

# Liquid Crystalline Perfluorocyclobutyl (PFCB) Aryl Ether Polymers Containing Oligophenylene Mesogens

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## Supporting information

### Experimental Section.

**General.** <sup>1</sup>H NMR (500 MHz), proton decoupled <sup>13</sup>C NMR (125 MHz) and <sup>19</sup>F NMR (470.6 MHz) spectra were obtained using a JOEL Eclipse<sup>+</sup> 500 spectrometer system. Matrix-assisted laser desorption/ionization Time-of-Flight (MALDI-TOF) mass analysis was performed on a Bruker Daltonics omniflex MALDI-TOF-MS, equipped with a N<sub>2</sub> laser, 337 nm. The matrix for all measurements was 2,5-dihydroxybenzoic acid (DHB). DSC data were obtained from a TA Q1000 DSC System at a heating rate of 10 °C /min in a nitrogen atmosphere. UV-Vis spectra of the complex were collected using a Shimadzu UV-2101 PC spectrometer. The photoluminescent spectra of the complex were collected with a Perkin Elmer LS50B Luminescence spectrometer. Cross-polarized optical microscopy experiments were performed using a James Swift Polarizing optical microscope (POM) MP3500 equipped with a Mettler-Toledo FP 82HT hot stage and FP900 programmable Thermosystem. High resolution synchrotron X-ray diffraction data were obtained on capillary samples at several different temperatures at the Advanced Photon Source (APS) facilities at the Argonne National Lab. X-ray wavelength is 0.765335 Å. The distance from sample to detector is 500.9 mm. MAR3450 area detector is used in high-res mode.

**Materials.** 4-bromo-4'-(trifluorovinyloxy) biphenyl was prepared as described previously.<sup>1</sup> 4-Bromo(trifluorovinyloxy)benzene, 4-(trifluorovinyloxy)benzene boronic acid, and 4,4'-bis(trifluorovinyloxy) biphenyl are commercially available from Tetramer Technologies, L.L.C. (<http://www.tetramertechnologies.com>) and distributed by Oakwood Chemicals, Inc., Columbia, SC (<http://www.oakwoodchemical.com>). Other chemicals and reagents were purchased from Aldrich or Fisher Scientific and used as received unless otherwise stated.

**Synthesis of 4,4''-bis(trifluorovinyloxy)-1,1':4',1''-terphenyl (1).**

**Method A.** 4-Bromo-4'-(trifluorovinyloxy)biphenyl (1.8 g, 5.5 mmol) and 4-(trifluorovinyloxy)benzene boronic acid (1.2 g, 5.5 mmol) were added to a 50 mL one neck flask containing 20 mL toluene, 4 mL of EtOH and 8 mL of 2M Na<sub>2</sub>CO<sub>3</sub> under an N<sub>2</sub> atmosphere. Tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) (0.21 g, 0.18 mmol) was added to the stirred mixture and heated to 100 °C for 24 hrs. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> and recrystallized from EtOH to give the product as white crystals in 70% yield. mp. 168 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.20 (4H, d, *J* = 8.7 Hz), 7.6283 (4H, d, *J* = 8.7 Hz), 7.6288 (s, 4H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 116.3, 127.44, 128.55, 133.9 (ddd, CF=CF<sub>2</sub>), 137.5, 139.1, 147.0 (ddd, CF=CF<sub>2</sub>), 154.5 ppm. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ: -119.4 (2F, dd, *cis*-CF=CF<sub>2</sub>, Fa), -126.3 (2F, dd, *trans*-CF=CF<sub>2</sub>, Fb), -133.7 (2F, dd, CF=CF<sub>2</sub>, Fc) ppm. MALDI-TOF/MS (M<sup>+</sup> calcd as C<sub>22</sub>H<sub>12</sub>O<sub>2</sub>F<sub>6</sub> 422) m/z: 422.

**Method B.** Monomer **1** can also be synthesized more practically from commercial available starting materials 4-bromo(trifluorovinyloxy)benzene and phenyl 1,4-diboronic acid. To a 50 mL one neck flask containing 30 mL toluene, 8 mL of EtOH and 10 mL of 2M Na<sub>2</sub>CO<sub>3</sub> equipped with N<sub>2</sub> purge were added 4-bromo-(trifluorovinyloxy)benzene (5.06g, 20 mmol) and phenyl 1,4-diboronic acid (1.66 g, 10 mmol) and 0.5g tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>). The solution mixture was heated to 100 °C and stirred for 24 hrs. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> and recrystallized from EtOH to give the product as white crystals in 60% yield.

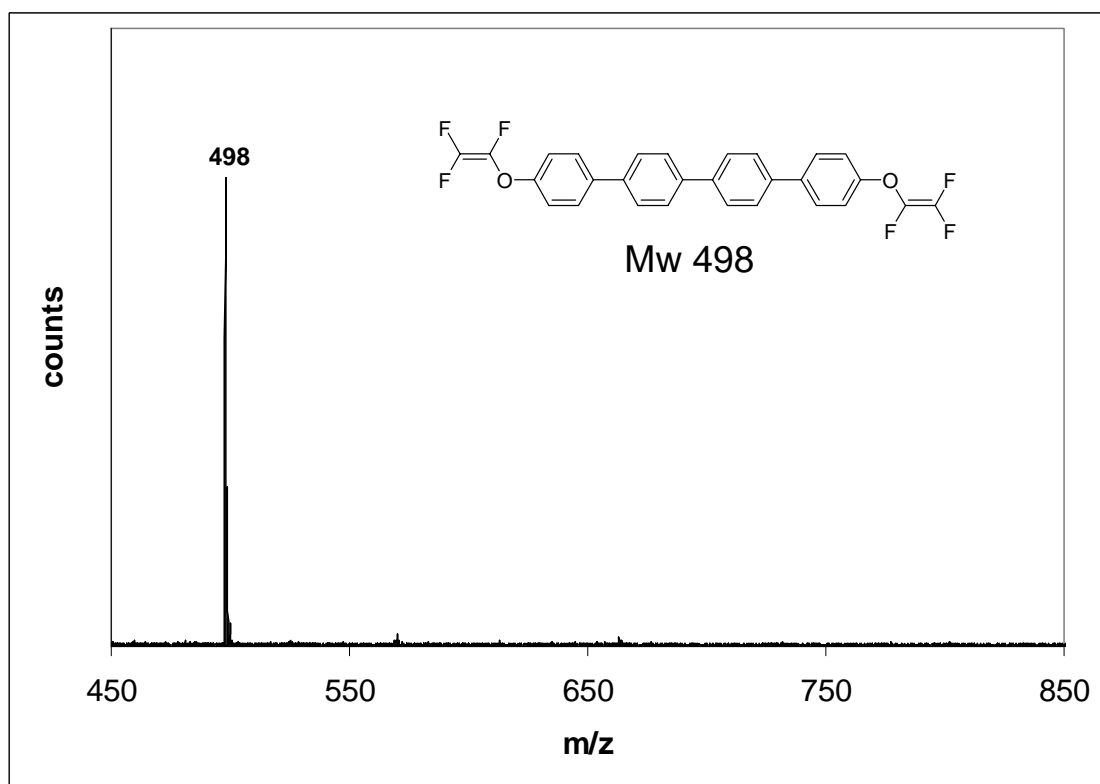
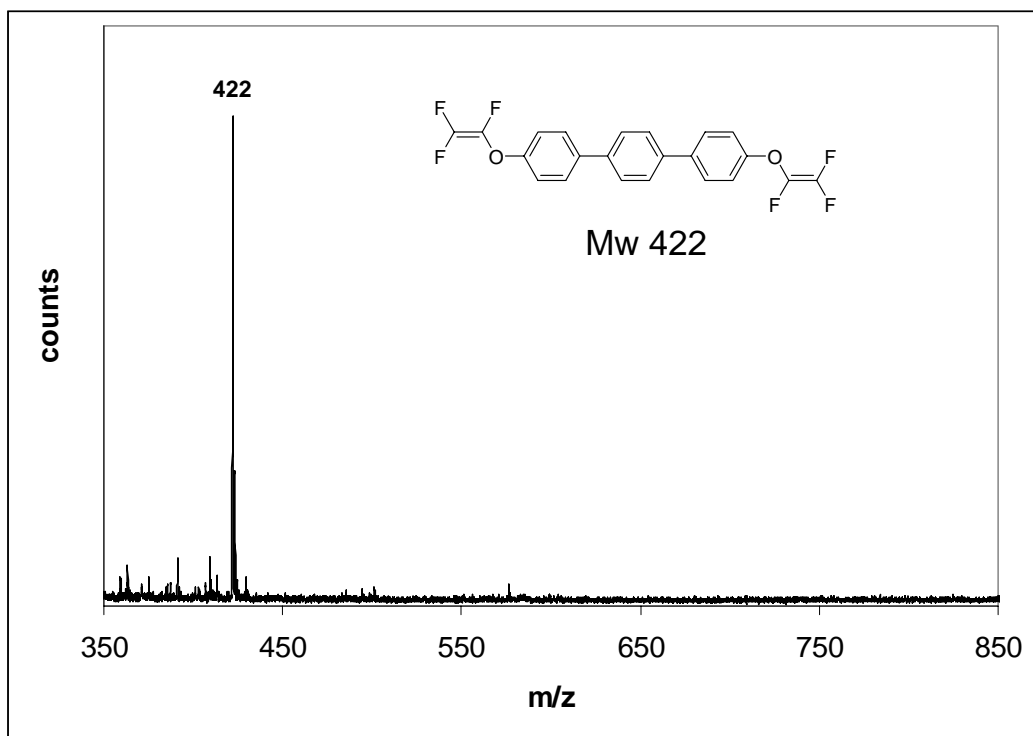
**Synthesis of 4,4'''-bis(trifluorovinyloxy)-1,1':4',1'':4'',1'''-quaterphenyl (2).** 4,4'-Dibromobiphenyl (0.936 g, 3 mmol) and 4-(trifluorovinyloxy)benzene boronic acid (1.31 g, 6 mmol) were added to a 50 mL single neck flask containing 20 mL toluene, 4 mL of EtOH and 8 mL of 2M Na<sub>2</sub>CO<sub>3</sub> under an N<sub>2</sub> atmosphere. Then tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) (0.22 g, 0.2 mmol) was added to the stirred mixture and heated to 100 °C for 24 hrs. During the reaction, the product (**2**) precipitated from the solution, filtered, and recrystallized from DMSO and toluene to give white crystals in 40% yield. mp. 226 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.21 (4H, d, *J* = 8.7 Hz), 7.648 (4H, d, *J* = 8.7 Hz), 7.65 (4H, d, *J* = 8.25 Hz), 7.72 (4H, d, *J* = 8.25 Hz) ppm. MALDI-TOF/MS (M<sup>+</sup> calcd as C<sub>28</sub>H<sub>16</sub>O<sub>2</sub>F<sub>6</sub> 496) m/z: 496.

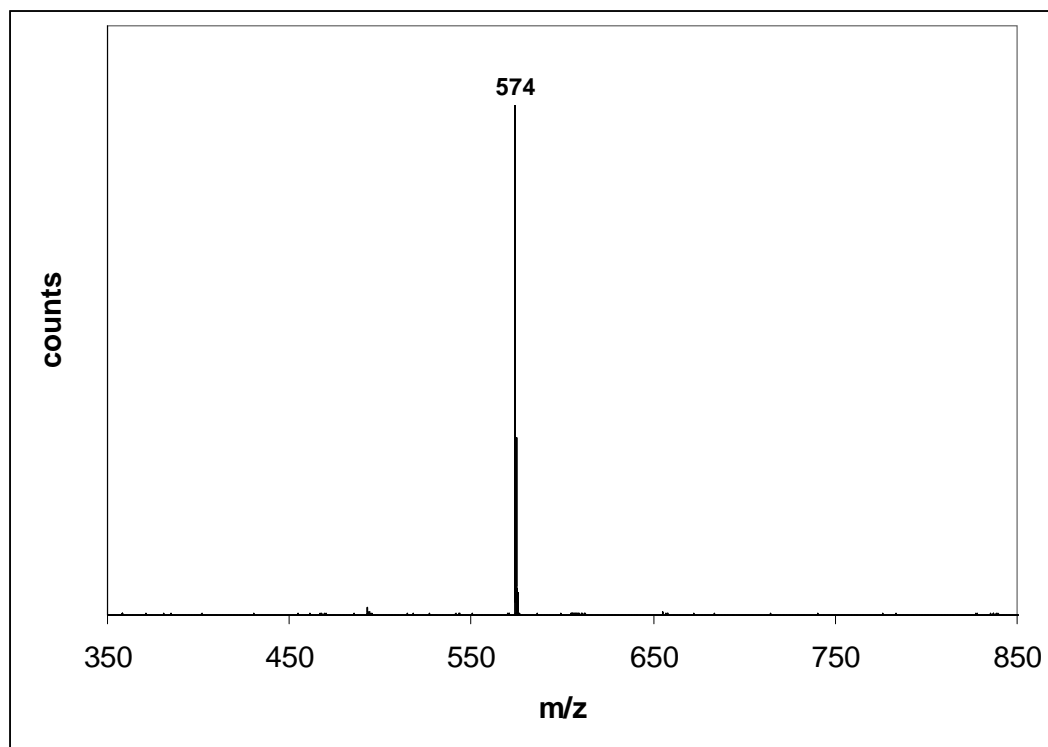
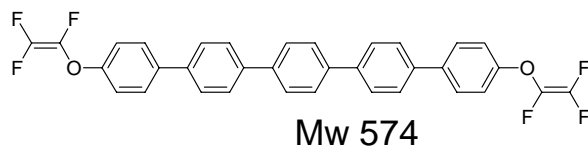
**Synthesis of 4,4''''-bis(trifluorovinyloxy)-1,1':4',1'':4'',1''':4''',1''''-pentaphenyl (3).** Similar to above, 4-bromo-4'-(trifluorovinyloxy)biphenyl (0.987 g, 3 mmol) and 1,4-phenylenebisboronic acid (0.249 g, 1.5 mmol) were added to a 50 mL one neck flask containing 20 mL toluene, 4 mL of EtOH and 8 mL of 2M Na<sub>2</sub>CO<sub>3</sub> under an N<sub>2</sub> atmosphere. Tetrakis(triphenylphosphine) palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) (0.11 g, 0.1 mmol)

was added to the stirred mixture solution and heated to 100 °C for 24 hrs. During the reaction, the product (**3**) precipitated from solution, filtered, and washed with hot DMSO to give a metallic solid in 40% yield. The product was confirmed by MALDI-TOF/MS. GC/MS ( $M^+$  calcd as  $C_{34}H_{20}O_2F_6$  574) m/z: 574.

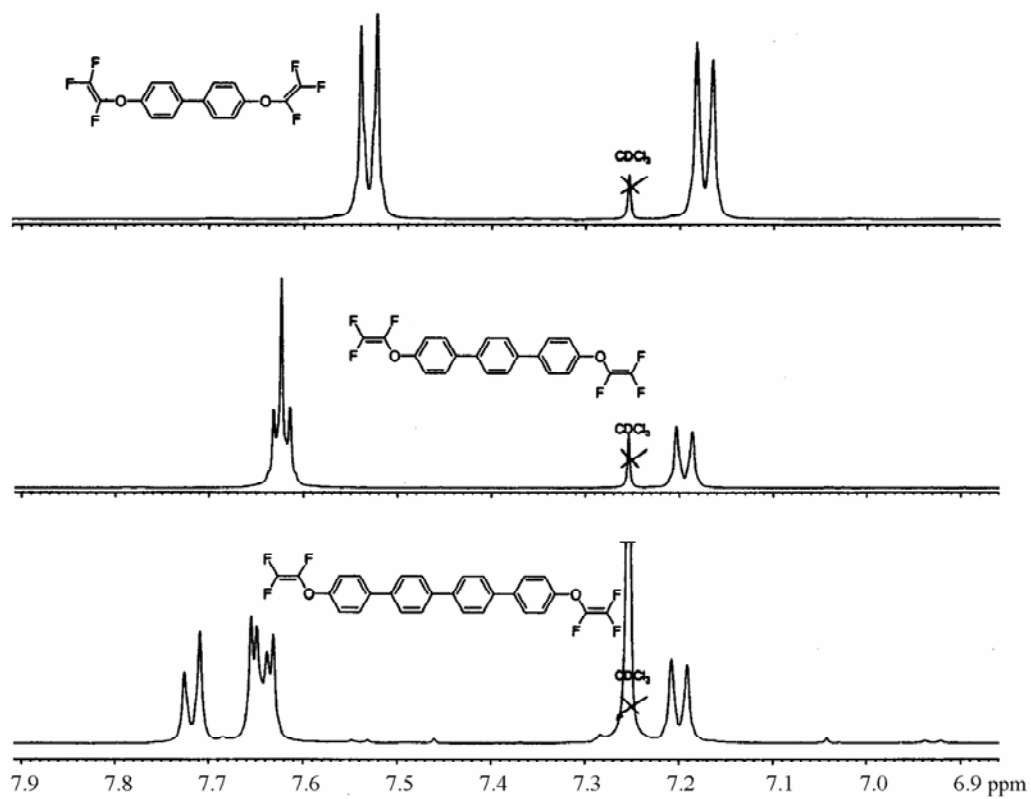
**Polymerization.** To a 5mL ample equipped with magnetic stirring bar was added monomer **1** (300 mg) and mesitylene (1 mL). The ample was sealed under  $N_2$  purge and polymerized at 180 °C for 24 hrs. The polymer (**poly1**) was precipitated in methanol. **Poly1** is slightly soluble in  $CHCl_3$  and mesitylene at room temperature but very soluble at elevated temperature.  $^{19}F$  NMR shows the characteristic series of multiplets representing the perfluorocyclobutyl fluorine signals ranging from –126 to –133 ppm. The number average molecular weight is about 5,064 determined by end group analysis. Monomer **1** was also packed into three quartz capillaries (i.d = 1.5mm) and polymerized at 180 °C for 30, 53 and 120 min for hi-res synchrotron X-ray diffraction study. The polymerization for monomer **2** and **3** was studied only in a DSC experiment. The resulting homopolymers of **2** and **3** were insoluble in all common organic solvents.

**X-ray Diffraction.** Monomer **1** was polymerized at 180 °C for 120 min in a 2.5mm quartz capillary. The sample was then quenched to room temperature and the evolution of the structure with increasing temperature was followed by X-ray scattering. Measurements were carried out at the Advanced Photon Source (APS) facilities at the Argonne National Laboratories at 6IDB with a wave length of 0.764Å. The temperature was controlled to +/- 0.1°C.

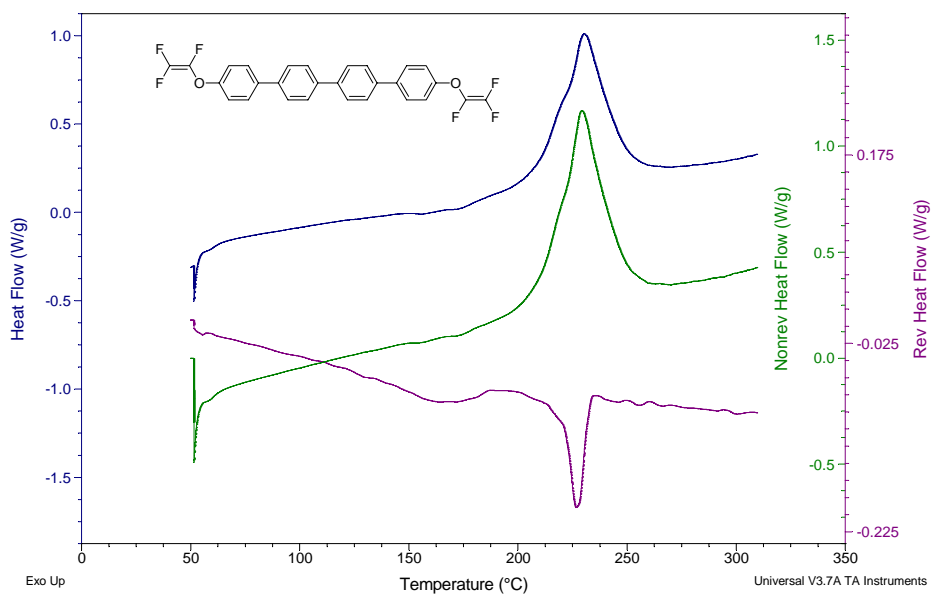




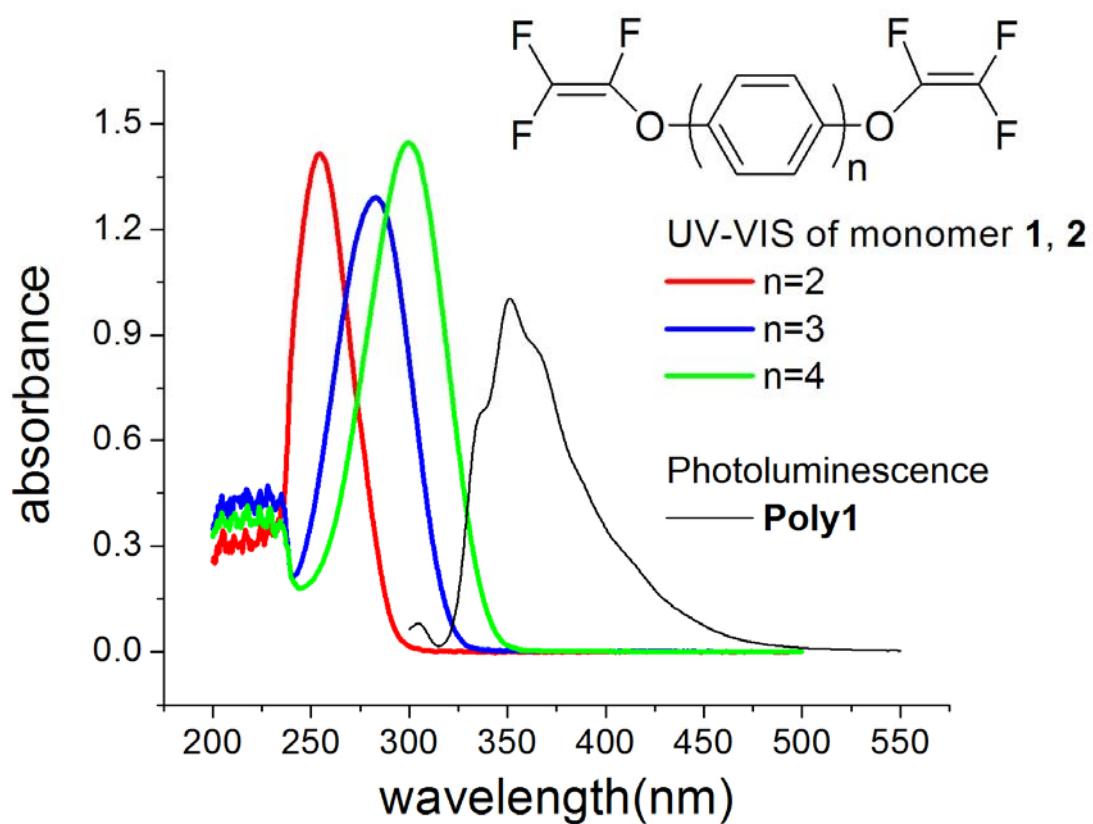
**Figure S1.** MALDI-TOF mass spectra of the monomers **1-3**.



**Figure S2.** <sup>1</sup>H NMR spectra of commercial 4,4'-bis(trifluorovinyl)oxy biphenyl and monomers **1** - **2**.

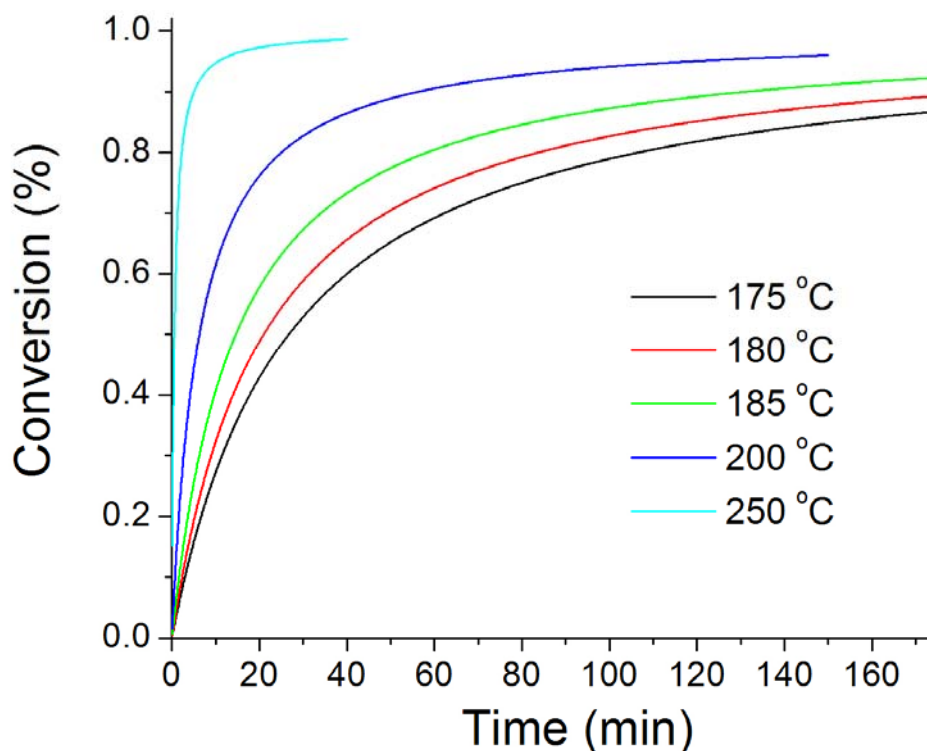


**Figure S3.** Modulated DSC of monomer **2** at 10 °C/min. A melting transition at 226 °C of monomer **2** is clearly observed in the reversible heat flow curve. While using regular DSC, the melt transition is embedded in the dominant exothermic peak from cyclopolymerization of trifluorovinyl ethers.



**Figure S4.** UV-Vis spectra of commercial 4,4'-bis(trifluorovinyloxy)biphenyl and monomers **1–2** and photoluminescence spectrum of **poly1**.





**Figure S5.** Conversion versus time at various polymerization temperatures.

The polymerization kinetics of trifluorovinyl ether monomers in the bulk has been characterized via Raman Spectroscopy by measuring the disappearance of the fluoroolefin Raman signal at  $1831\text{ cm}^{-1}$ .<sup>2</sup> Using this data to estimate monomer **1** conversion versus time, we found that the induction times for development of an LC phase at different temperatures all similarly point to a monomer conversion of 50%. From step growth polymerization statistics, 50% conversion represents an oligomer composition with average degree of polymerization of 2, or dimer.

The equation of conversion versus time for 2<sup>nd</sup> order reaction is as follows:

$$x/(1-x)=kt$$

where as      x : conversion  
                     k: rate constant ( $\text{min}^{-1}$ )  
                     t: time (min)

**Table S1.** Time comparison of formation of LC droplet and theoretic 50% monomer conversion

Temp °C	Rate constant $K^a$ (min <sup>-1</sup> )	Onset of Nematic droplet observed (min)	Theoretic Time for 50% Conversion (min) <sup>b</sup>
175	0.03746	23.79	26.7
185	0.068494	13.1	14.6
200	0.159429	6.91	6.5
250	1.781925	1.5	0.6

<sup>a)</sup> The rate constant K is calculated from previous publication.<sup>2</sup>

<sup>b)</sup> The data is obtained from Figure S7.

## Reference

- 1). Jin, J.; Smith, Jr. D.W.; Topping, C.; Suresh, S.; Chen, S.; Foulger, S.; Rice, N.; Mojazza, B. *Macromolecules* **2003**, *36*, 9000.
- 2). Cheatham, C.M.; Lee, S.-N.; Laane, J.; Babb, D.A.; Smith, Jr. D.W. *Polym. Inter.* **1998**, *46*, 320.