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Kazem D. Safa^a; Elham Sharifi^a; Shahin Tofangdarzadeh^a; Akbar Hassanpour^a

^a Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

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FACILE SYNTHESIS OF TRIS(ALKOXYDIMETHYLSILYL)METHANE DERIVATIVES VIA ALCOHOLYSIS UNDER OPEN-FLASK AND MILD CONDITIONS

**Kazem D. Safa, Elham Sharifi, Shahin Tofangdarzadeh,
and Akbar Hassanpour**

*Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz,
Tabriz, Iran*

The reactions between a variety of functionalized alcohols and tris(dimethylsilyl)methane, (HMe₂Si)₃CH, are described. Alcohols such as ethylene glycol monobutyl ether, ethylene glycol monoethyl ether, triethylene glycol monomethyl ether, 2-chloroethanol, 1-octanol, benzyl alcohol, glycidol, and allyl alcohol were converted in the presence of Karstedt's catalyst into the corresponding tris(alkoxydimethylsilyl)methanes, (ROMe₂Si)₃CH, in a convenient one-pot operation under aerobic conditions. The appearance of the products coincides with the generation of colloidal Pt(0) species. Moreover, poly(4-chloromethyl)styrene containing tris(dimethylsilyl)methyl groups reacts with benzyl alcohol or 2-chloroethanol in the presence of Karstedt's catalyst to give new macromolecules bearing tris(alkoxydimethylsilyl)methyl groups. The reaction rate is greatly influenced by the concentration of catalyst.

Keywords Alcoholysis reaction; Karstedt's catalyst; poly(chloromethyl)styrene; tris(alkoxydimethylsilyl)methane; tris(dimethylsilyl)methane

INTRODUCTION

Alcoholysis of organosilanes requires a catalyst because alcohols are not sufficiently nucleophilic to react with Si—H bonds under normal conditions. The standard method for preparation of alkoxysilanes is to treat the organosilyl chloride with the alcohol, in the presence of a base such as imidazole, in polar organic solvents such as DMF.¹ D'Sa et al.² have shown that organic solvents such as CH₃CN and CH₂Cl₂ can be used with a superbase. However, base-sensitive functional groups cannot be tolerated, and the production of an ammonium hydrochloride as byproduct makes this approach unattractive. Cationic iridium and iron catalysts have been employed for the alcoholysis of silanes.^{3–5} The mechanism is believed to proceed through nucleophilic attack by the alcohol on an η^2 -silane adduct. Drawbacks of these catalysts include the need for rigorously aerobic and water-free conditions, slow rates, especially with bulky tertiary silanes, and poor functional group tolerance. The highly Lewis acidic borane B(C₆F₅)₃ has also been shown to effect the dehydrogenative

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Address correspondence to Kazem D. Safa, Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, 51664 Tabriz, Iran. E-mail: dsafa@tabrizu.ac.ir

silylation of alcohols with various silanes, albeit at very slow rates.⁶ Substitution reactions of the Si-X (where X = F, Cl, Br) bond with alcohols or with water also leads to Si-O bonds. This reaction requires bases such as amines to act as acid scavengers, in stoichiometric amounts, making this method not very cost-effective.^{7,8}



We have recently developed a convenient procedure for the preparation of a series of tris(alkoxydimethylsilyl)methanes from reactions of $(\text{HMe}_2\text{Si})_3\text{CH}$ with mono-functionalized alcohols in the presence of chloroplatinic acid, $[\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}]$, as a catalyst.⁹ In this article, we report the use of Karstedt's catalyst as highly effective for the alcoholysis of tris(dimethylsilyl)methane under open-flask conditions. Moreover, analogous reactions with styrene-based polymers having Si-H groups in the side chain gave new functionalized polymers bearing silyl ether groups.

RESULTS AND DISCUSSION

Recently, we have embarked on a program directed toward the development of reactions of tris(dimethylsilyl)methane, $(\text{HMe}_2\text{Si})_3\text{CH}$, for the generation of synthetically useful organosilicon compounds.¹⁰⁻¹² We have reported the preparation of some tris(alkoxydimethylsilyl)methanes from the alcoholysis of tris(dimethylsilyl)methane in the presence of Speier's catalyst ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) under mild aerobic conditions.⁹ In ongoing efforts to exploit $(\text{HMe}_2\text{Si})_3\text{CH}$, the alcoholysis of tris(dimethylsilyl)methane with some functionalized alcohols in the presence of Karstedt's catalyst $[\text{Pt}_2(\text{CH}_2=\text{CHSiMe}_2\text{OSiMe}_2\text{CH}=\text{CH}_2)_3]$ is examined.

The compound $(\text{HMe}_2\text{Si})_3\text{CH}$ was made in 60% yield from HMe_2SiCl , CHBr_3 , and Mg in THF. Alcohols, such as ethylene glycol monobutyl ether, ethylene glycol monoethyl ether, triethylene glycol monomethyl ether, 2-chloroethanol, 1-octanol, benzyl alcohol, glycidol, and allyl alcohol, were treated with $(\text{HMe}_2\text{Si})_3\text{CH}$ in the presence of Karstedt's catalyst in air under mild conditions, and the related tris(alkoxydimethylsilyl)methanes were produced in good yields (Table I). The progress of the reactions was monitored by IR

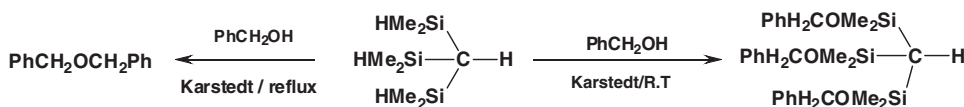
Table I Products, yields, and reaction conditions for the alcoholysis of $(\text{HMe}_2\text{Si})_3\text{CH}$ in the presence of Karstedt's catalyst

Entry	ROH	Product	Product yield (%)	Temp/time
1	$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	$(\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$	66	Reflux/1 h
2	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	$(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$	76	Reflux/3 h
3	$\text{CH}_3\text{OCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{OH}$	$(\text{CH}_3\text{OCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$	97	Reflux/2 h
4	$\text{ClCH}_2\text{CH}_2\text{OH}$	$(\text{ClCH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$	55	Reflux/30 min
5	$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$	$(\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$	64	Reflux/4 h
6		$(\text{C}_6\text{H}_5\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$	77	Rt/10 h
7		$(\text{glycidylOMe}_2\text{Si})_3\text{CH}$	71	Rt/2 h
8	$\text{CH}_2=\text{CHCH}_2\text{OH}$	$(\text{CH}_2=\text{CHCH}_2\text{OMe}_2\text{Si})_3\text{CH}$	75	Reflux/18 h

spectroscopy until the Si—H absorbance in the IR spectrum disappeared. The colorless reaction mixture gradually turned to a homogeneous black solution, indicating the generation of colloidal Pt(0) particles.

In all cases, reaction times are significantly shorter than those with Speier's catalyst, even for larger alcohols. Furthermore, good yields (Table I, entries 6 and 7) were obtained in reactions of benzyl alcohol and glycidol at room temperature. The alcoholysis in the presence of Karstedt's catalyst was carried out under aerobic conditions, unlike those in previous work.^{13,14}

Benzyl alcohol in the presence of Speier's catalyst gave dibenzyl ether, $\text{PhCH}_2\text{OCH}_2\text{Ph}$, instead of the expected $(\text{PhCH}_2\text{OSiMe}_2)_3\text{CH}$.⁹ The reaction of benzyl alcohol with $(\text{HMe}_2\text{Si})_3\text{CH}$ in the presence of Karstedt's catalyst at room temperature led to $(\text{PhCH}_2\text{OMe}_2\text{Si})_3\text{CH}$, but at higher temperature, coupling took place (Scheme 1). In the case of glycidol (Table I, entry 7), alcoholysis was successful at room temperature, but under reflux, polymerization instead of alcoholysis was observed.



Scheme 1 The alcoholysis of $(\text{HMe}_2\text{Si})_3\text{CH}$ with benzyl alcohol.

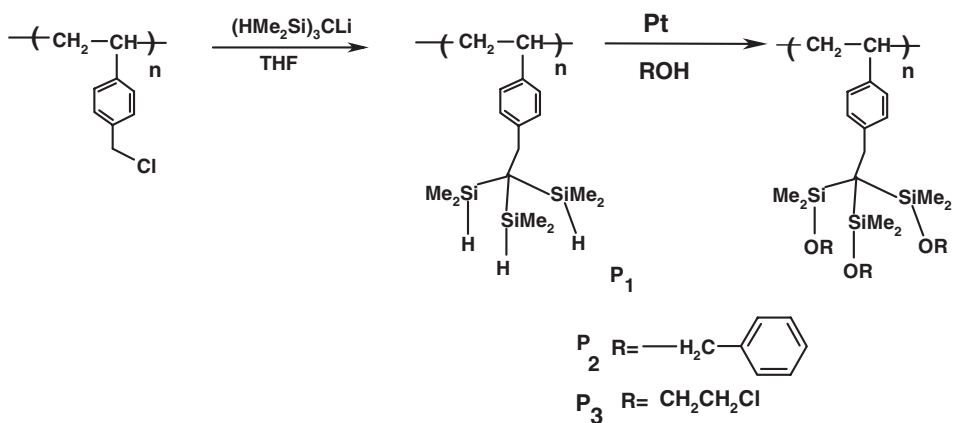
The amount of Karstedt's catalyst has a significant effect on the alcoholysis rate. The optimum amount was determined by experiments with ethylene glycol monoethyl ether. Table II shows that increasing amounts of catalyst leads to faster reactions and shorter alcoholysis times. For instance, by increasing the amount of catalyst from $[\text{Pt}^\circ]/[\text{Si—H}] = 1.10 \times 10^{-4}$ to $[\text{Pt}^\circ]/[\text{Si—H}] = 2.21 \times 10^{-4}$, we were able to reduce the reaction time from 3 h to 30 min.

The attachment of organosilyl groups to macromolecules leads to important modifications in polymer properties, such as gas permeability and permaselectivity parameters; mechanical, thermal, and surface properties; and photochemical reactivity; and constitutes an important research field in its own right. Alcoholyses of polymeric silicon compounds such as polysiloxanes and polysilanes, or copolymers containing such polymeric units, have been reported,^{15–17} but to our knowledge there are a few references in the literature to alcoholysis of groups attached to polystyrene side chains in the presence of Karstedt's catalyst.¹⁸ Alkoxy groups were attached to polymer side chains under the same conditions as those used for monomeric compounds, but the reactions were heterogeneous since the polymers were insoluble in alcohols.

4-Chloromethylstyrene (4-CMS) was homopolymerized at 70°C with AIBN as radical initiator. Then the homopolymer **P**₁ (0.5 g) was treated with an optimized amount of $(\text{HMe}_2\text{Si})_3\text{CLi}$ (25 mmol) in THF. The replacement of chlorine atoms by $(\text{HMe}_2\text{Si})_3\text{C}$ groups was easily followed by the appearance of the Si—H absorption at 2110–2130 cm^{-1} . A FTIR spectrum of the resulting polymer **P**_{1-SiH} exhibits the following characteristics.

Table II Effect of the amount of Karstedt's catalyst on the alcoholysis of glycol monoethyl ether

(Pt/Si—H)	0.55×10^{-4}	1.10×10^{-4}	1.65×10^{-4}	2.21×10^{-4}	2.75×10^{-4}	5.52×10^{-4}
Time	4 h	3 h	100 min	30 min	10 min	10 min



Scheme 2 Alcoholysis of polymer **P₁** with benzyl alcohol or 2-chloroethanol.

The Si—H bond is associated with the strong absorption at 2115 cm^{-1} and the Si—CH₃ bonds with absorptions at 1255 and 830 cm^{-1} . As shown in Scheme 2, the Si—H functional groups of the homopolymer were converted to alkoxy groups with benzyl alcohol or 2-chloroethanol in heterogeneous reactions in the presence of Karstedt's catalyst. The IR and NMR spectroscopic results indicated that under optimal conditions, replacement of H by OR at the silicon center was complete, as shown by the disappearance of both the Si—H peak at 2115 cm^{-1} and the signal ascribed to Si—H at 4.0 ppm in the ^1H NMR spectrum (see Figures 1 and 2).

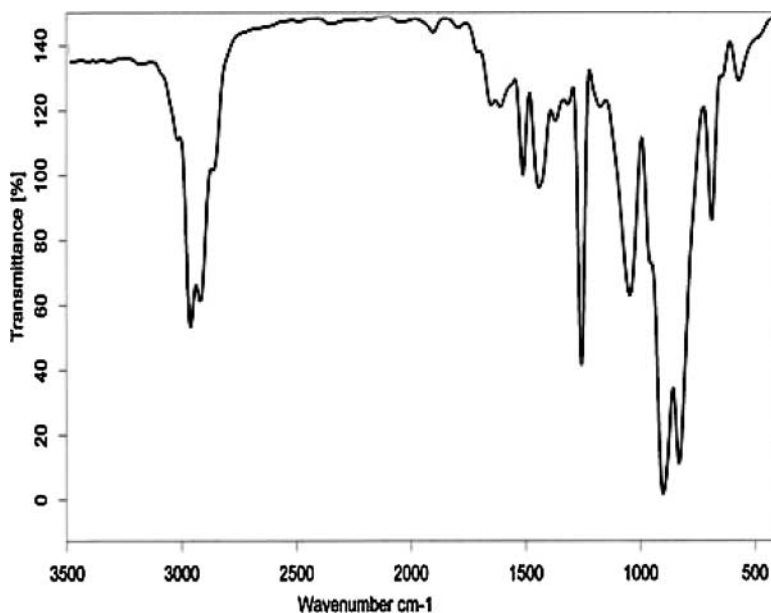


Figure 1 FT-IR spectrum of **P₃**.

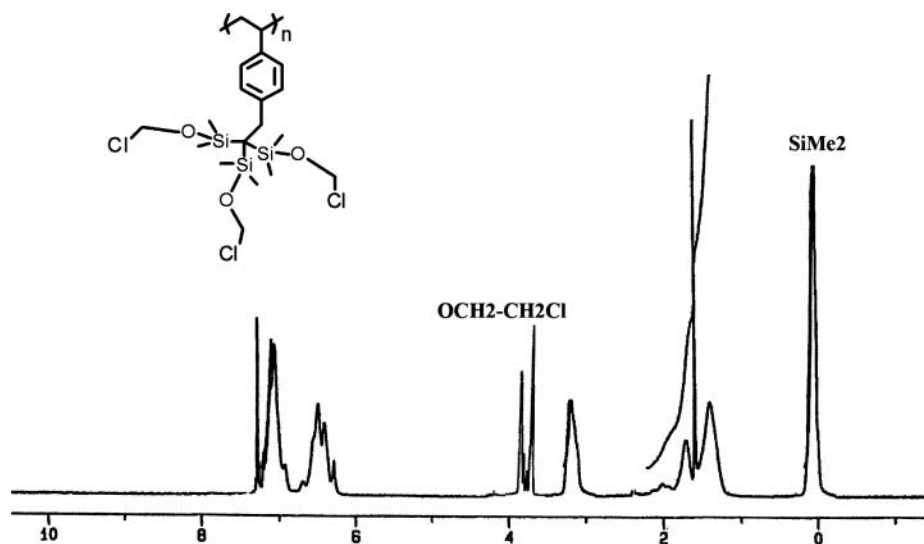


Figure 2 The ^1H NMR spectrum of P_3 .

EXPERIMENTAL

Materials

For the preparation of $(\text{HMe}_2\text{Si})_3\text{CH}$,¹⁹ bromoform (CHBr_3), THF, and Mg were all obtained from Merck and dried by standard methods. HMe_2SiCl (Aldrich) was used as received. All alcohols such as ethylene glycol monobutyl ether, ethylene glycol monoethylether, triethylene glycol monomethyl ether, 2-chloroethanol, glycidol, 1-octanol, benzyl alcohol, and allyl alcohol were obtained from Merck. The monomer CMS (Merck 99%) was distilled under reduced pressure to remove inhibitors before use. Toluene was stirred over calcium hydride for 24 h and distilled under a dry argon atmosphere. The initiator α, α' -azobis(isobutyronitrile) (Merck) was purified by crystallization from methanol. Platinum divinyltetramethyldisiloxane complex (Karstedt's catalyst, 0.10 M solution in xylenes) was purchased from Aldrich.

Measurements

Infrared spectra were recorded on KBr pellets with a 4600 Unicam FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer at room temperature with CDCl_3 as a solvent. The mass spectra were obtained with a GC-Mass Agilent quadrupole mode 5973N spectrometer operating at 70 eV. Elemental analyses were made with an Elementar, Vario EL III mode instrument.

General Procedures for Synthesis of $(\text{ROME}_2\text{Si})_3\text{CH}$ (1–5)

Karstedt's catalyst (40 μL) was added to a solution of $(\text{HMe}_2\text{Si})_3\text{CH}$ (2.0 g, 10.6 mmol) in ROH (40 mL). The mixture was heated under reflux, the solvent was evaporated off, and the residue was distilled to give the products $(\text{ROME}_2\text{Si})_3\text{CH}$.

Synthesis of $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$ (1). The general procedure gave $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$ after 1 h, (1.32 g, 66.4%), bp $90^\circ\text{C}/3$ mmHg; FT-IR (KBr, cm^{-1}) 2958, 2868 (C–H), 1253, 836 (Si–C), 1094 (Si–O), 1011 (C–O); ^1H NMR (CDCl_3 , 400 MHz): δ 0.02 (s, 1H, CH), 0.10 (s, 18H, SiMe_2), 0.81 (t, 9H, CH_2CH_3 , $^3J = 7.5$ Hz), 1.21–1.30 (m, 6H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.40–1.47 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.57 (t, 6H, CH_2OSi , $^3J = 5.7$ Hz), 3.30–3.41 (overlapped, 12H, $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$); ^{13}C NMR (CDCl_3 , 100 MHz): δ 0.0 (SiMe_2), 9.5 (CH), 12.7 (CH_2CH_3), 18.0 (CH_2CH_3), 30.6 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 60.3 (CH_2OSi), 69.7 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 70.9 (CH_2O); MS (EI) m/z (%) 523 (5, $[M - \text{Me}]^+$), 305 (90, $[M - 3\text{BuO} - \text{Me}]^+$), 205 (100, $[M - 3\text{BuOEtO} - 2\text{Me}]^+$), 189 (40, $[M - 3\text{BuOEtO}]^+$), 57 (36, $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2]^+$). Anal. Calc. for $\text{C}_{25}\text{H}_{58}\text{Si}_3\text{O}_6$: C, 55.7; H, 10.8. Found: C, 55.3; H, 10.7%.

Synthesis of $(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$ (2). The general procedure gave $(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$ after 3 h, (3.6 g, 76.5%), bp $70^\circ\text{C}/3$ mmHg; FT-IR (KBr, cm^{-1}) 2969, 2867 (C–H), 1254, 850 (Si–C), 1106 (Si–O), 1016 (C–O); ^1H NMR (CDCl_3 , 400 MHz): δ 0.09 (s, 1H, CH), 0.14 (s, 18H, SiMe_2), 1.12 (t, 9H, CH_3CH_2 , $^3J_{\text{HH}} = 7$ Hz), 3.61 (t, 6H, CH_2OSi , $^3J = 5.5$ Hz), 3.39–3.48 (overlapped, 12H, $\text{CH}_3\text{CH}_2\text{OCH}_2$); ^{13}C NMR (CDCl_3 , 100 MHz): δ 0.0 (SiMe_2), (CH), 14.0 (CH_3CH_2), 60.5 (CH_2OSi), 65.4 (CH_3CH_2), 70.7 ($\text{CH}_3\text{CH}_2\text{OCH}_2$); MS (EI) m/z (%) 439 (100, $[M - \text{Me}]^+$), 365 (68, $[M - \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2 - \text{Me}]^+$), 147 (79, $[M - 2\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2]^+$), 73 (54, $[\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2]^+$). Anal. Calc. for $\text{C}_{19}\text{H}_{46}\text{Si}_3\text{O}_6$: C, 50.2; H, 10.2. Found: C, 49.9; H, 10.5%.

Synthesis of $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$ (3). The general procedure gave $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$ after 2 h, (6.8 g, 96.9%), bp $152^\circ\text{C}/0$ mmHg; FT-IR (KBr, cm^{-1}) 2872 (C–H), 1253, 853 (Si–C), 1108 (Si–O), 1018 (C–O); ^1H NMR (CDCl_3 , 400 MHz): δ –0.26 (s, 1H, CH), –0.14 (s, 18H, SiMe_2), 3.34 (t, 6H, CH_2OSi , $^3J = 5$ Hz), 3.10–3.30 (overlapped, 30H, CH_2OCH_2); ^{13}C NMR (CDCl_3 , 100 MHz): δ 0.0 (SiMe_2), 9.4 (CH), 57.7 (CH_3), 60.1 (CH_2OSi), 69.2–69.3 ($\text{CH}_2\text{OCH}_2\text{CH}_2$), 70.6 (CH_3OCH_2), 71.2 ($\text{CH}_2\text{CH}_2\text{OSi}$); MS (EI) m/z (%) 367 ($[M - 3\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2]^+$), 225 (30, $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}]^+$), 205 (50, $[2\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2]^+$), 147 (28, $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2]^+$), 103 (100, $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2]^+$), 59 (96, $[\text{CH}_3\text{OCH}_2\text{CH}_2]^+$). Anal. Calc. for $\text{C}_{28}\text{H}_{64}\text{Si}_3\text{O}_{12}$: C, 49.6; H, 9.5. Found: C, 49.2; H, 9.3%.

Synthesis of $(\text{ClCH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$ (4). The general procedure gave $(\text{ClCH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$ after 30 min, (2.25 g, 54.7%), bp $80^\circ\text{C}/3$ mmHg; FT-IR (KBr, cm^{-1}) 2971 (C–H), 1255, 863 (Si–C), 1096 (Si–O), 1006 (C–O); ^1H NMR (CDCl_3 , 400 MHz): δ 0.05 (s, 1H, CH), 0.23 (s, 18H, SiMe_2), 3.52 (t, 6H, CH_2Cl , $^3J = 6$ Hz), 3.78 (t, 6H, CH_2O , $^3J = 6$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz): δ 0.0 (SiMe_2), 9.7 (CH), 44.1 (CH_2Cl), 61.9 (CH_2O); MS (EI) m/z (%) 411 (100, $[M - \text{Me}]^+$), 345 (25, $[M - \text{CH}_2\text{Cl} - \text{Me}]^+$), 279 (30, $[M - 3\text{CH}_2\text{Cl}]^+$), 223 (89, $[M - 3\text{CH}_2\text{Cl} - \text{Me}]^+$), 189 (10, $[M - 3\text{CH}_2\text{CH}_2\text{Cl}]^+$), 63 (10, $[\text{CH}_2\text{CH}_2\text{Cl}]^+$). Anal. Calc. for $\text{C}_{17}\text{H}_{43}\text{Si}_3\text{O}_3\text{Cl}_3$: C, 38.3; H, 7.5. Found: C, 38.0; H, 7.1%.

Synthesis of $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$ (5). The general procedure gave $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OMe}_2\text{Si})_3\text{CH}$ after 4 h (3.8 g, 63.6%), bp $130^\circ\text{C}/0$ mmHg; FT-IR (KBr, cm^{-1}) 2927, 2856 (C–H), 1253, 858 (Si–C), 1094 (Si–O), 1014 (C–O); ^1H NMR (CDCl_3 , 400 MHz): δ –0.19 (s, 1H, CH), 0.21 (s, 18H, SiMe_2), 0.90 (t, 9H, CH_3CH_2 , $^3J = 7$ Hz), 1.29 (s, 30H, $\text{CH}_3(\text{CH}_2)_4\text{CH}_2$), 1.49–1.53 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.53 (t, 6H, CH_2OSi , $^3J = 6.5$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz): δ 2.0 (SiMe_2), 9.5 (CH), 13.1 (CH_3), 21.7 (CH_3CH_2), 24.9 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 24.9

($\text{CH}_3(\text{CH}_2)_2\text{CH}_2$), 28.3 ($\text{CH}_3(\text{CH}_2)_3\text{CH}_2$); 30.8 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 31.7 ($\text{CH}_2\text{CH}_2\text{O}$), 64.3 (CH_2O); MS (EI) m/z (%) 445 (29, [$M - \text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{O}$] $^+$), 317 (24), 207 (23), 205 (100, [$M - 2\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{O} - \text{CH}_3(\text{CH}_2)_6\text{CH}_2$] $^+$), 203 (22), 57 (23, [$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$] $^+$). Anal. Calc. for $\text{C}_{31}\text{H}_{70}\text{Si}_3\text{O}_3$: C, 64.7; H, 12.2. Found: C, 64.9; H, 12.3%.

Reaction Between (HMe_2Si) $_3\text{CH}$ and Benzyl Alcohol (6)

Karstedt's catalyst (40 μL) was added to a solution of (HMe_2Si) $_3\text{CH}$ (2 g, 10.6 mmol) in benzyl alcohol (40 mL). The mixture was stirred at room temperature for 10 h. The solvent was evaporated off, and the residue was distilled to give ($\text{C}_6\text{H}_5\text{CH}_2\text{OMe}_2\text{Si}$) $_3\text{CH}$, (4.06 g, 77.1%), bp 120°C/3 mmHg; FT-IR (KBr, cm^{-1}) 3064, 3031 (Ar-H), 2956, 2898 (C-H), 1604 (C=C), 1255, 862 (Si-C), 1065 (Si-O), 1014 (C-O); ^1H NMR (CDCl_3 , 400 MHz): δ 0.12 (s, 1H, CH), 0.44 (s, 18H, SiMe_2), 4.85 (s, 6H, ArCH_2), 7.41–7.52 (m, 15H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz): δ 0.4 (SiMe_2), 10.1 (CH), 63.4 (CH_2O), 14.0 (C- CH_2), 125.8–127.0 (Ar); MS (EI) m/z (%) 493 (22, [$M - \text{Me}$] $^+$), 401 (43, [$M - \text{PhCH}_2\text{O}$] $^+$), 309 (58, [$M - \text{PhCH}_2\text{O} - \text{PhCH}_2$] $^+$), 295 (43), 203 (44), 181 (100, [2PhCH_2] $^+$). Anal. Calc. for $\text{C}_{28}\text{H}_{40}\text{Si}_3\text{O}_3$: C, 66.1; H, 7.9. Found: C, 65.9; H, 7.8%.

Reaction Between (HMe_2Si) $_3\text{CH}$ and Glycidol (7)

Karstedt's catalyst (40 μL) was added to a solution of (HMe_2Si) $_3\text{CH}$ (2 g, 10.6 mmol) in glycidol (40 mL). The mixture was stirred at room temperature for 2 h. The solvent was evaporated off, and the residue was distilled to give the product, (5.2 g, 71.1%), bp 35°C/0 mmHg; FT-IR (KBr, cm^{-1}) 2927, 2877 (C-H), 1258, 848 (Si-C), 1099 (Si-O), 1041 (C-O); ^1H NMR (CDCl_3 , 400 MHz): δ -0.14 (s, 1H, CH), 0.07 (s, 18H, SiMe_2), 42.43–2.61 (m, 6H, CH_2O), 3.30–3.42 (m, 3H, CH-CH_2), 3.61–4.15 (m, 6H, (CH_2OSi)); ^{13}C NMR (CDCl_3 , 100 MHz): δ 2.5 (SiMe_2), 16.8 (CH), 43.0 (CH_2O), 56.65 (C- CH_2), 69.5 (CH_2OSi); MS (EI) m/z (%) 205 (100, [$M - (3\text{RCH}_2 + \text{Me})$] $^+$), 189 (77, [$M - (3\text{RCH}_2\text{O})$] $^+$), 131 (45, [$\text{RCH}_2\text{OSiMe}_2$] $^+$), 73 (22, [RCH_2O] $^+$). Anal. Calc. for $\text{C}_{23}\text{H}_{58}\text{Si}_3\text{O}_6$: C, 47.2; H, 8.4. Found: C, 46.8; H, 8.8%.

Reaction Between (HMe_2Si) $_3\text{CH}$ and Allyl Alcohol (8)

Karstedt's catalyst (40 μL) was added to a solution of (HMe_2Si) $_3\text{CH}$ (2 g, 10.6 mmol) and allyl alcohol (40 mL) in toluene as a solvent. The mixture was stirred at room temperature for 18 h. The solvent was evaporated off, and the residue was distilled to give ($\text{CH}_2 = \text{CHCH}_2\text{OMe}_2\text{Si}$) $_3\text{CH}$ (1.24 g, 74.7%), bp 110°C/3 mmHg; FT-IR (KBr, cm^{-1}) 2952, 2862 (C-H), 1252, 862 (Si-C), 1093 (Si-O), 1013 (C-O); ^1H NMR (CDCl_3 , 400 MHz): δ 0.04 (s, 1H, CH), 0.21 (s, 18H, SiMe_2), 4.08 (d, 6H, CH_2O , $^3J = 3$ Hz), 5.00–5.05 (dd, 3H, $\text{HHC} = \text{CH}$), 5.17–5.23 (dd, 3H, $\text{HHC} = \text{CH}$), 5.82–5.91 (m, 3H, $\text{CH}_2 = \text{CHCH}_2$); ^{13}C NMR (CDCl_3 , 100 MHz): δ 0.1 (SiMe_2), 17.4 (CH), 62.3 (CH_2O), 133.5 ($\text{CH}_2 = \text{CHCH}_2$), 136.1 ($\text{CH}_2 = \text{CHCH}_2$); MS (EI) m/z (%) 343 (100, [$M - \text{Me}$] $^+$), 245 (26, [$M - 2\text{CH}_2 = \text{CHCH}_2\text{O} - 2\text{Me}$] $^+$), 203 (24), 189 (63, [$M - 3\text{CH}_2 = \text{CHCH}_2\text{O}$] $^+$). Anal. Calc. for $\text{C}_{17}\text{H}_{36}\text{Si}_3\text{O}_3$: C, 54.8; H, 9.7. Found: C, 54.6; H, 9.6%.

Synthesis of Polymers P_2 and P_3 Bearing $-\text{SiMe}_2\text{OR}$ Groups in the Side Chain

Karstedt's catalyst (40 μL) was added to a solution of polymer P_1 (0.5 g) in benzyl alcohol or 2-chloroethanol (40 mL). The heterogeneous mixture was heated under reflux,

and the progress of the alcoholysis was monitored by FT-IR spectroscopy. The resulting polymer was filtered off and washed several times with cold methanol. It was dissolved in chloroform (10 mL), the solution was filtered to remove Pt particles, and the polymer was precipitated from methanol to give **P₂** or **P₃**.

Spectroscopic Results for New Homopolymers

P₂: FT-IR (KBr, cm^{-1}) 3022, 2980, (C–H), 1255, 850 (Si–C), 1654, 1450 (C=C), 1010 (Si–O), 988 (C–O); ^1H NMR (CDCl_3 , 400 MHz): δ 0.10 (SiMe₂), 1.3, 1.8 (CH₂CH), 4.91 (PhCH₂), 7.20–8.12 (Ph); ^{13}C NMR (CDCl_3 , 100 MHz): δ – 5.0 (SiMe₂), –3.2 (CH), 70.9 (CH₂Ph), 126.1–140.0 (Ph).

P₃: FT-IR (KBr, cm^{-1}) 3024, 2959 (C–H), 1250, 850 (Si–C), 1010 (Si–O), 980 (C–O); ^1H NMR (CDCl_3 , 400 MHz): δ 0.10 (SiMe₂), 1.3, 1.8 (CH₂CH), 3.57 (ClCH₂), 3.95 (CH₂O); ^{13}C NMR (CDCl_3 , 100 MHz): δ –0.5 (SiMe₂), –3.6 (CH), 42.7 (CHCl), 63.4 (CH₂O).

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