Electronic Supplementary Information

Importance of reversible reaction for the synthesis of telechelic polymer by means of polycondensastion using an excess of one monomer

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1. Materials

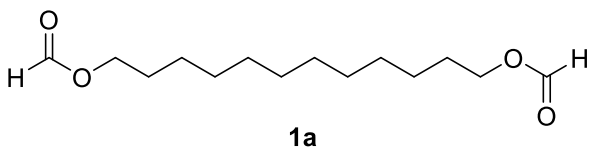
All starting materials were purchased from commercial suppliers (TCI, Aldrich, Wako and Kanto) and used without further purification. Commercially available dehydrated dichloromethane (Kanto), dehydrated tetrahydrofuran (THF, stabilizer-free, Kanto), deoxidized THF (Wako), deoxidized toluene (Wako), dehydrated *N*,*N*-dimethylformamide (DMF, Wako), dehydrated *N*,*N*-dimethylacetamide (DMAc, Aldrich), and dehydrated diethyleneglycol dimethyl ether (diglyme, Aldrich) were used as dry solvents. Monomers were used after drying over phosphoric oxide (V) in a desiccator or azeotropic distillation with dry toluene. 4-[(*Tert*-butyldimethylsilyloxy)methyl]benzoic acid (**8**) was synthesized according to the literature.[1]

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), 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-4600AC. All melting points were measured with a Yanagimoto hot stage melting point apparatus without correction. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with a specified solvent. 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 °C) with two Shodex KF-804L columns, Shodex UV-41, Shodex RI-71S. 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. All compounds for polycondensation were placed in a flask in a glove box MDB-1KH-YYO of Miwa Manufacturing Co., Ltd.

3. Synthesis of monomer and ExRs.

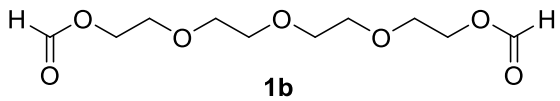
3-1. dodecane-1,12-diyl diformate (1a)



1a

A round-bottom flask was equipped with a three-way stopcock. Formic acid (2.8 mL, 74.2 mmol) was added to a solution of dodecane-1,12-diol (6.08 g, 30.1 mmol), 4-(*N*,*N*-dimethylamino) pyridine (DMAP) (8.87 g, 72.6 mmol), and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (13.8 g, 72.1 mmol) in dry dichloromethane (100 mL) at 0 °C. The solution was stirred at room temperature for 24 h. The mixture was washed with 1 M aqueous HCl, saturated aqueous $NaHCO_3$, and brine, and dried over anhydrous $MgSO_4$. The organic layer was concentrated under reduced pressure to afford **1a** as a white solid (7.24 g, 93%); mp. 38.0-38.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 2 H), 4.16 (t, *J* = 6.9 Hz, 4 H), 1.66 (quint, *J* = 7.2 Hz, 4 H), 1.36-1.27 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 64.1, 29.5, 29.4, 29.1, 28.5, 25.8; IR (KBr) 2925, 2855, 2362, 1718, 1478, 1375, 1184 cm^{-1}.

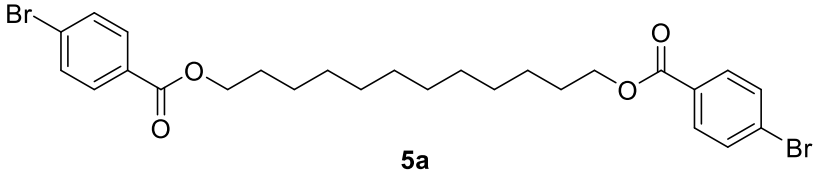
3-2. tetraethylene glycol diformate (1b)



1b

Diformate **1b** was synthesized in the same procedure as **1a** using tetraethylene glycol instead of dodecane-1,12-diol to afford colorless liquid (yield 84%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 2 H), 4.33 (t, *J* = 4.9 Hz, 4 H), 3.74 (t, *J* = 4.9 Hz, 4 H), 3.67 (s, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.9, 70.6, 68.8, 62.9; IR (KBr) 3426, 2876, 2354, 2191, 1722, 1646, 1561, 1454, 1383, 1350, 1294, 1250, 1182, 1129, 1042 cm^{-1}.

3-3. dodecane-1,12-diyl bis(4-bromobenzoate) (5a) [2]

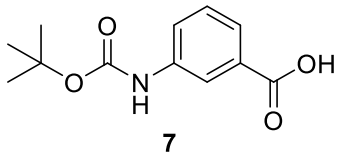


5a

A round-bottom flask was equipped with a three-way stopcock. To the flask were added dodecane-1,12-diol (0.500 g, 2.47 mmol), DMAP (0.711 g, 5.82 mmol), EDCI (1.09 g, 5.69 mmol), 4-bromobenzoic acid (1.14 g, 5.69 mmol), and dry DMF (8.0 mL). The solution was stirred at room temperature for 24 h. The mixture was washed with 1 M aqueous HCl, saturated aqueous $NaHCO_3$, and brine, dried over anhydrous $MgSO_4$, and

concentrated under reduced pressure. The residue was purified by means of column chromatography (SiO_2; ethyl acetate/hexane = 2/1) to afford **5a** as a white solid (1.27 g, 91%); mp. 64.8-65.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (dt, *J* = 8.4 and 1.8 Hz, 4 H), 7.58 (dt, *J* = 8.4 and 1.8 Hz, 4 H), 4.30 (t, *J* = 6.6 Hz, 4 H), 1.75 (quint, *J* = 7.8 Hz, 4 H), 1.42 (quint, *J* = 7.8 Hz, 4 H), 1.38-1.24 (m, 12 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ165.9, 131.7, 131.1, 129.4, 127.9, 65.4, 29.5, 29.4, 29.2, 28.7, 26.0; IR (KBr) 2920, 2852, 1715, 1589, 1474, 1398, 1293, 1176, 1131, 1068, 1012, 851, 755 cm^{-1}.

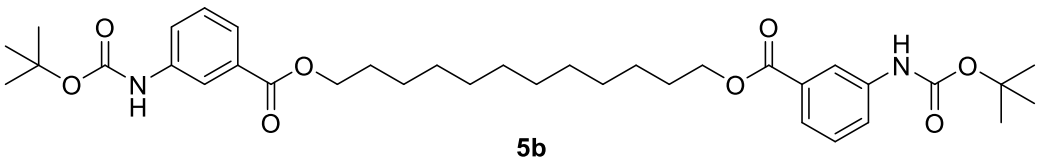
3-4. 3-(*tert*-butoxycarbonylamino)benzoic acid (7) [3]



7

To a round-bottom flask were added 3-aminobenzoic acid (2.04 g, 14.9 mmol), dioxane (40 mL), water (20 mL), triethylamine (3.2 mL, 22.3 mmol) and di-*tert*-butyl dicarbonate (5.2 mL, 22.6 mmol). The mixture was stirred at room temperature for 21 hand evaporated. To the residue was added 6 M aqueous HCl dropwise to acidify. Then the solution was extracted with ethyl acetate, dried over $MgSO_4$, and concentrated under reduced pressure to afford **7** as a white solid (3.03 g, 86%); mp 195-197 °C (lit[3]:189-190 °C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.53 (s, 1 H), 8.13 (s, 1 H), 7.61 (d, *J* = 9.6 Hz, 1 H), 7.52 (dt, *J* = 9.6 and 2.4 Hz, 1 H), 7.35 (t, *J* = 9.6 Hz, 1 H), 1.47 (s, 9 H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.3, 152.8, 139.8, 131.3, 128.8, 122.9, 122.2, 118.8, 79.3, 28.1; IR (KBr) 3354, 3006, 2972, 2645, 2586, 1694, 1594, 1529, 1452, 1292, 1242, 1158, 1058, 945, 747 cm^{-1}.

3-5. dodecane-1,12-diyl bis[3-(*tert*-butoxycarbonylamino)benzoate] (5b)

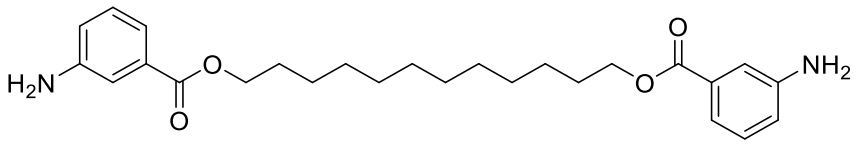


5b

Diester **5b** was prepared by similar procedures for diester **1a** using **7** instead of formic acid and purified by column chromatography (SiO_2; ethyl acetate/hexane = 1/4) to afford white solid (2.94 g, 86%); mp 115.1-118.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 2 H), 7.74 (br s, 2 H), 7.70 (d, *J* = 7.8 Hz, 2 H), 7.36 (t, *J* = 7.2 Hz, 2 H), 6.64 (s, 2 H), 4.30 (t, *J* = 6.6 Hz, 4 H), 1.75 (quint, *J* = 6.6 Hz, 4 H), 1.52 (s, 9 H), 1.42 (quint, *J* = 7.8 Hz, 4

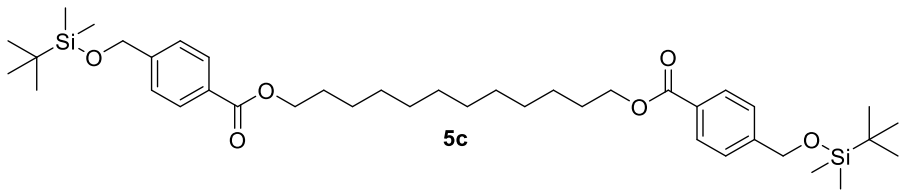
H), 1.38-1.26 (m, 12 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ166.4, 152.6, 138.6, 131.2, 129.0, 124.1, 122.8, 119.4, 65.2, 29.49, 29.45, 29.2, 28.7, 28.3, 26.0; IR (KBr) 3378, 2917, 2846, 1726, 1702, 1610, 1526, 1489, 1367, 1314, 1241, 1152, 964, 753 cm^{-1}.

3-6. dodecane-1,12-diyl bis(3-aminobenzoate) [1]



To a round-bottom flask were added **5b** (644 mg, 1.00 mmol) and dry dichloromethane (5.0mL), and the atmosphere was replaced with argon. Trifluoroacetic acid (1.5 mL, 20 mmol) was added to the flask at 0 ºC, and the mixture was stirring at room temperature for 18 h. The reaction was quenched with saturated aqueous Na_2CO_3, and the mixture was extracted with dichloromethane. The organic layer was washed with water, dried over $MgSO_4$, and was concentrated under reduced pressure to afford the desired diamine as a yellow solid (4.01 g, 91%); mp 65.0-66.0 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.8 Hz, 2 H), 7.35 (t, *J* = 1.8 Hz, 2 H), 7.21 (t, *J* = 7.8 Hz, 2 H), 6.85 (dd, *J* = 7.8 and 2.4 Hz, 2 H), 4.28 (t, *J* = 7.2 Hz, 4 H), 3.77 (br s, 4 H), 1.75 (quint, *J* = 6.6 Hz, 4 H), 1.42 (quint, *J* = 7.8 Hz, 4 H), 1.38-1.24 (m, 12 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 146.4, 131.5, 129,2, 119.7, 119.3, 115.7, 65.1, 29.53, 29.49, 29.3, 28.7, 26.0; IR (KBr) 3416, 3389, 3336, 2926, 2851, 1726, 1706, 1605, 1589, 1458, 1321, 1289, 1234, 1108, 1070, 1019, 995, 948, 883, 806, 752, 680 cm^{-1}.

3-7. dodecane-1,12-diyl bis(4-*tert*-butyldimethylsilyloxymethylbenzoate) (5c)

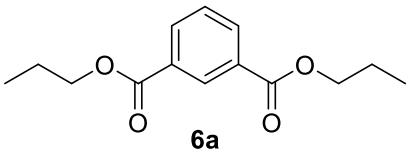


5c

Diester **5c** was synthesized by similar procedure for diester **1a** using **8** instead of formic acid and purified by column chromatography twice (SiO_2; ethyl acetate/hexane = 1/1 and 1/13) to afford colorless liquid (yield 61%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 4 H), 7.38 (d, *J* = 7.8 Hz, 4 H), 4.79 (s, 4 H), 4.30 (t, *J* = 6.6 Hz, 4 H), 1.76 (quint, *J* = 7.8 Hz, 4 H), 1.43 (quint, *J* = 7.8 Hz, 4 H), 1.38-1.24 (m, 12 H), 0.95 (s, 18 H),

0.10 (s, 12 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ166.7, 146.6, 129.5, 129.1, 125.6, 65.0, 64.5, 29.6, 29.5, 29.3, 28.7, 26.0, 25.9, 18.4, -5.30; IR (KBr) 3421, 2926, 1931, 1715, 1614, 1579, 1508, 1471, 1416, 1251, 1206, 1173, 1087, 1019, 835, 752 cm^{-1}.

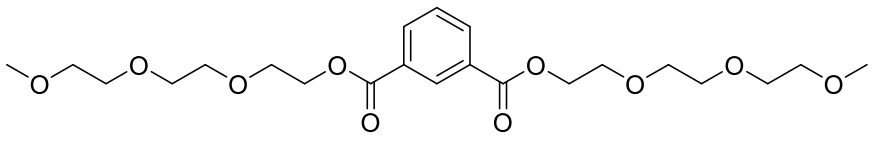
3-8. dipropyl isophthalate (6a) [4]



6a

Isophthaloyl chloride (2.41 g, 11.9 mmol), 1-propanol (12.0 mL, 160 mmol), and dry dichloromethane (12.0 mL) were placed in a round-bottom flask equipped with a three-way stopcock and cooled to 0 °C in an ice bath. The mixture was stirred at room temperature for 24 h and concentrated in *vacuo*. The residue was diluted with dichloromethane, washed with saturated aqueous $NaHCO_3$, and dried over anhydrous $MgSO_4$. The organic layer was concentrated under reduced pressure to afford **6a** as a colorless liquid (3.23 g, 108%);^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (t, *J* = 1.5 Hz, 1 H), 8.23 (dd, *J* = 8.0 and 2.0 Hz, 2 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 4.32 (t, *J* = 6.0 Hz, 4 H), 1.82 (sext, *J* = 7.5 Hz, 4 H), 1.05 (t, *J* = 8.0 Hz, 6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 133.4, 130.7, 130.4, 128.3, 66.6, 21.9, 10.3; IR (KBr) 3076, 2970, 2880, 1724, 1609, 1465, 1437, 1390, 1301, 1238, 1132, 1095, 1077, 981, 957, 730 cm^{-1}.

3-9. bis{[(2-methoxy)-2-ethoxy]-2-ethoxyl}-2-ethyl isophthalate (6b) [5]

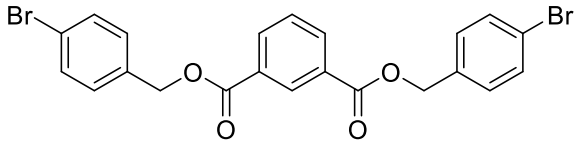


6b

Triethylene glycol monomethyl ether (2.31 mL, 14.7 mmol) was placed in a round-bottom flask equipped with a three-way stopcock, and the atmosphere was replaced with argon. Dry dichloromethane (3.0 mL) and dry pyridine (0.86 mL, 11 mmol) were added to the flask in a nitrogen flow and cooled to 0 °C. Another round-bottom flask was charged with isophthaloyl chloride (1.00 g, 4.94 mmol), and the atmosphere was replaced with argon. Dry dichloromethane (2.0 mL) was added to the flask in a nitrogen flow.The

solution of isophthaloyl chloride was then added dropwise to the first flask containing the alcohol and pyridine at 0 °C under nitrogen. The mixture was stirred at room temperature for 1 day. The organic layer was washed with 1 M aqueous HCl, saturated aqueous $NaHCO_3$, and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by means of column chromatography (SiO_2; ethyl acetate) to afford **6b** as a white liquid (1.65 g, 76%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (t, *J* = 2.0 Hz, 1 H), 8.25 (dd, *J* = 7.5 and 2.0 Hz, 2 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 4.51 (t, *J* = 4.5 Hz, 4 H), 3.85 (t, *J* = 6.0 Hz, 4 H), 3.74-3.71 (m, 4 H), 3.70-3.64 (m, 8 H), 3.55 (dd, *J* = 5.0 and 3.0 Hz, 4 H), 3.37 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 133.9, 130.9, 130.5, 128.5, 71.8, 70.63, 70.56, 70.52, 69.1, 64.4, 59.0; IR (KBr) 2875, 1952, 1724, 1609, 1454, 1353, 1303, 1239, 1104, 938, 853, 732, 656 cm^{-1}.

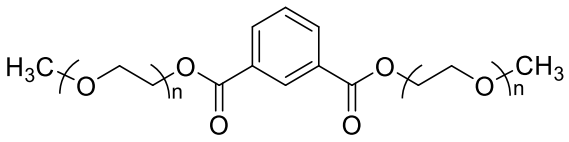
3-10. di(4-bromobenzyl) isophthalate (6c)



6c

To a round-bottom flask equipped with a three-way stopcock was added 4-bromobenzyl alcohol (1.96 g, 10.5 mmol), dry pyridine (1.0 mL, 12.4 mmol), and dry THF (5.0 mL). The mixture was cooled to 0 °C, and 2.32 M isophthloyl dichloride solution in THF (2.0 mL, 4.65 mmol) was added to the flask under nitrogen. The mixture was stirred at room temperature for 1 day. The reaction was quenched with water, and the mixture was concentrated under reduced pressure. The residue was washed with 1 M aqueous HCl, saturated aqueous $NaHCO_3$, and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by means of column chromatography (SiO_2, ethyl acetate/hexane = 1/4) to afford **6c** as a white solid (0.993 g, 42%); mp = 144.2-145.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (t, *J* = 1.8 Hz, 1 H), 8.25 (dd, *J* = 7.8 and 1.8 Hz, 2 H), 7.54 (t, *J* = 7.2 Hz, 1 H), 7.52 (d, *J* = 7.8 Hz, 4 H), 7.33 (d, *J* = 8.4 Hz, 4 H), 5.33 (s, 4 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 134.7, 134.1, 131.8, 130.9, 130.4, 130.0, 128.7, 122.5, 66.3; IR (KBr) 1722, 1493, 1372, 1321, 1240, 1149, 1072, 1016, 967, 797, 725 cm^{-1}.

3-11. bis(polyethylene gylocol) isophthalate (6d) [5]



6d

Dicarboxylic ester **6d** was prepared by similar procedures for dicarboxylic diester **6b** using polyethylene glycol monomethyl ether (M_n = 1000) instead of triethylene glycol monomethyl ether and purified by preparative HPLC (elutent: $CHCl_3$) to afford **6d** as a pale yellow viscous liquid (0.913 g, 57%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (t, J = 1.5 Hz, 1 H), 8.25 (dd, J = 8.0 and 2.0 Hz, 2 H), 7.54 (t, J = 8.0 Hz, 1 H), 4.50 (t, J = 4.5 Hz, 4 H), 3.85 (t, J = 5.0 Hz, 4 H), 3.72-3.69 (m, 4 H) 3.68-3.59 (m, 178 H), 3.55 (dd, J = 5.0 and 2.5 Hz, 4 H), 3.38 (s, 6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 133.9, 130.9, 130.6, 128.6, 71.9, 70.5, 69.1, 64.4, 59.0; IR (KBr) 2882, 1722, 1468, 1360, 1344, 1281, 1235, 1114, 946, 843 cm^{-1}.

4. Polymerization

4-1. General procedure for unstoichiometric polycondensation of 1 and 2

A round-bottomed flask was flame-dried, and the atmosphere was replaced with argon. To the flask were added 5 mol% of potassium *tert*-butoxide, **1**, **2**, and dry diglyme in a glove box, and stirred at 120 ºC under reduced pressure (90-100 Torr) for 1 day. The reaction was quenched with saturated aqueous NH_4Cl, and extracted with dichloromethane. The organic layer was washed with 1 M aqueous HCl and saturated aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in dichloromethane and precipitated into methanol. Clear solvent containing no precipitated polymer was removed by decantation. The precipitated viscous polymer was collected by dissolution with dichloromethane, and the solution was concentrated under reduced pressure to afford telechelic polyester.

4-2. General procedure for unstoichiometric polycondensation of 1 and 2 in the presence of ExR

A round-bottomed flask was flame-dried, and the atmosphere was replaced with argon. To the flask were added 5 mol% of potassium *tert*-butoxide, **1**, **2**, **ExR**, and dry diglyme in a glove box, and stirred at 120 ºC under reduced pressure (90-100 Torr) for 1 day. The reaction was quenched with saturated aqueous NH_4Cl, and extracted with dichloromethane. The organic layer was washed with 1 M aqueous HCl and saturated

aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in dichloromethane and precipitated into methanol. Clear solvent containing no precipitated polymer was removed by decantation. The precipitated viscous polymer was collected by dissolution with dichloromethane, and the solution was concentrated under reduced pressure to afford telechelic polyester.

4-3. Synthesis of triblock copolymer by means of polycondensation of 1a and 2a in the presence of 6d

Two round-bottomed flasks were flame-dried, and the atmosphere was replaced with argon. To one flask were added **1a** (155 mg, 0.601 mmol), **2a** (117 mg, 0.604 mmol), **6d** (247 mg, 0.116 mmol), and deoxidized toluene (0.8 mL), and to the other flask were added potassium *tert*-butoxide (6.6 mg, 0.059 mmol), 18-crown-6 (22.7 mg, 0.086 mmol), and deoxidized toluene (0.4 mL) in a glove box. Half the solution in the latter flask containing alkoxide and crown ether was added to the former flask containing monomers and **6d**, and the mixture was stirred at 65 °C under reduced pressure (90-100 Torr) for 1 day. The reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with dichloromethane, washed with 1 M aqueous HCl, saturated aqueous $NaHCO_3$, and saturated aqueous KCl, and dried over anhydrous $MgSO_4$. The organic layer was concentrated under reduced pressure, and the residue was dissolved in dichloromethane and precipitated into methanol at 0 °C. Clear solvent containing no precipitated polymer was removed by decantation. The precipitated viscous polymer was collected by dissolution with dichloromethane, and the solution was concentrated under reduced pressure to afford pale yellow viscos liquid (92.7 mg, 46%).

5. Figures

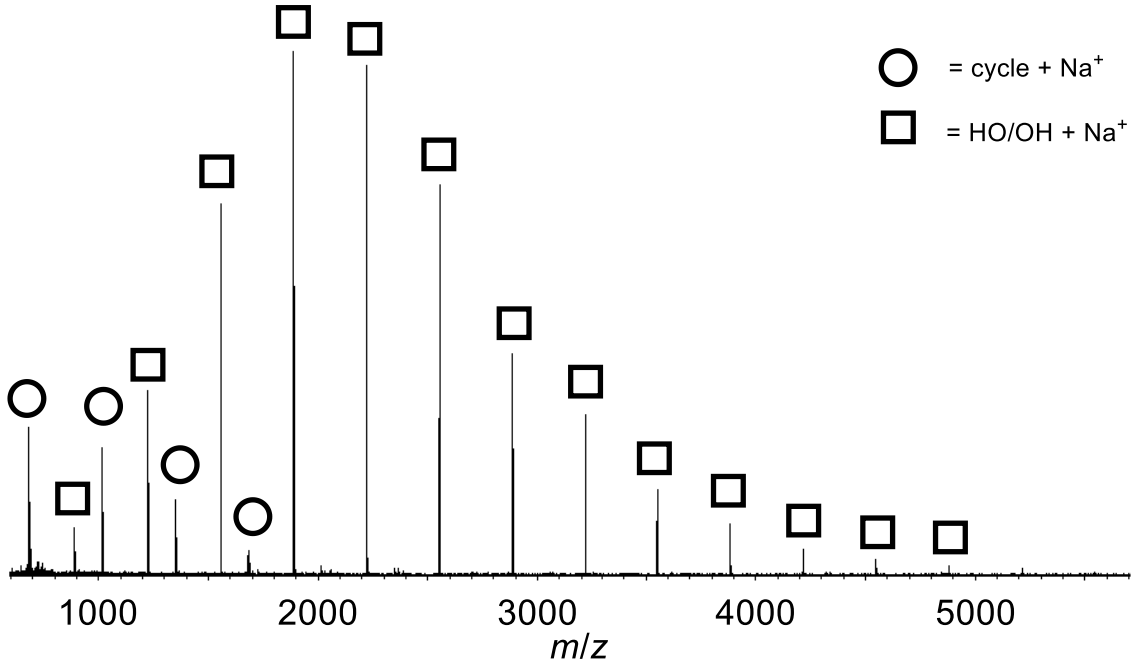


Figure S1. MALDI-TOF mass spectrum of the product obtained by the polymerization of 1.2 equiv of **1a** and 1.0 equiv of **2a** with 5 mol% of ^{t}BuOK in diglyme ([**2a**]$_0$ = 0.6 mol/L) at 120 ^{o}C under reduced pressure (90-100 Torr) for 1 day (Table 1, Entry 1).

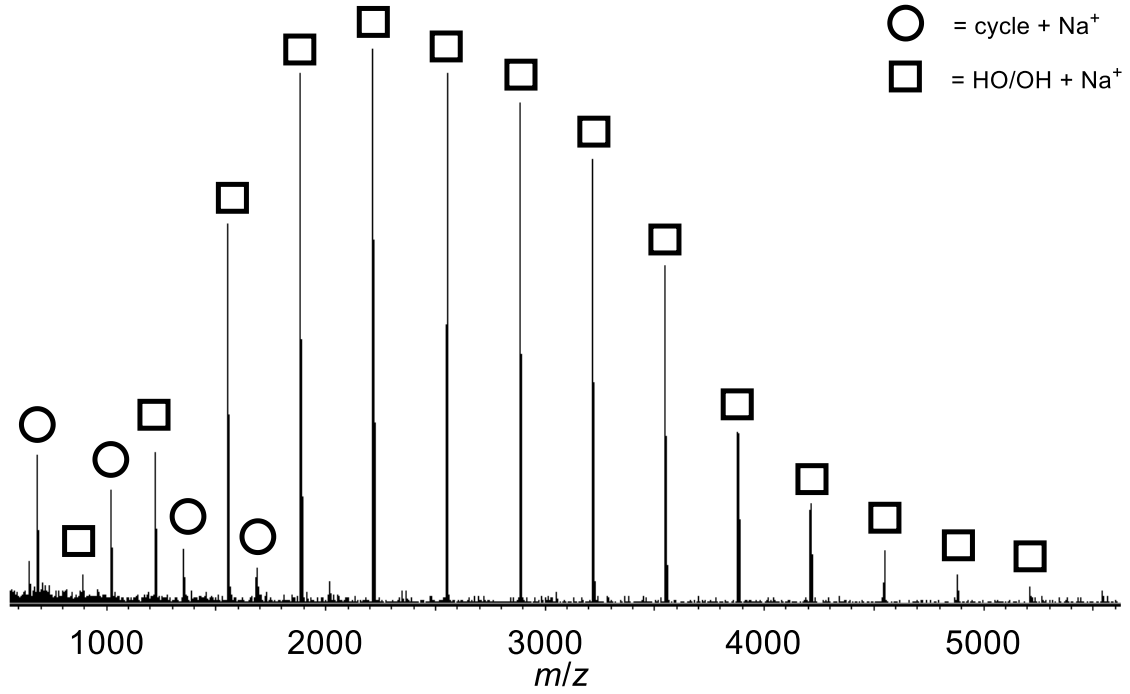


Figure S2. MALDI-TOF mass spectrum of the product obtained by the polymerization of 1.25 equiv of **1a** and 1.0 equiv of **2a** with 5 mol% of ^{t}BuOK in diglyme ([**2a**]$_0$ = 0.6

mol/L) at 120 ºC under reduced pressure (90-100 Torr) for 1 day (Table 1, Entry 2).

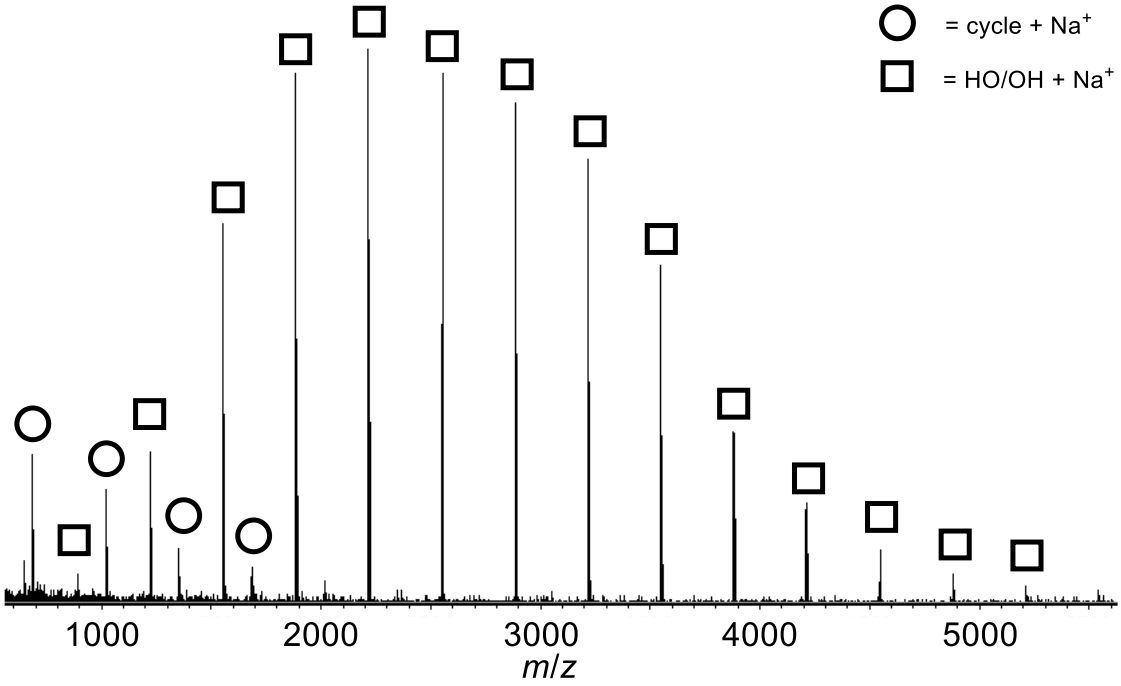


Figure S3. MALDI-TOF mass spectrum of the product obtained by the polymerization of 1.20 equiv of **1a** and 1.0 equiv of **2a** with 5 mol% of ^{t}BuOK in diglyme ([**2a**]$_0$ = 1.0 mol/L) at 120 ºC under reduced pressure (90-100 Torr) for 1 day (Table 1, Entry 3).

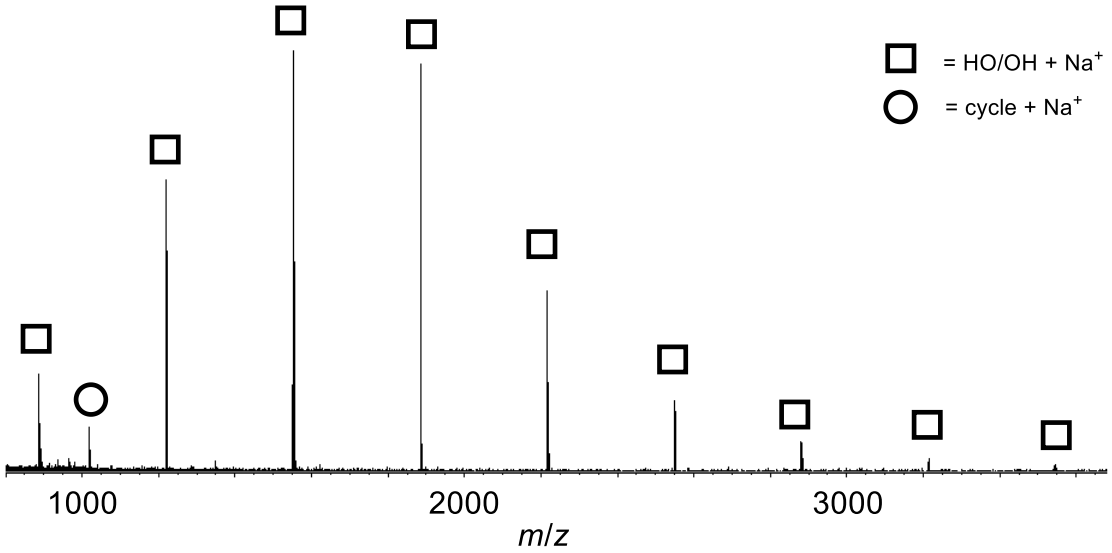


Figure S4. MALDI-TOF mass spectrum of the product obtained by the polymerization of 1.14 equiv of **1a** and 1.0 equiv of **2a** with 5 mol% of ^{t}BuOK in diglyme ([**2a**]$_0$ = 2.0 mol/L) at 120 ºC under reduced pressure (90-100 Torr) for 1 day (Table 1, Entry 5).

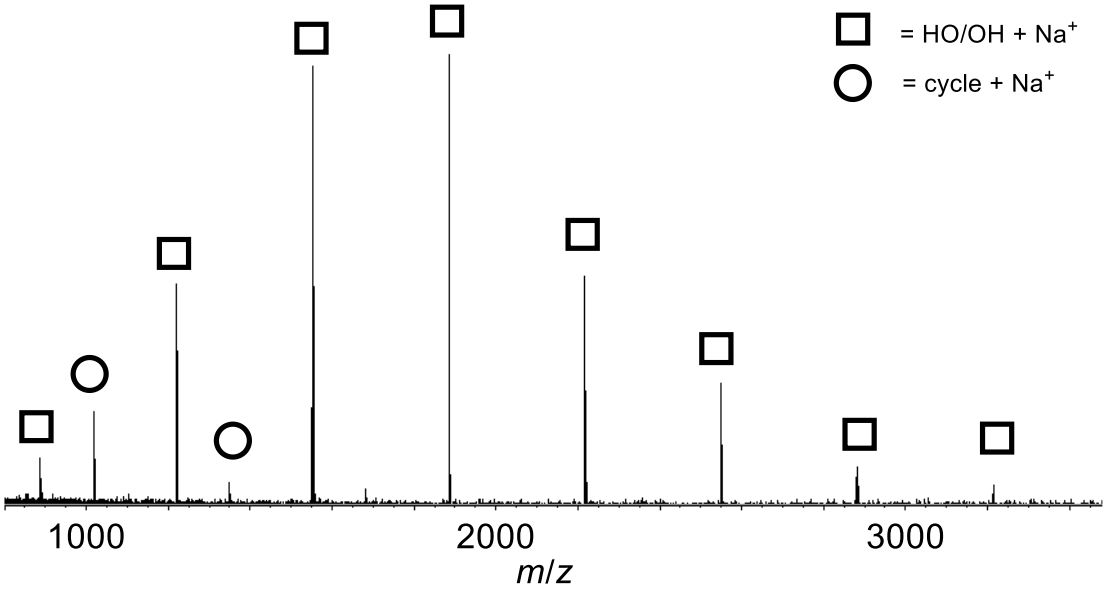


Figure S5. MALDI-TOF mass spectrum of the product obtained by the polymerization of 1.09 equiv of **1a** and 1.0 equiv of **2a** with 5 mol% of ^{t}BuOK in diglyme ([**2a**]$_0$ = 2.0 mol/L) at 120 ºC under reduced pressure (90-100 Torr) for 1 day (Table 1, Entry 6).

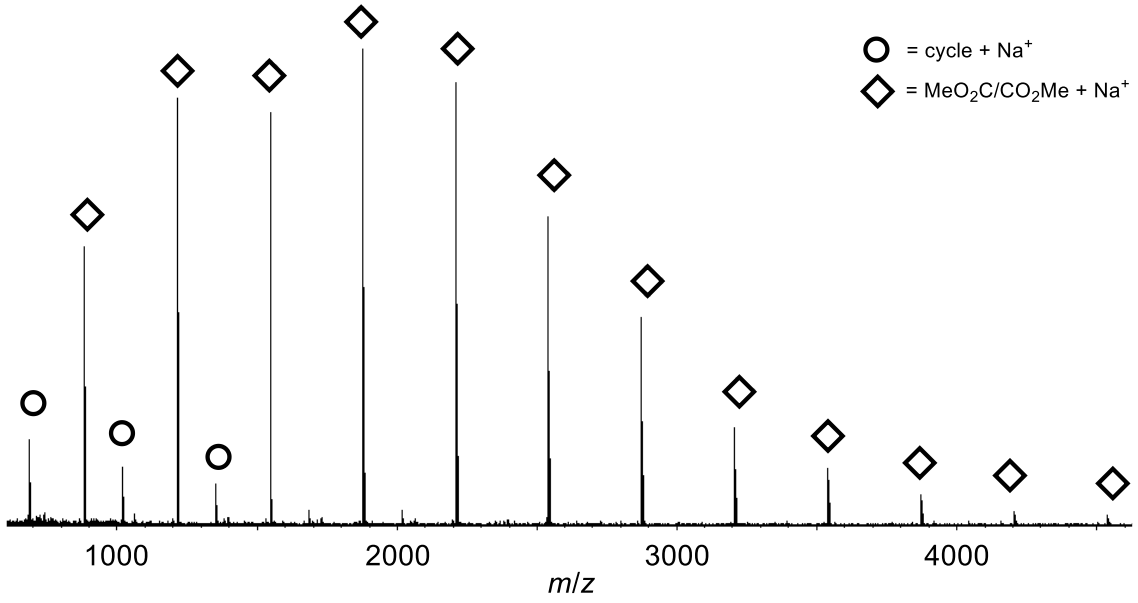


Figure S6. MALDI-TOF mass spectrum of the product obtained by the polymerization of 1.0 equiv of **1a** and 1.2 equiv of **2a** ([**1a**]$_0$/[**2a**]$_0$ = 0.83) with 5 mol% of ^{t}BuOK in diglyme ([**1a**]$_0$ = 0.6 mol/L) at 120 ºC for under reduced pressure (90-100 Torr) 1 day (Table 1, Entry 7).

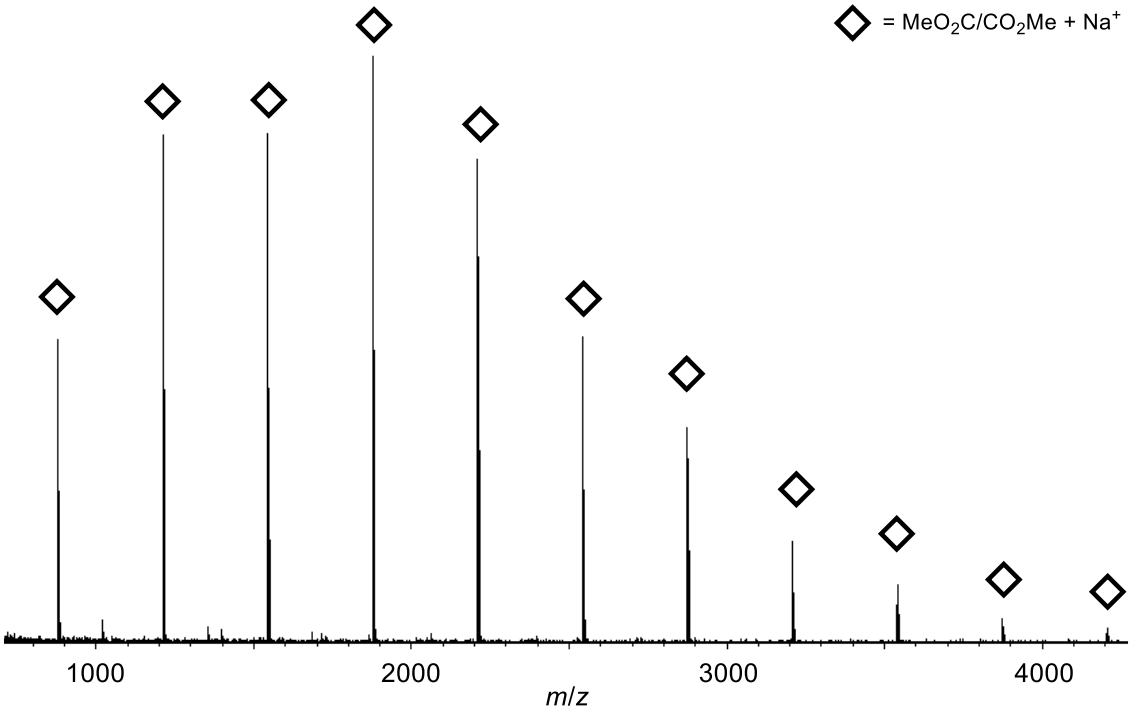
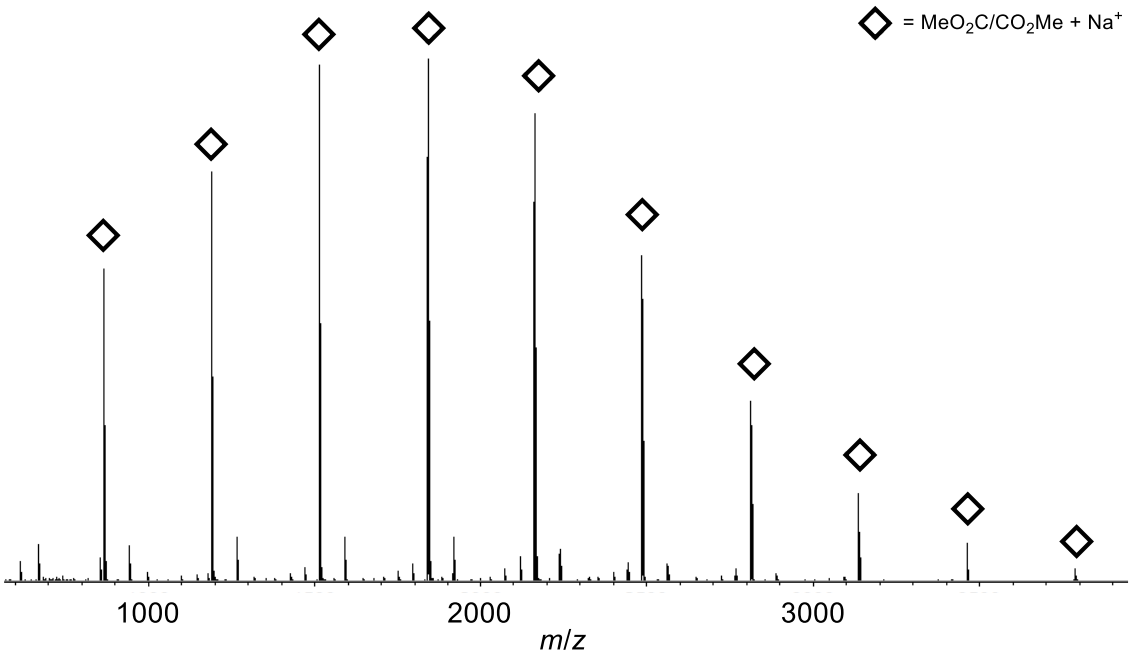


Figure S7. MALDI-TOF mass spectrum of the product obtained by the polymerization of 1.0 equiv of **1a** and 1.3 equiv of **2a** ($[\mathbf{1a}]_0/[\mathbf{2a}]_0$ = 0.77) with 5 mol% of ^{t}BuOK in diglyme ($[\mathbf{1a}]_0$ = 0.6 mol/L) at 120 °C under reduced pressure (90-100 Torr) for 1 day (Table 1, Entry 9).



FigureS8. MALDI-TOF mass spectrum of the product obtained by the polymerization of 1.0 equiv of **1b** and 1.25 equiv of **2a** ([**1b**]$_0$/[**2a**]$_0$ = 0.80) with 5 mol% of ^{t}BuOK and 6 mol% of 18-crown-6 in diglyme ([**1b**]$_0$ = 0.6 mol/L) at 120 °C under reduced pressure (90-100 Torr) for 1 day (Table 1, Entry 10).

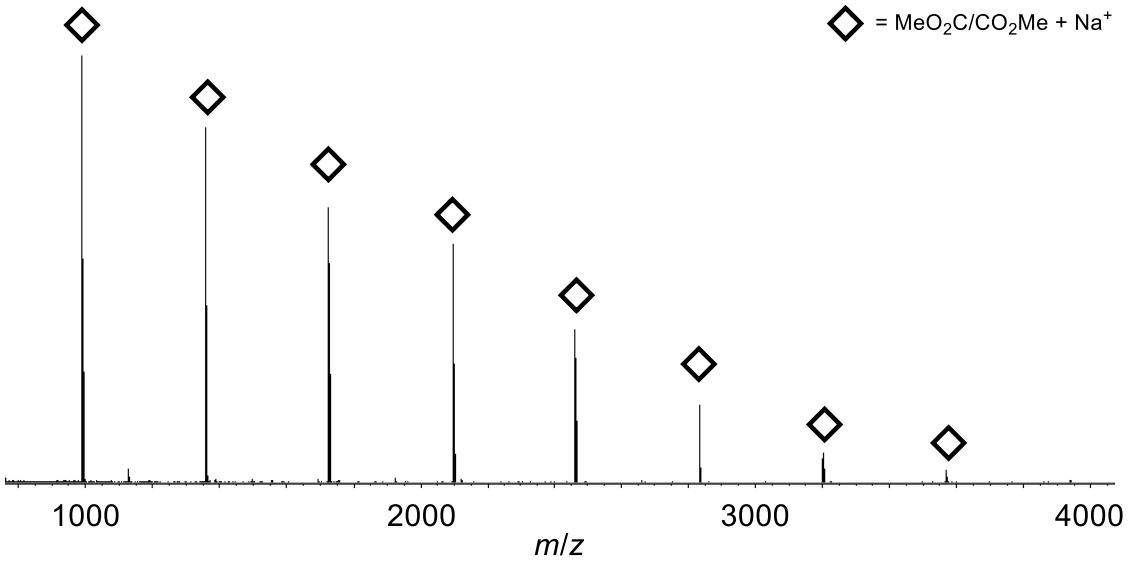


Figure S9. MALDI-TOF mass spectrum of the product obtained by the polymerization of 1.0 equiv of **1a** and 1.25 equiv of **2b** ([**1a**]$_0$/[**2b**]$_0$ = 0.80) with 5 mol% of ^{t}BuOK in diglyme ([**1a**]$_0$ = 0.60 mol/L) at 120 °C under reduced pressure (90-100 Torr) for 1 day (Table 1, Entry 11).

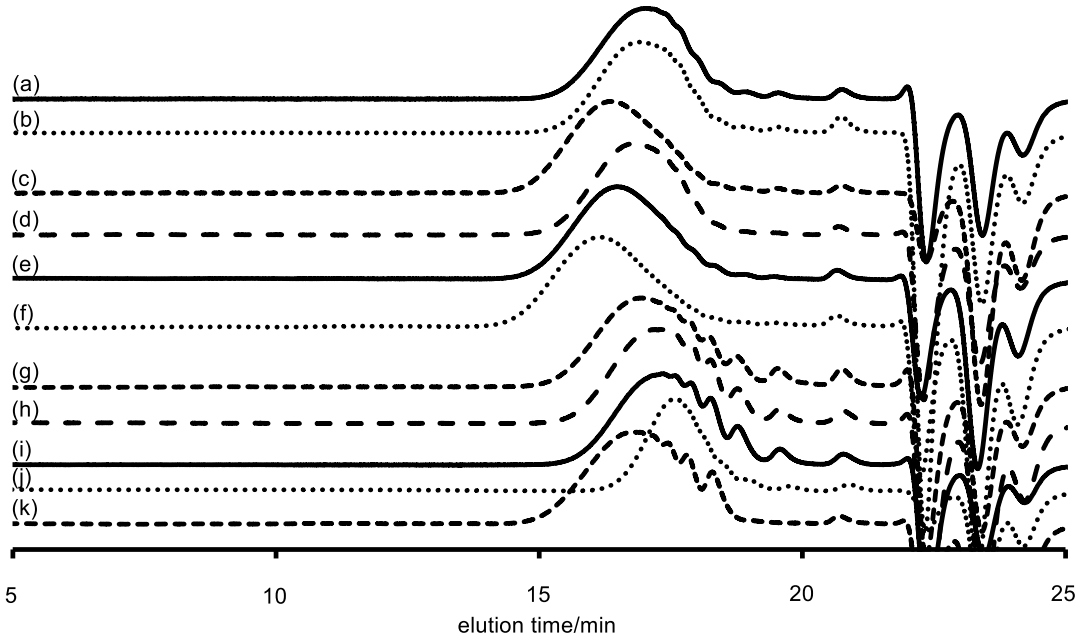


Figure S10. GPC elution curves of products obtained by the polymerization of **1** and **2** with 5 mol% of ^{t}BuOK in diglyme at 120 °C under reduced pressure (90-100 Torr) for 1 day: **1**, **2**, $[\mathbf{1}]_0/[\mathbf{2}]_0$, M_n, and M_w/M_n are(a) **1a**, **2a**, 1.20, 5170, 1.28 (Table 1, Entry 1), (b) **1a**, **2a**, 1.25, 4650, 1.31 (Entry 2), (c) **1a**, **2a**, 1.20, 6430, 1.41 (Entry 3), (d) **1a**, **2a**, 1.20, 5140, 1.31 (Entry 4), (e) **1a**, **2a**, 1.14, 5790, 1.37 (Entry 5), (f) **1a**, **2a**, 1.09, 7260, 1.39 (Entry 6), (g) **1a**, **2a**, 0.83, 4310, 1.45 (Entry 7), (h) **1a**, **2a**, 0.80, 3420, 1.40 (Entry 8), (i) **1a**, **2a**, 0.77, 3290, 1.39 (Entry 9), (j), **1b**, **2a**, 0.80, 3150, 1.16 (Entry 10), (k) **1a**, **2b**, 0.80, 4550, 1.46 (Entry 11).

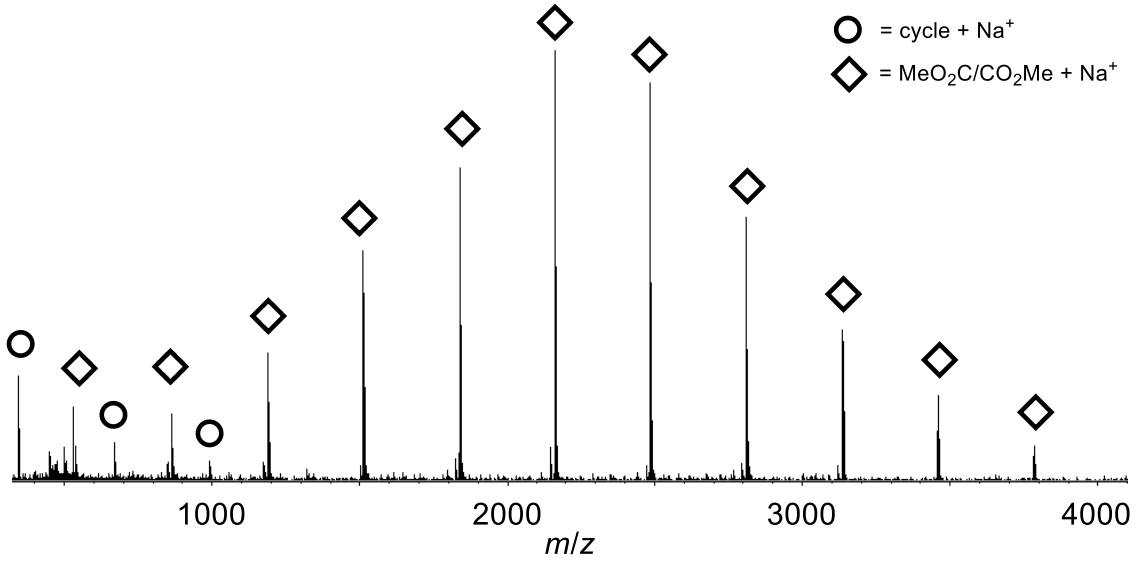


Figure S11. MALDI-TOF mass spectrum of the product obtained by the polymerization of 1.0 equiv of **3b** and 1.25 equiv of **4a** ([**3b**]$_0$/[**4a**]$_0$ = 0.80) with 2.2 equiv of pyridine in CH_2Cl_2 ([**3b**]$_0$ = 0.6 mol/L) at room temperature for 1 day (Table 2, Entry 3).

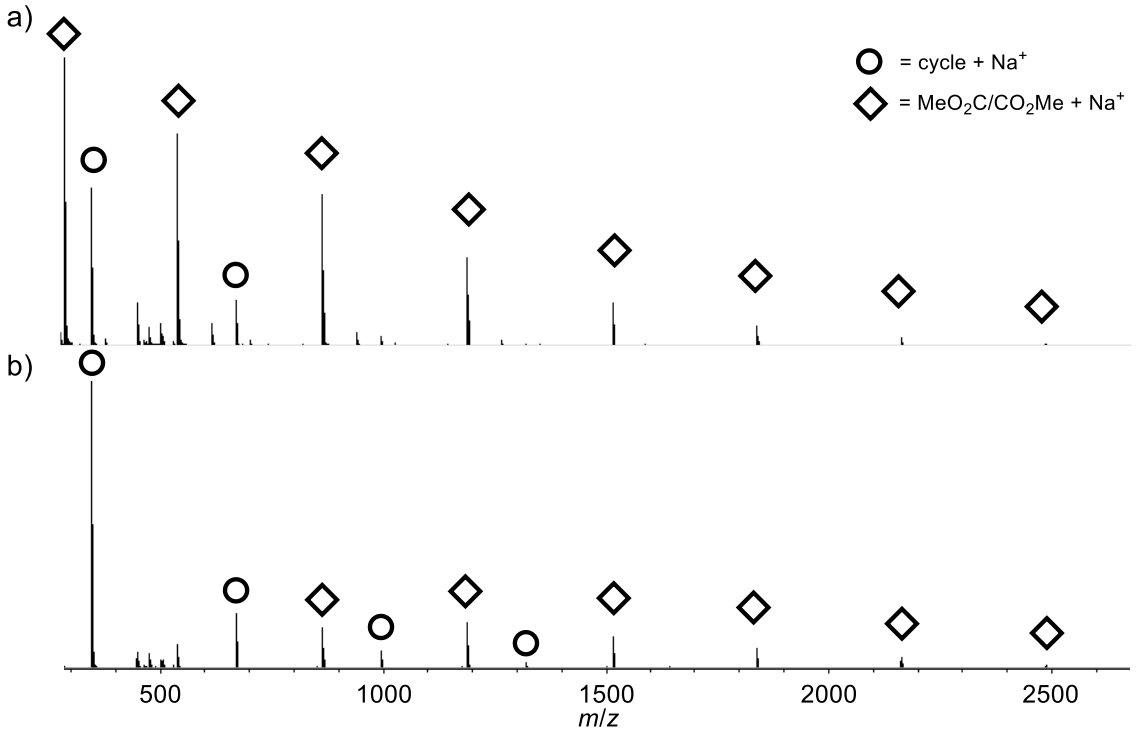


Figure S12. MALDI-TOF mass spectra of products in the methanol soluble part: (a) polymerization of 1.0 equiv of **1b** and 1.25 equiv of **2a** ([**1b**]$_0$/[**2a**]$_0$ = 0.80) in the presence

of 5 mol% of of ^{t}BuOK in diglyme ([**1b**]$_0$ = 0.6 mol/L) at 120 ^{o}C under reduced pressure (90-100 Torr) for 1 day (Table 1, Entry 10), (b) polymerization of 1.0 equiv of **3b** and 1.25 equiv of **4a** ([**3b**]$_0$/[**4a**]$_0$ = 0.80) in the presence of 2.2 equiv of pyridine in CH_2Cl_2 ([**3b**]$_0$ = 0.6 mol/L) at room temperature for 1 day (Table 2, Entry 3).

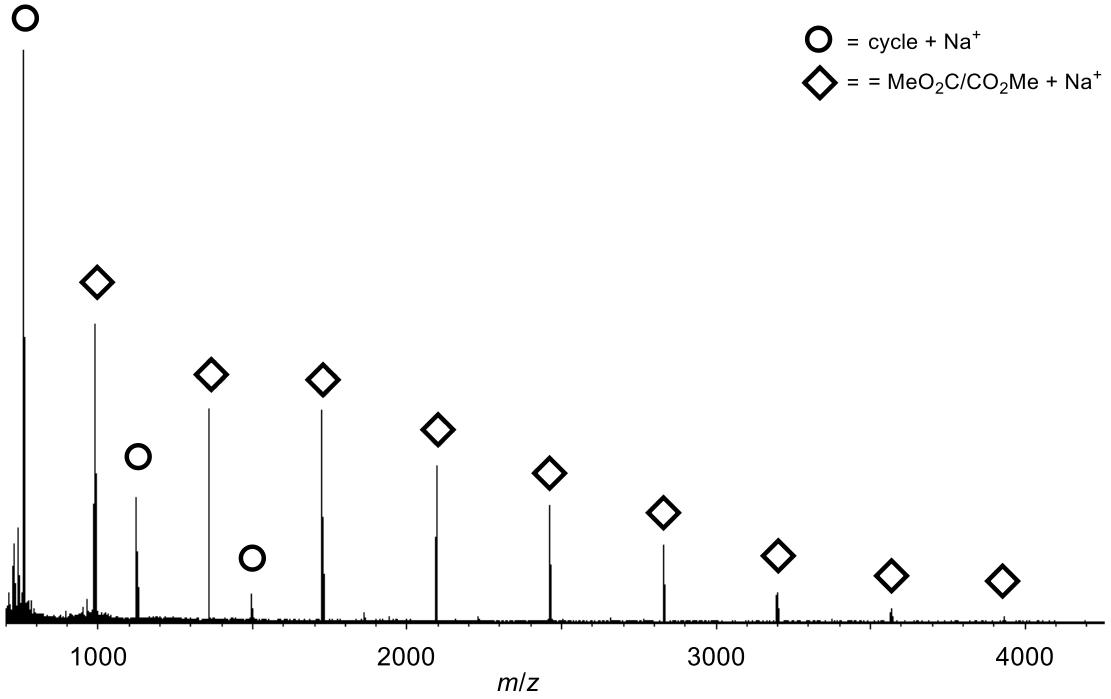


Figure S13. MALDI-TOF mass spectrum of the product obtained by the polymerization of 1.0 equiv of **3a** and 1.25 equiv of **4b** ([**3a**]$_0$/[**4b**]$_0$ = 0.80) with 2.2 equiv of pyridine in CH_2Cl_2 ([**3a**]$_0$ = 0.6 mol/L) at room temperature for 1 day (Table 2, Entry 4).

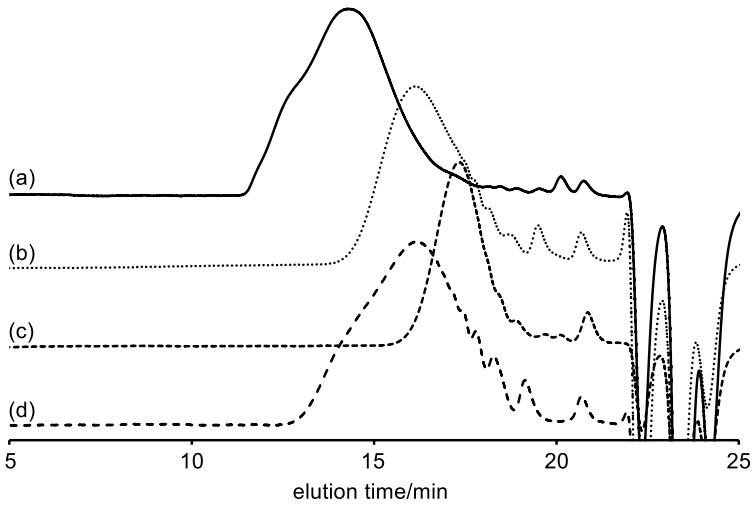


Figure S14. GPC elution curves of products obtained by the irreversible polymerization of **3** and **4** in the presence of 2.2 equiv of pyridine in CH_2Cl_2 at room temperature for 1 day: feed ratio, $M_{n,}$ and M_w/M_n are (a) $[\mathbf{3a}]_0/[\mathbf{4a}]_0$ = 1.18, 24600, 3.61 (Table 2, Entry 1), (b) $[\mathbf{3a}]_0/[\mathbf{4a}]_0$ = 0.80, 6330, 1.62 (Entry 2), (c) $[\mathbf{3b}]_0/[\mathbf{4a}]_0$ = 0.80, 3600, 1.20 (Entry 3), and (d) $[\mathbf{3a}]_0/[\mathbf{4b}]_0$ = 0.80, 7300, 2.40 (Entry 4).

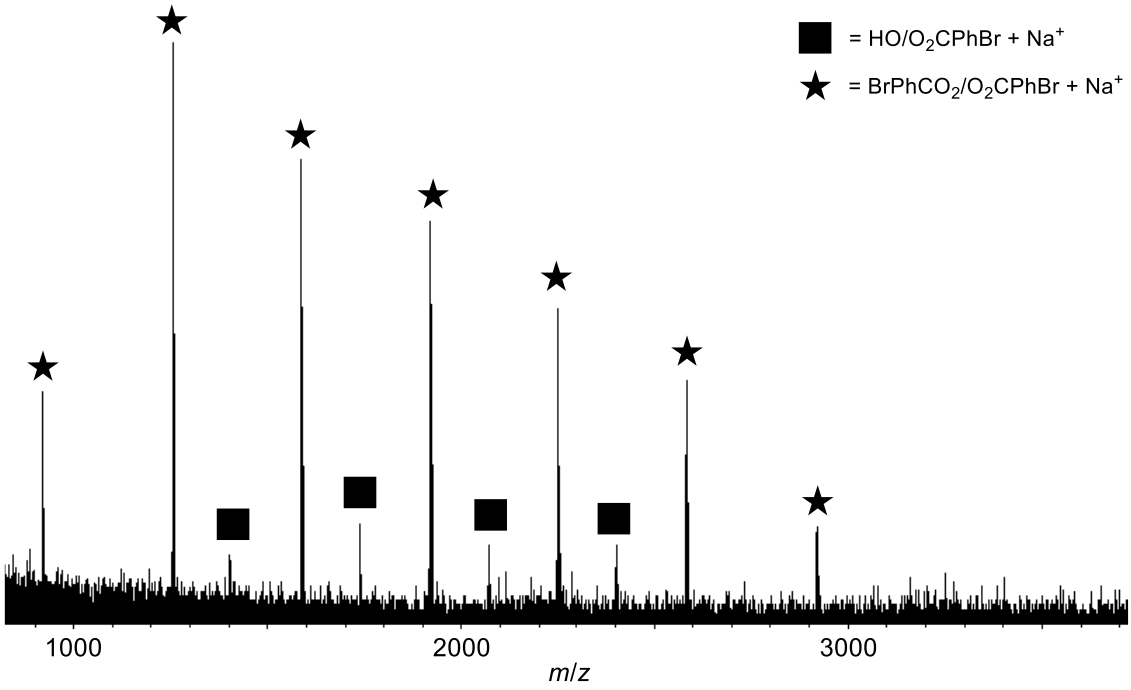


Figure S15. MALDI-TOF mass spectrum of the products obtained by the polymerization of equimolar **1a** and **2a** with 20 mol% of **5a** and 5 mol% of ^{t}BuOK in diglyme ($[\mathbf{2a}]_0$ = 1.0 mol/L) at 120 °C under reduced pressure (90-100 Torr) for 1 day (Table 3, Entry 1).

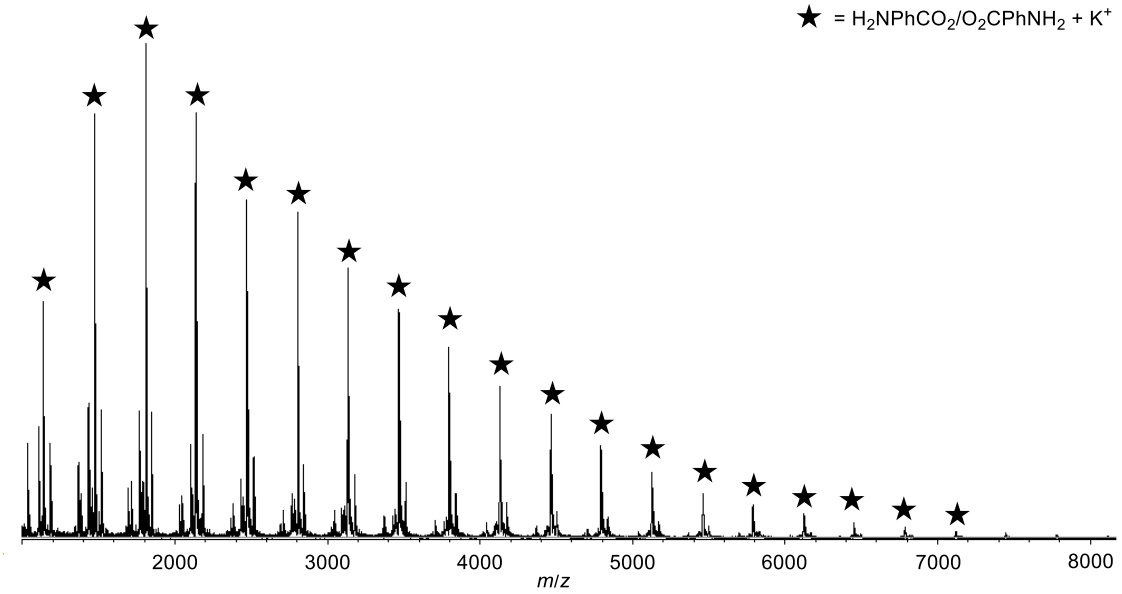


Figure S16. MALDI-TOF mass spectrum of the product by the polymerization of equimolar **1a** and **2a** with 20 mol% **5b** and 5 mol% of ^{t}BuOK in toluene ([**2a**]$_0$ = 1.0 mol/L) at 65 ^{o}C under reduced pressure (90-100 Torr) for 1 day, followed by deprotection with trifluoroacetic acid (Table 3, Entry 2).

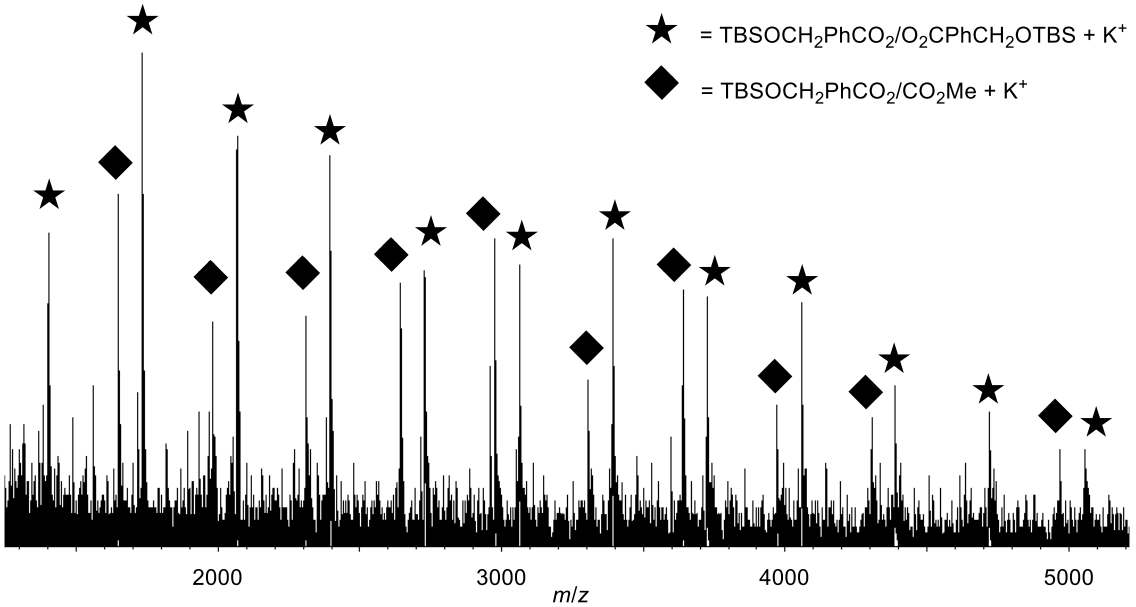


Figure S17. MALDI-TOF mass spectrum of the product by the polymerization of equimolar **1a** and **2a** with 20 mol% of **5c** and 5 mol% of ^{t}BuOK in toluene ([**2a**]$_0$ = 1.0 mol/L) at 65 ^{o}C under reduced pressure (90-100 Torr) for 1 day (Table 3, Entry 3).

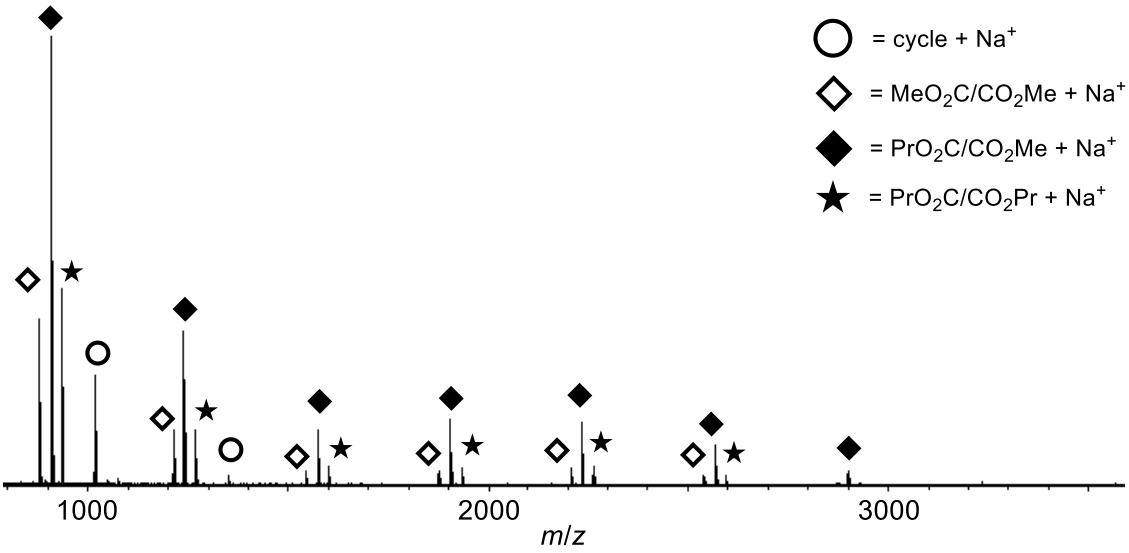


Figure S18. MALDI-TOF mass spectrum of the product obtained by the polymerization of equimolar **1a** and **2a** with 20 mol% of **6a** and 5 mol% of ^{t}BuOK in diglyme ([**2a**]$_0$ = 1.0 mol/L) at 120 °C under reduced pressure (90-100 Torr) for 1 day (Table 3, Entry 4).

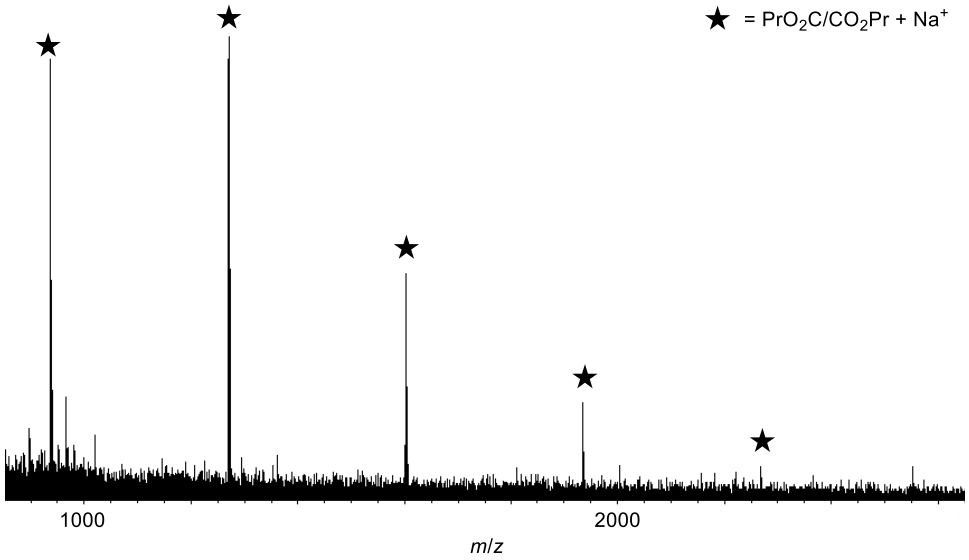


Figure S19. MALDI-TOF mass spectrum of the products obtained by the polymerization of equimolar **1a** and **2a** with 5 mol% of ^{t}BuOK in diglyme ([**2a**]$_0$ = 0.6 mol/L) at 120 °C under reduced pressure (90-100 Torr) for 4 h, followed by addition of a solution of 20 mol% of **6a** and 5 mol% of ^{t}BuOK in diglyme ([**2a**]$_0$ = 0.5 mol/L) and stirring at room temperature for 3 day (Table 3, Entry 5).

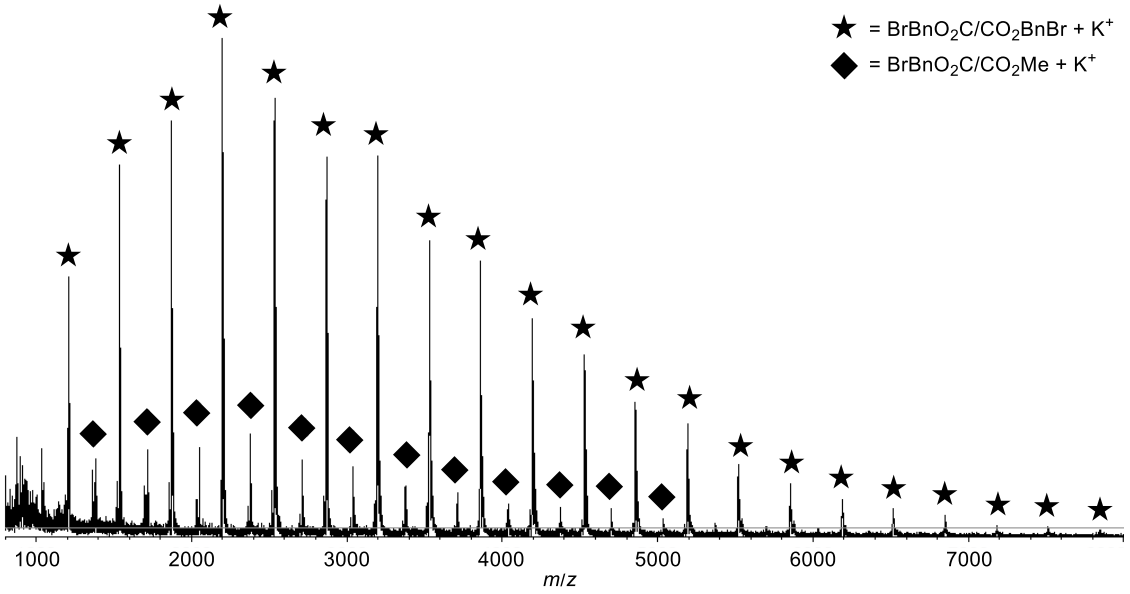


Figure S20. MALDI-TOF mass spectrum of the product by the polymerization of equimolar **1a** and **2a** with 20 mol% of **6c** and 5 mol% of ^{t}BuOK in toluene ([**2a**]$_0$ = 1.0 mol/L) at 65 ^{o}C under reduced pressure (90-100 Torr) for 1 day (Table 3, Entry 7).

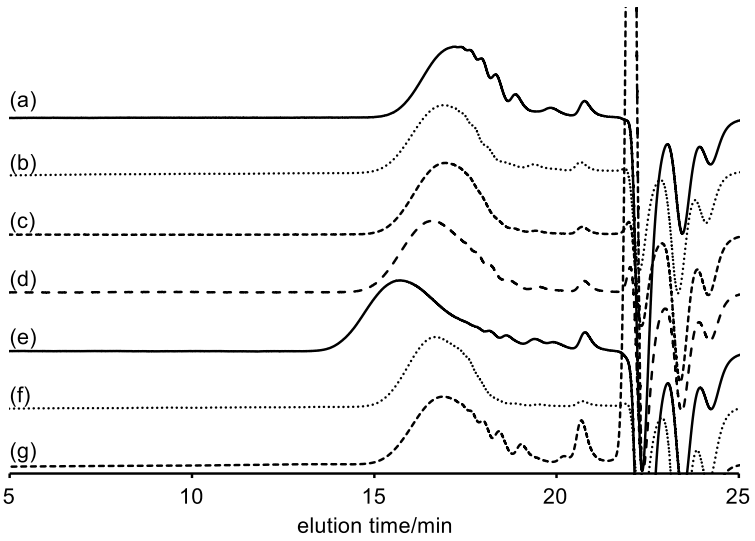


Figure S21. GPC elution curves of products obtained by the polymerization of equimolar of **1a** and **2a** was carried out in the presence of 20 mol% of ExR and 5 mol% of ^{t}BuOK in diglyme: ExR, M_n, and M_w/M_n are (a) **5a**, 3740, 1.41 (Table 3, Entry 1), (b) **5b**, 4630, 1.38 [after deprotection] (Entry 2), (c) **5c**, 4600, 1.32 (Entry 3), (d) **6a**, 4880, 1.65 (Entry 4), (e) **6a**, 4480, 2.87 (Entry 5), (f) **6b**, 5410, 1.32 (Entry 6), and (g) **6c**, 2940, 1.50 (Entry 7).

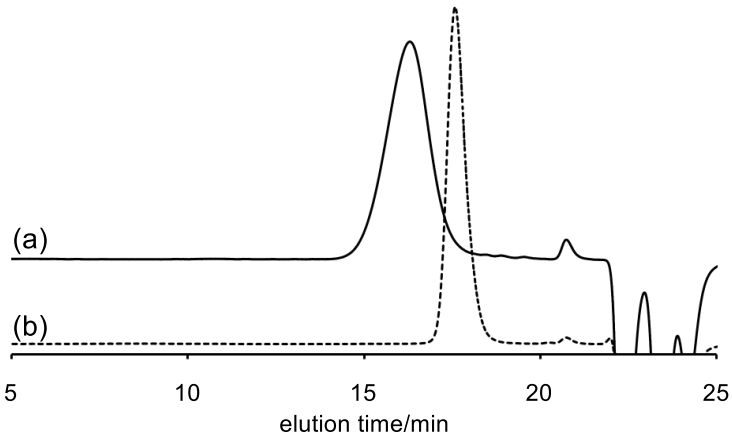


Figure S22. GPC elution curves of (a) the product obtained by the polymerization of equimolar **1a** and **2a** with 20 mol% of **6d** and 5 mol% of ^{t}BuOK in toluene ([**2a**]$_0$ = 1.0 mol/L) at 65 ^{o}C under reduced pressure (90-100 Torr) for 1 day (Table 3, Entry 8, M_n =8570, M_w/M_n = 1.20) and (b) **6d**.

References

1. Y. Ohta, Y. Kamijyo, S. Fujii, A. Yokoyama and T. Yokozawa, *Macromolecules*, 2011, **44**, 5112-5122.
2. T. O. Lopes, D. A. da Silva Filho, A. A. M. Lapis, H. C. B. de Oliveira and B. A. D. Neto, *J. Phys. Org. Chem.*, 2014, **27**, 303-309.
3. F. Mu, S. L. Coffing, D. J. Riese, R. L. Geahlen, P. Verdier-Pinard, E. Hamel, J. Johnson and M. Cushman, *J. Med. Chem.*, 2001, **44**, 441-452.
4. E. A. A. Wallén, J. A. M. Christiaans, M. M. Forsberg, J. I. Venäläinen, P. T. Männistö and J. Gynther, *J. Med. Chem.*, 2002, **45**, 4581-4584.
5. A. Borissov, I. Marques, J. Y. C. Lim, V. Félix, M. D. Smith and P. D. Beer, *J. Am. Chem. Soc.*, 2019, **141**, 4119-4129.