Supporting Information

Triblock and Pentablock Terpolymers by Sequential Base-Assisted Living Cationic Copolymerization of Functionalized Vinyl Ethers

Hassen Bouchékif, [a] Ahlam I Sulami, [a] Reem D. Alghamdi, [a] Yves Gnanou [b] and Nikos Hadjichristidis [a,]*

King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Kingdom of Saudi Arabia

[a] Division of Physical Sciences and Engineering, KAUST Catalysis Center, Polymer Synthesis Lab.

[b] Division of Physical Sciences and Engineering.

E-mail: (N.H.) nikolaos.hadjichristids@kaust.edu.sa

Experimental Section

S1. General procedure for the synthesis of monofunctional (nBEA, CEEA Sand iDEGEA) and difucntional (cHMDEA) initiators

S1.1 Synthesis of the nBVE-acetic acid adduct (nBEA). This was prepared by treatment of nBVE (9.7(7.51) mL(g), 0.075mol, bp = 94°C) with a default of AcOH (2.86(3) mL(g), 0.050 mol, bp =117-118°C) at 60 °C for 3 h. The crude product was distilled twice over calcium hydride under reduced pressure (60 °C) to give nBEA (bp = 120°C), a sweet smelling colorless oil: 75% isolated yield from acetic acid; purity >99%. ^{1}H NMR (CDCl$_3$, δ): 5.9 (m,1 H, -OCH(CH$_3$)O), 3.7 (m, 1 H, OCHHC), 3.4 (m, 1 H, OCHHC), 2.05 (s,3 H, OCOCH_3), 1.55 (m, 1 H, CH$_3$CH$_2$CH_2-), 1.4 (d, 2 H, CH$_3$CH_2-), 1.4 (d, 3 H, -OCH(CH_3)O), 0.9 (d, 3 H, CH_3CH$_2$-).^{13}C NMR (CDCl$_3$, δ): 171.03 (-OCOCH$_3$), 96.62 (-OCH(CH$_3$)O-), 69.19 (-OCH$_2$CH$_2$CH$_2$CH$_3$), 31.78 (-OCH$_2$$CH_2CH_2CH_3$), 21.51 (-OCO$CH_3$), 20.99 (-OCH($CH_3$)O-), 19.37 (-OCH$_2CH_2$$CH_2CH_3$), 14.01 (-OCH$_2CH_2CH_2$$CH_3$). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S1 in the Supporting Information.

S1.2 Synthesis of the SiDEGVE-acetic acid adduct (SiDEGEA). This was prepared by treatment of SiDEGVE (8(8.06) mL(g), 32.76 mmol, d = 1.01 g/mL) with an excess of AcOH (3(3.148) mL(g), 52.4 mmol, bp =117-118°C) at 60°C for 8 h. The mixture was washed at least 3 times with water (10 mL, each), pre-dried over MgSO$_4$, and distilled twice over calcium hydride under reduced pressure (60 °C) to give SiDEGEA (d = 1.01 g/mL), a colorless oil: 93% isolated yield from acetic acid; purity >99%. ^{1}H NMR (CDCl$_3$, δ): 5.9 (m,1 H, -OCH(CH$_3$)O), 3.5 (m, 2 H, -OCH_2CH$_2$OCH$_2$CH$_2$OSi), 3.57-3.75 (m, 6 H, OCH$_2$CH_2OCH_2CH_2OSi), 2 (m, 3 H, -OCOCH_3), 1.35 (d, 3 H, CH_3CH(OCOCH$_3$)O-), 0.84 (s, 12 H, -OSi(CH$_3$)$_2$C(CH_3)$_3$) and 0.03 (s, 6 H, -OSi(CH_3)$_2$C(CH$_3$)$_3$). ^{13}C NMR (CDCl$_3$, δ): 170.67 (-OCOCH$_3$), 96.56 (-OCH(CH$_3$)O-), 72.70 (-OCH$_2$CH$_2$OCH$_2$CH$_2$OSi), 70.26 (-OCH$_2$$CH_2OCH_2$$CH_2$OSi), 25.91 (-OSi(CH$_3$)$_2$C($CH_3$)$_3$), 21.23 (-OCO$CH_3$), 20.68 (-OSi(CH$_3$)$_2$$C$(CH$_3$)$_3$), 18.34 (C$H_3$CH(OCOCH$_3$)O-) and -

5.3 (-OSi(CH_3)$_2$C(CH_3)$_3$). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S2 in the Supporting Information.

S1.3 Synthesis of the CEVE-acetic acid/CEVE (62/38) adduct (CEEA). This was prepared by treatment of CEVE (5.7(5.95) mL(g), 55.9 mmol, d = 1.048 g/mL, bp = 109°C) with an default of AcOH (2(2.098) mL(g), 34.93 mmol, d = 1.049 g/mL, bp =117-118°C) at 60 °C in 8 h. The crude material was distilled twice over calcium hydride under reduced pressure (60 °C) to give a molar ratio of 62/38 CEEA/CEVE, a colorless oil with 100% isolated yield from acetic acid. ^{1}H NMR (CDCl$_3$, δ): 5.9 (m,1 H, -OCH(CH$_3$)O), 3.9 (m, 2 H, -OCH_2CH$_2$Cl), 3.57 (m, 6 H, OCH$_2$CH_2Cl), 2.04 (m, 3 H, -OCOCH_3) and 1.38 (d, 3 H, CH_3CH(OCOCH$_3$)O-). ^{13}C NMR (CDCl$_3$, δ): 170.87 (-OCOCH$_3$), 96.36 (-OCH(CH$_3$)O-), 69.34 (-OCH$_2$CH$_2$Cl), 42.75 (-OCH$_2$$CH_2$Cl), 21.39 (-OCO$CH_3$) and 20.7 (-OCH($CH_3$)O). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S3 in the Supporting Information.

S1.4 Synthesis of cHDMEA. This was prepared by treatment of cHDMVE (6.4(5.9) mL(g), 0.03mol, bp = 94°C) with an excess of AcOH (5.5(5.76) mL(g), 0.096 mol, bp =117-118°C) at 60 °C in 3 h. At room temperature, the product crystallizes. The product was then filtered and then recrystallized twice in di-ethyl ether at -20°C as white powder. It had 88% isolated yield from acetic acid; purity >99%. The product was stored at -20°C to prevent its decomposition at room temperature (Figure S4c, ESI). 'H NMR (CDCl$_3$, δ): 5.86 (m, 2 H, -OCH(CH$_3$)O-), 3.43 and 3.26 (m, 4 H, eq, CH$_3$CH(O-)OCH_2-), 2.04 (s, 6 H, -OCOCH_3), 1.76 and 0.93 (m, 8 H, -OCH$_2$CH(CH_2CH_2-)CH_2CH_2-), 1.48 (m, 2 H, -OCH$_2$CH(CH$_2$-)CH$_2$-), 1.36 (d, 6 H, CH_3CH(O-)O-).^{13}C NMR (CDCl$_3$, δ): 171.03 (2 C, -OCOCH$_3$), 96.5 (2 C, -OCH(CH$_3$)O-), 74.7 (2 C, -CH$_3$CH(O-)OCH$_2$-), 37.9 (2 C, CH$_3$CH(O-)OCH$_2$$C$H(CH$_2$-)CH$_2$-), 29.15 and 29.09 (4 C, -OCH$_2$CH(CH$_2$$CH_2$-)$CH_2$$CH_2$-), 21.3 (2 C, -OCO$CH_3$), 20.7 (2 C, -$CH_3$CH(O-)O-). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S4 in the Supporting Information.

S2. Monomer synthesis. Synthesis of 2-(tert-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE). A solution of *tert*-butyldimethylchlorosilane (25g, 0.17 mol) in *N,N*-dimethylformamide (DMF; 50 mL) was added dropwise to a mixture of ethylene glycol monovinyl ether (28.7 mL, 0.21 mol), imidazole (25 g, 0.37mol), and DMF (50 mL) at 0 °C under nitrogen. The mixture was stirred for 6 h at room temperature and washed with water. The crude monomer was distilled twice over calcium hydride under reduced pressure; bp: 80.0 °C at 10 mmHg. Isolated yield: 80%. Purity: 99% (by gas chromatography). ^{1}H NMR (CDCl$_3$, 30 °C, δ): 0.05 (s, 6H, -Si(C*H*$_3$)$_2$C(CH$_3$)$_3$), 0.83 (s, 9H, -Si(CH$_3$)$_2$C(C*H*$_3$)$_3$), 3.56 (m, 4H, -OCH$_2$CH$_2$OC*H*$_2$CH$_2$OSi), 3.71 (m, 2H, -OCH$_2$C*H*$_2$OCH$_2$CH$_2$OSi), 3.75 (m, 2H, OCH$_2$CH$_2$OCH$_2$C*H*$_2$OSi), 3.81 (m, 2H, -OC*H*$_2$CH$_2$OCH$_2$CH$_2$OSi), 3.97 and 4.15 (m, 2H, *H*$_2$C=), 6.48 (q, 1H,=C*H*-O-). ^{13}C NMR (CDCl$_3$, 30°C, δ): -3.36 (-Si(*C*H$_3$)$_2$C(CH$_3$)$_3$), 18.57 ((-Si(CH$_3$)$_2$*C*(CH$_3$)$_3$), 26.13 (-Si(CH$_3$)$_2$C(*C*H$_3$)$_3$), 72.57 (-O*C*H$_2$CH$_2$OCH$_2$CH$_2$OSi), 69.92 (-OCH$_2$*C*H$_2$OCH$_2$CH$_2$OSi), 62.96 (-OCH$_2$CH$_2$O*C*H$_2$CH$_2$OSi), 67.52 (-OCH$_2$CH$_2$OCH$_2$*C*H$_2$OSi), 86.77 (m, 2H, H$_2$*C*=), 151.99 (=*C*H-O-). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S5 in the Supporting Information.

S3. General Procedure for the homopolymerization of VE monomers using monofunctional (nBEA, CEEA and SiDEGEA) and difunctional (cHDMEA) initiators.

S3.1 Homopolymerization of nBVE using the nBEA initiator. In the polymerization experiments carried out, *e.g.,* in n-Hex, with 4 mM of nBEA (1 mL, 0.08 M in n-Hex), 2 and 4 mL of n-BVE were respectively added to attain an initial concentration in nBVE of 0.77 and 1.56 M, respectively, using either 0.1(4), 0.2(8) or 0.3(12) mL(M) of $Al_2Et_3Cl_3$. The total volume of the solution was 20 mL. As an example, the results obtained at -20°C with $[nBVE]_0 = 0.77$ M, $[nBEA]_0 = 4$ mM, $[DtBP]_0 = 0.4$ mM, $[Al_2Et_3Cl_3]_0 = 4$ mM, $[AcOEt]_0 = 1$ M were as follows: $x^{nBVE}_{42h} = 98\%$, $M_{n(GPC)} = 21,400$ g/mol, PDI = 1.08 (sample P2.6). For additional experimental data, see Tables S2 and S9 in the Supporting Information).

^{1}H NMR in (CDCl$_3$, δ): 3.5 (m, 2 H, -CH$_2$CH(OCH_2-)-), 3 (m, 1 H,-CH$_2$CH(O-)-), 1.79 (m, 1 H,-CHHCH(O-)-), 1.5 (m, 1 H,-CHHCH(O-)-), 1.47 (m, 2 H, CH$_3$CH$_2$CH_2-), 1.33 (m, 2 H, CH$_3$CH_2-), 0.87 (d, 3 H, CH_3CH$_2$-).^{13}C NMR (CDCl$_3$, δ): 73.9 (-CH$_2$CH(O-)-), 68.4-69.1 (-CH$_2$CH(OCH_2-)-), 41.5-39.5 9 (-CH$_2$CH(O-)-), 32.6 (CH$_3$CH$_2$CH_2-), 19.7 (CH$_3$CH_2CH$_2$-), 14.21 (CH_3CH$_2$CH$_2$-). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S7 in the Supporting Information.

S3.2 Homopolymerization of nBVE using cHDMEA. In the polymerization experiments carried out, *e.g.,* in n-Hex, with 4 mM of cHDMEA (2 mL, 0.04 M in n-Hex), 1, 1.5, 2, 3, 5 and 8 mL of n-BVE were respectively added to attain initial concentrations of nBVE(cHDMEA)(Al$_2$Et$_3$Cl$_3$)(Sample) of 0.38(4)(8)(P8.1), 0.57(4)(8)(P8.2), 0.76(4)(8)(P8.3), 1.15(4)(8)(P8.4), 1.92(4)(8)(P8.5), 3.08(4)(8)(P8.6) M(mM)(mM). Here, the polymerization was initiated at -20°C by adding 0.2 mL of Al$_2$Et$_3$Cl$_2$ (0.8 M in n-Hex). The total volume of the solution was 20 mL. As an example, the results obtained at -20°C for a targeted DP of 770 with $[nBVE]_0 = 3.08$ M, $[cHDMEA]_0 = 4$ mM, $[DtBP]_0 = 0.4$ mM, $[Al_2Et_3Cl_3]_0 = 8$ mM, $[AcOEt]_0 = 1$ M were as follows: $x^{nBVE}_{48h} = 100\%$, $M_{n(GPC)} = 80,200$ g/mol, PDI = 1.09 (Sample P8.6, ESI). For additional experimental data, see Table S8 in the Supporting Information.

S3.3 Homopolymerization of SiDEGVE using monofunctional initiator at -20°C. In the polymerization experiments carried out with 0.8, 1.6, 3 and 3.9 mL of SiDEGVE using 1 mL of the monofunctional initiator (*i.e.,* nBEA (series P3), SiDEGEA (series P4) or CEEA (series P5)) (0.08 M in n-Hex), 0.1 mL of $Al_2Et_3Cl_3$ (0.8 M in n-Hex) was respectively added to attain an initial concentrations of SiDEGVE(initiator)($Al_2Et_3Cl_3$) of 0.16(4)(4), 0.32(4)(4), 0.6(4)(4) and 0.8(4)(4) M(mM)(mM). The total volume of the solution was 20 mL. As an example, the results obtained at -20°C for $[nBVE]_0 = 0.32$ M, $[nBEA]_0 = 4$ mM, $[DtBP]_0 = 0.4$ mM, $[Al_2Et_3Cl_3]_0 = 4$ mM, $[AcOEt]_0 = 1$ M were as follows: $x_{384h}^{SiDEGVE} = $ 96%, $Mn_{(GPC)} = $ 21,400 g/mol, PDI = 1.14 (Sample P10.2). For additional experimental data, see Tables S3-S5 and S10 in the Supporting Information.

^{1}H NMR ($CDCl_3$, 30 °C, δ): 0.03 (s, 6H, $-Si(CH_3)_2C(CH_3)_3$), 0.86 (s, 9H, $-Si(CH_3)_2C(CH_3)_3$), 1.5 (m, 1 H,-CH*H*CH(O-)-), 1.78 (m, 1 H,-C*H*HCH(O-)-), 3.37 (m, 1 H, $-CH_2CH(O-)$-), 3.49 (m, 4H, -OC*H*$_2$C*H*$_2$OCH$_2$CH$_2$OSi), 3.55 (m, 2H, -OCH$_2$CH$_2$OC*H*$_2$CH$_2$OSi), 3.72 (m, 2H, OCH$_2$CH$_2$OCH$_2$C*H*$_2$OSi). ^{13}C NMR ($CDCl_3$, 30°C, δ): -3.36 ($-Si(CH_3)_2C(CH_3)_3$), 18.34 ((-Si(CH_3)_2C(CH_3)_3$), 25.96 ($-Si(CH_3)_2C(CH_3)_3$), 39.38-41.5 ($-CH_2CH(O-)$-), 62.64 (-OCH$_2CH_2OCH_2CH_2$OSi), 68.81 (-OCH$_2CH_2OCH_2CH_2$OSi), 70.87 (-OCH$_2CH_2OCH_2CH_2$OSi), 72.60 (-OCH$_2CH_2OCH_2CH_2$OSi), 73.71 5 (-CH$_2$CH(O-)-). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S9 in the Supporting Information.

S3.4 Homopolymerization of CEVE using nBEA at -20°C. The polymerization experiments were carried out as described above in the general procedure. In the polymerization experiments carried out, *e.g.,* in toluene, with 0.8 M of **CEVE** (1.6 mL) and 1 mL of **nBEA** (0.08 M in toluene), 0.1mL of $Al_2Et_2Cl_3$ (0.8 M in n-Hex)) was respectively added to attain an initial concentration in CEVE(nBEA)($Al_2Et_3Cl_3$) of 0.8(0.004)(0.004) M(mM)(M). The total volume of the solution was 20 mL. The results obtained in toluene at -20°C for $[CEVE]_0 = 0.8$ M, $[nBEA]_0 = 4$ mM, $[DtBP]_0 = 0.4$ mM, $[Al_2Et_3Cl_3]_0 = 4$ mM,

[AcOEt]$_0$ = 1 M were as follows: x_{312h}^{CEVE}= 94%, $Mn_{(GPC)}$ = 16,500 g/mol, PDI = 1.34 (Sample P13.6). For additional experimental data, see Table S13 in the Supporting Information.

^{1}H NMR (CDCl$_3$, δ): 3.8 (m, 1 H, (ClCH$_2$CH_2O-), 3.72 (m, 1 H, (ClCH_2CH$_2$O-), 3.63 (s, 1 H,-CH$_2$CH(O-)-), 1.89 (m, 1 H,-CHHCH(O-)-), 1.67 (m, 1 H,-CHHCH(O-)-). ^{13}C NMR (CDCl$_3$, δ): 74.2-73.9 (-CH$_2$CH(O-)-), 69.5-69.1 (ClCH$_2$CH$_2$O-), 43.9 (ClCH$_2$CH$_2$O-), 39.8-40.8 (-CH$_2$CH(O-)-). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S10 in the Supporting Information

S4. General Procedure for the synthesis of the block polymers by sequential monomer addition using the Schlenk technique at -20°C.

The polymerization was carried out under dry argon in a Schlenk reactor equipped with rotaflos (ESI, Figure S6) and ampules containing monomers for sequential additions and an empty ampule used to remove a base sample of the living polymer for molecular characterization. The reactor was heated under vacuum with a heat gun, cooled down and transferred into a glovebox. In a typical polymerization experiment, *e.g.* in n-Hex, the reagents were added in the main reactor in the following order: n-Hex (17-*x*-*y*-*z* mL), AcOEt (2.0 mL), monomer (*x* mL), DtBP (1.0 mL, 0.008 M in n-Hex) and initiator (*y* mL, 0.04 or 0.08 M in n-Hex). Then *p* mL of CEVE in n-Hex (50% v/v in n-Hex) containing 0.05*p* mL of DtBP (0.008 M in n-Hex) were introduced in ampoule A and *q* mL of SiDEGVE in n-Hex (50% v/v in hexane) containing 0.05*p* mL of DtBP (0.008 M in n-Hex) were introduced in ampoule B. The Schlenk reactor was then transferred outside the glovebox in a cryobath set at -20°C. The polymerization was initiated by adding either $z = 0.1y$ or 0.2y mL of $Al_2Et_3Cl_3$ (0.8 M in n-Hex) whether nBEA or cHDMEA initiator were used as nonfunctional or difunctional initiator, respectively. The initial concentrations were as follows: $[nBVE]_0$ = 2-0.76 M, $[initiator]_0$ = 4-9 mM, $[Et_3Al_2Cl_3]_0$ = 4-9 mM, $[AcOEt]_0$ = 1 M and $[DtBP]_0$ = 0.8 mM. After 48h, the CEVE solution contained in ampoule A was added into the main reactor through the bridge at -20°C by opening the rotaflo (A). After 120 h, an aliquot was taken from ampoule C to check at x^{CEVE}_{120h}= 100% the molecular dimension of the PnBVE-*b*-PCEVE diblock prior to the addition at -20°C by opening the rotaflo (B) of the SiDEGVE solution contained in ampoule B. After a given time, the polymerization was quenched with ammoniacal methanol (3% v/v). The quenched reaction mixtures were sequentially washed with diluted hydrochloric acid and with water to remove the catalyst residues. The n-Hex sample containing the polymer, *i.e.,* PnBVE-*b*-PCEVE-*b*-PSiDEGVE, was then dried over $MgSO_4$, evaporated to dryness under reduced pressure, and vacuum dried overnight to give the product polymers. The conversion of the monomer was measured by gravimetry of the product.

S4.1 Synthesis of the PnBVE-b-PCEVE at -20°C. The polymerization experiments were carried out as described above in the general procedure. n-Hex (14.9 mL), AcOEt (2.0 mL), nBVE (1.0 mL), DtBP (1.0 mL, 0.008 M in n-Hex), nBEA (1.0 mL, 0.08 M in n-Hex) and $Al_2Et_3Cl_3$ (0.1 mL, 0.8 M in n-Hex) were used at -20°C for targeting DP of 100; $x^{nBVE}_{48h} = 100\%$, $Mn_{(GPC)}$(PDI)(sample) = 9,800(1.08)(P7.1), 10,500(1.07)(P30) and 10,200(1.08)(P31) g/mol. After 48 h, 2(0)(0)(P7.5), 1(0)(1)(P30) and 0.2(0.8)(1.0)(P31) mL(mL)(mL) of CEVE(nBVE)(n-Hex)(series) were added to living PnBVE cations of the solution for the preparation of $PnBVE_{100}$-*b*-$PCEVE_{200}$, $PnBVE_{100}$-*b*-$PCEVE_{70}$ and $PnBVE_{117}$-*b*-$P(nBVE_{0.8}$-*co*-$CEVE_{0.2})_{70}$, respectively. As an example, the results obtained for the synthesis of $PnBVE_{100}$-*b*-$PCEVE_{70}$ were as follows: $x^{CEVE}_{72h} = 61\%$, $M_{n(GPC)} = 18,100$ g/mol, PDI = 1,09 (Sample P30, Table 1). The 400 MHz ^{1}H and ^{13}C NMR spectra of P30 and P31 are shown in Figures S11 and S12 in the Supporting Information.

S4.2 Synthesis of the PnBVE-b-PSiEGVE at -20°C. The polymerization experiments were carried out as described above in the general procedure. n-Hex (14.9 mL), AcOEt (2.0 mL), nBVE (1.0 mL), DtBP (1.0 mL, 0.008 M in n-Hex), nBEA (1.0 mL, 0.09 M in n-Hex) and $Al_2Et_3Cl_3$ (0.1 mL, 0.8 M in n-Hex) were used at -20°C for targeting DP of 84; $t(x^{nBVE}_t)(Mn_{(GPC)})$(PDI)(sample) = 42(96)(8,600)(1.08)(P32) and 48(100)(8,400)(1.07)(P33) h(%)(g/mol) (Table 1). After 42 and 48h, 2.6 mL of SiEGVE (50% v/v in n-Hex) was added to living PnBVE cations of the solution for the preparation of $PnBVE_{85}$-*b*-$PSiEGVE_{60}$ and $PnBVE_{85}$-*b*-$PSiEGVE_{62}$, respectively; $x^{SiDEGVE}_{72h}(M_{n(GPC)})$(PDI)(sample) = 82(21,400)(1.19)(P32) and (85)(23,800)(1.1)(P33) %(g/mol) (Table 1). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S13 in the Supporting Information.

S4.3 Synthesis of the PnBVE-b-PCEVE-b-PSiEGVE at -20°C. The polymerization experiments were carried out as described above in the general procedure using the stock solution nBEA1 (0.09 M in n-Hex), nBEA2 (0.08 M in n-Hex), DtBP (0.008 M in n-Hex) and $Al_2Et_3Cl_3$ (0.8 M in n-Hex). In the polymerization experiments carried out with 4 and 9 mM of nBEA, 12.6(2)(2)(2)(0)(1)(0.4)(P34) and

13.8(2)(2)(0)(1)(1)(0.2)(P35) mL(mL)(mL)(mL)(mL)(mL) of nHex(nBVE)(AcOEt)(nBEA1)(nBEA2)(DtBP)(Al$_2$Et$_3$Cl$_3$)(sample) were used to prepare living PnBVE cations of DP 88 and 200, respectively; $x^{nBVE}_{48h} = 100\%$, Mn$_{(GPC)}$(PDI)(series) = 8,800(1.08)(P34) and 20,100(1.09)(P35) g/mol. After 48 h, PnBVE$_{90}$-b-PCEVE$_{98}$ and PnBVE$_{200}$-b-PCEVE$_{216}$ were prepared by the addition of 3.4 mL of CEVE (50% v/v in n-Hex) containing of $M_{n(GPC)}$ DtBP (0.1 mL, 0.008M in n-Hex) on living PnBVE cations; $x^{CEVE}_{120h} = 100\%$, Mn$_{(GPC)}$(PDI)(series) = 17,800(1.17)(P34) and 43,200(1.18)(P35) g/mol. After 120 h, 4 mL of SiEGVE (50 % v/v in nHx) were added to the living PnBVE$_{90}$-b-PCEVE$_{98}$ cations and 7.6 mL of SiEGVE (50 % v/v in nHx) were added to PnBVE$_{200}$-b-PCEVE$_{216}$ cations, to obtain at -20°C PnBVE$_{90}$-b-PCEVE$_{98}$-b-PSieGVE$_{24}$ (P34) and PnBVE$_{200}$-b-PCEVE$_{216}$-b-PSieGVE$_{192}$ (S34), respectively; x^{SiEGVE}_{t}(time)(Mn$_{(GPC)}$)(PDI)(series) = (60)(120)(23,800)(1.17)(P34) and 100(240)(90,600)(1.18)(P35) %(h)(g/mol). For additional experimental data, see Table 1 and Tables S33-34 in the Supporting Information. The 400 MHz ^{1}H and ^{13}C NMR spectra of P34 and P35 are shown in Figure S14 and S15 in the Supporting Information.

S4.4 Synthesis of the PCEVE-b-PnBVE-b-PCEVE at -20°C. The polymerization experiments were carried out as described above in the general procedure. In the polymerization experiments carried out with 4 mM of cHDMEA (2 mL, 0.04 M in n-Hex) and x = 2 and 5.2 mL of nBVE, n-Hex (14.8-x mL), AcOEt (2.0 mL), DtBP (1.0 mL, 0.008 M in n-Hex) and Al$_2$Et$_3$Cl$_3$ (0.2 mL, 0.8 M in n-Hex) were used at -20°C for target DP of 200 and 500, respectively; x^{nBVE}(time)(Mn$_{(GPC)}$)(PDI)(series) = 100(42)(21,000)(1.06)(P36), 100(48)(55,100)(1.07)(P37) and 100(48)(53,200)(1.07)(P38) %(h)(g/mol). After 48 h, 3.4 mL of CEVE (50%v/v in n-Hex) containing of DtBP (0.1mL, 0.008M in n-Hx) were added to living α,ω-PnBVE cations for the preparation of PCEVE$_{82}$-*b*-PnBVE$_{200}$-*b*-PCEVE$_{82}$ (P36) and PCEVE$_{98}$-*b*-PnBVE$_{500}$-*b*-PCEVE$_{98}$ (P37), respectively. Similarly, PCEVE$_{20}$-*block*-PnBVE$_{500}$-*b*-PCEVE$_{20}$ (P38) was prepared using 0.4 mL of CEVE (50% v/v in nHex). The results obtained for the synthesis of PCEVE$_{82}$-*b*-PnBVE$_{200}$-*b*-PCEVE$_{82}$, PCEVE$_{98}$-*b*-PnBVE$_{500}$-*b*-PCEVE$_{98}$ and PCEVE$_{20}$-*b*-PnBVE$_{500}$-*b*-

PCEVE$_{20}$ were as follows: x^{CEVE}(time)($M_{n(GPC)}$)(PDI)(sample) = 81(72)(38,700)(1.2)(P36), 100(120)(75,700)(1.09)(P37) and 100(120)(57,100)(1.09)(P38) %(g/mol). For additional experimental data, see Table 2. The 400 MHz ^{1}H and ^{13}C NMR spectra of P36, P37 and P38 are shown in Figures S16-S18 in the Supporting Information.

S4.5 Synthesis of the PSiEGVE-b-PnBVE-b-PSiEGVE at -20°C. The polymerization experiments were carried out as described above in the general procedure. In the polymerization experiments carried out with 4 mM of **cHDMEA** (2 mL, 0.04 M in n-Hex) and x = 2 and 5.2 mL of **nBVE,** n-Hex (14.8-x mL), AcOEt (2.0 mL), DtBP (1.0 mL, 0.008 M in n-Hex) and Al$_2$Et$_3$Cl$_3$ (0.2 mL, 0.8 M in n-Hex) were used at -20°C to target a DP of 200 and 500, respectively; x^{nBVE}(time)(Mn$_{(GPC)}$)(PDI)(sample) = 97(42)(21,200)(1.06)(P39), 100(48)(54,800)(1.06)(P40) 100(48)(52,300)(1.06)(P41). After 48 h, 8 and 1 mL of SiEGVE (50% v/v in n-Hex) containing of DtBP (0.1mL, 0.008M in n-Hx) were added to living PnBVE$_{500}$ cations for the preparation of PSiEGVE$_{101}$-*b*-PnBVE$_{500}$-*b*-PSiEGVE$_{101}$ (P39) and PSiEGVE$_{10}$-*b*-PnBVE$_{500}$-*b*-PSiEGVE$_{10}$ (P40), respectively. Similarly, PSiEGVE$_{37}$-*b*-PnBVE$_{200}$-*b*-PSiEGVE$_{37}$ (P41) was prepared using 3 mL of SieGVE (50% v/v in nHex). The results obtained for the synthesis of PSiEGVE$_{101}$-*b*-PnBVE$_{500}$-*b*-PSiEGVE$_{101}$, PSiEGVE$_{10}$-*b*-PnBVE$_{500}$-*b*-PSiEGVE$_{10}$ and PSiDEGVE$_{37}$-*b*-PnBVE$_{200}$-*b*-PSiDEGVE$_{37}$ are $x^{SiDEGVE}_{time}$(time)($M_{n(GPC)}$)(PDI)(series) = 75(120)(38,200)(1.15)(P39) , 100(384)(105,600)(1.12)(P40) and 100(384)(58,000)(1.09)(P41) %(h)(g/mol). For additional experimental data, see Table 2 and Tables S39-S41 in the Supporting Information. The 400 MHz ^{1}H and ^{13}C NMR spectra of P39, P40 and P41 are shown in Figures S19-S21 in the Supporting Information.

S4.6 Synthesis of the PSiEGVE-b-PCEVE-b-PnBVE-b-PCEVE-b-PSiEGVE at -20°C. The polymerization experiments were carried out as described above in the general procedure. In the polymerization experiments carried out with 4 mM of cHDMEA (2.0 mL, 0.04 M in n-Hex)**,** n-Hex (14.8-x mL), nBVE (x=5.2 mL), AcOEt (2.0 mL), DtBP (1.0 mL, 0.008 M in n-Hex) and Al$_2$Et$_3$Cl$_3$ (0.2 mL, 0.8 M in n-Hex) were used at -20°C for target DP of 500; $M_{n(GPC)}$ = 53,000 g/mol, PDI = 1.08 and yield =

100% (P42). After 48 h, 3.4 mL of CEVE (50% v/v in n-Hex) containing DtBP (0.1mL, 0.008M in n-Hx) were added to living PnBVE cations for the preparation of $PCEVE_{97}$-b-$PnBVE_{500}$-b-$PCEVE_{97}$; $x_{120h}^{CEVE} = 100\%$, $M_{n(GPC)} = 73,200$ g/mol, PDI = 1.09 (P42). After 120 h, 4 mL of SiEGVE (50 % v/v in n-Hex) were used at -20°C to obtained the $PSiEGVE_{100}$-b-$PCEVE_{97}$-b-$PnBVE_{500}$-b-$PCEVE_{97}$-b-$PSiEGVE_{100}$; $x_{384h}^{SiDEGVE} = 100\%$, $M_{n(GPC)} = 98,400$ g/mol, PDI = 1.14 (sample P42). For additional experimental data, see Table 2 and Table S41 in the Supporting Information. The 400 MHz ^{1}H and ^{13}C NMR spectra of P42 are shown in Figure S22 in the Supporting Information.
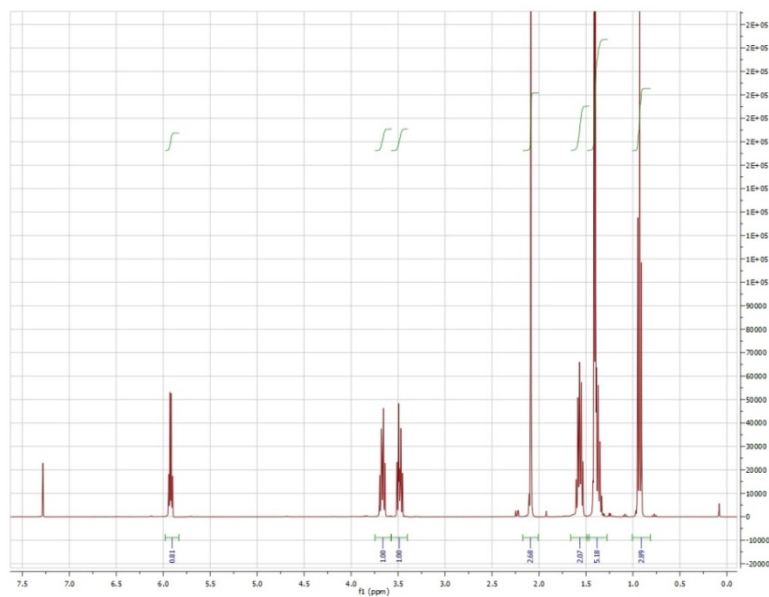
^{1}H NMR (CDCl$_3$, δ): 5.9 (m,1 H, -OC*H*(CH$_3$)O), 3.7 (m, 1 H, OC*H*HC), 3.4 (m, 1 H, OCH*H*C), 2.05 (s,3 H, OCOC*H*$_3$), 1.55 (m, 1 H, CH$_3$CH$_2$C*H*$_2$-), 1.4 (d, 2 H, CH$_3$C*H*$_2$-), 1.4 (d, 3 H, -OCH(C*H*$_3$)O), 0.9 (d, 3 H, C*H*$_3$CH$_2$-).

Fig S1a: 400 MHz ^{1}H NMR spectrum of nBVE-Acetic Acid Adduct (nBEA).
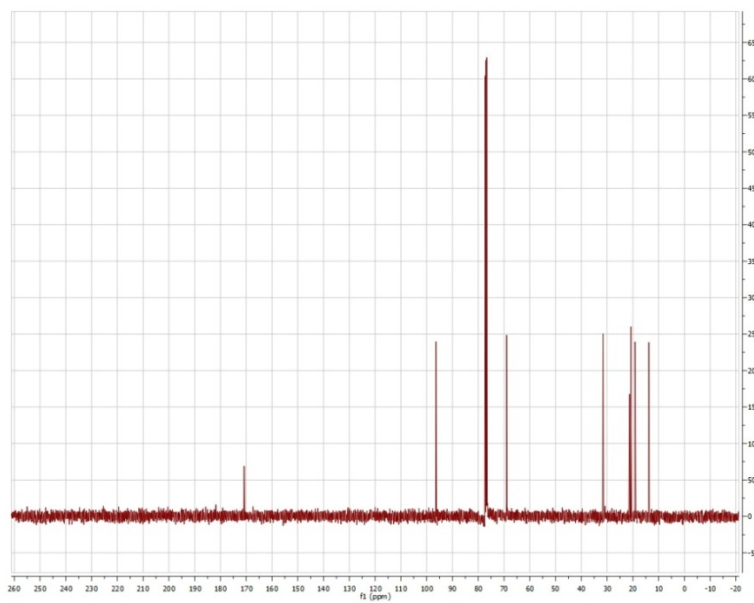
^{13}C NMR (CDCl$_3$, δ): 171.03 (-O*C*OCH$_3$), 96.62 (-O*C*H(CH$_3$)O-), 69.19 (-O*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.78 (-OCH$_2$*C*H$_2$CH$_2$CH$_3$), 21.51 (-OCO*C*H$_3$), 20.99 (-OCH(*C*H$_3$)O-), 19.37 (-OCH$_2$CH$_2$*C*H$_2$CH$_3$), 14.01 (-OCH$_2$CH$_2$CH$_2$*C*H$_3$).

Figure S1b: 400 MHz ^{13}C NMR spectrum of nBVE-Acetic Acid Adduct (nBEA)
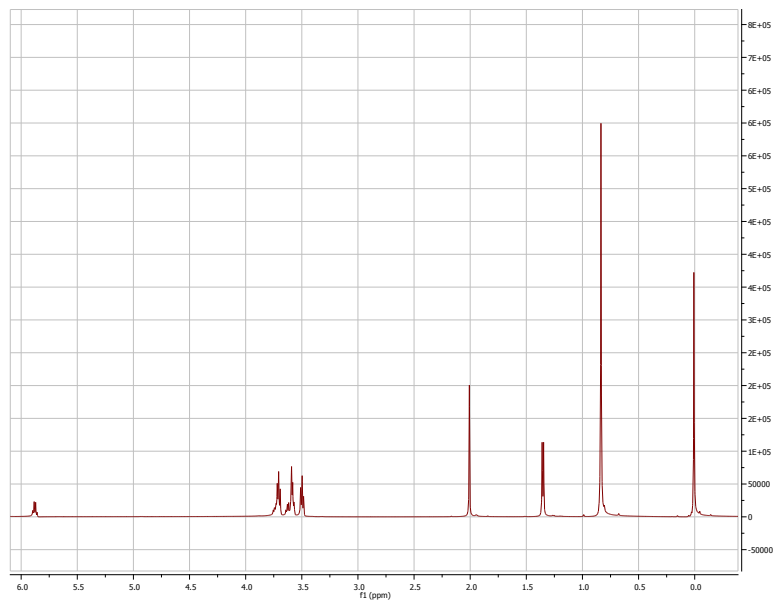
^{1}H NMR (CDCl$_3$, δ): 5.9 (m,1 H, -OC*H*(CH$_3$)O), 3.5 (m, 2 H, -OC*H$_2$*CH$_2$OCH$_2$CH$_2$OSi), 3.57-3.75 (m, 6 H, OCH$_2$C*H$_2$*OC*H$_2$*C*H$_2$*OSi), 2 (m, 3 H, -OCOC*H$_3$*), 1.35 (d, 3 H, C*H$_3$*CH(OCOCH$_3$)O-), 0.84 (s, 12 H, -OSi(CH$_3$)$_2$C(C*H$_3$*)$_3$) and 0.03 (s, 6 H, -OSi(C*H$_3$*)$_2$C(CH$_3$)$_3$).

Fig. S2a: 400 MHz ^{1}H NMR spectrum of tBDMSiEGVE-Acetic Acid Adduct (tBDMSiEGEA).
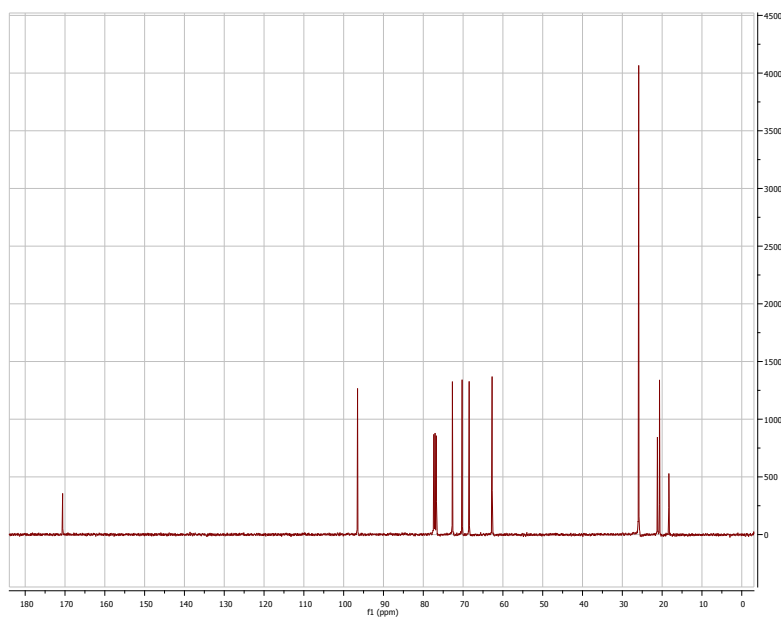
^{13}C NMR (CDCl$_3$, δ): 170.67 (-OC*OCH$_3$), 96.56 (-OCH(CH$_3$)O-), 72.70 (-OCH$_2$CH$_2$OC*H$_2$*CH$_2$OSi), 70.26 (-OCH$_2$C*H$_2$*OCH$_2$CH$_2$OSi), 25.91 (-OSi(CH$_3$)$_2$C(C*H$_3$*)$_3$), 21.23 (-OCOC*H$_3$*), 20.68 (-OSi(CH$_3$)$_2$*C*(CH$_3$)$_3$), 18.34 (C*H$_3$*CH(OCOCH$_3$)O-) and - 5.3 (-OSi(C*H$_3$*)$_2$C(CH$_3$)$_3$).

Fig. S2b: 400 MHz ^{13}C NMR spectrum of tBDMSiEGVE -Acetic Acid Adduct (tBDMSiEGEA).
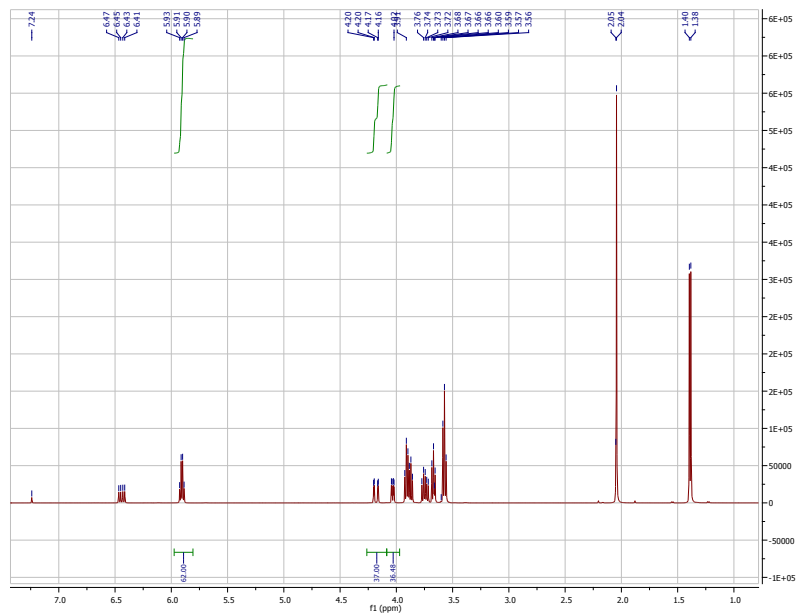
^{1}H NMR (CDCl$_3$, δ): 5.9 (m,1 H, -OC*H*(CH$_3$)O), 3.9 (m, 2 H, -OC*H*$_2$CH$_2$Cl), 3.57 (m, 6 H, OCH$_2$C*H*$_2$Cl), 2.04 (m, 3 H, -OCOC*H*$_3$) and 1.38 (d, 3 H, C*H*$_3$CH(OCOCH$_3$)O-).

Fig. S3a: 400 MHz ^{1}H NMR spectrum of CEVE-Acetic Acid/CEVE (62/38) Adduct (CEEA).
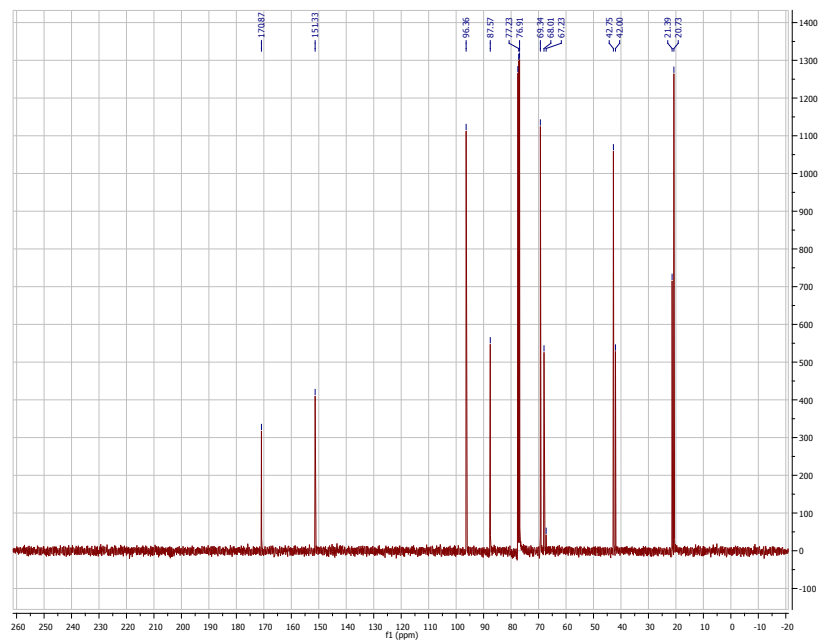
^{13}C NMR (CDCl$_3$, δ): 170.87 (-O*C*OCH$_3$), 96.36 (-O*C*H(CH$_3$)O-), 69.34 (-O*C*H$_2$CH$_2$Cl), 42.75 (-OCH$_2$*C*H$_2$Cl), 21.39 (-OCO*C*H$_3$) and 20.7 (-OCH(*C*H$_3$)O).

Fig. 3b: 400 MHz ^{13}C NMR spectrum of CEVE-Acetic Acid/CEVE (62/38) Adduct (CEEA).
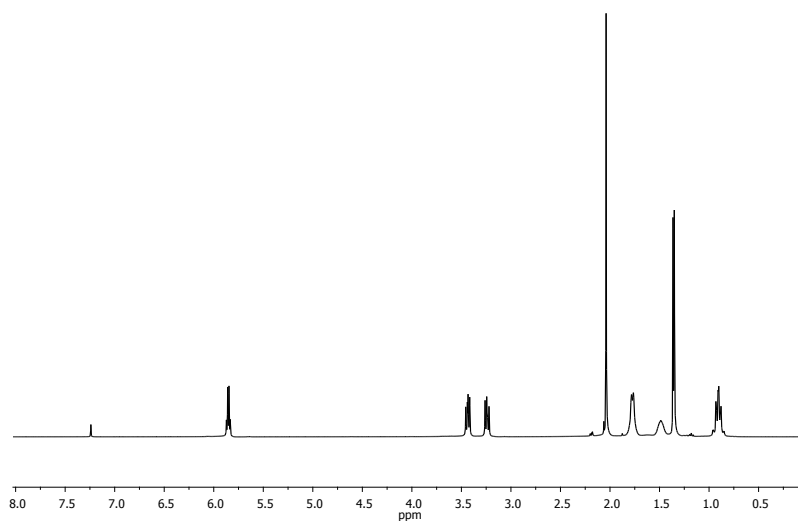
^{1}H NMR (CDCl$_3$, δ): 5.86 (m, 2 H, -OC*H*(CH$_3$)O-), 3.43 and 3.26 (m, 4 H, eq, CH$_3$CH(O-)OC*H*$_2$-), 2.04 (s, 6 H, -OCOC*H*$_3$), 1.76 and 0.93 (m, 8 H, -OCH$_2$CH(C*H*$_2$C*H*$_2$-)C*H*$_2$C*H*$_2$-), 1.48 (m, 2 H, -OCH$_2$C*H*(CH$_2$-)CH$_2$-), 1.36 (d, 6 H, C*H*$_3$CH(O-)O-).

Fig. S4a: 400 MHz ^{1H} NMR spectrum of cHMDEA
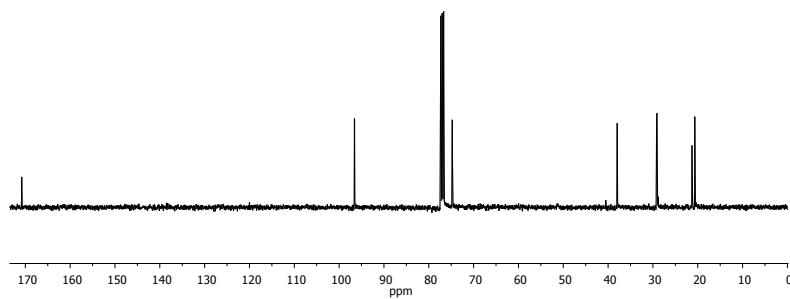
^{13}C NMR (CDCl$_3$, δ): 171.03 (2 C, -OCOCH$_3$), 96.5 (2 C, -OCH(CH$_3$)O-), 74.7 (2 C, -CH$_3$CH(O-)OCH$_2$-), 37.9 (2 C, CH$_3$CH(O-)OCH$_2$CH(CH$_2$-)CH$_2$-), 29.15 and 29.09 (4 C, -OCH$_2$CH(CH$_2$CH$_2$-)CH$_2$CH$_2$-), 21.3 (2 C, -OCOCH$_3$), 20.7 (2 C, -CH$_3$CH(O-)O-).

Fig. S4b: 400 MHz ^{13}C NMR spectrum of cHMDEA.
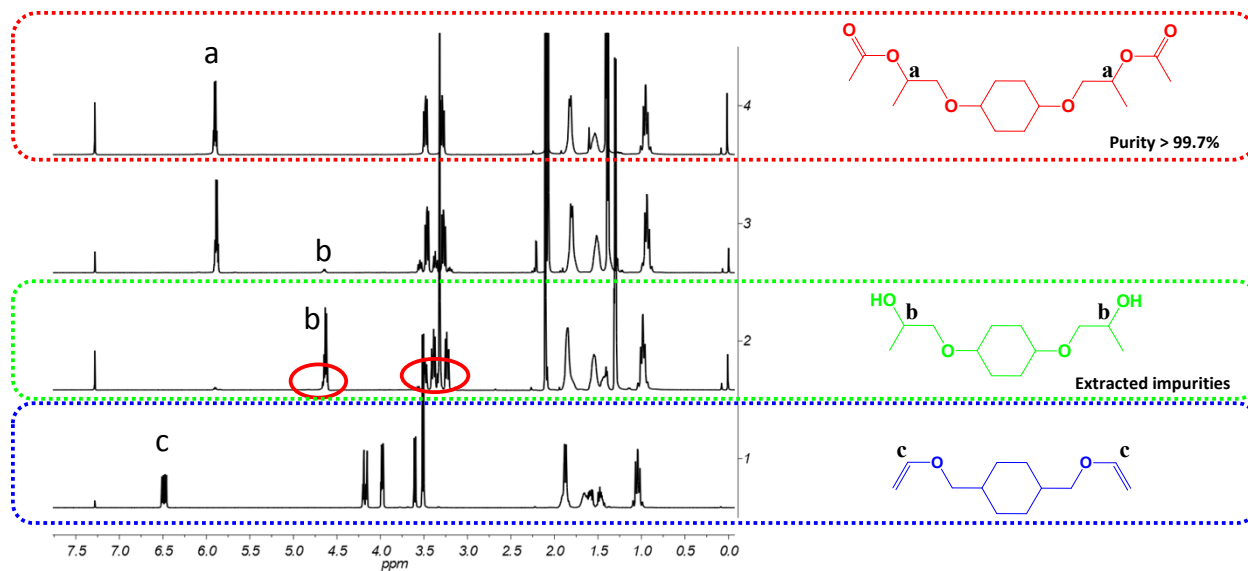
Figure S4c: 400 MHz ^{13}C NMR spectrum of cHMDEA after recrystallization (purity > 99.7%).
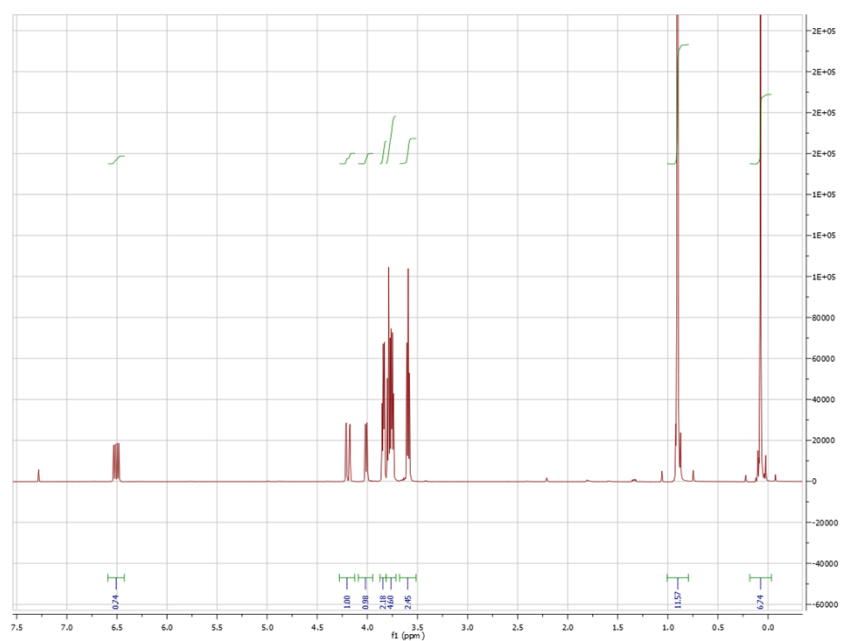
^{1}H NMR (CDCl$_3$, 30 °C, δ): 0.05 (s, 6H, -Si(CH_3)$_2$C(CH$_3$)$_3$), 0.83 (s, 9H, -Si(CH$_3$)$_2$C(CH_3)$_3$), 3.56 (m, 4H, -OCH$_2$CH$_2$OCH$_2$CH$_2$OSi), 3.71 (m, 2H, -OCH$_2$CH_2OCH$_2$CH$_2$OSi), 3.75 (m, 2H, OCH$_2$CH$_2$OCH$_2$CH_2OSi), 3.81 (m, 2H, -OCH_2CH$_2$OCH$_2$CH$_2$OSi), 3.97 and 4.15 (m, 2H, H_2C=), 6.48 (q, 1H,=CH-O-).

Fig. S5: 400 MHz ^{1}H NMR spectrum of tBDMSiEGVE.
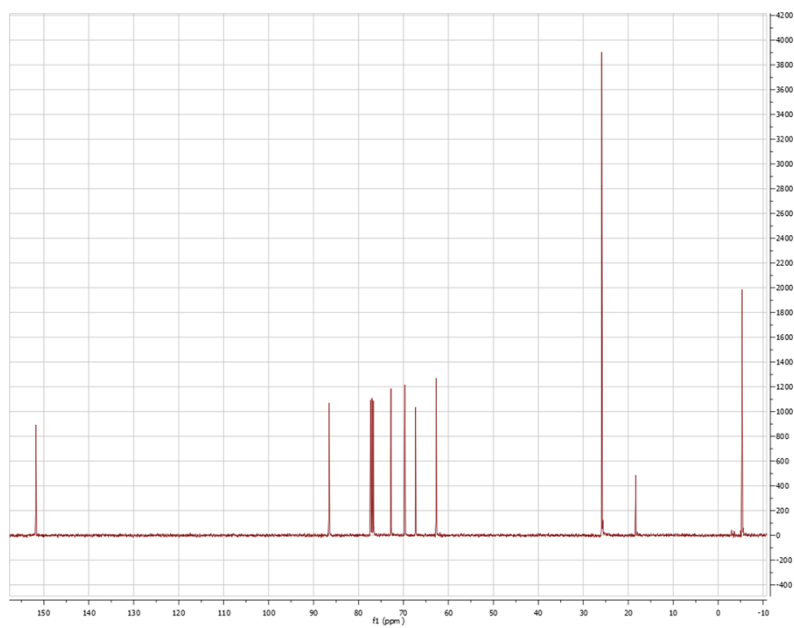
^{13}C NMR (CDCl$_3$, 30°C, δ): -3.36 (-Si(CH$_3$)$_2$C(CH$_3$)$_3$), 18.57 ((-Si(CH$_3$)$_2$C(CH$_3$)$_3$), 26.13 (-Si(CH$_3$)$_2$C(CH$_3$)$_3$), 72.57 (-OCH$_2$CH$_2$OCH$_2$CH$_2$OSi), 69.92 (-OCH$_2$CH$_2$OCH$_2$CH$_2$OSi), 62.96 (-OCH$_2$CH$_2$OCH$_2$CH$_2$OSi), 67.52 (-OCH$_2$CH$_2$OCH$_2$CH$_2$OSi), 86.77 (m, 2H, H$_2$C=), 151.99 (=CH-O-).

Fig. S5: 400 MHz ^{13}C NMR spectrum of tBDMSiEGVE
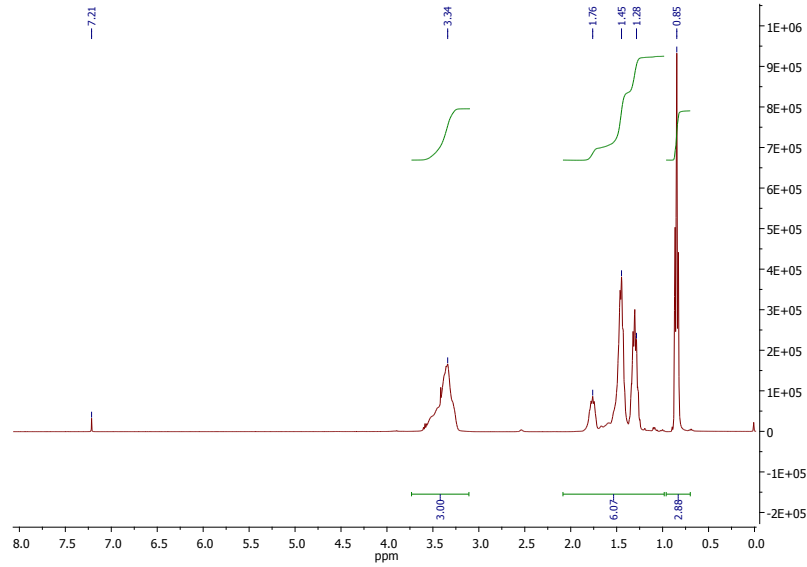
^{1}H NMR in (CDCl$_3$, δ): 3.5 (m, 2 H, -CH$_2$CH(OCH$_2$-)-), 3 (m, 1 H,-CH$_2$CH(O-)-), 1.79 (m, 1 H,-CHHCH(O-)-), 1.5 (m, 1 H,-CHHCH(O-)-), 1.47 (m, 2 H, CH$_3$CH$_2$CH$_2$-), 1.33 (m, 2 H, CH$_3$CH$_2$-), 0.87 (d, 3 H, CH$_3$CH$_2$-).

Fig. S7: 400 MHz ^{1}H NMR spectrum of PnBVE in CDCl$_3$
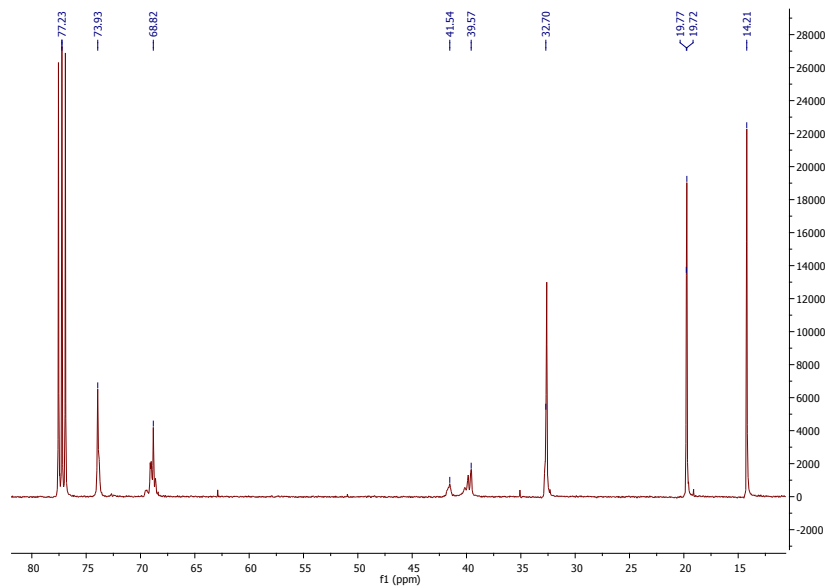
^{13}C NMR (CDCl$_3$, δ): 73.9 (-CH$_2$CH(O-)-), 68.4-69.1 (-CH$_2$CH(OCH$_2$-)-), 41.5-39.5 9 (-CH$_2$CH(O-)-), 32.6 (CH$_3$CH$_2$CH$_2$-), 19.7 (CH$_3$CH$_2$CH$_2$-), 14.21 (CH$_3$CH$_2$CH$_2$-).

Fig. S7: 400 MHz ^{13}C NMR spectrum of crude PnBVE in CDCl$_3$
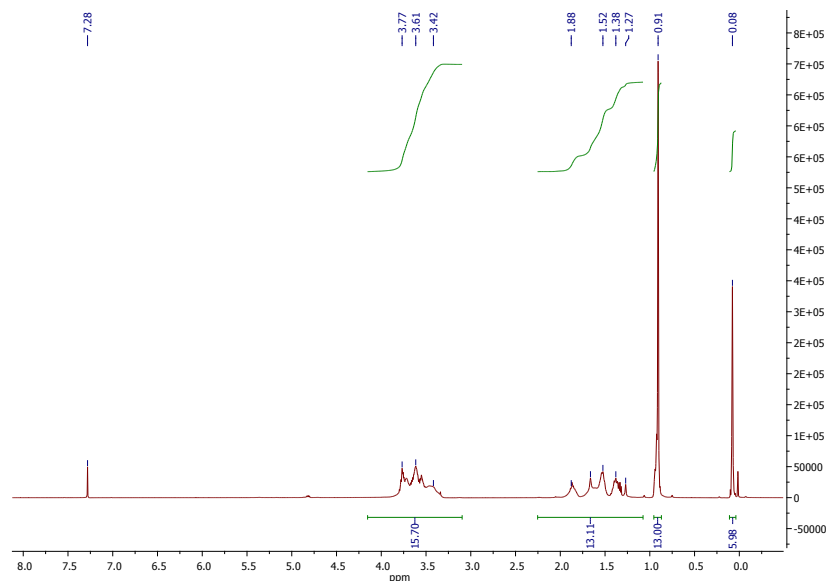
^{1}H NMR (CDCl$_3$, 30 °C, δ): 0.03 (s, 6H, -Si(C*H*$_3$)$_2$C(CH$_3$)$_3$), 0.86 (s, 9H, -Si(CH$_3$)$_2$C(C*H*$_3$)$_3$), 1.5 (m, 1 H,-CH*H*CH(O-)-), 1.78 (m, 1 H,-C*H*HCH(O-)-), 3.37 (m, 1 H, -CH$_2$C*H*(O-)-), 3.49 (m, 4H, -OC*H*$_2$CH$_2$OCH$_2$CH$_2$OSi), 3.55 (m, 2H, -OCH$_2$CH$_2$OC*H*$_2$CH$_2$OSi), 3.72 (m, 2H, OCH$_2$CH$_2$OCH$_2$C*H*$_2$OSi).

Fig. S9: 400 MHz ^{1}H NMR spectrum of PSiDEGVE in CDCl$_3$
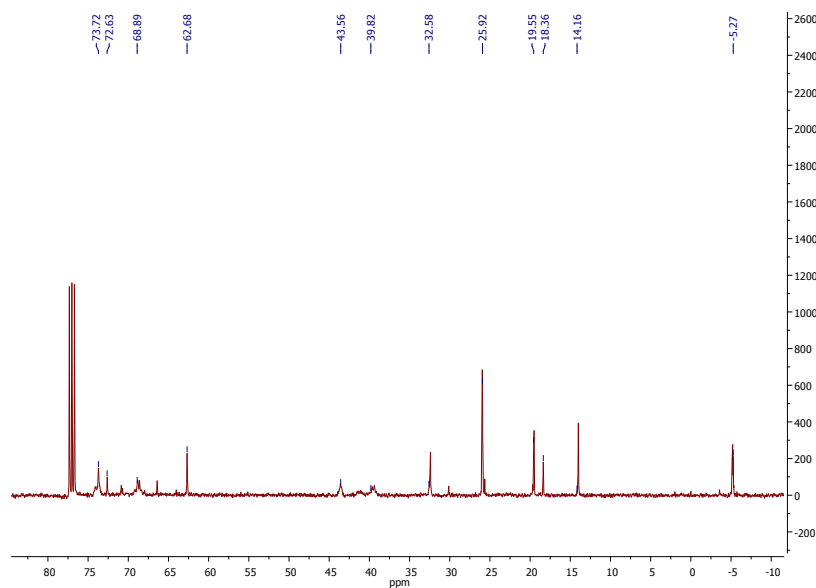
^{13}C NMR (CDCl$_3$, 30°C, δ): -3.36 (-Si(*C*H$_3$)$_2$C(CH$_3$)$_3$), 18.34 ((-Si(CH$_3$)$_2$*C*(CH$_3$)$_3$), 25.96 (-Si(CH$_3$)$_2$C(*C*H$_3$)$_3$), 39.38-41.5 (-*C*H$_2$CH(O-)-), 62.64 (-OCH$_2$CH$_2$O*C*H$_2$CH$_2$OSi), 68.81 (-O*C*H$_2$CH$_2$O*C*H$_2$CH$_2$OSi), 70.87 (-OCH$_2$*C*H$_2$OCH$_2$CH$_2$OSi), 72.60 (-OCH$_2$CH$_2$OCH$_2$*C*H$_2$OSi), 73.71 5 (-CH$_2$*C*H(O-)-).

Fig. S9: 400 MHz ^{13}C NMR spectrum of PSiDEGVE in CDCl$_3$
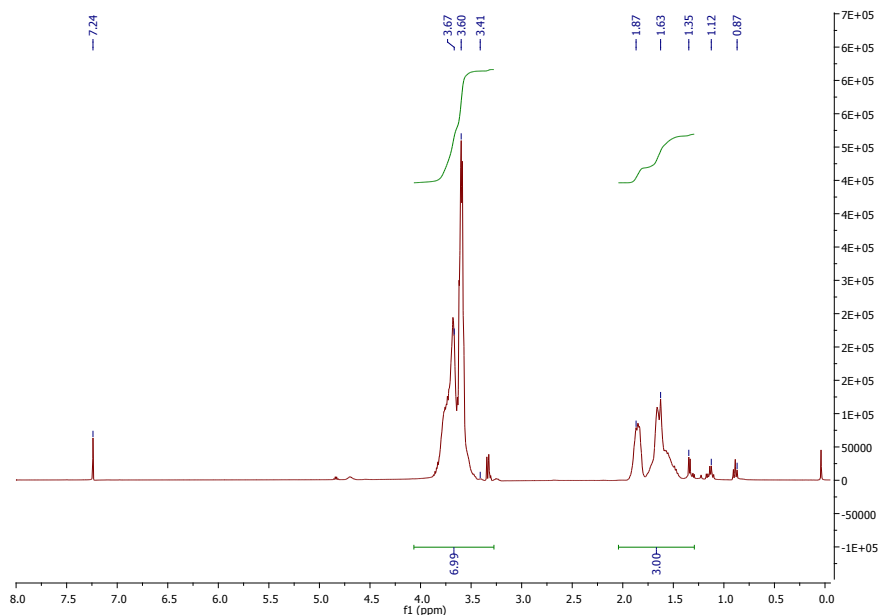
^{1}H NMR (CDCl$_3$, δ): 3.8 (m, 1 H, (ClCH$_2$C*H*$_2$O-), 3.72 (m, 1 H, (ClC*H*$_2$CH$_2$O-), 3.63 (s, 1 H,-CH$_2$C*H*(O-)-), 1.89 (m, 1 H,-C*H*HCH(O-)-), 1.67 (m, 1 H,-CH*H*CH(O-)-).

Fig. S10: 400 MHz ^{1}H NMR spectrum of crude PCEVE in CDCl$_3$
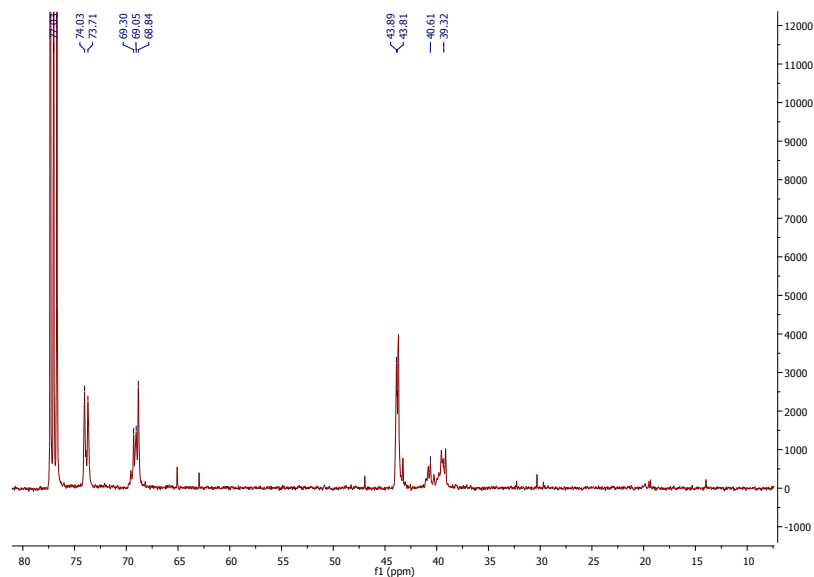
^{13}C NMR (CDCl$_3$, δ): 74.2-73.9 (-CH$_2$C*H*(O-)-), 69.5-69.1 (ClCH$_2$C*H*$_2$O-), 43.9 (Cl*C*H$_2$CH$_2$O-), 39.8-40.8 (-*C*H$_2$CH(O-)-).

Fig. S10: 400 MHz ^{1}H NMR spectrum of crude PCEVE in CDCl$_3$

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Fig. 6a. Schlenk reactors used for the synthesis at -20°C in n-hexane of triblocks ABC and pentablocks CBABC terpolymers by living cationic polymerization of vinyl ether by sequential monomer addition.

Figure 6b. Schlenk reactors, equipped with a sampling ampoule, used for the synthesis of block triblocks ABC and pentablocks CBABC terpolymers by living cationic polymerization of vinyl ether monomer by sequential monomer addition.

Table S1: Results from the polymerization of nBVE initiated by 1/2 n/n cHMDEA/$Al_2Et_3Cl_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

[nBVE]$_0$ = 2 M, [AcOEt]$_0$ = 1 M, [cHMDEA]$_0$ = 4 mM, [$Al_2Et_3Cl_3$]$_0$ = 8 mM and [DtBP]$_0$ = 0.4 mM.

Series	Time (h)	x_{time}^{VE} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P1.1	1h40mn	16.2	8,110	8,780	1.14
P1.2	3h20mn	39	19,530	21,000	1.14
P1.3	5h	48.7	24,400	26,300	1.12
P1.4	7h	58.4	29,300	31,600	1.1
P1.5	28h	97.4	48,700	54,400	1.09
P1.6	32h	100	50,100	55,000	1.08

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= [nBVE]$_0$/[cHMDEA]$_0$×x_{time}^{VE}×100.16 g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S2: Results from the polymerization of nBVE initiated by 1/1 n/n nBEA/$Al_2Et_3Cl_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

[nBVE]$_0$ = 0.77 M, [AcOEt]$_0$ = 1 M, [nBEA]$_0$ = 4 mM, [$Al_2Et_3Cl_3$]$_0$ = 4 mM and [DtBP]$_0$ = 0.4 mM.

Series	Time (h)	x_{time}^{nBVE} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P2.1	6h45mn	41	7,900	8,220	1.14
P2.2	10h	54	10,400	10,720	1.1
P2.3	11h10	58	11,200	11,400	1.09
P2.4	12h45	63	12,100	12,100	1.09
P2.5	20h40	80	15,400	18,100	1.08
P2.6	41h15	96	18,500	21,400	1.08

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= [nBVE]$_0$/[nBEA]$_0$×x_{time}^{nBVE}×100.16 g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S3: Results from the polymerization of SiDEGVE initiated by 1/1 n/n nBEA/$Al_2Et_3Cl_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

$[SiDEGVE]_0 = 0.32$ M, $[AcOEt]_0 = 1$ M, $[nBEA]_0 = 4$ mM, $[Al_2Et_3Cl_3]_0 = 4$ mM and $[DtBP]_0 = 0.4$ mM.

Series	Time (h)	$x^{SiDEGVE}_{time}$ [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P3.1	36	21	4,160	4,500	1.14
P3.2	50	30	5,940	6,200	1.12
P3.3	125	62	12,280	13,000	1.09
P3.4	260	87	17,230	17,500	1.09
P3.5	400	97	18,820	19,400	1.08

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] $M_{nth} = [SiDEGVE]_0/[nBEA]_0 \times x^{SiDEGVE}_{time} \times 246.42$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S4: Results from the polymerization of SiDEGVE initiated by 1/1 n/n SiDEGEA/$Al_2Et_3Cl_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

$[SiDEGVE]_0 = 0.32$ M, $[AcOEt]_0 = 1$ M, $[SiDEGEA]_0 = 4$ mM, $[Al_2Et_3Cl_3]_0 = 4$ mM and $[DtBP]_0 = 0.4$ mM.

Series	Time (h)	$x^{SiDEGVE}_{time}$ [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P4.1	13	10	1,980	2,500	1.2
P4.2	22	16.9	3,350	3,800	1.18
P4.3	38	27.3	5,400	5,700	1.16
P4.4	167	75.3	14,900	15,000	1.15
P4.5	384	96	19,000	19,200	1.14
P4.6	420	98	19,800	20,500	1.14

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] $M_{nth} = [SiDEGVE]_0/[SiDEGEA]_0 \times x^{SiDEGVE}_{time} \times 246.42$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S5: Results from the homopolymerization of SiDEGVE initiated by 1/1 n/n nCEEA/$Al_2Et_3Cl_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

$[SiDEGVE]_0 = 0.32$ M, $[AcOEt]_0 = 1$ M, $[nBEA]_0 = 4$ mM, $[Al_2Et_3Cl_3]_0 = 4$ mM and $[DtBP]_0 = 0.4$ mM.

Series	Time (h)	$x^{SiDEGVE}_{time}$ [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P5.1	80	42	8,320	9,100	1.16
P5.2	160	68	13,420	14,300	1.13
P5.3	400	94	18,620	20,100	1.12
P5.4	500	98	19,800	22,000	1.12

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] $M_{nth} = [SiDEGVE]_0/[CEEA]_0 \times x^{SiDEGVE}_{time} \times 246.42$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S6: Results from the homopolymerization of CEVE initiated by 1/1 n/n $PnBVE_{95}+/Al_2Et_3Cl_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

$[CEVE]_0 = 0.32$ M, $[AcOEt]_0 = 1$ M, $[PnBVE_{95}+]_0 = 4$ mM, $[Al_2Et_3Cl_3]_0 = 4$ mM and $[DtBP]_0 = 0.4$ mM. Time of polymerization of $t=120$h.

Series	Time (h)	x^{CEVE}_{time} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P7.0 [d]	0	0	N.A.	9,500	1.09
P6.1	14	37	16,500	16,900	1.09
P6.2	24	54	19,700	20,300	1.1
P6.3	42	75	23,670	24,500	1.09
P6.4	120	98	28,020	29,100	1.08

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] $M_{nth} = [CEVE]_0/[PnBVE_{95}+]_0 \times x^{CEVE}_{120h} \times 106.2$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

[d] Experimental conditions : Living $PnBVE_{100}$ cation ($[nBVE]_0 = 0.87$ M, $[nBEA]_0 = [Al_2Et_3Cl_3]_0 = 4.34$ mM), $[AcOEt]_0 = 1.09$ M $[DtBP]_0 = 0.44$ mM , $V_T = 18.4$ mL, $x^{nBVE}_{42h} = 100\%$, $Mn_{(GPC)} = 9,500$ g/mol; PDI = 1.08)

Table S8: Results from the dependence of $M_{n(GPC)}$ and $M_{w(GPC)}/M_{n(GPC0)}$ *vs* [nBVE]$_0$/[cHMDEA]$_0$x x^{nBVE}_{46h}, from the homopolymerization of nBVE initiated by 1/2 n/n nBEA/Al$_2$Et$_3$Cl$_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

[nBVE]$_0$ = 0.38-3.08 M, [AcOEt]$_0$ = 1 M, [cHMDEA]$_0$ = 4 mM, [Al$_2$Et$_3$Cl$_3$]$_0$ = 8 mM and [DtBP]$_0$ = 0.4 mM. Time of polymerization of *t*=46h.

Series	[nBVE]$_0$	Targeted DP	x^{nBVE}_{46h} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P8.1	0.38	95	100	9,270	8,900	1.1
P8.2	0.57	142.5	100	14,460	14,800	1.09
P8.3	0.76	190	100	19,250	23,200	1.08
P8.4	1.15	287.5	100	28,900	29,800	1.09
P8.5	1.92	480	100	46,200	46,500	1.08
P8.6	3.08	770	100	77,100	81,700	1.08

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= [nBVE]$_0$/[cHMDEA]$_0$xx^{nBVE}_{46h} ×100.16 g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S9: Results from the dependence of $M_{n(GPC)}$ and $M_{w(GPC)}/M_{n(GPC0)}$ *vs* [nBVE]$_0$/[nBEA]$_0$ x x^{nBVE}_{46h}, from the homopolymerization of nBVE initiated by 1/1 n/n nBEA/Al$_2$Et$_3$Cl$_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

[nBVE]$_0$ = 0.38-3.12 M, [AcOEt]$_0$ = 1 M, [nBEA]$_0$ = 4 mM, [Al$_2$Et$_3$Cl$_3$]$_0$ = 4 mM and [DtBP]$_0$ = 0.4 mM. Time of polymerization of *t*=46h.

Series	[nBVE]$_0$	Targeted DP	x^{nBVE}_{46h} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]

P9.1	0.38	95	99	9,500	10,100	1.07
P9.2	0.78	195	100	19,500	19,500	1.08
P9.3	1.56	390	100	39,000	41,600	1.08
P9.4	3.12	780	100	78,100	80,400	1.07

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] $M_{nth} = [nBVE]_0/[nBEA]_0 \times x^{nBVE}_{46h} \times 100.16$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S10: Results from the dependence of $M_{n(GPC)}$ and $M_{w(GPC)}/M_{n(GPC0}$ *vs* $[SiDEGVE]_0/[nBEA]_0$ x $x^{SiDEGVE}_{420h}$, from the homopolymerization of SiDEGVE initiated by 1/1 n/n nBEA/Al$_2$Et$_3$Cl$_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

$[SiDEGVE]_0$ = 0.38-3.12 M, $[AcOEt]_0$ = 1 M, $[nBEA]_0$ = 4 mM, $[Al_2Et_3Cl_3]_0$ = 4 mM and $[DtBP]_0$ = 0.4 mM. Time of polymerization of t=420h.

Series	$[SiDEGVE]_0$	Targeted DP	x^{SiDEVE}_{420h} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P10.1	0.2	50	98	12,300	11,500	1.16
P10.2	0.4	100	97	24,600	21,400	1.14
P10.3	0.6	150	98	36,970	39,100	1.15
P10.4	0.8	200	98	49,300	47,200	1.15

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] $M_{nth} = [SiDEGVE]_0/[nBEA]_0 \times x^{SiDEGVE}_{420h} \times 246.42$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S11: Results from the dependence $M_{n(GPC)}$ and $M_{w(GPC)}/M_{n(GPC0}$ *vs* $[CEVE]_0/[PnBVE_{95}+]_0$ x x^{CEVE}_{120h}, from the homopolymerization of CEVE initiated by 1/1 n/n PnBVE$_{95}$+/Al$_2$Et$_3$Cl$_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

$[CEVE]_0$ = 0.2 – 1.6 M, $[AcOEt]_0$ = 1 M, $[PnBVE+]_0$ = 4 mM, $[Al_2Et_3Cl_3]_0$ = 4 mM and $[DtBP]_0$ = 0.4 mM. Time of polymerization of t=120h.

Series	$[CEVE]_0$	Targeted DP	x^{CEVE}_{120h} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]

P7.0 [d]	0	0	N.A.	N.A.	9,500	1.08
P11.1	0.2	50	100	14,800	14,200	1.13
P11.2	0.4	100	99	20,100	20,100	1.12
P11.3	0.8	200	100	30,700	30,200	1.1
P11.4	1.6	290	100	40,300	36,000	1.3

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] $M_{nth} = [CEVE]_0/[nBEA]_0 \times x^{CEVE}_{120h} \times 106.2$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

[d] Experimental conditions : Living PnBVE$_{100}$ cation ([nBVE]$_0$ = 0.87 M, [nBEA]$_0$ = [Al$_2$Et$_3$Cl$_3$]$_0$ = 4.34 mM), [AcOEt]$_0$ = 1.09 M [DtBP]$_0$ = 0.44 mM , V_T = 18.4 mL, x^{nBVE}_{42h} = 100%, Mn$_{(GPC)}$ = 9,500 g/mol; PDI = 1.08)

Table S12: Results from the homopolymerization of nBVE initiated by 1/1 n/n nBEA/Al$_2$Et$_3$Cl$_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in toluene at -20°C.

[nBVE]$_0$ = 0.77 M, [AcOEt]$_0$ = 1 M, [nBEA]$_0$ = 4 mM, [Al$_2$Et$_3$Cl$_3$]$_0$ = 4 mM and [DtBP]$_0$ = 0.4 mM.

Series	Time (h)	x^{nBVE}_{time} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P12.1	25	53	10,200	10,300	1.13
P12.2	31	61	11,760	12,200	1.16
P12.3	35	66	12,730	12,600	1.18
P12.4	40	70	13,500	13,000	1.22
P12.5	57	82	15,810	15,600	1.28
P12.6	89	90	17,350	19,100	1.31
P12.7	112	95	18,320	22,000	1.37
P12.8	130	98	18,700	23,100	1.25
P12.9	160	100	19,280	24,500	1.37
P12.10	200	100	19,280	26,800	1.41

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] $M_{nth} = [nBVE]_0/[nBEA]_0 \times x^{nBVE}_{time} \times 100.16$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S13: Results from the homopolymerization of CEVE initiated by 1/1 n/n nBEA/Al$_2$Et$_3$Cl$_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in toluene at -20°C.

[CEVE]$_0$ = 0.8 M, [AcOEt]$_0$ = 1 M, [nBEA]$_0$ = 4 mM, [Al$_2$Et$_3$Cl$_3$]$_0$ = 4 mM and [DtBP]$_0$ = 0.4 mM.

Series	Time (h)	x_{time}^{nBVE} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P13.1	10	9	1,900	1,300	1.24
P13.2	36	28	5,900	4,400	1.21
P13.3	62	43	9,100	6,900	1.28
P13.4	77	50	10,600	8,000	1.31
P13.5	101	61	12,700	9,300	1.34
P13.6	312	94	19,900	20,000	1.35

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] $M_{nth} = [CEVE]_0/[nBEA]_0 \times x_{time}^{CEVE} \times 106.2$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S14: Results from the homopolymerization of SiDEGVE initiated by 1/1 n/n nBEA/Al$_2$Et$_3$Cl$_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in toluene at -20°C.

$[SiDEGVE]_0 = 0.32$ M, $[AcOEt]_0 = 1$ M, $[nBEA]_0 = 4$ mM, $[Al_2Et_3Cl_3]_0 = 4$ mM and $[DtBP]_0 = 0.4$ mM.

Series	Time (h)	$x_{time}^{SiDEGVE}$ [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P14.1	88	21	4,140	6,300	1.07
P14.2	250	54	10,600	10,800	1.09
P14.3	400	58	11,400	11,300	1.12
P14.4	425	64	12,600	14,100	1.15
P14.5	660	82	16,160	14,400	1.18
P14.6	1200	96	18,900	20,300	1.25

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] $M_{nth} = [nBVE]_0/[nBEA]_0 \times x_{time}^{nBVE} \times 246.42$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S15: Results from the homopolymerization of nBVE initiated by 1/1 n/n nBEA/Al$_2$Et$_3$Cl$_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in DCM at -20°C.

[nBVE]$_0$ = 0.77 M, [AcOEt]$_0$ = 1 M, [nBEA]$_0$ = 4 mM, [Al$_2$Et$_3$Cl$_3$]$_0$ = 4 mM and [DtBP]$_0$ = 0.4 mM.

Series	Time (h)	x^{nBVE}_{time} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P15	24	95	18,300	24,800	1.37

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= [nBVE]$_0$/[nBEA]$_0 \times x^{nBVE}_{time} \times$100.16 g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S16: Results from the homopolymerization of CEVE initiated by 1/1 n/n nBEA/Al$_2$Et$_3$Cl$_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in DCM at -20°C.

[CEVE]$_0$ = 0.8 M, [AcOEt]$_0$ = 1 M, [nBEA]$_0$ = 4 mM, [Al$_2$Et$_3$Cl$_3$]$_0$ = 4 mM and [DtBP]$_0$ = 0.4 mM.

Series	Time (h)	x^{nBVE}_{time} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P16	48	87	18,500	23,000	1.41

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= [CEVE]$_0$/[nBEA]$_0 \times x^{nBVE}_{time} \times$106.2 g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S17: Results from the homopolymerization of SiDEGVE initiated by 1/1 n/n nBEA/Al$_2$Et$_3$Cl$_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in DCM at -20°C.

[SiDEGVE]$_0$ = 0.32 M, [AcOEt]$_0$ = 1 M, [nBEA]$_0$ = 4 mM, [Al$_2$Et$_3$Cl$_3$]$_0$ = 4 mM and [DtBP]$_0$ = 0.4 mM.

Series	Time (h)	x^{nBVE}_{time} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P17	72	83	18,300	21,200	1.27

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= [SiDEGVE]$_0$/[nBEA]$_0 \times x^{nBVE}_{time} \times$246.42 g/mol

Table S21: Results from the homopolymerization of nBVE initiated by 1/2 n/n nBEA/$Al_2Et_3Cl_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

$[nBVE]_0$ = 0.385 – 1.5 M, $[AcOEt]_0$ = 1 M, $[nBEA]_0$ = 4 mM, $[Al_2Et_3Cl_3]_0$ = 8 mM and $[DtBP]_0$ = 0.4 mM. Time of polymerization t=48h.

Series	$[nBVE]_0$	Targeted DP	x^{nBVE}_{48h} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P21.1	0.385	96	100	9,640	9,000	1.12
P21.2	0.6	150	100	15,000	12,500	1.11
P21.3	0.77	192	100	19,280	16,720	1.11
P21.4	1.5	375	100	37,600	34,300	1.13

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= $[nBVE]_0/[nBEA]_0 \times x^{nBVE}_{48h} \times$100.16 g/mol

Table S22: Results from the homopolymerization of nBVE initiated by 1/3 n/n nBEA/$Al_2Et_3Cl_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C.

$[nBVE]_0$ = 0.385 – 2 M, $[AcOEt]_0$ = 1 M, $[nBEA]_0$ = 4 mM, $[Al_2Et_3Cl_3]_0$ = 12 mM and $[DtBP]_0$ = 0.4 mM. Time of polymerization t=48h.

Series	$[nBVE]_0$	Targeted DP	x^{nBVE}_{48h} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P22.1	0.385	96	100	9,640	6,900	1.12
P22.2	0.77	192	100	19,300	14,400	1.11
P22.3	1.5	375	100	37,600	27,900	1.11
P22.4	2	500	100	50,000	37,300	1.13

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= $[nBVE]_0/[nBEA]_0 \times x^{nBVE}_{48h} \times$100.16 g/mol

Table S23: Results from the homopolymerization of nBVE initiated by 1/4 n/n nBEA/AlEtCl$_2$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at -20°C. Time of polymerization t=48h.

[nBVE]$_0$ = 1.5 M, [AcOEt]$_0$ = 1 M, [nBEA]$_0$ = 4 mM, [Al$_2$Et$_3$Cl$_3$]$_0$ = 16 mM and [DtBP]$_0$ = 0.4 mM.

Series	[nBVE]$_0$	Targeted DP	x^{nBVE}_{48h} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P23	1.5	375	100	37,600	24,000	1.33

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M$_{nth}$= [nBVE]$_0$/[nBEA]$_0$×x^{nBVE}_{48h} ×100.16 g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S24: Results from the homopolymerization of SiDEGVE initiated by 1/4 n/n nBEA/AlEtCl$_2$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in n-Hex at 0°C.

[SiDEGVE]$_0$ = 0.13 - 0.5 M, [AcOEt]$_0$ = 1 M, [nBEA]$_0$ = 4 mM, [AlEtCl$_2$]$_0$ = 16 mM and [DtBP]$_0$ = 0.4 mM. Time of polymerization t=420h.

Series	[SiDEGVE]$_0$	Targeted DP	$x^{nSiDEGVE}_{420h}$ [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P24.1	0.13	32.5	96	5,500	8,000	1.14
P24.2	0.32	80	98	12,800	19,700	1.07
P24.3	0.5	125	98	30,800	30,800	1.17

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M$_{nth}$= [SiDEGVE]$_0$/[nBEA]$_0$×$x^{SiDEGVE}_{420h}$ ×246.42 g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S25: Results from the homopolymerization of SiDEGVE initiated by 1/4 n/n nBEA/AlEtCl$_2$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in toluene at 0°C.

[SiDEGVE]$_0$ = 0.32 – 0.64 M, [AcOEt]$_0$ = 1 M, [nBEA]$_0$ = 4 mM, [AlEtCl$_2$]$_0$ = 16 mM and [DtBP]$_0$ = 0.4 mM. Time of polymerization t=420h.

Series	[SiDEGVE]$_0$	Targeted DP	$x^{SiDEGVE}_{420h}$ [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P25.1	0.32	80	90	19,700	10,400	1.12
P25.2	0.64	160	91	38,200	19,400	1.21

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= [SiDEGVE]$_0$/[nBEA]$_0$×$x^{SiDEGVE}_{420h}$ ×246.42 g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Table S26: Results from the homopolymerization of CEVE initiated by 1/4 n/n nBEA/AlEtCl$_2$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in toluene at 0°C.

[CEVE]$_0$ = 0.76 - 1.5 M, [AcOEt]$_0$ = 1 M, [nBEA]$_0$ = 4 mM, [AlEtCl$_2$]$_0$ = 16 mM and [DtBP]$_0$ = 0.4 mM. Time of polymerization t=120h.

Series	[CEVE]$_0$	Targeted DP	x^{CEVE}_{120h} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P26.1	0.76	80	100	19,100	4,400	1.06
P26.2	1.5	160	100	37,800	10,170	1.14

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= [CEVE]$_0$/[nBEA]$_0$×x^{CEVE}_{48h} ×106.2 g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Controlled cationic polymerization of nBVE, CEVE and SiDEVE by Al$_2$Et$_3$Cl$_3$ in toluene and in DCM - Molecular weight controlled together with chain-end termination.
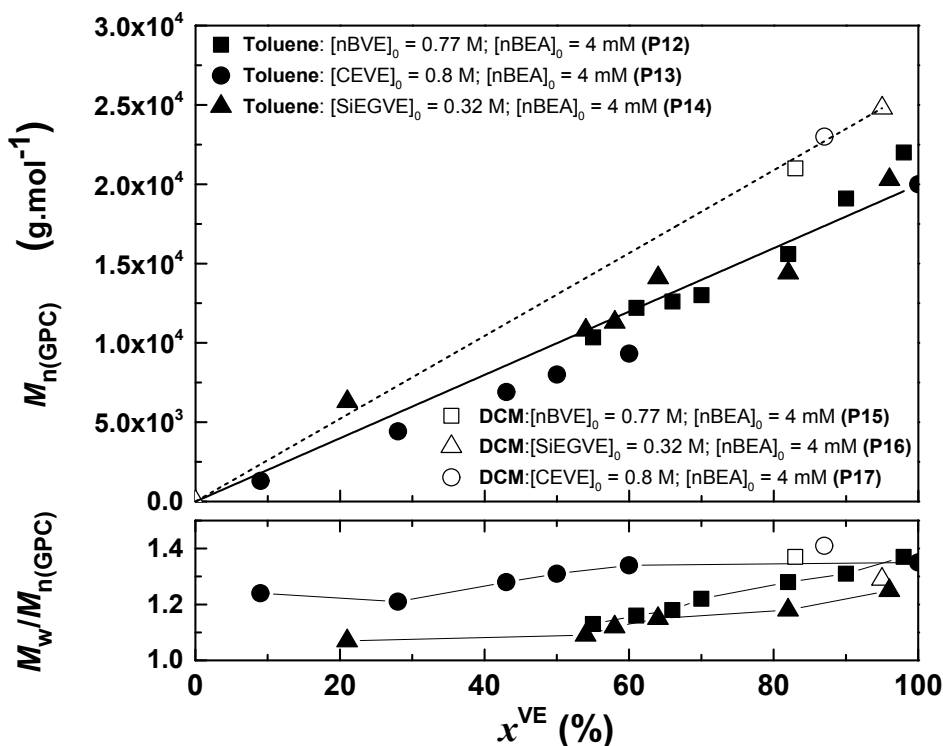
**Fig. S11**: Number average molecular weight ($M_{n(GPC)}$) and molecular weight distribution ($M_w/M_{n(GPC)}$) *vs* conversion (x^{VE}) for the polymerization at $-20°C$ in toluene (P12-14) (■,●,▲) and in dichloromethane (P15-P17) (□,○,Δ) of 0.77 M of n-butyl vinyl ether (nBVE) (P12, P15) (■,□), 0.8 M of 2-chloroethyl vinyl ether (CEVE) (P13, P16) (●,○) and 0.32 M of 2-(*tert*-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) (P14, P17) (▲,Δ) initiated by 4 mM of nBVE-acetic acid adduct (nBEA) in the presence of 0.4 mM of 2,6 di-tert-butylpyridine (DtBP), 1 M of ethyl acetate (AcOEt) and 4 mM of Et$_3$Al$_2$Cl$_3$. The total volume of the solutions (V$_T$) was 20 mL for a targeted M_n of 20,000 g/mol at x^{VE}=100%. For additional experimental data, see Table S12-S17 (Supporting Information)

Controlled cationic polymerization of nBVE, CEVE and SiDEVE by $Al_2Et_3Cl_3$ in toluene and in DCM - Molecular weight controlled together with chain-end termination.
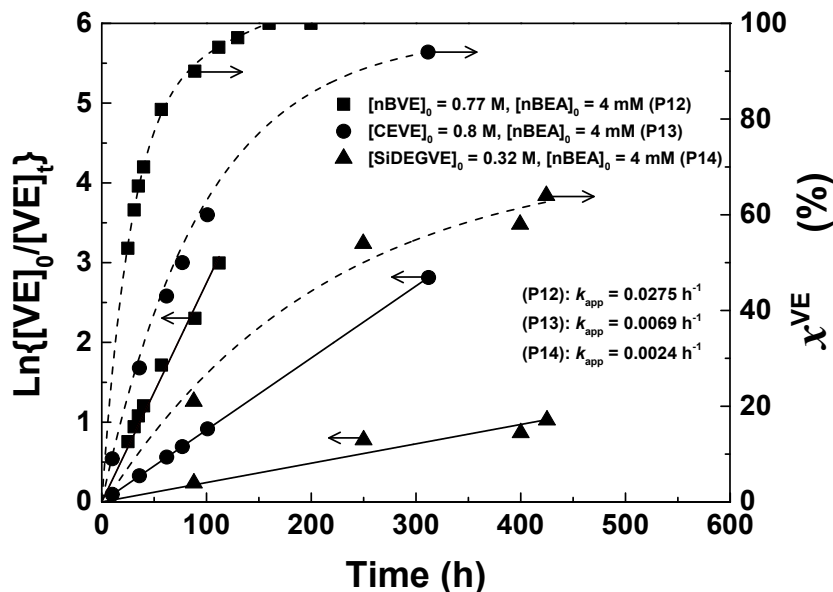
Fig. S12: First-order kinetic ($Ln\{[VE]_0/[VE]_t\}$) (full line —) and conversion (x^{VE}) (dash line ----) *vs* time for the polymerization in toluene at -20°C of 0.77 M of n-butyl vinyl ether (nBVE) (P12) (■), 0.8 M of 2-chloroethyl vinyl ether (CEVE) (P13) (●) and 0.32 M of 2-(*tert*-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) (P14) (▲) initiated by 4 mM of nBVE-Acetic Acid Adduct (nBEA) in the presence of 2,6 di-*tert*-butylpyridine (DtBP), 1 M of ethyl acetate (AcOEt) and 4 mM of $Et_3Al_2Cl_3$. The total volume of the solutions (V_T) is 20 mL for a targeted M_n of 20,000 g/mol at x^{VE}=100%. For additional experimental data, see Table S12-S14 (Supporting Information).

Controlled cationic polymerization of nBVE, CEVE and SiDEVE by Al$_2$Et$_3$Cl$_3$ in toluene and in DCM - Molecular weight controlled together with chain-end termination.
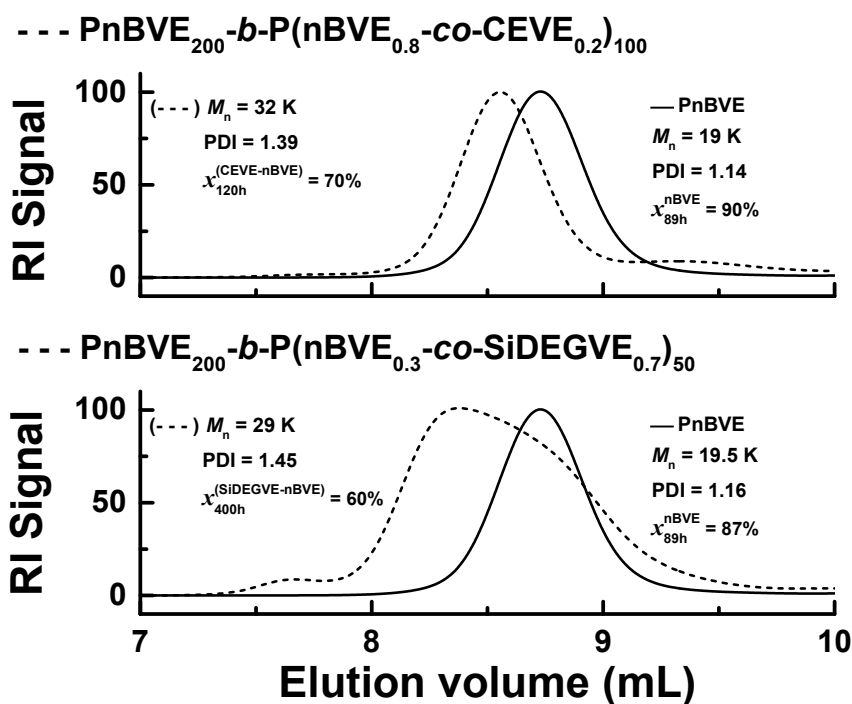
The existence of chain termination reactions in toluene, which happening more significantly for PnBVE cations than for PCEVE or PSIDEGVE cations (**Fig 3(iii)** in manuscript), was also demonstrated by the failure in yielding well-defined PnBVE$_{200}$-b-P(nBVE$_{0.8}$-co-CEVE$_{0.2}$)$_{100}$ (Sample P43) and PnBVE$_{200}$-b-P(nBVE$_{0.7}$-b-SiDEGVE$_{0.3}$)$_{50}$ (Sample P44) at -20°C by sequential monomer addition carried out at x^{nBVE}_{89h} < 90%, *i.e.* on living PnBVE cation showing no signal of UV absorbance at x^{nBVE}_{89h} < 90% (**Fig. 1(ii)** in manuscript).

- - - PnBVE$_{200}$-b-P(nBVE$_{0.8}$-co-CEVE$_{0.2}$)$_{100}$

(- - -) M_n = 32 K
PDI = 1.39
$x^{(CEVE-nBVE)}_{120h}$ = 70%

— PnBVE
M_n = 19 K
PDI = 1.14
x^{nBVE}_{89h} = 90%

- - - PnBVE$_{200}$-b-P(nBVE$_{0.3}$-co-SiDEGVE$_{0.7}$)$_{50}$

(- - -) M_n = 29 K
PDI = 1.45
$x^{(SiDEGVE-nBVE)}_{400h}$ = 60%

— PnBVE
M_n = 19.5 K
PDI = 1.16
x^{nBVE}_{89h} = 87%

Fig. S13: GPC RI traces of poly(n-butyl vinyl ether)-b-poly(chloro ethyl vinyl ether)(PnBVE-b-PCEVE) (**P42**), poly(n-butyl vinyl ether)-*block*- ethyl vinyl ether) (PnBVE-b-PSiDEGVE) (**P43**) obtained by sequential cationic polymerization of nBVE and CEVE (P42) or nBVE and SiDEGVE (**P43**) in toluene (Tol) at -20°C using 4 mM of the 1/1 n/n 1-butoxyethyl acetate /Al$_2$Et$_3$Cl$_3$ initiating system in the presence of 0.4 mM of di--butylypyridine (DtBP) and 1 M of ethyl acetate (AcOEt).

**Effect of the [Al₂Et₃Cl₃]/[nBEA] ratio on the living polymerization of nBVE, CEVE and SiDEGVE.**

The use of a large excess of $Al_2Et_3Cl_3$ (*i.e.,* $[Al_2Et_3Cl_3]/[nBEA] = 2$ and 3) to reduce the time of polymerization did not permit us to produce living PnBVE cations with predictable M_n (*i.e.,* based on the $[nBVE]_0/[nBEA]_0$ ratio) usable for the clean synthesis of PnBVE-*b*-PCEVE and PnBVE-*b*-PSiEGVE block copolymers. **Fig. S11** shows that polymers obtained at $[Al_2Et_3Cl_3]/[nBEA] > 1$ and at $[AlEtCl_2]/[nBEA] > 2$ have $M_{n(GPC)}$'s $< M_{n(th)}$, indicating that direct initiation from the catalyst can proceed independently of the monomer (*i.e.,* nBVE, CEVE, SiDEGVE), the nature of the solvent (*i.e.,* toluene, n-Hex and DCM) and the temperature of polymerization (*i.e.,* T = -20, 0, 20°C).
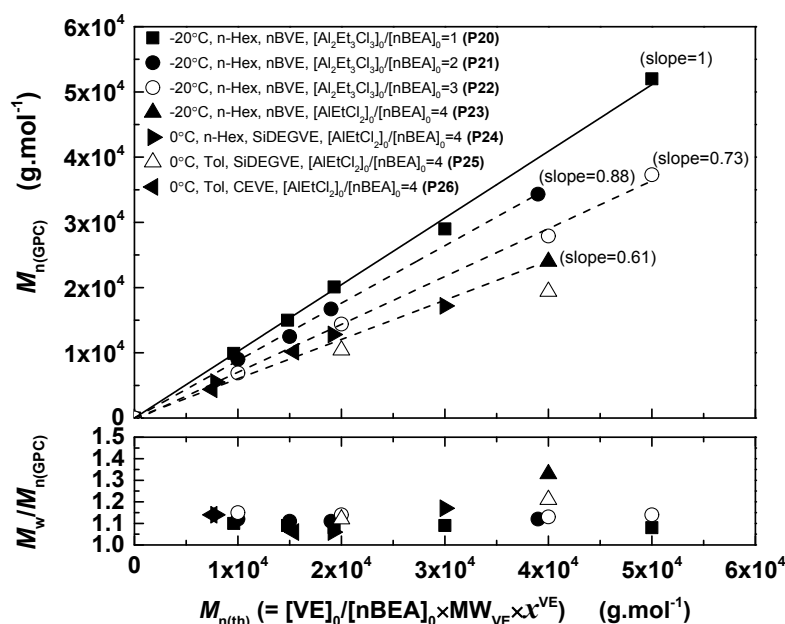
Fig. S14: Number average molecular weight ($M_{n(GPC)}$) and molecular weight distribution ($M_{n(GPC)}/M_{n(GPC)}$) *vs* theoretical number average molecular weight ($M_{n(th)}$) dependences plotted at various ratios $[catalyst]_0/[nBEA]_0$ (= 1, 2 or 3) for the polymerization of n-butyl vinyl ether (nBVE) (■,●,○,▲), 2-chloroethyl vinyl ether (CEVE) (◄) and 2-(tert-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) (►,Δ) initiated by 4 mM of nBVE-Acetic Acid Adduct (nBEA) with $Al_2Et_3Cl_3$ (■,●,○) and $AlEtCl_2$ (▲,◄,►,Δ)) catalyst in the presence of 0.4 mM of 2,6 di-tert-butylpyridine (DtBP) and 1 M of ethyl acetate (AcOEt) in n-hexane (n-Hex) (■,●,○,▲,►) and toluene (Tol) (◄,Δ) at 0 and -20°C. The total volume of the solutions (V_T) was 20 mL. Experiments: (**P20**) ($[nBVE]_0 = 0.38, 0.57, 0.76, 1.15$ and 1.93, $[Al_2Et_3Cl_3]_0 = [nBEA]_0 = 4$ mM, $x_{48h}^{nBVE} = 100\%$ in n-Hex at -20°C) (■); (**P21**) ($[nBVE]_0 = 0.385, 0.6, 0.77$ and 1.5 M, $[Al_2Et_3Cl_3]_0 = 2 \times [nBEA]_0 = 8$ mM, $x_{48h}^{nBVE} = 100\%$ in n-Hex at -20°C) (●); (**P22**) ($[nBVE]_0 = 0.385, 0.77, 1.5$ and 2 M, $[Al_2Et_3Cl_3]_0 = 3 \times [nBEA]_0 = 12$ mM, $x_{48h}^{nBVE} = 100\%$ in n-Hex at -20°C) (○); (**P23**) ($[nBVE]_0 = 1.5$ M, $[AlEtCl_2]_0 = 4 \times [nBEA]_0 = 16$ mM, $x_{48h}^{nBVE} = 100\%$ in n-Hex at -20°C) (▲); (**P24**) ($[SiDEGVE]_0 = 0.13, 0.32$ and 0.5 M, $[nBEA]_0 = 4$ mM, $[AlEtCl_2]_0/[nBEA]_0 = 4$, $x_{48h}^{nBVE} = 100\%$ in n-Hex at 0°C) (►); (**P25**) ($[SiDEGVE]_0 = 0.32$ and 0.64 M, $[nBEA]_0 = 4$ mM, $[AlEtCl_2]_0/[nBEA]_0 = 4$, $x_{48h}^{nBVE} < 100\%$ in Tol at 0°C) (◄); (**P26**) ($[CEVE]_0 = 0.76$ and 1.5 M, $[nBEA]_0 = 4$ mM, $[AlEtCl_2]_0/[nBEA]_0 = 4$, $x_{48h}^{nBVE} = 100\%$ in Tol at 0°C) (Δ). $M_{n(th)}$ was calculated assuming that one

polymer chain is formed per molecule of initiator. For additional experimental data, see Tables S20-S26 in the Supporting Information.

Effect of the [Al₂Et₃Cl₃]₀ (=[nBEA]₀) on the living polymerization of nBVE, CEVE and SiDEGVE.
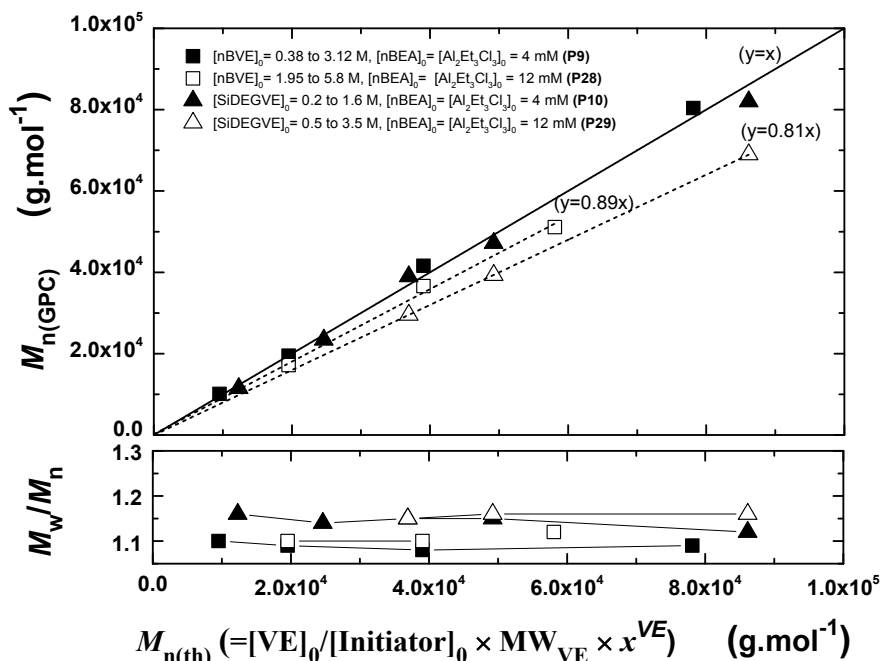
Fig. S15: Number average molecular weight ($M_{n(GPC)}$) and molecular weight distribution ($M_{n(GPC)}/M_{n(GPC)}$) *vs* theoretical number average molecular weight ($M_{n(th)}$) dependences plotted at various ratios [catalyst]₀/**[nBEA]₀** (= 1, 2 or 3) for the polymerization of n-butyl vinyl ether (nBVE) (∎) and 2-(tert-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) (▲) initiated by nBVE-Acetic Acid Adduct (nBEA) with Al₂Et₃Cl₃ (∎,●,○) catalyst in the presence of 0.4 mM of 2,6 di-tert-butylpyridine (DtBP) and 1 M of ethyl acetate (AcOEt) in n-hexane (n-Hex) (∎,●,○,▲,▶) at -20°C. The total volume of the solutions (V_T) was 20 mL. Experiments: **(P9)** ([nBVE]₀ = 0.38, 0.78, 1.56 and 3.12, [Al₂Et₃Cl₃]₀ = [nBEA]₀ = 4 mM, x^{nBVE}_{48h} = 100% in n-Hex at -20°C) (∎); **(P28)** ([nBVE]₀ = 1.92, 2.88 and 4.6 M, [Al₂Et₃Cl₃]₀ = [nBEA]₀ = 12 mM, x^{nBVE}_{48h} < 97% in n-Hex at -20°C) (●); **(P10)** ([SiDEGVE]₀ = 0.2, 0.4, 0.6 and 0.8 M, [Al₂Et₃Cl₃]₀ = [nBEA]₀ = 4 mM, x^{nBVE}_{420h} < 97% in n-Hex at -20°C) (○); **(P29)** ([SiDEGVE]₀ = 1.5, 2 and 3.5 M, [Al₂Et₃Cl₃]₀ = [nBEA]₀ = 12 mM, x^{nBVE}_{48h} < 97% in n-Hex at -20°C) (○). $M_{n(th)}$ was calculated assuming that one polymer chain is formed per molecule of initiator.

Copolymerization of nBVE with SiDEGVE

The polymerization of nBVE from 1/1 n/n SiDEGEA/$Al_2Et_3Cl_3$ initiating system in the presence of a tiny amount of SiDEGVE (4 and 10%) yield in n-Hex at -20°C polymers with PDI > 1.4 whereas in the absence of SiDEGVE, polymer with PDI < 1.1 were obtained (series P27). In this respect, SiDEGVE was polymerized last in sequential monomer addition..
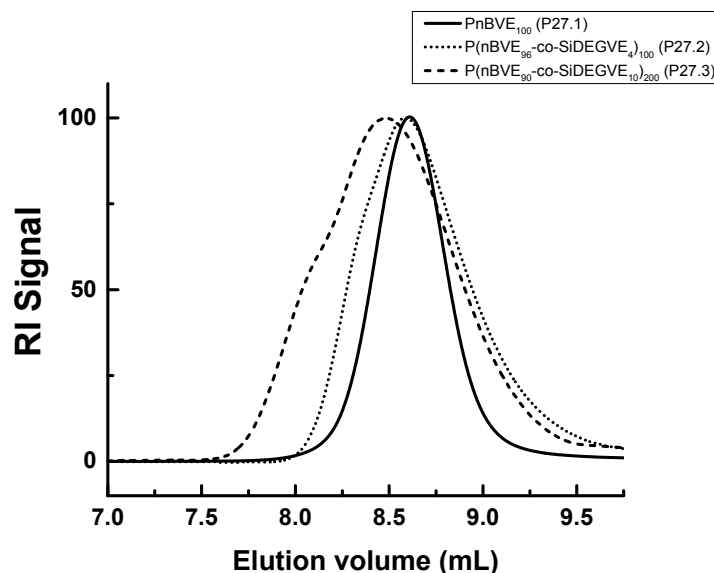
Fig. S16 GPC RI traces of poly(n-butyl vinyl ether) (PnBVE) and -poly(2-chloro ethyl vinyl ether) (PCEVE) (**P42**) obtained in the polymerization of nBVE (series P276) in n-hexane at -20°C in the presence (---) or in the absence (—) of a tiny amount of (SiDEGVE) (~5-10 %) using 4 mM of the 1/1 n/n SiDEGEA /$Al_2Et_3Cl_3$ initiating system in the presence of 0.4 mM of di-*tert*-butylypyridine (DtBP) and 1 M of ethyl acetate (AcOEt). For additional experimental data, see Tables S27 in the Supporting Information.

Table S27: Results from the copolymerization of nBVE with a tiny amount of SiDEGVE initiated by 1/1 n/n nBEA/$Al_2Et_3Cl_3$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) in nHex at -20°C.

$[nBVE]_0$ = 0.76, $[AcOEt]_0$ = 1 M, $[SiDEGEA]_0$ = 4 mM, $[Al_2Et_3Cl_3]_0$ = 4 mM and $[DtBP]_0$ = 0.4 mM. Time of polymerization t=48h.

| Series	$[nBVE]_0$ M	$[SiDEGVE]_0$ mM	Targeted DP	x^{nBVE}_{48h} [a] (%)	$M_{n(th)}$ [b] (g/mol)	$M_{n(GPC)}$ [c] (g/mol)	PDI [c]
P27.1	0.76	0	200	100	19,100	19,400	1.06
P27.2	0.76	40	200	100	19,100	23,500	1.43
P27.3	0.76	80	200	100	19,100	30,400	1.53

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= $[nBVE]_0/[nBEA]_0 \times x^{nBVE}_{48h} \times 100.16$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Homopolymerization of nBVE and CEVE from PSiDEGVE macroinitiator in n-Hexane at -20°C by sequential monomer addition in the presence of a tiny amount of SiDEGVE (4-5%)
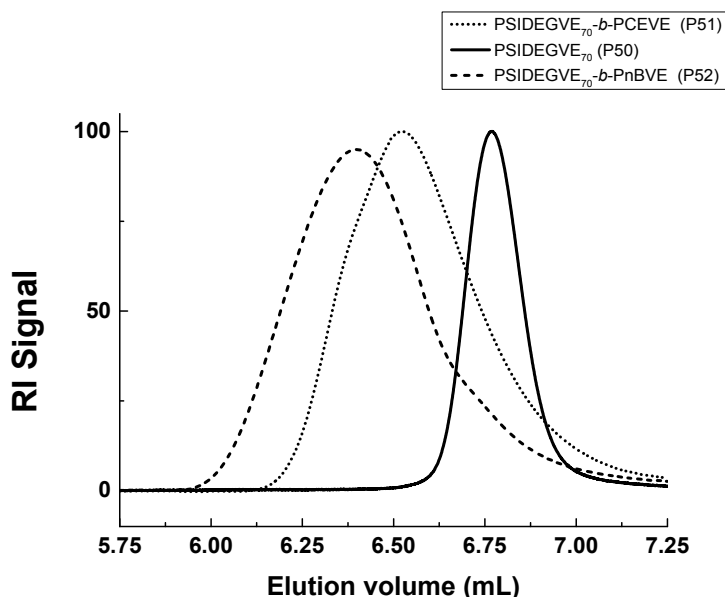
Fig S17. GPC RI traces of PSiDEVE-*b*-PCEVE (**P51**) and PSiDEGVE-*b*-PnBVE (**P52**) obtained by sequential cationic polymerization of 2-(tert-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) with n-butyl vinyl ether (nBVE) (**P52**) or 2-chloroethyl vinyl ether (CEVE) (**P51**) using 4 mM of the 1/1 n/n of SiDEGVE-Acetic Acid Adduct (SiDEGEA)/Al$_2$Et$_3$Cl$_3$ in the presence of Al$_2$Et$_3$Cl$_3$ ([Al$_2$Et$_3$Cl$_3$]$_0$/[nBEA]$_0$ = 1), 0.4 mM of 2,6 di-tert-butylpyridine (DtBP) and 1 M of ethyl acetate (AcOEt) in n-hexane at -20°C. For additional experimental data, see Table S28 in the Supporting Information.

Table S28. Results for the synthesis of PSiDEVE-*b*-PCEVE (**P51**) and PSiDEGVE-*b*-PnBVE (**P52**) obtained by sequential cationic polymerization of 2-(tert-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) with n-butyl vinyl ether (nBVE) (**P52**) or 2-chloroethyl vinyl ether (CEVE) (**P51**) using 4 mM of the 1/1 n/n of SiDEGVE-Acetic Acid Adduct (SiDEGEA)/Al$_2$Et$_3$Cl$_3$ in the presence of Al$_2$Et$_3$Cl$_3$ ([Al$_2$Et$_3$Cl$_3$]$_0$/[nBEA]$_0$ = 1), 0.4 mM of 2,6 di-tert-butylpyridine (DtBP) and 1 M of ethyl acetate (AcOEt) in n-hexane at -20°C.

Series	Block[g] sequence	DP	x_{time}^{VE}[a] h(%)	M_n (g/mol) calcd[a]	M_n (g/mol) GPC[b]	M_w/M_n GPC[b]	Solubility in n-Hex
P52	C	75	520(95)	17,500	18,600	1.11	yes
	CA	75+75	120(81)	26,000	38,700	1.55	
P51	C	75	520(96)	17,600	18,200	1.1	physical gel
	CB	75+75	120(100)	26,500	58,200	1.68	

[a] The fraction of the VE monomer converted into polymer was measured by gravimetry of the product.

[b] M_{nth}= [VE]$_0$/[initiator]$_0 \times x_{time}^{VE} \times$MW$_{VE}$ g/mol

[c] The average number molecular weight ($M_{n(GPC)}$) and molecular weight distribution (M_w/M_n) were determined by GPC in THF against PS standards

Fig S18: 400 MHz ^{1}H NMR spectrum of PnBVE synthesized in n-hexane and in toluene. Coupling reaction of PnBVE cations with toluene and toluene-ended PVE (PVE-S (A,B) and (PVE)$_2$-S (C)). Small resonances in the olefinic region suggest that the the formation of polyenes may also occur the formation of polyenes (S. Aoshima, T. Higashimura, *Polym. J.*, 1984, **16**, 249-258**).**