Facile Preparation of Fluorovinylene Aryl Ether Telechelic Polymers with Dual Functionality for Thermal Chain Extension and Tandem Crosslinking

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Supplementary Information

General Information. Chemicals and solvents were purchased through Aldrich or Alfa Aesar and used without purification unless otherwise stated. Bis(trifluorovinyloxy) aryl ether compounds (**1**), specifically 4,4'-bis(4-trifluorovinyloxy)biphenyl (X = –), 2,2-bis(4-trifluorovinyloxyphenyl)-1,1,1,3,3,3-hexafluoropropane (X = $C(CF_3)_2$), and 2,2-bis(4-trifluorovinyloxyphenyl)-1,1,1,3,3,3-propane (X = $C(CH_3)_2$), were donated and are commercially available from Tetramer Technologies, L.L.C., Pendelton, SC (www.tetramertechnologies.com) and distributed through Oakwood Chemicals, Inc., Columbia, SC (www.oakwoodchemical.com). All reactions were carried out under nitrogen (ultra high purity grade). Flasks and syringes were flamed-dried under vacuum and allowed to cool in dry box or desiccator prior to use. ^{1}H, ^{13}C (proton decoupled), and ^{19}F (proton decoupled) NMR data were obtained on a JOEL Eclipse$^+$ 300 and chemical shifts were reported in part per million (δ ppm).[S1] ^{1}H NMR was internally referenced to tetramethylsilane (δ 0.0), ^{13}C NMR chemical shifts were reported relative to the center peak of the multiplet for $CDCl_3$ (δ 77.0 (t)), and ^{19}F NMR was referenced to $CFCl_3$. Coupling constants for all spectra were reported in Hertz (Hz). Attenuated total reflectance Fourier transform infrared (ATR–FTIR) of neat samples and Fourier transform infrared (FTIR) analysis of samples prepared on KBr plates were performed on a ThermoNicolet Magna IR 550 FTIR Spectrophotometer. Gel permeation chromatography (GPC) data were collected in $CHCl_3$ using polystyrene as a standard (Polymer Labs Easical PS-2) using a Waters 2690 Alliance System with refractive index detection at 35 °C. GPC samples were eluted in series through Polymer Labs PLGel 5 mm Mixed-D and Mixed-E columns. Differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA) were performed on a TA Q1000 instrument and Mettler-Toledo 851 instrument, respectively. Glass transitions temperatures (T_g) of polymers were obtained from the second heating cycle using DSC analysis. Data collected with gas chromatography coupled with a mass spectrometer (GS–MS) were performed using a HP 5970. Melting points (mp) were measured using either DSC or a Mel-Temp melting point apparatus and are uncorrected. Yields are calculated from overall isolated mass.

Preparation of Polymer 3. 2,2-Bis(4-hydroxyphenyl)hexafluoropropane (336 mg, 1.00 mmol) dissolved in anhydrous DMF (2 mL) was added drop wise to a stirred suspension of NaH (52.8 mg, 2.20 mmol) in DMF (2 mL) at room temperature for 1 h. 4,4'-bis(4-trifluorovinyloxy)biphenyl (346 mg, 1.00 mmol) in DMF (2 ml) was transferred into the solution via syringe in a single portion. The solution was then heated to 80 °C for 24 h. The reaction was monitored the first few hours to see if solution gelled or solidified; at this time additional DMF was added to maintain a constant stirring rate. The solution contents were then precipitated in H_2O, filtered under vacuum, washed repeatedly with H_2O, MeOH, and hexanes. The solid was dried in a vacuum oven at 60 °C for 24 h to afford the title compound as a pale yellow solid (550 mg, 81%). ATR–FTIR (neat) ν 1607 (w), 1495 (m), 1172 (vs), 1114 (s), 829 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80–6.80 (m), 6.20–6.70 (m); ^{19}F NMR ($CDCl_3$, 283 MHz) δ –63.8 (s, $C(CF_3)_2$), –85.6 (s, $CHFCF_2$), 120.8 (d, *J* = 32.8 Hz, *cis*-CF=CF), –122.2 (d, *J* = 49.3 Hz, *cis*-CF=CF), –126.6 (d, *J* = 111.8 Hz, *trans*-CF=CF), –128.6 (d, *J* = 111.7, *trans*-CF=CF), –138.5 (d, *J* = 59.2 Hz, $CHFCF_2$). GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution of M_n = 12 100 (M_w/M_n = 2.0). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 88 °C and TGA (10 °C/min) gave T_d (onset) = 324 and 554 °C in nitrogen and 551 °C in air.

Preparation of Polymer 4a. 2,2-Bis(4-hydroxyphenyl)propane (500 mg, 2.20 mmol) was used for the addition to 4,4'-bis(4-trifluorovinyloxy)biphenyl (871 mg, 2.20 mmol) using the procedure outlined for the preparation of **3** to obtain the title compound as a white solid (1.20 g, 88%). ATR–FTIR (neat) ν 2967 (w), 1604 (w), 1494 (vs), 1260 (vs), 1169 (vs), 1116 (vs), 824 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.70–7.7.56 (m), 6.85–6.65 (m), 3.15 (d, *J* = 5.64 Hz); ^{19}F NMR (DMSO-d_6, 283 MHz) δ –84.5 (d, J_{ab} = 150.0, $CFHCF_2$), –85.4 (d, *J* = 150.0, $CFHCF_2$) –121.4 (d, *J* = 39.5 Hz, *cis*-CF=C*F*), –122.0 (d, *J* = 39.4 Hz, *cis*-CF=CF), –128.2 (d, *J* = 108.5 Hz, *trans*-CF=CF), –128.7 (d, *J* = 108.5 Hz, *trans*-CF=CF), –141.1 (d, *J* = 55.9 Hz, $CHFCF_2$). GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution of M_n = 23 409 (M_w/M_n = 1.3). As a comparison using ^{19}F NMR, molecular weight relative to *α,α,α*-trifluorotoluene as an internal standard gave a calculated M_n = 15 000. DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 95 °C and TGA (10 °C/min) gave T_d (onset) = 319 and 524 °C in nitrogen and 561 °C in air.

Preparation of Polymer 4b. 2,2-Bis(4-hydroxyphenyl)propane (500 mg, 2.20 mmol), 4,4'-bis(4-trifluorovinyloxy)biphenyl (871 mg, 2.20 mmol), and Cs_2CO_3 (358 mg, 1.10 mmol) in a minimal amount of DMF to initiate stirring was heated to 80 °C for 24 h. The reaction was monitored the first few hours to see if solution gelled or solidified; at this time additional DMF was added to maintain a constant stirring rate. The solution contents were then precipitated in H_2O, filtered under vacuum, washed repeatedly with H_2O, MeOH, and hexanes. The solid was dried in a vacuum oven at 60 °C for 24 h to afford the title compound as a yellow solid (1.10 mg, 80%). ATR–FTIR (neat) ν 2969 (w), 1604 (w), 1495 (vs), 1269 (m), 1172 (vs), 1095 (vs), 823 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55–7.45 (m), 7.25–7.7.16 (m), 6.03–5.82 (m), 1.68 (s); ^{19}F NMR ($CDCl_3$, 283 MHz) δ –85.4 (d, J_{ab} = 151.0 $CFHCF_2$), –86.2 (d, *J* = 151.0 $CFHCF_2$), –121.3 (d, *J* = 42.7 Hz, *cis*-CF=C*F*), –122.0 (d, *J* = 42.7 Hz, *cis*-CF=CF), –127.5 (d, *J* = 111.8 Hz, *trans*-CF=CF), –128.2 (d, *J* = 111.5 Hz, *trans*-CF=CF), –138.6 (d, *J* = 49.3 Hz, $CHFCF_2$). GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution of M_n = 11 771 (M_w/M_n = 1.7). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 34 °C and TGA (10 °C/min) gave T_d (onset) = 336 and 513 °C in nitrogen and 632 °C in air.

Preparation of Polymer 5. 2,2-Bis(4-hydroxyphenyl)hexafluoropropane (500 mg, 1.48 mmol) was used for the addition to 2,2-bis(4-trifluorovinyloxyphenyl)-1,1,1,3,3,3-hexafluoropropane (893 mg, 1.48 mmol) using the procedure outlined for the preparation of **3** to obtain the title compound as a pale yellow solid (450 mg, 32%). ATR–FTIR (neat) ν 1610 (w), 1511 (m), 1173 (vs), 1120 (m), 829 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.15 (m), 6.05–5.86 (m); ^{19}F NMR ($CDCl_3$, 283 MHz) δ –63.9 (s, $C(CF_3)_2$), –85.9 (s, $CFHCF_2$), –121.6 (s, *cis*-CF=C*F*), –127.7 (s, *trans*-CF=CF), –139.6 (d, *J* = 59.2 Hz, $CHFCF_2$). GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution of M_n = 15 766 (M_w/M_n = 1.8). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 102 °C and TGA (10 °C/min) gave T_d (onset) = 370 and 521 °C in nitrogen and 534 °C in air.

Preparation of Polymer 6. 2,2-Bis(4-hydroxyphenyl)propane (500 mg, 2.20 mmol) was used for the addition to 2,2-bis(4-trifluorovinyloxyphenyl)-1,1,1,3,3,3-hexafluoropropane (1.10 g, 2.20 mmol) using the procedure outlined for the preparation of **3** to obtain the title compound as a white solid (815 mg, 48%). ATR–FTIR (neat) ν 2160 (w), 1520 (w), 1105 (vs), 833 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 8.10–7.99 (m), 3.36 (s); ^{19}F NMR (DMSO-d_6, 283 MHz) δ –64.4 (s, $\mathrm{C(CF_3)_2}$), –85.8 (d, J_{ab} = 165.0 Hz, $\mathrm{CFHC}F_2$), –86.8 (d, J = 165.0 Hz, $\mathrm{CFHC}F_2$), –121.7 (d, J = 39.5 Hz, *cis*-CF=C*F*), –123.9 (d, J = 42.7 Hz, *cis*-CF=CF), –127.9 (d, J = 108.5 Hz, *trans*-CF=CF), –130.4 (d, J = 111.8 Hz, *trans*-CF=CF), –141.9 (d, J = 55.9 Hz, $\mathrm{CH}F\mathrm{CF_2}$). Using ^{19}F NMR, molecular weight relative to *α,α,α*-trifluorotoluene as an internal standard gave a calculated M_n = 11 764. DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 122 °C and TGA (10 °C/min) gave T_d (onset) = 302 and 543 °C in nitrogen and 566 °C in air.

Preparation of Polymer 7. 2,2-Bis(4-hydroxyphenyl)propane (500 mg, 2.19 mmol) was used for the addition to 2,2-bis(4-trifluorovinyloxyphenyl)-1,1,1,3,3,3-propane (850 mg, 2.19 mmol) using the procedure outlined for the preparation of **3** to obtain the title compound as a white solid (1.10 g, 81%). ATR–FTIR (neat) ν 2970 (w), 1604 (w), 1503 (vs), 1259 (vs), 1168 (s), 1118 (m), 832 (m) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$ with 20 vol % DMSO-d_6, 300 MHz) δ 6.53–6.29 (m), 0.93 (s); ^{19}F NMR ($\mathrm{CDCl_3}$, 283 MHz) δ –85.7 (s, $\mathrm{CFHC}F_2$), –122.0 (s, *cis*-CF=C*F*), –128.1 (s, *trans*-CF=CF), –138.6 (s, $\mathrm{CH}F\mathrm{CF_2}$). Using ^{19}F NMR, molecular weight relative to *α,α,α*-trifluorotoluene as an internal standard gave a calculated M_n = 14 269. DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 90 °C and TGA (10 °C/min) gave T_d (onset) = 321 and 534 °C in nitrogen and 512 °C in air.

Preparation of Polymer 8. 2,2-Bis(4-hydroxyphenyl)hexafluoropropane (736 mg, 2.19 mmol) was used for the addition to 2,2-bis(4-trifluorovinyloxyphenyl)-1,1,1,3,3,3-propane (850 mg, 2.19 mmol) using the procedure outlined for the preparation of **3** to obtain the title compound as a white solid (1.30 g, 82%). ATR–FTIR (neat) ν 1678 (w), 1596 (s), 1168 (vs), 1104 (s), 830 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.70–7.57 (m), 3.34 (s); ^{19}F NMR (DMSO-d_6, 283 MHz) δ –63.6 (s, $\mathrm{C(CF_3)_2}$), –84.8 (d, J_{ab} = 148.0 Hz, $\mathrm{CFHC}F_2$), –87.1 (d, J = 148.0 Hz, $\mathrm{CFHC}F_2$), –120.9 (d, J = 39.4 Hz, *cis*-CF=C*F*), –122.6 (d, J = 55.9 Hz, *cis*-CF=CF), –127.7 (d, J = 109.0 Hz, *trans*-CF=CF), –129.7 (d, J = 108.5 Hz, *trans*-CF=CF), –140.9 (d, J = 59.2 Hz, $\mathrm{CH}F\mathrm{CF_2}$). Using ^{19}F NMR, molecular weight relative to *α,α,α*-trifluorotoluene as an internal standard gave a calculated M_n = 35 500. DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 44 °C and TGA (10 °C/min) gave T_d (onset) = 343 and 439 °C in nitrogen and 565 °C in air.

Preparation of Polymer 9. 4,4'-Dihydroxydiphenyl (252 mg, 1.25 mmol) was used for the addition to 2,2-bis(4-trifluorovinyloxyphenyl)-1,1,1,3,3,3-propane (485 mg, 1.25 mmol) using the procedure outlined for the preparation of **3** to obtain the title compound as a white solid (514 g, 70%). ATIR/FTIR (neat) ν 2959 (w), 1604 (w), 1493 (vs), 1166 (vs), 1099 (vs), 829 (m) cm^{-1}; ^{19}F NMR (DMSO-d_6, 283 MHz) δ –84.5 (d, J_{ab} = 147.9 Hz, $\mathrm{CFHC}F_2$), –85.5 (d, J = 147.9 Hz, $\mathrm{CFHC}F_2$), –121.3 (d, J = 36.2 Hz, *cis*-CF=C*F*), –122.1 (d, J = 36.2 Hz, *cis*-CF=CF), –128.3 (d, J = 108.0 Hz, *trans*-CF=CF), –128.5 (d, J = 108.5 Hz, *trans*-CF=CF), –140.7 (d, J = 55.9 Hz, CH*F*CF$_2$). Using ^{19}F NMR, molecular weight relative to α,α,α-trifluorotoluene as an internal standard gave a calculated M_n = 13 605. DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 99 °C and TGA (10 °C/min) gave T_d (onset) = 313 and 523 °C in nitrogen and 436 °C in air.

Preparation of Polymer 10. 4,4'-Dihydroxydiphenyl (233 mg, 1.25 mmol) was used for the addition to 2,2-bis(4-hydroxyphenyl)hexafluoropropane (485 mg, 1.25 mmol) using the procedure outlined for the preparation of **3** to obtain the title compound as a white solid (341 mg, 47%). ATIR/FTIR (neat) ν 2954 (w), 1609 (w), 1494 (m), 1172 (vs), 1100 (vs), 829 (m) cm^{-1}; ^{19}F NMR (DMSO-*d$_6$*, 283 MHz) δ –63.4 (s, C(CF$_3$)$_2$), –84.5 (d, J_{ab} = 144.6 Hz, CFHC*F*$_2$), –84.5 (d, *J* = 144.6 Hz, CFHC*F*$_2$), –120.9 (d, *J* = 39.5 Hz, *cis*-CF=C*F*), –122.1 (d, *J* = 39.5 Hz, *cis*-CF=CF), –127.2 (d, *J* = 108.5 Hz, *trans*-CF=CF), –129.2 (d, *J* = 108.5 Hz, *trans*-CF=CF), –142.4 (d, *J* = 55.9 Hz, CH*F*CF$_2$). Using ^{19}F NMR, molecular weight relative to α,α,α-trifluorotoluene as an internal standard gave a calculated M_n = 15 000. DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 112 °C and TGA (10 °C/min) gave T_d (onset) = 310 and 528 °C in nitrogen and 486 °C in air.

Preparation of Telechelomer 11. 4,4'-Dihydroxydiphenyl ether (1.01 g, 5.00 mmol) dissolved in anhydrous DMF (5 mL) was added drop wise to a stirred suspension of NaH (300 mg, 12.5 mmol) in DMF (5 mL) at room temperature for 1 h. The suspension was then transferred via cannula while maintaining drop wise addition to a solution of 4,4'-bis(4-trifluorovinyloxy)biphenyl (5.20 g, 15.0 mmol) in DMF (10 mL) at 45 °C. After 24 h, the solution was treated with saturated aqueous NH$_4$Cl (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed successively with water (20 mL), brine (20 mL), and dried (MgSO$_4$). After filtration, the solvent was removed under reduced pressure affording a viscous yellow oil. Methanol (30 mL) was added to precipitate solids; the suspension was then filtered under vacuum and was successively washed with methanol (100 mL) and hexanes (100 mL). The solid was dried under vacuum to afford the title compound as a white solid (1.81 g, 50%). Mp 116 °C (DSC); ATR–FTIR (neat) ν 1605 (w), 1491 (m), 1161 (vs), 1111 (vs), 820 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.67–7.47 (m), 7.33–6.90 (m); ^{19}F NMR (CDCl$_3$, 283 MHz) δ –85.8 (s, CHFC*F*$_2$), –119.4 (dd, *J* = 95.5, 55.9 Hz, *cis*-CF=C*F*$_2$), –121.5 (d, *J* = 39.5 Hz, *cis*-CF=CF), –122.0 (d, *J* = 42.7 Hz, *cis*-CF=CF), –126.3 (dd, *J* = 111.9, 98.8 Hz, *trans*-CF=C*F*$_2$), –127.7 (d, *J* = 111.9 Hz, *trans*-CF=CF); –128.2 (d, *J* = 108.6 Hz, *trans*-CF=CF); –133.8 (dd, *J* = 129.4, 59.2 Hz, C*F*=CF$_2$), –138.67 (d, *J* = 49.3 Hz, CH*F*CF$_2$). GPC in CHCl$_3$ relative to polystyrene gave a multimodal distribution of M_n = 1290 ($M_\mathrm{w}/M_\mathrm{n}$ = 1.6). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 10 °C.

PFCB Aryl Ether Chain Extension of 11 at 210 °C (poly11). In a vacuum sealed glass ampoule, 50 mg of **11** was heated to 210 °C for 1 h affording a yellow organic soluble film in essentially quantitative yield. ^{19}F NMR (CDCl$_3$, 283 MHz) δ –85.7 (s, CHFC*F*$_2$), –119.4 (dd, *J* = 95.5, 55.9 Hz, *cis*-CF=C*F*$_2$), –121.3–(–121.5) (m, *cis*-CF=CF), –121.8–(–122.1) (m, *cis*-CF=CF), –126.3 (dd, *J* = 111.9, 98.8 Hz, *trans*-CF=C*F*$_2$), –128.0–(–131.4) (m, *trans*-CF=CF and cyclobutyl-*F*$_6$), –133.8 (dd, *J* = 129.4, 59.2 Hz, C*F*=CF$_2$), –138.5 (d, *J* = 59.2 Hz, CH*F*CF$_2$). GPC in CHCl$_3$ relative to polystyrene gave a monomodal distribution with M_n = 6250 ($M_\mathrm{w}/M_\mathrm{n}$ = 2.2). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 70 °C and TGA (10 °C/min) gave T_d (onset) = 283 and 534 °C in nitrogen and 262 and 525 °C in air.

Preparation of Telechelomer 12. 4,4'-Dihydroxy diphenyl sulfide (1.10 g, 5.00 mmol) was used for the addition to 4,4'-bis(4-trifluorovinyloxy)biphenyl (5.2 g, 15.0 mmol) using the procedure outlined for the preparation of **11** to obtain the title compound as a white solid (1.60 g, 23%). Mp 54 °C (DSC); ATR–FTIR (neat) ν 1600 (w), 1486 (m), 1161 (vs), 1109 (vs), 834 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.62–6.98 (m); ^{19}F NMR (CDCl$_3$, 283 MHz) δ –85.7 (s, CHFCF_2), –119.4 (dd, J = 95.5, 55.9 Hz, *cis*-CF=CF_2), –121.3 (d, J = 42.8 Hz, *cis*-CF=CF), –121.9 (d, J = 39.5 Hz, *cis*-CF=CF), –126.3 (dd, J = 111.9, 98.7 Hz, *trans*-CF=CF_2), –127.3 (d, J = 111.9 Hz, *trans*-CF=CF), –128.2 (d, J = 111.9 Hz, *trans*-CF=CF), –133.8 (dd, J = 111.9, 59.2 Hz, CF=CF$_2$), –138.5 (d, J = 59.2 Hz, CHFCF$_2$). GPC in CHCl$_3$ relative to polystyrene gave a multimodal distribution of M_n = 1223 (M_w/M_n = 1.6). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 27 °C

PFCB Aryl Ether Chain Extension of 12 at 210 °C (poly12). In a vacuum sealed glass ampoule, 50 mg of **12** was heated to 210 °C for 1 h affording a yellow organic soluble film in essentially quantitative yield. ^{19}F NMR (CDCl$_3$, 283 MHz) δ –86.8 (s, CHFCF_2), –119.4 (dd, J = 95.5, 55.9 Hz, *cis*-CF=CF_2), –122.4 (d, J = 42.7 Hz, *cis*-CF=CF), –123.1 (d, J = 42.7 Hz, *cis*-CF=CF), –128.0–(–131.4) (m, *cis*-CF=CF and cyclobutyl-F_6), –134.8 (dd, J = 129.4, 59.2 Hz, CF=CF$_2$), –140.5 (d, J = 59.2 Hz, CHFCF$_2$). GPC in CHCl$_3$ relative to polystyrene gave a monomodal distribution of M_n = 9771 (M_w/M_n = 3.3). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 57 °C and TGA (10 °C/min) gave T_d (onset) = 310 and 550 °C in nitrogen and 304 and 600 °C in air.

Preparation of Telechelomer 13. 2,2-Bis(4-hydroxyphenyl)hexafluoropropane (672 mg, 2.00 mmol) was used for the addition to 4,4'-bis(4-trifluorovinyloxy)biphenyl (2.08 g, 6.00 mmol) using the procedure outlined for the preparation of **11** to obtain the title compound as a white solid (600 mg, 35%). Mp 60 °C (Mel-Temp); ATR–FTIR (neat) ν 1607 (w), 1482 (m), 1162 (vs), 1059 (vs), 831 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.70–7.05 (m); ^{19}F NMR (CDCl$_3$, 283 MHz) δ –63.9 (s, C(CF_3)$_2$), –85.9 (s, CHFCF_2), –119.4 (dd, J = 98.7, 59.8 Hz, *cis*-CF=CF_2), –120.9 (d, J = 39.5 Hz, *cis*-CF=CF), –122.2 (d, J = 39.5 Hz, *cis*-CF=CF), –126.3 (dd, J = 111.9, 98.7 Hz, *trans*-CF=CF_2), –126.6 (d, J = 108.5 Hz, *trans*-CF=CF), –128.7 (d, J = 108.6 Hz, *trans*-CF=CF); –133.8 (dd, J = 108.6, 55.2 Hz, CF=CF$_2$), –138.5 (d, J = 59.2 Hz, CHFCF$_2$). GPC in CHCl$_3$ relative to polystyrene gave a multimodal distribution of M_n = 1737 (M_w/M_n = 1.4). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 12 °C

PFCB Aryl Ether Chain Extension of 13 at 210 °C (poly13). In a vacuum sealed glass ampoule, 50 mg of **13** was heated to 210 °C for 1 h affording a yellow organic soluble film in essentially quantitative yield. ^{19}F NMR (CDCl$_3$, 283 MHz) δ –64.3 (s, C(CF_3)$_2$), –86.6 (s, CHFCF_2), –120.3 (dd, J = 98.7, 59.8 Hz, *cis*-CF=CF_2), –121.6 (d, J = 39.5 Hz, *cis*-CF=CF), –123.0 (d, J = 39.5 Hz, *cis*-CF=CF), –127.3 (dd, J = 111.9, 98.7 Hz, *trans*-CF=CF_2), –127.2–(–131.6) (m, *cis*-CF=CF and cyclobutyl-F_6), –134.4 (dd, J = 108.6, 55.2 Hz, CF=CF$_2$), –139.9 (d, J = 59.2 Hz, CHFCF$_2$). GPC in CHCl$_3$ relative to polystyrene gave a monomodal distribution of M_n = 13 863 (M_w/M_n = 5.3). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 57 °C and TGA (10 °C/min) gave T_d (onset) = 340 and 543 °C in nitrogen and 560 °C in air.