Supporting Information:
A New Type of Silicon Super Lewis Acids for Polymerization of Silyl Vinyl Ethers

Masataka Oishi and Hisashi Yamamoto*
Graduate School of Engineering, Nagoya University
CREST, Japan Science and Technology Corporation (JST)
Chikusa, Nagoya, 464-8603, Japan

All manipulations of oxygen- and moisture-sensitive materials involving polymerization reactions were performed by standard Schlenk techniques. Toluene and tetrahydro-furan were distilled from Na/benzophenone ketyl before use. Methylenechloride solvent was dried over CaH$_2$ and distilled in vacuo. NMR spectra were recorded on either a Varian INOVA 500 (FT 500 MHz, $^1$H; 125 MHz, $^{13}$C) or Germini-300 (FT 300 MHz, $^1$H; 75 MHz, $^{13}$C) instrument. Chemical shifts for $^1$H and $^{13}$C NMR spectra were referenced to internal solvent resonances and are reported relative to tetramethylsilane. Elemental analyses were performed at the Faculty of Agriculture, Nagoya University. Infrared (IR) spectra were measured on a Shimadzu FTIR-9100 spectrometer. Vinyl ether monomers 1, diisopropyl bis(vinyloxy)silane (2), bis(vinyloxy)silacyclohexane (3), and 1,2,3,3-tetraisopropyl-1,3-bis(vinyloxy)disiloxane (4), were purified by distillation similarly to literature procedure$^1$ or flash chromatography on silica gel E. Merck 9385 or silica gel 60 extra pure. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Gel permeation chromatography (GPC) analyses of polymer samples were carried out at 40 °C on a Shimadzu LC-9A instrument and a Shimadzu RID-10A RI detector equipped with Tosoh TSKgel G5000H$_{HR}$-H and TSKgel G3000H$_{HR}$ (300 mm length x 7.8 mm inner diameter) in series. Solutions of polymer samples dissolved in THF were filtered through a Dismic-13JP PTFE 0.5 μm filter. All GPC data were analyzed using a System Instrument SIC 480 Data Station software. The molecular weight calibration curve was obtained using standard polystyrenes.

Methylaluminum bis(2,6-di-tert-butyl-4-methylphenoxide) (MAD)$^2$
methylaluminum bis(4-bromo-2,6-di-\textit{tert}-butylphenoxide) (MABR),\textsuperscript{3} \textit{tert}-butyldimethylsilyl vinyl ether 1a\textsuperscript{4} and 1,1-dichlorosilinane\textsuperscript{5} were prepared according to literature procedures. All other simple chemicals were purchased from commercial suppliers.

**Preparation of 1b.** Monomer 1b was readily prepared from \textit{tert}-butyltrimethylchlorosilane and propionaldehyde.\textsuperscript{6} \textit{tert}-Butyldimethylchlorosilane (100 mmol, 15 g) at 0 °C was added to a solution of propionaldehyde (150 mmol, 11.0 mL) and DBU (110 mmol, 16.5 mL) in dichloromethane (100 mL). The mixture was heated in reflux for 2 h. The solution was then cooled and most of solvent was removed under reduced pressure. The residue was poured into ice water and 1b was extracted with hexane. Dryness of organic layer, concentration and fractional distillation in the presence of CaH\textsubscript{2} furnished 1b quantitatively as a mixture of stereoisomers, which can be isolated from each other by chromatographic purification on silica gel (hexane only). The \textit{\textsuperscript{1}H NMR} spectra were consistent with literature data.\textsuperscript{7}

**Synthesis of 2-4.** Monomers 2-4 were synthesized in a similar manner reported for 1a. A solution of \textit{n}-BuLi in hexane (1.6 M) was exposed to THF at room temperature under Ar. The corresponding dichlorosilane was added in one portion. The mixture was stirred overnight at this temperature. The solution was cooled, washed with brine and the organic layer was dried over MgSO\textsubscript{4} and filtered. After removal of the solvent under reduced pressure and successive purification by chromatography on silica gel (using hexane) followed by distillation from CaH\textsubscript{2}, the desired vinyl ether was obtained as a colorless liquid. 2: \textit{\textsuperscript{1}H NMR (CDCl\textsubscript{3})} \(\delta\) 6.54 (2H, dd, J = 5.7, 13.8 Hz, C=CH-O), 4.55 (2H, dd, J = 0.9, 13.8 Hz, CHH=C-O), 4.21 (2H, dd, J = 0.9, 5.7 Hz, CHH=C-O), 1.05-1.15 (14H, m, Si-CH\textsubscript{3}, CH\textsubscript{2}); \textit{\textsuperscript{13}C NMR (CDCl\textsubscript{3})} \(\delta\) 145.51 (C=CH-O), 95.69 (C=C-O), 16.82 (C-CH\textsubscript{3}), 12.17 (Si-C); IR (liquid film) 2950, 1636, 1466, 1391, 1320, 1171, 1022, 885, 845, 776; Anal. Calcd for C\textsubscript{10}H\textsubscript{20}O\textsubscript{2}Si: C, 59.95; H, 10.06. Found: C, 59.80; H, 10.07. 3: \textit{\textsuperscript{1}H NMR (CDCl\textsubscript{3})} \(\delta\) 6.47 (2H, dd, J = 5.7, 13.8 Hz, C=CH-O), 4.57 (2H, dd, J = 0.9, 13.8 Hz, CHH=C-O), 4.25 (2H, dd, J = 0.9, 5.7 Hz, CHH=C-O), 1.71-1.82 (4H, m, C-CH\textsubscript{3}-C-CH\textsubscript{2}-C), 1.40-1.49 (2H, m, C-C-CH\textsubscript{3}-C-C), 0.84 (4H, t, J = 6.9 Hz, Si-CH\textsubscript{3}); \textit{\textsuperscript{13}C NMR (CDCl\textsubscript{3})} \(\delta\) 144.80 (C=C-O), 96.22 (C=C-O), 29.48 (C-C-CH\textsubscript{3}-C-C), 24.33 (C-CH\textsubscript{2}-C-CH\textsubscript{2}-C), 11.79 (Si-CH\textsubscript{3}); IR (liquid film) 2928, 1634, 1391, 1320, 1167, 1024, 990, 909, 847, 781; Anal. Calcd for C\textsubscript{12}H\textsubscript{24}O\textsubscript{2}Si: C, 58.65; H,
8.75. Found: C, 58.50; H, 9.00. 4: $^1$H NMR (CDCl$_3$) $\delta$ 6.54 (2H, dd, $J$ = 5.7, 13.5 Hz, C=CH-O), 4.49 (2H, d, $J$ = 13.5 Hz, CHH=C-O), 4.14 (2H, d, 5.7 Hz, CHH=C-O), 0.98-1.15 (14H, br, Si-CH, CH$_3$); $^{13}$C NMR (CDCl$_3$) $\delta$ 145.34 (C=C-O), 94.99 (C=C-O), 17.06 (CH$_3$), 13.04 (Si-CH). IR (liquid film) 2948, 1644, 1391, 1318, 1180, 1088, 1059, 1022, 885, 760. Anal. Calcd for C$_{18}$H$_{25}$O$_3$Si$_2$: C, 58.13; H, 10.37. Found: C, 58.14; H, 10.32.

**Polymerization Procedure:** Representative procedure for polymerization of 1a is as follows. In the glovebox, methylaluminum bis(aryloxide) (MAD or MABR) (0.25 mmol) was weighed into a flame-dried 100 mL-Schlenk flask with a magnetic stir bar. Under a argon flow the reaction vessel was interfaced with a vacuum line, dry CH$_2$Cl$_2$ (15 mL) was then condensed (at $\sim$ 78 °C, 10$^{-4}$ Torr). Me$_3$SiOTf (0.25 mmol, 50 µL), PhCHO (0.25 mmol, 25 µL) and 1a (10 mmol, 2.0 mL) were added at $\sim$ 78 °C under Ar via syringes in this order. Polymerization was quenched by addition of trace MeOH after continued under the given conditions. Typical precipitation of the resulting solution in large excess MeOH or MeOH-acetone mixture (800 mL) followed by dryness of the filtered solid in vacuo afforded the desired polymer as a white powder. Due to gelation only broad peaks were observed in $^1$H NMR spectra of poly(2) and poly(3).

**Poly(1b):** $^1$H NMR (CDCl$_3$) $\delta$ 3.30-4.38 (1H, CH-O), 1.64-2.10 (1H, CH-CH$_3$), 0.89 (12H, C-CH$_3$; SiC(CH$_3$)$_3$), -0.10-0.30 (6H, Si(CH$_3$)$_3$); $^{13}$C NMR (CDCl$_3$) $\delta$ 72-78 (CH-O), 43-47 (CH-CH$_3$), 26.82 (SiC(CH$_3$)$_3$), 18-20 (SiC(CH$_3$)$_3$), 10-15 (C-CH$_3$), -5-1 (SiCH$_3$)$_3$).

**Poly(4):** $^1$H NMR (CDCl$_3$) $\delta$ 3.85-4.23 (CH-O), 1.50-2.00 (CH$_2$-C-O), 0.80-1.40 (Si-CH(CH$_3$)$_2$); $^{13}$C NMR (CDCl$_3$) $\delta$ 69-72, 63-67, 42-51 (CH$_3$), 17.65 (CH$_3$), 13.60 (Si-CH)
References