New straightforward Route for the Synthesis of Some 1-Oxa-2-Silacyclopentane Derivatives

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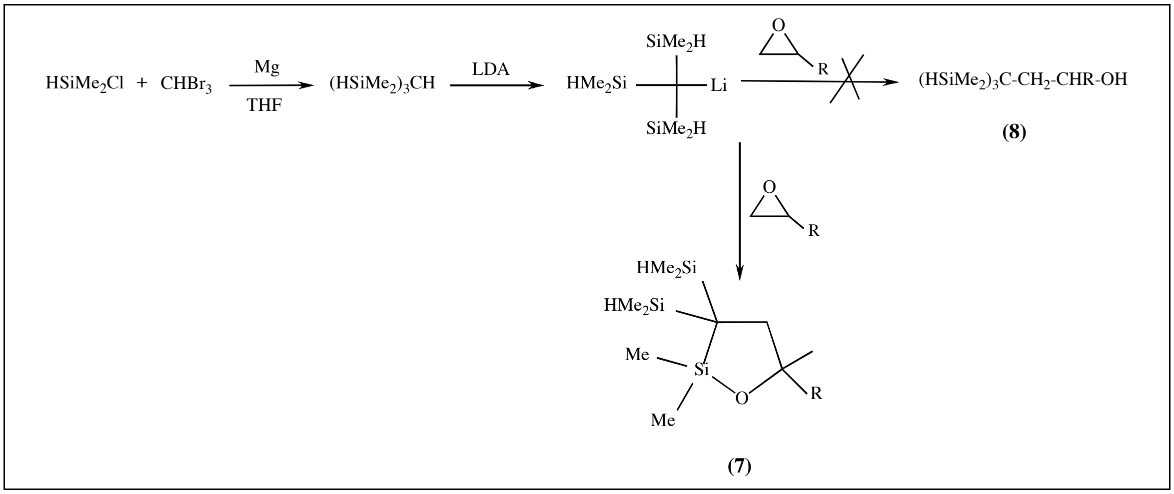
Received May 20, 2007



Tris(dimethylsilyl)methyl lithium, $(HSiMe_2)_3CLi$, reacts with allyl, phenyl, benzyl, *n*-propyl and *n*-butyl glycidyl ethers in THF at -5 °C to give 1-oxa-2-silacyclopentane derivatives. It seems that ring closure is facilitated by conversion of the Si-H bond into an Si-O bond. Glycidyl methacrylate (GM) random copolymers with 4-methyl- and 4-methoxy styrene, synthesized by solution free radical polymerization at 70 (±1) °C with α,α-azobis(isobutyronitrile) (AIBN) as initiator, contained pendant epoxide functions. Treatment of these with $(HSiMe_2)_3CLi$ did not lead to intramolecular nucleophilic attack as found for simple epoxides.

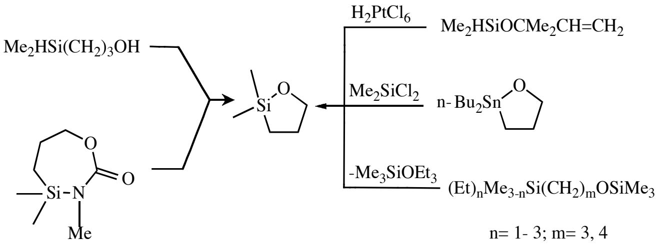
J. Heterocyclic Chem., **45**, 389 (2008).

INTRODUCTION

Silicon-substituted alkyllithium compounds, in particular $(Me_3Si)_3CLi$ have been used to synthesis organic compounds containing very bulky substituents, many of which possess unique structures and display novel reactivity [1-3]. It is also known that $[(HSiMe_2)_3\text{-}CLi].2THF$ is formed in excellent yield from the reaction of $(HSiMe_2)_3CH$ with $(Me_2CH)_2NLi$ in THF [4]. Attachment of tris(trimethylsilyl)methyl groups to macromolecular chains leads to important modifications of polymer properties such as potential membrane materials in separation processes and an increase in glass transition temperature [5-6].

1-Oxa-2-silacyclopentanes are powerful intermediates in organic synthesis, since they can be readily converted into diols after oxidation of the carbon-silicon bond [7]. These useful intermediates can be prepared by dehydrogenation [8], intramolecular hydrosilylation [9], extrusion of isocyanates [10], elimination of dibutyltin chloride from the 2-oxastannacyclopentane by reaction with dimethyldichlorosilane [11], cyclization of (ω-ethoxysilylalkoxy)trimethylsilanes [12] (Scheme 1), insertion of carbonyl groups to oxasilacyclopropane [13,14], and intramolecular bis-silylation [15] of alkenes promoted by a palladium isocyanide catalyst. Treatment of $(HSiMe_2)_3CLi$ with some simple epoxides gave 3,3-bis-(dimethylsilyl)-1-oxa-2-silacyclopentanes in an unusual but straightforward process [17]. To seek more evidence for the proposed mechanism we studied the reaction of $[(HSiMe_2)_3CLi].2THF$ with some other epoxides and polymers containing epoxy groups on the side chain.

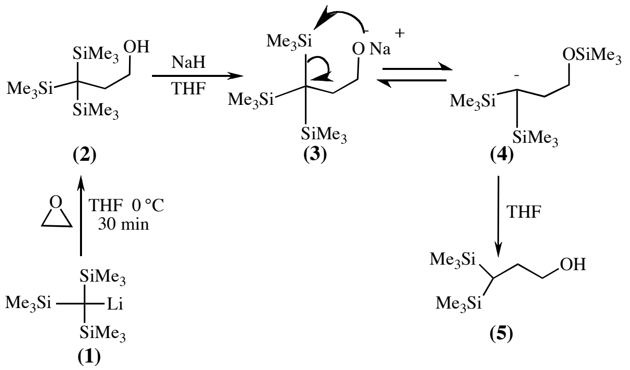
Scheme 1



RESULTS AND DISCUSSION

It was shown previously that the reaction of $(Me_3Si)_3CLi$ 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**, which has one fewer silyl group. The silicon transfer **3** → **4** → **5** takes *ca.* 90 min at room temperature. Potassium *t*-butoxide in THF worked comparably well, but the lithium and magnesium alkoxides did not react [16] (Scheme 2).

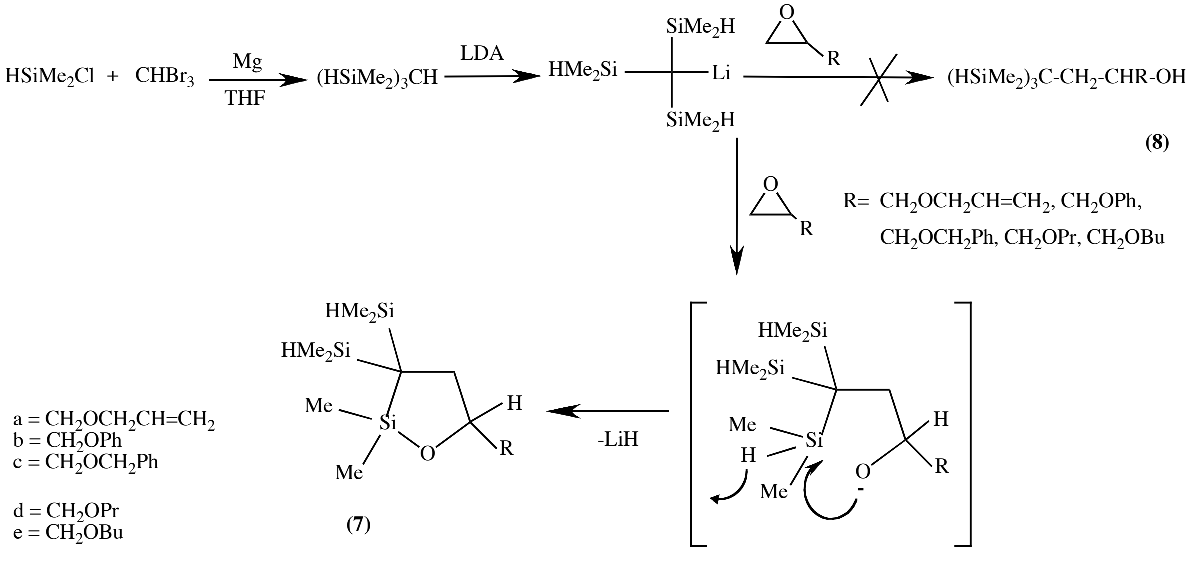
Scheme 2



The compound $(HSiMe_2)_3CH$ was made by treatment of $CHBr_3$ with HMe_2SiCl in the presence of magnesium [18]. The deep-red solution of the nucleophilic reagent $(HSiMe_2)_3CLi$ [4] was prepared from the reaction of $(HMe_2Si)_3CH$ with a solution of lithium diisopropylamide (LDA) in THF for 6 h at room temperature. The solvated organolithium reacted with allyl, phenyl, benzyl, propyl, and butyl glycidyl ethers in THF but the products were 1-oxa-2-silacyclopentane derivatives rather than the expected compounds $(HMe_2Si)_3CCH_2CHROH$ (8). For example, when the solution of $(HMe_2Si)_3CLi$ was quenched with allyl glycidyl ether at -5 °C in THF the color of the solution changed gradually from deep-red to yellow during the addition of the epoxide. In this reaction, because of the existence of the Si-H bond, an intramolecular alkoxylation takes place (Scheme 3).

The IR spectra of **7a** showed no peak above 3300 cm^{-1} as expected if an alcohol had been formed. A typical ^{1}H NMR spectrum (Figure 1) for this product showed three separate signals; a multiplet at 0.11-0.17 ppm for 12 protons (a) and two singlets at 0.18, 0.30 ppm for 6 protons (b, c). There was no broad peak corresponding to the OH group. Integration of the area peak at 4.04-4.14 corresponding to the Si-H bond showed two protons for the Si-H bond instead of three protons which clearly indicate liberation of a hydride ion. In the ^{13}C NMR spectrum, the resonance signals (b_1, b_2) at -0.7 and 0.2 ppm were due to the $(CH_3)_2SiO$ and four resonance signals at -4.2, -3.9, -3.7 and -3.4 ppm (a_1), (a_2), (a_3) and (a_4) related to four different CH_3 of two $SiMe_2H$ groups respectively (Figure 1). All these results clearly show that the ring opening reaction led to cyclic compound **7a** instead of the expected related alcohol.

Scheme 3



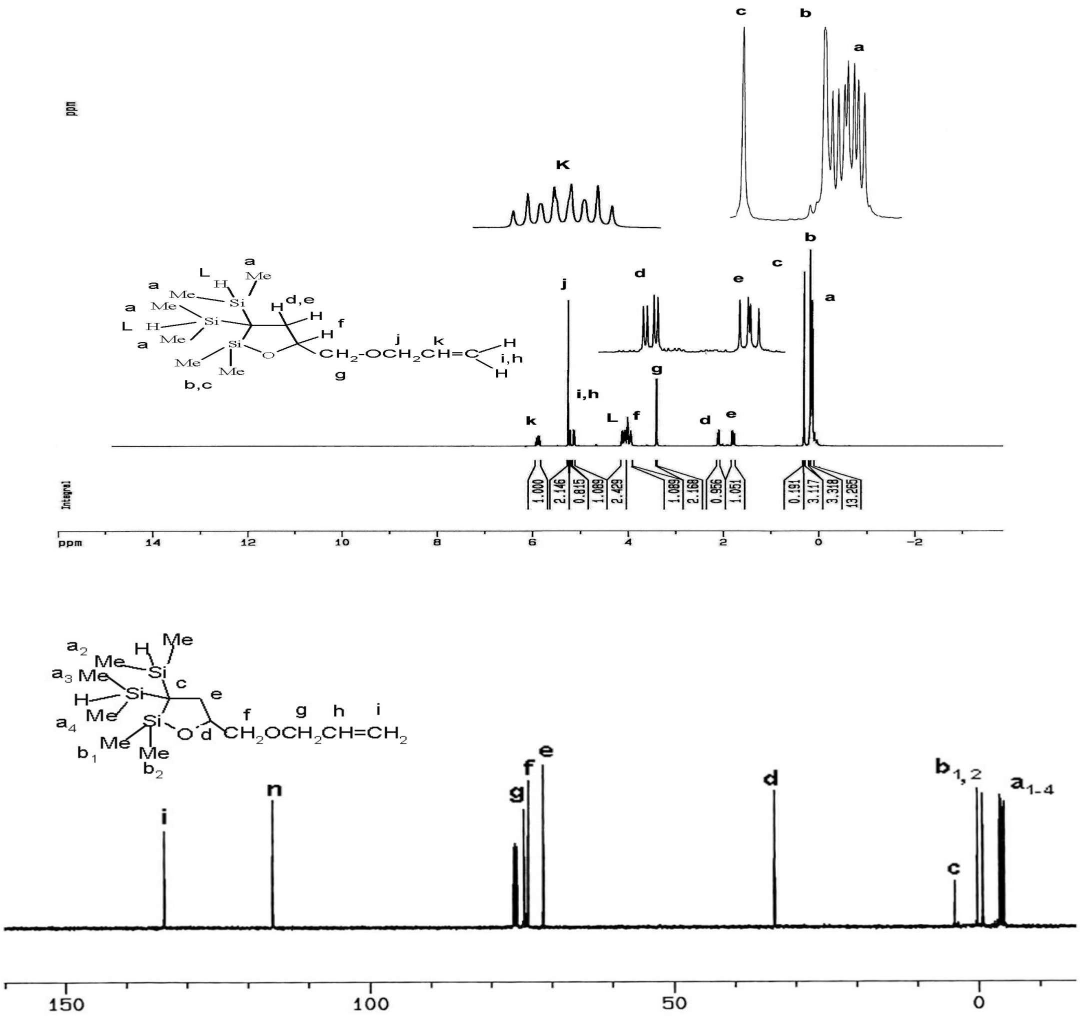
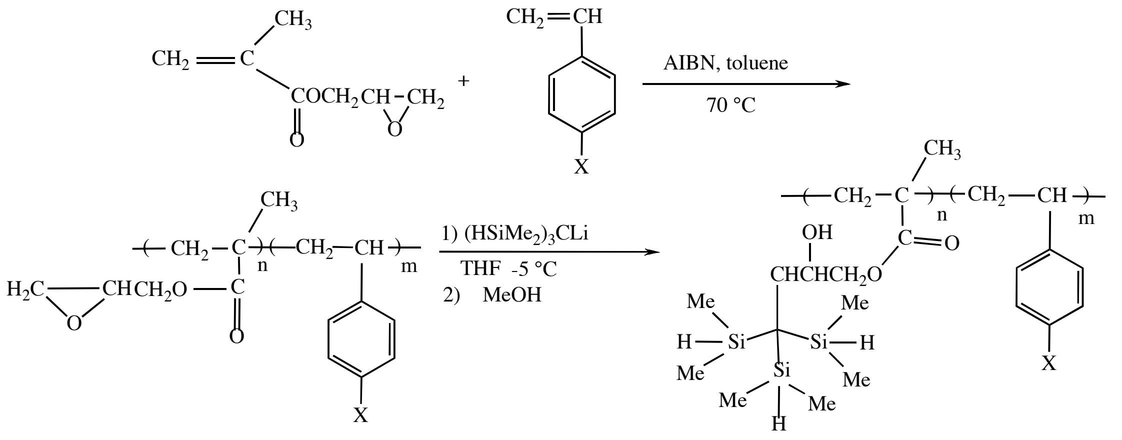


Figure 1. ^{1}H and ^{13}C NMR of the compound **7a** in $CDCl_3$ without tetramethylsilane.

Scheme 4



I X= Me
II X=OMe

II-SiH X=OMe
I-SiH X=Me

Poly glycidyl methacrylate (PGM) and its copolymers have been widely used as precursors for the synthesis of functional polymers. The interest in these polymers is largely due to the presence of the reactive epoxide ring, which can enter into wide range of chemical reactions. To examine the possibility of the formation of oxasilacyclopentane ring on the side chain of polymers, GM monomer was copolymerized with 4-methyl and 4-methoxy styrene at 70(±1) °C using AIBN as the radical initiator (Scheme 4). The composition, molecular weight, mole fraction of GM in the copolymers (obtained by ^{1}H NMR), and yield of the copolymers (I, II) are listed in Table 1. The resulting polymers are white solids and 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 become insoluble in organic solvents, probably due to intramolecular cross linking between epoxy units.

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Table 1

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

Copolymer	M_n ^{b} ×10^3	M_w ^{b} ×10^3	M_w/M_n	Mol% GM ^{a}	Weight (g)	Yield (%)
Poly(GM-co-MSt)$_{1:1}$(I)	29.5	53.8	1.80	50	3.77	83
Poly(GM-co-OMeSt)$_{1:1}$(II)	19.1	38.8	2.03	41	3.93	80

^{a} Mol% of both monomers were obtained via ^{1}H NMR; ^{b} Molecular weight was obtained by GPC analysis.

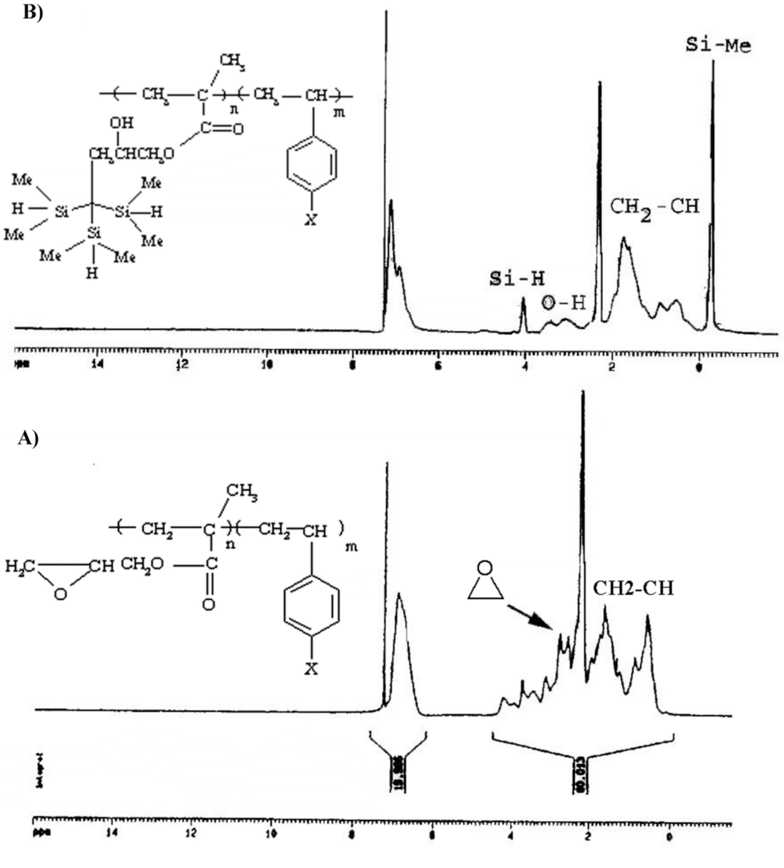


Figure 2. ^{1}H-NMR spectra: (A) **I** and (B) **I-SiH** in $CDCl_3$ without tetramethylsilane.

The resulting polymers are white solids and 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 become insoluble in organic solvents, probably due to intramolecular cross linking between epoxy units.

The copolymers (I, II) were treated with $(HSiMe_2)_3CLi$ with the expectation that 1-oxa-2-silacyclopentane side chain copolymers would be formed, but FT-IR spectra of the resulting copolymers showed 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. ^1H NMR spectra indicated a singlet for 18 protons of the $(HSi\mathit{Me}_2)_3C$- group (Figure 2). It seems possible that the high rigidity of the copolymers in comparison to simple monomer inhibits intramolecular reaction.

CONCLUSION

The reaction of epoxides with trisilylmethyllithium reagents bearing hydride groups on silicon gives oxasilacyclopentane products, which presumably by cyclization of the intermediate lithium alkoxide onto silicon with loss of a hydride leaving group. These transformations are quite different from those observed with the trimethylsilyl analogues. It is likely that the initial step of $(HSiMe_2)_3CLi$ reaction with epoxides proceeds *via* nucleophilic attack at the uncrowded carbon of the epoxides yielding **6** as intermediate. The intramolecular reaction between the Si-H and OLi groups of **6** results in ring closure and the formation of cyclic product **7** (Scheme 5). In contrast, the reactions of tris(trimethylsilyl)methyl group with epoxides lead only to alcohols. It is probable that the ease of ring closure of epoxide with tris(dimethylsilyl)methyl group is due to the existence of the Si-H bond and the enhancement of reactivity of the Si-H bond towards nucleophiles. It also seemed that the high rigidity of the copolymers makes them unfavorable towards intramolecular nucleophilic attack.

EXPERIMENTAL

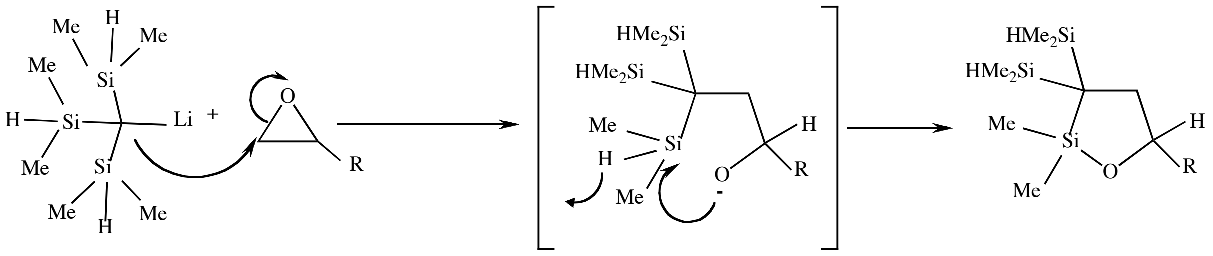
Solvents and reagents. The reactions involving organolithium reagents were carried out under dry argon atmosphere. Solvents were dried by standard methods. Glycidyl methacrylate (GM) (Merck) and 4-methyl- and 4-methoxy styrene (Merck) were distillated under reduced pressure to remove inhibitors before use and AIBN (Merck) was purified by crystallization from methanol.

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

Copolymerization of glycidyl methacrylate (GM) with 4-methyl styrene and 4-methoxy styrene copolymer (I, II). A mixture of GM (2.84 g, 20 mmol), AIBN (0.06 g, 0.4 mmol), 4-methyl styrene (2.36 g, 20 mmol) or 4-methoxy styrene (2.68 g, 20 mmol) was dissolved in toluene (15 ml) in a glass ampoule. The solution was degassed, and the ampoule sealed under vacuum and shaken at 70(±1) °C. The viscous solution was poured from the ampoule into 150 ml of cooled methanol. The precipitate was collected and washed with cooled acidic methanol several times and dried under vacuum at room temperature. For copolymer **I**: ν_{max}/cm^{-1} 3018 (Ar-H), 2922, 2850 (R-H), 1730 (C=O), 1650, 1488 (C=C), 1110 (C-O), 907, 846 (C-O epoxide); δ_H (400 MHz, $CDCl_3$) 0.58-2.24 (CH_2-CH,α-Me), 2.3 (Ar-CH_3) 2.5-3.4 (epoxide),3.5(OH), 3.7 ($COOCH_2$), 6.6-7.2 (Ar). For copolymer **II**: ν_{max}/cm^{-1} 3025 (Ar-H), 2994, 2840 (R-H), 1727 (C=O), 1613, 1456 (C=C), 1180, 1032 (C-O), 907, 784 (C-O epoxide); δ_H (400 MHz, $CDCl_3$) 0.6-1.7 (CH_2-CH,α-Me) 2.5-3.3 (epoxide), 3.6 (OMe), 3.8 ($COOCH_2$), 7.1-7.2 (Ar).

The ring opening reaction between the epoxy groups of Poly (GM-*co*-4-MeSt) and Poly (GM-*co*-4-MeOSt) with $(HSiMe_2)_3CLi$ (ISi-H, IISi-H). A solution of copolymer **I** (0.5 g, with 1.92 mmol of epoxy-containing monomer units) or copolymer **II** (0.5 g, with 1.5 mmol of epoxy-containing monomer units) in THF (30 ml) was transferred into dropping funnel under an argon atmosphere and added dropwise to a stirred solution of a $(HSiMe_2)_3CLi$ (2 g, 10.5 mmol) at -5 °C.

Scheme 5



(6) (7)

The reaction was quenched by addition of a small amount of acidic methanol after 3 h, and the reaction mixture was poured into cooled acidic methanol to precipitate the polymer. For copolymer **I-SiH**: ν_{max}/cm^{-1} 3443 (OH), 3066 (Ar-H), 2956 (R-H), 2110 (Si-H), 1728 (C=O), 1257, 850 (C-Si), 1034 (C-O); δ_H (400 MHz, CDCl$_3$) δ -0.2(Si-Me), 0.56-2.0 (CH$_2$-CH,α-Me), 2.3 (Ar-CH$_3$), 3.7 (COOCH$_2$), 4.0(Si-H), 6.6-7.2 (Ar). For copolymer **II-SiH**: ν_{max}/cm^{-1} 3443 (OH), 3066 (Ar-H), 2956 (R-H), 2110 (Si-H), 1728 (C=O), 1257, 850 (C-Si), 1034 (C-O); δ_H (400 MHz, CDCl$_3$) δ 0.1(Si-Me), 0.6-1.7 (CH$_2$-CH, α-Me) , 3.4 (OH), 3.6 (OMe), 4 (Si-H), 7.0-7.2 (Ar).

General procedure for reactions of tris(dimethylsilyl)-methyllithium with epoxides. Epoxides were added dropwise to a solution of tris(dimethylsilyl)methyllithium (15.8 mmol) at -5 °C and the mixtures kept for 1 h at this temperature, then the mixtures were 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 *N* 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 product obtained by preparative TLC (Silica gel).

Preparation of 3,3-bis(dimethylsilyl)-2,2-dimethyl-5-allyl-oxymethyl-1-oxa-2-sila-cyclopentane (7a). The reaction of allyl glycidyl ether (3.6 g, 31.6 mmol) with (HSiMe$_2$)$_3$CLi (15.8 mmol) for 3 h at -5 °C gave **7a**. A colorless liquid (Yield 61%) was obtained by preparative TLC (silica gel, 1: 1 n-hexane: CH$_2$Cl$_2$, R$_f$ = 0.70). ν_{max}/cm^{-1} 2105 (Si-H), 1255, 829 (Si-CH$_3$), 1070 (Si-O-C), 1496, 1633 (C=C); δ_H (400 MHz, CDCl$_3$) 0.12-0.17 (m, 12H, HSi(CH$_3$)$_2$, 0.18, 0.30 (2s, 2×3H, OSi(CH$_3$)$_2$), 1.76, 2.08 (2×d-d, 2×1H, J= 12.2, 10.1 Hz, CCH_2), 3.40 (d, 2H, J= 4.3, CH_2OCH$_2$CH=CH$_2$), 3.92-3.98 (m, 1H, CH$_2$CHOSiMe$_2$), 4.04-4.14 (m, 2H, Si-H), 5.13, 5.22 (2×d-d, 2×1H, J= 6.0, 6.0 Hz, CH=CH_2), 5.26 (d, 2H, J= 15.5, CH_2CH=CH$_2$), 5.84-5.93 (m, 1H, CH=CH2); δ_C (CDCl$_3$) -4.2, -3.9, -3.7, -3.4 (HSi(CH$_3$)$_2$), -0.7, 0.2 (OSi(CH$_3$)$_2$), 3.9 (CCH$_2$CH), 33.4 (CCH$_2$CH), 71.4 (CH$_2$$C$HO), 73.8 ($CH_2OCH_2$CH=CH$_2$), 74.5 ($CH_2$CH=CH$_2$), 115.9 (CH=$CH_2$), 133.7 ($C$H=CH$_2$); m/z (EI) 302 (6%, [M]$^+$), 287 (21%, [M-Me]$^+$), 243 (48%, [M-(HSiMe$_2$)]$^+$). *Anal.* Cal. for $C_{13}H_{30}Si_3O_2$: C, 51.6; H, 9.9. Found: C, 51.4; H, 10.0%.

Preparation of 3, 3-bis(dimethylsilyl)-2, 2 -dimethyl-5-phen-oxymethyl-1-oxa-2-sila-cyclopentane (7b). Similarly **7b** was obtained in 52% yield from phenyl glycidyl ether (4.7 g, 31.6 mmol) and (HSiMe$_2$)$_3$CLi (15.8 mmol) during 3 h at -5 °C and isolated as a colorless liquid by preparative TLC (silica gel, 1: 1 n-hexane: CH$_2$Cl$_2$, R$_f$ = 0.60). ν_{max}/cm^{-1} 2109 (Si-H), 1255, 833 (Si-CH$_3$), 1054 (Si-O-C), 1628, 1542 (C=C); δ_H (400 MHz, CDCl$_3$) 0.14-0.25 (m, 12H, HSi(CH_3)$_2$), 0.27, 0.40 (2s, 2×3H, OSi(CH_3)$_2$), 1.98, 2.25 (2×d-d, 2×1H, J=12.0, 10.1 Hz, CCH_2CH), 3.93-4.01 (m, 2H, Si-H), 4.19 (d, 2H, J= 4.2, CH_2OPh), 4.34-4.41 (m, 1H, CH$_2$CHO), 6.91-7.00 (m, 3H, Ph), 7.26-7.32 (m, 2H, Ph); δ_C (CDCl$_3$) -4.2, -3.8, -3.7, -3.4 (HSi(CH$_3$)$_2$), -0.6, 0.2 (OSi(CH$_3$)$_2$), 4.0 (CCH$_2$CH), 33.4 (CCH$_2$CH), 71.2 (CH$_2$$C$HO), 73.8 ($CH_2$OPh), 113.50, 113.53, 119.7, 120.1, 128.3, 158.4 (Ph); m/z (EI) 339 (4%, [M]$^+$), 324 (19%, [M-Me]$^+$), 280 (47%, [M-(HSiMe$_2$)]$^+$). *Anal.* Cal. for $C_{16}H_{30}Si_3O_2$: C, 56.7; H, 8.9. Found: C, 56.6; H, 8.9%.

Preparation of 3, 3-bis(dimethylsilyl)-2, 2-dimethyl-5-benzyl-oxymethyl-1-oxa-2-sila-cyclopentane (7c). 7c was obtained in 57 % yield from benzyl glycidyl ether (5.1 g, 31.6 mmol) and (HSiMe$_2$)$_3$CLi (15.8 mmol) during 3 h at -5 °C as a colorless liquid purified by preparative TLC (silica gel, 1: 1 n-hexane: CH$_2$Cl$_2$, R$_f$ = 0.60). ν_{max}/cm^{-1} 2108 (Si-H), 1251, 837 (Si-CH$_3$), 1043 (Si-O-C), 1595, 1532 (C=C); δ_H (400 MHz, CDCl$_3$) 0.12-0.24 (m, 12H, HSi(CH_3)$_2$), 0.26, 0.39 (2s, 2×3H, OSi(CH_3)$_2$), 1.85, 2.25 (2×d-d, 2×1H, J= 12.3, 10.4, CCH_2CH), 3.93-4.00 (m, 2H, Si-H), 4.34-4.41 (m, 1H, CH$_2$CHO), 4.20 (d, 2H, J= 4.1 Hz, CH_2OCH$_2$Ph), 4.57 (s, 2H, OCH_2Ph), 7.27-7.32 (m, 5H, OCH$_2$$Ph$); δ_C (CDCl$_3$) -4.1, -3.7, -3.6, -3.4 (HSi(CH$_3$)$_2$), -0.8, 0.2 (OSi(CH$_3$)$_2$), 4.0 (CCH$_2$CH), 33.3 (CCH$_2$CH), 72.6 (CH$_2$OCH$_2$Ph), 73.8 (OCH$_2$Ph), 80.9 (CH$_2$$C$HO), 114.51, 114.54, 118.8, 119.3, 131.2, 136.1 (Ph); m/z (EI) 353 (4%, [M]$^+$), 338 (19%, [M-Me]$^+$), 294 (43%, [M-(HSiMe$_2$)]$^+$). *Anal.* Cal. for $C_{17}H_{32}Si_3O_2$: C, 57.9; H, 9.1. Found: C, 57.6; H, 9.1%.

Preparation of 3, 3-bis(dimethylsilyl)-2, 2-dimethyl-5-propyl-oxymethyl-1-oxa-2- sila-cyclopentane (7d). *n*-Propyl glycidyl ether (3.6 g, 31.6 mmol) was treated with (HSiMe$_2$)$_3$CLi (15.8 mmol) at -5 °C for 2 h to give **7d** in 58% yield and the colorless liquid was purified by preparative TLC (silica gel, 1: 1 n-hexane: CH$_2$Cl$_2$, R$_f$ = 0.75). ν_{max}/cm^{-1} 2106 (Si-H), 1261, 834 (Si-CH$_3$), 1076 (Si-O-C); δ_H (400 MHz, CDCl$_3$) 0.11-0.18 (m, 12H, HSi(CH_3)$_2$), 0.20, 0.29 (2s, 2×3H, OSi(CH_3)$_2$), 0.86 (t, 3H, J= 12.2 Hz, CH$_2$CH_3), 1.24-1.31 (m, 2H, CH_2CH$_3$), 1.66, 2.10 (2×d-d, 2×1H, J= 12.1, 8.0 Hz, CCH_2CH), 3.50 (t, 2H, J= 12.0 Hz, OCH_2CH$_2$), 3.77 (d, 2H, J= 8.0 Hz, CH_2OPr), 3.86-3.94 (m, 1H, CH$_2$CHO), 4.04-4.13 (m, 2H, Si-H); δ_C (CDCl$_3$) -4.5, -4.1, -3.9, -3.6 (HSi(CH$_3$)$_2$), -0.9, 0.5 (OSi(CH$_3$)$_2$), 4.2 (CCH$_2$CH), 12.1 (CH$_3$), 24.3 (CH$_2$CH$_3$), 36.1 (CCH$_2$CH), 73.3 (CH$_2$CH$_2$CH$_3$), 83.3 (CH$_2$$C$HO), 87.1 ($CH_2$OPr); m/z (EI) 304 (6%, [M]$^+$), 289 (20%, [M-Me]$^+$), 245 (46%, [M-(HSiMe$_2$)]$^+$). *Anal.* Cal. for $C_{13}H_{32}Si_3O_2$: C, 51.2; H, 10.5. Found: C, 51.4; H, 10.1%.

Preparation of 3, 3-bis(dimethylsilyl)-2,2-dimethyl-5-butyl-oxymethyl-1-oxa-2- sila-cyclopentane (7e). *n*-Butyl glycidyl ether (4.1 g, 31.6 mmol) was treated with (HSiMe$_2$)$_3$CLi (15.8 mmol) at -5 °C for 2 h to give **7e** in 56% yield, and purified by preparative TLC (silica gel, 1: 1 n-hexane: CH$_2$Cl$_2$, R$_f$ = 0.80). A pure colorless liquid was obtained. ν_{max}/cm^{-1} 2104 (Si-H), 1258, 833 (Si-CH$_3$), 1073 (Si-O-C); δ_H (400 MHz, CDCl$_3$) 0.10-0.18 (m, 12H, HSi(CH_3)$_2$), 0.19, 0.28 (2s, 2×3H, OSi(CH_3)$_2$), 0.85 (t, 3H, J= 12.1 Hz, CH$_2$CH_3), 1.28-1.37 (m, 2H, CH_2CH$_3$), 1.38-1.43 (m, 2H, CH_2CH$_2$CH$_3$), 1.67, 2.12 (2×d-d, 2×1H, J= 12.2, 8.1 Hz, CCH_2CH), 3.54 (t, 2H, J= 12.4 Hz, OCH_2CH$_2$CH$_2$), 3.75 (d, 2H, J= 8 Hz, CH_2OCH$_2$CH$_2$), 3.87-3.92 (m, 1H, CH$_2$CHO), 4.04-4.14 (m, 2H, Si-H); δ_C (CDCl$_3$) -4.4, -4.0, -3.8, -3.5 (HSi(CH$_3$)$_2$), -0.8, 0.4 (OSi(CH$_3$)$_2$), 4.1 (CCH$_2$CH), 14.1 (CH$_2$$CH_3$), 20.4 ($CH_2CH_3$), 33.0 ($CH_2CH_2CH_3$), 36.1 (C$CH_2$CH), 66.3 ($CH_2CH_2CH_2$), 74.1 (CH$_2$$C$HO), 76.9 ($CH_2OCH_2CH_2$); m/z (EI) 318 (8%, [M]$^+$), 303 (25%, [M-Me]$^+$), 259 (44%, [M-(HSiMe$_2$)]$^+$). *Anal.* Cal. for $C_{14}H_{34}Si_3O_2$: C, 52.7; H, 10.7. Found: C, 51.4; H, 10.9%.

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