Electronic Supplementary Information (ESI)

Ring-Expansion Cationic Cyclopolymerization for Construction of Cyclic Cyclopolymer

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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 (mCPBA, 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 (SnBr₃, 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. 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
Measurement

$^1$H NMR. $^1$H NMR spectra were recorded in CDCl$_3$ or toluene-$d_6$ 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, Shimdazu; packed column: polyethylene glycol 1500, shimalite; temperature: injection 120 °C, column 80 °C; current: 120 mA with CCl$_4$ 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 CHCl$_3$ 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 CH$_2$Cl$_2$ 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 $T_{\text{max}}$: the temperature of maximum weight loss) of polymer samples (50 μL of 10wt% polymer solution in CH$_2$Cl$_2$ 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.

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$_2$Cl$_2$ 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$_2$SO$_4$ 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.

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C):
1: δ (ppm) 6.46 (q, J = 7.1 Hz, 2H), 4.19 (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 = 6.9, 2.3 Hz, 2H), 3.98 (dd, J = 6.9, 2.3 Hz, 2H), 3.64 (ddd, J = 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), 4.00 (dd, J = 6.9, 2.3 Hz, 2H), 3.79 (t, J = 6.0 Hz, 4H), 2.95 (m, 1H), 3.51 (s, 3H), 2.78 (m, 1H), 1.35 (s, 6H), 0.97 (s, 6H).

Synthesis of the cyclic initiator.

2-Methoxycyclohexanone (6.60 mL, 52.5 mmol) was slowly added to a CH$_2$Cl$_2$ solution (250 mL) of NaHCO$_3$ (5.91 g, 70.4 mmol) and mCPBA (18.6 g, 77.6 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 1.5 hour. Excess mCPBA was quenched with saturated aqueous Na$_2$CO$_3$ solution and saturated aqueous Na$_2$SO$_4$ solution, and the resulting mixture was extracted with CH$_2$Cl$_2$. The organic layer was separated, and washed with saturated aqueous Na$_2$CO$_3$ solution. Then the organic layer was dried over Na$_2$SO$_4$. After filtration, the solution was concentrated under reduced pressure. Finally, it was distilled under reduced pressure to afford the cyclic initiator (1.3 mL) as colorless oil.

$^1$H 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$_2$ 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]$_0$ = 50/12.5/5.0/0.15 mM. After a predetermined interval, the polymerization was quenched with precoilled methanol containing 1vol% of ammonia solution. Conversion of monomer’s vinyl groups was determined by $^1$H NMR from the integrated peak area of monomer’s olefinic protons with tetralin as an internal standard. The quenched polymerization solution was washed with precoilled water, evaporated to dryness under reduced pressure, and vacuum-dried. SEC curves, $M_n$, $M_w$, $M_M$, 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$_2$O (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$_2$O.
Effects of temperature on the cationic cyclopolymerization of 3

(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).

Fig S1. Effects of temperature on the cationic cyclopolymerization of 3. Polymerization: [3]/[IBEA]/[SnBr4]/[DTBMP] = 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: \([3]/[\text{IBEA}]/[\text{SnBr}_4]/[\text{DTBMP}] = 50/0.50/5.0/0.15 \text{ mM in toluene at } 0 \, ^\circ\text{C}.\) (a) Scheme of the cationic cyclopolymerization of 3. (b) Time-conversion plot. (c) SEC curves of the resultant polymers.

\(^1\text{H NMR spectra of cyclic and linear poly(3)s before and after acid treatment}\)

Fig S3. \(^1\text{H NMR spectra of cyclic and linear poly(3)s before and after acid treatment.} \) (a): in toluene-\(d_8\); (b-d) in CDCl\(_3\).
Synthesis of higher molecular weight cyclic poly(3) by sequential monomer addition

Polymerization:

\[
\begin{align*}
&\text{Cyclic Initiator (1 eq.)} \\
&\text{Conv. = 58\% (30 min)} \\
&\text{Conv. = 128\% (30 min × 2)} \\
&\text{Conv. = 195\% (30 min × 3)} \\
&\text{Conv. = 303\% (30 min × 4)} \\
\end{align*}
\]

As Polymerized

After Acidolysis

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<th>(M_w)</th>
<th>(M_n)</th>
<th>(M_w/M_n)</th>
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After Acidolysis

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Fig S4. Synthesis of the higher molecular weight (MW) cyclic cyclopolymer by sequential monomer addition. Polymerization: \([3]_0/\text{cyclic initiator}_0/[\text{SnBr}_4]/[\text{DTBMP}]_0 = 50/1.25/5/0.15\) 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: [IBVE]/[IBEA]/[SnBr\(_4\)]/[DTBMP] = 1000/5.0/5.0/0.15 mM in toluene at 0 \(^\circ\)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) \(^1\)H NMR spectrum of the resultant polymer (conversion of IBVE = 11%).
Synthesis of cyclic poly(IBVE)

Fig S6. Synthesis of cyclic-poly(IBVE) via ring-expansion living cationic polymerization of IBVE. Polymerization: [IBVE]/[cyclic initiator]/[SnBr4]/[DTBMP] = 200/5.0/5.0/0.15 mM in toluene at 0 °C. (a) Scheme of the ring-expansion cationic polymerization of IBVE. (b) Time-conversion plot. (c) Mₚ-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%).
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 $T_{\text{max}}$ was the temperature of maximum weight loss.
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.
$^1$H NMR Spectra of the divinyl ethers

Fig S9. $^1$H NMR spectra of divinyl ether 1 (upper), 2 (middle), and 3 (lower).
$^1$H NMR Spectra of the initiators

Fig S10. NMR spectrum of the cyclic initiator.

Fig S11. NMR spectrum of IBEA.
Table S1  Summary of the analysis of the polymers after removal of the residual monomers

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<th>$M_w$</th>
<th>$M_w/M_n$</th>
<th>HAE (%)</th>
<th>$T_g$ (˚C)</th>
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<sup>a</sup>Polymerization: $[\text{3}]_0/\text{[IBEA]}_0/\text{[SnBr}_4]_0/\text{[DTBMP]}_0 = 50/1.25/5.0/0.15 \text{ mM in toluene at } 0 \degree \text{C, sequential monomer addition (0-3 times) was performed for LCP2-5.}<br>
<sup>b</sup>Polymerization: $[\text{3}]_0/\text{[cyclic initiator]}_0/\text{[SnBr}_4]_0/\text{[DTBMP]}_0 = 50/1.25/5.0/0.15 \text{ mM in toluene at } 0 \degree \text{C, sequential monomer addition (0-3 times) was performed for CCP5-8.}<br>
<sup>c</sup>Polymerization: $[\text{IBVE}]_0/\text{[IBEA]}_0/\text{[SnBr}_4]_0/\text{[DTBMP]}_0 = 100/0.0/5.0/0.15 \text{ mM in toluene at } 0 \degree \text{C.}<br>
<sup>d</sup>Polymerization: $[\text{IBVE}]_0/\text{[cyclic initiator]}_0/\text{[SnBr}_4]_0/\text{[DTBMP]}_0 = 200 \text{ (for CP1-4) or 380 (for CP5) }/5.0/10/0.15 \text{ mM in toluene at } 0 \degree \text{C.}<br>
<sup>e</sup>Measured by SEC with polystyrene standard after removal of the residual monomers.<br>
<sup>f</sup>Retention of HAE bond in the resultant polymers measured by $^1\text{H NMR.}<br>
<sup>g</sup>Not found due to indistinct peaks from the relevant protons (HAE, aldehyde, and acetal).<br>
<sup>h</sup>Not measured.<br>
<sup>i</sup>Measured by DSC.