Supporting Information for:

Synthesis of poly[oligo(hexafluoropropylene oxide) perfluoroisopropenylether (PIPE)] graft copolymers with vinylidene fluoride (VDF) using CF_3 radicals

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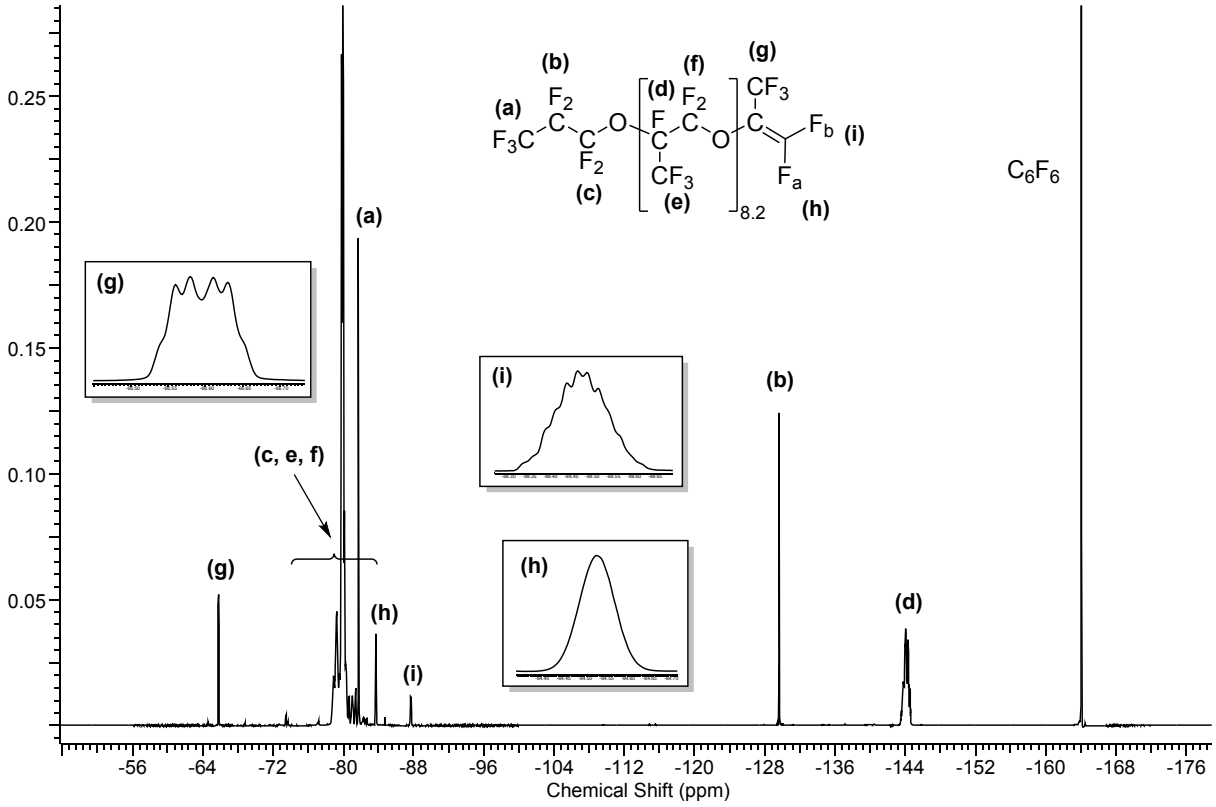

Figure S1:[19]F-NMR spectrum of oligo(hexafluoropropylene oxide) perfluoroisopropenyl ether.

δ ^{19}F NMR (376 MHz, C_6D_6, 25 ^{o}C): -66.50 (dd, -C(C**F**$_3$)=CF_aF_b, *3F*), -80 (m, -CF(C**F**$_3$*)*CF_2O-), -82.41 (s, C**F**$_3$$CF_2CF_2O$-, 3F), -84.42 (bs, -OC($CF_3$)=C**F**$_a$$F_b$, 1F), -88.40 (m, -OC($CF_3$)=$CF_a$**F**$_b$**,** 1F*),* -130.32 (s, CF_3C**F**$_2$$CF_2O$-, 2F), -144.83 (m, -C**F**(CF_3)CF_2O-, n=8.59 F)

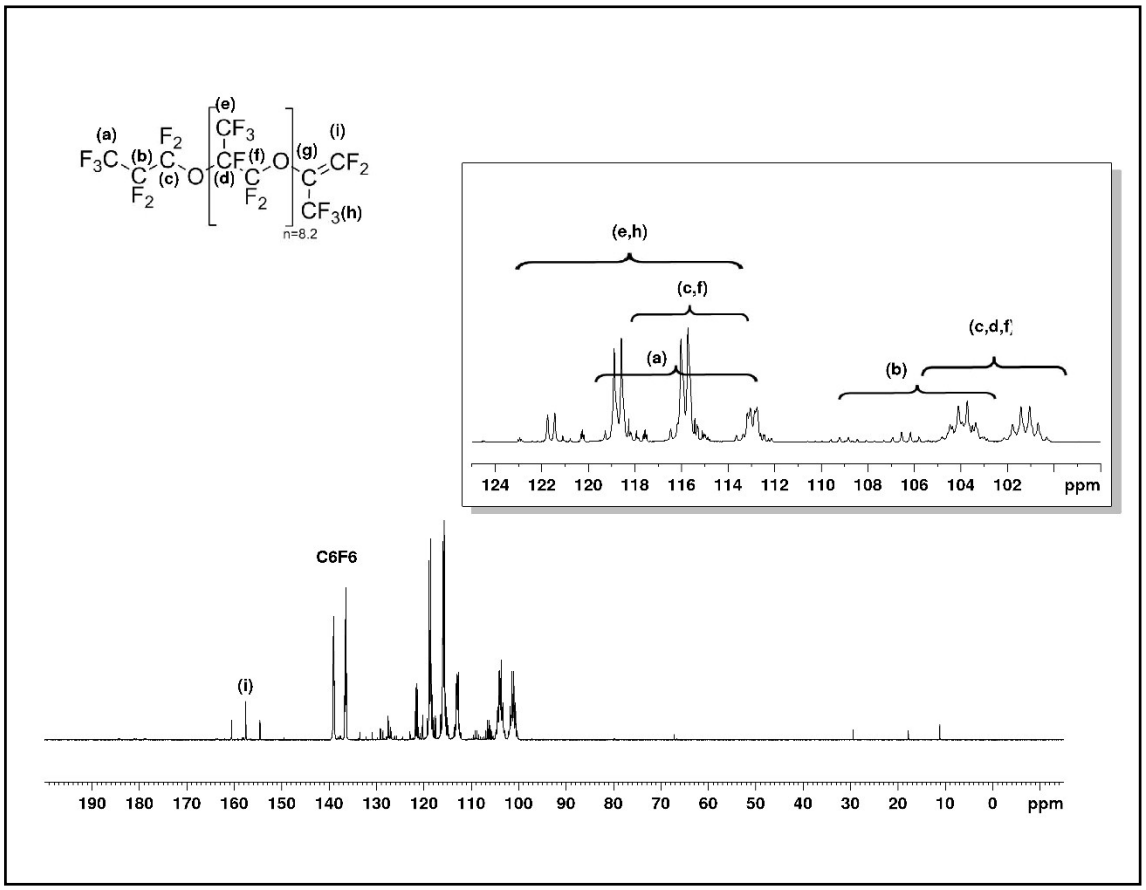

Figure S2: ^{13}C- NMR spectrum of oligo(hexafluoropropylene oxide) perfluoroisopropenyl ether.

^{13}C NMR (101 MHz, C_6D_6, 25 °C, δ): 102.52 (dsext, $^1J_{CF}$ = 265.8 Hz, $^2J_{CF}$ = 35.6 Hz, -O**C**F(CF_3)CF_2-), 106.34 (tsext, $^1J_{CF}$ = 265.37 Hz, $^2J_{CF}$ = 38.81 Hz, CF_3**C**F_2CF_2O-), 115.87 (td, $^1J_{CF}$=287.86 Hz, $^2J_{CF}$ = 30.75Hz, -CF(CF_3)**C**F_2O-), 117.73 (qd, $^1J_{CF}$ =286.13 Hz, $^2J_{CF}$ = 32.90 Hz, -CF(**C**F_3)CF_2O-), 157.57 (t, $^1J_{CF}$ = 301.45 Hz, -OC(CF_3)=**C**F_2)

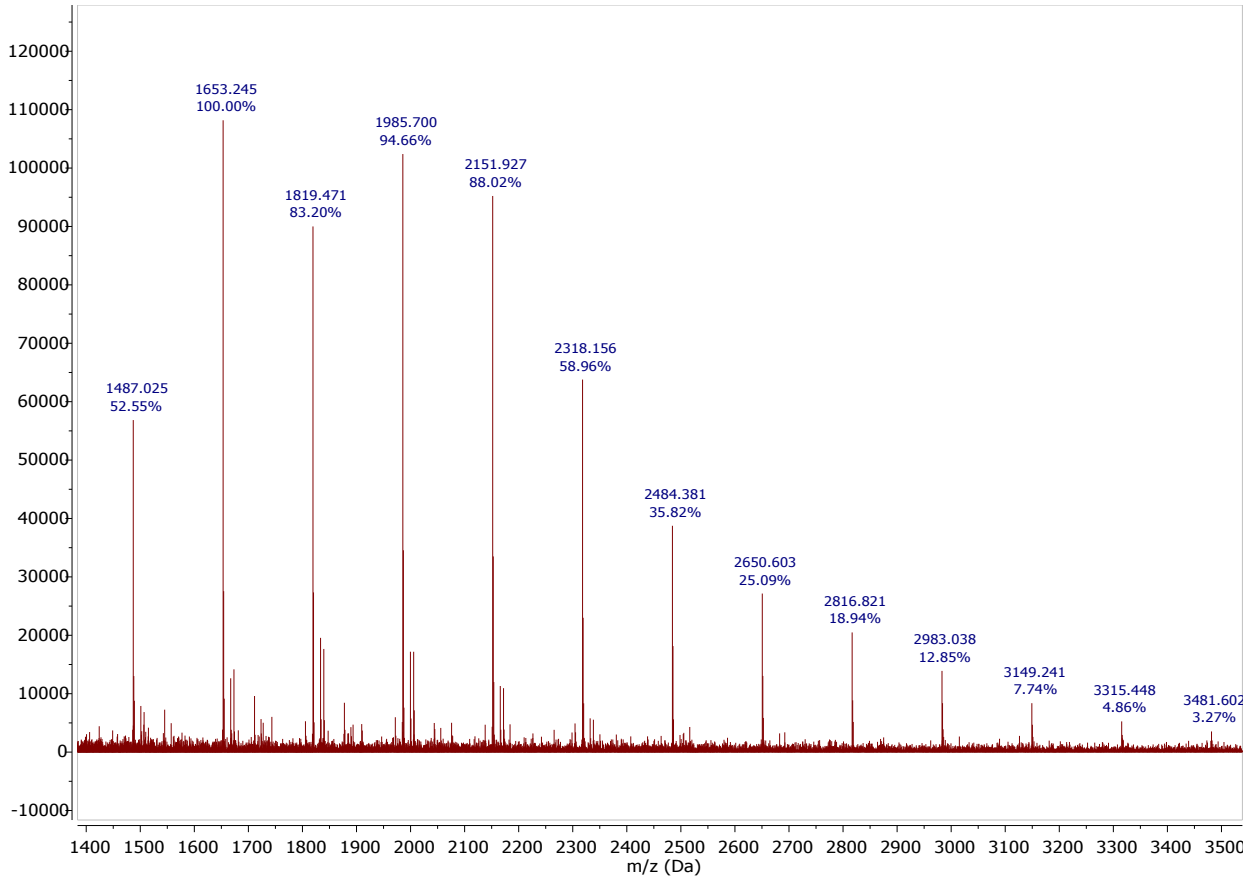

Figure S3: MALDI-TOF Spectrum of oligo(HFPO)-PIPE.

Maldi-TOF (Li+) = 1487.0, 1653.2, 1819.4, 1985.7, 2151.9, 2318.1, 2484.3, 2650.6, 2816.821, 3149.2, 3315.4, 3481.6

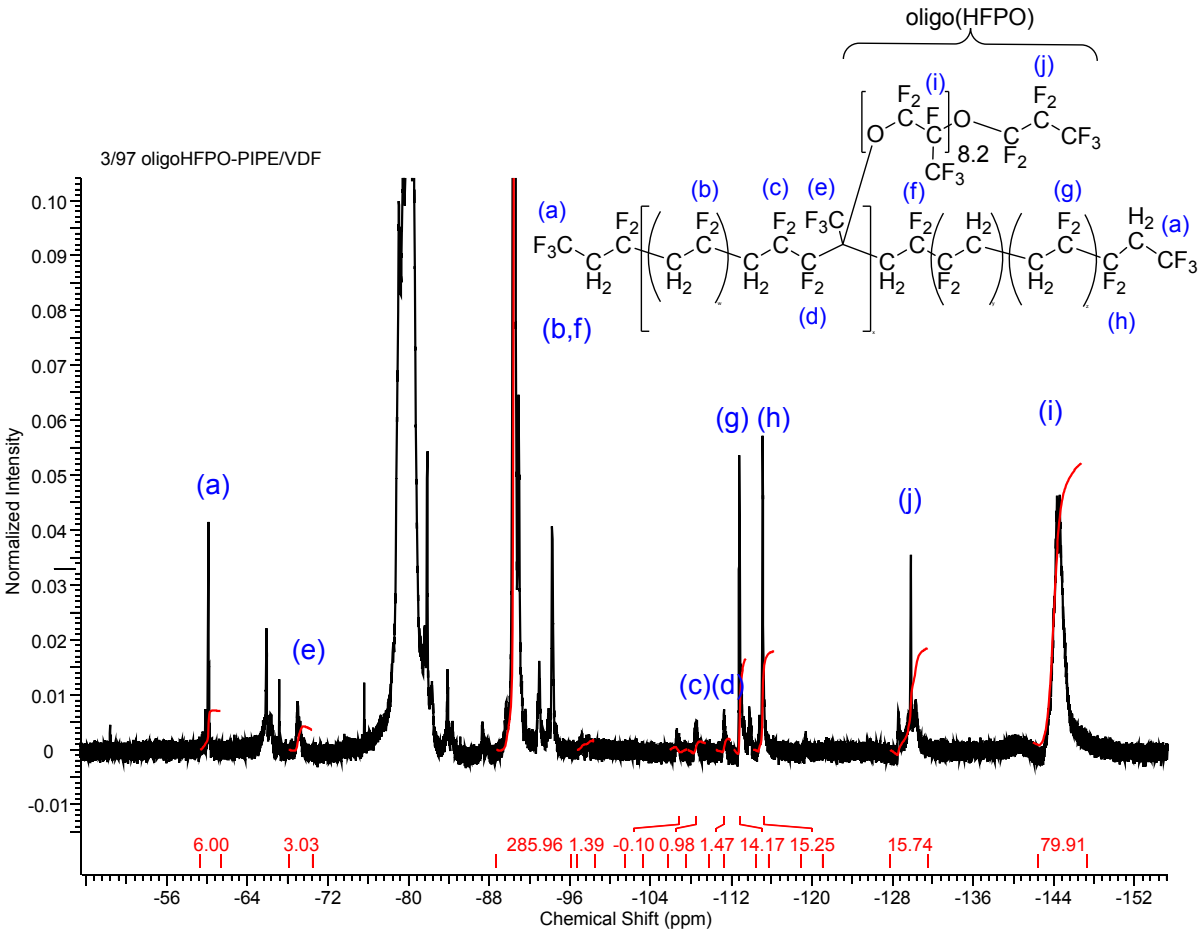

Figure S4: ^{19}F-NMR spectrum of the radical copolymerization of oligo(hexafluoropropylene oxide) perfluoroisopropenyl ether with VDF initiated by PPFR (Reaction #1).

^{19}F-NMR (376 MHz, C_6D_6 capillary/Acetone, 25 ^{o}C, δ): -61.3 ($C\underline{F}_3CH_2$- chain end), -70.2 (-$CF_2C(C\underline{F}_3)(ORf)CH_2$-, 3F) -81.6 (bs, $CF_3CF_2C\underline{F}_2O$-, 2F), -82.5 (bs, $C\underline{F}_3CF_2CF_2O$- , 3F), -79 to -84 (-[$CF(C\underline{F}_3)C\underline{F}_2O$]-),-90.3 to -95.8 (-$C\underline{F}_2$- of VDF, normal addition head-to-tail); -109.4 (-$CH_2C\underline{F}_2CF_2C(CF_3)CH_2$-, 2F), -112.3(-$CH_2CF_2C\underline{F}_2C(CF_3)CH_2$-), -113.8 and -116.0 ($CH_2$-$C\underline{F}_2$-$C\underline{F}_2$-$CH_2$ reverse addition of VDF, head to head). -130.7 (bs, $CF_3C\underline{F}_2CF_2$-, 2F), -145.8 (bm, -[$C\underline{F}(CF_3)CF_2O$]-, 7 x 1F).

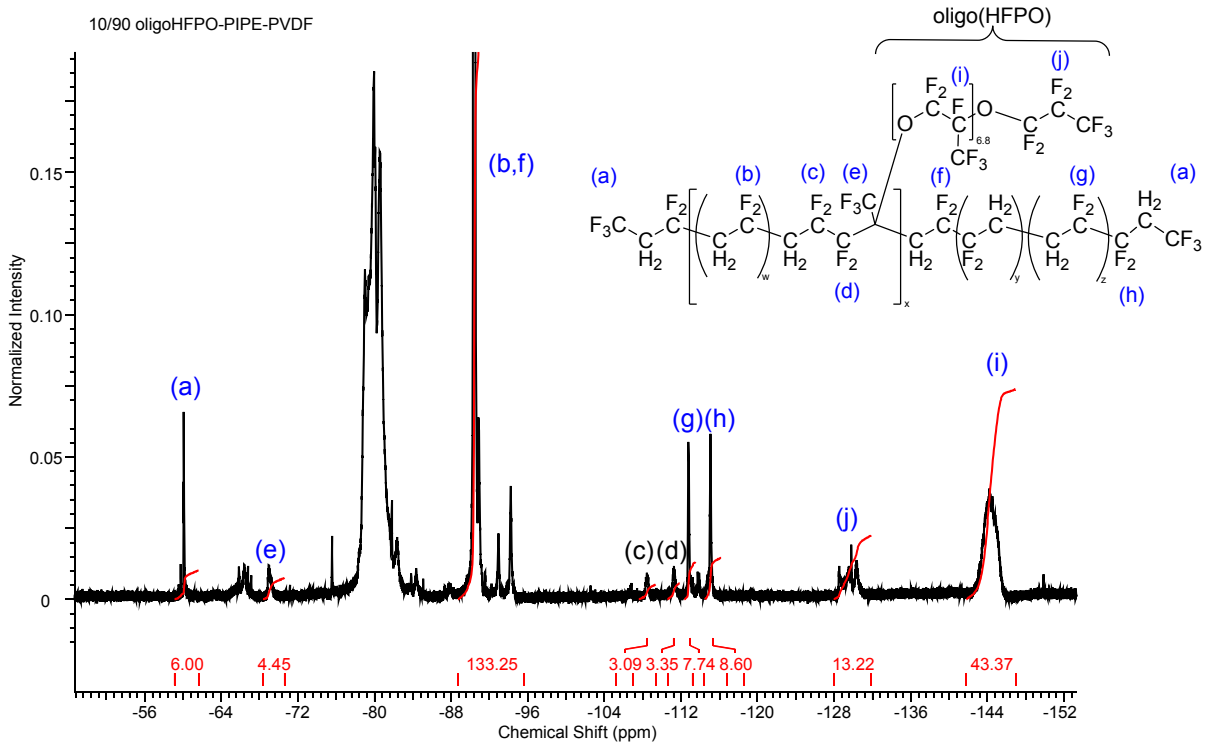

Figure S5: ^{19}F-NMR spectrum of the radical copolymerization of oligo(hexafluoropropylene oxide) perfluoroisopropenyl ether with VDF initiated by PPFR (Reaction #2).

^{19}F-NMR (376 MHz, C_6D_6 capillary/Acetone, 25 °C, δ): -61.3 ($C\underline{\mathbf{F}}_3CH_2$- chain end), -70.2 (-$CF_2C(C\underline{\mathbf{F}}_3)(ORf)CH_2$-, 3F) -81.6 (bs, $CF_3CF_2C\underline{\mathbf{F}}_2O$-, 2F), -82.5 (bs, $C\underline{\mathbf{F}}_3CF_2CF_2O$- , 3F), -79 to -84 (-[$CF(C\underline{\mathbf{F}}_3)C\underline{\mathbf{F}}_2O$]-),-90.3 to -95.8 (-$C\underline{\mathbf{F}}_2$- of VDF, normal addition head-to-tail); -109.4 (-$CH_2C\underline{\mathbf{F}}_2CF_2C(CF_3)CH_2$-, 2F), -112.3(-$CH_2CF_2C\underline{\mathbf{F}}_2C(CF_3)CH_2$-), -113.8 and -116.0 ($CH_2$-$C\underline{\mathbf{F}}_2$-$C\underline{\mathbf{F}}_2$-$CH_2$ reverse addition of VDF, head to head). -130.7 (bs, $CF_3C\underline{\mathbf{F}}_2CF_2$-, 2F), -145.8 (bm, -[$C\underline{\mathbf{F}}(CF_3)CF_2O$]-, 7 x 1F).

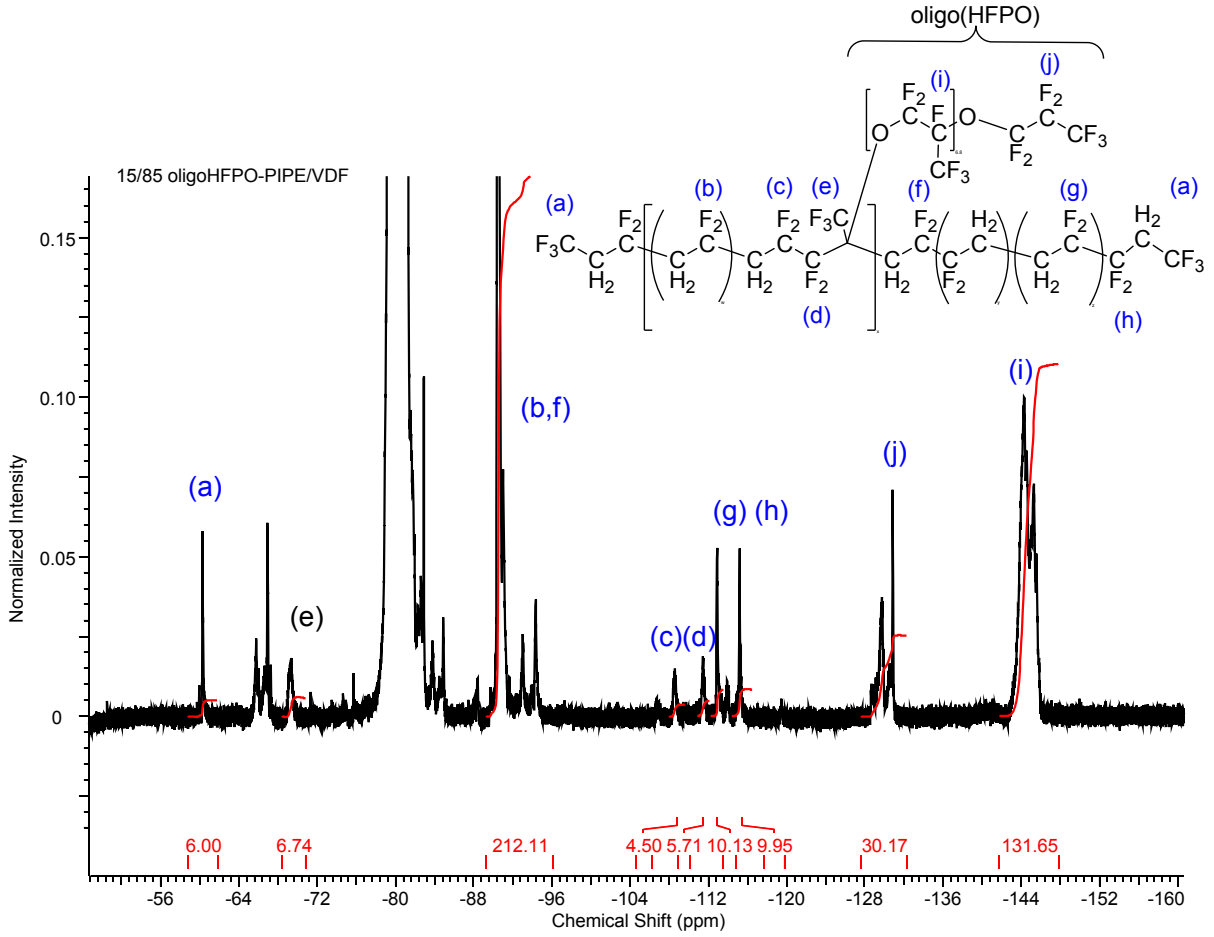

Figure S6: ^{19}F-NMR spectrum of the radical copolymerization of oligo(hexafluoropropylene oxide) perfluoroisopropenyl ether with VDF initiated by PPFR (Reaction #3).

^{19}F-NMR (376 MHz, C_6D_6 capillary/Acetone, 25 °C, δ): -61.3 ($C\underline{F}_3CH_2$- chain end), -70.2 (-$CF_2C(C\underline{F}_3)(ORf)CH_2$-, 3F) -81.6 (bs, $CF_3CF_2C\underline{F}_2O$-, 2F), -82.5 (bs, $C\underline{F}_3CF_2CF_2O$- , 3F), -79 to -84 (-[$CF(C\underline{F}_3)C\underline{F}_2O$]-),-90.3 to -95.8 (-$C\underline{F}_2$- of VDF, normal addition head-to-tail); -109.4 (-$CH_2C\underline{F}_2CF_2C(CF_3)CH_2$-, 2F), -112.3(-$CH_2CF_2C\underline{F}_2C(CF_3)CH_2$-), -113.8 and -116.0 ($CH_2$-$C\underline{F}_2$-$C\underline{F}_2$-$CH_2$ reverse addition of VDF, head to head). -130.7 (bs, $CF_3C\underline{F}_2CF_2$-, 2F), -145.8 (bm, -[$C\underline{F}(CF_3)CF_2O$]-, 7 x 1F).

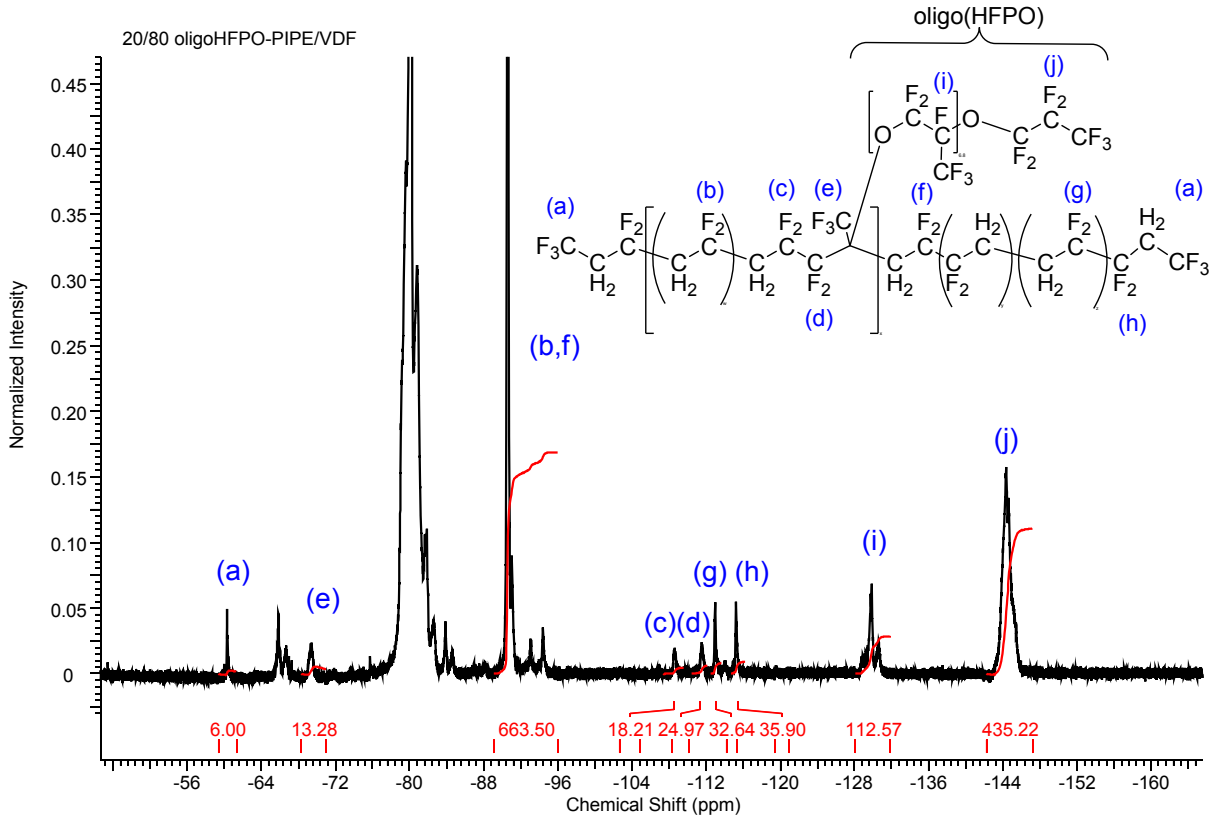

Figure S7: ^{19}F-NMR spectrum of the radical copolymerization of oligo(hexafluoropropylene oxide) perfluoroisopropenyl ether with VDF initiated by PPFR (Reaction #4).

^{19}F-NMR (376.41 MHz, C_6D_6 capillary THF/$CClF_2CFCl_2$, 25°C) δ (ppm) -79 to -84 (-[CF(C**F**$_3$)C**F**$_2$O]-), -82.03 ($CF_3CF_2C\underline{F}_2O$-, 2F), -83.73 (s, C**F**$_3$$CF_2CF_2O$- , 3F), -91.5 (C**F**$_2$ of VDF, normal addition head-to-tail); -113 and -116 (CH_2-C**F**$_2$-C**F**$_2$-CH_2 reverse addition of VDF, head to head). -131.69 (s, CF_3C**F**$_2$$CF_2$-, 2F), -146.31 (m, -[C**F**(CF_3)CF_2O]-, 5.73 x 1F).

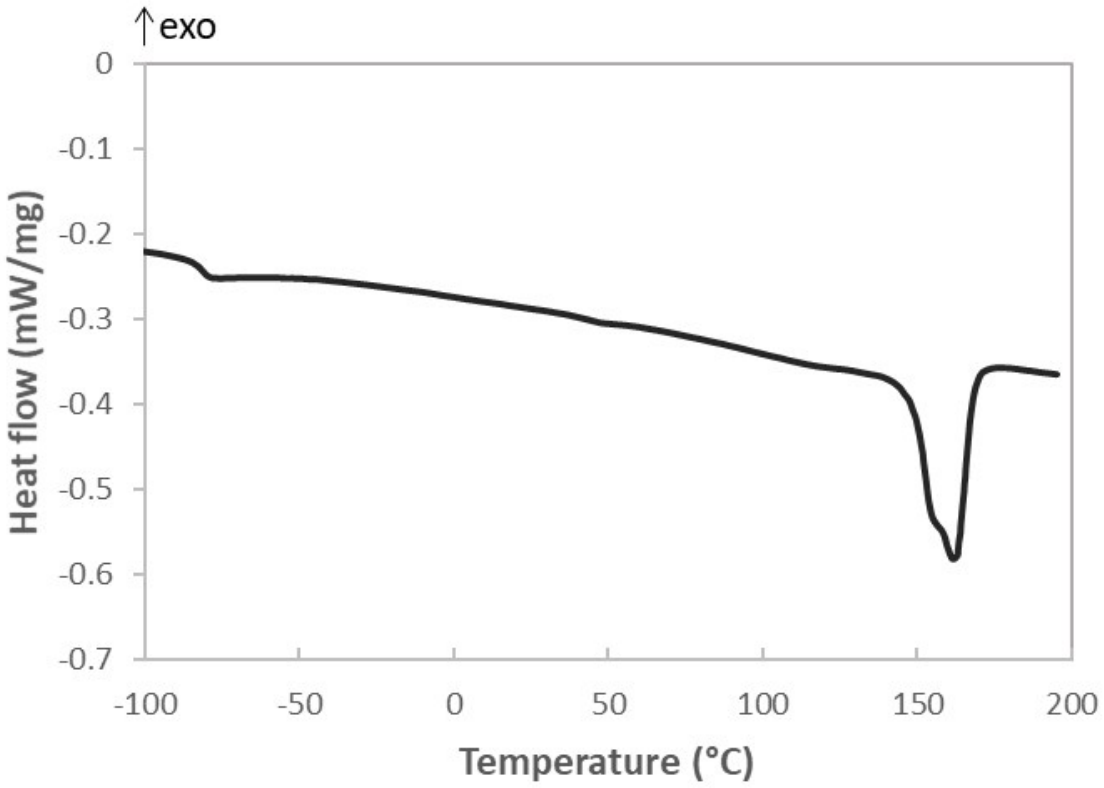

Figure S8: Differential scanning calorimetry (DSC) thermogram of the copolymer from the radical copolymerization of oligo(hexafluoropropylene oxide) perfluoroisopropenyl ether with VDF initiated by PPFR (Reaction #1).

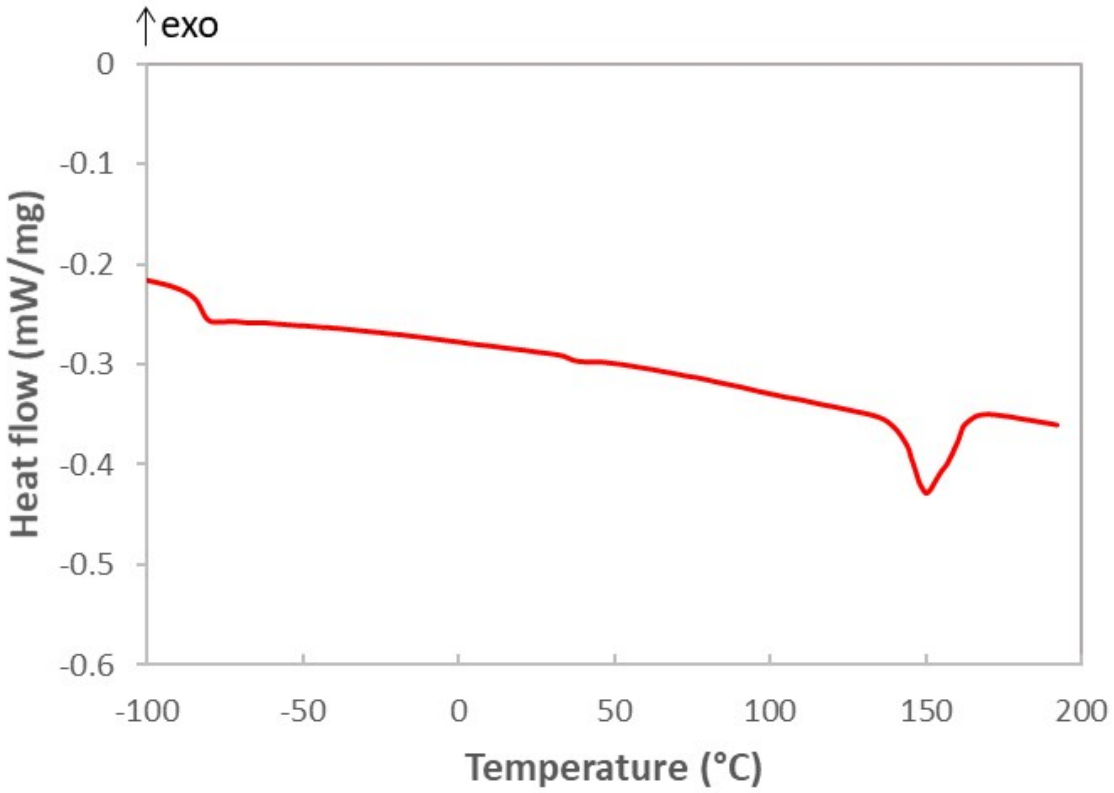

Figure S9: Differential scanning calorimetry (DSC) thermogram of the copolymer from the radical copolymerization of oligo(hexafluoropropylene oxide) perfluoroisopropenyl ether with VDF initiated by PPFR (Reaction #2).

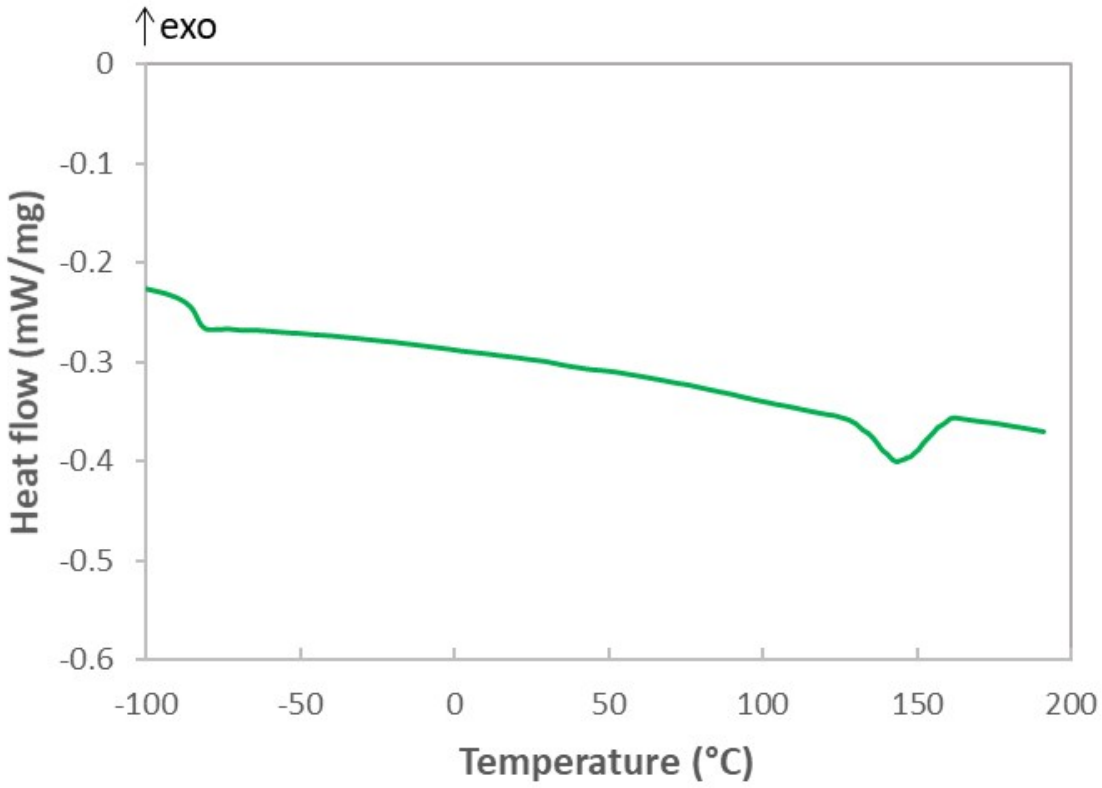

Figure S10: Differential scanning calorimetry (DSC) thermogram of the copolymer from the radical copolymerization of oligo(hexafluoropropylene oxide) perfluoroisopropenyl ether with VDF initiated by PPFR (Reaction #3).

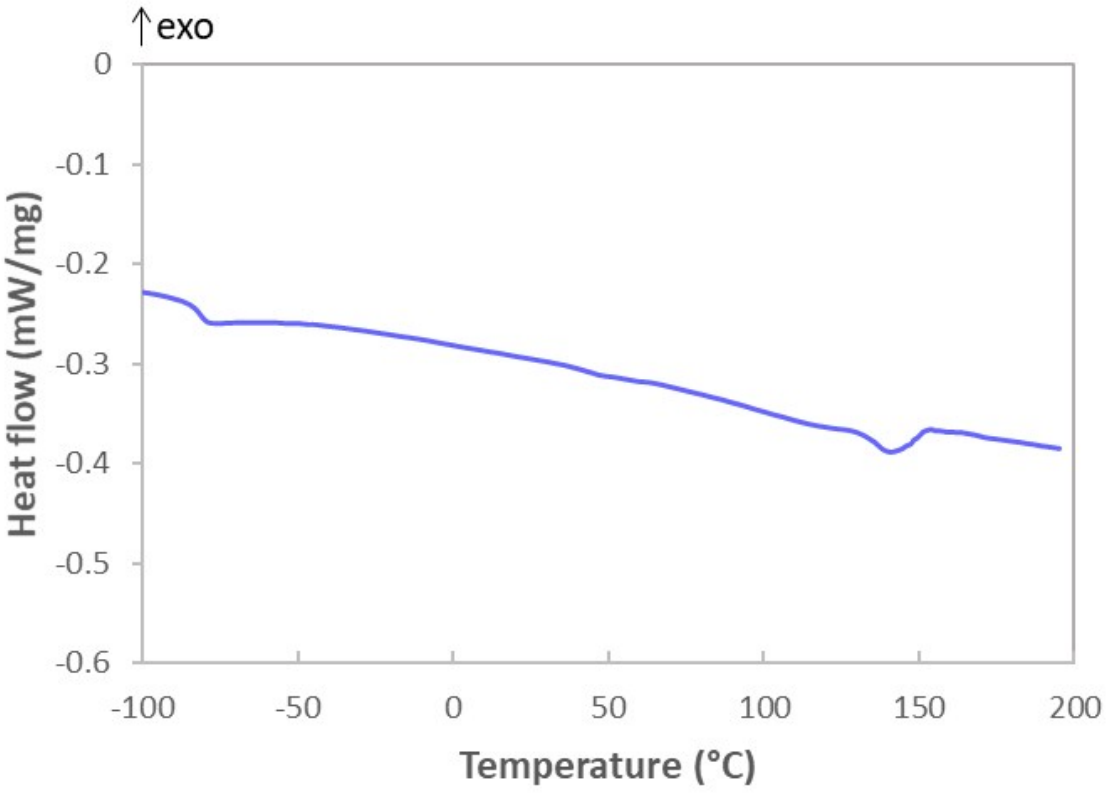

Figure S11: Differential scanning calorimetry (DSC) thermogram of the copolymer from the radical copolymerization of oligo(hexafluoropropylene oxide) perfluoroisopropenyl ether with VDF initiated by PPFR (Reaction #4).

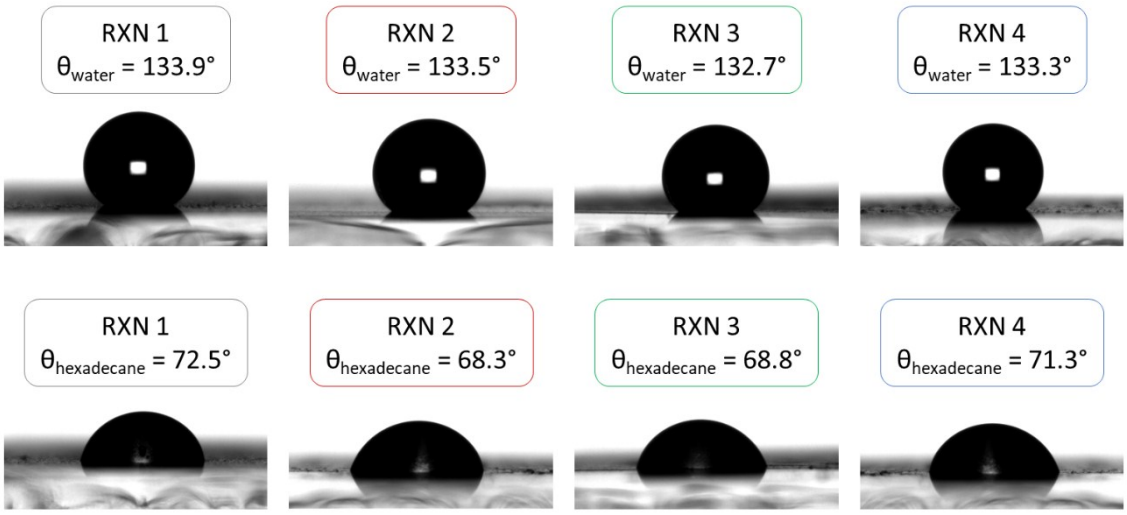

Figure S12: Images of water and hexadecane droplets deposited on the polymer film surface during contact angle measurements.

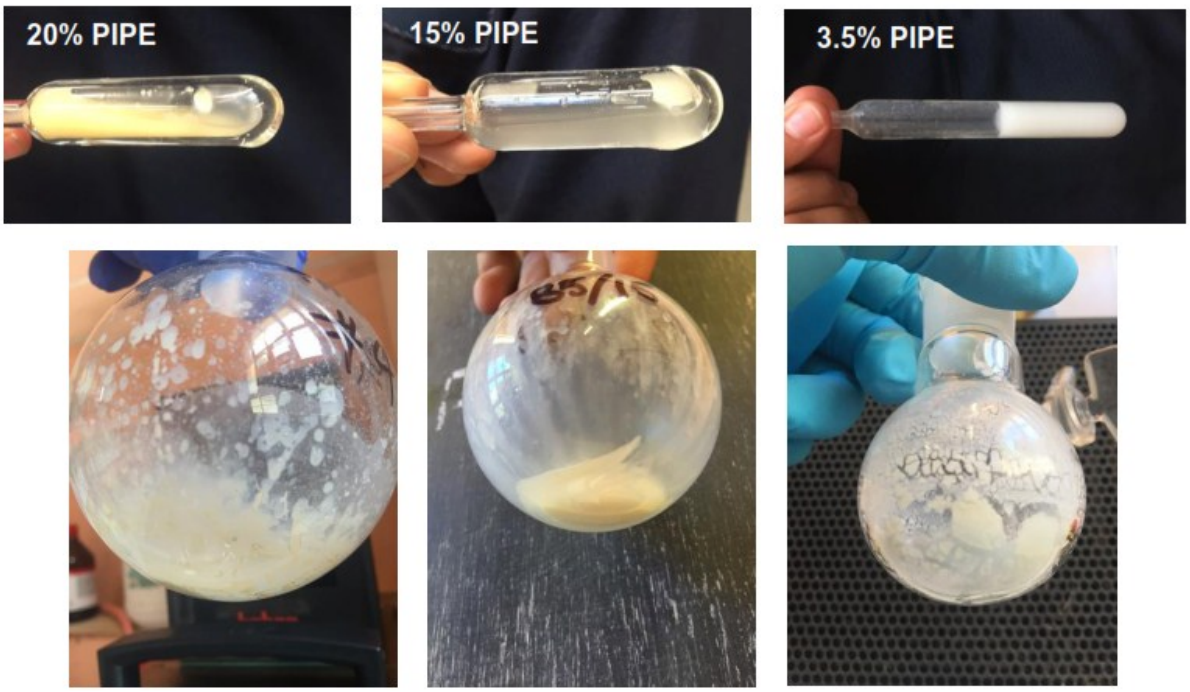

Figure S13: Images of polymerization products, prior to work-up (top) and post-transfer and isolated by vacuum distillation (bottom). Polymers trend from a thick, pale tan wax at 20% PIPE (left) and 15% PIPE (center), to a white powder at 3.5% PIPE (right).