Electronic Supplementary Information for

Ryouichi Okabayashi, Yoshihiro Ohta, and Tsutomu Yokozawa*

*To whom correspondence should be addressed. E-mail: T.Y. (yokozt01@kanagawa-u.ac.jp)

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1. Materials

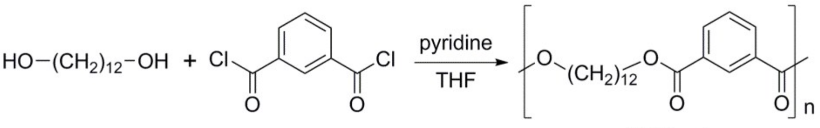
All starting materials were purchased from commercial suppliers (TCI, Aldrich, Wako and Kanto). Isophthaloyl dichloride was refluxed with thionyl chloride followed by distillation under reduced pressure, and stored in a flask under argon. 1,12-dodecanediol, synthesized cyclic polyester (**CPEs-1**) and ExR **1** were dried in vacuo over P_2O_5 overnight immediately before use. Other starting materials were used without further purification. Commercially available dehydrated tetrahydrofuran (THF, stabilizer-free; Kanto) and dehydrated diglyme (Aldrich) were used as dry solvents.

2. General

^{1}H and ^{13}C NMR spectra were obtained on JEOL ECA-500 and ECA-600 spectrometers. The internal standard for ^{1}H NMR spectra in $CDCl_3$ was tetramethylsilane (0.00 ppm), and the internal standard for ^{13}C NMR spectra in $CDCl_3$ was the midpoint of $CDCl_3$ (77.0 ppm). IR spectra were recorded on a JASCO FT/IR-410. The M_n and M_w/M_n values of polymers were measured on a Shodex GPC-101 gel permeation chromatography unit (eluent, THF 1.00 mL/min; calibration, polystyrene standards; column temperature, 40 ^{o}C) with two Shodex KF-804L columns and Shodex UV-41 and RI-71S detectors. Purification of polyester after the transesterification was conducted with a JAI LC-908 preparative HPLC (eluent: $CHCl_3$, flow rate: 6.0 mL/min) equipped with a JAI UV detector 310, JAI RI detector RI-5, and two TOSOH TSKgel columns (2 × G2000H_{HR}). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Shimadzu Biotech AXIMA Confidence in the reflectron mode by use of a laser (λ = 337 nm). Dithranol (1,8-dihydroxy-9[10*H*]-anthracenone) was used as the matrix for the MALDI-TOF mass measurements. All reactions described below were conducted under an inert gas atmosphere. Column chromatography was performed on silica gel (Silica gel 60, 230–400 mesh; Merck) with a specified solvent.

3. Syntheses

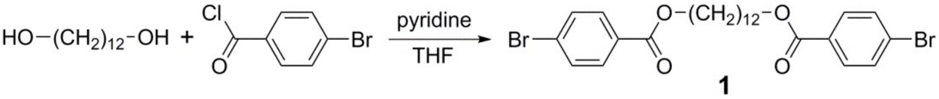
3-1. Synthesis of cyclic polyester



CPEs-1

A round-bottomed flask was flame-dried and flushed with argon. 1,12-dodecanediol (0.6070 g, 3.000 mmol) and isophthaloyl dichloride (0.6157 g, 3.033 mmol) were added to the flask and the flask was flushed with argon again. Dehydrated THF (6.0 mL) was added to the flask via a syringe, and the mixture was cooled to 0 °C. To the stirred reaction mixture, dehydrated pyridine (0.97 mL, 12 mmol) was added dropwise via a syringe at 0 °C. The reaction mixture was stirred at room temperature for 73 h, and then the reaction was quenched with 0.50 mL of dehydrated methanol. The mixture was diluted with dichloromethane (150 mL) and washed with 1 M HCl twice, saturated aqueous solution of $NaHCO_3$ once, and H_2O twice sequentially. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to afford a crude product as a white translucent elastic solid (0.9780 g, 98%). The crude product was dissolved in dichloromethane and precipitated into methanol. The precipitate was filtrated, dissolved in THF and dried in vacuo to afford **CPEs-1** as a white translucent elastic solid (0.9439 g, 95%): $M_n = 54100$, $M_w/M_n = 2.63$.

3-2. Synthesis of ExR



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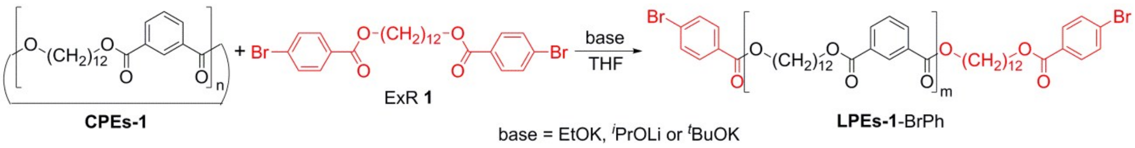
To a stirred solution of 1,12-dodecanediol (0.101 g, 0.499 mmol) and pyridine (0.095 mL, 1.2 mmol) in dehydrated THF (3.0 mL), a solution of 4-bromobenzoyl chloride (0.242 g, 1.10 mmol) in dehydrated THF (2.4 mL) was added dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 1 hour followed by room temperature for 18 hours. The mixture was filtered and concentrated under reduced pressure. The residue was diluted with dichloromethane, washed with water 4 times, dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to afford a crude product as a white solid (0.258 g, 91%). The crude product was purified by means of column chromatography (SiO_2, hexane/dichloromethane = 1/1) to afford **1** as a white solid (0.233 g, 82%): $R_f = 0.41$ (hexane/dichloromethane = 1/1); mp 64.5-64.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 4 H), 7.58 (d, *J* = 8.6 Hz, 4 H), 4.30 (t, *J* = 6.7 Hz, 4 H), 1.75 (quint, *J* = 7.1 Hz, 4 H), 1.42 (quint, *J* = 7.6 Hz, 4 H), 1.37-1.25 (m, 12 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.90, 131.63, 131.05, 129.40, 127.86, 65.38, 29.50, 29.47, 29.23, 28.64, 25.98; IR (KBr crystal) 2920, 2852, 1715, 1590, 1474, 1398, 1317, 1293, 1277, 1177, 1132, 1068, 1012, 968, 850, 755 cm^{-1}.

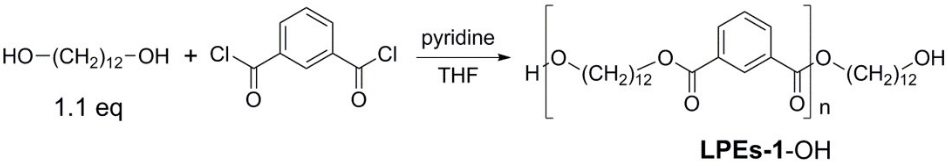
3-3. Transesterification of cyclic polyester with diester



General procedure of transesterification

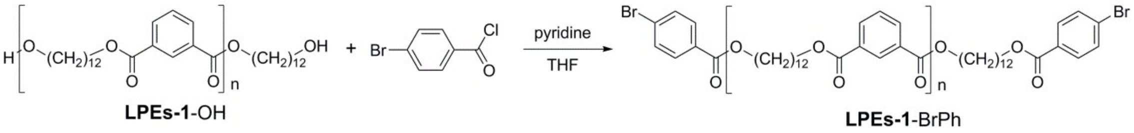
A round-bottomed flask was flame-dried and flushed with argon. **CPE-1** and **1** were placed in the flask, and the atmosphere in the flask was replaced with argon again. Dehydrated THF was added to the flask via a syringe. Another flask was flame-dried and flushed with argon. This flask was put into a glove box and potassium *tert*-butoxide was placed in it. The flask was sealed and removed from the glove box, and dehydrated THF was added to it via a syringe under a stream of nitrogen. The resulting solution of potassium *tert*-butoxide was added via a syringe to the stirred solution of **CPE-1** and **1** in the first flask, and the reaction mixture was stirred at room temperature for predetermined time. The reaction was quenched with saturated aqueous ammonium chloride, and the resulting mixture was extracted with dichloromethane. The organic solution was washed with water twice, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to afford a crude product.

3-4. Synthesis of hydroxide-terminated linear polyester



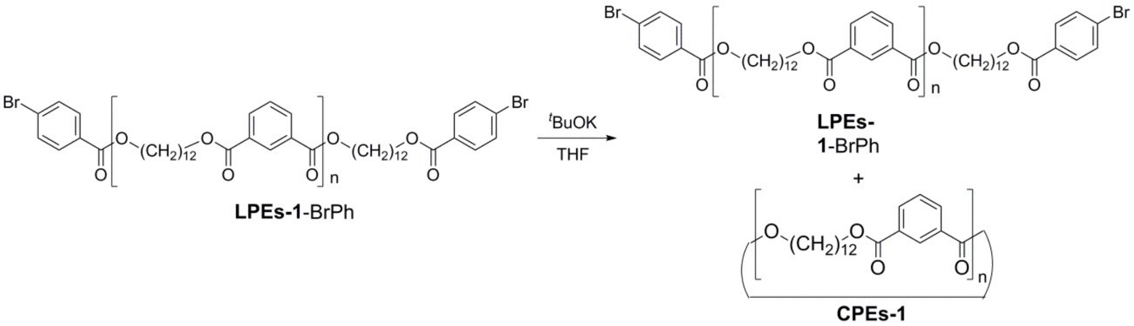
A round-bottomed flask was flame-dried and flushed with argon. 1,12-dodecanediol (0.4450 g, 2.199) and isophthaloyl dichloride (0.4064 g, 2.002 mmol) were added to the flask and the flask was flushed with argon again. Dehydrated THF (4.0 mL) was added to the flask via a syringe, and the mixture was cooled to 0 °C. To the stirred reaction mixture, dehydrated pyridine (0.650 mL, 8.04 mmol) was added dropwise via a syringe at 0 °C. The reaction mixture was stirred at room temperature for 44.5 h, and then the reaction was quenched with 0.30 mL of dehydrated methanol. The mixture was diluted with dichloromethane (100 mL) and washed with 1 M HCl twice, saturated aqueous solution of $NaHCO_3$ once, and H_2O twice sequentially. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to afford a crude product as a white soft solid (0.6929 g, 104%). The crude product was dissolved in dichloromethane and precipitated into methanol. The supernatant liquid was removed by decantation. The precipitated viscous liquid was taken up in dichloromethane and the solution was concentrated in vacuo to afford **LPEs-1**-OH as a white soft solid (0.5867 g, 88%): $M_n = 8310$, $M_w/M_n = 1.57$.

3-5. Synthesis of bromophenyl terminated linear polyester



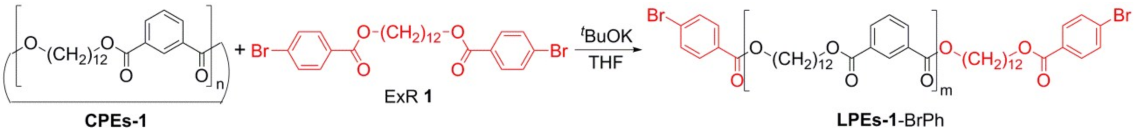
To a solution of **LPEs-1**-OH (0.149 g) and pyridine (0.0067 mL, 0.082 mmol) in dehydrated THF (0.80 mL), 4-bromobenzoyl chloride (17.3 mg, 0.0788 mmol) in dehydrated THF (0.20 mL) was added dropwise and stirred at rt for 45 h, and then the reaction was quenched with water. The mixture was diluted with methylene chloride and washed with water four times. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to afford a crude product as a pale yellow translucent sticky liquid (0.1583 g, 100%). The crude product was dissolved in dichloromethane and precipitated into methanol. The supernatant liquid was removed by decantation. The precipitated viscous liquid was taken up in dichloromethane and the solution was concentrated in vacuo. To convert remaining hydroxide end group to bromophenyl group, same work was conducted again, to afford **LPEs-1**-BrPh as a pale yellowish white soft and sticky solid (0.0983 g, 62%): $M_n = 7720$, $M_w/M_n = 1.50$.

3-6. Transesterification of linear polyester without ExR



A round-bottomed flask was flame-dried and flushed with argon. **LPEs-1**-BrPh (33.5 mg) was added to the flask and the flask was flushed with argon again. Dehydrated THF (0.40 mL) was added to the flask via a syringe. Another flask was flame-dried and flushed with argon. This flask was put into a glove box and potassium *tert*-butoxide (22.8 mg, 0.203 mmol) was placed in it. The flask was sealed and removed from the glove box, and dehydrated THF (8.00 mL) was added to it via a syringe under a stream of nitrogen. The resulting solution of potassium *tert*-butoxide (0.200 mL, ^{t}BuOK = 0.570 mg, 0.00508 mmol) was added via a syringe to the stirred solution of **LPEs-1**-BrPh in the first flask, and the reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with saturated aqueous ammonium chloride (0.5 mL), and the resulting mixture was extracted with dichloromethane twice. The organic solution was washed with water twice, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to afford a mixture of **LPEs-1**-BrPh and **CPEs-1** as a pale yellow translucent sticky liquid (32.7 mg, 98%): $M_n = 4390$, $M_w/M_n = 1.80$.

3-7. Optimized reaction condition of transesterification of cyclic polyester with diester (Table 2, entry 5)



A round-bottomed flask was flame-dried and replaced with argon. **CPEs-1** (66.2 mg, 0.199 mmol) and **1** (22.6 mg, 0.0398 mmol) were added to the flask and the flask was replaced with argon again. Another flask was flame-dried and replaced with argon. This flask was put into a glove box and potassium *tert*-butoxide (22.7 mg, 0.202 mmol) was placed in it. The flask was sealed and removed from the glove box, and dehydrated THF (4.00 mL) was added to it via a syringe under a stream of nitrogen. The resulting solution of potassium *tert*-butoxide (0.200 mL, ^{t}BuOK = 1.14 mg, 0.0101 mmol) was added via a syringe to **CPEs-1** and **1** in the first flask, and the reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with saturated aqueous ammonium chloride (0.5 mL), and the resulting mixture was extracted with dichloromethane. The organic solution was washed with water twice, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to afford a crude product as a pale yellow viscous liquid (85.7 mg, 97%): $M_n = 2730$, $M_w/M_n = 1.49$. 43.0 mg of the crude product was purified by preparative HPLC with SEC columns to remove low-molecular-weight CPEs and afford pure **LPEs-1**-BrPh as a slightly yellowish viscous liquid (27.6 mg, collection rate: 64%): $M_n = 4400$, $M_w/M_n = 1.21$.

4. Supporting figures

4-1. Synthesis of cyclic polyester

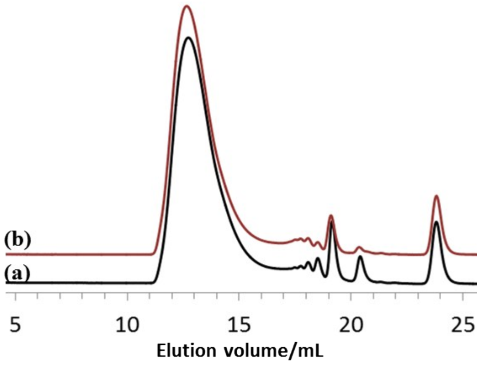


Figure S1. GPC elution curves of **CPEs-1** obtained by the polycondensation of 1.00 equiv of dodecane-1,12-diol and 1.01 equiv of isophthaloyl dichloride: (a) crude product (M_n = 45300, M_w/M_n = 2.87) and (b) after the purification (M_n = 54100, M_w/M_n = 2.63).

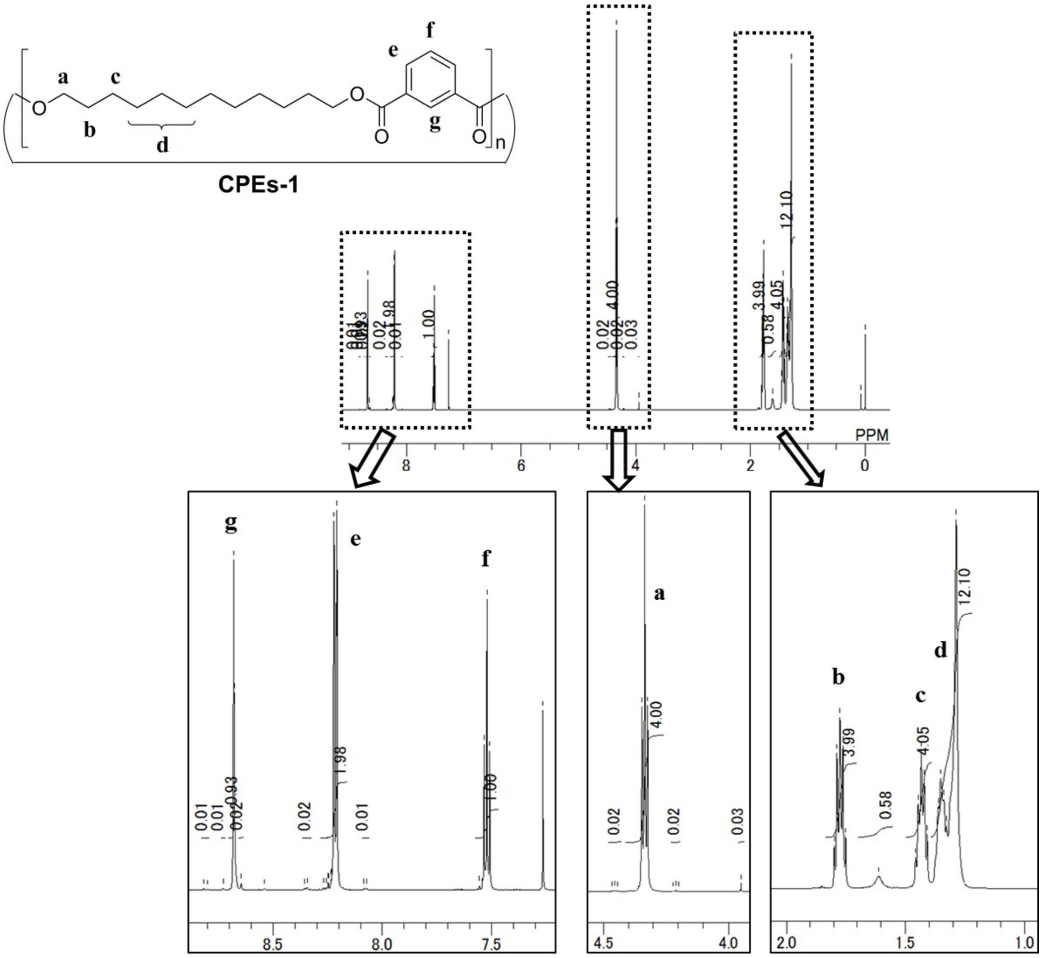


Figure S2. ^{1}H NMR spectrum of **CPEs-1** obtained by the polycondensation of 1.00 equiv of dodecane-1,12-diol and 1.01 equiv of isophthaloyl dichloride after the purification in $CDCl_3$ at 25 ^{o}C.

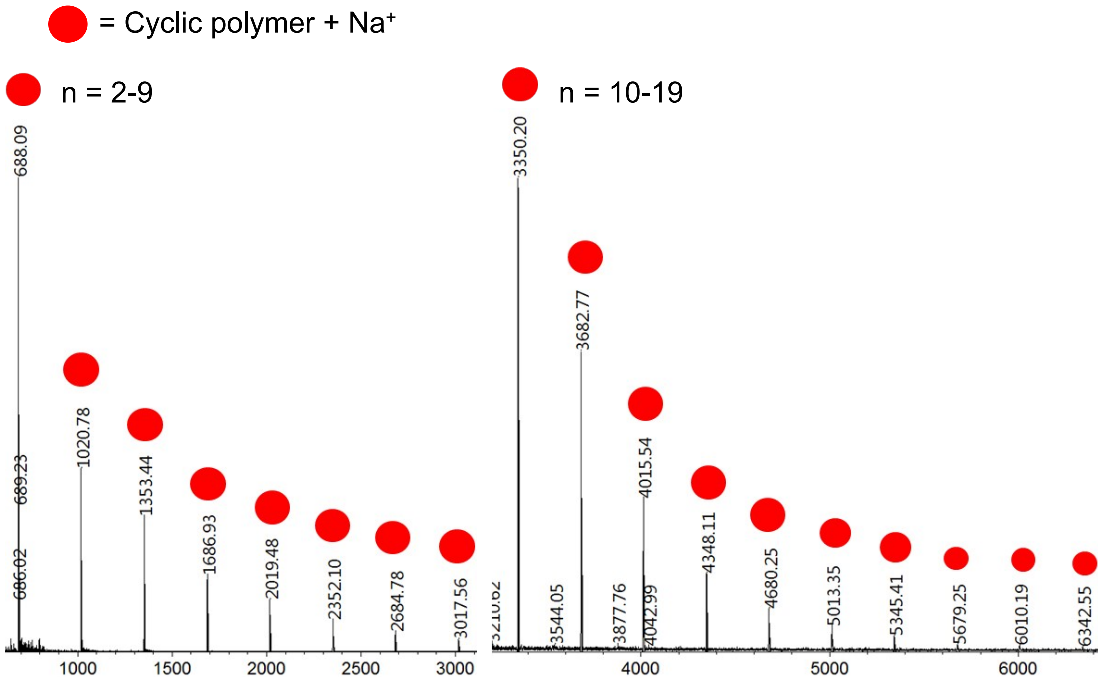
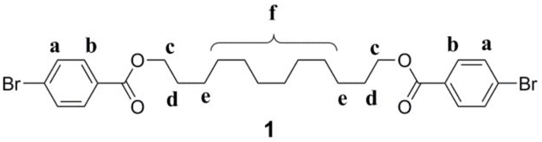


Figure S3. MALDI-TOF mass spectrum of **CPEs-1** obtained by the polycondensation of 1.00 equiv of dodecane-1,12-diol and 1.01 equiv of isophthaloyl dichloride after the purification.

4-2. Transesterification of cyclic polyester and low-molecular-weight diester

4-2-1 Synthesis of ExR



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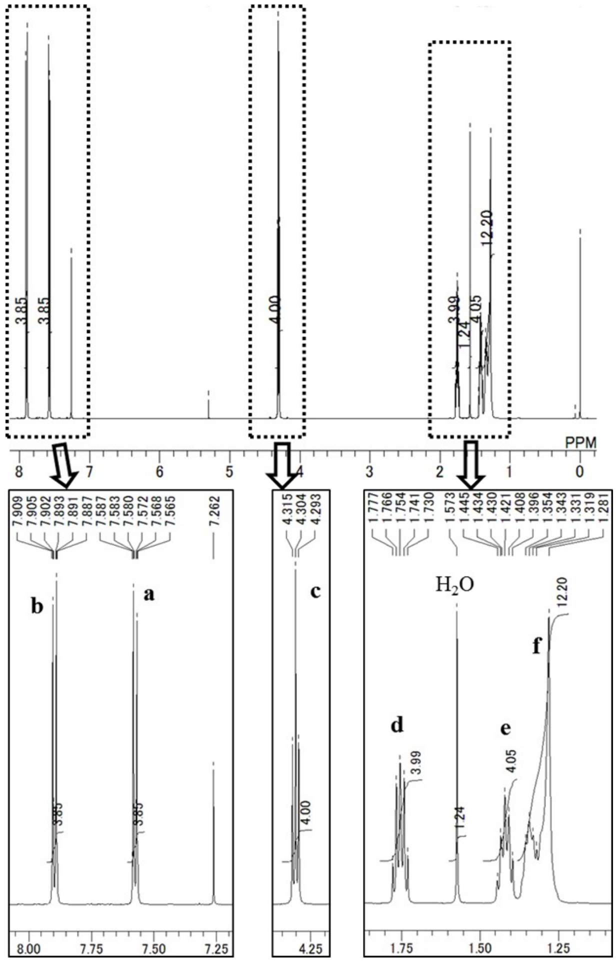

Figure S4. ^{1}H NMR spectrum of **1** in $CDCl_3$ at 25 ^{o}C.

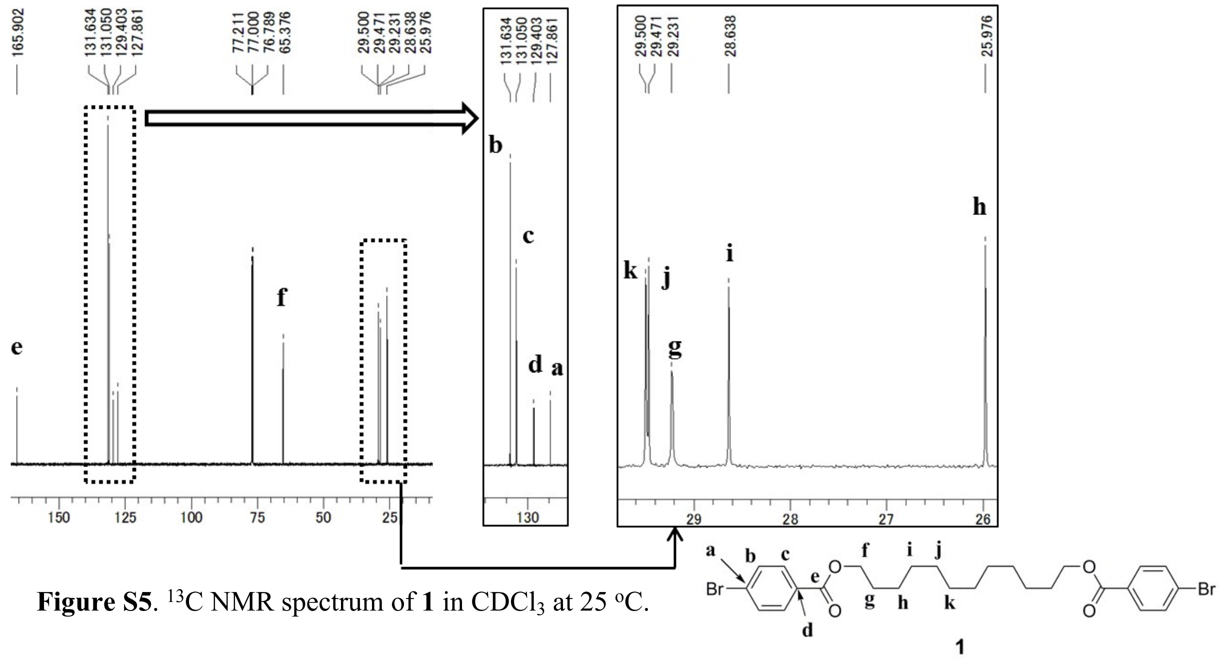

Figure S5. ^{13}C NMR spectrum of **1** in $CDCl_3$ at 25 ^{o}C.

4-2-2. Screening of catalyst

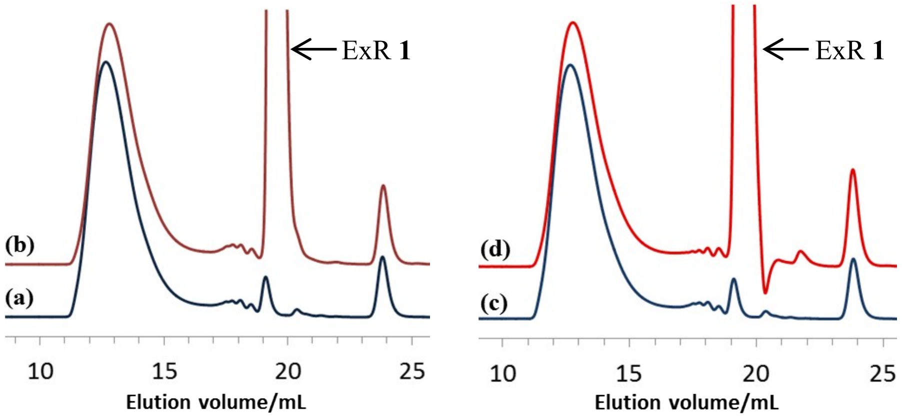

Figure S6. GPC elution curves of (a, c) **CPEs-1** (M_n = 54100, M_w/M_n = 2.63), and the product of the transesterification of **CPEs-1** and 20 mol% of **1** with (b) 1 mol% and (d) 4 mol% of EtOK (M_n = 49100, M_w/M_n = 2.53 and M_n = 51500, M_w/M_n = 2.52 respectively) (Table 1, entries 1 and 2).

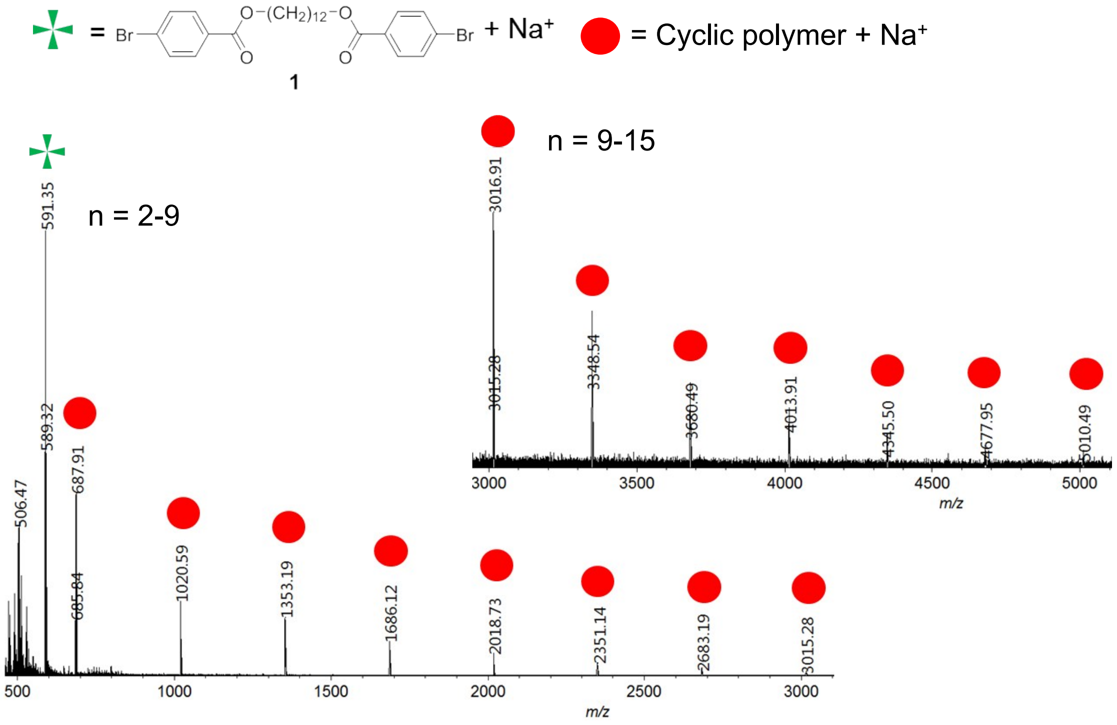

Figure S7. MALDI-TOF mass spectrum of the product of the transesterification of **CPEs-1** and 20 mol% of **1** with 1 mol% of EtOK (Table 1, entry 1).

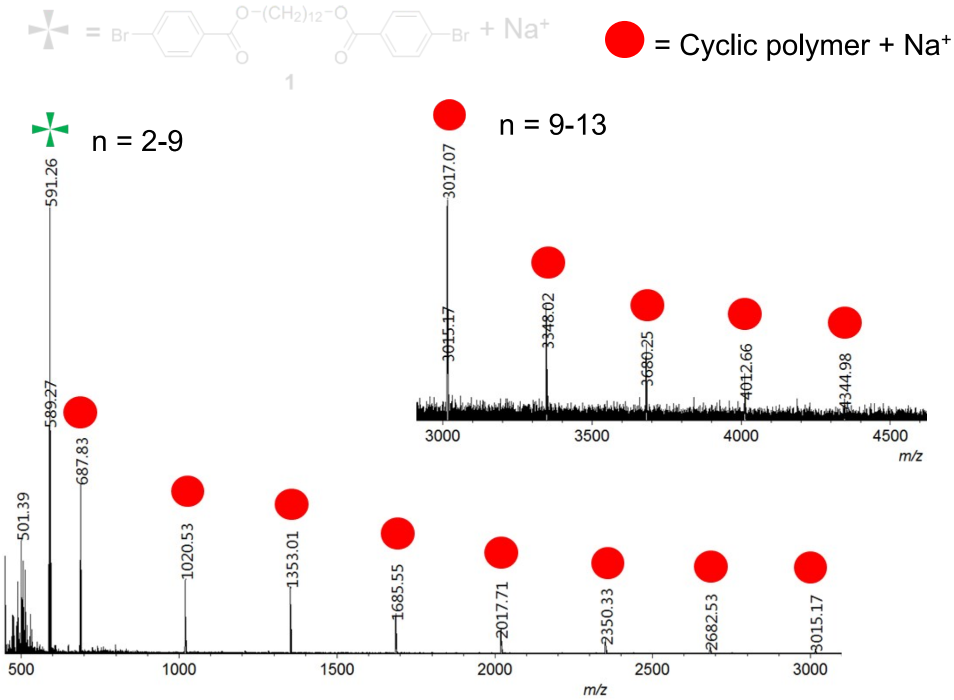

Figure S8. MALDI-TOF mass spectrum of the product of the transesterification of **CPEs-1** and 20 mol% of **1** with 4 mol% of EtOK (Table 1, entry 2).

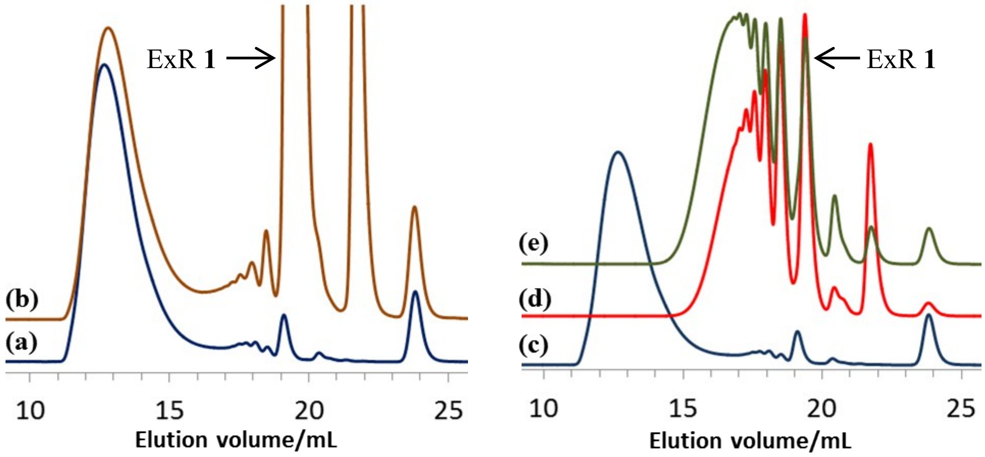

Figure S9. GPC elution curves of (a, c) **CPEs-1** (M_n = 54100, M_w/M_n = 2.63), and the product of the transesterification of **CPEs-1** and **1** with ^{t}BuOK: (b) with 20 mol% of **1** and 1 mol% of ^{t}BuOK (M_n = 48100, M_w/M_n = 2.60) (Table 1, entry 3), (d) with 20 mol% of **1** and 5 mol% of ^{t}BuOK (M_n = 2420, M_w/M_n = 1.41) (Table 1, entry 4) and (e) with 10 mol% of **1** and 5 mol% of ^{t}BuOK (M_n = 2940, M_w/M_n = 1.56) (Table 1, entry 5).

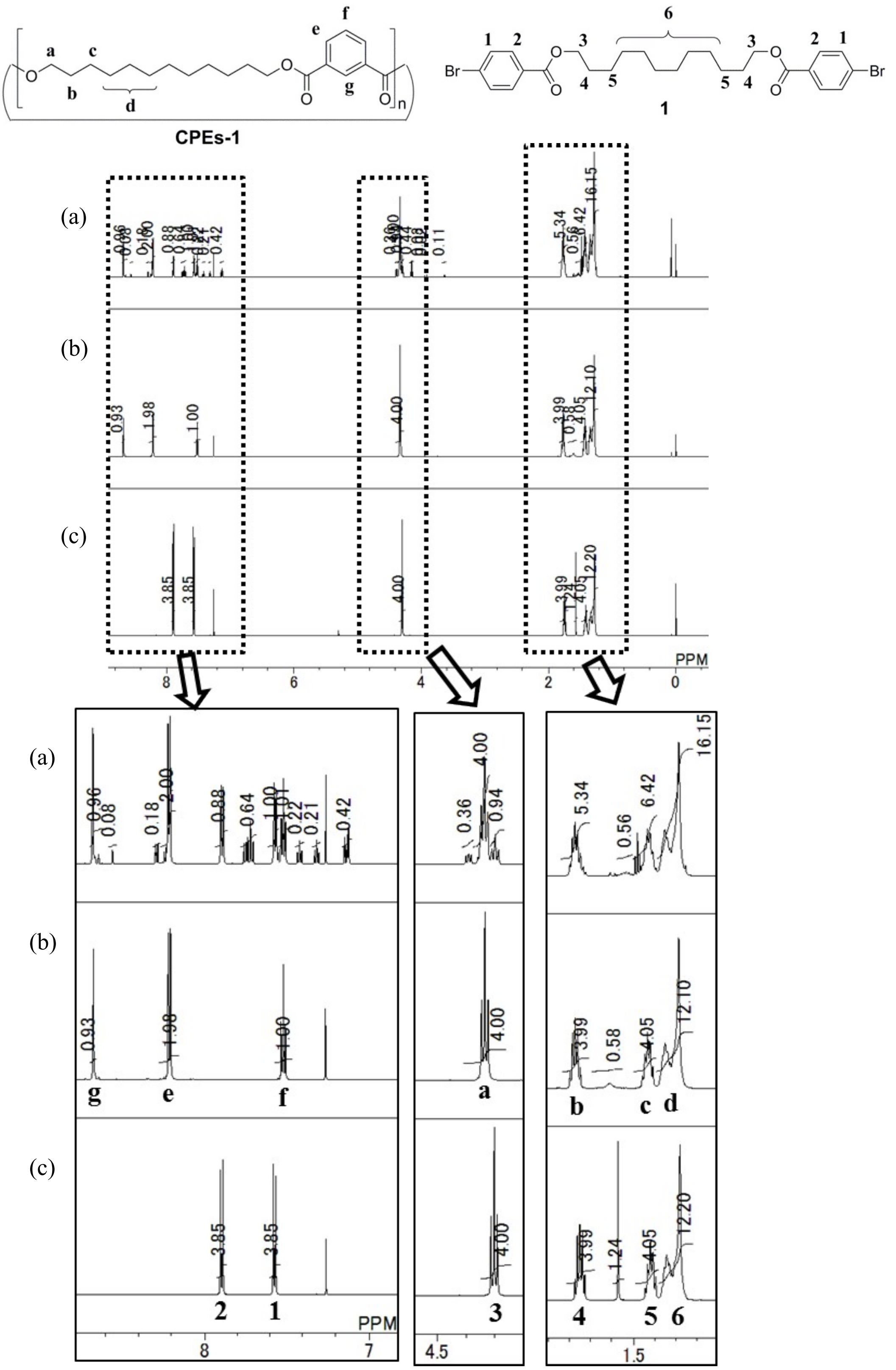

Figure S10. ^{1}H NMR spectra of (a) the product of the transesterification of **CPEs-1** with 20 mol% of **1** and 5 mol% of ^{t}BuOK (Table 1, entry 4), (b) **CPEs-1** after the purification and (c) **1** in $CDCl_3$ at 25 °C.

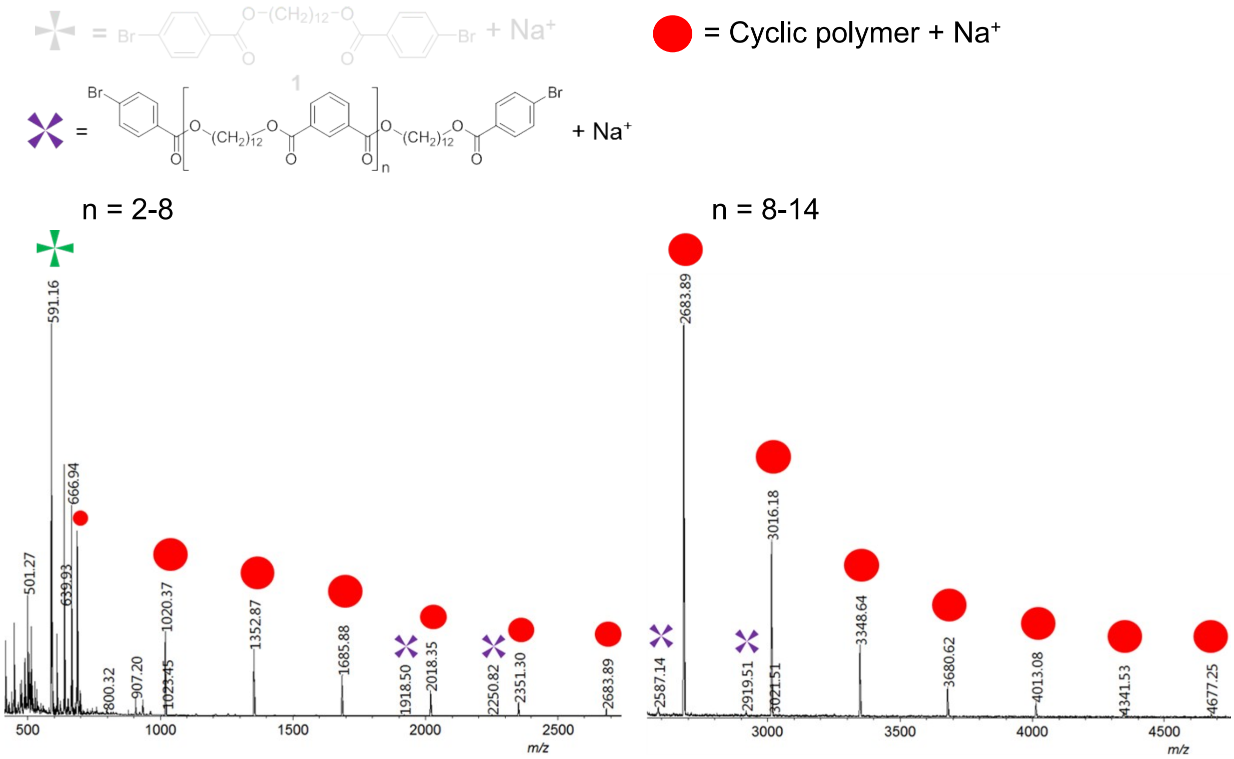

Figure S11. MALDI-TOF mass spectrum of the product of the transesterification of **CPEs-1** and 20 mol% of **1** with 1 mol% of ^{t}BuOK (Table 1, entry 3).

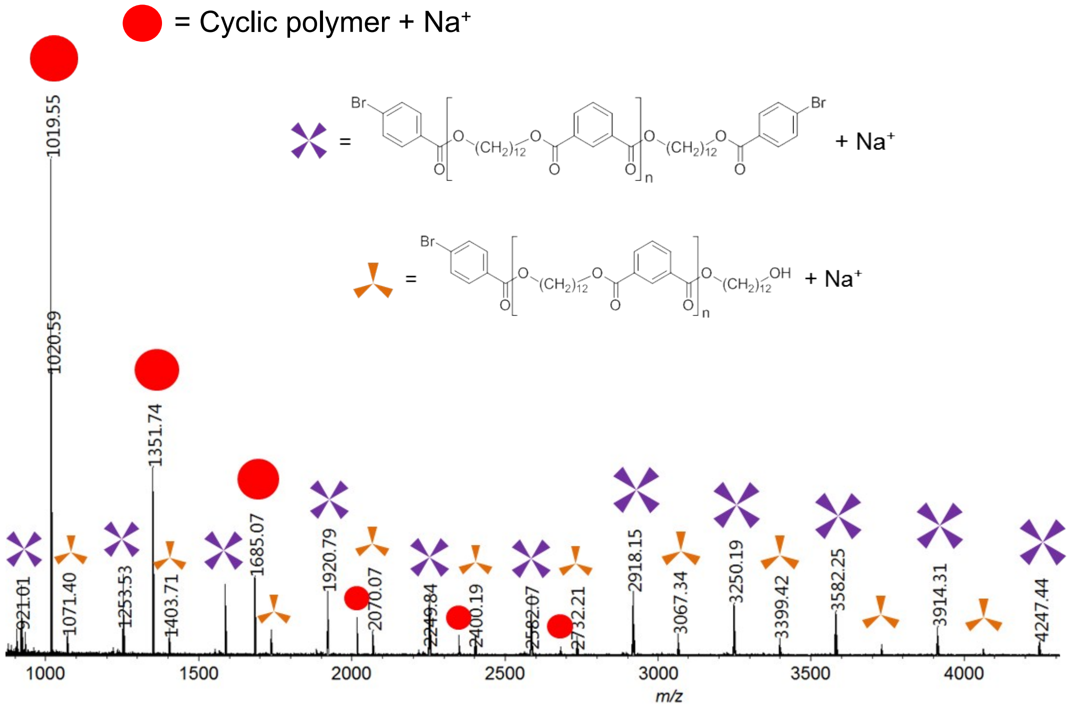

Figure S12. MALDI-TOF mass spectrum of the product of the transesterification of **CPEs-1** and 10 mol% of **1** with 5 mol% of ^{t}BuOK (Table 1, entry 5).

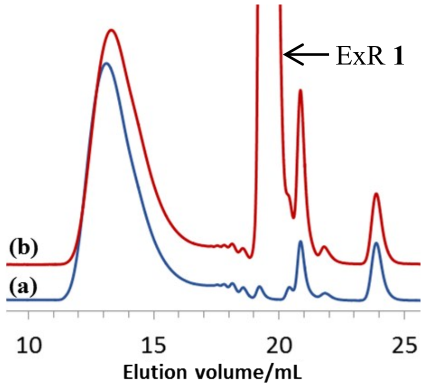

Figure S13. GPC elution curves of (a) **CPEs-1** (M_n = 48000, M_w/M_n = 2.54) and (b) the product of the transesterification of **CPEs-1** and 20 mol% of **1** with 5 mol% of ^{i}PrOLi (M_n = 41400, M_w/M_n = 2.33) (Table 1, entry 6).

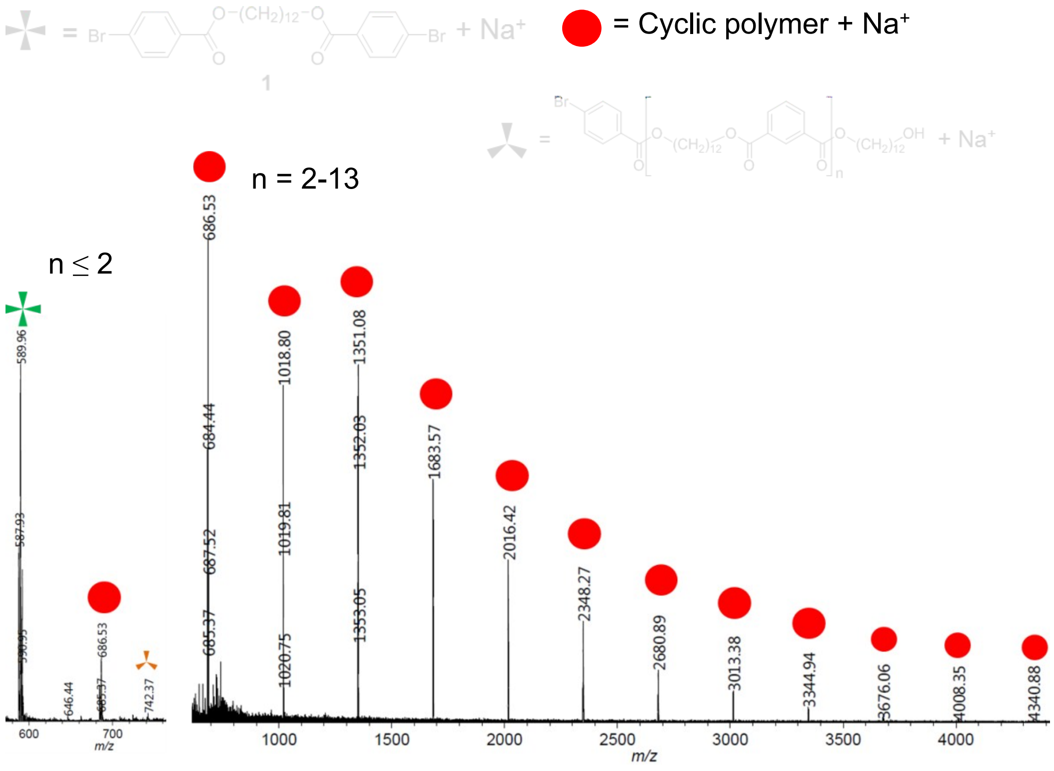

Figure S14. MALDI-TOF mass spectrum of the product of the transesterification of **CPEs-1** and 20 mol% of **1** with 5 mol% of ^{i}PrOLi (Table 1, entry 6).

4-2-3. Analysis of the equilibrium

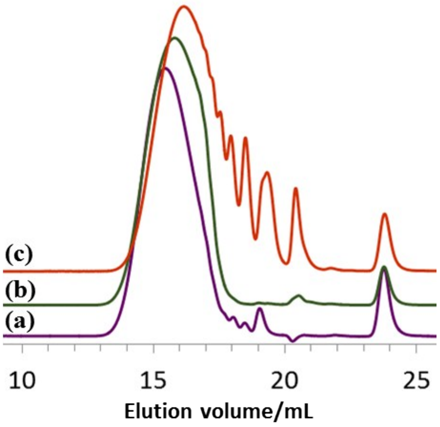

Figure S15. GPC elution curves of (a) **LPEs-1**-OH obtained by the polycondensation of 1.10 equiv of dodecane-1,12-diol and 1.00 equiv of isophthaloyl dichloride (M_n = 8310, M_w/M_n = 1.57), (b) **LPEs-1**-BrPh obtained by the reaction of **LPEs-1**-OH with 4-bromobenzoyl chlorideand (M_n = 7720, M_w/M_n = 1.50) and (c) the product of the reaction of **LPEs-1**-BrPh with 5 mol% of ^{t}BuOK (M_n = 4390, M_w/M_n = 1.80).

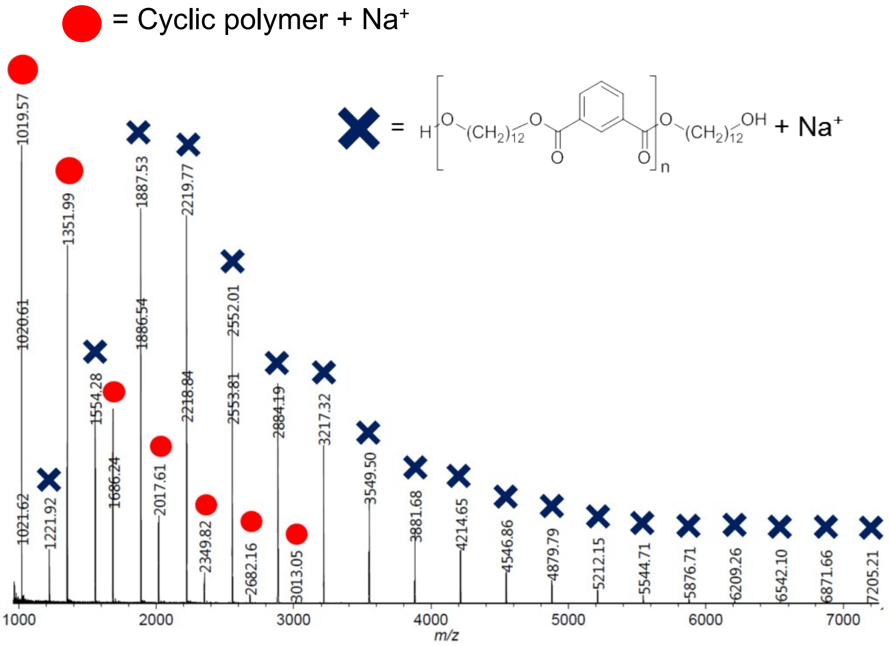

Figure S16. MALDI-TOF mass spectrum of **LPEs-1**-OH obtained by the polycondensation of 1.10 equiv of dodecane-1,12-diol and 1.00 equiv of isophthaloyl dichloride.

4-2-4. Optimization of the reaction condition

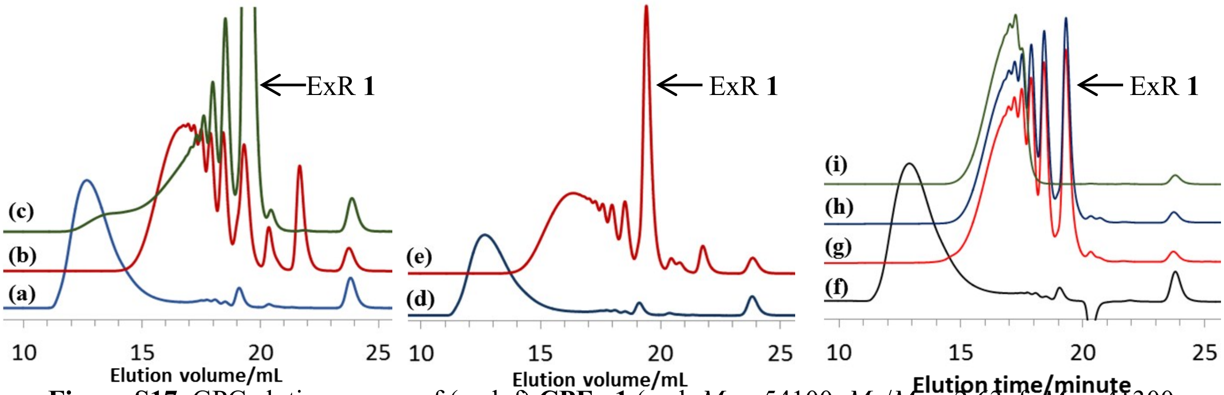

Figure S17. GPC elution curves of (a, d, f) **CPEs-1** (a, d: M_n = 54100, M_w/M_n = 2.63, f: M_n = 41300, M_w/M_n = 2.66) and products of transesterification of **CPEs-1** and **1** with ^{t}BuOK: (b) with 10 mol% of **1**, 017 mol/L, in THF at 50 °C (M_n = 3190, M_w/M_n = 1.58) (Table 2, entry 1), (c) with 20 mol% of **1**, 0.17 mol/L, in diglyme at 100 °C (M_n = 2800, M_w/M_n = 3.87) (entry 2), (e) with 10 mol% of **1**, 033 mol/L, in THF at rt (M_n = 3550, M_w/M_n = 1.82) (entry 3), (g) with 20 mol% of **1**, 050 mol/L, in THF at rt (M_n = 2780, M_w/M_n = 1.56) (entry 4), (h) with 20 mol% of **1**, 1.0 mol/L, in THF at rt before the purification (M_n = 2730, M_w/M_n = 1.49) and (i) after the purification (M_n = 4400, M_w/M_n = 1.21) (entry 5).

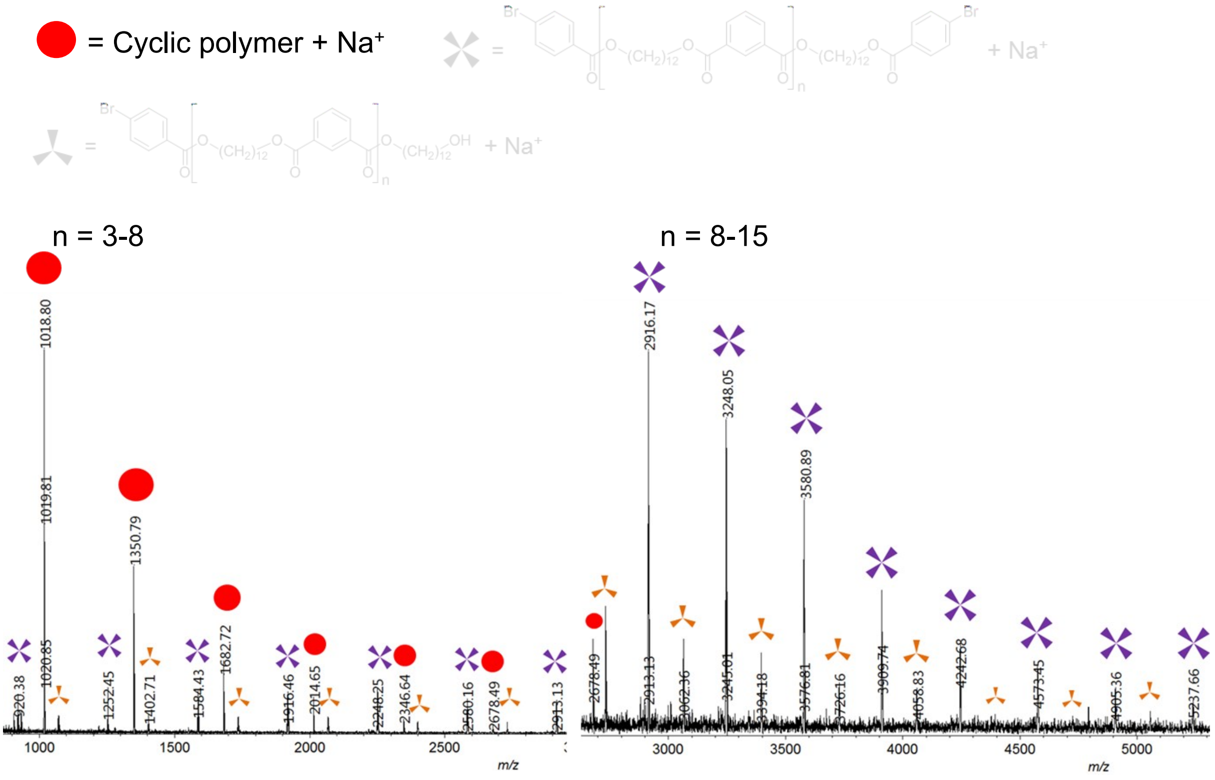

Figure S18. MALDI-TOF mass spectrum of the product of the transesterification of **CPEs-1** and 10 mol% of **1** with 5 mol% of ^{t}BuOK at 50 °C in THF (0.17 mol/L) (Table 2, entry 1).

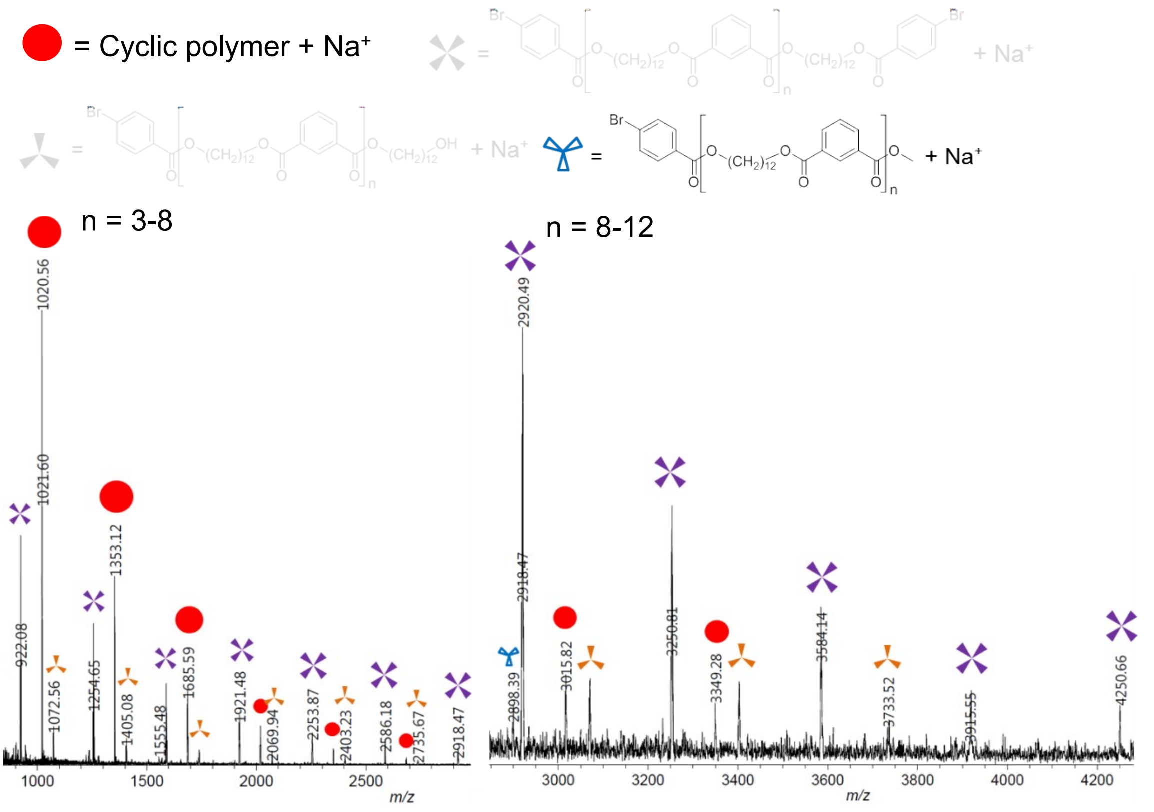

Figure S19. MALDI-TOF mass spectrum of the product of the transesterification of **CPEs-1** and 20 mol% of **1** with 5 mol% of ^{t}BuOK at 100 °C in diglyme (0.17 mol/L) (Table 2, entry 2).

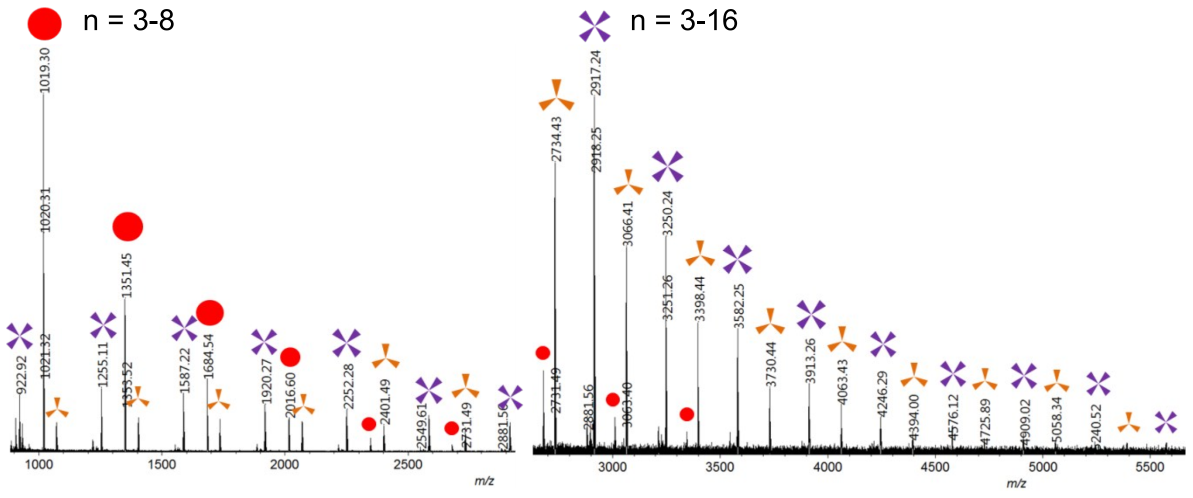

Figure S20. MALDI-TOF mass spectrum of the product of the transesterification of **CPEs-1** and 20 mol% of **1** with 5 mol% of ^{t}BuOK at rt in THF (0.33 mol/L) (Table 2, entry 3).

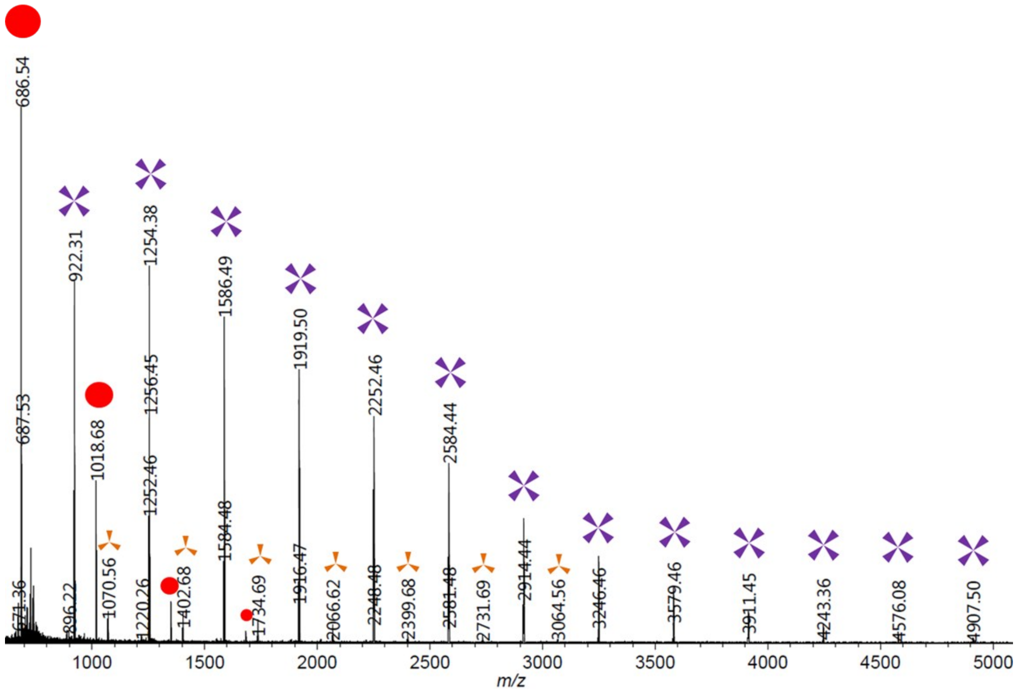

Figure S21. MALDI-TOF mass spectrum of the product of the transesterification of **CPEs-1** and 20 mol% of **1** with 5 mol% of ^{t}BuOK at rt in THF (0.50 mol/L) (Table 2, entry 4).