RAFT Polymerization of Trifluoroethylene: The importance of understanding reverse additions.

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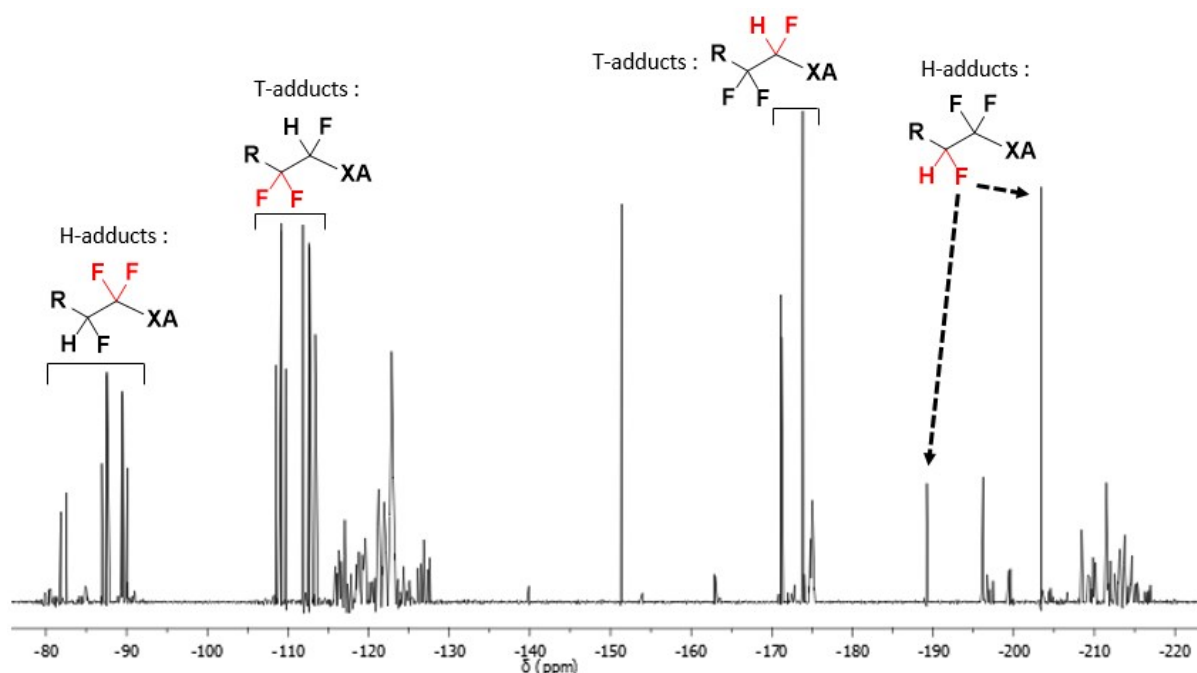
Supplementary Information

Figure S1. $^{19}F\{^1H\}$ NMR spectrum of PTrFE (yield = 4.3%) made by RAFT (Entry 1, Table 1) recorded in acetone-d6.

Equation S1 to S3 :

$$CFH\text{-}XA\ (\%) = \frac{\displaystyle\int_{-170}^{-176} CFH}{\displaystyle\int_{-244}^{-245.5} CFH + \ 1/2 \int_{-130.3}^{-135.3} CF2H + \int_{-170}^{-176} CFH2 + 1/2 \int_{-81.5}^{-91.5} CF2-XA} * 100 \quad (1)$$

$$CF_2\text{-}XA\ (\%) = \tfrac{1}{2}* \frac{\displaystyle\int_{-81.5}^{-91.5} CF2-XA}{\displaystyle\int_{-244}^{-245.5} CFH + \ 1/2 \int_{-130.3}^{-135.3} CF2H + \int_{-170}^{-176} CFH2 + 1/2 \int_{-81.5}^{-91.5} CF2-XA} * 100 \quad (2)$$

$$\text{Irreversible transfer (\%)} = \frac{\frac{1}{2}\int_{-130.3}^{-135.3} CF2H + \int_{-170}^{-176} CFH2}{\int_{-244}^{-245.5} CFH + \frac{1}{2}\int_{-130.3}^{-135.3} CF2H + \int_{-170}^{-176} CFH2 + \frac{1}{2}\int_{-81.5}^{-91.5} CF2-XA} * 100 \tag{3}$$

Table S1. Chain end functionality for DP 50 with and without considering H-adducts in CFH- percentage

Time (h)	Conversion (%)	with T-adducts (%)			without T-adducts (%)		
		CF_2-XA	CFH-XA	Transfer	CF_2-XA	CFH-XA	Transfer
2	4.7	45.5	54.5	0	56.8	43.2	0
4	13.3	3.4	94.5	2.1	4.6	92.5	2.9
6	40.7	0	80.1	19.9	0	77	23
15	56.7	0	56.3	43.7	0	50.5	49.5

Table S2. Chain end functionality for DP 100 with and without considering H-adducts in CFH- percentage

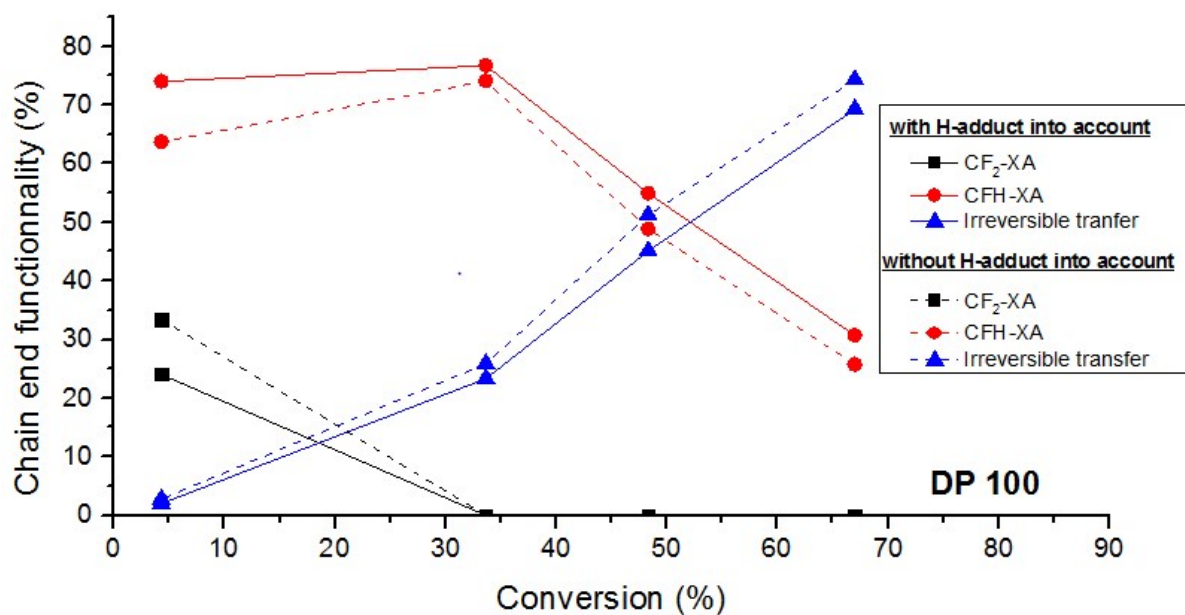| Time (h)	Conversion (%)	with T-adduct (%)			without T-adduct (%)		
		CF_2-XA	CFH-XA	Transfer	CF_2-XA	CFH-XA	Transfer
2	4.3	24	74	2	33.4	63.7	2.8
4	33.6	0	76.7	23.3	0	74.1	25.9
8	48.3	0	54.9	45.1	0	48.8	51.2
15	67	0	30.7	69.3	0	25.7	74.3

Figure S2. Comparison of the chain end functionalities of DP100 with and without taking T-adducts into account in the calculations of -CFH-XA percentage
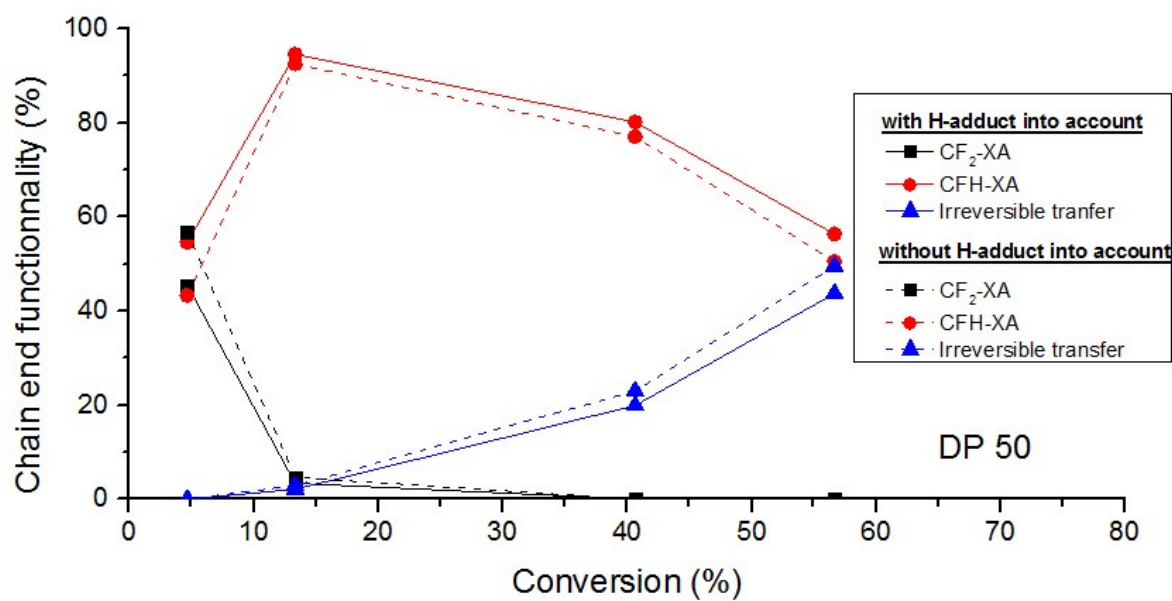

Figure S3. Comparison of the chain end functionality of DP50 with and with taking T-adducts into account in the calculations of -CFH-XA percentage

At 25°C

At 70°C

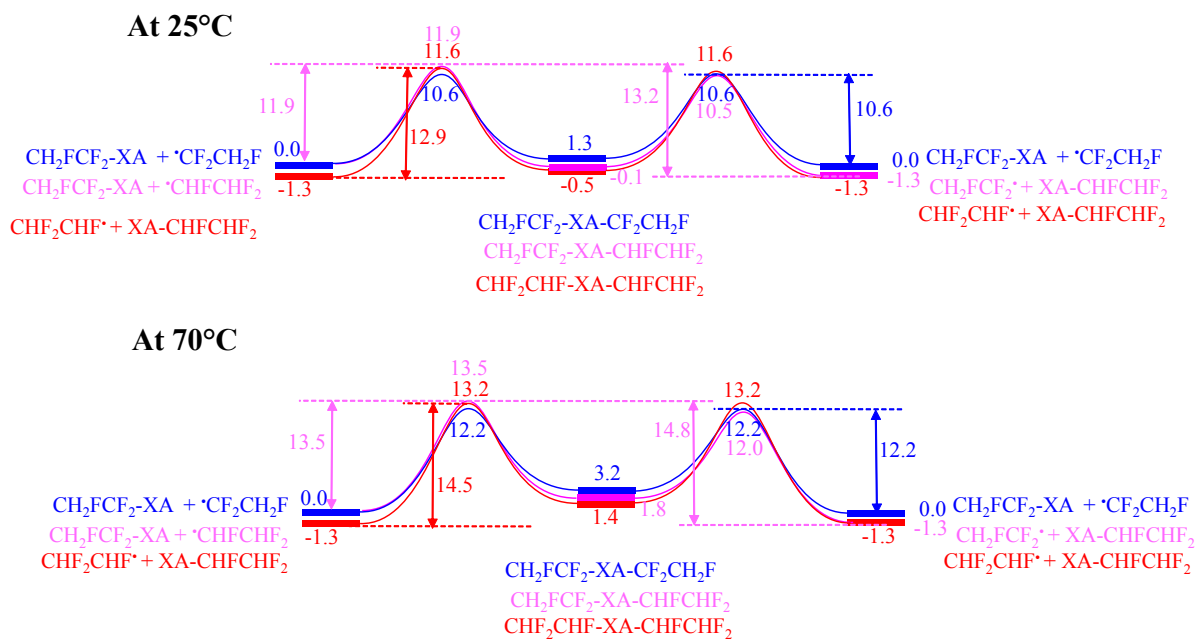*Figure S4. Comparison of the energy profiles (ΔG in kcal/mol) for the degenerative (H/H and T/T) and nondegenerative (H/T) radical exchange for the PTrFE radical and CTA models at 298.15 and 343.15 K.*

At 25°C   **At 70°C**

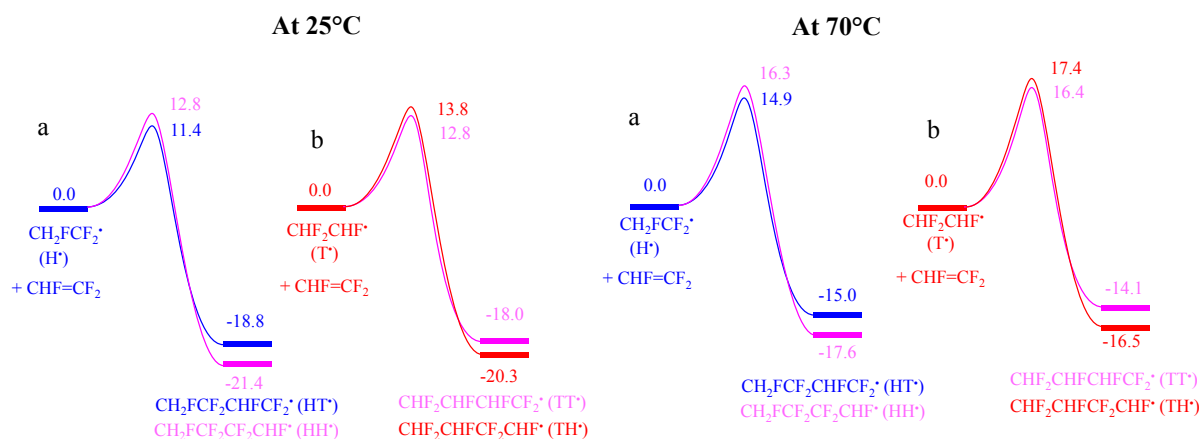*Figure S5. Comparison of the energy profiles (ΔG in kcal/mol) for the four possible TrFE homopropagation modes at 298.15 and 343.15 K.*
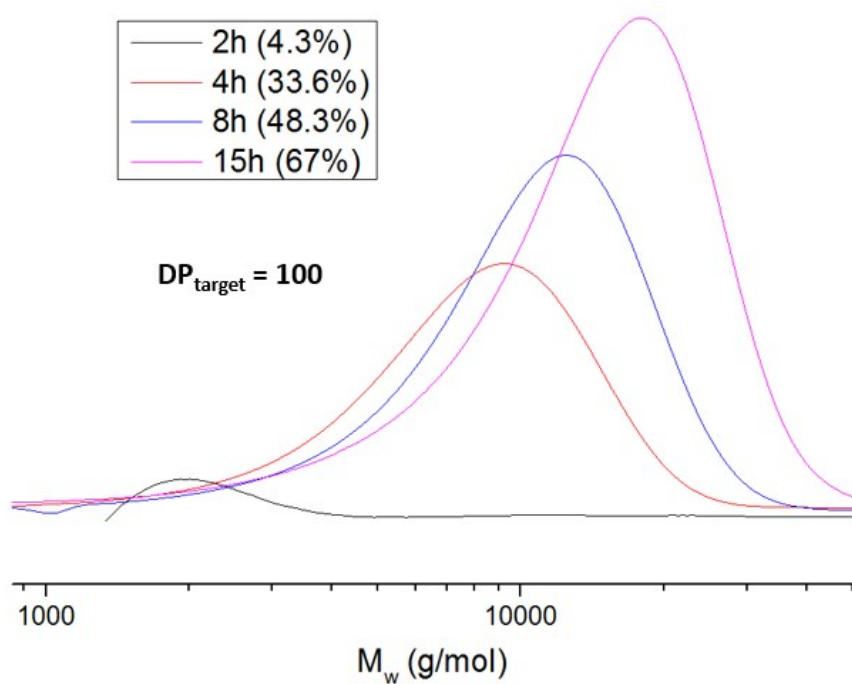
Figure S6. Evolution of the GPC traces with conversion for the RAFT polymerisation of TrFE (DPtarget = 100).
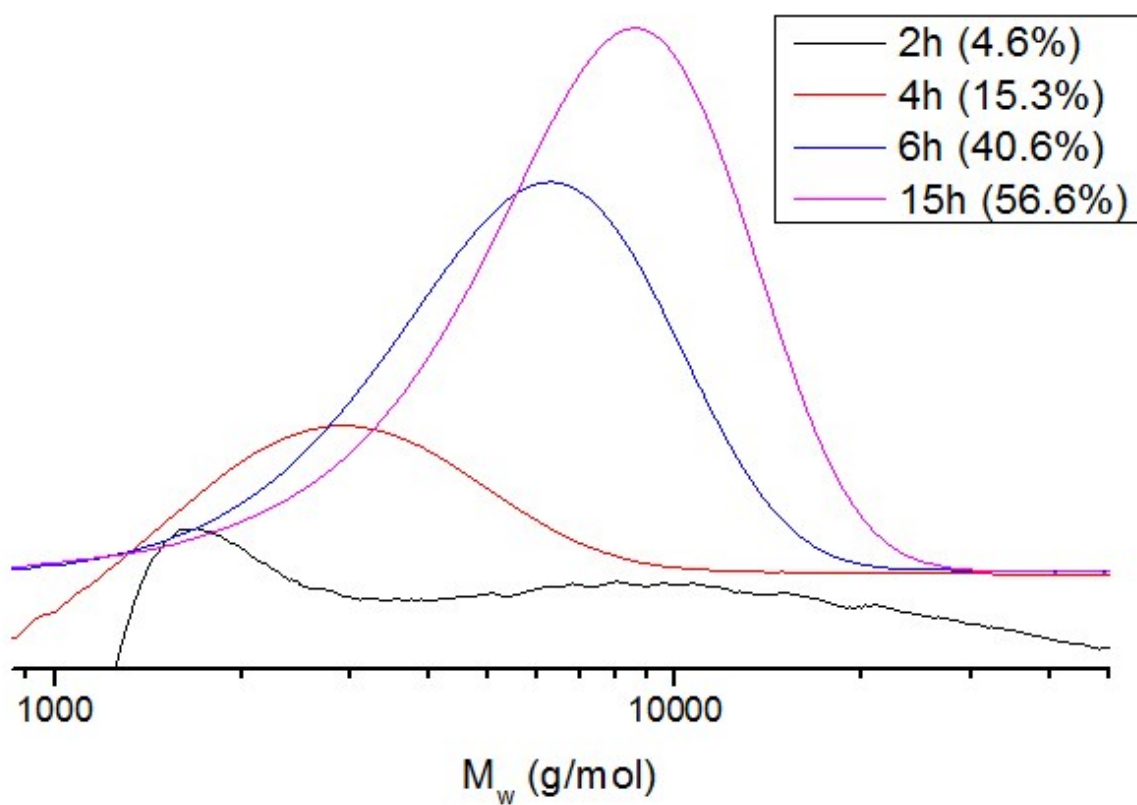
Figure S7. Evolution of the GPC traces with conversion for the RAFT polymerisation of TrFE (DPtarget = 50). TrFE conversion is indicated in brackets.
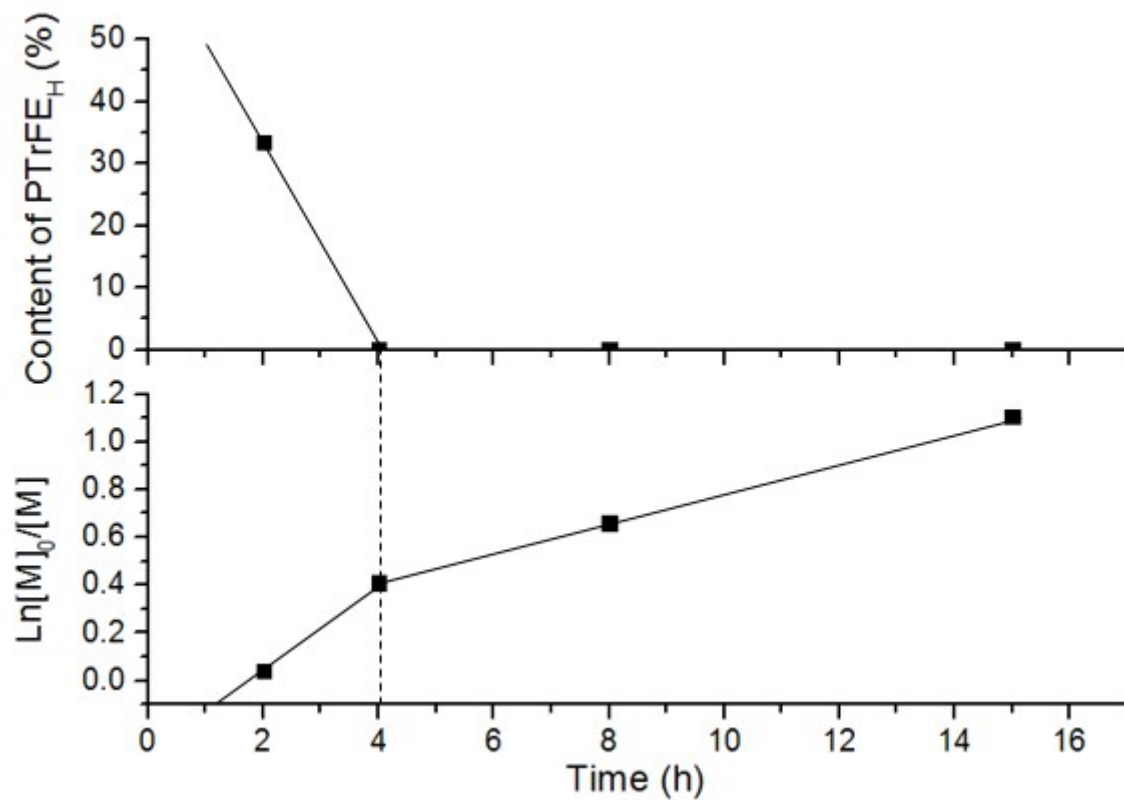
Figure S8. Correlation between the evolution vs time of the proportion of PTrFE_H-XA chains top) and the corresponding first-order kinetic plot (bottom) for TrFE RAFT polymerisation. DPtarget = 100
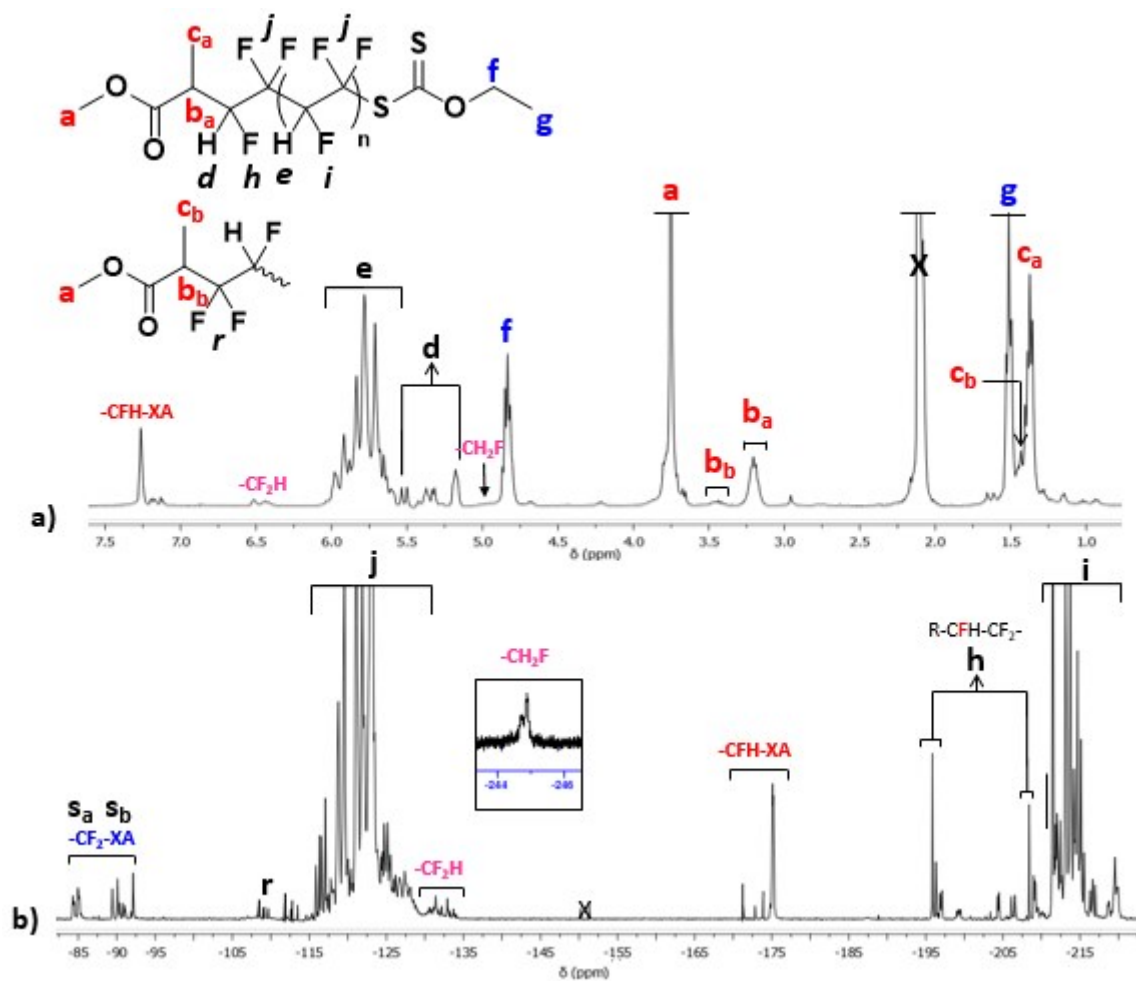
Figure S9. a) $^1H\{^{19}F\}\{^{13}C\}$ and b) $^{19}F\{^1H\}\{^{13}C\}$ NMR spectra in acetone-d_6 of PTrFE made by RAFT (Entry 4, Table 1).
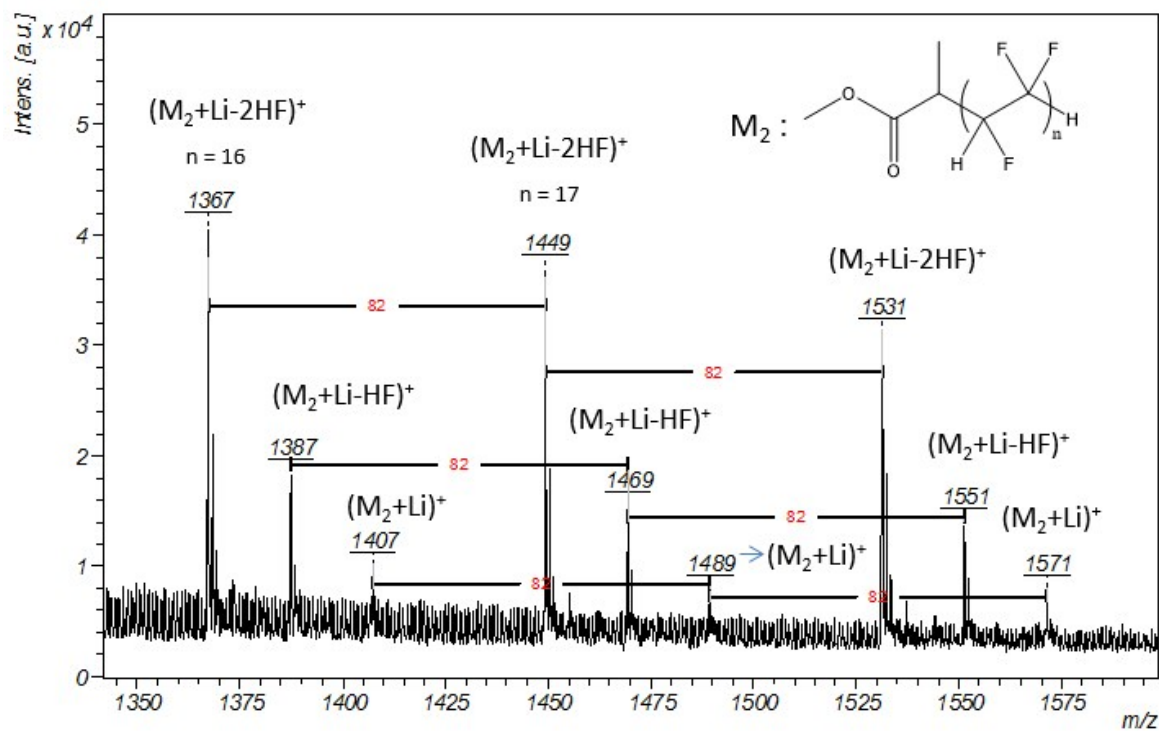
Figure S10. MALDI-TOF mass spectrum of PTrFE prepared by RAFT polymerisation in positive ion mode (Entry 11, Table 1). Reaction conditions: [M]0:[CTA]0:[I]0 = 100:1:0.2, reaction time = 15h at 73°C, conversion = 67%.

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Table S3. Energies (hartrees), views and Cartesian coordinates of all optimized geometries

A. Monomer and radicals

CHF=CF$_2$ (TrFE)

E = -375.95420183
G(298K,1M) = -375.949636

6	0.000000000	0.434876000	0.000000000
6	-0.700700000	-0.694241000	0.000000000
1	-1.783820000	-0.714613000	0.000000000
9	-0.569891000	1.628873000	0.000000000
9	1.317177000	0.508113000	0.000000000
9	-0.081951000	-1.884674000	0.000000000

H-CHFCF$_2$• (head radical)

E = -376.533111838
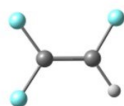G(298K,1M) = -376.519101

6	-0.553867000	-0.000143000	0.374307000
6	0.910090000	-0.000932000	0.619183000
1	1.173997000	0.893390000	1.195975000
1	1.172983000	-0.897239000	1.193377000
9	1.639360000	0.000477000	-0.568893000
9	-1.069194000	-1.097689000	-0.179943000
9	-1.068424000	1.098357000	-0.178974000

H-CF$_2$CHF• (tail radical)

E = -376.531949464
G(298K,1M) = -376.519132
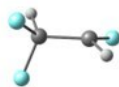
6	0.816217000	-0.457615000	-0.329519000
6	-0.436246000	0.005025000	0.310202000
1	0.863603000	-0.801253000	-1.359893000
1	-0.329183000	0.106041000	1.399395000
9	-0.839576000	1.223963000	-0.184535000
9	-1.422259000	-0.891573000	0.023719000
9	1.949142000	0.046583000	0.169305000

**B. Chain transfer agents
(dormant chain models)**

MeOC(S)S-CF$_2$CHF-H (head)

E = -1325.76139338
G(298K,1M) = -1325.703360

6	-1.393333000	0.408143000	0.133356000
6	-2.819137000	-0.078872000	0.361254000
16	-0.240833000	-1.034823000	0.110861000
6	1.363467000	-0.299784000	0.001358000
8	1.322212000	1.018258000	-0.132063000
6	2.566426000	1.729648000	-0.231710000
1	3.126822000	1.393227000	-1.110390000
1	3.170879000	1.566079000	0.666806000
1	-2.898447000	-0.502455000	1.369982000
9	-3.161281000	-1.022299000	-0.577345000
16	2.689426000	-1.268847000	0.056461000
1	-3.473767000	0.798655000	0.273072000
1	2.279989000	2.778422000	-0.326592000

9	-1.103226000	1.264129000	1.149120000
9	-1.320518000	1.105272000	-1.025005000

MeOC(S)S-CHFCF$_2$-H (tail)

E = -1325.76373361
G(298K,1M) = -1325.705499

6	1.162948000	0.383109000	-0.007846000
6	2.484028000	-0.138646000	-0.563582000
16	-0.024364000	-1.005126000	0.063984000
6	-1.593997000	-0.197155000	-0.042686000
8	-1.490281000	1.128225000	-0.102190000
6	-2.699923000	1.901768000	-0.174151000
1	-3.319999000	1.714985000	0.708709000
1	-3.265687000	1.641111000	-1.074872000
1	2.372378000	-0.505674000	-1.594661000
9	2.956609000	-1.147434000	0.216329000
16	-2.969104000	-1.093918000	-0.047064000
1	-2.365948000	2.940396000	-0.205796000
1	0.764167000	1.154525000	-0.676906000
9	1.381313000	0.927889000	1.230805000
9	3.385910000	0.877224000	-0.544921000

C. Propagation

C1. Head-to-tail

H-CHFCF$_2$•···CHFCF$_2$ TS

E = -752.483480424
G(298K,1M) = -752.450603

1	-2.873530000	-0.886997000	0.748148000
9	-1.937374000	-1.360159000	-0.982694000
6	-1.852564000	-0.959711000	0.340340000
1	-1.283257000	-1.699556000	0.915522000
6	-1.144834000	0.359499000	0.418084000
6	0.790640000	0.140260000	-0.913107000
6	1.753272000	-0.343169000	-0.098163000
9	2.591954000	0.397843000	0.596533000
9	-1.833901000	1.390284000	-0.082742000
9	-0.729085000	0.641539000	1.664131000
1	0.212155000	-0.516321000	-1.553184000
9	0.836296000	1.436689000	-1.266154000
9	1.812727000	-1.626017000	0.227214000

H-CHFCF$_2$-CHFCF$_2$•

E = -752.537601103
G(298K,1M) = -752.498657

1	2.807695000	0.931988000	-0.298200000
9	2.556695000	-0.985044000	0.309429000
6	2.143623000	0.072413000	-0.458503000
1	2.159616000	-0.203763000	-1.520996000
6	0.740369000	0.518112000	-0.061653000
6	-0.391627000	-0.444270000	-0.439156000
6	-1.692899000	-0.119894000	0.251003000
9	-2.682947000	-0.951271000	-0.069317000
9	0.717515000	0.766024000	1.274005000

9

9	0.504401000	1.697345000	-0.718303000
1	-0.520575000	-0.395211000	-1.534553000
9	-0.044111000	-1.731993000	-0.099998000
9	-2.078612000	1.150364000	0.149028000

9	-1.483321000	-0.135122000	1.478750000
9	2.854201000	-0.001204000	0.624353000

C2. Head-to-head

H-CHFCF₂•···CF₂CHF TS

E = -752.481566263
G(298K,1M) = -752.448419
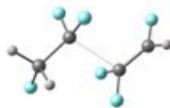
1	-2.985877000	0.609654000	0.165616000
9	-2.175850000	-1.105518000	-0.538216000
6	-2.107316000	-0.038074000	0.326179000
1	-2.105719000	-0.389732000	1.364517000
6	-0.847465000	0.740396000	0.077947000
6	0.988551000	-0.737831000	0.184442000
6	2.012349000	0.096590000	0.473680000
9	2.644537000	0.741029000	-0.513047000
1	2.248296000	0.410163000	1.483484000
9	-0.764176000	1.294173000	-1.133433000
9	-0.631301000	1.664521000	1.027510000
9	0.443690000	-1.487782000	1.141864000
9	0.768278000	-1.217153000	-1.027690000

H-CF₂CHF•···CF₂CHF

H-CHFCF₂-CF₂CHF•

E = -752.540618784
G(298K,1M) = -752.502894

1	-2.799598000	0.661504000	0.209365000
9	-2.221340000	-1.223340000	-0.275006000
6	-1.991053000	-0.054433000	0.407181000
1	-1.925212000	-0.252957000	1.482456000
6	-0.694498000	0.583749000	-0.063570000
6	0.588560000	-0.241920000	0.163207000
6	1.816835000	0.541614000	-0.115057000
9	2.928684000	-0.165992000	-0.296206000
1	1.947587000	1.578757000	0.172860000
9	-0.770683000	0.885464000	-1.383945000
9	-0.553586000	1.757527000	0.631238000
9	0.553688000	-0.678904000	1.474979000
9	0.558588000	-1.348239000	-0.619421000

C3. Tail-to-head

H-CF₂CHF•···CF₂CHF TS

E = -752.480316546
G(298K,1M) = -752.446792
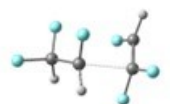
9	1.449017000	1.186272000	-0.586589000
6	1.523633000	0.294598000	0.439357000
1	1.147947000	0.762206000	1.359613000
6	0.746410000	-0.928206000	0.103754000
6	-1.507707000	-0.288051000	0.156822000
6	-1.590921000	0.763685000	-0.689243000
9	-1.314451000	1.989859000	-0.235956000
1	-1.697445000	0.653187000	-1.761488000
9	0.957440000	-1.405486000	-1.131329000
1	0.623628000	-1.703169000	0.860810000
9	-1.918733000	-1.497028000	-0.207348000

H-CF₂CHF-CF₂CHF•

E = -752.538031274
G(298K,1M) = -752.501074
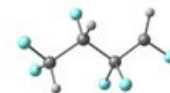
9	1.944861000	-0.446507000	1.176817000
6	1.698230000	-0.395623000	-0.152246000
1	1.539502000	-1.412026000	-0.536096000
6	0.492838000	0.501451000	-0.425571000
6	-0.831099000	-0.204810000	-0.130200000
6	-1.990949000	0.711058000	-0.186171000
9	-3.167894000	0.192973000	0.153373000
1	-2.021034000	1.635814000	-0.752932000
9	0.583783000	1.644591000	0.334461000
1	0.501553000	0.771711000	-1.490362000
9	-0.935979000	-1.219927000	-1.071557000
9	-0.794530000	-0.831880000	1.080733000
9	2.788187000	0.142089000	-0.768880000

C4. Tail-to-tail

H-CF₂CHF•···CHFCF₂ TS

E = -752.48202861
G(298K,1M) = -752.448338

9	-0.957111000	-1.395781000	0.165396000
6	-1.516203000	-0.210791000	0.548594000
1	-1.205108000	0.022529000	1.575962000
6	-1.106358000	0.870676000	-0.382634000
6	1.210077000	1.034520000	-0.003235000
6	1.765224000	-0.192765000	-0.103342000
9	1.877776000	-1.034044000	0.901775000
9	-1.254265000	0.583586000	-1.686806000
1	-1.353583000	1.901189000	-0.126531000
1	1.265405000	1.739290000	-0.825072000
9	1.025804000	1.556458000	1.229942000
9	-2.879372000	-0.392074000	0.542808000
9	2.095706000	-0.726239000	-1.262077000

H-CF₂CHF-CHFCF₂•

E = -752.536357402
G(298K,1M) = -752.497367
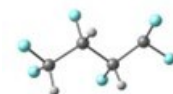
9	-2.223815000	1.088600000	0.314534000
6	-1.867061000	0.079609000	-0.512197000
1	-1.837499000	0.454567000	-1.546898000
6	-0.527383000	-0.513470000	-0.084746000
6	0.652129000	0.393551000	-0.397867000
6	1.943119000	-0.167175000	0.142490000
9	3.013904000	0.576593000	-0.120582000
9	-0.571972000	-0.781589000	1.264619000
1	-0.387920000	-1.456376000	-0.633616000
1	0.734044000	0.501244000	-1.496520000
9	0.477113000	1.649085000	0.141064000
9	-2.817166000	-0.893094000	-0.434606000
9	2.153777000	-1.445653000	-0.188257000

D. Radical exchange (chain transfer)

D1. Head-head

H-CHFCF$_2$-SC(OMe)(S)···•CF$_2$CHF-H TS

E = -1702.29268901
G(298K,1M) = -1702.205557
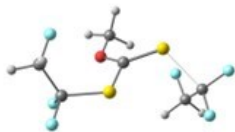
6	2.834802000	-0.618663000	0.429446000
6	3.784447000	0.168762000	-0.463316000
16	1.244800000	-1.135394000	-0.360922000
6	0.237862000	0.316251000	-0.483324000
8	0.652634000	1.330771000	0.267115000
6	-0.116062000	2.544374000	0.234473000
1	-1.132981000	2.354741000	0.590496000
1	-0.152310000	2.942903000	-0.784773000
16	-1.141993000	0.229804000	-1.386170000
1	4.667751000	0.425667000	0.137899000
1	0.415145000	3.228250000	0.898902000
1	4.079410000	-0.472580000	-1.302022000
9	3.456786000	-1.804192000	0.698837000
9	2.635384000	0.020173000	1.600702000
6	-3.172241000	-0.690567000	-0.022464000
6	-3.223764000	-0.051775000	1.333796000
1	-4.146650000	-0.351565000	1.858377000
9	-3.218724000	1.323282000	1.217982000
1	-2.356696000	-0.386132000	1.915850000
9	3.197440000	1.313843000	-0.937075000
9	-3.022355000	-2.017755000	0.056880000
9	-4.194078000	-0.380718000	-0.822863000

H-CHFCF$_2$-SC•(OMe)-S-CF$_2$CHF-H

E = -1702.31155023
G(298K,1M) = -1702.220359
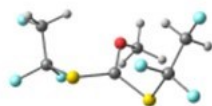
6	-2.633167000	-0.476795000	0.026144000
6	-2.958032000	0.415046000	1.208326000
16	-0.937249000	-1.226334000	0.161552000
6	0.011041000	0.047925000	-0.555193000
8	-0.238441000	1.310179000	-0.103883000
6	-0.287583000	2.328086000	-1.115432000
1	-1.109004000	2.117891000	-1.809187000
1	0.661963000	2.383782000	-1.662143000
16	1.491723000	-0.358448000	-1.382597000
6	2.702722000	-0.394897000	0.038921000
6	2.950280000	0.989145000	0.604388000
1	-2.219467000	1.223481000	1.249904000
1	-2.904584000	-0.185672000	2.125401000
1	1.992602000	1.410072000	0.935705000
1	3.377304000	1.619432000	-0.186124000
9	3.845474000	-0.922816000	-0.461681000
9	2.245810000	-1.216574000	1.013523000
9	-2.749384000	0.220991000	-1.131136000
9	-3.497307000	-1.519621000	-0.022306000
1	-0.468055000	3.266539000	-0.586290000
9	-4.226269000	0.931053000	1.054553000
9	3.825409000	0.905686000	1.664558000

D2. Head-tail

H-CHFCF$_2$-SC(OMe)(S)···•CHFCF$_2$-H TS

E = -1702.29056738
G(298K,1M) = -1702.203563
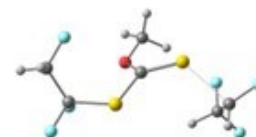
6	2.902237000	-0.722671000	0.287689000
6	3.841696000	0.350643000	-0.246423000
16	1.375545000	-1.011081000	-0.716894000
6	0.317164000	0.380518000	-0.439503000
8	0.633727000	1.099915000	0.632275000
6	-0.144611000	2.276033000	0.907519000
1	-1.186287000	2.004561000	1.101243000
1	-0.096678000	2.968548000	0.060682000
16	-1.003888000	0.562202000	-1.421745000
1	4.684286000	0.431097000	0.454381000
1	0.318388000	2.715464000	1.792767000
1	4.205047000	0.031284000	-1.230043000
9	3.575058000	-1.906372000	0.191843000
9	2.618521000	-0.510578000	1.588657000
6	-3.042236000	-0.709919000	-0.677320000
6	-3.112632000	-0.585020000	0.802992000
9	-3.257811000	0.721557000	1.171078000
1	-2.209606000	-0.997571000	1.274464000
9	3.211356000	1.563859000	-0.354634000
1	-2.790524000	-1.679634000	-1.104403000
9	-4.002604000	-0.056641000	-1.343987000
9	-4.201260000	-1.259437000	1.302731000

H-CHFCF$_2$-SC•(OMe)-S-CHFCF$_2$H

E = -1702.31410889
G(298K,1M) = -1702.222660
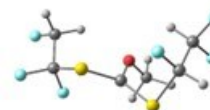
6	-2.644408000	-0.359495000	0.002720000
6	-2.870664000	0.487619000	1.239511000
16	-1.024904000	-1.273599000	0.070572000
6	0.027899000	-0.055957000	-0.597332000
8	-0.054694000	1.173289000	-0.015089000
6	0.197936000	2.297258000	-0.873609000
1	-0.483881000	2.271219000	-1.731248000
1	1.239715000	2.300561000	-1.210925000
16	1.441363000	-0.562259000	-1.495765000
6	2.657342000	-0.817078000	-0.146036000
6	2.869369000	0.409275000	0.735631000
1	-2.061560000	1.223121000	1.310927000
1	-2.858032000	-0.166955000	2.120528000
1	1.960040000	0.685378000	1.283674000
1	3.605839000	-1.079526000	-0.635849000
9	2.255058000	-1.836301000	0.686576000
9	-2.701715000	0.412533000	-1.108560000
9	-3.605836000	-1.311059000	-0.091254000
1	0.002088000	3.181388000	-0.262821000
9	-4.089302000	1.123309000	1.141469000
9	3.865398000	0.129794000	1.617979000
9	3.270300000	1.459780000	-0.036854000

H-CHFCF$_2$•···(S)C(OMe)S-CHFCF$_2$-H TS

E = -1702.29310613
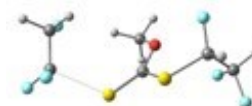
G(298K,1M) = -1702.205814

6	2.698639000	-0.550637000	0.962757000
6	3.709771000	-0.009607000	-0.049739000
16	1.165191000	-1.235609000	0.247416000
6	0.238618000	0.134785000	-0.389837000
8	0.630317000	1.312032000	0.086845000
6	-0.067178000	2.482962000	-0.367434000
1	-1.122227000	2.426676000	-0.083875000
1	0.015069000	2.575530000	-1.455530000
16	-1.062015000	-0.175896000	-1.356726000
1	4.545202000	0.471788000	0.480059000
1	0.432074000	3.316003000	0.130871000
1	3.160450000	-1.433565000	1.428957000
9	2.481596000	0.403849000	1.924148000
6	-3.223013000	-0.671312000	0.059338000
6	-3.356036000	0.355891000	1.143729000
1	-4.317486000	0.230056000	1.669776000
9	-3.318712000	1.626556000	0.607601000
1	-2.536150000	0.222550000	1.859558000
9	3.166582000	0.885201000	-0.906325000
9	-3.092417000	-1.907763000	0.553572000
9	-4.184004000	-0.634167000	-0.865381000
9	4.183057000	-1.059643000	-0.772336000

D3. Tal-tail

H-CF$_2$CHF-SC(OMe)(S)···$^•$CHFCF$_2$-H TS

E = -1702.29102577
G(298K,1M) = -1702.204080

6	2.749811000	0.076306000	1.145736000
6	3.760533000	0.096171000	-0.002931000
16	1.284510000	-0.978193000	0.874121000
6	0.313020000	-0.188789000	-0.380147000
8	0.605242000	1.096657000	-0.555423000
6	-0.108096000	1.814723000	-1.574882000
1	-1.176523000	1.840016000	-1.342362000
1	0.044762000	1.340421000	-2.549952000
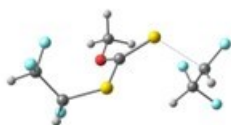
16	-0.924848000	-1.043724000	-1.071514000
1	4.549114000	0.833577000	0.208350000
1	0.320564000	2.818403000	-1.561233000
1	3.245494000	-0.415741000	1.995564000
9	2.442606000	1.367866000	1.488815000
6	-3.084150000	-0.969259000	0.239413000
6	-3.199904000	0.411736000	0.778391000
9	-3.305074000	1.318248000	-0.236557000
1	-2.330388000	0.662748000	1.401932000
9	3.193648000	0.396338000	-1.193827000
1	-2.866889000	-1.781291000	0.931695000
9	-3.980117000	-1.284866000	-0.703975000
9	4.316304000	-1.141084000	-0.093992000
9	-4.330692000	0.547269000	1.548891000

H-CF$_2$CHF-SC$^•$(OMe)S-CHFCF$_2$-H

E = -1702.31527463
G(298K,1M) = -1702.223374

6	-2.616336000	-0.323361000	-0.574500000
6	-2.932791000	-0.175191000	0.911216000
16	-0.986327000	-1.098875000	-0.914037000
6	0.045923000	0.293371000	-0.721355000
8	-0.168913000	1.039498000	0.399177000
6	0.058915000	2.451232000	0.262796000
1	-0.566683000	2.852047000	-0.542889000
1	1.116787000	2.655141000	0.066248000
16	1.566087000	0.334839000	-1.583814000
6	2.665615000	-0.588236000	-0.441972000
6	2.699545000	-0.021405000	0.973801000
1	-2.212510000	0.461868000	1.435805000
1	1.726502000	-0.100842000	1.474158000
1	3.673381000	-0.532833000	-0.877857000
9	2.267467000	-1.900782000	-0.333332000
9	-2.696166000	0.918976000	-1.152496000
1	-3.364734000	-0.996237000	-1.016338000
1	-0.231244000	2.889584000	1.220404000
9	-4.180528000	0.359754000	1.021030000
9	3.633065000	-0.709652000	1.683804000
9	3.081421000	1.287406000	0.928504000
9	-2.948769000	-1.415547000	1.469463000

Table S4 GPC results of the sample used for DSC and DRX measurements.

Sample	Mn$_{GPC}$ (g/mol)	Mw$_{GPC}$ (g/mol)	Đ
PTrFE	5700	24000	4.30
PTrFE-XA	5700	9000	1.58