

Supporting Information

**Construction of Ring-Based Architectures via Ring-Expansion
Cationic Polymerization and Post-Polymerization Modification:
Design of Cyclic Initiators from Divinyl Ether and Dicarboxylic Acid**

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Materials

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%), 1,2,3,4-tetrahydronaphthalene (tetralin, TCI; >98%) and tetrachloromethane (Wako; >99.5%) were distilled from calcium hydride once before use. ϵ -Caprolactone (ϵ -CL, TCI; >99%) was distilled under reduced pressure.

For polymerization or reaction solvent, toluene (Wako; Deoxidized), tetrahydrofuran (THF, Wako; Dehydrated) and dichloromethane (DCM, Wako; Deoxidized) were used as received. For the quencher of cationic polymerization, *N,N*-dimethylformamide (DMF, Wako; Dehydrated) was kept over molecular sieves 4A (Wako).

4-Methylphthalic acid (TCI; >98%), 4-bromophthalic acid (TCI; >98%), tin bromide (SnBr₄, Aldrich; >99%), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl benzoate (TCI ; >98%), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl alcohol (TCI ; >98%), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (BLD pharm; >97%), 1,4- benzenediboronic acid bis(pinacol) ester (TCI; >98%), [1,1'-bis(diphenylphosphino)ferrocene] dichloropalladium(II) dichloromethane adduct (PdCl₂(dppf) · CH₂Cl₂; Aldrich), cesium carbonate (TCI; >98%), triazabicyclo [4.4.0] dec-5-ene (TBD, TCI; >98%), and benzoic acid (Wako; >99.5%) were used as received. 2,2-Dimethyl-1,3-divinyloxy propane (DVE-1), 1,3-divinyloxy propane (DVE-2) and 7-membered cyclic initiator (7-CyInit) were synthesized according to the literature.¹ 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styrene (vinyl- substituted Bpin) was synthesized according to the literature.²

- 1) Kubota, H.; Yoshida, S.; Ouchi, M.; *Polym. Chem.*, **2020**, *11*, 3964-3971.
- 2) Wu, J. et. al., *J. Am. Chem. Soc.*, **2018**, *140*, 16360-16367.

Instruments

¹H NMR

¹H NMR spectra were recorded in CDCl₃ 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 with CCl₄ as an internal standard by using GC-2014 (Shimadzu) equipped with a packed column (polyethyleneglycol 1500/shimalite): Temperature: 120 °C for injection, 80 °C for column; Current: 120 mA.

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 (Shodex LF-404) at 0.35 mL/ min of flow rate. 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). For the analyses of cyclic initiators, TOSOH H2000 column was used instead of LF-404.

Preparative SEC

Cyclic initiators and polymer samples were purified for removal of undesired portions or lower molecular weight compounds with preparative SEC, LaboACE LC-5060 (Japan Analytical Industry). Eluent: CHCl₃; Column: JAIGEL-2.5HR (exclusion limit = 20000) or combination of JAIGEL-2HR and JAIGEL-1HR: Flow rate: 10 mL/ min.

Intrinsic Viscosity

Intrinsic viscosity and absolute molecular weight of polymer samples were measured by Viscotek TDAMax (Malvern). Eluent: THF; Column: polystyrene-gel columns (Shodex KF-805); Flow rate: 1.0 mL/min; Temperature: 40 °C. PS105K (Malvern) was used for the calibration of light scattering.

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 DCTB as matrix and sodium trifluoroacetate as cationizing agent.

Procedures

Syntheses of cyclic initiators

The typical procedure for the synthesis of the cyclic initiator is as follows: 4-Methylphthalic acid (0.311 g, 1.72 mmol), 2,2-dimethyl-1,3-divinyloxy propane (0.30 mL, 1.72 mmol) and toluene (8.6 mL) were added to glass tube under argon. Note that the solvent polarity was tuned depending on the solubility of the product (see Table S1). The reaction mixture was heated to 60 °C under magnetic stirring until the insoluble part was completely dissolved. In 4 hours, the reaction solution was diluted with toluene and washed with saturated aqueous Na₂CO₃ solution and then water. The organic layer was dried over Na₂SO₄ for 30 min, followed by filtration. The solution was concentrated under reduced pressure, and the product was purified by preparative SEC to give the 1:1 cyclic adduct. Finally, the product was dehydrated by azeotrope with toluene three times, and the colorless oil product **1** was obtained (0.211 g, 0.64 mmol, 37%). See Figure S1 for the ¹H NMR spectrum. ESI-MS: 359.1472 (m/z) (Calcd: 359.1465 for Na⁺ adduct).

Table S1. Conditions for the Cyclic Initiator Synthesis.^a

DCA	DVE	Solvent	Reaction Time (hr)	Rate of 1:1 Ring (%) ^g
MePA ^b	DVE-1 ^e	Toluene	4.0	87.2
MePA	DVE-2 ^f	Toluene	4.0	69.4
SA ^c	DVE-1	Toluene/Acetonitrile (1/1 v/v)	24	65.2
BrPA ^d	DVE-1	Toluene	3.0	85.9

^a[DCA]/[DVE] = 200/200 mM at 60 °C. ^bMePA = 4-methyl phthalic acid. ^cSA = succinic acid. ^dBrPA = 4-bromo phthalic acid. ^eDVE-1 = 2,2-Dimethyl-1,3-divinyloxy propane. ^fDVE-2 = 1,3-divinyloxy propane. ^gDetermined by the peak area ratio of SEC.

Ring-Expansion Cationic Polymerization

The typical procedure of ring-expansion cationic polymerization is as follows: A glass tube equipped with a three-way stopcock and a magnetic stirring bar was dried using a heating gun (Hakko; 880B; ~400 °C) under dry nitrogen and the polymerization solution was prepared here under the inert gas atmosphere. The polymerization was initiated by adding solution of SnBr₄ (50

mM in toluene, 0.3 mL) via a dry syringe into a mixture containing IBVE, **1**, DTBMP, and CCl₄ (internal standard) in toluene (2.7mL) at 0 °C: [IBVE]₀/[**1**]₀/[SnBr₄]₀/[DTBMP]₀ = 380/2.5/5.0/0.15 mM. After a predetermined interval, the polymerization was quenched with 0.3 mL dehydrated DMF. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl₄ 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 1 mL of a cyclic poly(IBVE) solution (0.1 wt% in THF) and added 0.1 mL of a TFA/H₂O (2/1 v/v) solution was added. The solution was kept at room temperature for more than 2 hours, and the resultant solution was evaporated to dryness under reduced pressure to remove THF, TFA and H₂O.

Synthesis of acyclic initiator 2

4-Methylphthalic acid (0.433g, 2.40 mmol) and IBVE (1.6 mL, 12.2 mmol) were added to glass tube under argon. The reaction mixture was heated to 60 °C with magnetic stirring until the powder was completely dissolved. The unreacted IBVE was evaporated under reduced pressure to give colorless oil. The product was dehydrated by azeotrope with toluene three times.

Living Cationic Polymerization with the acyclic initiator

The typical procedure of ring-expansion cationic polymerization is as follows: A glass tube equipped with a three-way stopcock and a magnetic stirring bar was dried using a heating gun (Hakko; 880B; ~400 °C) under dry nitrogen and the polymerization solution was prepared here under the inert gas atmosphere. The polymerization was initiated by adding solution of SnBr₄ (50 mM in toluene, 0.3 mL) via a dry syringe into a mixture containing IBVE, **2**, DTBMP, and CCl₄ (internal standard) in toluene (2.7mL) at 0 °C: [IBVE]₀/[**2**]₀/[SnBr₄]₀/[DTBMP]₀ = 380/2.5/5.0/0.15 mM. After a predetermined interval, the polymerization was quenched with 0.3 mL dehydrated DMF. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl₄ 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 opening polymerization of ϵ -CL from the cyclic macroinitiator for synthesis of tadpole polymer

To a flame-dried glass tube, the cyclic macroinitiator (39.7 mg, 0.011 mmol for hydroxy group), DCM (0.85 mL), tetralin (0.02 mL) and ϵ -CL (0.115 mL, 1.1 mmol) were added under argon. The polymerization was initiated by adding the solution of triazabicyclo [4.4.0] dec-5-ene (TBD) in DCM (0.11 mL of 100 mM,) at room temperature under magnetic stirring. The polymerization was quenched with small amount of benzoic acid. Monomer conversion was determined by ^1H NMR from the integrated peak area of ϵ -CL for that of tetralin as an internal standard. The product was purified via three times dialysis (MWCO = 1000; Spectra/PorVR7, diameter 29 mm) with THF for removal of the residual low molecular weight compounds.

Suzuki-Miyaura cross coupling (SMC) to cyclic polymer

The typical procedure of SMC reaction with the cyclic polymer is as follows: 4-(Hydroxymethyl)-phenylboronic acid pinacol ester (0.031 g, 0.13 mmol), [1,1'-Bis(diphenylphosphino)-ferrocene]palladium(II) dichloride dichloromethane adduct (0.014 g, 0.017 mmol), cesium carbonate (0.081 g, 0.25 mmol), and the cyclic polymer solution in THF (0.2880 g /1.6 mL) were added to glass tube under argon. Water (bubbled with N_2 in advance, 0.4 mL) was then added, and the solution was heated to 40 °C under magnetic stirring for 12 hr. The reaction mixture was evaporated under reduced pressure to remove THF. The crude product was dissolved in DCM and washed with water three times. The organic layer was filtrated with an ISOLUTE[®] Phase Separator (Biotage) followed by evaporation. The crude product was then dissolved in chloroform and purified by preparative SEC to give the hydroxy-functionalized cyclic polymer (0.040 g).

¹H NMR spectra

Initiator **1**

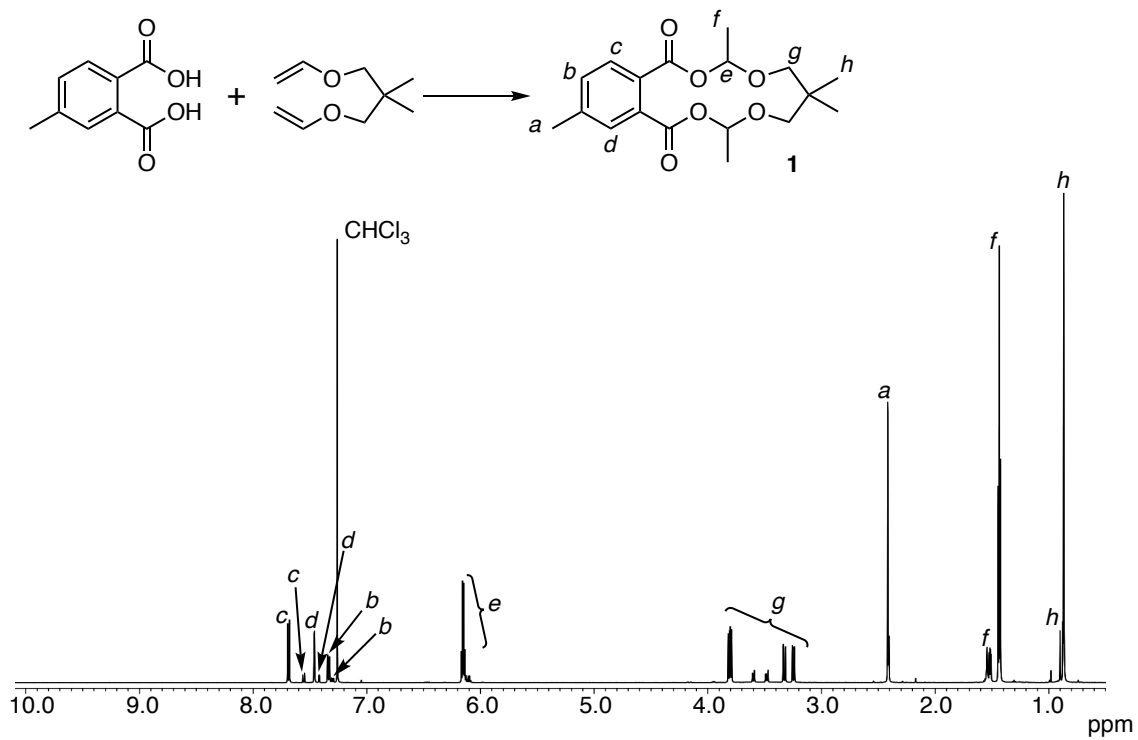


Figure S1. ¹H NMR spectra of cyclic initiator **1** in CDCl₃.

Initiator **2**

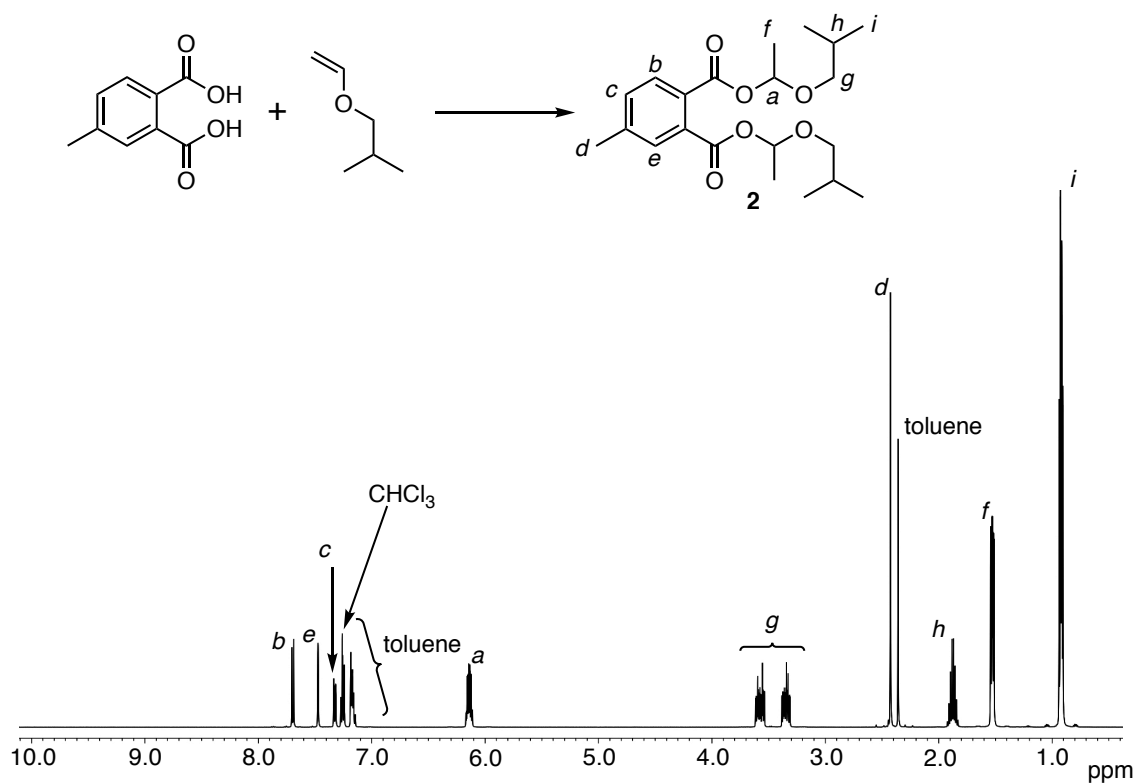


Figure S2. ¹H NMR spectra of cyclic initiator **2** in CDCl₃.

Initiator **3**

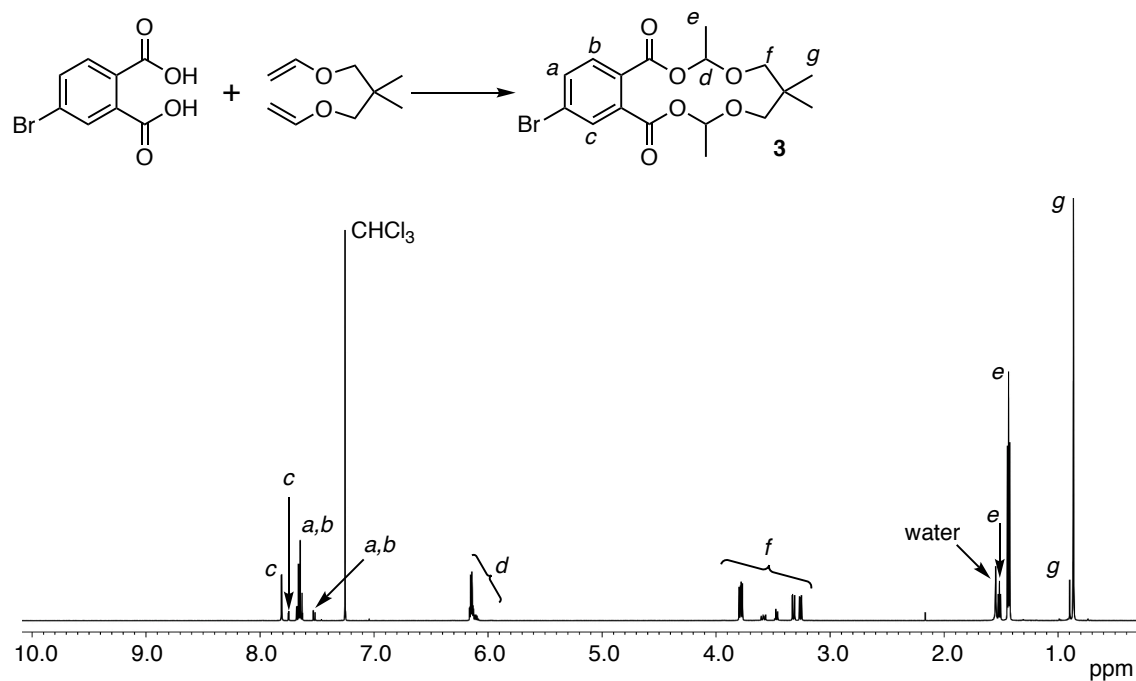


Figure S3. ¹H NMR spectra of cyclic initiator **3** in CDCl₃.

Purification of Cyclic Initiators by preparative SEC

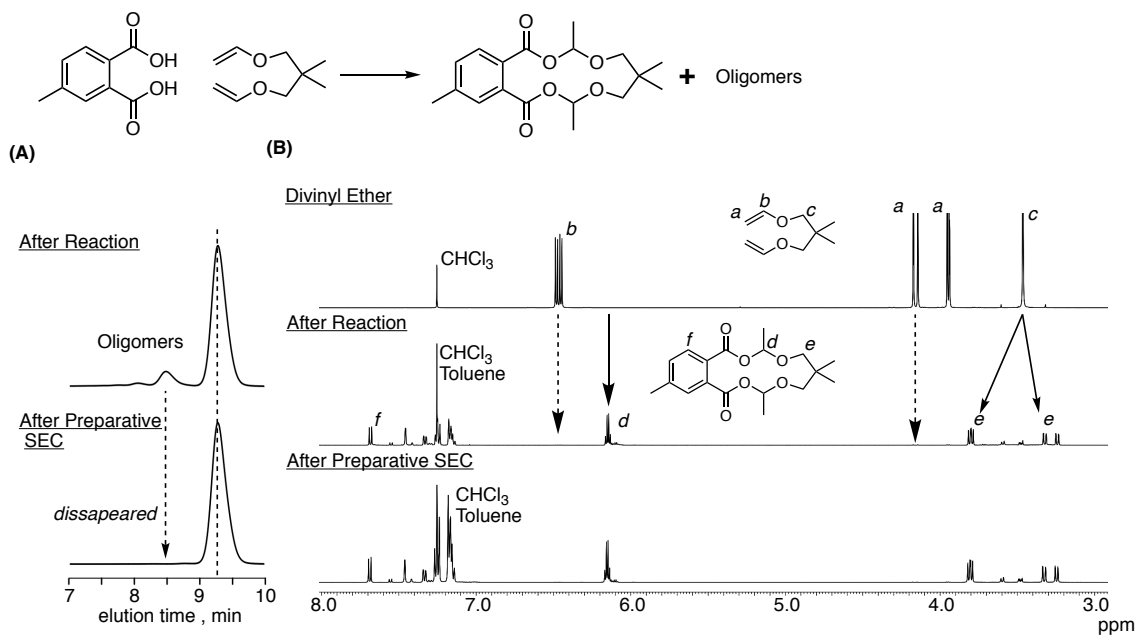


Figure S4. Synthesis and purification of cyclic initiator **1**. (A) SEC curves of the product after reaction (upper) and that after purification by preparative SEC (lower). (B) ¹H NMR spectra of the divinyl ether (DVE-1, upper), the product after the reaction (middle), and that after purification by preparative SEC in CDCl₃. See Figure S1 for the detailed peak assignment.

Conversion- M_n for the polymers after acidolysis treatment

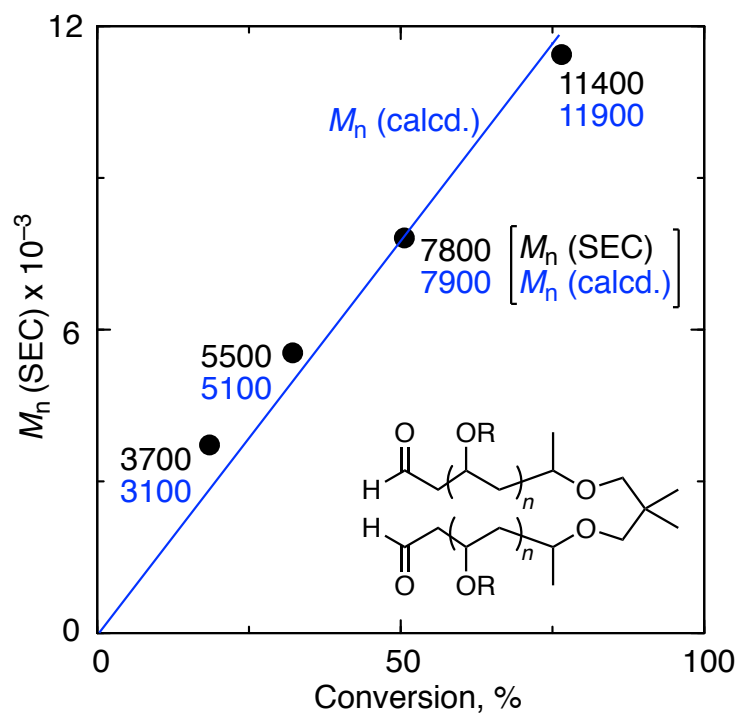


Figure S5. Conversion- M_n plots of poly(IBVE)s after acidolysis. Polymerization: $[\text{IBVE}]_0/[\mathbf{1}]_0/[\text{SnBr}_4]_0/[\text{DTBMP}]_0 = 380/2.5/5.0/0.15$ mM in toluene at 0 °C. See above for the acidolysis treatment.

Ring-Expansion Cationic Polymerization with **1** ($[1]_0 = 5.0 \text{ mM}$)

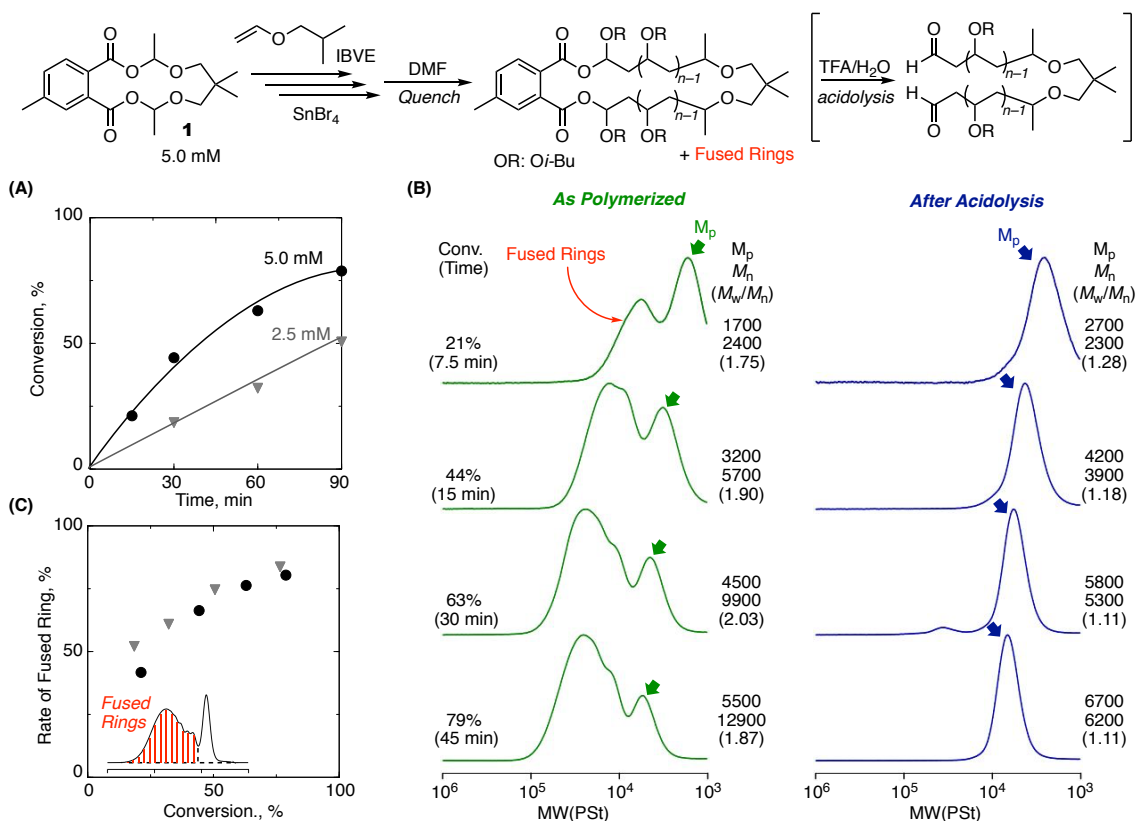


Figure S6. RECP of IBVE with **1** at higher concentration ($[1]_0 = 5.0 \text{ mM}$): $[\text{IBVE}]_0/[\mathbf{1}]_0/[\text{SnBr}_4]_0/[\text{DTBMP}]_0 = 380/5.0/5.0/0.15 \text{ mM}$ in toluene at 0°C . (A) Time-conversion curve of the polymerization (black) in comparison with the 2.5 mM condition (gray). (B) SEC curves of obtained poly(IBVE)s (green) and those after acidolysis (blue). (C) Comparison of fused ring rates between 5.0 mM (black) and 2.5 mM (gray) of $[1]_0$.

MALDI-TOF-MS spectra

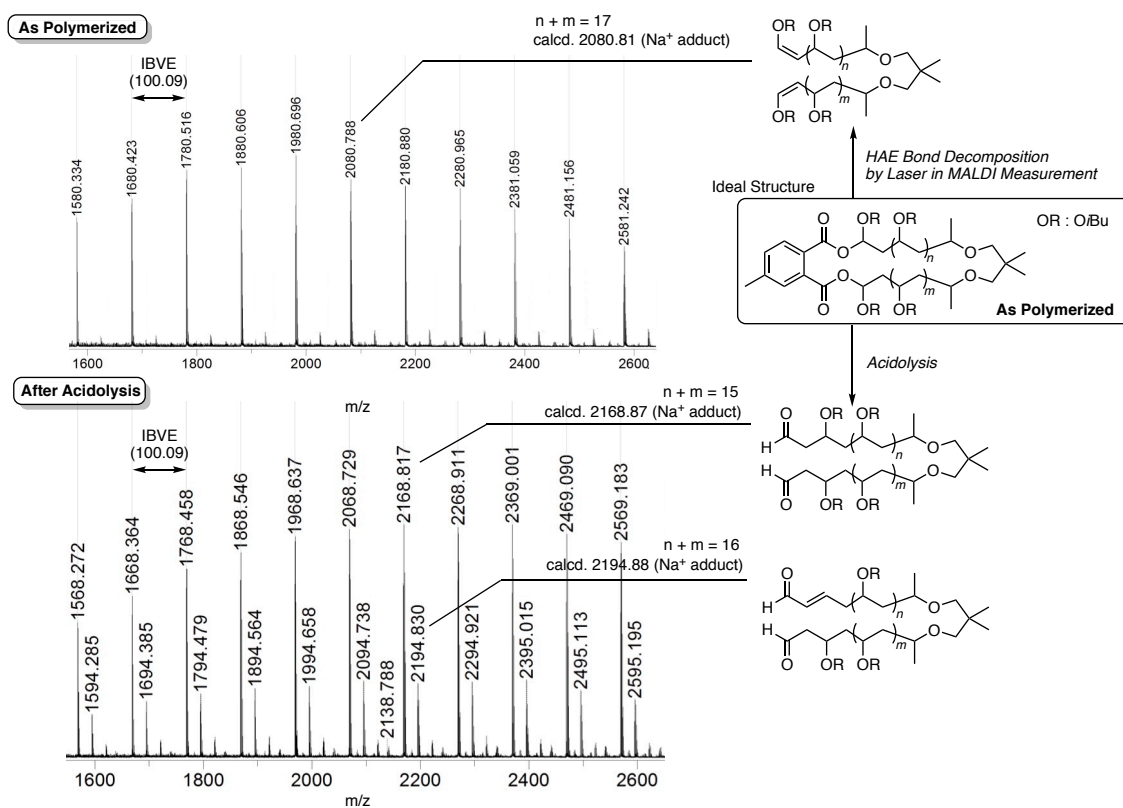


Figure S7. MALDI-TOF-MS spectra of the obtained poly(IBVE)s before (upper) and after (lower) the acidolysis. M_n , M_w/M_n (SEC) = 4300, 1.72 (conversion = 19%, as polymerized), 3700, 1.21 (after acidolysis).

Ring-Expansion Cationic Polymerization with **3**

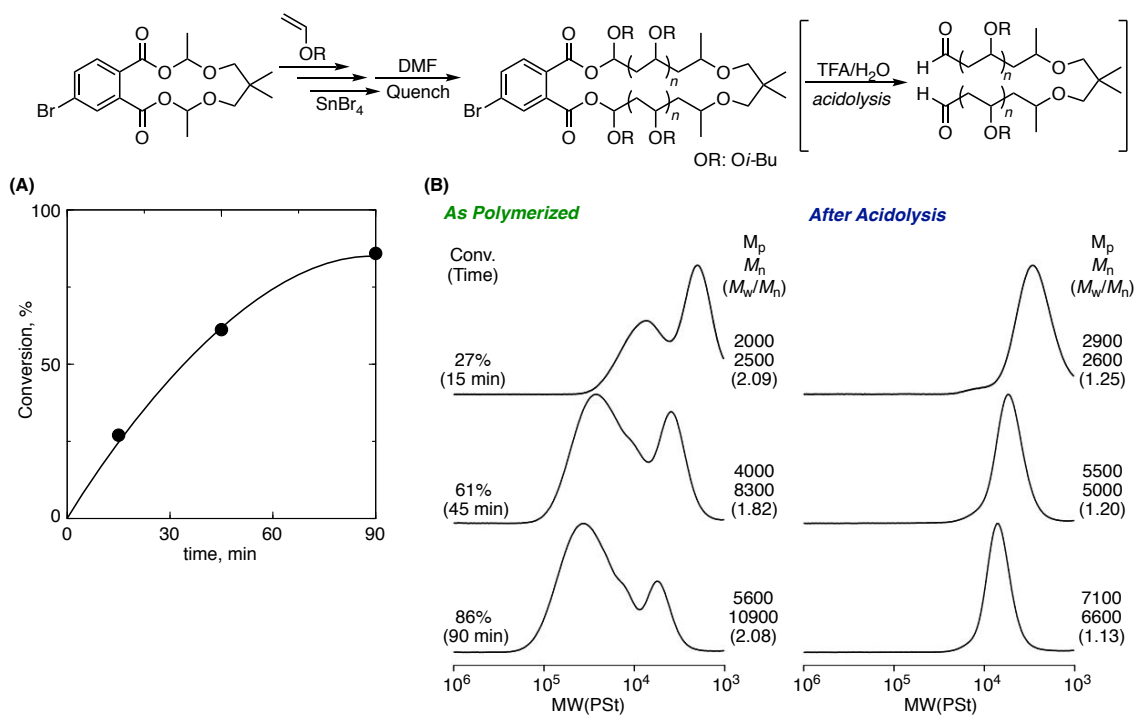


Figure S8. (A) Scheme of ring-expansion cationic polymerization of IBVE with **3** as an initiator. (B) Time-conversion curves of the polymerization initiated with **3**. (C) SEC curves of obtained poly(IBVE)s and those after acidolysis. $[\text{IBVE}]_0/[\mathbf{3}]_0/[\text{SnBr}_4]_0/[\text{DTBMP}]_0 = 380/2.5/5.0/0.15$ mM in toluene at 0 °C.

SMC of the bromine-functionalized cyclic polymer with hydroxymethyl-Bpin

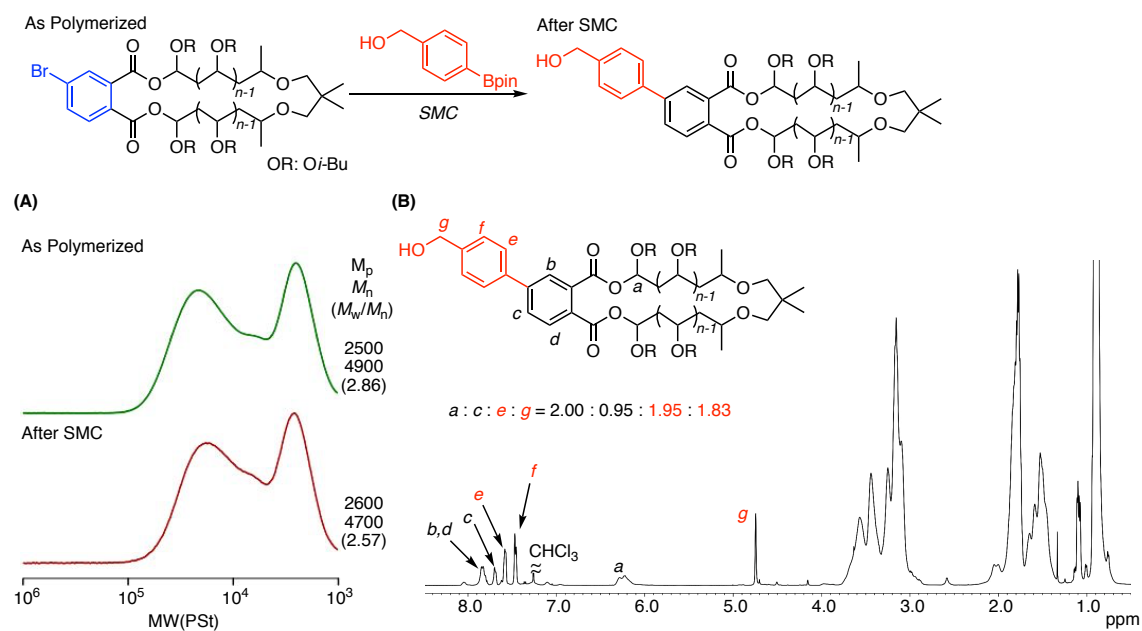


Figure S9. (A) SEC curves of the product via RECP of IBVE with 3 (as polymerized, conv. = 62%, upper) and that after SMC with hydroxymethyl-Bpin (lower). (B) ¹H NMR spectra (500 MHz, CDCl₃) of the cyclic poly(IBVE) carrying the hydroxymethyl group.

Amino group introduction to cyclic polymer by SMC

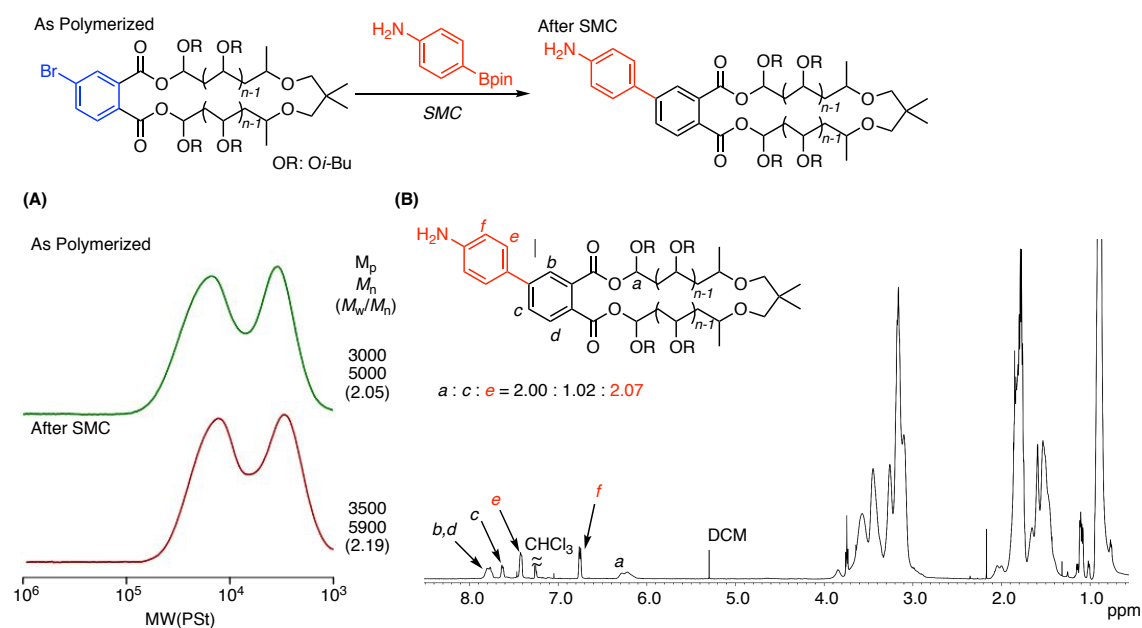


Figure S10. (A) SEC curves of the product via RECP of IBVE with 3 (as polymerized, conv. = 30%, upper) and that after SMC with hydroxymethyl-Bpin (lower). (B) ^1H NMR spectra (500 MHz, CDCl_3) of the cyclic poly(IBVE) carrying the hydroxymethyl group.

Vinyl group introduction to cyclic polymer by SMC

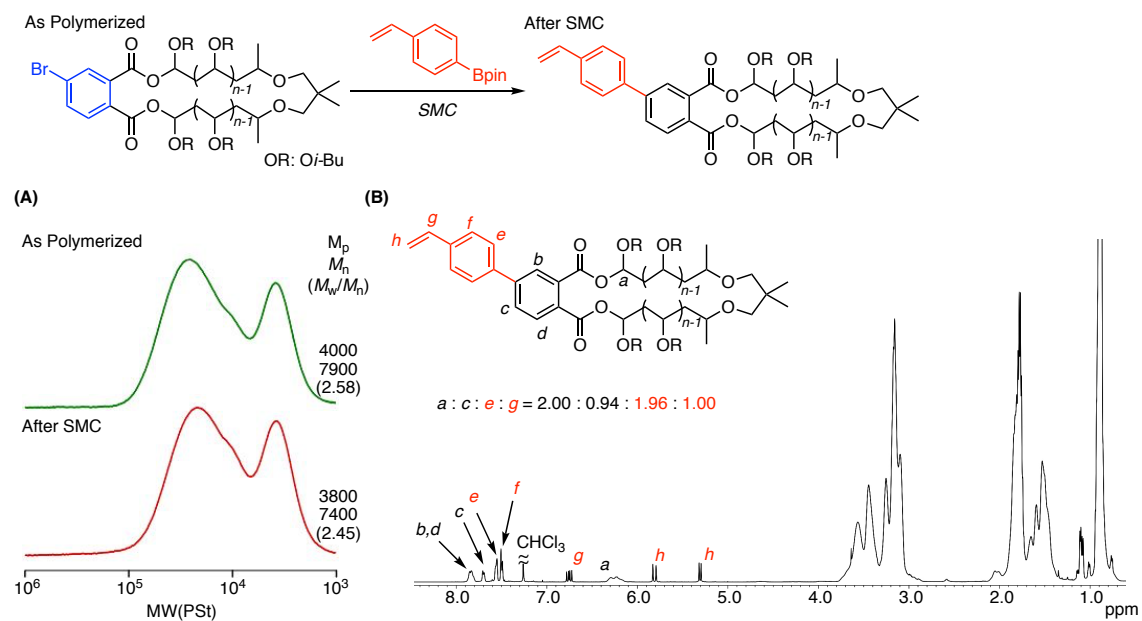


Figure S11. (A) SEC curves of the product via RECP of IBVE with 3 (as polymerized, conv. = 55%, upper) and that after SMC with hydroxymethyl-Bpin (lower). (B) ^1H NMR spectra (500 MHz, CDCl_3) of the cyclic poly(IBVE) carrying the hydroxymethyl group.

ROP of ϵ -CL with the cyclic poly(IBVE) carrying the hydroxymethyl group as a macroinitiator

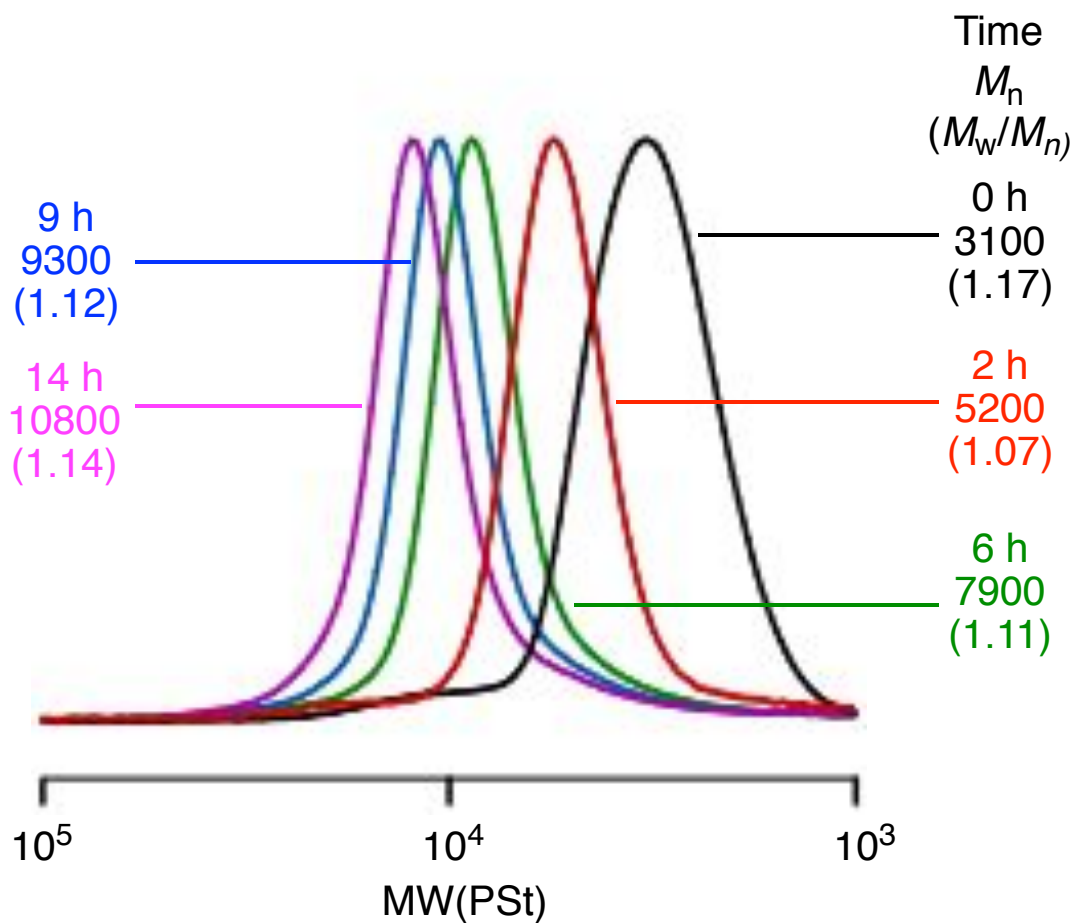


Figure S12. SEC curves of the products in ROP of ϵ -CL with the cyclic poly(IBVE) carrying the hydroxymethyl group as a macroinitiator. See the caption of Figure 9 in the main text for the polymerization condition.

Table S2. Molecular Weight Characterizations for the Synthesis of the Tadpole Polymer

Polymer	$M_n(\text{SEC})^a$	$M_w/M_n(\text{SEC})^a$	$M_n(\text{NMR})^b$	$M_n(\text{LS})^c$
Cyclic Poly(IBVE) (Before Preparative SEC)	5500	1.99	n.d. ^d	n.d.
Cyclic Poly(IBVE) (Macroinitiator)	3100	1.19	3600	n.d.
Tadpole Polymer (After ROP of ϵ -CL)	11100	1.20	8600	10500

^aMeasured by SEC calibrated with polystyrene standard. ^bCalculated by the integral values of peaks from the HAE bond and the repeating units. ^cMeasured by light scattering detector in Viscotek TDAmix. ^dNot determined.

Table S3. Molecular Weight Characterizations for the Synthesis of the Figure-Eight Polymer and the Related Samples for the Elucidation of Intrinsic Viscosity

Polymer	$M_n(\text{SEC})^b$	$M_w/M_n(\text{SEC})^b$	$M_n(\text{NMR})^c$	$M_n(\text{LS})^d$
Cyclic Poly(IBVE) (Before Preparative SEC)	5500	1.99	n.d. ^c	n.d.
Cyclic Poly(IBVE) (Single Ring)	2400	1.10	3300	4300
Figure-eight Poly(IBVE) (After SMC and Preparative SEC)	5600	1.06	6800	7900
Linear Poly(IBVE) ^a	9100	1.06	n.d.	8600

^aPolymerization: [IBVE]₀/[IBEA (IBVE-AcOH adduct)]₀/[SnBr₄]₀/[DTBMP]₀ = 380/2.5/5.0/0.15 mM in toluene at 0 °C. ^bMeasured by SEC calibrated with polystyrene standard. ^cCalculated by the integral values of peaks from the HAE bond and the repeating units. ^dMeasured by Viscotek TDAmx equipped with a light scattering detector. ^eNot determined.