

SHORT COMMUNICATIONS

A Novel Synthesis of Poly(silyl ether)s by Addition Reactions of Diepoxide with Dichlorosilane Compounds

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The addition reaction of trimethylsilyl halides with cyclic ethers is a very useful reaction¹ in various organic syntheses. It was found² that both the rate and regioselectivity of the reaction were strongly enhanced by addition of either triphenylphosphine or tetrabutylammonium chloride as catalysts. Poly(siloxane)s are usually synthesized³ by the catalytic ring opening polymerization of cyclic siloxanes, and poly(silane)s, which can be used as positive type photo-resists, are obtained⁴ by the reaction of dichlorosilane compounds with sodium metal. However, there is no report on the synthesis of organosilicone polymers by the reaction of a dichlorosilane compound with a cyclic ether.

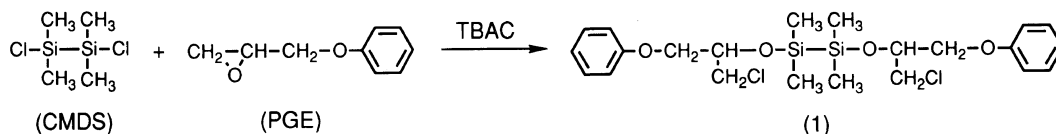
Recently, we found^{5,6} the regioselective addition reactions of diepoxide with diacyl chlorides or active diesters proceeded very smoothly to give the corresponding poly(ester)s when catalyzed by quaternary onium salts. In this paper, we report a novel synthesis of new poly(silyl ether)s by addition reactions of diepoxide with dichlorosilane compounds using quaternary onium salts as catalysts.

Dichlorotetramethyldisilane (CMDS) (bp 146—148 °C) was synthesized in 44% yield by the reaction of hexamethyldisilane with acetyl

chloride using aluminum chloride as a catalyst, as reported previously.⁷ Bisphenol A diglycidyl ether (BPGE) (epoxy equivalent; 171.1) was recrystallized four times from the mixed solvent of methanol and methylethyl ketone (4 : 1, v/v). Reagent grade dichlorodiphenylsilane (CPS) was used without further purification.

The addition reaction of CMDS (0.9361 g; 5 mmol) with phenyl glycidyl ether (PGE) (1.5018 g; 10 mmol) was carried out in toluene (4 ml) using tetrabutylammonium chloride (TBAC) (0.0035 g; 0.125 mmol) as a catalyst at 0°C for 1 h, and then at room temperature for 7 h. The reaction mixture was washed twice with minimal amounts of water, and the solvent was evaporated *in vacuo*. The crude product thus obtained was purified by silica gel column chromatography using chloroform as the eluent: The isolated yield of the resulting silyl ether (**1**) was 2.06 g (84.5%). The IR spectrum of **1** showed absorption peaks at 3036, 2960, 1247, 1093, and 770 cm⁻¹ due to aromatic C—H, aliphatic C—H, C—O—C, Si—O, and C—Cl stretching, respectively. The ¹H NMR spectrum (90 MHz, CDCl₃, TMS) of this compound showed proton signals at δ = 0.27 (s, 12H, Si—CH₃), 3.42—3.85 (m, 4H, CH₂Cl),

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Scheme 1.

Table I. Polyaddition reactions of CMDS and CPS with BPGE using various catalysts^a

Silyl chloride	Catalyst	Solvent	Yield		
			%	\bar{M}_n^b	\bar{M}_w/\bar{M}_n
CMDS	TBAC	toluene	91	25400	1.54
CMDS	TBAC	nitrobenzene	80	19200	1.38
CMDS	TBAC	THF	88	28700	1.59
CMDS	TBAC	DMAc	88	24300	1.54
CMDS	TBAB	toluene	91	29000	1.62
CMDS	TBPC	toluene	87	26400	1.54
CMDS	TPP	toluene	90	9300	1.49
CPS	TBAC	toluene	90	11000	1.44

^a The reactions were carried out with 2.5 mmol of CMDS (or CPS) and 2.5 mmol of BPGE in the solvent (2 ml) using 1 mol% of the catalyst at 0°C for 1 h, and then at room temperature for 23 h.

^b From GPC elution volume, relative to poly(styrene).

3.90–4.05 (m, 4H, O–CH₂–C), 4.10–4.35 (m, 2H, CH), and 6.80–7.40 ppm (m, 10H, aromatic protons). This result means that the addition reaction of CMDS with PGE, which is considered as a model of the polymerization reaction, proceeded very smoothly and regioselectively under mild reaction conditions using a quaternary ammonium salt as the catalyst.

Polyaddition reaction of CMDS (0.4680 g; 2.5 mmol) with BPGE (0.8511 g; 2.5 mmol) was carried out in various solvents (2 ml) in the presence 1 mol% of the catalyst at 0–5 °C for 1 h, and then at room temperature for 23 h. The reaction mixture was washed twice using little water, then poured into hexane. The polymer obtained was reprecipitated twice from chloroform by hexane, and dried *in vacuo* at 90 °C. As summarized in Table I, the reaction proceeded successfully in various solvents using 1 mol% of TBAC as the catalyst, and the cor-

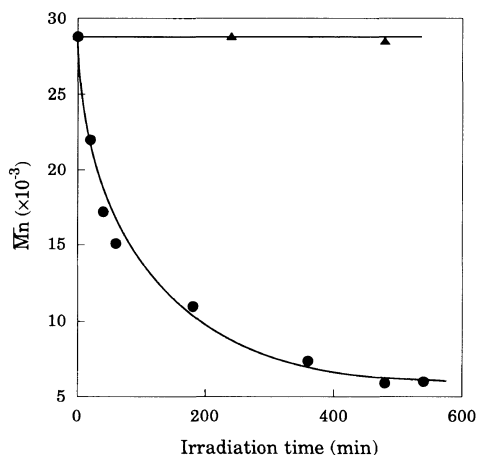
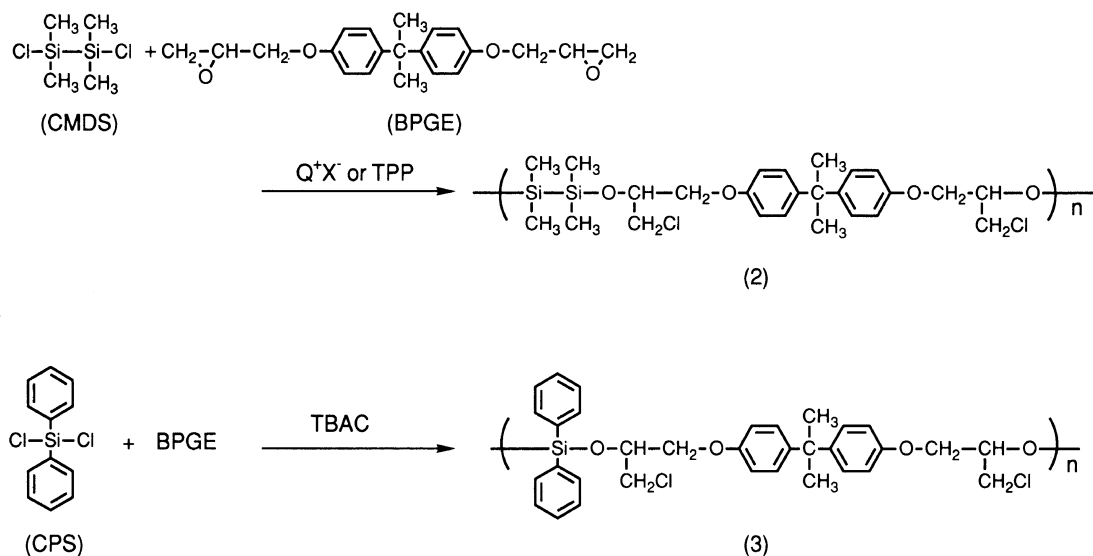


Figure 1. Plots of the molecular weight of polymer 2 vs. irradiation time by high-pressure mercury lamp: (●) with irradiation; (▲) without irradiation.

responding poly(silyl ether) with Si–Si bond in the main chain (2) was obtained. However, these results also suggest that the degree of polymerization was strongly affected by the reaction solvent. That is, polymer 2 with relatively high molecular weight was obtained in toluene, THF, and DMAc. It was also found that quaternary onium salts such as TBAC, tetrabutylammonium bromide (TBAB), and tetrabutylphosphonium chloride (TBPC) had higher catalytic activity than triphenylphosphine (TPP) in the reaction of CMDS with BPGE. The IR spectrum of polymer 2 showed absorption peaks at 3032, 2958, 1247, 1093, and 769 cm⁻¹ due to aromatic C–H, aliphatic C–H, C–O–C, Si–O, and C–Cl stretching, respectively. The ¹H NMR spectrum (90 MHz, CDCl₃, TMS) of this compound showed proton signals at δ=0.31 (s, 12H, Si–CH₃), 1.61 (s, 6H, C–CH₃), 3.52–3.80 (m, 4H, CH₂Cl), 3.82–4.00 (m, 4H, O–CH₂–C),

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Scheme 2.

4.05—4.35 (m, 2H, CH), and 6.76—7.12 ppm (m, 8H, aromatic protons).

As shown in Figure 1, the molecular weight of polymer 2 decreased rapidly when irradiation was carried out in THF solution (0.132 g/100 ml), which was charged into a quartz flask, using 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D) under nitrogen. This result suggests that polymer 2 has a function as positive type photo-resist.

The reaction of CPS with BPGE was performed under the same reaction conditions as above. As summarized in Table I, corresponding poly(silyl ether) (3) was formed in high yield. The IR spectrum of polymer 3 showed absorption peaks at 3046, 2964, 1247, 1095, and 755 cm^{-1} due to aromatic C-H, aliphatic C-H, C-O-C, Si-O, and C-Cl stretching, respectively. The ^1H NMR spectrum (90 MHz, CDCl_3 , TMS) of this compound showed proton signals at $\delta = 1.60$ (s, 6H, C-CH₃), 3.55—3.82 (m, 4H, CH₂Cl), 3.85—4.35 (m, 4H, O-CH₂-C), 4.37—4.57 (m, 2H, CH), 6.58—7.18 (m, 8H, aromatic protons of

O-Ar), and 7.30—7.82 ppm (m, 10H, aromatic protons of Si-Ar).

From these results, it is clear that two new poly(silyl ether)s, polymer 2 and polymer 3, were synthesized by the novel addition reactions of both CMDS and CPS with BPGE under mild reaction conditions using quaternary onium salts or TPP as catalysts.

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