Polymerization of Monomers Containing Functional Silyl Groups. 11. Anionic Living Polymerization of 3-(Tri-2-propoxysilyl)propyl Methacrylate

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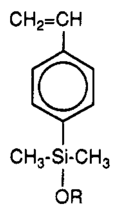
ABSTRACT: Anionic polymerizations of 3-(trimethoxysilyl)propyl (**3a**), 3-(triethoxysilyl)propyl (**3b**), and 3-(tri-2-propoxysilyl)propyl methacrylates (**3c**) were investigated in THF at −78 °C with a variety of initiators. They included butyllithium, 1,1-diphenylhexyllithium, 1,1-diphenylhexyllithium–LiCl, cumylpotassium capped with 1,1-diphenylethylene (DPE), 1,4-dipotassio-1,1,4,4-tetraphenylbutane from potassium naphthalenide and DPE, benzylmagnesium chloride, potassium *tert*-butoxide, and $LiAlH_4$. The polymerization of **3c** proceeded well to give poly(**3c**) quantitatively with each of all the initiators except for $LiAlH_4$. Among these, the combination of 1,1-diphenylhexyllithium and LiCl is particularly an excellent initiator system which produces polymers of predictable molecular weights and of very narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.05$). Thus, the living character of the polymerization of **3c** with this system has been demonstrated. A novel well-defined block copolymer, poly(**3c**-*b*-methyl methacrylate), could be synthesized by the sequential anionic living polymerization of **3c** with methyl methacrylate. Similarly, block copolymers of poly(methyl methacrylate-*b*-**3c**) and poly(styrene-*b*-**3c**) were also synthesized quantitatively. The hydrolytic behavior of poly(**3c**) was studied in detail in water, 2 N HCl, or 1 N NaOH.

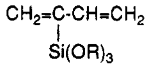
Introduction

Some basic properties of polymer are known to be strongly dependent on their molecular weights. Therefore, it is desirable for the polymer chemist to use polymer samples with known molecular weights and narrow molecular weight distributions in order to clarify the properties of polymer in solution as well as in bulk. Currently, the best established method to get such samples is undoubtedly the method of anionic living polymerization of vinyl monomers. Molecular weight can be practically controlled in a wide range of 10^2–10^6 by this anionic method. Moreover, the resulting polymers have extremely narrow molecular weight distributions.

For the anionic living polymerization, the best vinyl monomers are conjugated hydrocarbons such as styrenes and 1,3-dienes. Recently, the living polymerizations of some styrenes with functional groups have been successfully realized by suitably protecting these functional groups during the polymerization.[1] Under certain specific conditions, vinylpyridines and alkyl methacrylates can undergo anionic living polymerization without side reactions.[2] However, the number of vinyl monomers amenable to anionic living polymerization is still limited.

We have previously demonstrated that the styrenes (**1**)[3,4] and 1,3-butadienes (**2**)[5,6] with alkoxysilyl groups are anionically polymerized to afford stable living polymers similar to those from styrene and 1,3-butadiene. Although it is believed that alkoxysilyl groups are susceptible to nucleophilic attack by strong nucleophiles and basic reagents like organolithium compounds, they are surprisingly stable under the anionic living polymerization conditions. It was found that the resulting polymers retained the desirable characteristics of living polymers such as controllable molecular weights and narrow molecular weight distributions. Furthermore, new types of well-defined block copolymers of **1** and **2** with styrene and isoprene could be prepared by living polymerizations of **1** and **2**. The presence of alkoxysilyl functions which can react with silanols and metal oxides on the surfaces of glass and metallic materials is a useful property. From this viewpoint, they are attractive polymers for modifying these inorganic surfaces and for making organic–inorganic composite materials.

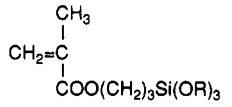

(**1**)



$$CH_2{=}C(Si(OR)_3){-}CH{=}CH_2$$

(**2**)

As a part of a series of studies on the anionic polymerization of monomers with functional silyl groups, we report here the anionic polymerization of alkyl methacrylates with alkoxysilyl groups such as 3-(trialkoxysilyl)propyl methacrylates (**3a–c**). The monomers **3a–c** are expected to undergo living polymerization, since the anionic living polymerizations of some methacrylate monomers have previously been reported[7-12] and the Si–OR bonds are stable enough under the conditions of anionic living polymerization as mentioned above. Therefore, the polymerization behavior of **3a–c** will be carefully examined with emphasis on the living nature of the polymerization.



$$CH_2{=}C(CH_3)COO(CH_2)_3Si(OR)_3$$

3a : R= CH_3

3b : R= C_2H_5

3c : R=$CH(CH_3)_2$

(**3a-c**)

Experimental Section

Materials. Triethylaluminum and trioctylaluminum were kindly supplied by Mitsui Petrochemical Industries Ltd. They were used as heptane solutions without purification. Heptane was washed with concentrated H_2SO_4 and then with water and was dried over $MgSO_4$. It was refluxed for 5 h over P_2O_5 and its butyllithium solution distilled under an atmosphere of nitrogen. Tetrahydrofuran (THF) was refluxed over a Na wire and distilled over $LiAlH_4$. Finally, its sodium naphthalenide solution was distilled on a vacuum line. Commercially available methanol,

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ethanol, propanol, 2-propanol, butanol, 2-butanol, *tert*-butanol, and *p*-toluenesulfonic acid hydrate were used without purification. Methyl methacrylate (MMA) and styrene were washed with 5% NaOH and then with water. They were dried over MgSO$_4$ at first and then over CaH$_2$ for 48 h and distilled over CaH$_2$ under reduced pressure. Further purifications of MMA and styrene will be described later. Commercially available 1,1-diphenylethylene (DPE) was dried over CaH$_2$ and distilled over CaH$_2$. Then, it was distilled from its 1,1-diphenylhexyllithium solution under reduced pressure. LiCl was dried under high vacuum (10^{-6} mmHg) for 48 h with baking for every 1 h. Commercially available butyllithium (BuLi) was used without further purification. Cumylpotassium was prepared according to the method previously reported.[13] The concentration was determined by the colorimetric titration from a red to colorless end point. The titration was carried out in a sealed reactor with break-seals using standardized octanol in THF. Metal naphthalenides were prepared by the reactions of a slight excess of naphthalene with the corresponding metals in THF. Similar to the case of cumylpotassium, the concentrations of green solutions were determined by colorimetric titration using standardized octanol in THF. 1,1-Diphenylhexyllithium was prepared just prior to the polymerization from BuLi and an excess of DPE in THF at 30 °C for 20 s and then −78 °C for 10 min. 1,4-Dipotassio-1,1,4,4-tetraphenylbutane was prepared just prior to the polymerization from potassium naphthalenide and an excess of DPE in THF at 30 °C for 1 min and then −78 °C for 15 min. Potassium *tert*-butoxide was prepared by the reaction of potassium naphthalenide and *tert*-butanol and purified by sublimation under high-vacuum conditions. Benzylmagnesium chloride was prepared by the reaction of benzyl chloride with an excess of Mg in THF. Benzyl chloride was found to be completely reacted by gas chromatography. The concentrations of potassium *tert*-butoxide and benzylmagnesium chloride were determined by conventional acid (HCl)–base (NaOH) titration. LiAlH$_4$ was recrystallized from absolute diethyl ether and used as a THF solution.

3-(Triethoxysilyl)propyl Methacrylate (3b). A 500-mL flask equipped with a 20-cm Vigreux column was charged with 3-(trimethoxysilyl)propyl methacrylate (**3a**; 9.18 g, 37 mmol), ethanol (50 mL), and a catalytic amount of *p*-toluenesulfonic acid. Methanol together with ethanol was distilled from the mixture at 70–80 °C over 5 h while 20 mL of ethanol was added to the mixture for each 1 h. The reaction was traced by gas chromatography and was found to generally be complete within 3 h. The reaction mixture was poured into a NaHCO$_3$-saturated aqueous solution (100 mL), and the product was extracted with hexane three times. The hexane layer was dried over MgSO$_4$ and filtered. The solvent was removed under reduced pressure to give a colorless oil. The product was twice distilled at 91–92 °C (0.5 mm) to give 8.79 g (81%) of colorless, liquid 3-(triethoxysilyl)propyl methacrylate (**3b**): ^{1}H NMR (90 MHz, CDCl$_3$) δ 6.10 (s, 1 H, *H*C=C, trans), 5.54 (s, 1 H, *H*C=C, cis), 4.12 (t, 2 H, J = 13.7 Hz, COOCH$_2$), 3.80 (q, 6 H, SiOCH$_2$), 1.94 (s, 3 H, =CCH$_3$), 1.89–1.70 (m, 2 H, COOCH$_2$*C*H$_2$), 1.22 (t, 9 H, SiOCH$_2$*C*H$_3$), 0.77–0.58 (m, 2 H, SiCH$_2$); ^{13}C NMR (22.5 Hz, CDCl$_3$) δ 167.5 (C=O), 136.6 (CH$_2$=*C*), 125.2 (*C*H$_2$=C), 66.7 (COO*C*H$_2$), 58.5 (SiOCH$_2$), 22.3 (COOCH$_2$*C*H$_2$), 18.4 (CH$_3$), 18.3 (SiOCH$_2$*C*H$_3$), 6.6 (SiCH$_2$). Anal. Calcd for $C_{13}H_{26}O_5Si$: C, 53.24; H, 8.89; N, 0.00. Found: C, 53.76; H, 9.02; N, 0.00.

3-(Tri-2-propoxysilyl)propyl Methacrylate (3c). A reaction similar to the one above was run with **3a** (20.5 g, 83 mmol), 2-propanol (50 mL), and a catalytic amount of *p*-toluenesulfonic acid. Methanol together with 2-propanol was distilled from the mixture at 85–95 °C over 5 h while 20 mL of 2-propanol was added to the mixture for each 1 h. The reaction was traced by gas chromatography and was found to generally be complete within 3 h. The reaction mixture was poured into a NaHCO$_3$-saturated aqueous solution (100 mL), and the product was extracted with hexane three times. The hexane layer was dried over MgSO$_4$ and filtered. The solvent was removed under reduced pressure to give a colorless oil. The product was twice distilled at 99–100 °C (0.5 mm) to give 23.7 g (86%) of colorless, liquid 3-(tri-2-propoxysilyl)propyl methacrylate (**3c**): ^{1}H NMR (90 MHz, CDCl$_3$) δ 6.09 (s, 1 H, *H*C=C, trans), 5.53 (s, 1 H, *H*C=C, cis), 4.21 (hept, 3 H, SiOCH), 4.11 (t, 2 H, J = 13.7 Hz, COOCH$_2$), 1.93 (s, 3 H, =CCH$_3$), 1.87–1.61 (m, 2 H, COOCH$_2$*C*H$_2$), 1.15 (d, 18 H, SiOCH(C*H*$_3$)), 0.71–0.52 (m, 2 H, SiCH$_2$); ^{13}C NMR (22.5 Hz, CDCl$_3$) δ 167.0 (C=O), 136.5 (CH$_2$=*C*), 124.5 (*C*H$_2$=C), 66.6 (COO*C*H$_2$), 64.8 (SiOCH), 25.3 (SiOCH*C*H$_3$), 22.4 (COOCH$_2$*C*H$_2$), 18.1 (CH$_3$), 8.2 (SiCH$_2$). Anal. Calcd for $C_{16}H_{32}O_5Si$: C, 57.49; H, 9.61; N, 0.00. Found: C, 57.80; H, 9.90; N, 0.00.

Purification of Monomers. The monomers **3a–c** were purified similarly by the previous method of Allen, Long, and McGrath.[14] They were degassed and stirred over finely ground CaH$_2$ for 48 h and were distilled on a vacuum line into the round-bottomed flask equipped with break-seals. After adding an appropriate amount of trioctylaluminum in heptane solution into the monomer through the break-seal, the mixture was stirred for 1 h and the monomer was then distilled on a vacuum line into the break-seal-attached round-bottomed flask prewashed with 1,1-diphenylhexyllithium. About 1 mol % of trioctylaluminum to the monomer was generally used. The monomer thus distilled was diluted to 0.2–0.3M solutions with THF and stored at −30 °C until ready for polymerization.

Similarly, MMA was purified by distillations first over CaH$_2$ and then over triethylaluminum on a vacuum line according to the method previously reported by Allen, Long, and McGrath.[14]

Styrene was distilled on a vacuum line in the presence of benzyl chloride free benzylmagnesium chloride.

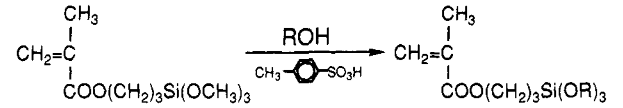
Polymerization Procedure. All the polymerizations were carried out at −78 °C for 1 h with stirring under high-vacuum conditions (10^{-6} mmHg) in an all-glass apparatus equipped with break-seals in the usual manner. The desired charge of monomer in a THF solution was added to a THF solution of the initiator. Both solutions must be kept at −78 °C. The polymerization was then terminated with an excess of methanol degassed at −78 °C. The mixture was evaporated with a vacuum pump; the residual polymer was dissolved in a small amount of THF and precipitated into methanol. Special care is needed for handling the polymers obtained from **3a** and **3b**, because they were readily hydrolyzed. The polymer was purified by repeated precipitation from THF solution into methanol and freeze-dried from its benzene solution. The polymers obtained were characterized by IR, ^{1}H and ^{13}C NMR, vapor-pressure osmometry (VPO), and size-exclusion chromatography (SEC).

Similarly, block copolymerizations were carried out by the sequential polymerizations by **3c** with MMA, MMA with **3c**, and styrene with **3c**.

Measurements. Infrared (IR) spectra were recorded on a Jasco IR-G spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q in CDCl$_3$. Chemical shifts are reported in ppm downfield relative to (CH$_3$)$_4$Si (δ 0) for ^{1}H NMR and relative to CDCl$_3$ (δ 77.1) for ^{13}C NMR, respectively. Size-exclusion chromatograms were obtained at 40 °C with a Toyo Soda HLC-8020 instrument with ultraviolet or refractive index detection. THF was the carrier solvent at a flow rate of 0.8 mL/min. Vapor-pressure osmometry (VPO) measurement was made with a Corona 117 instrument in benzene solutions with a highly sensitive thermoelectric couple and equipment of very exact control of temperature. The number-average molecular weights ($\bar{M}_n$) up to 10^5 were determined possibly within an analytical error of ±5%.

Results and Discussion

Synthesis of Monomers. 3-(Trimethoxysilyl)propyl methacrylate (**3a**) is generally synthesized by the hydrosilylation of allyl methacrylate with trimethoxysilane. It is now commercially available and is widely used as a silane coupling reagent. Little attention, however, has been paid for the synthesis and use of other related methacrylates with alkoxysilyl groups. During this study, we have readily synthesized these alkoxysilyl derivatives such as 3-(triethoxysilyl)- (**3b**) and 3-(tri-2-propoxysilyl)propyl methacrylates (**3c**) by a simple acid-catalyzed alcohol exchange reaction of **3a** with a large excess of the corresponding alcohol as shown below:



It was also found that reaction occurred between **3a** and a variety of alcohols such as propanol, butanol, and 2-butanol in the presence of a catalytic amount of *p*-toluenesulfonic acid. In each of all these cases, a quantitative conversion was realized. On the other hand, with the use of bulky *tert*-butanol, the reaction always gave a mixture of mainly mono-*tert*-butoxysilyl derivative and small amounts of di- and tri-*tert*-butoxysilyl derivatives even after longer reaction times (24 h) at higher temperatures to 100 °C. It is noteworthy that no detectable transesterification reaction occurred under the reaction conditions employed here. Thus, the method is simple, and it allows for the straightforward and convenient synthesis of a wide variety of 3-(alkoxysilyl)alkyl methacrylates in which the alkoxy substituent on the silicon atom can be varied except for tertiary alkoxy ones.

Purification of Monomers. The purification of monomer is especially important for achieving anionic living polymerization with success. The monomers **3a–c** were readily purified up to more than 99.9% by the repeated fractional distillations under reduced pressure. They were then stirred over finely divided CaH_2 for 2 days and distilled under high-vacuum conditions (10^{-6} mmHg). When the monomers at this stage were used in the anionic polymerization, the results were always less satisfactory. The polymers with predetermined molecular weights and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.1$) were not produced even at the monomer to initiator molar ratios of less than 50, although the polymerizations occurred quantitatively.

We also tried to purify the monomers by the method where the monomers were distilled after addition of a small amount of an anionic initiator such as butyllithium, 1,1-diphenylhexyllithium, or oligo(α-methylstyryl)lithium. Again, the polymerization of monomers thus purified gave the polymers of relatively broad molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.2–1.4). Furthermore, one often encountered undesirable polymerizations during the process of addition of the initiator to monomer.

The rigorously purified monomers usable for anionic living polymerization could be obtained by a method similar to that recently developed by Allen, Long, and McGrath, who used triethylaluminum as an impurity scavenger.[14] Our monomers were first distilled over CaH_2 and then distilled in the presence of trioctylaluminum. The use of triethylaluminum more reactive than trioctylaluminum was not suitable for **3a–c**, because the distilled monomers were always contaminated with the aluminum compound. The results of anionic polymerization with these purified monomers are satisfactory with respect to the molecular weight and the molecular weight distribution of the resulting polymer. They will be described in the next section.

Anionic Polymerization of 3a–c. In contrast to the polymerizations of styrene and 1,3-dienes, anionic living polymerizations of alkyl methacrylates proceed only with very careful selection of solvent, temperature, and initiator. For example, in the anionic polymerization of methyl methacrylate (MMA), it is preferable to use the bulky and less nucleophilic initiator in a polar solvent like THF at a low temperature generally lower than −65 °C. It has been already established that the polymerization of MMA with 1,1-diphenylhexyllithium at −78 °C has the characteristic of a truly living system.[8] Therefore, polymerization of **3a–c** was first conducted under the conditions as described above.

Table I
Anionic Polymerizations of 3a–c with 1,1-Diphenylhexyllithium–LiCl in THF at −78 °C for 1 h[a]

monomer (mmol)	BuLi, mmol	1,1-diphenylethylene, mmol	LiCl, mmol	$10^{-3}\bar{M}_n$-(calcd)	$10^{-3}\bar{M}_n$-(obsd)[b]	$\bar{M}_w/\bar{M}_n$[c]
3a (2.99)	0.0920	0.190		8.3	12	1.31
3b (3.15)	0.0894	0.184		10	16	1.31
3c (2.34)	0.0990	0.156		8.1	14	1.28
3a (4.54)	0.120	0.158	0.398	9.6	8.2	1.05
3b (3.25)	0.0972	0.143	0.354	9.9	9.2	1.03
3c (1.60)	0.0418	0.109	0.0676	13	14	1.03

[a] Yields of polymers were quantitative in all cases. [b] $\bar{M}_n$(obsd) was obtained by VPO. [c] $\bar{M}_w/\bar{M}_n$ was determined from the SEC curve.

The polymerization proceeded very fast and was complete within less than 5 min. The results are summarized in Table I. As was seen, the observed molecular weights of polymers from **3a–c** were always definitely higher than those calculated from monomer to initiator ratios. The SEC profiles of the polymers all showed unimodal peaks with relatively broad distributions. The values of $\bar{M}_w/\bar{M}_n$ were in the range of 1.28–1.31. Either slow addition of the monomer to the initiator or use of a very diluted monomer solution gave similar results. These results indicate that the competitive side reactions occur to some extent possibly at an early stage in the polymerizations of **3a–c**. Since MMA undergoes anionic living polymerization under the same conditions, one of the possible candidates of a side reaction is the nucleophilic attack of a silicon atom by 1,1-diphenylhexyllithium and/or the propagating active ends of the polymers.

Teyssié and his co-workers recently found a striking effect of LiCl on the anionic living polymerizations of *tert*-butyl acrylate[10] and MMA.[15] They suggest that LiCl can control the dissociation of the active sites of propagating polymer chain ends and/or create enough steric hindrance around them to eliminate the undesirable side reactions. We have also examined the effect of LiCl to our polymerization system.

Again as can be seen in Table I, good agreement between the observed and calculated $\bar{M}_n$ values was observed. In addition, the resulting polymers were found to possess very narrow molecular weight distributions, the $\bar{M}_w/\bar{M}_n$ ratios being less than 1.05. Thus, the results on the molecular weights and their distributions are clearly improved by addition of LiCl to the polymerization system. The presence of LiCl may successfully contribute to suppress side reactions like a silicon attack as mentioned before. Thus, the living nature of the polymerizations of **3a–c** with LiCl is strongly supported by the above results.

Unfortunately, both poly(**3a**) and poly(**3b**) are particularly troublesome to handle. Broadening in their molecular weight distributions was often observed after reprecipitation of polymers. This is possibly due to the hydrolysis of either the trimethoxy or triethoxysilyl groups, followed by subsequent condensation of silanols formed in the polymer chains. The evidence is provided by the IR spectra of the resulting polymers which contain very broad bands at around 1050 cm^{-1} characteristic of the Si–O–Si bond. Practically, purification of the polymers was difficult, especially in the cases of high molecular weight polymers. Very careful handling using absolute solvents under a nitrogen atmosphere is required to purify both poly(**3a**) and poly(**3b**). Under this circumstance, their molecular weights and distributions measured were not

Table II
Anionic Polymerization of 3c with Various Initiators in THF at −78 °C for 1 h

3c, mmol	initiator		DPE,[a] mmol	LiCl, mmol	$10^{-3}\bar{M}_n$(calcd)	$10^{-3}\bar{M}_n$(obsd)[b]	$\bar{M}_w/\bar{M}_n$[c]
	type	mmol					
1.41	BuLi	0.0378				no polymer	
2.34	BuLi	0.0990	0.156		8.1	14	1.28
1.48	BuLi	0.0769	0.128	0.180	6.6	6.0	1.04
1.60	BuLi	0.0418	0.109	0.0676	13	14	1.03
3.26	BuLi	0.0449	0.161	0.353	24	26	1.02
6.01	BuLi	0.0558	0.131	0.395	36	34	1.03
7.99	BuLi	0.0533	0.105	0.170	50	58	1.02
3.14	cumyl K[d]	0.0490	0.112		22	24	1.21
2.34	K-Nap[e]	0.0923	0.154		17	24	1.35
3.14	*t*-BuOK[f]	0.276			3.9	24	1.33
2.95	BzMgCl[g]	0.0815			12	110	1.15
3.32	$LiAlH_4$	0.158				no polymer	

[a] 1,1-Diphenylethylene. [b] $\bar{M}_n$(obsd) obtained by VPO. [c] $\bar{M}_w/\bar{M}_n$ determined by SEC. [d] Cumylpotassium. [e] Potassium naphthalenide. [f] Potassium *tert*-butoxide. [g] Benzylmagnesium chloride.

reproducible. On the other hand, the polymer from **3c** was quite stable during handling. No change of the molecular weight distribution was in fact observed after reprecipitation and upon storage for months in the air. Therefore, **3c** was conveniently employed for examining in detail the general behavior of anionic polymerization of alkyl methacrylate bearing an alkoxysilyl group.

Table II presents the results of the anionic polymerization of **3c** in THF at −78 °C with a variety of anionic initiators. The initiators involved were BuLi, 1,1-diphenylhexyllithium, 1,1-diphenylhexyllithium–LiCl, cumylpotassium capped with DPE, 1,4-dipotassio-1,1,4,4-tetraphenylbutane, potassium *tert*-butoxide, lithium aluminum hydride ($LiAlH_4$), and benzylmagnesium chloride.

No polymer was produced with BuLi in THF at −78 °C. As mentioned above, the 1,1-diphenylhexyllithium-initiated polymerization gave quantitatively the polymer of higher M_n than the predicted value and of relatively broad distribution. The combination of 1,1-diphenylhexyllithium and LiCl is an excellent initiator system for the polymerization of **3c**.[16] Good agreement is observed between the measured and calculated $\bar{M}_n$ values. The molecular weight distributions are very narrow and the $\bar{M}_w/\bar{M}_n$ values are less than 1.1 in all runs. These are consistent with the living character of the polymerization. As a result, a series of nearly monodisperse poly(**3c**) of known molecular weight is possible by this system.

It should be noted that a precise molecular weight control was possibly achieved up to around 50 × 10^3 when trioctylaluminum-purified **3c** was used. At higher ratios of monomer to initiator in the polymerization, there were deviations between the calculated and observed $\bar{M}_n$ values of the resulting polymers and the latter were always higher than the calculated values. This is probably due to partial destruction of the initiator and/or the active end of the polymer chain by impurities in **3c** during the course of the polymerization. Therefore, more careful purification of **3c** is needed to obtain the polymers of higher M_n values than 10^5.

Organopotassium reagents of both cumylpotassium capped with DPE and 1,4-dipotassio-1,1,4,4-tetraphenylbutane were not excellent initiators for the polymerization of **3c**. It is obvious from the results that side reactions occur to a little extent in these polymerization systems. Both potassium *tert*-butoxide and benzylmagnesium chloride initiate the polymerization of **3c** with low initiator efficiencies, although the yields of polymers were quantitative. Unexpectedly, no polymerization of **3c** occurred with the use of $LiAlH_4$, which was previously reported to be an active initiator for the polymerization of MMA.[17] From these results with various anionic initiators, the polymerization behavior of **3c** is almost the same as that of MMA except for the case with $LiAlH_4$.

Table III
Synthesis of Block Copolymers of A–B Type[a]

A monomer	B monomer	block copolymer (homopolymer)[b]		
		$10^{-3}\bar{M}_n$(calcd)	$10^{-3}\bar{M}_n$(obsd)[c]	$\bar{M}_w/\bar{M}_n$[d]
3c	MMA	25 (8.7)	27 (7.3)	1.11 (1.08)[e]
MMA	**3c**	17 (11)	19 (14)	1.03 (1.02)[e]
styrene	**3c**	18 (9.0)	17 (10)	1.06 (1.03)[f]

[a] Block copolymerizations were carried out in THF at −78 °C for each 1 h at the first and second polymerizations. [b] Homopolymers were obtained at the first-stage polymerization. [c] $\bar{M}_n$(obsd) obtained by VPO. [d] $\bar{M}_w/\bar{M}_n$ determined by SEC. [e] 1,1-Diphenylhexyllithium–LiCl was used as an initiator. [f] BuLi was used as an initiator. Living polystyrene was capped with DPE before the second polymerization.

Block Copolymerization. One of the most attractive features in living polymerization is the feasibility of synthesizing block copolymers with well-defined structures. Therefore, we have synthesized an A–B diblock copolymer by the sequential polymerization of **3c** as monomer A and MMA as monomer B with 1,1-diphenylhexyllithium in the presence of LiCl. A yield of polymer was quantitative based on both monomer weights. The results are summarized in Table III.

As can be seen, the observed $\bar{M}_n$ value agrees well with that calculated from {[**3c**] + [MMA]}/[I]. The SEC profile showed that the peak of the starting polymer from **3c** shifted completely to the higher molecular weight side after addition of MMA. The resulting polymer possessed a fairly narrow molecular weight distribution. The ^1H NMR exhibited that the molar ratio of poly(**3c**) and PMMA segments was almost equal to that of [**3c**]/[MMA] fed at the polymerization. Thus, the expected block copolymer of poly(**3c**-*b*-MMA) can be successfully synthesized. This result also provides clear evidence for the living character of the anionic polymerization of **3c**.

The reverse order of monomer addition also resulted in the formation of the B–A diblock copolymer in 100% yield. The resulting poly(MMA-*b*-**3c**) was found to have the expected structure from both monomers to initiator molar ratio (Table III). Thus, the living polymer of MMA also initiates the polymerization of **3c**. Similarly, a novel diblock copolymer of poly(styrene-*b*-**3c**) could be synthesized by the addition of **3c** to the BuLi-initiated living polystyrene capped with DPE, also shown in Table III.

Hydrolysis of Poly(3c). The resulting poly(**3c**) is a colorless grease and soluble in a wide variety of solvents such as pentane, hexane, benzene, toluene, diethyl ether, THF, 1,4-dioxane, acetone, ethyl acetate, carbon tetrachloride, chloroform, dichloromethane, pyridine, *N*,*N*-dimethylformamide, and ethanol. It is insoluble only in methanol and water.

As mentioned before, both poly(**3a**) and poly(**3b**) were readily hydrolyzed even under neutral conditions. They were only stable under a nitrogen atmosphere but became gradually insoluble even with moisture in the air. On the other hand, poly(**3c**) is sufficiently stable in air and during the workup of the polymer purification using water and methanol. No evidence for the hydrolysis of the Si–OCH(CH_3)$_2$ bond could be detected by the ^{1}H NMR and IR analyses. There is no problem for long time storage in air.

In order to know in more detail the hydrolytic behavior of poly(**3c**), films (25 μm thick) cast from 5 wt % benzene solution were soaked in water, 2 N HCl, and 1 N NaOH aqueous solutions, respectively. The degree of hydrolysis was traced by IR measurement. No change was observed at all in water for weeks. Surprisingly, the film was still stable in 2 N HCl solution for 6 h at 25 °C, but after that it was gradually hydrolyzed. The absorption band corresponding to the Si–O–Si stretching vibration was observed to increase significantly in the film after 12 h by the IR spectrum. The film became completely insoluble in organic solvents as expected. In a 1 N NaOH solution, the absorption band for the Si–O–Si bond was not observed in the film after 8 h at 25 °C. Furthermore, the peak for an ester carbonyl was not reduced at all, indicating a strong resistibility of the ester linkage of poly(**3c**) to the base-catalyzed hydrolysis.

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(16) LiCl was found to be very effective in maintaining the living character of the polymerization of **3c**. Of particular interest in this effect is know what molar ratio of LiCl to 1,1-diphenylhexyllithium is required in the polymerization. Therefore, we have carried out the polymerization of **3c** in THF at −78 °C at different molar ratios of LiCl to 1,1-diphenylhexyllithium. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the resulting polymers were analyzed by VPO and SEC, respectively. The results show that the molecular weight distribution narrows as the ratio of [LiCl]/[initiator] increases, and the $\bar{M}_w/\bar{M}_n$ value as low as 1.04 is found to be leveled off at an equal molar ratio of LiCl to initiator. Good agreement between $\bar{M}_n$ values was observed at the ratio of more than 1, although the values of $\bar{M}_n$(obsd) were always higher than those of $\bar{M}_n$(calcd) at the ratio of [LiCl]/[initiator] less than 1. These results indicate that an equal amount of LiCl is enough to achieve the anionic living polymerization of **3c**. Thus, the effect of LiCl is similar to that on the polymerization of MMA reported by Teyssié and his co-workers.[15]

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Registry No. 3a (homopolymer), 52004-97-4; **3b** (homopolymer), 126843-37-6; **3c** (homopolymer), 138606-39-0; (**3c**)(MMa) (block copolymer), 138606-40-3; (**3c**)(St) (block polymer), 138606-41-4; BuLi, 109-72-8; $(Ph_2)(Li)C(CH_2)_5H$, 3462-81-5; $(Ph_2)(Li)C(CH_2)_5H{\cdot}ClLi$, 138606-38-9; $LiAlH_4$, 16853-85-3; 1,4-dipotassio-1,1,4,4-tetraphenylbutane, 52681-96-6; benzylmagnesium chloride, 6921-34-2; potassium *tert*-butoxide, 865-47-4.