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Supporting Information for

Selective synthesis of cyclic-polymer-free poly(ether sulfone)s with OH ends or F ends by non-stoichiometric, reversible polycondensation

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Table of Contents

1. Materials

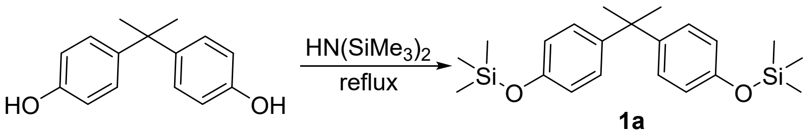
All starting materials were purchased from commercial suppliers (TCI, Aldrich, Wako, and Kanto) and used without further purification. Commercially available dehydrated *N*-methyl-2-pyrrolidone (NMP, Wako), dehydrated *N*,*N*-dimethylacetamide (DMAc, Wako) were used as dry solvents. The compounds were used after drying over phosphorous(V) oxide.

2. General

^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained on JEOL ECZ-400R, ECX-400II and ECA-600 spectrometers. The internal standard for ^{1}H NMR spectra in $CDCl_3$ was tetramethylsilane (0.00 ppm), the internal standard for ^{13}C NMR spectra in $CDCl_3$ was the midpoint of $CDCl_3$ (77.0 ppm), the internal standard for ^{19}F NMR spectra in $CDCl_3$ was C_6F_6 (-161.6 ppm). IR spectra were recorded on a JASCO FT/IR-4600AC. The M_n and M_w/M_n values of polymers were measured on Tosoh HLC-8420 gel permeation chromatography unit (eluent, THF 1.00 mL/min; calibration, polystyrene standards; column temperature, 40 °C) with two TSK-gel columns (2 x G4000H_{XL}). Purification of polymer was carried out by LC908-C60 recycling preparative HPLC (eluent, $CHCl_3$) with two JAIGEL columns (1H-40 and 2H-40). MALDI-TOF mass spectra were recorded on a Shimazu/Biotech AXIMA-Confidence in the reflectron ion mode and linear ion 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. TG-DTA was recorded on Shimazu DTG-60H. DSC was recorded on Hitachi High-Tech Science X-DSC7000.

3. Syntheses and monomers

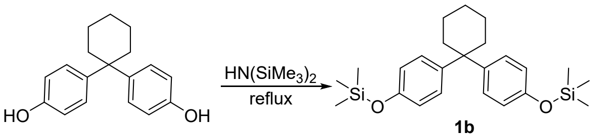
3-1. Synthesis of **1a**



1a

4,4'-Isopropylidenediphenol (11.4 g, 50.0 mmol) was placed in a round-bottomed flask, and the atmosphere in the flask was replaced with argon. 1,1,1,3,3,3-Hexamethyldisilazane (21.0 mL, 100 mmol) was added to the flask via a syringe, and the mixture was refluxed at 200 °C for 11 hours. The crude product was purified by means of distillation under reduced pressure (191-193 °C/4.8 mmHg) to afford bis(trimetylsilyl) bisphenol A ether as a colorless liquid (14.8 g, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.6 Hz, 4 H), 6.72 (d, *J* = 8.6 Hz, 4 H), 1.62 (s, 6 H), 0.25 (s, 18 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.81, 143.73, 127.69, 119.13, 41.71, 31.07, 0.27; IR (neat) 1384, 1409, 1256, 843, 757 cm^{-1}.

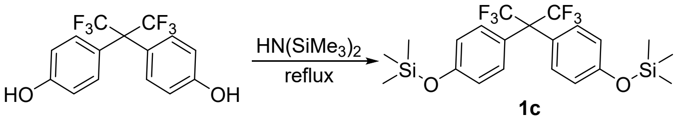
3-2. Synthesis of **1b**



1b

Bis(trimethylsilyl) ether **1b** was synthesized by the same procedures for the synthesis of **1a** using 4,4'-(cyclohexylidene)diphenol instead of 4,4'-(isopropylidene)diphenol. Crude product was purified by distillation (230 °C/1 mmHg) to afford a yellow viscous liquid (97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.8 Hz, 4 H), 6.71 (d, *J* = 8.8 Hz, 4 H), 2.19 (t, *J* = 5.2 Hz, 4 H), 1.53-1.47 (m, 6 H), 0.24 (s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 141.4, 127.8, 119.0, 44.9, 37.2, 26.2, 22.6, 2.17; IR (neat) 3036, 2937, 2859, 2860, 1606, 1177, 1107, 1012 cm^{-1}.

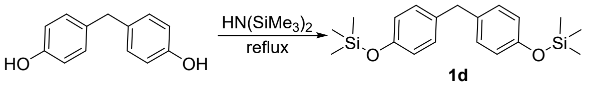
3-3. Synthesis of **1c**



1c

Bis(trimethylsilyl) ether **1c** was synthesized by the same procedures for the synthesis of **1a** using 4,4'-(hexafluoroisopropylidene)diphenol instead of 4,4'-(isopropylidene)diphenol. Crude product was purified by distillation (230 °C/0.1 mmHg) to afford a clear colorless viscous liquid (84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 9.2 Hz, 4 H), 6.80 (d, *J* = 9.2 Hz, 4 H), 0.29 (s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 131.2, 125.9, 125.6, 122.7, 119.1, 63.9, 63.6, 63.4, 63.1, 0.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0; IR (neat) 3051, 2962, 1610, 1515, 1419, 1017 cm^{-1}.

3-4. Synthesis of **1d**



1d

Bis(trimethylsilyl) ether **1d** was synthesized by the same procedures for the synthesis of **1a** using 4,4'-(methylene)diphenol instead 4,4'-(isopropylidene)diphenol. Crude product was purified by distillation (230 °C/0.1 mmHg) to afford a clear colorless viscous liquid (84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.8 Hz, 4 H), 6.75 (d, *J* = 8.4 Hz, 4 H), 3.84 (s, 2 H), 0.25 (s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 134.1, 129.5, 119.6, 40.0, 0.0; IR (neat) 3051, 2962, 1610, 1515, 1419, 1017 cm^{-1}.

4. Polymerization

4-1. Polymerization of 1.2 equivalents of **1a** and 1.0 equivalent of **2** ([**2**]$_0$ = 1.0 M) (Table 1, Entry 2)

A round-bottomed flask was flame-dried under reduced pressure, and the atmosphere was replaced with argon. **1a** (448 mg, 1.20 mmol), **2** (255 mg, 1.00 mmol) and dry K_2CO_3 (139 mg, 1.01 mmol) were placed in the flask, and the atmosphere was replaced with argon. Dry NMP (1.0 mL) was added under a stream of nitrogen, and the mixture was stirred at 145 °C for 48 h. The flask was cooled to room temperature, and NMP (10 mL) was added to the flask. The mixture was poured into water (500 mL), and the precipitate was filtrated and dried in a vacuum desiccator over phosphorous(V) oxide to afford PES with HO/OH ends as a brown powder (421 mg, 95%).

4-2. Polymerization of 1.0 equivalent of **1a** and 1.2 equivalents of **2** in the presence of K_2CO_3 ($[\mathbf{1a}]_0 = 1.0$ M)

A round-bottomed flask was flame-dried under reduced pressure, and the atmosphere was replaced with argon. **1a** (375 mg, 1.01 mmol), **2** (306 mg, 1.20 mmol) and dry K_2CO_3 (139 mg, 1.00 mmol) were placed in the flask, and the atmosphere was replaced with argon. Dry NMP (1.0 mL) was added under a stream of nitrogen, and the mixture was stirred at 145 °C for 72 h. The flask was cooled to room temperature, and NMP (20 mL) was added to the flask. The mixture was poured into water (250 mL), and the precipitate was filtrated and dried in a vacuum desiccator over phosphorous(V) oxide. The obtained solid was dissolved in dichloromethane (14 mL) and precipitated upon methanol (250 mL), filtrated, and dried under reduced pressure to afford PES as a pale yellow powder (165 mg, 37%).

4-3. Polymerization of 1.0 equivalent of **1a** and 1.2 equivalents of **2** ($[\mathbf{1}]_0 = 1.0$ M) (Table 2, Entry 1)

A round-bottomed flask was flame-dried under reduced pressure, and the atmosphere was replaced with argon. **1a** (373 mg, 1.00 mmol) and **2** (305 mg, 1.20 mmol) were placed in the flask, and the atmosphere was replaced with argon. Dry DMAc (1.0 mL) was added under a stream of nitrogen. Dry CsF (77.0 mg, 0.511 mmol) was placed in another round-bottomed flask and flame-dried under reduced pressure, and the atmosphere was replaced with argon. A solution of monomers in DMAc in the former flask was added to the latter flask containing CsF, and the mixture was stirred at 165 ^{o}C for 72 h. The flask was cooled to room temperature, and DMAc (10 mL) was added to the flask. The mixture was poured into water (500 mL), and the precipitate was filtrated and dried in a vacuum desiccator over phosphorous(V) oxide to afford PES with F/F ends as a white powder (419 mg, 85%).

4-4. Polymerization of 1.1 equivalents of **1c** and 1.0 equivalent of **2** ($[\mathbf{2}]_0 = 1.0$ M) (Table 3, Entry 2)

A round-bottomed flask was flame-dried under reduced pressure, and the atmosphere was replaced with argon. **1c** (528 mg, 1.10 mmol), **2** (254 mg, 1.00 mmol) and dry K_2CO_3 (138 mg, 1.00 mmol) were placed in the flask, and the atmosphere was replaced with argon. Dry NMP (1.0 mL) was added under a stream of nitrogen, and the mixture was stirred at 145 ^{o}C for 26 h. The flask was cooled to room temperature, and NMP (5 mL) was added to the flask. The mixture was poured into water (500 mL), and the precipitate was filtrated and dried in a vacuum desiccator over phosphorous(V) oxide to afford PES with HO/OH ends as a pale yellow powder (532 mg, 89%).

4-5. Polymerization of 1.0 equivalent of **1b** and 1.1 equivalents of **2** ($[\mathbf{1b}]_0 = 1.0$ M) (Table 4, Entry 1)

A round-bottomed flask was flame-dried under reduced pressure, and the atmosphere was replaced with argon. **1b** (412 mg, 1.00 mmol), **2** (280 mg, 1.10 mmol) were placed in a flask, and the atmosphere was replaced with argon. Dry DMAc (1.0 mL) was added to the flask under a stream of nitrogen. Dry CsF (75 mg, 0.49 mmol) was placed in another round-bottomed flask and flame-dried under reduced pressure, and the atmosphere was replaced with argon. A solution of monomers in DMAc in the former flask was added to the latter flask containing CsF, and the mixture was stirred at 165 ^{o}C for 72 h. The flask was cooled to room temperature, and DMAc (5 mL) was added to the flask. The mixture was poured into water (500 mL), and the precipitate was filtrated and dried in a vacuum desiccator over phosphorous(V) oxide to afford PES with F/F ends as a white powder (300 mg, 59%).

4-6. Reaction of **2** and K_2CO_3 in NMP

In a round bottomed flask, were placed **2** (305 mg, 1.200 mmol) and K_2CO_3 (138 mg, 1.00 mmol), and the atmosphere was replaced with argon. Dry NMP (1.0 mL) was added under a stream of nitrogen, and the mixture was stirred at 145 ^{o}C for 40 h. The flask was cooled to room temperature, and NMP (5 mL) was added to the flask. The mixture was poured into water (500 mL), and the precipitate was filtrated and dried in a vacuum desiccator over phosphorous(V) oxide to afford an oligomer as a brown powder (174 mg, 62%).

5. Figures

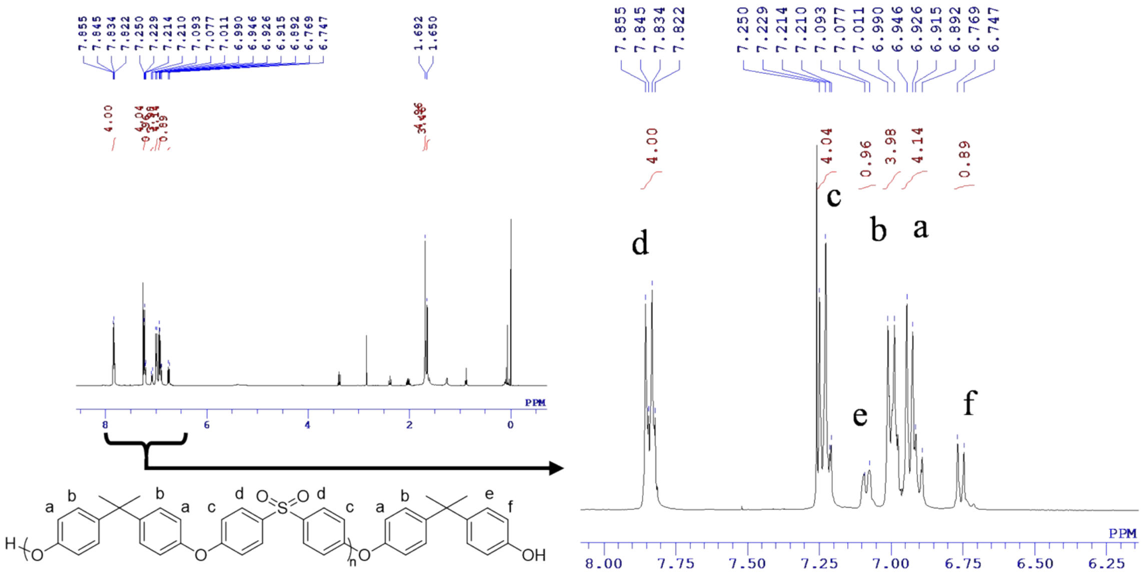


Figure S1. ^{1}H NMR spectrum of PES with HO/OH ends obtained by the polycondensation of 1.3 equivalents of **1a** and 1.0 equivalent of **2** in the presence of 1.0 equivalent of K_2CO_3 in NMP at 145 °C for 48 h (Table 1, Entry 1).

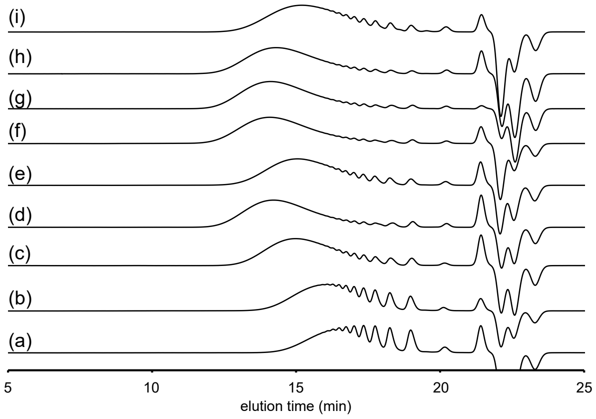


Figure S2. GPC elution curves of PES obtained by the polycondensation of excess **1a** and 1.0 equivalent

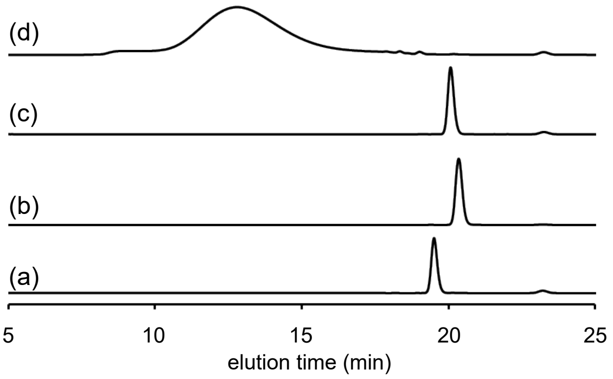


Figure S3. GPC elution curves of (a) **1a**, (b) **2**, (c) bisphenol A, and (d) PES obtained by the polycondensation of 1.0 equivalent of **1a** with 1.2 equivalents of **2** in the presence of 1.0 equivalent of K_2CO_3 in NMP at 140 °C for 72 h.

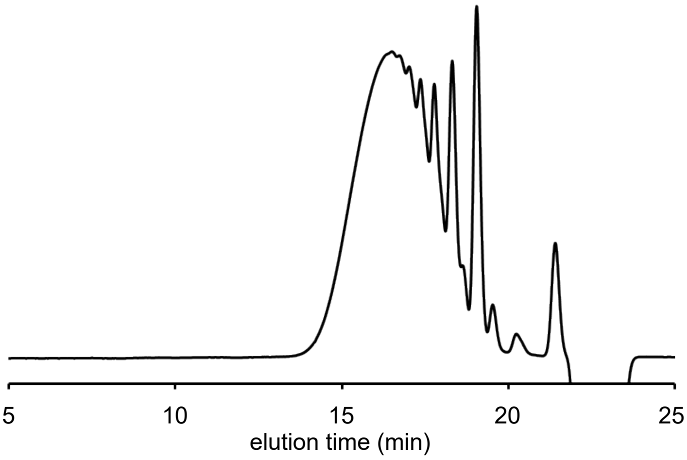


Figure S4. GPC elution curve of the polymer obtained by the polycondensation of 1.0 equivalent of **1a** and 1.5 equivalents of **2** in the presence of K_2CO_3 in NMP at 140 °C for 72 h.

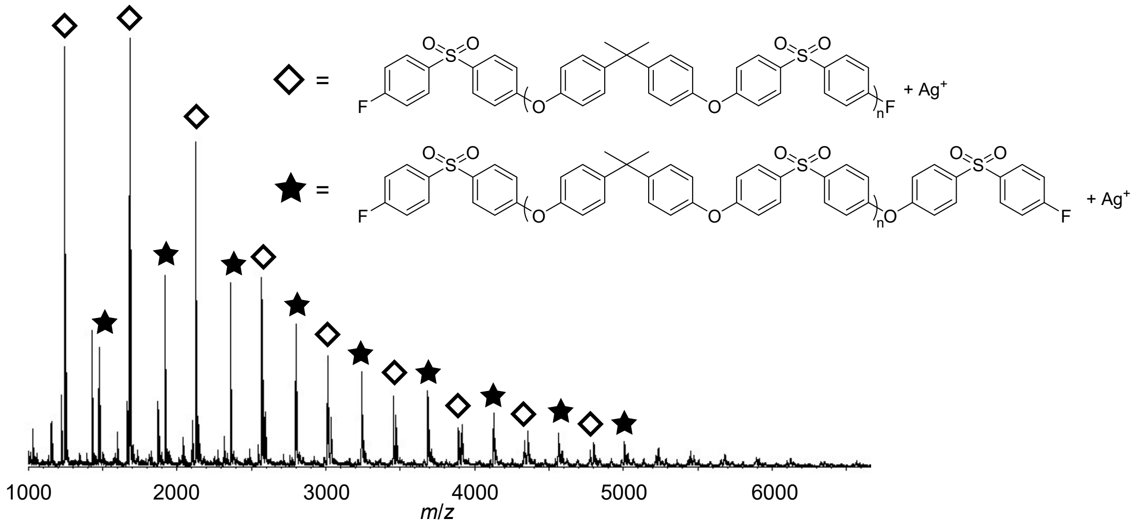


Figure S5. MALDI-TOF mass spectrum of the polymer obtained by the polycondensation of 1.0 equivalent of **1a** and 1.5 equivalents of **2** in the presence of K_2CO_3 in NMP at 140 °C for 72 h.

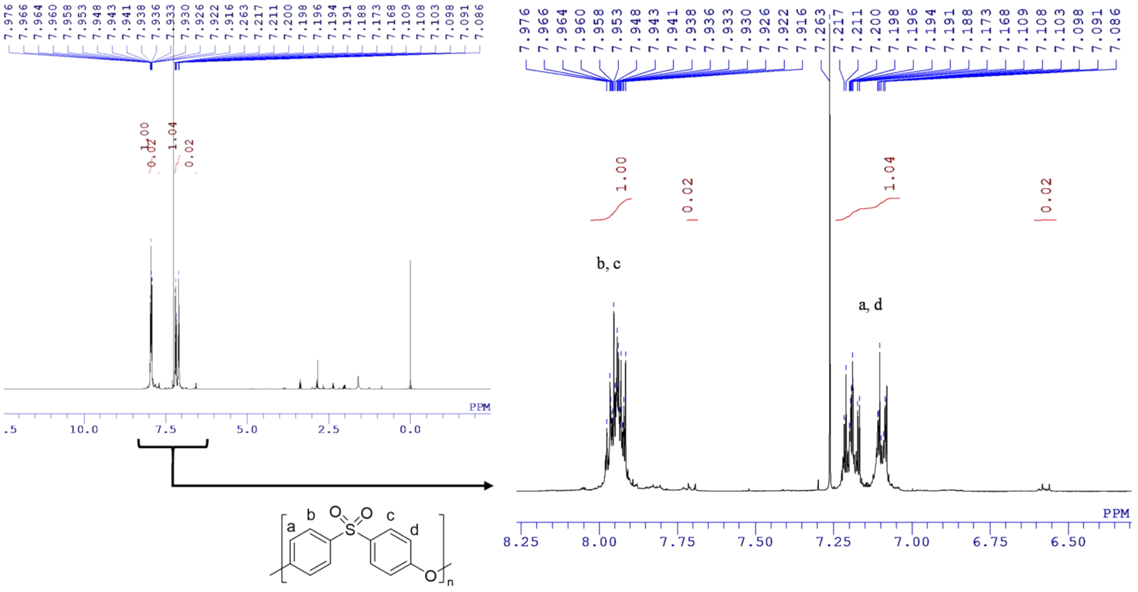


Figure S6. ^{1}H NMR spectrum of the oligomer obtained by the reaction 1.2 equivalents of **2** and 1.0 equivalent of K_2CO_3 in NMP at 145 °C for 40 h.

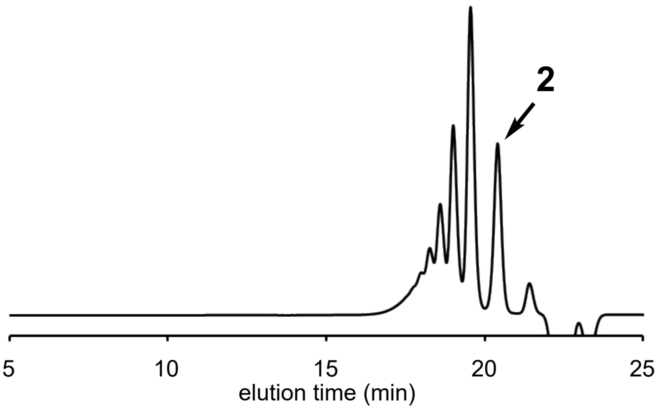


Figure S7. GPC elution curve of the oligomer obtained by the reaction of 1.2 equivalents of **2** and 1.0 equivalent of K_2CO_3 in NMP at 145 °C for 40 h (M_n = 747, M_w/M_n = 1.27).

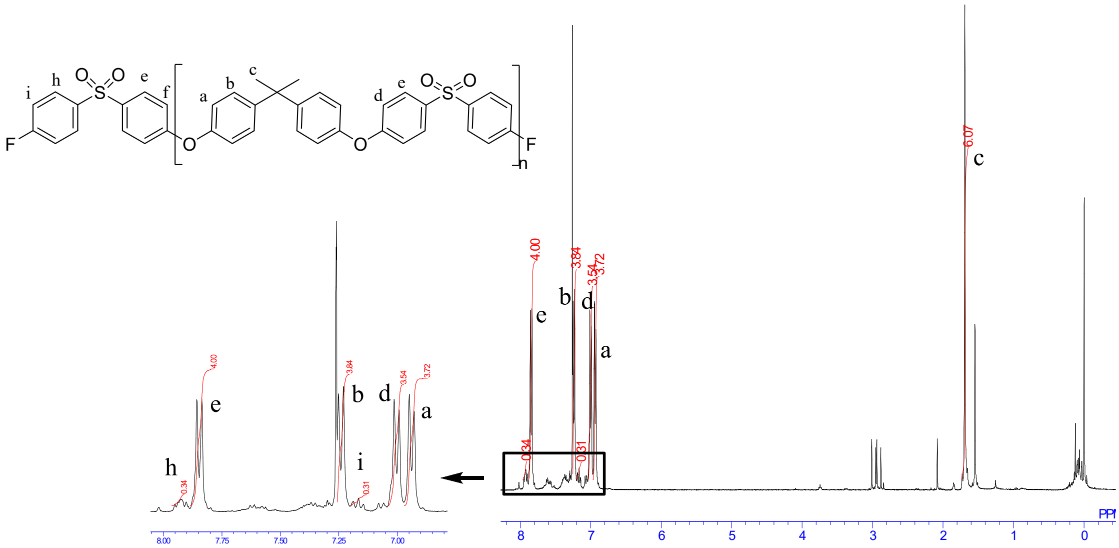


Figure S8. ^{1}H NMR spectrum of PES with F/F ends obtained by the polycondensation of 1 equivalent of **1a** and 1.2 equivalents of **2** in the presence of 0.5 equivalents of CsF in DMAc at 165 °C for 72 h (Table 2, Entry 1).

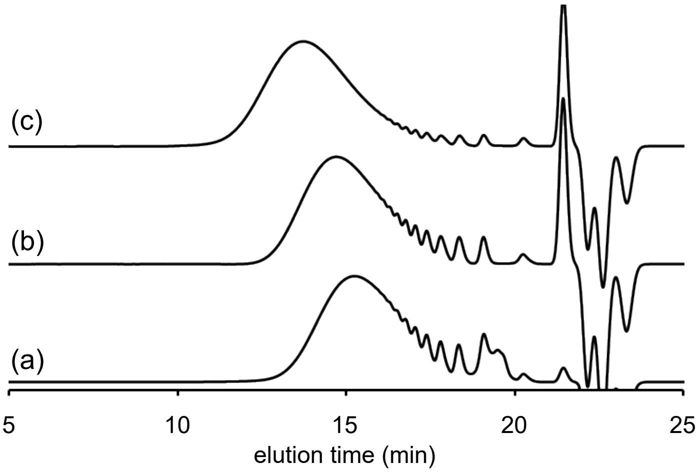


Figure S9. GPC elution curves of PES with F/F ends obtained by the polycondensation of **1a** and excess **2** in the presence of 0.5 equivalents of CsF in DMAc ($[\mathbf{1a}]_0$ = 1.0 M) at 165 °C for 72 h; Table 2: (a) Entry 1, (b) Entry 2, (c) Entry 3.

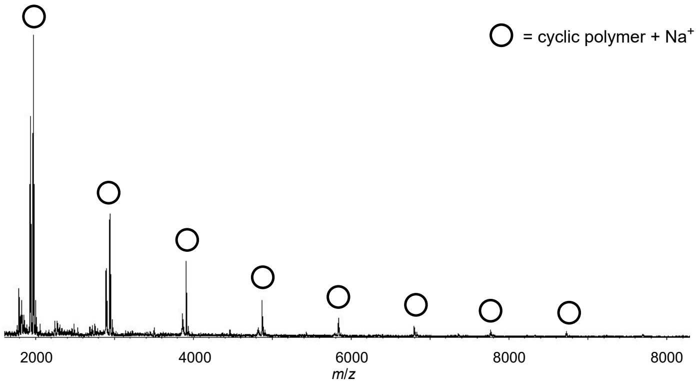


Figure S10. MALDI-TOF mass spectrum of PES in NMP-soluble fraction, obtained by the polycondensation of 1.1 equivalents of **1b** and 1.0 equivalent of **2** in the presence of K_2CO_3 in NMP at 145 °C for 24 h.

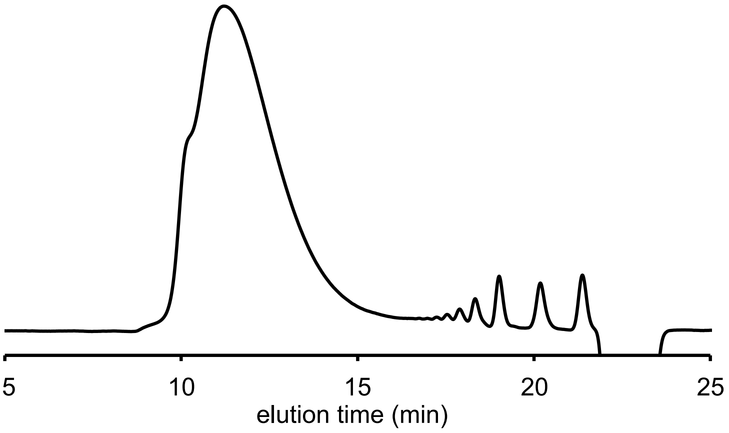


Figure S11. GPC elution curve of PES in NMP-soluble fraction, obtained by the polycondensation of 1.1 equivalents of **1b** and 1.0 equivalent of **2** in the presence of K_2CO_3 in NMP at 145 °C for 24 h.

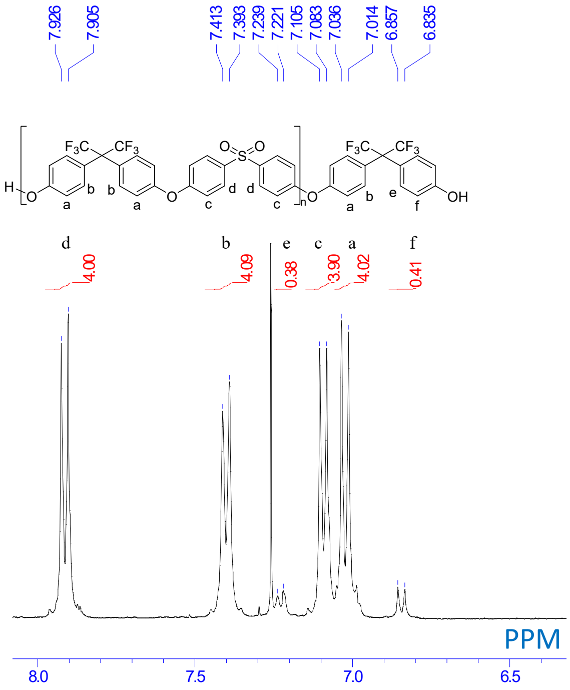


Figure S12. ^{1}H NMR spectrum of PES with HO/OH ends obtained by the polycondensation of 1.1 equivalents of **1c** and 1.0 equivalent of **2** in the presence of K_2CO_3 in NMP at 145 ^{o}C for 24 h.

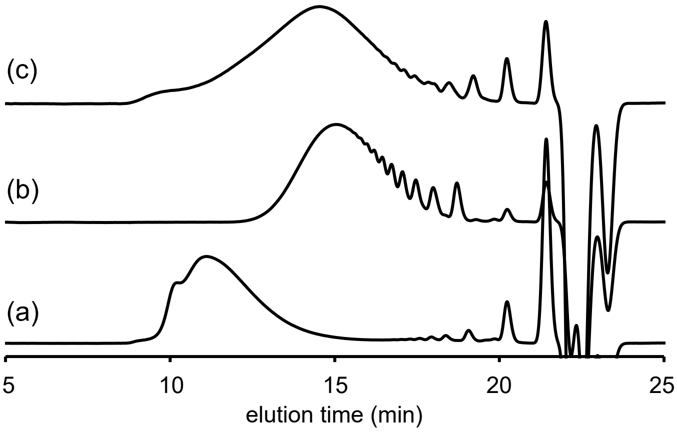


Figure S13. GPC elution curves of PES obtained by the polycondensation of 1.1 equivalents of **1** and 1.0 equivalent of **2** in the presence of K_2CO_3 in NMP at 145 °C for 24 h; Table 3: (a) Entry 1, (b) Entry 2, (c) Entry 3.

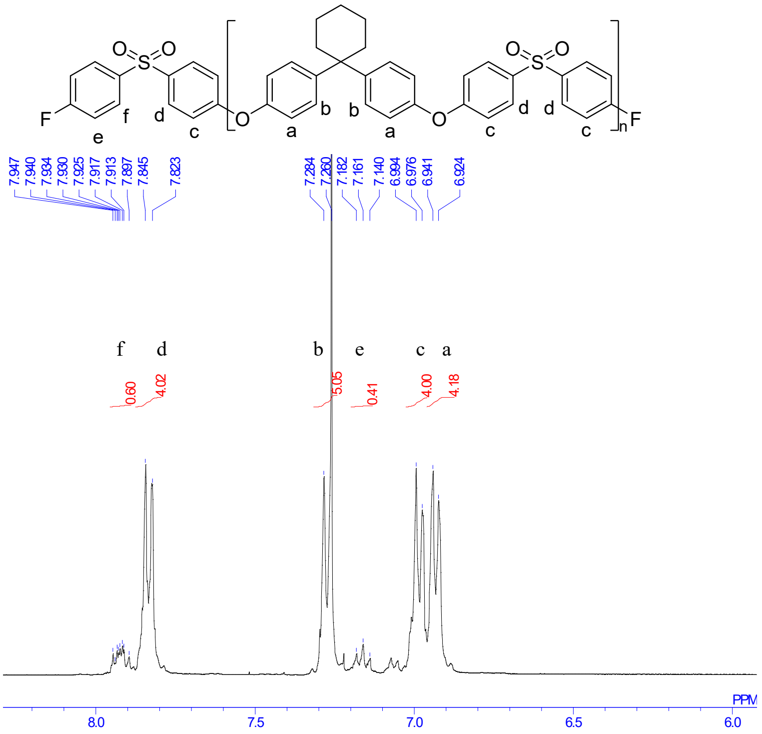


Figure S14. ^{1}H NMR spectrum of PES with F/F ends obtained by the polycondensation of 1.0 equivalent of **1b** and 1.1 equivalents of **2** in the presence of 0.50 equivalents of CsF in DMAc at 165 °C for 3 days.

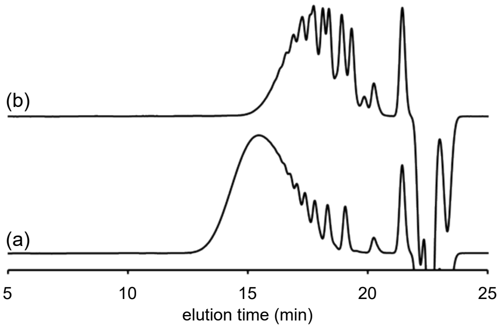


Figure S15. GPC elution curves of PES obtained by the polycondensation of 1.0 equivalent of **1** and 1.1 equivalents of **2** in the presence of 0.50 equivalents of CsF in DMAc at 165 °C for 3 days; Table 4: (a) Entry 1, (b) Entry 2.

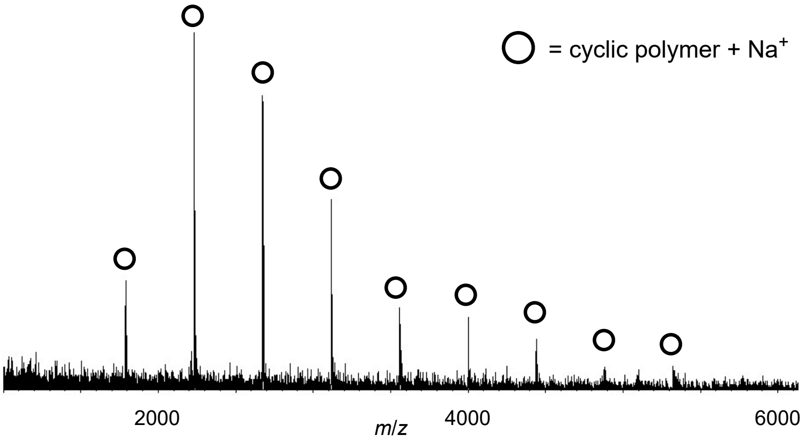


Figure S16. MALDI-TOF mass spectrum of PES obtained by the polycondensation of equimolar of **1a** and **2** in the presence of K_2CO_3 in NMP at 145 °C for 68 h.

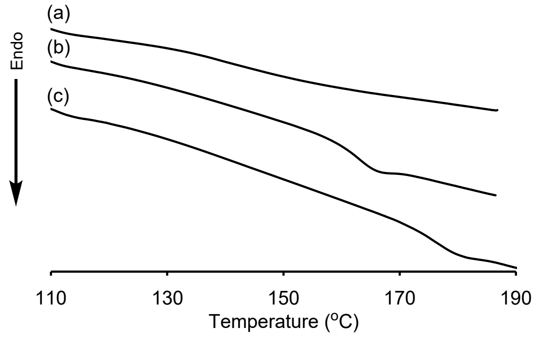


Figure S17. DSC curves during heating of PES; (a) polymer ends with HO/OH (Table 1, Entry 8), (b) polymer ends with F/F (Table 2, Entry 2), (c) cyclic polymer (Figure S16).

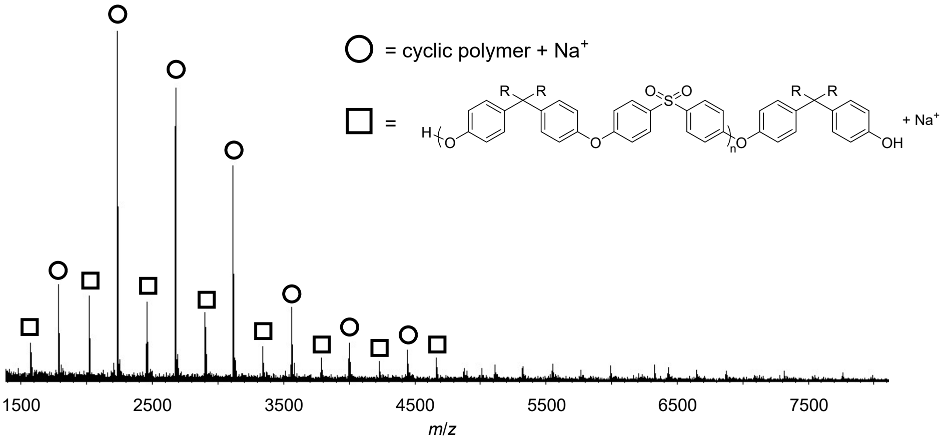


Figure S18. MALDI-TOF mass spectrum of a mixture of equal amount of cyclic polymer (Table 3, Entry 1; M_n = 6440, M_w/M_n = 2.63) and polymer with HO/OH ends (Table 3, Entry 2; M_n = 8380, M_w/M_n = 1.98).

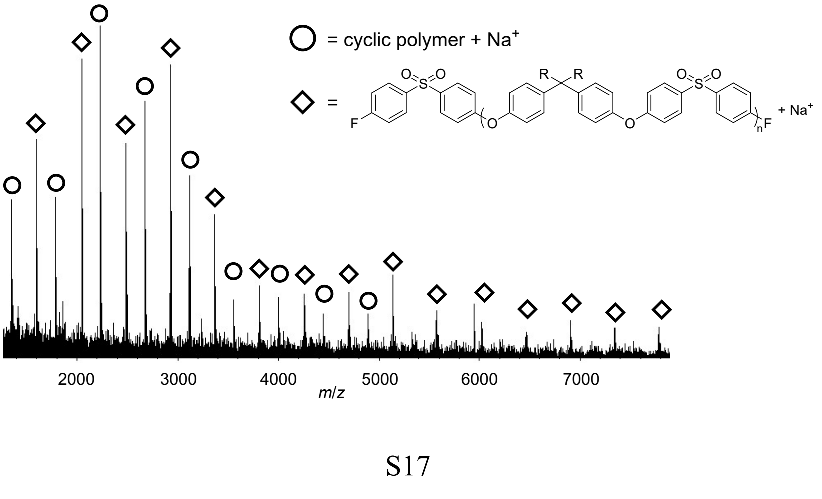


Figure S19. MALDI-TOF mass spectrum of a mixture of equal amount of cyclic polymer (Table 3, Entry 1; M_n = 6440, M_w/M_n = 2.63) and polymer with F/F ends (Table 3, Entry 3; M_n = 6300, M_w/M_n = 2.02).