Supporting Information

Magnesium Bromide ($MgBr_2$) as a Catalyst for Living Cationic Polymerization and Ring-Expansion Cationic Polymerization

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Materials

For Polymerization

Isobutyl vinyl ether (IBVE, TCI; >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. 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, Aldrich; 98%) and CCl_4 (Wako; >99.5%) were distilled from calcium hydride once before use. Toluene (Kishida Kagaku, Osaka; 99.5%) 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. Et_2O (Wako; >99.5%, super dehydrated) were kept over molecular sieves 4A for more than one day. $MgBr_2$ (Strem Chemicals, Inc.; anhydrous, 98%), $MgBr_2 \cdot OEt_2$ (Aldrich; 99%), $MgCl_2$ (Toho Catalyst Co., Ltd; D grade), MgI_2 (Aldrich; 98%), $Mg(OTf)_2$ (TCI; >98.0%) and $SnBr_4$ (Aldrich; 99%) were used as received.

For Acidolysis

trifluoroacetic acid (TFA, TCI; >99.0%) and THF (Wako; >99.5%, with stabilizer) were used as received.

For Thiol-ene Reaction

α-thioglycerol (TCI; >95.0%), Et_3N (TCI; >99.0%) and THF (Wako; >99.5%, super dehydrated, stabilizer free) were used as received.

Measurement

^{1}H NMR

^{1}H NMR spectra were recorded in $CDCl_3$, benzene-d_6, or toluene-d_8 at 25 ˚C on a JEOL JNM-ECA500 spectrometer, operating at 500.16 MHz.

Gas Chromatography (GC)

Conversion of IBVE was determined from its residual concentration from GC-2014, Shimadzu; packed column: polyethyleneglycol 1500, shimalite; temperature: injection 120 ˚C, column 80 ˚C; current: 120 mA with CCl_4 as an internal standard.

Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) was measured at 40˚C in THF as an eluent on three polystyrene-gel columns (Shodex LF-404) connected to DU-H2000 pump, RI-74S refractive-index detector, and UV-41 ultraviolet detector (Shodex). The columns were calibrated against 12 standard poly(St) samples (Tosoh, PS-Oligomer Kit; $M_w = 500–1090000$; $M_w/M_n = 1.01–1.14$).

MALDI-TOF-MS

MALDI-TOF-MS analyses were performed on an ultrafleXtreme (MALDI-TOF mass spectrometer, Bruker Daltonics) equipped with 337 nm nitrogen laser with dithranol or DCTB as matrix and sodium trifluoroacetate as cationizing agent.

Procedures

$MgBr_2$-Catalyzed Living Cationic Polymerization

The following is a typical living cationic polymerization procedure with **1**/$MgBr_2$: A glass tube equipped with a three-way stopcock was dried using a heating gun (Hakko; 880B; the blow temperature was ~400˚C) under dry nitrogen and the polymerization solution was prepared here under the inert gas atmosphere. The polymerization was initiated by adding solutions of $MgBr_2$ (100 mM in Et_2O: 0.5 mL) via a dry syringe into a mixture (4.5 mL) containing IBVE, the initiator **2**, DTBMP, and CCl_4 (0.025 mL, internal standard) in toluene at 0 ˚C: $[IBVE]_0/[\mathbf{2}]_0/[MgBr_2]_0/[DTBMP]_0$ = 380/5.0/10/0.15 mM. After a predetermined interval, the polymerization was quenched with prechilled methanol containing 1vol% of ammonia solution (0.5 mL). Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl_4 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).

$MgBr_2$-Catalyzed Ring-Expansion Cationic Polymerization

The following is a typical ring-expansion polymerization procedure with **1**/$MgBr_2$: A glass tube equipped with a three-way stopcock was dried using a heating gun (Hakko; 880B; the blow temperature was ~400˚C) under dry nitrogen and the polymerization solution was prepared here under the inert gas atmosphere. The polymerization was initiated by adding solutions of $MgBr_2$ (100 mM in Et_2O: 0.5 mL) via a dry syringe into a mixture (4.5 mL) containing IBVE, the cyclic initiator **1**, DTBMP, and CCl_4 (0.025 mL, internal standard) in toluene at 0 ˚C: $[IBVE]_0/[\mathbf{1}]_0/[MgBr_2]_0/[DTBMP]_0$ = 380/5.0/10/0.15 mM. After a predetermined interval, the polymerization was quenched with prechilled DMF (0.5 mL). Note that dehydrated DMF should be used. Otherwise, linear chains are partially formed via hydrolysis of the in-chain HAE bond. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl_4 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).

Acidolysis for cleavage of HAE bond

In a vial was placed 2 mL of a cyclic poly(IBVE) solution (1 wt% in THF) and added 0.1 mL of a TFA/H_2O (2/1 v/v) solution was added. The solution was kept at room temperature for 1 hour, and the resultant solution was evaporated to dryness under reduced pressure to remove THF, TFA and H_2O.

Post polymerization (thiol-ene reaction) for cyclic poly(IBVE) carrying methacrylate vinylidene group

In a glass tube equipped with a a three-way stopcock was place 2.5 mL of 5wt% THF solution of the cyclic poly(IBVE) ($M_{\mathrm{n,\ Conv.}}$ = 3900, $M_{\mathrm{n,\ SEC.}}$ = 8000) that was synthesized with the methacrylate vinylidene-embedded initiator (**5**) and added 0.28 mL of α-thioglycerol (3.2 mmol, ~100 eq for the vinylidene group) and 0.22 mL of Et_3N (1.6 mmol). The solution was kept at room temperature for 2 days, the resultant solution was evaporated to dryness under reduced pressure. Finally, the polymer was dissolved in toluene and the solution was washed with distilled water three times.

Syntheses of initiators (1, 2, 4, and 5) and the model compound of cyclic initiator (3)

7-Membered cyclic initiator (**1**)[1], IBVE-AcOH (**2**)[2], 4*H*-benzo[*d*][1,3]dioxin-4-one (**3**)[3], 6-membered cyclic initiator (**4**)[4], and 2,6-dimethyl-5-methylene-1,3-dioxa-4-one (**5**)[5] were synthesized according to the literature.

1) Kammiyada, H.; Konishi, A.; Ouchi, M.; Sawamoto, M. *ACS Macro Lett.* **2013**, *2*, 531-534.
2) Aoshima, S.; Higashimura, T. *Macromolecules*. **1989**, *22*, 1009-1013.
3) Lin, F.; Song, Q.; Gao, Y; Cui, X. *RSC Adv.*, **2014**, *4*, 19856-19860.
4) Neitzel, A. E.; Petersen, M. A.; Kokkoli, E.; Hillmyer, M. A. *ACS Macro Lett.* **2014**, *3*, 1156-1160.
5) Kohsaka, Y.; Matsumoto, T.; Zhang, Y.; Matsuhashi, T.; Kitayama, J. *Polym. Sci. Part A: Polym. Chem*. **2016**, *54*, 955-961.

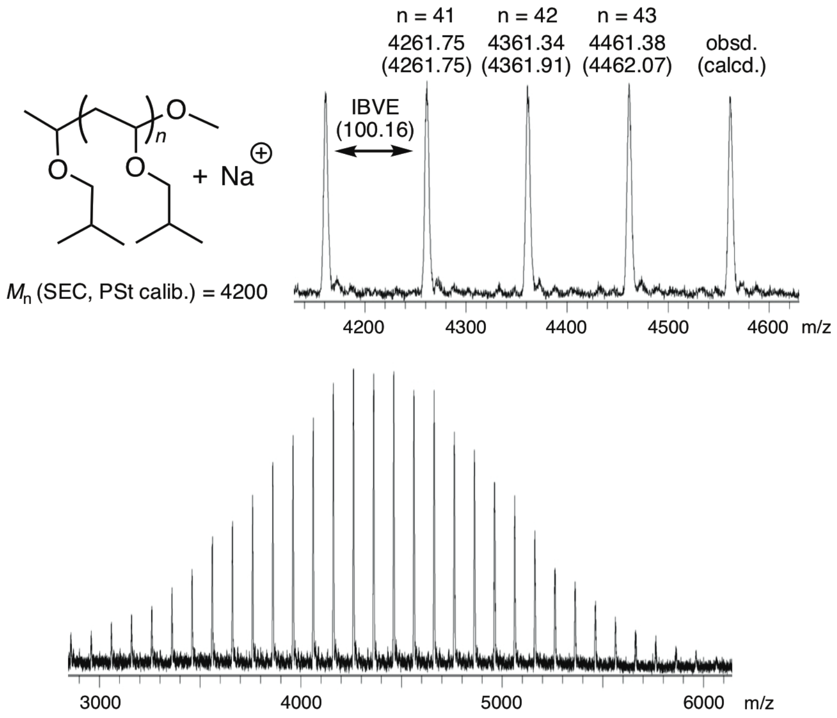

Figure S1. MALDI-TOF-MS spectrum of poly(IBVE): $[IBVE]_0/[\mathbf{2}]_0/[MgBr_2]_0/[DTBMP]_0$ = 190/5.0/10/0.15 mM in toluene/Et_2O (90/10 vol%) at 0˚C.

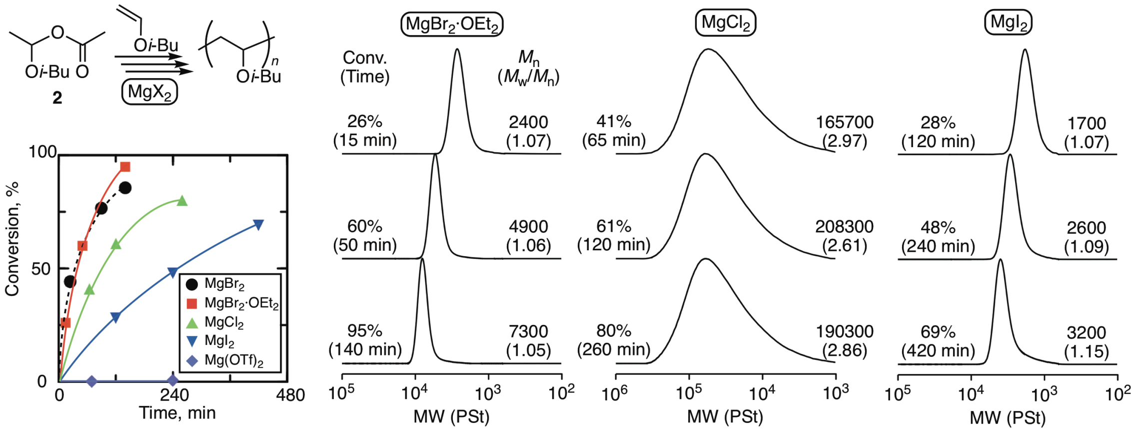

Figure S2. Cationic polymerizations of IBVE with **2** in conjunction with various magnesium complexes as catalysts: $[IBVE]_0/[\mathbf{2}]_0/[MgX_2]_0/[DTBMP]_0$ = 380/5.0/10/0.15 mM in toluene (for $MgCl_2$), toluene/Et_2O (90/10 vol%) (for $MgBr_2{\cdot}OEt_2$ and MgI_2), or toluene/CH_2Cl_2 (90/10 vol%) [for $Mg(OTf)_2$] at 0˚C.

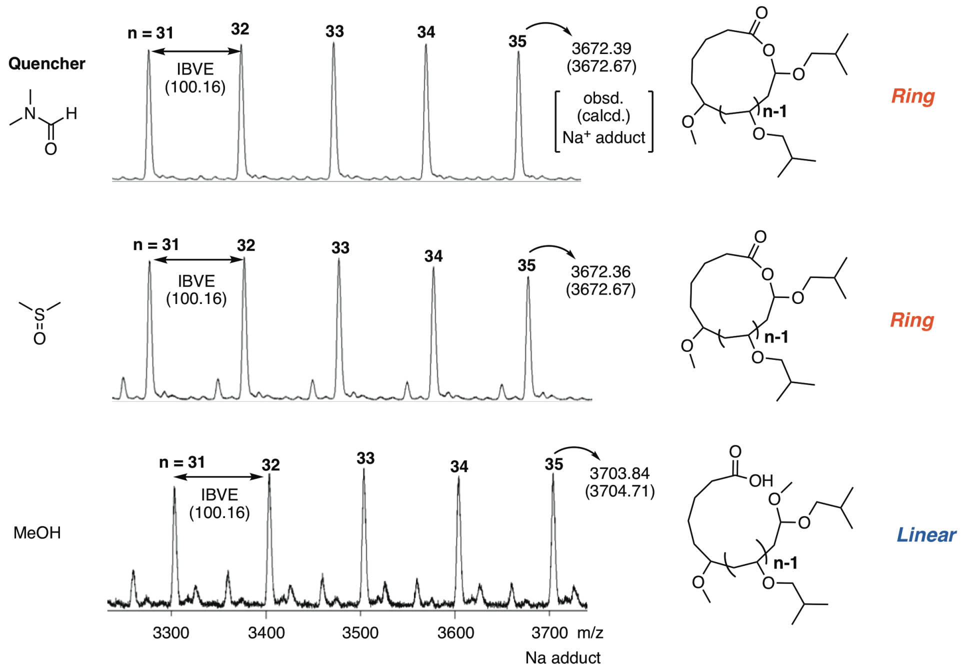

Figure S3. MALDI-TOF-MS spectra of poly(IBVE)s with DMF, DMSO, and methanol as the quencher for cationic polymerization of IBVE with **1** and $MgBr_2$. See Figure 3 in the main text.

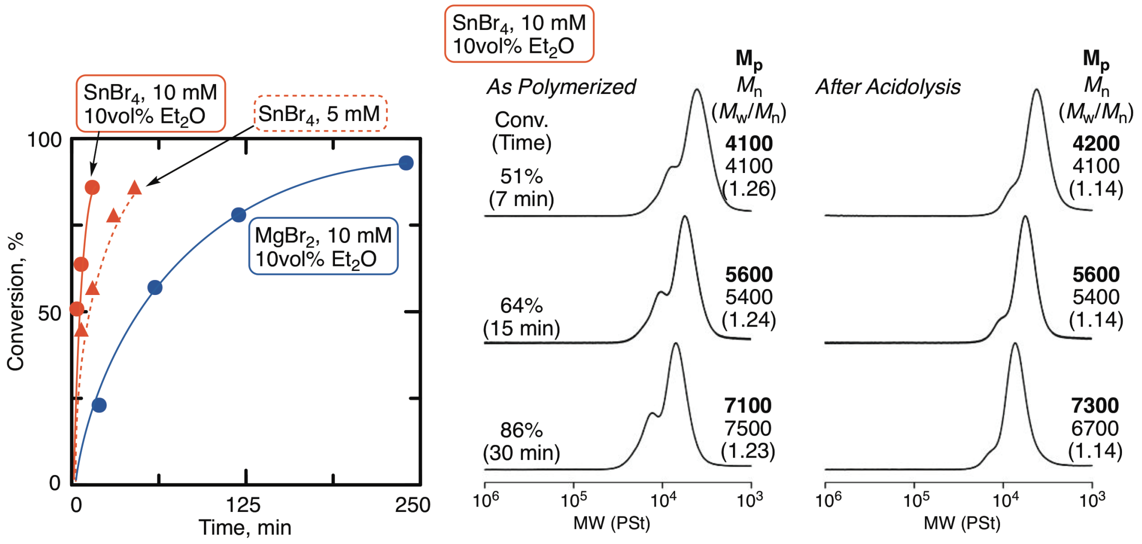

Figure S4. Cationic polymerization of IBVE with **1**/SnBr$_4$ for comparison of the catalytic activity with MgBr$_2$: [IBVE]$_0$/[**1**]$_0$/[SnBr$_4$]$_0$/[DTBMP]$_0$ = 380/10/10/0.15 mM in toluene/Et$_2$O (90/10 vol%) at 0˚C.

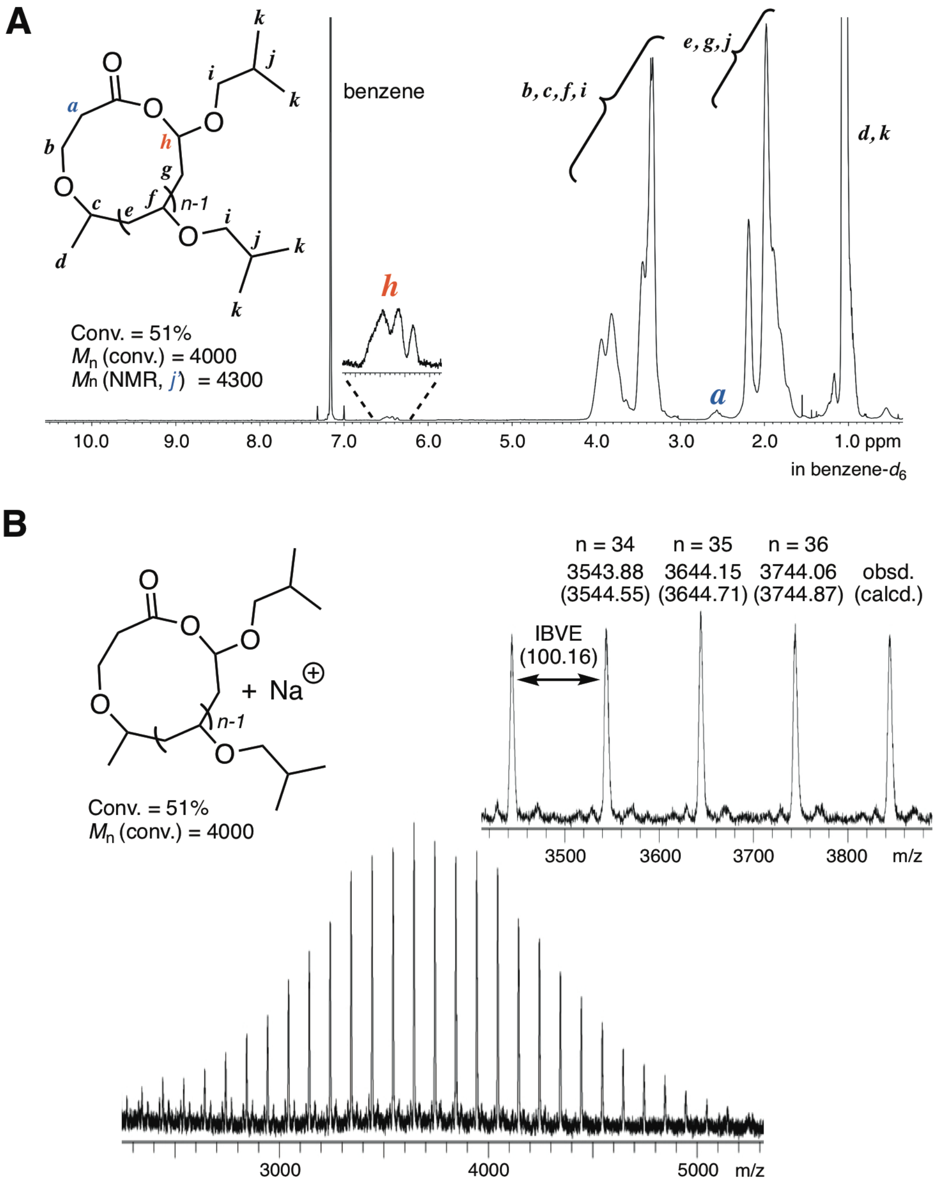

Figure S5. ^{1}H NMR (A) and MALDI-TOF-MS (B) spectrum of cyclic poly(IBVE) synthesized via ring-expansion cationic polymerization of IBVE with **4**/$MgBr_2$: $[IBVE]_0/[\mathbf{4}]_0/[MgBr_2]_0/[DTBMP]_0$ = 380/5.0/10/0.15 mM in toluene/Et_2O (90/10 vol%) at 0°C.

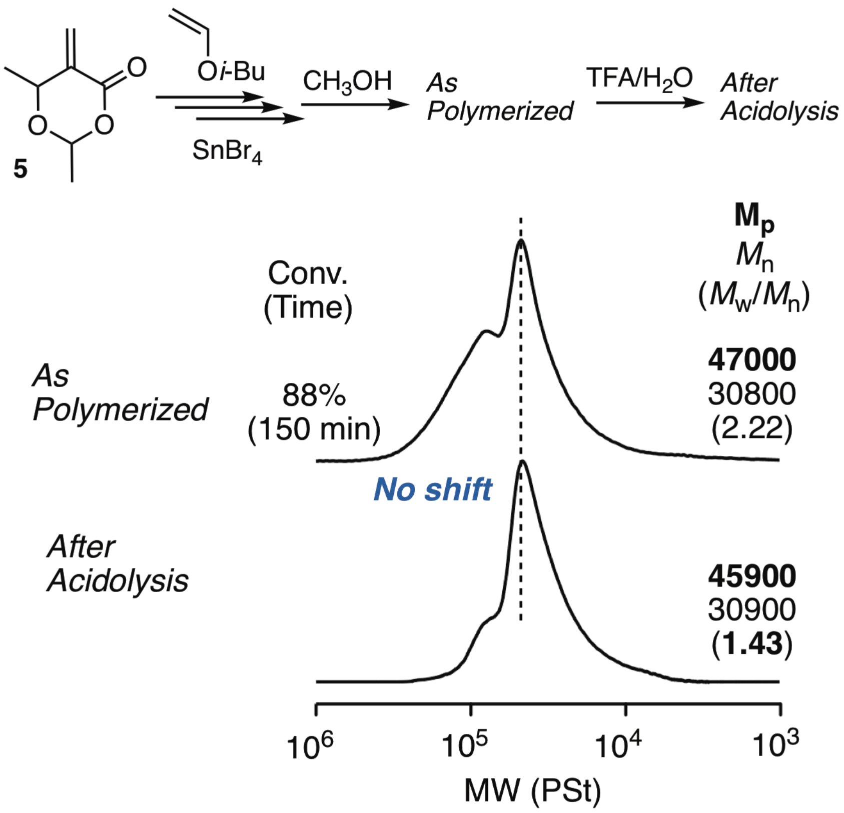

Figure S6. SEC curves of poly(IBVE)s via cationic polymerization of IBVE with **5** and $SnBr_4$ and after acidolysis reaction: $[IBVE]_0/[\mathbf{5}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5.0/5.0/0.15 mM in toluene at 0˚C.

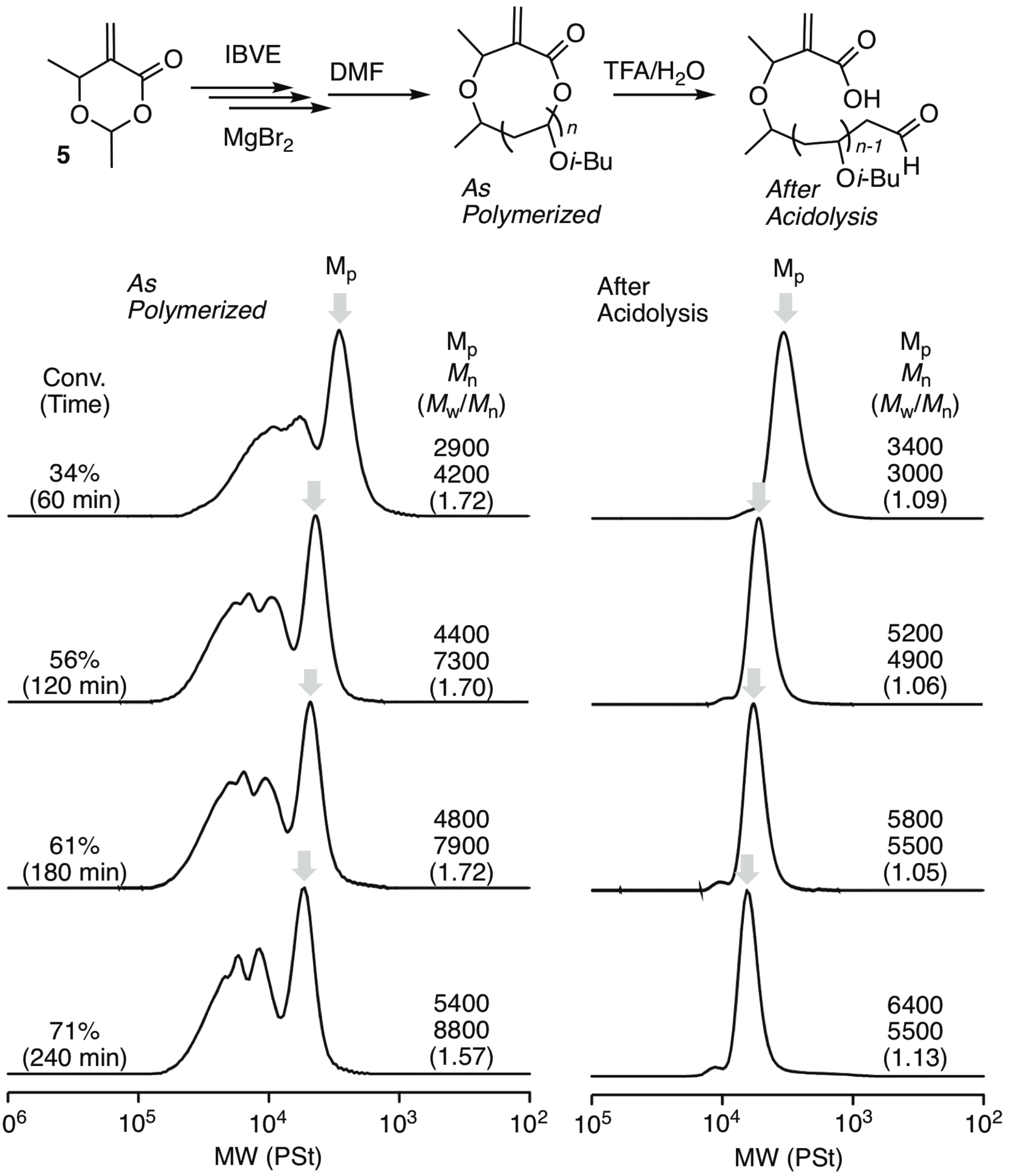

Figure S7. SEC curves of poly(IBVE)s via ring-expansion cationic polymerization of IBVE with **5** and $MgBr_2$ and after acidolysis reaction: $[IBVE]_0/[\mathbf{5}]_0/[MgBr_2]_0/[DTBMP]_0$ = 380/5.0/10/0.15 mM in toluene/Et_2O (90/10 vol%) at 0°C.