

Utilization of a Meldrum's acid towards functionalized fluoropolymers possessing dual reactivity for thermal crosslinking and post-polymerization modification

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Experimental

Materials

Meldrum's acid or 2,2-dimethyl-1,3-dioxane-4,6-dione was purchased from Alfa Aesar, recrystallization from absolute ethanol and dried in vacuum before use. 1-Bromo-4-(trifluorovinyloxy)benzene (**1**) and 4,4'-bis[(1,2,2-trifluoroethenyl)oxy]-1,1'-biphenyl (**BP-TFVE**) were purchased from Tetramer Technologies, L.L.C., Pendleton, SC and are commercially available from Oakwood Chemical. All other reagents and solvents were purchased from Aldrich and Alfa Aesar and used without further purification unless otherwise noted.

Instrumentation

^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker 400 MHz and chemical shifts were measured in ppm (δ) with reference to internal tetramethylsilane (0 ppm), deuterated chloroform (77 ppm), and trichlorofluoromethane (0 ppm) for ^1H , ^{13}C and ^{19}F NMR, respectively. Differential scanning calorimetry (DSC) analysis was performed on a Mettler Toledo DSC 1 system in nitrogen at a heating rate of 10 °C/min. The glass transition temperature (T_g) was obtained from a second heating cycle using Star E version 10.0 software suite. Thermal gravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/DSC 1 LF instrument in nitrogen at a heating rate of 10 °C/min up to 800 °C. Gel permeation chromatography (GPC) data were collected in THF from a Waters 2690 Alliance System with photodiode array detection. GPC samples were eluted in series through Polymer Labs PLGel 5 mm Mixed-D and Mixed-E columns at 35 °C. Molecular weights were obtained using polystyrene as a standard (Polymer Labs Easical PS-2). Single crystal X-ray diffraction data was collected at low

temperature (Oxford Cryosystems cryostream, $T = 100$ K) using a Bruker Kappa D8 Quest diffractometer equipped with Incoatec microfocus Mo $K\alpha$ radiation source and Photon 100 CMOS detector. Afterwards, the data was integrated, scaled, and evaluated for space group determination using Bruker SAINT, SADABS (multi-scan absorption correction), and XPREP, respectively. A starting model was generated using SHELXT (intrinsic phasing method)¹ and further atomic site assignments, anisotropic refinement of non-hydrogen atomic positions, and addition of “riding” hydrogen atomic sites were completed with SHELXL2014.2

Synthesis and Characterization of Monomers and Polymers

Synthesis of compounds 1–4 (see Scheme S1)

Compounds **1–4** were prepared according to the previously reported procedures.^{3, 4} All the compounds are confirmed by ^1H NMR and ^{19}F NMR spectra.

Compound **4**: ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.39 (m, 2H), 7.10 (d, $J = 8.2$ Hz, 2H), 4.51 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -119.45 (ddd, $J = 96.1, 58.5, 2.6$ Hz), -126.26 (ddd, $J = 109.9, 96.3, 3.4$ Hz), -134.17 (dd, $J = 109.9, 58.5$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 154.93 (s), 134.55 (s), 130.80 (s), 116.21 (s), 32.38 (s), 2.53 – -0.49 (m).

Synthesis of monomer 5

Anhydrous K_2CO_3 (340 mg, 2.5 mmol) was added to a solution of Meldrum's acid (144 mg, 1 mmol) in DMF (1 mL). To this vigorously stirred suspension was dropwise added a solution of **4** (587 mg, 2.2 mmol) in dry DMF (1 mL) at 0°C , then the reaction mixture was stirred at room temperature for 20 h. The reaction was quenched by slowly adding 1 M HCl until the solution became acidic. The mixture was extracted with EtOAc three times and the combined organic

layers were washed with water, brine. The separated organic layer was dried over anhydrous MgSO_4 , filtered, and concentrated to give a white solid as a crude product. The crude product was purified by flash chromatography on silica gel to afford the titled compound **5** as a white powder (412 mg, 80%). ^1H NMR (400 MHz, CDCl_3) δ 7.27 – 7.20 (m, 4H), 7.06 (d, $J = 8.3$ Hz, 4H), 3.45 (s, 4H), 0.73 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.04 (s), 154.80 (dd, $J = 7.8$, 3.2 Hz), 146.82 (ddd, $J = 279.7$, 273.2, 61.7 Hz), 133.68 (ddd, $J = 264.0$, 48.1, 41.8 Hz), 131.81 (s), 131.45 (s), 116.32 (s), 106.07 (s), 60.07 (s), 43.98 (s), 28.63 (s). ^{19}F NMR (376 MHz, CDCl_3) δ -119.58 (dd, $J = 96.8$, 58.5 Hz), -126.80 (dd, $J = 109.8$, 96.8 Hz), -134.43 (dd, $J = 109.9$, 58.5 Hz). ATR-FTIR (cm^{-1}): ν 729, 746, 826, 843, 854, 953, 1015, 1045, 1090, 1119, 1138, 1171, 1194, 1275, 1312, 1360, 1396, 1445, 1506, 1605, 1732 (C=O of Meldrum's acid ring), 1769 (O-CF=CF₂). HR-MS (CI) Calculated (found) for $\text{C}_{24}\text{H}_{18}\text{O}_6\text{F}_6$ 516.1009 (516.1013).

Preparation of polymer 6

Monomer **5** was polymerized in isothermal DSC experiments (25-160 °C, 10 °C/min, 160 °C, 8h, and then 160-25 °C, -10 °C/min, under N_2). The soluble oligomer **6** was obtained as a white powder. ^1H NMR (500 MHz, CDCl_3) δ 7.22 (ddd, $J = 13.4$, 8.5, 5.3 Hz, 4H), 7.16 – 7.04 (m, 4H), 3.55 – 3.32 (m, 4H), 0.80 – 0.56 (m, 6H). ^{19}F NMR (376 MHz, CDCl_3) δ -119.53 (dd, $J = 96.8$, 58.5 Hz), -126.21 – -127.33 (m), -127.58 (s), -127.89 (s), -128.17 (s), -128.48 (s), -129.47 (s), -130.11 (d, $J = 32.9$ Hz), -130.75 (s), -131.27 (d, $J = 62.3$ Hz), -134.41 (dd, $J = 109.8$, 58.5 Hz). ATR-FTIR (cm^{-1}): ν 660, 667, 687, 702, 835, 851, 961 (PFCB ring), 1018, 1045, 1115, 1142, 1179, 1200, 1271, 1308, 1360, 1379, 1395, 1429, 1435, 1447, 1506, 1609, 1738 (C=O of Meldrum's acid ring), 1767 (OCF=CF₂).

Preparation of copolymer 7

Monomer **5** (18 mg, 0.035mmol) and **BP-TFVE** (202 mg, 58 mmol) were transferred into a glass ampule (10 mL) with a magnetic stir bar, and then the ampule was sealed under high vacuum.

The reaction mixture was heated at 160 °C on oil bath for 12 h and then at 170 °C for 12 h. The ampule was allowed to cool to room temperature and opened to yield a viscous and clear liquid.

The raw copolymer was dissolved in a minimal amount of THF, and then precipitated in hexane, filtered, washed repeatedly with hexane, and dried under vacuum to afford a white fibrous solid of **7** (130 mg, 74%). ¹H NMR (500 MHz, CDCl₃) δ 7.62 – 7.42 (m, 61H), 7.26 (d, J = 7.7 Hz, 29H), 7.21 (d, J = 7.7 Hz, 32H), 3.43 (s, 4H), 0.77 – 0.57 (m, 6H). ¹⁹F NMR (471 MHz, CDCl₃) δ -126.70 (s), -128.08 (s), -128.24 (s), -128.64 (d, J = 75.3 Hz), -129.59 (s), -130.07 (s), -130.30 (s), -130.77 (s), -131.07 (s), -131.33 (s). ATR-FTIR (cm⁻¹): ν 824, 851, 899, 959 (PFCB ring), 1007, 1119, 1140, 1167, 1196, 1267, 1304, 1497, 1607, 1738 (C=O of Meldrum's acid ring).

Thermolysis of polymers 6 and 7

The polymerization of monomer **5** and thermolysis of polymer **6** were performed via isothermal DSC experiments (25–160 °C, 10°C/min: 160 °C, 8 h; and 8 repeated heating-cooling cycles: 25–260 °C, 10°C/min: 260–25 °C, -10°C/min). The *T*_gs of resulting polymers were measured by DSC thermograms of the corresponding heating cycles. Then resulting highly cross-linked polymer **9** was studied by ATR-FTIR technology (See Figure S15).

A sample of polymer **7** was subjected to an isothermal DSC experiment (25–260 °C, 10 °C/min: 260 °C, 3 h: 260–25 °C, -10 °C/min: 25–260 °C, 10 °C/min : 260–25 °C, -10 °C/min). The *T*_gs of resulting copolymer were measured from DSC thermograms of the first heating cycle and the final heating cycle. The resulting cross-linked copolymer was also studied by ATR-FTIR (See Figure S16).

Functionalization of polymer 7 with Disperse Red 1 (DR-1)

Polymer **7** (40 mg) and Disperse Red 1 (22 mg) was put into a 3 mL vial and diphenyl ether (3 mL) was added. The reaction mixture was heated to 200 °C for 3 h. The resulting solution was pour into a 10 mL evaporating dish to get rid of solvent. The resulting residue was dissolved in a minimal amount of THF and precipitate into DI water and methanol solution (v/v 50:50), filtered, washed repeatedly with methanol, and dried under vacuum to afford a reddish fibrous powder of polymer **10** (38 mg, 94%). The raw polymer was purified by soxhlet extraction using methanol for 24 h. ¹H NMR (500 MHz, CDCl₃) δ 8.36 (d, J = 8.9 Hz, 5H), 8.01 – 7.82 (m, 9H), 7.54 (d, J = 37.9 Hz, 115H), 7.27 (d, J = 6.9 Hz, 54H), 7.21 (d, J = 7.7 Hz, 55H), 4.69 (s, 1H), 4.02 (s, 2H), 3.71 (s, 2H), 3.45 (s, 2H), 3.29 (d, J = 20.3 Hz, 4H), 0.96 – 0.90 (m, 10H). ¹⁹F NMR (471 MHz, CDCl₃) δ -126.69 (s), -128.14 (d, J = 75.5 Hz), -128.62 (d, J = 75.7 Hz), -129.58 (s), -130.17 (d, J = 108.7 Hz), -130.76 (s), -131.19 (d, J = 124.1 Hz). ATR-FTIR (cm⁻¹): v 824, 853, 899, 959 (PFCB ring), 1007, 1018, 1026, 1119, 1167, 1196, 1240, 1265, 1304, 1398, 1497, 1605, 1721(C=O of ester unit).

Results and Discussion

Preparation of polymer 6 at higher temperature

Heating monomer **5** at 180 °C for 8 h yielded insoluble homopolymer. ATR-FTIR spectrum of this insoluble homopolymer showed a sharp and intensive perfluorocyclobutyl peak appeared at 961 cm⁻¹, which indicated cyclopolymerization took place (Figure S13). ATR-FTIR spectrum also showed several typical absorption peaks at 1700–1850 cm⁻¹ (Figure S13): the C=O stretching mode of Meldrum's acid group at 1741 cm⁻¹, the OCF=CF₂ stretching vibration peak at 1774 cm⁻¹, and the C=O stretching mode of the cyclobutance-1,3-dione (ketene dimerization

product) at 1813 cm^{-1} . There is an extra peak at 1840 cm^{-1} , which may be the C=O stretching peak of the [2+2] cycloaddition product of ketene intermediate with TFVE groups,⁵ which indicated the thermolysis of small amount of Meldrum's acid groups took place at temperature around $180\text{ }^{\circ}\text{C}$ and the resulting reactive ketene intermediates reacted with each other or with TFVE groups to give a high cross-linked and insoluble polymeric network. Usually the thermolysis of dialkyl Meldrum's acid should take place at higher temperatures (above $200\text{ }^{\circ}\text{C}$). Because the cyclopolymerization of monomer **5** is an exothermic process, the internal temperature of reaction mixture may be much higher than external heating temperature during polymerization, which can induce thermolysis of dialkyl Meldrum's acid at lower external heating temperatures. To avoid the thermolysis of Meldrum's acid taking place, the polymerization temperature should be around $160\text{ }^{\circ}\text{C}$.

DSC study of monomer 5

The thermal properties of monomer **5** were studied by DSC by heating and cooling it from $25\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$ for several cycles. As showed in Figure S14, the curve of the first heating cycle show a clear and sharp endothermic process at around $138\text{ }^{\circ}\text{C}$ presuming the melting process and a small exothermic process taking place at around $150\text{ }^{\circ}\text{C}$ which is associated with [2+2] cyclodimerization of TFVE groups.

Thermolysis of polymer 7

After the thermolysis of copolymer **7**, the characteristic absorbance peaks for ketenes and cyclobutane-1,3-diones were not shown in the ATR-FTIR spectrum of the resulting PFCB aryl ether polymer (Figure S16). Because the polymer backbone contains only a very small amount of

Meldrum's acid, it is hard to detect the absorbance of ketenes and their alkyl dimers using ATR-FTIR technique. As showed in Figure S16, the characteristic peak at 1732 cm^{-1} corresponding to the diester of Meldrum's acid disappeared after heating, indicating a complete thermolysis of Meldrum's acid groups in copolymer matrix.

DSC studies of polymer 7

DSC studies on the thermal properties of polymer **7** reveal well-defined T_g before and after thermolysis. As showed in Figure S17, DSC thermogram of the first heating cycle shows well-defined glass transition at $125\text{ }^\circ\text{C}$ and an endothermic process beginning with $220\text{ }^\circ\text{C}$, resulting from a combination of the exothermic [2+2] cyclodimerization of TFVE end groups and the endothermic thermolysis of Meldrum's acid groups. Heating polymer **7** to $300\text{ }^\circ\text{C}$ for several cycles caused the T_g of the resulting copolymer to shift dramatically from $125\text{ }^\circ\text{C}$ to $156\text{ }^\circ\text{C}$. Two major factors lead this shift: one is the chain extension via [2+2] cyclodimerization of TFVE end groups and the other one is the cross-linking via [2+2] cyclodimerization of ketene intermediates from the thermolysis of Meldrum's acid groups in the polymer **7**.

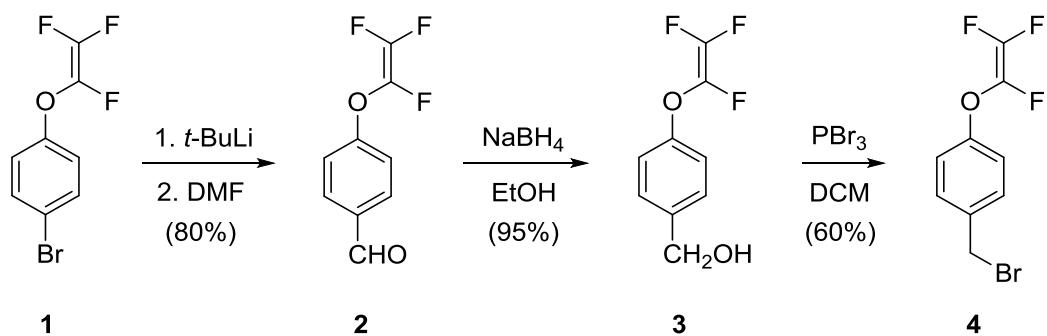
ATR-FTIR of polymer 10

After PPM, the characteristic peak at 1741 cm^{-1} corresponding to C=O stretching mode of the diester derived from the Meldrum's acid was disappeared and the new characteristic peak at 1721 cm^{-1} corresponding to the newly formed ester bond was clearly showed in Figure S18. ATR-FTIR spectrum corroborates the full conversion of Meldrum's acid functionality.

X-Ray Structure Elucidation of **5**

Crystallographic data for monomer **5** has been submitted to the Cambridge Crystallographic Data Center with deposition number CCDC 1053394. Copies can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

A colorless crystalline fragment ($-0.04 \times 0.2 \times 0.3 \text{ mm}^3$) of monomer **5** was chosen to study the crystal structure. Crystal data for monomer **5**: $\text{C}_{24}\text{H}_{18}\text{F}_6\text{O}_6$, $M = 516.38$, triclinic, $a = 8.917(3) \text{ \AA}$, $b = 11.888(4) \text{ \AA}$, $c = 12.165(4) \text{ \AA}$, $\alpha = 62.137(7)^\circ$, $\beta = 81.719(7)^\circ$, $\gamma = 78.834(7)^\circ$, $V = 1116.4(6) \text{ \AA}^3$, $T = 100(2) \text{ K}$, space group $P-1$, $Z = 2$, $\mu(\text{MoK}\alpha) = 0.14 \text{ mm}^{-1}$, 44146 reflections measured, 6785 independent reflections ($R_{int} = 0.047$). The final R_I values were 0.051 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.114 ($I > 2\sigma(I)$). The final R_I values were 0.076 (all data). The final $wR(F^2)$ values were 0.125 (all data). The goodness of fit on F^2 was 1.02. CCDC number CCDC 1053394. Note: Largest positive ($\Delta\rho_{\max} = 0.94 \text{ e \AA}^{-3}$) and negative ($\Delta\rho_{\min} = -0.57 \text{ e \AA}^{-3}$) residuals in the final difference map are located $\sim 1.02 \text{ \AA}$ and $\sim 0.74 \text{ \AA}$, respectively, from atomic site “F3” in Figure S20 – the least “well-behaved” site amongst the fluorine atoms in the average structure. The packing view of crystal structure is also shown in Figure S20 (bottom).



Scheme S1. Synthesis of benzyl bromide **4**

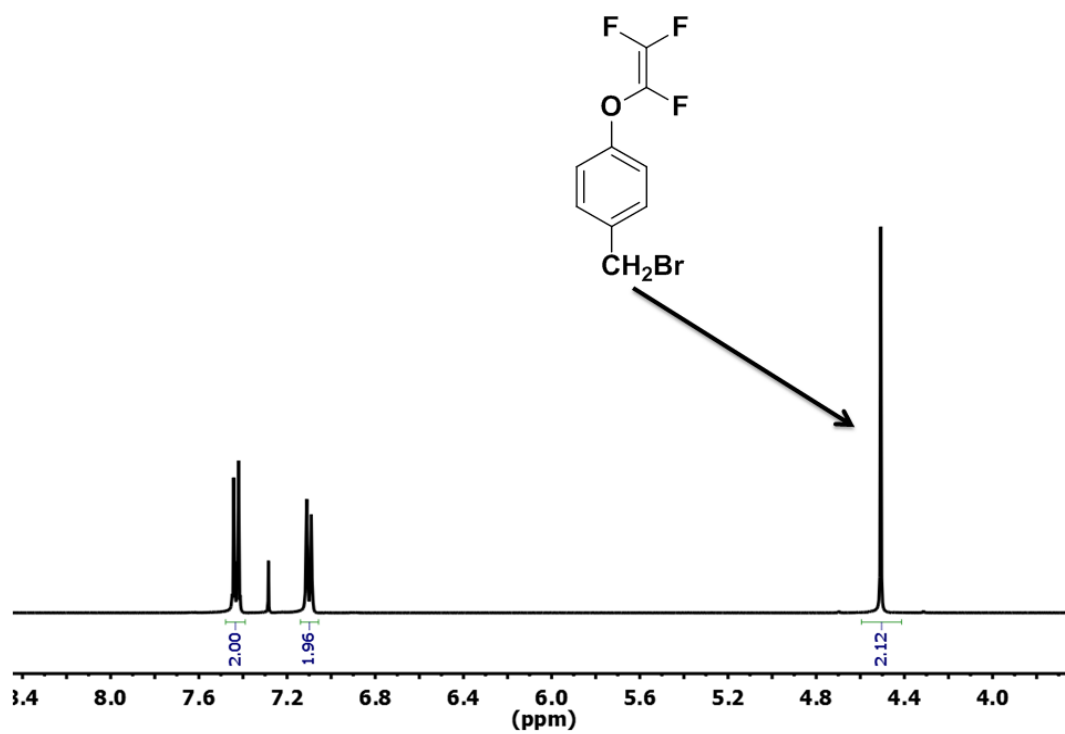


Figure S1. ^1H NMR spectrum of compound **4**

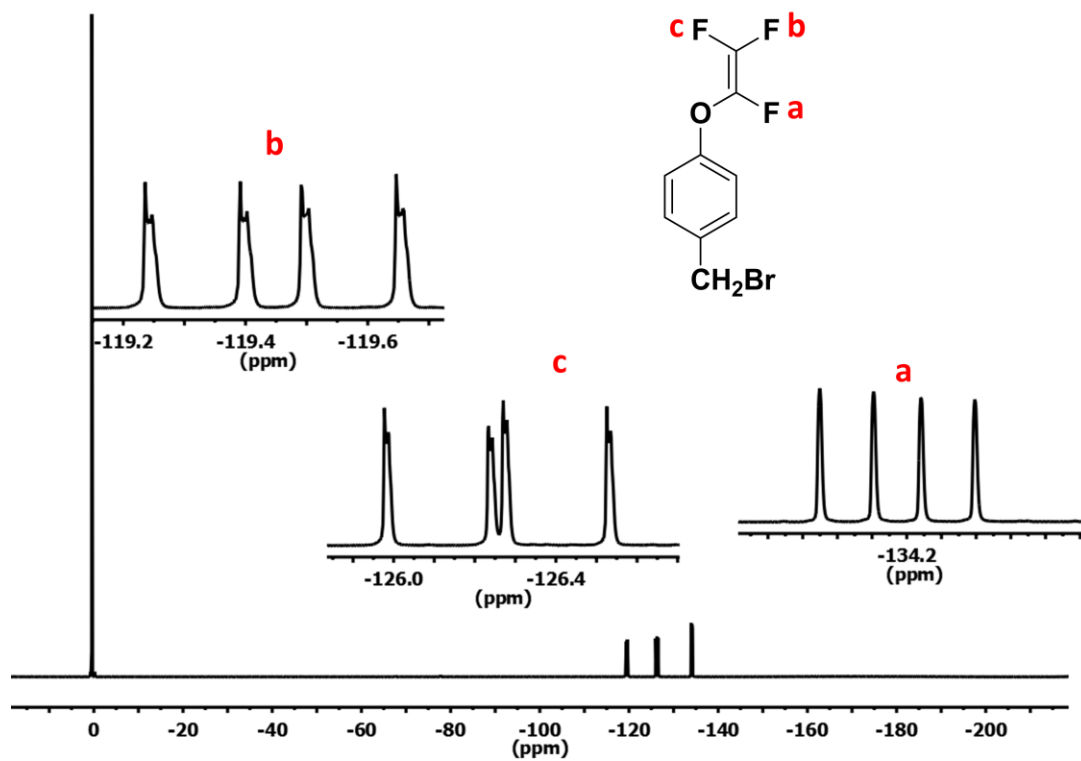


Figure S2. ^{19}F NMR spectrum of compound 4

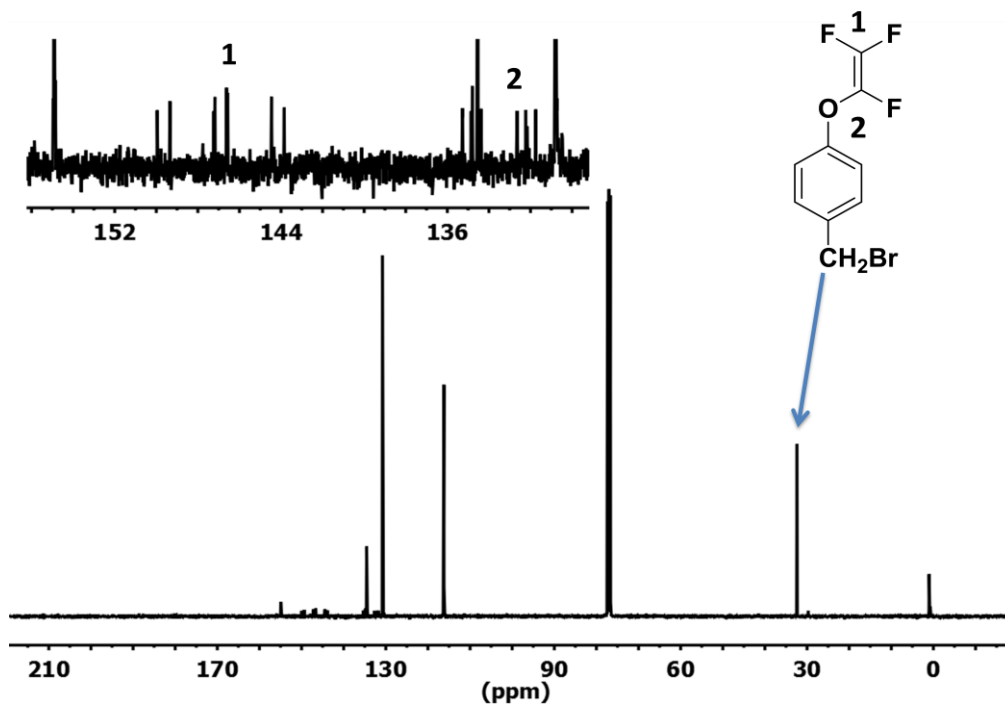


Figure S3. ^{13}C NMR spectrum of compound 4

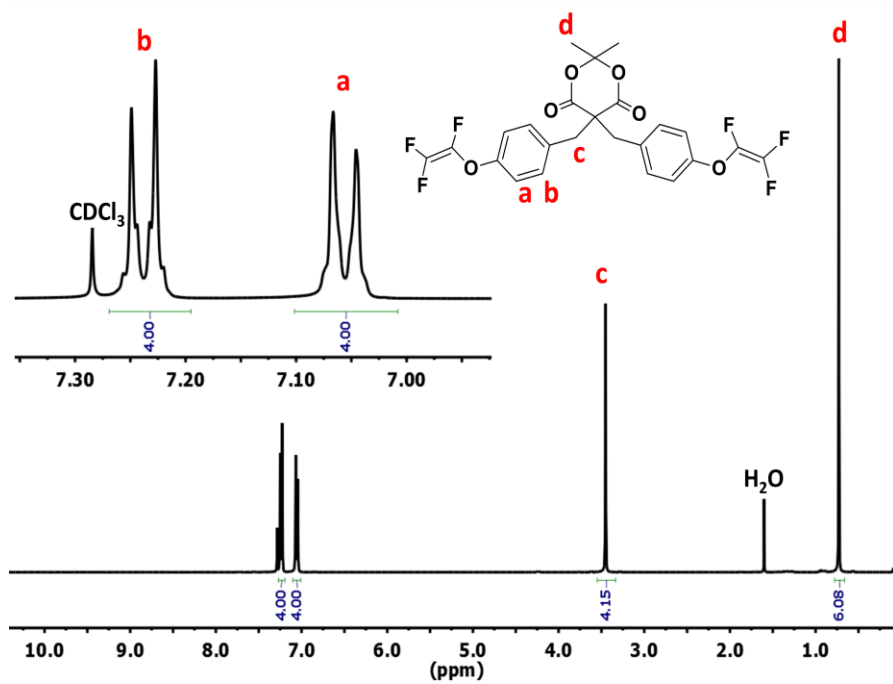


Figure S4. ^1H NMR spectrum of monomer **5**

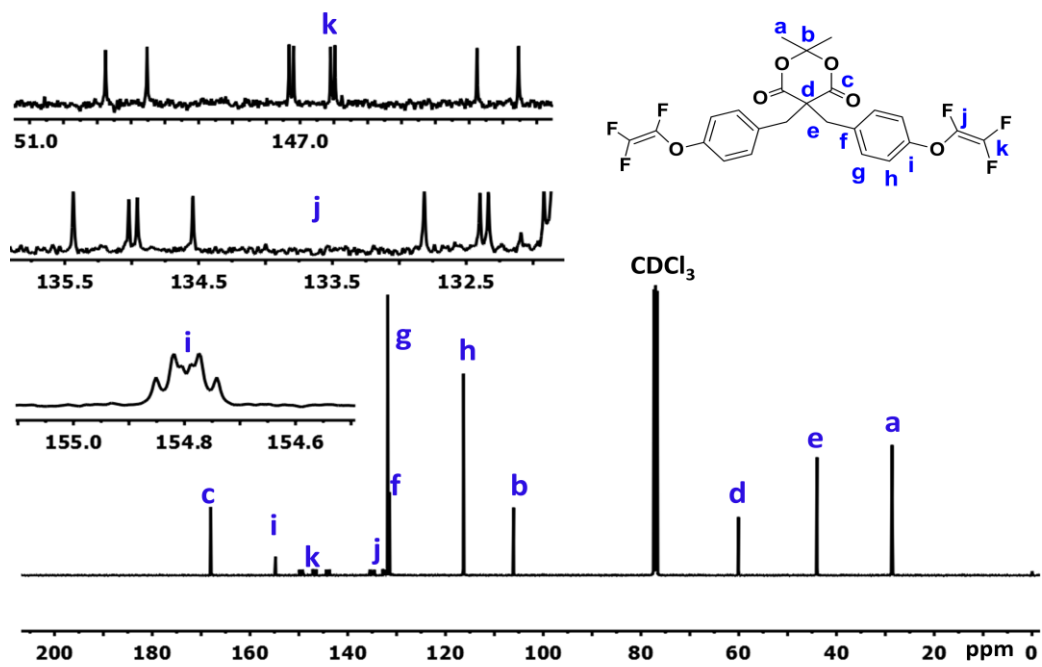


Figure S5. ^{13}C NMR spectrum of monomer **5**.

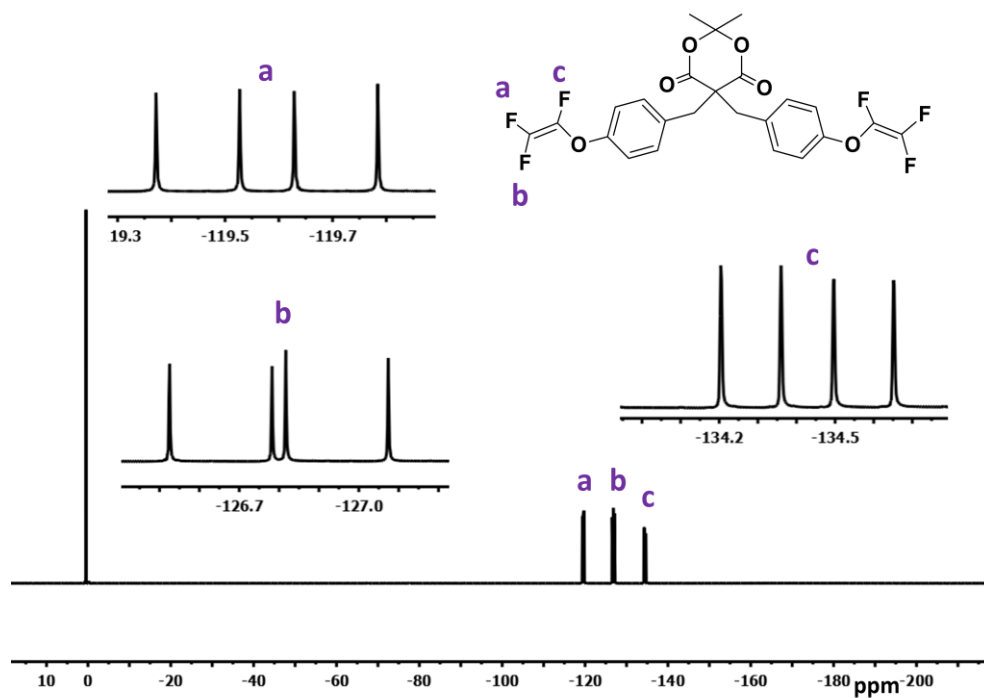


Figure S6. ^{19}F NMR spectrum of monomer 5.

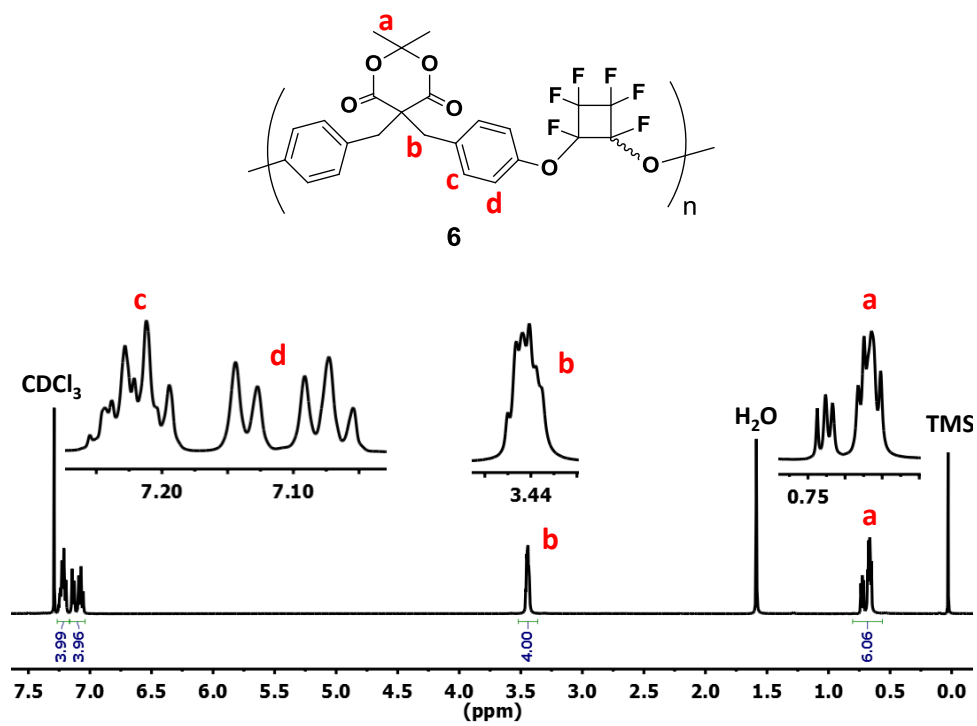


Figure S7. ^1H NMR spectrum of homopolymer 6

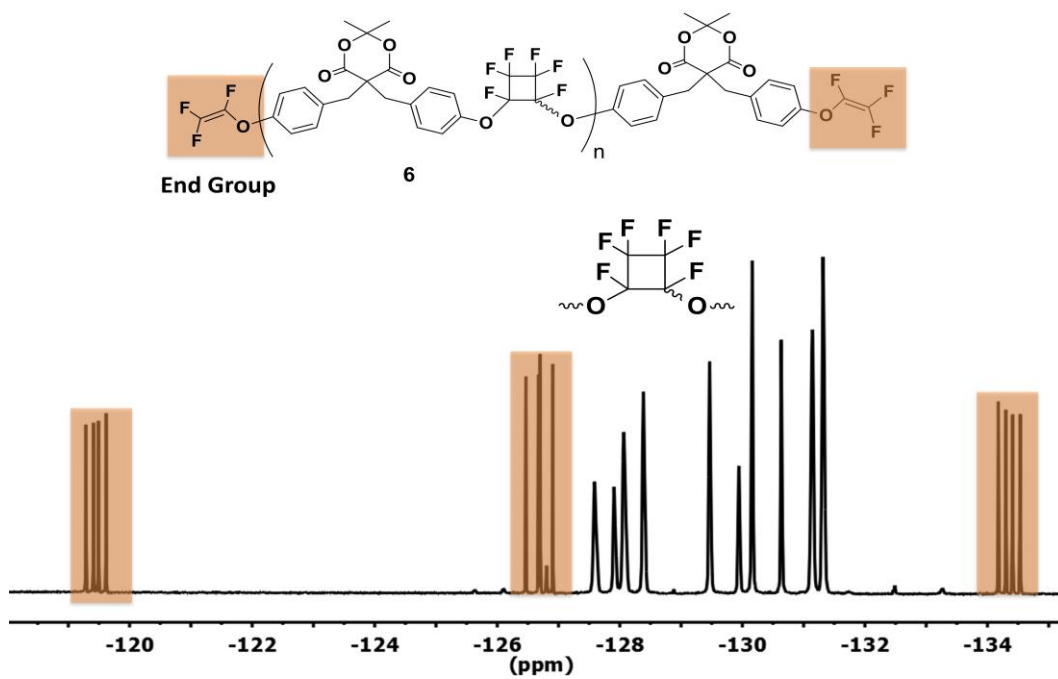


Figure S8. ^{19}F NMR spectrum of homopolymer 6

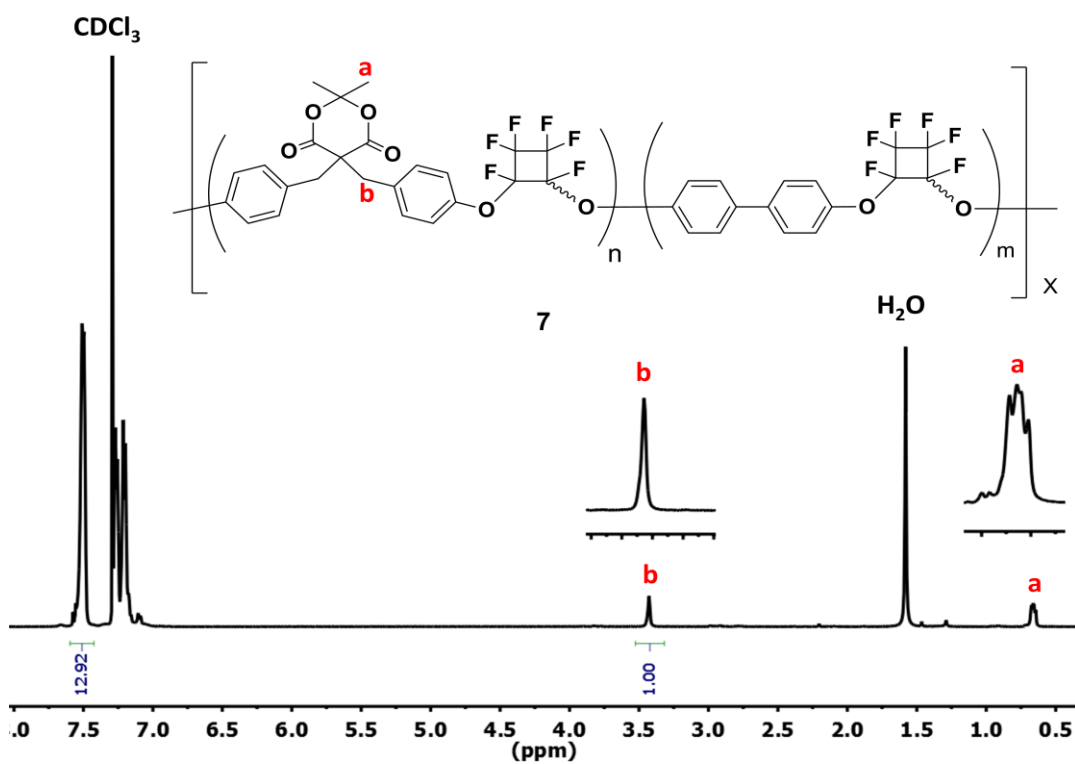


Figure S9. ^1H NMR spectrum of copolymer 7

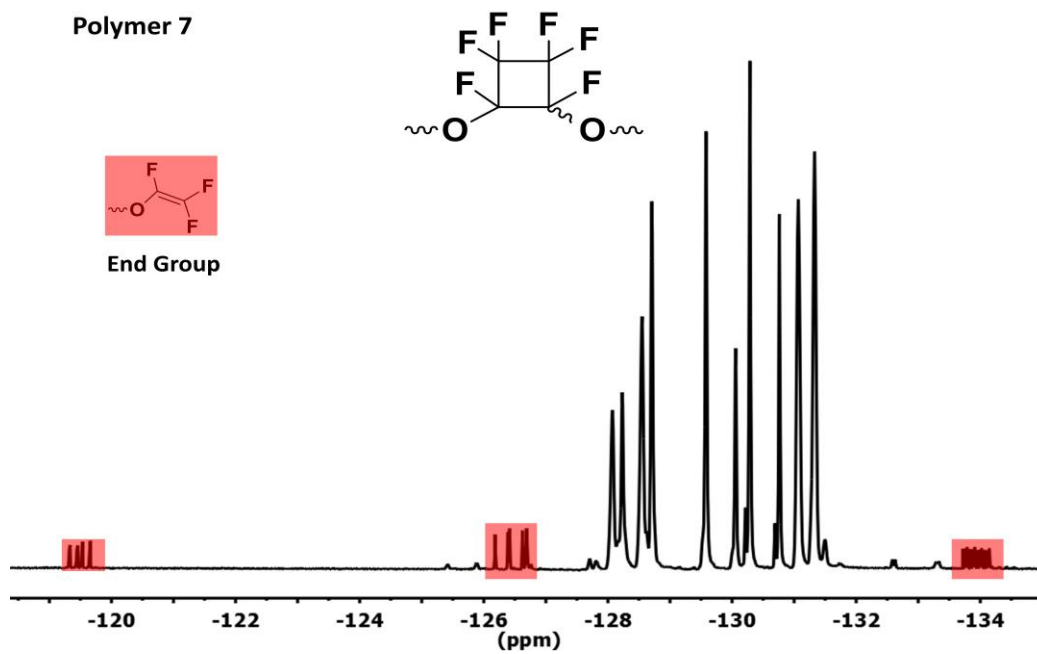


Figure S10. ^{19}F NMR spectrum of copolymer 7

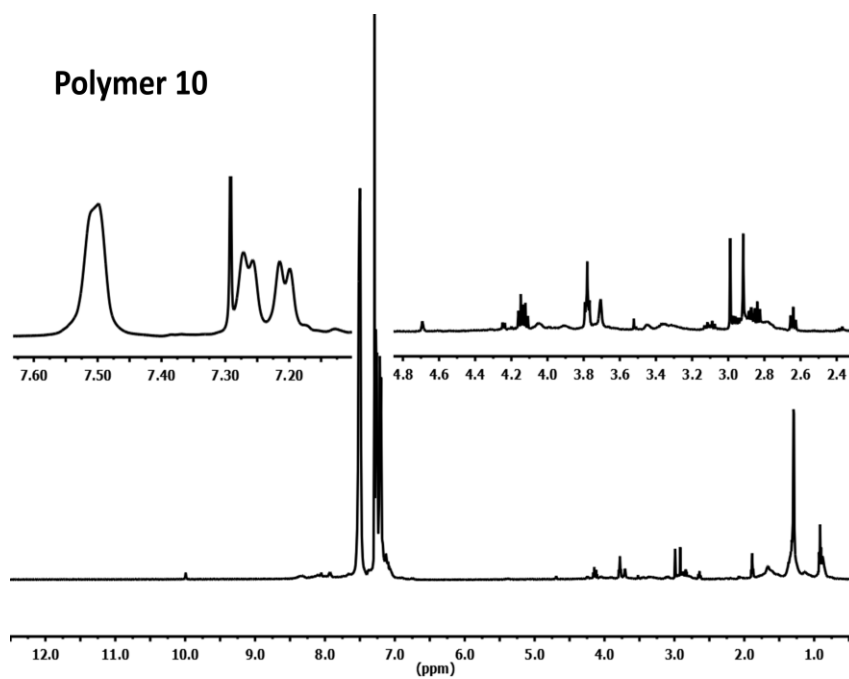


Figure S11. ^1H NMR spectrum of polymer 10

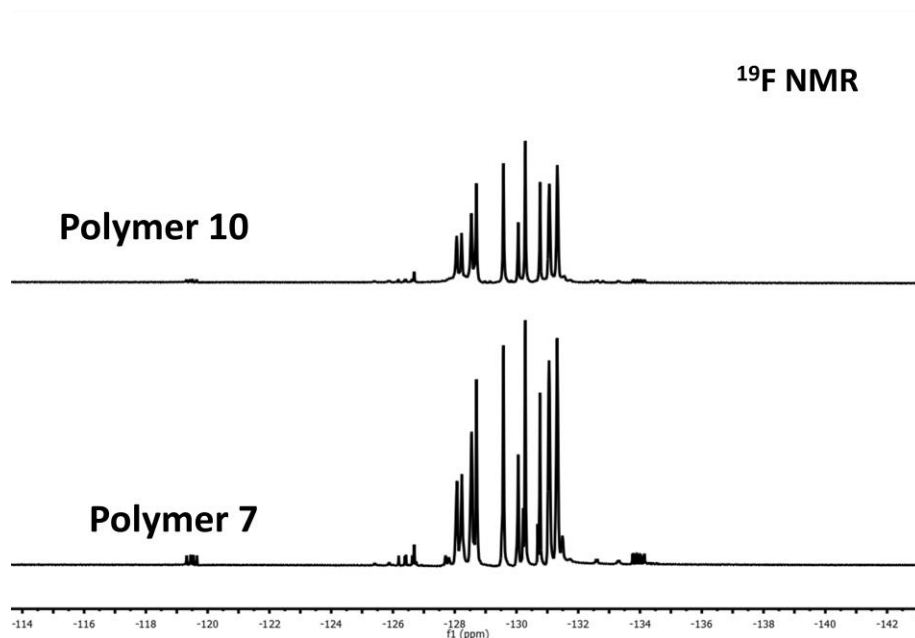


Figure S12. ¹⁹F NMR spectra of polymers 7 and 10

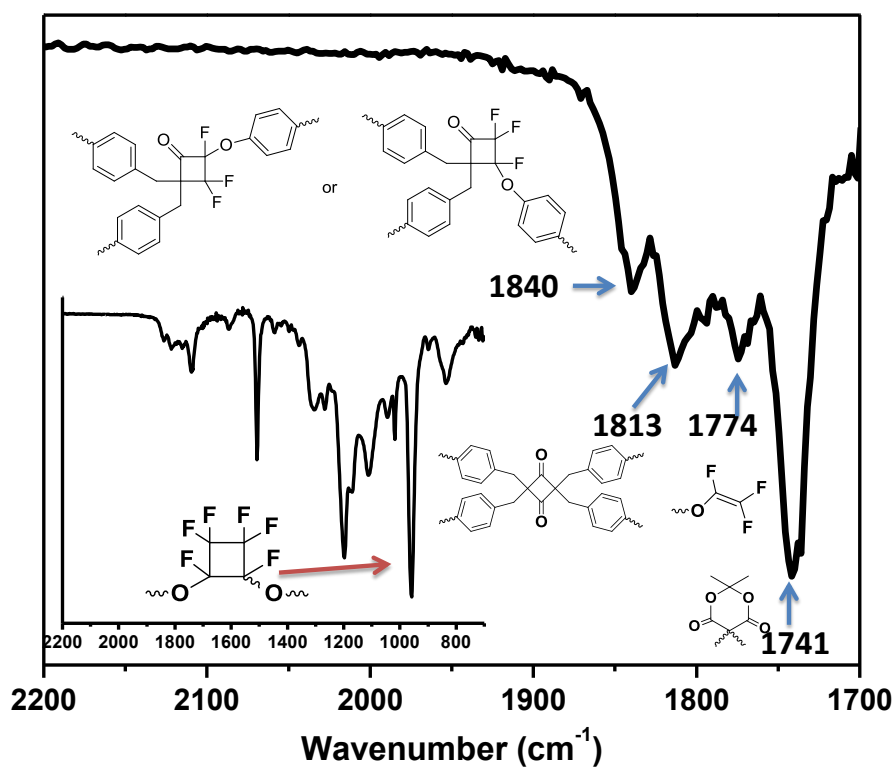


Figure S13. ATR-FTIR spectrum of insoluble PFCB homopolymer

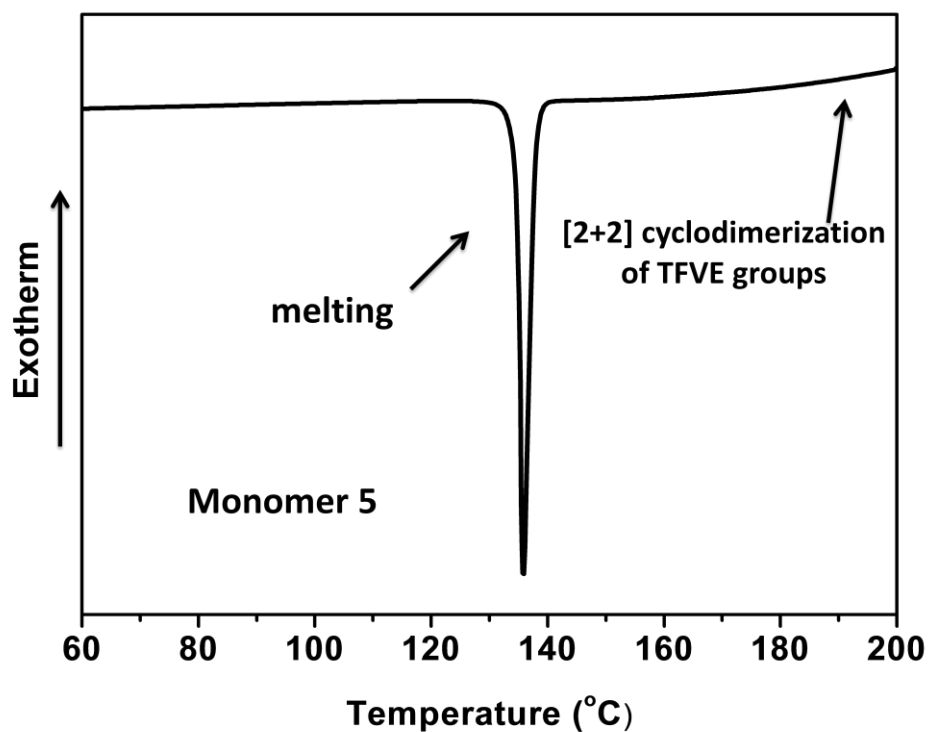


Figure S14. DSC thermogram of the first heating cycle of monomer 5

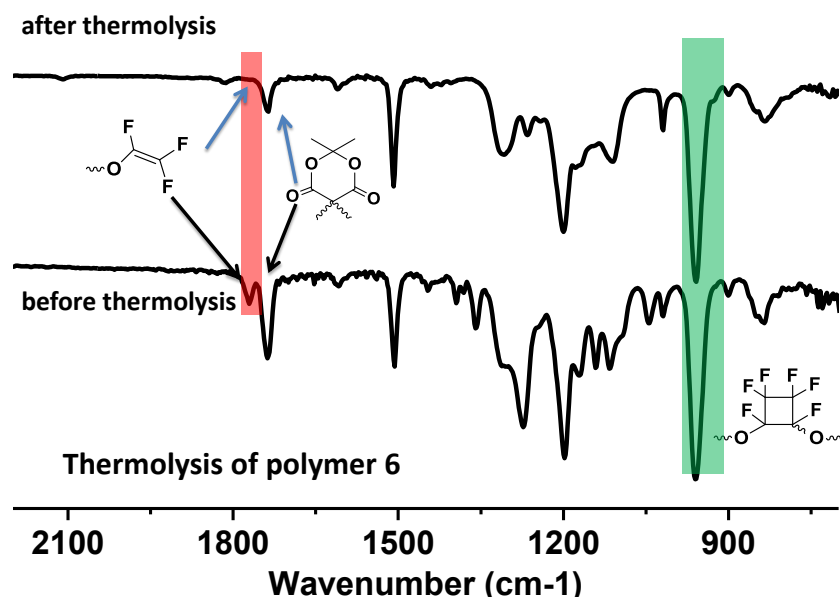


Figure S15. ATR-FTIR spectra of polymer 6 and 9

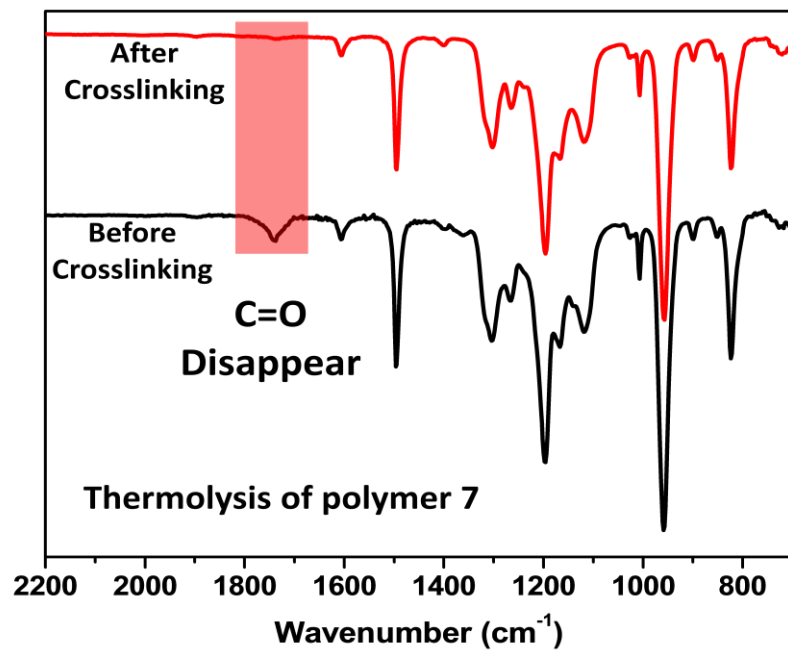


Figure S16. ATR-FTIR spectra of copolymer 7 before and after thermolysis

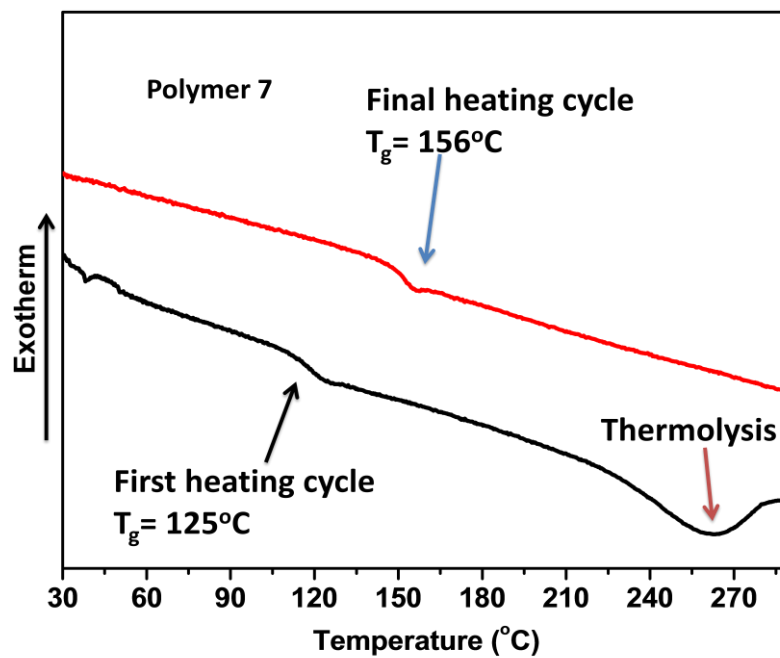


Figure S17. DSC thermograms of polymer 7

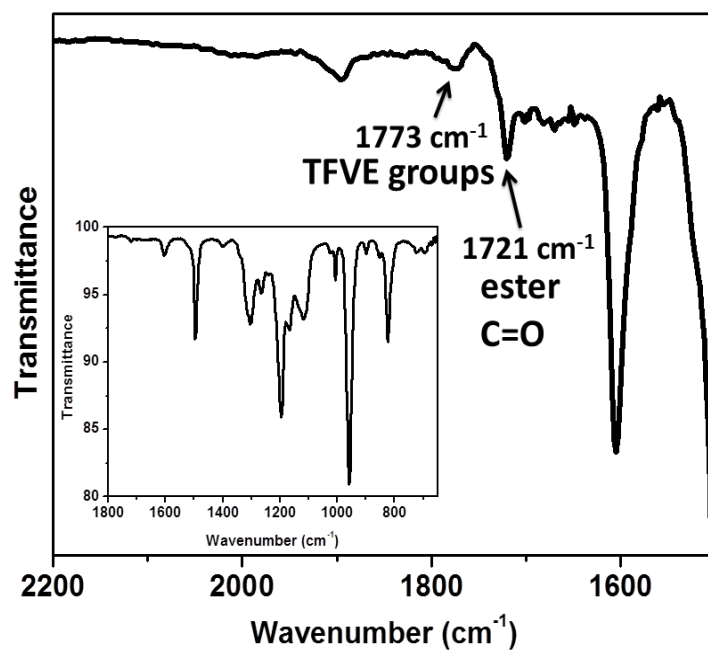


Figure S18. ATR-FTIR spectrum of polymer **10**

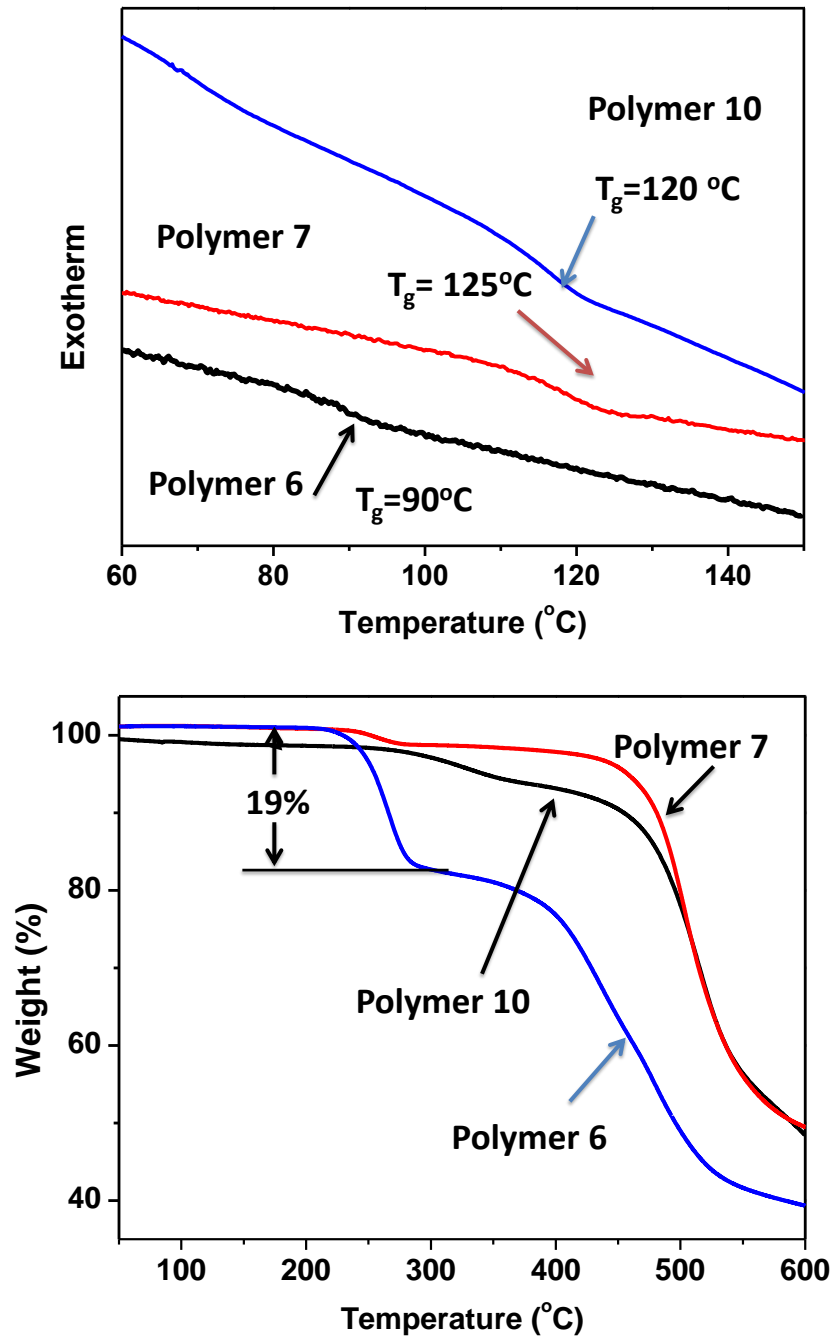


Figure S19. DSC (top) and TGA (bottom) thermograms of polymers 6, 7, and 10

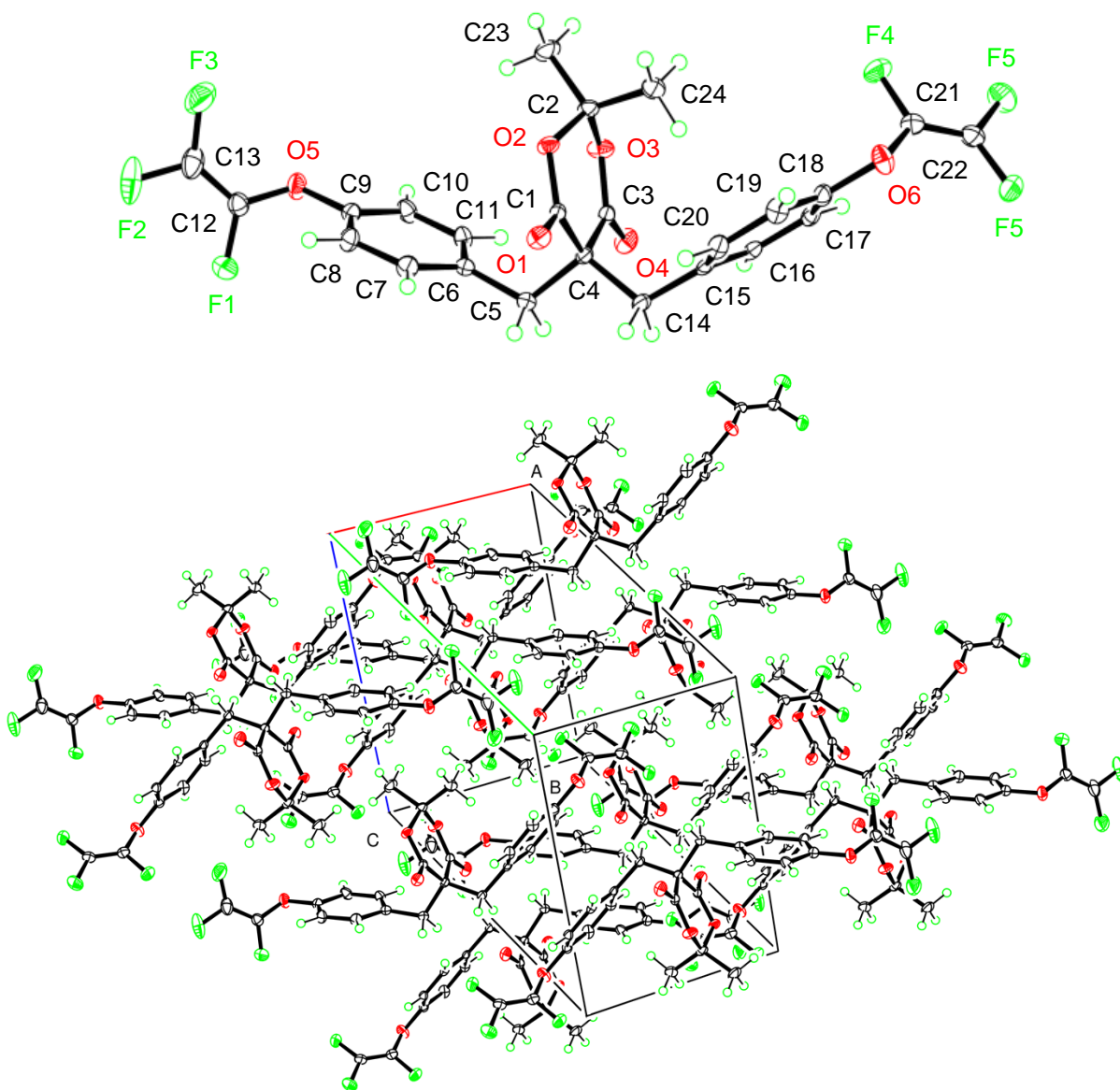


Figure S20. X-ray crystal structure and packing diagram of monomer **5**

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