Novel Synthesis of Poly(silyl ether)s by the Addition Reaction of Bis(epoxide)s with Dichlorosilanes or Bis(chlorosilane)s

Tadatomi Nishikubo,* Atsushi Kameyama, Yasuhiro Kimura, and Kunitoshi Fukuyo

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama, 221 Japan

Received November 4, 1994; Revised Manuscript Received March 17, 1995[⊗]

ABSTRACT: Certain new poly(silyl ether)s with reactive pendant chloromethyl groups were synthesized by the polyaddition of bis(epoxide)s with dichlorosilanes or bis(chlorosilane)s. The polyaddition proceeded very smoothly and regioselectively in toluene catalyzed by quaternary ammonium or phosphonium salts such as tetrabutylammonium chloride (TBAC) and tetrabutylphosphonium chloride (TBPC) under mild reaction conditions to give the corresponding poly(silyl ether)s having high molecular weights, although the reaction did not occur without a catalyst nor with 4-(dimethylamino)pyridine (DMAP) as the catalyst under the same reaction conditions. The polyaddition also proceeded using either triphenylphosphine (TPP) or a complex of 18-crown-6 with potassium chloride as catalysts to afford the poly(silyl ether), but with low molecular weights. That is, the catalytic activity of the above quaternary onium salts such as TBAC and TBPC was higher than that of DMAP, TPP, or the crown ether complex. Furthermore, it was found that the resulting poly(silyl ether)s with reactive pendant chloromethyl groups exhibited excellent solubility in common organic solvents.

Introduction

Polymers containing silicon in the main chain are noteworthy as high-performance and functional materials. Polysiloxanes with excellent low-temperature flexibility and high-temperature stability derived from their siloxane bonds have been used widely as elastomers and plastics in various industries. Polysiloxanes have also been studied as useful materials for medical applications, photolithography, and polymer supports for liquid crystal compounds, since these polymers have further attractive characteristics such as good transparency, oxygen permeability, flexibility, resistance to oxygen-reactive ion etching, and so on. Polysiloxanes have been ordinarily synthesized by the anionic ring-opening polymerization[1] of cyclic siloxane monomers. Polysiloxanes with phenylene units in the backbone have been prepared by the condensation reaction of silanediols with active silane monomers such as dialkyldichlorosilane,[2] bis(ureidosilane),[3] or bis(dimethylamino)silane[4] monomers through the nucleophilic substitution reaction.

Recently, polysilanes have been of increasing interest as a new type of silicon polymer in the field of electronics and optoelectronics. These polymers are usually obtained[5] by the polycondensation of dichlorosilanes with sodium metal. Poly(silyl ether)s are among the interesting new silicon polymers and have been synthesized by the polycondensation of dichlorosilanes,[6] diphenoxysilanes,[7] or diaminosilanes[7,8] with various diols.

The authors reported[9,10] recently that addition reactions of bis(epoxide)s with diacyl chlorides or active diesters proceed very smoothly and regioselectively using quaternary onium salts or crown ether complexes as catalysts to give the corresponding polyesters. It is known[11,12] that the addition reaction of silyl chlorides with cyclic ethers produces the corresponding silyl ethers with high yields. However, there is no report on the synthesis of poly(silyl ether)s by the polyaddition of bis(epoxide) with dichlorosilanes or bis(chlorosilane)s.

In this paper, the authors report a novel synthesis of new poly(silyl ether)s by the addition reaction of bis(epoxide)s with certain dichlorosilanes and bis(chlorosilane)s using quaternary onium salts, triphenylphosphine, or a crown ether complex as catalyst.

Experimental Section

Materials. Solvents were dried using P_2O_5, CaH_2, or Na metal wire and purified in the usual way before use. Reagent grade dichlorodiphenylsilane (CPS) and 1,2-bis(chlorodimethylsilyl)ethane (CMSE) were purified by vacuum distillation. Cyclopentamethylenedichlorosilane (CPMCS) and bis[(2-(chlorodimethylsilyl)ethyl)benzene] (CMSEB) 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. Tetrabutylammonium bromide (TBAB) was recrystallized from ethyl acetate. Triphenylphosphine (TPP) was purified by recrystallization from methanol. Tetrabutylammonium chloride (TBAC), tetrahexylammonium bromide (THAB), tetrabutylphosphonium chloride (TBPC), tetrabutylphosphonium bromide (TBPB), 4-(dimethylamino)pyridine (DMAP), 18-crown-6 (18-C-6), and potassium chloride (KCl) 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 (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).

Addition Reaction of PGE with CPS. To the solution of PGE (0.4506 g, 3.0 mmol) and TBAB (9.7 mg, 0.03 mmol) in toluene (0.25 mL) was added dropwise a solution of CPS (0.3798 g, 1.5 mmol) dissolved in toluene (0.5 mL) under stirring at 0–5 °C for 1 h, and then stirred at room temperature for 23 h. The solution was diluted with chloroform (10 mL), washed twice with minimal amounts of water, and the solvent was evaporated *in vacuo*. The crude product obtained was purified by silica gel column chromatography using chloroform as the eluent: The isolated yield of the resulting

---

* To whom all correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1995.

0024-9297/95/2228-4361$09.00/0

silyl ether **1** was 0.652 g (79%). IR (neat): 3066 ($\nu_{\text{aromatic C-H}}$), 2934 ($\nu_{\text{aliphatic C-H}}$), 1243 ($\nu_{\text{C-O-C}}$), 1095 ($\nu_{\text{Si-O}}$), 753 cm^{-1} ($\nu_{\text{C-Cl}}$). ^{1}H NMR (90 MHz, CDCl$_3$, TMS): δ 3.68–3.75 (m, 4H, CH$_2$-Cl), 4.00–4.11 (m, 4H, C–CH$_2$–O), 4.36–4.58 (m, 1.9H, O–CH), 6.68–7.79 ppm (m, 20H, aromatic protons). Anal. Calcd for $C_{30}H_{30}O_4Cl_2Si$: C, 65.09; H, 5.46. Found: C, 64.87; H, 5.38.

Synthesis of Poly(silyl ether) 2a from BPGE with CPS. A typical procedure for polyaddition of BPGE with CPS was as follows: BPGE (0.5107 g, 1.5 mmol), CPS (0.3798 g, 1.5 mmol), and TBPC (4.4 mg, 0.015 mmol) were dissolved in toluene (1.5 mL), and then the reaction was carried out at 50 °C for 24 h. The reaction mixture was diluted by the addition of chloroform (10 mL) and washed with water (7 mL), and then some amount of chloroform was evaporated. The concentrated polymer solution was poured into hexane, reprecipitated twice from chloroform into hexane, and dried *in vacuo* at 50 °C. The yield of polymer **2a** was 0.80 g (90%). The number average molecular weight (M_n) of the polymer determined from GPC was 38 300 (M_w/M_n = 1.54). IR (film): 3070 ($\nu_{\text{aromatic C-H}}$), 2967 ($\nu_{\text{aliphatic C-H}}$), 1250 ($\nu_{\text{C-O-C}}$), 1098 ($\nu_{\text{Si-O}}$), 758 cm^{-1} ($\nu_{\text{C-Cl}}$). ^{1}H NMR (90 MHz, CDCl$_3$, TMS): δ 1.59 (s, 6H, CH$_3$), 3.68–3.72 (m, 4H, CH$_2$Cl), 3.98–4.07 (m, 4H, C–CH$_2$–O), 4.39–4.51 (m, 1.9H, O–CHO, 6.59–7.74 ppm (m, 18H, aromatic protons). Anal. Calcd for $C_{33}H_{34}O_4Cl_2Si$: C, 66.77; H, 5.77. Found: C, 66.86; H, 5.49.

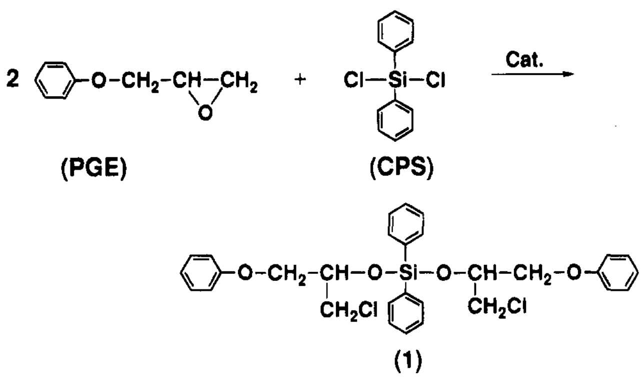
Synthesis of Poly(silyl ether) 2b from BPGE with CMSE. BPGE (0.5107 g, 1.5 mmol) was made to react with CMSE (0.3229 g, 1.5 mmol) in the presence of TBPC (4.4 mg, 0.015 mmol) in toluene (1.5 mL) at 50 °C for 24 h. The reaction mixture was diluted with chloroform and washed with water, and some amount of chloroform was evaporated. The polymer solution was poured into hexane, reprecipitated twice from chloroform into hexane, and dried *in vacuo* at 50 °C. The yield of polymer **2b** was 0.556 g (67%). The M_n of the polymer determined from GPC was 23 200 (M_w/M_n = 1.39). IR (film): 3032 ($\nu_{\text{aromatic C-H}}$), 2962 ($\nu_{\text{aliphatic C-H}}$), 1251 ($\nu_{\text{C-O-C}}$), 1101 ($\nu_{\text{Si-O}}$), 754 cm^{-1} ($\nu_{\text{C-Cl}}$). ^{1}H NMR (90 MHz, CDCl$_3$, TMS): δ 0.09–0.14 (m, 12H, Si–CH$_3$), 0.52–0.57 (m, 4H, Si–CH$_2$), 1.62 (s, 6H, CH$_3$), 3.55–3.64 (m, 4H, CH$_2$Cl), 3.89–3.98 (m, 4H, C–CH$_2$–O), 4.08–4.25 (m, 1.8H, O–CH), 6.72–7.17 ppm (m, 8H, aromatic protons). Anal. Calcd for $C_{27}H_{40}O_4Cl_2Si_2$: C, 58.36; H, 7.26. Found: C, 58.22; H, 7.57.

Synthesis of Poly(silyl ether) 2c from BPGE with CPMCS. The polyaddition of BPGE (0.5107 g, 1.5 mmol) and CPMCS (0.2537 g, 1.5 mmol) was carried out in the presence of TBPC (4.4 mg, 0.015 mmol) in toluene (1.5 mL) at 50 °C for 24 h, and the product was purified by the same procedure as described for **2a**. The final yield of polymer **2c** was 0.709 g (93%). The M_n of the polymer determined from GPC was 21 900 (M_w/M_n = 1.78). IR (film): 3032 ($\nu_{\text{aromatic C-H}}$), 2962 ($\nu_{\text{aliphatic C-H}}$), 1246 ($\nu_{\text{C-O-C}}$), 1095 ($\nu_{\text{Si-O}}$), 774 cm^{-1} ($\nu_{\text{C-Cl}}$). ^{1}H NMR (90 MHz, CDCl$_3$, TMS): δ 0.57–1.93 (br, 16H, Si–CH$_2$, C–CH$_2$–C, and CH$_3$), 3.62–3.70 (m, 4H, CH$_2$Cl), 3.97–4.03 (m, 4H, C–CH$_2$–O), 4.28–4.51 (m, 1.9H, O–CH), 6.72–7.66 ppm (m, 8H, aromatic protons). Anal. Calcd for $C_{26}H_{34}O_4Cl_2Si$: C, 61.29; H, 6.73. Found: C, 60.88; H, 6.96.

Synthesis of Poly(silyl ether) 2d from BPGE with CMSEB. BPGE (0.5107 g, 1.5 mmol), CMSEB (0.4792 g, 1.5 mmol), and TBPC (4.4 mg, 0.015 mmol) were dissolved in toluene (1.5 mL), and the solution was stirred at 50 °C for 24 h. The final yield of polymer **2d** was 0.369 g (37%). The M_n of the polymer determined from GPC was 9000 (M_w/M_n = 1.26). IR (film): 3034 ($\nu_{\text{aromatic C-H}}$), 2956 ($\nu_{\text{aliphatic C-H}}$), 1249 ($\nu_{\text{C-O-C}}$), 1129 ($\nu_{\text{Si-O}}$), 782 cm^{-1} ($\nu_{\text{C-Cl}}$). ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ 0.04–0.27 (m, 12H, Si–CH$_3$), 0.89–1.07 and 1.43–1.52 (m, 4H, Si–CH$_2$), 1.62 (s, 6H, CH$_3$), 2.18–2.30 and 2.46–2.74 (m, 4H, Ph–CH$_2$), 3.36–4.09 (m, 8H, CH$_2$Cl and O–CH$_2$–C), 4.13–4.28 (m, 1.9H, CH), 6.64–7.48 ppm (m, 12H, aromatic protons).

Synthesis of Poly(silyl ether) 2e from EGGE with CPS. EGGE (0.2613 g, 1.5 mmol) was allowed to react with CPS (0.3798 g, 1.5 mmol) in the presence of TBPC (4.4 mg, 0.015 mmol) in toluene (1.5 mL) at 50 °C for 24 h. The final yield of polymer **2e** was 0.492 g (77%). The M_n of the polymer determined from GPC was 17 400 (M_w/M_n = 1.38). IR (film): 3066 ($\nu_{\text{aromatic C-H}}$), 2868 ($\nu_{\text{aliphatic C-H}}$), 1124 ($\nu_{\text{C-O-C}}$), 1089 ($\nu_{\text{Si-O}}$), 741 cm^{-1} ($\nu_{\text{C-Cl}}$). ^{1}H NMR (90 MHz, CDCl$_3$, TMS): δ 3.38–3.64 (m, 12H, CH$_2$Cl and O–CH$_2$–C), 4.08–4.26 (m, 1.8H, O–CH), 7.33–7.71 ppm (m, 10H, aromatic protons). Anal. Calcd for $C_{20}H_{24}O_4Cl_2Si$: C, 56.21; H, 5.66. Found: C, 56.09; H, 5.64.

Scheme 1



Synthesis of Poly(silyl ether) 2f from EGGE with CMSE. To EGGE (0.2613 g, 1.5 mmol) in toluene (1.5 mL) was added CMSE (0.3229 g, 1.5 mmol) and TBPC (4.4 mg, 0.015 mmol). The mixture was stirred at 50 °C for 24 h. The final yield of polymer **2f** was 0.323 g (55%). The M_n of the polymer determined from GPC was 10 800 (M_w/M_n = 1.31). IR (film): 2952 and 2896 ($\nu_{\text{aliphatic C-H}}$), 1134 ($\nu_{\text{C-O-C}}$), 1052 ($\nu_{\text{Si-O}}$), 750 cm^{-1} ($\nu_{\text{C-Cl}}$). ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ 0.04–0.28 (m, 12H, Si–CH$_3$), 0.54 (s, 4H, Si–CH$_2$), 3.48–3.75 (m, 12H, C–CH$_2$–O and CH$_2$Cl), 3.92–4.19 ppm (m, 1.9H, O–CH). Anal. Calcd for $C_{14}H_{30}O_4Cl_2Si_2$: C, 43.18; H, 7.76. Found: C, 43.53; H, 7.73.

Results and Discussion

The addition reaction of PGE with CPS was performed as a model reaction for the polyaddition of bis(epoxide)s with dichlorosilanes or bis(chlorosilane)s. The reaction proceeded very smoothly using TBAB as a catalyst in toluene at 0–5 °C for 1 h, continuing at room temperature for 23 h to give the corresponding silyl ether **1** in 79% yield. The structure of the obtained adduct **1** was determined by IR and ^{1}H NMR spectra. The IR spectrum of **1** showed absorption peaks at 3066, 2934, 1243, 1095, and 753 cm^{-1} due to aromatic C–H, aliphatic C–H, C–O–C, Si–O, and C–Cl stretchings, respectively. The ^{1}H NMR spectrum of this compound exhibited the corresponding proton signals at 3.68–3.75 due to CH$_2$Cl, at 4.00–4.11 due to CH$_2$–O, at 4.36–4.58 due to O–CH, and at 6.68–7.79 ppm due to the aromatic protons. Furthermore, from the intensity ratio of methine protons at 4.36–4.58 ppm vs the aromatic protons at 6.68–7.79 ppm, the ratio of β-scission of the epoxy group of PGE was calculated as about 95%. This result suggests that the addition reaction of PGE with CPS proceeded with high regioselectivity to give silyl ether **1** as shown in Scheme 1, although about 5 mol % of α-scission of the epoxy group of PGE also occurred upon the reaction with CPS.

As summarized in Table 1, the polyaddition of BPGE with CPS was carried out without catalyst or with DMAP as a catalyst at 0 °C for 1 h, and then at room temperature for 23 h; however, the polymer was not obtained at all. On the other hand, poly(silyl ether)s **2a** with relatively low molecular weights such as M_n = 5800–6800 were obtained in 44 and 62% yields under the same conditions when TPP and 18-C-6/KCl complex were used as catalysts, respectively. Poly(silyl ether)s **2a** with relatively high molecular weights such as M_n = 10 700–23 500 were prepared in 81–99% yields

Table 1. Polyaddition of BPGE with CPS using Various Catalysts[a]

run no.	catalyst	yield, %	$10^{-4}M_n$[b]	M_w/M_n[b]
1	none	0		
2	DMAP	0		
3	TPP	44	0.58	1.08
4	18-C-6/KCl	62	0.68	1.08
5	TBAB	81	1.07	1.25
6	TBAC	97	2.35	1.47
7	TBPB	81	1.82	1.39
8	TBPC	99	2.10	1.48
9	THAB	86	1.67	1.39

[a] The reactions were carried out with 1.5 mmol of BPGE and 1.5 mmol of CPS in toluene (0.75 mL) using the catalyst (0.015 mmol) at 0 °C for 1 h, and then at room temperature for 23 h. [b] Estimated by GPC based on polystyrene standards.

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

run no.	solvent	yield, %	$10^{-4}M_n$[b]	M_w/M_n[b]
10	toluene	99	2.10	1.48
11	anisole	87	1.96	1.40
12	*o*-dichlorobenzene	80	1.50	1.37
13	THF	81	1.15	1.30
14	DMF	83	1.19	1.34
15	DMAc	78	0.99	1.21
16	NMP	81	1.31	1.35

[a] The reactions were carried out with 1.5 mmol of CPS and 1.5 mmol of BPGE in toluene (0.75 mL) using TBPC (0.015 mmol) as a catalyst at 0 °C for 1 h, and then at room temperature for 23 h. [b] Estimated by GPC based on polystyrene standards.

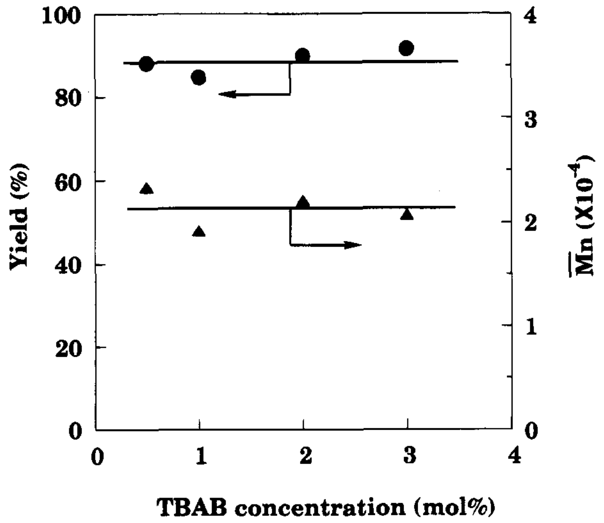


Figure 1. Effect of the TBAB concentration on the reaction of BPGE (1.5 mmol) with CPS (1.5 mmol) in toluene (0.75 mL) at 0 °C for 1 h, and then at room temperature for 23 h.

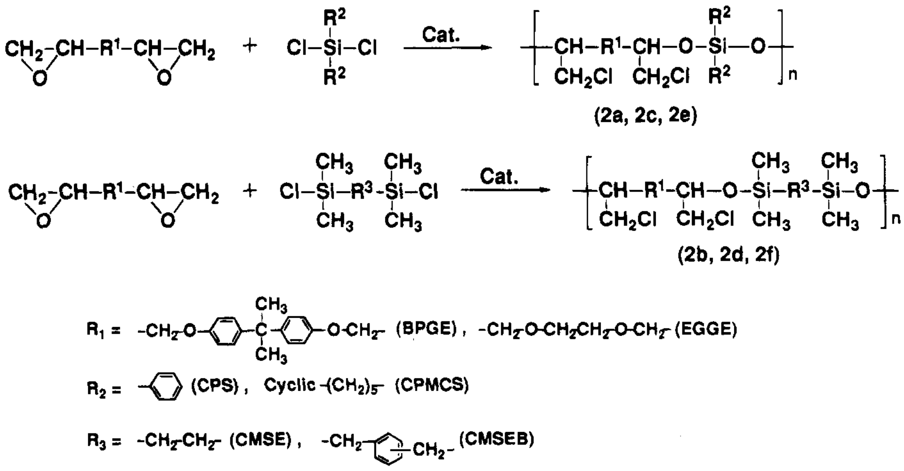
under the same reaction conditions, when TBAB, TBAC, TBPC, TBPB, or THAB was used as catalyst. These results show that the polyaddition of BPGE with CPS proceeded very smoothly using TPP, 18-C-6/KCl, and quaternary onium salts as catalysts under mild reaction conditions and that quaternary onium salts such as TBAC and TBPC also have very high 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 1250, 1098, and 758 cm^{-1} due to C–O–C, Si–O, and C–Cl stretchings, respectively. In the ^{1}H NMR spectrum of polymer **2a**, the corresponding proton signals were observed at 1.59 (C–CH$_3$), 3.68–3.72 (CH$_2$Cl), 3.98–4.07 (CH$_2$–O), 4.39–4.51 (O–CH), and 6.59–7.74 ppm (aromatic protons), respectively. The intensity ratio calculated from methine protons at 4.39–4.51 ppm vs the aromatic protons at 6.59–7.74 was 0.95. This shows that poly(silyl ether) **2a** with pendant chloromethyl groups in the side chain was synthesized by the polyaddition of BPGE with CPS using certain suitable catalysts; however, the regioselectivity of the obtained polymer was about 95%, the same as the addition reaction of PGE with CPS. Therefore, almost all polymer **2a** has the structure shown in Scheme 2.

The polyaddition of BPGE with CPS was also performed in various organic solvents using 2 mol % TBPC as the catalyst at 0 °C for 1 h, and then at room temperature for 23 h. As summarized in Table 2, polymers **2a** with relatively high molecular weights were obtained, when the reactions were carried out in aromatic and lipophilic solvents such as toluene, anisole, and *o*-dichlorobenzene. Molecular weights (M_n) of the polymers **2a** prepared in hydrophilic solvents such as THF, DMF, DMAc, and NMP were slightly lower than those of the polymer obtained in the former solvents. It seems that trace water contained in the hydrophilic solvents, which could not be removed completely, caused the hydrolysis of dichlorosilane compound CPS.

The effect of the catalyst concentration on the polyaddition of BPGE with CPS in the presence of TBAB in toluene under the same conditions was examined. As shown in Figure 1, polymers **2a** with mostly the same molecular weights (about M_n = 21 000) were obtained with about 90% yields within the 0.5–3 mol % range of catalyst concentration. It seems that the polyaddition of BPGE with CPS was mostly finished under the these

Scheme 2



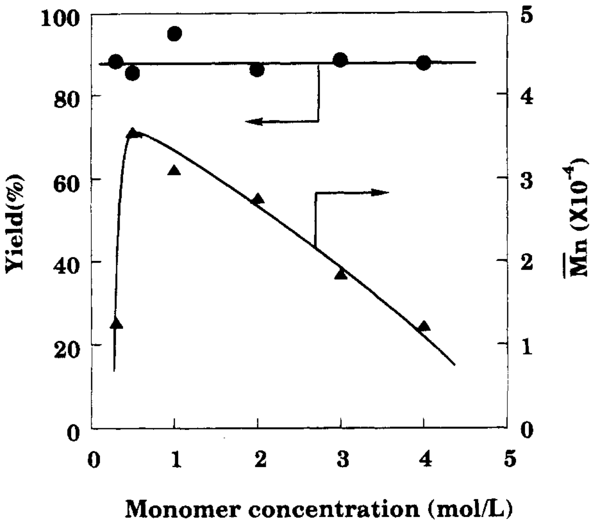


Figure 2. Effect of the monomer concentration on the reaction of BPGE with CPS in toluene using 2 mol % TBAC as the catalyst at 0 °C for 1 h, and then at room temperature for 23 h.

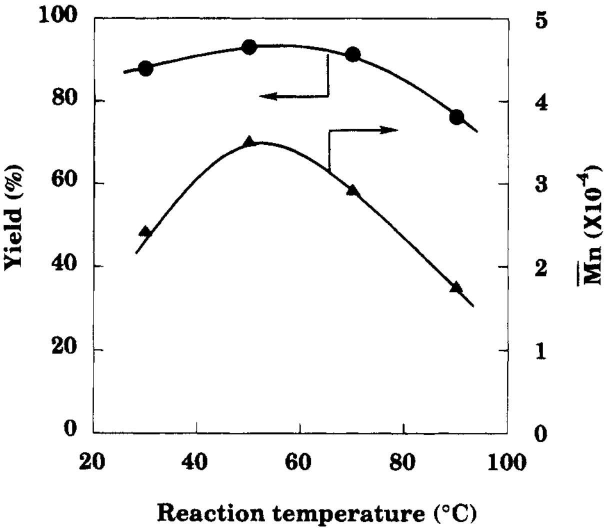


Figure 3. Effect of the reaction temperature on the reaction of BPGE (1.5 mmol) with CPS (1.5 mmol) in toluene (0.75 mL) using 2 mol % TBAC for 24 h.

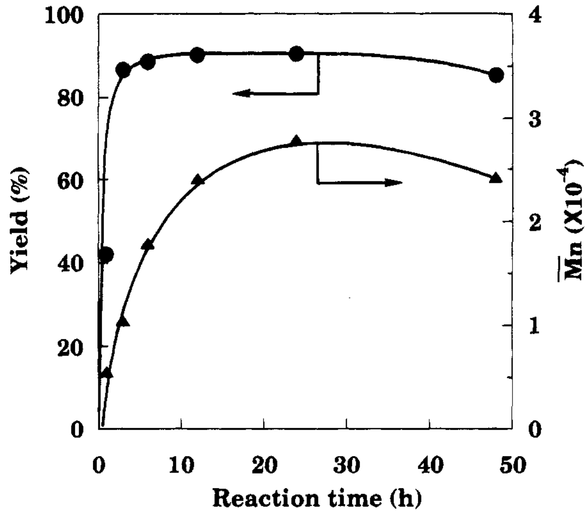


Figure 4. Effect of the reaction time on the reaction of BPGE (1.5 mmol) with CPS (1.5 mmol) in toluene (0.75 mL) using 2 mol % TBAC at 50 °C.

conditions, although the initial rate of the reaction was enhanced by increasing the catalyst concentration.

As shwon in Figure 2, although the yield of the polymer was not related to the monomer concentration, the molecular weight of the resulting polymer was strongly affected by the monomer concentration on the polyaddition of BPGE with CPS in toluene using TBAC as the catalyst at 0 °C for 1 h, and then at room temperature for 23 h. The number average molecular weight of polymer **2a** increased with monomer concentration and showed the highest molecular weight at 1 mol/L of the monomer concentration. However, the molecular weight of the polymer decreased gradually with increasing concentration. This result means that the polyaddition of terminal reactive groups in the polymer chains was hindered in the last stage of the reaction due to high viscosity of the produced polymer, when the reaction was carried out under high monomer concentrations.

The effect of the reaction temperature was examined in toluene for 24 h, in which 2 mol % TBAC was used as the catalyst. As shown in Figure 3, polymer **2a** with the highest molecular weight was obtained at 50 °C, and the molecular weight of the polymer decreased with increasing or decreasing temperature. The same tendency was also found with regard to the yield of polymer. These results indicate that the produced poly(silyl ether) **2a** decomposed gradually with heating, although the initial rate of the polyaddition was enhanced by heating.

The effect of the reaction time on the polyaddition of BPGE with CPS was investigated using 2 mol % TBAC as the catalyst in toluene at 50 °C. As shown in Figure 4, both the yield and the molecular weight of the resulting polymer increased with reaction times up to 2 and 24 h, respectively. However, both the yield and the molecular weight decreased slightly at 48 h. This result suggests that the produced poly(silyl ether) **2a** decomposed gradually due to stirring or heating for a longer time.

Polyaddition of various bis(epoxide)s with dichlorosilane or bis(chlorosilane)s was performed using 2 mol % TBPC as the catalyst in toluene at 50 °C for 24 h. As summarized in Table 3, the polyaddition of BPGE with CPS gave the corresponding polymer **2a** with high

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

	monomer					
polym no.	bis(epoxide)	dichlorosilane	yield, %	$10^{-4} M_n$[b]	M_w/M_n[b]	$S\beta$,[c] %
2a	BPGE	CPS	90	3.83	1.54	95
2b	BPGE	CMSE	67	2.32	1.39	90
2c	BPGE	CPMCS	93	2.19	1.78	95
2d	BPGE	CMSEB	37	0.90	1.26	95
2e	EGGE	CPS	77	1.74	1.38	90
2f	EGGE	CMSE	55	1.08	1.31	95

[a] The reactions were carried out with 1.5 mmol of bis(epoxide) and 1.5 mmol of dichlorosilane or bis(chlorosilane) in toluene (1.5 mL) using TBPC (0.015 mmol) as a catalyst at 50 °C for 24 h. [b] Estimated by GPC based on polystyrene standards. [c] Selectivity of β-cleavage.

Table 4. Solubility of Poly(silyl ether)s[a]

solvent	polymer 2a	2b	2c	2d	2e	2f
methanol	−	−	−	−	−	−
hexane	−	−	−	−	−	−
acetonitrile	−	−	−	−	++	++
acetone	++	++	++	++	++	++
ethyl acetate	++	++	++	++	++	++
chloroform	++	++	++	++	++	++
toluene	++	++	++	++	++	++
anisole	++	++	++	++	++	++
o-dichlorobenzene	++	++	++	++	++	++
THF	++	++	++	++	++	++
DMF	++	++	++	++	++	++
NMP	++	++	++	++	++	++
DMSO	++	++	++	++	++	++

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

molecular weight (M_n = 38 300). The polyaddition of BPGE with CMSE and CPMCS produced the corresponding poly(silyl ether)s **2b** and **2c** with high molecular weights, respectively. Poly(silyl ether) **2d** was also synthesized by the polyaddition of BPGE with CMSEB; however, the yield and the molecular weight of the resulting polymer were both too low. Poly(silyl ether)s **2e** and **2f** with relatively high molecular weights were obtained in 77 and 55% yields from the polyaddition of EGGE with CPS and CMSE, respectively.

The solubility of the poly(silyl ether)s (**2a**−**2f**) was examined. As summarized in Table 4, all of the poly(silyl ether)s were insoluble in methanol and hexane. Furthermore, poly(silyl ether)s **2a**, **2b**, **2c**, and **2d** prepared by the polyaddition with BPGE were insoluble in acetonitrile, although poly(silyl ether)s **2e** and **2f** prepared by the polyaddition with EGGE were soluble in acetonitrile. However, all the obtained poly(silyl ether)s were soluble in various organic solvents such as acetone, ethyl acetate, chloroform, toluene, anisole, *o*-dichlorobenzene, THF, DMF, NMP, and DMSO. Poly(silyl ether)s with a pendant chloromethyl group synthesized by the polyaddition of bis(epoxide)s with dichlorosilanes or bis(chlorosilane)s had very good solubilities in common organic solvents probably due to the poly(silyl ether) linkage, while poly(silyl ether)s **2e** and **2f** due to the oxyethylene chain showed higher solubilities than poly(silyl ether)s **2a**, **2b**, **2c**, and **2d** with the Bisphenol A skeleton in the main chain.

Acknowledgment. This work was supported by a grant from the Ministry of Education, Science, and Culture of Japan (No. 05650907), which is gratefully acknowledged.

References and Notes

(1) For example: Wright, P. V. In *Ring Opening Polymerization*; Ivin, K. J.; Saegusa, T., Eds.; Elsevier: London, **1984**; Vol. 2, pp 1055−1133.
(2) Lai, Yu-C.; Dvornic, P. R.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2277.
(3) (a) Dvornic, P. R.; Lenz, R. W. *J. Appl. Polym. Sci.* **1980**, *25*, 641. (b) Dvornic, P. R.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 593. (c) Dvornic, P. R.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 951.
(4) (a) Breed, L. W.; Elliott, R. L. Whitehead, M. E. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 2745. (b) Pittman, C. U., Jr.; Patterson, W. J.; Mcmanus, S. P. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1715. (c) Babu, N. G.; Newmark, R. A. *Macromolecules* **1991**, *24*, 4503.
(5) For example: (a) Zhang, X. H.; West, R. *J. Polym. Sci., Part A: Polym. Chem.* **1984**, *22*, 225. (b) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.
(6) (a) Carraher, C. E., Jr. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 2351. (b) Carraher, C. E., Jr.; Klimiuk, C. H. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 973.
(7) (a) Dunnavant, W. R.; Markle, R. A.; Stickney, P. B.; Curry, J. E.; Byrd, J. D. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 707. (b) Dunnavant, W. R.; Markle, R. A.; Sinclair, R. G.; Stickney, P. B.; Curry, J. E.; Byrd, J. D. *Macromolecules* **1968**, *1*, 249.
(8) Padamanaban, M.; Kakimoto, M.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 2997.
(9) (a) Nishikubo, T.; Iizawa, T.; Matsumura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 1975. (b) Nishikubo, T. Kameyama, A. *Prog. Polym. Sci.* **1993**, *18*, 963.
(10) Kameyama, A.; Watanabe, S.; Kobayashi, E.; Nishikubo, T. *Macromolecules* **1992**, *25*, 2307.
(11) For example: Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer: Berlin, 1983; pp 21−39.
(12) Andrews, G. C.; Crawford, T. C.; Contillo, L. D., Jr. *Tetrahedron Lett.* **1981**, *22*, 3803.

MA946219D