Silacyclobutanes as “Carbanion Pump” in Anionic Polymerization I. Anionic Polymerization of Styrene by Potassium *t*-Butoxide in the Presence of Silacyclobutanes

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Since the concept was established by Szwarc in 1956,¹ living anionic polymerization has been utilized to synthesize unique polymers, such as A-B-A triblock copolymers and star-shaped polymers. However, anionic multi-block polymerization has some limitation in selection of monomers, because of the difference in the reactivity of the propagating anionic species.² For instance, block polymerization from poly(styrene) to ethylene oxide is possible, but impossible *vice versa* because the propagating oxyanion (*O-anion*) cannot initiate the polymerization of styrene to form carbanion (*C-anion*).

Since silacyclobutanes give polymers by thermal,³ transition metal-catalyzed,⁴ and anionic⁵ polymerization due to their high ring-opening reactivity resulting from the large distortional energies (24.5 kcal mol⁻¹),⁶ it was anticipated that *O-anion* might open silacyclobutane ring to form *C-anion*. We actually showed the ring opening reaction of 1-trialkylsiloxysilacyclobutanes by lithium alkoxide.⁷ Similar ring opening of benzosilacyclobutanes by alcohols was also reported.⁸ This ring opening could be a method to convert less reactive propagating *O-anion* into more reactive *C-anion*. This function is significant from the viewpoint of the unrestricted design of multi-block copolymers from various combination of ring-opening and vinyl monomers. A similar idea using 1,1,2,2-tetramethyl- or 1-phenyl-1,2,2-trimethyl-1,2-disilacyclopentane was reported by Teyssié *et al.* to polymerize vinyl monomers by potassium silanolate and poly(ethylene oxide) potassium salt.⁹

In this communication, we report our preliminary results of the anionic polymerization of styrene with potassium *t*-butoxide in the presence of a silacyclobutane derivative (SB).

1,1-Dimethylsilacyclobutane (DMSB),¹⁰ 1-methyl-1-phenylsilacyclobutane (MPSB)¹¹ and 1,1-diphenylsilacyclobutane (DPSB)^{12,13} were synthesized according to the literature and purified by distillation over calcium hydride. Styrene (St) and potassium *t*-butoxide (BuOK) were purified in a common way. Tetrahydrofuran (THF) was dried over sodium and vacuum-transferred. Polymerization was initiated by injection of a silacyclobutane to the mixture of St and BuOK in THF under argon at-

mosphere and terminated by addition of triphenylchlorosilane (TPCS).

When DMSB (2.5 mmol) was injected into a THF (40 mL) solution of BuOK (2.5 mmol) and St (75 mmol), red-dish color of poly(St) anion immediately appeared. Figure 1 shows size exclusion chromatograms of the products without [(a)] and with [(b)] DMSB after the termination by TPCS detected by UV (254 nm). In Figure 1a, only one peak at retention time (rt) = 22.6 min ascribable to St monomer was observed in the absence of any polymers. In Figure 1b, the original peak at rt = 22.6 min disappeared, instead, new peaks at rt = 12.9 and 21.0 min appeared. The low molecular weight peak is assigned to *t*-butoxytriphenylsilane, formed by the reaction of remaining BuOK with TPCS. The conversion of styrene was quantitative.

Figure 1. Size exclusion chromatograms* (a) before and (b) after injection of DMSB into the THF solution of BuOK and St (reaction time: 30 min).

*on the combination of Shodex KF-803L (exclusion limit: $M_n = 7 \times 10^4$, poly(styrene)) and KF-804 (exclusion limit: $M_n = 4 \times 10^5$, poly(styrene)) columns (linear calibration down to $M_n = 100$, poly(styrene)) using THF as an eluent.

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Figure 2. ^1H NMR spectrum of the polymer obtained by the anionic polymerization of St in the presence of DMSB and BuOK.

A high molecular weight component ($\text{rt} = 12.9$) was separated by reprecipitation and characterized by ^1H NMR to be poly(St) (Figure 2). Signals due to the protons of methyl and methylene groups attached to silicon atom were also observed in the spectrum at -0.03 and 0.57 ppm, almost identical positions with those of poly(DMSB), in the ratio of *ca.* 6 : 4. These signals are assigned to the terminal $t\text{-BuOSi}(\text{CH}_3)_2\text{CH}_2\text{—}$ and $\text{—}[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{—}]$ in the polymer chain. The signal due to initiating $t\text{-butoxy}$ group (1.24 ppm) was also observed, overlapped with the broad signal of methylene group of poly(St) backbone ($1.2\text{—}1.8$ ppm). It was considered that BuOK formed a carbanion by ring opening of DMSB, and the formed carbanion initiated St and DMSB polymerizations, and finally gave poly(St) with the incorporation of DMSB during the polymerization.

In order to confirm the formation of carbanion, the reaction between BuOK and DMSB was carried out in the presence of 1,1-diphenylethylene (DPE). The solution of BuOK and DPE was transparent even after one day in the absence of DMSB. On addition of DMSB, reddish orange color immediately appeared. However, the reaction mixture (1 : 1 : 1 molar ratio, 25 mmol dm^{-3}) gave too strong absorption, and only an absorption tail at 600 nm could be distinguished. To detect the λ_{max} , the reaction between BuOK (0.2 mmol) and DMSB (0.4 mmol) was carried out in the presence of DPE ($0.13\text{ }\mu\text{mol}$) in THF (5 mL). A new absorption band was observed in the region from 400 to 600 nm ($\lambda_{\text{max}} = 498\text{ nm}$) (Figure 3). This band is almost identical to the absorption of 1,1-diphenylhexyllithium.¹⁴ Based on these data, it was concluded that BuOK, in the presence of DMSB, formed 3-($t\text{-butoxy}$)dimethylsilylpropyl and propagated $\sim\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$ anions which added to DPE to give alkylidiphenylmethyl anions. We named the function of DMSB to convert an oxyanion into carbanion as “*carbanion pump*” (Scheme 1).

In the presence of St, the formed carbanion by the reaction of BuOK and DMSB polymerized DMSB and St in anionic mechanism. Overall “*carbanion pump*” efficiency (oCPE)¹⁵ will strongly depend on the polymerization conditions. The molecular weight of the resulting poly(St) was much higher than that expected from the ratio of BuOK : DMSB : St, for example, *ca.* 30000 from the system of the feed ratio of 1 : 1 : 30, when DMSB was injected as neat in short period of time. The oCPE was es-

Figure 3. Electronic absorption spectra of (a) before (dashed line) and (b) after (solid line) injection of DMSB into the THF solution of BuOK and DPE. ($[\text{DPE}] = 26\text{ }\mu\text{mol dm}^{-3}$).

timated *ca.* 10% irrespective of the substituents on silicon atom in SB (Table I).

It is crucial to establish the reaction conditions to convert oxyanion efficiently into carbanion to synthesize a block copolymer through the cross propagation from polymeric oxyanion to styrene. Since it was anticipated that this might be a slow initiation and fast propagation system, the dependence of apparent CPE (aCPE)¹⁶ on the reaction conditions was also examined in the presence of excess BuOK over a SB as a preliminary study. The results with the molar ratio of BuOK : SB = 1.0 : 0.5 are shown in Table II. When the feed ratio of SB is reduced to less than BuOK, the aCPE increased, although oCPE decreased (run 1). The effects of the temperature (run 2), solvent polarity (run 3), and concentration of the reagents (run 4) which will strongly affect the efficiency of the initial ring opening are not significant on the aCPE . The addition of diluted DMSB to suppress the ho-

Scheme 1. Concept of "carbanion pump".

Table I. CPE in anionic polymerization of St with BuOK and SBs^a

Run	SB	$M_n (\times 10^{-4})^b$	M_w/M_n^b	$\alpha\text{CPE}^c/\%$
1	DMSB	3.1	1.8	11
2	MPSB	3.4	2.1	9.5
3	DPSB	4.3	2.1	7.5

^a Reaction temperature: -50°C , Solvent: THF (20 mL), SB: neat, $[\text{BuOK}]/[\text{SB}]/[\text{St}] = 1/1/30$ ($[\text{BuOK}] = 0.13 \text{ mol dm}^{-3}$, $[\text{St}] = 3.8 \text{ mol dm}^{-3}$). ^b M_n and M_w/M_n were measured by GPC (poly(styrene) standard). ^c ref 15.

Table II. CPE in anionic polymerization of St with BuOK and DMSB^a

Run	Varied condition	$M_n (\times 10^{-4})^b$	M_w/M_n^b	$\alpha\text{CPE}^c/\%$
1	None	5.4	1.8	11
2	0°C	5.3	1.9	12
3	THF/Toluene = 1/1(v/v)	6.7	1.9	9.3
4	THF (30 mL)	5.5	1.6	11
5	$[\text{DMSB}] = 0.5 \text{ mol dm}^{-3}$	4.7	1.7	13
6	$[\text{BuOK}]/[\text{DMSB}]/[\text{St}] = 1/0.5/60$	6.7	1.8	18

^a Except for the above-mentioned condition, the reaction was carried out as follows. Reaction temperature: -50°C , Solvent: THF (20 mL), DMSB: neat, $[\text{BuOK}]/[\text{DMSB}]/[\text{St}] = 1/0.5/30$ ($[\text{BuOK}] = 0.13 \text{ mol dm}^{-3}$, $[\text{St}] = 3.8 \text{ mol dm}^{-3}$). ^b M_n and M_w/M_n were measured by GPC (poly(styrene) standard). ^c ref 16.

homopolymerization of DMSB did not improve the efficiency (run 5). When the feed ratio of St increases, αCPE increased (run 6).

It was shown that not only the efficient ring opening of SB by BuOK, but also suppression of homopolymerization reaction of DMSB and styrene as monomers are important to achieve the high αCPE by BuOK. Trapping of the formed carbanion as stable carbanion in the absence of styrene may give a clue to improve the αCPE . More detailed investigation on the effect of the chemical structure of the silacyclobutanes and trapping of the formed carbanion are still under way.¹⁷

In summary, we presented a new concept of "carbanion pump" to convert *O*-anion into *C*-anion. This new concept will give a clue to develop a variety of block polymers from various combinations of ring-opening and vi-

nyl monomers.

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- The overall CPE (αCPE) is defined as follows,

$$M_{n(\text{calcd})} = \frac{[\text{St}]}{[\text{BuOK}]} \bullet M_{\text{St}} + M_{\text{BuO}} + M_{\text{SB}} + M_{\text{TPS}}$$

$$M_{n(\text{GPC})} = \frac{[\text{St}]}{[\text{C-anion}]} \bullet M_{\text{St}} + M_{\text{BuO}} + M_{\text{SB}} + M_{\text{TPS}}$$

$$[\text{O-anion}] = [\text{BuOK}]$$

$$\alpha\text{CPE} = \frac{[\text{C-anion}]}{[\text{O-anion}]} = \frac{M_{n(\text{calcd})} - (M_{\text{BuO}} + M_{\text{SB}} + M_{\text{TPS}})}{M_{n(\text{GPC})} - (M_{\text{BuO}} + M_{\text{SB}} + M_{\text{TPS}})} \approx \frac{M_{n(\text{calcd})}}{M_{n(\text{GPC})}}$$

where M_{St} , M_{BuO} , M_{SB} , and M_{TPS} are molecular weight of styrene, *t*-butoxy, (dimethylsilylene)trimethylene, triphenylsilyl units in the polymer chain.

- The apparent CPE (αCPE) is calculated using $M_{n(\text{calcd})\text{SB}}$ based on the concentration of SB, as follows.

$$M_{n(\text{calcd})\text{SB}} = \frac{[\text{St}]}{[\text{SB}]} \bullet M_{\text{St}} + M_{\text{BuO}} + M_{\text{SB}} + M_{\text{TPS}}$$

$$a\text{CPE} \approx \frac{M_{n(\text{calcd})\text{SB}}}{M_{n(\text{GPC})}}$$

17. M. R. K. Sheikh, K. Tharanikkarasu, I. Imae, and Y. Kawakami, in preparation.