

Electronic Supplementary Information (ESI)

**Ring-Expansion Cationic Cyclopolymerization
for Construction of Cyclic Cyclopolymers**

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Materials

For synthesis of monomers. Ethyl vinyl ether (EVE, TCI; stabilized with KOH, >98.0%) was bubbled with nitrogen for more than 15 min before use. 1,3-Propanediol (TCI; >98.0%), 2-methyl-1,3-propanediol (TCI; >98.0%), 2,2-Dimethyl-1,3-propanediol (TCI; >98.0%), palladium (II) acetate (Pd(OAc)₂, Aldrich; 98%), 1,10-phenanthroline (phen, Aldrich; >99%), dichloromethane (CH₂Cl₂, Wako; stabilized with 2-methyl-2-butane, super dehydrated), sodium hydrogen carbonate (NaHCO₃, Wako; 99.5-100.3%), sodium chloride (NaCl, Wako; >99.5%) and sodium sulfate (Na₂SO₄, Wako; anhydrous, >99.0%) was used as received. For purification with column chromatography, Wakogel C-200 (Wako) and *n*-hexane (Wako; >96%) were used. For further purification with distillation, calcium hydride (CaH₂, Wako; >80.0%) was used.

For synthesis of the cyclic initiator. Methoxycyclohexan-one (TCI; >95.0%), *m*-chloroperbenzoic acid (*m*CPBA, Wako; with water, 69.0-75.0%), sodium hydrogen carbonate (NaHCO₃, Wako; 99.5-100.3%), dichloromethane (CH₂Cl₂, Wako; stabilized with 2-methyl-2-butane, >99.5%), sodium carbonate (Na₂CO₃, Wako; anhydrous, >99.8%), sodium thiosulfate (Na₂S₂O₃, Wako; anhydrous, >95.0%), and sodium sulfate (Na₂SO₄, Wako; anhydrous, >99.0%) were used as received.

For polymerization. Isobutyl vinyl ether (IBVE, TCI; >99%) was washed with 10% aqueous sodium hydroxide (NaOH, Wako; >97.0%) and then with water, dried overnight over potassium hydroxide (KOH, Wako; >85.0%), and distilled twice from calcium hydride (CaH₂, Wako; >80.0%) before use. 2,6-Di-*tert*-butyl-4-methylpyridine (DTBMP, Aldrich; 98%), tetrachloromethane (CCl₄, Wako; >99.5%) and 1,2,3,4-tetrahydronaphthalene (tetralin, TCI; >98.0%) was distilled from calcium hydride (CaH₂, Wako; >80.0%) 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 (Wako) for more than one day. Tin bromide (SnBr₄, Aldrich; 99%) was used as received. An adduct of acetic acid (Wako; >99.7%) to IBVE (TCI; >99%) (IBEA) as an acyclic initiator was prepared according to the literature.¹ For quenching polymerization, methanol (MeOH, Wako; >99.8%) containing 1vol% of ammonia solution (Wako; 25.0-27.9%) was used without further purification.

For acid treatment of polymers. Trifluoroacetic acid (TFA, TCI; >99.0%), ultrapure water (H₂O, Wako), and tetrahydrofuran (THF, Wako; with stabilizer, >99.5%) were used as received. For extraction, *n*-hexane (Wako; >96%) was used.

Reference

- 1 S. Aoshima and T. Higashimura, *Macromolecules*, 1989, **22**, 1009–1013.

Measurement

¹H NMR. ¹H NMR spectra were recorded in CDCl₃ 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 CCl₄ as an internal standard.

Size exclusion chromatography (SEC). SEC curves, number-average molecular weight (M_n), weight-average molecular weight (M_w), peak top molecular weight (M_p), and molecular weight distribution (MWD; M_w/M_n) of the polymers were measured by HLC-8320GPC (TOSOH) in THF as an eluent at 40 °C on two polystyrene-gel columns (TOSOH TSKgel Super Multipore HZ-M: column size = 4.6 mm I.D. × 15 cm; particle size = 4 μm; flow rate = 0.35 mL/min). The columns were calibrated against standard polystyrene samples (TOSOH PStQuick series).

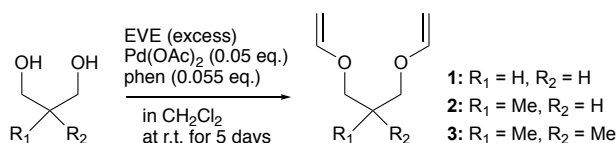
Preparative SEC. Preparative SEC was performed to remove the residual divinyl monomers from the polymers by LaboACE LC-5060 Dell Latitude 3380 (Japan Analytical Industry) in CHCl₃ for linear poly(3) or toluene for cyclic poly(3) as an eluent at ambient temperature on one polystyrene-gel column (JAIGEL-2.5HR: exclusion limit = 20000; column size = 20 mm I.D. × 600 mmL; flow rate = 10 mL/min).

Differential scanning calorimetry (DSC). Glass transition temperature (T_g) of polymer samples (50 μL of 10wt% polymer solution in CH₂Cl₂ was placed into an aluminum pan and vacuum-dried overnight; ca. 3-10 mg) was measured by a DSC Q200 calorimeter (TA instruments) equipped with a RCS 90 electric machine under dry nitrogen flow at a heating or cooling rate of 10 °C/min. First heating: 40 °C to 80 °C, first cooling: 80 °C to -80 °C, second heating: -80 °C to 150 °C, second cooling: 150 °C to -80 °C, third heating: -80 °C to 150 °C. The second heating scan was employed to determine T_g .

Thermogravimetric analysis (TGA). Decomposition temperature (T_d ; the temperature of 5% weight loss and T_{max} ; the temperature of maximum weight loss) of polymer samples (50 μL of 10wt% polymer solution in CH₂Cl₂ was placed into an aluminum pan and vacuum-dried overnight; ca. 3-10 mg) was performed under dry nitrogen flow on a STA 2500 Regulus (NETZSCH). The heating rate was at 10 °C/min, between 20 °C and 500 °C.

Procedure

Synthesis of divinyl ethers 1-3.



Scheme S1 Synthesis of Divinyl Ethers 1-3

The following is a typical procedure for the synthesis of divinyl ether **1** as an example. EVE (250 mL) and 1,3-propanediol (7.30 mL, 100 mmol) were added to a CH_2Cl_2 solution (30 mL) of $Pd(OAc)_2$ (1.12 g, 4.99 mmol), and phen (1.00 g, 5.55 mmol) under dry argon or nitrogen. The resulting mixture was stirred at room temperature for 5 days. The precipitate was separated by filtration and the filtrate was washed with saturated aqueous $NaHCO_3$ solution and then brine. The organic layer was dried over Na_2SO_4 for 30 min. After filtration, the solution was concentrated under reduced pressure. The obtained yellow liquid was purified by short column chromatography (*n*-hexane as an eluent) and then distillation under reduced pressure from CaH_2 to afford divinyl ether **1** (3.5 mL) as colorless oil.

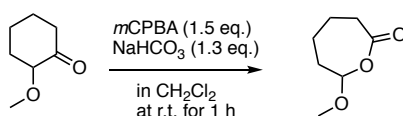
1H NMR (500 MHz, $CDCl_3$, 25 °C):

1; δ (ppm) 6.46 (q, $J = 7.1$ Hz, 2H), 4.19 (dd, $J = 14.3, 1.7$ Hz, 2H), 4.00 (dd, $J = 6.9, 2.3$ Hz, 2H), 3.79 (t, $J = 6.0$ Hz, 4H), 2.01 (t, $J = 6.0$ Hz, 2H).

2; δ (ppm) 6.47 (q, $J = 7.1$ Hz, 2H), 4.18 (dd, $J = 14.3, 1.7$ Hz, 2H), 3.98 (dd, $J = 6.9, 2.3$ Hz, 2H), 3.64 (ddd, $J = 32.5, 9.6, 6.2$ Hz, 4H), 1.02 (d, $J = 6.9$ Hz, 3H).

3; δ (ppm) 6.46 (d, $J = 14.3$ Hz, 2H), 4.16 (d, $J = 14.3$ Hz, 2H), 3.95 (d, $J = 4.6$ Hz, 2H), 3.46 (s, 4H), 0.97 (s, 6H).

Synthesis of the cyclic initiator.



Scheme S2 Synthesis of the Cyclic Initiator

2-Methoxycyclohexanone (6.60 mL, 52.5 mmol) was slowly added to a CH_2Cl_2 solution (250 mL) of $NaHCO_3$ (5.91 g, 70.4 mmol) and *m*CPBA (18.6 g, 77.6 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 1.5 hour. Excess *m*CPBA was quenched with saturated aqueous Na_2CO_3 solution and saturated aqueous $Na_2S_2O_3$ solution, and the resulting mixture was extracted with CH_2Cl_2 . The organic layer was separated, and washed with saturated aqueous Na_2CO_3 solution. Then the organic layer was dried over Na_2SO_4 . After filtration, the solution was concentrated under reduced pressure. Finally, it was distilled under reduced pressure to afford the cyclic initiator (1.3mL) as colorless oil.

1H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) 5.14-5.13 (m, 1H), 3.51 (s, 3H), 2.78-2.57 (m, 2H), 2.09-1.65 (m, 6H).

Polymerization. The following is a typical cationic polymerization procedure (the divinyl ether **3**/the cyclic initiator/ $SnBr_4$ system as an example). 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 argon. The polymerization was initiated by adding solutions of $SnBr_4$ (50 mM in toluene: 1.0 mL) via a dry syringe into a mixture (9.0 mL) containing the monomer **3**, the cyclic initiator, DTBMP, and tetralin (0.025 mL) in toluene at 0 °C: $[3]_0/[cyclic\ initiator]_0/[SnBr_4]_0/[DTBMP]_0 = 50/1.25/5.0/0.15$ mM. After a predetermined interval, the polymerization was quenched with prechilled methanol containing 1 vol% of ammonia solution. Conversion of monomer's vinyl groups was determined by 1H NMR from the integrated peak area of monomer's olefinic protons with tetralin as an internal standard. The quenched polymerization solution was washed with prechilled water, evaporated to dryness under reduced pressure, and vacuum-dried. SEC curves, M_n , M_w , M_p , and M_w/M_n ratio of the polymers were measured by SEC.

Acid treatment of cyclic and linear poly(3)s. The following is a typical procedure for acid treatment of cyclic and linear poly(3)s (cyclic poly(3) as an example). In a vial (2 mL) was placed 0.1 mL of a cyclic poly(3) solution (0.5wt% in THF) and added 0.1 mL of a TFA/ H_2O (2/1 v/v) solution was added. Kept at room temperature for 1 hour, the resultant solution was diluted with *n*-hexane and washed with water. Then the organic layer was evaporated to dryness under reduced pressure, and vacuum-dried to remove THF, TFA and H_2O .

Effects of temperature on the cationic cyclopolymerization of **3**

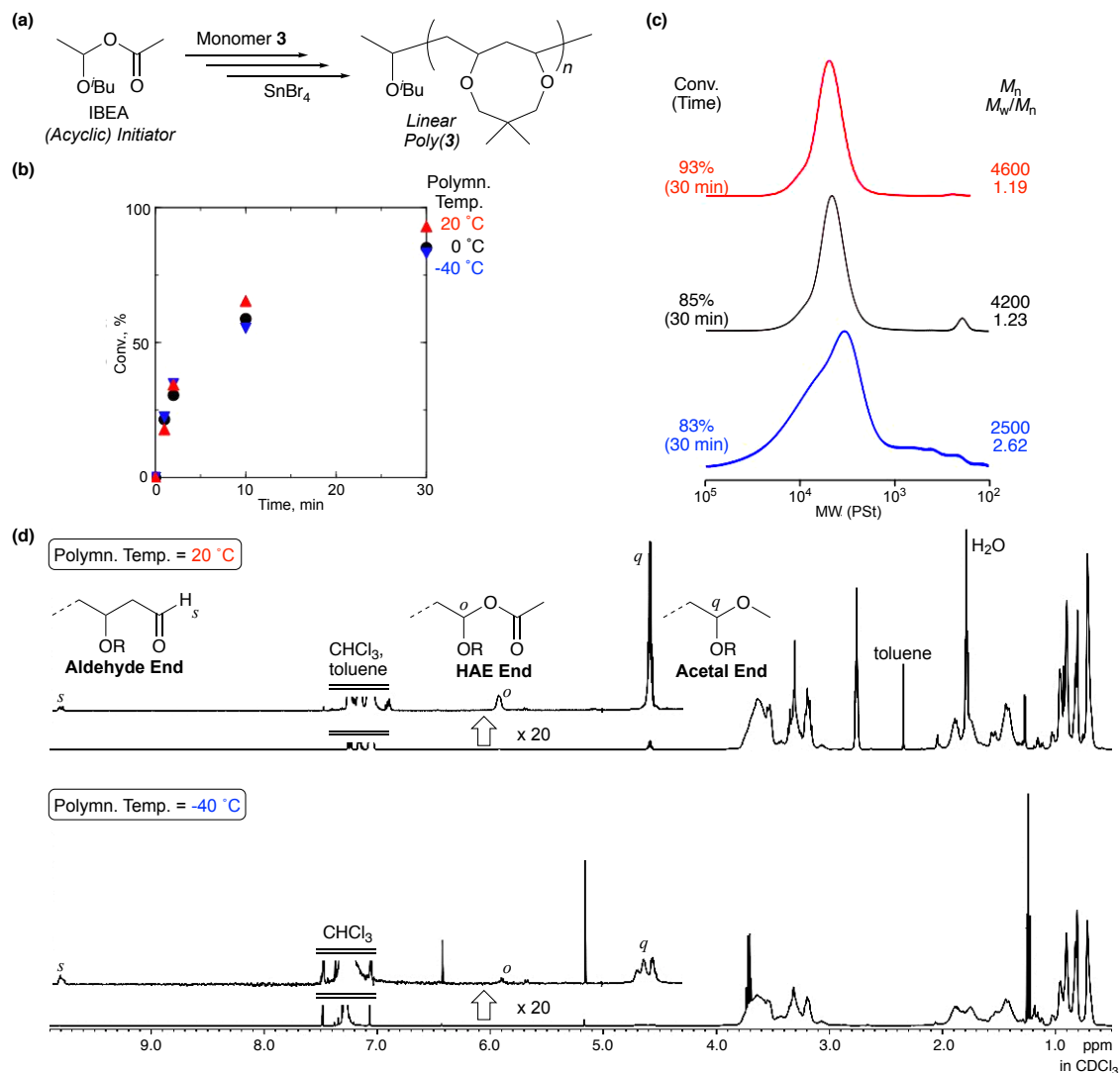


Fig S1. Effects of temperature on the cationic cyclopolymerization of **3**. Polymerization: $[\mathbf{3}]_0/[\text{IBEA}]_0/[\text{SnBr}_4]_0/[\text{DTBMP}]_0 = 200/5.0/5.0/0.15$ mM in toluene at 20 °C, 0 °C, or -40 °C. (a) Scheme of the cationic cyclopolymerization of **3**. (b) Time-conversion plots. Polymerization temperature: 20 °C (red), 0 °C (black), -40 °C (blue). (c) SEC curves of the resultant polymers. Polymerization temperature: 20 °C (red), 0 °C (black), -40 °C (blue). (d) ^1H NMR spectra of the resultant polymers (polymerization time: 30 min). Polymerization temperature: 20 °C (upper), -40 °C (lower).

Synthesis of higher molecular weight linear poly(3) by decreasing the initiator concentration

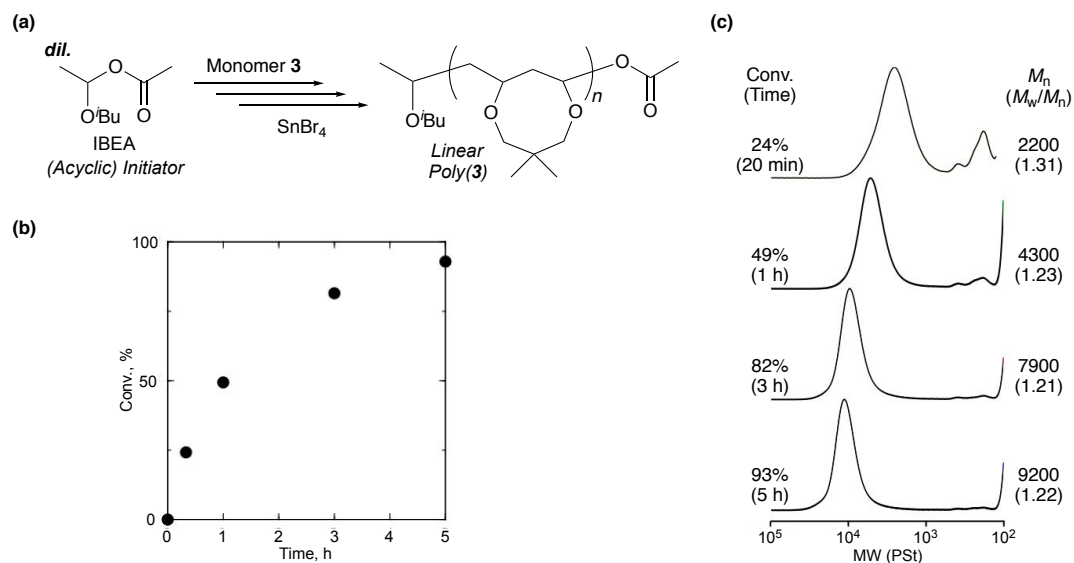


Fig S2. Synthesis of higher molecular weight linear poly(3) by decreasing the initiator concentration. Polymerization: $[3]_0/[IBEA]_0/[SnBr_4]_0/[DTBMP]_0 = 50/0.50/5.0/0.15$ mM in toluene at 0 °C. (a) Scheme of the cationic cyclopolymerization of 3. (b) Time-conversion plot. (c) SEC curves of the resultant polymers.

¹H NMR spectra of cyclic and linear poly(3)s before and after acid treatment

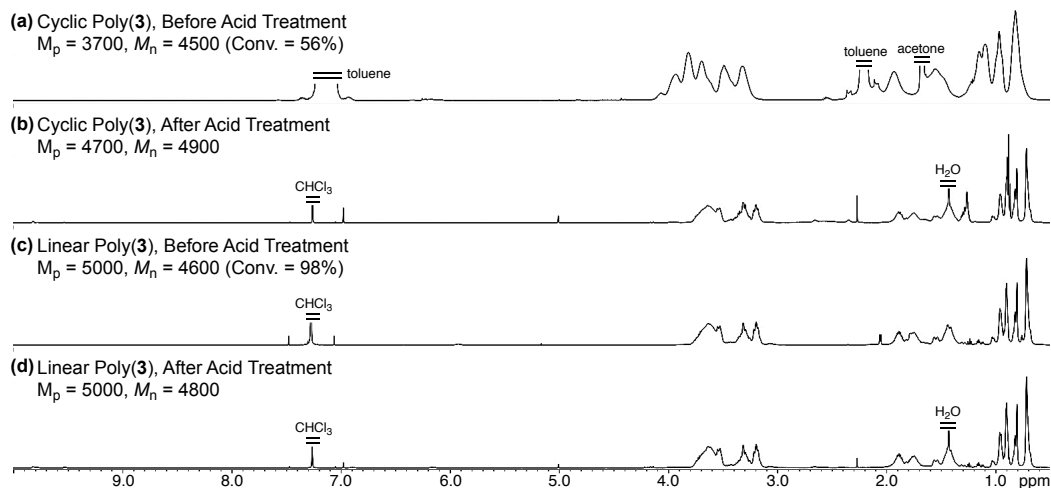


Fig S3. ¹H NMR spectra of cyclic and linear poly(3)s before and after acid treatment. (a): in toluene-*d*₈; (b-d) in CDCl₃.

Synthesis of higher molecular weight cyclic poly(3) by sequential monomer addition

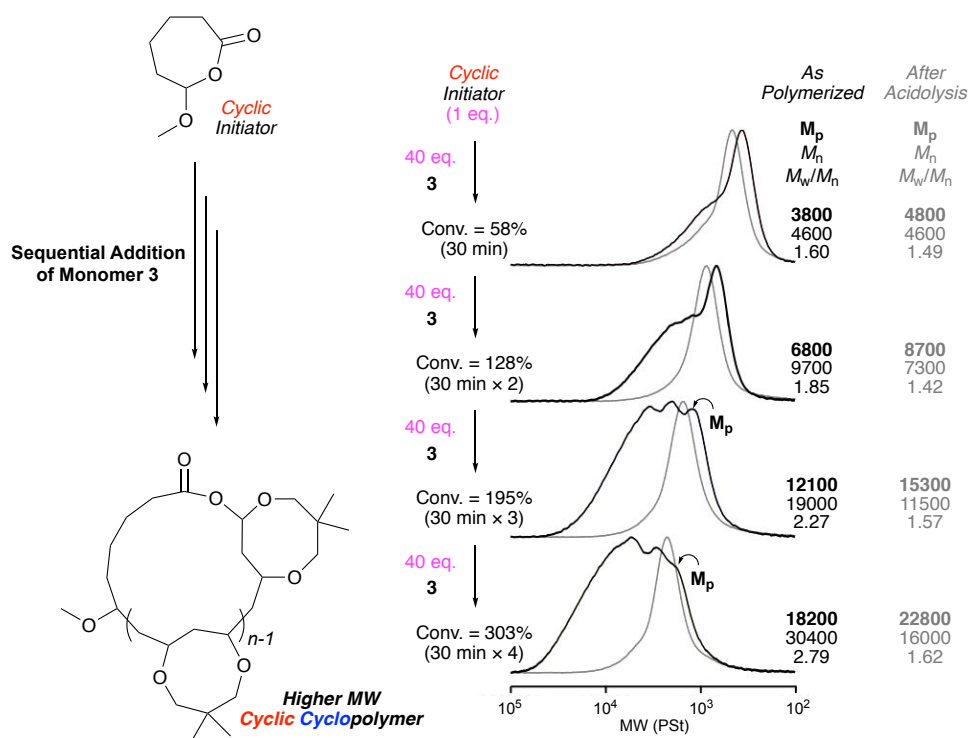


Fig S4. Synthesis of the higher molecular weight (MW) cyclic cyclopolymer by sequential monomer addition. Polymerization: $[3]_0/[cyclic\ initiator]_0/[SnBr_4]_0/[DTBMP]_0 = 50/1.25/5.0/0.15$ mM in toluene at 0 °C, the fresh monomer (40 eq. for the initiator) was added every 30 minutes.

Synthesis of linear poly(IBVE)

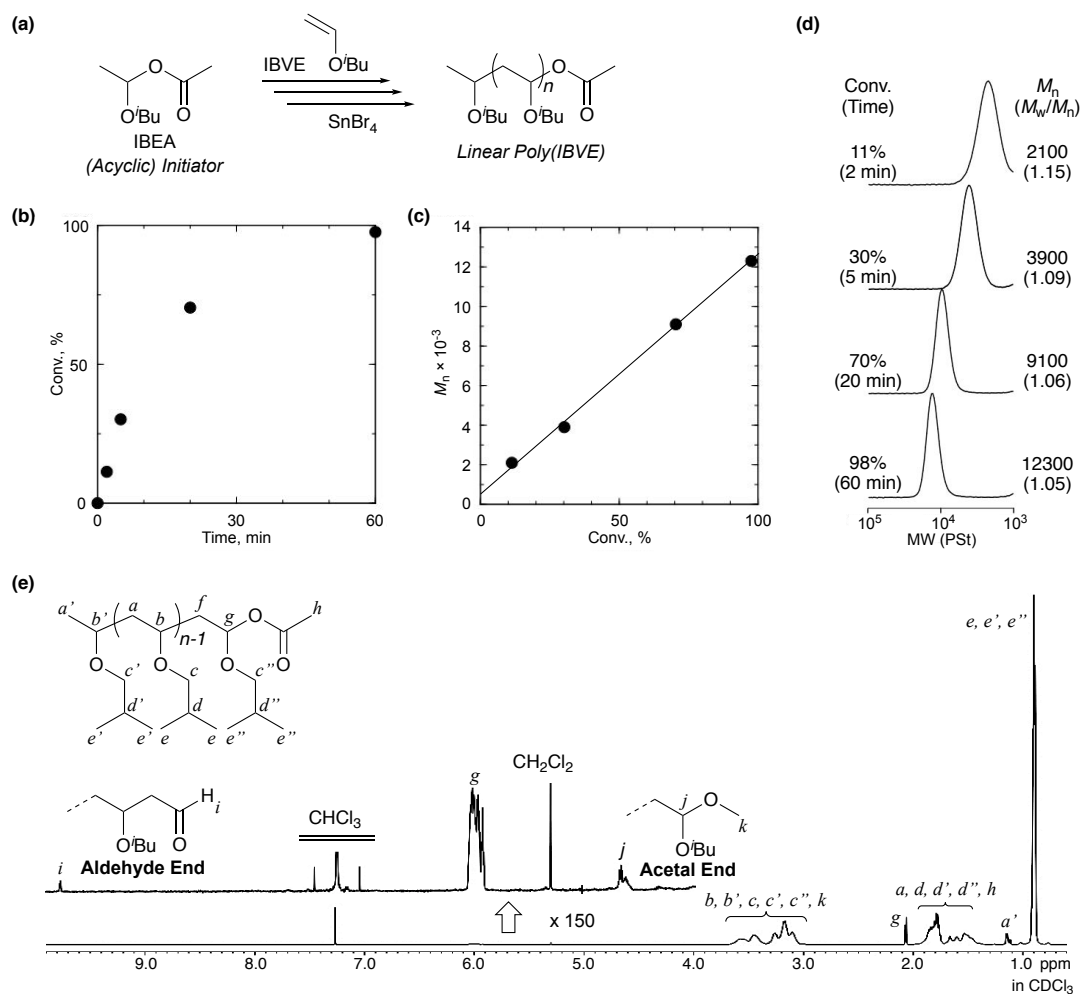


Fig S5. Synthesis of linear poly(IBVE) via living cationic polymerization of IBVE. Polymerization: $[\text{IBVE}]_0/[\text{IBEA}]_0/[\text{SnBr}_4]_0/[\text{DTBMP}]_0 = 1000/5.0/5.0/0.15$ mM in toluene at 0 °C. (a) Scheme of the cationic polymerization of IBVE. (b) Time-conversion plot. (c) Conversion- M_n plot. M_n was measured by SEC with polystyrene standard. (d) SEC curves of the resultant polymers. (e) ^1H NMR spectrum of the resultant polymer (conversion of IBVE = 11%).

Synthesis of cyclic poly(IBVE)

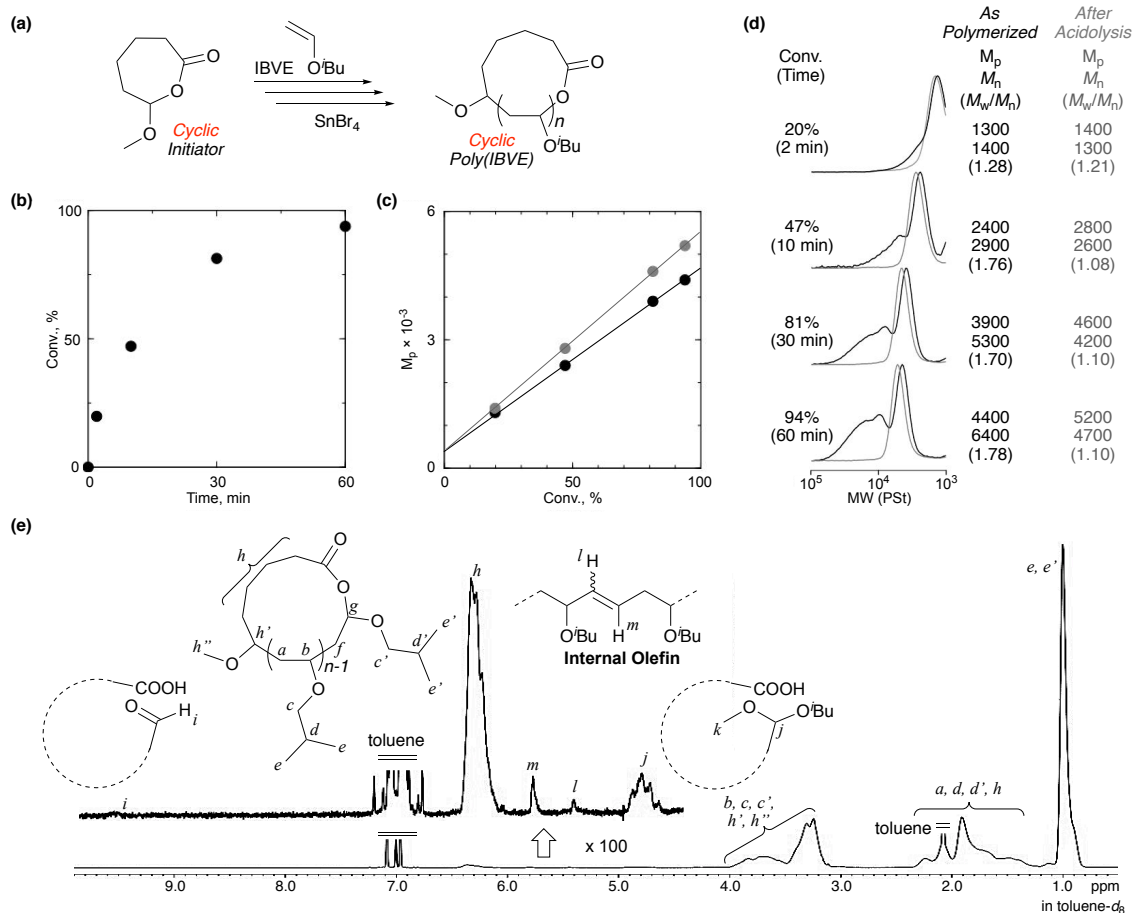


Fig S6. Synthesis of cyclic-polyIBVE via ring-expansion living cationic polymerization of IBVE. Polymerization: $[IBVE]_0/[cyclic\ initiator]_0/[SnBr_4]_0/[DTBMP]_0 = 200/5.0/5.0/0.15\text{ mM}$ in toluene at $0\text{ }^\circ\text{C}$. (a) Scheme of the ring-expansion cationic polymerization of IBVE. (b) Time-conversion plot. (c) M_p -conversion plots of the polymeric products (black) and the acidolyzed products (gray). (d) SEC curves of the polymeric products (black) and the acidolyzed products (gray). (e) ^1H NMR spectrum of the polymeric product (conversion of IBVE = 20%).

TGA chart

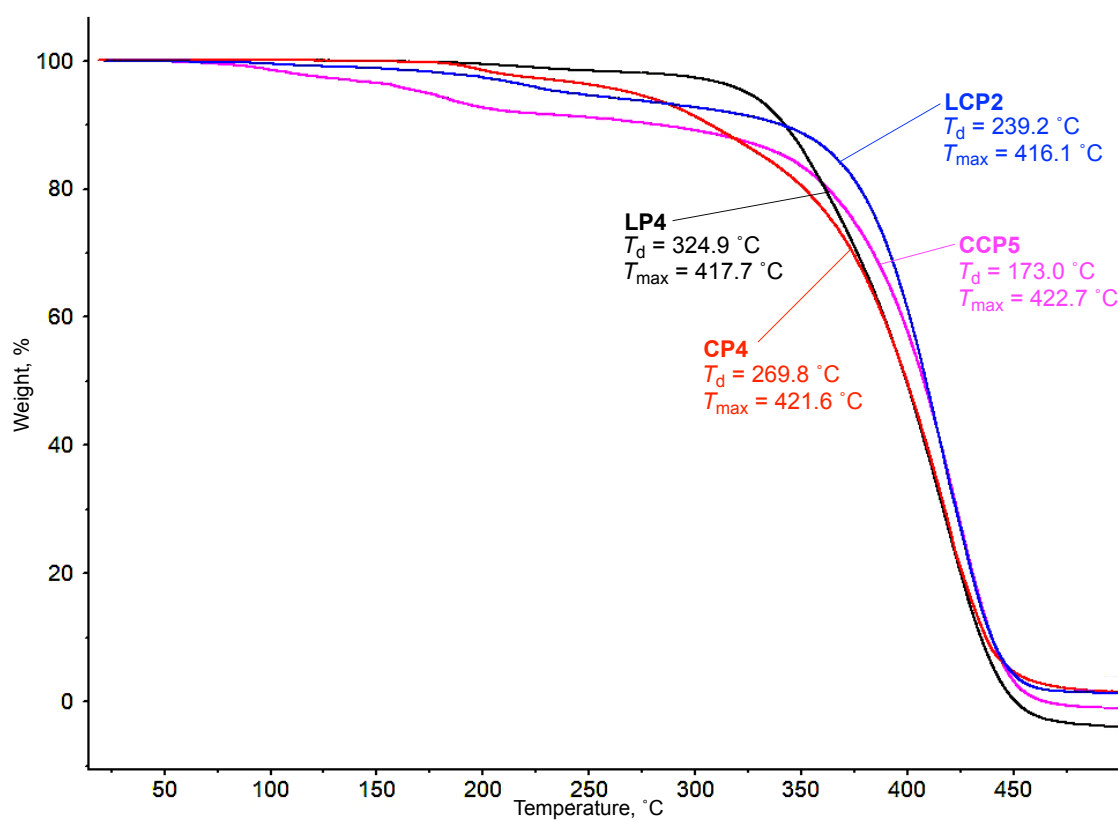


Fig S7. TGA chart of LCP2 (blue), CCP5 (pink), CP4 (red), and LP4 (black). The heating rate was 10 °C/min from 20 to 500 °C. T_d was the temperature of 5% weight loss and T_{max} was the temperature of maximum weight loss.

DSC chart

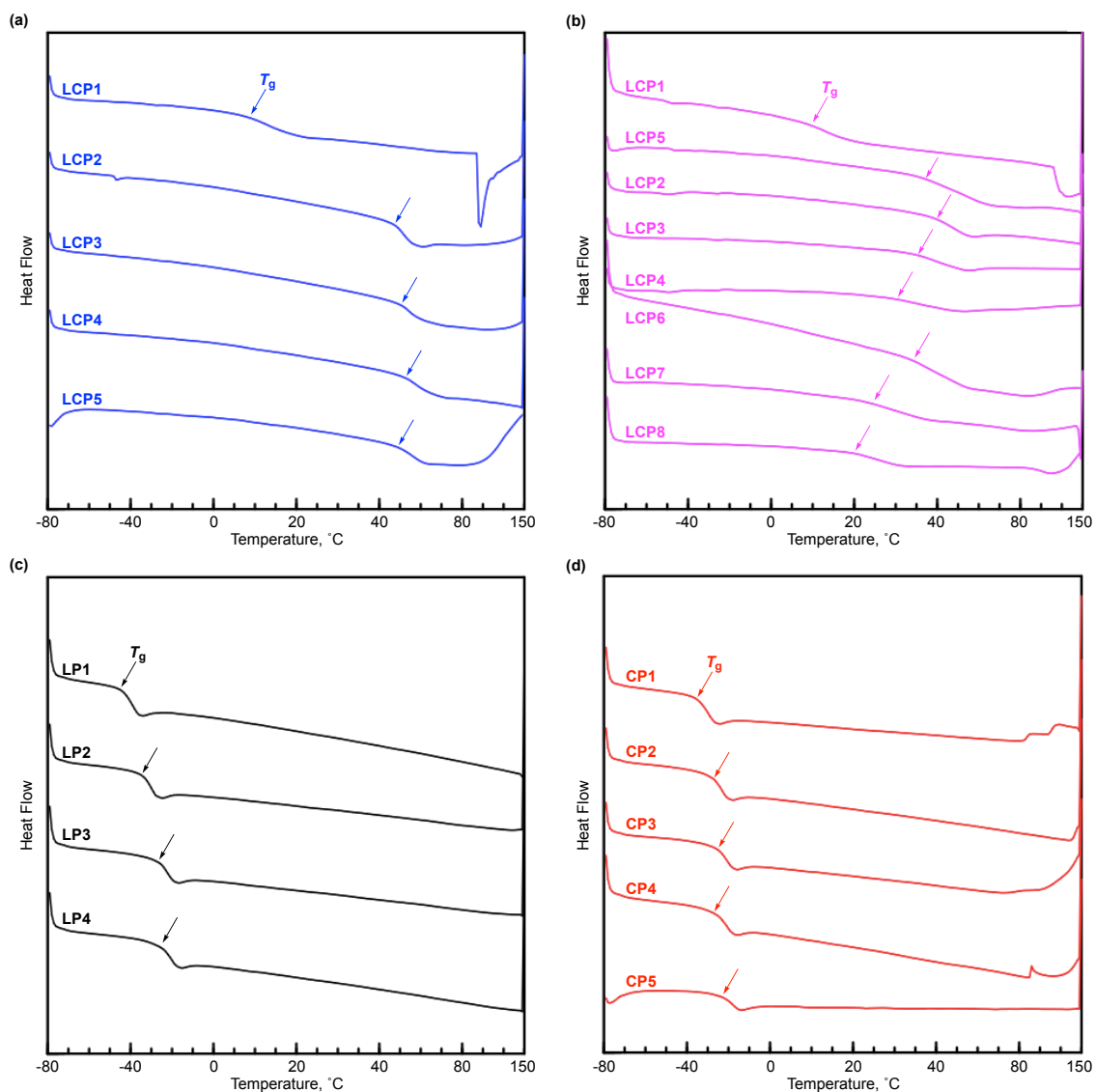


Fig S8. DSC charts of the polymer samples [LCP (a), CCP (b), LP (c), and CP (d)]. Second heating process from -80 to 150 °C after heating and cooling process. Heating rate: 10 °C/min.

¹H NMR Spectra of the divinyl ethers

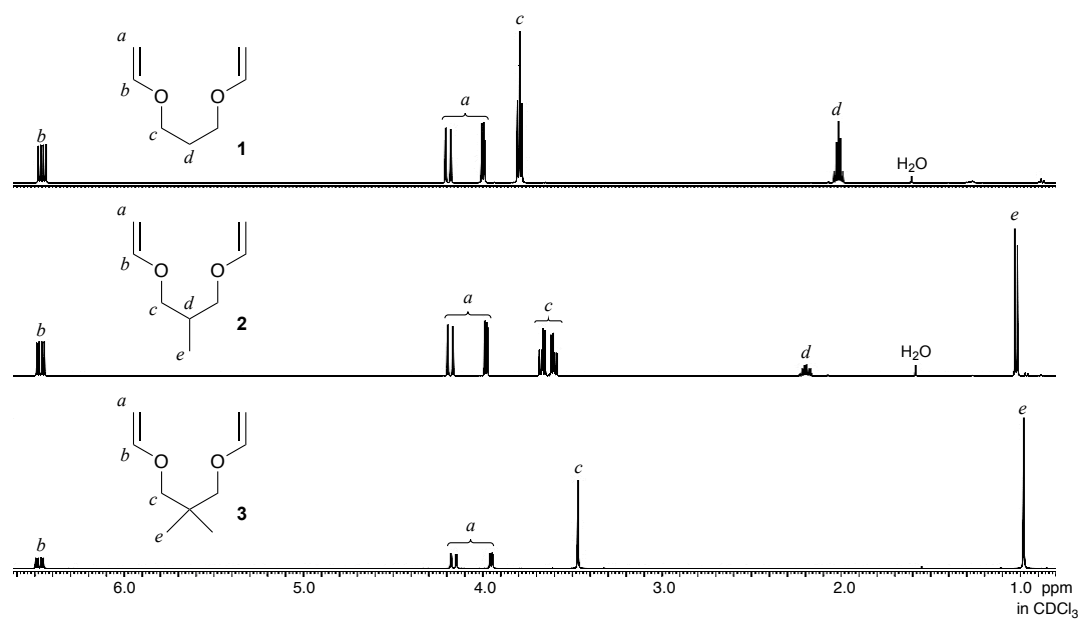


Fig S9. ¹H NMR spectra of divinyl ether **1** (upper), **2** (middle), and **3** (lower).

¹H NMR Spectra of the initiators

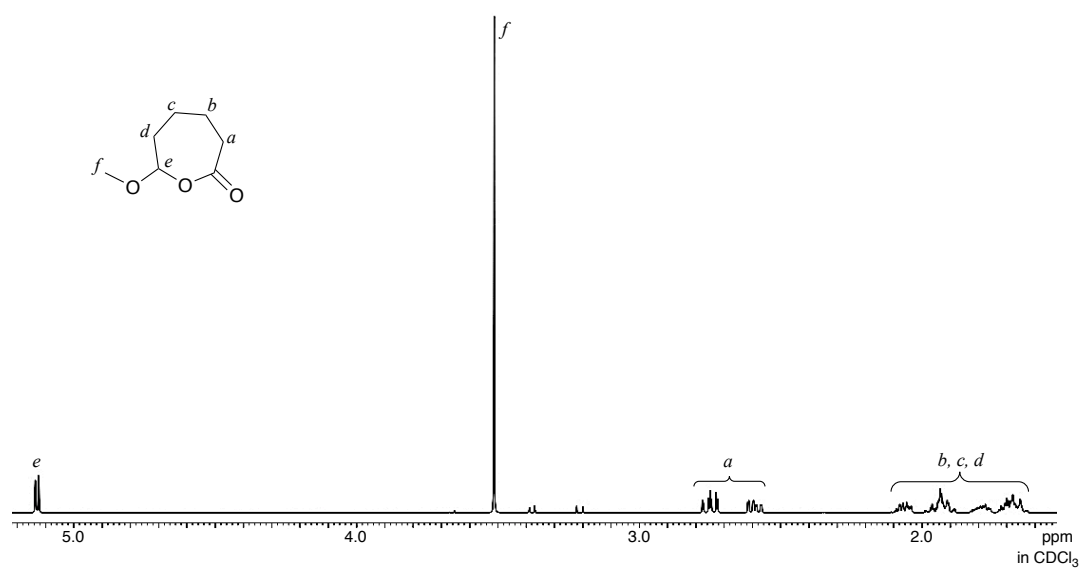


Fig S10. NMR spectrum of the cyclic initiator.

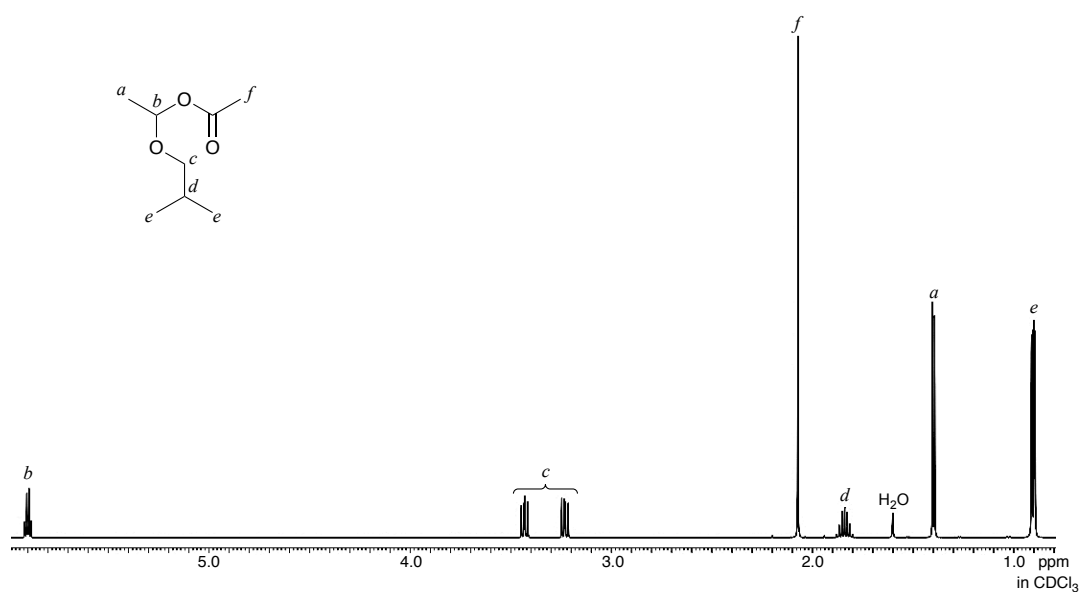


Fig S11. NMR spectrum of IBEA.

Polymer list

Table S1 Summary of the analysis of the polymers after removal of the residual monomers

Polymer	Code	M_n^e	M_w^e	M_w/M_n^e	HAE (%) ^f	T_g (°C) ⁱ
Linear Poly(3) ^a (Linear Cyclopolymer)	LCP1	2100	2500	1.19	85.3	16.9
	LCP2	4600	5100	1.13	85.3	87.0
	LCP3	8500	9600	1.14	82.6	89.9
	LCP4	12500	14100	1.13	83.4	92.4
	LCP5	16300	19100	1.17	79.4	90.8
Cyclic Poly(3) ^b (Cyclic Cyclopolymer)	CCP1	2300	3800	1.65	91.7	18.2
	CCP2	4600	7300	1.58	92.1	78.9
	CCP3	5900	9900	1.67	92.0	70.4
	CCP4	9000	16900	1.88	74.8	56.4
	CCP5	4300	6500	1.52	80.6	74.0
	CCP6	9800	17200	1.76	82.7	63.0
	CCP7	19100	41300	2.16	– ^g	44.6
	CCP8	31500	83500	2.65	– ^g	40.3
Linear Poly(IBVE) ^c (Linear Polymer)	LP1	2100	2400	1.15	87.5	-43.1
	LP2	3900	4200	1.09	– ^h	-33.7
	LP3	9100	9600	1.06	– ^h	-25.9
	LP4	12300	12900	1.05	77.7	-24.5
Cyclic Poly(IBVE) ^d (Cyclic Polymer)	CP1	1400	1800	1.28	85.4	-34.4
	CP2	2900	4000	1.76	– ^h	-27.3
	CP3	5300	9000	1.78	– ^h	-24.4
	CP4	6400	11500	1.70	76.8	-24.7
	CP5	13400	27600	2.06	73.8	-24.3

^aPolymerization: [**3**]₀/[IBEA]₀/[SnBr₄]₀/[DTBMP]₀ = 50/1.25/5.0/0.15 mM in toluene at 0 °C, sequential monomer addition (0-3 times) was performed for **LCP2-5**. ^bPolymerization: [**3**]₀/[cyclic initiator]₀/[SnBr₄]₀/[DTBMP]₀ = 50/1.25/5.0/0.15 mM in toluene at 0 °C, sequential monomer addition (0-3 times) was performed for **CCP5-8**. ^cPolymerization: [IBVE]₀/[IBEA]₀/[SnBr₄]₀/[DTBMP]₀ = 1000/5.0/5.0/0.15 mM in toluene at 0 °C. ^dPolymerization: [IBVE]₀/[cyclic initiator]₀/[SnBr₄]₀/[DTBMP]₀ = 200 (for **CP1-4**) or 380 (for **CP5**)/5.0/10/0.15 mM in toluene at 0 °C. ^eMeasured by SEC with polystyrene standard after removal of the residual monomers. ^fRetention of HAE bond in the resultant polymers measured by ¹H NMR. ^gNot found due to indistinct peaks from the relevant protons (HAE, aldehyde, and acetal). ^hNot measured. ⁱMeasured by DSC.