Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Suzuki–Miyaura Catalyst-Transfer Polycondensation of Triolborate-Type Fluorene Monomer: Toward Rapid Access to Polyfluorene-Containing Block and Graft Copolymers from Various Macroinitiators

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Materials

2-(7-Bromo-9,9-dihexyl-9*H*-fluorene-2-yl)4,4,5,5-tetramethyl-1,2,3dioxaborolane [1] and tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ($Pd_2(dba)_3$•$CHCl_3$),[2] were prepared according to reported methods. Benzoic acid, 2-bromoisobutyryl bromide, *n*-butyl acrylate, *ε*-caprolactone (*ε*-CL), 18-crown 6-ether (18-crown-6), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), 2,2-diethyl-1,3-propanediol, 4-(dimethylamino)pyridine (DMAP), diphenyl phosphate (DPP), ethyl 2-bromoisobutyrate, ethyl 4-iodobenzoate, 4-hydroxybutyl acrylate, 4'-iodoacetophenone, 4-iodoaniline, 4-iodobenzoyl chloride, 4-iodobenzyl alcohol, 4-iodotoluene, *rac*-lactide (*rac*-LA), *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA), styrene, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]malononitrile, triisopropyl borate, and trimethylolethane were purchased from Tokyo Chemical Industry Co., Ltd. (TCI), and used as received. *n*-Butyllithium (*n*-BuLi; in *n*-hexane as 1.6 mol L^{-1} solution), 2,7-dibromo-9,9-dihexylfluorene, potassium hydroxide (KOH), and triethylamine (Et_3N) were purchased from Kanto Chemical Co., Inc., and used as received. Tri(*t*-butyl)phosphine (*t*-Bu_3P) and tripotassium phosphate (K_3PO_4) were purchased from Fujifilm Wako Pure Chemical Co. and used as received. 4-Iodophenol was purchased from Manac Co., Inc., and used as received. Amberlyst® A21, copper (I) bromide (CuBr), (4-iodophenylethynyl)trimethylsilane, and poly(ethylene oxide) monomethyl ether ($M_{n,NMR}$ = 5,000 g mol^{-1}) were purchased from Sigma-Aldrich Chemicals Co. and used as received. *rac*-Lactide (*rac*-LA; TCI, >98%) was purified by recrystallization (twice) from dry toluene and stored in a glovebox. DBU, *ε*-CL, and styrene were purified by distillation over CaH_2 under reduced pressure and stored in a glovebox.

Commercially-available dry-CH_2Cl_2, dry-THF and dry-toluene (Kanto Chemical Co., Inc., >99.5%, water content, <0.001%) was further purified by an MBRAUN MB SPS Compact solvent purification system equipped with a MB-KOL-C column and a MB-KOL-A column, which was then directly used for the polymerizations.

Instruments

Polymerization was carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and a copper catalyst) under a dry argon atmosphere (H_2O, O_2 <0.1 ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 moisture sensor and an MB-OX-SE 1 oxygen sensor, respectively.

^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained using a JEOL JNM-ECS400 instrument at 25 °C.

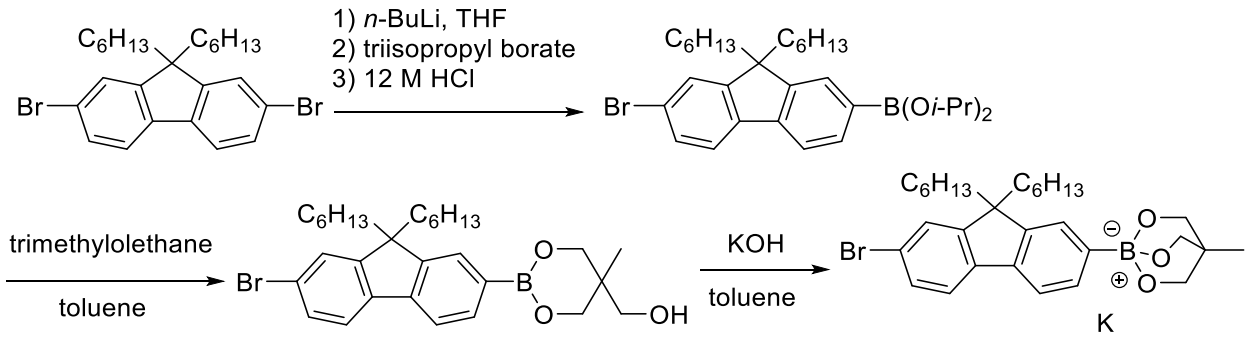
DOSY NMR measurement was performed at 30 °C on a JEOL JNM-ECZ600R NMR spectrometer operating at 600 MHz and equipped with a ROYAL probe (NM100006) capable of producing gradients in the z direction with strength 90 G cm^{-1}. The pulse sequence used was stimulated-echo and longitudinal eddy current delay. The gradient strength was logarithmically incremented in 16 steps from 50 mT up to 200 mT of the maximum gradient strength. The gradient duration was 2 ms and the diffusion delay was 0.1 s. The spectra were collected with a spectral window from −2.5 to 12.5 ppm in 8 transients and with 4 dummy transients in the beginning, with an acquisition time of 3 s and relaxation delay of 15 s.

Size exclusion chromatography (SEC) was performed at 40 °C using a Jasco high-performance liquid chromatography system (PU-2080Plus Intelligent HPLC pump, CO-2065Plus Column oven, RI-2031Plus Intelligent RI detector, and Shodex DG-2080-54) equipped with a Shodex KF-G guard column (4.6 mm × 10 mm; particle size, 8 μm) and two Shodex KF-804 columns (linear; particle size, 7 μm; 8.0 mm × 300 mm; exclusion limit, 4×10^5) in THF at a flow rate of 1.0 mL min^{-1}. The number-average molecular weight ($M_{n,SEC}$) and dispersity ($Đ_M$) of the polymer were calculated on the basis of a polystyrene calibration.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurement of the polymer was carried out in the reflector mode using an ABSCIEX TOF/TOF/5800 equipped with a 337 nm nitrogen laser (3 ns pulse width). The MALDI-TOF MS samples were prepared by depositing a mixture of the polymer and matrix in THF onto a sample plate. A 1:80 (v/v) ratio of [PF (1.0 g L^{-1} in THF)]/[*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]malononitrile (10 g L^{-1} in THF)] was used.

Synthesis of potassium 2-(7-bromo-9,9-dihexyl-9*H*-fluorene-2-yl)triolborate

Scheme S1. Synthesis of triolborate salt fluorene monomer



To a 500 mL three-necked round bottom flask, 2,7-dibromo-9,9-dihexylfluorene (40.0 g, 81.2 mmol) was added and dried under vacuum at room temperature for 6 h. Dry-THF (320 mL) was introduced to this flask and cooled to −78 °C. *n*-BuLi (50.8 mL, 81.2 mmol, 1.6 mol L^{-1} in *n*-hexane) was injected slowly via a syringe, and the whole mixture was stirred for 1.5 h under argon atmosphere. Triisopropyl borate (28.0 mL, 121.9 mmol) was then added to this reaction mixture. The mixture was gradually brought back to room temperature and stirred for 9 h under argon atmosphere. The reaction was quenched by the addition of 12 mol L^{-1} HCl (30 mL). The solvent was removed by evaporation, and the residue was dissolved in CH_2Cl_2 and washed with brine. The organic layer was dried over Na_2SO_4 and evaporated completely. The residue was purified by silica gel column chromatography (*n*-hexane → MeOH) to give 2-(7-bromo-9,9-dihexyl-9*H*-fluorene-2-yl)diisopropyl boronate (41.7 g, 90.5% yield) as a white powder.

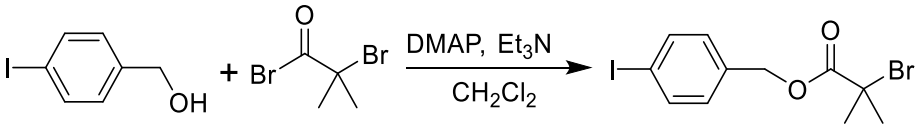
2-(7-Bromo-9,9-dihexyl-9*H*-fluorene-2-yl)diisopropyl boronate (30.0 g, 55.4 mmol) and trimethylolethane (6.7 g, 55.4 mmol) were then dissolved in toluene (150 ml). Isopropanol was removed by azeotropic distillation for 4 h by a Dean-Stark apparatus. Then, KOH (3.1 g, 55.4 mmol) was added, and the mixture was refluxed for 4 h. The precipitate was collected by filtration, washed with cyclohexane, and dried under reduced pressure to give 2-(7-bromo-9,9-dihexyl-9*H*-fluorene-2-yl)triolborate (25.7 g, 44.3 mmol, 80% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.93–7.77 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 3.56 (s, –O(C*H*$_2$)$_3$CCH$_3$), 2.12 (br, –C*H*$_2$(CH$_2$)$_4$CH$_3$), 1.36–0.66 (m, –CH$_2$(C*H*$_2$)$_4$C*H*$_3$), 0.47 (s, –O(CH$_2$)$_3$CC*H*$_3$).
^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 150, 147.8, 141.0, 140, 137.9, 134.8, 133.5, 131.4, 130.6, 129.6, 128.4, 122.5, 69.1, 52.6, 43.9, 32.9, 31.8, 29.9, 24.4, 22.7, 14.9, 14.1.

HRMS (ESI): *m*/*z* calcd for $C_{30}H_{41}BO_3Br^-$: 539.2337; found: 539.23407 $[M–K]^-$

Synthesis of 4-iodobenzyl 2-bromo-2-methylpropanoate

Scheme S2. Synthesis of iodobenzene-functionalized ATRP initiator



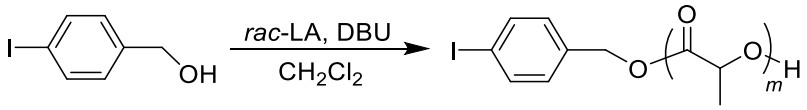
4-Iodobenzyl alcohol (10 g, 42.7 mmol), DMAP (260 mg, 2.1 μmol), and Et_3N (7.7 mL, 55.5 mmol) in dry-CH_2Cl_2 was added 2-bromo-2-dimethylpropionyl bromaide (6.3 mL, 51.3 mmol). After stirring at room temperature for 2 h, the reaction mature was filtered, and the filtrate was washed with saturated Na_2CO_3 and 1 mol L^{-1} HCl solutions. The combined organic layers were then dried over $MgSO_4$ and evaporated to dryness to give 4-iodobenzyl 2-bromo-2-methylpropanoate (13.1 g, 80% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.22-7.49 (m, Ar–*H*), 5.13 (s, 2H, –C*H*$_2$O–), 1.92 (s, 6H, –C*H*$_3$).
^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 171.3, 134.4, 131.8, 129.6, 122.4, 66.75, 55.50, 30.74.

HRMS (EI): *m*/*z* calcd for $C_{11}H_{12}O_2BrI$: 381.9065; found: 381.90496 $[M^{\bullet}]^+$

Synthesis of iodobenzene-terminated poly(*rac*-lactide)

Scheme S3. Synthesis of iodobenzene-terminated poly(*rac*-lactide)

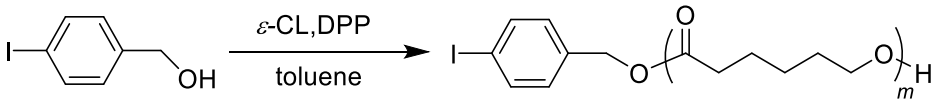


In the glovebox, DBU (51.9 μL, 347 μmol, 1.0 eq.) was added to a stirred solution of the 4-iodobenzyl alcohol (81.2 mg, 347 mmol, 1.0 eq.) and *rac*-LA (2.50 g, 17.35 mmol, 50 eq.) in dry-CH_2Cl_2 (25 mL). After 10 min, an excess of benzoic acid (ca. 500 mg) was added to the reaction mixture to terminate the polymerization. The mixture was purified by reprecipitation using THF as a good solvent and cold MeOH as a poor solvent to give iodobenzene-terminated poly(*rac*-lactide) (**PLA−I**; 1.81 g, 72.6% yield) as a white powder.

$M_{n,SEC}$ = 5,800 g mol^{-1} (THF); $M_{n,NMR}$ = 6,000 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.06.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (m, Ar–*H*), 5.19 (m, –C*H*$_2$O–, –C(=O)C*H*CH$_3$O–), 4.40–4.25 (m, –C(=O)C*H*CH$_3$OH), 1.58 (m, –C(=O)CHC*H*$_3$O–).

Synthesis of iodobenzene-terminated poly(ε-caprolactone)

Scheme S4. Synthesis of iodobenzene-terminated poly(ε-caprolactone)



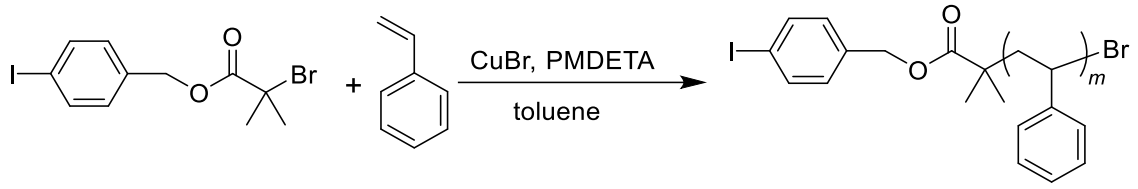
In the glovebox, DPP (73.1 mg, 292 μmol, 0.8 eq.) was added to a stirred solution of the 4-iodobenzyl alcohol (85.4 mg, 365 μmol, 1.0 eq.) and ε-CL (2.50 g, 21.9 mmol, 60 eq.) in dry-toluene (25 mL). After 6 h, an excess of Amberlyst® A21 was added to the reaction mixture to terminate the polymerization. The mixture was purified by reprecipitation using THF as a good solvent and cold MeOH as a poor solvent to give iodobenzene-terminated poly(ε-caprolactone) (**PCL−I**; 1.91 g, 76.5% yield) as a white powder.

$M_{n,SEC}$ = 6,500 g mol^{-1} (THF); $M_{n,NMR}$ = 6,700 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.07.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (m, Ar–*H*), 5.19 (s, –C*H*$_2$O–), 4.06 (t, –COCH$_2$–), 3.65 (m, –C*H*$_2$OH), 2.31 (t, –C(=O)C*H*$_2$–), 1.60–1.70 (m, –C(=O)CH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$O–), 1.37 (m, –CO(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_2$O–).

Synthesis of iodobenzene-terminated polystyrene

Scheme S5. Synthesis of iodobenzene-terminated polystyrene

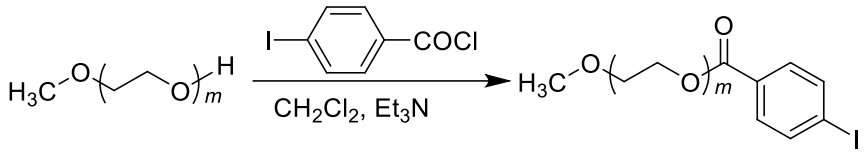


CuBr (230 mg, 1.60 mmol, 1.0 eq.) was evacuated for 30 min in a Schlenk flask and backfilled with argon. Styrene monomer was passed through a basic Al_2O_3 column in order to remove the inhibitor. A mixture of styrene monomer (5.0 g, 48.0 mmol, 30 eq.), PMDETA (334 μL, 1.60 mmol, 1.0 eq.), and 4-iodobenzyl 2-bromo-2-methylpropanoate (613 mg, 1.60 mmol, 1.0 eq.) in dry-toluene was subjected to three freeze-pump-thaw cycles. Next, the liquid mixture was transferred to the Schlenk flask containing CuBr for the polymerization. The polymerization was performed in a preheated oil bath at 50 °C, and the monomer conversion was monitored by ^{1}H NMR at different polymerization time interval. The polymerization was terminated by bubbling air into the solution. The crude product was passed through a neutral Al_2O_3 column and eluted with THF to remove the catalyst. The mixture was purified by reprecipitation using THF as a good solvent and cold MeOH as a poor solvent to give iodobenzene-terminated polystyrene (**PSt−I**; 2.70 g, 53.9% yield) as white powder.

$M_{n,SEC}$ = 2,500 g mol^{-1} (THF); $M_{n,NMR}$ = 2,150 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.17.
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.22–7.49 (m, Ar–*H*), 6.49–6.39 (m, Ar–*H*), 5.13 (s, 2H, –C*H*$_2$O–), 2.00–1.54 (s, 2H, Ar−C*H*$_2$−), 1.92 (s, 6H, –C*H*$_3$).

Synthesis of iodobenzene-terminated poly(ethylene oxide)

Scheme S6. Synthesis of iodobenzene-terminated poly(ethylene oxide)

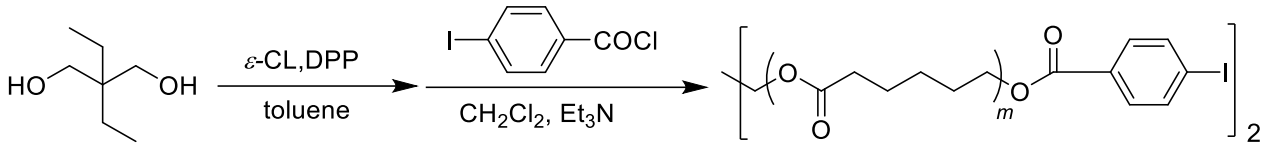


Poly(ethylene oxide) monomethyl ether ($M_{n,NMR}$ = 5,000 g mol^{-1}, 1.0 g, 0.20 mmol) was added to a 200 mL three-necked flask and was dried under vacuum at room temperature for 9 h. A solution of 4-iodobenzoyl chloride (60 mg, 0.22 mmol) and Et_3N (35 μL, 0.25 mmol) in dry-CH_2Cl_2 (50 mL) was degassed by bubbling with Ar gas for 30 min, then it was transferred to the three-necked flask using a cannula. After stirring at room temperature for 24 h, the reaction mature was filtered, and the filtrate was washed with saturated Na_2CO_3 and 1 mol L^{-1} HCl solutions. The organic layers was concentrated by rotary evaporation, and the residue was precipitated using THF as a good solvent and cold *n*-hexane as a poor solvent to give iodobenzene-terminated poly(ethylene oxide) (**PEO−I**; 1.04 g, 99.5% yield) as a white powder.

$M_{n,SEC}$ = 3,100 g mol^{-1} (THF); $M_{n,NMR}$ = 5,300 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.25.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (m, Ar–*H*), 3.67–3.56 (m, –C*H*$_2$C*H*$_2$–, –C*H*$_3$).

Synthesis of linear poly(ε-caprolactone) possessing an iodobenzene moiety each chan end

Scheme S7. Synthesis of linear PCL possessing an iodobenzene moiety each chain end



In the glovebox, DPP (146 mg, 584 μmol, 1.6 eq.) was added to a stirred solution of the 2,2-diethyl-1,3-propanediol (48.3 mg, 365 μmol, 1.0 eq.) and ε-CL (2.50 g, 21.9 mmol, 60 eq.) in dry-toluene (25 mL). After 1.5 h, an excess of Amberlyst® A21 was added to the reaction mixture to terminate the polymerization. The mixture was purified by reprecipitation using THF as a good solvent and cold MeOH as a poor solvent to give linear poly(ε-caprolactone) (1.91 g, 76.5% yield) as a white powder.

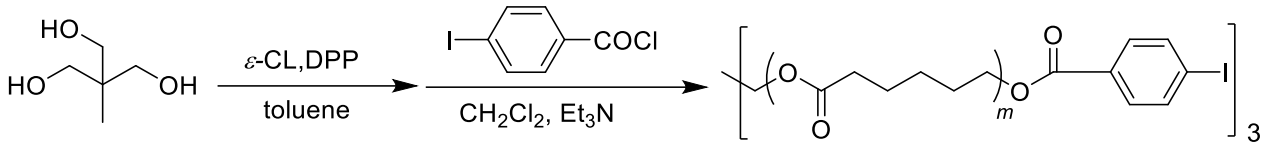
Linear poly(ε-caprolactone) ($M_{n,SEC}$ = 8,440 g mol^{-1}, $M_{n,NMR}$ = 7,460 g mol^{-1}, $Đ_M$ = 1.06, 1.0 g, 0.13 mmol) was added to a 20 mL three-necked flask and was dried under vacuum at room temperature for 3 h. A solution of 4-iodobenzoyl chloride (80 mg, 0.29 mmol) and Et_3N (47 μL, 0.34 mmol) in dry-CH_2Cl_2 (50 mL) was degassed by bubbling with Ar gas for 30 min, and then it was transferred to the three-necked flask using a cannula. After stirring at room temperature for 24 h, the reaction mature was filtered, and the filtrate was washed with saturated Na_2CO_3 and 1 mol L^{-1} HCl solutions. The organic layers were concentrated by rotary evaporation, and the residue was precipitated using THF as a good solvent and cold MeOH as a poor solvent to give linear poly(ε-caprolactone) possessing an iodobenzene moiety each chain end (**(PCL−I)$_2$**; 940 mg, 93.9% yield) as a white powder.

$M_{n,SEC}$ = 9,400 g mol^{-1} (THF); $M_{n,NMR}$ = 7,900 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.05.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94–7.74 (m, Ar–*H*), 4.32 (t, –C*H*$_2$OBz–I), 4.07 (t, –COCH$_2$–), 2.32 (t, –C(=O)C*H*$_2$–), 1.70–1.60 (m, –C(=O)CH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$O–), 1.43–1.35 (m, –CO(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_2$O–, –C*H*$_2$CH$_3$), 0.84 (s, –C*H*$_3$).

Synthesis of three-armed star-shaped PCL with an iodobenzene moiety at each chain end

Scheme S8. Synthesis of three-armed star-shaped PCL



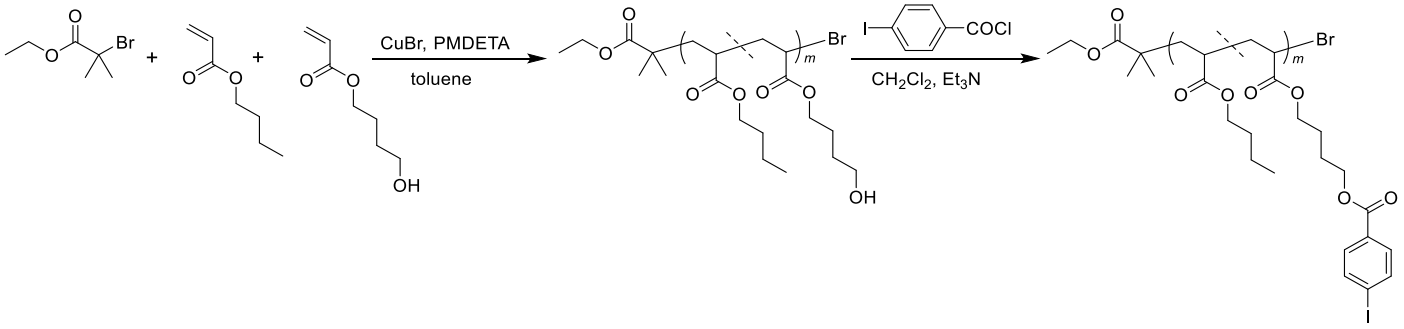
The star-shaped PCL was synthesis by the ring-opening polymerization of ε-CL (2.50 g, 21.9 mmol, 60 eq.) with trimethylolethane (43.9 mg, 365μmol, 1.0 eq.), DPP (219 mg, 876 μmol, 2.4 eq.) in dry-toluene (25 mL). Then, 4-iodobenzoyl chloride (130 mg, 0.50 mmol), Et_3N (106 μL, 0.76 mmol), and dry-CH_2Cl_2 (50 mL) were added to the residue, and the solution was stirred at room temperature for 24 h. The reaction mature was filtered and washed with saturated Na_2CO_3 and 1 mol L^{-1} HCl solutions, and the combined organic layer was concentrated by rotary evaporation. The residue was precipitated using THF as a good solvent and cold MeOH as a poor solvent to give three-armed star-shaped PCL with an iodobenzene moiety at each chain end (**(PCL−I)$_3$**; 930 mg, 71.1% yield) as a white powder.

$M_{n,SEC}$ = 12,350 g mol^{-1} (THF); $M_{n,NMR}$ = 7,300 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.05.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94–7.74 (m, Ar–*H*), 4.30 (t, –C*H*$_2$OBz–I), 4.06 (t, –COC*H*$_2$–), 2.31 (t, –C(=O)C*H*$_2$–), 1.89–1.55 (m, –C(=O)CH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$O–), 1.38 (m, –CO(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_2$O–), 1.00 (s, –C*H*$_3$).

Synthesis of poly(*n*-butyl acrylate) possessing iodobenzene side chain

Scheme S9. Synthesis of poly(*n*-butyl acrylate) possessing iodobenzene side chain



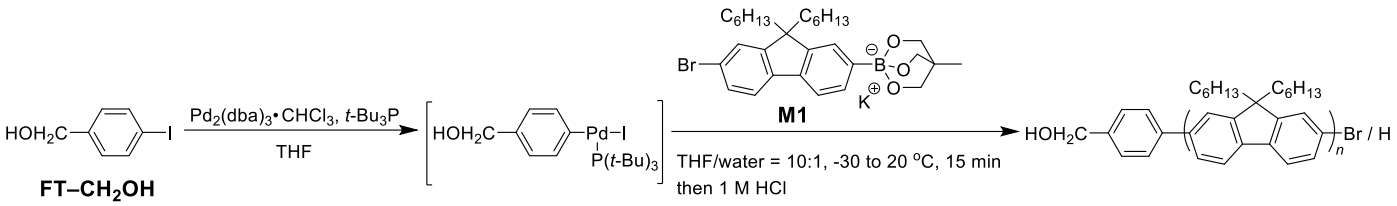
CuBr (336 mg, 2.34 mmol, 1.0 eq.) was evacuated for 30 min in a Schlenk flask and backfilled with argon. *n*-Butyl acrylate and 4-hydroxybutyl acrylate were passed through a basic Al_2O_3 column in order to remove the inhibitor. A mixture of *n*-butyl acrylate (15 g, 117 mmol, 50 eq.), 4-hydroxybutyl acrylate (1.69 g, 2.34 mmol, 5 eq.), PMDETA (489 μL, 2.34 mmol, 1.0 eq.), and ethyl 2-bromoisobutyrate (457 mg, 2.34 mmol, 1.0 eq.) in dry-toluene was subjected to three freeze-pump-thaw cycles. Next, the liquid mixture was transferred to the Schlenk flask containing CuBr for the polymerization. The polymerization was performed in a preheated oil bath at 50 °C, and the monomer conversion was monitored by ^{1}H NMR at different polymerization time interval. The reaction mixture was quenched in liquid nitrogen and allowed to warm to room temperature. After removing the remaining *n*-butyl acrylate and 4-hydroxy acrylate by evaporation under reduced pressure, 4-iodobenzoyl chloride (55 mg, 2.08 mmol), Et_3N (229 μL, 3.12 mmol), and dry-CH_2Cl_2 (50 mL) were added to the residue, and the solution was stirred at room temperature for 24 h. The reaction mature was filtered and washed with saturated Na_2CO_3 and 1 mol L^{-1} HCl solutions, and the combined organic layer was concentrated by rotary evaporation. The residue was precipitated using THF as a good solvent and cold *n*-hexane as a poor solvent to give poly(*n*-butyl acrylate) possessing iodobenzene at the side chain (**P(BA$_{50}$-*co*-BzI$_4$)**; 6.67 g, 40.0%) as a yellow viscous liquid.

$M_{n,SEC}$ = 7,630 g mol^{-1} (THF); $M_{n,NMR}$ = 8,100 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.09.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.94–7.74 (m, Ar–*H*), 4.35 (t, –C*H*$_2$OBz–I), 4.04 (t, –C(=O)OC*H*$_2$CH$_2$–), 2.28 (br, –C*H*$_2$CH–), 1.92 (br, –CH$_2$C*H*–), 1.60–1.38 (m, –(C*H*$_2$)$_2$–), 1.24 (t, –CH$_2$C*H*$_3$), 1.09 (d, –C(=O)C(C*H*$_3$)$_2$–), 0.94 (t, –C*H*$_3$).

Polymerization of potassium 2-(7-bromo-9,9-dihexyl-9*H*-fluorene-2-yl)triolborate

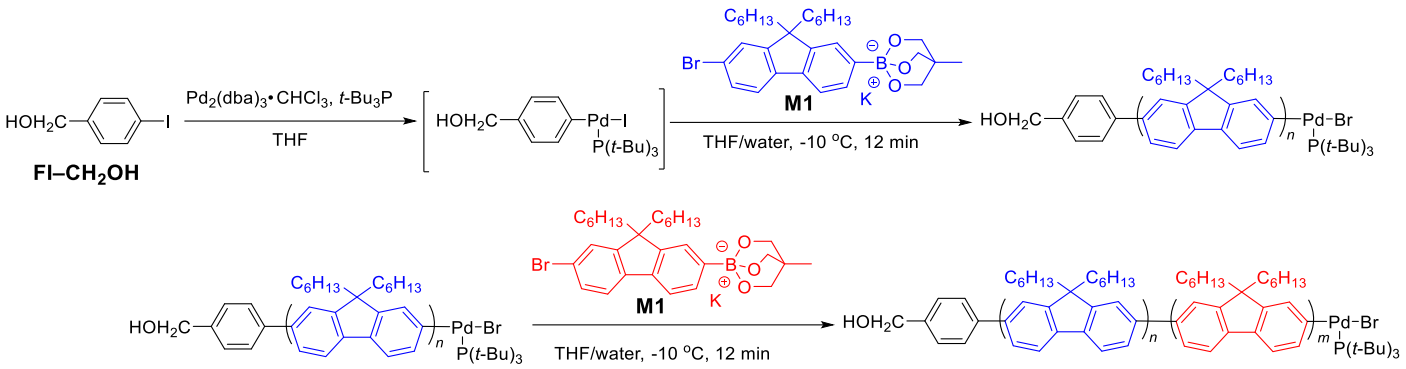
Scheme S10. Polymerization of triolborate-type fluorene monomer



In the glovebox, 4-iodobenzyl alcohol (**FI−CH$_2$OH**; 115 μL, 57.5 μmol, as 0.50 mol L^{-1} stock solution in THF), $Pd_2(dba)_3$•$CHCl_3$ (17.9 mg, 17.2 μmol), and *t*-Bu_3P (253 μL, 127 μmol, as 0.5 mol L^{-1} stock solution in THF) were placed in a vial and dissolved in THF (5 mL), after stirring for 1 h at room temperature. The vial containing the stock solution of the Pd-initiator was sealed and taken out from the glovebox. In a 300 mL recovery flask, a mixture of THF (86 mL) and deionized water (8.6 mL) was deoxygenated by argon bubbling at least for 1 h. The stock solution of the Pd-initiator was transferred to the flask using a cannula under an argon atmosphere, and the entire mixture was cooled to −10 °C. Potassium 2-(7-bromo-9,9-dihexyl-9*H*-fluorene-2-yl)triolborate (**M1**; 3.45 mL, 0.86 mmol, as 0.25 mol L^{-1} stock solution in THF) was quickly added to the mixture under an argon atmosphere, and the entire mixture was vigorously stirred for 15 min at −10 °C. To the reaction mixture, 1 mol L^{-1} HCl (5 mL) was added to terminate the polymerization. The solvent was removed by evaporation, and the residue was dissolved in CH_2Cl_2 and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated. The mixture was filtered, and the filtrate was evaporated under reduced pressure. The resulting solution was concentrated and precipitated using THF as a good solvent and cold acetone as a poor solvent to give **HOCH$_2$−PF**. The polymerization results are listed in **Table 1**.

Evaluation of the living nature of the SCTP of triolborate salt monomer

Scheme S11. Post-polymerization experiment for the SCTP



In the glovebox, **FI−CH₂OH** (1.15 mL, 0.58 mmol, as 0.5 mol L^{-1} stock solution in THF), $Pd_2(dba)_3$•$CHCl_3$ (178.6 mg, 0.173mmol), and *t*-Bu_3P (2.53 mL, 1.27 mmol, as 0.5 mol L^{-1} stock solution in THF) were placed in a vial and dissolved in THF (15 mL), then stirring for 1 h at room temperature. The vial containing the stock solution of the Pd-initiator was sealed and taken out from the glovebox. In a 1000 mL recovery flask, a mixture of THF (860 mL) and water (86 mL) was deoxygenated by argon bubbling at least for 1 h. The stock solution of the Pd-initiator was transferred to the flask using a cannula under an argon atmosphere, and the entire mixture was cooled to −10 °C. **M1** (34.5 mL, 8.63 mmol, as 0.25 mol L^{-1} stock solution in THF) was quickly added to the mixture under an argon atmosphere, and the entire mixture was vigorously stirred for 12 min at −10 °C. Then, **M1** (34.5 mL, 8.63 mmol, as 0.25 mol L^{-1} stock solution in THF) was added. A small aliquot (0.3 mL) of the reaction mixture was collected at 0.5, 1.0, 2.0, 5.0, 10, 12.5, 13, 14, 17, and 24 min. Each aliquot was quenched with 1 mol L^{-1} HCl solution and extracted with CH_2Cl_2. The separated organic layer was evaporated under reduced pressure to get a residue. Half of the residue was dissolved in $CDCl_3$ to determine the conversion of monomer by ^1H NMR (conversions of 31%, 39%, 65%, 85%, 99%, 119%, 146%, 161%, 176%, and 199% were observed for 0.5, 1.0, 2.0, 5.0, 10, 12.5, 13, 14, 17, and 24 min, respectively). The other half of the residue was dissolved in THF, and the solution was filtered. The filtrate was analyzed by SEC to determine the *M*n and $Đ_M$ values of the polymers. The $M_{n,SEC}$ ($Đ_M$) values of each polymer initiated by $Pd_2(dba)_3$•$CHCl_3$/*t*-Bu_3P/**FI−CH₂OH** for 0.5, 1.0, 2.0, 5.0, 10, 12.5, 13, 14, 17, and 24 min were 1960 (1.22), 2400 (1.22), 3860 (1.23), 4970 (1.23), 5760 (1.23), 6940 (1.25), 8450 (1.25), 9280 (1.26), 9850 (1.27), and 11460 g mol^{-1} (1.28) respectively. The polymerization results are listed in **Table S1**.

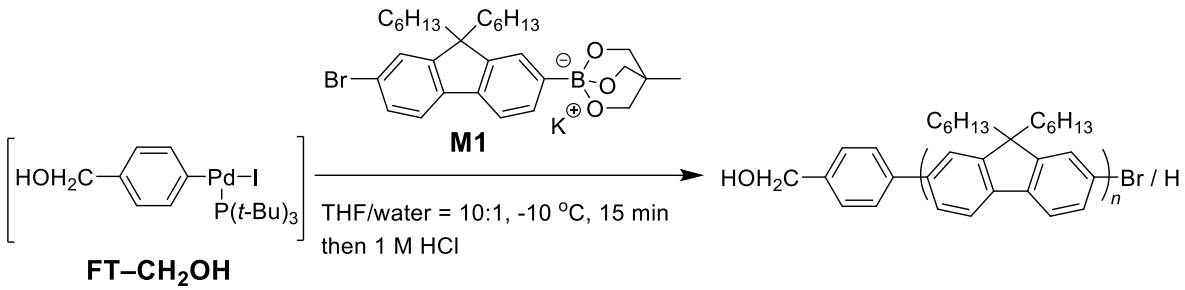
Table S1. Monomer conversion, molecular weight, and dispersity at each reaction time[a]

reaction time (min)	conversion (%)	$M_{n,SEC}$[b] (g mol^{-1})	$Đ_M$[b]	$M_{n,NMR}$[c] (g mol^{-1})
0.5	31	2,100	1.22	1,960
1.0	39	2,500	1.22	2,400
2.0	65	3,700	1.23	3,860
5.0	85	5,000	1.23	4,970
10.0	99	6,100	1.24	5,760
12.5	119	7,100	1.25	6,940
13.0	146	8,600	1.25	8,450
14.0	161	9,400	1.26	9,280
17.0	176	10,000	1.27	9,850
24.0	199	12,000	1.28	11,460

[a] Polymerization conditions: Ar atmosphere; solvent, THF/water (v/v) = 10:1; [**M1**]$_0$ = 10 mmol L^{-1}; [**M1**]$_0$/[**FI−CH$_2$OH**]$_0$/[$Pd_2(dba)_3$•$CHCl_3$]/[*t*-Bu_3P] = 15:1:0.3:2.2. [b] Determined by SEC (PSt standards, THF, 40 °C). [c] Determined by ^{1}H NMR spectrum in $CDCl_3$.

Molecular weight control

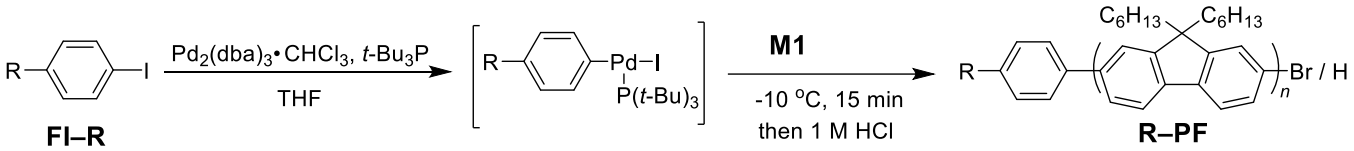
Scheme S12. Molecular weight control of PF



The SCTP of **M1** was conducted with the optimized condition while varying the [**M1**]$_0$/[**FI−CH$_2$OH**]$_0$ ratio (30:1, 45:1, 90:1, 180:1 and 270:1) for aiming at synthesizing the higher molecular weight PFs. The final product of **HOCH$_2$−PF** was obtained as a yellow solid. The polymerization results are listed in **Table 1**.

Synthesis of *α*-end-functionalized PFs using functional initiators

Scheme S13. Polymerization with various initiators



FI–R

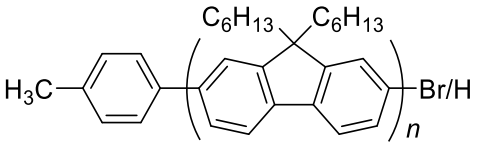
R = CH_3: **FI–CH_3**
R = OH: **FI–OH**
R = NH_2: **FI–NH_2**
R = $(C=O)CH_3$: **FI–$(C=O)CH_3$**
R = (C=O)OEt: **FI–(C=O)OEt**
R = C≡C–TMS: **FI–C≡C–TMS**

R–PF

R = CH_3: **CH_3PF**
R = OH: **HO–PF**
R = NH_2: **NH_2–PF**
R = $(C=O)CH_3$: **CH_3CO–PF**
R = (C=O)OEt: **EtOOC–PF**
R = C≡C–TMS: **TMS–C≡C–PF**

The *α*-end-functionalized PF was synthesized by the SCTP of **M1** (3.45 mL, 0.86 mmol, as 0.25 mol L^{-1} stock solution in THF) with aryl halide (**FI−R**; 115 μL, 57.5 μmol, as 0.50 mol L^{-1} stock solution in THF), $Pd_2(dba)_3$•$CHCl_3$ (17.9 mg, 17.2 μmol), *t*-Bu_3P (253 μL, 127 μmol, as 0.5 mol L^{-1} stock solution in THF) in a mixture of THF (86 mL), K_3PO_4 (18.3 mg, 86.3 μmol), and deionized water (8.6 μL). The final products of *α*-end-functionalized PF was obtained as a yellow solid.

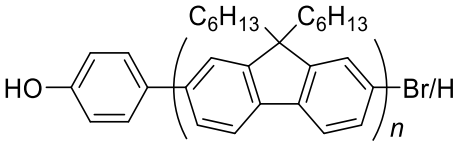
α-Methyl-functionalized poly(9,9-dihexyl-2,7-fluorene)



248 mg, 86.8% yield: Yellow solid. $M_{n,SEC}$ = 4,800 g mol^{-1} (THF); $M_{n,NMR}$ = 4,400 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.35.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.93–7.77 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 2.45 (s, –C*H*$_3$), 2.12 (br, –C*H*$_2$(CH_2)$_4$$CH_3$), 1.36–0.66 (m, –$CH_2$(C*H*$_2$)$_4$C*H*$_3$).

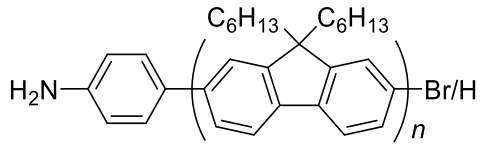
α-Hydroxyl-functionalized poly(9,9-dihexyl-2,7-fluorene)



245 mg, 85.8% yield: Yellow solid. $M_{n,SEC}$ = 5,100 g mol^{-1} (THF); $M_{n,NMR}$ = 5,300 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.27.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.93–7.77 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 2.12 (br, –C*H*$_2$(CH_2)$_4$$CH_3$), 1.36–0.66 (m, –$CH_2$(C*H*$_2$)$_4$C*H*$_3$).

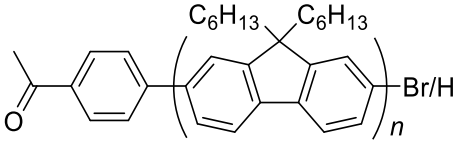
α-Amino-functionalized poly(9,9-dihexyl-2,7-fluorene)



208 mg, 73.0% yield: Yellow solid. $M_{n,SEC}$ = 5,000 g mol^{-1} (THF); $M_{n,NMR}$ = 5,100 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.19.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.77 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 2.37 (s, -C*H*$_3$), 2.12 (br, –C*H*$_2$(CH$_2$)$_4$CH$_3$), 1.36–0.66 (m, –CH$_2$(C*H*$_2$)$_4$C*H*$_3$).

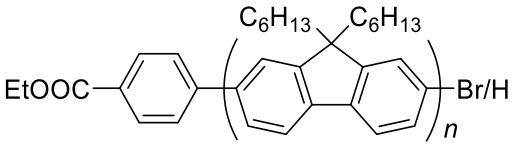
α-Acetyl-functionalized poly(9,9-dihexyl-2,7-fluorene)



238 mg, 83.3% yield: Yellow solid. $M_{n,SEC}$ = 5,300 g mol^{-1} (THF); $M_{n,NMR}$ = 5,700 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.36.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.77 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 3.51 (d, –COC*H*$_3$), 2.12 (br, –C*H*$_2$(CH$_2$)$_4$CH$_3$), 1.36–0.66 (m, –CH$_2$(C*H*$_2$)$_4$C*H*$_3$).

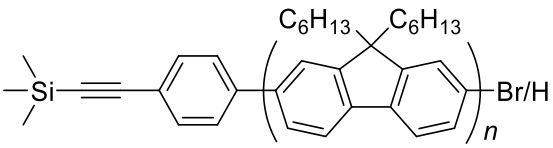
α-Ethyl ester-functionalized poly(9,9-dihexyl-2,7-fluorene)



234 mg, 81.7% yield: Yellow solid. $M_{n,SEC}$ = 5,200 g mol^{-1} (THF); $M_{n,NMR}$ = 4,100 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.23.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.77 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 4.45 (m, –C*H*$_2$CH$_3$), 2.12 (br, –C*H*$_2$(CH$_2$)$_4$CH$_3$), 1.45 (–C*H*$_3$), 1.36–0.66 (m, –CH$_2$(C*H*$_2$)$_4$C*H*$_3$).

α-Trimethylsilylethynyl-functionalized poly(9,9-dihexyl-2,7-fluorene)



237 mg, 82.8% yield: Yellow solid. $M_{n,SEC}$ = 6,000 g mol^{-1} (THF); $M_{n,NMR}$ = 7,700 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.35.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.77 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 2.12 (br, –C*H*$_2$(CH$_2$)$_4$CH$_3$), 1.36–0.66 (m, –CH$_2$(C*H*$_2$)$_4$C*H*$_3$), 0.8 (–Si–C≡C–(C*H*$_3$)$_3$).

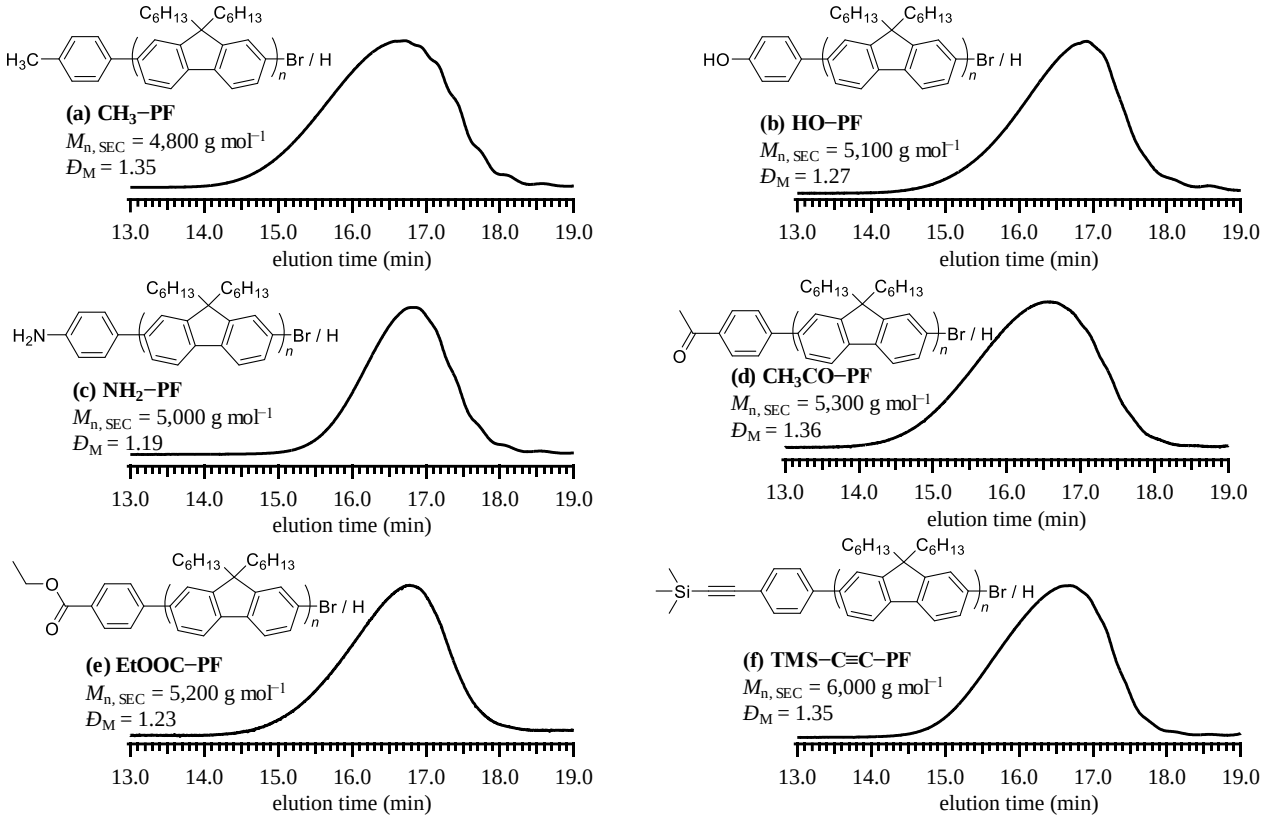


Figure S1. SEC traces of (a) **CH₃−PF**, (b) **HO−PF**, (c) **H₂N−PF**, (d) **CH₃CO−PF**, (e) **EtOOC−PF**, and (f) **TMS−C≡C−PF** detected by RI detector (eluent, THF; flow rate 1.0 mL min^{-1}).

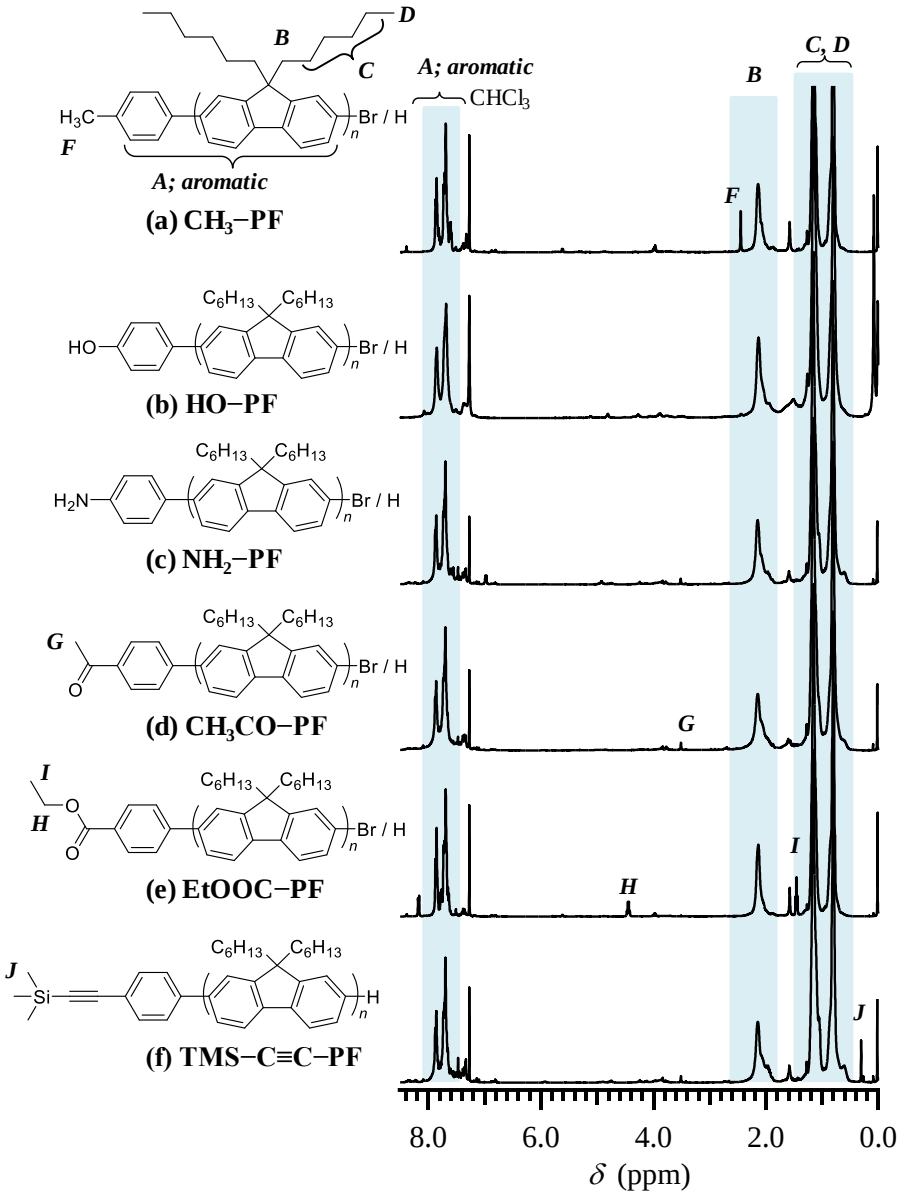
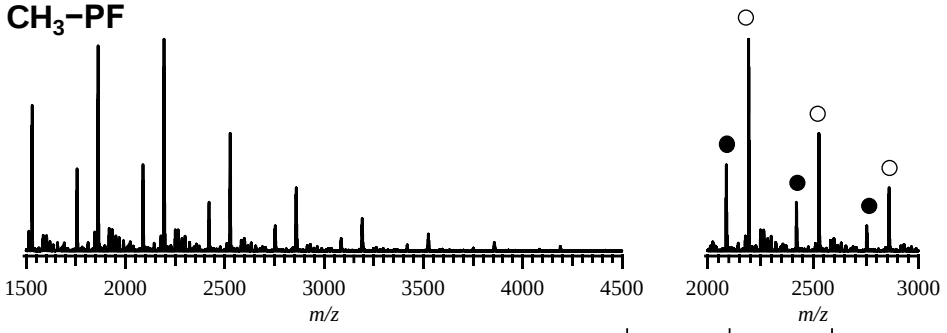


Figure S2. ^{1}H NMR spectra of (a) **CH_3−PF**, (b)**HO−PF**, (c) **H_2N−PF**, (d) **CH_3CO−PF**, (e) **EtOOC−PF**, and (f) **TMS−C≡C−PF** (solvent, $CDCl_3$).

(a) CH_3−PF



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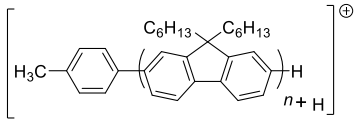
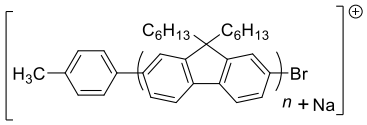


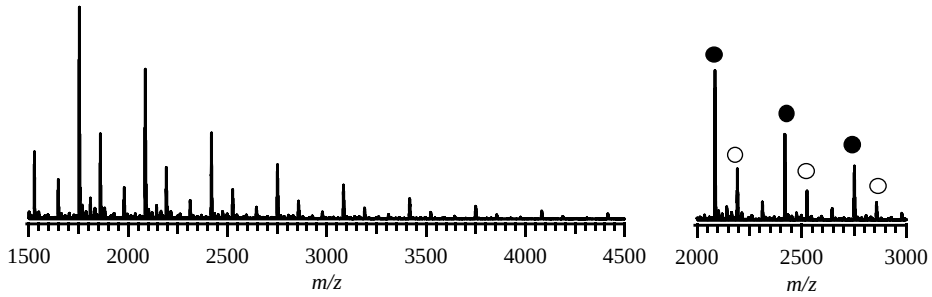
	n = 6	*n* = 7	*n* = 8
Clcd.	2085.57	2417.82	2750.07
Found	2085.54	2418.65	2750.90

○ =



	n = 6	*n* = 7	*n* = 8
Clcd.	2186.47	2518.72	2850.97
Found	2185.60	2519.66	2850.19

(b) HO−PF



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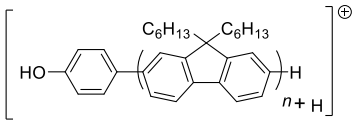
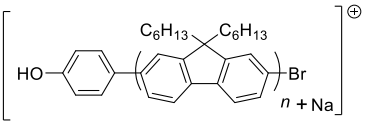


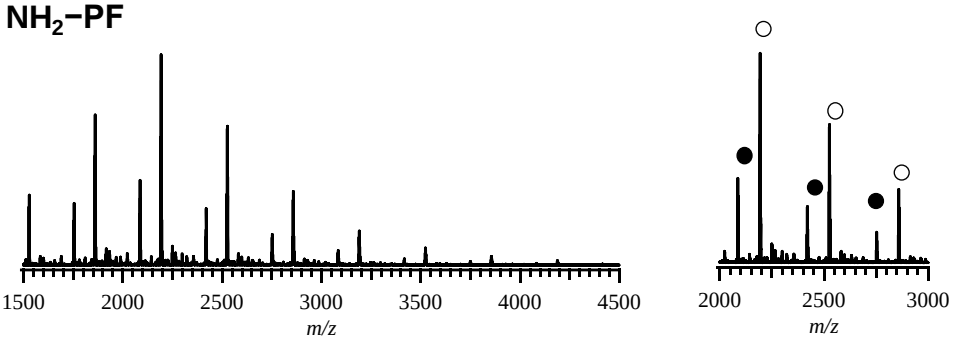
	n = 6	*n* = 7	*n* = 8
Clcd.	2087.54	2419.79	2752.05
Found	2087.62	2419.90	2752.57

○ =



	n = 6	*n* = 7	*n* = 8
Clcd.	2188.44	2520.70	2852.95
Found	2188.66	2520.94	2852.10

(c) NH_2−PF



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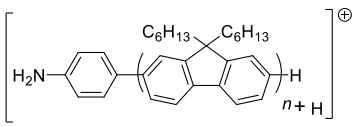
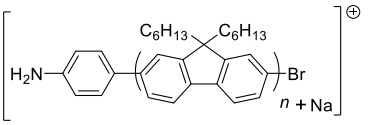


	n = 6	*n* = 7	*n* = 8
Clcd.	2086.00	2418.81	2751.06
Found	2087.52	2418.85	2751.12

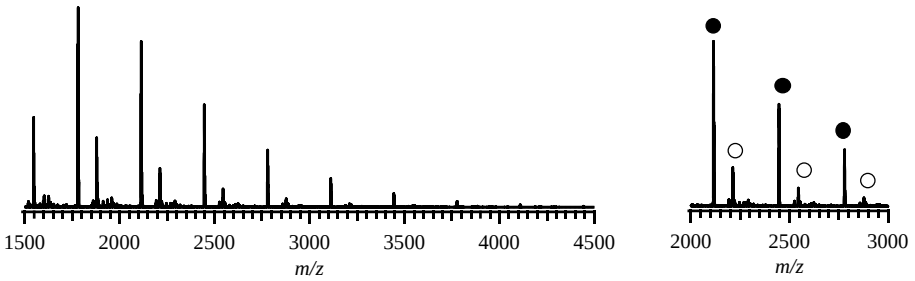
○ =

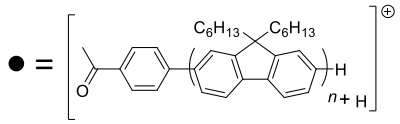


	n = 6	*n* = 7	*n* = 8
Clcd.	2187.46	2519.71	2851.96
Found	2189.04	2520.00	2852.50

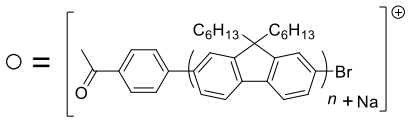
Figure S3 (continue)

(d) CH_3CO−PF



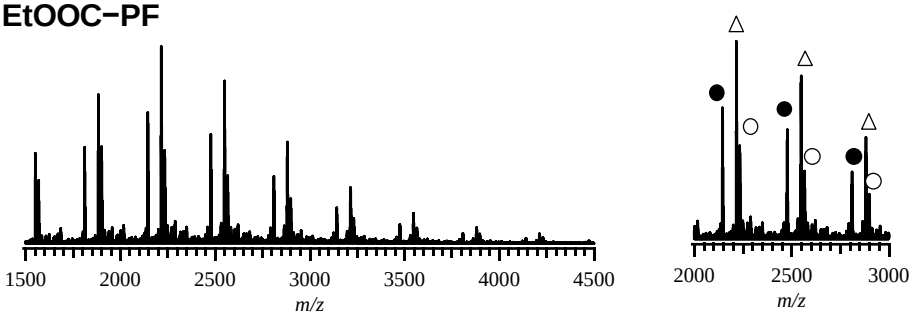


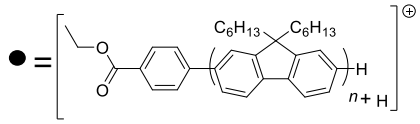
	n = 6	*n* = 7	*n* = 8
Clcd.	2113.56	2445.81	2778.06
Found	2113.56	2445.76	2778.14



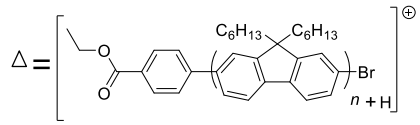
	n = 6	*n* = 7	*n* = 8
Clcd.	2211.78	2543.97	2875.65
Found	2211.46	2544.71	2876.96

(e) EtOOC−PF

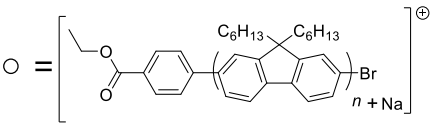




	n = 6	*n* = 7	*n* = 8
Clcd.	2097.57	2429.82	2762.07
Found	2097.54	2429.81	2762.10

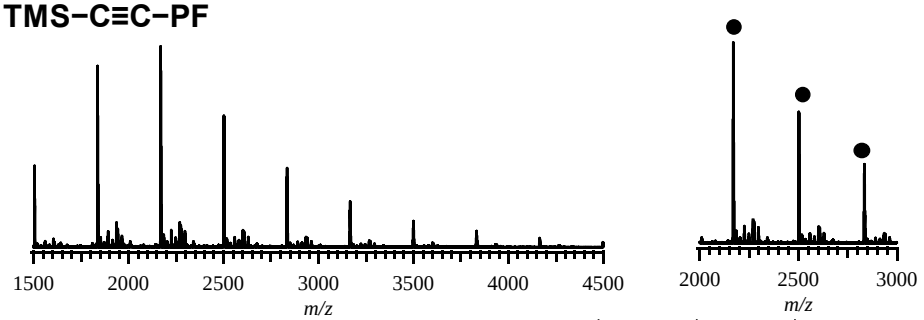


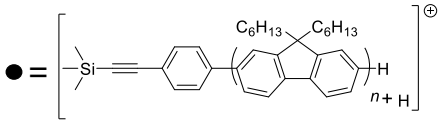
	n = 6	*n* = 7	*n* = 8
Clcd.	2221.48	2553.73	2885.98
Found	2222.66	2552.93	2886.27



	n = 6	*n* = 7	*n* = 8
Clcd.	2244.47	2576.72	2908.97
Found	2242.87	2575.09	2899.45

(f) TMS−C≡C−PF



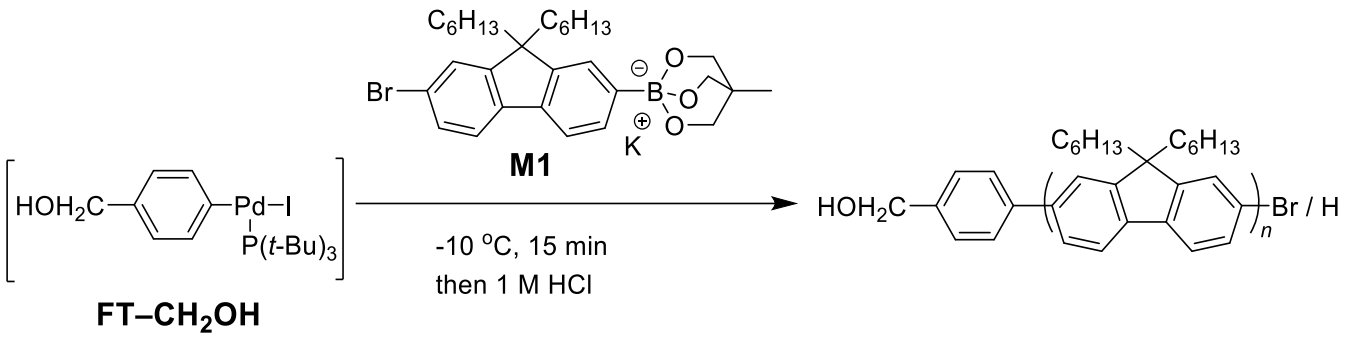


	n = 6	*n* = 7	*n* = 8
Clcd.	2167.59	2499.84	2832.09
Found	2168.10	2500.87	2833.00

Figure S3. MALDI-TOF MS spectra of (a) **CH_3−PF**, (b) **HO−PF**, (c) **H_2N−PF**, (d) **CH_3CO−PF**, (e) **EtOOC−PF**, and (f) **TMS−C≡C−PF**.

Effect of water content in the solvent on the polymerization properties

Scheme S14. Polymerization in THF/water cosolvent with varied water content



In order to elucidate the effect of water content in the solvent on the polymerization properties, the SCTP of **M1** was performed with varying the THF/water ratio (THF/water (v/v) =10:1, 100:1, 1000:1 and 5000:1). The final product of **HOCH₂−PF** was obtained as a yellow solid. The polymerization results are listed in **Table S2**.

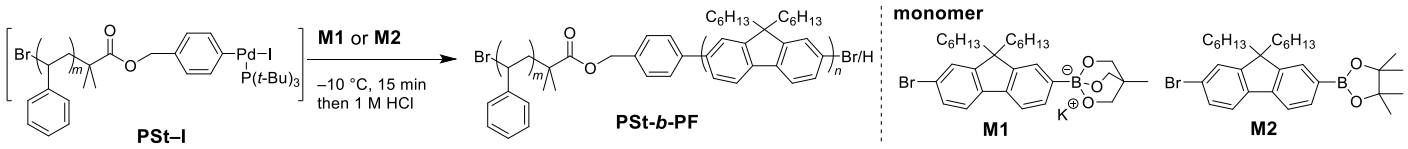
Table S2. Effect of M1 SCTP on varying water content in solvent[a]

run	THF/H_2O (v/v)	$M_{n,SEC}$[b] (g mol^{-1})	$M_{n,NMR}$[c] (g mol^{-1})	$Đ_M$[b]	yield[d] (%)
1	10/1	12,300	12,600	1.24	83.2
2	100/1	11,400	12,400	1.22	85.2
3	1000/1	11,100	12,000	1.22	84.3
4[e]	5000/1	10,500	11,900	1.20	84.3

[a]Polymerization conditions: Ar atmosphere; temperature, −10 °C; [**M1**]$_0$ = 10 mmol L^{-1}; [**FI−CH₂OH**]$_0$/[**M1**]$_0$/[$Pd_2(dba)_3$•$CHCl_3$]/[*t*-Bu_3P]/[K_3PO_4] = 1:30:0.3:2.2:1.5. [b]Determined by SEC (PSt standards, THF, 40 °C). [c]Determined by ^1H NMR spectrum in $CDCl_3$. [d]Isolated yields. [e]Saturated aqueous solution of K_3PO_4.

The effect of water in the solvent on the block copolymer synthesis

Scheme S15. The effect of water in the solvent on the PF-*b*-PSt synthesis



In order to investigate the effect of water content in the solvent on the block copolymer synthesis, polymerizations of **M1** and **M2** was performed while varying the THF/water (v/v) ratio (10:1 and 5000:1). The polymerization results are listed in **Table S3**. The SEC traces of each product and macroiniators are depicted in **Figure S4**.

Table S3. SCTP of M1 or M2[a]

run	THF/H_2O (v/v)	**[PSt–I]**$_0$/[K_3PO_4]/[18-crown-6]	monomer	$M_{n,SEC}$[b] (g mol^{-1})	$M_{n,NMR}$[c] (g mol^{-1})	$Đ_M$[b]	yield[d] (%)
1[e]	5000/1	1/1.5/0	**M1**	12,700	12,700	1.20	87.0
2	10/1	1/150/0	**M1**	—	—	—	—
3[e]	5000/1	1/1.5/0	**M2**	—	—	—	—
4	10/1	1/150/50	**M2**	—	—	—	—

[a] Polymerization conditions: Ar atmosphere; [**M1**]$_0$ = 10 mmol L^{-1}; [**PSt–I**]$_0$/[monomer]$_0$/[$Pd_2(dba)_3$•$CHCl_3$]/[*t*-Bu_3P] = 1:15:0.3:2.2. [b] Determined by SEC (PSt standards, THF, 40 °C). [c] Determined by ^{1}H NMR spectrum in $CDCl_3$. [d] Isolated yields. [e] Saturated aqueous solution of K_3PO_4.

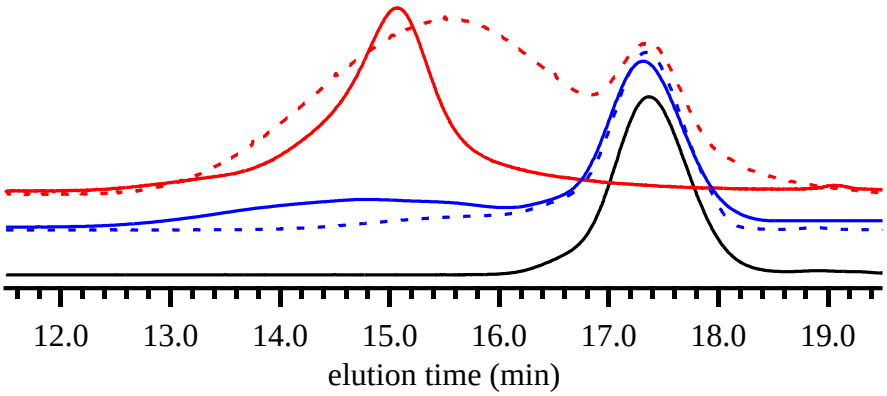
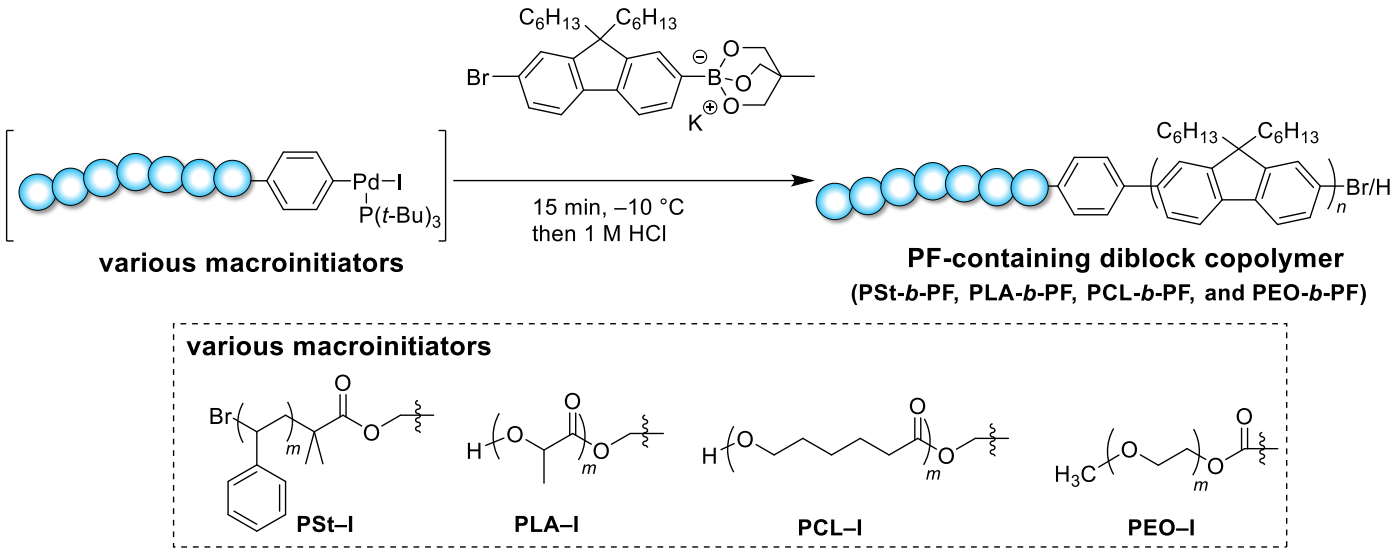


Figure S4. SEC traces of the product (red solid line; run 1 in Table S3, red broken line; run 2 in Table S3, blue solid line; run 3 in Table S3, blue broken line; run 4 in Table S3) and corresponding macroinitiator (black line) detected by RI detector (eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of PF-containing diblock copolymers using macroinitiators

Scheme S16. Synthesis of PF-containing diblock copolymers by SCTP with various macroinitiators



The PF-containing diblock copolymers were synthesized by the SCTP of **M1** (10.4 mL, 2.59 mmol, as 0.25 mol L^{-1} stock solution in THF) with the macroinitiators (86.3 μmol, 1.0 eq.; **PSt−I**, $M_{n,\,NMR}$ = 2,150, $Đ_M$ = 1.17; **PLA−I**, $M_{n,\,NMR}$ = 6,000, $Đ_M$ = 1.06; **PCL−I**, $M_{n,\,NMR}$ = 6,700, $Đ_M$ = 1.07; **PEO−I**, $M_{n,\,NMR}$ = 5,300, $Đ_M$ = 1.25), $Pd_2(dba)_3$•$CHCl_3$ (26.8 mg, 25.9 μmol, 0.5 eq.), and *t*-Bu_3P (380 μL, 190 μmol, as 0.5 mol L^{-1} stock solution in THF, 2.2 eq.) in a mixture of THF (248 mL), K_3PO_4 (2.7 mg, 13 μmol, 1.5 eq.), and deionized water (50 μL). The resulting solution was concentrated and precipitated using THF as a good solvent and cold mixed solvent of MeOH/acetone (= 1/1 (v/v)) as a poor solvent to give the PF-containing diblock copolymers. The final products were obtained as a yellow solid.

PSt-*b*-PF

0.93 g, 87.0% yield: Yellow solid. $M_{n,SEC}$ = 12,700 g mol^{-1} (THF); $M_{n,NMR}$ = 12,700 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.20.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.77 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 7.30–6.30 (m, Ar–*H*), 2.12 (br, –C*H*$_2$(CH_2)$_4$$CH_3$), 2.00–1.54 (m, –C*H*C*H*$_2$–), 1.36–0.66 (m, –CH_2(C*H*$_2$)$_4$C*H*$_3$).

PLA-*b*-PF

1.30 g, 90.0% yield: Yellow solid. $M_{n,SEC}$ = 16,800 g mol^{-1} (THF); $M_{n,NMR}$ = 15,700 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.19.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.77 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 5.29-5.11 (m, –COC*H*(CH_3)O–), 1.66-1.43 (m, –COCH(C*H*$_3$)O–), 2.12 (br, –C*H*$_2$(CH_2)$_4$$CH_3$), 1.36–0.66 (m, –$CH_2$(C*H*$_2$)$_4$C*H*$_3$).

PCL-*b*-PF

1.33 g, 85.0% yield: Yellow solid. $M_{n,SEC}$ = 17,700 g mol^{-1} (THF); $M_{n,NMR}$ = 16,000 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.11.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.77 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 4.06 (t, –COC*H*$_2$–), 3.65 (m, –C*H*$_2$OH), 2.31 (t, –COOC*H*$_2$–), 2.12 (br, –C*H*$_2$(CH_2)$_4$$CH_3$), 1.60-1.70 (m, –$COCH_2$C*H*$_2$($CH_2$)$_2$$CH_2CH_2$O–),1.37 (m, –CO($CH_2$)$_2$C*H*$_2$($CH_2$)$_2$O–), 1.36–0.66 (m, –$CH_2$(C*H*$_2$)$_4$C*H*$_3$).

PEO-*b*-PF

1.04 g, 67.3% yield: Yellow solid. $M_{n,SEC}$ = 10,300 g mol^{-1} (THF); $M_{n,NMR}$ = 14,200 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.50.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.77 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 3.67-3.55 (m, –OC*H*$_2$C*H*$_2$–, –OC*H*$_3$), 2.12 (br, –C*H*$_2$(CH$_2$)$_4$CH$_3$), 2.00–1.54 (m, –C*H*C*H*$_2$–), 1.36–0.66 (m, –CH$_2$(C*H*$_2$)$_4$C*H*$_3$).

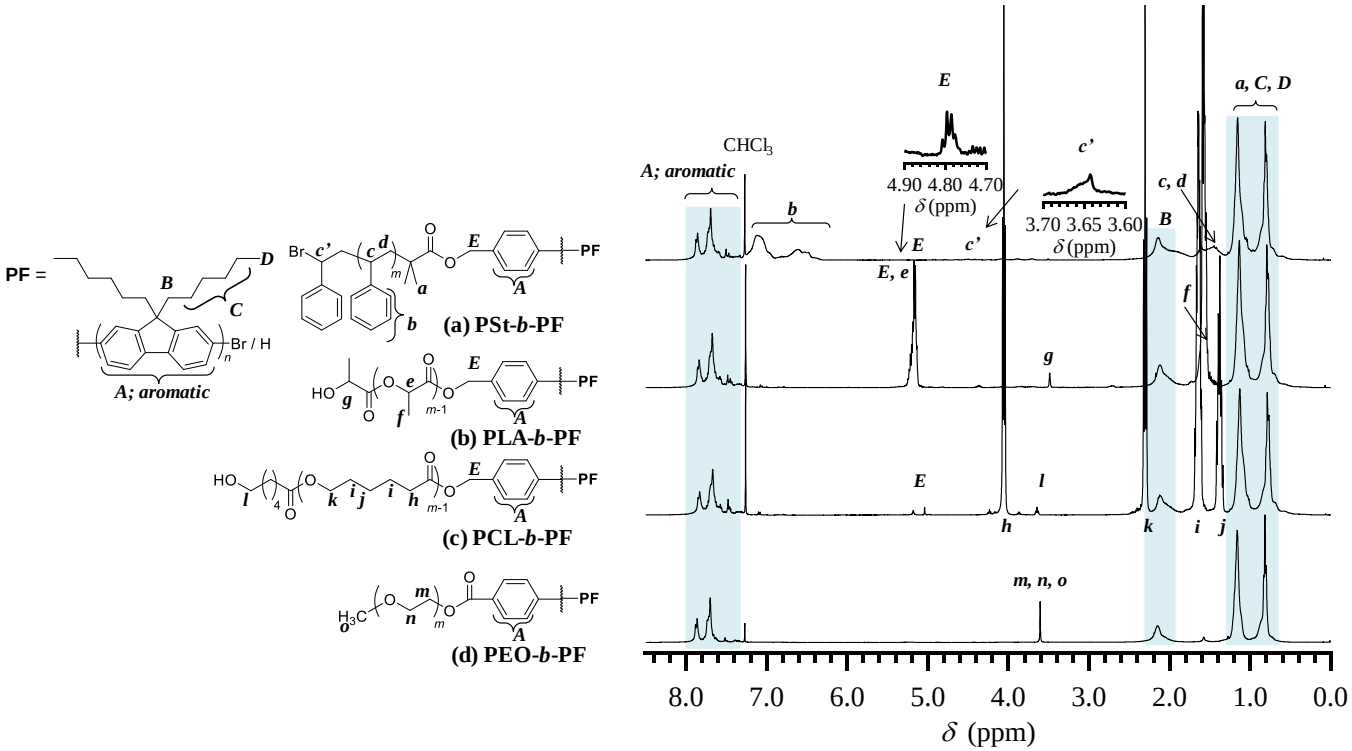
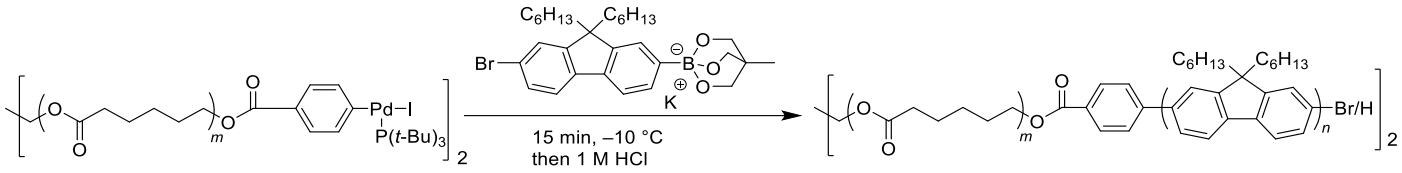


Figure S5. ^{1}H NMR spectra of (a) **PSt-*b*-PF**, (b) **PLA-*b*-PF**, (c) **PCL-*b*-PF**, and (d) **PEO-*b*-PF** (solvent, $CDCl_3$).

Synthesis of PF-containing triblock copolymer using macroinitiator

Scheme S17. Synthesis of PF-containing triblock copolymer using linear PCL with an iodobenzene moiety at each chain end as the macroinitiator



The PF-containing triblock copolymer was synthesized by the SCTP of **M1** (10.4 mL, 2.59 mmol, as 0.25 mol L^{-1} stock solution in THF) with the linear PCL possessing an iodobenzene moiety at each chain end (**(PCL−I)2**; $M_{n,NMR}$ = 7,900 g mol^{-1}, $Đ_M$ = 1.05) as the macroinitiator (68.3 mg, 86.3 μmol, 1.0 eq.), $Pd_2(dba)_3$•$CHCl_3$ (8.9 mg, 8.63 μmol, 1.0 eq.), and *t*-Bu_3P (76 μL, 38 μmol, as 0.5 mol L^{-1} stock solution in THF, 4.4 eq.) in a mixture of THF (248 mL), K_3PO_4 (5.5 mg, 26 μmol, 3.0, eq.), and deionized water (50 μL). The final product (**PF-*b*-PCL-*b*-PF**) was obtained as a yellow solid.

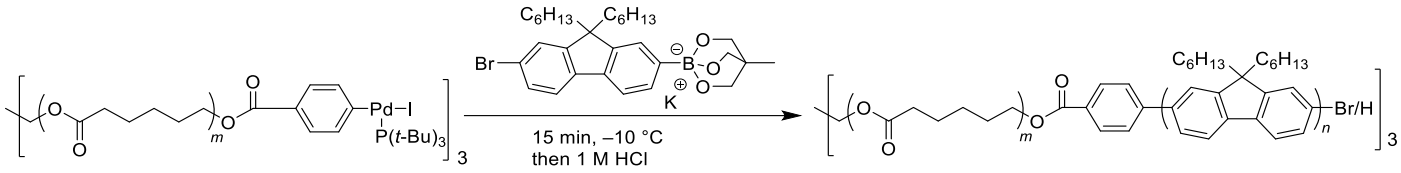
PF-*b*-PCL-*b*-PF

96.6 mg, 88.5% yield: Yellow solid. $M_{n,SEC}$ = 15,800 g mol^{-1} (THF); $M_{n,NMR}$ = 17,800 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.10.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94–7.74 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 4.32 (t, –C*H*$_2$OBz–I), 4.07 (t, –COC*H*$_2$-), 2.32 (t, –COOC*H*$_2$–), 1.70–1.60 (m, –C(=O)CH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$O–), 2.12 (br, –C*H*$_2$(CH$_2$)$_4$CH$_3$), 1.70–1.60 (m, –COCH$_2$C*H*$_2$(CH$_2$)$_2$CH$_2$CH$_2$O–),1.43–1.35 (m, –CO(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_2$O–), 1.36–0.66 (m, –CH$_2$(C*H*$_2$)$_4$C*H*$_3$, –C*H*$_3$).

Synthesis of PF-containing star-block copolymer using macroinitiator

Scheme S18. Synthesis of PF-containing star-block copolymer by SCTP using three-armed star-shaped PCL with an iodobenzene moiety at each chain end as the initiator



The PF-containing star-block copolymer was synthesized by the SCTP of **M1** (10.4 mL, 2.59 mmol, as 0.25 mol L^{-1} stock solution in THF) with the three-armed star-shaped PCL with an iodobenzene moiety at each chain end (**(PCL−I)3**; $M_{n,NMR}$ = 7,900 g mol^{-1}, $Đ_M$ = 1.05) as the macroinitiator (62.9 mg, 86.3 μmol, 1.0 eq.), $Pd_2(dba)_3$•$CHCl_3$ (13.4 mg, 13 μmol, 1.5 eq.), and *t*-Bu_3P (114 μL, 57 μmol, as 0.5 mol L^{-1} stock solution in THF, 6.6 eq.) in a mixture of THF (248 mL), K_3PO_4 (8.2 mg, 39 μmol, 4.5 e.q), and deionized water (50 μL). The final product (**(PCL-*b*-PF)3**) was obtained as a yellow solid.

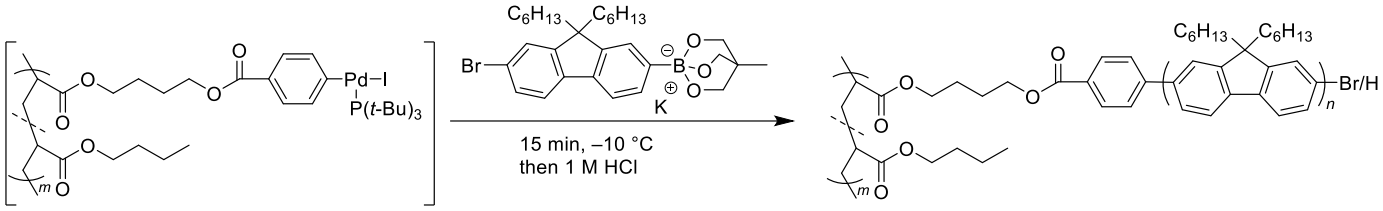
(PCL-*b*-PF)3

87.9 mg, 82.6% yield: Yellow solid. $M_{n,SEC}$ = 15,300 g mol^{-1} (THF); $M_{n,NMR}$ = 17,100 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.07.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.74 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 4.30 (t, –C*H*$_2$OBz–I), 4.06 (t, –COCH_2–), 2.31 (t, –C(=O)C*H*$_2$–), 1.89–1.55 (m, –C(=O)CH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$O–), 2.12 (br, –C*H*$_2$(CH$_2$)$_4$CH$_3$), 1.60–1.70 (m, –COCH$_2$C*H*$_2$(CH$_2$)$_2$CH$_2$CH$_2$O–), 1.38 (m, –CO(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_2$O–, –C*H*$_3$), 1.36–0.66 (m, –CH$_2$(C*H*$_2$)$_4$C*H*$_3$).

Synthesis of PF-containing graft copolymer using macroinitiator

Scheme S19. Synthesis of PF-containing graft copolymer by SCTP using poly(*n*-butyl acrylate) possessing iodobenzene side chain as the macroinitiator



The PF-containing graft copolymer was synthesized by the SCTP of **M1** (10.4 mL, 2.59 mmol, as 0.25 mol L^{-1} stock solution in THF) with the poly(*n*-butyl acrylate) possessing iodobenzene side chain (**P(BA$_{50}$-*co*-BzI$_4$)**; $M_{n,NMR}$ = 8,100 g mol^{-1}, $Đ_M$ = 1.09) as the macroinitiator (52.6 mg, 86.3 μmol, 1.0 eq.), $Pd_2(dba)_3$•$CHCl_3$ (26.8 mg, 25.9 μmol, 2.0 eq.), and *t*-Bu_3P (114 μL, 57 μmol, as 0.5 mol L^{-1} stock solution in THF, 8.8 eq.) in a mixture of THF (248 mL), K_3PO_4 (8.2 mg, 39 μmol, 6.0 e.q.), and deionized water (25 μL). The final product (**PBA-*g*-PF**) was obtained as a yellow solid.

PBA-*g*-PF

76.3 mg, 75.3% yield: Yellow solid. $M_{n,SEC}$ = 14,900 g mol^{-1} (THF); $M_{n,NMR}$ = 21,300 g mol^{-1} ($CDCl_3$), $Đ_M$ = 1.08.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.74 (m, Ar–*H*), 7.75–7.57 (m, Ar–*H*), 7.50 (d, Ar–*H*), 4.06 (t, –COCH_2–), 4.35 (t, –CH_2OBz–), 4.04 (t, –C(=O)OCH_2CH$_2$–), 2.28 (br, –CH_2CH–), 2.12 (br, –CH_2(CH$_2$)$_4$CH$_3$), 1.92 (br, –CH$_2$C*H*–), 1.60–1.38 (m, –(CH_2)$_2$–),1.36–0.66 (m, –CH$_2$(CH_2)$_4$CH_3, –CH$_2$CH_3, –CH_3).

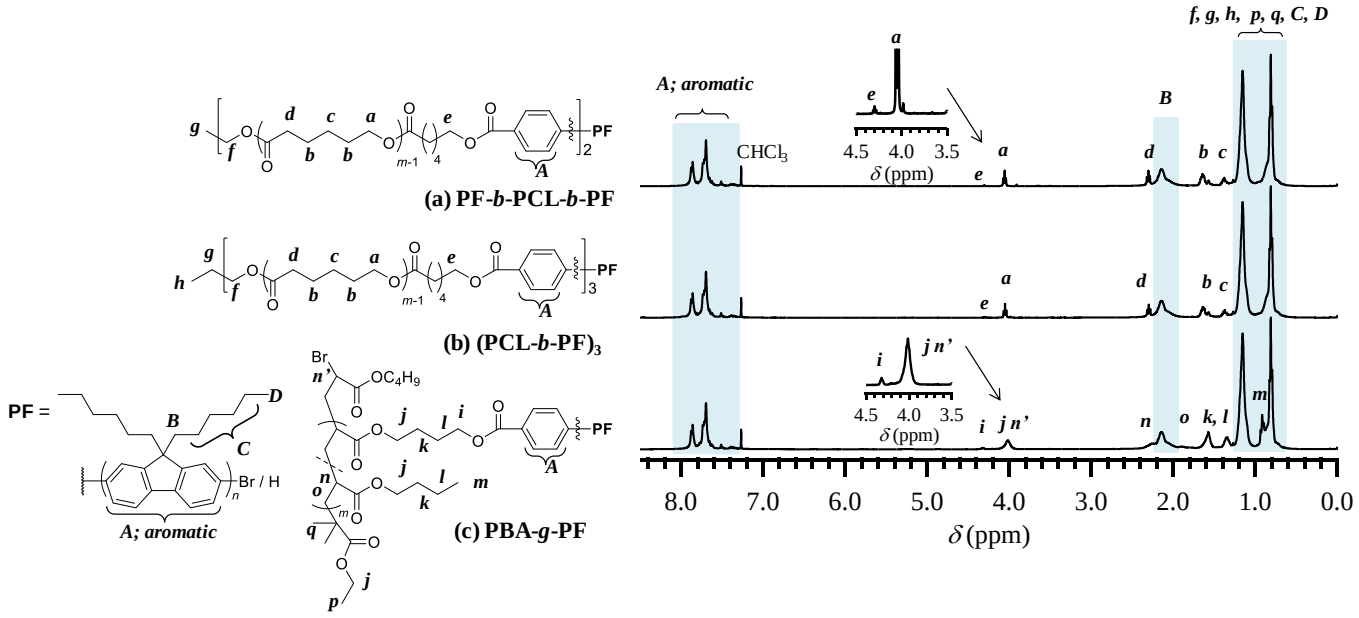


Figure S6. ^{1}H NMR spectra of (a) **PF-*b*-PCL-*b*-PF**, (b) **(PCL-*b*-PF)$_3$**, and (c) **PBA-*g*-PF** (solvent, $CDCl_3$).

Reference and notes

1. A. Yokoyama, H. Suzuki, Y. Kubota, K. Ohuchi, H. Higashimura, and T. Yokozawa, *J. Am. Chem. Soc*., **2007**, 129, 7236−7237.
2. S. Zalesskiy and V. P. Ananikov, *Organometallics*, **2012**, 31, 2302−2309.