Anionic Ring-opening Polymerization of 1,1,2,2-Tetramethyl-1,2-disilacyclohexane: Homopolymerization, Alternating Copolymerization with 1,2-Epoxycyclohexane and Oxygen-abstracting Polymerization with 1,2-Epoxybutane

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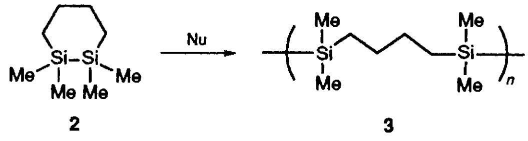
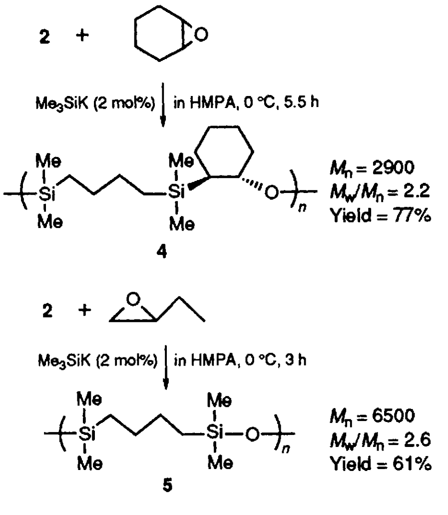
The ring-opening polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclohexane was conducted by anionic initiators; the homopolymer, the alternating copolymer with 1,2-epoxycyclohexane, and the siloxane polymer by oxygen-abstracting polymerization with 1,2-epoxybutane are produced.

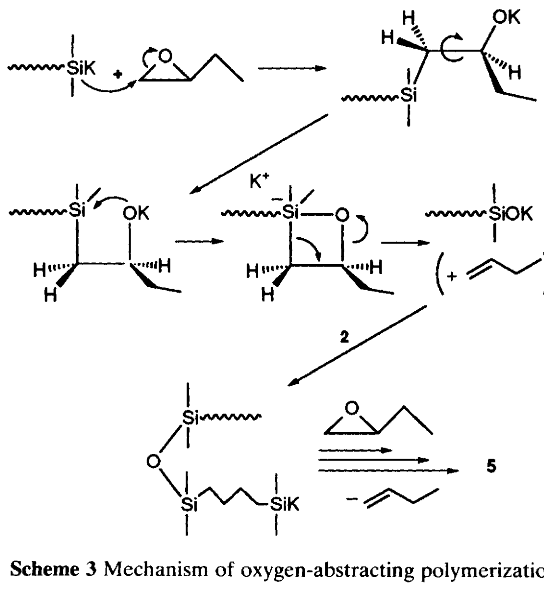
In order to shed light on the chemistry of silicon active species in polymerization, we are investigating the ring-opening polymerization of cyclic compounds having a Si–Si bond(s), whose scission is the key step to generate a silicon active species. In this context, we have recently published the anionic ring-opening polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane **1**.[1] This paper deals with the ring-opening polymerization of the six-membered homologue, *i.e.* 1,1,2,2-tetramethyl-1,2-disilacyclohexane **2**,[2] including not only the anionic homopolymerization but also the unique copolymerization with epoxides.



Scheme 1



Scheme 2



Scheme 3 Mechanism of oxygen-abstracting polymerization

The polymerization of **2** took place under conditions similar to those of the polymerization of **1** (Scheme 1, Table 1). Anionic initiators such as Me$_3$SiK,[3] MeLi and Bu$_4$NF conducted the polymerization in HMPA or in THF with HMPA (or with crown ether). In contrast with the polymerization of **1**, which was almost completely consumed within a few hours, the reaction of **2** became very slow or stopped before the complete conversion of **2**. This is ascribable to the smaller ring strain of **2** than **1**.[2] The ^{13}C NMR spectroscopy indicated that the product polymers **3**‡ were contaminated by a siloxane unit, whose amount was dependent on the initiator and the reaction solvent [see footnote (*h*) of Table 1]. Since the contamination was too much in some cases (runs 5 and 7), we supposed that HMPA supplied its oxygen to the polymer. However, the deoxygenated product, *i.e.* hexamethylphosphorous triamide, was not detected in the reaction mixture; the source of oxygen is still unknown. To make the polymer, which is hardly contaminated with the siloxane unit, quickly and in high yield, Me$_3$SiK is the preferred initiator.

Since low homopolymerizability is rather advantageous for controlled copolymerization, we subsequently proceeded to explore the copolymerization of **2**.[4] Taking the oxygen affinity of silicon into account, we employed epoxides as a partner for **2** in the copolymerization and consequently found interesting behaviour in the anionic copolymerization with epoxides. Two specific copolymerization styles, which were defined by the epoxide structure, took place in HMPA with Me$_3$SiK as the initiator (Scheme 2). Alternating copolymer **4**‡ was produced from **2** with 1,2-epoxycyclohexane, whereas poly-[tetramethylene(tetramethyl)disiloxane] **5**‡ from **2** with 1,2-epoxybutane. In the latter copolymerization, only the oxygen of 1,2-epoxybutane was incorporated into the product polymer, and but-1-ene was released simultaneously. Thus, we termed this unique polymerization 'oxygen-abstracting polymerization', whose occurrence we anticipated because it had been known that hexamethyldisilane with a catalytic amount of potassium methoxide conducts the deoxygenation of epoxides to produce olefin and hexamethyldisiloxane.[5] Scheme 3 shows the mechanism of the oxygen-abstracting polymerization of **2** with 1,2-epoxybutane. The key step is the *syn*-elimination of siloxy potassium, namely the Peterson elimination.[6] The striking contrast between 1,2-epoxycyclohexane and 1,2-epoxybutane in the copolymerization with **2** is attributed to this step. Since the back-side attack of silyl potassium opens an epoxy ring to position the silyl group and the oxypotassium group to the *anti*-configuration, C–C bond rotation is required for the *syn*-elimination (Scheme 3). The cyclohexane ring does not allow this rotation. Thus, the copolymerization of **2** with 1,2-epoxycyclohexane proceeded without the Peterson elimination. It should be noted that the selective polymerization required Me$_3$SiK as the initiator and HMPA as the reaction solvent. When the copolymerization was initiated by MeLi (or Bu$_4$NF) or carried out in THF–

Table 1 Anionic ring-opening polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclohexane **2**

Run	Initiator[a]	Solvent	T/°C	t/h	Conv. (%)	Yield (%)[b,c]	M_n[d]	M_w/M_n[d]
1	Me_3SiK	THF–18-crown-6[e]	0	3	60	30	1600	1.4
2	Me_3SiK	HMPA[f]	0	2.5	60	54	3500	1.9
3	Me_3SiK	THF–HMPA[g]	0	2	70	45	5500	2.9
4	Me_3SiK	THF–HMPA[g]	−25	14	90	80	6200	1.9
5	MeLi	HMPA[f]	0	11	65	35[h]	2800	1.4
6	MeLi	THF–HMPA[g]	0	96		54	5600	1.9
7	Bu_4NF	HMPA[f]	0	20	98	57[h]	4700	2.0
8	Bu_4NF	THF–HMPA[g]	0	6	20	0		

[a] 2 mol% for **2**. [b] MeOH insoluble part. [c] The contamination with the siloxane unit was less than 5% (evaluated by ^{13}C NMR spectra) unless otherwise noted. [d] GPC (PSt standard, eluent: $CHCl_3$). [e] 18-Crown-6 = 2 mol% for **2**. [f] Containing THF (8 vol%) to avoid freezing. [g] THF : HMPA = 1 : 1 (v/v). [h] The contamination with the siloxane unit = 10% (run 5), 25% (run 7).

HMPA (1 : 1), the product polymer consisted of the mixed structure of two or three components, *i.e.* the homopolymer unit of **2**, the alternating copolymer unit and the siloxane unit. The reaction solvent and the counter cation of the propagating end apparently exerted considerable influence upon the relative reactivities of the monomers and the relative rate of the Peterson elimination to the polymerization.

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Footnotes

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‡ Precipitation into methanol gave the oily polymers. *Selected NMR data*: **3** ^{13}C NMR ($CDCl_3$) δ −3.0, 15.8, 29.1; **4** ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 6H), −0.01 (s, 6H), 0.27–0.74 (br, 4H), 0.74–2.14 (br, 13H), 3.37–3.61 (br, 1H); ^{13}C NMR ($CDCl_3$) δ −3.0, −2.8, 0.1, 15.3, 18.4, 25.9, 27.0, 27.2, 27.9, 28.6, 34.8, 38.4, 74.5; **5** ^{13}C NMR ($CDCl_3$) δ 1.2, 18.7, 27.4. Anal.: **4** Calc. for $C_{14}H_{30}OSi_2$: C, 62.15; H, 11.18. Found: C, 61.38; H, 11.29. **5** Calc. for $C_8H_{20}OSi_2$: C, 51.00; H, 10.70. Found: C, 50.51; H, 10.96.

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