

**Electronic Supplementary Information for:  
Tandem polymerization consisting of cyclotrimerization and the Tishchenko  
reaction: synthesis of acid- and alkali-degradable polymers with cyclic acetal  
and ester structures in the main chain**

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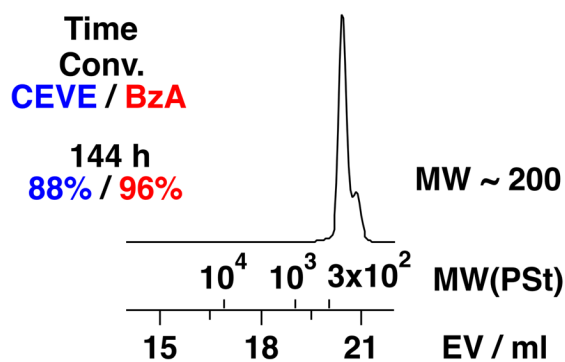
## Experimental Section

### Materials

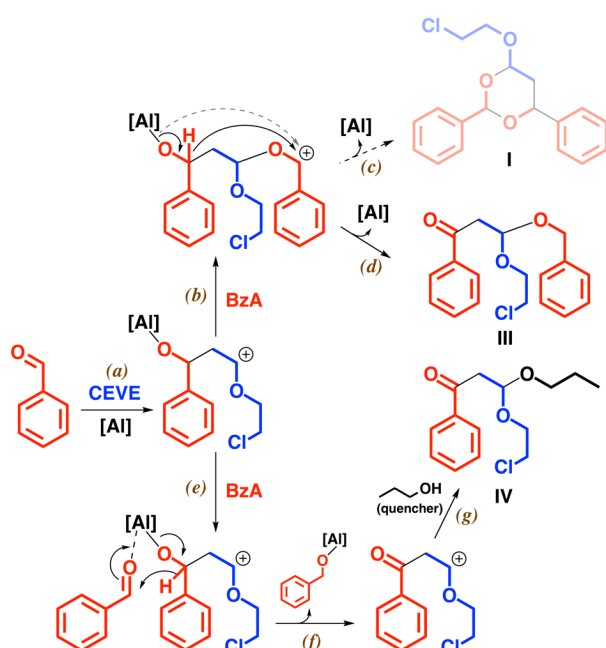
CEVE (TCI, >97.0%) was washed with a 10% aqueous sodium hydroxide solution and then water and was distilled twice over calcium hydride under reduced pressure. IBVE (TCI, >99.0%) was washed with a 10% aqueous sodium hydroxide solution and then water and was distilled twice over calcium hydride. BzA (Wako, >98.0%), DEF (TCI, >98.0%), and DiPF (TCI, >98.0%) were distilled twice over calcium hydride under reduced pressure. IPA (TCI, >98.0%) and TPA (Nacalai Tesque, >98.0%) were recrystallized from *n*-hexane and toluene, vacuum dried for more than 3 h, and then dried by azeotropy with toluene. Commercially available EtAlCl<sub>2</sub> (Wako, 1.0 M solution in hexane), Al(O*i*Pr)<sub>3</sub> (Nacalai Tesque, >98.0%), Al(OPh)<sub>3</sub> (Sigma–Aldrich, >99.9%), and Al(O*t*Bu)<sub>3</sub> (TCI, >98.0%) were used as received. Dichloromethane (Wako, 99.0%) was dried by passing it through solvent purification columns (Glass Contour). Hydrochloric acid (Nacalai Tesque), sodium hydroxide (Nacalai Tesque), and 1,2-dimethoxyethane (Nacalai Tesque) for acid and alkali hydrolysis were used as received. CEVE, IBVE, BzA, DEF, DiPF, and a solution of EtAlCl<sub>2</sub> were stored in brown ampules.

### Characterization

The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [TSKgel GMH<sub>HR</sub>-M × 2 (exclusive limit molecular weight =  $4 \times 10^6$ ; bead size = 5 μm; column size = 7.8 mm I.D. × 300 mm); flow rate = 1.0 mL min<sup>-1</sup>] connected to a JASCO PU-4580 pump, a Tosoh CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive index detector. The weight-average molecular weight ( $M_w$ ) and the polydispersity ratio (weight-average molecular weight/number-average molecular weight [ $M_w/M_n$ ]) were calculated from the chromatograms with respect to 16 polystyrene standards (Tosoh;  $M_n = 5.0 \times 10^2$ — $1.09 \times 10^6$ ,  $M_w/M_n \leq 1.1$ ). NMR spectra were recorded using a JEOL JNM-ECA 500 (500.16 MHz for <sup>1</sup>H and 125.77 MHz for <sup>13</sup>C) spectrometer. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded using an LTQ orbitrap XL spectrometer (Thermo Scientific). DSC was conducted with a Shimadzu DSC-60 Plus differential scanning calorimeter.

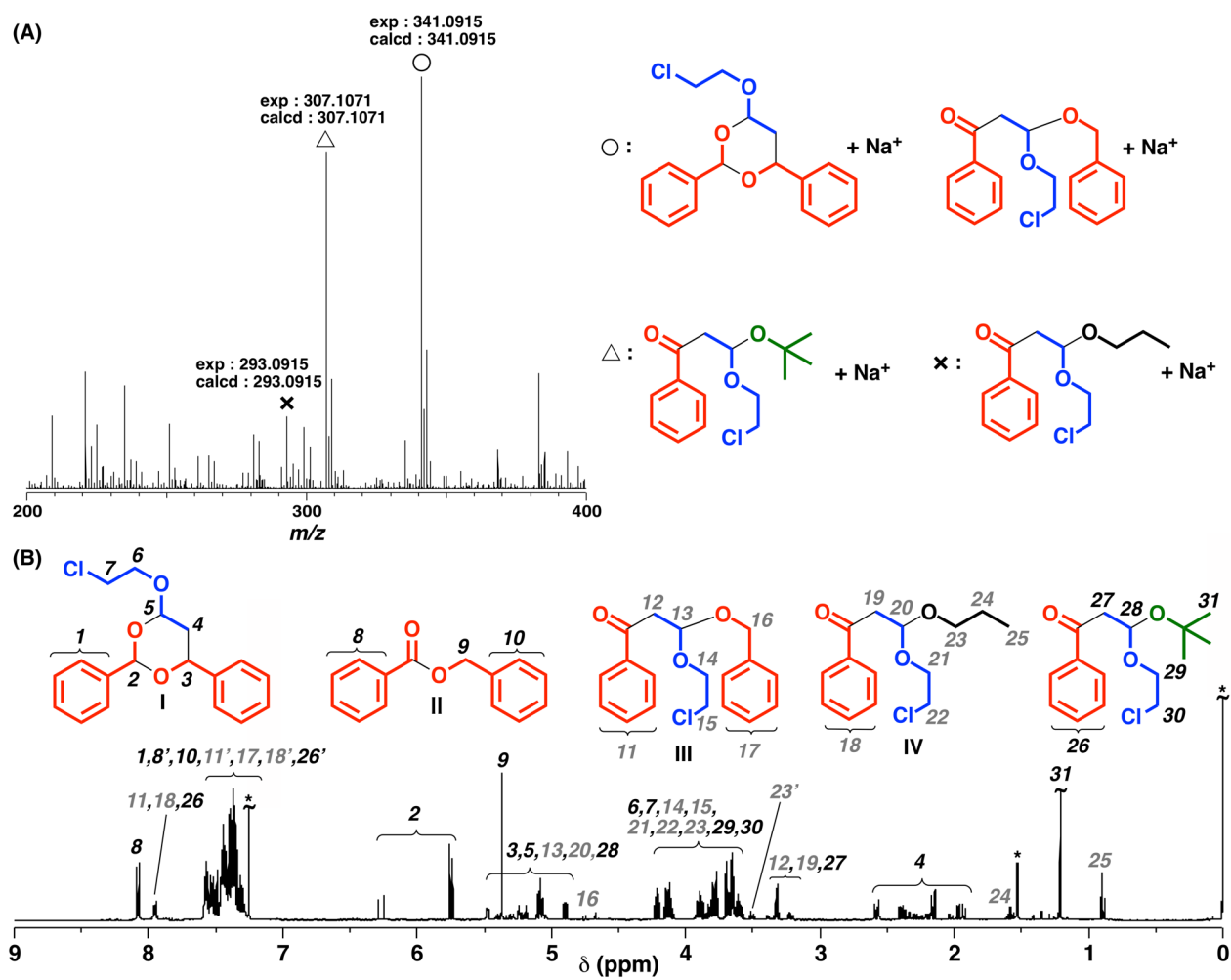


**Figure S1.** MWD curve of the product obtained in the model reaction of CEVE and BzA (entry 3 in Table 1).

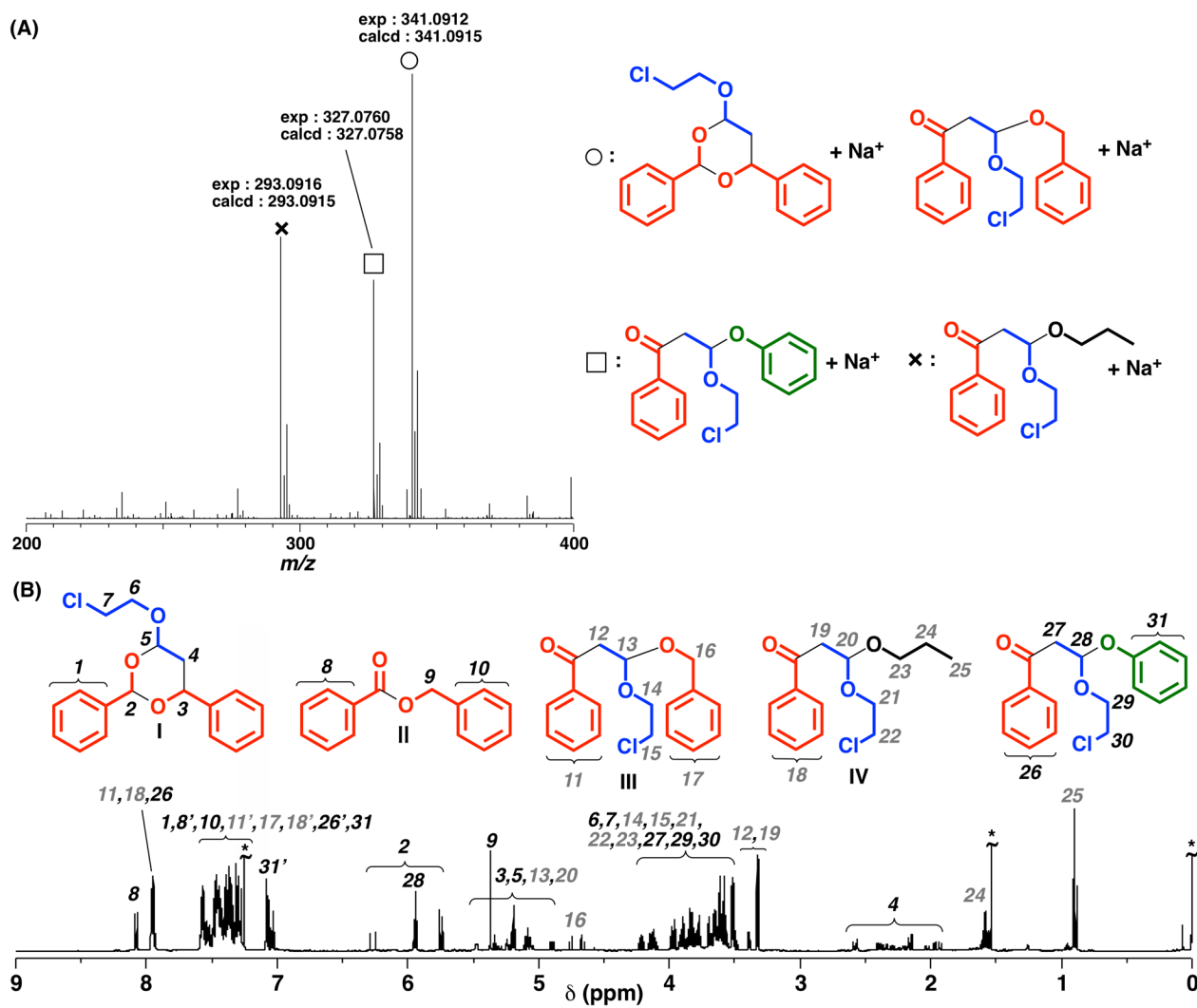


**Scheme S1.** Possible pathways of generation of two linear acetals ([Al]:  $\text{Al}(\text{OR})_n\text{Cl}_{2-n}$ ; dormant species with a covalent bond, such as a carbon–chlorine bond, generated from carbocations are ignored).

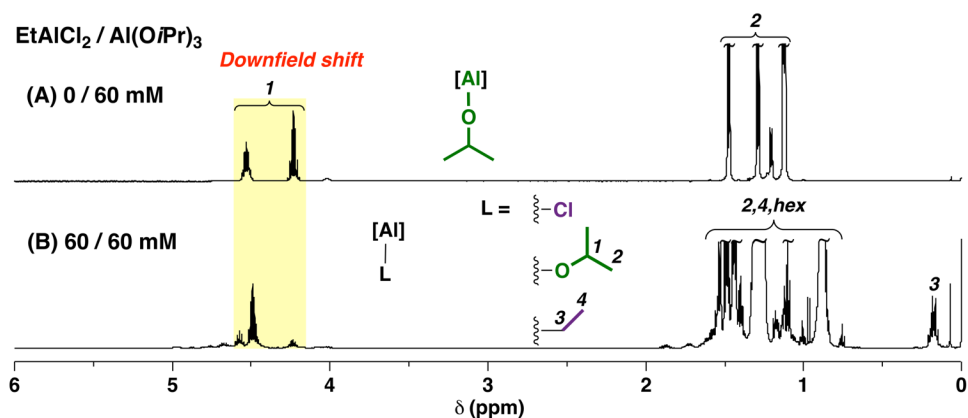
**Note for Scheme S1:** A BzA molecule activated by the Al catalyst reacts with CEVE (path (a)) and another BzA (path (b)). The subsequent reaction of the Al-coordinated oxygen atom with the carbocation results in the cyclotrimerization (path (c); compound I), whereas the intramolecular hydride transfer results in a linear acetal consisting of one CEVE and two BzAs (path (d); compound III). The other linear acetal (path (g); compound IV) is produced by the reaction of 1-propanol, which was used as a quencher, with a carbocation derived from the undesired hydride transfer after the reaction of one BzA and one CEVE (paths (e) and (f)).



**Figure S2.** (A) ESI-MS and (B)  $^1\text{H}$  NMR spectra of the product obtained in the model reaction using  $\text{EtAlCl}_2$  and  $\text{Al}(\text{O}t\text{Bu})_3$  (in  $\text{CDCl}_3$  at  $30^\circ\text{C}$ ; entry 5 in Table 1; \*  $\text{CHCl}_3$ , water, or TMS).

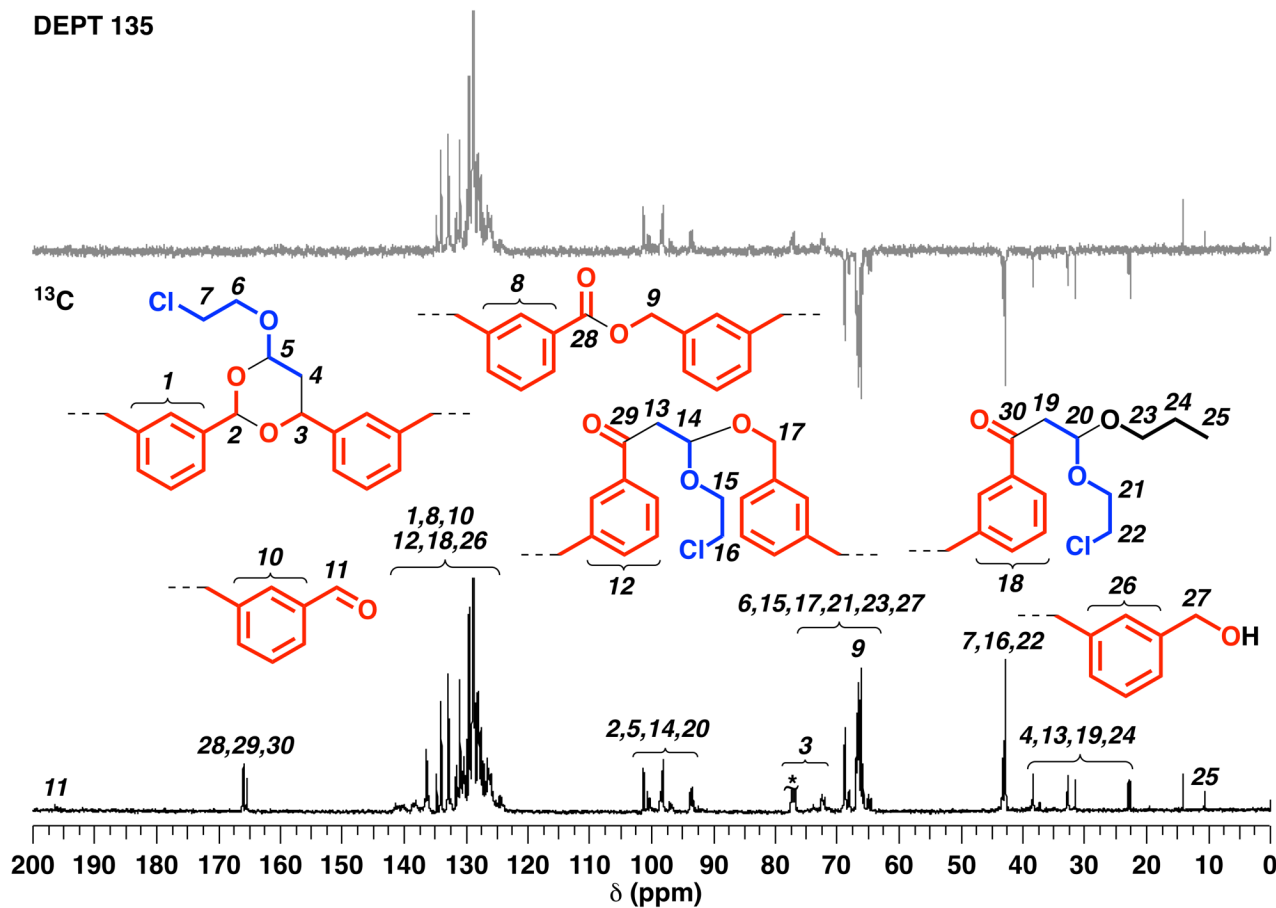


**Figure S3.** (A) ESI-MS and (B)  $^1\text{H}$  NMR spectra of the product obtained in the model reaction using  $\text{EtAlCl}_2$  and  $\text{Al}(\text{OPh})_3$  (in  $\text{CDCl}_3$  at  $30^\circ\text{C}$ ; entry 6 in Table 1; \*  $\text{CHCl}_3$ , water, or TMS).



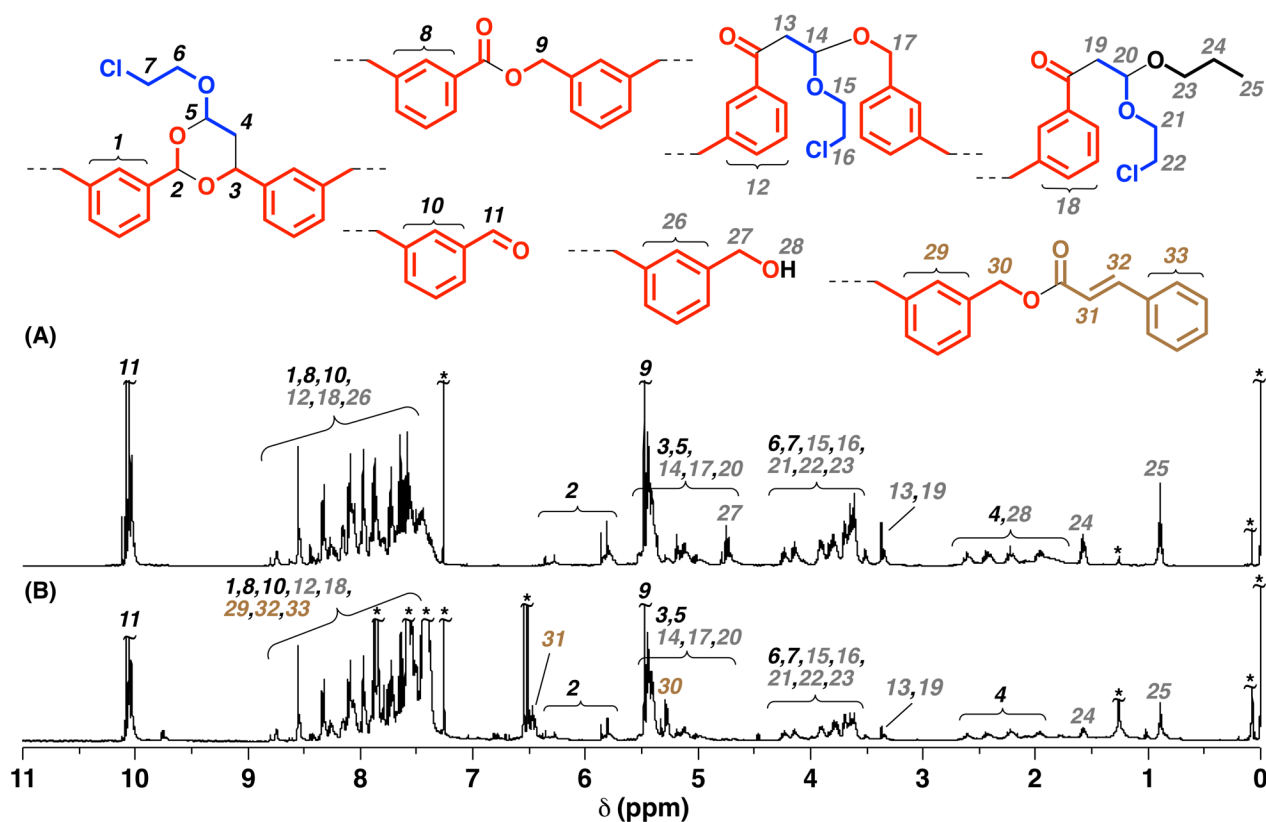
**Figure S4.**  $^1\text{H}$  NMR spectra of (A)  $\text{Al}(\text{O}i\text{Pr})_3$  and (B) the mixture of an equimolar amount of  $\text{EtAlCl}_2$  and  $\text{Al}(\text{O}i\text{Pr})_3$  (in  $\text{CDCl}_3$  at  $30\text{ }^\circ\text{C}$ ; hex: *n*-hexane).

**Note for Figure S4.** Aluminum alkoxides exist as various aggregation forms. The  $^1\text{H}$  NMR spectrum (Figure S4A) indicated that commercially available  $\text{Al}(\text{O}i\text{Pr})_3$  likely aggregated into a tetramer, which is supported by the study on ring-opening polymerization of  $\epsilon\text{-CL}$  using different aggregated forms of  $\text{Al}(\text{O}i\text{Pr})_3$  (reference: A. Duda and S. Penczek, *Macromol. Rapid Commun.*, 1995, **16**, 67–76).

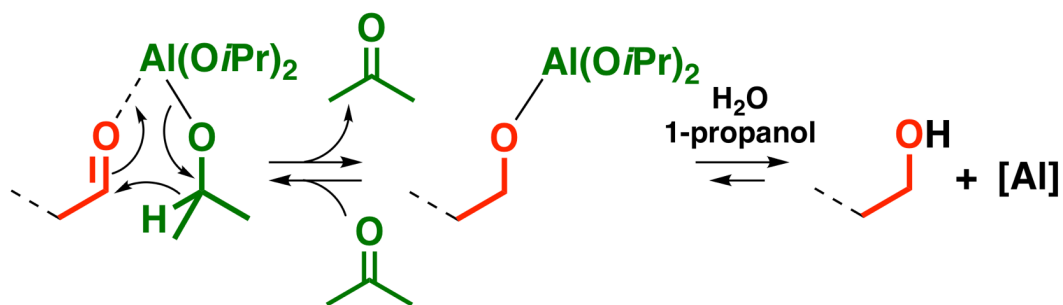


**Figure S5.** <sup>13</sup>C and DEPT 135 NMR spectra of the product obtained by the tandem polymerization of CEVE and IPA (in CDCl<sub>3</sub> at 30 °C; entry 3 in Table 2; after purification by reprecipitation in *n*-hexane; \* CDCl<sub>3</sub>).

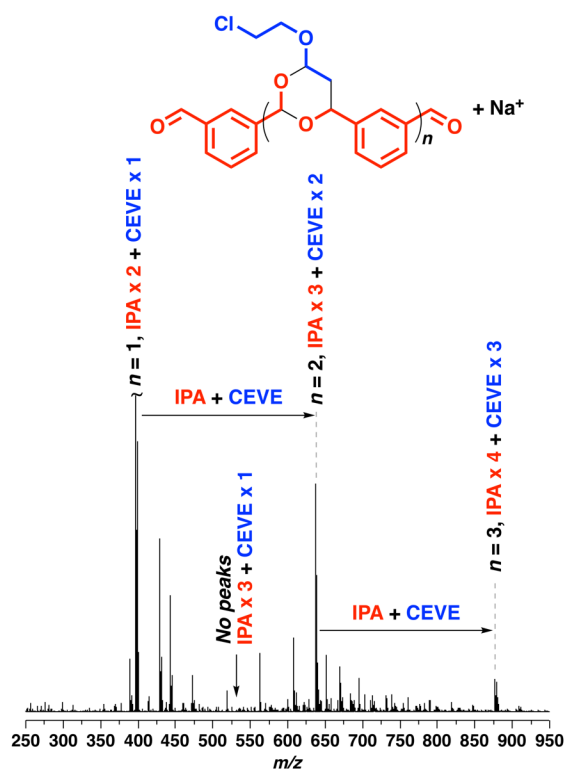




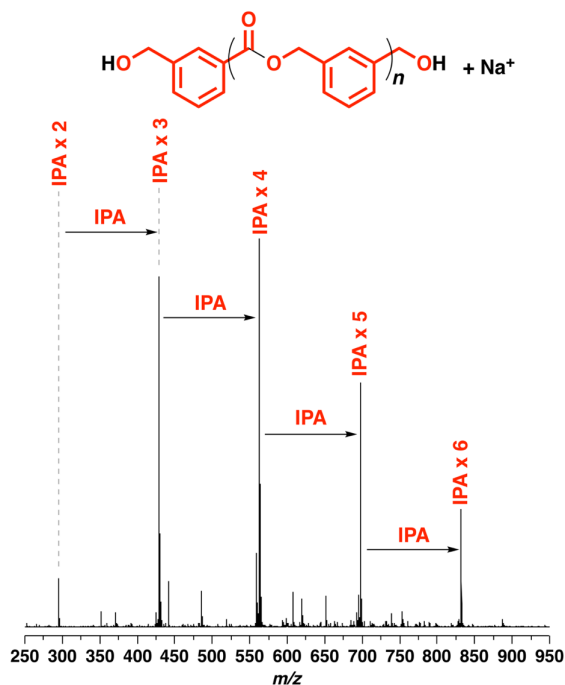
**Figure S6.**  $^1\text{H}$  NMR spectra of (A) the oligomer obtained by the tandem polymerization of CEVE and IPA ( $[\text{CEVE}]_0 = 0.50 \text{ M}$ ,  $[\text{IPA}]_0 = 0.70 \text{ M}$ ,  $[\text{EtAlCl}_2]_0 = 30 \text{ mM}$ ,  $[\text{Al}(\text{O}i\text{Pr})_3]_0 = 10 \text{ mM}$ , in dichloromethane at  $0^\circ\text{C}$  for 4 h) and (B) the product obtained by acetylation of this oligomer: polymer (3 mg), cinnamoyl chloride (6 mg), 4-dimethylaminopyridine (1 mg), and anhydrous pyridine (3  $\mu\text{L}$ ) were dissolved in dichloromethane (5.0 mL) (in  $\text{CDCl}_3$  at  $30^\circ\text{C}$ ; \* cinnamic acid,  $\text{CHCl}_3$ , water, grease, or TMS).



**Scheme S2.** A postulated mechanism of the transformation of a formyl group into a hydroxy group after termination reaction (the MPV reduction).

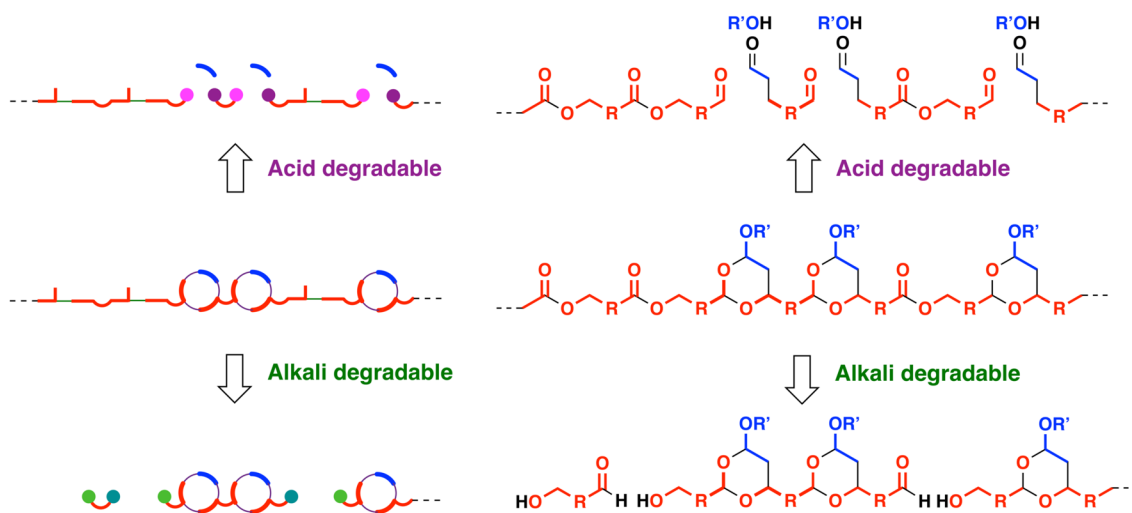


**Figure S7.** ESI-MS spectrum of the product obtained by the cyclotrimerization of CEVE and IPA ( $[\text{CEVE}]_0 = 0.50 \text{ M}$ ,  $[\text{IPA}]_0 = 0.50 \text{ M}$ ,  $[\text{EtAlCl}_2]_0 = 50 \text{ mM}$ ,  $[\text{THF}] = 1.0 \text{ M}$ , in dichloromethane at  $0 \text{ }^\circ\text{C}$ ).

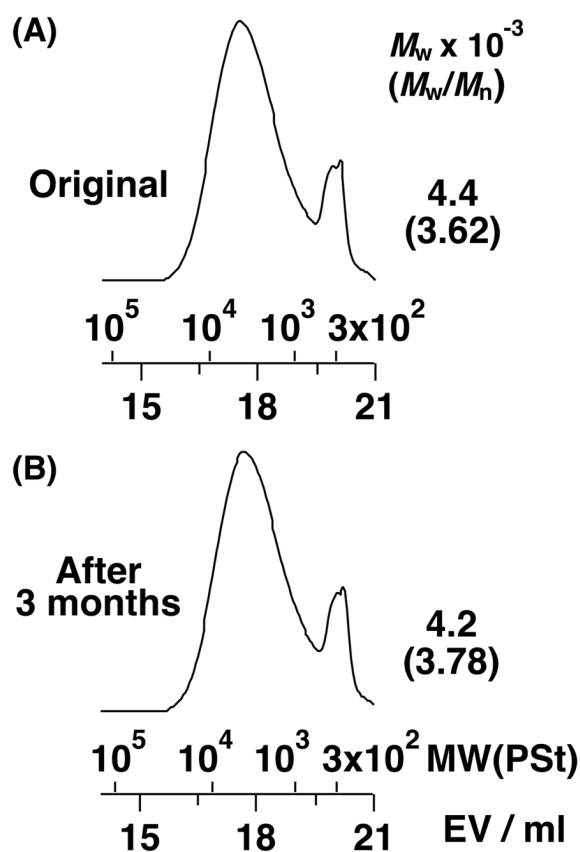


**Figure S8.** ESI-MS spectrum of the product obtained in the Tishchenko reaction of IPA ( $[\text{IPA}]_0 = 0.50 \text{ M}$ ,  $[\text{Al}(\text{O}i\text{Pr})_3]_0 = 100 \text{ mM}$  in dichloromethane at  $0 \text{ }^\circ\text{C}$ ).

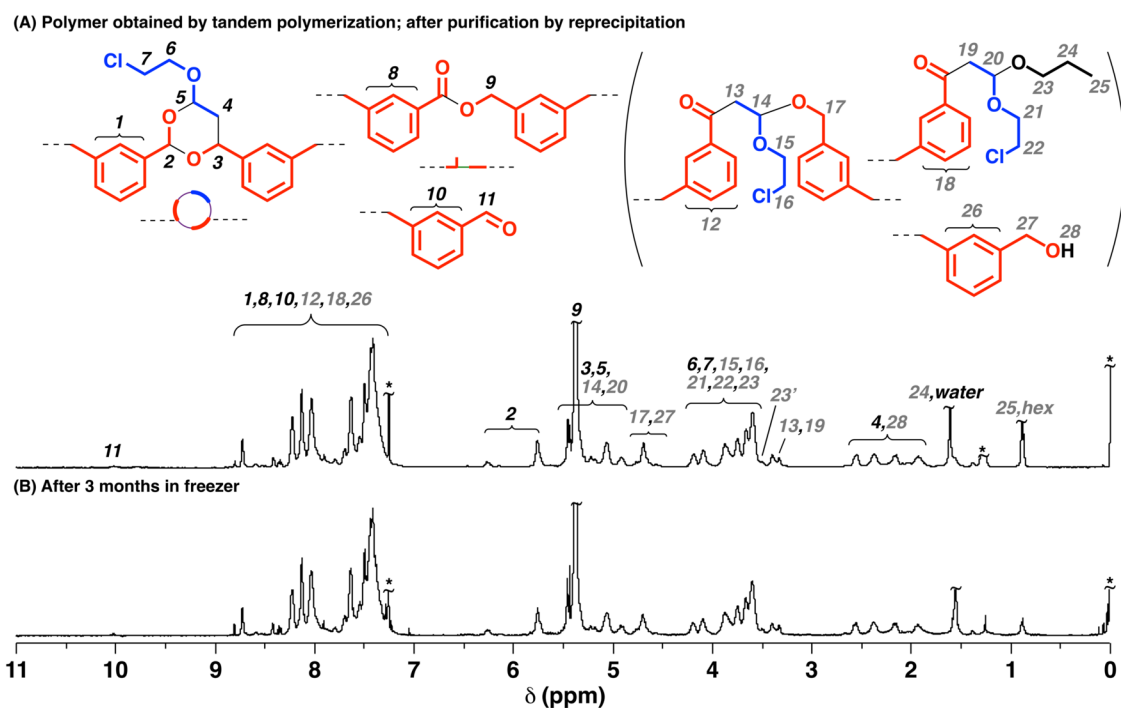
**Note for Figure S8.** The aldehyde moieties at polymer chain ends were most likely converted into the alcohol moieties via the MPV reduction after termination reaction.



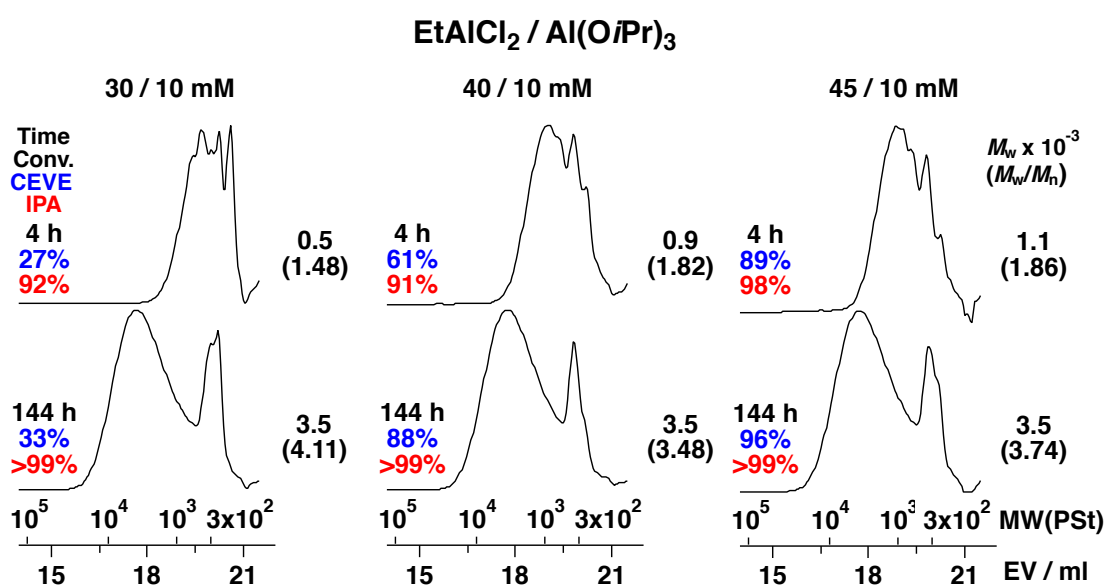
**Scheme S3.** Schematic illustration of acid and alkali hydrolysis of the obtained polymer.



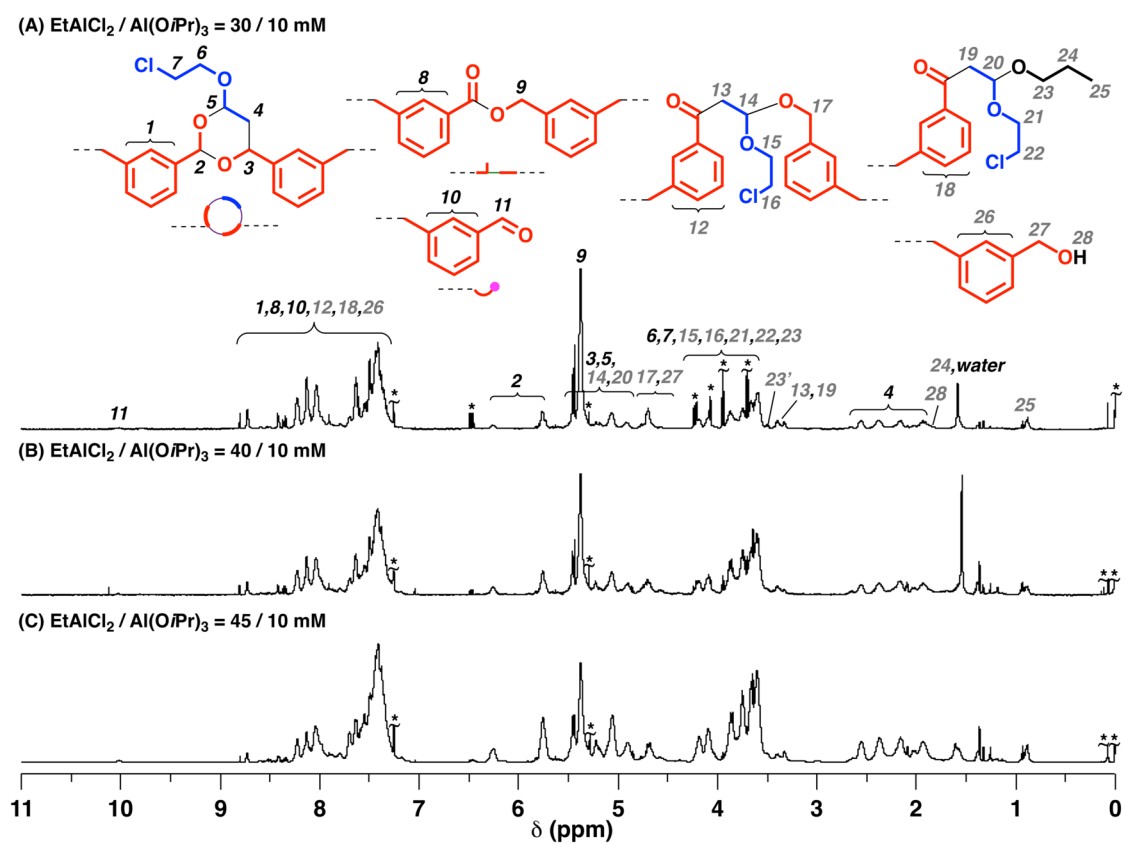
**Figure S9.** MWD curves of the polymer obtained by the tandem polymerization of CEVE and IPA (entry 3 in Table 2); after (A) purification by reprecipitation in *n*-hexane and (B) storage for 3 months in a freezer (approximately at  $-18$  °C).



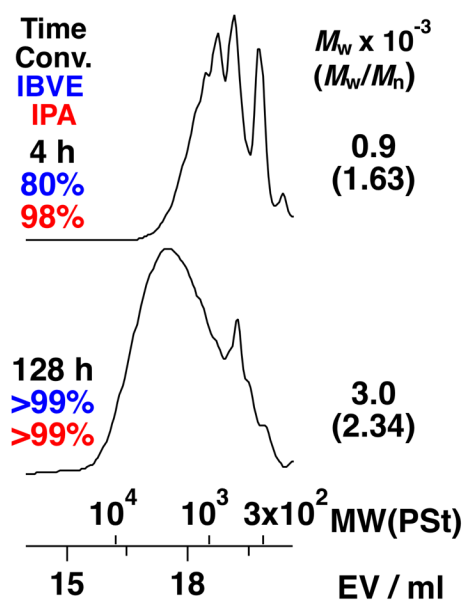
**Figure S10.**  $^1\text{H}$  NMR spectra of the obtained polymer by the tandem polymerization of CEVE and IPA (entry 3 in Table 2); after (A) purification by reprecipitation in *n*-hexane and (B) storage for 3 months in a freezer (approximately at  $-18^\circ\text{C}$ ) (in  $\text{CDCl}_3$  at  $30^\circ\text{C}$ ; \* solvents or TMS; hex: *n*-hexane).



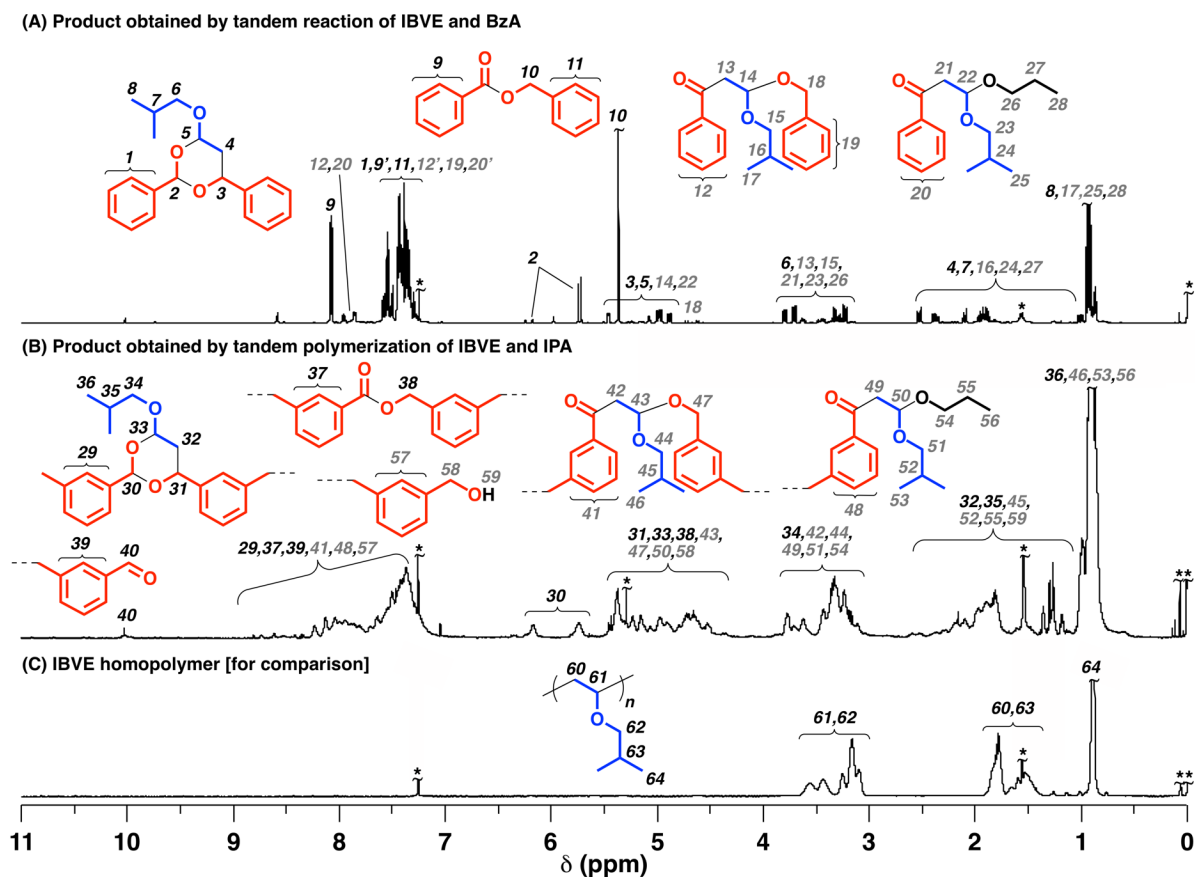
**Figure S11.** MWD curves of the polymers obtained by the tandem polymerization with different catalyst molar ratios (entries 3–5 in Table 2).



**Figure S12.** <sup>1</sup>H NMR spectra of the obtained polymers by the tandem polymerization with different catalyst molar ratios (in CDCl<sub>3</sub> at 30 °C; entries 3–5 in Table 2; \* solvents, residual monomer, grease, or TMS).



**Figure S13.** MWD curves of the products obtained by the tandem polymerization of IBVE and IPA (entry 6 in Table 2).

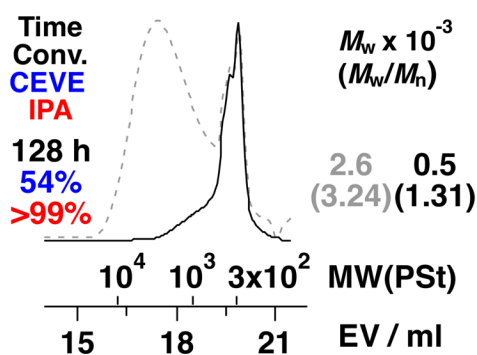


**Figure S14.**  $^1\text{H}$  NMR spectra of (A) the product obtained by the tandem reaction of IBVE and BzA, (B) the product obtained by the tandem polymerization of IBVE and IPA (entry 6 in Table 2), and (C) IBVE homopolymer (in  $\text{CDCl}_3$  at 30 °C; \* solvents, water, grease, or TMS).

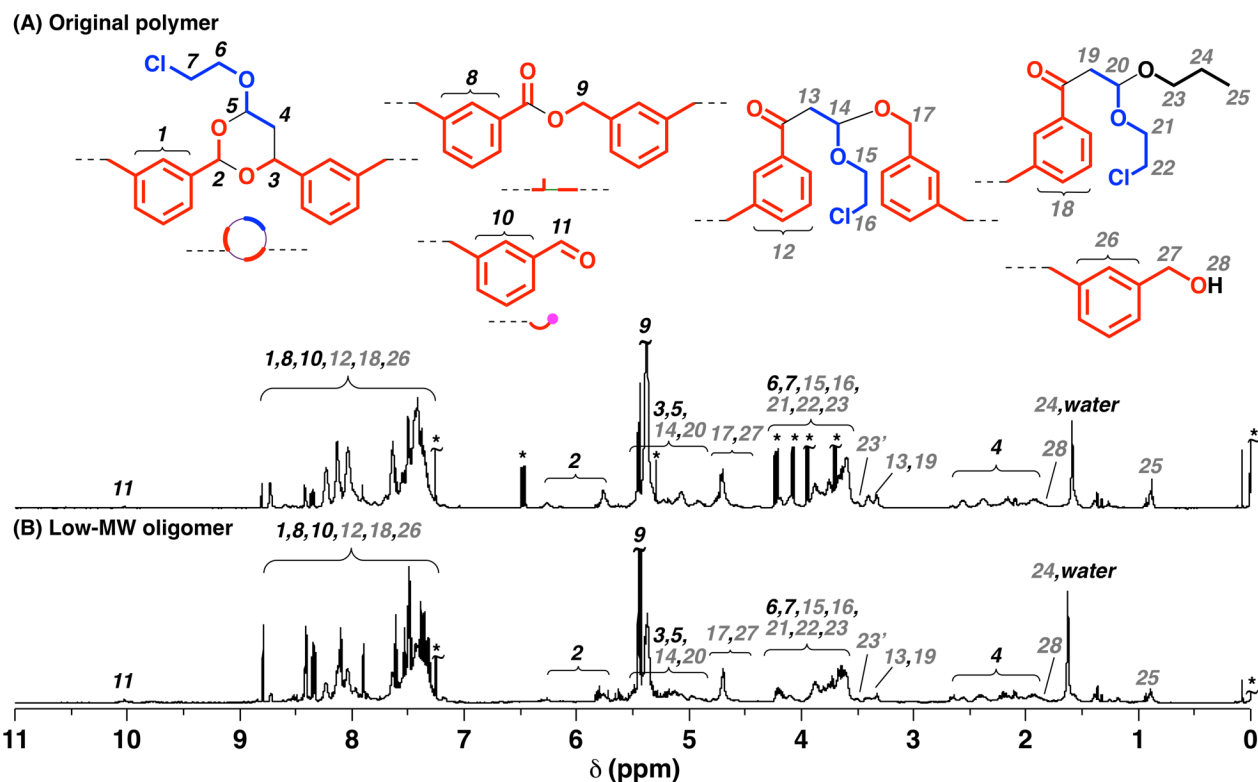
**Table S1** Tandem polymerization of CEVE and IPA at various monomer concentrations<sup>a</sup>

| Entry | CEVE<br>(M) | IPA<br>(M) | Time<br>(h) | Conv. (%) <sup>b</sup> |     |                       |             | Ratio of products <sup>d</sup> |                     |                       |                          |
|-------|-------------|------------|-------------|------------------------|-----|-----------------------|-------------|--------------------------------|---------------------|-----------------------|--------------------------|
|       |             |            |             | CEVE                   | IPA | $M_w \times 10^{-3c}$ | $M_w/M_n^c$ | Cyclotrimerization             | Tishchenko reaction | VE homopolymerization | Linear acetal generation |
| 1     | 0.50        | 0.50       | 168         | 47                     | >99 | 3.8                   | 4.43        | 17                             | 67                  | 9                     | 7                        |
| 2     | 0.50        | 0.60       | 168         | 31                     | >99 | 3.7                   | 5.17        | 13                             | 76                  | 6                     | 5                        |
| 3     | 0.50        | 0.70       | 144         | 33                     | >99 | 3.5                   | 4.11        | 21                             | 68                  | 5                     | 6                        |

<sup>a</sup> [EtAlCl<sub>2</sub>]<sub>0</sub> = 30 mM, [Al(OiPr)<sub>3</sub>]<sub>0</sub> = 10 mM, in dichloromethane at 0 °C. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of quenched reaction mixtures. <sup>c</sup> Determined by GPC (polystyrene standards). <sup>d</sup> Estimated by <sup>1</sup>H NMR analysis of the obtained polymers.



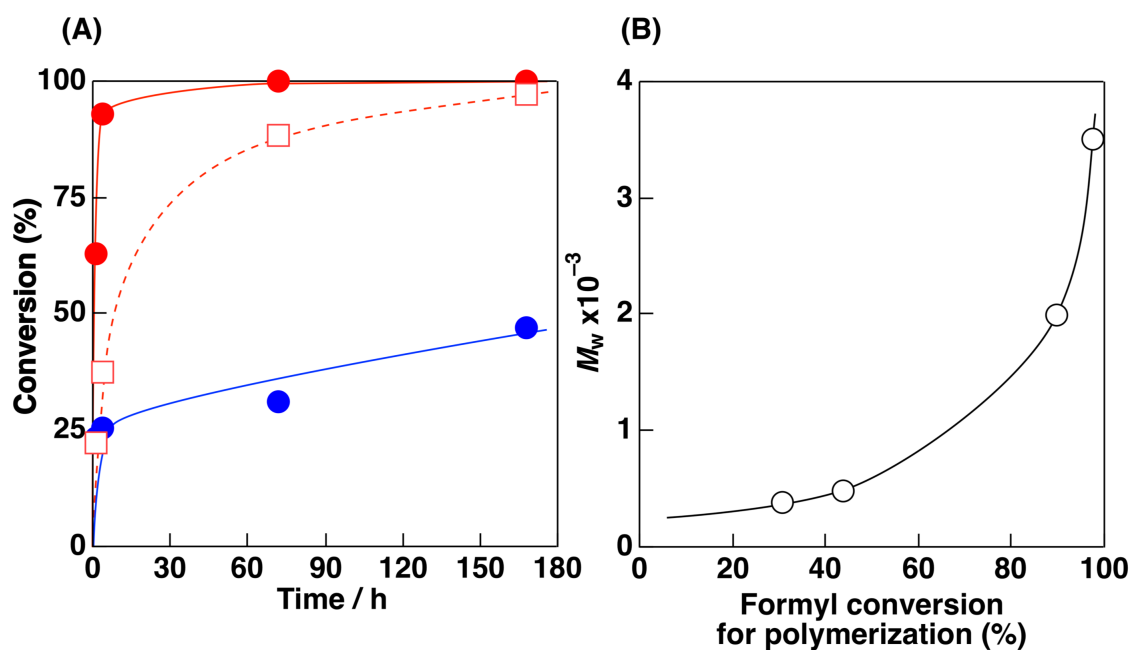
**Figure S15.** MWD curves of the obtained polymer (dashed line) by the tandem polymerization of CEVE and IPA and the low-MW fraction separated by preparative GPC (solid line) ([CEVE]<sub>0</sub> = 0.50 M, [IPA]<sub>0</sub> = 0.70 M, [EtAlCl<sub>2</sub>]<sub>0</sub> = 30 mM, [Al(OiPr)<sub>3</sub>]<sub>0</sub> = 10 mM, in dichloromethane at 0 °C; a different sample from that shown in entry 3 in Table 2).



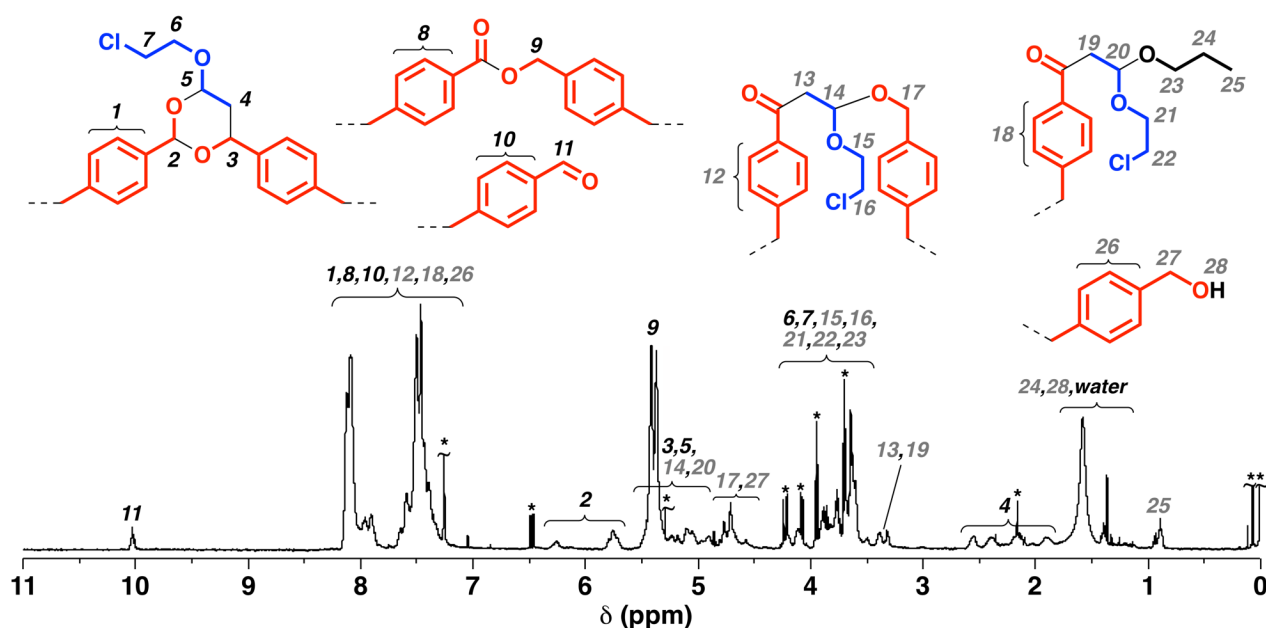
**Figure S16.**  $^1\text{H}$  NMR spectra of (A) the obtained polymer and (B) the low-MW fraction separated by preparative GPC (in  $\text{CDCl}_3$  at  $30\text{ }^\circ\text{C}$ ;  $[\text{CEVE}]_0 = 0.50\text{ M}$ ,  $[\text{IPA}]_0 = 0.70\text{ M}$ ,  $[\text{EtAlCl}_2]_0 = 30\text{ mM}$ ,  $[\text{Al}(\text{O}i\text{Pr})_3]_0 = 10\text{ mM}$ , in dichloromethane at  $0\text{ }^\circ\text{C}$ ; a different sample from those shown in entry 3 in Table 2; \* solvents, residual monomer, water, grease, or TMS).

**Note for Figure S16.** In Figure S16B, the peaks of the remaining aldehyde and hydroxy moieties at polymer chain ends (peaks 11 and 27) are very small considering the MW determined by GPC. This result indicates that low-MW oligomers most likely had cyclic structures.

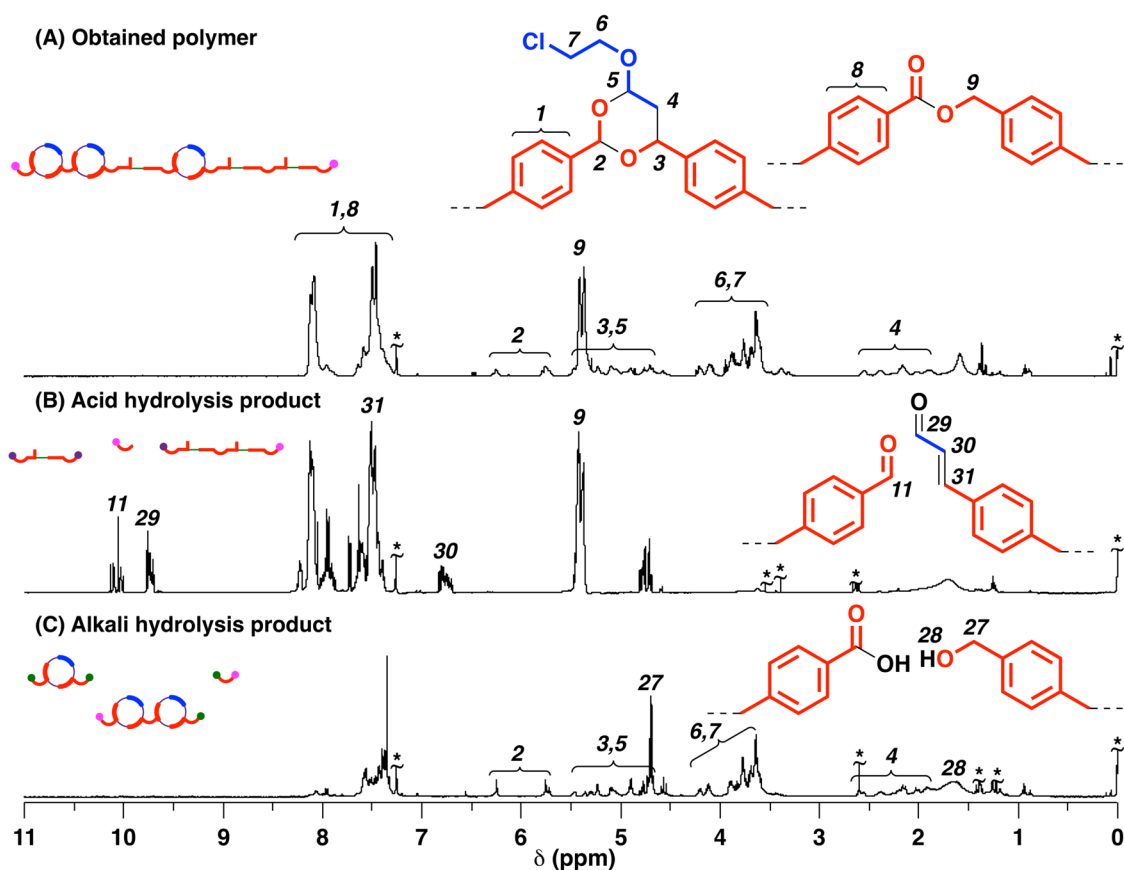




**Figure S17.** (A) Time–conversion curves of the tandem polymerization of CEVE and TPA and (B) the  $M_w$  values of the product polymers (entry 3 in Table 3;  $[\text{CEVE}]_0 = 0.50 \text{ M}$ ,  $[\text{TPA}]_0 = 0.70 \text{ M}$ ,  $[\text{EtAlCl}_2]_0 = 30 \text{ mM}$ ,  $[\text{Al}(\text{OiPr})_3]_0 = 10 \text{ mM}$ , in dichloromethane at  $0^\circ \text{C}$ ).



**Figure S18.**  $^1\text{H}$  NMR spectrum of the product obtained in the tandem polymerization of CEVE and TPA (in  $\text{CDCl}_3$  at  $30^\circ \text{C}$ ; entry 3 in Table 3; \* solvents, residual monomer, grease, or TMS).

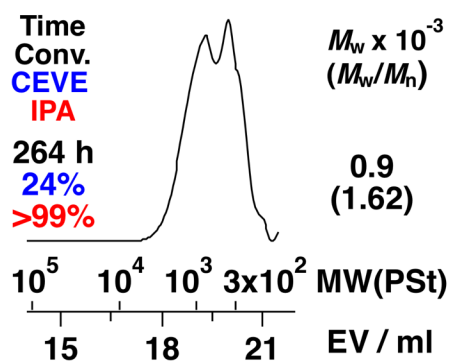


**Figure S19.** <sup>1</sup>H NMR spectra of (A) the product obtained by the tandem polymerization of CEVE and TPA and its (B) acid or (C) alkali hydrolysis product (in CDCl<sub>3</sub> at 30 °C; entry 4 in Table 3; \* solvents or TMS).

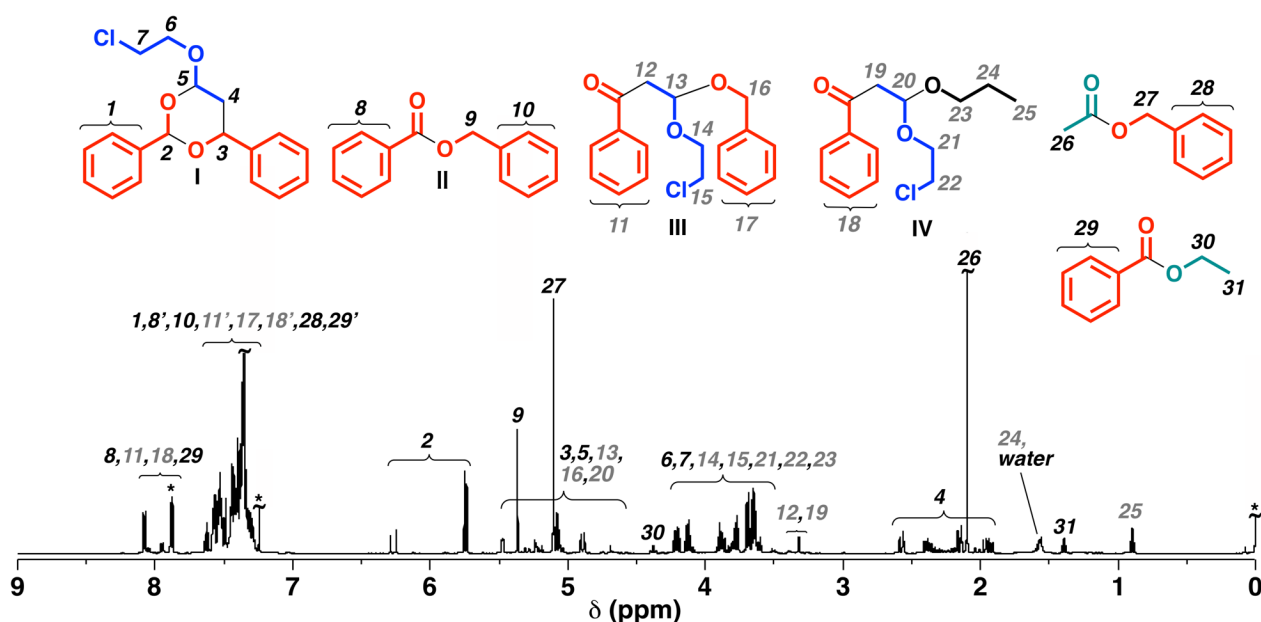
**Table S2.** Tandem polymerization of CEVE and IPA with various additives<sup>a</sup>

| Entry | Additives       | Time (h) | Conv. (%) <sup>b</sup> |     | $M_w \times 10^{-3}$ <sup>c</sup> | $M_w/M_n$ <sup>c</sup> |
|-------|-----------------|----------|------------------------|-----|-----------------------------------|------------------------|
|       |                 |          | CEVE                   | IPA |                                   |                        |
| 1     | tetrahydrofuran | 432      | 62                     | >99 | 1.0                               | 1.91                   |
| 2     | ethyl acetate   | 264      | 24                     | >99 | 0.9                               | 1.62                   |
| 3     | 1,4-dioxane     | 432      | 45                     | >99 | 1.6                               | 2.69                   |

<sup>a</sup> [CEVE]<sub>0</sub> = 0.50 M, [IPA]<sub>0</sub> = 0.70 M, [EtAlCl<sub>2</sub>]<sub>0</sub> = 30 mM, [Al(OiPr)<sub>3</sub>]<sub>0</sub> = 10 mM, [additive]<sub>0</sub> = 1.0 M, in dichloromethane at 0 °C. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of quenched reaction mixtures. <sup>c</sup> Determined by GPC (polystyrene standards).



**Figure S20.** MWD curve of the product obtained by the tandem polymerization of CEVE and IPA in the presence of ethyl acetate (entry 2 in Table S2;  $[CEVE]_0 = 0.50$  M,  $[IPA]_0 = 0.70$  M,  $[ethyl\ acetate]_0 = 1.0$  M,  $[EtAlCl_2]_0 = 30$  mM,  $[Al(OiPr)_3]_0 = 10$  mM, in dichloromethane at 0 °C).

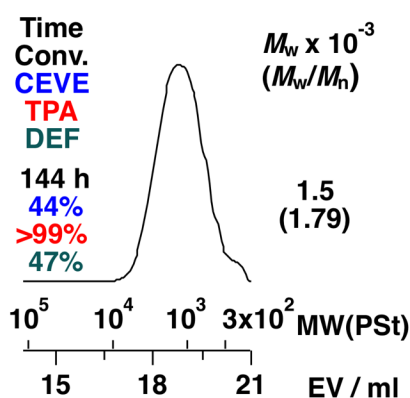


**Figure S21.**  $^1H$  NMR spectrum of the product obtained by the tandem reaction of CEVE and BzA in the presence of ethyl acetate (in  $CDCl_3$  at 30 °C;  $[CEVE]_0 = 0.50$  M,  $[BzA]_0 = 1.0$  M,  $[ethyl\ acetate]_0 = 1.0$  M,  $[EtAlCl_2]_0 = 30$  mM,  $[Al(OiPr)_3]_0 = 10$  mM, in dichloromethane at 0 °C; \* residual monomer,  $CHCl_3$ , or TMS).

**Table S3.** Three-component tandem polymerization with different catalyst molar ratios<sup>a</sup>

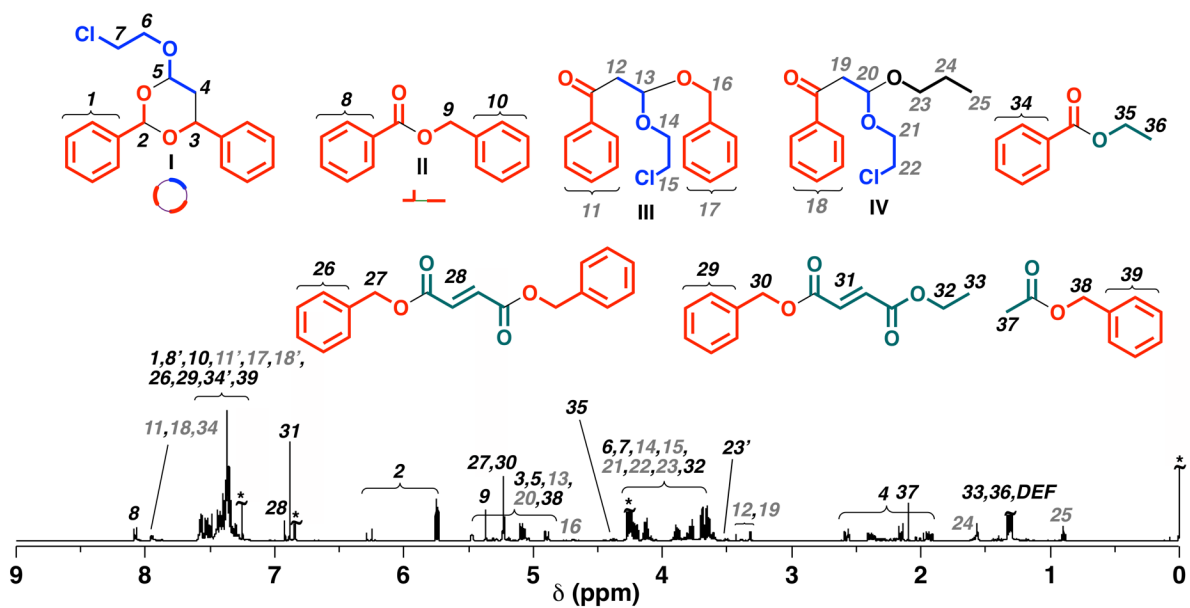
| Entry | IPA<br>(M) | DEF<br>(M) | EtAlCl <sub>2</sub><br>(mM) | Al(OiPr) <sub>3</sub><br>(mM) | Time<br>(h) | Conv. (%) <sup>b</sup> |     |     | Ratio of products <sup>d</sup> |           |                    |                     |                     |        |
|-------|------------|------------|-----------------------------|-------------------------------|-------------|------------------------|-----|-----|--------------------------------|-----------|--------------------|---------------------|---------------------|--------|
|       |            |            |                             |                               |             | CEVE                   | IPA | DEF | $M_w \times 10^{-3}$           | $M_w/M_n$ | Cyclotrimerization | Tishchenko reaction | Transesterification | Others |
| 1     | 0.70       | 0.40       | 40                          | 10                            | 168         | 31                     | 97  | 8   | 0.6                            | 1.67      | 5                  | 70                  | 1                   | 24     |
| 2     | 0.70       | 0.40       | 45                          | 10                            | 168         | 50                     | >99 | 8   | 1.1                            | 1.96      | 5                  | 68                  | 2                   | 25     |
| 3     | 0.50       | 0.40       | 40                          | 10                            | 168         | 59                     | >99 | 35  | 1.6                            | 1.86      | 22                 | 54                  | 10                  | 14     |
| 4     | 0.50       | 0.40       | 45                          | 10                            | 168         | 74                     | >99 | 20  | 1.7                            | 2.00      | 30                 | 45                  | 7                   | 18     |

<sup>a</sup> [CEVE]<sub>0</sub> = 0.50 (entries 1 and 2) and 0.49 (entries 3 and 4) M, in dichloromethane at 0 °C. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of quenched reaction mixtures. <sup>c</sup> Determined by GPC (polystyrene standards). <sup>d</sup> Estimated by <sup>1</sup>H NMR analysis of the obtained polymers.

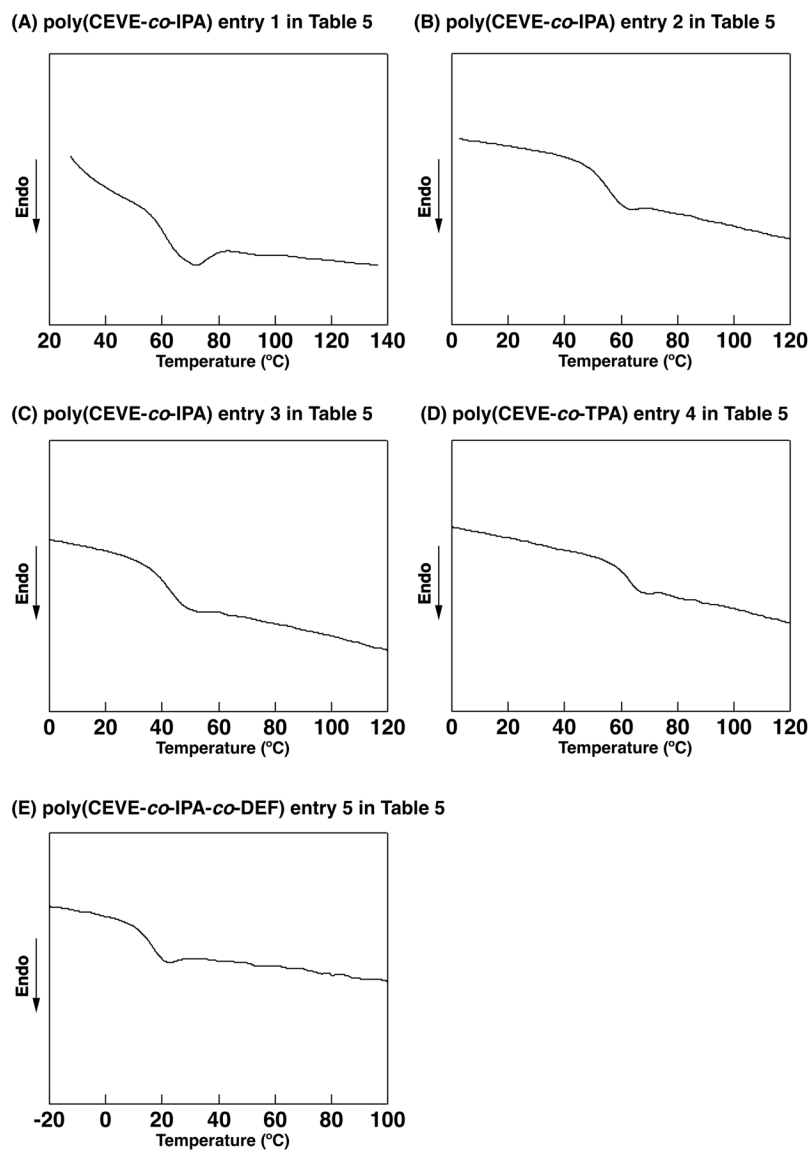
**Figure S22.** MWD curve of the obtained polymer by three-component tandem polymerization of CEVE, TPA, and DEF (entry 6 in Table 4).**Table S4.** Three component tandem reaction at various monomer concentrations<sup>a</sup>

| Entry | Dicarboxylic acid ester | (M)  | Time (h) | Conv. (%) <sup>b</sup> |     |                         | Ratio of products <sup>c</sup> |                     |                     |        |
|-------|-------------------------|------|----------|------------------------|-----|-------------------------|--------------------------------|---------------------|---------------------|--------|
|       |                         |      |          | CEVE                   | BzA | Dicarboxylic acid ester | Cyclotrimerization             | Tishchenko reaction | Transesterification | Others |
| 1     | DEF                     | 0.20 | 72       | 60                     | 81  | 41                      | 55                             | 18                  | 14                  | 13     |
| 2     | DEF                     | 0.40 | 72       | 60                     | 85  | 32                      | 55                             | 8                   | 24                  | 13     |
| 3     | DEF                     | 0.60 | 72       | 62                     | 65  | 16                      | 73                             | 5                   | 4                   | 18     |
| 4     | DiPF                    | 0.40 | 96       | 40                     | 61  | 0                       | 61                             | 28                  | 0                   | 11     |

<sup>a</sup> [CEVE]<sub>0</sub> = 0.50 M, [BzA]<sub>0</sub> = 1.0 M, [EtAlCl<sub>2</sub>]<sub>0</sub> = 30 mM, [Al(OiPr)<sub>3</sub>]<sub>0</sub> = 10 mM, in dichloromethane at 0 °C. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of quenched reaction mixtures. <sup>c</sup> Estimated by <sup>1</sup>H NMR analysis of the obtained products.



**Figure S23.**  $^1\text{H}$  NMR spectrum of the product obtained in the model reaction of CEVE, BzA, and DEF (in  $\text{CDCl}_3$  at  $30^\circ\text{C}$ ; entry 2 in Table S4; \*  $\text{CHCl}_3$ , residual monomer, or TMS).



**Figure S24.** DSC thermograms (the 2nd heating scan; heating rate: 10 °C/min) of the polymers listed in Table 5.