

# **Convergent Approach to Ring Polymers with Narrow Molecular Weight Distribution through Post Dilution in Ring Expansion Living Cationic Polymerization**

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## Experimental Section

### Materials.

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. Chloroethyl vinyl ether (CEVE) (Tokyo Kasei; >97%) was dried overnight over calcium chloride, and distilled once before use. Carbon tetrachloride was distilled from calcium hydride once before use. Toluene (Kishida Kagaku, Osaka; 99.5%) and *n*-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.  $\text{SnBr}_4$  (Aldrich; >99%), 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, Aldrich; >99%) trifluoroacetic acid (TFA, Wako; >98%) were used as received. The ring initiator (**1**) was synthesized according to our previous paper.<sup>1</sup>

### Ring-Expansion 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 procedure is given below: the polymerization was initiated by adding solutions of  $\text{SnBr}_4$  (50 mM in toluene; 0.5 mL) via a dry syringe into a mixture

(4.5 mL) containing IBVE (0.25 mL), CCl<sub>4</sub> (internal standard, 0.10 mL), ring initiator **1**, and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) in toluene at -40°C: [IBVE]<sub>0</sub>/[**1**]<sub>0</sub>/[SnBr<sub>4</sub>]<sub>0</sub>/[DTBMP]<sub>0</sub> = 380/5/5/0.15 mM. After a predetermined interval, the polymerization was terminated with prechilled ammoniacal methanol. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl<sub>4</sub> 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).

#### **Ring fission via post-dilution of polymerization solution**

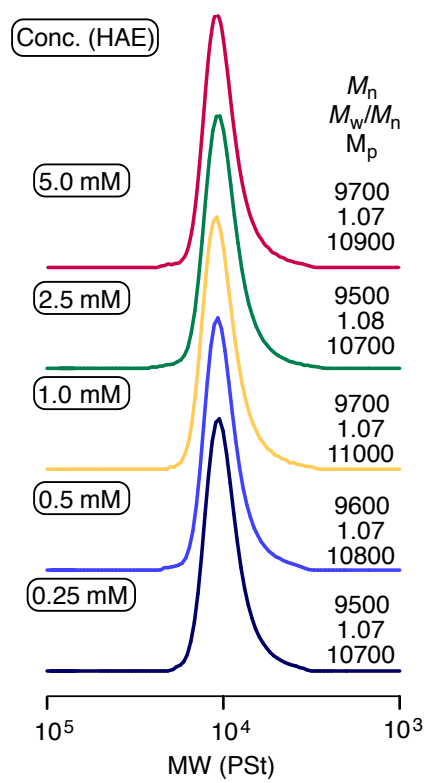
When IBVE was almost consumed (Conv. > 98%) for the cationic polymerization with **1**/SnBr<sub>4</sub>, predetermined amount of dried *n*-hexane was added to the solution under dry nitrogen, followed by stirring. A typical procedure is given below: when the monomer conversion reached 100% for the ring expansion cationic polymerization, *n*-hexane (45 mL) was added to the polymerization solution. At predetermined interval, prechilled ammoniacal methanol was added to deactivate Lewis acid catalyst. The quenched reaction mixture was washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(IBVE).

#### **HAE cleavage of ring poly(IBVE) via Acidolysis**

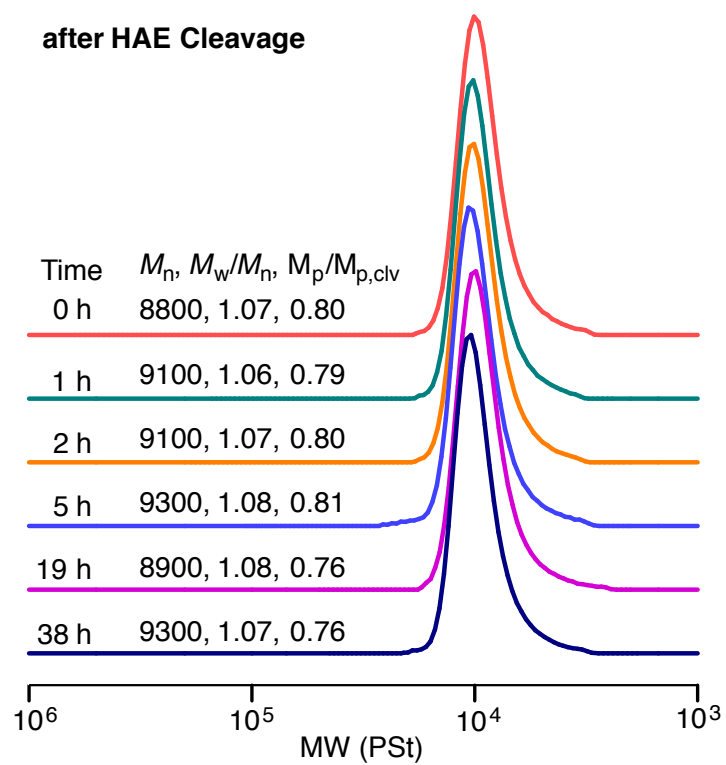
A typical procedure for cleavage of HAE bond in ring poly(IBVE) is given below. In a vial (2 mL) was placed 1.0 mL of ring poly(IBVE) solution (1wt% in THF) and added 5 drops of  $\text{H}_2\text{O}/\text{THF}(1/2 \text{ v/v})$  solution was added. The resultant solution was kept at ambient temperature for 12 hours, and the resultant solution was vacuum dried to remove THF, water and trifluoroacetic acid to obtain linear poly(IBVE).

## Measurements

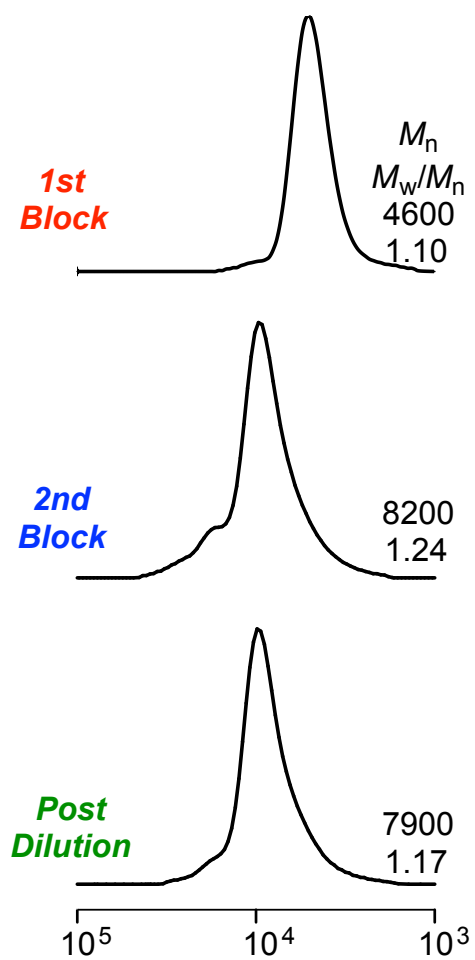
The molecular weight distribution,  $M_n$ , and  $M_w/M_n$  values of polymers were measured by size exclusion chromatography (SEC) at 40°C in THF as an eluent on three polystyrene-gel columns (Shodex KF-803; pore size, 20–1000 Å; 8.0 mm i.d. x 30 cm; flow rate, 1.0 mL min<sup>-1</sup>) connected to 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). <sup>1</sup>H NMR spectra of the obtained polymers were recorded in benzene-*d*<sub>6</sub> at 25°C on a JEOL JNM-ECA500 spectrometer, operating at 500.16 MHz.



**Figure S1.** SEC traces after HAE cleavage of polymers in Figure 6.



**Figure S2.** SEC traces after HAE cleavage of polymers in Figure 7.



**Figure S3.** SEC traces after HAE cleavage of polymers in Figure 10.

## Reference

1. H. Kammiyada, A. Konishi, M. Ouchi and M. Sawamoto, *ACS Macro Lett*, 2013, **2**, 531-534.