Microflow System Controlled Anionic Polymerization of Styrenes

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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 over CaH$_2$ before use. Stainless steel (SUS304) T-shaped micromixers having inner diameter of 250 and 500 µm were manufactured by Sanko Seiki Co., Inc (Figure S-1). Stainless steel (SUS316) microtube reactors having 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 typical microflow system composed of micromixers and microtube reactors is shown in Figure S-2. The microflow system was dipped in a cooling bath to control the temperature. Solutions were introduced to a microflow system using syringe pumps, Harvard Model 11, equipped with gastight syringes purchased from SGE.

Figure S-1. The structure of the T-shaped micromixer.
Figure S-2. A microflow system composed of two micromixers and two microtube reactors for controlled anionic polymerization followed by the termination with dichlorodimethylsilane. Syringe pumping are used to feed solutions into the system. The system was dipped in a cooling bath to control the temperature.

Molecular Weight and Molecular Weight Distribution.

The molecular weight (Mn) and molecular weight distribution (Mw/Mn) were determined in THF at 40 °C with a Shodex GPC-101 equipped with two LF-804L columns (Shodex) and an RI detector using a polystyrene (polySt) standard sample for calibration.

Sec-BuLi Initiated Polymerization of Styrene in a Macrobatch Reactor.

To a solution of sec-BuLi (0.20 M, 1 mL) in hexane was added a solution of styrene (1.0 M, 6 mL, 0 °C) in THF in a 25 mL flask by syringe pumping (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 with the calibration using standard polystyrene samples.

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 was used. Microtube pre-cooling units (inner diameter (φ) = 1000 μm, length (L) = 100 cm) were connected to an inlet of the micromixer 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 pumping. The resulting solution was passed through R (inner diameter (φ) = 1000 μm, length (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 polymer samples were analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-11~S-25) and the results are summarized in Table S-1.

**Table S-1. Microflow system controlled anionic polymerization of styrene initiated by sec-BuLi.**

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<th>entry</th>
<th>flow rate of sec-buLi/hexane (mL min⁻¹)</th>
<th>flow rate of styrene/THF (mL min⁻¹)</th>
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<th>bath temperature (°C)</th>
<th>residence time (s)</th>
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Table S-2. The control of molecular weights of polymers by modulating flow rates.

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<th>concentration of sec-BuLi/hexane (M)</th>
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sec-BuLi Initiated Polymerization of 4-Dimethylsilylstyrene in a Microflow System.

A microflow system composed of a T-shaped micromixer M and a microtube reactor R was used. Microtube pre-cooling units (ϕ = 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 (2.0 M) in THF (flow rate = 6.0 mL min⁻¹) and a solution of sec-BuLi (0.2 or 0.05 M) in hexane were introduced to M (ϕ = 250 µm) by syringe pumping. The resulting solution was passed through R (ϕ = 1000 µm, L = 50 cm). After a steady state was reached, the product solution was collected for 15 s was treated with methanol. The solvent was removed under reduced pressure to obtain the polymer product in quantitative yields. The polymer samples were analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-26-S-36) and the results are summarized in Table S-2.
4-dimethylsilylstyrene (2.0 M) in THF (flow rate: 6.0 mL min$^{-1}$) and a solution of sec-BuLi (0.20 M) in hexane (flow rate: 2.0 mL min$^{-1}$) were introduced to M ($\phi = 250 \mu$m) by syringe pumping. The resulting solution was passed through R ($\phi = 1000 \mu$m, 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 crude product. The crude product was subjected to gel permeation chromatography (CHCl$_3$) to afford the polymer product (451.2 mg, 92%). The polymer sample was analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-37).

**sec-BuLi Initiated Polymerization of 4-Methoxystyrene in a Microflow System.**

A microflow system composed of a T-shaped micromixer M and a microtube reactor R was used. Microtube pre-cooling units ($\phi = 1000 \mu$m, L = 100 cm) were connected to the inlets of M. The whole microflow system was dipped in a cooling bath (24 °C). A solution of 4-methoxystyrene (1.0 M) in THF (flow rate: 6.0 mL min$^{-1}$) and a solution of sec-BuLi (0.20 M) in hexane (flow rate: 1.0 mL min$^{-1}$) were introduced to M ($\phi = 250 \mu$m) by syringe pumping. The resulting solution was passed through R ($\phi = 1000 \mu$m, 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 crude product. The crude product was subjected to gel permeation chromatography (CHCl$_3$) to afford the polymer product in quantitative yield. The polymer sample was analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-38).

**sec-BuLi Initiated Polymerization of 4-tert-Butyldimethylsiloxystyrene in a Microflow System.**

A microflow system composed of a T-shaped micromixer M and a microtube reactor R was used. Microtube pre-cooling units ($\phi = 1000 \mu$m, L = 100 cm) were connected to the inlets of M. The whole microflow system was dipped in a cooling bath (24 °C). A solution of 4-tert-butyldimethylsiloxystyrene (2.0 M) in THF (flow rate = 6.0 mL min$^{-1}$) and a solution of sec-BuLi (0.20 M) in hexane (flow rate = 2.0 mL min$^{-1}$) were introduced to M ($\phi = 250 \mu$m) by syringe pumping. The resulting solution was passed through R ($\phi = 1000 \mu$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 polymer product (94% conversion determined by $^1$H NMR). The polymer sample was analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-39).

**sec-BuLi Initiated Polymerization of 4-Methylthiostyrene in a Microflow System.**

A microflow system composed of a T-shaped micromixer M and a microtube reactor R was used. Microtube pre-cooling units ($\phi = 1000 \mu$m, 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
4-methylthiostyrene (2.0 M) in THF (flow rate = 6.0 mL min$^{-1}$) and a solution of sec-BuLi (0.20 M) in hexane (flow rate = 2.0 mL min$^{-1}$) were introduced to M ($\phi = 250 \mu$m) by syringe pumping. The resulting solution was passed through R ($\phi = 1000 \mu$m, 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 crude product. The crude product was subjected to gel permeation chromatography (CHCl$_3$) to afford the polymer product in quantitative yield. The polymer sample was analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-40).

**sec-BuLi Initiated Polymerization of 4-(1-Hexynyl)styrene in a Microflow System.**

A microflow system composed of a T-shaped micromixer M and a microtube reactor R was used. Microtube pre-cooling units ($\phi = 1000 \mu$m, 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 4-(1-hexynyl)styrene (0.50 M) in THF (flow rate: 6.0 mL min$^{-1}$) and a solution of sec-BuLi (0.10 M) in hexane (flow rate = 1.0 mL min$^{-1}$) were introduced to M ($\phi = 250 \mu$m) by syringe pumping. The resulting solution was passed through R ($\phi = 1000 \mu$m, 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 crude product. The crude product was subjected to gel permeation chromatography (CHCl$_3$) to afford the polymer product in quantitative yield. The polymer sample was analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-41).

**sec-BuLi Initiated Polymerization Followed by the Termination with Chlorotrimethylsilane 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 pre-cooling units ($\phi = 1000 \mu$m, 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 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 (\(\phi = 250 \mu\text{m}\)) by syringe pumping. The resulting solution was passed through R1 (\(\phi = 1000 \mu\text{m}, L = 50 \text{ cm}\)) and was mixed with chlorotrimethylsilane (2.0 M) in THF (flow rate = 3.0 mL min\(^{-1}\)) in M2 (\(\phi = 250 \mu\text{m}\)). The resulting solution was passed through R2 (\(\phi = 1000 \mu\text{m}, L = 50 \text{ cm}\)). 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 polymer samples were analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-42 and S-43). \(^1\)H NMR spectrum was shown in Figure S-3.

**sec-BuLi Initiated Polymerization Followed by the Termination with Chlorodimethylvinylsilane 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 pre-cooling units (\(\phi = 1000 \mu\text{m}, L = 100 \text{ cm}\)) were connected to the inlets of M1 and M2. The whole microflow system was dipped in a cooling bath (24 °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 (\(\phi = 250 \mu\text{m}\)) by syringe pumping. The resulting solution was passed through R1 (\(\phi = 1000 \mu\text{m}, L = 50 \text{ cm}\)) and was mixed with chlorodimethylvinylsilane (0.050 M) in THF (flow rate: 3.0 mL min\(^{-1}\)) in M2 (\(\phi = 250 \mu\text{m}\)). The resulting solution was passed through R2 (\(\phi = 1000 \mu\text{m}, L = 200 \text{ cm}\)). 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 yield. The polymer samples were analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-44). \(^1\)H NMR spectrum was shown in Figure S-4.

**Epoxidation of the Polymer Obtained by the Reaction of sec-BuLi Initiated Polymer End with Chlorodimethylvinylsilane.**

A mixture of the polymer (0.33 g, 0.30 mmol) and 3-chloroperoxybenzoic acid, 77% max. (100.9 mg 0.45 mmol) in CH\(_2\)Cl (6.0 ml) was stirred at room temperature for 113 h. To the reaction mixture was added sat. aq Na\(_2\)S\(_2\)O\(_3\) • 5H\(_2\)O. The mixture was extracted with CHCl\(_3\). The combined organic phase was washed with sat. aq NaHCO\(_3\) and brine, and was dried over Na\(_2\)SO\(_4\). 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 with the calibration using standard polystyrene samples (Figure S-45). \(^1\)H
NMR spectrum was shown in Figure S-5.

**Cationic Ring-Opening Polymerization of the Macromonomer.**

A solution of the macromonomer (110 mg, 0.10 mmol) in dry CH$_2$Cl$_2$ (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 sat. K$_2$CO$_3$ in methanol (1 ml). The mixture was added sat. aq NaHCO$_3$. The organic phase was separated and the aqueous phase was extracted with CHCl$_3$. The combined organic phase was washed with sat. aq NaHCO$_3$ and brine, and was dried over Na$_2$SO$_4$. 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 with the calibration using standard polystyrene samples (Figure S-46).

**Block Polymerizations 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 pre-cooling units ($\phi = 1000 \mu m$, $L = 100$ 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 ($\phi = 250 \mu m$) by syringe pumping. The resulting solution was passed through R1 ($\phi = 1000 \mu m$, $L = 50$ cm) and was mixed with monomer 2 (0.50 M) in THF (flow rate = 3.0 mL min$^{-1}$) in M2 ($\phi = 250 \mu m$). The resulting solution was passed through R2 ($\phi = 1000 \mu m$, $L = 200$ 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 polymer samples were analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-47~S-54). $^1$H NMR spectra are shown in Figures S-6 (monomer 2:
sec-BuLi Initiated Polymerization Followed by the Reaction with Dichlorodimethylsilane (1.0 eq) 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 pre-cooling units (ϕ = 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 (ϕ = 250 µm) by syringe pumping. The resulting solution was passed through R1 (ϕ = 1000 µm, L = 50 cm) and was mixed with dichlorodimethylsilane (0.050 M) in THF (flow rate = 3.0 mL min⁻¹) in M2 (ϕ = 250 µm). The resulting solution was passed through R2 (ϕ = 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 (CHCl₃) to afford the polymer product (84.6 mg, 95%). The polymer samples were analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figures S-55 and S-56). ¹H NMR spectrum is shown in Figure S-8.

sec-BuLi Initiated Polymerization in a Microflow System Followed by the Reaction with Dichlorodimethylsilane (0.5 eq) 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 pre-cooling units (ϕ = 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 (ϕ = 250 µm) by syringe pumping. The resulting solution was passed through R1 (ϕ = 1000 µm, L = 50 cm) and was mixed with dichlorodimethylsilane (0.20 M) in THF (flow rate = 3.0 mL min⁻¹) in M2 (ϕ = 250 µm). The resulting solution was passed through R2 (ϕ = 1000 µm, L = 200 cm). After a steady state was reached, the product solution was collected for 15 s 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 (CHCl₃) to afford the polymer product (158.8 mg, 94%). The polymer samples were analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figures S-57 and S-58).

sec-BuLi Initiated Polymerization in a Microflow System Followed by the Reaction with Dichlorodimethylsilane (1.0 eq) in a Macrobatch Reactor.

A microflow system composed of a T-shaped micromixer M and a microtube reactor R
was used. Microtube pre-cooling units ($\phi = 1000 \mu m$, $L = 100 cm$) were connected to the inlets of $M$. The whole microflow system was dipped in a cooling bath. 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 $M$ ($\phi = 250 \mu m$) by syringe pumping. The resulting solution was passed through $R$ ($\phi = 1000 \mu m$, $L = 50 cm$). After a steady state was reached, the product solution was collected for 30 s and was treated with a solution of dichlorodimethylsilane (0.050 M, 1.5 mL) in a flask under argon gas and was stirred for 10 min. To the product solution was added methanol (neat, 1 mL) to quench the polymerization. The solvent was removed under reduced pressure to obtain a polymer product in quantitative yield. The polymer samples were analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figures S-59 and S-60).

**sec-BuLi Initiated Polymerization Followed by the Termination with Dichlorodimethylsilane (1.0 eq) in a Microflow System and Subsequent Reaction with Methanol.**

A microflow system composed of two T-shaped micromixers ($M_1$ and $M_2$) and two microtube reactors ($R_1$ and $R_2$) was used. Microtube pre-cooling units ($\phi = 1000 \mu m$, $L = 100 cm$) were connected to the inlets of $M_1$ and $M_2$. 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 $M_1$ ($\phi = 250 \mu m$) by syringe pumping. The resulting solution was passed through $R_1$ ($\phi = 1000 \mu m$, $L = 50 cm$) and was mixed with dichlorodimethylsilane (0.050 M) in THF (flow rate: 3.0 mL min$^{-1}$) in $M_2$ ($\phi = 250 \mu m$). The resulting solution was passed through $R_2$ ($\phi = 1000 \mu m$, $L = 200 cm$). 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$_3$N (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 was subjected to gel permeation chromatography (CHCl$_3$) to afford the polymer product (84.0 mg, 94%). The polymer sample was analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-61). $^1$H NMR spectrum is shown in Figure S-9.

**sec-BuLi Initiated Polymerization Followed by the Termination with Dichlorodimethylsilane (1.0 eq) in a Microflow System and Subsequent Reaction with 4-Methoxyphenyl Magnesium Bromide.**

A microflow system composed of two T-shaped micromixers ($M_1$ and $M_2$) and two microtube reactors ($R_1$ and $R_2$) was used. Microtube pre-cooling units ($\phi = 1000 \mu m$, $L = 100 cm$) were connected to the inlets of $M_1$ and $M_2$. 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 $M_1$.
The resulting solution was passed through R1 (φ = 1000 µm, L = 50 cm) and was mixed with dichlorodimethylsilane (0.050 M) in THF (flow rate: 3.0 mL min⁻¹) in M2 (φ = 250 µm). The resulting solution was passed through R2 (φ = 1000 µm, L = 200 cm). After a steady state was reached, the product solution was collected for 30 s. A solution of 4-methoxyphenyl magnesium 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 quenched by 1N HCl. The organic phase was separated and the aqueous phase was extracted with CHCl₃. The combined organic phase was dried over sodium carbonate. After filtration, the solvent was removed under reduced pressure to obtain the crude product. The crude product was subjected to gel permeation chromatography (CHCl₃) to afford the polymer product (91.4 mg, 95%). The polymer sample was analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-62). ¹H NMR spectrum is shown in Figure S-10.

**Typical Procedure for the Synthesis of Star Polymers 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 pre-cooling units (φ = 1000 µm, 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 \textit{sec}-BuLi (0.025 M) in hexane (flow rate: 2.0 mL min\(^{-1}\)) were introduced to \textbf{M1} (\(\phi = 250 \mu\text{m}\)) by syringe pumping. The resulting solution was passed through \textbf{R1} (\(\phi = 1000 \mu\text{m}\), L = 50 cm) and was mixed with dichlorodimethylsilane (0.017 M) in THF (flow rate = 3.0 mL min\(^{-1}\)) in \textbf{M2} (\(\phi = 250 \mu\text{m}\)). A solution of monomer 2 (1.0 M) in THF (flow rate = 3.0 mL min\(^{-1}\)) and a solution of \textit{sec}-BuLi (0.10 M) in hexane (flow rate = 3.0 mL min\(^{-1}\)) were introduced to \textbf{M3} (\(\phi = 250 \mu\text{m}\)) by syringe pumping. The resulting solution was passed through \textbf{R3} (\(\phi = 1000 \mu\text{m}\), L = 50 or 200 cm) and was introduced to \textbf{M4} (\(\phi = 500 \mu\text{m}\)) where the solution was mixed with the solution from \textbf{R2} (\(\phi = 1000 \mu\text{m}\), L = 200 cm). The resulting solution was passed through \textbf{R4} (\(\phi = 1000 \mu\text{m}, L = 200 \text{ cm}\)). 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. The crude product was subjected to gel permeation chromatography (CHCl\(_3\)) to afford the polymer product in quantitative yields. The polymer samples were analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (Figure S-63–S-65).
Figure S-3. $^1$H NMR spectrum (600 MHz, in CDCl$_3$) of the polymer obtained by the sec-BuLi-initiated polymerization of styrene followed by the termination with chlorotrimethylsilane.
Figure S-4. $^1$H NMR spectrum (600 MHz, in CDCl$_3$) of the polymer obtained by the sec-BuLi-initiated polymerization of styrene followed by the termination with chlorodimethylvinylsilane.
Figure S-5. $^1$H NMR spectrum (600 MHz, in CDCl$_3$) of the polymer obtained by the epoxidation of the polymer obtained by the reaction of sec-BuLi initiated polymer end with chlorodimethylvinylsilane.
Figure S-6. $^1$H NMR spectrum (600 MHz, in CDCl$_3$) of the polymer obtained by the block polymerization (monomer 2: 4-dimethylsilylstyrene).
Figure S-7. $^1$H NMR spectrum (600 MHz, in CDCl$_3$) of the polymer obtained by the block polymerization (monomer 2: 4-tert-butyldimethylsiloxystyrene).
Figure S-8. $^1$H NMR spectrum (600 MHz, in CDCl$_3$) of the polymer obtained by the sec-BuLi initiated polymerization of styrene followed by the termination with dichlorodimethylsilane (1.0 equiv).
Figure S-9. $^1$H NMR spectrum (600 MHz, in CDCl$_3$) of the polymer obtained by the sec-BuLi initiated polymerization of styrene followed by the termination with dichlorodimethylsilane (1.0 equiv) and sequential reaction with methanol.
Figure S-10. $^1$H NMR spectrum (600 MHz, in CDCl$_3$) of the polymer obtained by the sec-BuLi initiated polymerization of styrene followed by the termination with dichlorodimethylsilane (1.0 equiv) and sequential reaction with 4-methoxyphenyl magnesium bromide.
Figure S-11. \textit{sec}-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of \textit{sec}-BuLi/hexane = 2 mL/min, flow rate of the monomer solution = 6 mL/min, M: φ = 250 µm, -78 °C).
Figure S-12. sec-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of sec-BuLi/hexane = 2 mL/min, flow rate of the monomer solution = 6 mL/min, M: φ = 250 µm, -48 °C).
Figure S-13. sec-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of sec-BuLi/hexane = 2 mL/min, flow rate of the monomer solution, M: φ = 250 µm, -28 °C).
Figure S-14. sec-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of sec-BuLi/hexane = 2 mL/min, flow rate of the monomer solution = 6 mL/min, M: φ = 250 µm, 0 °C).
Figure S-15. *sec*-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of *sec*-BuLi/hexane = 2 mL/min, flow rate of the monomer solution = 6 mL/min, M: φ = 250 μm, 24 °C).
Figure S-16. sec-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of sec-BuLi/hexane = 3 mL/min, flow rate of the monomer solution = 9 mL/min, M: φ = 250 µm, 0 °C)
Figure S-17. sec-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of sec-BuLi/hexane = 1 mL/min, flow rate of the monomer solution = 3 mL/min, M: φ = 250 µm, 0 °C)
Figure S-18. sec-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of sec-BuLi/hexane = 0.5 mL/min, flow rate of the monomer solution = 1.5 mL/min, M: φ = 250 µm, 0 °C)
Figure S-19. sec-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of sec-BuLi/hexane = 0.25 mL/min, flow rate of the monomer solution = 0.75 mL/min, $M$: $\phi = 250 \text{ } \mu \text{m}$, 0 $^\circ$C)
Figure S-20. *sec*-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of *sec*-BuLi/hexane = 2 mL/min, flow rate of the monomer solution = 6 mL/min, M: \( \phi = 500 \) \( \mu \)m, 0 \( ^\circ \)C)
**Figure S-21.** sec-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of sec-BuLi/hexane = 3 mL/min, flow rate of the monomer solution = 9 mL/min, M: φ = 500 µm, 0 °C)
Figure S-22. sec-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of sec-BuLi/hexane = 1 mL/min, flow rate of the monomer solution = 3 mL/min, M: φ = 500 µm, 0 °C)
Figure S-23. *sec*-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of *sec*-BuLi/hexane = 0.5 mL/min, flow rate of the monomer solution = 1.5 mL/min, M: φ = 500 µm, 0 °C)
Figure S-24. sec-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of sec-BuLi/hexane = 0.25 mL/min, flow rate of the monomer solution = 0.75 mL, M: φ = 500 µm, 0 °C)
Figure S-25. sec-BuLi Initiated Polymerization of Styrene in a Microflow System (flow rate of sec-BuLi/hexane = 2 mL/min, flow rate of the monomer solution = 6 mL/min, M: φ = 800 µm, 0 °C)

平均分子量
Mn (数平均分子量) = 3344
Mw (重量平均分子量) = 5250
Mz (Z平均分子量) = 8368
Mv (粘度平均分子量) = 5250
I. V (固有粘度) = 5250

分散度
Mw/Mn = 1.56991  Mz/Mn = 2.50227  Mv/Mn = 1.56991
Figure S-26. Control of Molecular Weights of Polymers by Modulating Flow Rates in sec-BuLi Initiated Polymerization of Styrene (concentration of sec-BuLi/hexane = 0.20 M, flow rate of sec-BuLi/hexane = 6 mL/min).
Figure S-27. Control of Molecular Weights of Polymers by Modulating Flow Rates in sec-BuLi Initiated Polymerization of Styrene (concentration of sec-BuLi = 0.20 M, flow rate of sec-BuLi/hexane = 5 mL/min).
Figure S-28. Control of Molecular Weights of Polymers by Modulating Flow Rates in *sec*-BuLi Initiated Polymerization of Styrene (concentration of *sec*-BuLi = 0.20 M, flow rate of *sec*-BuLi/hexane = 4 mL/min).
Figure S-29. Control of Molecular Weights of Polymers by Modulating Flow Rates in sec-BuLi Initiated Polymerization of Styrene (concentration of sec-BuLi = 0.20 M, flow rate of sec-BuLi/hexane = 3 mL/min).
Figure S-30. Control of Molecular Weights of Polymers by Modulating Flow Rates in sec-BuLi Initiated Polymerization of Styrene (concentration of sec-BuLi = 0.20 M, flow rate of sec-BuLi/hexane = 2 mL/min).
Figure S-31. Control of Molecular Weights of Polymers by Modulating Flow Rates in sec-BuLi Initiated Polymerization of Styrene (concentration of sec-BuLi = 0.20 M, flow rate of sec-BuLi/hexane = 1.5 mL/min).
Figure S-32. Control of Molecular Weights of Polymers by Modulating Flow Rates in sec-BuLi Initiated Polymerization of Styrene (concentration of sec-BuLi = 0.20 M, flow rate of sec-BuLi/hexane = 1 mL/min).
Figure S-33. Control of Molecular Weights of Polymers by Modulating Flow Rates in sec-BuLi Initiated Polymerization of Styrene (concentration of sec-BuLi = 0.05 M, flow rate of sec-BuLi/hexane = 3 mL/min).
Figure S-34. Control of Molecular Weights of Polymers by Modulating Flow Rates in \textit{sec}-BuLi Initiated Polymerization of Styrene (concentration of \textit{sec}-BuLi = 0.05 M, flow rate of the \textit{sec}-BuLi/hexane = 2.5 mL/min).
**Figure S-35.** Control of Molecular Weights of Polymers by Modulating Flow Rates in sec-BuLi Initiated Polymerization of Styrene (concentration of sec-BuLi = 0.05 M, flow rate of the sec-BuLi/hexane = 2 mL/min).
**Figure S-36.** Control of Molecular Weights of Polymers by Modulating Flow Rates in sec-BuLi Initiated Polymerization of Styrene (concentration of sec-BuLi = 0.05 M, flow rate of the sec-BuLi/hexane = 1.5 mL/min).
Figure S-37. sec-BuLi Initiated Polymerization of 4-Dimethylsilylstyrene in a Microflow System.
Figure S-38. sec-BuLi Initiated Polymerization of 4-Methoxystyrene in a Microflow System.
Figure S-39. sec-BuLi Initiated Polymerization of 4-tert-Butyldimethylsiloxystyrene in a Microflow System.
Figure S-40. sec-BuLi Initiated Polymerization of 4-Methylthiostyrene in a Microflow System.
Figure S-41. sec-BuLi Initiated Polymerization of 4-(1-Hexynyl)styrene in a Microflow System.
Figure S-42. sec-BuLi Initiated Polymerization Followed by the Reaction with Chlorotrimethylsilane in a Microflow System (0 °C).
Figure S-43. sec-BuLi Initiated Polymerization Followed by the Reaction with Chlorotrimethylsilane in a Microflow System (24 °C).
Figure S-44. sec-BuLi Initiated Polymerization Followed by the Reaction with Chlorodimethylvinylsilane in a Microflow System.
**Figure S-45.** Polymer Obtained by the Reaction of with Chlorodimethylvinylsilane followed by Epoxidation.
Figure S-46. Cationic Ring-Opening Polymerization of the Macromonomer.
Figure S-47. Block Polymerizations in a Microflow System (monomer 1 = styrene, monomer 2 = none, 0 °C).
Figure S-48. Block Polymerizations in a Microflow System (monomer 1 = styrene, monomer 2 = none, 24 °C).
**Figure S-49.** Block Polymerizations in a Microflow System (monomer 1 = styrene, monomer 2 = styrene, 0 °C).
Figure S-50. Block Polymerizations in a Microflow System (monomer 1 = styrene, monomer 2 = styrene, 24 °C).
**Figure S-51.** Block Polymerizations in a Microflow System (monomer 1 = styrene, monomer 2 = 4-tert-butyldimethylsiloxystyrene, 0 °C).
Figure S-52. Block Polymerizations in a Microflow System (monomer 1 = styrene, monomer 2 = 4-tert-butyldimethylsiloxystyrene, 24 °C).
Figure S-53. Block Polymerizations in a Microflow System (monomer 1 = styrene, monomer 2 = 4-dimethylsilylstyrene, 0 °C).
Figure S-54. Block Polymerizations in a Microflow System (monomer 1 = styrene, monomer 2 = 4-dimethylsilylstyrene, 24 °C).
Figure S-55. sec-BuLi Initiated Polymerization of Styrene Followed by the Reaction with Dichlorodimethylsilane (1.0 eq) in a Microflow System (0 °C).
Figure S-56. *sec*-BuLi Initiated Polymerization of Styrene Followed by the Reaction with Dichlorodimethylsilane (1.0 eq) in a Microflow System (24 °C).
Figure S-57. *sec*-BuLi Initiated Polymerization of Styrene Followed by the Reaction with Dichlorodimethylsilane (0.5 eq) in a Microflow System (0 °C).
Figure S-58. sec-BuLi Initiated Polymerization of Styrene Followed by the Reaction with Dichlorodimethylsilane (0.5 eq) in a Microflow System (24 °C).
**Figure S-59.** sec-BuLi Initiated Polymerization of Styrene Followed by the Reaction with Dichlorodimethylsilane (1.0 eq) in a Macrobatch Reactor (0 °C).
Figure S-60. *sec*-BuLi Initiated Polymerization of Styrene Followed by the Reaction with Dichlorodimethylsilane (1.0 eq) in a Macrobatch Reactor (24 °C).
Figure S-61. *sec*-BuLi Initiated Polymerization of Styrene Followed by the Reaction with Dichlorodimethylsilane (1.0 eq) in a Microflow System and Sequential Reaction with Methanol.
Figure S-62. sec-BuLi Initiated Polymerization of Styrene Followed by the Reaction with Dichlorodimethylsilane (1.0 eq) in a Microflow System and Sequential Reaction with 4-Methoxyphenyl Magnesium Bromide.
Figure S-63. Synthesis of Block Copolymers Having Dichlorodimethylsilane in a Microflow System (monomer 1 = styrene, monomer 2 = none).
**Figure S-64.** Synthesis of Block Copolymers Having Dichlorodimethylsilane in a Microflow System (monomer 1 = styrene, monomer 2 = 4-tert-butyldimethylsiloxy styrene).
Figure S-65. Synthesis of Block Copolymers Having Dichlorodimethylsilane in a Microflow System (monomer 1 = styrene, monomer 2 = 4-dimethylsilylstyrene).