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Silacyclobutane as “Carbanion Pump” in Anionic Polymerization. 2. Effective Trapping of the Initially Formed Carbanion by Diphenylethylene

Md. Rezaul Karim Sheikh, Kannan Tharanikkarasu, Ichiro Imae, and Yusuke Kawakami*

Graduate School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), Asahidai 1-1, Tatsunokuchi, Ishikawa 923 1292, Japan

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ABSTRACT: The initially formed carbanion from dimethylsilacyclobutane and potassium *tert*-butoxide was trapped in as high as 88% yield in the presence of 1,1-diphenylethylene as evidenced by quenching with methyl iodide. The initiator efficiency of 76% was obtained by using a combination of potassium *tert*-butoxide, dimethylsilacyclobutane, and 1,1-diphenylethylene carbanion pump system as an initiator in the polymerization of methyl methacrylate.

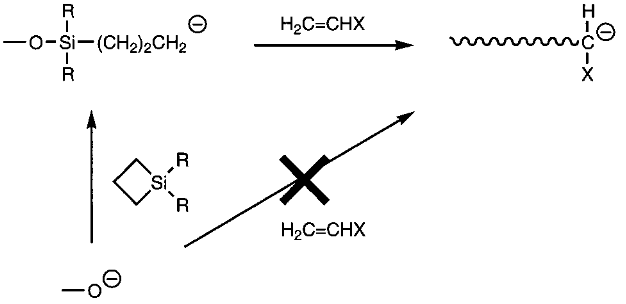
Introduction

Anionic polymerization is widely used to prepare polymers with narrow molecular weight distributions.[1] In this method, the formation of block copolymers by sequential monomer addition depends mainly on the nucleophilic reactivity of the living chain end. For instance, the highly nucleophilic polystyrene carbanion can initiate the polymerization of ethylene oxide to form polystyrene-*block*-poly(ethylene oxide), whereas the comparatively less nucleophilic poly(ethylene oxide) oxyanion cannot initiate the polymerization of styrene. As a result, polystyrene-*block*-poly(ethylene oxide)-*block*-polystyrene triblock copolymers and poly(ethylene oxide)−polystyrene multiblock copolymers cannot be prepared[2,3] by sequential addition in the living anionic polymerization system. This has long been an obstacle in the unrestricted synthesis of tri- and multiblock copolymers from hydrocarbon and oxirane monomers.

Some exceptions have been reported for methacrylates and acrylates as polar vinyl monomers. Trekoval[4] used lithium *tert*-butoxide for the polymerization of methyl methacrylate. Tomoi[5] described the polymerization of methacrylates by lithium, sodium, and potassium alkoxides. Tsvetanov[6,7] studied the polymerization of methyl methacrylate and 2-vinylpyridine in the presence of lithium *tert*-butoxide and also used a poly(ethylene oxide) salt as an active anionic initiator. Nagasaki,[8,9] Lascelles,[10] and Vamvakaki[11] showed that potassium alkoxides are able to polymerize (dialkylamino)ethyl methacrylates and 2-trialkylsiloxyethyl methacrylate in a living fashion and obtained polymers with relatively narrow polydispersity. Vamvakaki[11] showed that well-defined poly(ethylene oxide)-based block copolymers can be obtained when the potassium salt of monohydroxy-ended poly(ethylene oxide) is used as a macroinitiator.

There have only been a few reports on the polymerization of styrene initiated by an oxyanion. In 1974, Boileau[12] reported the polymerization of styrene by sodium *tert*-amylalkoxide in the presence of cryptand-[2.2.2]. Very recently, Stolarzewicz[13] et al. reported the polymerization of styrene at room temperature by potassium alkoxides and oligo(ethylene oxide) alkoxide without any additional ligand. They insisted that the rate of polymerization and molecular weight of the polymer were controlled by the number of ether oxygen atoms in the initiator system. However, the yield was only 36% after 14 days. They also did not mention the formation of color of styrene anion. We therefore cannot conclude that the polymerization proceeded by an anionic mechanism.

Scheme 1. Concept of Carbanion Pump



We recently proposed the concept of a “carbanion pump”, where a silacyclobutane having high ring distortional energy[14] was used to convert an oxyanion into a carbanion (Scheme 1), which can further initiate polymerization of styrene.[15] Similarly, Teyssié[16] used disilacyclopentane derivatives to convert oxyanion into silyl anion, and the resulting silyl anion was used to polymerize styrene and methyl methacrylate. However, the initiator efficiency was not high enough in either our[15] (∼11%) or Teyssié’s system (35%). To improve the initiator efficiency, this report uses 1,1-diphenylethylene and α-methylstyrene to trap the initially formed carbanion from potassium *tert*-butoxide (BuOK) and dimethylsilacyclobutane. To confirm the efficient trapping of the initially formed carbanion by 1,1-diphenylethylene, the (BuOK-dimethylsilacyclobutane carbanion pump)−1,1-diphenylethylene system was used to polymerize methyl methacrylate, since 1,1-diphenylhexyllithium initiation is almost quantitative and produces polymer with well-controlled molecular weight and narrow polydispersity.[17]

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* Corresponding author. Telephone +81-761-51-1630; Fax +81-761-51-1635; E-mail kawakami@jaist.ac.jp.

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Table 1. Trapping of Carbanion from BuOK and Dimethylsilacyclobutane by 1,1-Diphenylethylene[a]

	feed	solvent (v/v)	yield (%)		
run	BuOK:DPE:DMSB[b]	THF:Hex[c]	hex soluble	compd **C**	compd **E**
1	1.0:1.0:1.0	10:0	97	52	12
2	1.0:2.0:1.0	10:0	93	59	13
3[d]	1.0:2.0:1.0	10:0	91	21	24
4	1.0:2.0:1.0	9:1	96	60	13
5	1.0:2.0:1.0	7:3	95	42	21
6	1.0:2.0:1.0	5:5	94	29	32
7	1.0:2.0:1.0	1:9	93	23	36
8[e]	1.0:2.0:1.0	9:1	95	80[f]	5[g]
9[e,h]	1.0:2.0:1.5	9:1	97	83[f]	1[g]
10[e,h]	1.0:2.0:2.0	9:1	100	88[f]	
11[e,h,i]	1.0:2.0:1.0	9:1	100	86[f]	

[a] $[\mathrm{BuOK}]_0 = 0.45$ mol/L, dimethylsilacyclobutane: neat (0.45 g, 4.5 mmol), solvent = 10 mL, temperature = 30 °C. [b] DPE = 1,1-diphenylethylene, DMSB = dimethylsilacyclobutane. [c] THF = tetrahydrofuran, Hex = *n*−hexane. [d] Temperature = −78 °C. [e] MeI was used as a quenching agent. [f] Compound **F**. [g] Compound **H**. [h] Twofold excess of MeI was used. [i] Dimethylsilacyclobutane was added as 1.5 mol/L THF solution for 2 h.

Experimental Section

Materials. Dimethylsilacyclobutane (Shin-Etsu Chemical, ∼99%), α-methylstyrene (Wako Pure Chemical, >98%), methyl methacrylate (Wako Pure Chemical, >98%), 1,1-diphenylethylene (Kanto Chemical, 93%), and *n*-hexane were dried and distilled over CaH_2 and stored under argon atmosphere. They were again distilled and purified just before reaction. Methyl iodide (MeI) (Wako Pure Chemical, >95%) and trimethylsilyl chloride (Me_3SiCl) (Shin-Etsu Chemical, 98%) were used as received. BuOK was purified by sublimation under vacuum (175 °C at 0.11 mmHg).[18] Tetrahydrofuran was refluxed over Na−benzophenone and used freshly. All liquid reagents were transferred using a stainless steel needle with a gastight syringe under an argon atmosphere.

Trapping Reactions of the Initial Products by α-Methylstyrene or 1,1-Diphenylethylene. A typical example (run 4 in Table 1) is given for the trapping reaction by 1,1-diphenylethylene. Freshly sublimed BuOK (0.51 g, 4.5 mmol) was taken in a 50 mL two-necked flask fitted with a three-way stopcock, and a tetrahydrofuran/*n*-hexane mixture (9/1 v/v, 10 mL) was added. To this was added 1,1-diphenylethylene (1.6 g, 9.0 mmol). When the reaction mixture reached 30 °C, dimethylsilacyclobutane (0.45 g, 4.5 mmol) was added slowly for 30 min. The resulting red solution was stirred at the same temperature for another 30 min. After Me_3SiCl (0.49 g, 4.5 mmol) was added to quench the reaction, volatile materials were removed by vacuum evaporation. To remove all of the inorganic salt (KCl), 30 mL of ether was added into the flask, and the reaction system was washed three times with water (10 mL × 3). Finally ether was removed by vacuum evaporation. *n*-Hexane was added into the crude product, and soluble (2.6 g) and insoluble (0.10 g) portions were separated.

To determine the amounts of trapped products, the trapped products were separated by recycling preparative gel permeation chromatography (GPC), and the standard calibration curve was prepared with internal standard 1,3,5-tri-*tert*-butylbenzene (see Analysis and Characterization). Two major products, 2,2,4,4,10,10-hexamethyl-9,9-diphenyl-3-oxa-4,10-disilaundecane (1.2 g) and 2,2,4,4,10,10-hexamethyl-9-phenyl-9-(4-trimethylsilylphenyl)-3-oxa-4,10-disilaundecane (0.3 g), were isolated.

Anionic Polymerization of Methyl Methacrylate Using Trapped Carbanion from BuOK, Dimethylsilacyclobutane, and 1,1-Diphenylethylene. Freshly sublimed BuOK (0.15 g, 1.4 mmol) was taken in a 100 mL two-necked flask fitted with a three-way stopcock. 1,1-Diphenylethylene (0.49 g, 2.7 mmol) and freshly distilled tetrahydrofuran/*n*-hexane mixture (9/1 v/v, 15 mL) were added into the flask. At 30 °C, dimethylsilacyclobutane (1.4 g, 1.4 mmol) was added slowly for 90 min with stirring. The stirring was continued for another 30 min. Then the red anionic solution was cooled to −50 °C, and methyl methacrylate (8.2 g, 82 mmol) was added. At the end of 30 min, the reaction mixture was quenched by adding an excess amount of Me_3SiCl and poured into 15-fold excess of methanol. The formed poly(methyl methacrylate) was obtained by filtration, dried, and characterized by GPC to have $M_n = 8.3 \times 10^3$.

Analysis and Characterization. GPC was performed to determine the amounts of the initial trapped products and molecular weights of the polymer on a JASCO GPC apparatus (Gulliver series) equipped with a series of Shodex columns KF-800P (precolumn), KF-801 (exclusion limit, polystyrene $M_n = 1.5 \times 10^3$), and KF-802 (exclusion limit, polystyrene $M_n = 4.0 \times 10^4$) detected by UV (JASCO UV-970, monitored at 254 nm) working at 40 °C with tetrahydrofuran as an eluent at a flow rate of 1 mL $\min^{-1}$. Molar mass of the polymer was determined from the calibration curve based on linear polystyrene standard (Tosoh).

The initial trapped products by 1,1-diphenylethylene or α-methylstyrene were separated by preparative GPC (JASCO Gulliver series) on a combination of a series of KF-2001 (20 diameter × 600 mm, exclusion limit, polystyrene $M_n = 1.5 \times 10^3$) and KF-2002 (20 diameter × 600 mm, exclusion limit, polystyrene $M_n = 4.0 \times 10^4$) detected by a UV (JASCO UV-970, monitored at 254 nm) detector working at 40 °C with tetrahydrofuran as an eluent at a flow rate of 2 mL $\min^{-1}$.

The molecular mass of the trapped products was determined by SHIMADZU QP-5000 gas chromatography−mass spectroscopy (GC-MS). An acetone solution of each sample (0.5 μL) was injected into the GC in split mode at a ratio of ∼10:1 with helium as the carrier gas. The injection port temperature was held at 230 °C. The capillary column was 30 m in length, with a 0.32 mm i.d. and with a stationary phase DB-17 (J&W Scientific, (50%-phenyl)methylpolysiloxane). The oven temperature was held at 50 °C for 5 min and then ramped at 10 °C $\min^{-1}$ to 230 °C, where the temperature was held for 35 min. The mass filter was scanned from m/z 70 to m/z 700 under electron ionization conditions.

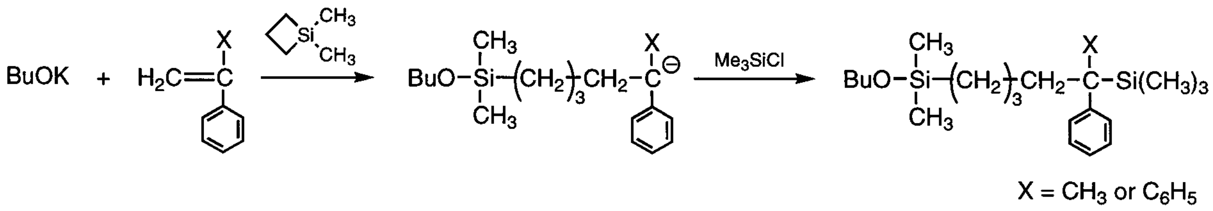
^1H (300 MHz) and ^{13}C (75.4 MHz) spectra were obtained on a Varian NMR spectrometer, model Gemini 2000. Chemical shifts are referenced in ppm relative to $CHCl_3$ ($\delta = 7.26$) in ^1H NMR and $CDCl_3$ ($\delta = 77.00$) in ^{13}C NMR.

Results and Discussion

In our previous article,[15] we reported that the carbanion produced from BuOK and a silacyclobutane can initiate the polymerization of styrene. However, the initiator efficiency was only around ∼11%. Among the silacyclobutanes used, dimethylsilacyclobutane was the most efficient. To improve the initiator efficiency, we attempted to trap the formed carbanion from BuOK and dimethylsilacyclobutane by α-methylstyrene or 1,1-diphenylethylene.

Trapping Reactions. The trapping reaction by α-methylstyrene was carried out above its ceiling temperature using 1:2:1 molar ratio of BuOK, α-methylstyrene, and dimethylsilacyclobutane by adding neat dimethylsilacyclobutane. An *n*-hexane soluble fraction contained only oligomers, and an insoluble fraction contained small amounts of oligomers and polymers. The α-methylstyrene-based trapped products in the *n*-hexane soluble fraction showed several peaks by GPC as shown in Figure 1a. The major three fractions of the product were separated by recycling preparative GPC and characterized by GC-MS. The strongest mass peak of fraction **1** was close to the expected molecular weight of the product of the trapping reaction shown in Scheme 2. Fraction **1** was further separated into two fractions **1x** and **1y** by recycling preparative GPC as shown in Figure 1b. The ^1H NMR spectra of fractions **1x** and **1y**

Scheme 2. Expected Product by α-Methylstyrene or 1,1-Diphenylethylene Trapping System



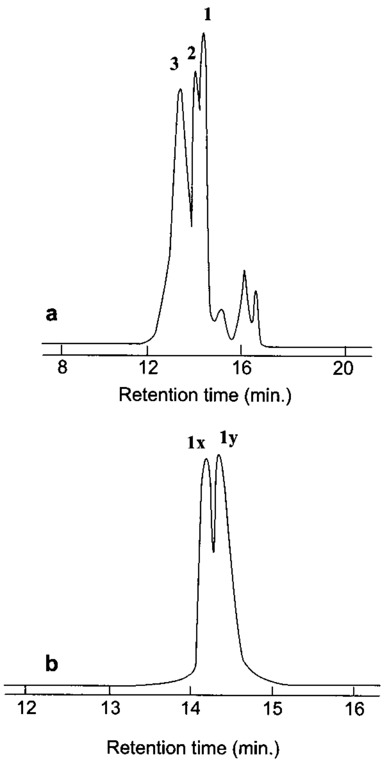


Figure 1. (a) GPC trace of the products by α-methylstyrene trapping reaction. (b) GPC trace (recycled) of fraction **1** (vertical scale: arbitrary unit).

showed the peaks of the expected product, but with impurities including some broad peaks. This may indicate that co-oligomer of α-methylstyrene and dimethylsilacyclobutane is present in the system. The situation is similar for fractions **2** and **3**. Therefore, the carbanion trapping reaction by α-methylstyrene is not the clean reaction shown in Scheme 2. α-Methylstyrene cannot trap the initially formed carbanion cleanly as an α-methylstyrene anion, and the α-methylstyrene anion cannot suppress the homo- or copolymerization of dimethylsilacyclobutane effectively because of its high reactivity.

The trapping reaction by 1,1-diphenylethylene was typically carried out using a 1:2:1 molar ratio of BuOK, 1,1-diphenylethylene, and dimethylsilacyclobutane by adding neat dimethylsilacyclobutane. The GPC chromatograms of the trapped products by 1,1-diphenylethylene in a *n*-hexane soluble fraction after quenching by Me_3SiCl (addition time of dimethylsilacyclobutane is 30 min) are shown in Figure 2. Figure 2a shows that the formation of high molecular weight species is suppressed, in contrast to the trapping by α-methylstyrene, and that the chromatographic peaks are quite sharp. The suppression is more effective in tetrahydrofuran/*n*-hexane (9/1 v/v) mixed solvent (Figure 2b).

To further understand the 1,1-diphenylethylene-based trapping reactions, a *n*-hexane soluble portion was separated and characterized. According to thin-layer chromatography and GPC, the *n*-hexane soluble portion contains two major products. The two compounds (**C** and **E**) were separated by recycling preparative GPC using tetrahydrofuran as an eluent. According to mass spectroscopy, the molecular weight of compounds **C** and **E** are 426 and 498, respectively. The ^1H and ^{13}C NMR spectra of compounds **C** and **E** are shown in Figures 3–5. The major difference in the ^1H NMR spectra of **E** and **C** is the new singlet (9H) at 0.28 ppm and part of a quartet at 7.38 ppm (2H, $J = 7.8$ Hz) in the aromatic

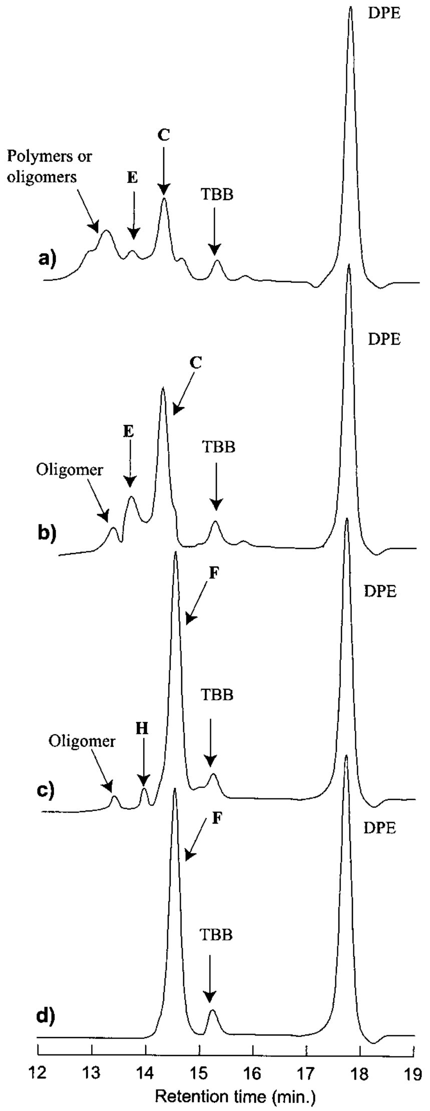


Figure 2. GPC of the products by 1,1-diphenylethylene trapping reaction: (a) in THF, quenched by Me_3SiCl; (b) in THF/Hex (9/1 v/v), quenched by Me_3SiCl; (c) in THF/Hex (9/1 v/v), quenched by MeI; (d) in THF/Hex (9/1 v/v), quenched by MeI, [dimethylsilacyclobutane]/[BuOK] = 2 [DPE = 1,1-diphenylethylene, TBB = 1,3,5-tri-*tert*-butylbenzene, THF = tetrahydrofuran, Hex = *n*-hexane] (vertical scale: arbitrary unit).

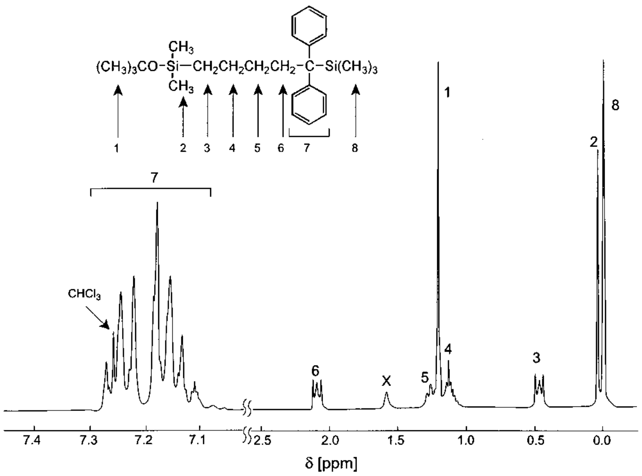


Figure 3. ^{1}H NMR spectrum of compound **C** (MS, $m/z = 426$) from BuOK, dimethylsilacyclobutane, and 1,1-diphenylethylene quenched by Me$_3$SiCl.

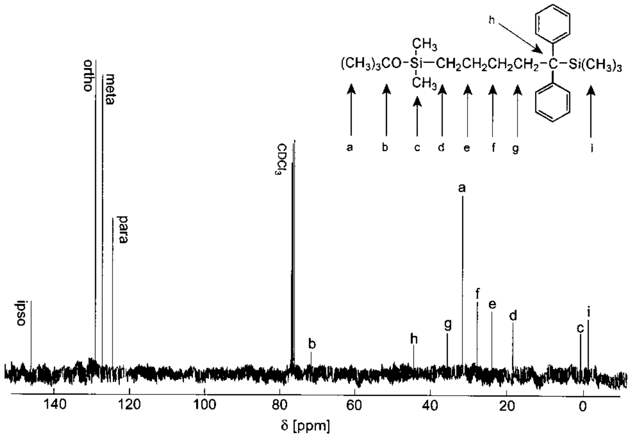


Figure 4. ^{13}C NMR spectrum of compound **C** from BuOK, dimethylsilacyclobutane, and 1,1-diphenylethylene quenched by Me$_3$SiCl.

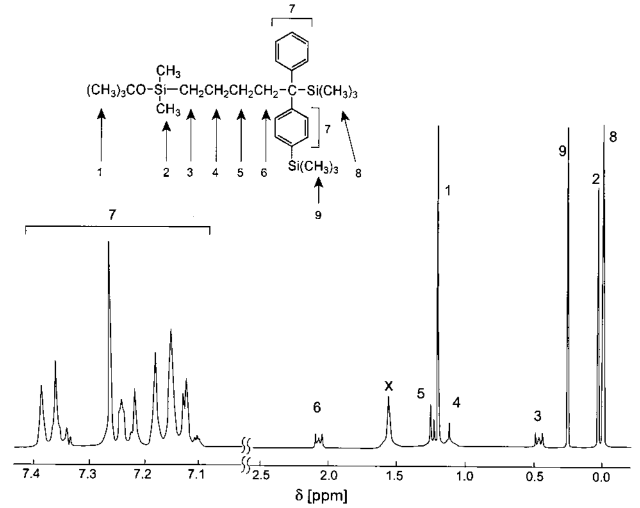


Figure 5. ^{1}H NMR spectrum of compound **E** (MS, $m/z = 498$) from BuOK, dimethylsilacyclobutane, and 1,1-diphenylethylene quenched by Me$_3$SiCl.

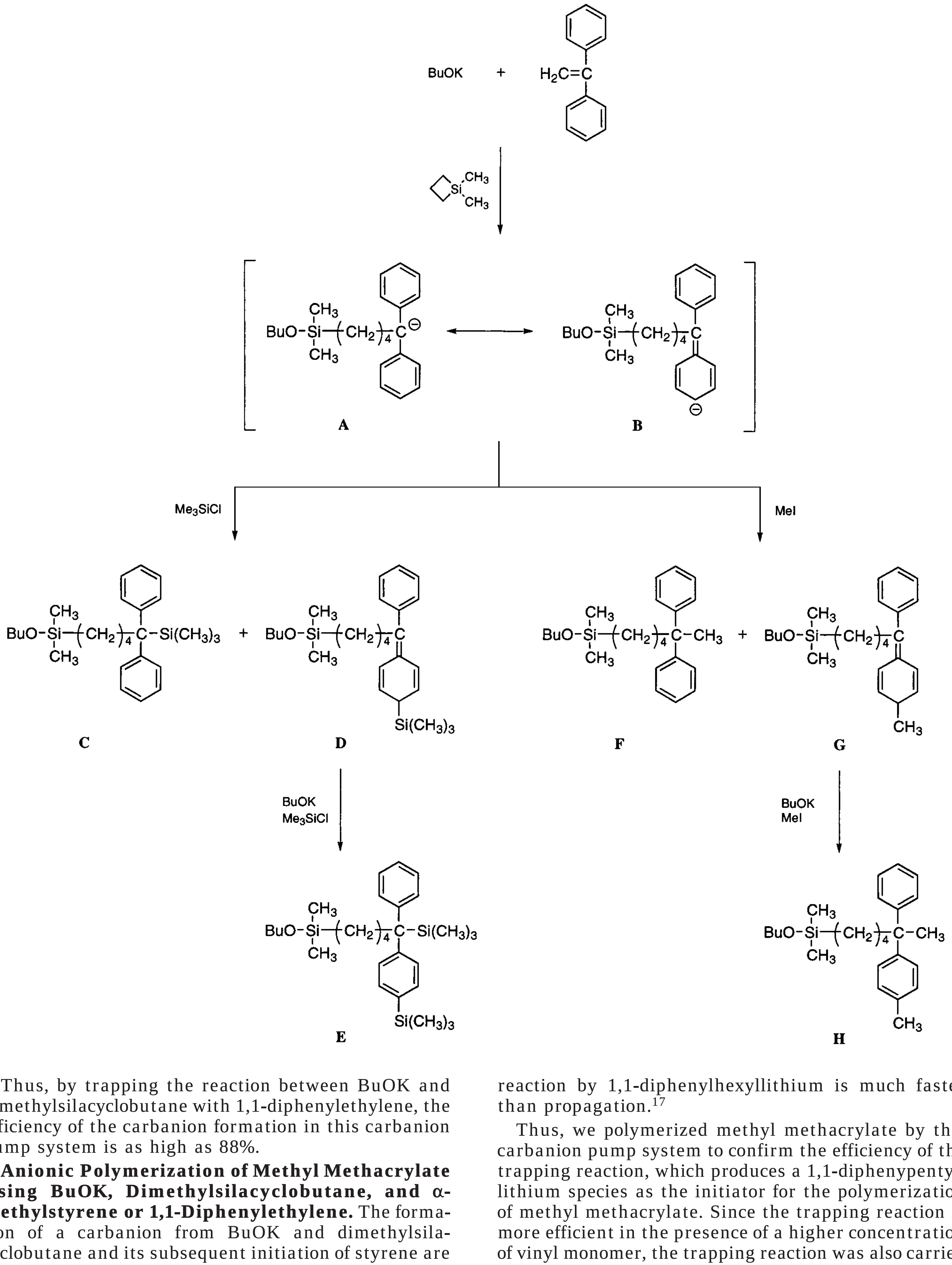
region corresponding to 9H. This strongly indicates the presence of *p*-phenylene structure in compound **E**. On the basis of the MS and NMR data, compound **C** is the expected compound shown in Scheme 2 (X = C$_6$H$_5$). Compound **E** is a trimethylsilylated product of compound **C**. However, when MeI was used instead of Me$_3$SiCl as a quenching agent, compound **F** (Scheme 3) was preferentially formed as the quenched product (Figure 2c). When a 2-fold excess of Me$_3$SiCl was used as the quenching agent, the formation of compound **E** was suppressed by increasing amounts of **C**. Compound **D** could not be isolated even when the initially trapped carbanion solution was added dropwise to the Me$_3$SiCl solution. Apparently, hydrogen abstraction from **D** is faster than trimethylsilylation of intermediate **A**. Our proposed series of trapping reactions is shown in Scheme 3.

The carbanion formed from BuOK, dimethylsilacyclobutane, and 1,1-diphenylethylene has two resonance structures, **A** and **B**. When a bulky and hard electrophile like Me$_3$SiCl is used, compounds **C** and **D** should be obtained as the initial products. In the presence of unreacted BuOK, the *ipso* allylic hydrogen of **D** is abstracted to regenerate a carbanion on diphenyl-substituted methyl carbon to give compound **E** in the following trimethylsilylation with Me$_3$SiCl. Some BuOK may also react directly with Me$_3$SiCl. The reason for the clean trapping by 1,1-diphenylethylene is apparently because the reactivity of the initially formed diphenylpentyl anion toward dimethylsilacyclobutane is low. We have also found that the homopolymerization of dimethylsilacyclobutane is quite slow when initiated by 1,1-diphenylhexyllithium compared to the polymerization initiated by butyllithium or BuOK, since almost no conversion was observed, and the red color of 1,1-diphenylhexyllithium was maintained after 1 h. The amounts of compounds **C**, **E**, and **F** were determined using a calibration curve with 1,3,5-tri-*tert*-butylbenzene as an internal standard. The results are presented in Table 1.

The reaction at −78 °C is apparently incomplete and remaining BuOK converts about half of **C** into **E** (run 3). When the amount of *n*-hexane is increased in the mixed solvent, the yield of the trapped products decreases, and more compound **E** forms by reaction of the unreacted BuOK (runs 5−7). When dimethylsilacyclobutane was added dropwise over 30 min, the highest trapping efficiency observed in the tetrahydrofuran/*n*-hexane system (9/1 v/v) was 73% by Me$_3$SiCl (run 4) and 85% by MeI (run 8) with equimolar amounts of dimethylsilacyclobutane. These values should be basically the same if the quenching reaction occurs at the same efficiency. The lower efficiency with Me$_3$SiCl may be because 2 mol of Me$_3$SiCl is consumed in the formation of compound **E** and because of direct reaction of BuOK with Me$_3$SiCl and separation procedure. When a soft electrophile MeI is used as the quenching agent, preferential methylation of the softer carbanion center occurs to give compound **F** over **H** as the major trapped product (run 8). Trapping with excess MeI gave higher yield of **F** with less amounts of **H** (run 9).

The amounts of compounds **F** and **H** (**C** and **E**) also depend on the addition time and concentration of dimethylsilacyclobutane. Use of excess dimethylsilacyclobutane improved the trapping efficiency (runs 9 and 10). When a 2-fold excess of dimethylsilacyclobutane was added over 90 min, the formation of **H** was almost completely suppressed (Figure 2d and run 10 in Table 1), and compound **F** was formed in 88% yield. Addition of an equimolar amount of dimethylsilacyclobutane in solution (1.5 mol/L) also gave product **F** in comparable yield (run 11).

Scheme 3. Reaction of the 1,1-Diphenylethylene Trapping System



Thus, by trapping the reaction between BuOK and dimethylsilacyclobutane with 1,1-diphenylethylene, the efficiency of the carbanion formation in this carbanion pump system is as high as 88%.

Anionic Polymerization of Methyl Methacrylate Using BuOK, Dimethylsilacyclobutane, and α-Methylstyrene or 1,1-Diphenylethylene. The formation of a carbanion from BuOK and dimethylsilacyclobutane and its subsequent initiation of styrene are essentially simultaneous.[15] Hence, it is difficult to reliably confirm the trapping efficiency by examining the initiation reaction of styrene polymerization by this carbanion pump system. On the other hand, in the polymerization of methyl methacrylate, the initiation reaction by 1,1-diphenylhexyllithium is much faster than propagation.[17]

Thus, we polymerized methyl methacrylate by this carbanion pump system to confirm the efficiency of the trapping reaction, which produces a 1,1-diphenypentyllithium species as the initiator for the polymerization of methyl methacrylate. Since the trapping reaction is more efficient in the presence of a higher concentration of vinyl monomer, the trapping reaction was also carried out in the presence of concentrated 1,1-diphenylethylene. However, the polymerization system became highly viscous when the same initiator concentration was used. The amount of solvent was thus increased (15 mL) from the original carbanion trapping stage to avoid the unnecessary death of the living end by dilution and to realize efficient stirring during the polymerization. The molecular weight of poly(methyl methacrylate) produced in tetrahydrofuran/*n*-hexane mixed solvent estimated by GPC and NMR is consistent with the calculated value ($[M]_0/[I]_0 = 60$, $M_{n(calc)} = 6470$, $M_{n(NMR)} = 8470$, $M_{n(GPC)} = 8340$, $M_w/M_n = 2.0$), and the initiator efficiency was 76%. By the aid of this carbanion pump, various types of block copolymer from vinyl and oxirane monomers should be prepared by the successive addition in the anionic polymerization system.[19]

Conclusion

Though oxyanions cannot initiate polymerization of hydrocarbon monomers, they can be combined with silacyclobutane to produce a carbanion pump that will polymerize hydrocarbon monomers. 1,1-Diphenylethylene efficiently traps the initially formed carbanion in the carbanion pump system, and the trapped carbanion can be used to polymerize methyl methacrylate. The polymer yield was quantitative, and the initiator efficiency was 76%.

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