

Anionic Ring-opening Polymerization of 1,1,2,2-Tetramethyl-1,2-disilacyclopentane

Masato Suzuki,* Tatsuhiko Obayashi and Takeo Saegusa

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Ring-opening polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane took place with the aid of Me_3SiM ($\text{M} = \text{Na}, \text{K}, \text{Li}$) as initiator.

Silicon-containing polymers such as polysilanes, polycarbosilanes and polysilazanes are of current interest as new materials. New synthetic methods for their production are important not only for material science but also for the study of silicon chemistry, which has hardly been explored in polymerization chemistry to date. We are interested in ring-opening polymerization of cyclic compounds containing a Si-Si bond(s), whose scission is the key step in generating silicon active species. Interestingly, the silicon-silicon σ bond has some analogous character and reactivity to the carbon-carbon π bond,¹ so reference to vinyl polymerization should assist in the design of monomers as well as the ring-opening method (Fig. 1). It is of interest to investigate the similarities and differences between silicon and carbon polymerization chemistry.

To gain fundamental information, we have started our investigation by employing the simplest cyclic compounds containing one silicon-silicon σ bond, *i.e.*, 1,2-disilacycloalkanes. This communication is the first report in this context, dealing with the anionic ring-opening polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane **1** (Scheme 1).² Several examples of ring-opening polymerization of silicon containing compounds, excluding siloxane derivatives, have been reported.³ However, only two papers have reported polymerization involving a silicon-silicon bond. Shiina reported the first example: thermal and AlCl_3 -catalysed (cationic?) ring-opening polymerization of 1,1,2,2-tetramethyl-1,2-disilabenzocyclobutane.⁴ During the course of our investigation, Cypryk *et al.* have published the first finding of an anionic ring-opening polymerization employing 1,2,3,4-tetra-

methyl-1,2,3,4-tetraphenyltetrasilacyclobutane as monomer.⁵ Both of these reports dealt with four-membered cyclic compounds which were much more strained than **1**.

The monomer **1**† was readily polymerized using trimethylsilyl anions, as the initiator, generated *in situ* by the reaction of Me_6Si_2 with MeOK, MeONa or MeLi (Table 1).⁶ After almost complete conversion of **1** (examined by gas chromatography), MeI was added to stop the reaction, causing the characteristic pale yellow colour due to silyl anions to vanish. Precipitation into MeOH gave a colourless oily polymer.‡ The addition of a polar aprotic solvent such as hexamethylphosphoramide (HMPA) and 1,3-dimethylimidazolidin-2-one (DMI) or a small amount of a crown ether into the reaction medium of tetrahydrofuran (THF) was required to realize the progress of the polymerization. A reaction temperature of 0 °C seemed to be optimum, since the polymer produced at room temp. showed a bimodal curve on gel permeation chromatography (GPC) analysis and the reaction below 0 °C was too slow. In any case, the molecular mass of the polymer was lower or higher than the value calculated on the monomer: initiator ratio and also a wide molecular mass

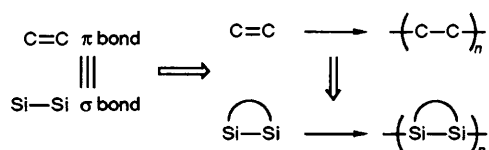
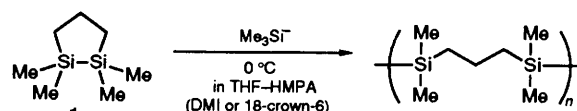


Fig. 1 Design of a new polymerization method

† Monomer **1** was prepared as follows: 2-chloro-2,6,6-trimethyl-2,6-disilaheptane, which was prepared by H_2PtCl_6 -catalysed hydrosilation of allyltrimethylsilane with chlorodimethylsilane, was treated with chlorotrimethylsilane in the presence of AlCl_3 catalyst to give 2,6-dichloro-2,6-dimethyl-2,6-disilaheptane, which was subsequently cyclized to **1** with the aid of lithium metal in THF-HMPA.

‡ ¹H NMR (CDCl_3): δ -0.03 (s, 12H), 0.34-0.77 (t, 4H), 0.94-1.68 (br, 2H). ¹³C NMR (CDCl_3): δ -3.16, 20.26, 20.61. Satisfactory C and H analyses were obtained.

Table 1 Anionic ring-opening polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane **1** at 0 °C

Run	Initiator ^a	Solvent ^b	t/h	Yield (%) ^c	\bar{M}_n^d	\bar{M}_w/\bar{M}_n^e
1	KOMe–Me ₆ Si ₂	THF–HMPA	1.5	69	2800	2.1
2	NaOMe–Me ₆ Si ₂	THF–HMPA	21	64	3000	2.5
3	MeLi–Me ₆ Si ₂	THF–HMPA	22.5	86	13000	1.9
4	KOMe–Me ₆ Si ₂	THF–18-crown-6 ^f	1.5	79	2300	1.9
5	KOMe–Me ₆ Si ₂	THF–DMI ^g	2	57	5200	2.1

^a 2 mol% for the monomer. ^b THF:HMPA (or DMI) = 1:1 (v/v). ^c MeOH insoluble part. ^d Vapour pressure osmometry (in CHCl₃ at 40 °C). ^e GPC (PSt standard, eluent: CHCl₃). ^f 18-crown-6 was added in 3 mol% for **1**. ^g 1,3-Dimethylimidazolidin-2-one.

distribution was observed. Thus, it seems likely that an unfavourable side reaction of chain transfer is occurring.

The propagating end of the polymerization of **1** is assumed to be a silyl anion. Although model reactions of **1** with an equimolar or excess amount of trimethylsilyl anion under various conditions resulted in failure to isolate a 1:1 adduct, it has previously been reported that the reaction of octamethyl-1,2-disilacyclobutane with alkyl lithium caused the Si–Si bond scission.⁷

Further studies are ongoing to disclose the substituent and ring-size effect along with exploring other polymerization methods and monomers. Although, in the present study, **1** was inert under the condition of cationic and radical polymerization, transition metal-catalysed polymerization will be reported in a forthcoming paper.

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