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Reactions of Tris(dimethylsilyl)methane and Polymers Containing Si–H Groups with Various Hydroxy Compounds under Aerobic and Mild Conditions

Kazem D. Safa,[1,2] Shahin Tofangdarzadeh,[1]
and Hossein Heydari Ayenadeh[1]

[1]*Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, 51664 Tabriz, Iran*

[2]*Research Institute for Fundamental Sciences, Tabriz, Iran*

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ABSTRACT: *Tris(dimethylsilyl)methane, $(HMe_2Si)_3CH$, reacts with n-propyl, iso-propyl, n-butyl, s-butyl, iso-butyl, n-pentyl, s-pentyl, n-hexyl alcohol, and phenol in the presence of chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) in air to give products $(ROMe_2Si)_3CH$ (where R is n-propyl, iso-propyl, n-butyl, s-butyl, iso-butyl, n-pentyl, s-pentyl, n-hexyl, phenyl). Similar reactions with benzyl alcohol and acetic acid lead to the unexpected products, $(PhCH_2)_2O$ and $HC(Me_2SiOSiMe_2)_3CH$, respectively. The compound $(n\text{-}BuOMe_2Si)_3CSiMe_2H$ was made from $(n\text{-}BuOMe_2Si)_3CH$ by treatment with lithium diisopropylamide, followed by quenching with HMe_2SiCl. The homopolymer poly{(4-chloromethyl)styrene} and copolymers with styrene (in 1:1 and 1:3 mol ratio) were synthesized by free radical polymerization, and $(HMe_2Si)_3C$ groups were linked to them by nucleophilic substitution reactions between $(HMe_2Si)_3CLi$ and the chloromethyl groups of the polymer side chains. The resulting functional polymers containing Si—H bonds reacted with various alcohols in the presence of chloroplatinic acid under heterogeneous conditions.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:365–376, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20440

INTRODUCTION

Among the diverse reactions at silicon centers, those involving silicon–oxygen bond formation are particularly important and silyl ethers are among the most widely used protecting groups for hydroxyl functions in organic synthesis [1]. They also play an important role in inorganic synthesis as precursors in the preparation of sol–gels and other condensed siloxane materials [2]. Silyl ethers are most commonly prepared from chlorosilanes, by the reaction with alcohols or alkoxides, under acidic or basic conditions [3].

The addition of hydrosilanes to alcohols is, however, also an attractive route to silyl ethers because the only side product is hydrogen gas (Eq. (1)).

$$R_{4-x}SiH_x + xR'OH \xrightarrow{\text{catalyst}} R_{4-x}Si(OR')_x + xH_2 \qquad (1)$$

The alcoholysis requires a catalyst because alcohols are not generally sufficiently nucleophilic to attack hydrosilanes. Strongly nucleophilic or electrophilic catalysts can be used [2], and a limited number of transition metal complexes [4–10]. It has been found that chloroplatinic acid, even in minute amounts, is

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Correspondence to: Kazem D. Safa; e-mail: dsafa@tabrizu.ac.ir.

Contract grant sponsor: Research Institute for Fundamental Sciences, Tabriz, Iran.

an extremely potent catalyst, but few examples have been reported in the literature [11].

The work described in this paper centers on the preparation of tris(alkoxydimethysilyl)methanes under mild aerobic conditions and a study of their lithiation. We also report the synthesis of new polymers containing $(HMe_2Si)_3C$ functions and the preparation of homo- and co-polymers by the reaction of several Si—H-containing polymers with alcohols in the presence of the Pt catalyst.

EXPERIMENTAL

Materials

For the synthesis of $(HMe_2Si)_3CH$ [12], bromoform, THF, and Mg were obtained from Merck (Germany, Frankfurter Str. 250, 64293 Darmstadt) and dried by standard methods. HMe_2SiCl Aldrich (Aldrich Chemical Co. P.O. Box 2060. Milwaukee, WI 53201) was used as received. Alcohols such as methanol, ethanol, *n*-propanol, iso- propanol, *n*-butanol, *s*-butanol, iso-butanol, *n*-pentanol, *s*-pentanol, *n*-hexanol, and phenol (Merck) were distilled before use. The monomer styrene (Merck) and 4-chloromethylstyrene (CMS) (Merck; 99%) were distilled under reduced pressure to remove inhibitors. Toluene was stirred over calcium hydride for 24 h and distilled under dry argon. The initiator α,α'-azobis(isobutyronitrile) (AIBN) (Merck) was purified by crystallization from methanol.

Measurements

Infrared spectra from KBr pellets were recorded with a 4600 Unicam FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were run 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 instrument operating at 70 eV. Elemental analyses were carried out with an Elementar, Vario EL III mode 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. Glass transition temperatures (T_g) were determined by a Shimadzu DSC-50 instrument with a heating rate of 10 K/min and 5 K/min in air or N_2. The T_gs were taken from inflections in the heat flow plots.

General Procedure for the Synthesis of $(ROMe_2Si)_3CH$

Four drops of 0.04 M $H_2PtCl_6{\cdot}6H_2O$ in EtOH were added to a solution of $(HMe_2Si)_3CH$ (2 g, 10.6 mmol) in ROH (50 mL). The mixture was heated under reflux for 24 h, during which eight more drops of the $H_2PtCl_6{\cdot}6H_2O$ solution were added. The solution was filtered, the solvent was evaporated from the filtrate, and the residue was distilled to give $(ROMe_2Si)_3CH$. Analytical and spectroscopic data are given below.

*$(CH_3CH_2CH_2OMe_2Si)_3CH$ (**1**).* Yield: 2.34 g, 61.1%, b.p. 110°C/2 mmHg; IR: 2962 (C—H), 1255, 832 (Si—C), 1088 (Si—O), 1008 (C—O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ −0.03 (s, 1H, CH), 0.18 (s, 18H, $SiMe_2$), 0.87 (t, 9H, $CH_2\mathit{CH_3}$, $^3J_{HH} = 8$ Hz), 1.51 (m, 6H, $\mathit{CH_2}CH_3$, $^3J_{HH} = 8$ Hz), 3.47 (t, 6H, CH_2O, $^3J_{HH} = 8$ Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 0.1 ($SiMe_2$), 3.1 (CH), 9.5 ($CH_2\mathit{CH_3}$), 24.8 ($\mathit{CH_2}CH_3$), 63.0 (CH_2O); MS (EI) *m/z* (%): 349 (100, $[M - Me]^+$), 305 (20), 247 (30), 205 (70), 189 (25). Anal. Calcd for $C_{16}H_{40}Si_3O_3$: C, 52.7; H, 10.9. Found: C, 52.3; H, 10.5.

*$[(CH_3)_2CHOMe_2Si]_3CH$ (**2**).* Yield 2 g, 52.2%, b.p. 100°C/2 mmHg; IR: 2968 (C—H), 1252, 837 (Si—C), 1128 (Si—O), 1021 (C—O) cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.11 (s, 1H, CH), 0.19 (s, 18H, $SiMe_2$), 1.10 (d, 18H $(\mathit{CH_3})_2CH$, $^3J_{HH} = 8$ Hz), 3.95 (m, 3H, CHO, $^3J_{HH} = 8$ Hz); ^{13}C NMR ($CDCl_3$,): δ 0.9 ($SiMe_2$), 10.2 (CH), 24.8 ($(\mathit{CH_3})_2CH$), 63.4 (CHO); MS (EI) *m/z* (%): 349 (50, $[M - Me]^+$), 305 (10), 247 (20), 205 (100), 189 (20). Anal. Calcd for $C_{16}H_{40}Si_3O_3$: C, 52.7; H, 10.9. Found: C, 52.5; H, 10.9.

*$(CH_3CH_2CH_2CH_2OMe_2Si)_3CH$ (**3**).* Yield: 3.1 g, 72%, b.p. 120°C/2 mmHg; IR: 2957 (C—H), 1251, 851 (Si—C), 1092 (Si—O), 1012 (C—O) cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.04 (s, 1H, CH), 0.17 (s, 18H, $SiMe_2$), 0.89 (t, 9H, $\mathit{CH_3}CH_2$, $^3J_{HH} = 8$ Hz), 1.33 (m, 6H, $CH_3\mathit{CH_2}CH_2$, $^3J_{HH} = 4$ Hz), 1.46 (m, 6H, $CH_3CH_2\mathit{CH_2}$, $^3J_{HH} = 4$ Hz), 3.51(t, 6H, CH_2O, $^3J_{HH} = 8$ Hz); ^{13}C NMR ($CDCl_3$): δ 0.1 ($SiMe_2$), 9.6 (CH), 12.9 ($\mathit{CH_3}CH_2$), 18.1 ($CH_3\mathit{CH_2}CH_2$), 33.8 ($CH_3CH_2\mathit{CH_2}$), 60.9 (CH_2O); MS (EI) *m/z* (%): 391(100, $[M - Me]^+$), 333 (10), 261 (25), 205 (70), 189 (20). Anal. Calcd for $C_{19}H_{46}Si_3O_3$: C, 56.1; H, 11.3. Found: C, 55.8; H, 11.2.

*$[(CH_3CH_2)(CH_3)CHOMe_2Si]_3CH$ (**4**).* Yield 1.72 g, 40.2%, b.p. 60°C/2 mmHg; IR: 2971 (C—H), 1255, 863 (Si—C), 1096 (Si—O), 1006 (C—O) cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.08 (s, 1H, CH), 0.20 (d, 18H, $SiMe_2$, $^3J_{HH} = 8$ Hz), 0.86 (t, 9H, $\mathit{CH_3}CH_2$, $^3J_{HH} = 8$ Hz), 1.08 (d, 9H, $\mathit{CH_3}CHO$, $^3J_{HH} = 8$ Hz), 1.42 (m, 6H, $CH_3\mathit{CH_2}$, $^3J_{HH} = 8$ Hz), 3.69 (m, 3H, CHO, $^3J_{HH} = 4$ Hz); ^{13}C

NMR ($CDCl_3$): δ 1.0, 1.1 ($SiMe_2$), 10.6 (CH), 14.2 (CH_3CH_2), 21.9 (CH_3CHO), 31.22 (CH_3CH_2), 68.37 (CHO); MS (EI) *m/z* (%): 391 (30, [M − Me]$^+$), 333 (20), 261 (18), 205 (100), 189 (17). Anal. Calcd for $C_{19}H_{46}Si_3O_3$: C, 56.1; H, 11.3. Found: C, 55.9; H, 11.3.

$[(CH_3)_2CHCH_2OMe_2Si]_3CH$ (**5**). Yield 2.4 g, 56.2%, b.p. 90°C/2 mmHg; IR (KBr): 2960 (C—H), 1253, 865 (Si—C), 1086 (Si—O), 1016 (C—O) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.0 (s, 1H, CH), 0.2 (s, 18H, $SiMe_2$), 0.9 (d, 18H, $(CH_3)_2CH$, $^3J_{HH} = 8$ Hz), 1.7 (m, 3H, $(CH_3)_2CH$, $^3J(H—H) = 8$ Hz), 3.3 (d, 6H, CH_2O, $^3J_{HH} = 8$ Hz), ^{13}C NMR ($CDCl_3$): δ 0.1 ($SiMe_2$), 9.7 (CH), 18.2 ($(CH_3)_2CH$), 29.7 ($(CH_3)_2CH$), 68.2 (CH_2O); MS (EI) *m/z* (%): 391 (70, [M − Me]$^+$), 333 (20), 261(25), 205 (100), 189 (18). Anal. Calcd for $C_{19}H_{46}Si_3O_3$: C, 56.1; H, 11.3. Found: C, 56.1; H, 11.2.

$(CH_3CH_2CH_2CH_2CH_2OMe_2Si)_3CH$ (**6**). Yield 3.31 g, 70%), b.p. 130°C/2 mmHg; IR: 2953 (C—H), 1251, 858 (Si—C), 1094 (Si—O), 1008 (C—O) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.04 (s, 1H, CH), 0.18 (s, 18H, $SiMe_2$), 0.88 (t, 9H, CH_3CH_2, $^3J_{HH} = 8$ Hz), 1.29 (m, 12H, $CH_3(CH_2)_2CH_2$, $^3J_{HH} = 4$ Hz), 1.48 (m, 6H, $CH_3(CH_2)_2CH_2$ $^3J_{HH} = 4$ Hz), 3.51 (t, 6H, CH_2O, $^3J_{HH} = 8$ Hz); ^{13}C NMR ($CDCl_3$,): δ 0.0 ($SiMe_2$), 9.6 (CH), 13.0 (CH_3CH_2), 21.5 (CH_3CH_2), 27.2 ($CH_3CH_2CH_2$), 31.4 ($CH_3(CH_2)_2CH_2$), 61.2 (CH_2O); MS (EI) *m/z* (%): 433 (100, [M − Me]$^+$), 361 (15), 275 (18), 205 (60),189 (18). Anal. Calcd for $C_{22}H_{52}Si_3O_3$: C, 58.9; H, 11.6. Found: C, 58.9; H, 11.5.

$[(CH_3CH_2CH_2)(CH_3)CHOMe_2Si]_3CH$ (**7**). Yield: 2.4 g, 50.8%, b.p. 120°C/2 mmHg; IR: 2963 (C—H), 1251, 846 (Si—C), 1127 (Si—O), 1018(C—O) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.09 (s, 1H, CH), 0.19 (d, 18H, $SiMe_2$,$^3J_{HH} = 8$ Hz), 0.87 (t, 9H, CH_3CH_2, $^3J_{HH} = 8$ Hz), 1.07 (d, 9H, CH_3CHO, $^3J_{HH} = 8$ Hz), 1.32 (m, 12H, $CH_3(CH_2)_2$, $^3J_{HH} = 4$ Hz), 3.74 (m, 3H, CHO, $^3J_{HH} = 4$ Hz); ^{13}C NMR $CDCl_3$): δ 0.9, 1.0 ($SiMe_2$), 10.6 (CH), 13.2 (CH_3CH_2), 17.9 (CH_3CHO), 22.5 (CH_3CH_2), 41.0 ($CH_3CH_2CH_2$), 66.9 (CHO); MS (EI) *m/z* (%): 433 (25, [M − Me]$^+$), 361 (20), 275 (15), 205 (100), 189 (14). Anal. Calcd for $C_{22}H_{52}Si_3O_3$: C, 58.9; H, 11.6. Found: C, 59.0; H, 11.5.

$(CH_3CH_2CH_2CH_2CH_2CH_2OMe_2Si)_3CH$ (**8**). Yield 3.2 g, 62.1%), b.p. 100°C/2 mmHg; IR: 2952 (C—H), 1252, 862 (Si—C), 1093 (Si—O), 1013(C—O) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.0 (s, 1H, CH), 0.2 (s, 18H, $SiMe_2$), 0.9 (t, 9H, CH_3CH_2, $^3J_{HH} = 8$ Hz), 1.3 (m, 18H, $CH_3(CH_2)_3CH_2$, $^3J_{HH} = 4$ Hz), 1.5 (m, 6H, $CH_3(CH_2)_3CH_2$, $^3J_{HH} = 8$ Hz), 3.5 (t, 6H, CH_2O, $^3J_{HH} = 8$ Hz); ^{13}C NMR ($CDCl_3$): δ 0.12 ($SiMe_2$), 9.6 (CH), 13.0 (CH_3CH_2), 21.7 (CH_3CH_2), 24.7 ($CH_3CH_2CH_2$), 30.7 ($CH_3(CH_2)_2CH_2$), 31.7 ($CH_3(CH_2)_3CH_2$), 61.3 (CH_2O); MS (EI) *m/z* (%): 475(5, [M − Me]$^+$), 391 (35), 375 (8), 291 (10), 205 (100), 189 (38). Anal. Calcd for $C_{25}H_{58}Si_3O_3$: C, 61.2; H, 11.8. Found: C, 61.3; H, 11.7.

$(PhOMe_2Si)_3CH$ (**10**). Yield: 2.22 g, 45.3%, m.p. 48–50°C; IR (cm^{-1}): 3029 (Ar—H), 2960 (C—H), 1597, 1497 (C=C), 1272, 852 (Si—C), 1060 (Si—O), 1027 (C—O); ^{1}H NMR ($CDCl_3$): δ 0.43 (s, 1H, CH), 0.49 (s, 18H, $SiMe_2$), 6.85–6.87 (dd, 6H, *m*-H), 6.96–6.99 (t, 3H, *p*-H), 7.23–7.27 (t, 6H, *o*-H); ^{13}C NMR ($CDCl_3$): δ 0.1 ($SiMe_2$), 9.8 (CH), 118.0 (*m*-C), 119.3 (*p*-C), 127.5 (*o*-C), 153.0 (*i*-C); MS (EI) *m/z* (%): 391 (8, [M − Ph]$^+$), 316 (4), 301 (7), 281 (7), 253 (4), 223 (100), 207 (25), 93 (5). Anal. Calcd for $C_{25}H_{34}$ Si_3O_3: C, 64.3; H, 7.3. Found: C, 63.9; H, 7.1.

Reaction between $(HMe_2Si)_3CH$ and $PhCH_2OH$

An attempt to synthesize $PhCH_2OMe_2Si)_3CH$ by the general procedure unexpectedly gave the product $(PhCH_2)_2O$ (**9**), b.p. 120°C/2 mmHg; IR: 3031 (Ar—H), 2922 (C—H), 1645, 1453 (C=C), 1093 (C—O), 741 (Ar—H bend.) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.66 (s, 4H, CH_2O), 7.45–7.47 (10H, Ph); ^{13}C NMR ($CDCl_3$): δ 70.9 (CH_2O), 126.3, 126.5, 127.3, 137.1 (Ph); MS (EI) *m/z* (%): 107 (20), 92 (100), 77 (19). Anal. Calcd for $C_{14}H_{14}O$: C, 84.8; H, 7.1. Found: C, 84.4; H, 6.9.

Attempted Synthesis of $(CH_3COOMe_2Si)_3CH$

The reaction between $(HMe_2Si)_3CH$ and acetic acid with the general procedure described above gave the known compound $HC(Me_2SiOSiMe_2)_3CH$ **(11)**, 1.25 g, 56.3%, m.p. 275–276°C; IR 2952 (C—H), 1258, 868 (Si—C), 1051 (Si—O—Si) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.85 (s, 2H, CH) and 0.18 (s, 36H, $SiMe_2$); ^{13}C NMR ($CDCl_3$): δ 5.2 ($SiMe_2$), 12.3 (CH); MS (EI) *m/z* (%): 422 (2, M$^+$), 407 (100, [M − Me]$^+$), 391 (5), 319 (8), 303 (10), 188 (7). Anal. Calcd for $C_{14}H_{38}$ Si_6O_3: C, 39.7; H, 8.9. Found: C, 39.7; H, 8.9.

*Synthesis of $(n\text{-}BuOMe_2Si)_3CSiMe_2H$ (**12**)*

A 50-mL round-bottom flask equipped with a stirrer, septum, and gas-inlet needle was charged with diisopropylamine (0.25 g, 2.5 mmol) and THF (5 mL). The flask was placed in a water/ice bath and then *n*-BuLi (0.93 mL, 2.7 M solution in hexane) was added dropwise via a syringe to give a clear yellow solution that was stirred for an additional 30 min. The lithium diisopropylamide (LDA) solution was transferred into a dropping funnel and added to a 100-mL round-bottom flask containing tris(butoxydimethylsilyl)methane, (n-$BuOMe_2Si)_3CH$ (1.00 g, 2.5 mmol), in THF (10 mL) under argon at −78°C during 2 h. Then, the silane HMe_2SiCl (0.24 g, 2.5 mmol) was added dropwise via a syringe at −78°C. A white precipitate of LiCl formed immediately. The mixture was allowed to warm up to room temperature during 2 h. Solvent was removed, and the residue was extracted with pentane (20 mL) to leave a white solid. This was filtered off, and solvents were removed from the filtrate to give a yellow oil. An analytically pure colorless liquid was obtained by preparative TLC (silica gel, 1:2 n-hexane: CH_2Cl_2), (0.55 g, 48.2%). IR: 2961 (C—H), 2123 (Si—H), 1256, 816 (Si—C), 1050 (Si—O), 1010 (C—O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.23 (s, 18H, $SiMe_2$), 0.24 (d, 6H,$SiMe_2H$, $^3J_{HH} = 4$ Hz), 0.89 (t, 9H, CH_3CH_2, $^3J_{HH} = 8$ Hz), 1.34 (m, 6H, $CH_3CH_2CH_2$, $^3J_{HH} = 4$ Hz), 1.47 (m, 6H, $CH_3CH_2CH_2$, $^3J_{HH} = 4$ Hz), 3.51 (t, 6H, CH_2O, $^3J_{HH} = 8$ Hz), 4.68 (m, 1H, SiH); ^{13}C NMR ($CDCl_3$): δ −0.16 ($SiMe_2H$), 0.0 ($SiMe_2$), 4.6 (C), 12.8 (CH_3CH_2), 18.10 ($CH_3CH_2CH_2$), 33.82 ($CH_3CH_2CH_2$), 60.94 (CH_2O); MS (EI) m/z (%): 407 (100, $[M - Bu]^+$), 392 (2), 377 (4), 351 (20), 335 (80), 319 (10), 303 (5), 263 (25), 247 (28), 205 (10), 189 (15). Anal. Calcd for $C_{21}H_{52}Si_4O_3$:C, 54.3; H, 11.2. Found: C, 54.2; H, 11.1

*Synthesis of $(HMe_2Si)_3CCH_2Ph$ (**13**)*

A solution of $(HMe_2Si)_3CLi$ in THF was prepared from $(HMe_2Si)_3CH$ and LDA according to the literature [13]. In a 50-mL two-necked flask equipped with a condenser, a solution of 10.5 mmol of $(HMe_2Si)_3CLi$ in THF was prepared from $(HMe_2Si)_3CH$ (2.00 g,10.5 mmol) and LDA (6.5 mL, 13 mmol). The red-brown solution was stirred at ambient temperature for 6 h under argon. Then, a solution of 1.32 g benzyl chloride (10.5 mmol) in 15 mL THF was added dropwise. The mixture was heated under reflux for 3 h, then allowed to cool and poured into aqueous NH_4Cl. The products were extracted with ether, and the etheral layer was dried with anhydrous Na_2SO_4, filtered and solvent was evaporated from the filtrate. The residue was purified by TLC (silica gel, n-hexane as eluent) to give a clear gel. IR: 3020 (aromatic C—H), 1930 (aliphatic C—H), 2120 (Si—H), 1590, 1480 (aromatic C=C), 1250, 895 (C—Si) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.2 (d, 18H, $SiMe_2$), 3.1 (s, 2H, CH_2Ph), 4.2 (sept, 3H, SiH), 7.3–7.4 (m, 5H, ArH); ^{13}C NMR: ($CDCl_3$): δ −3.8 (6C, SiMe), 3.8 ($(SiMe_2H)_3C$), 34.9 (CH_2-Ph), 125.2–139.3 (aromatic); MS (EI) m/z (%): 175 (100), $[M - SiMe_2H]^+$), 189 (60), 59 (40), 91 (50, $[C_6H_5CH_2]^+$). Anal. Calcd for $C_{14}H_{28}Si_3$: C, 59.9; H, 9.9. Found: C, 60.0; H, 10.0.

Synthesis and Characterization of Homopolymer P_1 and Copolymers (P_2, P_3)

The homopolymerization of 4-chloromethylstyrene to give polymer P_1 and copolymerizations of 4-chloromethylstyrene with styrene to give P_2 and P_3 were carried out according to the standard procedure described previously [14] (see also Table 3). Spectroscopic results for P_1: IR (KBr, cm^{-1}) 3030 (aromatic C—H), 2910–2860 (aliphatic C—H), 1590, 1480 (aromatic C=C); ^1H NMR ($CDCl_3$) δ: 1.4 (2H, CH_2CH), 1.9 (1H, CH_2CH), 4.6 (2H, CH_2Cl), 7.2–8.4 (4H, Ar—H); ^{13}C NMR ($CDCl_3$): δ 40.0 (CH_2CH), 41.0 (CH_2CH), 48.2 (CH_2Cl), 125–145.5 (aromatic). Anal. Calcd for C_9H_9Cl (per polymeric unit): C, 70.8; H, 5.9. Found: C, 70.7; H, 5.8.

Spectroscopic results for copolymer P_3, IR (KBr, cm^{-1}): 3030 (aromatic C—H), 2900, 2850 (aliphatic C—H), 1600, 1485 (aromatic C=C); ^1H NMR ($CDCl_3$): δ 1.4 (2H,CH_2CH), 1.8 (1H,CH_2CH) 4.6 (2H,CH_2Cl), 7.4–8.3 (4H, Ar—H); ^{13}C NMR ($CDCl_3$): δ 41.0 (CH_2-CH), 41.5(CH_2-CH), 48.0(CH_2-Cl), 125–145 (aromatic). Anal. Calcd for $C_{17}H_{17}Cl$ (one polymeric unit): C, 79.5; H, 6.6. Found: C, 79.3; H, 6.5.

Addition of $(HMe_2Si)_3C$ Groups to Polymer Side Chains (Polymers $P_{1\text{-SiH}}$, $P_{2\text{-SiH}}$, $P_{3\text{-SiH}}$)

In a 100-mL two-necked flask equipped with a dropping funnel and a reflux condenser, 0.5 g of polymer P_1 (with 3.3 mmol of chlorine-containing monomer units) was dissolved in 30 mL THF. A gas inlet was attached to the top of the dropping funnel, and the system was maintained under a slight pressure of argon. A solution of $(HMe_2Si)_3CLi$ (25 mmol) was prepared as described above, transferred into the dropping funnel under argon and added dropwise with stirring to the solution of P_1 at room temperature. The reaction mixture was heated under reflux for 6 h, allowed to cool, and poured into an excess of methanol. The yellow precipitate was dissolved in THF (15 mL), and the solution was poured into 50 mL of cooled methanol. The precipitate was washed with methanol several times to give white polymer $P_{1\text{-SiH}}$ that was dried under vacuum at room temperature.

A solution of P_2 (0.5 g with 1 mmol of chlorine-containing monomer units) or 0.5 g P_3 (with 2 mmol of chlorine-containing monomer units) in THF (30 mL) was treated with an excess of $(HMe_2Si)_3CLi$ (20 mmol) and heated under reflux for 8 h as described above. After workup, white solids $P_{2\text{-SiH}}$ or $P_{3-\text{SiH}}$ were collected and dried under vacuum at room temperature. Spectroscopic results for homopolymer $P_{1\text{-SiH}}$: IR (KBr, cm^{-1}) 3029 (aromatic

C—H), 2910–2860 (aliphatic C—H), 2115 (Si—H), 1590, 1480 (aromatic C=C), 1255, 850 (C—Si); ^{1}H NMR ($CDCl_3$): δ 0.16 (18H, $Si(CH_3)_2$), 1.4–1.9 (3H, CH_2CH), 3.1 (2H, CH_2Ph), 4.0 (3H, Si—H),7.2–8.4 (4H, Ar—H); ^{13}C NMR ($CDCl_3$): δ 2.6 (CH_3Si), 5 (($HMe_2Si)_3C$), 35.0 (CH_2-Ph), 40.0 (CH_2CH), 41.0 (CH_2CH), 125–145.5 (aromatic carbons). Anal. Calcd for $C_{16}H_{30}Si_3$ (one polymeric unit): C, 62.8; H, 9.8. Found: C, 62.5; H, 9.8. Elemental analysis for copolymer P_{3-SiH}: Anal. Calcd for $C_{17}H_{21}Si_3$ (one polymeric unit): C, 67.9; H, 9.0. Found: C, 67.6; H, 8.9.

General Procedures for Synthesis of Polymers (P-OR) Containing SiMe$_2$R-Substituted Side Chains

Four drops of 0.04 M $H_2PtCl_6{\cdot}6H_2O$ in EtOH were added to a mixture of polymer $P_{Si\text{-}H}$ (0.5 g) in ROH (50 mL).The heterogeneous mixture was heated under reflux for 48 h, during which eight more drops of the catalyst were added. The color gradually changed to black, and the progress of the alcoholysis reaction 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 reprecipitated from methanol.

Spectroscopic results for homopolymers are as follows:

P$_1$-OMe. IR (KBr, cm^{-1}): 3029 (aromatic C—H), 2910–2860 (aliphatic C—H) 1590, 1480 (aromatic C=C), 1094 (Si—O), 1008 (C—O), 1255, 850 (C-Si); ^{1}H NMR ($CDCl_3$): δ 0.18 (18H, $Si(CH_3)_2$), 1.4–1.9 (3H, CH_2CH), 3.1 (2H, CH_2Ph), 3.60 (s, 3H, OMe), 7.2–8.4 (4H, Ar-H); ^{13}C NMR ($CDCl_3$,): δ 2.6 (CH_3Si), 7.0 ($C(SiMe_2OR)_3$), 34.0 (CH_2Ph), 40.0 (CH_2CH), 41.0 (CH_2CH), 56.2 (OMe), 125–145.5 (aromatic). Anal. Calcd for $C_{19}H_{36}Si_3O_3$ (one polymeric unit): C, 57.5; H, 9.09. Found: C, 57.2; H, 9.1.

P$_1$-OEt. IR (KBr, cm^{-1}): 3029 (aromatic C—H), 2910–2860 (aliphatic C—H) 1590, 1480 (aromatic C=C), 1092 (Si—O), 1005 (C—O), 1255, 850 (C—Si); ^{1}H NMR ($CDCl_3$): δ 0.18 (18H, $Si(CH_3)_2$), 1.4–1.9 (3H, CH_2-CH), 1.32 (t, 9H, CH_2CH_3,), 3.1 (2H, CH_2Ph), 3.57 (6H, CH_2O), 7.2–8.4 (4H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 2.6 (6C, CH_3-Si), 7.0 ($C(SiMe_2OR)_3$), 14.0 (CH_2CH_3), 34.0 (CH_2Ph), 41.0 (CH_2CH), 44.0 (CH_2CH), 60.2 (CH_2O), 125–145.5 (aromatic). Anal. Calcd for $C_{22}H_{42}Si_3O_3$ (one polymeric unit): C, 60.2; H, 9.5. Found: C, 60.5; H, 9.8.

P$_1$-OPr. IR (KBr, cm^{-1}): 3018 (aromatic C—H), 2920–2860 (aliphatic C—H), 1592, 1482 (aromatic C=C), 1090 (Si—O), 1000 (C—O), 1254, 850 (C—Si); ^{1}H NMR ($CDCl_3$): δ 0.18 (18H, $Si(CH_3)_2$), 0.92 (9H, CH_2CH_3,), 1.4–1.9 (3H, CH_2-CH), 1.56 (6H, CH_2CH_3,), 3.31 (2H, CH_2Ph), 3.50 (6H, CH_2O), 7.2–8.4 (4H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 2.6 (CH_3-Si), 7.0 ($C(SiMe_2OR)_3$), 10.2 (CH_2CH_3), 25.83 (CH_2CH_3), 34.0 (CH_2-Ph), 40.0 (CH_2CH), 41.0 (CH_2CH), 62.99 (CH_2O), 125–145.5 (aromatic). Anal. Calcd for $C_{25}H_{48}Si_3O_3$ (one polymeric unit): C, 62.5; H, 10.2. Found: C, 62.1; H, 10.3.

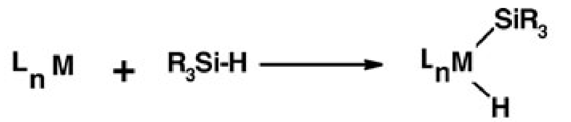
P$_1$-OBu. IR (KBr, cm^{-1}): 2953 (C—H), 1251, 858 (Si—C), 1094 (Si—O), 1008 (C—O), 1254, 850 (C—Si); ^{1}H NMR ($CDCl_3$): δ 0.22 (18H, $Si(CH_3)_2$), 0.82 (9H, CH_2CH_3), 1.4–1.9 (3H, CH_2CH, 6H, CH_2CH_2O), 1.56 (6H, CH_2CH_3), 3.31 (2H, CH_2Ph), 3.55 (6H, CH_2O), 7.2–8.4 (4H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 2.2 ($SiMe_2$), 8.5 (CH), 12.00 (CH_3CH_2), 22.47 (CH_3CH_2), 28.19 ($CH_3CH_2CH_2$), 32.39 ($CH_3(CH_2)_2CH_2$), 35.0 (CH_2-Ph), 41.0 (CH_2CH), 43.0 (CH_2CH), 62.19 (CH_2O); Anal. Calcd for $C_{28}H_{54}Si_3O_3$ (one polymeric unit): C, 64.3; H, 10.3. Found: C, 64.5; H, 10.2.

Spectroscopic data for copolymers $P_{2\text{-}OR}$ and $P_{3\text{-}OR}$ were similar to those for the homopolymer.

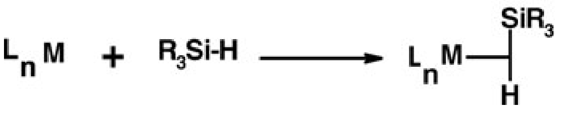
RESULTS AND DISCUSSION

The metals of groups 8–10 and some of their salts are known to catalyze the cleavage of the silicon-hydrogen bond by a wide variety of nucleophilic reagents. The most widely studied nucleophiles have been alcohols and carboxylic acids [15]. This general class of reaction constitutes a convenient method for the preparation of substances containing the silicon-oxygen bonds in high yields.

Transition metal catalyzed activation of silanes can occur by oxidative addition Eq. (2) or by formation of a σ complex (Eq. (3)).

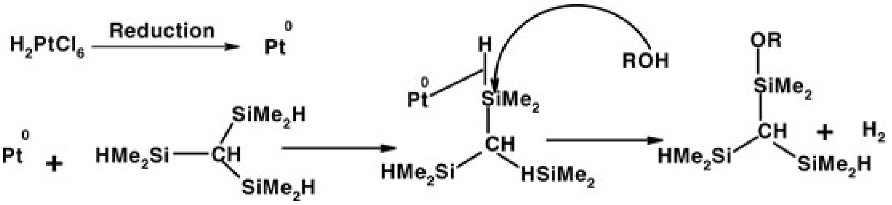


(2)



(3)

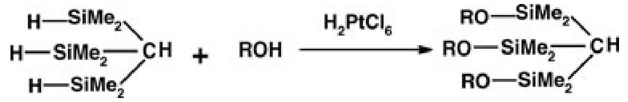
Oxidative addition appears to be implicated in the catalysis of alkene hydrosilylation, because the key step is the insertion of the unsaturated substrate into an M—H or M—Si bond. Silane alcoholysis (eq. 1) is thought to be catalyzed most efficiently by formation of an intermediate σ-complex. The metal is believed to polarize the Si—H bond and so favors nucleophilic attack by ROH (Scheme 1) [16].



SCHEME 1 Proposed mechanism for the alcoholysis reaction of $(HMe_2Si)_3CH$.

Synthesis of $(ROMe_2Si)_3CH$

The compound $(HMe_2Si)_3CH$ was made from the reaction between HMe_2SiCl and $CHBr_3$ in the presence of Mg in THF. Monofunctional alcohols (*n*-propyl, iso-propyl, *n*-butyl, *s*-butyl, iso-butyl, *n*-pentyl, *s*-pentyl, and *n*-hexyl) were treated with $(HMe_2Si)_3CH$ in the presence of $H_2PtCl_6 \cdot 6H_2O$ as a catalyst in air under mild conditions. The related tris(alkoxydimethylsilyl)methanes were produced in good yields (Table 1). The progress of the reaction was monitored by IR spectroscopy until the Si–H absorbance in the IR spectrum had disappeared (Scheme 2). The reaction is assumed to proceed through reduction of the Pt(IV) catalyst to colloidal Pt(0), as metallic particles can be observed at the end. These reactions occurred in air. In contrast, most reported alcoholysis reactions promoted by transition metal catalysts have been carried out under inert atmospheres such as argon or nitrogen. Reactions of $(HMe_2Si)_3CH$ with primary alcohols gave higher yields than analogous reactions with secondary alcohols, probably because of the increase in steric hindrance (see Table 1). No reaction was observed with the tertiary alcohol Bu^tOH (entry 12). Similarly, $(PhOMe_2Si)_3CH$ was obtained from the reaction of phenol with $(HMe_2Si)_3CH$ in the presence of the Pt-catalyst. In the case of benzyl alcohol, the spectroscopic results show that treatment with $(HMe_2Si)_3CH$ gave dibenzyl ether instead of the expected $(PhCH_2OMe_2Si)_3CH$.



SCHEME 2 Alcoholysis reaction of $(HMe_2Si)_3CH$ with various alcohols.

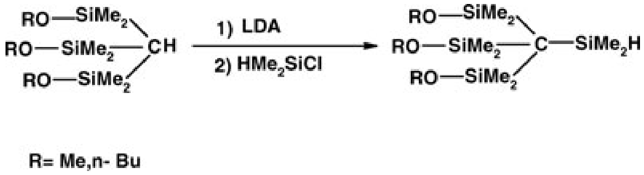
The reaction between acetic acid and $(HMe_2Si)_3CH$ in the presence of chloroplatinic acid as catalyst gave $(Me_2SiOSiMe_2)_3CH$. This compound was made previously by Eaborn and coworkers by a different method, but we have obtained it in high yield and in a one-pot process.

Lithiation of $(ROMe_2Si)_3CH$ (R = Me, n-Bu)

Organometallic compounds containing $(MeOMe_2Si)_2(Me_3Si)C$ and $(MeOMe_2Si)_3C$ ligands have been reported previously. We describe the lithiation of $(ROMe_2Si)_3CH$, and a new organosilicon compound containing the $(BuOMe_2Si)_3C$-ligand. Eaborn and coworkers [17] have previously shown that treatment of $(Me_3Si)_3CCl$ with ICl followed by MeOH-Et_3N gave $(MeOMe_2Si)_3CCl$. This compound was treated with *n*-BuLi at −78°C to give $(MeOMe_2Si)_3CLi$, which reacted

TABLE 1 Product Yields from Pt-Catalyzed Reactions of Various Hydroxy Compounds with $(HMe_2Si)_3CH$

Entry	*Hydroxy Compounds*	*Products*	*Yield (%)*
1	$CH_3CH_2CH_2OH$	$(CH_3CH_2CH_2OMe_2Si)_3CH$ (**1**)	61.1
2	$(CH_3)_2CHOH$	$[(CH_3)_2CHOMe_2Si]_3CH$ (**2**)	52.2
3	$CH_3CH_2CH_2CH_2OH$	$(CH_3CH_2CH_2CH_2OMe_2Si)_3CH$ (**3**)	72.6
4	$(CH_3CH_2)(CH_3)CHOH$	$[(CH_3CH_2)(CH_3)CHOMe_2Si]_3CH$ (**4**)	40.2
5	$(CH_3)_2CHCH_2OH$	$[(CH_3)_2CHCH_2OMe_2Si]_3CH$ (**5**)	56.2
6	$CH_3CH_2CH_2CH_2CH_2OH$	$(CH_3CH_2CH_2CH_2CH_2OMe_2Si)_3CH$ (**6**)	70.1
7	$(CH_3CH_2CH_2)(CH_3)CHOH$	$[(CH_3CH_2CH_2)(CH_3)CHOMe_2Si]_3CH$ (**7**)	50.8
8	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	$(CH_3CH_2CH_2CH_2CH_2CH_2OMe_2Si)_3CH$ (**8**)	62.1
9	$PhCH_2OH$	$PhCH_2OCH_2Ph$ (**9**)	–
10	PhOH	$(PhOMe_2Si)_3CH$ (**10**)	45.3
11	CH_3COOH	$HC(Me_2SiOSiMe_2)_3CH$ (**11**)	56.3
12	$(CH_3)_3COH$	No Product obtained	–



SCHEME 3 Synthetic pathway leading to the new compounds $(ROMe_2Si)_3CSiMe_2H$.

with HMe_2SiCl to give $(MeOMe_2Si)_3CSiMe_2H$. In view of the previous observation that lithiation of $(MeOMe_2Si)_2(Me_3Si)CH$ with MeLi was not reproducible as MeLi attacked Si—OMe as well as C—H bonds [18], we turned to LDA as an alternative metalating agent. The reaction between $(MeOMe_2Si)_3CH$ and LDA proceeded smoothly at −78°C and, after addition of HMe_2SiCl, gave $(MeOMe_2Si)_3CSiMe_2H$. To throw light on the effect of the alkyl group on lithiation, we chose to study $(n\text{-}BuOMe_2Si)_3CH$ because the alkoxy-substituted derivative is obtained in the highest yield. The final product was $(n\text{-}BuOMe_2Si)_3CSiMe_2H$ (Scheme 3) (see also Fig. 1).

Preparation of New Polymers Containing Si—H Group in Side Chains

The attachment of organosilyl groups to macromolecules chain leads to important modifications in polymer properties such as gas permeability and permselectivity parameters, mechanical, thermal, surface properties, and photochemical reactivity, and constitutes an important research field in its own right [19–22].

Preparation of CMS Homopolymer and Copolymes with Styrene by Free Radical Polymerization. The monomer of 4-CMS was homopolymerized and copolymerized with styrene at 70°C with AIBN as radical initiator. The reaction conditions are shown in Table 2. The composition of P_2 and P_3 was determined by use of ^1H NMR spectroscopy. The mole fractions of CMS and styrene were calculated from the ratio of the areas of the peaks at 4.6 ppm corresponding to two protons of the chloromethyl group in CMS to the total area between 7.4 and 8.3 ppm, attributed to four aromatic protons of CMS and five aromatic protons of styrene. Gel permeation chromatography (GPC) with THF as solvent was used to determine the number and weight-average molecular weights of the homopolymer (P_1) and copolymers (P_2, P_3). The results are listed in Tables 2 and 3.

Attachment of Bulky $(HMe_2Si)_3C$ Groups via Nucleophilic Substitution. The reaction of $(HMe_2Si)_3CH$ with 1 equivalent of LDA in THF resulted in quantitative formation of $(HMe_2Si)_3CLi{\cdot}2THF$. A few coupling reactions between $(HMe_2Si)_3CLi$ and chlorosilanes have been reported but, as far as we are aware, there has hitherto been no reference in the literature to the reaction between $(HMe_2Si)_3CLi$ and benzyl chloride. We carried out this reaction to examine the possibility of attaching $(HMe_2Si)_3C$ groups to polymer side chains. The model compound $(HMe_2Si)_3CCH_2Ph$ was

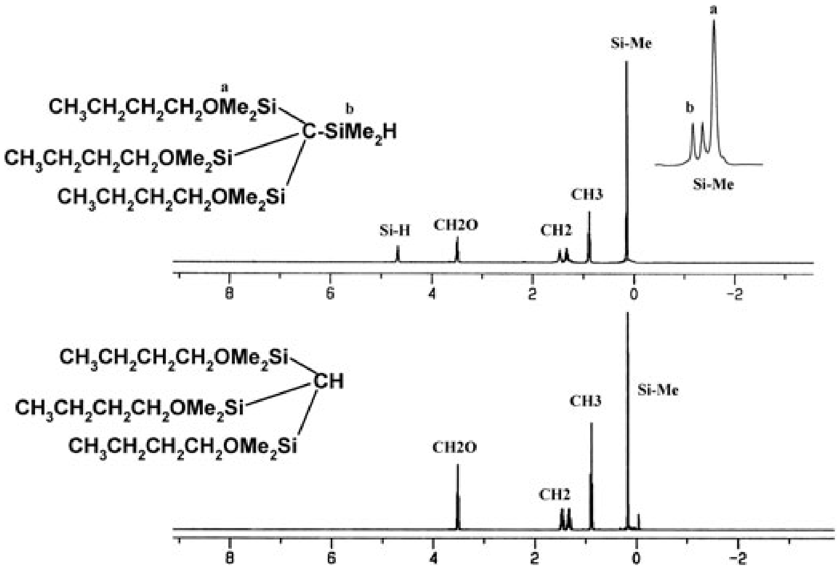


FIGURE 1 ^1H NMR spectra: (a) $(n\text{-}BuOMe_2Si)_3CH$ and (b) $(n\text{-}BuOMe_2Si)_3CSiMe_2H$ in $CDCl_3$ without tetramethylsilane.

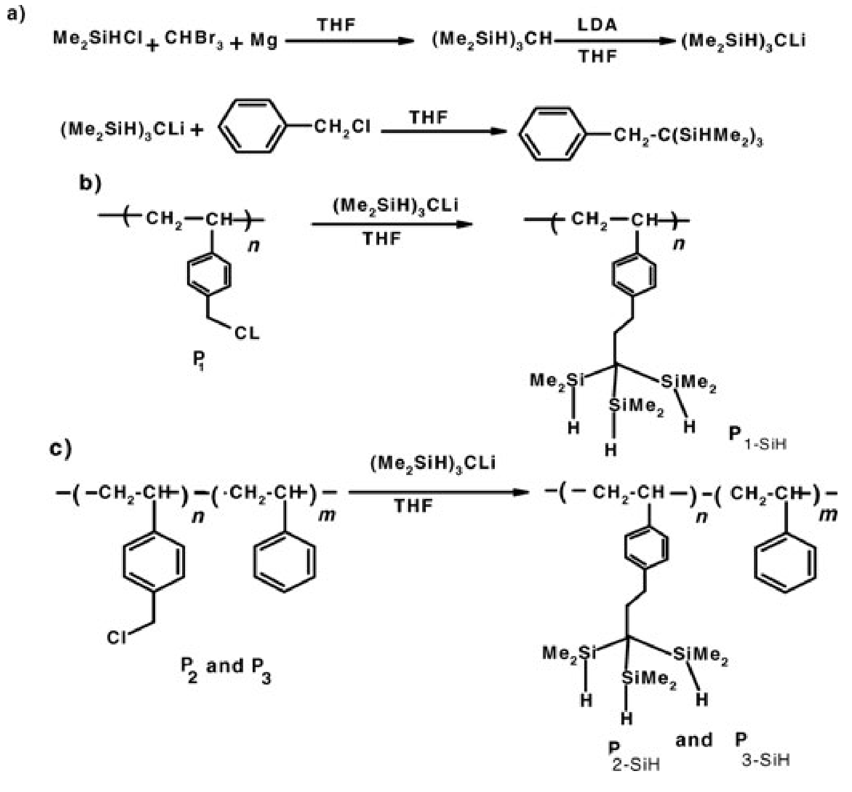
TABLE 2 Conditions of Preparation of Homopolymer and Copolymers at 70 ± 1°C

Sample No.	*Monomer 1*	*Monomer 2*	*Amount of 1 (mmol)*	*Amount of 2 (mmol)*	*Solvent*	*Time (h)*	*Nonsolvent*
P_1	CMS	–	20	–	–	12	MeOH
P_2	CMS	Styrene	10	30	Toluene	30	MeOH
P_3	CMS	Styrene	20	20	Toluene	30	MeOH

TABLE 3 Compositions and Molecular Weights of P_1, P_2, and P_3

Sample	*mol% CMS*	*mol% Styrene*	$M_w \times 10^3$	$M_n \times 10^3$	M_w/M_n	T_g (°C)
P_1	100	–	20.4	12.3	1.65	103
P_2	25	75	30.4	18.9	1.60	93
P_3	52	48	31.5	19.3	1.63	98

isolated as a clear gel in fairly good yield (Scheme 4a). Therefore, a mixture of homopolymer P_1 (0.5 g) was treated with optimized amount of $(HMe_2Si)_3CLi$ (25 mmol) in THF (Scheme 4b). The replacement of chlorine atoms by $(HMe_2Si)_3C$ groups was easily followed by the appearance of the Si—H absorption at 2110–2130 cm^{-1}. A FTIR spectrum of the obtained polymer $P_{1\text{-SiH}}$ exhibits the following characteristics: The appearance of Si—H bonds is associated with the strong absorption at 2115 cm^{-1} and the appearance of $Si—CH_3$ bonds with absorption at 1255 and 830 cm^{-1}. In the ^{1}H NMR spectrum (Fig. 2b) of the homoplymer $P_{1\text{-SiH}}$, the absorption at 4.6 ppm, assigned to the methylene protons of benzyl chloride, disappeared completely and a new signal appeared at 3.1 ppm due to methylene protons adjacent to the $(HMe_2Si)_3C$ groups. A new 18-proton signal from $(HMe_2Si)_3C$ appeared at 0.16 ppm. The peaks at 4.0 ppm are assigned to the Si—H resonance. Other assignments for P_4 are the same as



SCHEME 4 Synthetic routes for preparation of (a) model compound, (b) substitution of $(HMe_2Si)_3C$ groups in P_1, and (c) substitution of $(HMe_2Si)_3C$ groups at copolymers P_2 and P_3.

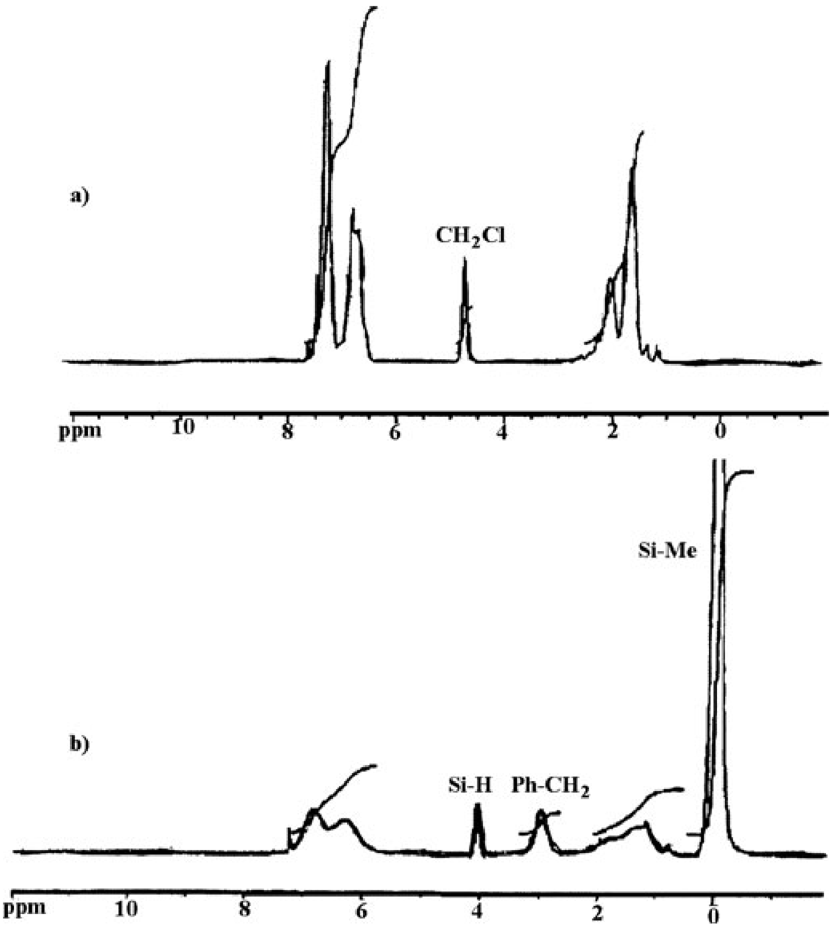


FIGURE 2 ^{1}H NMR spectra: (a) P_1 and (b) $P_{1\text{-SiH}}$ in $CDCl_3$ without tetramethylsilane. The Si—H (δ 4.0 ppm), which are well defined in the $P_{1\text{-SiH}}$.

those observed for the homopolymer P_1. In the ^{13}C NMR spectrum of $P_{1\text{-SiH}}$, the peak at 46 ppm corresponding to the methylene carbon of benzyl chloride is replaced by a new signal at 35 ppm, corresponding to the methylene carbon adjacent to the $(HMe_2Si)_3C$ subsitutent. In addition, the peaks at 5 and 2.6 ppm are the resonance peaks, respectively, of the central carbon and the six methyl carbon atoms of the $(HMe_2Si)_3C$ group. All spectroscopic results indicate that coupling reactions with an excess of $(HMe_2Si)_3CLi$ (25 mmol) were successful and complete, i.e. that all the chlorine atoms in homopolymer P_1 were replaced by $(HMe_2Si)_3C$ groups. The complete replacement of the chlorine atoms was also confirmed by comparison of elemental analyses of homopolymer P_1 with homopolymer $P_{1\text{-SiH}}$. Treatment of 0.5 g of polymers P_2 and P_3 with an excess of $(HMe_2Si)_3CLi$ in THF solution led to complete substitution of chlorine atoms by $(HMe_2Si)_3C$ groups to give new copolymers ($P_{2\text{-SiH}}$ and $P_{3\text{-SiH}}$) (Scheme 4c). The appearance of peaks attributed to Si—H vibrations in IR spectra and the concomitant disappearance of peaks at 4.6 and 46 ppm in ^{1}H and ^{13}C NMR spectra, respectively, clearly indicated that the coupling reactions (as with P_1) were successful and complete (see also Figs. 3a and 3b). The result was confirmed by elemental analysis.

Glass transition temperatures (T_g) of the new polymers were determined by DSC analysis. As shown in Fig. 4, the curves showed that incorporation of $(HMe_2Si)_3C$ into polymer side chain increases the rigidity. The glass transition temperature of the homopolymer $P_{1\text{-SiH}}$ was found to be 197°C (Fig. 4a), which is 94°C higher than that (105°C) found for homopolymer P_1. T_gs of P_2 and P_3 are 93 and 98°C, respectively, whereas those of $P_{2\text{-SiH}}$ and $P_{3\text{-SiH}}$ are 150°C and 177°C (Figs. 4b and 4c). The bulkiness of the $(HMe_2Si)_3C$ substituent effectively restricts the free volume of the macromolecules. In addition, with increasing CMS mole fraction in the copolymer, bulky groups are incorporated in higher yields and, therefore, the free volumes of the macromolecules

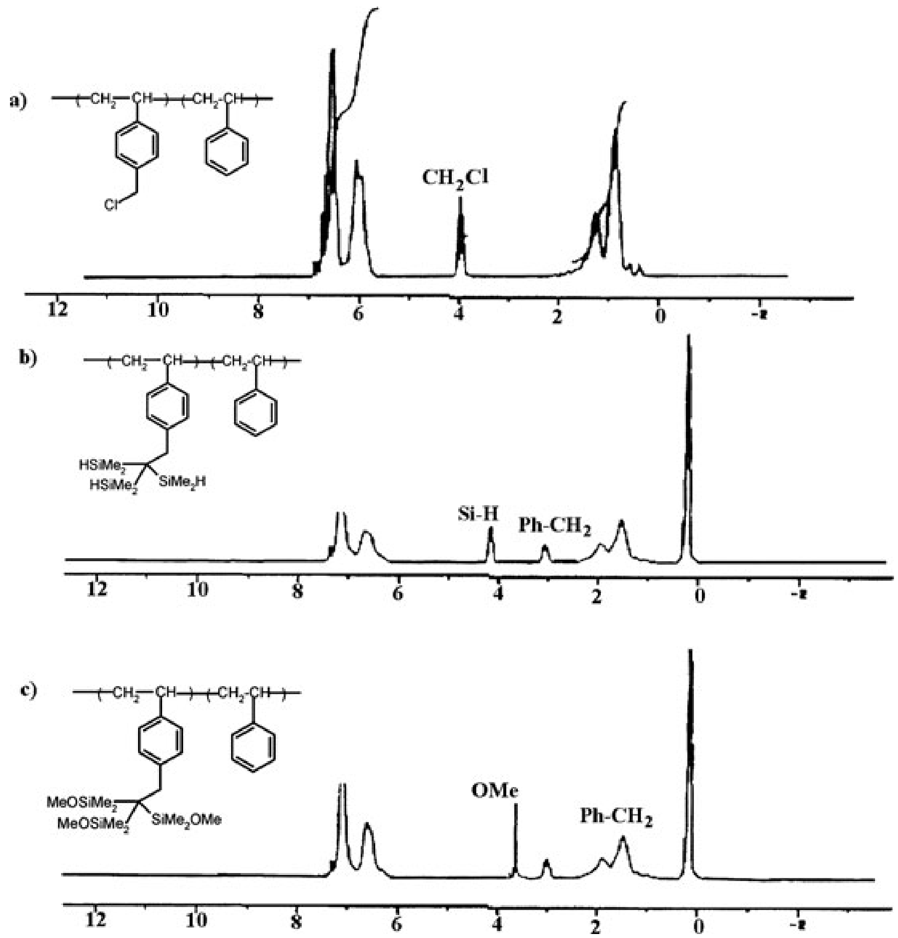


FIGURE 3 ^{1}H NMR spectra: (a) P_3 and (b) $P_{2\text{-SiH}}$ (c) P_2-OMe in $CDCl_3$ without tetramethylsilane. The Si—H (δ 4.0 ppm), which are well defined in the $P_{2\text{-SiH}}$.

further decreased. The higher T_g value of homopolymer $P_{1\text{-SiH}}$ is ascribed to the high $(HMe_2Si)_3C$ content of P_1. For the same reason the T_g of the polymer, $P_{3\text{-SiH}}$ (177°C) is higher than that of $P_{2\text{-SiH}}$ (150°C).

Alcoholyses of the Side Chains of Polymers $P_{1\text{-}OMe}$, $P_{1\text{-}OEt}$, $P_{1\text{-}OPr}$, and $P_{1\text{-}OBu}$

Alcoholysis reactions of polymeric silicon compounds such as polysiloxanes and polysilanes or copolymers containing such polymeric units have been reported [11], but to our knowledge there are no references in the literature to alcoholyses of groups attached to polystyrene side chains. 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. The spectroscopic results indicated that under optimal conditions replacement of H by OR at the silicon center was complete. This was proven by complete

TABLE 4 Compositions and molecular weights of P_1, P_2, and P_3

Sample	$M_n \times 10^3$	$M_w \times 10^3$	M_w/M_n	T_g(°C)
$P_{1\text{-SiH}}$	12.1	19.2	1.58	197
$P_{2\text{-SiH}}$	17.9	30.0	1.67	177
$P_{3\text{-SiH}}$	18.3	30.5	1.66	150
$P_{1\text{-OMe}}$	12.1	19.2	1.58	199
$P_{1\text{-OEt}}$	12.1	19.1	1.57	205
$P_{1\text{-OPr}}$	12.1	19.1	1.57	220
$P_{1\text{-OBu}}$	12.0	19.0	1.58	250

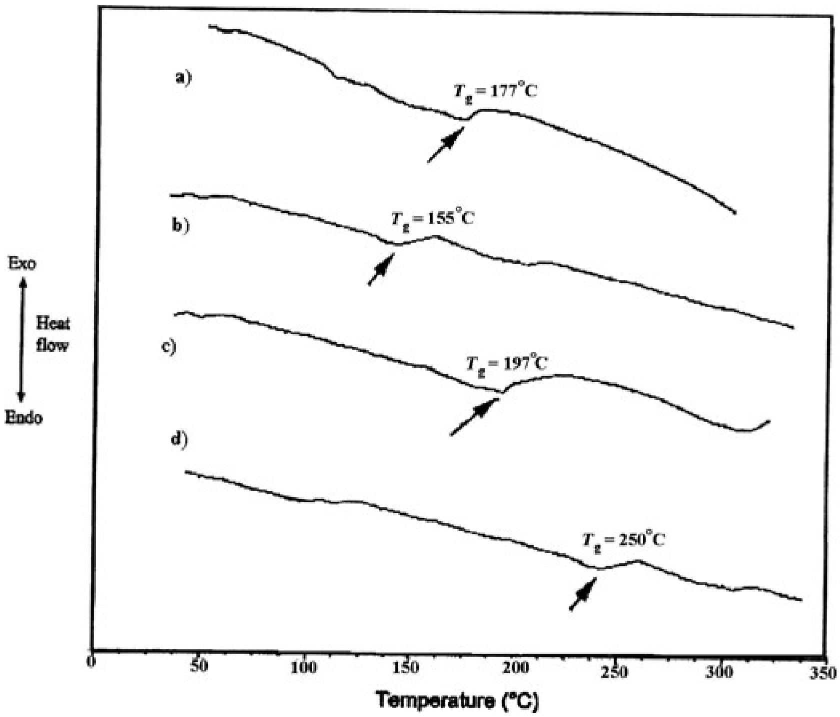
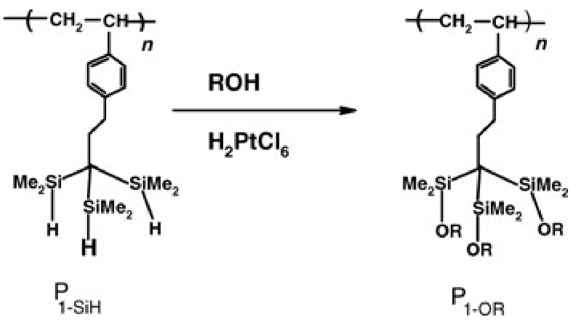


FIGURE 4 DSC curves of polymers: (a) $P_{2\text{-SiH}}$ (b) $P_{3\text{-SiH}}$, (c) $P_{1\text{-SiH}}$ and (d) P_1-OBu at 10°C/min in air.



SCHEME 5 Preparation of silyl ether on the side chain of polymer.

disappearance of Si—H peak at 2115 cm^{-1} and the concomitant disappearance of signals corresponding to Si—H at 4.0 ppm in the ^1H NMR spectra of the polymers (Scheme 5). The results were verified by elemental analysis. As shown in Table 4, the T_g of the polymer increased with alkyl groups of increasing bulk. For the same reason, the T_g of the polymer $P_{1\text{-OBu}}$ (250°C) was higher than that of $P_{1\text{-OPr}}$ (220°C) or $P_{1\text{-OEt}}$ (205°C).

CONCLUSIONS

The present study shows that chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) is a mild catalyst for alcoholysis of hydrosilanes in air. A series of tris(alkoxydimethysilyl)methanes are obtained in near quantitative yields from the catalytic reaction of $(HMe_2Si)_3CH$ with monofunctional alcohols. Primary alcohols gave higher yields than secondary, and no reaction took place with t-butanol. Reactions with benzyl alcohol and acetic acid led to unexpected products. The compound $(BuOSiMe_2)_3CH$ (**3**) was metalated with LDA at low temperatures. $(HMe_2Si)_3C$ groups have been attached to polymer side chains, and alcoholyses have been effected under the same conditions as those for monomeric compounds. DSC showed that introduction of bulky groups into the side chains of polymers gave big increases in the glass transition temperatures of the polymers.

ACKNOWLEDGMENTS

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