Silacyclobutane as "Carbanion Pump" in Anionic Polymerization. III. Synthesis of Di- and Tri-block Copolymer by "Diphenylsilacyclobutane–Potassium *tert*-Butoxide System"

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ABSTRACT: Efficiency of formation of carbanion from a combination of an alkaline metal *tert*-butoxide and a silacycle (carbanion pump efficiency) was studied in the presence of diphenylethylene. Combination of a silacyclobutane with potassium counter ion was the most effective among the silacycles studied (1:1 molar ratio). Sodium and lithium counter ions gave low efficiency. When 2-times 1,1-diphenylethylene was used, diphenylsilacyclobutane with potassium counter ion was found superior to dimethylsilacyclobutane–potassium, and produced (*tert*-butoxy)diphenyl-(5,5-diphenylhexyl)silane as the major trapped product of initially formed carbanion. However, (*tert*-butoxy)diphenylpropylsilane and diphenylpropylsilanol were also formed as non-trapped products in 1 to 27% depending on the reaction conditions, especially when tetrahydrofuran–hexane (9:1) was used. Hydrogen elimination from initially formed intermediate was suggested. With 4-times diphenylethylene, or reaction in tetrahydrofuran–hexane (1:1), (*tert*-butoxy)(5,5-diphenylhexyl)silane was produced in 95% yield after treatment with methyl iodide, accompanied by only 1–2% (*tert*-butoxy)diphenylpropylsilane as non-trapped product, and *tert*-butoxy anion was converted to carbanion in as high as 97% yield. This carbanion pump system was applied in the syntheses of poly(ethylene oxide)-*block*-polystyrene, poly(ethylene oxide)-*block*-polystyrene-*block*-poly(ethylene oxide), poly(ethylene oxide)-*block*-poly(methyl methacrylate), and poly(ethylene oxide)-*block*-poly(methyl methacrylate)-*block*-poly(ethylene oxide).
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Block copolymers show very interesting microphase separation, self-assembly phenomena,[1–6] and exhibit unique properties, such as thermal behavior, dielectric properties and solubility.[7] The properties are determined by polymer architecture, sequence length, and molecular weight distribution (MWD). Multi-block copolymers consisting of amphiphilic components are especially of importance not only in actual applications, but also as model polymers to study the physical property of such polymers with new chemical structure.

To make it possible to freely synthesize multi-block copolymers from various combinations of monomers by anionic mechanism, it is essential to modify the reactivity of growing anionic chain end of each monomer so as to attack the co-monomer. We proposed a concept of "carbanion pump", which converted oxyanion (typically *tert*-butoxy anion) to carbanion with the aid of the ring-opening of 1,1-dimethylsilacyclobutane (**DMSB**) (11% efficiency).[8] One of the reasons for the low efficiency of the system was in the homopolymerization of **DMSB**. To improve the efficiency, 2-times 1,1-diphenylethylene (**DPE**) to potassium *tert*-butoxide (**BuOK**) was used to end-cap the initial-

ly formed carbanion, and 86% efficiency was realized.[9] Recently, the function of **DMSB–DPE** was proved quite effective to synthesize well-defined block copolymer from highly purified (1,1′-ferrocenediyl)dimethylsilane and methyl methacrylate.[10] Teyssié used disilacyclopentane to convert oxyanion into silyl anion (35%).[11]

In this paper, four types of silacycle derivatives, namely 1,1-dimethylsilacyclopent-3-ene (**DMSP**), 2,3-benzo-1-silacyclobutene (**BSB**), 1,1-dimethylsilacyclobutane (**DMSB**), and 1,1-diphenylsilacyclobutane (**DPSB**) were used with alkaline metal *tert*-butoxide to study the effect of the structure of silacycles, and Li, Na, and K as counter ion of *tert*-butoxy anion (Scheme 1). During the study, we found that a part of the formed carbanion species was not end-capped by **DPE** in the reaction system of **BuOK–DPSB–DPE** (1:1:2). Discussion is made on an insight of carbanion pump function of **BuOK–DPSB–DPE** system. Efforts were made to obtain high carbanion pump efficiency, and the carbanion pump system was actually applied in block copolymer syntheses.

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EXPERIMENTAL

Materials

1,1-Dimethylsilacyclobutane (**DMSB**) (Shin-Etsu Chemical, ~99%) and **DPE** (Kanto Chemical, 93%) were distilled over CaH_2 and stored under argon atmosphere. Methyl iodide (MeI) (Wako Pure Chemical, >95%) was distilled before use. Lithium *tert*-butoxide (**BuOLi**, Aldrich, 1.0 M THF solution) and sodium *tert*-butoxide (**BuONa**, Aldrich, 97%) were used as received. **BuOK** was purified by sublimation under vacuum (175 °C at 0.11 mmHg).[12] *tert*-Butanol-d_{10} (Aldrich, 99% D atom) was used as received. Ethylene oxide (**EO**) was purified by trap to trap distillation after drying with calcium hydride. Styrene (**St**) and methyl methacrylate (**MMA**) were purified by distillation after drying with calcium hydride. Tetrahydrofuran (THF), hexane (Hex) and toluene (Tol) were stirred over Na–naphthalene in vacuum line and transferred by trap to trap method before use. All liquid reagents were transferred using a stainless steel needle with a gas-tight syringe under an argon atmosphere.

1,1-Dimethylsilacyclopent-3-ene (DMSP). 1,1-Dimethylsilacyclopent-3-ene was synthesized by modification of the method of Weber.[13] Cuprous chloride (0.234, 2.36 mmol) and triethylamine (26.6 g, 0.263 mol) in ether (180 mL) were added drop-wise during 1 h to 1,4-dichloro-*cis*-2-butene (29 g, 0.232 mol) and trichlorosilane (35.6 g, 0.263 mol) in ether (22 mL) in a 500 mL round flask. After refluxing for 24 h, the product 4-chloro-1-trichlorosilyl-*cis*-2-butene was extracted with pentane and distilled (72–73 °C/ 3 mmHg).

Mg turnings (21 g, 0.87 mol) were dried and activated by stirring under heating in vacuum at 120 °C for 5 h. The reaction flask was cooled, dry ether was added just to cover the Mg surface, and mole 5% 1,2-dibromoethane was added slowly to further activate the Mg surface. After cooling the system, a solution of 4-chloro-1-trichlorosilyl-*cis*-2-butene (47.9 g, 0.25 mol) in 100 mL dry ether was added drop-wise over 4 h at 40 °C. After 40 h, the mixture was filtered, and the solvent was removed. The product 1,1-dichlorosilacyclopent-3-ene was distilled over CaH_2 (bp 130–133 °C, 61% yield). ^1H NMR ($CDCl_3$) δ 1.86 (d, $J = 2.1$ Hz, 4H, SiCH_2), 5.99 (t, $J = 2.1$ Hz, 2H, C=CH). ^{13}C NMR δ 21.89, 129.06. ^{29}Si NMR δ 40.76.

1,1-Dichlorosilacyclopent-3-ene was methylated by treating with methylmagnesium bromide in THF (0.9 mol/L 30 mL, 27 mmol) for 3 h at −52 °C, and 2 h at room temperature. The solution was extracted with ether after washing with water. The extracted product was dried over anhydrous Na_2SO_4, and distill-

ed over CaH_2 (99–100 °C). ^1H NMR ($CDCl_3$) δ 0.16 (s, 6H, CH_3), 1.28 (d, $J = 1.2$ Hz, 4H, SiCH_2), 5.98 (t, $J = 2.1$ Hz, 2H, C=CH).

1,1-Dimethylbenzosilacylobutene (BSB).[14] To activated Mg turnings (7.3 g, 0.3 mol), a mixture of *o*-bromobenzyl bromide (24.5 g, 0.1 mol) and dichlorodimethylsilane (13.8 g, 0.107 mol) in ether (100 mL) was dropped for 12 h and stirred another 12 h at room temperature. The product was extracted with ether after washing with aq. NH_4Cl, and purified by fractional distillation (bp 35 °C/4 mmHg, 17 g, 35% yield). ^1H NMR δ 0.36 (s, 6H), 2.06 (s, 2H), 7.03 (m, 2H), 7.18 (m, 2H). ^{13}C NMR: δ −0.45, 20.13, 126.18, 126.91, 130.38, 130.46, 145.94, 150.55, ^{29}Si NMR: δ 9.14, mass M^+ 148.

1,1-Diphenylsilacyclobutane (DPSB). 1,1-Diphenylsilacyclobutane was synthesized by modification of the reported method.[15–17] Purified THF was added just to cover dry Mg turnings (10 g, 0.42 mol) surface and about 5 mol % of 1,2-dibromoethane was added slowly to further activate the Mg surface. 3-Chloropropyl-1-phenyldichlorosilane (22.8 g, 0.107 mol) in 100 mL dry THF was added dropwise over 5 h period at 45–50 °C, and maintained at the same temperature for 24 h. To the resulting reaction mixture, bromobenzene (19.6 g, 0.125 mol) in 60 mL dry THF was added dropwise, and reacted for further 24 h at the temperature. The reaction system was decomposed with water and extracted with ether. After drying with anhydrous Na_2SO_4, the product was obtained by distillation (bp 120 °C at 1 mmHg). The yield was 86%. ^1H NMR ($CDCl_3$): δ 1.50 (t, $J = 8.4$ Hz, 4H, SiCH_2), 2.3 (quintet, $J = 8.4$ Hz, 2H, CH_2), 7.4–7.7 (m, 10H, aromatics).

Trapping of the Initial Products in the Presence of DPE

Trapping reaction was carried out similarly as reported.[12,13] Typical example is given for **BuOK**. Freshly sublimed **BuOK** (0.51 g, 4.5 mmol) was taken into a 50 mL two-necked round flask fitted with a three way stopcock in the glove box, and purified THF/Hex mixture (9/1 v/v, 10 mL) was added by trap to trap method, followed by **DPE** (1.6 g, 9.0 mmol). To this mixture, **DPSB** (0.45 g, 4.5 mmol) was added slowly during 30 min at r.t. The resulting solution was stirred at the same temperature for another 30 min. After MeI (0.49 g, 4.5 mmol) was added to quench the reaction, volatile materials were evaporated. When it was desirable to avoid hydrolysis of the product, the residue was extracted only with dry Hex. When the change of the product distribution by hydrolysis was studied, the solution was treated with saturated NH_4Cl (10 mL × 3), and extracted with Hex. Finally ether was removed by vacuum evapora-

tion (≈100% yield). The trapped products were separated by recycling preparative SEC, and the amounts were determined by weight.

Lithium *tert*-butoxide (**BuOLi**, 1 M solution in THF, 4.8 mL) (4.5 mmol) and **BuONa** (0.45 g, 4.5 mmol) were also used in trapping reaction under similar conditions.

In the trapping reaction with **BuOK**-d_9. **BuOK**-d_9 was prepared from potassium hydride (min 30% in oil, 1.90 g; 0.57 g, 14.3 mmol after washing with Hex) and *tert*-butanol-d_{10} (1 g, 11.9 mmol), and sublimated under vacuum (175 °C at 0.11 mmHg)[12] before use.

Conversion of the Poly(ethylene oxide) Oxyanion to Carbanion Terminal

Freshly distilled **EO** (4 mL, 80 mmol) was transferred to a 50 mL round bottom flask equipped with a three way stop cock by trap to trap technique. To this, **BuOK** (0.52 g, 4.6 mmol) in THF (10 mL) was added, and stirred for 2 d at 25 °C. To this reaction mixture, **DPE** (1.7 g, 9.4 mmol) was added, and **DPSB** (1.03–2.58 g, 4.6–11.5 mmol) was added during 10 h, 24 h, and 48 h. Extent of conversion of oxyanion terminal to carbanion terminal was evaluated by evaluating the consumed **DPE** after stopping the reaction with excess methanol.

Synthesis of Model Block Copolymers

THF solution (1 mL) of poly**EO** with carbanion terminal as prepared above was added to THF or Tol (10 mL) solution of **St** (0.95 g, 9.1 mmol) or **MMA** (0.7 g, 7.0 mmol) at −78 °C or at room temperature. After **St** or **MMA** was polymerized for 1 h, fresh **EO** (1 mL, 20 mmol) was added, and the polymerization system was stirred for further 2 d at room temperature. Excess methanol was added to stop the reaction and the formed block copolymers was separated by preparative SEC.

Analysis and Characterization

Size exclusion chromatography (SEC) was performed on a JASCO GPC (Gulliver series) equipped with Shodex column KF-800P (pre-column) detected by UV (JASCO UV-970, monitored at 254 nm) operating at 40 °C with THF at a flow rate of 1 mL min^{-1}. The low molecular weight compounds were performed with KF-801 (exclusion limit, polystyrene $M_n = 1.5 \times 10^3$) and KF-802 (exclusion limit, polystyrene $M_n = 4.0 \times 10^4$). KF-803L (exclusion limit, polystyrene $M_n = 7.0 \times 10^4$) and KF-804 (exclusion limit, polystyrene $M_n = 4.0 \times 10^5$) were used for the analysis of block copolymers.

The low molecular weight products were separated by recycling preparative SEC (JASCO Gulliver series)

equipped with KF-2001 ($20\phi \times 600$ mm, exclusion limit, polystyrene $M_n = 1.5 \times 10^3$) and KF-2002 ($20\phi \times 600$ mm, exclusion limit, polystyrene $M_n = 4.0 \times 10^4$) detected by UV (JASCO UV-970, monitored at 254 nm) at 40 °C with THF (flow rate = 2 mL min^{-1}). The molecular mass of the separated product was determined by SHIMADZU QP-5000 gas chromatography–mass spectroscopy (GC–MS) An ether solution of each sample (0.5 μL) was injected into the GC in split mode at a ratio of ∼10:1 with helium as the carrier gas. The capillary column was 30 m in length, with a 0.32 mm i.d. with a stationary phase DB-17 (J&W Scientific, [poly(methylsiloxane) containing 50% phenyl group]). The oven temperature was held at 80 °C for 5 min and then ramped at 10 °C min^{-1} to 230 °C, where the temperature was held for 35 min. The mass filter was scanned from m/z 100 to m/z 700 under electron ionization conditions. To determine more accurate molecular mass, bioAPEX 70e FT-ICR mass spectrometer (Bruker Daltonics Inc., Billerica, MA) with an external ESI source (Analytica of Branford Inc.) was used. A compound in solution (80% methanol + 20% dichloromethane) was infused into the ESI source in the positive ion mode by a syringe pump at a rate of 60 μL h^{-1} and were desolvated by countercurrent nitrogen gas heated to 250 °C. ESI-generated ions were accumulated externally in the hexapole ion guide prior to being transferred into the trapped-ion cell. The trapped-ion cell used in the Bruker FT-ICR system is the "Infinity Cell", a cylindrical cell of 63 mm long and 74 mm in diameter with a pair of nine-segment trapping plates, which models the rf excitation field of an infinitely long cell and is thought to eliminate the *z*-ejection effect during broadband rf excitation and/or ion selection events in multi-tandem mass spectrometric experiments. The exact composition of peak **2** (Figures 1 and 3) was determined by YANACO G6800 gas chromatography. The capillary column was Beta Dex™ 120 (30 m × 0.25 mm) of SUPELCO. Inc., and helium carrier was used. The oven temperature was held at 50 °C for 5 min and increase at 10 °C min^{-1} to 300 °C. ^{1}H (500 MHz), ^{13}C (125.7 MHz) and ^{29}Si (98 MHz) spectra were obtained in CDCl$_3$ on a Varian 500 MHz Unity INOVA spectrometer. Chemical shifts are reported in ppm relative to CHCl$_3$ ($\delta = 7.26$ for ^{1}H) in ^{1}H NMR, CDCl$_3$ ($\delta = 77.00$ for ^{13}C) in ^{13}C NMR and tetramethylsilane ($\delta = 0.00$ for ^{29}Si) in ^{29}Si NMR.

RESULTS AND DISCUSSION

Reaction scheme to trap the initially formed carbanion with a silacycle is typically shown for the case of silacyclobutane in Scheme 1. The reaction of formed
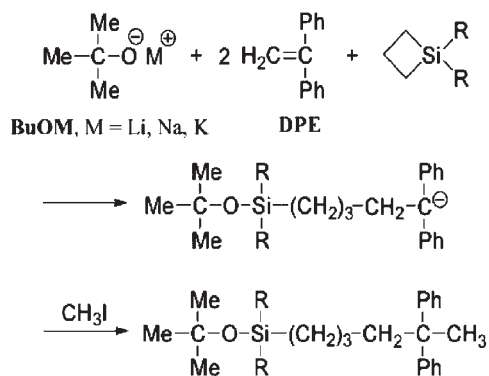
Scheme 1. Reaction scheme of "Carbanion pump" and trapping of the initially formed carbanion.

carbanion with methyl iodide (MeI) was quantitative.

Structural Effect of Silacycle

Figure 1 shows size exclusion chromatogram (SEC) of trapping reaction with various silacycles.

Unreacted **DPE** peak appeared at 17.5 min. **DMSP** was not ring-opened by oxyanion because of low ring strain, and **BSB** system produced a lot of oligomers, which were seen from 12 min to 14 min in Figure 1b. Although only one **DPE** end-capped peak, (*tert*-butoxy)dimethyl(5,5-diphenylhexyl)silane, was observed at 14.6 min for **DMSB** system, Homopolymerization could not be suppressed perfectly as can be seen in Figure 1c.[9] Compared to **DMSB**, **DPSB** system produced less oligomers, and new peak **1** and peak **2** appeared. The major peak **1**, separated by preparative SEC, was determined as (*tert*-butoxy)diphenyl(5,5-diphenylhexyl)silane (M^+ 560), by referring (*tert*-butoxy)dimethyl(5,5-diphenylhexyl)silane,[9]
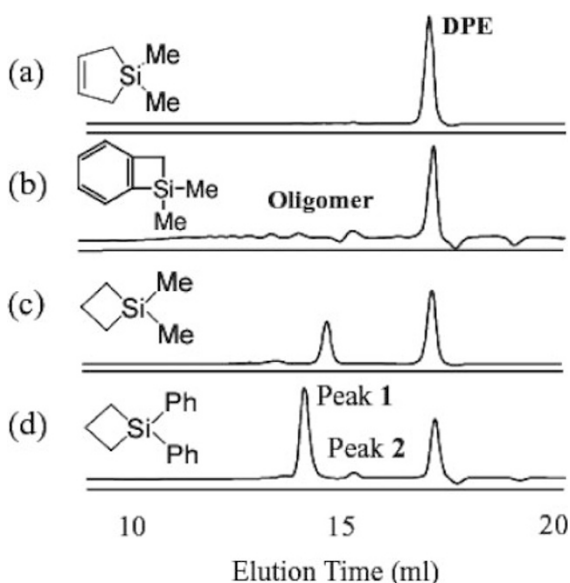
as the methylated product of initially formed carbanion from **BuOK** and **DPSB** after attacking **DPE** as shown in Scheme 1 (R = phenyl).

The reason for the formation of (*tert*-butoxy)diphenyl(5,5diphenylhexyl)silane is attributed to the fact that the reactivity of the initially formed diphenylpentyl anion towards **DPSB** is low. Homopolymerization of **DPSB** was scarcely initiated by 1,1-diphenylhexyllithium in tetrahydrofuran (THF). Almost no conversion of **DPSB** was observed, and the red color of 1,1-diphenylhexyllithium was maintained even after 1 h. The nucleophilic attack by 1,1-diphenylpentylpotassium is assumed also slow. Preferential methylation of the soft carbanion center occurred to give (*tert*-butoxy)diphenyl(5,5diphenylhexyl)silane as the major product.[9] Detailed reaction mechanism will be discussed later.

Effect of Counter Cation

tert-Butoxy anion is a highly reactive anion due to the electron donating effect of three methyl groups. The nucleophilic reactivity of an oxyanion changes by counter ion in the following order K > Na > Li (**BuOK** > **BuONa** > **BuOLi**)[18] reflecting the radius of the atom and aggregation of the compound. Figure 2 shows ^{29}Si NMR spectra of the product mixture in trapping experiment with different counter ion.

The silicon atom linked to *tert*-butoxy group appeared at -13 ppm, and Si of **DPSB** homopolymer at -7.9 ppm. *tert*-Butoxy anion with Li and Na as
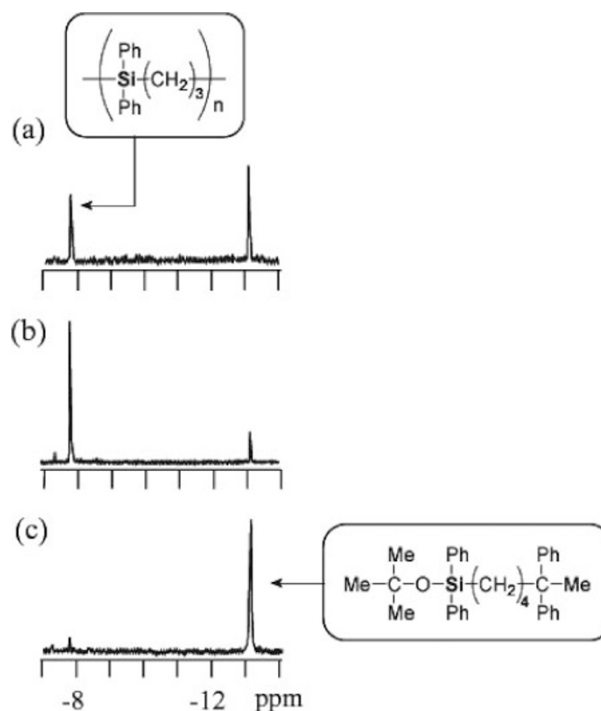

Figure 1. SEC of the products in trapping reaction in the presence of **DPE**: (a) **DMSP**, (b) **BSB**, (c) **DMSB**, (d) **DPSB**.

Figure 2. ^{29}Si NMR of the product mixture: (a) **BuOLi**, (b) **BuONa**, (c) **BuOK**.
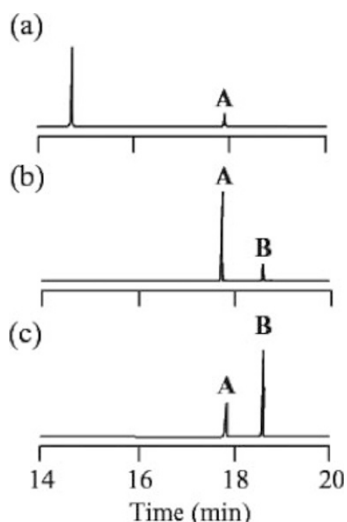
Figure 3. Change in GC of the peak **2** under various work-up conditions: (a) as reacted (b) isolated by preparative SEC from the Hex extract after quenched with MeI (c) isolated by preparative SEC from the Hex extract after shaking with NH_4Cl–water.

counter ion formed homopolymer of **DPSB** as the major product, contrary K as counter ion produced principally the ring-opened product without the formation of oligomers or polymers. Addition of HMPA or 18-crown-6 produced more oligomers.

Peak **2** in Figure 1d was also observed for the hydrolyzed sample without treatment by MeI. Formation of product **2** was further analyzed by gas chromatogram (GC) under various working-up conditions as shown in Figure 3.

In as produced sample, only small peak **A** was observed at retention time 17.8 min. When isolated sample by preparative SEC from the crude product after treating with MeI followed by extraction with Hex was injected, major peak **A** and minor peak **B** were observed at retention time 17.8 and 18.6 min. Isolated sample after shaking with NH_4Cl–water gave stronger peak **B**. When the products were thoroughly treated with NH_4Cl–water, peak **A** completely disappeared and only peak **B** was obtained. Peak **B** seemed to be mainly produced by the hydrolysis of peak **A**. The peak **B** in Figure 3b seemed to have been produced during chromatographic procedure.

The peak **2** produced by treatment of MeI and following extraction with Hex was separated by preparative SEC. The separated peak **2** was further separated by column chromatography (Hex–ethyl acetate = 8:1). ^1H, ^{13}C NMR and gradient-enhanced heteronuclear multiple quantum coherence (*g*-HMQC) of the separated compound **A** are shown in Figure 4.

The compound was assigned as (*tert*-butoxy)diphenylpropylsilane by further support using electro spray ionization (ESI)–mass spectrometry (*m/z* 321.1618, m/z_{cal} 321.1650). The compound **B** was as-
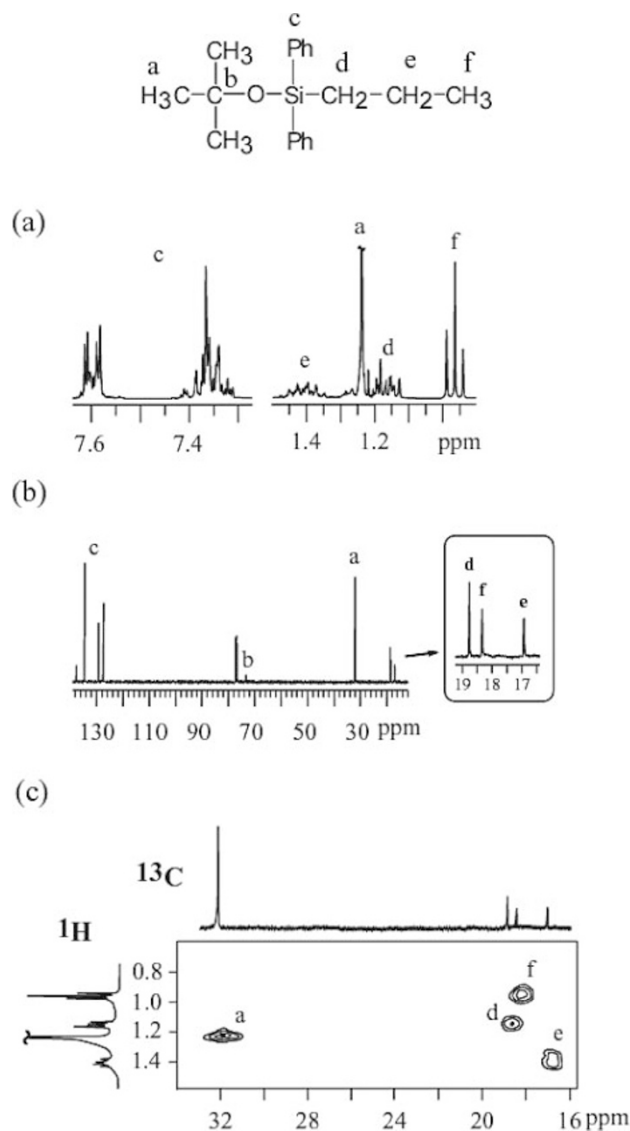

Figure 4. NMR spectra of compound **A**: (a) ^1H, (b) ^{13}C, (c) *g*-HMQC spectra.

signed as diphenylpropylsilanol (*m/z* 265. 1018, m/z_{cal} 265.1024), which showed identical aliphatic ^1H NMR signals with compound **A**. These separated compounds had the same retention time with peaks **A** and **B**. Thus, peak **A** and **B** were concluded to be (*tert*-butoxy)diphenylpropylsilane and diphenylpropylsilanol, respectively. It is very important to comment that both compounds (*tert*-butoxy)diphenylpropylsilane and diphenylpropylsilanol are the propyl derivatives. These compounds were apparently produced by the protonation of the carbanion formed from **BuOK** and **DPSB** without end-capping by **DPE**.

Major portion of diphenylpropylsilanol in Figure 3c seemed to be apparently produced by the cleavage of *tert*-butoxy group during the NH_4Cl treatment. Diphenylpropylsilanol could be also produced by the hydrolysis of potassium diphenylpropylsilanolate during chromatographic separation.

When deuterium oxide was used to quench the reaction before trapping with methyl iodide, no deuterium was incorporated in the propyl group, which indicates that major part of (*tert*-butoxy)diphenylpropylsilane and diphenylpropylsilanol were not produced by the moisture or water treatment.

The amounts of the products under different reaction conditions are summarized in Table I, and the change in the product distribution is shown in Figure 5.

Peak **2** was observed only under the condition of Figure 5a, where the solvent composition is THF:hexane (Hex) = 9:1. Change of the amounts of peak **2** after complete hydrolysis of the product (peak **2** contains only diphenylpropylsilanol) is shown in Figure 6.

It should be noted that the peak **2** [(*tert*-butoxy)di-

Table I. Distribution of the products in the reaction between *tert*-**BuOK** and **DPSB**[a] in the presence of **DPE**

Run No	Peak 1	Peak 2	Oligomers	Total Carbanion Pump Efficiency (%)
	Yield (%)			
1	85	11	3	96
2[b]	77	18	4	95
3[c]	68	20	11	88
4[d]	46	27	27	73
5[e]	95	2	3	97
6[f]	95	1	2	96
7[g]	68	1	29	70
DPSB	78	—	18	78

[a][**BuOK**] = 0.505 g (4.5 mmol); [**DPE**] = 1.62 g (9 mmol); [**DPSB**] = 1.02 (4.5 mmol); Solvent = THF 9 mL + Hex 1 mL; at r.t. [b]18 mL THF + 2 mL Hex was used as solvent. [c]at 0 °C. [d]**DPSB** was added as in one portion. [e]4-times of **DPE** (18 mmol). [f]In THF 5 mL + Hex 5 mL. [g]In THF 1 mL + Hex 9 mL.
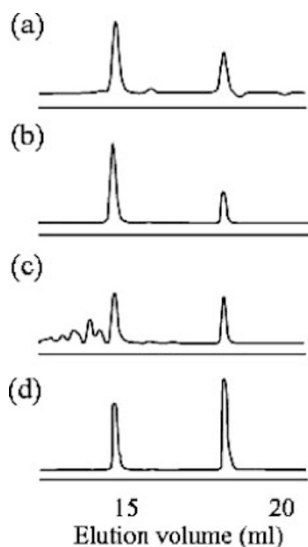

Figure 5. Change in SEC of the products with composition of the solvent: (a) THF:Hex = 9:1, (b) THF:Hex = 1:1, (c) THF:Hex = 1:9, (d) THF:Hex = 9:1 with 4 times **DPE**.
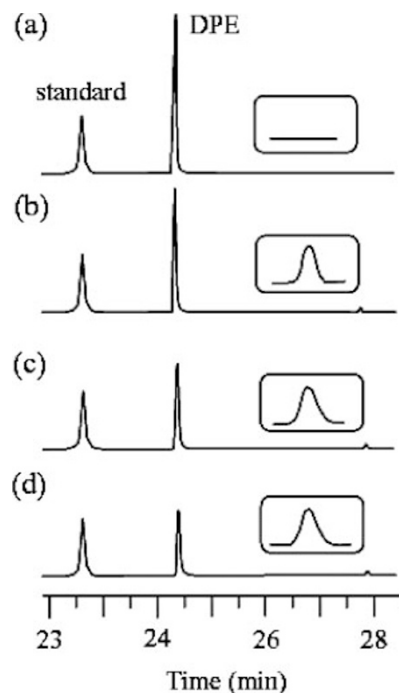
Figure 6. Change in GC with the addition of **DPSB**: (a) 0%, (b) 33%, (c) 66%, (d) 99% addition.

phenylpropylsilane + diphenylpropylsilanol] was formed only in the initial stage of the reaction, and that no peak **2** was observed in mixed solvent system of higher Hex content (THF:Hex = 1:1 or higher Hex). Since the sample was prepared by extraction with ether, there might remain some diphenylpropylsilanol component not extracted, and the actual amounts of diphenylpropylsilanol may be a little higher than analyzed.

The species present in the system was studied by *in situ* NMR. The NMR taken immediately after mixing the reagents was shown in Figure 7.

It might be reasonable to consider that the peak observed at −0.07 ppm was assignable to the methylene proton of the propyl carbanion initially formed, and the signal at 2.38 ppm to methylene protons adjacent to the anionic carbon of diphenylalkyl anion produced
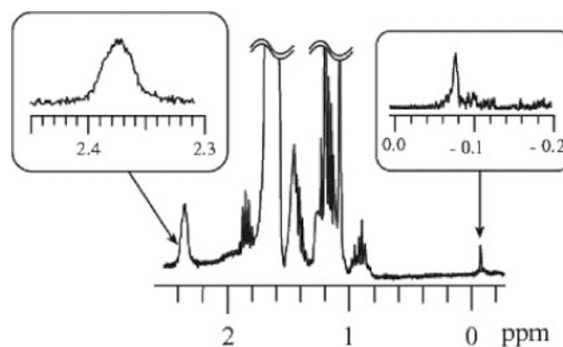

Figure 7. ^{1}H NMR spectra of **BuOK–DPSB** *in situ* system in THF.

by trapping with **DPE**, since these peaks disappeared (-0.07 ppm) or shifted (2.38 ppm) to 1.95 ppm by the reaction with MeI.

The ratio of these two peaks is about 10 to 90 after 10 min, indicating that only a part of initially formed carbanion is present alive in the system. The peak at -0.07 ppm became weaker with longer reaction time, and also disappeared with the treatment by water.

More important fact was obtained by the use of **BuOK**-d_9 and **THF**-d_8. In the initial stage of the reaction in THF–Hex (9:1) system, formation of butene was confirmed by mass spectroscopy, and deuterium was incorporated in the propyl groups of diphenylpropylsilanol and t-butoxydiphenylpropylsilane when **BuOK**-d_9 was used, as evidenced by ^{1}H NMR (Figure 8).

Considering the fact that (*tert*-butoxy)diphenylpropylsilane (major) and diphenylpropylsilanol (minor) were formed in the initial stage of the reaction as observed as one peak in Figure 6, and that the amount did not change with reaction time after the addition of 33% **DPSB**, these compounds seemed to be produced by the reactions of initially formed (*tert*-butoxy)diphenylsilylpropyl anion, and not from **BuOK**
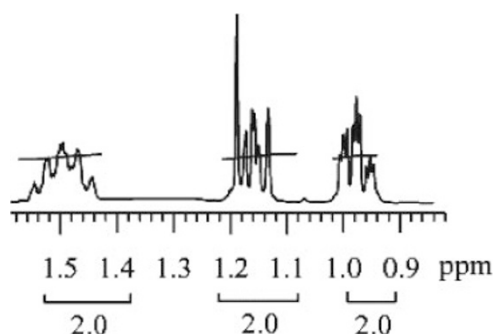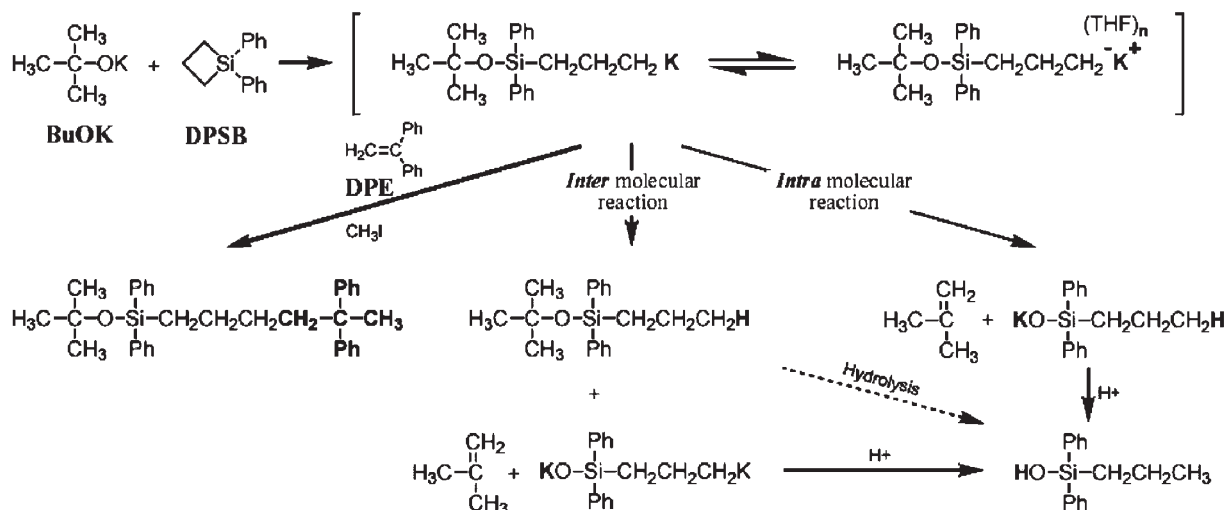

Figure 8. ^{1}H NMR of diphenyl(propyl-d_1)silanol.

as hydrogen source. No deuterium was incorporated when THF-d_8 was used as the solvent. If the hydrogen source was **BuOK**, the amounts should increase with addition of **DPSB**.

Two pathways are conceivable as the major paths for the formation of (*tert*-butoxy)diphenylpropylsilane and diphenylpropylsilanol as proposed in Scheme 2.

Initially formed potassium propyl species can exist in equilibrium with solvent separated or free ionic species. Although all species can add to diphenylethylene, unimolecular proton elimination from *tert*-butoxy group would become easier, probably by the aid of the coordination of oxygen atom to potassium cation which withdraws electron from *tert*-butyl group, to produce potassium diphenylpropylsilanolate. Contact or free ionic species will eliminate hydrogen bimolecularly to produce (*tert*-butoxy)diphenylpropylsilane and potassium diphenylpropylsilanolate. Such hydrogen abstraction reaction might be suppressed by the presence of potassium silanolate because of the stabilization of the initially formed carbanion by complexation with potassium silanolate. Change of the reactivity of a carbanion in the presence of alkoxide is well known.[19,20]

When considered that (*tert*-butoxy)diphenylpropylsilane is the major product over diphenylpropylsilanol, the major path seemed to be hydrogen abstraction through intermolecular reaction. The fact that potassium 2-methoxyethoxide was used as the initiator, which would coordinate to the initially formed anion more efficiently, propyldiphenylsilanol was formed more than in the case of **BuOK**, strongly supports the proposed mechanism.

The overall carbanion pump efficiency after trapping is closely related to kinetic aspect of the reaction. Potassium *tert*-butoxide having K as counter ion can

Scheme 2. Plausible scheme of formation of (*tert*-butoxy)diphenylpropylsilane and propyldiphenylsilanol.

more effectively ring-open the silacyclobutane than **BuONa**, or **BuOLi**, because it is less aggregated and more nucleophilic. The nucleophilicity is reversed after ring-opening of silacyclobutane, because the carbanion formed by ring-opening of silacyclobutane with Li or Na has smaller radius than K, and become more dissociated in THF, especially for Li. The highly reactive carbanion will indiscriminatively initiate the polymerization of silacyclobutane over addition to diphenylethylene. With BuLi as the initiator for the polymerization of the 1:1 mixture of silacyclobutane and **DPE**, silacyclobutane was selectively homopolymerized without the incorporation of **DPE** in the polymer. Addition of HMPA and 18-crown-6 crown ether dramatically increased the homopolymerization of silacyclobutane.

Conversion of Poly(ethylene oxide) Oxyanion to Carbanion Terminal

Conversion of poly**EO** oxyanion to carbanion terminal was indirectly evaluated by tracing the disappearance of **DPE** by ^{1}H NMR. By changing the dropping time of one equivalent **DPSB** to initial **BuOK** from 10 h to 50 h, the efficiency increased from 20% to 65%. When 2.5 times **DPSB** was added during 50 h, the efficiency reached 85%. The conversion of poly**EO** terminal to carbanion terminal was also confirmed by the appearance of methylene signal adjacent to silicon atom as indicated in Figure 4. The amount of **BuO** terminal and **DPE** end-capped terminal well coincided. The formation of block copolymers were studied by SEC and ^{1}H NMR. The change in SEC
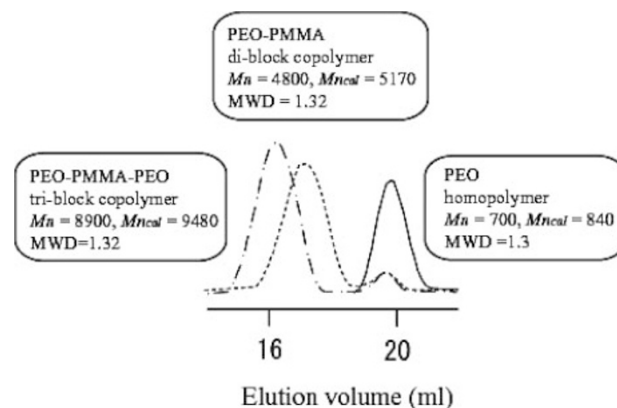

Figure 9. Change in SEC in di- and tri-block copolymer formation from **EO** and **MMA**[a]. [a]Di- and tri-block copolymer formations were carried out in THF at $-78\,^\circ$C, and at room temperature, respectively. Molecular weight of di- and tri-block copolymers were calculated by $[65(\mathbf{BuO}) + 44(\mathbf{EO})m + 224(\mathbf{DPSB}) \times 2.5 + 180(\mathbf{DPE}) + 100(\mathbf{MMA})n + 1]$ and $[65(\mathbf{BuO}) + 44(\mathbf{EO})(m + o) + 224(\mathbf{DPSB}) \times 2.5 + 180(\mathbf{DPE}) + 100(\mathbf{MMA})n + 1]$, respectively. Estimated molecular weight was correlated to standard polystyrene.

in the case of block copolymer of **MMA** in THF is shown in Figure 9.

Initially formed poly**EO** ($M_n = 700$, $M_{WD} = 1.3$) was converted to higher molecular weight product by the addition of **MMA**. The conversion of poly**EO** anion was about 85%, which was well coincided with the efficiency of the conversion of oxyanion to carbanion terminal. The di-block copolymer was converted into tri-block copolymer by further addition of new **EO**. The peak of di-block copolymer was shifted to

Table II. Molecular weight and composition of the poly**EO** di- and tri-block copolymers

No.	Polymer (ratio[a])	Solvent	Temp ($^\circ$C)	M_n ($\times 10^{-3}$ g/mol) Calcd.	M_n ($\times 10^{-3}$ g/mol) SEC[b]	M_w/M_n	[EO]/[M][c]
1	Poly**EO** (DP = 17.4) ([**BuOK**]:[**EO**] = 4.6:80.0)	THF	r.t.	0.84	0.70	1.30	—
2[d]	Poly**EO**–Poly**MMA** ([**EO**]:[**MMA**] = 3.5:7.0)	THF	-78	5.17	4.8	1.32	1.0/1.9
3		THF	r.t.		5.9	1.33	1.0/1.9
4		Tol	-78[e]		—	—	—
5		Tol	r.t.		5.7	1.32	1.0/1.8
6	Poly**EO**–Poly**MMA**–Poly**EO** ([**EO**]:[**MMA**]:[**EO**] = 3.5:7.0:20)	THF[f]	r.t.	9.48	8.9	1.32	3.6/1.0
7		To[g]	r.t.		9.3	1.32	3.8/1.0
8[d]	Poly**EO**–Poly**St** ([**EO**]:[**St**] = 3.5:6.8)	THF	r.t.	6.31	bimodal	—	—
9		Tol	r.t.		7.6	1.80	1.0/2.6
10[h]	Poly**EO**–Poly**St**–Poly**EO** ([**EO**]:[**St**]:[**EO**] = 3.5:6.8:20)	Tol	r.t.	10.7	broad	—	4.1/1.0[i]

[a]number in mmole. [b]correlated to polystyrene standard. [c]M = **MMA** or **St**, determined by ^{1}H NMR. [d]0.20 mmole of diphenylalkyl carbanion formed by carpanion pump (85% efficiency from **BuOK**) was used as the initiator. [e]reaction system became heterogeneous. [f]di-block copolymer **2** was used. [g]di-block copolymer **5** was used. [h]diblockcopolymer **9** was used. [i]contamination with homo poly**EO** was evidenced by RI detection in SEC.
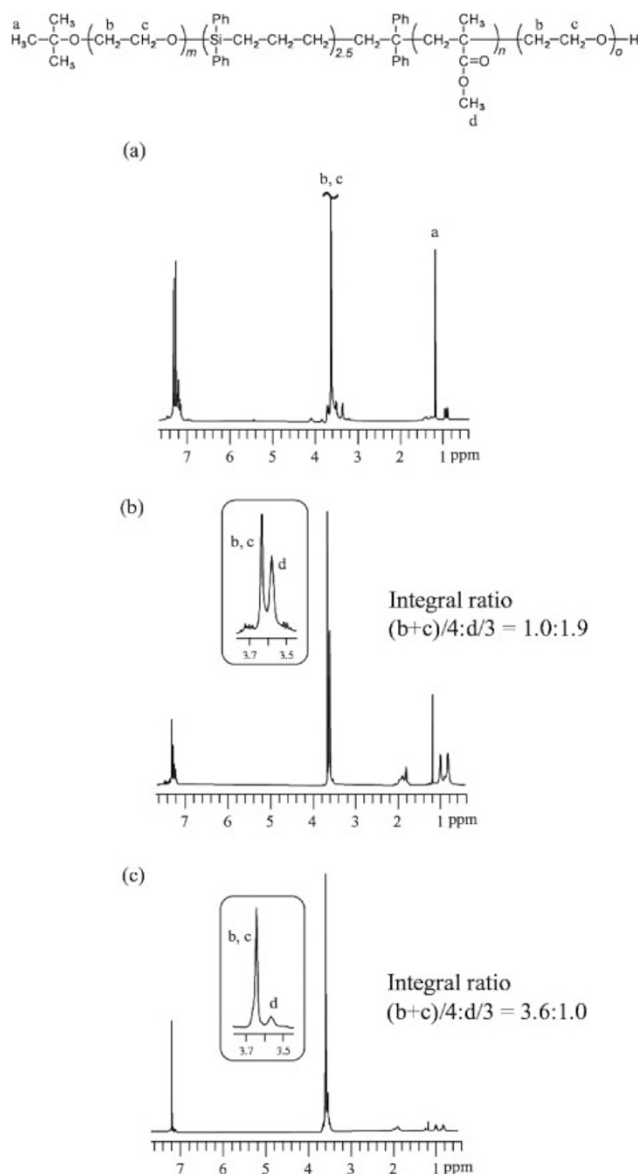
Figure 10. Change of ^{1}H NMR in the synthesis of poly**EO**-*block*-poly**MMA**-*block*-poly**EO** tri-block copolymer using **BuOK–DPSB** "Carbanion Pump": (a) Poly**EO** ([**BuOK**]:[**EO**] = 1.0:17.4), (b) poly**EO**-*block*-poly**MMA** ([**EO**]:[**MMA**] = 3.5: 7.0), (c) poly**EO**-*block*-poly**MMA**-*block*-poly**EO** ([**EO**]:[**MMA**] = 23.5:7.0).

higher molecular weight and completely disappeared. Some of the initially remaining poly**EO** did not react in the tri-block copolymer synthesis. The reason is not clear. It might have been deactivated by some reason. The results of the synthesis of block copolymers are summarized in Table II.

The change in ^{1}H NMR in poly**EO** poly**MMA** block copolymer syntheses in THF is shown in Figure 10.

Increase in **MMA** and **EO** content was clearly seen in di-block and tri-block copolymers. The molar ratio of **EO** and **MMA** well coincided with the feed ratio in di-block copolymer synthesis. The value was a little

higher in tri-block copolymer. Initiation of **EO** from **MMA** terminal might not efficiently occur in the present procedure. The synthesis in Tol was also successful, but the tacticity of the formed polymer, which could be evaluated from methyl signal at 0.7–1.1 ppm, was different.

Block copolymer with **St** was similarly synthesized. Reaction in THF could not be controlled, yet. Synthesis in Tol gave reasonable result, but molecular weight distribution was wider than the case of di-block copolymer with **MMA**, probably because of the relatively higher reactivity of **St** anion in propagation than the initiation reaction by diphenylalkyl anion. Tri-block copolymer could be synthesized in Tol, but contamination with homo poly**EO** was evidenced by RI-detected SEC analysis. This situation might be also true in the synthesis of tri-block copolymer with **MMA**. Further refinement of the reaction conditions is needed to cleanly synthesize tri-block copolymers.

SUMMARY

Homopolymerization of 1,1-diphenylsilacyclobutane by potassium *tert*-butoxide was effectively suppressed, and initially formed carbanion was trapped in 97% yield with 4-times 1,1-diphenylethylene as trapping agent. When 2-times 1,1-diphenylethylene was used, (*tert*-butoxy)diphenylpropylsilane and diphenylpropylsilanol were formed in 1 to 27% yield depending on the reaction conditions. These compounds were formed mainly by bimolecular hydrogen abstraction reaction from the initially formed carbanion. Formation of these compounds were almost completely suppressed by decreasing the polarity of the solvent or by increasing the concentration of 1,1-diphenylsilacyclobutane or diphenylethylene. Potassium as counter cation was more effective than Na or Li as counter ion. Although further refinement of the reaction conditions is needed, di-block copolymers from **EO** and **MMA** or **St** were synthesized by this system in 85% efficiency. Synthesis of tri-block copolymers were also possible, although some contamination of poly**EO** was noticed.

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