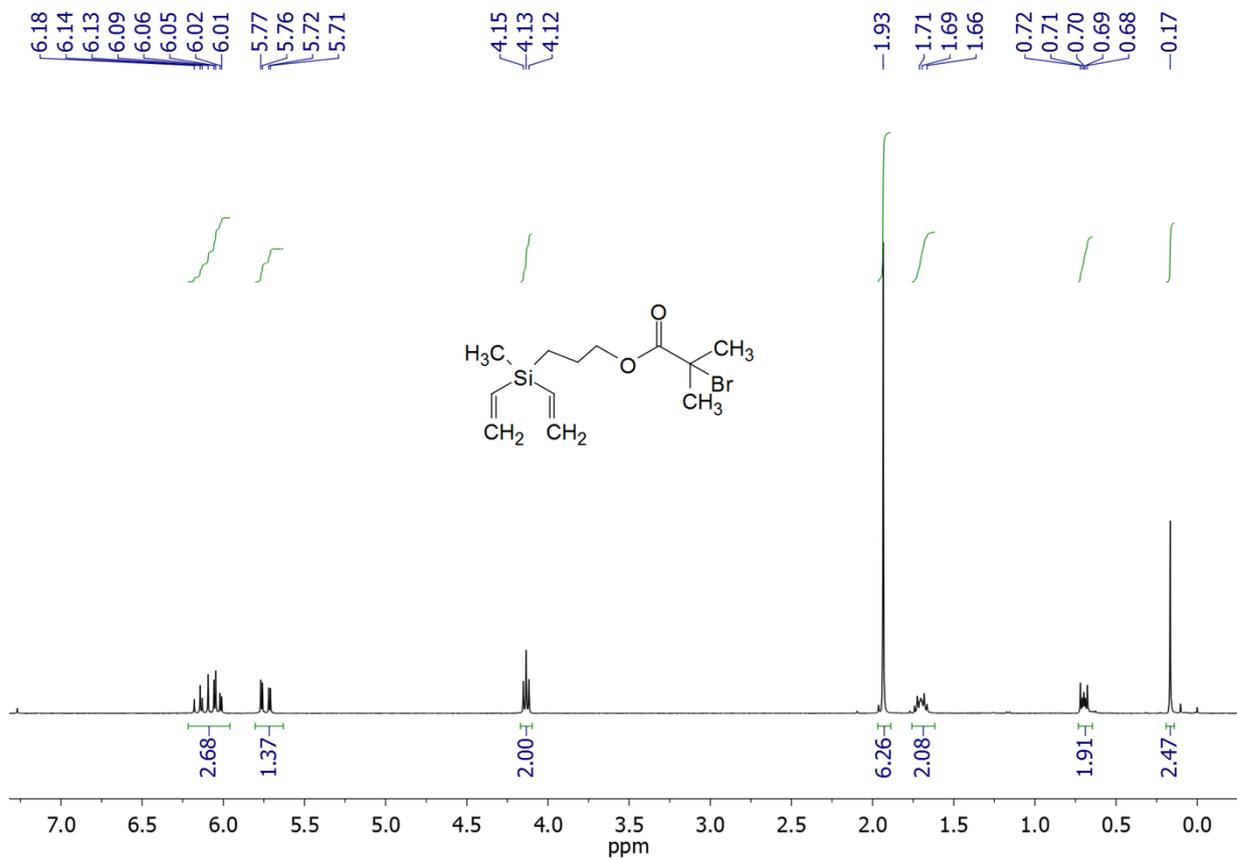
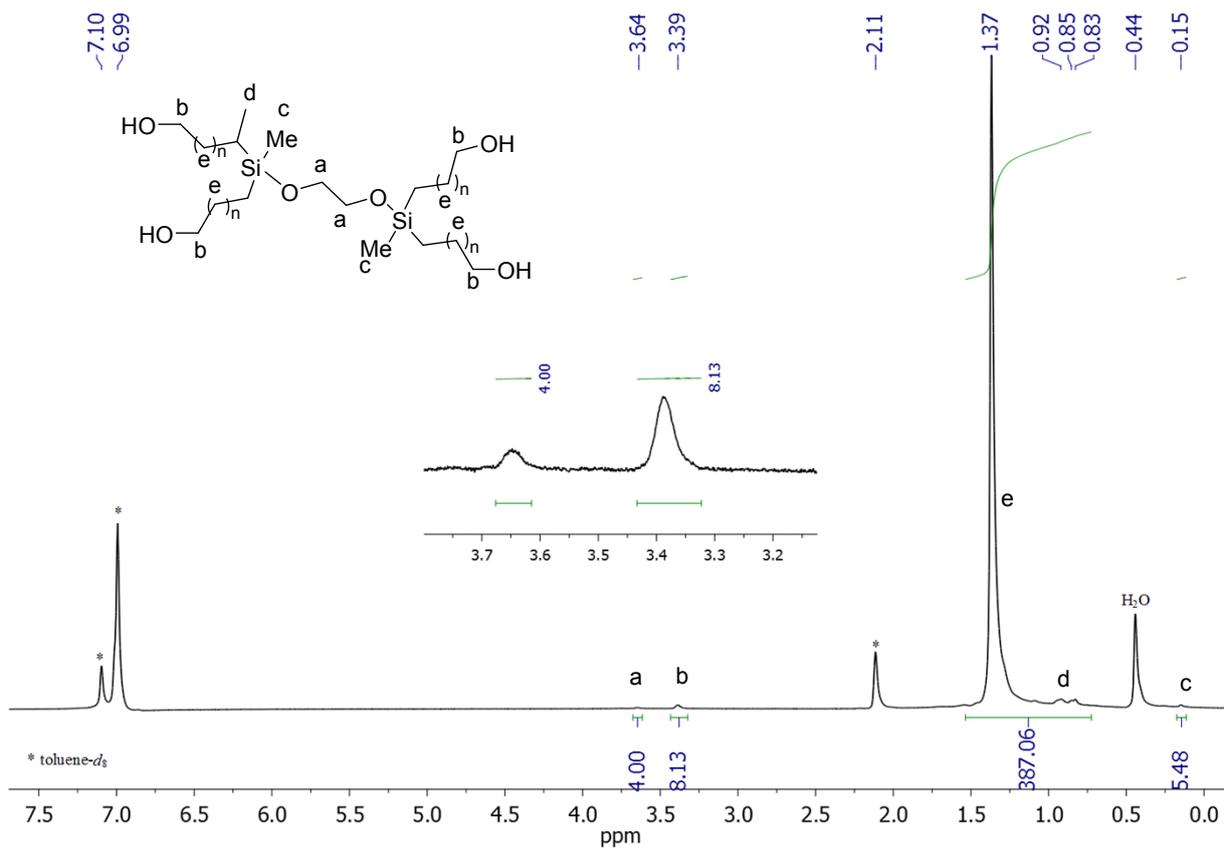


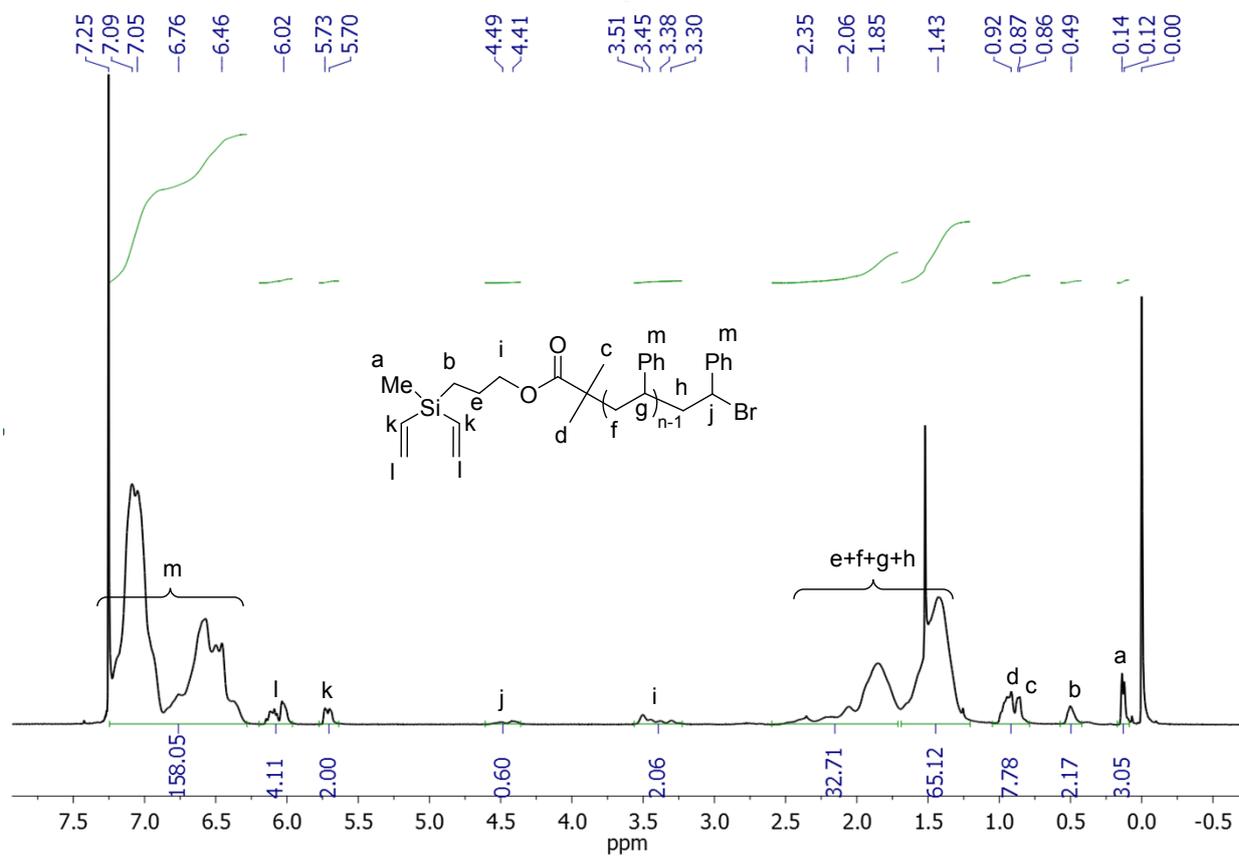
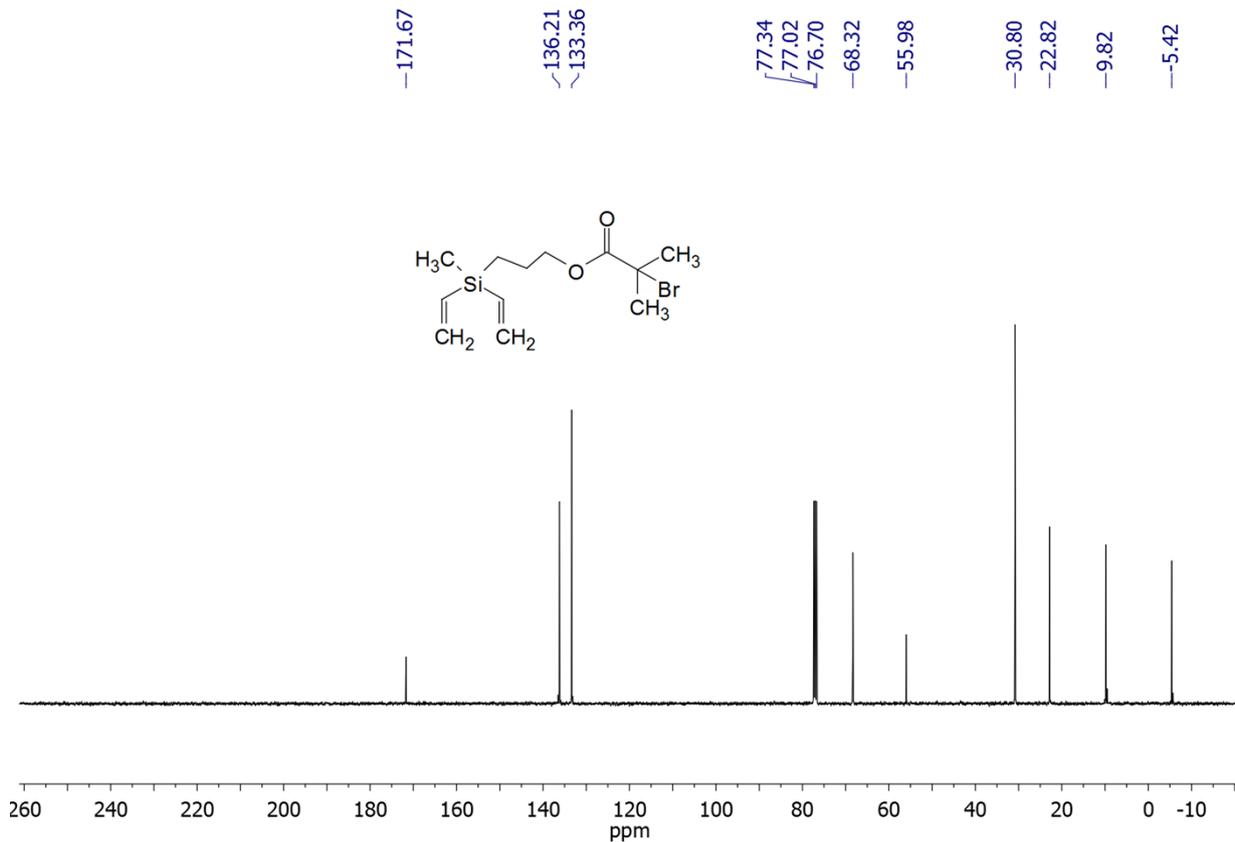
Figure S7. Mark-Houwink-Sakurada plots of PE-branched double graft copolymer **13** and a PE standard (M_p = 119.6×10³ g/mol, PDI = 1.20) for comparison (HT-GPC system, TCB at 150 °C).

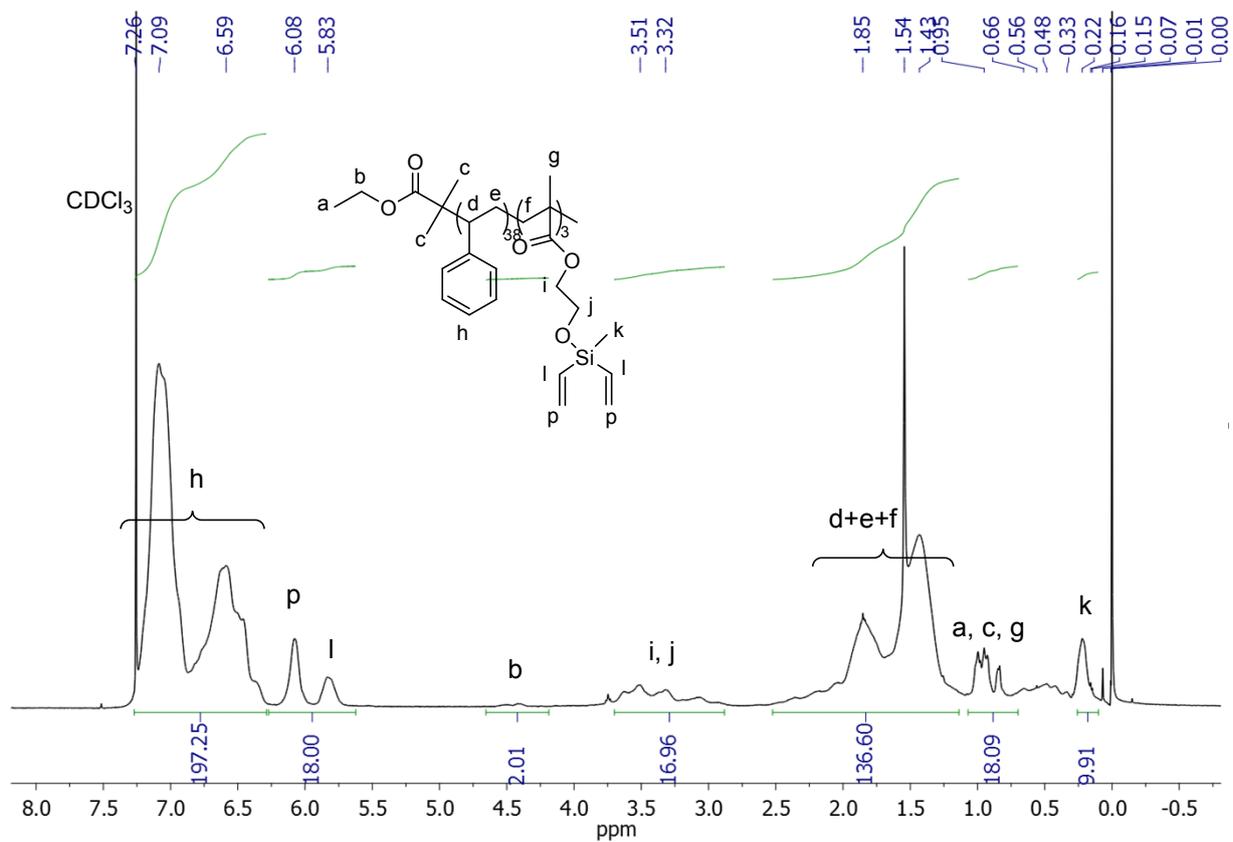
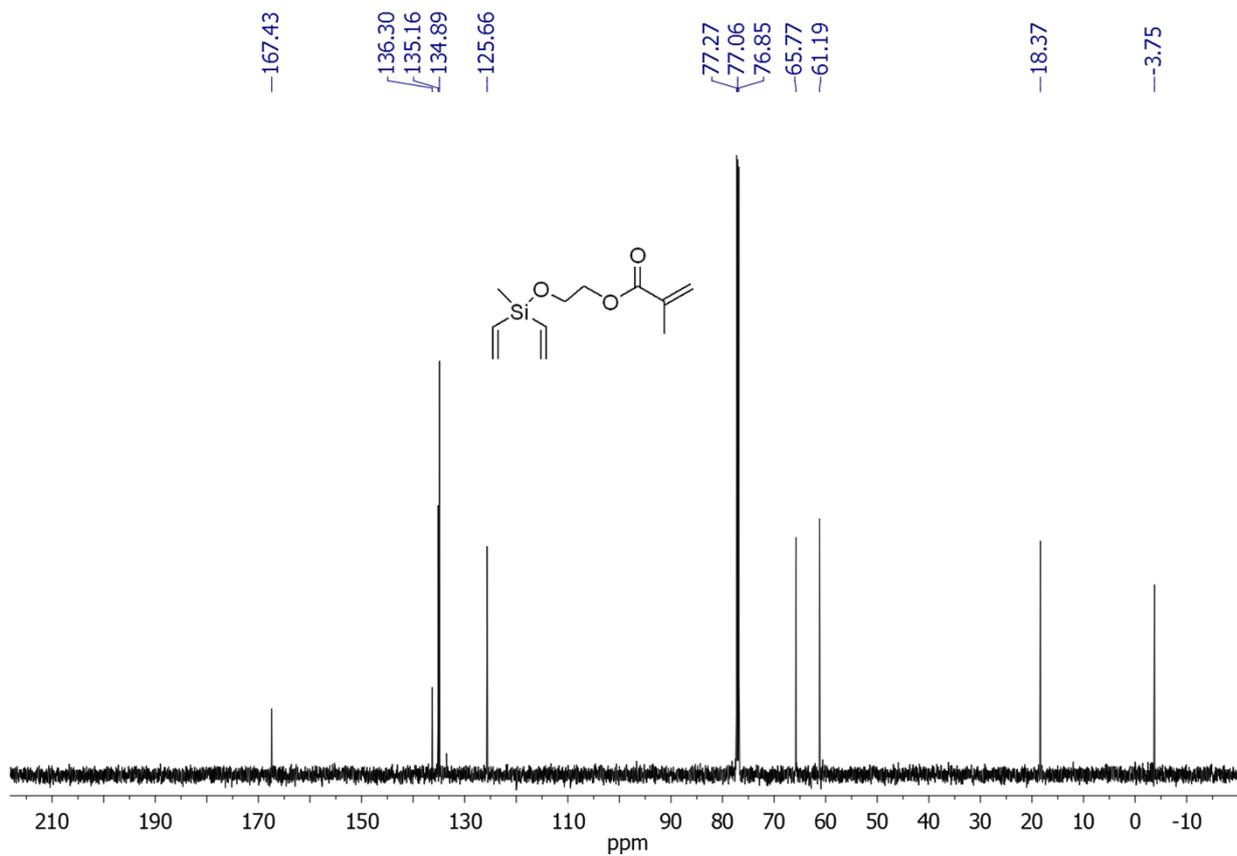
3. Spectroscopic Data of Synthesized Compounds

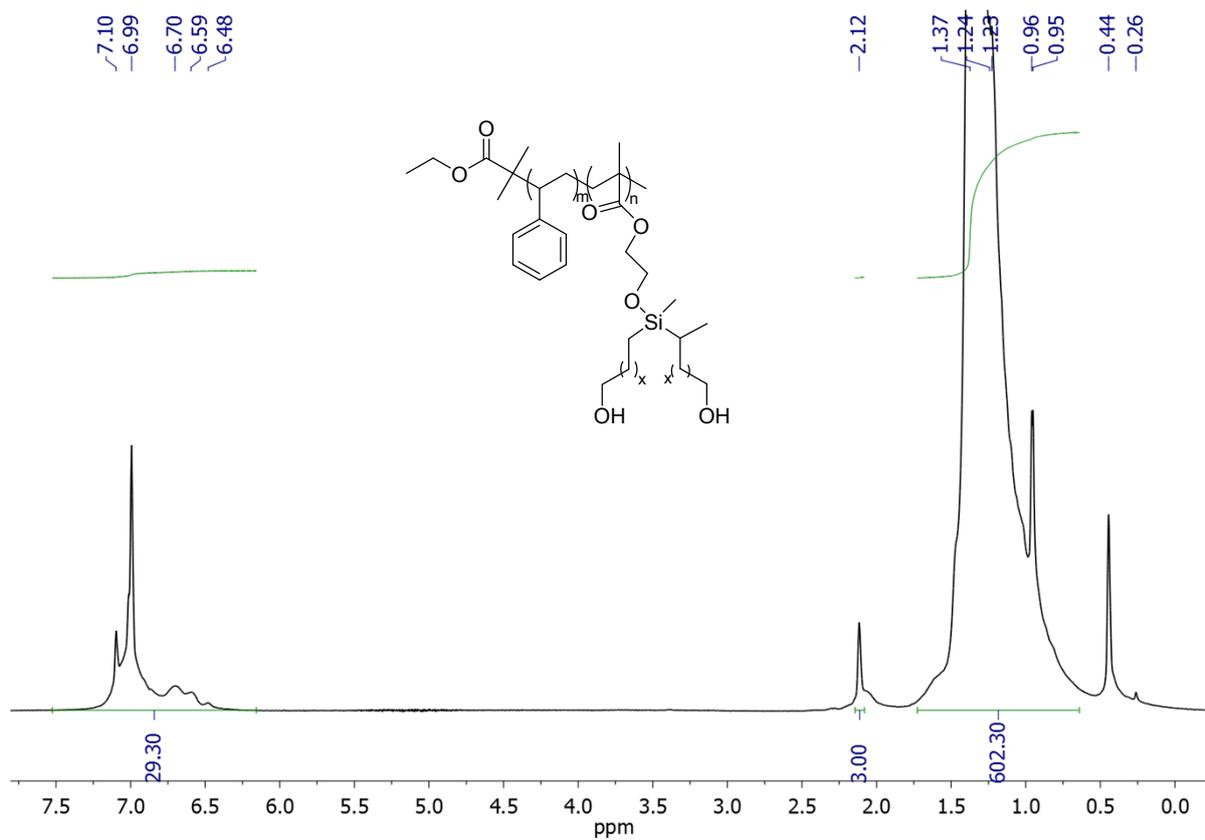












4. References

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