

((Supporting Information can be included here using this template))

Supporting Information

Photocurable Hypervalent Fluorinated Sulfur Containing Thin Films with Remarkable Hardness and Modulus

Kelly A. Bonetti¹, Denis Rende³, Michael Murphy², Prof. John T. Welch^{1,}*

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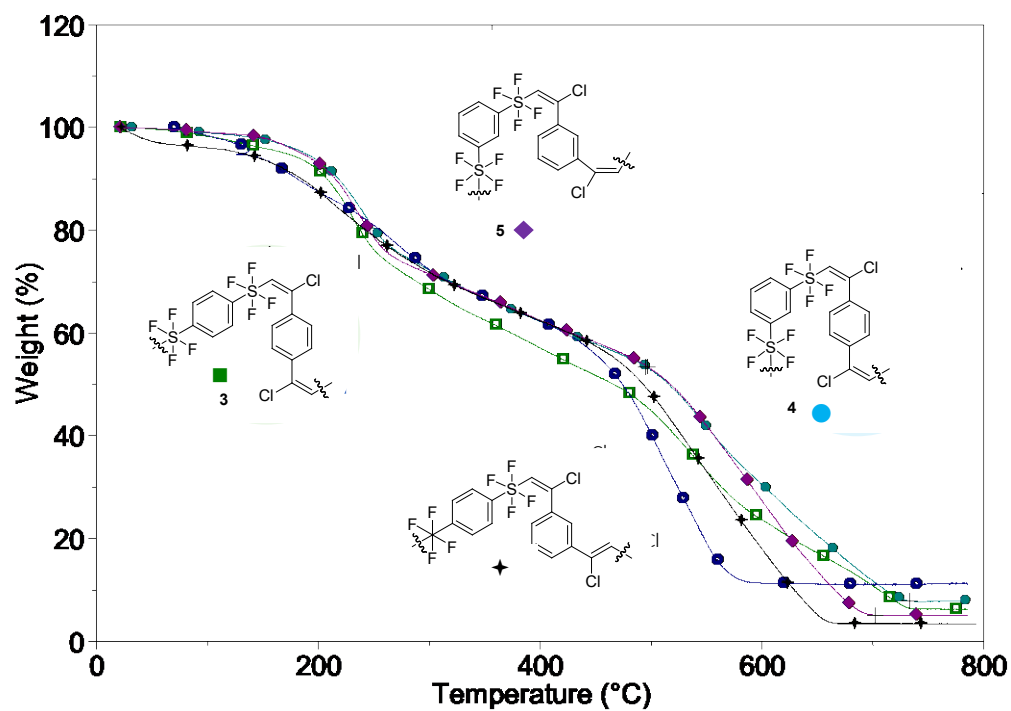


Figure S1. Thermogravimetric analyses of polymers **3**, **4** and **5**. Tetrafluorosulfonyl-containing polymers **3**, **4** and **5** demonstrate two major weight losses..

NMR Characterization

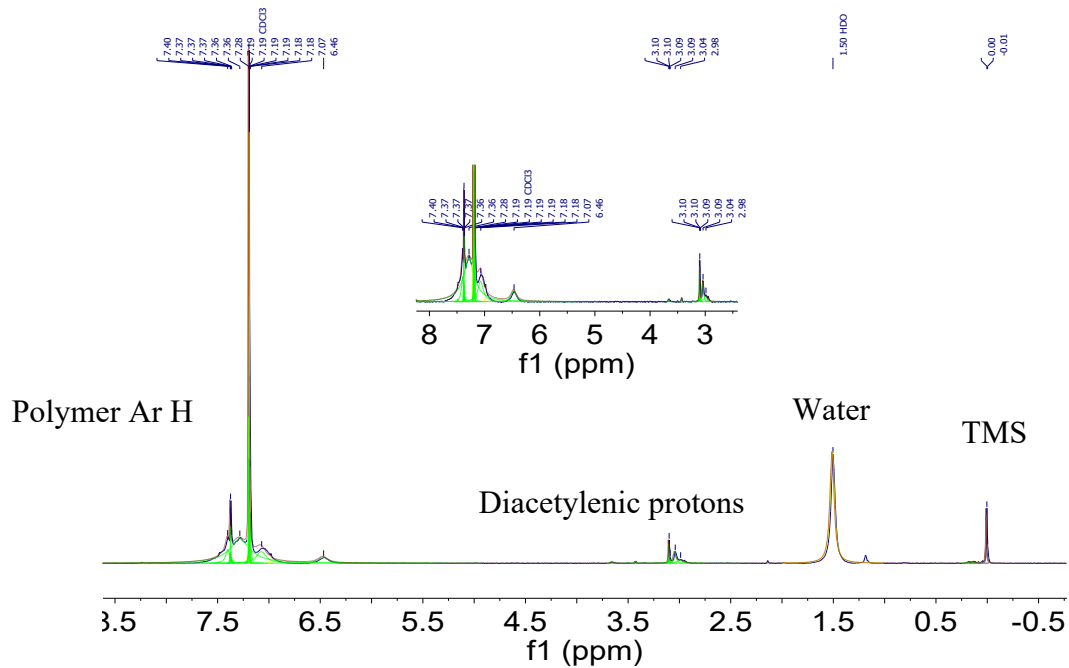


Figure S2. ^1H NMR polymer **3** in chloroform- d .^[1]

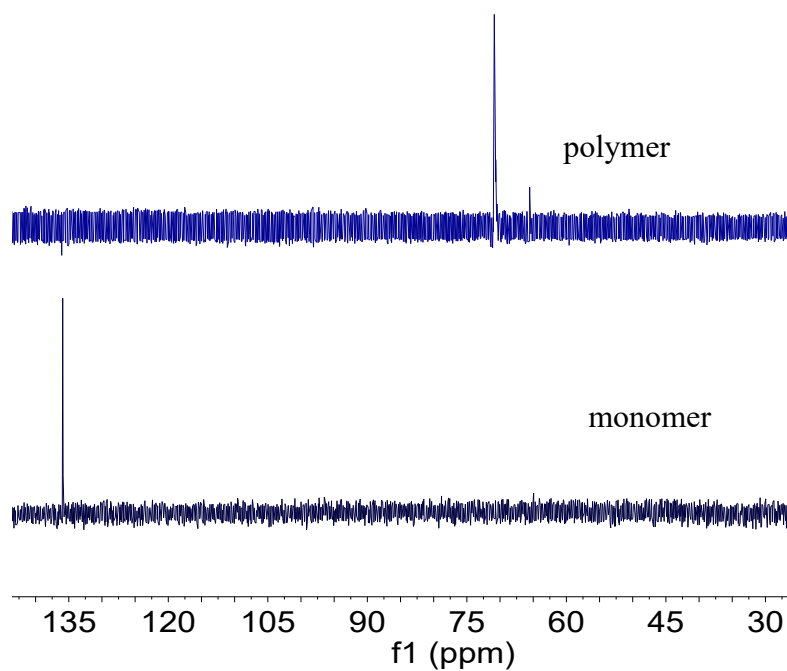


Figure S3. ^{19}F NMR of monomer **1** compared with polymer **3** with baseline smoothing. Samples dissolved in chloroform- d .^[1]

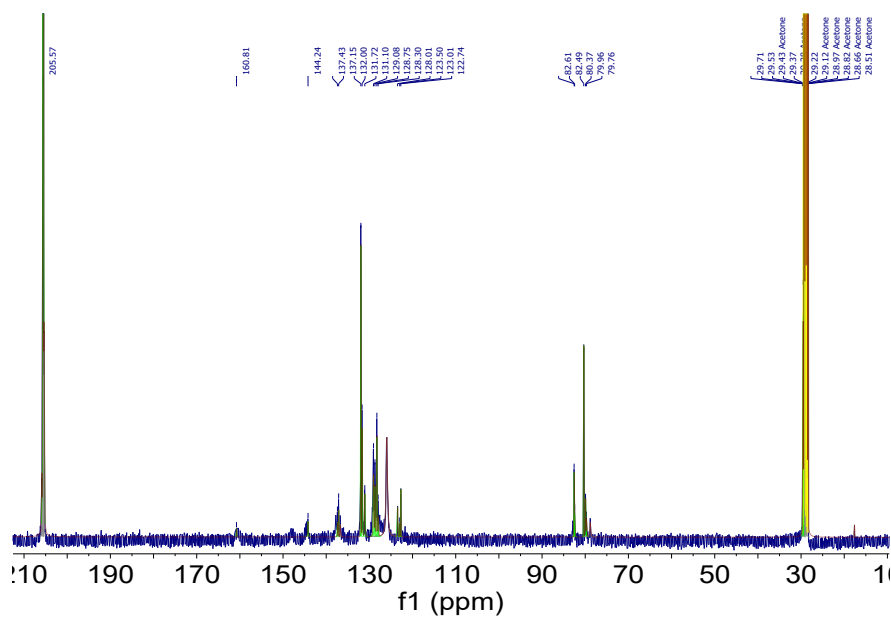


Figure S4. Polymer **3** ^{13}C in acetone- d_6 . ^{13}C (500 MHz, acetone- d_6): δ 160.8 (p, 2C, ArSF_4Cl), 144.2 (m, 2C, alkene $\text{SF}_4\text{-C}$), 137.2 (m, 2C, alkene $\text{SF}_4\text{-C}$), 132.0 (s, 4C, Ar C), 131.7 (s, 4C, Ar C), 131.09 (s, 4C, Ar C), 129.1 (p, 2C, alkene C-Cl), 128.7 (m, 2C, Ar C), 128.3 (m, 2C, Ar C), 126.1 (m, 2C, Ar SF_4), 123.5 (s, 2C, Ar C), 82.6 (s, 1C, alkyne C), 79.8 (s, 1C, Alkyne C).[1]

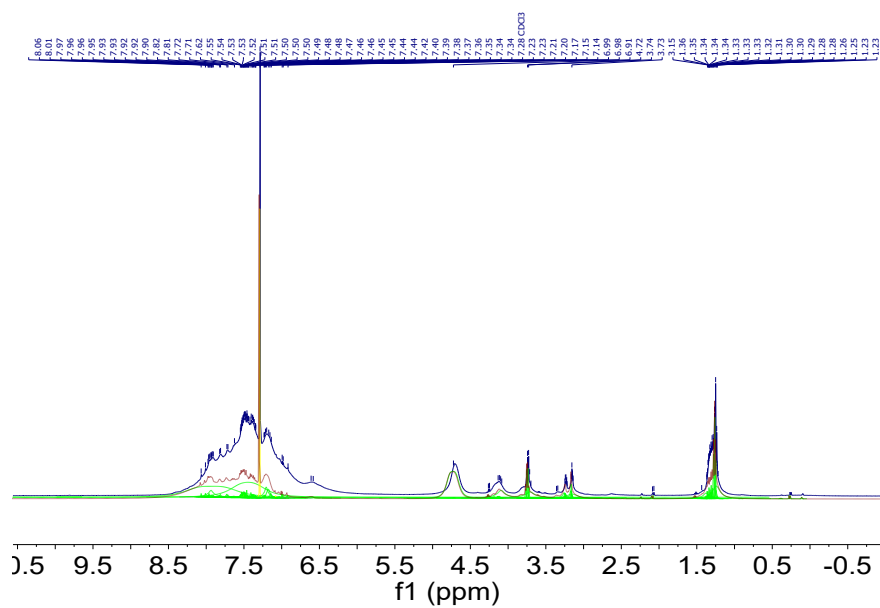
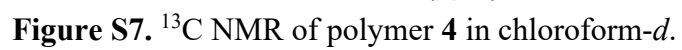
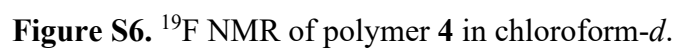


Figure S5. ^1H NMR of polymer **4** in chloroform- d .



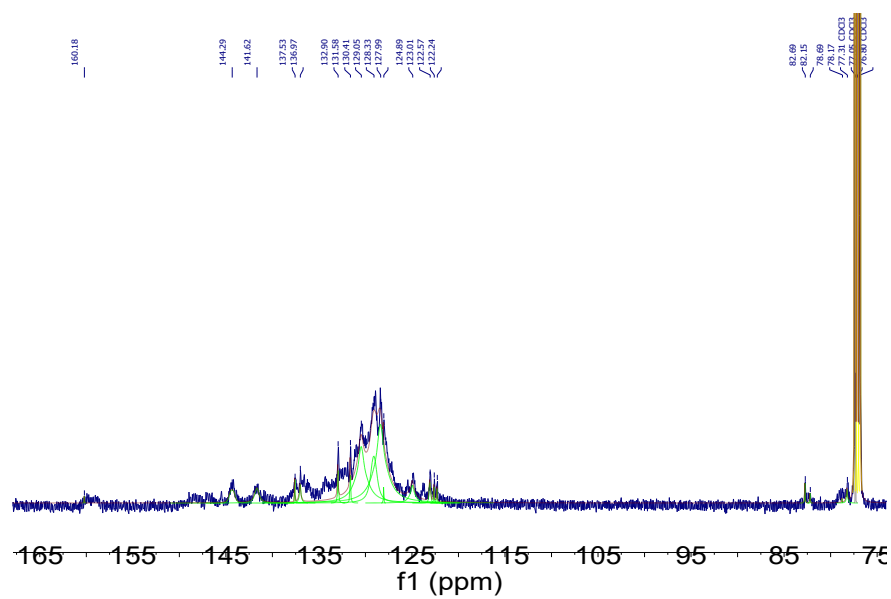


Figure S10. ^{13}C NMR of polymer **5** in chloroform-*d*.

Infrared Spectra

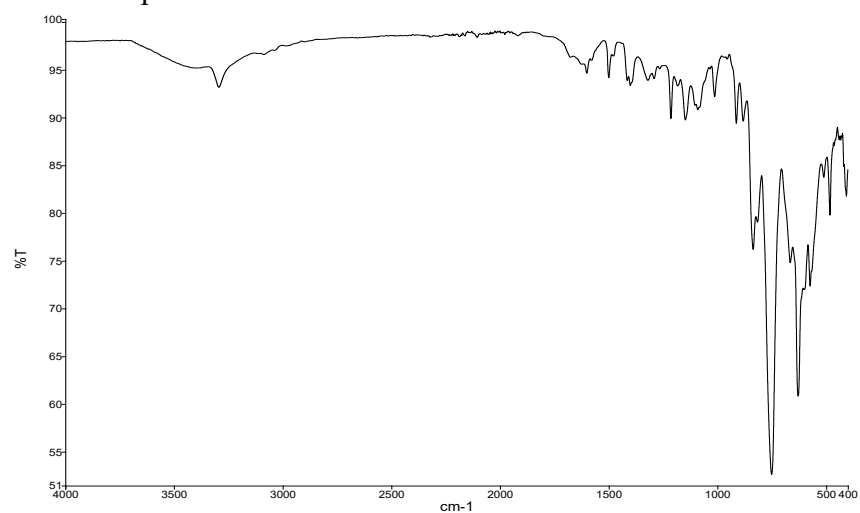


Figure S11. IR of the polymer **3**.

Table S1. IR peaks of polymer **3**.

Peak Name	X (cm-1)	Y (%T)
1	3296.21	93.25
2	1602.31	94.73
3	1501.03	94.26
4	1402.11	93.44
5	1214.9	89.98
6	1148.64	89.82
7	1091.25	90.89
8	1013.34	92.27
9	913.86	89.48
10	882.11	89.7
11	836.16	76.24
12	751.25	52.62
13	665.95	74.84
14	628.8	60.84
15	574.1	72.4
16	482.57	79.83
17	406.84	81.83

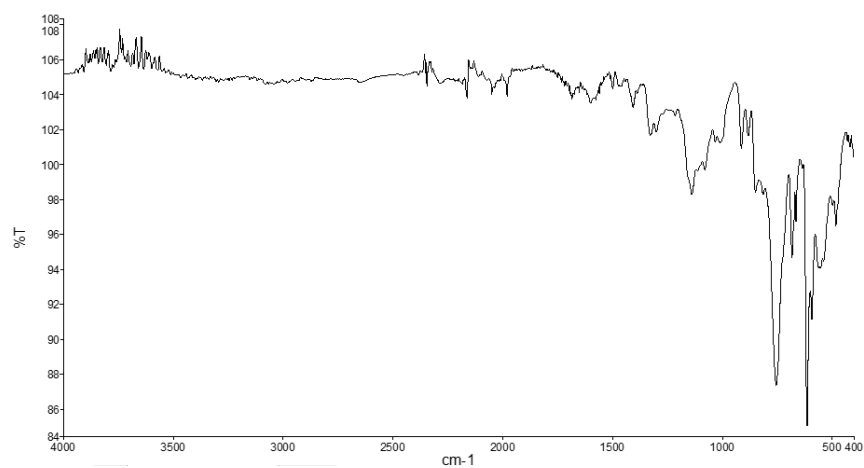


Figure S12. IR of polymer **4**

Table S2. Peak Labels of polymer **4**

Peak Name	X (cm-1)	Y (%T)
1	912.41	100.94
2	753.28	87.35
3	681.77	94.67
4	612.92	85.01
5	552.43	94.06

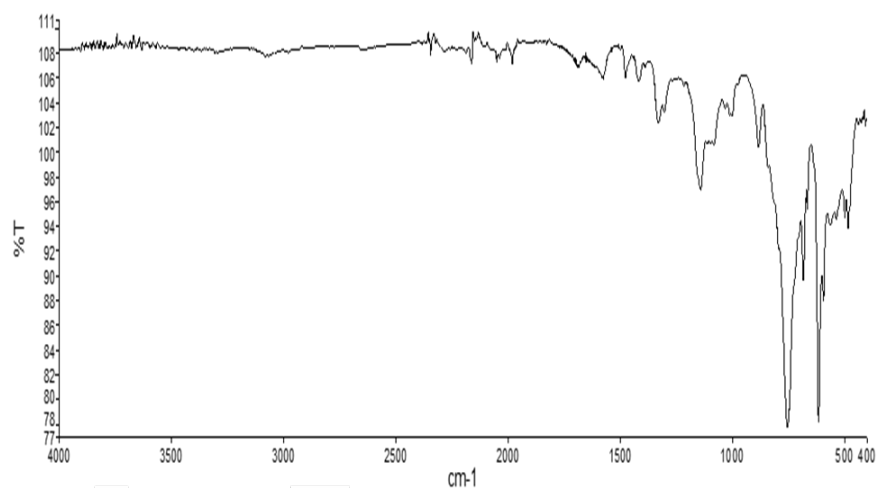


Figure S13. IR of polymer **5**.

Table S3. IR Peaks of polymer **5**.

Peak Name	X (cm-1)	Y (%T)
1	3678.64	108.44
2	3079.38	107.81
3	2345.23	107.95
4	2161.49	107.25
5	2049.75	107.41
6	1979.42	107.17
7	1682.27	106.9
8	1574.24	105.98
9	1475.17	106.08
10	1416.7	105.8
11	1328.46	102.42
12	1141.06	97.01
13	999.96	103.03
14	881.59	100.44
15	752.48	77.73
16	682.02	89.63
17	664.36	95.44
18	613.76	78.19
19	592.22	88.07
20	496.77	94.79
21	481.88	93.85

Thermal Characterization

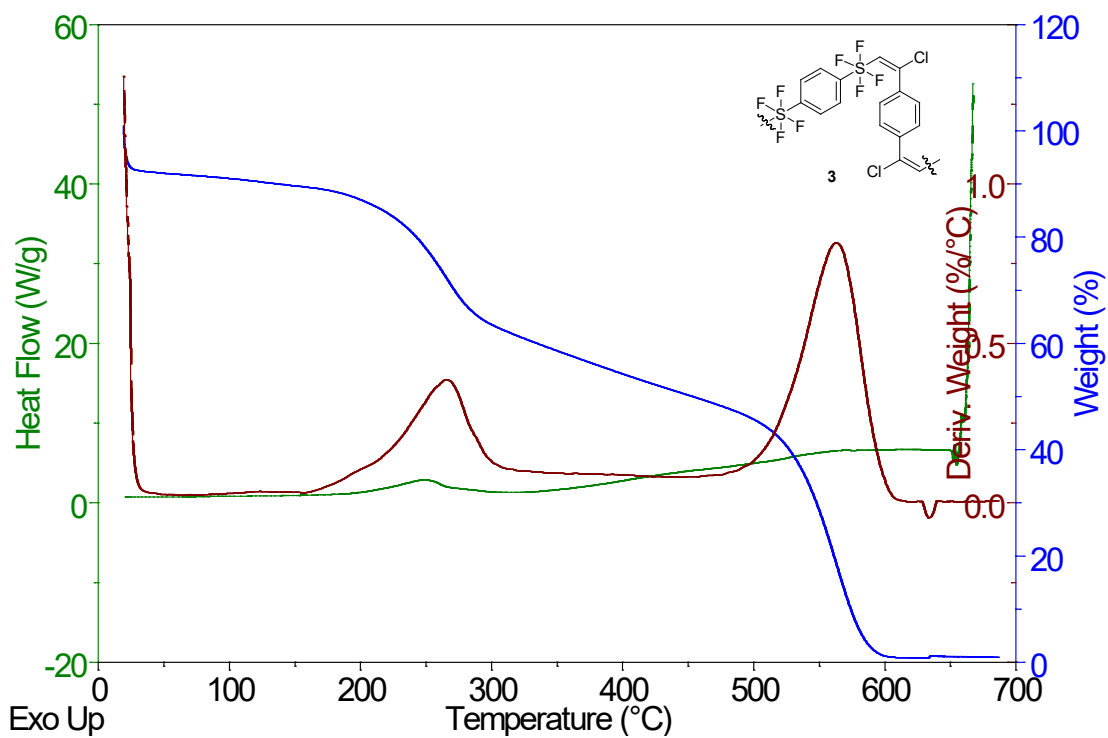


Figure S14. TGA and DSC of polymer 3.

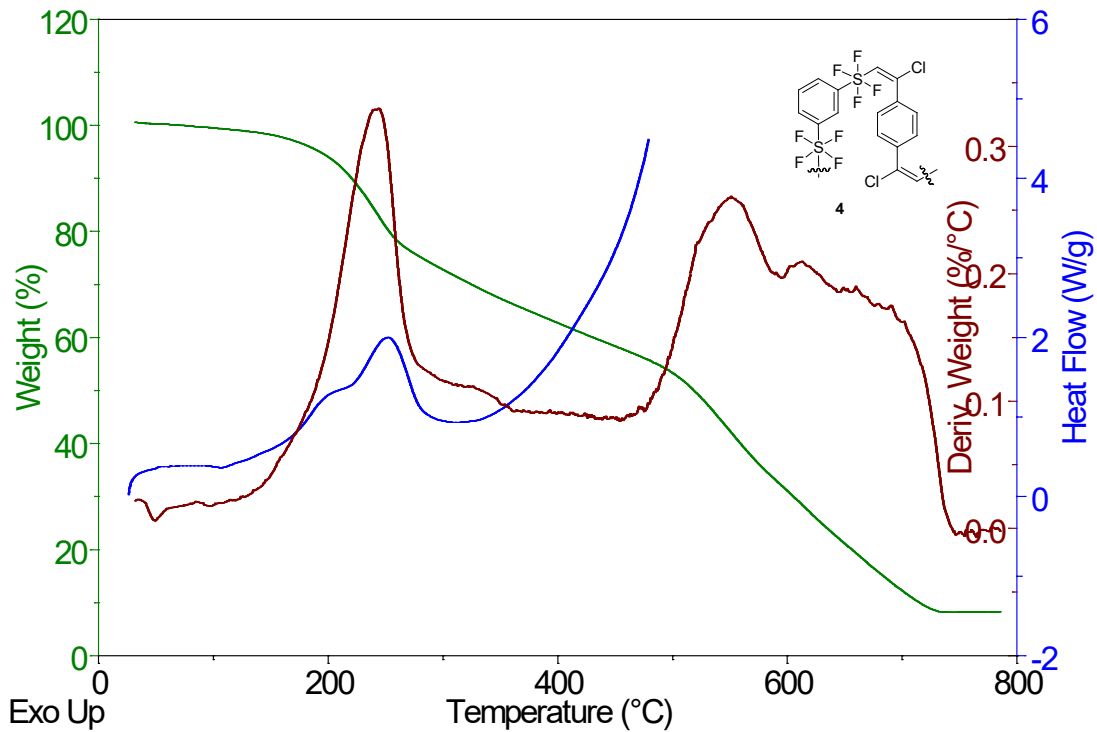


Figure S15. TGA and DSC of polymer 4.

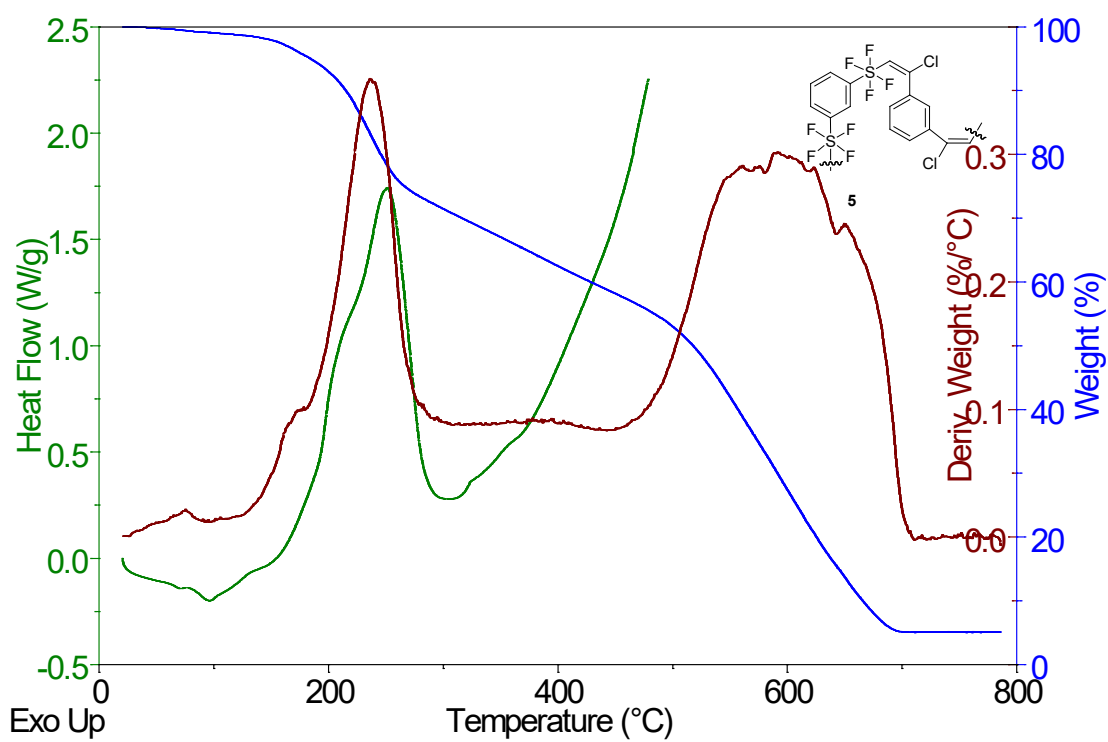
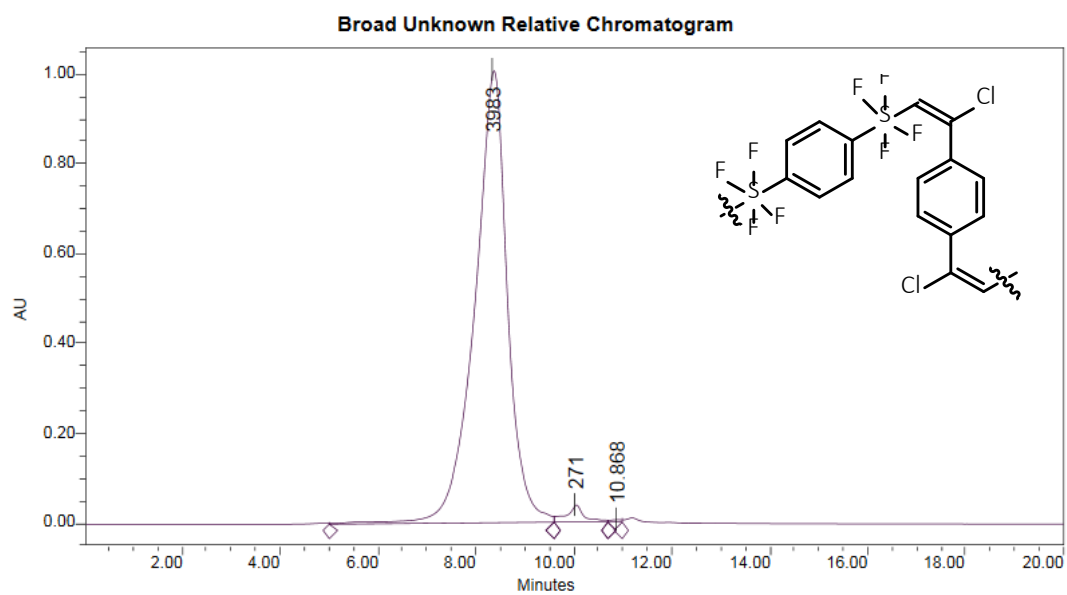


Figure S16. TGA and DSC of polymer **5**.

Gel Permeation Chromatography

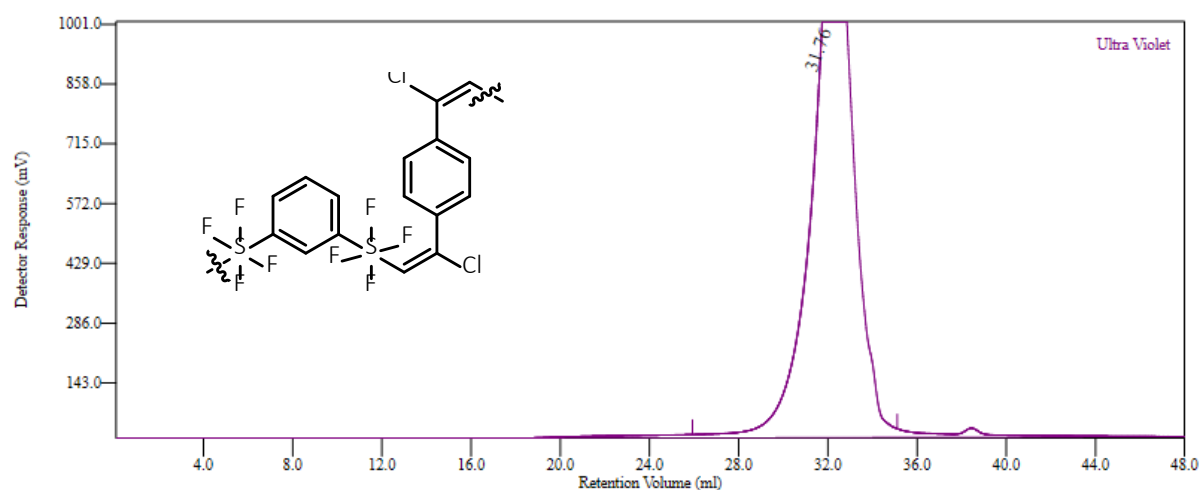
Figure S17. GPC data for **3**



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		3758	5833	3983	10720	22683	1.552072	1.837888	3.889080
2				271					

Figure S18. GPC data for **4**.



Warning: No flow rate marker was found.

Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	31.760
Mn - (Daltons)	1,801
Mw - (Daltons)	4,310
Mz - (Daltons)	18,926
Mp - (Daltons)	3,716
Mw / Mn	2.393
Percent Above Mw:	0
Percent Below Mw:	0
Mw 10.0% Low	617
Mw 10.0% High	18,542
RI Area - (mVml)	0.00
UV Area - (mVml)	2541.11

Annotation	
Method File	cc-0002.vcm
Limits File	49:54_13_MONOMER_14_DEB_01-cc-0002-0000.lim
Date Acquired	Nov 16, 2018 - 15:49:34
Solvent	THF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	GAHcd
System	System 1
Flow Rate - (ml/min)	0.800
Inj Volume - (ul)	100.0
Volume Increment - (ml)	0.00267
Detector Temp. - (deg C)	30.0
Column Temp. - (deg C)	30.0
OmniSEC Build Number	210

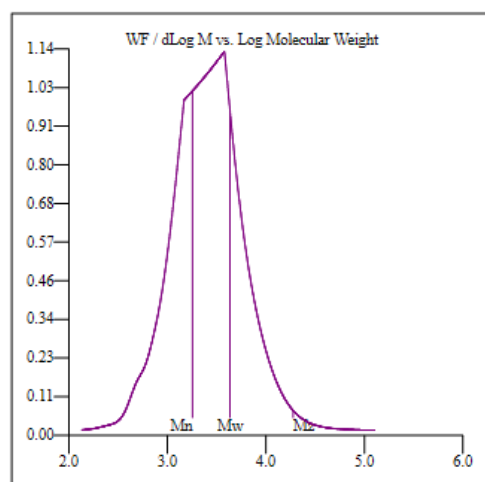
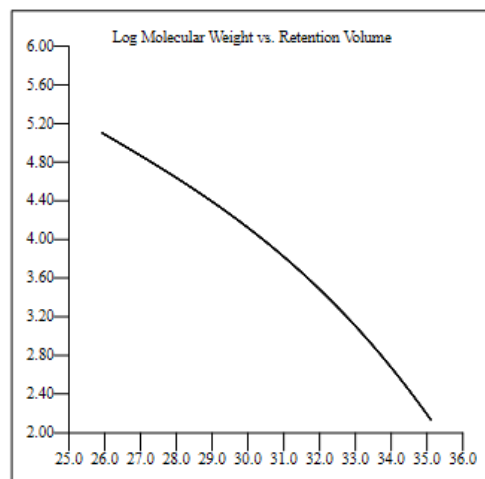
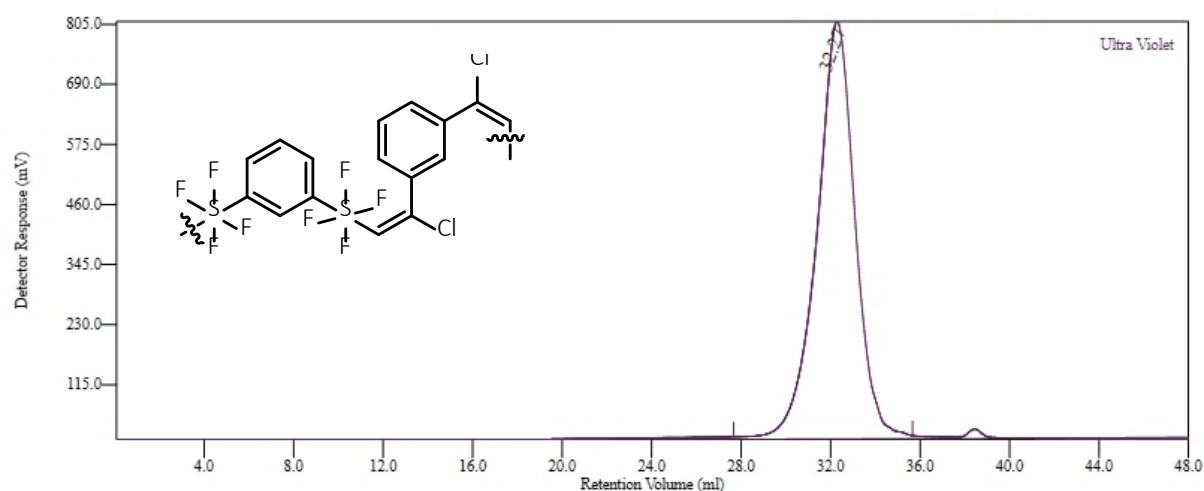


Figure S19. GPC data for **5**.



Warning: No flow rate marker was found.

Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	32.275
Mn - (Daltons)	1,753
Mw - (Daltons)	3,402
Mz - (Daltons)	7,085
Mp - (Daltons)	2,429
Mw / Mn	1.940
Percent Above Mw:	0
Percent Below Mw:	0
Mw 10.0% Low	652
Mw 10.0% High	10,891
RI Area - (mVml)	0.00
UV Area - (mVml)	1587.45

Annotation	
Method File	cc-0002.vcm
Limits File	48:58 13 MONOMER 13 DEB 01-cc-0002-0001.lim
Date Acquired	Nov 16, 2018 - 14:48:58
Solvent	THF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	GMHxL
System	System 1
Flow Rate - (ml/min)	0.800
Inj Volume - (ul)	100.0
Volume Increment - (ml)	0.00267
Detector Temp. - (deg C)	30.0
Column Temp. - (deg C)	30.0
OmniSEC Build Number	210

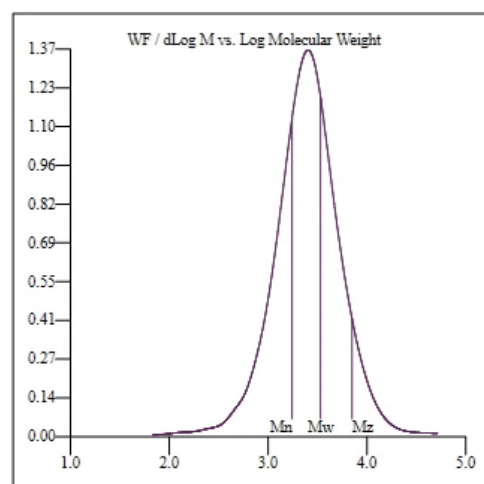
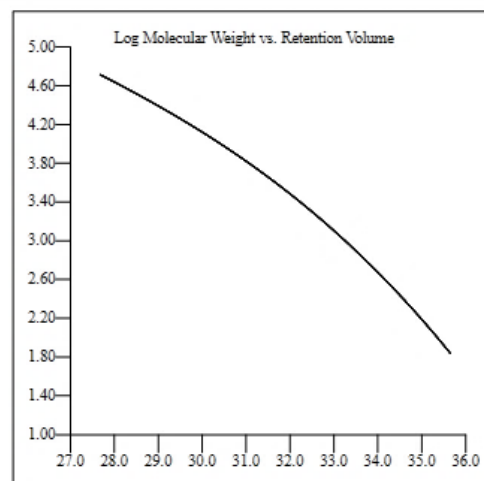
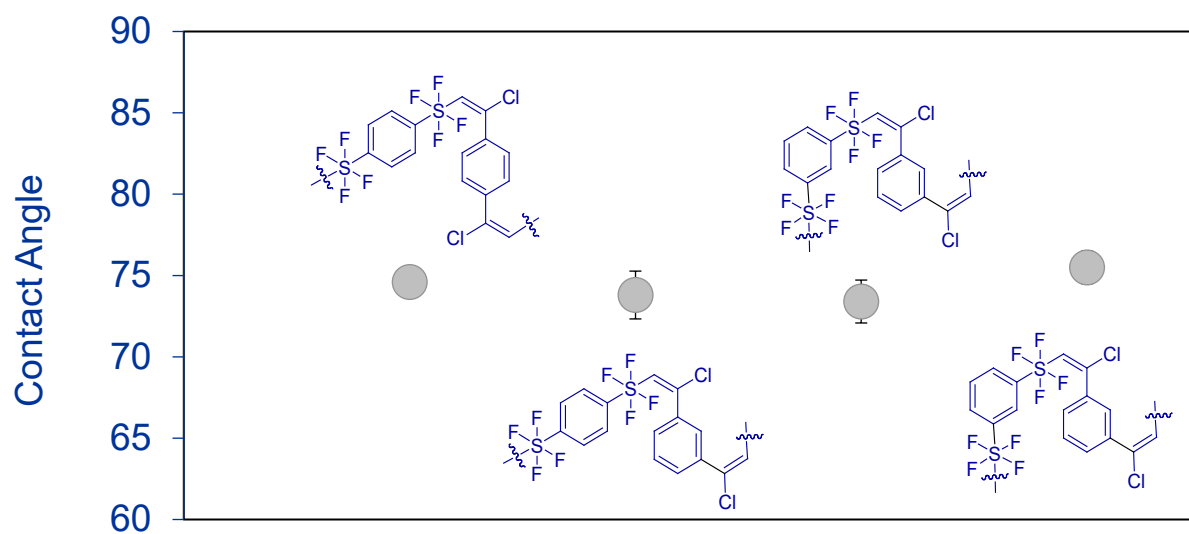
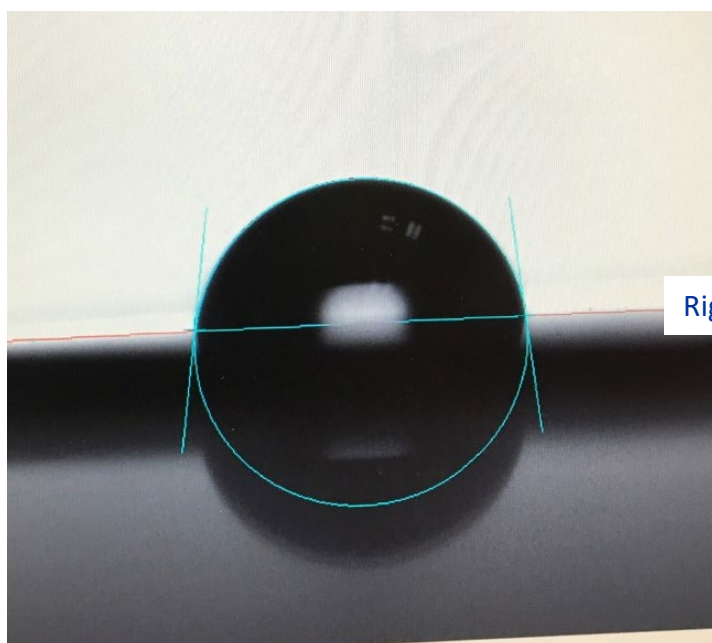


Figure S20. Water contact angles for **3,4** and **5**..



	Contact Angle
1414	74.6±0.49 °
1413	73.8±1.5 °
1313	73.4±1.3 °
1314	75.5±1.0 °



Right and left contact angle of the same water spot.

References

1. Bonetti, K.A.; Murphy, M.; Brainard, R.L.; Zhong, L.; Welch, J.T. Photosensitive Hypervalent Fluorinated Sulfur Containing Polymers for Light Sensitive Applications. *J. Polym. Sci. (Hoboken, NJ, U. S.)* **2020**, *58*, 787-791, doi:10.1002/pol.20190104.