6322 *Macromolecules* **2008**, *41*, 6322−6330

Microflow-System-Controlled Anionic Polymerization of Styrenes

Aiichiro Nagaki, Yutaka Tomida, and Jun-ichi Yoshida*

*Department of Synthetic and Biological Chemistry, Graduate School of Engineering, Kyoto University
Nishikyo-ku, Kyoto 615-8510, Japan*

Received April 5, 2008; Revised Manuscript Received June 21, 2008

ABSTRACT: Anionic polymerization of styrene using *sec*-BuLi as an initiator was conducted in a microflow system. A high level of molecular-weight distribution control was achieved under easily accessible conditions, such as at 0 °C ($M_w/M_n = 1.08$) and 24 °C ($M_w/M_n = 1.10$). The polymerization of styrene derivatives having silyl, methoxy, silyloxy, alkynyl, and alkylthio groups on the benzene ring also took place in a highly controlled manner using *sec*-BuLi as an initiator. The end functionalization using chlorosilanes and block copolymerization were also achieved in microflow systems. The end functionalization with dichlorodimethylsilane led to the formation of a chlorosilane having a single polymer chain on silicon. The subsequent reaction with another active polymer chain gave block copolymers having two different polymer chains on a silicon core.

Introduction

Polymerization in microflow systems has attracted a great deal of attention,[1] and extensive studies on radical polymerization of vinyl monomers,[2] coordination polymerization,[3] polycondensation,[4] and ring-opening polymerization[5] using microflow systems have been reported.[6,7] We recently reported that the cationic polymerization of vinyl monomers could be achieved in a microflow system with excellent molecular-weight distribution control without adding a capping agent, which decelerates the propagation by the equilibrium between active and dormant species.[8] The characteristic features of microflow systems, including fast mixing,[9] fast heat transfer,[10] and short residence time,[11] seem to be responsible for the excellent molecular-weight distribution control.

Among various methods of polymerization, anionic polymerization of vinyl monomers[12] serves as an excellent method for the synthesis of polymers of well-defined end structures because the anionic polymer ends are living even in the absence of a capping agent[13] and can be utilized for end functionalization reactions with various electrophiles and block copolymerization.[14] Major drawbacks of conventional anionic polymerization in polar solvents in macrobatch reactors include the requirement of low temperatures, such as −78 °C. Such an requirement causes severe limitations in the use of this highly useful polymerization in industry. Using nonpolar solvents, the polymerization can be conducted at higher temperatures,[15] but much longer reaction time is needed for completion. We envisaged that such a drawback can be overcome using microflow systems. Moreover, we hope that the use of microflow systems will enable more precise control of polymer structures compared with conventional macrobatch polymerization. However, to the best of our knowledge, there is no report on the use of microflow systems for anionic polymerization of vinyl monomers in the literature. In this paper, we report that alkyllithium-initiated anionic polymerization of styrenes takes place in a highly controlled manner in a microflow system under easily accessible conditions such as at 0 °C or room temperature. We also report that selective functionalization of the active polymer chains and block copolymerization can be achieved in the microflow system.

Results and Discussion

***sec*-BuLi-Initiated Polymerization of Styrene in a Macrobatch Reactor.** We focused on *sec*-BuLi-initiated polymerization of styrene, which is one of the most fundamental anionic polymerization reactions. Before using a microflow system, the polymerization in a macrobatch reactor was examined. A solution of styrene in tetrahydrofuran (THF) (1.0 M, 6 mL, 0 °C) was added to a solution of *sec*-BuLi in hexane (0.20 M, 1 mL) in a 25 mL flask using a syringe pump (flow rate = 6.0 mL min^{-1}) at 0 °C. The reaction was complete within 10 s. The polymerization was quenched with methanol (neat, 3 mL) at 0 °C. The number-average molecular weight of the resulting polystyrene ($M_n = 5200$) was higher than that calculated based on the monomer/initiator ratio ([M]/[I] = 30, $M_n = 3180$), and the molecular-weight distribution was not very narrow ($M_w/M_n = 1.36$). These phenomena are well-known for conventional macrobatch reactors. In general, *sec*-BuLi-initiated polymerization of styrene derivatives in polar solvents such as THF should be carried out at low temperatures such as −78 °C to obtain narrow molecular weight distributions.

***sec*-BuLi-Initiated Polymerization of Styrene in a Microflow System.** A microflow system composed of a T-shaped micromixer **M** and a microtube reactor **R** (inner diameter (ϕ) = 1000 μm, length (L) = 50 cm) was used for the anionic polymerization of styrene (Figure 1). A solution of styrene in THF (2.0 M) and a solution of *sec*-BuLi in hexane (0.2 M) were mixed using **M**, and the resulting solution was introduced to **R**, where the polymerization took place.

The results obtained with varying temperature, flow rate, and inner diameter of **M** are summarized in Table 1. The polymerizations were complete within the residence time of 2.0−24 s to give the polymers in quantitative yields. When **M** of 250 μm inner diameter was used (entries 1−5), high level of

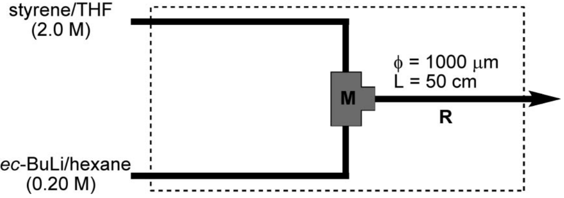


Figure 1. Schematic diagram of a microflow system for controlled anionic polymerization (**M**: T-shaped micromixer; **R**: microtube reactor; THF = tetrahydrofuran).

---

* To whom correspondence should be addressed.

10.1021/ma800769n CCC: $40.75

Table 1. Microflow-System-Controlled Anionic Polymerization of Styrene Initiated by *sec*-BuLi[a]

entry	flow rate of *sec*-BuLi/hexane (mL/min)	flow rate of styrene/THF (mL/min)	inner diameter of M (μm)	bath temperature (°C)	M_n[b]	M_w/M_n[b]
1	2.0	6.0	250	−78	4000	1.43
2	2.0	6.0	250	−48	3700	1.08
3	2.0	6.0	250	−28	3600	1.07
4	2.0	6.0	250	0	3300	1.08
5	2.0	6.0	250	24	3400	1.10
6	3.0	9.0	250	0	3200	1.08
7	1.0	3.0	250	0	3400	1.08
8	0.50	1.5	250	0	4300	2.77
9	0.25	0.75	250	0	4600	3.24
10	3.0	9.0	500	0	3300	1.10
11	2.0	6.0	500	0	3300	1.34
12	1.0	3.0	500	0	4700	2.32
13	0.50	1.5	500	0	5000	2.72
14	0.25	0.75	500	0	6100	3.30
15	2.0	6.0	800	0	3300	1.57

[a] A solution of styrene in THF (tetrahydrofuran) (2.0 M) and a solution of *sec*-BuLi in hexane (0.20 M) were reacted in the microflow system. [b] Polymers were analyzed with size-exclusion chromatography calibrated with polystyrene.

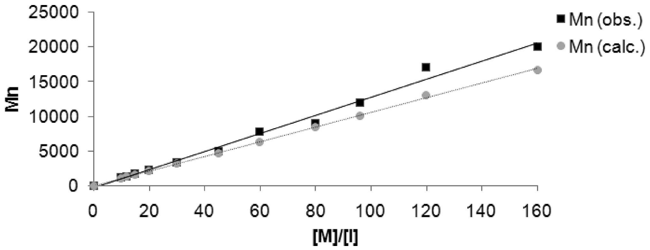
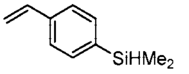
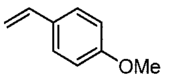
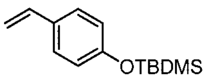
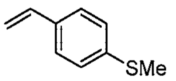
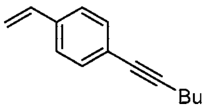


Figure 2. Plots of the molecular weight against the monomer/initiator ratio in anionic polymerization of styrene in THF at 0 °C using the microflow system.

molecular-weight distribution control was attained, although M_w/M_n obtained at −78 °C was larger, presumably because of slow initiation (entry 1). A high level of controllability was attained even at 0 °C (entry 4) and room temperature (entry 5). The number-average molecular weights (M_n) determined by size-exclusion chromatography were close to those calculated based on the monomer/initiator ratio ([M]/[I] = 30, M_n = 3180). The degree of molecular-weight distribution control strongly depended on the flow rate. M_w/M_n increased with a decrease in the flow rate (entries 4 and 6−9), which corresponds to a decrease in mixing speed.[16] The degree of molecular-weight distribution control also depended on the inner diameter of micromixer **M**. The use of **M** with 500 or 800 μm inner diameter resulted in lower controllability (entries 10−15). The mixing speed decreases with an increase in the inner diameter because the diffusion path increases. However, at high flow rates such as 3 mL/min, good control was attained, presumably because of high mixing speed caused by high flow rate (entry 10). Thus, the present results indicate that extremely fast mixing is required for excellent controllability of molecular-weight distribution in microflow system at higher temperatures. Very recently, a similar tendency in the control of molecular-weight distribution and reaction condition using the microflow system was also demonstrated by Löwe and Frey.[17]

M_n increased linearly with an increase in the monomer/initiator ratio ([M]/[I]) as shown in Figure 2. M_n also can be controlled simply by changing the relative flow rate of the solutions of the monomer and the initiator. These results indicate that microflow systems serve as a convenient and powerful method for synthesizing polymers of different molecular weights.

Table 2. Microflow-System-Controlled Anionic Polymerization of Styrene Derivatives

monomer	temperature (°C)	Mn[d]	Mw/Mn[d]
 [a]	0	5700	1.10
 [b]	24	4300	1.14
 [a]	24	6900	1.06
 [a]	0	4500	1.20
 [c]	0	9500	1.18

[a] A solution of styrene derivatives in THF (tetrahydrofuran) (2.0 M) (6 mL/min) and *sec*-BuLi in hexane (0.20 M) (2 mL/min) were reacted in the microflow system. [b] *p*-Methoxystyrene in THF (1.0 M) (6 mL/min) and *sec*-BuLi in hexane (0.20 M) (1 mL/min) were reacted in the microflow system. [c] *p*-(1-Hexynyl)styrene in THF (0.50 M) (6 mL/min) and *sec*-BuLi in hexane (0.10 M) (1 mL/min) were reacted in the microflow system. [d] Polymers were analyzed with size-exclusion chromatography calibrated with polystyrene.

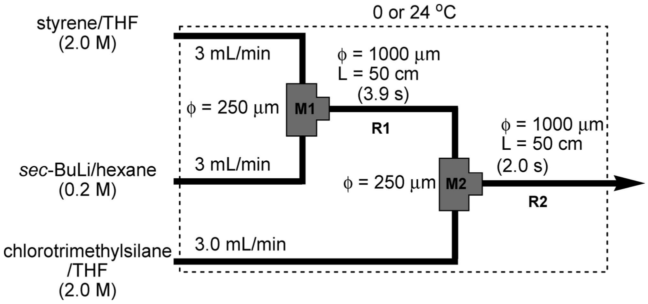


Figure 3. Schematic diagram of the microflow system for controlled anionic polymerization of styrene followed by reaction with chlorotrimethylsilane (**M1**, **M2**: T-shaped micromixers; **R1**, **R2**: microtube reactors; THF = tetrahydrofuran).

***sec*-BuLi-Initiated Polymerization of Styrene Derivatives.** The *sec*-BuLi-initiated polymerization of functionalized styrene derivatives was examined using the optimized conditions (temperature = 0 or 24 °C, inner diameter of **M** = 250 μm, flow rate of *sec*-BuLi/hexane = 2 mL/min, flow rate of the monomer/THF = 6.0 mL/min). Styrenes substituted with silyl,[18] methoxy,[19] and silyloxy[20] groups on the benzene ring underwent the polymerization in a highly controlled manner as shown in Table 2. Styrene derivatives having an alkynyl[21] and an alkylthio[22] groups, which are difficult to polymerize by cationic and radical living polymerizations, could also be polymerized in a highly controlled manner at 0 °C.

End Functionalization of the Polymer Using Chlorosilanes. Synthesis of structurally well-defined polymers and copolymers requires a living polymer end. Thus, end functionalization reactions using chlorosilanes were examined. Styrene was polymerized with 0.1 equiv of *sec*-BuLi, and the polymerization was terminated by chlorotrimethylsilane (10 equiv, 3 mL/min)[23] in the microflow system (Figure 3). The residence time in the first microtube reactor **R1**, where the polymerization took place, was 3.9 s. The polymers were obtained in quantitative yields with narrow molecular-weight distribution at 0 and 24 °C (0 °C: M_n = 1200, M_w/M_n = 1.10; 24 °C: M_n = 1200, M_w/M_n = 1.08). The M_n

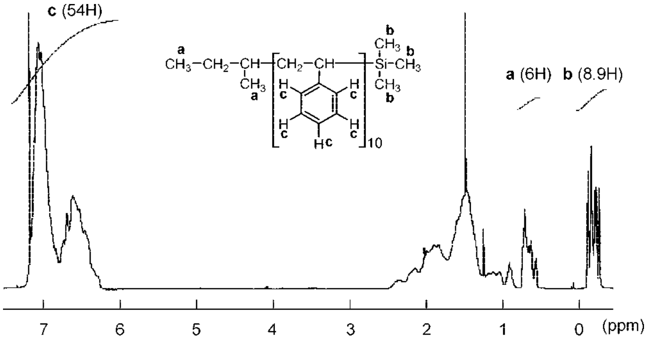
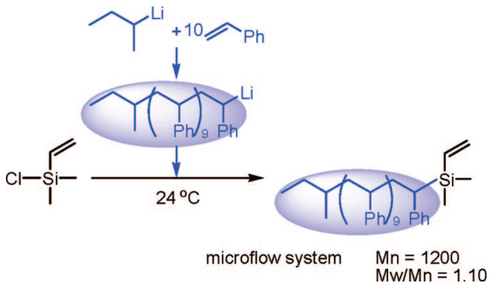


Figure 4. ^{1}H NMR spectrum (600 MHz, in $CDCl_3$) of the polymer obtained by *sec*-BuLi-initiated polymerization of styrene followed by reaction with chlorotrimethylsilane at 24 °C.

Scheme 1. Controlled Anionic Polymerization of Styrene Followed by Reaction with Chlorodimethylvinylsilane



was very close to the calculated value based on the monomer/initiator ratio ([M]/[I] = 10, M_n = 1170).

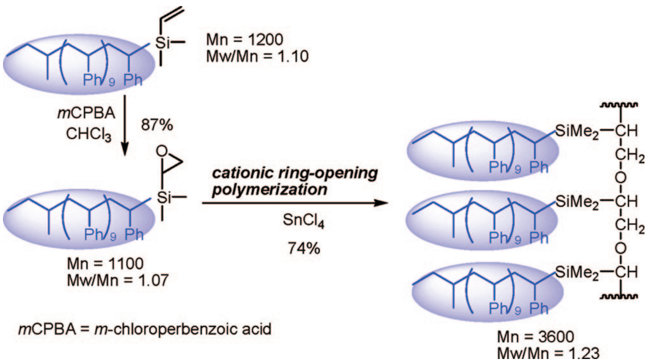
The obtained polymer was analyzed by ^{1}H NMR spectroscopy. As shown in Figure 4, signals due to a trimethylsilyl group were observed at −0.3 to −0.1 ppm. The number of protons of the trimethylsilyl group, which was determined based on that of the initiating *sec*-Bu group in the polymer chain, was 8.9, indicating that the active polymer end was quantitatively trapped by chlorotrimethylsilane. The number of protons of the phenyl groups in the polymer chain (6.2−7.3 ppm) was 54, indicating that an average of 11 monomer units were incorporated into a single polymer chain. This number is reasonable because 10 equiv of the monomer relative to *sec*-BuLi was used. The present observations indicate that the polymer end was really living in the microflow system even at room temperature within the residence time of 3.9 s.

Chlorodimethylvinylsilane was also effective as a trapping agent, and the polymer containing a vinylsilyl group was obtained in quantitative yield (M_n = 1200, M_w/M_n = 1.10) (Scheme 1).[24]

The vinyl group in the polymer could be converted into an epoxy group by the oxidation with *m*CPBA (*m*CPBA = *m*-chloroperbenzoic acid) (87%, M_n = 1100, M_w/M_n = 1.07). The resulting polymer was used as a macromonomer for the cationic ring-opening polymerization using $SnCl_4$ to obtain a polymer brush having polystyrene side chains of narrow molecular-weight distribution as shown in Scheme 2 (74%, M_n = 3600, M_w/M_n = 1.23).[25]

Block Copolymerization. On the basis of the livingness of the polymer end, we synthesized structurally defined block copolymers composed of two different monomers[26] using the microflow system shown in Figure 5. The polymerization reactions were carried out at lower concentrations (concentration of monomer solutions = 0.50 M, concentration of *sec*-BuLi/hexane = 0.05 M) to suppress the pressure increase because an increase in the numbers of micromixers and microtube reactors in a flow system usually causes a significant pressure increase.

Scheme 2. Oxidation of the Vinyl Group in the Polymer with *m*CPBA Followed by Cationic Ring-Opening Polymerization with $SnCl_4$



Solutions of styrene (0.50 M) and *sec*-BuLi (0.05 M) were introduced to T-shaped micromixer **M1** (flow rate = 3.0 mL/min) at 0 or 24 °C. The reaction mixture was introduced to microtube reactor **R1** (ϕ = 1000 μm, L = 50 cm), in which the polymerization took place. In the next stage, a solution of styrene or substituted styrene (0.50 M) was introduced to T-shaped micromixer **M2** (flow rate = 3.0 mL/min). The mixture was introduced to microtube reactor **R2** (ϕ = 1000 μm, L = 50 cm), in which the second polymerization took place. The polymers of higher molecular weight with narrow molecular-weight distribution were obtained (Table 3, Figure 6), indicating that the microflow controlled anionic polymerization serves as an effective method for the synthesis of block copolymers.

Synthesis of Block Copolymers Having Two Polymer Chains on a Silicon Core. We examined the synthesis of block copolymers having two different polymer chains on a silicon core by the reaction of an active polymer chain with dichlorodimethylsilane followed by the reaction with another active polymer chain as a proof of principle. To accomplish this, selective 1:1 reaction of an active polymer chain with dichlorodimethylsilane in the first step is essential. It is noteworthy that an excess amount of dichlorodimethylsilane should be used to obtain the monosubstituted compound selectively in a conventional macrobatch reactor.[27] This requirement of a macrobatch process is problematic because an excess amount of dichlorodimethylsilane should remain unchanged in the first step, and therefore, a large excess amount of another active polymer chain should be used in the second step.

The use of a microflow system serves as a powerful method for solving this kind of problem. For example, we have reported highly selective Friedel−Crafts monoalkylation of aromatic compounds with an *N*-acyliminium ion using a microflow system.[9] The second alkylation was greatly retarded by extremely fast 1:1 mixing. Other examples of the improvement

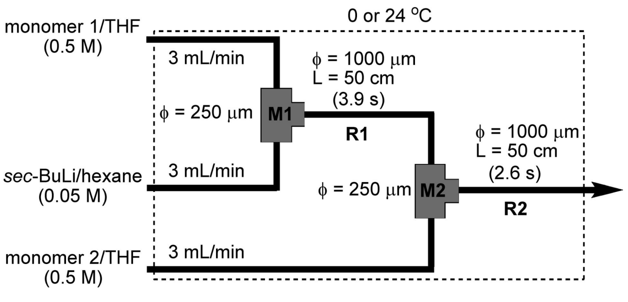
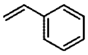
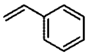
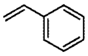
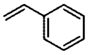
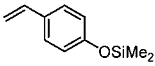
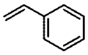
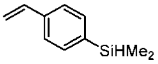


Figure 5. Schematic diagram of the microflow system for controlled anionic block copolymerization (**M1**, **M2**: T-shaped micromixers; **R1**, **R2**: microtube reactors; THF = tetrahydrofuran).

Table 3. Block Copolymerization Using a Microflow System[a]

monomer 1	monomer 2	temperature (°C)	yield (%)	Mn[b]	Mw/Mn[b]
		0	quant	1000	1.11
		24	quant	1100	1.14
		0	quant	2300	1.10
		24	quant	2400	1.10
		0	quant	2700	1.06
		24	quant	3100	1.07
		0	quant	2900	1.06
		24	quant	3000	1.08

[a] Polymerization reactions were carried out with 10 equiv of monomer 1 in THF (0.50 M) and 10 equiv of monomer 2 in THF (tetrahydrofuran) (0.50 M) based on *sec*-BuLi in hexane (0.050 M) at 0 °C. [b] Polymers were analyzed with size-exclusion chromatography calibrated with polystyrene.

of product selectivity in competitive consecutive reactions using microflow systems have also been reported in the literature.[28]

We examined the reaction of an active polymer chain with dichlorodimethylsilane using a microflow system (Figure 7). An active polymer chain, which was prepared in **M1** and **R1**, was allowed to react with dichlorodimethylsilane (1 equiv based on the amount of *sec*-BuLi, which corresponds to the amount of the active polymer ends) in **M2** and **R2**. The corresponding chlorosilane having a single polymer chain was obtained in 95% yield with good molecular-weight distribution control (0 °C: $M_n = 1300$, $M_w/M_n = 1.12$; 24 °C: $M_n = 1400$, $M_w/M_n = 1.13$) as shown in Scheme 3. In contrast, the use of a macrobatch reactor for the reaction with dichlorodimethylsilane led to lower controllability of the polymer structure (0 °C: $M_n = 1300$, $M_w/M_n = 1.21$; 24 °C: $M_n = 1300$, $M_w/M_n = 1.21$). The use of 0.5 equiv of dichlorodimethylsilane in the microflow system gave the silane having two polymer chains on silicon in 94% yield with good molecular-weight distribution control (0 °C: $M_n = 2100$, $M_w/M_n = 1.09$; 24 °C: $M_n = 2000$, $M_w/M_n = 1.10$) (Scheme 3).

The chlorosilane having a single polymer chain was subjected to the subsequent reaction with an alcohol or a Grignard reagent. For example, the reaction with methanol gave the corresponding methoxysilane having a single polymer chain (94%, $M_n = 1300$, $M_w/M_n = 1.14$). The reaction with *p*-methoxyphenylmagnesium bromide gave the *p*-methoxyphenylsilane having a single polymer chain (95%, $M_n = 1300$, $M_w/M_n = 1.12$).

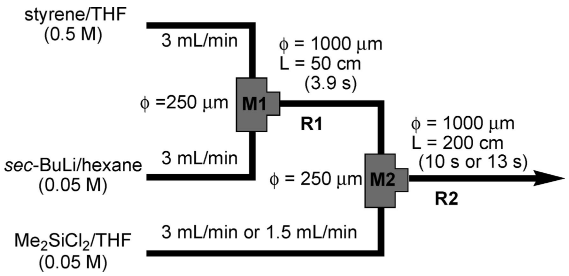
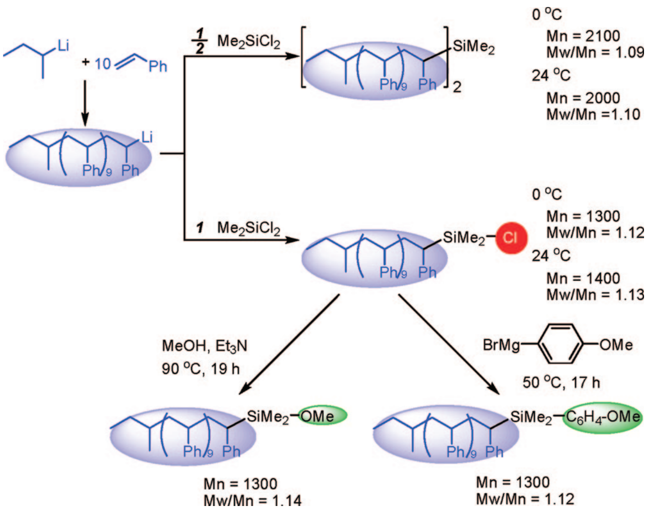


Figure 7. Schematic diagram of the microflow system for *sec*-BuLi-initiated polymerization of styrene followed by the reaction with dichlorodimethylsilane (**M1**, **M2**: T-shaped micromixers; **R1**, **R2**: microtube reactors; THF = tetrahydrofuran).

Scheme 3. Reaction of an Active Polymer Chain with Dichlorodimethylsilane Followed by Reaction with an Alcohol or a Grignard Reagent



The polymer obtained by the reaction with dichlorodimethylsilane was analyzed by ^{1}H NMR (Figure 8a). Signals due to a dimethylsilyl group were observed at −0.3 to 0.1 ppm. The number of protons, which was determined based on that of the initiating *sec*-Bu group in the polymer chain, was 5.1. The NMR spectra of the polymers obtained by the reactions with the Grignard reagent and methanol are also shown in parts b and c of Figure 8, respectively. The signals due to methoxyphenyl group (3.7−3.9 ppm) and those due to methoxysilyl group (3.1−3.5 ppm) were observed. These observations indicate that a single polymer chain was selectively introduced on silicon by extremely fast 1:1 micromixing of the active polymer chain and dichlorodimethylsilane.

With the method for the selective introduction of a single polymer chain on silicon, block copolymers having two different polymer chains on a silicon core were synthesized in the

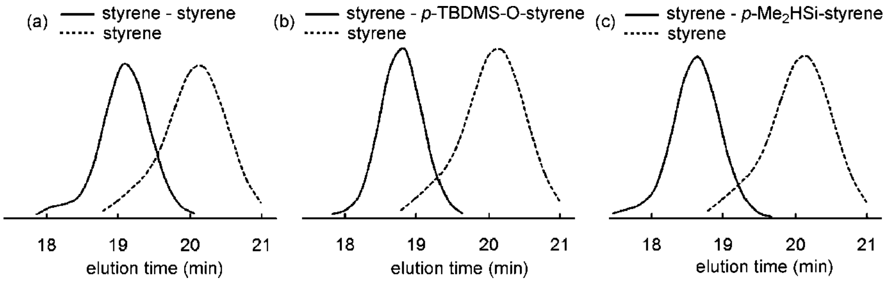


Figure 6. Size exclusion chromatography traces of block copolymerization with the same and different monomers using the microflow system (a) styrene−styrene, (b) styrene−*p*-*tert*-butyldimethylsiloxystyrene, and (c) styrene−*p*-dimethylsilylstyrene.

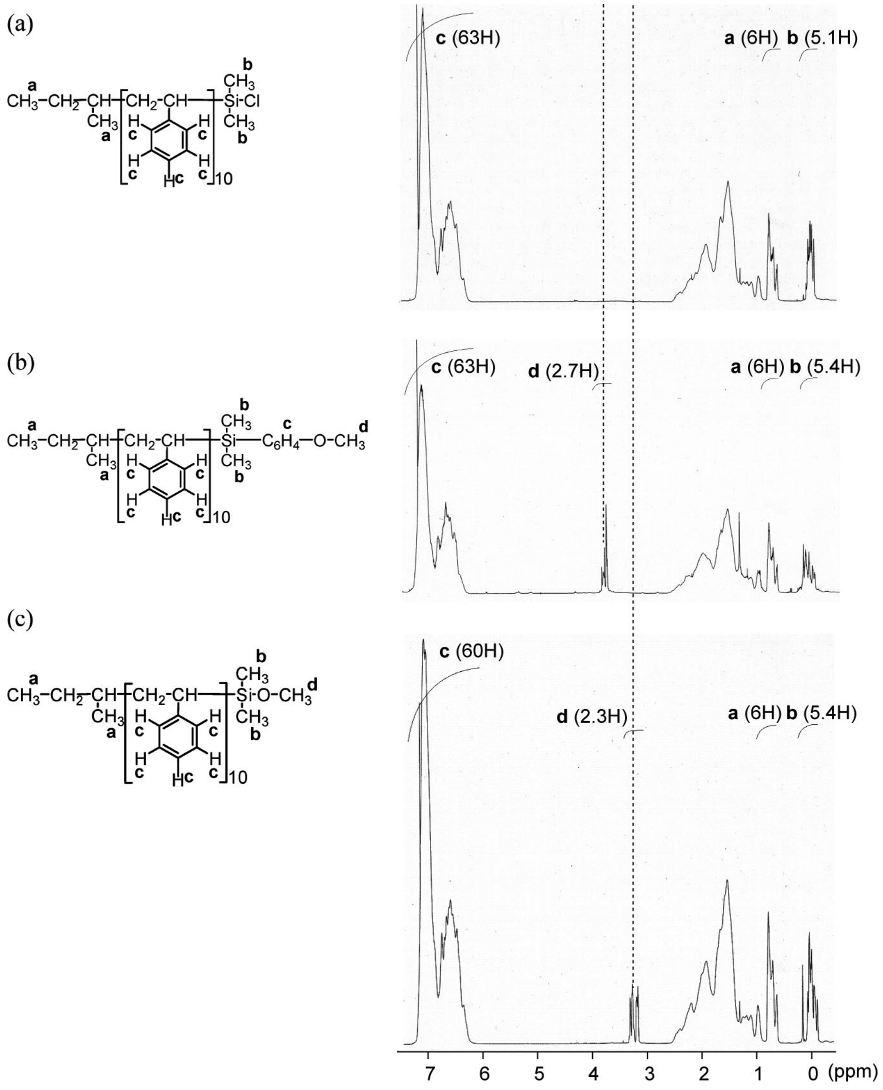
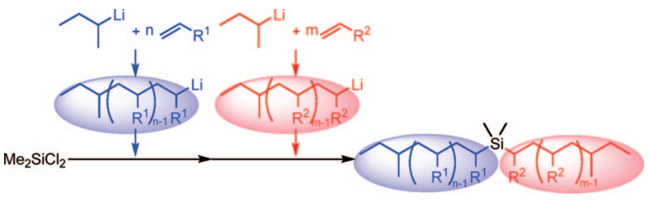


Figure 8. ^{1}H NMR spectra (600 MHz, in $CDCl_3$) of the polymers obtained with reaction with dichlorodimethylsilane: (a) no subsequent treatment was performed, (b) after the treatment with *p*-methoxyphenylmagnesium bromide, and (c) after the treatment with methanol in the presence of triethylamine.

Scheme 4. Reaction of an Active Polymer Chain with Dichlorodimethylsilane Followed by Reaction with Another Active Polymer Chain



microflow system using another active polymer chain as a second nucleophile (Scheme 4).

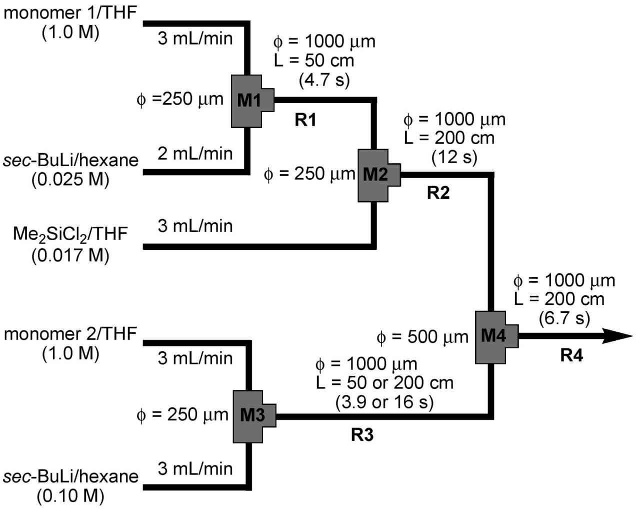


Figure 9. Schematic diagram of the microflow system for the synthesis of block copolymers having two different polymer chains on a silicon core (**M1**, **M2**, **M3**, **M4**: T-shaped micromixers; **R1**, **R2**, **R3**, **R4**: microtube reactors; THF = tetrahydrofuran).

Thus, the polymerization of monomer 1 (60 equiv based on *sec*-BuLi) using *sec*-BuLi was carried out in micromixer **M1** and microtube reactor **R1** (Figure 9). The resulting active polymer was allowed to react with dichlorodimethylsilane (1 equiv based on the active polymer chain) in **M2** and **R2** to produce a chlorosilane having a single polymer chain. The polymerization of monomer 2 (10 equiv based on *sec*-BuLi) to obtain another active polymer chain was carried out in **M3** and **R3**. The reaction of this active polymer chain with the chlorosilane having a single polymer chain in **M4** and **R4** gave the final products in quantitative yields. The block copolymers thus obtained had higher molecular weight with narrow molecular-weight distribution (Figure 10 and Table 4). Therefore,

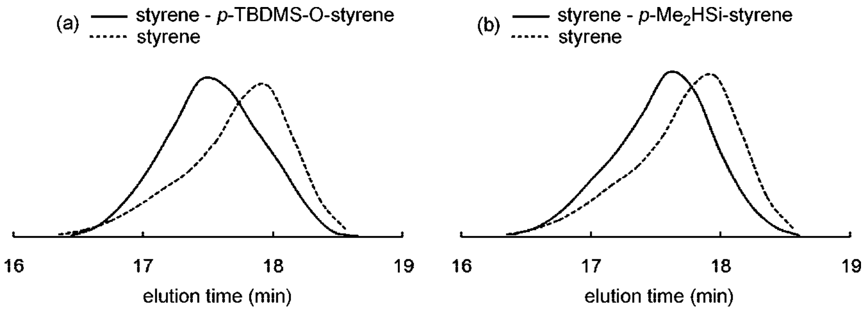
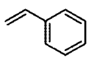
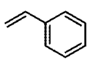
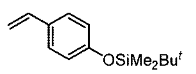
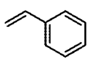
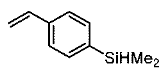


Figure 10. Size exclusion chromatography traces of block copolymers two polymer chains on a silicon core: (a) styrene−*p*-*tert*-butyldimethylsiloxystyrene and (b) styrene−*p*-dimethylsilylstyrene.

Table 4. Synthesis of Block Copolymers Having Two Polymer Chains on a Silicon Core Using a Microflow System[a]

monomer 1	monomer 2	Mn[b]	Mw/Mn[b]
	-	7400 Mn(theory) = 6400	1.14
		8700 Mn(theory) = 8800	1.11
		8600 Mn(theory) = 8000	1.12

[a] Polymerizations were carried out with 60 equiv of monomer 1 and 10 equiv of monomer 2 based on *sec*-BuLi initiator at 24 °C. [b] Polymers were analyzed with size-exclusion chromatography calibrated with polystyrene.

Table 5. Control of Molecular Weights of Polymers by Modulating Flow Rates

concn of *sec*-BuLi/hexane (M)	flow rate of *sec*-BuLi/hexane (mL/min)	[M]/[I]	M_n	M_w/M_n
0.20	6	10	1200	1.13
	5	12	1300	1.12
	4	15	1700	1.11
	3	20	2200	1.11
	2	30	3300	1.10
	1.5	40	4900	1.07
	1	60	7800	1.09
0.05	3	80	9000	1.10
	2.5	96	12000	1.11
	2	120	17000	1.11
	1.5	160	20000	1.11

structurally well-defined block copolymers having two different polymer chains on silicon core could be easily synthesized using microflow systems.

Conclusions. Controlled anionic polymerization of styrenes using *sec*-BuLi as an initiator in a polar solvent can be successfully conducted in a microflow system. The polymerization reactions were complete within 10 s. High level of molecular-weight distribution control was achieved under easily accessible conditions such as at 0 and 24 °C. End functionalization and block copolymerization were also achieved using the microflow system. Selective introduction of a single polymer chain on silicon by fast 1:1 micromixing of an active polymer chain and dichlorodimethylsilane followed by the subsequent reaction with the second active polymer chain in the microflow system led to the synthesis of block copolymers having two different polymer chains on a silicon core. The observations illustrated here open a new possibility for the synthesis of structurally well-defined polymers, copolymers, and block copolymers using microflow system controlled anionic polymerization.

Experimental Section

General. ^{1}H NMR spectra were recorded on a JEOL ECA-600 (^{1}H 600 MHz) spectrometer in $CDCl_3$. Hexane was purchased from Wako, distilled before use, and stored over molecular sieves 4A. THF was purchased from Kanto as a dry solvent and used as obtained. Styrene was distilled twice from CaH_2 before use. Stainless steel (SUS304) T-shaped micromixers with inner diameter of 250, 500, and 800 μm were manufactured by Sanko Seiki Co., Inc. Stainless steel (SUS316) microtube reactors with inner diameter of 1000 μm were purchased from GL Sciences. Micromixers and microtube reactors were connected with stainless steel fittings (GL Sciences, 1/16 OUW). A microflow system composed of micromixers and microtube reactors was dipped in a cooling bath to control the temperature. Solutions were introduced to the microflow system using syringe pumps, Harvard Model 11, equipped with gastight syringes purchased from SGE.

Molecular Weight and Molecular-Weight Distribution. The molecular weight (M_n) and molecular-weight distribution (M_w/M_n) were determined by size exclusion chromatography in THF at 40 °C with a Shodex GPC-101 equipped with two LF-804 columns (pore size: 3000 Å; bead size: 8.0 × 300 mm; range of separation of molecular weight (polystyrene): 200−2 000 000) (Shodex) and an RI detector using a polystyrene standard sample for calibration (flow rate: 1.0 mL/min).

***sec*-BuLi-Initiated Polymerization of Styrene in a Macrobatch Reactor.** A solution of styrene (1.0 M, 6 mL, 0 °C) in THF was added to a solution of *sec*-BuLi (0.20 M, 1 mL) in hexane in a 25 mL flask by a syringe pump (flow rate = 6.0 mL min^{-1}) at 0 °C. After 10 s, the polymerization was quenched with methanol (neat, 3 mL) at 0 °C. The solvent was removed under reduced pressure to obtain the polymer product in quantitative yields. The polymer sample was analyzed with size-exclusion chromatography calibrated with polystyrene ($M_n = 5200$, $M_w/M_n = 1.36$).

Typical Procedure for *sec*-BuLi-Initiated Polymerization of Styrene in a Microflow System. A microflow system composed of a T-shaped micromixer **M** and a microtube reactor **R** (inner diameter (ϕ) = 1000 μm, length (L) = 50 cm) was used. Microtube precooling units ($\phi = 1000$ μm, $L = 100$ cm) were connected to the inlets of **M**. The whole microflow system was dipped in a cooling bath. A solution of styrene (2.0 M) in THF and a solution of *sec*-BuLi (0.20 M) in hexane were introduced to **M** by syringe pumps. The resulting solution was passed through **R**. After a steady state was reached, the product solution was collected for 15 s and was treated with methanol. The solvent was removed under reduced pressure to obtain the polymer products in quantitative yields. The results are summarized in Tables 1 and 2.

Typical Procedure for Polymerization at Various Flow Rates of the Initiator Solution. A microflow system composed of a T-shaped micromixer **M** and a microtube reactor **R** was used. Microtube precooling units ($\phi = 1000$ μm, $L = 100$ cm) were connected to the inlets of **M**. The whole microflow system was dipped in a cooling bath (0 °C). A solution of styrene in THF (2.0 M flow rate = 6.0 mL min^{-1}) and a solution of *sec*-BuLi in hexane (0.20 or 0.05 M) were introduced to **M** ($\phi = 250$ μm) by syringe pumps. The resulting solution was passed through **R** ($\phi = 1000$ μm, $L = 50$ cm). After a steady state was reached, the product solution was collected for 15 s and was treated with methanol. The solvent was removed under reduced pressure to obtain the polymer product in quantitative yields. The results are summarized in Figure 2 and Table 5.

Epoxidation of the Polymer Obtained by the Reaction of *sec*-BuLi-Initiated Polymer End with Chlorodimethylvinylsilane Followed by Cationic Ring-Opening Polymerization. A mixture of the polymer (0.33 g, 0.30 mmol) and 3-chloroperoxybenzoic acid, 77% maximum (100.9 mg 0.45 mmol), in CH_3Cl (6.0 mL) was stirred at room temperature for 113 h. To the reaction mixture was added saturated aqueous $Na_2S_2O_3 \cdot 5H_2O$. The mixture was extracted with $CHCl_3$. The combined organic phase was washed with saturated aqueous $NaHCO_3$ and brine and dried over Na_2SO_4. After filtration, the solvent was removed to give the crude product. The crude product was subjected to gel permeation chromatography ($CHCl_3$) to afford the product (0.287 g, 0.26 mmol, 87%). The polymer samples were analyzed with size exclusion chromatography calibrated with polystyrene ($M_n = 1100$, $M_w/M_n = 1.07$). Then, a solution of the macromonomer (110 mg, 0.10 mmol) in dry CH_2Cl_2 (1 mL) was stirred at room temperature. To the solution was added tetrachlorostannane (50.1 mg, 0.19 mmol), and the reaction mixture was stirred at room temperature for 21 h. To the reaction mixture was added saturated K_2CO_3 in methanol (1 mL). The mixture was added saturated aqueous $NaHCO_3$. The organic phase was separated, and the aqueous phase was extracted with $CHCl_3$. The combined organic phase was washed with saturated aqueous $NaHCO_3$ and brine and dried over Na_2SO_4. After filtration, the solvent was removed to give the crude product. The crude product was subjected to gel permeation chromatography ($CHCl_3$) to afford the product (81.6 mg, 0.074 mmol, 74%). The polymer samples were analyzed with size exclusion chromatography calibrated with polystyrene ($M_n = 3600$, $M_w/M_n = 1.23$).

Block Copolymerizations in a Microflow System. A microflow system composed of two T-shaped micromixers (**M1** and **M2**) and two microtube reactors (**R1** and **R2**) was used. Microtube precooling units ($\phi = 1000$ μm, $L = 100$ cm) were connected to the inlets of **M1** and **M2**. The whole microflow system was dipped in a cooling bath. A solution of monomer 1 (styrene) (0.50 M) in THF (flow rate = 3.0 mL min^{-1}) and a solution of *sec*-BuLi (0.050 M) in hexane (flow rate = 3.0 mL min^{-1}) were introduced to **M1** ($\phi = 250$ μm) by syringe pumps. The resulting solution was passed through **R1** ($\phi = 1000$ μm, $L = 50$ cm) and was mixed with monomer 2 (0.50 M) in THF (flow rate = 3.0 mL min^{-1}) in **M2** ($\phi = 250$ μm). The resulting solution was passed through **R2** ($\phi = 1000$ μm, $L = 200$ cm). After a steady state was reached, the product solution was collected for 15 s and was treated with methanol. The solvent was removed under reduced pressure to obtain the crude product. The crude product was subjected to gel permeation chromatography ($CHCl_3$) to afford the polymer product in quantitative yields (monomers 1 and 2: 100% conversion). The results are summarized in Table 3.

***sec*-BuLi-Initiated Polymerization Followed by the Reaction with Dichlorodimethylsilane (1.0 equiv) in a Microflow System.** A microflow system composed of two T-shaped micromixers (**M1** and **M2**) and two microtube reactors (**R1** and **R2**) was used. Microtube precooling units ($\phi = 1000$ μm, $L = 100$ cm) were connected to the inlets of **M1** and **M2**. The whole microflow system was dipped in a cooling bath (0 °C). A solution of styrene (0.50 M) in THF (flow rate = 3.0 mL min^{-1}) and a solution of *sec*-BuLi (0.050 M) in hexane (flow rate = 3.0 mL min^{-1}) were introduced to **M1** ($\phi = 250$ μm) by syringe pumps. The resulting solution was passed through **R1** ($\phi = 1000$ μm, $L = 50$ cm) and was mixed with dichlorodimethylsilane (0.050 M) in THF (flow rate = 3.0 mL min^{-1}) in **M2** ($\phi = 250$ μm). The resulting solution was passed through **R2** ($\phi = 1000$ μm, $L = 200$ cm). After a steady state was reached, the product solution was collected for 15 s and was treated with methanol. The solvent was removed under reduced pressure to obtain the crude product. The crude product was subjected to gel permeation chromatography ($CHCl_3$) to afford the polymer product (84.6 mg, 95%). The polymer samples were analyzed with size exclusion chromatography calibrated with polystyrene ($M_n = 1300$, $M_w/M_n = 1.12$).

***sec*-BuLi-Initiated Polymerization Followed by the Reaction with Dichlorodimethylsilane (0.5 equiv) in a Microflow System.** A microflow system composed of two T-shaped micromixers (**M1** and **M2**) and two microtube reactors (**R1** and **R2**) was used. Microtube precooling units ($\phi = 1000$ μm, $L = 100$ cm) were connected to the inlets of **M1** and **M2**. The whole microflow system was dipped in a cooling bath (0 °C). A solution of styrene (2.0 M) in THF (flow rate = 3.0 mL min^{-1}) and a solution of *sec*-BuLi (0.20 M) in hexane (flow rate = 3.0 mL min^{-1}) were introduced to **M1** ($\phi = 250$ μm) by syringe pumps. The resulting solution was passed through **R1** ($\phi = 1000$ μm, $L = 50$ cm) and was mixed with dichlorodimethylsilane (0.20 M) in THF (flow rate = 1.5 mL min^{-1}) in **M2** ($\phi = 250$ μm). The resulting solution was passed through **R2** ($\phi = 1000$ μm, $L = 200$ cm). After a steady state was reached, the product solution was collected for 15 s and was treated with methanol. The solvent was removed under reduced pressure to obtain the crude product. The crude product was subjected to gel permeation chromatography ($CHCl_3$) to afford the polymer product (158.8 mg, 94%). The polymer samples were analyzed with size exclusion chromatography calibrated with polystyrene ($M_n = 2100$, $M_w/M_n = 1.09$).

***sec*-BuLi-Initiated Polymerization Followed by the Termination with Dichlorodimethylsilane (1.0 equiv) in a Microflow System and Subsequent Reaction with Methanol.** A microflow system composed of two T-shaped micromixers (**M1** and **M2**) and two microtube reactors (**R1** and **R2**) was used. Microtube precooling units ($\phi = 1000$ μm, $L = 100$ cm) were connected to the inlets of **M1** and **M2**. The whole microflow system was dipped in a cooling bath (0 °C). A solution of styrene (0.50 M) in THF (flow rate = 3.0 mL min^{-1}) and a solution of *sec*-BuLi (0.050 M) in hexane (flow rate = 3.0 mL min^{-1}) were introduced to **M1** ($\phi = 250$ μm) by syringe pumps. The resulting solution was passed through **R1** ($\phi = 1000$ μm, $L = 50$ cm) and was mixed with dichlorodimethylsilane (0.050 M) in THF (flow rate = 3.0 mL min^{-1}) in **M2** ($\phi = 250$ μm). The resulting solution was passed through **R2** ($\phi = 1000$ μm, $L = 200$ cm). After a steady state was reached, the product solution was collected for 30 s. A mixture of methanol (0.75 mmol, 24 mg) and Et_3N (0.75 mmol, 76 mg) was added at 0 °C. Then the reaction mixture was refluxed for 19 h. After filtration, the solvent was removed under reduced pressure. The crude product thus obtained was subjected to gel permeation chromatography ($CHCl_3$) to afford the polymer product (84.0 mg, 94%). The polymer samples were analyzed with size exclusion chromatography calibrated with polystyrene ($M_n = 1300$, $M_w/M_n = 1.14$).

***sec*-BuLi-Initiated Polymerization Followed by the Termination with Dichlorodimethylsilane (1.0 equiv) in a Microflow System and Subsequent Reaction with 4-Methoxyphenylmagnesium Bromide.** A microflow system composed of two T-shaped micromixers (**M1** and **M2**) and two microtube reactors (**R1** and **R2**) was used. Microtube precooling units ($\phi = 1000$ μm, $L = 100$ cm) were connected to the inlets of **M1** and **M2**. The whole microflow system was dipped in a cooling bath (0 °C). A solution of styrene (0.50 M) in THF (flow rate = 3.0 mL min^{-1}) and a solution of *sec*-BuLi (0.050 M) in hexane (flow rate = 3.0 mL min^{-1}) were introduced to **M1** ($\phi = 250$ μm) by syringe pumps. The resulting solution was passed through **R1** ($\phi = 1000$ μm, $L = 50$ cm) and was mixed with dichlorodimethylsilane (0.050 M) in THF (flow rate = 3.0 mL min^{-1}) in **M2** ($\phi = 250$ μm). The resulting solution was passed through **R2** ($\phi = 1000$ μm, $L = 200$ cm). After a steady state was reached, the product solution was collected for 30 s. A solution of 4-methoxyphenylmagnesium bromide in THF (0.50 M, 0.75 mmol) was added at 0 °C. Then the reaction mixture was stirred at 50 °C for 17 h. The resulting solution was treated with 1 N HCl. The organic phase was separated, and the aqueous phase was extracted with $CHCl_3$. The combined organic phase was dried over sodium carbonate. After filtration, the solvent was removed under reduced pressure. The crude product thus obtained was subjected to gel permeation chromatography ($CHCl_3$) to afford the polymer product (91.4 mg, 95%). The polymer samples were analyzed with size exclusion chromatography calibrated with polystyrene ($M_n = 1300$, $M_w/M_n = 1.12$).

Typical Procedure for the Synthesis of Block Copolymers Having Two Different Polymer Chains on a Silicon Core Using a Microflow System. A microflow system composed of four T-shaped micromixers (**M1**, **M2**, **M3**, and **M4**) and four microtube reactors (**R1**, **R2**, **R3**, and **R4**) was used. Microtube precooling units ($\phi = 1000\ \mu$m, $L = 100$ cm) were connected to the inlets of **M1**, **M2**, and **M3**. The whole microflow system was dipped in a cooling bath (24 °C). A solution of monomer 1 (1.0 M) in THF (flow rate = 3.0 mL min^{-1}) and a solution of *sec*-BuLi (0.025 M) in hexane (flow rate = 2.0 mL min^{-1}) were introduced to **M1** ($\phi = 250\ \mu$m) by syringe pumps. The resulting solution was passed through **R1** ($\phi = 1000\ \mu$m, $L = 50$ cm) and was mixed with dichlorodimethylsilane (0.017 M) in THF (flow rate = 3.0 mL min^{-1}) in **M2** ($\phi = 250\ \mu$m). A solution of monomer 2 (1.0 M) in THF (flow rate = 3.0 mL min^{-1}) and a solution of *sec*-BuLi (0.10 M) in hexane (flow rate = 3.0 mL min^{-1}) were introduced to **M3** ($\phi = 250\ \mu$m) by syringe pumps. The resulting solution was passed through **R3** ($\phi = 1000\ \mu$m, $L = 50$ or 200 cm) and was introduced to **M4** ($\phi = 500\ \mu$m), where the solution was mixed with the solution from **R2** ($\phi = 1000\ \mu$m, $L = 200$ cm). The resulting solution was passed through **R4** ($\phi = 1000\ \mu$m, $L = 200$ cm). After a steady state was reached, the product solution was collected for 15 s and was treated with methanol. The solvent was removed under reduced pressure to obtain the crude product. The crude product was subjected to gel permeation chromatography ($CHCl_3$) to afford the polymer product in quantitative yields. The results are summarized in Table 4.

Acknowledgment. This work was partially supported by the Grant-in-Aid for Scientific Research and NEDO projects.

Supporting Information Available: Experimental procedures and spectroscopic data of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Review: Hessel, V.; Serra, C.; Löwe, H.; Hadziioannou, G. *Chem. Ing. Tech.* **2005**, *77*, 1693−1714, and references therein.

(2) (a) Wu, T.; Mei, Y.; Cabral, J. T.; Xu, C.; Beers, K. L. *J. Am. Chem. Soc.* **2004**, *126*, 9880–9881. (b) Russum, J. P.; Jones, C. W.; Schork, F. J. *Macromol. Rapid Commun.* **2004**, *25*, 1064–1068. (c) Wu, T.; Mei, Y.; Xu, C.; Byrd, H. C. M.; Beers, K. L. *Macromol. Rapid Commun.* **2005**, *26*, 1037–1042. (d) Serra, C.; Sary, N.; Schlatter, G.; Hadziioannou, G.; Hessel, V. *Lab Chip* **2005**, *5*, 966–973. (e) Enright, T. E.; Cunningham, M. F.; Keoshkerian, B. *Macromol. Rapid Commun.* **2005**, *26*, 221–225. (f) Russum, J. P.; Jones, C. W.; Schork, F. J. *Ind. Eng. Chem. Res.* **2005**, *44*, 2484–2493. (g) Xu, C.; Wu, T.; Drain, C. M.; Batteas, J. D.; Beers, K. L. *Macromolecules* **2005**, *38*, 6–8. (h) Iwasaki, T.; Kawano, N.; Yoshida, J. *Org. Process Res. Dev.* **2006**, *10*, 1126–1131. (i) Rosenfeld, C.; Serra, C.; Brochon, C.; Hadziioannou, G. *Chem. Eng. Sci.* **2007**, *62*, 5245–5250.

(3) Miyazawa, A.; Kase, T.; Shibuya, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1841–1844.

(4) Yoshida, J.; Okamoto, H. In *Advanced Micro & Nanosystems*; Kockmann, N., Ed.; Wiley: Weinheim, 2006; Vol. *5*.

(5) (a) Yamaguchi, Y.; Ogino, K.; Yamashita, K.; Maeda, H. *J. Chem. Eng. Jpn.* **2004**, *37*, 1265–1270. (b) Honda, T.; Miyazaki, M.; Nakamura, H.; Maeda, H. *Lab Chip* **2005**, *5*, 812–818. (c) Miyazaki, M.; Honda, T.; Nakamura, H.; Maeda, H. *Chem. Eng. Technol.* **2007**, *30*, 300–304. (d) Wilms, D.; Nieberle, J.; Klos, J.; Lowe, H.; Frey, H. *Chem. Eng. Technol.* **2007**, *30*, 1519–1524.

(6) Reviews for microreactor: (a) Fletcher, P. D. I.; Haswell, S. J.; Pombo-Villar, E.; Warrington, B. H.; Watts, P.; Wong, S. Y. F.; Zhang, X. *Tetrahedron* **2002**, *58*, 4735–4757. (b) Jähnisch, K.; Hessel, V.; Löwe, H.; Baerns, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 406–446. (c) Doku, G. N.; Verboom, W.; Reinhoudt, D. N.; van den Berg, A. *Tetrahedron* **2005**, *61*, 2733–2742. (d) Yoshida, J. *Chem. Commun.* **2005**, 4509–4516.

(7) Recent examples: (a) de Bellefon, C.; Tanchoux, N.; Caravieilhes, S.; Grenouillet, P.; Hessel, V. *Angew. Chem., Int. Ed.* **2000**, *39*, 3442–3445. (b) Watts, P.; Wiles, C.; Haswell, S. J.; Pombo-Villar, E.; Styring, P. *Chem. Commun.* **2001**, 990–991. (c) Hisamoto, H.; Saito, T.; Tokeshi, M.; Hibara, A.; Kitamori, T. *Chem. Commun.* **2001**, 2662–2663. (d) Suga, S.; Okajima, M.; Fujiwara, K.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 7941–7942. (e) Wiles, C.; Watts, P.; Haswell, S. J.; Pombo-Villar, E. *Chem. Commun.* **2002**, 1034–1035. (f) Fukuyama, T.; Shinmen, M.; Nishitani, S.; Sato, M.; Ryu, I. *Org. Lett.* **2002**, *4*, 1691–1694. (g) Ueno, M.; Hisamoto, H.; Kitamori, T.; Kobayashi, S. *Chem. Commun.* **2003**, 936–937. (h) Garcia-Egido, E.; Spikmans, V.; Wong, S. Y. F.; Warrington, B. H. *Lab Chip* **2003**, *3*, 73–76. (i) Lai, S. M.; Martin-Aranda, R.; Yeung, K. L. *Chem. Commun.* **2003**, 218–219. (j) Mikami, K.; Yamanaka, M.; Islam, M. N.; Kudo, K.; Seino, N.; Shinoda, M. *Tetrahedron Lett.* **2003**, *44*, 7545–7548. (k) Suga, S.; Nagaki, A.; Tsutsui, Y.; Yoshida, J. *Org. Lett.* **2003**, *5*, 945–947. (l) Kobayashi, J.; Mori, Y.; Okamoto, K.; Akiyama, R.; Ueno, M.; Kitamori, T.; Kobayashi, S. *Science* **2004**, *304*, 1305–1308. (m) Horcajada, R.; Okajima, M.; Suga, S.; Yoshida, J. *Chem. Commun.* **2005**, 1303–1305. (n) Ducry, L.; Roberge, D. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 7972–7975. (o) He, P.; Watts, P.; Marken, F.; Haswell, S. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 4146–4149. (p) Uozumi, Y.; Yamada, Y.; Beppu, T.; Fukuyama, N.; Ueno, M.; Kitamori, T. *J. Am. Chem. Soc.* **2006**, *128*, 15994–15995. (q) Tanaka, K.; Motomatsu, S.; Koyama, K.; Tanaka, S.; Fukase, K. *Org. Lett.* **2007**, *9*, 299–302. (r) Ushiogi, Y.; Hase, T.; Iinuma, Y.; Takata, A.; Yoshida, J. *Chem. Commun.* **2007**, 2947–2949.

(8) (a) Nagaki, A.; Kawamura, K.; Suga, S.; Ando, T.; Sawamoto, M.; Yoshida, J. *J. Am. Chem. Soc.* **2004**, *126*, 14702–14703. (b) Iwasaki, T.; Nagaki, A.; Yoshida, J. *Chem. Commun.* **2007**, 1263–1265.

(9) For example: (a) Nagaki, A.; Togai, M.; Suga, S.; Aoki, N.; Mae, K.; Yoshida, J. *J. Am. Chem. Soc.* **2005**, *127*, 11666–11675. (b) Suga, S.; Nagaki, A.; Yoshida, J. *Chem. Commun.* **2003**, 354–355. (c) Yoshida, J.; Nagaki, A.; Iwasaki, T.; Suga, S. *Chem. Eng. Technol.* **2005**, *28*, 259–266.

(10) Iwasaki, T.; Yoshida, J. *Macromolecules* **2005**, *38*, 1159–1163.

(11) (a) Kawaguchi, T.; Miyata, H.; Ataka, K.; Mae, K.; Yoshida, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 2413–2416. (b) Usutani, H.; Tomida, Y.; Nagaki, A.; Okamoto, H.; Nokami, T.; Yoshida, J. *J. Am. Chem. Soc.* **2007**, *129*, 3046–3047. (c) Nagaki, A.; Tomida, Y.; Usutani, H.; Kim, H.; Takabayashi, N.; Nokami, T.; Okamoto, H.; Yoshida, J. *Chem. Asian J.* **2007**, *2*, 1513–1523.

(12) (a) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996. (b) Jagur-grodzinski, J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2116–2133. (c) Hong, K.; Uhrig, D.; Mays, J. W. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 531–538. (d) Smid, J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2101–2107. (e) Hirao, A.; Loykulnant, S.; Ishizone, T. *Prog. Polym. Sci.* **2002**, *27*, 1399–1471. (f) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747−3792, and references therein.

(13) (a) Szwarc, M. *Nature (London)* **1956**, *178*, 1168–1169. (b) Geacintov, C.; Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1962**, *84*, 2508–2514. (c) Bhattacharyya, D. N.; Lee, C. L.; Smid, J. Szwarc. *J. Phys. Chem.* **1965**, *69*, 612–623.

(14) (a) Morton, M.; Fetters, L. J. *J. Polym. Sci., Macromol. Rev.* **1967**, *2*, 71–113. (b) French, D. M. *Rubber Chem. Technol.* **1969**, *42*, 71–109. (c) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1–90. (d) Quirk, R. P.; Yin, J.; Guo, S.-H.; Hu, X.-W.; Summers, G.; Kim, J.; Zhu, L.-F.; Schock, L. E. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 47–59. (e) Zhao, Y.; Higashihara, T.; Sugiyama, K.; Hirao, A. *J. Am. Chem. Soc.* **2005**, *127*, 14158–14159. (f) Hirao, A.; Nagahama, H.; Ishizone, T.; Nakahama, S. *Macromolecules* **1993**, *26*, 2145–2150. (g) Avgeropoulos, A.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 813–816. (h) Bi, L.-K.; Fetters, L. J. *Macromolecules* **1976**, *9*, 732–742. (i) Hirao, A.; Hattori, I.; Sasagawa, T.; Yamaguchi, K.; Nakahama, S. *Makromol. Chem.* **1982**, *RC3*, 59–63. (j) Uhrig, D.; Mays, J. W. *Macromolecules* **2002**, *35*, 7182–7190. (k) Beyer, F. L.; Gido, S. P.; Poulos, Y.; Avgeropoulos, A.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 2373–2376. (l) Allgaier, J.; Young, R. N.; Efstratiadis, V.; Hadjichristidis, N. *Macromolecules* **1996**, *29*, 1794–1797. (m) Floudas, G.; Pispas, S.; Hadjichristidis, N.; Pakula, T.; Erukhimovich, I. *Macromolecules* **1996**, *29*, 4142–4154. (n) Schappacher, M.; Deffieux, A. *Macromolecules* **2005**, *38*, 7209–7213. (o) Ji, H.; Sakellariou, G.; Mays, J. W. *Macromolecules* **2007**, *40*, 3461–3467.

(15) Living anionic polymerization of styrene in cyclohexane as nonpolar solvent was achieved under the condition of 30−60 °C.

(16) Ehrfeld, W.; Golbig, K.; Hessel, V.; Löwe, H.; Richter, T. *Ind. Eng. Chem. Res.* **1999**, *38*, 1075–1082.

(17) Wurm, F.; Wilms, D.; Klos, J.; Löwe, H.; Frey, H. *Macromol. Chem. Phys.* **2008**, *209*, 1106–1114.

(18) Han, Y.-H.; Pearce, E. M.; Kwei, T. K. *Macromolecules* **2000**, *33*, 1321–1329.

(19) Geerts, J.; Van Beylen, M.; Smets, G. *J. Polym. Sci., Polym. Chem.* **1969**, *7*, 2859–2873.

(20) (a) Hirao, A.; Yamaguchi, K.; Takenaka, K.; Suzuki, K.; Nakahama, S.; Yamazaki, N. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 941–

946. (b) Hirao, A.; Takenaka, K.; Packirisamy, S.; Yamaguchi, K.; Nakahama, S. *Makromol. Chem.* **1985**, *186*, 1157–1166.

(21) Ishizone, T.; Uehara, G.; Hirao, A.; Nakahama, S. *Macromolecules* **1998**, *31*, 3764–3774.

(22) Hirao, A.; Shione, H.; Ishizone, T.; Nakahama, S. *Macromolecules* **1997**, *30*, 3728–3731.

(23) (a) Kobayashi, M.; Uchino, K.; Ishizone, T. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4126–4135. (b) Cernohous, J. J.; Macosko, C. W.; Hoye, R. T. *Macromolecules* **1998**, *31*, 3759–3763.

(24) (a) Itoh, M.; Iwata, K.; Kobayashi, M.; Takeuchi, R.; Kabeya, T. *Macromolecules* **1998**, *31*, 5609–5615. (b) Asami, R.; Oku, J.; Takeuchi, M.; Nakamura, K.; Takaki, M. *Polym. J.* **1988**, *20*, 699–702. (c) Oku, J.; Hasegawa, T.; Nakamura, K.; Takeuchi, M.; Asami, R. *Polym. J.* **1991**, *23*, 195–199. (d) Oku, J.; Hasegawa, T.; Takeuchi, T.; Takaki, M. *Polym. J.* **1991**, *23*, 1377–1382.

(25) For cationic ring-opening polymerization: Worsfold, D. J.; Eastham, A. M. *J. Am. Chem. Soc.* **1957**, *79*, 897–899.

(26) (a) Yan, X.; Liu, G.; Li, Z. *J. Am. Chem. Soc.* **2004**, *126*, 10059–10066. (b) Yan, X.; Liu, F.; Li, Z.; Liu, G. *Macromolecules* **2001**, *34*, 9112–9116. (c) Liu, G.; Qiao, L.; Guo, A. *Macromolecules* **1996**, *29*, 5508–5510. (d) Hirao, A.; Nakahama, S. *Acta Polym.* **1998**, *49*, 133–144, and references therein.

(27) (a) Pennisi, R. W.; Fetters, L. J. *Macromolecules* **1988**, *21*, 1094–1099. (b) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 4649–4651. (c) Rózga-Wijas, K.; Chojnowski, J.; Fortuniak, W.; Ścibiorek, M.; Michalska, Z.; Rogalski, L. *J. Mater. Chem.* **2003**, *13*, 2301–2310.

(28) (a) Suga, S.; Nagaki, A.; Tsutsui, Y.; Yoshida, J. *Org. Lett.* **2003**, *5*, 945–947. (b) Hessel, V.; Hofmann, C.; Löwe, H.; Meudt, A.; Scherer, S.; Schönfeld, F.; Werner, B. *Org. Process Res. Dev.* **2004**, *8*, 511–523. (c) Suga, S.; Tsutsui, Y.; Nagaki, A.; Yoshida, J. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1206–1217. (d) Midorikawa, K.; Suga, S.; Yoshida, J. *Chem. Commun.* **2006**, 3794–3796.

MA800769N