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

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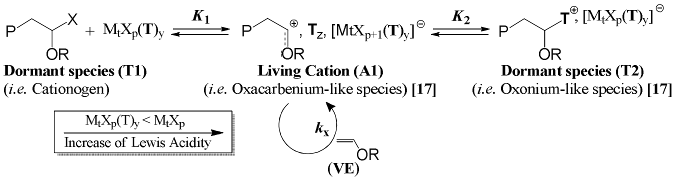
A series of novel, well-defined triblock (PnBVE-*b*-PCEVE-*b*-PSiDEGVE) and pentablock (PSiDEGVE-*b*-PCEVE-*b*-PnBVE-*b*-PCEVE-*b*-PSiDEGVE) terpolymers of n-butyl vinyl ether (nBVE), 2-chloroethyl vinyl ether (CEVE) and *tert*-butyldimethylsilyl ethylene glycol vinyl ether (SiEGVE) were synthesized by sequential base-assisted living cationic polymerization. The living character of the homopolymerization of the three VE monomers and the crossover reaction resulting in the formation of well-defined block copolymers were investigated in various solvents (toluene, dichloromethane and n-hexane) using either a monofunctional [nBVE-acetic acid adduct (nBEA), CEVE-acetic acid adduct (CEEA) and SiDEGVE-acetic acid adduct (SiDEGEA)] or a difunctional [1,4-cyclohexane-1,4-diyl bis(2-methoxyethyl acetate) (cHDMEA)] initiator. All initiators are structurally equivalent to the dormant species of the corresponding monomers in order to achieve fast initiation. The optimal conditions of polymerizations were achieved in n-hexane at -20°C, in the presence of 1 M AcOEt (base). Good control over the number average molecular weight (M_n) and the polydispersity index (PDI) was obtained only at $[Et_3Al_2Cl_3]_0$ = [Chain-end]$_0$ ≤ 10 mM. 2,6-di-*tert*-butylpyridine (DtBP) was used as a non-nucleophilic proton trap to neutralize any protonic initiation from moisture (*i.e.*, $Et_3Al_2Cl_3.H_2O$). Well-defined PnBVE$_n$-*b*-PCEVE$_p$-*b*-PSiDEGVE$_q$ and PSiDEGVE$_q$-*b*-PCEVE$_p$-*b*-PnBVE$_n$-*b*-PCEVE$_p$-*b*-PSiDEGVE$_q$ terpolymers with high crossover efficiency, no PCEVE-induced physical gelation, predictable M_n and PDI < 1.15 were synthesized successfully provided that the targeted DP_{CEVE}/DP_{nBVE} ratio (*i.e.*, *p*/*n*) did not exceed 2 and 0.2, respectively. The quantitative desilylation of the PSiEGVE by $n\text{-}Bu_4N^+F^-$ in THF at 0°C led to triblock and pentablock terpolymers in which the PCEVE is the central block and the polyalcohol is the outer block. The thermal properties of the synthesized materials were examined by differential scanning calorimetry.

Introduction

The cationic polymerization of vinyl ether (VE) monomers with long-lived growing species[1] has received considerable attention after the discovery of Highashimura and Sawamoto in 1984 that hydrogen iodide/iodine (HI/I_2) initiating system can lead to living polymerization.[2,3] This ground breaking work was followed in the late 1980's by the development of binary living initiating systems, *i.e.*, a combination of a protonic acid (HB) and a weak Lewis acid (M_tX_p).[4-9] Typical examples of HB/M_tX_p systems include hydrogen halide[3,4] and acetic acid[5,6] in conjunction with zinc halide,[3,4,6] zinc acetate,[5] and tin(IV) bromide[4]. In an attempt to expand further the scope of living cationic polymerization of VE, strong Lewis acids (*e.g.,* M_t = Fe, Ga, Sn, In, Zn, Al, Ti, Hf, Zr, Bi, Si, Ge, Sb)[10], were associated with a suitable nucleophilic oxygen-base additives **(T)** (*e.g.* ethyl acetate, 1,4-dioxane, etc.)[11,12] per se capable to form dormant oxonium-like ions (**T2**)[13] in equilibrium with living propagating oxacarbenium ions (**A1**) and cationogen non-propagating species (**T1**) (**Scheme 1**).



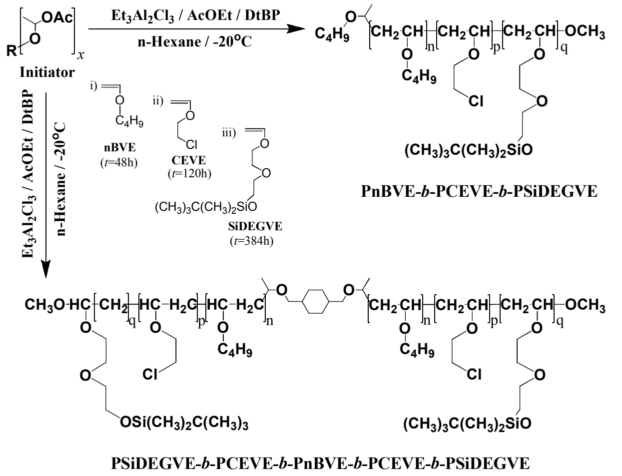
P: Polymer (P = P(VE)$_n$) or initiator (P = H)
T: Additive (AcOEt, THF, 1,4-D, Et_2O, etc ...) **[15-16]**
VE: Vinyl ether monomer
k_x: Initiation rate constante k_i (P = H) or propagation rate constante k_p (P = P(VE)$_n$)

Scheme 1: Living cationic polymerization of vinyl ether (VE) monomers at catalyzed high temperature using Lewis acid (MtX_p) and cationogen species in the presence of additive (T).[15-17]

Such system, known as a *base-assisted living polymerization system* was successfully employed to polymerize in a living/controlled manner VE monomers with various pendant groups, such as esters[14], alcohols (via benzyl,[15] cyclic acetal,[16,17] silyloxy,[16,18,19] and acetoxy,[17,20,21] moiety), amine (via phthalimide moiety),[22] polyoxyethylenes,[15,18,19,23,26] chlorine,[25] azide,[27] carboxylic amide,[28] azobenzene,[29,30] imidazolium and pyridinium,[31] dihydrofuran,[32] carbohydrate,[33,34] cellobiose heptadecanoate residue,[35] urethane,[36] oligooxetylene carbonate,[37] fluorine,[20,21,38] cycloalkyl,[39,40] a mesogenic substituent,[41,42] and a liquid crystalline mesogenic structure [43,44]. Well-defined stimuliresponsive homo-[14-44] and copolymers with comb/graft,[18-23] random,[16,18,28,29,38,42,43,44] gradient,[18,19,30] block[17,18,21,22,25,27,34,35,38,42,43] structures was produced, including thermally-,[16,22-24,31,33,44] pH-,[14,22] photo-,[29] mesomorphic,[33-35,41,42] selective solvent-[20,21,30,38] and pressure-[15] responsive polymeric materials.

A large number of well-defined block copolymers and terpolymers having two different functional groups has also been prepared by sequential living cationic polymerization of alkyl[17,20,21,37,48-59] or 2-chloroethyl [25,27] VE with oxyethylene VE [17,20,21,25,49,56-59] or with VE carrying either hydrophilic functions such as hydroxyl,[27,48-51,54-58] carboxy,[27,52,59] and amino,[27,53] groups in protected forms or hydrophobic functions such as azido[27] group. More difficult is obviously the synthesis of block terpolymers carrying three different pendant groups due to the fact that livingness and polymerization kinetics are strongly dependent on an appropriate combination of the Lewis acid with added base which varies as a function of the pendant group and the nature of the solvent.[60]

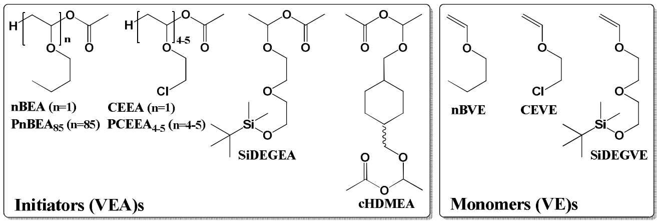
In this contribution, well-defined triblock and pentablock VE-based terpolymers, containing an unreactive alkyl group and two antagonist functions, namely, hydroxyl- and chloro-pendant groups, were synthesized. These terpolymers are aimed to be subsequently subjected to grafting-from and grafting-onto reactions for the preparation of complex macromolecular architectures (*e.g.* grafts, star-grafts, etc.).



nBEA (**Initiator** with R- = C_4H_9-; *x* = 1); **cHMDEA** (**Initiator** with -R- = -CH_2-C_6H_{10}-CH_2-, *x* = 2)
$[nBEA]_0 = [Al_2Et_3Cl_3]_0 = 4$ mM ($[nBEA]_0/[Al_2Et_3Cl_3]_0=1$, $[AcOEt]_0 = 1$ M and $[DtBP]_0 = 0.4$ mM

Scheme 2: Synthesis of block copolymers and terpolymers by sequential base-assisted living cationic polymerization of nBVE with CEVE and SiDEGVE in n-hexane at -20°C using monofunctional (nBEA) and difunctional (cHMDEA) initiators.

The synthesis was achieved by sequential base-assisted living cationic polymerization (**Scheme 2**) of n-butyl vinyl ether (nBVE), 2-chloroethyl vinyl ether (CEVE) and *tert*-butyldimethylsilyl ethylene glycol vinyl ether (SiEGVE) using mono-functional [n-butoxyethyl acetate (nBEA)] and di-functional [1,4-cyclohexanedimethanol-di(1-ethyl acetate) (cHMDEA)] initiators in the presence of $Al_2Et_3Cl_3$ (catalyst) and AcOEt (base) (**Scheme 3**). The focus of this work is to investigate the living character of the polymerization of the three monomers and the crossover resulting in the formation of well-defined block copolymers and terpolymers.



Scheme 3: Initiators and monomers used.

Experimental

Materials. *n*-Hexane (*n*-Hex) (99%, Fisher Scientific) was rendered olefin free by refluxing over concentrated sulfuric acid for 48 h. *n*-Hex as well as *n*-butyl vinyl ether (n-BVE) (99%, Sigma Aldrich), toluene (99%, Fisher Scientific) and dichloromethane (DCM) (99%, Fisher Scientific) were washed with an aqueous alkali solution (KOH, 10% w/w) and then water until neutral, pre-dried over $MgSO_4$ overnight, and distilled twice over calcium hydride just before use. *n*-Hex and toluene were further dried by distillation over *sec*-BuLi using diphenylethylene as indicator. 2-Chloroethyl vinyl ether (CEVE) (99%, TCI) was washed with an aqueous alkali solution (KOH, 10% w/w) and then water, pre-dried over Na_2SO_4, and distilled twice over calcium hydride before use. 2,6-Di-*tert*-butylypyridine (DtBP) (Sigma Aldrich, 99%) was vacuum-distilled twice over calcium at 90°C to remove any traces of monosubstituted pyridine, and used as a 0.08 or 0.16 M solution in dried *n*-Hex. Ethylaluminum sesquichloride ($Et_3Al_2Cl_3$) (97%, Sigma Aldrich) and diethylaluminum chloride (Et_2AlCl) (97%, Sigma Aldrich) were used without further purification as a 0.8 M solution in dried *n*-Hex. Ethyl acetate (AcOEt) (99%, Sigma Aldrich) was distilled twice over calcium hydride. Diethylene glycol monovinyl ether (DEGVE) (99%, TCI), 1,4-cyclohexanedimethanol divinyl ether (cHDMVE) (Sigma Aldrich, 98%, mixture of isomer), tetrahydrofurane (THF) (99%, Sigma Aldrich), *N,N*-dimethylformamide anhydrous (DMF) (99.8%, Sigma Aldrich), acetic acid (AcOH) (99%, Sigma Aldrich), -butylchlorodimethylsilane (98%, Acros Organics), tetra-*n*-butylammonium bromide (99%, Acros Organics), imidazole (99%, Acros Organics) were used as received without any further purification.

Synthesis of initiators. The synthesis of $CH_3CH(O(CH_2)_3CH_3)OCOCH_3$ (1-butoxyethyl acetate, nBEA), *p*-$C_6H_{10}(CH_2OCH(CH_3)OCOCH_3)_2$ [1,4-cyclohexane-1,4-diyl bis(2-methoxyethyl acetate), cHDMEA], and $ClCH_2CH_2OCH(CH_3)OCOCH_3$ [1-(2-chloroethoxy)ethyl acetate, CEEA] and $(CH_3)_3C(CH_3)_2SiO(CH_2CH_2O)_2CH(CH_3)OCOCH_3$ [1-(2-(2-(*tert*-butyldimethylsilyloxy)ethoxy)ethoxy)ethyl acetate, SiDEGEA] were based on the reported synthesis of 1-isobutoxyethyl acetate.[13] For additional experimental data, see the general procedure S1 (Supporting Information).

Monomer Synthesis. The synthesis of 2-(-butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) was based on the reported synthesis of 2-(tert-Butyldimethylsilyloxy) ethylene glycol vinyl ether.[16] For additional experimental data, see the general procedure S2 (Supporting Information).

Living Cationic Polymerization of Vinyl Ethers

The polymerizations were carried out under a dry argon atmosphere in a 30 ml glass tube or in a 50 mL Schlenk reactor equipped with a rotaflos (ESI, Figure S6), in n-Hex, in toluene and in DCM at 3 different temperatures (T: -20, 0 and 30°C) using the following stock solutions: $[\text{Initiator}]_0$ = 0.04 or 0.08 M, $[\text{DtBP}]_0$ = 0.004 M, $[\text{Al}_2\text{Et}_3\text{Cl}_3]_0$ = 0.8 M. AcOEt and the monomers (nBVE, SiDEGVE and CEVE) were added without dilution. 0.4 mM of D*t*BP (0.008 M in n-Hex) was used as a non-nucleophilic proton trap in concentrations comparable to those of protic impurities coming from the reaction of moisture with the catalysts to prevent any side initiation. [61,62]

General procedure for the homopolymerization of vinyl ethers using monofunctional (nBEA, CEEA and SiDEGEA) and difunctional (cHDMEA) initiator. The polymerization was carried out under dry argon in a baked 50 mL glass tube equipped with a septum. The reactor was heated under vacuum with a heat gun, cooled down and transferred into a glovebox (M Braun model LabMaster sp). In a typical polymerization experiment, *e.g.* in n-Hex, the reagents were added 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). The glass tube reactor was then transferred outside the glovebox to carry out the polymerization in a cryobath set at -20 or 0°C or in an oil bath at 30°C. The polymerization was initiated by adding either z = 0.1*yp* or 0.2*yp* mL of $\text{Al}_2\text{Et}_3\text{Cl}_3$ (0.8 M in n-Hex) when monofunctional (nBEA, SiDEGVA, CEEA) or difunctional (cHDMEA) initiator was used respectively, at $[\text{Al}_2\text{Et}_3\text{Cl}_3]_0$ / [chain-end]$_0$ =*p* with *p* = 1, 2 or 3. The total volume of the solution was 20 mL. In a typical experiment, the concentrations were the following: $[\text{VE}]_0$ = 0.16-3.08 M, $[\text{AcOEt}]_0$ = 1 M, $[\text{initiator}]_0$ = 1-12 mM, $[\text{Al}_2\text{Et}_3\text{Cl}_3]_0$ = 1-12 mM with $[\text{Al}_2\text{Et}_3\text{Cl}_3]_0/[\text{initiator}]_0$ = 1- 3 and $[\text{DtBP}]_0$ = 0.4 mM. After a given time, the polymerization was quenched with ammoniacal methanol (0.3% v/v). The quenched reaction mixtures were sequentially washed with diluted hydrochloric acid and with water to remove the catalyst residues. The n-Hex mixture containing the polymer was then dried over MgSO_4, evaporated to dryness under reduced pressure, and vacuum dried overnight to give the product polymers. The fraction of VE monomer converted into polymer (x_{time}^{VE}) was measured by gravimetry of the product.

Homopolymerization of nBVE using nBEA initiator. As an example, the results obtained in n-Hex at -20°C with $[\text{nBVE}]_0$ = 0.77 M, $[\text{nBEA}]_0$ = 4 mM, $[\text{DtBP}]_0$ = 0.4 mM, $[\text{Al}_2\text{Et}_3\text{Cl}_3]_0$ = 4 mM, $[\text{AcOEt}]_0$ = 1 M were as follows: x_{42h}^{nBVE} = 98%, $M_{\text{n(GPC)}}$ = 21,400 g/mol, PDI = 1.08 (P2.6). For additional experimental data, see general procedure S3.1 and Table S2 (Supporting Information). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S7 (Supporting Information).

Homopolymerization of nBVE using cHDMEA. As an example, the results obtained in n-Hex at -20°C for a targeted degree of polymerization (DP) of 770 with $[\text{nBVE}]_0$ = 3.08 M, $[\text{cHDMEA}]_0$ = 4 mM, $[\text{DtBP}]_0$ = 0.4 mM, $[\text{Al}_2\text{Et}_3\text{Cl}_3]_0$ = 8 mM, $[\text{AcOEt}]_0$ = 1 M were as follows: x_{48h}^{nBVE} = 100%, $M_{\text{n(GPC)}}$ = 80,200 g/mol, PDI = 1.09 (P8.6). For additional experimental data, see general procedure S3.2 and Table S8 (Supporting Information).

Homopolymerization of SiDEGVE using a monofunctional initiator at -20°C. As an example, the results obtained in n-Hex at -20°C for $[\text{nBVE}]_0$ = 0.32 M, $[\text{nBEA}]_0$ = 4 mM, $[\text{DtBP}]_0$ = 0.4 mM, $[\text{Al}_2\text{Et}_3\text{Cl}_3]_0$ = 4 mM, $[\text{AcOEt}]_0$ = 1 M were as follows: $x_{384h}^{SiDEGVE}$= 96%, Mn$_{\text{(GPC)}}$ = 21,400 g/mol, PDI = 1.14 (P10.2). For additional experimental data, see general procedure S3.3 and Table S10 (Supporting Information). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S9 (Supporting Information).

Homopolymerization of CEVE using nBEA at -20°C. The results obtained in toluene at -20°C for $[\text{CEVE}]_0$ = 0.8 M, $[\text{nBEA}]_0$ = 4 mM, $[\text{DtBP}]_0$ = 0.4 mM, $[\text{Al}_2\text{Et}_3\text{Cl}_3]_0$ = 4 mM, $[\text{AcOEt}]_0$ = 1 M were as follows: x_{312h}^{CEVE}= 94%, *M*n$_{\text{(GPC)}}$ = 16,500 g/mol, PDI = 1.34 (P13.6). For additional experimental data, see general procedure S3.4 and Table S13 (Supporting Information). The 400 MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S10 (Supporting Information).

General Procedure for the synthesis of block co- and terpolymers by sequential monomer addition using the Schlenk technique at -20°C in n-Hex. The polymerization was carried out under dry argon in a Schlenk reactor equipped with rotaflos (SI, Figure S6) and ampules containing monomers for sequential additions and an empty ampule used to remove a sample of the living polymer for molecular characterization. For additional experimental information, see general procedure S4 (Supporting Information).

Synthesis of PnBVE-b-PCEVE in n-Hex at -20°C. As an example, the results obtained for the one pot synthesis of PnBVE$_{100}$-*b*-PCEVE$_{70}$ (P30) (Table 1) were as follows: time(x_{time}^{VE})($M_{\text{n(GPC)}}$)(PDI) = 48(100)(10,500)(1.07) and 72(61)(18,100)(1.09) h(%)(g/mol) for PnBVE$_{100}$ and PnBVE$_{100}$-*b*-PCEVE$_{70}$, respectively. For additional experimental data, see general procedure S4.1 (Supporting Information).

Synthesis of PnBVE-b-PSiEGVE in n-Hex at -20°C. As an example, the results obtained for the one pot synthesis of PnBVE$_{85}$-*b*-PSiEGVE$_{60}$ (P33) (Table 1) were as follows: time(x_{time}^{VE})($M_{\text{n(GPC)}}$)(PDI) = 42(96)(8,600)(1.08) and 72(85)(23,400)(1.9) h(%)(g/mol) for PnBVE$_{85}$ and PnBVE$_{85}$-*b*-PSiEGVE$_{60}$, respectively. For additional experimental data, see general procedure S4.2 (Supporting Information).

Synthesis of PnBVE-b-PCEVE-b-PSiEGVE in n-Hex at -20°C. As an example, the results obtained for the one pot synthesis of PnBVE$_{200}$-b-PCEVE$_{216}$-b-PSieGVE$_{192}$ (P35) (Table 1) were as follows: time(x_{time}^{VE})($M_{\text{n(GPC)}}$)(PDI) = 48(100)(20,100)(1.09), 120(100)(43,200)(1.18) and 240(100)(90,600)(1.18) h(%)(g/mol) for PnBVE$_{200}$, PnBVE$_{200}$-b-PCEVE$_{216}$ and PnBVE$_{200}$-b-PCEVE$_{216}$-b-PSieGVE$_{192}$, respectively. For additional experimental data, see general procedure S4.3 (Supporting Information).

Synthesis of PCEVE-b-PnBVE-b-PCEVE in n-Hex at -20°C. As an example, the results obtained for the one pot synthesis of PCEVE$_{98}$-*b*-PnBVE$_{500}$-*b*-PCEVE$_{98}$ (P37) (Table 2) were as follows: time(x_{time}^{VE})($M_{\text{n(GPC)}}$)(PDI) = 48(100)(55,100)(1.07) and 120(100)(75,700)(1.09) h(%)(g/mol) for PnBVE$_{500}$ and PCEVE$_{98}$-*b*-PnBVE$_{500}$-*b*-PCEVE$_{98}$, respectively. For additional experimental data, see general procedure S4.4 (Supporting Information). The 400

MHz ^{1}H and ^{13}C NMR spectra are shown in Figure S17 (Supporting Information).

Synthesis of the PSiEGVE-b-PnBVE-b-PSiEGVE in n-Hex at -20°C. As an example, the results obtained for the synthesis of PSiEGVE$_{101}$-*b*-PnBVE$_{500}$-*b*-PSiEGVE$_{101}$ (P40) (Table 2) were as follows: time(x_{time}^{VE})($M_{\text{n(GPC)}}$)(PDI) = 100(48)(54,800)(1.06) and 100(384)(105,600)(1.12) h(%)(g/mol) for PnBVE$_{500}$ and PSiEGVE$_{101}$-*b*-PnBVE$_{500}$-*b*- PSiEGVE$_{101}$, respectively. For additional experimental data, see general procedure S4.5 (Supporting Information).

Synthesis of the PSiEGVE-b-PCEVE-b-PnBVE-b-PCEVE-b-PSiEGVE in n-Hex at -20°C. As an example, the results obtained for the one pot synthesis of PSiEGVE$_{100}$-*b*-PCEVE$_{97}$-*b*-PnBVE$_{500}$-*b*-PCEVE$_{97}$-*b*-PSiEGVE$_{100}$ (P42) (Table 2) were as follows: time(x_{time}^{VE})($M_{\text{n(GPC)}}$)(PDI) = 48(100)(53,000)(1.08), 120(100)(73,2000)(1.09) and 100(384)(98,400)(1.14) h(%)(g/mol) for PnBVE$_{500}$, PCEVE$_{97}$-*b*-PnBVE$_{500}$-*b*-PCEVE$_{97}$ and pentablock, respectively. For additional experimental data, see general procedure S4.6 in the Supporting

Desilylation of the PSiDEGVE segment. The desilylation of the copolymers with PSiDEGVE segments was conducted using n-Bu_4N^+,F^- (3 equivalents with respect to the terbutyl dimethylsilyl ether group) in THF at 0°C. After the removal of the organic solvents, the polymer was purified either by precipitation in large excess of methanol or by dialysis in the case of water soluble polymers. The aqueous solutions were dialyzed against pure water for a week in a cellulose tube (7Speactra/Por® Dialysis corresponding to a cut off molecular weight of 1000). The water soluble polymers containing polyalcohol (*i.e.,* poly(diethylene glycol vinyl ether) (PDEGVE)) segments were finally recovered by evaporation of water under reduced pressure and vacuum-dried. Quantitative desilylation was confirmed by the disappearance of the ^{1}H NMR signals at 0.03 ppm (s, 6H, -Si(CH_3)$_2$-) and 0.86 ppm (s, 6H, -Si(CH$_3$)$_2$-C(CH_3)$_3$), as well as ,of ^{13}C NMR signals at -3.36 ppm (s, 2C, -Si(CH$_3$)$_2$-), 18.34 ppm (s, C, -Si(CH$_3$)$_2$-C(CH$_3$)$_3$) and 25.96 ppm (s, 3C, -Si(CH$_3$)$_2$-C(CH$_3$)$_3$) and of the -butyl dimethyl silyl group. The 400 MHz ^{13}C NMR spectra of the triblock terpolymer PnBVE-*b*-PCEVE-*b*-PDEGVE is shown in **Fig. 8.**

Measurement. ^{1}H NMR and ^{13}C NMR spectra were recorded in a Bruker spectrometer (400 MHz) with CDCl$_3$ as the solvent (Cambridge Isotope Laboratories Inc.). ^{1}H NMR spectra of solutions in CDCl$_3$ were calibrated to the solvent signal (δ_H) at 7.24 ppm.

For the GPC characterization the polymer solution was dissolved in THF to a concentration of 2-5 mg/mL. The solution was then filtered through a 0.45 μm PTFE syringe filter (Fisher Scientific). The molecular weight and molecular weight distribution were measured with a Viscotek Gel Permeation Chromatography GPC equipped with a model pump/autosampler/degasser Viscotek GPCmax module; a temperature controlled TDA 305 (RI, MALS, Viscometer) online with a Viscotek UV-PDA detector, and two GPC Waters columns connected in the following series: Styragel HR 4 and Stryragel HR 2 (molecular weight range: 1,000 and 600,000 g/mol). THF (Sigma Aldrich) was used as an eluent at a flow rate of 1.0 mL/min at 40°C. Data acquisition was performed with Viscotek OmniGPC 4.6 software. The instruments were calibrated by using narrow molecular weight polystyrene standards in the range of 162 to 600,000 g/mol. Differential scanning calorimetry (DSC) measurements of polymer samples (~10 mg) were performed using a Mettler Toledo DSC 1 Star System over a temperature range from -90 to 100 °C at the heating and cooling temperature of 10 °C min^{-1}. Both temperature and heat flow were calibrated with ultra-pure indium. The glass transition temperature (T_g) was calculated using the inflection tangent as a method in determining the midpoint between the onset and the end of the step/glass transition region. Data acquisition was performed using STARe version 9.20 software.

Results and Discussions

1. Living cationic polymerization of of n-butyl vinyl ether (nBVE), 2-chloroethyl vinyl ether (CEVE) and *tert*-butyldimethylsilyl ethylene glycol vinyl ether (SiEGVE). Before to attempting to synthesize the block copolymers targeted, we first defined the optimal conditions. A few polymerizations were thus carried out at three different temperatures (T: -20°C, 0°C and 20°C) in various solvents (toluene, DCM and n-Hex) using either a monofunctional (nBEA, CEEA, SiDEGEA) or difunctional (cHDMEA) initiator, in the presence of $Al_2Et_3Cl_3$, with AcOEt as additive (**Scheme 3**). DtBP (*i.e.,* $[DtBP]_0 < 0.1x[\text{Chain-end}]_0$) was used as a non-nucleophilic proton trap to neutralize any protonic initiation produced from reaction of moisture with $Et_3Al_2Cl_3$. [63-65] The total volume of polymerization solutions was 20 mL, the $[VE]_0 = 0.3$-2 M, $[AcOEt]_0 = 1$ M, $[\text{initiator}]_0 = 4$-8 mM, $[Al_2Et_3Cl_3]_0 = 4$-8 mM and $[DtBP]_0 = 0.4$ mM. As PCEVE is hardly soluble in n-hexane, attempts were first made to use toluene and DCM as solvent for the polymerization of the three monomers.

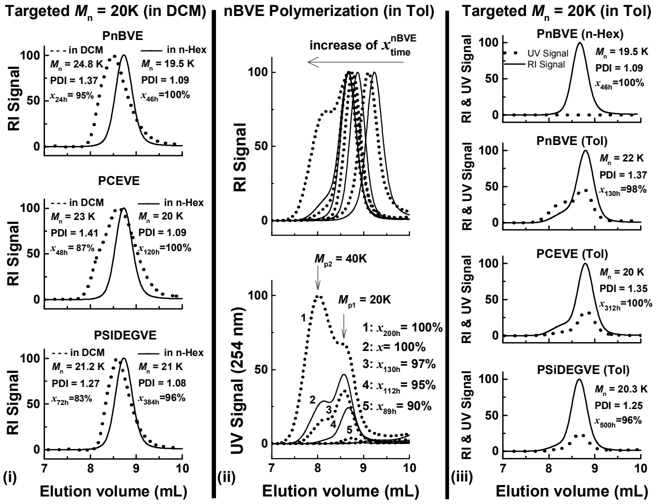
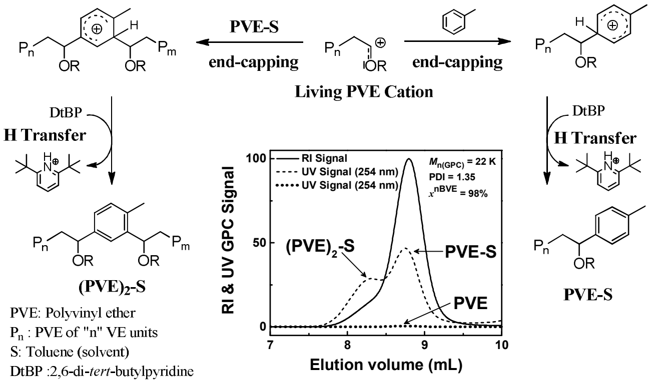


Fig. 1: GPC RI and UV traces of PnBVE (P2, P12, P15), PCEVE (P13, P17) and PSiDEGVE (P16, P18) synthesized in toluene (Tol) (P12, P13, P18), in n-hexane (n-Hex) (P2) and in dichloromethane (DCM) (P15, P16, P17) at -20°C using 4 mM (P2, P12, S13 and P15-P17) and 8 mM (P18) of the 1/1 n/n 1-butoxyethyl acetate /$Al_2Et_3Cl_3$ initiating system in the presence of 0.4 mM of 2,6-di-*tert*-butylpyridine (DtBP) and 1 M of ethyl acetate (AcOEt). For additional experimental data, see Tables S2, S12, S13 and S15-S18 (Supporting Information).

1.1 Toluene and Dichloromethane. In the investigation of the dependence of the number average molecular weight ($M_{\text{n(GPC)}}$) *vs* polymer conversion of the VE-monomer, x^{VE}, in toluene (**Fig. S11**

in SI), a first-order linear variation was only observed at -20°C (**Fig. S12 in SI**). The RI and UV-GPC traces revealed the presence of a shoulder at the high molecular weight region with a strong UV absorbance beyond x^{nBVE} > 90% (**Fig. 1(ii)**) with UV and RI signal almost identical in shape. The ^{1}H NMR spectroscopy (**Fig. S18** in SI) showed that chain termination by coupling of PVE cations with toluene occurred even at -20°C yielding first a small amount of monosubstituted toluene-ended PVE (PVE-S). The produced PVE-S is responsible for further termination of the growing chains, leading to molecular weights twice as large (*i.e.,* $M_{P2} = 2 \times M_{P1}$, **Fig. 1(ii)**) as those of the main population (**Scheme 4**). The formed proton cannot initiate and produced new chains since it is captured by DtBP (**Scheme 4**). The formation of trisubstituted toluene-ended PVE ($(PVE)_3$-S) could also been observed (**Fig S18** in SI) by ^{1}H NMR spectroscopy. Small resonances observed in the olefinic region (4-6ppm) also suggested the formation of polyene by *β*-proton elimination of PVE cations and successive dealcoholation.[68] The existence of chain termination reactions in toluene, which happening more significantly for PnBVE cations than for PCEVE or PSIDEGVE cations (**Fig 3(iii)**), 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) (**Fig. S13 in SI**) 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)**).



(4i) RI and UV GPC traces of PnBVE synthesized in toluene (—, ----) (P12) and in n-hexane (…) (P2) at T=-20°C using 1-butoxyethyl acetate/Al2Et3Cl3 initiating system.

Scheme 4: Mechanism for the coupling reaction of PVE cations with toluene (S) and toluene-ended PVE (PVE-S).

In DCM, also at -20°C the polymerization of nBVE, CEVE and SiEGVE did not occur under truly living condition as indicated by the self-inhibition of the polymerization at x^{VE} < 95%,[67] the broadening of the GPC traces (**Fig. 1(i)**) and the formation of polymer with $M_{n(GPC)}$ higher than the theoretical one initiation (*i.e.,* low initiator efficiency, **Fig. S11** in SI). No UV absorption related to the formation of conjugated polyene was detected. [68]

1.2 Hexane. The polymerization of nBVE and SiDEGVE were carried out using n-Hex at -20°C, $[Initiator]_0$ = 4 mM at various targeted DP in nBVE {*i.e.,* $[nBVE]_0/[cHDMEA]_0$ = 96, 143, 190, 288, 482, 770 (series P1 and P8) and $[nBVE]_0/[nBEA]_0$ = 97, 195, 390, 780 (series P2 and P9)} and in SiDEGVE {*i.e.,* $[SiDEGVE]_0/[nBEA]_0$ = 40, 80, 150, 200 (series P3 and P10), $[SiDEGVE]_0/[SiDEGEA]_0$ = 80 (series P4) and $[SiDEGVE]_0/[CEEA]_0$ = 80 (series P5)} with $[CE]_0/[Al_2Et_3Cl_3]_0$ = 1, $[DtBP]_0$ = 0.4 mM and $[AcOEt]_0$ = 1 M. As expected, the $M_{n(GPC)}$ vs x^{VE} dependence (**Fig. 2(i)**) followed a linear first-order variation

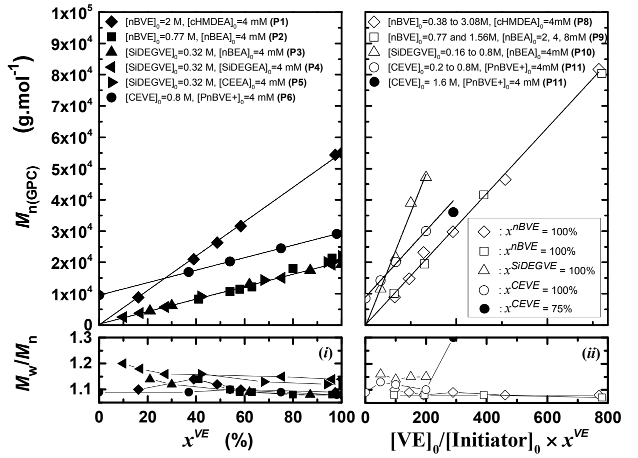


Fig. 2: Number average molecular weight ($M_{n(GPC)}$) and molecular weight distribution ($M_{w(GPC)}$/ $M_{n(GPC)}$) plotted (i) *vs* conversion in vinyl ether (x^{VE}) and (ii) *vs* $[VE]_0/[Initiator]_0$ x x^{VE}, for the polymerization in n-hexane at -20°C of n-butyl vinyl ether (nBVE) (■,□,♦,◊), 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) (**P2**,**P3, P9**) or by 4 mM of SiDEGVE-Acetic acid adduct (SiDEGEA) (**P4**) or by 4 mM of CEVE-Acetic Acid Adduct (CEEA) (**P5**) or by 4 mM of 1,4-cyclohexane-1,4-diyl bis(dimethanol di(1-ethyl acetate (cHMDEA) (**P1, P8**) or by 4 mM of living $PnBVE_{85}$ cations (**P6, P10**) in the presence of 0.4 mM of 2,6 di-*tert*-butylpyridine (DtBP) and 1 M of ethyl acetate (AcOEt). The total volume of the solutions (V_T) was 20 mL. The full straight line indicates the M_n assuming that one polymer chain is formed per molecule of initiator. For additional experimental data, see Tables S1-S11 (Supporting Information)

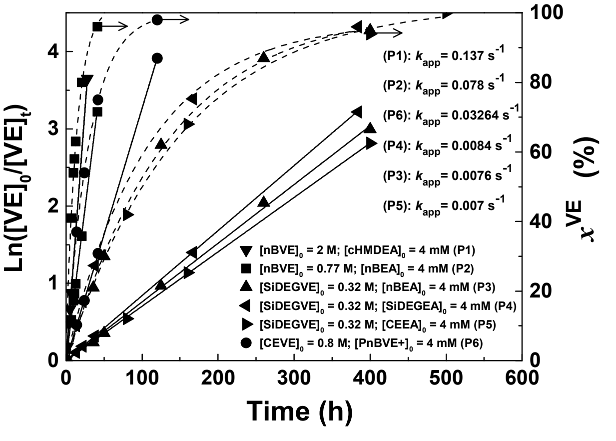


Fig. 3: First-order kinetic (Ln{$[M]_0/[M]_t$}) (full line —) and conversion (x^{VE}) (dash line ----) vs time dependences for the polymerization in n-hexane at -20°C of n-butyl vinyl ether (nBVE) (■,▼), 2-chloroethyl vinyl ether (CEVE) (●) and 2-(*tert*-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) (▲,◄,►) initiated by 4 mM of nBVE-acetic acid adduct (nBEA) (**P2**, **P3**) or by 4 mM of 1,4-cyclohexane-1,4-diyl bis(2-methoxyethyl acetate) (cHDMEA) (**P1**) or by 4 mM of living $PnBVE_{85}$ cations (**P6**) or by 4 mM of SiDEGVE-Acetic acid adduct (SiDEGEA) (**P4**) or by 4 mM of CEVE-Acetic Acid Adduct (CEEA) (**P5**) in the presence of

0.4 mM of 2,6 di-*tert*-butylpyridine (DtBP) and 1 M of ethyl acetate (AcOEt). The total volume of the solutions (V_T) was 20 mL. The full straight line indicates the M_n assuming that one polymer chain is formed per molecule of initiator. For additional experimental data, see Tables S1-S7 (Supporting Information).

(Fig. 3) and the $M_{n(GPC)}$'s of the resulting homopolymers had, throughout the polymerization process (**Fig. 2(i)**) and at various targeted DPs (**Fig. 2(ii)**), a value close to $M_{n(th)}$ and 1.06 < PDI < 1.15 at x^{VE} > 90% (**Fig. 4**). This demonstrates that the stationary concentration in the living chain end **(A1)** (**Scheme 1**) is reached at the fairly early stages of the polymerization and stays constant throughout the polymerization without any significant irreversible chain-end (CE) termination reactions.

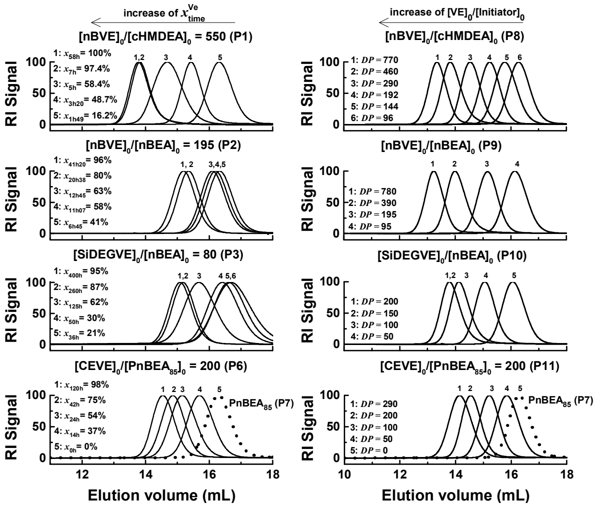


Fig. 4: GPC RI traces of PnBVE (**P1**, **P2, P8, P9**), PCEVE (**P6**, **P11**) and PSiDEGVE (**P3, P10**) obtained by cationic polymerization in n-hexane at -20°C of n-butyl vinyl ether (nBVE) (**P1**, **P2, P8, P9**), 2-chloroethyl vinyl ether (CEVE) and 2-(*tert*-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) using either nBVE-Acetic Acid Adduct (nBEA) (**P2**,**P3, P9, P10**), 1,4-cyclohexane-1,4-diyl bis(dimethanol di(1-ethyl acetate (cHMDEA) (**P1, P8**) or $PnBEA_{85}$ (**P6, P11**) in the presence of 0.4 mM of 2,6 di-*tert*-butylpyridine (DtBP) and 1 M of ethyl acetate (AcOEt). The total volume of the solutions (V_T) was 20 mL. For additional experimental data, see Tables S1-S3, S6, S8-S11 (Supporting Information).

As for CEVE, the resulting polymer being insoluble in n-hexane, living $PnBVE_{85}$ cations ($M_{n(GPC)}$ = 8,600 g/mol and PDI =1.08) was used as macromolecular initiator to keep growing chains in solution. **Fig. 2(ii)** shows that CEVE can be quantitatively polymerized (*i.e.,* $M_{n(GPC)}$ close to $M_{n(th)}$ with PDI < 1.1) (samples P37 and P38, **Table 2**) as long as the PCEVE block length does not exceed one-fifth the length of the PnBVE segment when **cHDMEA** is used as a di-functional initiator (sample P36, **Table 2**) or twice the length of the length of the PnBVE block when **nBEA** is used as a monofunctional initiator (Sample P11.4, Table S11 in ESI). Indeed, using living $PnBVE_{85}$ cation ($M_{n(GPC)}$ = 8,600 g/mol and PDI =1.08) as a mono-functional macroinitiator at the ratio of $[CEVE]_0/[PnBVE_{85}+]_0$ = 400, gelation was reached at x_{120h}^{CEVE} = 75 %, yielding $PnBVE_{85}$-*b*-$PCEVE_{300}$ with a PDI of 1.3 and a $M_{n(GPC)}$ of 37,000 g/mol slightly smaller than the calculated value assuming that one polymer chain is formed per molecule of nBEA (sample P11.4, **Fig. 2(ii)**, Table S11 in ESI). Similarly, $PCEVE_{82}$-*b*-$PnBVE_{200}$-*b*-$PCEVE_{82}$ with PDI of 1.23 was obtained at gelation (*i.e.*, $x_{42h}^{nBVE}(x_{120h}^{CEVE})$ = 100(81) %(%)) when the $[CEVE]_0/[nBVE]_0/[cHMDEA]_0$ ratio of 200/200/1 was targeted (sample P36, **Table 2**).

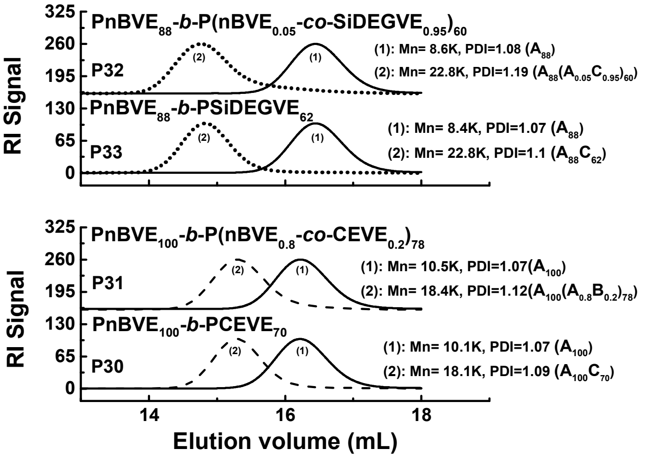


Fig. 5: GPC RI traces of $PnBVE_{100}$-*b*-$PCEVE_{70}$ (**P30**), $PnBVE_{100}$-*b*-P($CEVE_{0.2}$-co-$nBVE_{0.8})_{78}$ (**P31**), $PnBVE_{88}$-*b*-P($nBVE_{0.05}$-co-$SiDEGVE_{0.95})_{60}$ (**P32**) and $PnBVE_{88}$-*b*-$PSiDEGVE_{62}$ (**P33**) obtained by sequential cationic polymerization of n-butyl vinyl ether (nBVE) with 2-chloroethyl vinyl ether (CEVE) or 2-(*tert*-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) and initiated by the 1/1 n/n 1-butoxyethyl acetate (nBEA)/$Al_2Et_3Cl_3$ initiating system) in n-hexane at -20°C in the presence of 0.4 mM of 2,6 di-*tert*-butylpyridine (DtBP) and 1 M of ethyl acetate (AcOEt). For additional experimental data, see Table 1.

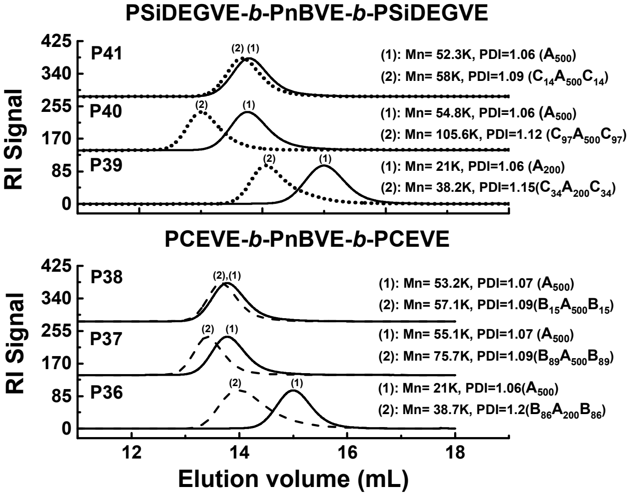


Fig. 6: GPC RI traces of PCEVE-*b*-PnBVE-b-PCEVE (**P36-P38**) and PSiDEGVE-*b*-PnBVE-b-PSiDEGVE (**P39-P41**) obtained by sequential cationic polymerization of n-butyl vinyl ether (nBVE) with 2-chloroethyl vinyl ether (CEVE) or 2-(tert-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) and initiated by the 1/1 n/n 1,4-cyclohexane-1,4-diyl bis(dimethanol di(1-ethyl acetate (cHMDEA)/$Al_2Et_3Cl_3$ initiating system in n-hexane at -20°C in the presence of 0.4 mM of 2,6 di-*tert*-butylpyridine (DtBP) and 1 M of ethyl acetate (AcOEt). For additional experimental data, see Table 2.

Using the following concentrations: $[CE]_0$ = 4 and 8 mM with $[Al_2Et_3Cl_3]_0/[CE]_0$ not higher than 1, $[AcOEt]_0$ = 1 M and $[DtBP]_0$ = 0.4 mM, we were able to determine the time required to polymerize quantitatively nBVE (x_{42h}^{nBVE} = 98% and x_{46h}^{nBVE} = 100%), CEVE (x_{120h}^{nBVE} = 100%) and SiDEGVE (x_{384h}^{SIDEGE} = 96% , x_{420h}^{SIDEGE} = 97% and x_{520h}^{SIDEGE} = 98%) in n-Hex at -20°C. The apparent rate

Table 1: Results for PnBVE-*b*-PCEVE (AB type), PnBVE-*b*-P(CEVE$_{0.2}$-co-nBVE$_{0.8}$) (A(A$_{0.8}$B$_{0.2}$) type), PnBVE-*b*-PSiDEGVE (AC type) and PnBVE-*b*-PCEVE-*b*-PSiDEGVE (ABC type) obtained by cationic polymerization of n-butyl vinyl ether (nBVE), 2-chloroethyl vinyl ether (CEVE) and 2-(tert-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) initiated by the 1/1 n/n 1-butoxyethyl acetate (nBEA) / $Al_2Et_3Cl_3$ initiating system in n-hexane at -20°C.

Samples	block[g] sequence	x_{time}^{VE} [a] h(%)	M_n (g/mol)		M_w/M_n	Composition $F_{(nBVE)}/F_{(CEVE)}/F_{(SiDGVE)}$ n/n/n	
			calcd[a]	GPC[b]	GPC[b]	calcd[c]	^{1}H NMR[d,e,f]
P30[h]	A	48(100)	9,600	10,500	1.07	104/72	100/70
	AB	72(61)	17,300	18,100	1.09		
P31[h]	A	48(100)	9,600	10,100	1.07	160/18	164/17
	A(A$_{0.8}$B$_{0.2}$)	72(80)	17,800	18,400	1.12		
P32[h]	A	42(96)	8,800	8,600	1.08	86/53	88/60
	A(A$_{0.05}$C$_{0.95}$)	72(82)	21,900	21,400	1.19		
P33[h]	A	42(100)	8,800	8,400	1.07	84/60	88/63
	AC	72(85)	21,900	23,800	1.09		
P34[h]	A	48(100)	8,800	8,400	1.06	88/93/24	85/100/25
	AB	120(100)	18,600	17,800	1.09		
	ABC	120(48)	24,500	23,800	1.13		
P35[h]	A	120(100)	19,300	20,100	1.08	200/210/192	200/204/195
	AB	120(100)	41,600	43,000	1.1		
	ABC	384(100)	89,100	90,600	1.2		

[a] Calculated $M_{n(th)}$ = (DP$_{n(nBVE)}$×100.16×x_{48h}^{nBVE}+ DP$_{n(CEVE)}$×100.16×x_{120h}^{CEVE} + DP$_{n,(SiDEGVE)}$x100.16x$x_{384h}^{SiDEGVE}$) where x_{time}^{VE}denotes the fraction of monomer VE converted into polymer at a given time, DP$_{n(VE)}$ =[VE]$_0$/[nBEA]$_0$.

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

[c] The calculated copolymer composition in moles is given by $F_{(nBVE)}$ = ($M_{n(th)}$ - MW$_{nBEA}$)/MW$_{nBVE}$, $F_{(CEVE)}$ = ($M_{n(th)}$ - $M_{n(precursor)}$)/MW$_{CEVE}$ and $F_{(CEVE)}$ = ($M_{n(th)}$ - $M_{n(precursor)}$)/MW$_{SiDEGVE}$ where MW$_{VE}$ denote the molecular weight of VE (*i.e.,* nBEA, nBVE, CEVE or SiDEGVE).

[d] The copolymer composition ratio on PnBVE-*b*-PCEVE, on the basis of ^{1}H NMR data, in moles is given by $F_{(nBVE)}/F_{(CEVE)} = [5/3\times f_{(0.9\ ppm)}/(f_{(4\text{-}3\ ppm)}\text{-}f_{(0.9\ ppm)}) + 2/3\times f_{(0.9\ ppm)}/(f_{(2.2\text{-}1\ ppm)}\text{-}2\times f_{(0.9\ ppm)})]/2$ where $f_{(\delta ppm)}$ *denote de intensity of peak at the given chemical shift* δ *ppm*

[e] The copolymer composition ratio on PnBVE-*b*-PSiDEGVE, on the basis of ^{1}H NMR data in CDCl$_3$, in moles is given by $F_{(nBVE)}/F_{(SiDEGVE)} = [2\times(f_{(0.9\ ppm)}\text{-}9/6\times f_{(0.03\ ppm)})/f_{(0.03\ ppm)} + 2\times(f_{(4\text{-}3.2\ ppm)}\text{-}9/6\times f_{(0.03\ ppm)})/f_{(0.03\ ppm)} + (f_{(2\text{-}1.2\ ppm)}\text{-}f_{(0.03\ ppm)}/3)/f_{(0.03\ ppm)}]/3$.

[f] The copolymer composition ratio on PnBVE-*b*-PSiDEGVE, on the basis of ^{1}H NMR data, in moles is given by $F_{(nBVE)}/F_{(SiDEGVE)} = 5/3\times(f_{(0.9\ ppm)}\text{-}9/6\times f_{(0.03\ ppm)})/f_{(0.03\ ppm)}$ and $F_{(CEVE)}/F_{(SiDEGVE)} = 6/5\times(f_{(4\text{-}3\ ppm)} - 9/6\times f_{(0.03\ ppm)} - 3/6\times(f_{(0.03\ ppm)}\times F_{(nBVE)}/F_{(SiDEGVE)})/f_{(0.03\ ppm)}$.

[g] Blocks A, B and C denote PnBVE, PCEVE and PSiDEGVE, respectively. The blocks (A_xB_{1-x}) and (A_xC_{1-x}) (with $x<1$) represent the statistical copolymers of nBVE/CEVE and nBVE/SiDEGVE, respectively, where *x* denotes the copolymer composition in number of nBVE monomer units.

[h] For additional experimental data, see general procedure S2 (Supporting Information)

constant values k_{app} in **Fig. 3** show that no significant change in nBVE polymerization time was observed when cHDMEA was used instead of nBEA at $[CE]_0/[Al_2Et_3Cl_3]_0 = 1$. Unfortunately, the use of a an excess of $Al_2Et_3Cl_3$ (*i.e.,* $[Al_2Et_3Cl_3]_0/[nBEA]_0$ = 2 and 3) to reduce the time of polymerization did not permit to produce at $[Al_2Et_3Cl_3]_0 > 10$ mM 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. The polymers obtained at $[Al_2Et_3Cl_3]_0/[nBEA]_0 > 1$ (**Fig. S14 in SI**) and at $[Al_2Et_3Cl_3]_0=[nBEA]_0 \geq 12$ mM (**Fig. S15 in SI**) 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 and n-Hex) and the temperature of polymerization (*i.e.,* T = -20, 0, 20°C). Besides, 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 (4-10%) 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 and 28) (**Fig S16 in SI**). Similar results were also obtained in n-Hex when the polymerization of nBVE or CEVE were initiated from living PSIDEGVE$_{75}$ cation ($M_{n(GPC)}$ = 17,500 g/mol and PDI =1.11) at -20°C by sequential monomer addition carried out at $x_{520h}^{SiDEGVE}$ ~ 96% (series P50 to P52) (**Fig S17** in ESI). In this respect, SiDEGVE was polymerized last in sequential monomer addition.

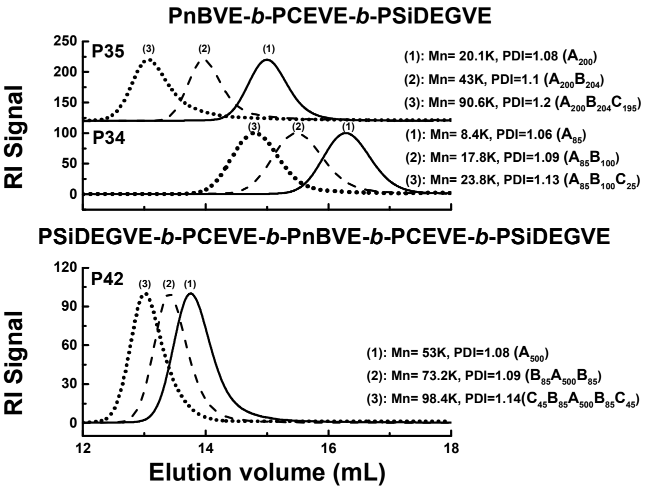


Fig. 7: GPC RI traces of PnBVE-*b*-PCEVE-*b*-PSiDEGVE (**P34,P35**) and PSiDEGVE-*b*-PCEVE-*b*-PnBVE-*b*-PCEVE-*b*-PSiDEGVE (**P42**) obtained by sequential cationic polymerization of n-butyl vinyl ether (nBVE), 2-chloroethyl vinyl ether (CEVE) and 2-(tert-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) using either 4 mM of the 1/1 n/n of nBVE-Acetic Acid Adduct (nBEA)/$Al_2Et_3Cl_3$ (**P34,P35**) or 4 mM of the 2/1 n/n 1,4-cyclohexane-1,4-diyl bis(dimethanol di(1-ethyl acetate (cHMDEA)/$Al_2Et_3Cl_3$ (**P42**) in the presence $Al_2Et_3Cl_3$ ($[Al_2Et_3Cl_3]_0/[\text{chain-end}]_0 = 1$) of 0.4 mM of 2,6 di-tert-butylpyridine (DtBP) and 1 M of ethyl acetate (AcOEt). For additional experimental data, see Tables 1 and 2.

Table 2: Results for PCEVE-*b*-PnBVE-*b*-PCEVE, PSiDEGVE-*b*-PnBVE-*b*-PSiDEGVE and PnBVE-*b*-PCEVE-*b*-PSiDEGVE obtained by cationic polymerization via sequential monomer addition of n-butyl vinyl ether (nBVE), 2-chloroethyl vinyl ether (CEVE) and 2-(tert-Butyldimethylsilyloxy) diethylene glycol vinyl ether (SiDEGVE) using the 1/2 n/n 1,4-cyclohexane-1,4-diyl bis(dimethanol di(1-ethyl acetate)) (cHDMEA) / $Al_2Et_3Cl_3$ initiating system in n-hexane at -20°C.

Series	Block[g] sequence	x_{time}^{VE} [a] h(%)	M_n (g/mol) calcd[a]	M_n (g/mol) GPC[b]	M_w/M_n GPC[b]	Composition $F_{(nBVE)}/F_{(CEVE)}/F_{(SiDGVE)}$ n/n/n calc[c]	Composition $F_{(nBVE)}/F_{(CEVE)}/F_{(SiDGVE)}$ n/n/n ¹H NMR[d,e,f]
P36[h]	A	42(100)	19,300	21,000	1.06	200/164/0	200/172/0
	BAB	120(81)	37,300	38,700	1.23[i]		
P37[h]	A	42(100)	50,100	55,100	1.07	550/195/0	500/188/0
	BAB	120(100)	72,400	75,700	1.09		
P38[h]	A	48(100)	50,100	53,200	1.07	531/36/0	500/28/0
	BAB	120(100)	52,800	57,100	1.09		
P39[h]	A	42(97)	19,300	21,000	1.06	200/74/0	200/68
	CAC	120(75)	38,700	38,200	1.15		
P40[h]	A	48(100)	50,100	54,800	1.06	547/206/0	500/194
	CAC	384(100)	102,800	105,600	1.12		
P41[h]	A	48(100)	50,100	52,300	1.06	522/23/0	500/28/0
	CAC	384(100)	59,400	58,000	1.09		
P42[h]	A	48(100)	50,100	53,000	1.08	550/192/100	500/190/90
	BAB	120(100)	72,400	73,200	1.09		
	CBABC	384(100)	91,700	98,400	1.14		

[a,b,c,d,e,f] See Table 1

[g] Blocks A, B and C denote PnBVE, PCEVE and PSiDEGVE, respectively.

[h] For additional experimental data, see general procedure S2 (Supporting Information)

2. Sequential base-assisted living cationic polymerization of nBVE, CEVE and SiDEGVE in n-Hex at -20°C – One pot synthesis of well-defined block copolymers and terpolymers. The block copolymers and terpolymers were synthesized at -20°C in n-Hex according to the following monomer addition sequence: nBVE, CEVE and SiDEGVE using either the 1/1 n/n nBEA/$Et_3Al_2Cl_3$ or the 1/2 n/n cHDMEA/$Et_3Al_2Cl_3$ initiating system.[66] The molecular weight and composition of the synthesized block copolymers and terpolymers are compiled in **Tables 1** and **2**.

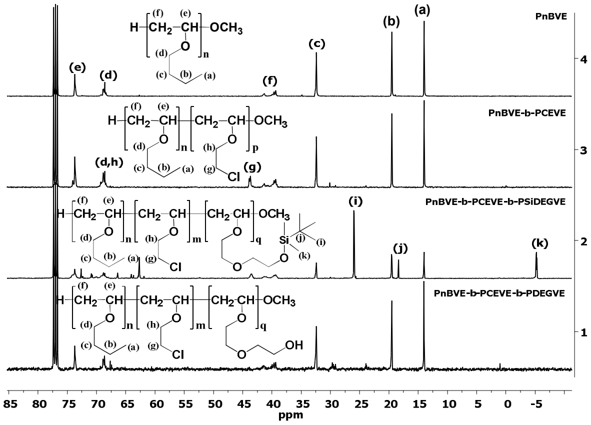


Fig. 8: ¹H NMR spectra ($CDCl_3$, r.t.) of triblock terpolymer PnBVE-*b*-PCEVE-*b*-PDEGVE (**P35**) and its precursors obtained by sequential living cationic polymerization of 0.77 M of nBVE, 0.8 M of CEVE and 0.33 M of SiDEGVE monomers using the 1/1 n/n nBEA/$Al_2Et_3Cl_3$ initiating system in n-Hexane at -20°C in the presence of 1 M of AcOEt and 0.8 mM of DtBP. For Additional experimental data, see Table 1

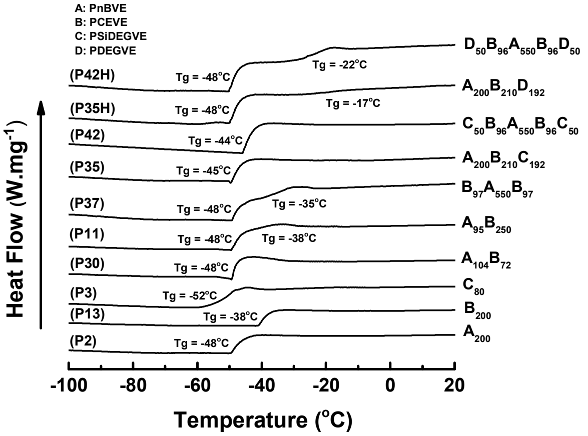


Fig. 9: Comparison of differential scanning calorimetry (DSC) curves between A, B, C homopolymers and their three corresponding AB diblock and ABC diblock copolymers and triblock terpolymers obtained with monofunctional nBEA and difunctional cHMDEA initiators when the polymerizations of nBVE, CEVE and SiDEGVE were carried out in the presence of $Al_2Et_3Cl_3$ in n-hexane at -20°C. ABD and DBABD are the terpolymer obtained after desilylation of the PSiDEGVE segment C.

2.1 Synthesis of well-defined PnBVE-based diblock and triblock copolymers with PCEVE or PSiEGVE as terminal blocks. The GPC traces of the block copolymers PnBVE-*b*-PCEVE (AB type),

Table 3: Glass transition temperatures (T_g) of the homopolymers, block copolymers and terpolymers

Series	Polymer [j]	Polymer segment	$M_{n(GPC)}$ [a] g/mol	PDI [a] g/mol	*Solubility* [k] *in n-Hex*	*Segment miscibility in bulk*	T_g [m]
P2[i]	A_{200}	PnBVE	21,400	1.08	yes	N.A.	-48
P13[j]	B_{200}	PCEVE	20,000	1.35	no [l]	N.A.	-38
P3[i]	C_{80}	PSiDEGVE	19,400	1.08	yes	N.A.	-52
P11[i]	$A_{95}B_{250}$	PnBVE PCEVE	9,500 36,000	1.09 1.2	gelation	no	-48 -38
P30[h]	$A_{104}B_{72}$	PnBVE PCEVE	10,500 7,600	1.07 1.09	yes	yes	-47
P31[h]	$A_{160}(A_{0.8}B_{0.2})_{18}$	PnBVE P(nBVE$_{0.8}$-co-CEVE$_{0.2}$)	10,100 8,300	1.07 1.12	yes	yes	-48
P32[h]	$A_{86}(A_{0.05}C_{0.95})_{53}$	PnBVE P(nBVE$_{0.05}$-b-SiDEGVE$_{0.95}$)	8,600 12,800	1.08 1.19	yes	yes	-49
P33[h]	$A_{84}C_{60}$	PnBVE PSiDEGVE	8,400 15,400	1.07 1.09	yes	yes	-50
P34[h]	$A_{88}B_{93}C_{24}$	PnBVE PCEVE PSiDEGVE	8,400 9,400 6,000	1.06 1.09 1.13	yes	yes	-47
P35[h]	$A_{200}B_{210}C_{92}$	PnBVE PCEVE PSiDEGVE	20,100 22,900 47,600	1.08 1.1 1.2	yes	yes	-45
P36[h]	$B_{82}A_{200}B_{82}$	PnBVE PCEVE	21,000 8,600	1.06 1.23	gelation	no	-48 -33
P37[h]	$B_{97}A_{550}B_{97}$	PnBVE PCEVE	55,100 10,300	1.07 1.09	limit to gelation	no	-48 -35
P38[h]	$B_{18}A_{531}B_{18}$	PnBVE PCEVE	53,200 1,950	1.07 1.09	yes	yes	-48
P39[h]	$C_{37}A_{200}C_{37}$	PnBVE PSiDEGVE	21,000 8,600	1.06 1.15	yes	yes	-48
P40[h]	$C_{103}A_{547}C_{103}$	PnBVE PSiDEGVE	54,800 25,400	1.06 1.12	yes	yes	-49
P41[h]	$C_{12}A_{522}C_{12}$	PnBVE PSiDEGVE	52,300 2,850	1.06 1.09	yes	yes	-48
P42[h]	$C_{55}B_{96}A_{550}B_{96}C_{55}$	PnBVE PCEVE PSiDEGVE	53,000 10,100 12,600	1.08 1.09 1.14	yes	yes	-44

[a,h] See Table 1

[i] For additional experimental data, see Tables S2,S3 and S11 in the Supporting Information

[j] Blocks A_n, B_m and C_p denote PnBVE$_n$, PCEVE$_m$ and PSiDEGVE$_p$, respectively, and n, m, p the corresponding degree of polymerization. The blocks (A_xB_{1-x}) and (A_xC_{1-x}) (with x<1) represent the statistical copolymers of nBVE/CEVE and nBVE/SiDEGVE, respectively, where *x* denotes the copolymer composition in number of nBVE monomer units.

[k] Solubility in n-Hex at the end of the polymerization

[l] PCEVE was synthesized in toluene. For additional experimental data, see Table S13 (Supporting Information)

[m] Mettler Toledo DSC 1 Star System over temperature range from -120 to 150 °C at the heating and cooling temperature of 5°C min^{-1}

PnBVE-*b*-PSiDEGVE (AC type), PCEVE-*b*-PnBVE-*b*-PCEVE (BAB type) and PSiDEGVE-*b*-PnBVE-*b*-PSiDEGVE (CAC type) **(Fig. 5** and **6)** shift clearly to higher molecular weights and virtually no peak corresponding to the unreacted precursor (*i.e.,* living PnBVE chains) and homopolymer (*i.e.,* PSiDEGVE or PCEVE formed by direct initiation from the $Al_2Et_3Cl_3$:VE initiating system) can be seen. The crossover efficiency is close to be quantitative, *i.e.,* higher than 98%. From comparisons of the integral value of the -Si-C-CH_3 and -Si(CH_3)$_2$- **NMR** peaks due to SiDEGVE and centered at 0.86 and 0.03 ppm, respectively, with the integral value of the -CH_3 peak in nBVE centered at 0.87 ppm and the integral value of the -CH_2-CHO- peak due to PCEVE, PSiDEGVE and PnBVE centered at 1.5-1.67 and 1.7-1.89 ppm, respectively, the copolymer composition $F_{nBVE}/F_{CEVE}/F_{SiDEGVE}$ as well as $M_{n(H\ NMR)}$ (the theoretical molecular number average molecular weight calculated by ^{1}H NMR for 100% monomer efficiency) were calculated according to the equation listed in the **Table 1**. The data listed in **Tables 1** and **2** show that the block copolymers and terpolymers obtained in this study have $M_{n(GPC)}$ close to the calculated $M_{n(NMR)}$ and the copolymer compositions are in agreement with targeted $M_{n(th)}$ values calculated from the targeted DP.

2.2 Synthesis of well-defined PnBVE-based triblock and pentablock terpolymers with a PCEVE central block and a PSiEGVE outer block. When PnBVE-*b*-PCEVE (**Fig. 5**) and PCEVE-*b*-PnBVE-*b*-PCEVE (**Fig. 6**) were synthesized using nBEA as the monofunctional initiator and cHMDEA as the difunctional initiator, gelation could be prevented by targeting a $F_{(nBVE)}/F_{(CEVE)} >$ 5 and 0.5, respectively; this allowed the quantitative polymerization of CEVE (samples P37 and P38) with the formation of a block copolymer with PDI lower than that of the PnBVE precursor. In this respect, triblock (samples P34 andP35) and pentablock (P42) terpolymers were synthesized successfully with GPC traces (**Fig. 7**) showing a clear shift to higher molecular weights with $M_{n(GPC)}$ close to $M_{n(NMR)}$ and PDI close to 1.15-1.18. Here, the increase in PDI is due to a lower initiation rate with respect to propagation when the polymerization of SiDEGVE is initiated from PCEVE macroinitiators (samples P34, P35 and P42). Indeed, at $[\text{SiDEGVE}]_0$ = 0.4 M, $[\text{AcOEt}]_0$ = 1 M, $[\text{Initiator}]_0$ = 4 mM, $[Al_2Et_3Cl_3]_0$ = 4 mM and $[\text{DtBP}]_0$ = 0.4 mM, PSiDEGVE with PDI < 1.1 was obtained only with SiDEGEA and nBEA initiators (**Fig. 1 and 2**). Under similar conditions, the use of PCEEA (PCEVE cation of DP = 4-5) as the in-situ monofunctional initiator yielded PSiDEGVE with a PDI higher than the one obtained with SiDEGEA, *i.e.,* 1.08 and 1.19 with SiDEGEA and PCEEA, respectively. This shows that the initiation rate to propagation rate ratio during cationic polymerization of SiDEGVE increases in the following order: SiDEGEA > PCEEA. Slow initiation rate to that of propagation rate ratios were also observed when nBVE was not quantitatively converted into a polymer in the block copolymer experiments; *e.g.,* PnBVE-*b*-PSiDEGEA of 23 K with PDI of 1.09 (sample P33, Table 1) and 1.2 (sample P32, Table 1) were obtained when SiDEGVE was added at x_{48h}^{nBVE} = 100% and x_{42h}^{nBVE} = 98%, respectively.

The desilylation of the PSiDEGVE segment in block copolymers and terpolymers was carried out using n-Bu_4N^+,F^- (3 equivalents with respect to the terbutyl dimethylsilyl ether group) in THF at 0°C. Quantitative desilylation was confirmed, *e.g.,* as shown in the **Fig. 8** for ABC-type terpolymers P35 by the disappearance of the ^{1}H NMR signals at 0.03 ppm (s, 6H, -Si(CH_3)$_2$-) and 0.86 ppm (s, 6H, -Si(CH_3)$_2$-C(CH_3)$_3$) and by the disappearance of ^{13}C NMR signals at -3.36 ppm (s, 2C, -Si(CH_3)$_2$-), 18.34 ppm (s, C, -Si(CH_3)$_2$-C(CH_3)$_3$) and 25.96 ppm (s, 3C, -Si(CH_3)$_2$-C(CH_3)$_3$) of the -butyl dimethyl silyl group.

2.3 Thermal analysis. Differential Scanning Calorimetry (DSC) experiments were performed to investigate the miscibility of the PnBVE, PCEVE and PSiDEGVE blocks present in the copolymers and terpolymers. The glass-transition temperatures (T_g) of the investigated copolymers and terpolymers are summarized in **Table 3** as well as those of the individual homopolymers. The T_g, at around -48°C, corresponds to the PnBVE segment. The other T_g's at about -38 and -52°C correspond to PCEVE and PSiDEGVE segments, respectively (**Fig. 9**, **Table 3**). The presence of two T_g's in PnBVE-*b*-PCEVE and in PCEVE-*b*-PnBVE-*b*-PCEVE copolymers, indicative of a phase separation between the PnBVE and PCEVE segments, was observed only for the copolymers that self-aggregated in n-Hex at -20°C when the content in PCEVE exceeded the p/n value of 2 in A_nB_p-type copolymers [*i.e.*, in PnBVE_{95}-*b*-PCEVE_{250} (sample P11)] and the p/n value of 0.2 in $B_pA_nB_p$-type copolymers (*i.e.*, PCEVE_{97}-*b*-PnBVE_{550}-b-PCEVE_{97} (sample P37)). For all other composition ranges, a single T_g, which was between the T_g values of the individual homopolymers, was observed, which indicated that PnBVE, PCEVE and/or PSiDEGVE segments are miscible. T_g's of both of the samples remained relatively constant between the first and second heating. The desilylation of the PSiDEGVE segment was confirmed by the appearance of a new T_g at around -20°C associated to the poly(di-ethylene glycol vinyl ether) (PDEGVE) segment in the $\text{PnBVE}_{200}\text{PCEVE}_{210}\text{PDEGVE}_{192}$ triblock and in the $\text{PDEGVE}_{50}\text{PCEVE}_{96}\text{PnBVE}_{550}\text{PCEVE}_{96}\text{PDEGVE}_{50}$ terpolymers (**Fig. 9**).

Conclusions

The sequential base-assisted living cationic polymerizations of nBVE, CEVE and SiDEGVE by $Al_2Et_3Cl_3$ were achieved at -20°C in the presence of 1 M of AcOEt in n-Hex, a solvent in which PCEVE is insoluble. Using nBEA and cHMDEA as initiators witgh structure equivalent to dormant species allowed fast initiation; well-defined PnBVE_n-*b*-PCEVE_p-*b*-PSiDEGVE_q and PSiDEGVE_q-*b*-PCEVE_p-*b*-PnBVE_n-*b*-PCEVE_p-*b*-PSiDEGVE_q terpolymers with high crossover efficiency, no PCEVE-induced physical gelation, predictable $M_{n(GPC)}$ and PDI < 1.15 were synthesized successfully provided that the targeted DP_{CEVE}/DP_{nBVE} ratio (*i.e.*, *p*/*n*) did not exceed 2 and 0.2, respectively. Good control over $M_{n(GPC)}$ and PDI could only be achieved at $[Et_3Al_2Cl_3]_0$ < 10 mM with the proviso that 0.4 μmol/mL of DtBP is used as a non-nucleophilic proton trap to prevent any initiation from the $Et_3Al_2Cl_3{:}H_2O$ complex (*i.e.,* $[Et_3Al_2Cl_3{:}H_2O]_0$ = 0). The use of an excess of $Et_3Al_2Cl_3$ (*i.e.*, $[Et_3Al_2Cl_3]_0$/[Chain end]$_0$ > 1) was also not beneficial as direct initiation from the $Et_3Al_2Cl_3{:}$VE complex can occur yielding P(VE)s with $M_{n(GPC)} < M_{n(th)}$ (*i.e.*, $[\text{initiator}]_0 = [\text{VEA}]_0 + [Et_3Al_2Cl_3{:}\text{VE}]_0$) and PDI > 1.2). In toluene, where PCEVE is fully soluble, chain termination reactions takes place at -20°C, yielding beyond at x^{VE} = 90% a toluene-ended PVE (*i.e.,* $(\text{PVE})_x$S with x =1 or 2) species unable to propagate further in the presence of VE. In DCM, the propagation rate was much faster than the initiation, which led to an incomplete initiation (*i.e.,* low initiator efficiency) and hence a drift of the linear dependence, M_n *vs*. $M_{n(th)}$. A higher molecular weight was observed at -20°C together with the increase of the PDI. The DSC revealed that the synthesized block co- and terpolymers have a single T_g, between the T_g s of the individual homopolymers, indicating no phase separation, except in the case of PnBVE_n-*b*-PCEVE_p and PCEVE_p-*b*-PnbVE_n-*b*-PCEVE_p with *p*/*n* higher than 2 and 0.2, respectively. The quantitative desilylation of the PSiDEGVE segment, using n-Bu_4N^+,F^- in THF at 0°C, was confirmed by NMR and by the appearance of a new T_g at around -22°C in block copolymers and terpolymers containing PDEGVE segments. This system represents a significant advance in terms of synthesis of polyvinyl ether-based materials with functional groups that could be subsequently be subjected to grafting-from and grafting-onto reactions.

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Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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67 In DCM at -20°C, the polymerization of nBVE, CEVE and SiDEGVE in the presence of $Al_2Et_3Cl_3$ (catalyst) become dark drown during the polymerization and stopped before the monomers is quantitatively converted into polymers.

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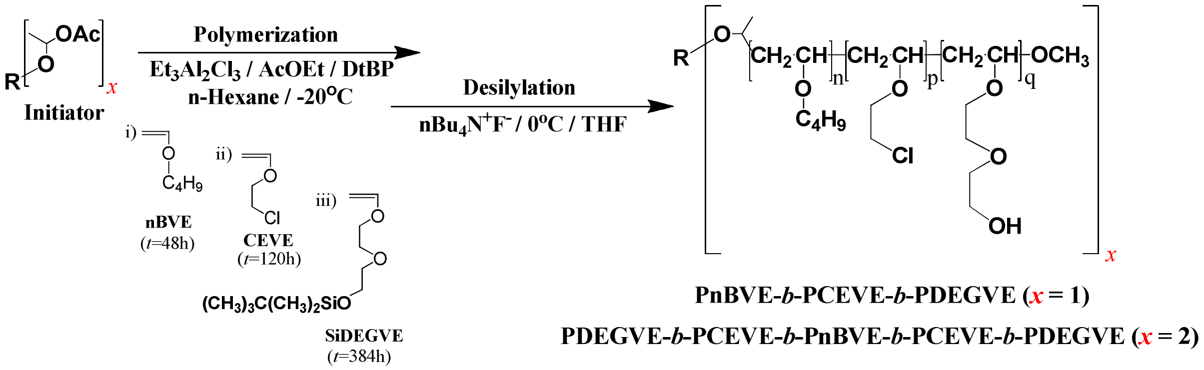
SYNOPSIS TOC

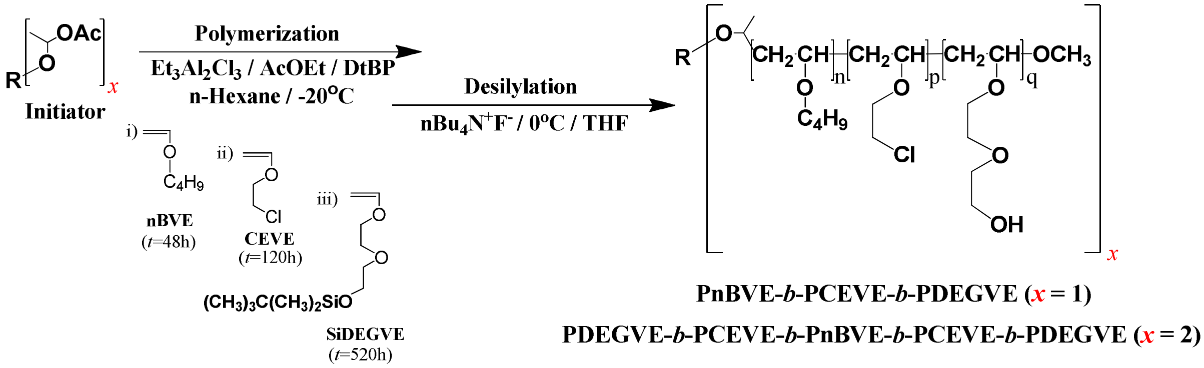


Livingness at ($x = 1$; p/n < 2) and ($x = 2$; p/n < 0.2)

nBEA (**Initiator** with R- = C_4H_9-; $x = 1$); **cHMDEA** (**Initiator** with -R- = -CH_2-C_6H_{10}-CH_2-, $x = 2$)

$[\mathrm{nBEA}]_0 = [\mathrm{Al_2Et_3Cl_3}]_0 = 4$ mM ($[\mathrm{nBEA}]_0/[\mathrm{Al_2Et_3Cl_3}]_0 = 1$, $[\mathrm{AcOEt}]_0 = 1$ M and $[\mathrm{DtBP}]_0 = 0.4$ mM

SYNOPSIS TOC



Livingness at ($x = 1$; p/n < 2) and ($x = 2$; p/n < 0.2)

nBEA (**Initiator** with R- = C_4H_9-; $x = 1$); **cHMDEA** (**Initiator** with -R- = -CH_2-C_6H_{10}-CH_2-, $x = 2$)

$[\text{nBEA}]_0 = [Al_2Et_3Cl_3]_0 = 4$ mM ($[\text{nBEA}]_0/[Al_2Et_3Cl_3]_0=1$, $[\text{AcOEt}]_0 = 1$ M and $[\text{DtBP}]_0 = 0.4$ mM