

Ring-Expansion Living Cationic Polymerization via Reversible Activation of Hemiacetal Ester Bond

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Experimental Section

Materials.

For Synthesis of 1: Dichloromethane (Wako, >99.5%), tetrahydrofuran (THF) (Wako; >99.5%), *m*-chloroperbenzoic acid (Wako; >69%, with water), and sodium hydrogen carbonate (Wako; >99.5%) were used as received without further purification.

2-methoxycyclohexan-1-one (TCI; >95.0%) was purified by column chromatography (silica gel) before use.

For Polymerization and Hydrolytic Cleavage: Isobutyl vinyl ether (IBVE) (Tokyo Kasei; >99%) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide, and distilled twice from calcium hydride before use. 1,4-Dioxane (DO) was dried overnight over calcium chloride and distilled from sodium benzophenone ketyl. Toluene (Kishida Kagaku, Osaka; 99.5%), dichromethane (Kishida Kagaku, Osaka; 99.5%) and hexane (Kishida Kagaku, Osaka; 96%) were dried and purified by passing through purification columns (Solvent Dispensing System, SG Water USA, Nashua, NH; Glass Contour), kept over molecular sieves 4A for more than one day. SnBr_4 (Aldrich; >99%), 2,6-di-*tert*-butyl-4-methylpyridine (Aldrich; >99%) trifluoroacetic acid (Wako; >98%) were used as received.

Synthesis of cyclic initiator 1 via Baeyer-Villiger oxidation.

To a dichloromethane solution of 2-methoxycyclohexan-1-one were added sodium hydrogen carbonate (1.3 equiv) and *m*-chloroperbenzoic acid (*m*-CPBA, 1.5 equiv). The resulting mixture was stirred at 0 °C to room temperature. Excess *m*-CPBA was quenched with aqueous sodium sulfite solution, and the resulting mixture was extracted with chloroform. The organic layer was separated, washed with aqueous sodium hydrogen

carbonate, and then with aqueous sodium chloride. Finally, it was concentrated with toluene under reduced pressure to remove water by azeotrope.

Living cationic polymerization of IBVE with 1.

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example is given below. The reaction was initiated by adding solutions of SnBr_4 (5.0 mM in CH_2Cl_2 ; 0.5 mL) via a dry syringe into a mixture (4.5 mL) containing IBVE (0.25 mL), 1,4-dioxane (0.13 mL), hexane (0.10 mL), cyclic initiator **1** and 2,6-di-*tert*-butyl-4-methylpyridine in CH_2Cl_2 at 0°C. After a predetermined interval, the polymerization was terminated with prechilled methanol. Monomer conversion was determined from its residual concentration measured by gas chromatography with hexane as an internal standard. The quenched reaction mixture was washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(IBVE).

Hydrolytic cleavage of hemiacetal ester in cyclic Poly(IBVE)

A typical example of hydrolysis of hemiacetal ester linkage in cyclic poly(IBVE) is given below. In a round-bottom flask (50 mL) was placed “as-obtained” (i.e., cyclic) poly(IBVE) (0.15 g) and it was dissolved into THF (4 mL) and trifluoroacetic acid (1.0 mL). To the resultant solution was added H_2O (0.2 mL) and it was stirred at room

temperature for 12 hours. The solution was washed with water and hexane to remove trifluoroacetic acid and the organic layer was evaporated under vacuum to obtain linear-PIBVE.

Measurements (SEC and ^1H NMR)

The molecular weight distribution, M_n , and M_w/M_n values of polymers were measured by size exclusion chromatography (SEC) at 40°C in THF as an eluent on three polystyrene-gel columns (Shodex KF-803; pore size, 20–1000 Å; 8.0 mm i.d. x 30 cm; flow rate, 1.0 mL min⁻¹) connected to a DU-H2000 pump, a 74S-RI refractive-index detector, and a 41-UV ultraviolet detector (all from Shodex). The columns were calibrated against 13 standard poly(St) samples (Polymer Laboratories; M_n = 500–3840000; M_w/M_n = 1.01–1.14). ^1H NMR spectra of the obtained polymers were recorded in CDCl_3 at 25°C on a JEOL JNM-ECA500 spectrometer, operating at 500.16 MHz. Polymer purification was performed by preparative SEC in CHCl_3 at room temperature (flow rate: 10 mL min⁻¹) on a polystyrene gel fractional column (K-5003: exclusion limit = 7×10^4 ; particle size = 15 mm; 5.0 cm i.d. x 30 cm) that was connected to a Jasco PU-2086 precision pump, a Jasco RI-2031 refractive index detector, and a Jasco UV-2075 UV/vis detector set at 250 nm.

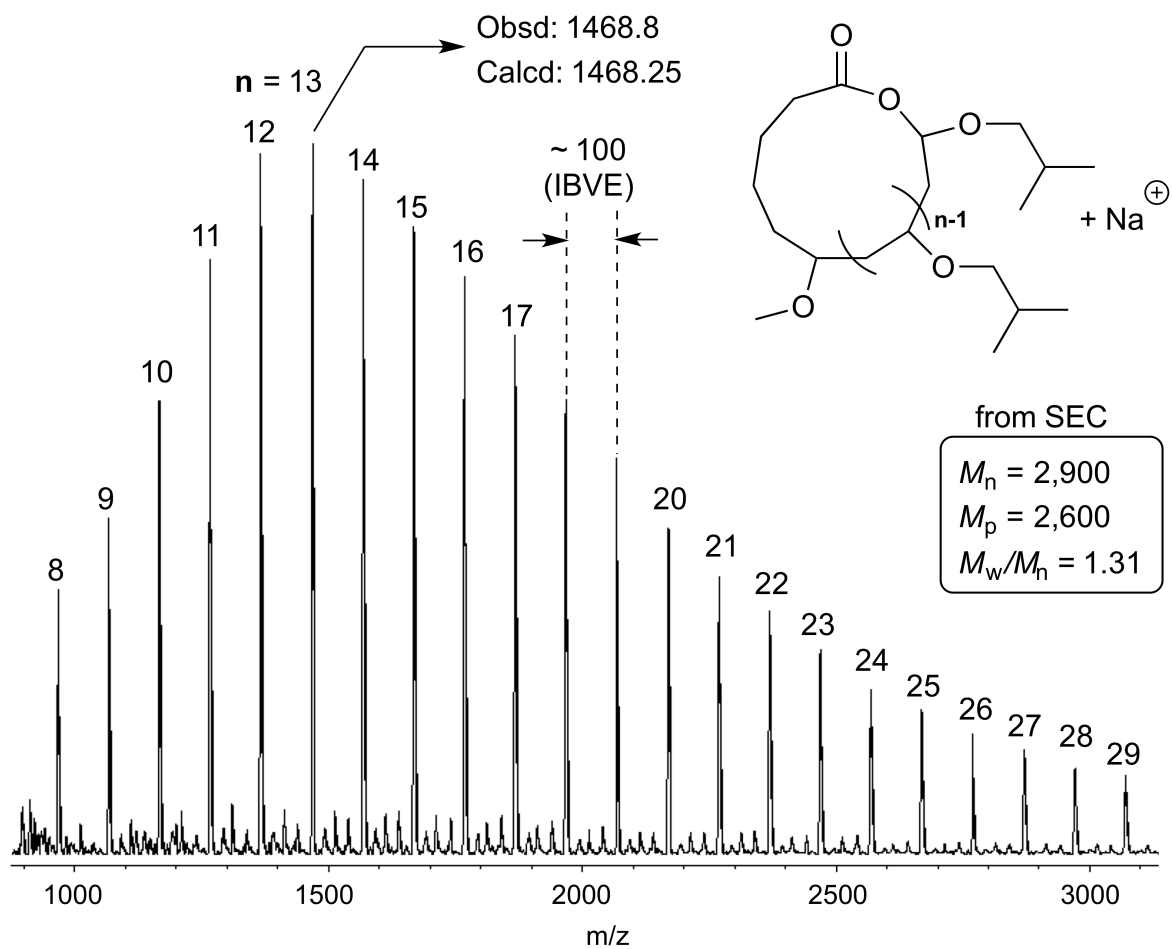


Figure S1. MALDI-TOF-MS spectrum of poly(IBVE) obtained with cyclic initiator **1**: $[\text{IBVE}]_0/[\mathbf{1}]_0/[\text{SnBr}_4]_0/[\text{DTBMP}]_0 = 380/5.0/0.50/0.15\text{mM}$ in CH_2Cl_2 with 2.5 vol% dioxane at 0°C .