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Synthesis of 1-oxa-2-silacyclopentane derivatives via intramolecular nucleophilic attack at silicon

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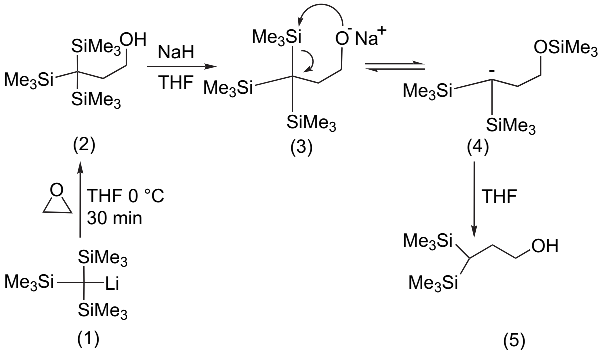
Abstract—Metalation of $(HSiMe_2)_3CH$ with lithium diisopropylamide (LDA) in THF gives $(HSiMe_2)_3CLi$, which reacts with ethylene oxide, propylene oxide, 1,2-epoxy butane, 1,2-epoxy pentane, 1,2-epoxy hexane, and epichlorohydrin to give the corresponding 1-oxa-2-silacyclopentane derivatives. Then, glycidylmethacrylate (GM) random copolymers with styrene (St) (in a 1:1 and 1:3 mol ratio) were synthesized by solution free radical polymerization at 70(±1) °C using α,α′-azobis(isobutyronitrile) (AIBN) as an initiator. Both types of copolymers were treated with $(HSiMe_2)_3CLi$ to give new modified copolymers. The reaction of $(HSiMe_2)_3CLi$ with epoxides on the side chains of the copolymers does not lead to intramolecular nucleophilic attack contrary to simple epoxides. All the products have been characterized by spectroscopic techniques.

1. Introduction

Cyclic silanes have been the targets of recent synthesis methods because these heterocycles can be readily converted into alcohols after the oxidation of a carbon–silicon bond.[1–4] The 1-oxa-2-silacyclopentane moiety, in particular, is an useful intermediate for the stereoselective formation of 1,3-diols.[5–7] Much novel chemistry has emerged from the studies of compounds in which the bulky ligand $(Me_3Si)_3C$, or to a lesser extent the related ligand $(HSiMe_2)_3C$, is attached to metals or metalloid centers.[8–12]

The synthesis of the compound $(HSiMe_2)_3CH$ was reported in 1983, but little attention was paid to it until it was shown that it could be metalated by LDA in THF to give $(HSiMe_2)_3CLi$.[13,14] Extensive studies in this area led to the characterization of novel stable compounds and new reaction mechanisms, but there are only few studies about attaching bulky organosilicon groups to the carbon atom. In this work, we were interested in studying of the reaction of $(HSiMe_2)_3CLi$ with some epoxides and then comparison of the reaction of $(SiMe_3)_3CLi$ and $(HSiMe_2)_3CLi$ groups toward epoxides. We then report the synthesis and properties of poly(GM-*co*-St) modified with $(HSiMe_2)_3C$ groups (Scheme 1).



Scheme 1.

2. Results and discussion

The ligand precursor $(HSiMe_2)_3CH$ was made by the reaction of $CHBr_3$ and Mg with $HSiMe_2Cl$ in THF.[13,14] The solvated organolithium reagent $(HSiMe_2)_3CLi$, which was obtained by the treatment of $(HSiMe_2)_3CH$ with LDA at room temperature, reacts with ethylene oxide in THF to give the 1-oxa-2-silacyclopentane derivative **7a**. It has been shown previously that the reaction of $(Me_3Si)_3CLi$ (tris(trimethylsilyl)methyllithium is referred to as trisyl lithium and commonly denoted by TsiLi) with ethylene oxide gave the alcohol **2**, which reacted with sodium hydride in THF to yield the silyl ether **4** and hence, by hydrolysis, the alcohol **5**,[15] which has one fewer silyl group. The silicon transfer **3**→**4**→**5** takes ca. 90 min at room temperature. Potassium *tert*-butoxide in THF worked comparably well, but the lithium and magnesium alkoxides did not react.

Keywords: Tris(dimethylsilyl)methyl; Ring opening reaction; Epoxides; Intramolecular alkoxide attack; 1-Oxa-2-silacyclopentane.

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Solvents such as diethyl ether, dioxane, dimethoxyethane, and benzene were ineffective with the sodium alkoxide. By analogy with the Brook rearrangement, one would expect 1,4-silyl shifts **2**→**4** to be endothermic, so that the equilibrium will be pulled over only when a proton source is available. It seems likely that the alkyl-sodium intermediate **4** is such a base (although the slightly more hindered and slightly better stabilized lithium base **1** is stable in THF at room temperature), which explains why the rearrangement **3**→**5** is only noticeable in THF and not in other aprotic solvents.[15] We postulate that when $(HSiMe_2)_3CLi$ is treated with ethylene oxide, it initially forms the alkoxide **6** then because of the presence of the Si–H bond, an intramolecular alkoxide attack takes place (Scheme 2). FTIR, NMR (^1H and ^{13}C), and mass spectrometry data confirmed the formulation given for the related cyclic compounds.

The FTIR spectrum of the obtained product **7a** does not show a broad peak above 3000 cm^{-1}, which indicates the absence of OH group. The $SiMe_2$ signals in the ^1H NMR spectrum show two separated signals; a multiplet at 0.15–0.18 ppm for 12 protons (a) and a singlet at 0.25 ppm for 6 protons (b). No broad peak appears for the OH group. Integration of the peak at 4.00–4.04 ppm corresponding to the Si–H bond shows two protons for the Si–H bond instead of three protons, which clearly indicates the liberation of a hydride anion. A typical ^1H NMR spectrum of the cyclic compound **7a** is given in Figure 1A. In the ^{13}C NMR spectrum, the resonance signals at 64.9 and 31.0 ppm were due to the CH_2O (f′) and CH_2CSiMe_2H (e′), respectively. The signal at 7.5 ppm was attributed to $CSiMe_2H$ (c′). The resonance signal at −0.5 ppm was due to the $(CH_3)_2SiO$ and two resonance signals at −3.9 (a′) and −3.5 ppm (b′), related to two different $SiMe_2H$ groups. A typical ^{13}C NMR spectrum of cyclic compound **7a** is shown in Figure 1B. Mass spectrometry showed *m/z* 232 (5%, M^+), 217 (8%, $[M-Me]^+$), and 59 (100%, $[SiMe_2H]^+$). All these results clearly show that the ring opening reaction led to cyclic compound **7a** instead of the expected alcohol **8**. However, unlike TsiLi, which is protonated toward propylene oxide,[10] $(HSiMe_2)_3CLi$ reacts with propylene oxide and clearly gives **7b**. The structure of the product was proven by spectroscopic data. We also treated $(HSiMe_2)_3CLi$ with 1,2-epoxy butane, 1,2-epoxy pentane, 1,2-epoxy hexane, and epichlorohydrin and obtained the corresponding products **7c–f**, respectively. In the case of epichlorohydrin, because of the high reactivity of the epoxide group due to the considerable strain in the three-membered epoxide ring, the CH_2–Cl bond remained unchanged during the reaction (when the experimental conditions were carefully chosen).

We were interested in carrying out analogous reactions with polymers containing epoxide groups in the side chains. For this reason glycidylmethacrylate was chosen as a monomer in free radical polymerization. The GM monomer was copolymerized with styrene at 70(±1) °C using azobis(isobutyronitrile) (AIBN) as the radical initiator in two ratios (1:1 and 1:3) (Scheme 3). Composition, molecular weight, and yield of copolymers (**I**, **II**) are shown in Table 1.

The resulting polymer is a white solid and is soluble in chloroform, dichloromethane, benzene, toluene, xylene, THF, *N*,*N*-dimethyl formamide, and dimethyl sulfoxide and insoluble in *n*-hexane, methanol, ethanol, and water. After standing for a long period of time even at room temperature, the GM copolymers became insoluble in organic solvents, probably due to intermolecular cross-linking between epoxy units.[16,17]

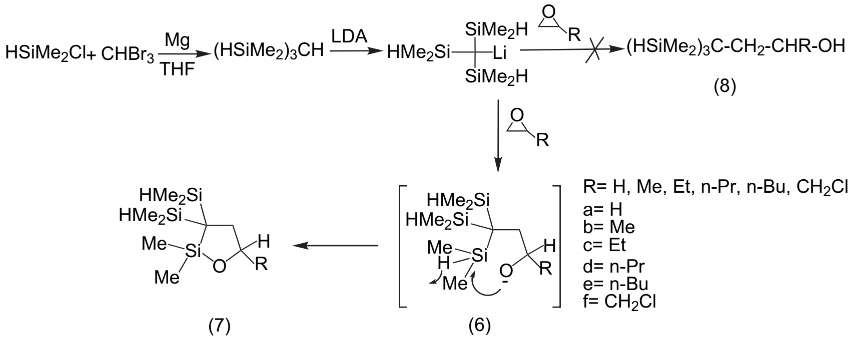
Gel permeation chromatography (GPC) was used to determine the number- and weight-average molecular weights of copolymers (**I**, **II**) soluble in THF and the results are listed in Table 1. The copolymer compositions were determined using ^1H NMR spectra.[18,19] The mole fraction of GM in the copolymer chains was calculated by measuring the integrated peak areas of aromatic protons of the styrene and aliphatic protons of the GM and other monomer units. The expression in Eq. 1 was used to determine the composition of copolymers **I** and **II**, where m_1 is the mole fraction of GM and $1-m_1$ is that of the styrene monomer. The styrene contains 5 aromatic protons and 3 aliphatic protons, and GM contains 10 aliphatic protons:

$$\frac{I_A}{I_a}=\frac{\text{Integrated peak area of aromatic protons}}{\text{Integrated peak area of aliphatic protons}}=\frac{5m_1}{3m_1+10(1-m_1)} \qquad (1)$$

on simplification, this gives:

$$m_1=\frac{10I_A}{5I_a+7I_A} \qquad (2)$$

Therefore, the mole fraction of GM in the copolymers (**I**, **II**) was determined from Eq. 2. Table 1 also shows mole fractions of GM and related co-monomer in the copolymers.



Scheme 2. The postulated mechanism for the formation of 1-oxa-2-silacyclopentane derivatives.

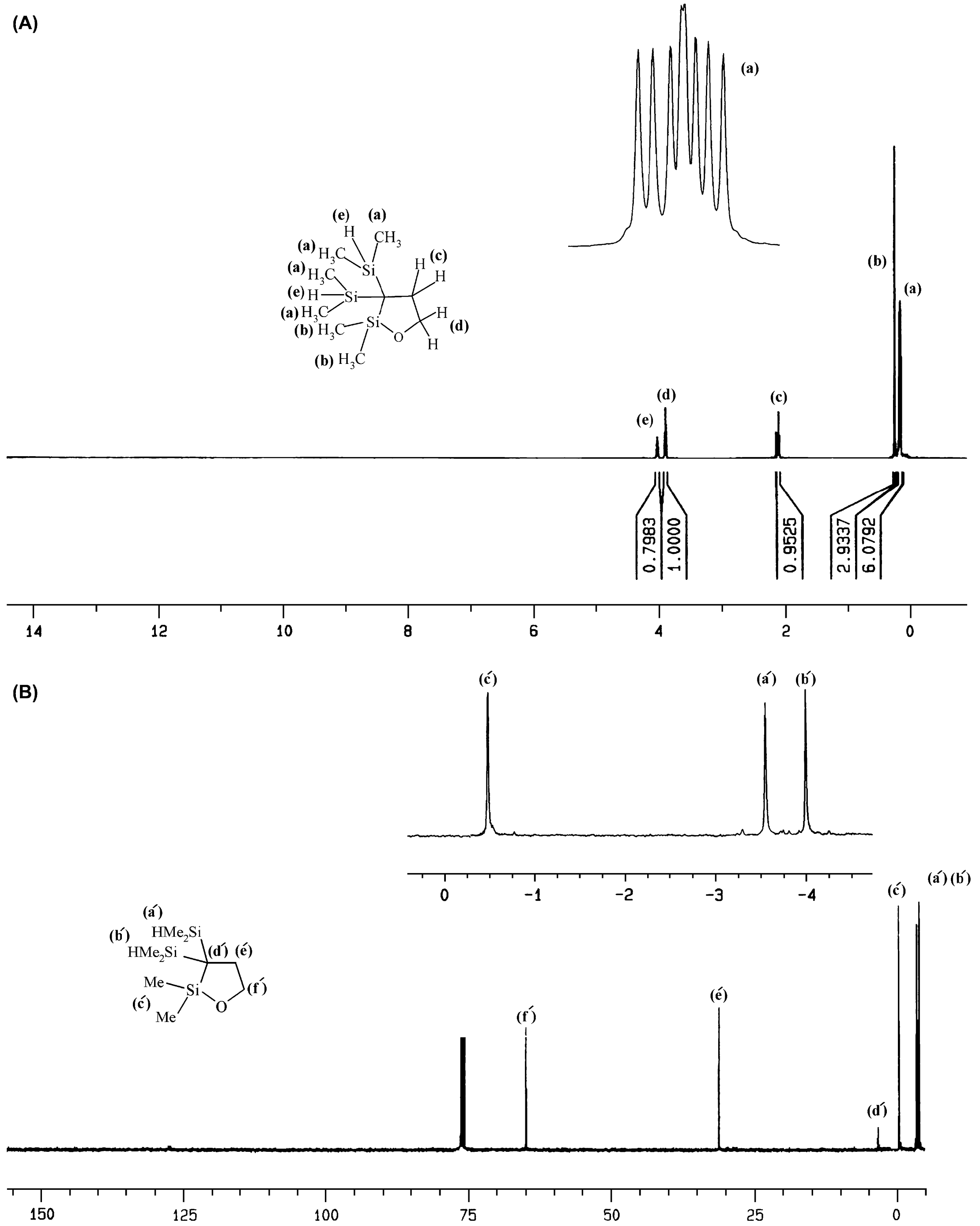
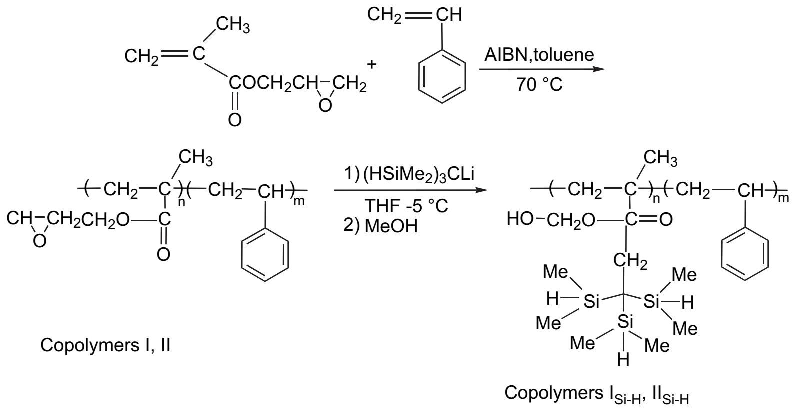


Figure 1. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of compound (**7a**) in $CDCl_3$ without tetramethylsilane.

A solution of $(HSiMe_2)_3CLi$ as a nucleophilic reagent reacted with epoxide groups in copolymers (**I**, **II**) with ring opening of all epoxide groups to give new modified copolymers. These new organosilylated copolymers ($\mathbf{I}_{Si-H}$, $\mathbf{II}_{Si-H}$) were isolated in high yields in cooled methanol as a nonsolvent. The structures of these new copolymers were supported by the spectra. The FTIR spectra of the modified copolymers ($\mathbf{I}_{Si-H}$, $\mathbf{II}_{Si-H}$) show that the broad band characteristic of hydroxyl groups at wave number 3500 cm^{-1}, a sign of hydroxyl formation following the breaking of the epoxy ring, and the ^{1}H NMR spectra, indicate a singlet for 18 protons of $(HSiMe_2)_3CH$ (also see Fig. 2).

3. Conclusion

A novel synthetic method for the preparation of 1-oxa-2-silacyclopentane derivatives with Si–H functional groups on the ring has been described. Unlike TsiLi, when $(HSiMe_2)_3CLi$ reacts with epoxides, cyclic products have been obtained. Because of the presence of the Si–H bond, an intramolecular alkoxide attack takes place after the ring opening reaction. In contrast to simple epoxides, when $(HSiMe_2)_3CLi$ is treated with epoxide groups on the side chain of poly(GM-*co*-St), ring opening reactions do not lead to the above intramolecular attack. Probably, the high



Scheme 3. Reaction of $(HSiMe_2)_3CLi$ with copolymer **I** and **II**.

Table 1. Compositions, molecular weights and yields of copolymers (**I**, **II**)

Copolymer	M_n[a]×10^3	M_w[a]×10^3	M_w/M_n	GM[b] (mol %)	St[b] (mol %)	Weight (g)	Yield (%)
Poly(GM-co-St)$_{1:1}$(**I**)	29	52	1.80	53	47	3.77	83
Poly(GM-co-St)$_{1:3}$(**II**)	10.6	20.7	1.95	31	69	3.93	80

[a] Molecular weight was obtained by GPC analysis.

[b] Mol % of both monomers were obtained via Eq. 2.

rigidity of the copolymers makes them unfavorable to intramolecular reaction.

4. Experimental

4.1. Solvents and reagents

The reactions involving organolithium reagents were carried out under dry argon. Solvents were dried by standard methods. Substrates for the preparation of tris(dimethylsilyl)methyllithium, viz. $HSiMe_2Cl$ (Merck), Mg (Merck), $CHBr_3$ (Merck), and all epoxides (Merck), were used as received. Glycidylmethacrylate (GM) (Merck) and styrene (Merck) were distilled under reduced pressure to remove inhibitors before use. AIBN (Merck) was purified by crystallization from methanol.

4.2. Spectra

The ^1H NMR and ^{13}C NMR recorded with a NMR Bruker FT-400 MHz spectrometer at room temperature used $CDCl_3$ as a solvent. The mass spectra were obtained with Finnigan-Mat mode 8400, operating at 70 eV. The FTIR

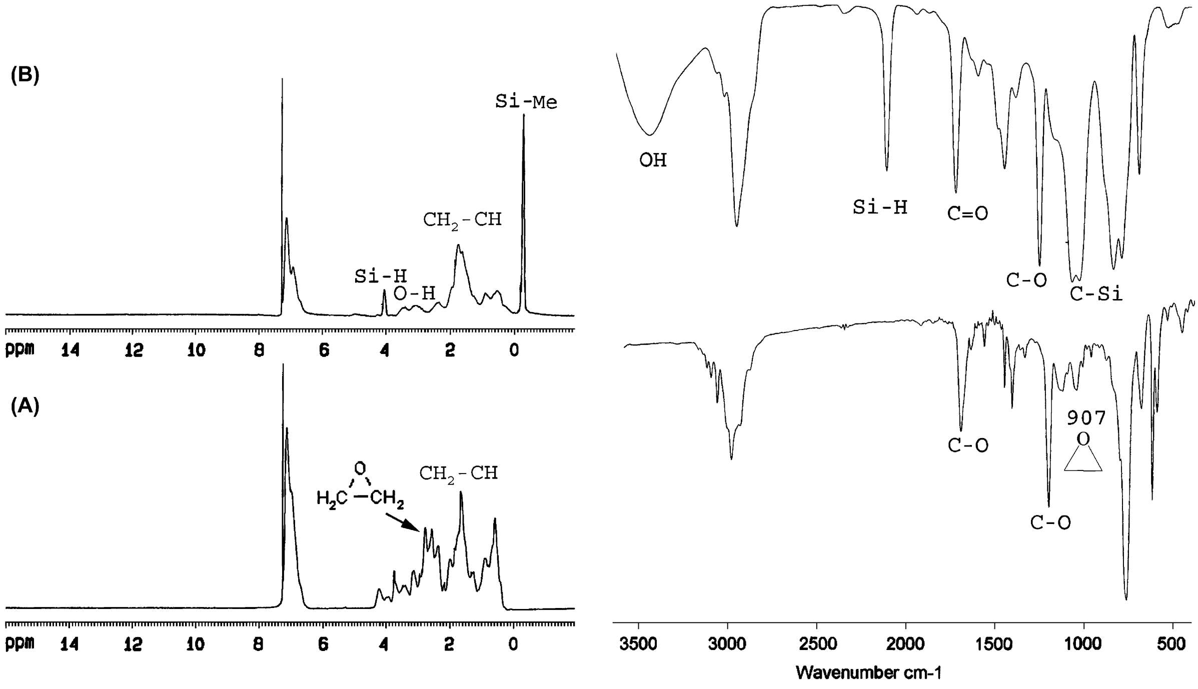


Figure 2. ^1H NMR and FTIR spectra of (A) **I** and (B) $\mathbf{I}_{Si-H}$.

spectra were recorded on a FTIR Bruker-Tensor 270 spectrometer. Elemental analyses were carried out with Heareus CHN-RAPID instrument. The molecular weights (M_w and M_n) were determined using a Waters 501 gel permeation chromatograph fitted with 10^2 and 10^3 nm Waters Styragel columns. THF was used as an elution solvent at a flow rate of 1 ml/min and polystyrene standards were employed for calibration.

4.3. Preparation of tris(dimethylsilyl)methyllithium, $(HSiMe_2)_3CLi$, solution in THF[14]

A 50 ml round-bottom flask equipped with a stirrer, septum, and gas-inlet needle was charged with diisopropylamine (1.6 g, 15.8 mmol) and 20 ml of THF. The flask was placed in a water/ice bath and then *n*-BuLi (11.5 ml, 1.5 M solution in hexane) was added dropwise via syringe to make a clear yellow solution. The solution was stirred for an additional 30 min. The lithium diisopropylamide (LDA) solution was transferred into a dropping funnel after which it was added dropwise to a 100 ml round-bottom flask containing tris(dimethylsilyl)methane, $(HSiMe_2)_3CH$ (3 g, 15.8 mmol), in 10 ml THF under argon atmosphere at room temperature. The orange-red solution was stirred at ambient temperature for 10 h.

4.4. Copolymerization of glycidylmethacrylate (GM) with styrene copolymer (I, II)

Poly(GM-*co*-St) was synthesized by following the general method. In a Pyrex glass ampoule, a mixture of GM (2.84 g, 20 mmol), AIBN (0.06 g, 0.4 mmol), and styrene (2.08 g, 20 mmol) was dissolved in toluene (15 ml) then the ampoule was degassed, sealed under vacuum, and maintained at 70(±1) °C in a water bath and shaken by a shaker machine for about 24 h. The viscous solution was poured from the ampoule into 150 ml of cooled methanol. The precipitate was collected and washed with cooled acidic methanol for several times and dried under vacuum at room temperature to give 3.77 g of white copolymer. The yield of copolymer is 83%. Also, a mixture of GM (1.42 g, 10 mmol), styrene (3.12 g, 30 mmol), and AIBN (0.06 g, 0.4 mmol) in toluene (15 ml) was copolymerized as described above to give 3.93 g of copolymer **II**. The yield of copolymer is 80%. FTIR (KBr, cm^{-1}): 3026 (Ar–H), 2927 (R–H), 1728 (C=O), 1601, 1450 (C=C), 1116 (C–O), 907, 846 (C–O epoxide); ^1H NMR (400 MHz, $CDCl_3$) δ 1.6–2, 2.5–3.4, 3.7–4.2, 6.9–7.2.

4.5. The ring opening reaction between the epoxy groups of poly(GM-*co*-St) with $(HSiMe_2)_3CLi$ (I_{Si-H}, II_{Si-H})

The ring opening reaction was carried out with vigorous magnetic stirring at −5 °C for 3 h. A solution of copolymer **I** (0.5 g, with 2.13 mmol of epoxy-containing monomer units) or copolymer **II** (0.5 g, with 1.34 mmol of epoxy-containing monomer units) in THF (30 ml) was transferred into a dropping funnel under argon atmosphere. Then, copolymer was added dropwise with stirring to a solution of a $(HSiMe_2)_3CLi$ (2 g, 10.5 mmol) into the flask at −5 °C. The reaction was quenched by adding a small amount of acidic methanol after 2 h and the reaction mixture was poured into cooled acidic methanol to precipitate the polymer. FTIR (KBr, cm^{-1}): 3443 (OH), 3066 (Ar–H), 2956 (R–H), 2110 (Si–H), 1728 (C=O), 1257, 850 (C–Si), 1034 (C–O); ^1H NMR (400 MHz, $CDCl_3$) δ 0.1, 1.6–2, 4.2, 6.9–7.2.

4.6. General procedure

Epoxides were added dropwise to a solution of tris(dimethylsilyl)methyllithium (15.8 mmol) at −5 °C and the mixtures were kept for some hours at the mentioned temperature, then poured into ice-cold solution. The organic layer was separated and the aqueous layer was extracted twice with 100 ml ether. The organic layers were combined and washed twice with 50 ml 2 M aqueous hydrochloric acid, twice with 50 ml distilled water, and once with 50 ml saturated aqueous sodium chloride solution. The clear yellow organic layer was dried over anhydrous sodium sulfate and filtered. The solvent was evaporated and the residue purified by preparative TLC (silica gel) to give the products.

4.6.1. Preparation of 3,3-bis(dimethylsilyl)-2,2-dimethyl-1-oxa-2-silacyclopentane (7a). The reaction was carried out according to the general procedure (23.7 mmol ethylene oxide with 15.8 mmol tris(dimethylsilyl)methyllithium) and the reaction mixture was stirred for 1 h at −5 °C (crude product 2.2 g). A pure colorless liquid was obtained by preparative TLC (silica gel, 1:1 *n*-hexane:CH_2Cl_2, R_f=0.8). FTIR (KBr, cm^{-1}): 2105 (Si–H), 1255, 865 ($Si–CH_3$), 1052 (Si–O–C); ^1H NMR (400 MHz, $CDCl_3$): δ 0.15–0.18 (m, 12H, $HSi(CH_3)_2$), 0.25 (s, 6H, $OSi(CH_3)_2$), 2.09 (t, 2H, J=8 Hz, CH_2CH_2O), 3.88 (t, 2H, J=6 Hz, CH_2CH_2O), 4.00–4.04 (m, 2H, Si–H); ^{13}C NMR ($CDCl_3$): δ −3.9, −3.5 ($HSi(CH_3)_2$), −0.5 ($OSi(CH_3)_2$), 7.5 (CCH_2CH_2), 31.0 (CH_2CH_2O), 64.9 (CH_2CH_2O); *m*/*z* (EI): 232 (4%, $[M]^+$), 217 (8%, $[M-Me]^+$), 173 (46%, $[M-(HSiMe_2)]^+$), 59 (100%, $[HSiMe_2]^+$). Anal. Calcd for $C_9H_{24}Si_3O$: C, 46.5; H, 10.4. Found: C, 46.6; H, 10.2%.

4.6.2. Preparation of 3,3-bis(dimethylsilyl)-2,2,5-trimethyl-1-oxa-2-silacyclopentane (7b). The ring opening reaction of propylene oxide (31.6 mmol, 7.8 g) with $(HSiMe_2)_3CLi$ (15.8 mmol) was carried out under the general procedure and the reaction mixture was stirred for 2 h at −5 °C (crude product 2.2 g). A pure colorless liquid was obtained by preparative TLC (silica gel, 1:1 *n*-hexane: CH_2Cl_2, R_f=0.80). FTIR (KBr, cm^{-1}): 2106 (Si–H), 1255, 872 ($Si–CH_3$), 1074 (Si–O–C); ^1H NMR (400 MHz, $CDCl_3$): δ 0.12–0.17 (m, 12H, $HSi(CH_3)_2$), 0.19, 0.29 (2×s, 2×3H, $OSi(CH_3)_2$), 1.22 (d, 3H, J=8 Hz, $OCHCH_3$), 1.64, 2.12 (2×dd, 2×1H, J=12, 8 Hz, CH_2CHO), 3.93–3.97 (m, 1H, CH_2CHO), 4.03–4.09 (m, 2H, Si–H); ^{13}C NMR ($CDCl_3$): δ −3.8, −3.6, −3.4, −3.2 ($HSi(CH_3)_2$), −0.8, 0.4 ($OSi(CH_3)_2$), 5.1 (CCH_2CH), 22.6 ($OCHCH_3$), 39.2 (CH_2CHO), 71.8 (CH_2CHO); *m*/*z* (EI): 247 (5%, $[M]^+$), 232 (18%, $[M-Me]^+$), 188 (44%, $[M-(HSiMe_2)]^+$), 59 (100%, $[HSiMe_2]^+$). Anal. Calcd for $C_{10}H_{26}Si_3O$: C, 48.7; H, 10.6. Found: C, 48.5; H, 10.6%.

4.6.3. Preparation of 3,3-bis(dimethylsilyl)-2,2-dimethyl-5-ethyl-1-oxa-2-silacyclopentane (7c). The ring opening reaction of 1,2-epoxy butane (31.6 mmol, 8.2 g) with $(HSiMe_2)_3CLi$ (15.8 mmol) was carried out according to the general procedure. After stirring the reaction mixture for 2 h (crude product 2.3 g), a pure colorless liquid was obtained by preparative TLC (silica gel, 1:1 *n*-hexane:CH$_2$Cl$_2$, *R*$_f$=0.8). FTIR (KBr, cm^{-1}): 2104 (Si–H), 1256, 883 (Si–CH$_3$), 1099 (Si–O–C); ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.10–0.14 (m, 12H, HSi(C*H*$_3$)$_2$), 0.15, 0.28 (2×s, 2×3H, OSi(C*H*$_3$)$_2$), 0.87 (t, 3H, *J*=8 Hz, OCHCH$_2$C*H*$_3$), 1.39–1.59 (m, 2H, OCHC*H*$_2$CH$_3$), 1.64, 2.09 (2×dd, 2×1H, *J*=12, 8 Hz, C*H*$_2$CHO), 3.80–3.87 (m, 1H, CH$_2$C*H*O), 4.04–4.09 (m, 2H, Si–*H*); ^{13}C NMR (CDCl$_3$): δ −4.2, −3.9 −3.6, −3.4 (HSi(*C*H$_3$)$_2$), −0.7, 0.2 (OSi(*C*H$_3$)$_2$), 4.5 (*C*CH$_2$CH), 8.9 (OCHCH$_2$*C*H$_3$), 29.9 (OCH*C*H$_2$CH$_3$), 36.5 (*C*H$_2$CHO), 76.9 (CH$_2$*C*HO); *m/z* (EI): 260 (5%, [M]$^+$), 246 (16%, [M−Me]$^+$), 202 (44%, [M−(HSiMe$_2$)]$^+$), 59 (100%, [HSiMe$_2$]$^+$). Anal. Calcd for C$_{11}$H$_{28}$Si$_3$O: C, 50.7; H, 10.8. Found: C, 50.5; H, 10.6%.

4.6.4. Preparation of 3,3-bis(dimethylsilyl)-2,2-dimethyl-5-propyl-1-oxa-2-silacyclopentane (7d). 1,2-Epoxy pentane (31.6 mmol, 8.7 g) was reacted with (HSiMe$_2$)$_3$CLi (15.8 mmol) at −5 °C for 2 h according to the general procedure (crude product 2.4 g). A pure colorless liquid was obtained by preparative TLC (silica gel, 1:1 *n*-hexane:CH$_2$Cl$_2$, *R*$_f$=0.75). FTIR (KBr, cm^{-1}): 2103 (Si–H), 1255, 880 (Si–CH$_3$), 1047 (Si–O–C); ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.09–0.13 (m, 12H, HSi(C*H*$_3$)$_2$), 0.15, 0.27 (2×s, 2×3H, OSi(C*H*$_3$)$_2$), 0.86 (t, 3H, *J*=6 Hz, OCHCH$_2$CH$_2$C*H*$_3$), 1.29–1.39 (m, 2H, OCHCH$_2$C*H*$_2$CH$_3$), 1.40–1.57 (m, 2H, OCHC*H*$_2$CH$_2$CH$_3$), 1.70, 2.09 (2×dd, 2×1H, *J*=20, 8 Hz, C*H*$_2$CHO), 3.83–3.89 (m, 1H, CH$_2$C*H*O), 4.08–4.14 (m, 2H, Si–*H*); ^{13}C NMR (CDCl$_3$): δ −4.3, −3.9, −3.6, −3.4 (HSi(*C*H$_3$)$_2$), −0.7, 0.5 (OSi(*C*H$_3$)$_2$), 4.6 (*C*CH$_2$CH), 14.9 (OCHCH$_2$CH$_2$*C*H$_3$), 22.8 (OCHCH$_2$*C*H$_2$CH$_3$), 26.9 (OCH*C*H$_2$CH$_2$CH$_3$), 37.2 (*C*H$_2$CHO), 75.5 (CH$_2$*C*HO); *m/z* (EI): 275 (9%, [M]$^+$), 260 (17%, [M−Me]$^+$), 216 (37%, [M−(HSiMe$_2$)]$^+$), 59 (100%, [HSiMe$_2$]$^+$). Anal. Calcd for C$_{12}$H$_{30}$Si$_3$O: C, 52.5; H, 11.0. Found: C, 52.5; H, 11.1%.

4.6.5. Preparation of 3,3-bis(dimethylsilyl)-2,2-dimethyl-5-butyl-1-oxa-2-silacyclopentane (7e). To a stirred mixture of (HSiMe$_2$)$_3$CLi (15.8 mmol) was added dropwise 1,2-epoxy hexane (31.6 mmol, 9.1 g) at −5 °C for 3 h under analogous reaction condition (crude product 2.3 g), then a pure colorless product was obtained by preparative TLC (silica gel, 1:1 *n*-hexane:CH$_2$Cl$_2$, *R*$_f$=0.75). FTIR (KBr, cm^{-1}): 2107 (Si–H), 1255, 829 (Si–CH$_3$), 1041 (Si–O–C); ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.11–0.16 (m, 12H, HSi(C*H*$_3$)$_2$), 0.17, 0.29 (2×s, 2×3H, OSi(C*H*$_3$)$_2$), 0.85 (t, 3H, *J*=8 Hz, OCHCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.27–1.35 (m, 2H, OCHCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.36–1.45 (m, 2H, OCHCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.52–1.64 (m, 2H, OCHC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.65, 2.10 (2×dd, 2×1H, *J*=12, 10 Hz, C*H*$_2$CHO), 3.92–3.97 (m, 1H, CH$_2$C*H*O), 4.04–4.10 (m, 2H, Si–*H*); ^{13}C NMR (CDCl$_3$): δ −4.2, −3.8, −3.6, −3.4 (HSi(*C*H$_3$)$_2$), −0.7, 0.2 (OSi(*C*H$_3$)$_2$), 4.5 (*C*CH$_2$CH), 13.0 (OCHCH$_2$CH$_2$CH$_2$*C*H$_3$), 21.8 (OCHCH$_2$CH$_2$*C*H$_2$CH$_3$), 27.0 (OCHCH$_2$*C*H$_2$CH$_2$CH$_3$), 37.1 (OCH*C*H$_2$CH$_2$CH$_2$CH$_3$), 37.2 (*C*H$_2$CHO), 75.5 (CH$_2$*C*HO); *m/z* (EI): 289 (4%, [M]$^+$), 274 (22%, [M−Me]$^+$), 230 (27%, [M−(HSiMe$_2$)]$^+$), 59 (100%, [HSiMe$_2$]$^+$). Anal. Calcd for C$_{13}$H$_{32}$Si$_3$O: C, 54.1; H, 11.1. Found: C, 54.1; H, 11.1%.

4.6.6. Preparation of 3,3-bis(dimethylsilyl)-2,2-dimethyl-5-chloromethyl-1-oxa-2-silacyclopentane (7f). A mixture of (HSiMe$_2$)$_3$CLi (15.8 mmol) and epichlorohydrin (23.7 mmol, 6.7 g) was stirred for 3 h at −5 °C under the general procedure (crude product 2.5 g). A pure colorless liquid was obtained by preparative TLC (silica gel, *n*-hexane, *R*$_f$=0.50). FTIR (KBr, cm^{-1}): 2108 (Si–H), 1257, 832 (Si–CH$_3$), 1082 (Si–O–C); ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.10–0.34 (m, 18H, Si(C*H*$_3$)$_2$), 1.71, 2.13 (2×dd, 2×1H, *J*=12, 10 Hz, C*H*$_2$CHO), 3.87 (d, 2H, *J*=4 Hz, OCHC*H*$_2$Cl), 4.03–4.10 (m, 2H, Si–*H*), 4.18–4.22 (m, 1H, CH$_2$C*H*O); ^{13}C NMR (CDCl$_3$): δ −3.9, −3.7, −3.5, −3.4 (HSi(*C*H$_3$)$_2$), −2.6, −0.90 (OSi(*C*H$_3$)$_2$), 6.27 (*C*CH$_2$CH), 37.3 (*C*H$_2$CHO), 38.4 (OCH*C*H$_2$Cl), 75.7 (CH$_2$*C*HO); *m/z* (EI): 281 (3%, [M]$^+$), 283 (1.1%, [M+2]$^+$), 266 (18%, [M−Me]$^+$), 222 (38%, [M−(HSiMe$_2$)]$^+$), 59 (100%, [HSiMe$_2$]$^+$). Anal. Calcd for C$_{10}$H$_{25}$Si$_3$OCl: C, 42.7 H, 8.9. Found: C, 42.9, H, 8.9%.

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