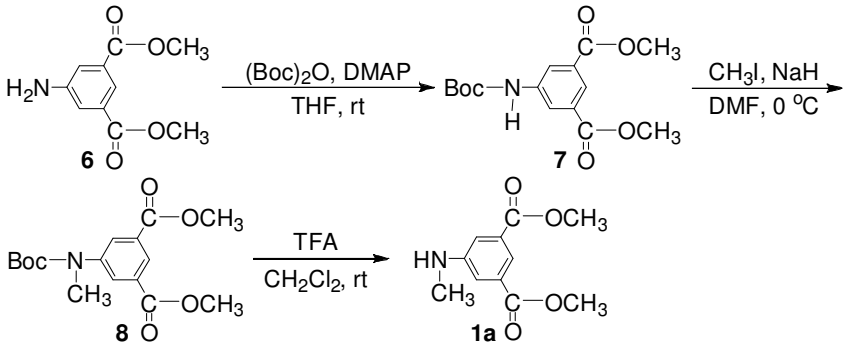
Supporting Information

Synthesis and Properties of a Variety of Well-Defined Hyperbranched *N*-Alkyl and *N*-H Polyamides by Chain-Growth Condensation Polymerization of AB_2 Monomers

*Yoshihiro Ohta, Yusuke Kamijyo, Shuichi Fujii, Akihiro Yokoyama, and Tsutomu Yokozawa**

Department of Material and Life Chemistry, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

Synthesis of 5-(methylamino)isophthalic acid methyl ester 1a.



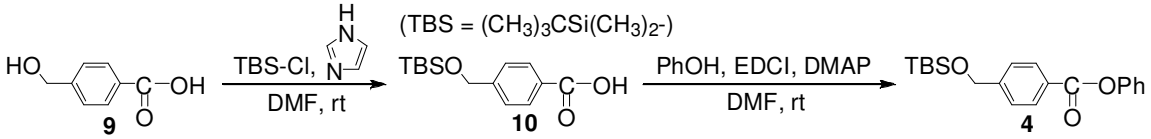
Scheme S1

Compound 7. Into a solution of 5-aminoisophthalic acid methyl ester **6** (5.23 g, 25.0 mmol) and 4-(dimethylamino)pyridine (DMAP) (3.91 g, 32.0 mmol) in dry THF (100 mL) was added di-*tert*-butyl dicarbonate (6.67 g, 30.6 mmol) at 0 °C. The mixture was stirred at 0 °C for 19 h, then the reaction was quenched with water and the whole was extracted with ether. The combined organic layers were washed with 1M HCl and water, and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 3/1) to give 5.86 g of **7** as a white solid (76%): mp 155.9-157.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (t, *J* = 1.4 Hz, 1 H), 8.26 (d, *J* = 1.1 Hz, 2 H), 6.77 (br s, 1 H), 3.94 (s, 6 H), 1.54 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 152.4, 139.1, 131.3, 125.1, 123.3, 83.5, 52.4, 28.3; IR (KBr) 3365, 2953, 1734, 1707, 1609, 1550, 1440, 1392, 1366, 1352, 1320, 1270, 1252, 1161, 1004 cm^{-1}.

Compound 8. Into a suspension of NaH (0.467 g, 19.5 mmol) in dry DMF (80 mL) was added a solution of 5-(*N*-*tert*-butoxycarbonylamino)isophthalic acid methyl ester **7** (5.02 g, 16.2 mmol) in dry DMF (20 mL) at 0 °C. The mixture was stirred at 0 °C for 40 min and then iodomethane (2.02 mL, 32.4 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 4 h, then the reaction was quenched with water, followed by extraction with ether. The combined organic layers were washed with 1 M HCl and water, and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to give 4.89 g of 5-(*N*-methyl-*N*-*tert*-butoxycarbonylamino)isophthalic acid methyl ester as a white solid (93%): mp 177.4-179.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (t, *J* = 1.4 Hz, 1 H), 8.13 (d, *J* = 1.4 Hz, 2 H), 3.95 (s, 6 H), 3.32 (s, 3 H), 1.47 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 154.1, 144.3, 130.9, 130.3, 127.1, 81.2, 52.5, 36.9, 28.2; IR (KBr) 2974, 1737, 1700, 1595, 1479, 1428, 1362, 1315, 1252, 1159, 1004, 756 cm^{-1}.

5-(methylamino)isophthalic acid methyl ester 1a. Into a solution of 5-(*N*-methyl-*N*-*tert*-butoxycarbonylamino)isophthalic acid methyl ester (5.61 g, 17.4 mmol) in dry CH_2Cl_2 (14 mL) was added trifluoroacetic acid (10 mL) at 0 ^oC. The mixture was stirred at 0 ^oC for 16 h, then the reaction was quenched with sat. $NaHCO_3$ and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 3/1) to give 3.41 g of **1a** as a slightly yellow solid (88%): mp 155.9-156.9 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (t, *J* = 1.4 Hz, 1 H), 7.43 (d, *J* = 1.4 Hz, 2 H), 4.03 (br s, 1 H), 3.92 (s, 6 H), 2.91 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 149.3, 131.3, 119.2, 117.0, 52.2, 30.6; IR (KBr) 3403, 2954, 1721, 1699, 1602, 1531, 1483, 1438, 1365, 1260, 1006, 755 cm^{-1}.

Synthesis of monofunctional initiator 4.



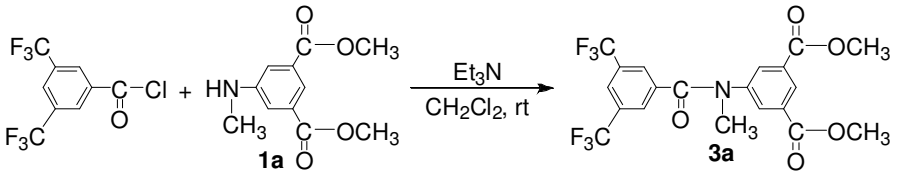
Scheme S2

Compound 10. Into a solution of imidazole (0.538 g, 7.90 mmol) and *tert*-butyldimethylchlorosilane (1.09 g, 7.23 mmol) in dry DMF (2.0 mL) at room temperature was slowly added a solution of 4-hydroxymethylbenzoic acid **9** (0.501 g, 3.29 mmol) in dry DMF (3.0 mL). The solution was stirred at room temperature for 15 h, and then the reaction was quenched with water and the whole was extracted with ether. The combined organic layers were washed with sat. $NaHCO_3$, water and brine, and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane, hexane/ethyl acetate = 10/1, hexane/ethyl acetate = 3/1) to give 0.407 g of **10** as a white solid (46%): mp 154.3-156.9 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 2 H), 7.43 (d, *J* = 8.2 Hz, 2 H), 4.82 (s, 2 H), 0.96 (s, 9 H), 0.12 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.0, 147.8, 130.2, 127.9, 125.7, 64.5, 25.9, 18.4, -5.3; IR (KBr) 3449, 2928, 2857, 1686, 1255, 1090, 1019, 835 cm^{-1}.

Monofunctional initiator 4. Into a solution of **10** (0.348 g, 1.31 mmol), phenol (0.281 g, 2.99 mmol) and DMAP (0.196 g, 1.60 mmol) in dry CH_2Cl_2 (5.0 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (0.305 g, 1.59 mmol) at 0 ^oC. The mixture was stirred at room temperature for 15 h, then the reaction was quenched with water. The whole was extracted with CH_2Cl_2, and the combined organic layers were washed with 1 M HCl and sat. $NaHCO_3$,

followed by drying over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/$CHCl_2$ = 2/1) to give 0.213 g of **4** as a viscous colorless oil (47%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.6 Hz, 2 H), 7.46 (d, *J* = 8.6 Hz, 2 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.27 (t, *J* = 7.4 Hz, 1 H), 7.22 (d, *J* = 8.7 Hz, 2 H), 4.83 (s, 2 H), 0.96 (s, 9 H), 0.13 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.2, 151.0, 147.6, 130.2, 129.5, 128.1, 125.84, 125.82, 121.8, 64.5, 25.9, 18.4, -5.3; IR (neat) 2954, 2929, 1739, 1265, 1198, 1070, 839, 743, 688 cm^{-1}.

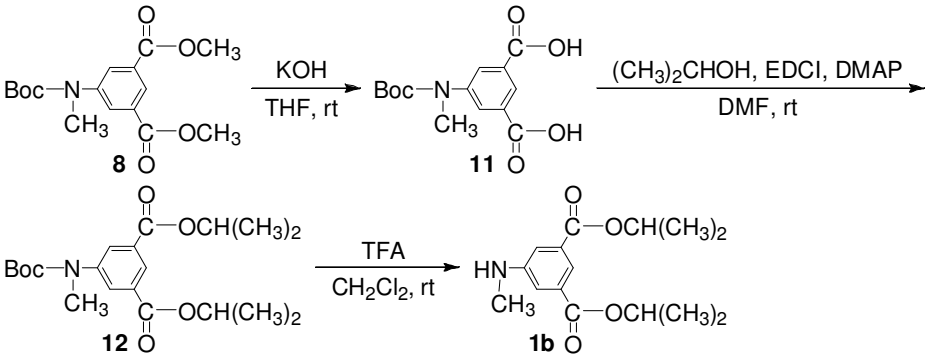
Synthesis of bifunctional initiator 3a.



Scheme S3

Bifunctional initiator 3a. Into a solution of **1a** (0.117 g, 0.524 mmol) and triethylamine (0.08 mL, 0.58 mmol) in dry CH_2Cl_2 (10 mL) at 0 ^{o}C was slowly added a solution of 3,5-bis(trifluoromethyl)benzoyl chloride (0.160 g, 0.579 mmol) in dry CH_2Cl_2 (10 mL). The solution was stirred at room temperature for 3 h, and then the reaction was quenched with water and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with 1 M HCl and sat. $NaHCO_3$, and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (CH_2Cl_2) to give 0.207 g of **3a** as a slightly yellow solid (85%): mp 126.5-128.8 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (t, *J* = 1.4 Hz, 1 H), 7.93 (s, 2 H), 7.78 (s, 1 H), 7.76 (s, 2 H), 3.92 (s, 6 H), 3.56 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4, 164.8, 144.2, 137.2, 132.2, 131.7, 131.6 (q, *J* = 34.0 Hz), 129.2, 128.9-128.8 (m), 123.6-123.5 (m), 122.6 (q, *J* = 273 Hz), 52.7, 38.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ 98.6; IR (KBr) 3075, 2958, 2856, 1720, 1656, 1617, 1599, 1446, 1396, 1360, 1339, 1282, 1256, 1196, 1174, 1129, 1052, 1052, 987, 753 cm^{-1}.

Synthesis of 5-(methylamino)isophthalic acid isopropyl ester 1b.



Scheme S4

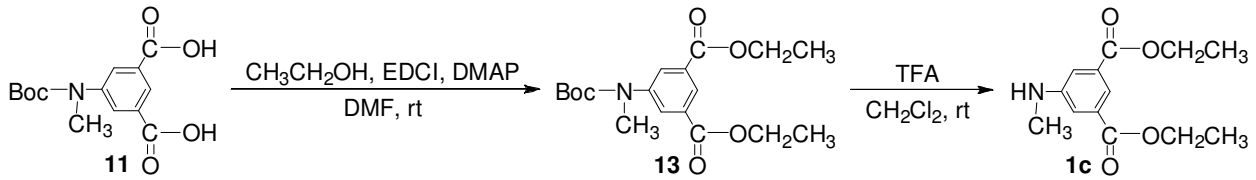
Compound 11. A mixture of **8** (4.51 g, 13.9 mmol) and KOH (8.07 g, 122 mmol) in THF (30 mL) and water (5 mL) was stirred at room temperature for 25 h. The reaction was quenched with 1 M HCl, and the whole was extracted with ether. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to give 3.90 g of **11** as a white solid (95%): mp 275.7-277.5 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.35 (br s, 2 H), 8.25 (t, J = 1.5 Hz, 1 H), 8.05 (d, J = 1.5 Hz, 2 H), 3.26 (s, 3 H), 1.41 (s, 9 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 166.2, 153.4, 144.0, 131.6, 129.3, 126.1, 80.3, 36.5, 27.8; IR (KBr) 3449, 2979, 1707, 1602, 1460, 1431, 1359, 1280, 1252, 1155, 1118, 760 cm^{-1}.

Compound 12. Into a solution of **11** (2.00 g, 6.77 mmol), dry 2-propanol (1.15 mL, 15.1 mmol), and DMAP (1.83 g, 15.0 mmol) in dry CH_2Cl_2 (40 mL) was added EDCI (3.03 g, 15.8 mmol) at 0 ^{o}C. The mixture was stirred at room temperature for 40 h, then the reaction was quenched with water. The whole was extracted with CH_2Cl_2, and the combined organic layers were washed with 1 M HCl, sat. $NaHCO_3$, and brine, followed by drying over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 5/1) to give 2.07 g of **12** as a viscous colorless oil (80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (t, J = 1.7 Hz, 1 H), 8.08 (d, J = 1.7 Hz, 2 H), 5.29 (sept, J = 6.3 Hz, 2 H), 3.32 (s, 3 H), 1.47 (s, 9 H), 1.38 (d, J = 6.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 154.2, 144.1, 131.6, 130.2, 127.0, 81.0, 69.0, 36.9, 28.2, 21.9; IR (neat) 3630, 2980, 2935, 1718, 1602, 1454, 1368, 1242, 1155, 1108, 1011, 956, 883, 760 cm^{-1}.

5-(methylamino)isophthalic acid isopropyl ester 1b. Into a solution of **12** (2.05 g, 5.40 mmol) in dry CH_2Cl_2 (20 mL) was added trifluoroacetic acid (5.0 mL) at 0 ^{o}C. The mixture was stirred at room temperature for 20 h, then the reaction was quenched with sat. $NaHCO_3$ and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. the solvent was removed in vacuo to give 1.48 g of **1b** as a white solid (88%): mp 81.1-82.7 ^{o}C; ^{1}H

NMR (500 MHz, $CDCl_3$) δ 7.98 (t, *J* = 1.4 Hz, 1 H), 7.42 (d, *J* = 1.4 Hz, 2 H), 5.25 (sept, *J* = 6.3 Hz, 2 H), 3.99 (br s, 1 H), 2.91 (s, 3 H), 1.37 (d, *J* = 6.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 149.2, 132.0, 119,0 116.9, 68.6, 30.7, 21.9; IR (KBr) 3408, 2981, 1704, 1608, 1523, 1373, 1319, 1253, 1118, 1091, 993, 963, 952, 883, 752 cm^{-1}.

Synthesis of 5-(methylamino)isophthalic acid ethyl ester 1c.

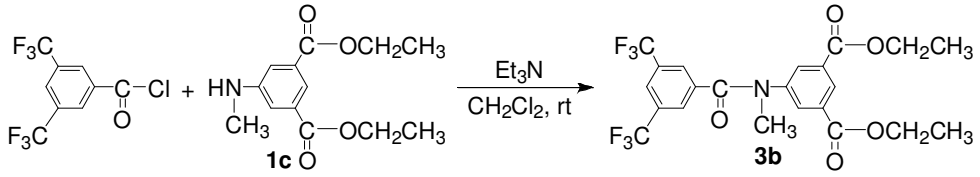


Scheme S5

Compound 13. Into a solution of **11** (4.45 g, 15.1 mmol) in dry DMF (40 mL) was added DMAP (4.06 g, 33.2 mmol), dry ethanol (1.95 mL, 33.4 mmol), and EDCI (6.70 g, 35.0 mmol) was added at 0 ^oC. The mixture was stirred at room temperature for 7.5 h, then the reaction was quenched with water. The whole was extracted with ether, and the combined organic layers were washed with 1 M HCl, sat. $NaHCO_3$, and brine, followed by drying over anhydrous $MgSO_4$. The solvent was removed in vacuo to give 4.61 g of **13** as a viscous yellow oil (87%); ^1H NMR (500 MHz, $CDCl_3$) δ 8.47 (t, *J* = 1.4 Hz, 1 H), 8.11 (d, *J* = 1.7 Hz, 2 H), 4.41 (q, *J* = 7.2 Hz, 4 H), 3.32 (s, 3 H), 1.47 (s, 9 H), 1.42 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 154.2, 144.2, 131.3, 130.2, 127.1, 81.1, 61.4, 36.9, 28.2, 14.3; IR (neat) 3086, 2979, 1724, 1603, 1455, 1369, 1350, 1238, 1153, 1028, 894, 863, 758, 703 cm^{-1}.

5-(methylamino)isophthalic acid ethyl ester 1c. Into a solution of **13** (4.53 g, 12.9 mmol) in dry CH_2Cl_2 (20 mL) was added trifluoroacetic acid (5 mL) at 0 ^oC. The mixture was stirred at room temperature for 19 h, then the reaction was quenched with sat. $NaHCO_3$ and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 3/1) to give 2.67 g of **1a** as a white solid (82%): mp 82.0-83.0 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (t, *J* = 1.4 Hz, 1 H), 7.43 (d, *J* = 1.4 Hz, 2 H), 4.38 (q, *J* = 7.2 Hz, 4 H), 4.01 (br s, 1 H), 2.91 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 149.3, 131.6, 119.0, 116.9, 61.1, 30.6, 14.3; IR (KBr) 3403, 2980, 1715, 1692, 1609, 1528, 1473, 1373, 1315, 1267, 1235, 1137, 1085, 1025, 988, 894, 866, 756 cm^{-1}; HRMS (M + Na^+) (ESI) calcd for $C_{13}H_{17}NO_4\ Na^+$ 274.1055, found 274.1009.

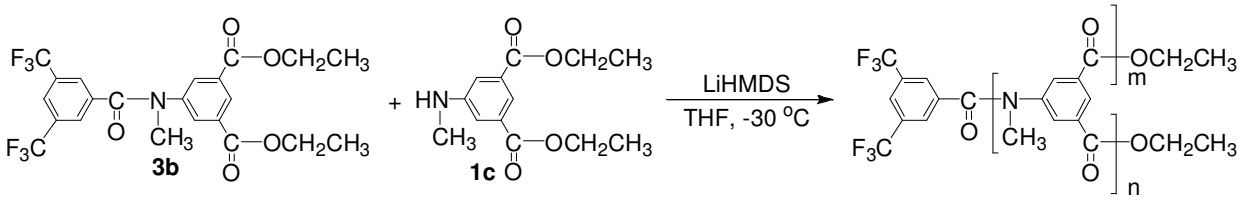
Synthesis of bifunctional initiator 3b.



Scheme S6

Bifunctional initiator 3b. Into a solution of **1c** (0.200 g, 0.796 mmol) and triethylamine (0.140 mL, 1.01 mmol) in dry CH_2Cl_2 (5.0 mL) at 0 ^oC was slowly added a solution of 3,5-bis(trifluoromethyl)benzoyl chloride (0.264 g, 0.955 mmol) in dry CH_2Cl_2 (5.0 mL). The solution was stirred at room temperature for 15 h, and then the reaction was quenched with water and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with 1 M HCl and sat. $NaHCO_3$, and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (CH_2Cl_2) to give 0.336 g of **3b** as a white solid (86%): mp 77.0-78.5 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.51 (t, *J* = 1.4 Hz, 1 H), 7.91 (s, 2 H), 7.82-7.70 (m, 3 H), 4.37 (q, *J* = 7.2 Hz, 4 H), 3.57 (s, 3 H), 1.37 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4, 164.4, 144.0, 137.3, 132.5, 131.6 (q, *J* = 34.0 Hz), 131.5, 129.2, 128.9-128.8 (m), 123.6-123.5 (m), 122.6 (q, *J* = 273.1 Hz), 61.8, 38.4, 14.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ 98.6; IR (KBr) 3430, 2986, 1725, 1657, 1603, 1352, 1334, 1279, 1250, 1198, 1173, 1126, 1050, 1024, 906, 757 cm^{-1}; HRMS (M + Na^+) (ESI) calcd for $C_{22}H_{19}F_6NO_5Na^+$ 514.1065, found 514.1038.

Polymerization of 1c with 3b in the absence of LiCl.

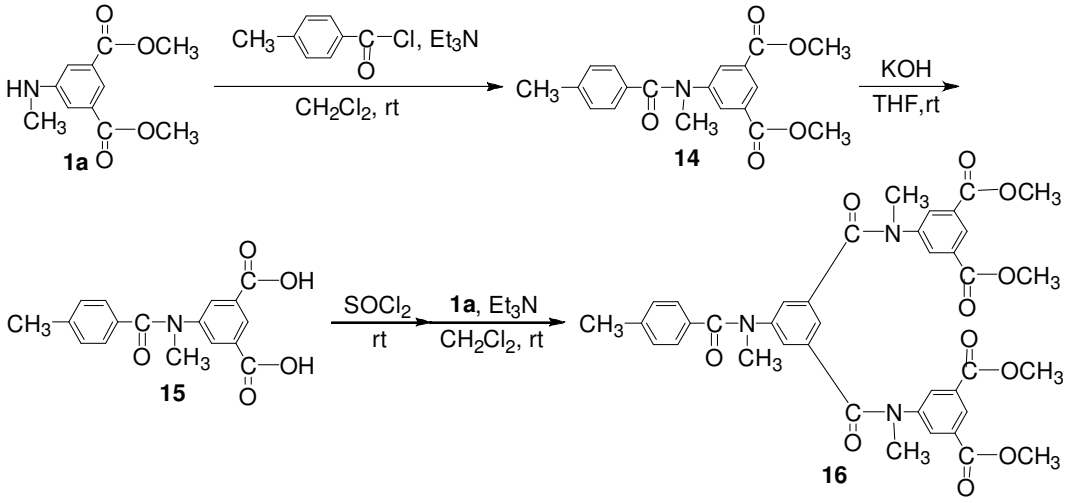


Scheme S7

A flask, equipped with a three-way stopcock, was purged with argon and then charged with 1.0 M LiHMDS in THF (0.720 mL, 0.720 mmol). The flask was cooled to -30 ^oC under an argon atmosphere with stirring. Into the flask was added a solution of **3a** (0.0212 g, 0.0431 mmol) and naphthalene (internal standard, 0.0102 g, 0.0796 mmol) in dry THF (1.0 mL) under dry nitrogen, followed by a solution of **1a** (0.163 g, 0.649 mmol) in dry THF (4.0 mL) dropwise over ca. 40 min at -30 ^oC with stirring under dry nitrogen. The mixture was stirred at -30 ^oC for 1 h, then the reaction was quenched with sat. NH_4Cl. A small portion of the THF layer was withdrawn by a syringe and analyzed by GC to

determine the conversion of **3a** and **1a** (conversion = 100%), and the whole was extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (2.0 mL), and the solution was added to hexane (150 mL). After filtration, the insoluble material was washed with hexane, and dried in desiccator to give HBPA as a white solid (0.126 g, 82%, M_n(MALLS) = 3500, M_w/M_n = 1.28)

Synthesis of model compound of D and T unit 16.



Scheme S8

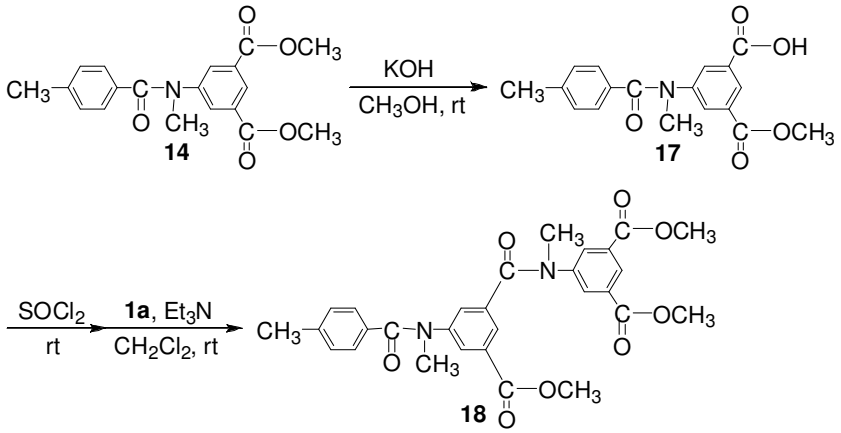
Compound 14. Into a solution of **1a** (0.303 g, 1.36 mmol) and triethylamine (0.210 mL, 1.51 mmol) in dry CH_2Cl_2 (10.0 mL) at 0 ^oC was added dropwise a solution of *p*-toluoyl chloride (0.254 g, 1.64 mmol) in dry CH_2Cl_2 (5.0 mL). After stirring at room temperature for 19 h, the reaction was quenched with water, and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with water and sat. $NaHCO_3$, and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 4/1) to give 0.420 g of **14** as a white solid (91%): mp 126.3-127.7 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 8.45 (s, 1 H), 7.92 (s, 2 H), 7.20 (d, J = 7.9 Hz, 2 H), 6.99 (d, J = 7.9 Hz, 2 H), 3.91 (s, 6 H), 3.51 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 165.3, 145.7, 140.3, 132.1, 131.8, 131.6, 128.8, 128.7, 128.2, 52.5, 38.4, 21.3; IR (KBr) 3422, 2953, 1721, 1644, 1597, 1460, 1436, 1359, 1330, 1283, 1265, 1038, 1002, 839, 753, 733 cm^{-1}.

Compound 15. A mixture of **14** (0.217 g, 0.636 mmol) and KOH (0.311 g, 4.71 mmol) in THF (10 mL) and water (14 mL) was stirred at room temperature for 7 h. The reaction was quenched with 1 MHCl and the whole was extracted with ether. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to give 0.191 g of **15** as a white

solid (96%): mp 280.3-282.0 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.38 (br s, 2 H), 8.23 (t, J = 1.5 Hz, 1 H), 7.91 (d, J = 1.5 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.07 (d, J = 8.0 Hz, 2 H), 3.40 (s, 3 H), 2.23 (s, 3 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.6, 165.9, 145.4, 139.5, 132.8, 132.1, 131.4, 128.6, 128.3, 127.4, 37.9, 20.8; IR (KBr) 3437, 2925, 1724, 1693, 1637, 1432, 1376, 1286, 1248, 1218, 749 cm^{-1}.

Model compound of D and T unit 16. The dicarboxylic acid **15** (0.101 g, 0.322 mmol) was treated with $SOCl_2$ (2.0 mL) at room temperature with stirring for 26 h, and the unreacted $SOCl_2$ was removed under reduce pressure. The residue was dissolved in dry CH_2Cl_2 (5.0 mL), and triethylamine (0.05 mL, 0.4 mmol) was added to the solution at 0 °C. A solution of **1a** (0.147 g, 0.659 mmol) in dry CH_2Cl_2 (5.0 mL) was added dropwise to the mixture at 0 °C, and the mixture was stirred at room temperature for 21 h. The reaction was quenched with water and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with 1 M HCl and sat. $NaHCO_3$, and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 1/1) to give 0.154 g of **16** as a light yellow solid (66%): mp 106.0-108.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (t, J = 1.7 Hz, 2 H), 7.92 (m, 4 H), 7.30 (m, 1 H), 7.07-6.96 (m, 4 H), 6.93 (d, J = 7.9 Hz, 2 H), 3.94 (s, 12 H), 3.38-3.04 (m, 9 H), 2.27 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 168.4, 165.1, 144.8, 144.3, 140.5, 136.6, 131.9, 131.8, 131.4, 128.9, 128.8, 128.6, 127.9, 126.2, 52.6, 38.6, 38.2, 21.3; IR (KBr) 3448, 2953, 1727, 1655, 1593, 1436, 1356, 1249, 1111, 1000, 833, 759, 694 cm^{-1}; HRMS (M + Na$^+$) (ESI) calcd for $C_{39}H_{37}N_3O_{11}Na^+$ 746.2326, found 746.2329.

Synthesis of model compound of L and T unit 18.



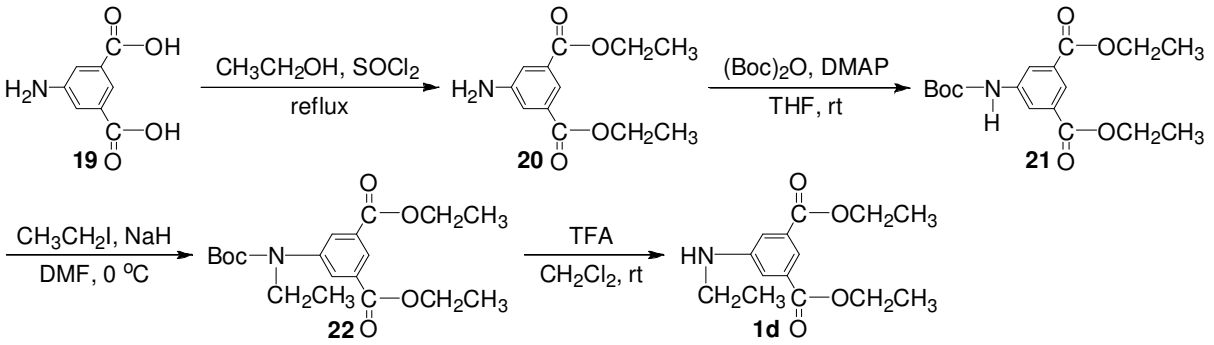
Scheme S9

Compound 17. A mixture of **14** (0.212 g, 0.621 mmol) and KOH (0.049 g, 0.74 mmol) in CH_3OH (10 mL) and water (6.0 mL) was stirred at room temperature for 2.5 h. The reaction was quenched with 1 M HCl and the whole was extracted with ether. The combined organic layers were washed with brine

and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (ethyl acetate) to give 0.098 g of **17** as a light yellow solid (49%): mp 192.4-195.2 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 8.52 (s, 1 H), 7.99 (s, 1 H), 7.95 (s, 1 H), 7.21 (d, *J* = 7.9 Hz, 2 H), 7.00 (d, *J* = 7.9 Hz, 2 H), 3.93 (s, 3 H), 3.53 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 169.3, 165.2, 145.8, 140.5, 132.4, 132.3, 131.9, 131.8, 130.9, 128.9, 128.8, 128.7, 52.6, 38.5, 21.4; IR (KBr) 3448, 2954, 1732, 1613, 1591, 1561, 1430, 1422, 1380, 1324, 1254, 1228, 1123, 984, 756 cm^{-1}.

Model compound of L and T unit 18. The monocarboxylic acid **17** (0.086 g, 0.26 mmol) was treated with $SOCl_2$ (2.0 mL) at room temperature with stirring for 137 h, and the unreacted $SOCl_2$ was removed under reduced pressure. The residue was dissolved in dry CH_2Cl_2 (5.0 mL), and triethylamine (0.04 mL, 0.3 mmol) was added to the solution at 0 ^oC. A solution of **1a** (0.060 g, 0.27 mmol) in dry CH_2Cl_2 (5.0 mL) was added dropwise to the mixture at 0 ^oC. The mixture was stirred at room temperature for 49 h. The reaction was quenched with water and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with 1 M HCl and sat. $NaHCO_3$, and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 1/1) to give 0.110 g of **18** as a light yellow solid (79%): mp 75.4-77.5 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.50 (t, *J* = 1.7 Hz, 1 H), 7.95 (m, 2 H), 7.83 (m, 1 H), 7.59 (m, 1 H), 7.25 (t, *J* = 1.7 Hz, 1 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.94 (d, *J* = 7.7 Hz, 2 H), 3.94 (s, 6 H), 3.82 (s, 3 H), 3.39 (br s, 3 H), 3.31 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 168.6, 165.1, 165.0, 145.3, 140.4, 136.6, 132.0, 131.9, 131.7, 131.3, 130.4, 129.3, 128.83, 128.81, 128.7, 127.33, 127.32, 52.7, 52.4, 38.5, 38.3, 21.3; IR (KBr) 2953, 1727, 1654, 1595, 1436, 1368, 1319, 1249, 1198, 1111, 1037, 998, 833, 758 cm^{-1}; HRMS (M + Na^+) (ESI) calcd for $C_{29}H_{28}N_2O_8Na^+$ 555.1743, found 555.1744.

Synthesis of 5-(ethylamino)isophthalic acid ethyl ester 1d.



Scheme S10

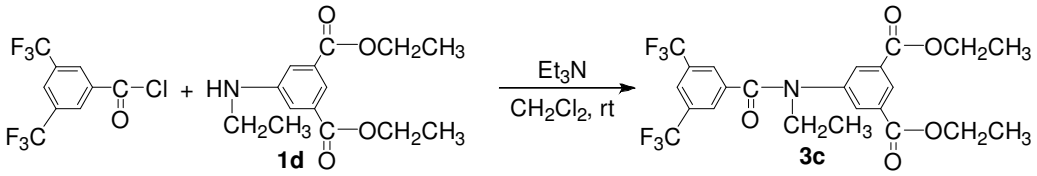
Compound 20. Into a solution of 5-aminoisophthalic acid **19** (4.02 g, 22.2 mmol) in dry ethanol (70 mL) was added thionyl chloride (5.0 mL, 69 mmol) at 0 ^{o}C. The mixture was stirred under reflux for 5 h, then the reaction was quenched with sat. $NaHCO_3$ and the whole was extracted with ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to give 4.45 g of **20** as a white solid (85%): mp ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (t, *J* = 1.4 Hz, 1 H), 7.52 (d, *J* = 1.4 Hz, 2 H), 4.38 (q, *J* = 7.3 Hz, 4 H), 3.93 (br s, 2 H), 1.40 (t, *J* = 7.3 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 146.6, 131.8, 120.6, 119.6, 61.2, 14.3; IR (KBr) 3456, 3362, 2997, 1699, 1626, 1607, 1442, 1398, 1376, 1338, 1241, 1136, 995, 977, 899, 756.

5-(*N*-*tert*-butoxycarbonylamino)isophthalic acid ethyl ester 21. Into a solution of 5-aminoisophthalic acid ethyl ester **20** (0.207 g, 0.872 mmol) in dry THF (2.0 mL) was added DMAP (0.142g, 1.16 mmol), and then the solution was cooled to 0 ^{o}C, followed by addition of di-*tert*-butyl dicarbonate (0.214 g, 0.981 mmol). The mixture was stirred at room temperature for 13 h, then the reaction was quenched with water and the whole was extracted with ether. The combined organic layers were washed with 1 M HCl, water and brine, and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 3/1) to give 0.143 g of **21** as a white solid (49%): mp 138.3-140.2 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (t, *J* = 1.4 Hz, 1 H), 8.25 (s, 2 H), 6.77 (br s, 1 H), 4.40 (q, *J* = 7.3 Hz, 4 H), 1.54 (s, 9 H), 1.41 (t, *J* = 7.3 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 152.5, 139.1, 131.6, 125.0, 123.4, 81.2, 61.4, 28.3, 14.3; IR (KBr) 3346, 2988, 1723, 1704, 1608, 1546, 1449, 1377, 1368, 1336, 1314, 1270, 1243, 1157, 1133, 1025, 1004, 758 cm^{-1}.

5-(*N*-ethyl-*N*-*tert*-butoxycarbonylamino)isophthalic acid ethyl ester 22. Into a suspension of NaH (0.391 g, 16.3 mmol) in dry DMF (50 mL) was added a solution of 5-(*N*-*tert*-butoxycarbonylamino)isophthalic acid ethyl ester **21** (5.02 g, 14.9 mmol) in dry DMF (10 mL) at 0 ^{o}C. The mixture was stirred at 0 ^{o}C for 20 min and then iodoethane (1.40 mL, 17.4 mmol) was added at 0 ^{o}C. The mixture was stirred at 0 ^{o}C for 3 h, then the reaction was quenched with water, followed by extraction with ether. The combined organic layers were washed with 1 M HCl, water and brine, and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to give 5.11 g of **22** as a viscous yellow oil (92%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (t, *J* = 1.4 Hz, 1 H), 8.06 (d, *J* = 1.4 Hz, 2 H), 4.41 (q, *J* = 7.3 Hz, 4 H), 3.75 (q, *J* = 7.3 Hz, 2 H), 1.42 (t, *J* = 7.3 Hz, 6 H), 1.17 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 154.0, 144.0, 131.9, 131.5, 127.7, 80.8, 61.5, 44.7, 28.3, 14.3, 13.8; IR (neat) 2979, 1703, 1603, 1452, 1368, 1326, 1286, 1236, 1152, 1029, 859, 758 cm^{-1}.

5-(ethylamino)isophthalic acid ethyl ester 1d. Into a solution of 5-(*N*-ethyl-*N*-*tert*-butoxycarbonylamino)isophthalic acid ethyl ester **22** (4.40 g, 12.0 mmol) in dry CH_2Cl_2 (50 mL) was added trifluoroacetic acid (10 mL) at 0 ^oC. The mixture was stirred at 0 ^oC for 24 h, then the reaction was quenched with sat. $NaHCO_3$ and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (CH_2Cl_2) to give 2.67 g of **1d** as a white solid (83%): mp 91.2-92.8 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 7.96 (t, *J* = 1.4 Hz, 1 H), 7.42 (d, *J* = 1.4 Hz, 2 H), 4.38 (q, *J* = 7.3 Hz, 4 H), 3.83 (m, 1 H), 3.26-3.21 (m, 2 H), 1.40 (t, *J* = 7.3 Hz, 6 H), 1.28 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 148.4, 131.6, 119,1 117.3, 61.1, 38.4, 14.6, 14.3; IR (KBr) 3392, 2977, 1696, 1605, 1523, 1449, 1373, 1344, 1308, 1265, 1234, 1151, 1133, 1103, 1066, 1025, 995, 890, 868, 757 cm^{-1}.

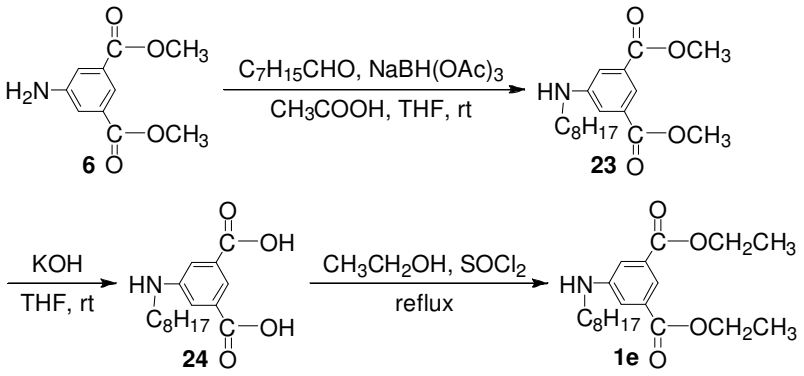
Synthesis of bifunctional initiator 3c.



Scheme S11

Bifunctional initiator 3c. Into a solution of **1d** (0.320 g, 1.21 mmol) and triethylamine (0.20 mL, 1.4 mmol) in dry CH_2Cl_2 (1.0 mL) at 0 ^oC was slowly added a solution of 3,5-bis(trifluoromethyl)benzoyl chloride (0.375 g, 1.36 mmol) in dry CH_2Cl_2 (1.0 mL). The solution was stirred at room temperature for 3 h, and then the reaction was quenched with water and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with 1 M HCl and water, and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (CH_2Cl_2) to give 0.609 g of **3c** as a yellow solid (99%): mp 77.1-78.6 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.51 (m, 1 H), 7.88 (m, 2 H), 7.74 (m, 1 H), 4.38 (q, *J* = 7.3 Hz, 4 H), 4.05-4.04 (m, 2 H), 1.38 (t, *J* = 7.3 Hz, 6 H), 1.27 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.0, 164.4, 142.5, 134.4, 132.6, 132.5, 131.6 (q, *J* = 34.0 Hz), 129.3, 128.9-128.8 (m), 123.4-123.3 (m), 122.7 (q, *J* = 272 Hz), 61.8, 45.6, 14.1, 12.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ 98.6; IR (KBr) 3067, 2983, 1719, 1661, 1600, 1451, 1415, 1367, 1325, 1284, 1236, 1191, 1172, 1128, 1058, 1021, 901, 760 cm^{-1}.

Synthesis of 5-(octylamino)isophthalic acid ethyl ester 1e.



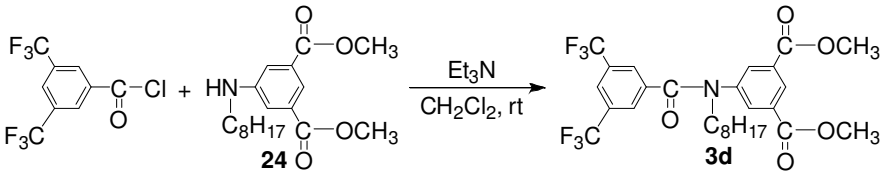
Scheme S12

5-(octylamino)isophthalic acid methyl ester 23. Into a solution of 5-aminoisophthalic acid methyl ester **6** (3.01 g, 14.4 mmol) in dry THF (46 mL) was added *n*-octanal (2.21 g, 17.2 mmol), sodium triacetoxyborohydride (4.57 g, 21.6 mmol), and acetic acid (1.0 mL, 18 mmol) successively. The mixture was stirred at room temperature for 42 h, then the reaction was quenched with sat. $NaHCO_3$ and the whole was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 4/1) to give 2.20 g of **23** as a white solid (48%): mp 83.5-85.0 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (t, *J* = 1.4 Hz, 1 H), 7.39 (d, *J* = 1.4 Hz, 2 H), 3.90-3.87 (m, 7 H), 3.14 (q, *J* = 6.4 Hz, 2 H), 1.60 (quint, *J* = 7.3 Hz, 2 H), 1.40-1.25 (m, 10 H), 0.85 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 148.6, 131.2, 119.0, 117.3, 52.2, 43.8, 31.8, 29.3, 29.27, 29.20, 27.0, 22.6, 14.1; IR (KBr) 3396, 2952, 2930, 2852, 2361, 1726, 1706, 1607, 1530, 1443, 1366, 1316, 1242, 1191, 1100, 1000, 761 cm^{-1}.

Synthesis of 5-(octylamino)isophthalic acid 24. A mixture of 5-(octylamino)isophthalic acid methyl ester **23** (1.60 g, 4.98 mmol) and KOH (3.40 g, 51.5 mmol) in THF (18 mL) and water (5 mL) was stirred at room temperature for 17 h. The reaction was quenched with 1 M HCl, and the whole was extracted with ether, followed by drying over anhydrous $MgSO_4$. The solvent was removed in vacuo to give 1.38 g of **24** as a white solid (99%): mp 227.0-232.0 ^oC; ^1H NMR (500 MHz, DMSO-d_6) δ 12.9 (br s, 2 H), 7.64 (t, *J* = 1.3 Hz, 1 H), 7.31 (d, *J* = 1.5 Hz, 2 H), 6.14 (br s, 1 H), 3.01 (br s, 2 H), 1.54 (quint, *J* = 7.3 Hz, 2 H), 1.38-1.34 (m, 2 H), 1.28-1.24 (m, 8 H), 0.84 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.3, 149.2, 131.7, 117.0, 116.0, 42.7, 31.2, 28.8, 28.7, 28.3, 26.6, 22.1, 13.9; IR (KBr) 3421, 2929, 2860, 1702, 1605, 1508, 1430, 1278, 760, 688 cm^{-1}.

Synthesis of 5-(octylamino)isophthalic acid ethyl ester 1e. Into a solution of 5-(octylamino)isophthalic acid **24** (0.362 g, 1.23 mmol) in dry ethanol (7.0 mL, 33 mmol) was added thionyl chloride (0.30 mL, 4.2 mmol) at 0 °C. The mixture was stirred at room temperature for 24 h, then concentrated in vacuo. CH_2Cl_2 and water was added in the residue, and then the whole was extracted with CH_2Cl_2, and the combined organic layers were washed with water and sat. $NaHCO_3$, followed by drying over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 3/1) to give 0.387 g of **1e** as a white solid (89%): mp 50.2-52.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (t, *J* = 1.4 Hz, 1 H), 7.43 (d, *J* = 1.4 Hz, 2 H), 4.39 (q, *J* = 7.2 Hz, 4 H), 3.89 (br s, 1 H), 3.18 (q, *J* = 5.9 Hz, 2 H), 1.64 (quint, *J* = 7.3 Hz, 2 H), 1.46-1.40 (m, 8 H), 1.36-1.26 (m, 8 H), 0.90 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 148.5, 131.6, 118.9, 117.3, 61.1, 43.9, 31.8, 29.34, 29.32, 29.2, 27.1, 22.6, 14.3, 14.1; IR (KBr) 3396, 2927, 2853, 1704, 1608, 1530, 1375, 1232, 1097, 1022, 761, 717 cm^{-1}.

Synthesis of bifunctional initiator 3d.

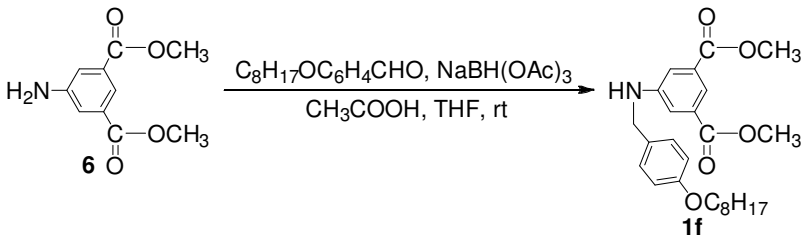


Scheme S13

Bifunctional initiator 3d. Into a solution of 5-(octylamino)isophthalic acid methyl ester **24** (0.323 g, 1.00 mmol) and triethylamine (0.17 mL, 1.2 mmol) in dry CH_2Cl_2 (5.0 mL) at 0 °C was slowly added a solution of 3,5-bis(trifluoromethyl)benzoyl chloride (0.334 g, 1.21 mmol) in dry CH_2Cl_2 (1.0 mL). The solution was stirred at room temperature for 14 h, and then triethylamine (0.10 mL, 0.72 mmol) and a solution of 3,5-bis(trifluoromethyl)benzoyl chloride (0.240 g, 0.868 mmol) in dry CH_2Cl_2 (0.5 mL) was added the reaction mixture and further stirred at room temperature for 1.5 h. The reaction was quenched with water and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with 1 M HCl and sat. $NaHCO_3$, followed by drying over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 5/1) to give 0.518 g of **3d** as a white solid (91%): mp 105.0-107.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (s, 1 H), 7.89 (s, 2 H), 7.75-7.72 (m, 3 H), 3.97-3.91 (m, 8 H), 1.62 (quint, *J* = 7.4 Hz, 2 H), 1.35-1.31 (m, 2 H), 1.31-1.21 (m, 8 H), 0.87 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.1, 164.9, 137.7, 133.2, 132.6, 132.2, 131.6 (q, *J* = 35.4 Hz), 129.3, 128.9-128.7 (m), 123.4-123.3 (m), 122.6 (q, *J* = 274

Hz), 52.7, 50.7, 31.7, 29.1, 29.0, 27.6, 26.7, 22.6, 14.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ 98.7; IR (KBr) 2929, 2856, 1719, 1664, 1460, 1332, 1279, 1251, 1132, 905, 759, 681 cm^{-1}.

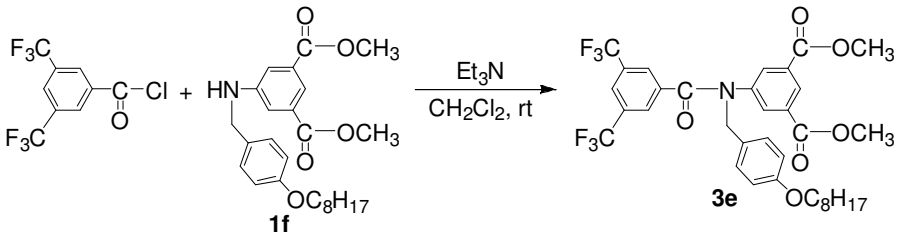
Synthesis of 5-(4-octyloxybenzylamino)isophthalic acid methyl ester 1f.



Scheme S14

5-(4-octyloxybenzylamino)isophthalic acid methyl ester 1f. Into a solution of 5-aminoisophthalic acid methyl ester **6** (2.96 g, 14.1 mmol) in dry THF (55 mL) was added 4-octyloxybenzaldehyde (2.17 g, 9.26 mmol), sodium triacetoxyborohydride (4.46 g, 21.0 mmol), and acetic acid (1.0 mL, 18 mmol) successively. The mixture was stirred at room temperature for 19 h, then the reaction was quenched with sat. $NaHCO_3$ and the whole was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 5/1) to give 2.17 g of **1f** as a white solid (55%): mp 88.8-92.5 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (t, *J* = 1.6 Hz, 1 H), 7.47 (d, *J* = 1.4 Hz, 2 H), 7.26 (d, *J* = 8.6 Hz, 2 H), 6.88 (d, *J* = 8.9 Hz, 2 H), 4.30 (d, *J* = 5.5 Hz, 2 H), 4.22 (t, *J* = 5.2 Hz, 1 H), 3.94 (t, *J* = 6.5 Hz, 2 H), 3.90 (s, 6 H), 1.77 (quint, *J* = 7.1 Hz, 2 H), 1.45 (quint, *J* = 7.4 Hz, 2 H), 1.37-1.32 (m, 8 H), 0.89 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 158.7, 148.3, 131.4, 130.1, 128.9, 119.5, 117.6, 114.7, 68.1, 52.2, 47.7, 31.8, 29.4, 29.3, 29.2, 26.1, 22.7, 14.1; IR (KBr) 3384, 2921, 2853, 1709, 1607, 1512, 1437, 1357, 1304, 1249, 1127, 1092, 1019, 824, 760 cm^{-1}.

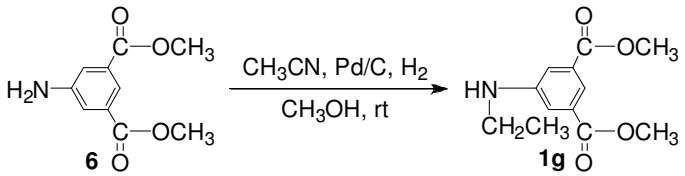
Synthesis of bifunctional initiator 3e.



Scheme S15

Bifunctional initiator 3e. Into a solution of **1f** (0.287 g, 0.671 mmol) and triethylamine (0.12 mL, 0.86 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 ^oC was slowly added a solution of 3,5-bis(trifluoromethyl)benzoyl chloride (0.225 g, 0.814 mmol) in dry CH_2Cl_2 (1.0 mL). The solution was stirred at room temperature for 21 h, and then triethylamine (0.07 mL, 0.50 mmol) and a solution of 3,5-bis(trifluoromethyl)benzoyl chloride (0.160 g, 0.579 mmol) in dry CH_2Cl_2 (0.5 mL) was added the reaction mixture and further stirred at room temperature for 38 h, then triethylamine (0.09 mL, 0.65 mmol) and a solution of 3,5-bis(trifluoromethyl)benzoyl chloride (0.184 g, 0.665 mmol) in dry CH_2Cl_2 (0.75 mL) was added the reaction mixture and further stirred at room temperature for 5 h. The reaction was quenched with water and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with 1 M HCl and sat. $NaHCO_3$, followed by drying over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 6/1) to give 0.422 g of **3e** as a white solid (94%): mp 69.5-75.7 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 8.46 (s, 1 H), 7.79-7.70 (m, 5 H), 7.14 (d, *J* = 8.3 Hz, 2 H), 6.80 (d, *J* = 8.6 Hz, 2 H), 5.10 (s, 2 H), 3.92-3.88 (m, 8 H), 1.75 (quint, *J* = 7.1 Hz, 2 H), 1.43 (quint, *J* = 7.5 Hz, 2 H), 1.34-1.24 (m, 8 H), 0.88 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.2, 164.8, 159.0, 142.6, 137.4, 132.9, 132.0, 131.5 (q, *J* = 34.6 Hz), 130.1, 129.4, 129.0-128.8 (m), 127.5, 123.6-123.4 (m), 122.6 (q, *J* = 273 Hz), 114.7, 68.0, 53.5, 52.6, 31.8, 29.3, 29.22, 29.20, 26.0, 22.6, 14.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ 98.7; IR (KBr) 2931, 2860, 2361, 1733, 1647, 1510, 1440, 1333, 1276, 1246, 1141, 905, 762, 681 cm^{-1}.

Synthesis of 5-(ethylamino)isophthalic acid methyl ester 1g.

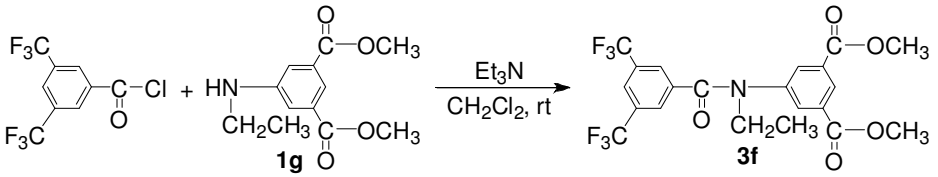


Scheme S16

5-(ethylamino)isophthalic acid methyl ester 1g. A mixture of 5-aminoisophthalic acid methyl ester **6** (3.08 g, 14.7 mmol), acetonitrile (1.6 mL, 30 mmol) and 5% Pd/C (0.604 g) in dry methanol (30 mL) was stirred at room temperature for 45 h under a hydrogen atmosphere. The reaction mixture was filtered and evaporated, and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2/1) to give 1.91 g of **1g** as a white solid (55%): mp 113.6-115.6 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (t, *J* = 1.4 Hz, 1 H), 7.42 (d, *J* = 1.4 Hz, 2 H), 3.92 (s, 6 H), 3.85 (br s, 1 H), 3.26-3.21 (m, 2 H), 1.28 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 148.5, 131.3, 119.1, 117.4,

52.2, 38.4, 14.6; IR (KBr) 3391, 2967, 1727, 1707, 1613, 1528, 1460, 1436, 1370, 1310, 1276, 1239, 1161, 1127, 1018, 995, 753 cm^{-1}.

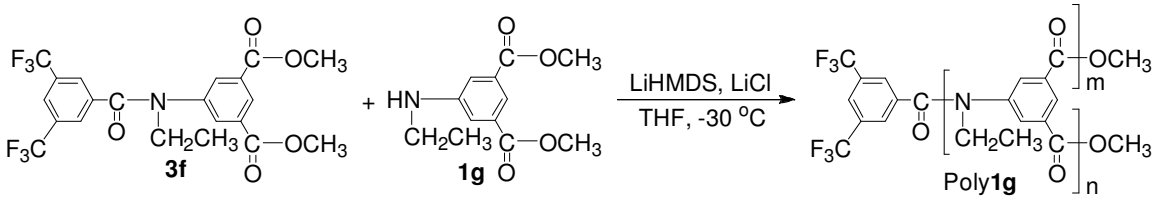
Synthesis of bifunctional initiator 3f.



Scheme S17

Bifunctional initiator 3f. Into a solution of **1g** (0.203 g, 0.856 mmol) and triethylamine (0.14 mL, 1.00 mmol) in dry CH_2Cl_2 (1.0 mL) at 0 ^oC was slowly added a solution of 3,5-bis(trifluoromethyl)benzoyl chloride (0.260 g, 0.940 mmol) in dry CH_2Cl_2 (0.5 mL). The solution was stirred at room temperature for 7 h, and then the reaction was quenched with water and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with 1 M HCl and water, and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (CH_2Cl_2) to give 0.374 g of **3f** as a white solid (92%): mp 119.0-121.5 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 8.52 (m, 1 H), 7.90 (m, 2 H), 7.75-7.74 (m, 3 H), 4.04 (q, *J* = 7.3 Hz, 2 H), 3.92 (s, 6 H), 1.26 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.0, 164.8, 142.6, 137.5, 132.7, 132.2, 131.6 (q, *J* = 34.0 Hz), 129.4, 128.9-128.8 (m), 123.5-123.4 (m), 122.6 (q, *J* = 273 Hz), 52.7, 45.7, 12.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ 98.6; IR (KBr) 3076, 2972, 1731, 1714, 1662, 1644, 1602, 1451, 1335, 1287, 1245, 1190, 1169, 1125, 1062, 1004, 907, 760 cm^{-1}.

Polymerization of AB_2 monomer 1g with bifunctional initiator 3f.



Scheme S18

Poly1g. LiCl (0.152 g, 3.59 mmol) was placed in a flask equipped with a three-way stopcock, and dried at 250 ^oC under reduced pressure. The flask was cooled to room temperature under an argon atmosphere, and then charged with 1.0 M LiHMDS in THF (0.720 mL, 0.720 mmol). The flask was cooled to -30 ^oC under an argon atmosphere with stirring. Into the flask was added a solution of **3f** (0.0206 g, 0.0432 mmol) and naphthalene (internal standard, 0.0128 g, 0.0999 mmol) in dry THF (1.0

mL) under dry nitrogen, followed by a solution of **1g** (0.154 g, 0.649 mmol) in dry THF (4.0 mL), added dropwise over ca. 40 min at -30 ^{o}C with stirring under dry nitrogen. The mixture was stirred at -30 ^{o}C for 1 h, and then the reaction was quenched with sat. NH_4Cl. A small portion of the THF layer was withdrawn into a syringe and analyzed by GC to determine the conversion of **3f** and **1g** (conversion = 100%). After that, the whole was extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (4.0 mL), and the solution was added into hexane/ether = 9/1 (v/v) (200 mL). After filtration, the insoluble material was washed with hexane, and dried in desiccator to give 0.181 g of HBPA as a white solid (83%, M_n(MALLS) = 4120, M_w/M_n = 1.12).

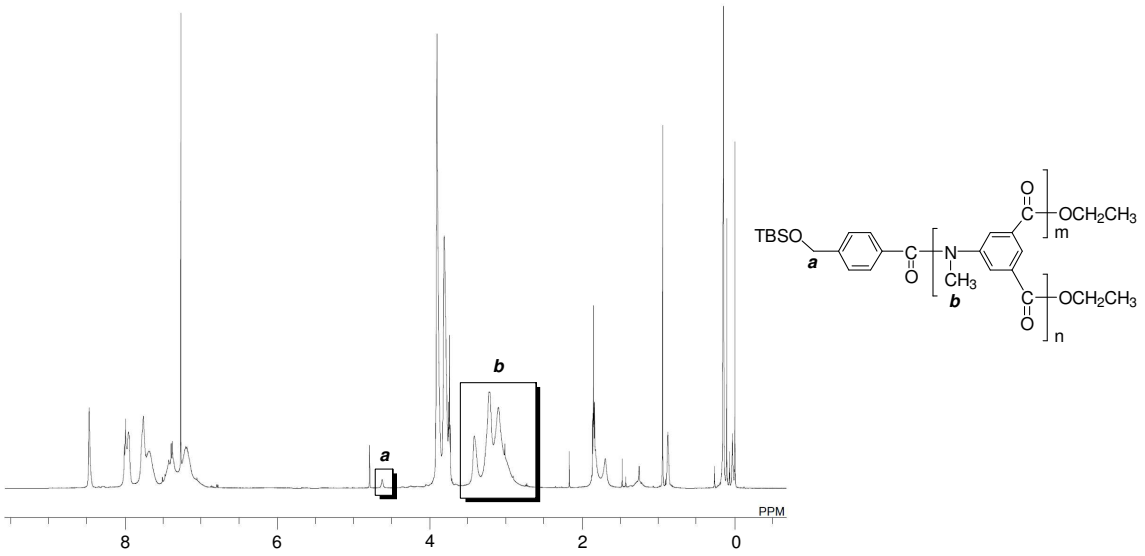


Figure S1. ^{1}H NMR spectrum of HBPA obtained from **1a** and **4** ($CDCl_3$ at 25 ^{o}C).

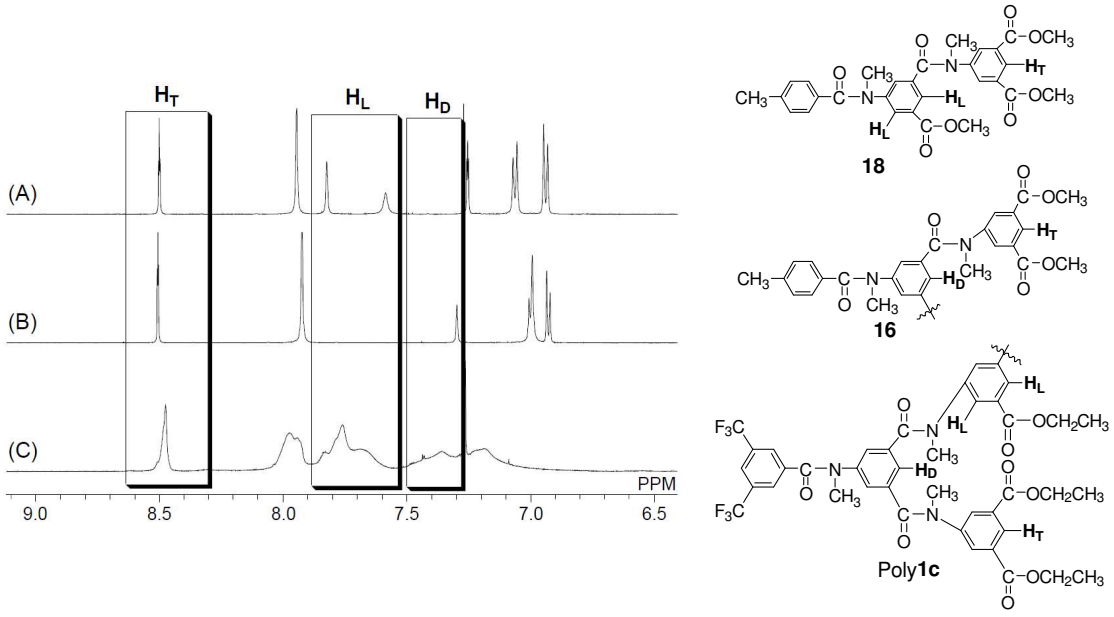


Figure S2. ^{1}H NMR spectra in $CDCl_3$ at 25 ^{o}C: (A) **18**, (B) **16**, and (C) Poly**1c**.

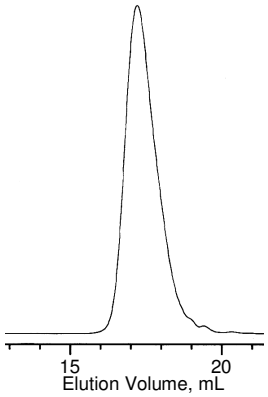


Figure S3. GPC profile of products obtained by the polymerization of **1c** with **3b** in the presence of LiCl: **1c** was added at once.

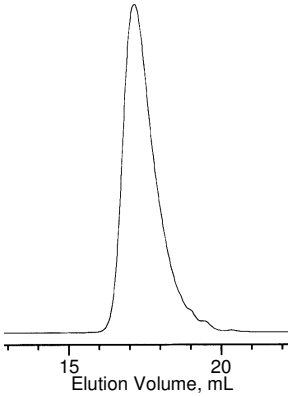


Figure S4. GPC profile of products obtained by the polymerization of **1c** with **3b** ($[\mathbf{1c}]_0/[\mathbf{3b}]_0 = 15$) in the absence of LiCl.

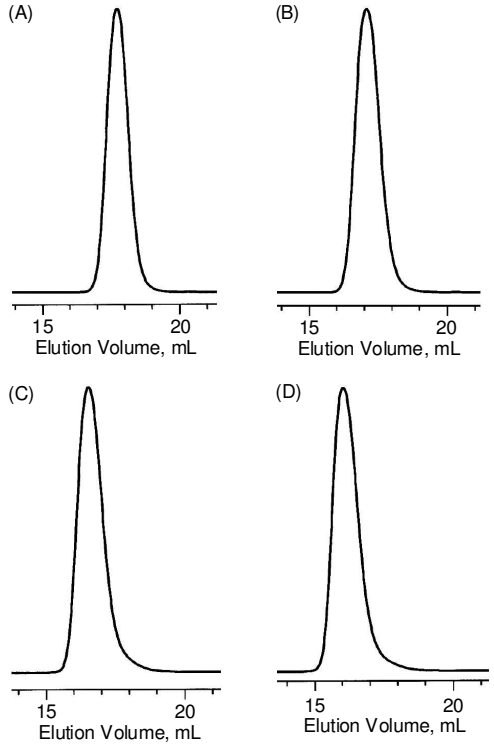


Figure S5. GPC profiles of products obtained by the polymerization of **1d** with **3c** in the presence of LiHMDS and LiCl: $[\mathbf{1d}]_0/[\mathbf{3c}]_0$ = (A) 7, (B) 15, (C) 31, (D) 50.

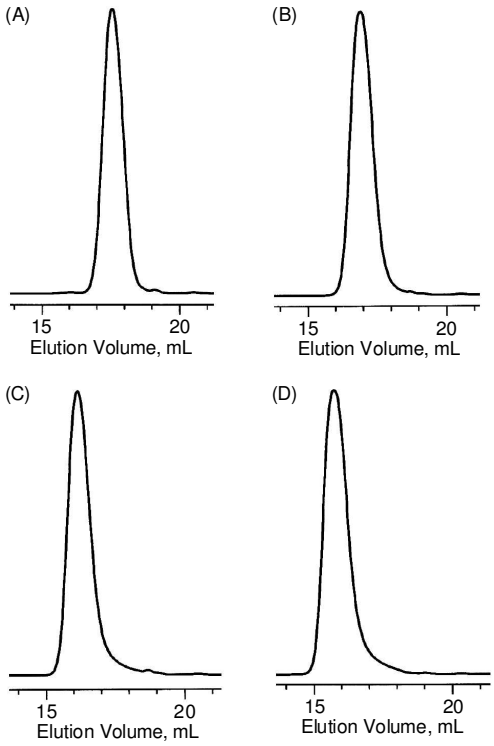


Figure S6. GPC profiles of products obtained by the polymerization of **1e** with **3d** in the presence of LiHMDS and LiCl: $[\mathbf{1e}]_0/[\mathbf{3d}]_0$ = (A) 7, (B) 15, (C) 32, (D) 46.

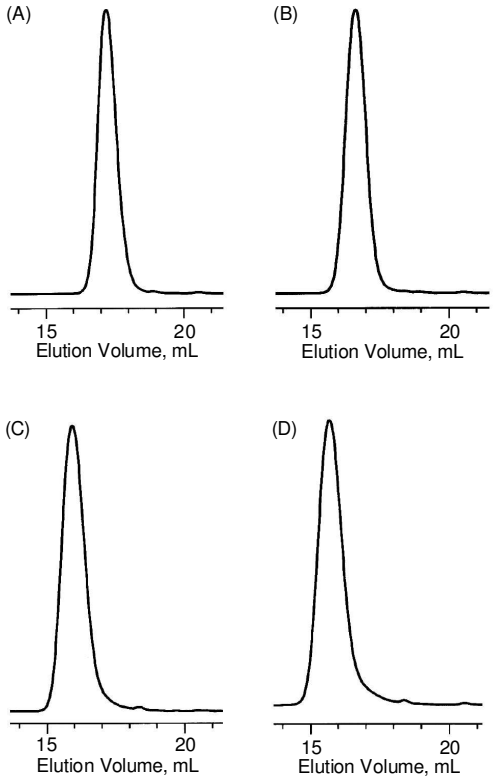


Figure S7. GPC profiles of products obtained by the polymerization of **1f** with **3e** in the presence of LiHMDS and LiCl: $[\mathbf{1f}]_0/[\mathbf{3e}]_0$ = (A) 7, (B) 15, (C) 31, (D) 43.

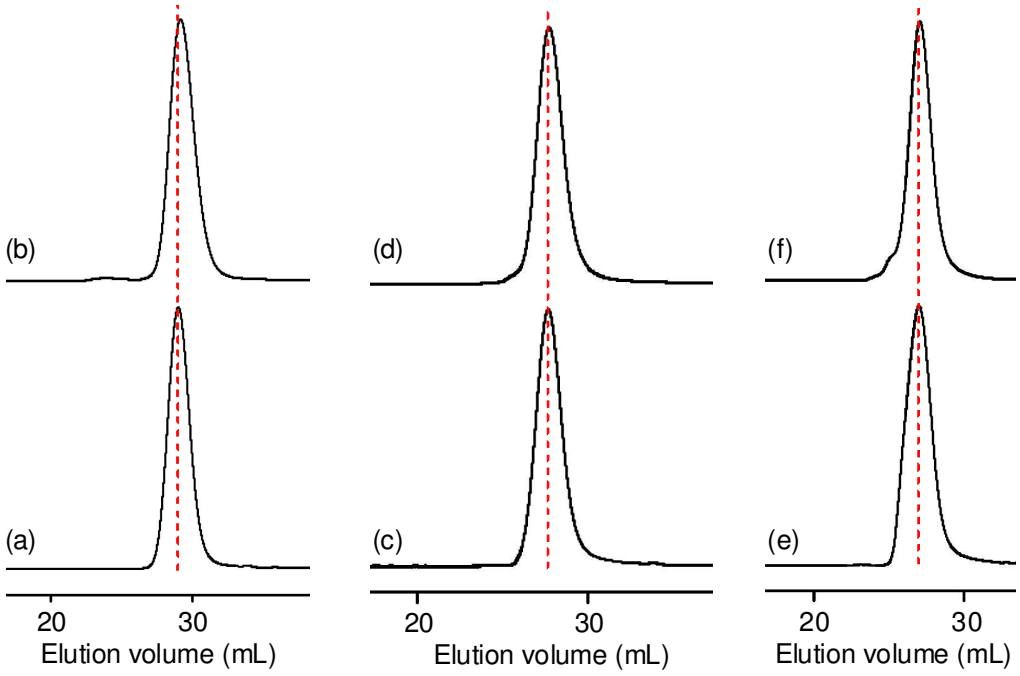


Figure S8. GPC (eluent: DMF) profiles of (a) Poly**1f** (M_n = 5510, M_w/M_n = 1.08), (b) product (M_n = 5040, M_w/M_n = 1.09) obtained by deprotection of Poly**1f** (M_n = 5510, M_w/M_n = 1.08), (c) Poly**1f** (M_n = 8440, M_w/M_n = 1.14), (d) product (M_n = 8370, M_w/M_n = 1.15) obtained by deprotection of Poly**1f** (M_n = 8440, M_w/M_n = 1.14), (e) Poly**1f** (M_n = 11400, M_w/M_n = 1.18), (f) product (M_n = 11100, M_w/M_n = 1.24) obtained by deprotection of Poly**1f** (M_n = 11400, M_w/M_n = 1.18)

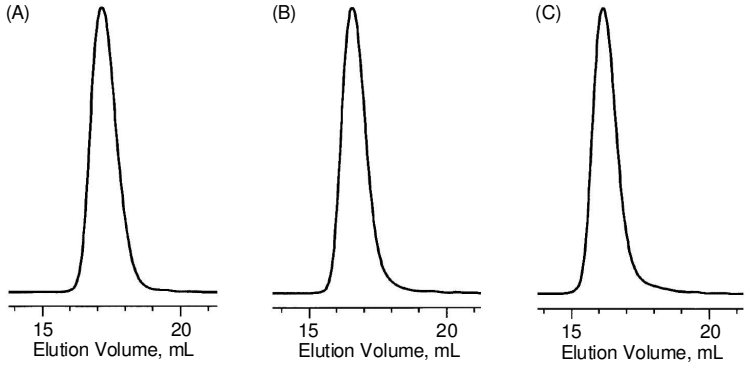


Figure S9. GPC profiles of products obtained by the polymerization of **1g** with **3f** in the presence of LiHMDS and LiCl: $[\mathbf{1g}]_0/[\mathbf{3f}]_0$ = (A) 15, (B) 31, (C) 50.

Table S1. Polymerization of **1a** with **3a** in the presence of LiHMDS and LiCl in THF[a]

	Conv of	M_n					T_g	T_d[10]
$[\mathbf{1a}]_0/[\mathbf{3a}]_0$	**3a** (%)[b]	calcd[c]	GPC[d]	MALLS[e]	M_w/M_n[d]	DB[f]	(°C)[g]	(°C)[h]
7	97	1840	2020	2260	1.16	0.48	120	361
15	87	3710	3170	4420	1.13	0.52	135	370
31	91	6960	5180	7470	1.11	0.52	147	388
46	94	9830	6730	11100	1.07	0.51	151	393
63	84	14800	7430	15200	1.11	0.52	-[i]	-[i]
100	-[i]	-	8750	22100	1.10	-[i]	152	405
150	-[i]	-	11100	32500	1.14	-[i]	153	408

[a] Polymerization of **1a** with **3a** was carried out in the presence of 1.1 equiv of LiHMDS and 5 equiv of LiCl in THF ($[\mathbf{1a}]_0$ = 0.11 M). [b] Determined by GC. [c] The M_n value was calculated on the basis of conversion of **3a**. [d] Determined by GPC based on polystyrene standards (eluent: THF). [e] Determined by GPC-MALLS (eluent: THF). [f] Determined by ^{1}H NMR. [g] Determined by DSC at heating rate 10 °C/min under nitrogen. [h] Determined by TG-DTA at heating rate 10 °C/min under nitrogen. [i] Not determined.

Table S2. Polymerization of **1b** with **3a** in the presence of LiHMDS and LiCl in THF[a]

	Conv of	M_n				
$[\mathbf{1b}]_0/[\mathbf{3a}]_0$	**3a** (%)[b]	calcd	GPC[c]	MALLS[d]	M_w/M_n[c]	DB[e]
7	100	2050	2180	2080	1.09	0.47
15	100	3810	3170	3770	1.11	0.43
31	100	7320	4840	7220	1.14	0.41
46	100	10600	5460	8800	1.17	0.43
60	100	13700	5870	9010	1.21	0.41

[a] Polymerization of **1b** with **3a** was carried out in the presence of 1.1 equiv of LiHMDS and 5 equiv of LiCl in THF ($[\mathbf{1b}]_0$ = 0.11 M). [b] Determined by GC. [c] Determined by GPC based on polystyrene standards (eluent: THF). [d] Determined by GPC-MALLS (eluent: THF). [e] Determined by ^{1}H NMR.

Table S3. Polymerization of **1c** with **3b** in the presence of LiHMDS and LiCl in THF[a]

$[\mathbf{1c}]_0/[\mathbf{3b}]_0$	Conv of **3b** (%)[b]	M_n calcd	M_n GPC[c]	M_n MALLS[d]	M_w/M_n[c]	DB[e]	T_g (°C)[f]	T_d^{10} (°C)[g]
7	100	1930	2200	2370	1.10	0.49	95	365
15	100	3570	3360	3920	1.11	0.52	-[h]	-[h]
31	100	6850	5500	7480	1.08	0.51	116	376
60	100	12800	7460	13500	1.11	0.50	119[i]	379[i]
100	100	21000	10200	22500	1.09	0.52	122	383
200	100	41500	14900	39300	1.13	0.52	122	382

[a] Polymerization of **1c** with **3b** was carried out in the presence of 1.1 equiv of LiHMDS and 5 equiv of LiCl in THF ($[\mathbf{1c}]_0$ = 0.11 M). [b] Determined by GC. [c] Determined by GPC based on polystyrene standards (eluent: THF). [d] Determined by GPC-MALLS (eluent: THF). [e] Determined by ^{1}H NMR. [f] Determined by DSC at heating rate 10 °C/min under nitrogen. [g] Determined by TG-DTA at heating rate 10 °C/min under nitrogen. [h] Not investigated. [i] M_n(MALLS), M_w/M_n and DB of Poly**1c** are 14400, 1.07 and 0.51 respectively.

Table S4. Polymerization of **1d** with **3c** in the presence of LiHMDS and LiCl in THF[a]

$[\mathbf{1d}]_0/[\mathbf{3c}]_0$	Conv of **3c** (%)[b]	M_n calcd	M_n GPC[c]	M_n MALLS[d]	M_w/M_n[c]	DB[e]	T_g (°C)[f]	T_d^{10} (°C)[g]
7	100	2040	2520	2530	1.07	0.38	89	373
15	100	3790	3830	4230	1.09	0.39	100	376
31	100	7300	5170	6780	1.13	0.40	106	379
50	100	11500	7080	10700	1.13	0.39	110	380

[a] Polymerization of **1d** with **3c** was carried out in the presence of 1.1 equiv of LiHMDS and 5 equiv of LiCl in THF ($[\mathbf{1d}]_0$ = 0.11 M). [b] Determined by GC. [c] Determined by GPC based on polystyrene standards (eluent: THF). [d] Determined by GPC-MALLS (eluent: THF). [e] Determined by ^{1}H NMR. [f] Determined by DSC at heating rate 10 °C/min under nitrogen. [g] Determined by TG-DTA at heating rate 10 °C/min under nitrogen.

Table S5. Polymerization of **1e** with **3d** in the presence of LiHMDS and LiCl in THF[a]

	Conv of	M_n					T_g
$[\mathbf{1e}]_0/[\mathbf{3d}]_0$	**3d** (%)[b]	calcd	GPC[c]	MALLS[d]	M_w/M_n[c]	DB[e]	(°C)[f]
7	100	2700	2970	3140	1.10	0.37	22
15	100	5130	4610	5500	1.10	0.33	25
31	100	9990	6990	9090	1.16	0.32	30
46	100	14500	8530	13000	1.15	0.32	-[h]

[a] Polymerization of **1e** with **3d** was carried out in the presence of 1.1 equiv of LiHMDS and 5 equiv of LiCl in THF ($[\mathbf{1e}]_0$ = 0.11 M). [b] Determined by GC. [c] Determined by GPC based on polystyrene standards (eluent: THF). [d] Determined by GPC-MALLS (eluent: THF). [e] Determined by ^{1}H NMR. [f] Determined by DSC at heating rate 10 °C/min under nitrogen. [g] Determined by TG-DTA at heating rate 10 °C/min under nitrogen. [h] Not investigated.

Table S6. Polymerization of **1f** with **3e** in the presence of LiHMDS and LiCl in THF[a]

	Conv of	M_n				
$[\mathbf{1f}]_0/[\mathbf{3e}]_0$	**3e** (%)[b]	calcd	GPC[c]	MALLS[d]	M_w/M_n[c]	DB[e]
7	100	3440	3840	3860	1.08	-[f]
15	100	6600	5910	7000	1.08	-[f]
31	100	12900	8710	11600	1.13	-[f]
43	100	17700	9970	16000	1.15	-[f]

[a] Polymerization of **1f** with **3e** was carried out in the presence of 1.1 equiv of LiHMDS and 5 equiv of LiCl in THF ($[\mathbf{1f}]_0$ = 0.11 M). [b] Determined by GC. [c] Determined by GPC based on polystyrene standards (eluent: THF). [d] Determined by GPC-MALLS (eluent: THF). [e] Determined by ^{1}H NMR. [f] Not determined.

Table S7. Polymerization of **1g** with **3f** in the presence of LiHMDS and LiCl in THF[a]

$[\mathbf{1g}]_0/[\mathbf{3e}]_0$	Conv of **3f** (%)[b]	M_n			M_w/M_n[c]	DB[e]	T_g (°C)[f]	T_d^{10} (°C)[g]
		calcd	GPC[c]	MALLS[d]				
15	100	3560	3480	4120	1.12	0.44	121	396
31	100	6840	5140	7690	1.11	0.44	130	399
50	100	10700	6580	10300	1.14	0.45	133	399

[a] Polymerization of **1g** with **3f** was carried out in the presence of 1.1 equiv of LiHMDS and 5 equiv of LiCl in THF ($[\mathbf{1g}]_0$ = 0.11 M). [b] Determined by GC. [c] Determined by GPC based on polystyrene standards (eluent: THF). [d] Determined by GPC-MALLS (eluent: THF). [e] Determined by ^{1}H NMR. [f] Determined by DSC at heating rate 10 °C/min under nitrogen. [g] Determined by TG-DTA at heating rate 10 °C/min under nitrogen.