New Synthesis of Poly(silyl ether) and Poly(germyl ether) by Addition Reactions of Bisepoxides with Dimethyldiphenoxysilane and Dimethyldiphenoxygermane

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ABSTRACT: Certain new poly(silyl ether)s and a poly(germyl ether) were synthesized by the polyaddition of bisepoxides with dimethyldiphenoxysilane (MPS) and dimethyldiphenoxygermane (MPG). The polyaddition of Bisphenol A diglycidyl ether (BPGE) with MPS proceeded very smoothly and regioselectively using quaternary onium salts such as tetrabutylammonium chloride (TBAC) and tetrabutylphosphonium chloride (TBPC) as catalysts at 100 °C to give the corresponding poly(silyl ether)s having high molecular weights, although the reaction did not occur without a catalyst under the same reaction conditions. The polyaddition also proceeded using either triphenylphosphine (TPP), triethylamine (TEA), or a complex of 18-crown-6 with potassium chloride as catalysts to give the poly(silyl ether)s, but with low molecular weights. The polyaddition of BPGE with MPG produced the corresponding poly(germyl ether) with good yield using TBAC as a catalyst; however, the molecular weight of the isolated poly(germyl ether) was lower than that of the obtained poly(silyl ether) under the same conditions.

Introduction

Polymers containing metallic and inorganic atoms have been noted for their special characteristics. The polymers with silicon in the main chain have received much attention as high-performance and functional polymers. Polysiloxanes with excellent low-temperature flexibility and high-temperature stability derived from the Si−O−Si skeleton have been used widely as elastomers and plastics in various industries. Since polysiloxanes have further attractive characteristics such as good transparency, oxygen permeability, flexibility, and resistance to oxygen-reactive ion etching, these polymers were also useful materials for medical applications, photolithography, and polymer supports for liquid crystal compounds. Polysilanes with Si−Si bonds have been of interest as a new type of silicon polymer in the field of electronics and optoelectronics due to their unique physical and chemical properties. Poly(silyl ether)s are also among the interesting new silicon polymers. Polysiloxanes have been ordinarily prepared[1] by the anionic ring-opening polymerization of cyclic siloxane monomers. Polysilanes have usually been obtained[2] by the coupling reaction of dichlorosilanes using sodium metal. Poly(silyl ether)s have normally been synthesized by the polycondensation of dichlorosilanes,[3] diphenoxysilanes,[4] or diaminosilanes[4−6] with various diols. However, there is no report on the synthesis of poly(silyl ether) by polyaddition except our recent paper[7,8] on the polyaddition of bisepoxides with dichlorosilanes.

Polymers with germanium in the main chain have also been of interest as new functional materials due to their unique characteristics. Polyesters with germanium in the main chain have been synthesized[9] by the polycondensation of dichlorogermanes with sodium dicarboxylates. Polygermanes have also been prepared[10] by Wurtz-type polycondensation in toluene as have polysilanes. Kobayashi et al. recently reported[11] the synthesis of certain germanium-containing polymers by the polyaddition of germylenes with *p*-benzoquinones, α,*β*-unsaturated ketones, and acetylene monomers.

The authors reported finding[12] that the polyaddition of bisepoxides with active diesters proceed very smoothly and regioselectively when catalyzed by quaternary onium salts or crown ether complexes to give the corresponding polyesters. This reaction system can be further extended[13] for the reaction of cyclic ethers with appropriate nucleophilic reagents to produce new polymers. This article reports on the novel synthesis of poly(silyl ether)s and a poly(germyl ether) by the polyaddition of bisepoxides with dimethyldiphenoxysilane (MPS) and dimethyldiphenoxygermane (MPG) using quaternary onium salts, triphenylphosphine, or a crown ether complex as catalysts, respectively.

Experimental Section

Materials. Solvents and triethylamine (TEA) were dried using P_2O_5, CaH_2, or Na metal wire and purified in the usual way before use. Reagent grade dichlorodimethylsilane (CMS) (Aldrich) and dichlorodimethylgermane (CMG) (Aldrich) were used without further purification. Bisphenol A diglycidyl ether (BPGE) was recrystallized four times from the mixed solvent of methanol and methyl ethyl ketone (4:1 v/v). Phenyl glycidyl ether (PGE) and ethylene glycol diglycidyl ether (EGGE) were purified twice by distillation under reduced pressure. 3,3′,5,5′-Tetramethylbiphenyl-4,4′-diol 4,4′-diglycidyl ether (MBGE), biphenyl-4,4′-diol 4,4′-diglycidyl ether (BGE), donated from Yuka-Shell Epoxy Co. Ltd., were recrystallized four times from the mixed solvent of methyl isobutyl ketone and methyl ethyl ketone (3:1 v/v), respectively. Tetrabutylammonium bromide (TBAB) was recrystallized from ethyl acetate. Triphenylphosphine (TPP) was purified by recrystallization from methanol. Tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrabutylphosphonium chloride (TBPC), tetrabutylphosphonium bromide (TBPB), 18-crown-6 (18-C-6), potassium chloride (KCl), potassium bromide (KBr), cesium fluoride (CsF), and cesium chloride (CsCl) were used without further purification.

Measurement. Infrared (IR) spectra were measured on a JASCO Model IR-700 spectrometer. The ^{1}H NMR spectra were recorded on JEOL Models JNM EX-90 (90 MHz) and JNM FX-200 (200 MHz) instruments in $CDCl_3$ using Me_4Si

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(TMS) as an internal standard. The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with the use of a TOSO Model HLC-8020 GPC equipped with a refractive index detector using TSK gel columns (eluent: DMF, calibrated with narrow molecular weight polystyrene standards).

Synthesis of Dimethyldiphenoxysilane (MPS). To a solution of phenol (22.58 g, 0.24 mol) and TEA (24.29 g, 0.24 mol) in THF (200 mL) was added CMS (12.91 g, 0.10 mol) at 0 °C for 1 h under dried nitrogen. The mixture was stirred at 0 °C for 1 h and then at room temperature for 3 h. The precipitated salts of TEA/HCl were filtered off, and then the solvents were evaporated. The residue was distilled twice under reduced pressure. The yield of MPS was 12.41 g (51%): bp 104−105 °C/0.3 mmHg (lit.[14] bp 94−100 °C/1 mmHg); IR (neat) 3034 (aromatic C−H), 2926 (aliphatic C−H), 1490 (C═C), 1290 cm^{-1} (Si−O); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 0.76 (s, 6H, CH_3), 6.80−7.26 (m, 10H, aromatic protons).

Synthesis of Dimethyldiphenoxygermane (MPG). MPG was obtained in 44% yield by the reaction of CMG (4.86 g, 28 mmol) with phenol (6.40 g, 68 mmol) in toluene (68 mL) using TEA (6.88 g, 68 mmol) as HCl acceptor using the same method for the synthesis of MPS, and an oily crude product was purified by distillation three times under reduced pressure (125−126 °C/0.8 mmHg). The yield of MPG was 3.58 g (44%). IR (neat) 3036 (aromatic C−H), 2942 (aliphatic C−H), 1500 (C═C), 1236 cm^{-1} (Ge−O); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 0.76 (s, 6H, CH_3), 6.80−7.28 (m, 10H, aromatic protons).

Addition Reaction of MPS with PGE. MPS (0.4887 g, 2 mmol), PGE (0.6007 g, 4 mmol), TBPC (0.0294 g, 0.1 mmol) as a catalyst, and NMP (1 mL) as a reaction solvent were all charged into a glass tube in a drybox, after which the tube was evacuated and then sealed using a gas torch. The reaction of MPS with PGE was carried out in the sealed tube at 100 °C for 24 h under stirring. The reaction mixture was diluted with 10 mL of chloroform and washed thrice with minimal amounts of water, and the solvent was evaporated *in vacuo*. The crude product obtained was purified using recycling preparative HPLC. The isolated yield of the resulting silyl ether **1** was 1.019 g (94%). IR (neat) 3036 (aromatic C−H), 2964 (aliphatic C−H), 1494 (C═C), 1240 (C−O−C), 1051 cm^{-1} (Si−O); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 0.30 (s, 6H, CH_3), 3.98−4.18 (m, 8H, OCH_2), 4.52−4.68 (m, 2H, OCH), 6.78−7.36 (m, 20H, aromatic protons). Anal. Calcd for $C_{32}H_{36}O_6Si$: C, 70.56; H, 6.66. Found: C, 70.77; H, 6.83.

Synthesis of Poly(silyl ether) 2a by the Reaction of MPS with BPGE. A typical procedure for polyaddition of MPS with BPGE was as follows: MPS (0.4887 g, 2 mmol), BPGE (0.6809 g, 2 mmol), TBPC (0.0294 g, 0.1 mmol), and NMP (1 mL) were charged into a glass tube in a drybox, and then the tube was sealed as explained above. The reaction was performed at 100 °C in the sealed tube for 24 h under stirring, and then the solution was diluted with 10 mL of chloroform. The polymer solution was washed thrice with minimal amounts of water, and the solution was poured into 150 mL of *n*-hexane to precipitate the polymer. The resulting polymer was reprecipitated twice from chloroform into *n*-hexane and dried in vacuo. The yield of polymer **2a** was 1.157 g (99%). The number-average molecular weight (M_n) of the polymer determined from GPC was 16 300 (M_w/M_n = 1.57). IR (film) 3042 (aromatic C−H), 2966 (aliphatic C−H), 1510 (C═C), 1242 (C−O−C), 1051 cm^{-1} (Si−O); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 0.28 (s, 6H, CH_3), 1.60 (s, 6H, CH_3), 3.92−4.16 (m, 8H, OCH_2), 4.48−4.64 (m, 2.0H, OCH), 6.68−7.28 (m, 18H, aromatic protons). Anal. Calcd for $C_{35}H_{40}O_6Si$: C, 71.89; H, 6.89. Found: C, 71.44; H, 7.07.

Synthesis of Poly(silyl ether) 2b by the Reaction of MPS with BGE. MPS (0.4887 g, 2 mmol) was made to react with BGE (0.5967 g, 2 mmol) in the presence of TBPC (0.0236 g, 0.08 mmol) in toluene (0.67 mL) at 120 °C in a sealed tube for 36 h. The reaction mixture was diluted with chloroform and washed with water. The polymer solution was poured into *n*-hexane, reprecipitated twice from chloroform into *n*-hexane, and dried *in vacuo*. The yield of polymer **2b** was 1.062 g (98%). The M_n of the polymer determined from GPC was 18 500 (M_w/M_n = 3.22). IR (film) 3042 (aromatic C−H), 2936 (aliphatic C−H), 1497 (C═C), 1239 (C−O−C), 1052 cm^{-1} (Si−O); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 0.30 (s, 6H, CH_3), 3.96−4.24 (m, 8H, OCH_2), 4.48−4.68 (m, 2.0H, OCH), 6.76−7.48 (m, 18H, aromatic protons).

Synthesis of Poly(silyl ether) 2c by the Reaction of MPS with MBGE. The polyaddition of MPS (0.4887 g, 2 mmol) and MBGE (0.7089 g, 2 mmol) was carried out in the presence of TBPC (0.0236 g, 0.08 mmol) in toluene (0.67 mL) at 120 °C in a sealed tube for 36 h, and the product was purified by the same procedure as described for **2a**. The final yield of polymer **2c** was 1.164 g (97%). The M_n of the polymer determined from GPC was 20 200 (M_w/M_n = 2.01). IR (film) 3034 (aromatic C−H), 2926 (aliphatic C−H), 1495 (C═C), 1245 (C−O−C), 1048 cm^{-1} (Si−O); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 0.32 (s, 6H, CH_3), 2.28 (s, 12H, CH_3), 3.88−4.30 (m, 8H, OCH_3), 4.56−4.68 (m, 2.0H, OCH), 6.82−7.32 (m, 14H, aromatic protons).

Synthesis of Poly(silyl ether) 2d by the Reaction of MPS with EGGE. MBGE (0.7089 g, 2 mmol), EGGE (0.3484 g, 2 mmol), and TBPC (0.0236 g, 0.08 mmol) were dissolved in toluene (0.67 mL) in a sealed tube, and the solution was stirred at 120 °C for 36 h under stirring. The final yield of polymer **2d** was 0.665 g (79%). The M_n of the polymer determined from GPC was 12 500 (M_w/M_n = 1.33). IR (film) 3042 (aromatic C−H), 2876 (aliphatic C−H), 1496 (C═C), 1247 (C−O−C), 1048 cm^{-1} (Si−O); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 0.19 (s, 6H, CH_3), 3.44−3.64 (m, 8H, OCH_2), 3.80−4.08 (m, 4H, OCH_2), 4.20−4.36 (m, 2.0H, OCH), 6.72−7.30 (m, 10H, aromatic protons).

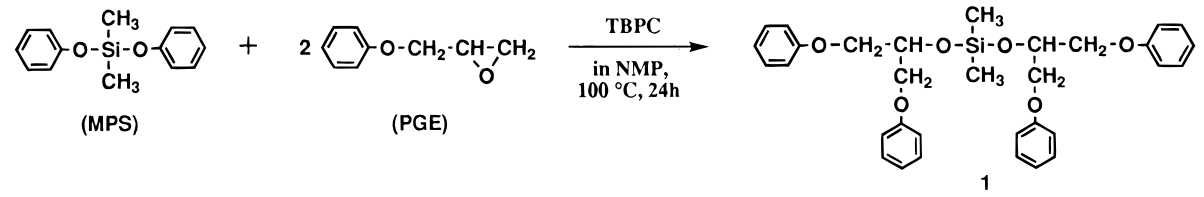
Synthesis of Poly(germyl ether) 3 by the Reaction of MPG with BPGE. MPG (0.1156 g, 0.4 mmol) was allowed to react with BPGE (0.1362 g, 0.4 mmol) in the presence of TBPC (0.0129 g, 0.04 mmol) in toluene-d_8 (0.4 mL) at 100 °C in a sealed tube for 36 h, and then the ^1H NMR spectrum (200 MHz, toluene-d_8, TMS) of polymer **3** was measured as follows: δ 0.655 (s, 6H, CH_3), 1.60 (s, 6H, CH_3), 3.84−4.16 (m, 8H, OCH_2), 4.46−4.64 (m, 2H, OCH), 6.72−7.19 (m, 18H, aromatic protons). The polymer solution was poured into *n*-hexane to precipitate polymer **3**. The recovered polymer was reprecipitated twice from chloroform into *n*-hexane and dried *in vacuo*. The final yield of polymer **3** was 0.237 g (94%). The M_n of the polymer determined from GPC was 3090 (M_w/M_n = 1.57). IR (film) 3228 (weak O−H), 3062 (aromatic C−H), 2966 (aliphatic C−H), 1510 (C═C), 1242 cm^{-1} (C−O−C).

Results and Discussion

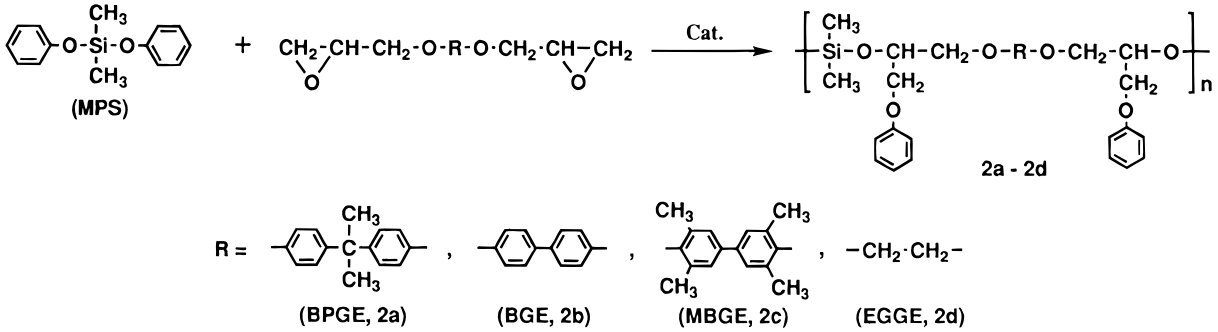
MPS[14] was prepared in 51% yield from the reaction of CMS with phenol followed by vacuum distillation. MPG was also synthesized in 44% yield by the reaction of CMG with phenol using the same method as for the synthesis of MPS and confirmed by IR and ^1H NMR spectra. However, it was found that MPG is unstable to the moisture in the air, although MPS is stable under the same conditions.

The addition reaction of MPS with PGE was performed as a model reaction for the polyaddition of MPS with bisepoxides. The reaction proceeded smoothly using TBPC as a catalyst in NMP at 100 °C for 24 h to give the resulting silyl ether **1** in 94% yield. The structure of the obtained silyl ether **1** was determined by IR and ^1H NMR spectra and elemental analysis. The IR spectrum of **1** showed absorption peaks at 3036, 2964, 1492, 1240, and 1051 cm^{-1} due to aromatic C−H, aliphatic C−H, C═C, C−O−C, and Si−O stretching, respectively. The ^1H NMR spectrum of this compound exhibited the proton signals at 0.30 ppm due to the $SiCH_3$, at 3.98−4.18 ppm due to the CH_2O, at 4.52−4.68 ppm due to the OCH, and at 6.78−7.36 ppm due to the aromatic protons. From the intensity ratio of methine protons at 4.52−4.68 ppm vs aromatic protons at 6.78−7.36 ppm, the ratio of β-cleavage of the epoxy ring of PGE was calculated as 100%. This result means

Scheme 1



Scheme 2



that the addition reaction of MPS with PGE occurred regioselectively to give the corresponding silyl ether **1** as shown in Scheme 1. Nambu and Endo[15] also reported the reaction of (trimethylsilyl)phenoxide with PGE catalyzed by cesium fluoride without solvent at 130 °C produced the corresponding 1:1 adduct. Although they also synthesized an epoxy resin with a pendant silyloxy group by the reaction of a bifunctional aryl silyl ether with 2 equiv of BPGE catalyzed by cesium fluoride, the reaction of equivalent amounts of those monomers to produce the corresponding polyethers with a pendant silyloxy group was not reported.

The addition reaction of MPG with PGE was not performed, because the reaction product is very unstable[16] to the moisture in the air and to the water in solution, and the isolation and purification may be impossible.

Based on the above model reaction of MPS with PGE, the polyaddition of MPS with BPGE was carried out with or without catalyst in NMP at 100 °C for 24 h (Table 1). Although the polymer was not obtained at all when the reaction was performed without catalyst, poly(silyl ether)s **2a** with relatively low molecular weight (M_n = 3800−8300) were obtained in 64−90% yields when TBAB, TBAI, TBPB, 18-C-6/KBr, 18-C-6/CsF, and TPP were used as catalysts. Poly(silyl ether)s **2a** with relatively high molecular weight (M_n = 10 300−16 900) were prepared in 87−99% yields under the same reaction conditions when TBAC, TBPC, 18-C-6/KCl, 18-C-6/CsCl, and TEA were used as catalysts. These results suggest that the polyaddition of MPS with BPGE proceeded smoothly using TBAC, TBPC, 18-C-6/KCl, 18-C-6/CsCl, and TEA as catalysts and that quaternary onium salts with Cl^- as a counteranion such as TBAC and TBPC have the highest catalytic activity.

The structure of the obtained polymer **2a** was confirmed by IR and ^{1}H NMR spectra. In the IR spectrum, polymer **2a** showed absorption peaks at 3042, 2966, 1510, 1242, and 1051 cm^{-1} due to aromatic C−H, aliphatic C−H, C=C, C−O−C, and Si−O stretching, respectively. In the ^{1}H NMR spectrum of polymer **2a**, the corresponding proton signals were observed at 0.28 ($SiCH_3$), 1.60 (CCH_3), 3.92−4.16 (CH_2O), 4.48−4.64 (OCH), and 6.68−7.28 ppm (aromatic protons), respectively. The intensity ratio calculated from methine protons at 4.48−4.64 ppm vs aromatic protons at 6.68−7.28 was 1.0. This means that poly(silyl ether) **2a** with pendant phenoxy groups in the side chain was synthesized regioselectively by the polyaddition of MPS with BPGE using certain suitable catalysts as shown in Scheme 2.

Table 1. Polyaddition of MPS with BPGE Using Various Catalysts[a]

run no.	catalyst	yield, %	M_n[b] × 10^{-4}	M_w/M_n[b]
1	none	0		
2	TBAC	96	1.69	1.62
3	TBAB	85	0.75	1.26
4	TBAI	64	0.43	1.13
5	TBPC	99	1.63	1.57
6	TBPB	90	0.50	1.31
7	18-C-6/KCl	89	1.18	1.39
8	18-C-6/KBr	81	0.83	1.30
9	18-C-6/CsF	73	0.38	1.10
10	18-C-6/CsCl	87	1.04	1.34
11	TPP	85	0.56	1.33
12	TEA	87	1.03	1.35

[a] The reactions were carried out with MPS (2 mmol) and BPGE (2 mmol) using the catalyst (5 mol %) in NMP (1 mL) at 100 °C for 24 h. [b] Estimated by GPC based on polystyrene standards.

Table 2. Polyaddition of MPS with BPGE in Various Solvents[a]

run no.	solvent	yield, %	M_n[b] × 10^{-4}	M_w/M_n[b]
13	toluene	95	1.20	1.41
14	anisole	97	1.29	1.44
15	chlorobenzene	97	1.24	1.41
16	diglyme	98	1.50	1.52
17	DMF	92	1.60	1.57
18	DMAc	95	1.41	1.54
5	NMP	99	1.63	1.57
19	HMPA	99	1.56	1.60

[a] The reactions were carried out with MPS (2 mmol) and BPGE (2 mmol) in the solvent (1 mL) using TBPC (5 mol %) as the catalyst at 100 °C for 24 h. [b] Estimated by GPC based on polystyrene standards.

The polyaddition of MPS with BPGE was also examined in various organic solvents using 5 mol % of TBPC as the catalyst at 100 °C for 24 h. As summarized in Table 2, polymers **2a** with relatively high molecular weight were obtained quantitatively when the reactions were carried out in aprotic polar solvents such as DMF, DMAc, NMP, and HMPA. Molecular weights (M_n) of the polymers **2a** prepared in aromatic solvents such as

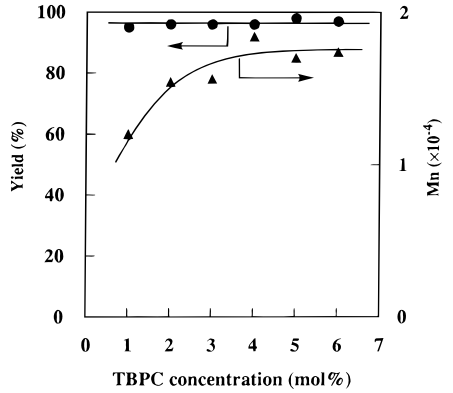


Figure 1. Effect of the catalyst concentration on the reaction of MPS (2 mmol) with BPGE (2 mmol) in NMP (1 mL) at 100 °C for 24 h: (●) yield; (▲) M_n of polymer.

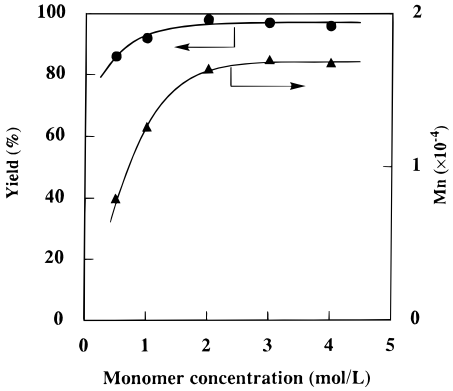


Figure 2. Effect of the monomer concentration on the reaction of MPS with BPGE in NMP using TBPC (5 mol %) as the catalyst at 100 °C for 24 h: (●) yield; (▲) M_n of polymer.

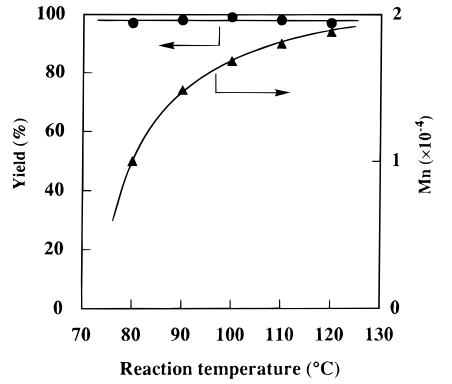


Figure 3. Effect of the temperature on the reaction of MPS (2 mmol) with BPGE (2 mmol) in NMP (1 mL) using TBPC (5 mol %) for 24 h: (●) yield; (▲) M_n of polymer.

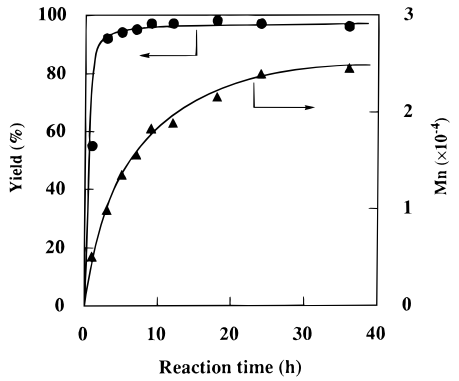


Figure 4. Effect of the time on the reaction of MPS (2 mmol) with BPGE (2 mmol) in NMP (1 mL) using TBPC (5 mol %) at 100 °C: (●) yield; (▲) M_n of polymer.

toluene, anisole, and chlorobenzene were slightly lower than those of the polymer obtained in the former solvents. When the reaction was performed in diglyme, the polymer with moderate molecular weight was obtained. This result suggests that the polarity of the reaction solvent affected the reaction of BPGE with MPS, which has a lower reactivity than CMS toward epoxy compound, at high reaction temperature.

The effect of the catalyst concentration on the polyaddition of MPS with BPGE in the presence of TBPC in NMP under the same conditions was examined. As shown in Figure 1, polymers **2a** with mostly the same molecular weights were obtained quantitatively within the 3−6 mol % range of the catalyst concentration, although the molecular weight of the polymer increased gradually with catalyst concentration at 1−3%. It seems that the polyaddition of MPS with BPGE was mostly finished at 100 °C for 24 h under 3−6 mol % of the catalyst concentration, although the initial rate of the reaction was enhanced by increasing the catalyst concentration.

As shown in Figure 2, the yield and molecular weight of the polymer increased with monomer concentration at 0.5−2 mol/L, and both the yield and the molecular weight of the resulting polymers were nearly the same within 2−4 mol/L of the monomer concentration.

The effect of the reaction temperature was examined in NMP at 80−120 °C for 24 h using 5 mol % of TBPC as the catalyst. As shown in Figure 3, although the polymer was obtained in quantitative yield under each reaction condition, the molecular weight of the resulting polymer increased with reaction temperature. This result suggests that the reaction temperature is an important factor to obtain the polymer by the reaction of BPGE with MPS, because the reactivity of the silylphenoxy group to oxirane is lower than that[8] of silyl chloride.

The effect of the reaction time on the polyaddition of MPS with BPGE was investigated in the presence of 5 mol % of TBPC as the catalyst in NMP at 100 °C. As shown in Figure 4, the yield of the polymer increased strongly until 5 h, and then the polymer was obtained in quantitative yield within 5−35 h. On the other hand, the molecular weight of the resulting polymer gradually increased with reaction time from 2 to 35 h. These results indicate that poly(silyl ether) **2a** with high molecular weight can be obtained under appropriate conditions such as catalyst concentration, monomer concentration, reaction temperature, and reaction time using TBPC as the catalyst.

Polyaddition of MPS with various bisepoxides was performed using 4 mol % of TBPC as the catalyst in NMP at 120 °C for 36 h. As summarized in Table 3, the polyaddition of MPS with BPGE gave quantitative yields of the corresponding polymer **2a** with high molecular weight. The polyaddition of MPS with BGE and MBGE produced in high yields the corresponding poly(silyl ether)s **2b** and **2c** with high molecular weights, respectively. Poly(silyl ether) **2d** was also prepared in 79% yield by the polyaddition of MPS with EGGE; however, the molecular weight of the resulting polymer was relatively low. Regioselectivity of the resulting polymers was confirmed by ^{1}H NMR spectra, and it was found that the reactions of MPS with BGE, MBGE, and EGGE produced regioselectively the corresponding poly(silyl ether)s such as **2b**, **2c**, and **2d** as shown in Scheme 2. However, the reaction of dimethyldimethoxysilane

Scheme 3

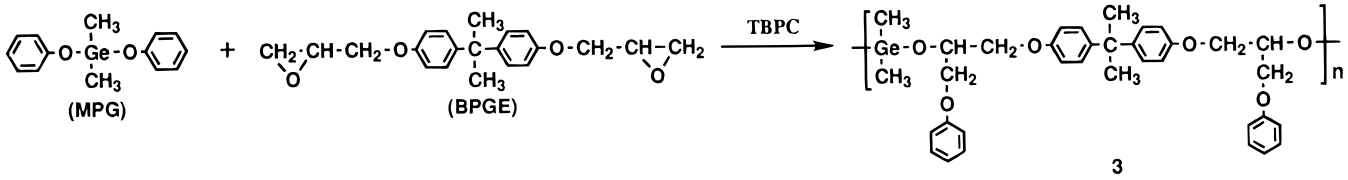


Table 3. Synthesis of Various Poly(silyl ether)s[a]

polym no.	monomer: dialkoxysilane	monomer: bisepoxide	yield, %	M_n[b] × 10^{-4}	M_w/M_n[b]	S_β,[c] %
2a	MPS	BPGE	98	1.84	1.68	100
2b	MPS	BGE	98	1.85	3.22	100
2c	MPS	MBGE	97	2.02	2.01	100
2d	MPS	EGGE	79	1.25	1.33	100
2e	MMS	BPGE	0			

[a] The reactions were carried out with dialkoxysilane (2 mmol) and bisepoxide (2 mmol) using TBPC (4 mol %) as a catalyst in NMP (0.67 mL) at 120 °C for 36 h. [b] Estimated by GPC based on polystyrene standards. [c] Selectivity of β-cleavage.

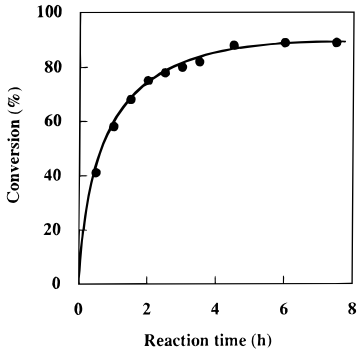


Figure 5. Effect of the time on the reaction of MPG (0.4 mmol) with BPGE (0.4 mmol) in toluene-d_8 (0.4 mL) using TBPC (5 mol %) at 100 °C.

(MMS) with BPGE did not produce polymer under the same reaction conditions. This result suggests that the reactivity of the silylmethoxy group of MMS is much lower than that of the silylphenoxy group of MPS.

Polyaddition of MPG with BPGE was carried out using 5 mol % of TBPC as a catalyst in toluene-d_8 at 100 °C in a sealed tube. The ^{1}H NMR spectra of the mixture of MPG and BPGE in toluene-d_8 exhibited signals at 2.22−2.46 ppm due to the methylene protons of the epoxy ring. These proton signals decreased gradually with reaction time, and then new proton signals appeared at 3.84−4.16 ppm due to the CH_2O groups and at 4.46−4.64 ppm due to CHO groups in the polymer chains. The intensity ratio calculated from the methine protons at 4.46−4.64 ppm vs the aromatic protons at 6.72−7.19 was 1.0. This means that the polyaddition of MPG with BPGE proceeded regioselectively using TBPC as the catalyst to give poly(germyl ether) **3** with pendant phenoxy groups in the side chain as shown in Scheme 3.

Correlation between reaction time and conversion of the epoxy ring in BPGE is showed in Figure 5. This indicates that the polyaddition of MPG with BPGE proceeded smoothly as did the reaction of MPS with BPGE. The polyaddition was performed for 36 h, and the resulting poly(germyl ether) **3** was recovered with 94% yield by precipitation from *n*-hexane. However, the molecular weight of poly(germyl ether) **3** was disappointingly low (M_n = 3090), although poly(silyl ether) **2a** obtained by the reaction of MPS with BPGE under the same conditions had high molecular weight. There are two reasons that poly(germyl ether) with high molecular weight was not obtained. That is, the reactivity of MPG to oxirane was lower than that of MPS. Furthermore, the resulting polymer decomposed gradually by contact with water during the treatment of the polymer. Indeed, as summarized in Table 4, the M_n of poly(germyl ether) **3** dissolved in THF decreased with time. Although Kobayashi et al.[11] reported that poly(germyl ether)s prepared by the polyaddition of bis[bis(trimethylsilyl)amido]germanium(II) with benzoquinone derivative were hydrolytically stable, we found[16] that poly(germyl ether) obtained by the polyaddition of dichlorodiphenylgermane with BPGE was vulnerable to water in the solution.

Table 4. Decomposition of Poly(germyl ether) 3

time, h	M_n[a] × 10^{-3}	M_w/M_n
0	3.09	1.57
3	1.22	1.59
6	0.95	1.37

[a] Estimated by GPC based on polystyrene standards.

Table 5. Solubility of Poly(silyl ether)s[a]

solvent	polymer: **2a**	**2b**	**2c**	**2d**
methanol	−	−	−	−
n-hexane	−	−	−	−
acetonitrile	−	−	−	−
acetone	++	−	++	++
ethyl acetate	++	++	++	++
chloroform	++	++	++	++
toluene	++	++	++	++
anisole	++	++	++	++
chlorobenzene	++	++	++	++
THF	++	++	++	++
DMF	++	++	++	++
DMAc	++	++	++	++
NMP	++	++	++	++
DMSO	++	++	++	++
HMPA	++	++	++	++

[a] ++, soluble at room temperature; +, soluble by heating; + −, partially soluble or swelling; −, insoluble.

The solubility of the poly(silyl ether)s **2a**−**d** was examined. As summarized in Table 5, all of the poly(silyl ether)s were insoluble in methanol, *n*-hexane, and acetonitrile. Furthermore, poly(silyl ether) **2b** was insoluble in acetone. However, all the obtained poly(silyl ether)s were soluble in ethyl acetate, chloroform, toluene, anisole, chlorobenzene, THF, DMF, DMAc, NMP, DMSO, and HMPA.

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References and Notes

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