

Step-Growth Copolymerization of Cyclic and Acyclic Perfluoroolefins with Bisphenols

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 <i>poly(1-co-2)A</i> – The copolymer based on perfluoro-4-methylpent-2-ene (PFP), perfluorohept-1-ene (PFH) and bisphenol-A (BPA).		
<i>poly(1-co-4)A</i> - The copolymer based on perfluoro-4-methylpent-2-ene (PFP), perfluorocyclohexene (PFCH) and bisphenol-A (BPA).		
<i>poly(2-co-4)A</i> - The copolymer based on perfluorohept-1-ene (PFH), perfluorocyclohexene (PFCH) and bisphenol-A (BPA).		
<i>poly(2-co-4)AF</i> - The copolymer based on perfluorohept-1-ene (PFH), perfluorocyclohexene (PFCH) and bisphenol-AF (BPF).		
<i>poly(1-co-4)AF</i> - The copolymer based on perfluoro-4-methylpent-2-ene (PFP), perfluorocyclohexene (PFCH) and bisphenol-AF (BPF).		
<i>poly(1-co-3)AF</i> - The copolymer based on perfluoro-4-methylpent-2-ene (PFP), perfluorocyclopentene (PFCP) and bisphenol-AF (BPF).		

S1. Addition-Elimination Mechanism

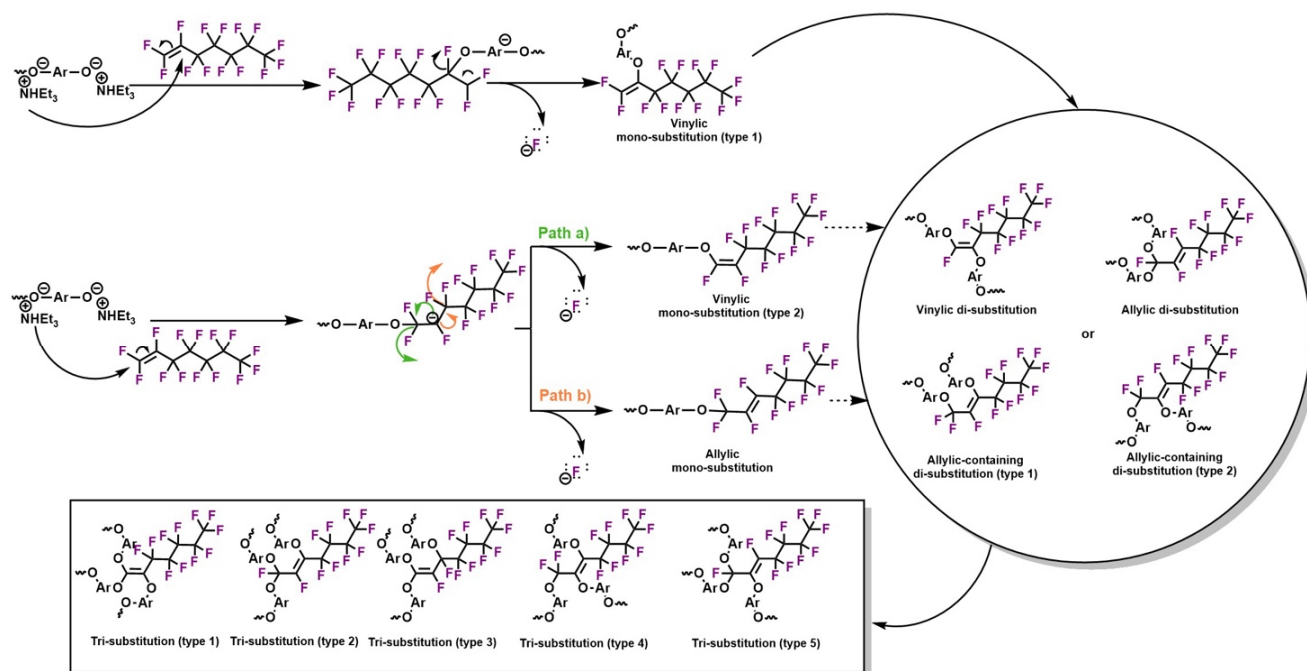


Figure S1. The addition-elimination mechanism of the reaction between PFH and bisphenols involves the formation of linear chains upon di-substitution and crosslinks upon tri-substitution of given perfluoroolefin monomers.

S2. ^1H NMR, ^{19}F NMR, GPC, Thermal Analysis (TGA /DSC), and ATR-FTIR Data of *poly(1-co-2)A* Copolymer

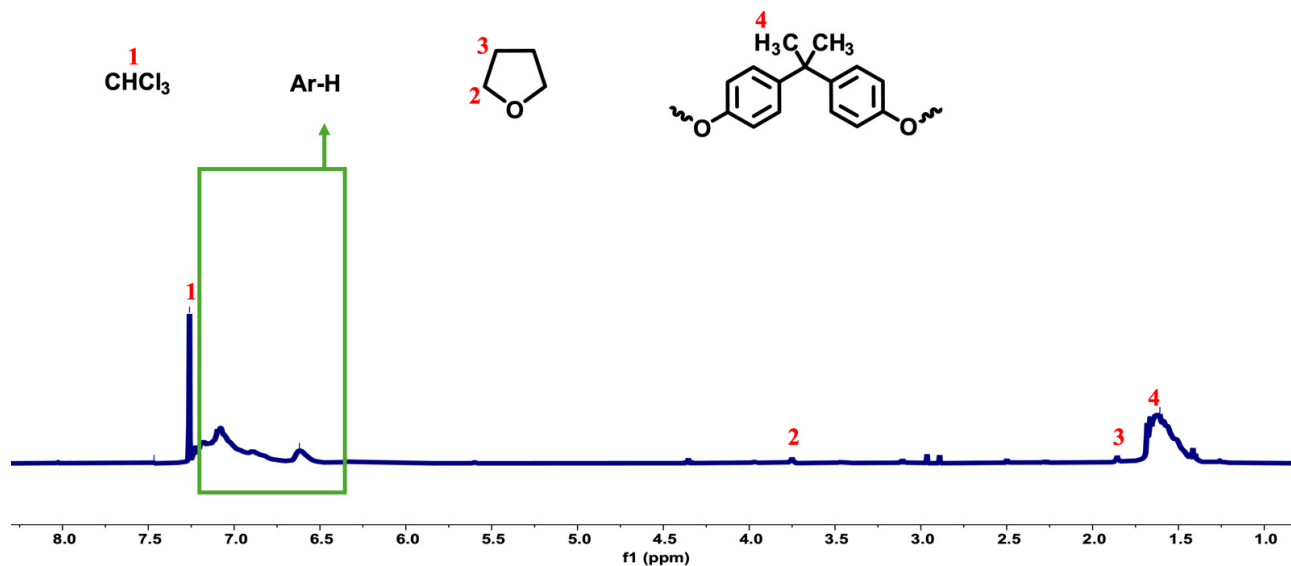


Figure S2. ^1H NMR (500 MHz, CDCl_3) of isolated *poly(1-co-2)A*.

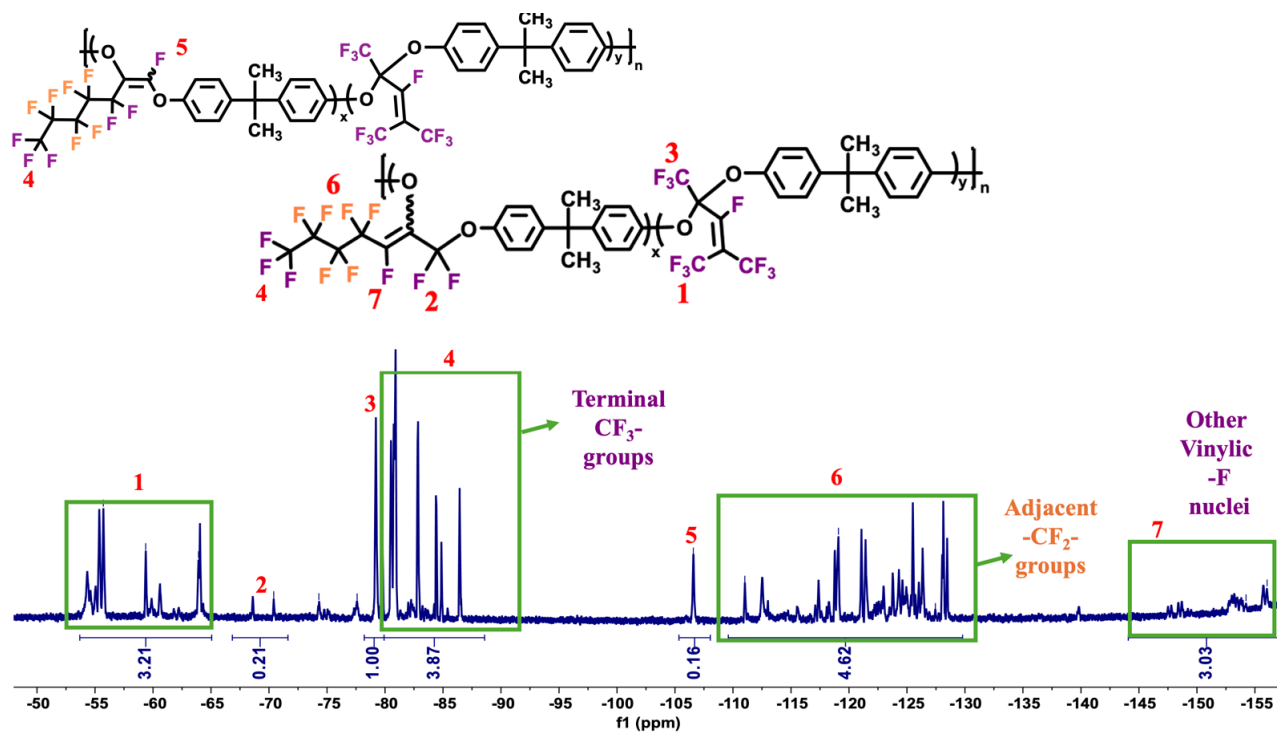


Figure S3. ^{19}F NMR (470 MHz, CDCl_3) analysis of *poly(1-co-2)A* copolymer.

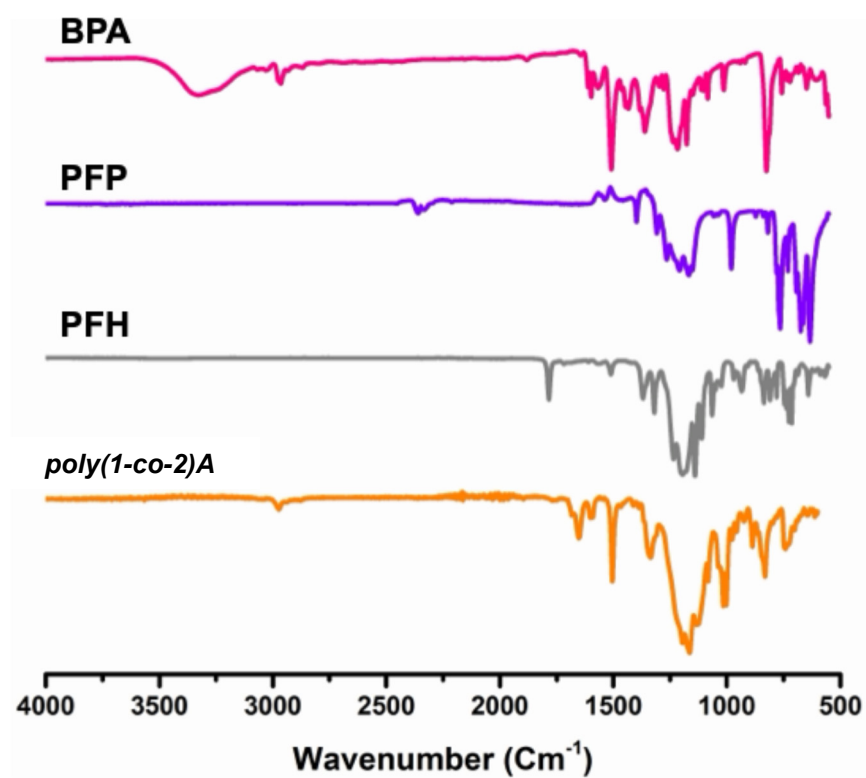


Figure S4. Stacked ATR-FTIR of starting materials and isolated copolymer *poly(1-co-2)A*.

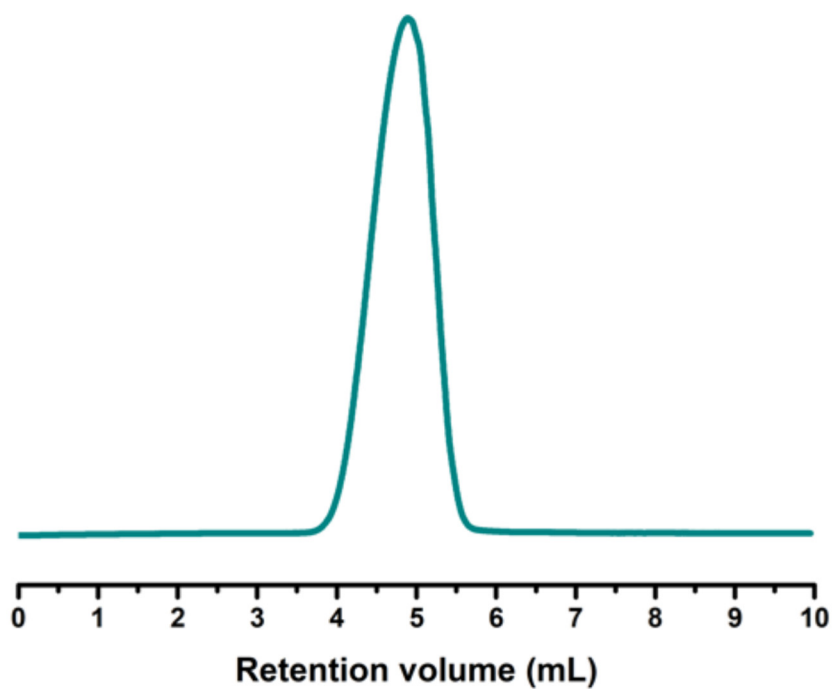


Figure S5. Copolymer *poly(1-co-2)A* GPC (THF) with $M_n = 13.2$ kDa and PDI (M_w/M_n) = 1.3, respectively.

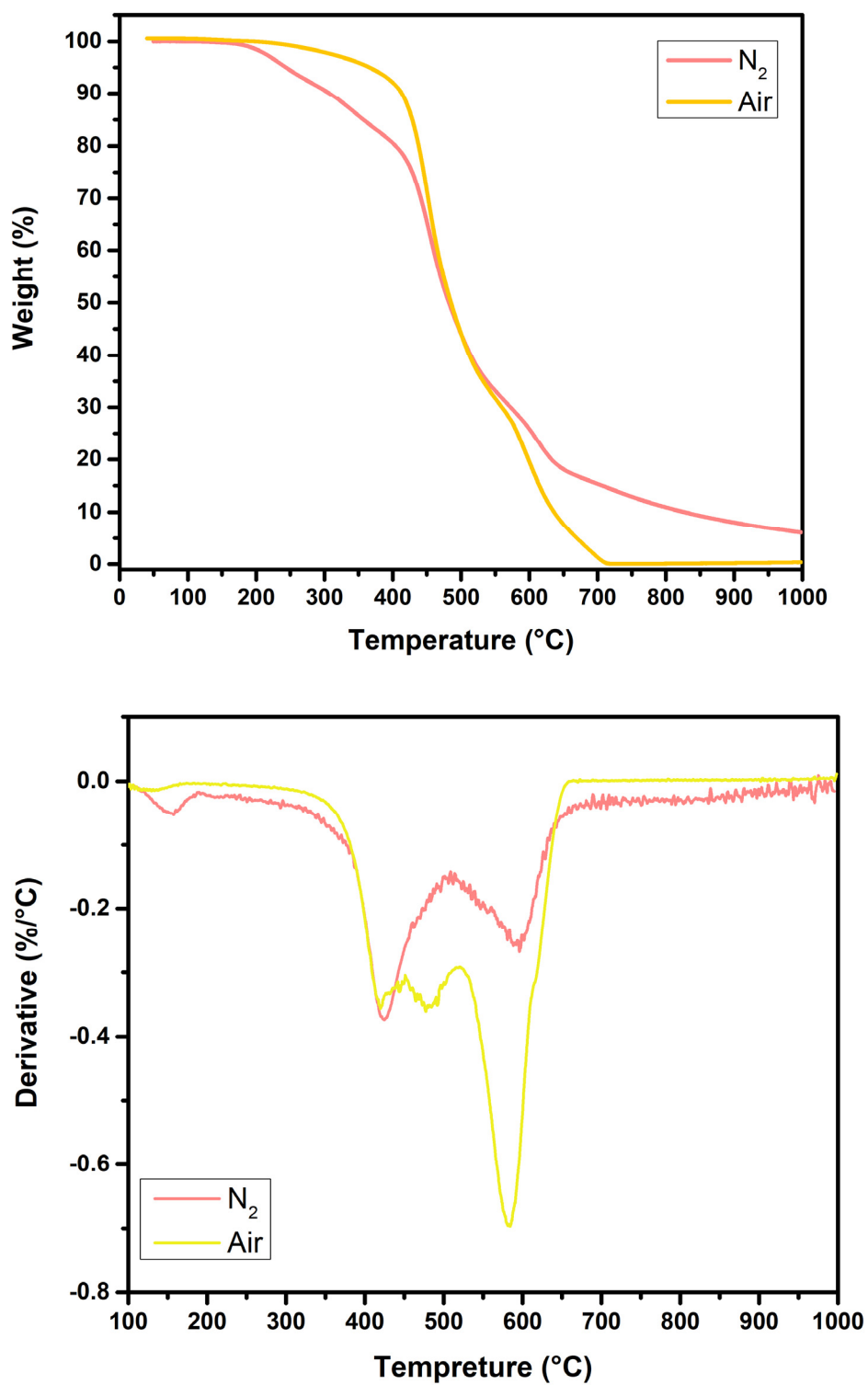


Figure S6. TGA (10 °C/min) of *poly(1-co-2)A* (Top), DTG of *poly(1-co-2)A* (Bottom).

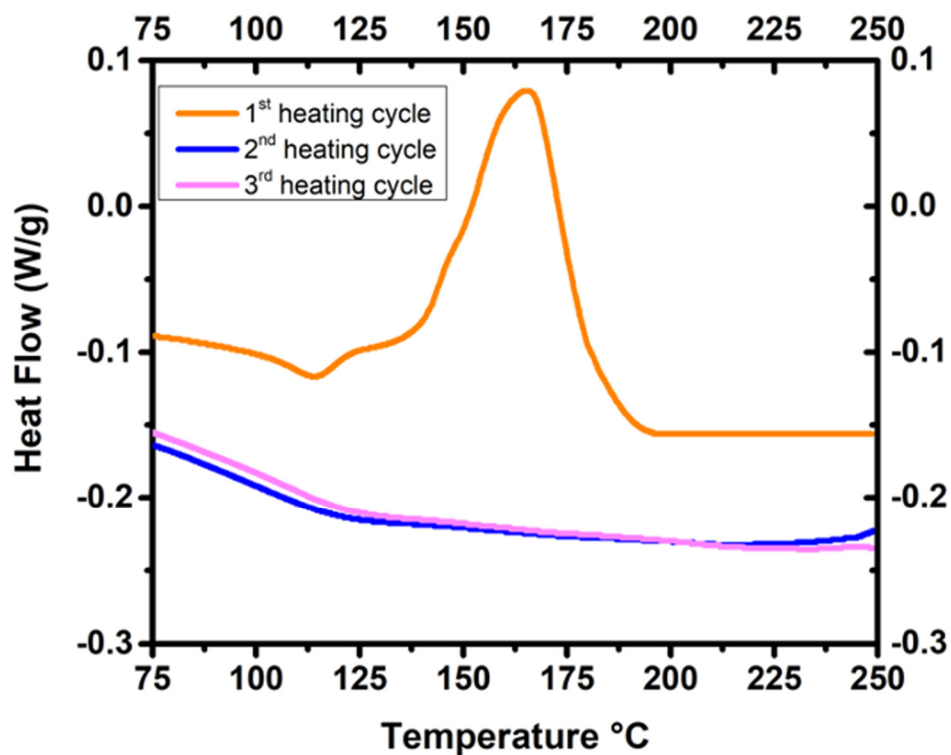


Figure S7. DSC analysis (10 °C/min in N₂) of *poly(1-co-2)A*.

S3. ¹H NMR, ¹⁹F NMR, GPC, Thermal Analysis (TGA/DSC), and ATR-FTIR Data of *poly(1-co-4)A/AF* Copolymers

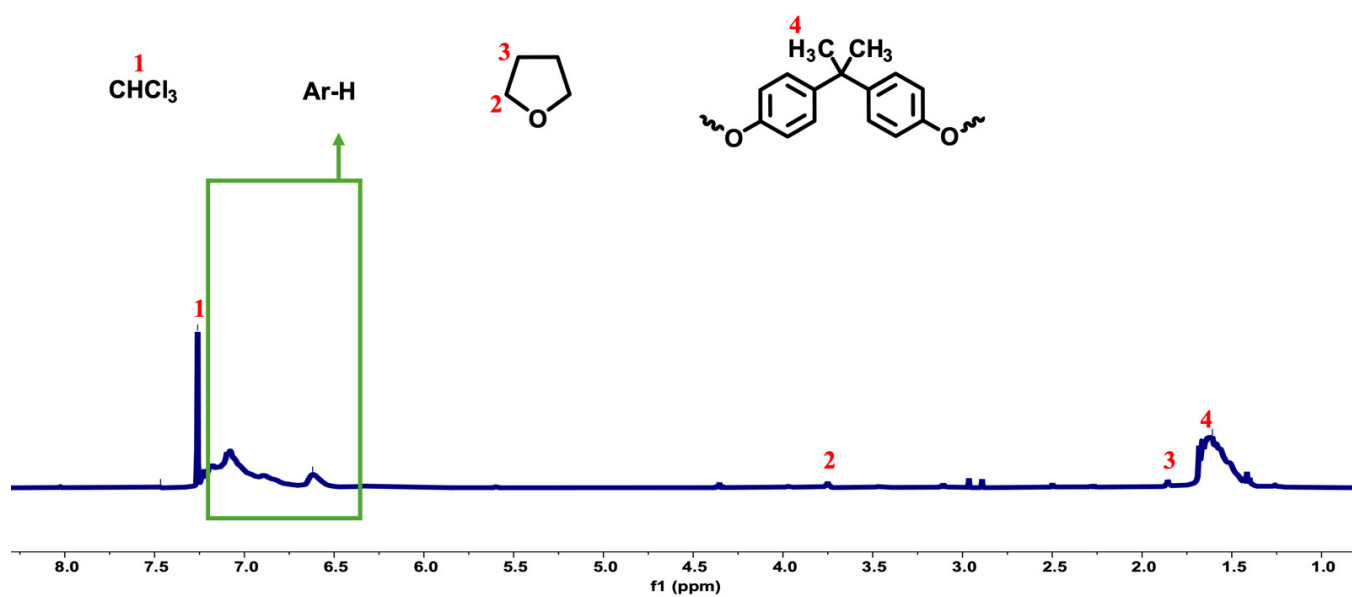


Figure S8. ¹H NMR (500 MHz, CDCl₃) of isolated copolymer *poly(1-co-4)A*.

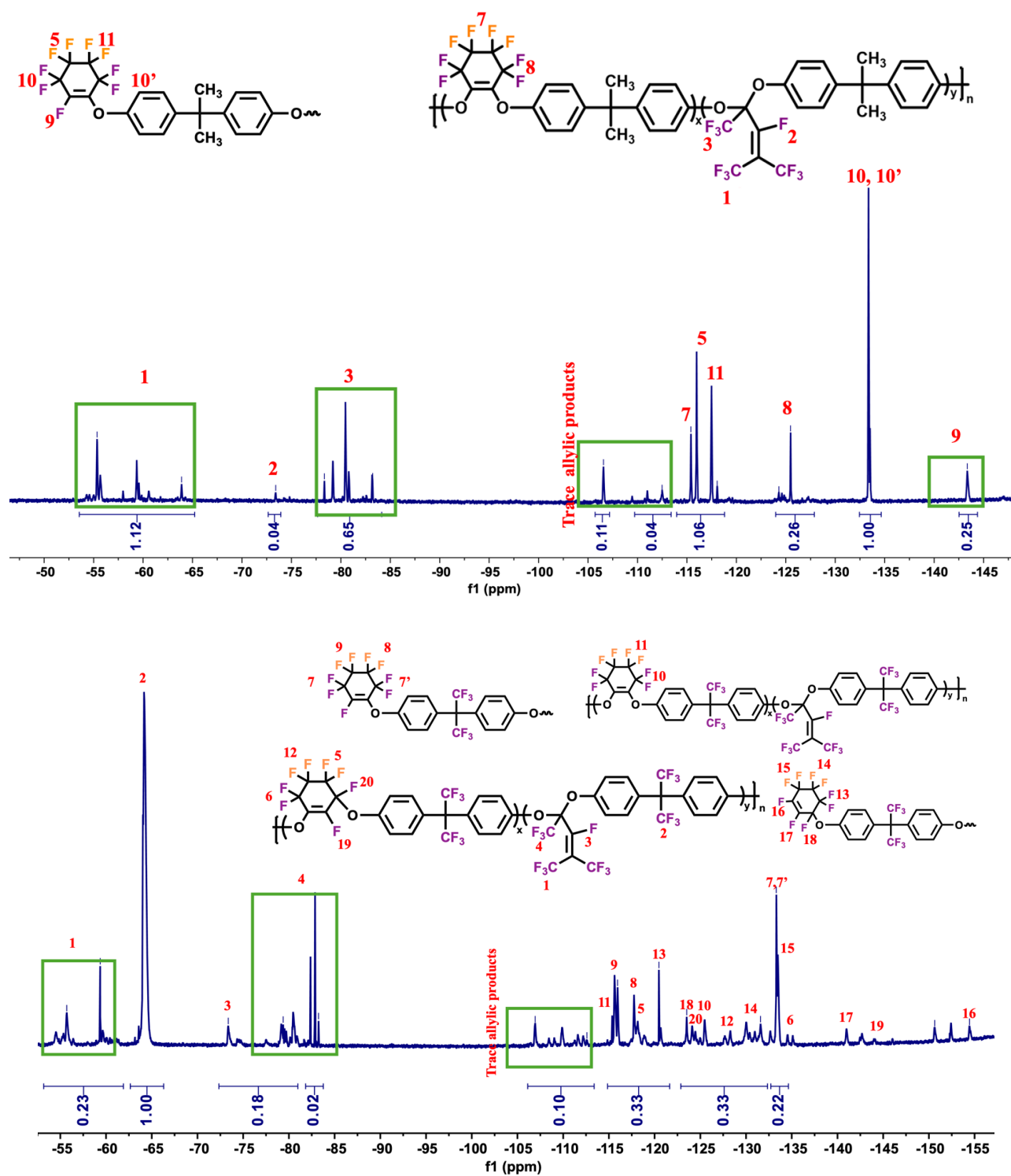


Figure S9. ^{19}F NMR (470 MHz, CDCl_3) analysis of copolymers $poly(1-co-4)A$ (Top), and $poly(1-co-4)AF$ (Bottom) copolymers.

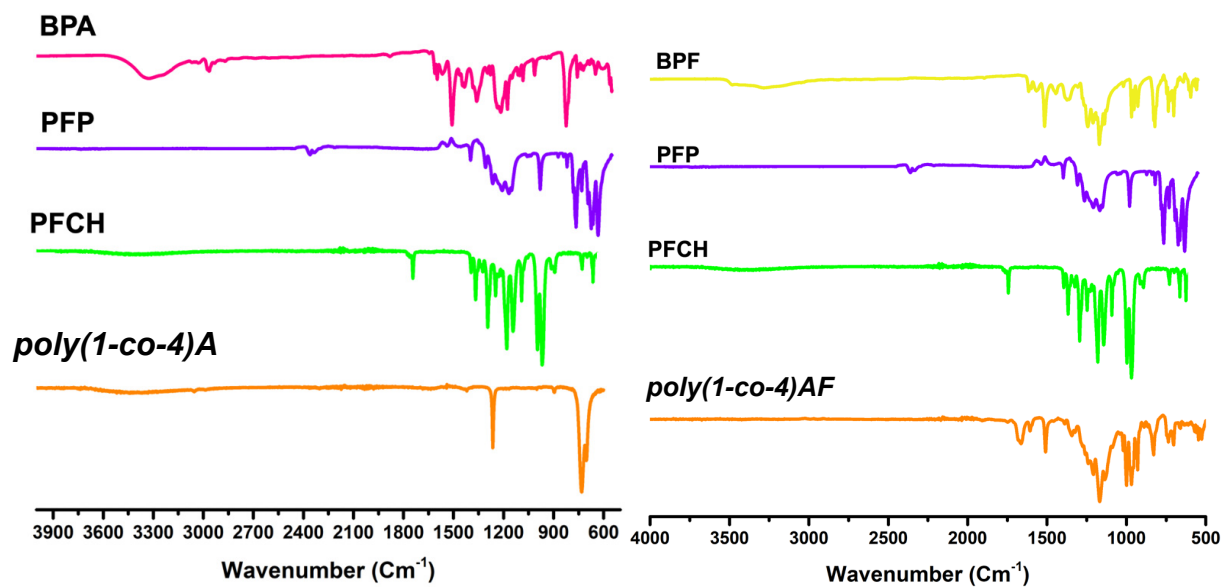


Figure S10. Stacked ATR-FTIR of starting materials and isolated *poly(1-co-4)A* (left) and *poly(1-co-4)AF* (right).

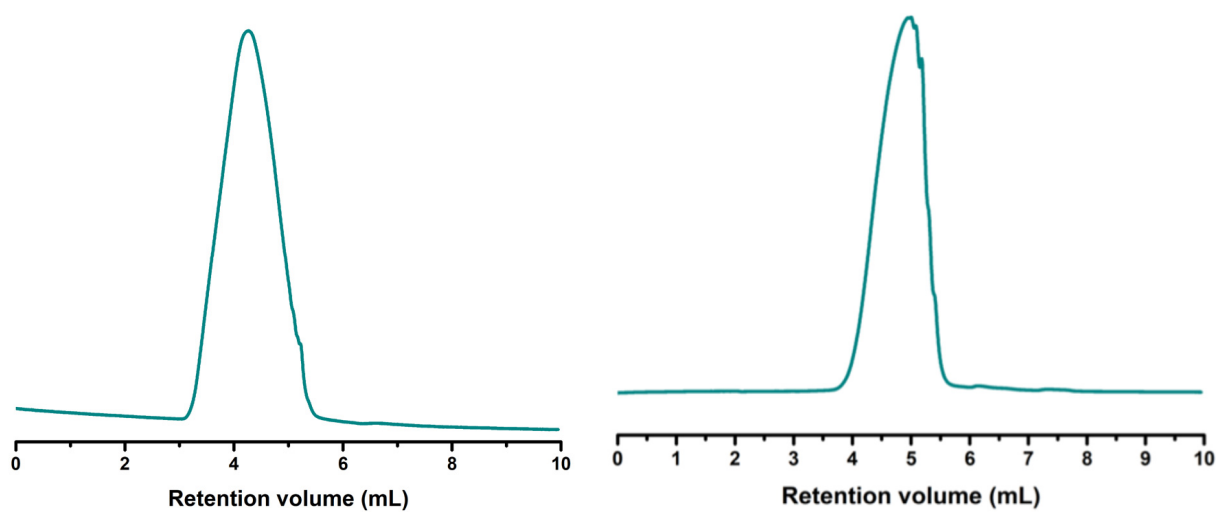


Figure S11. Copolymers *poly(1-co-4)A* (left), and *poly(1-co-4)AF* (right) GPC (THF) with $M_n = 13.1$ and 16.2 kDa and PDI (M_w/M_n) = 1.9, 1.1, respectively.

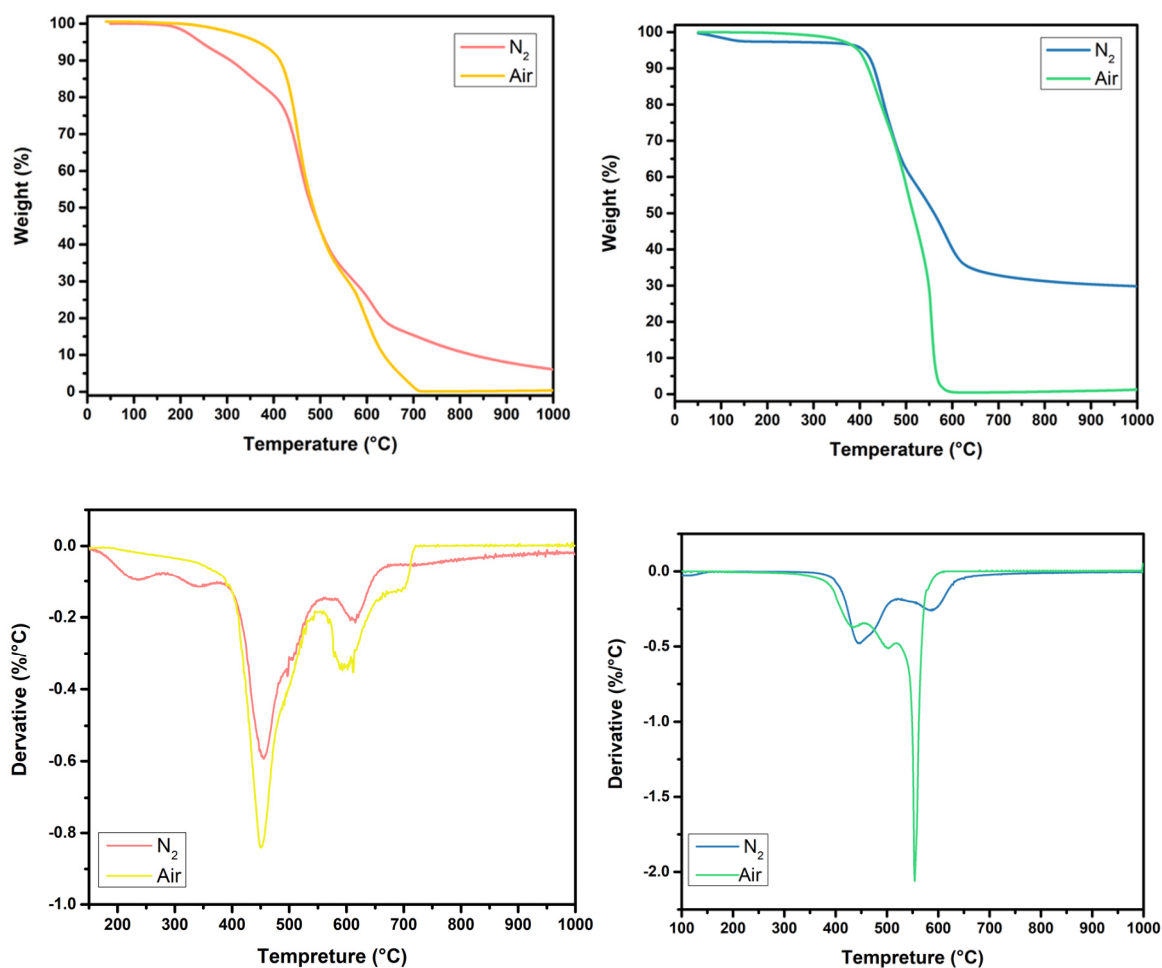


Figure S12. TGA analysis (10 °C/min) of *poly(1-co-4)A* (Top-Left) and *poly(1-co-4)AF* (Top-Right), DTG analysis of *poly(1-co-4)A* (Bottom-Left) and *poly(1-co-4)AF* (Bottom-Right).

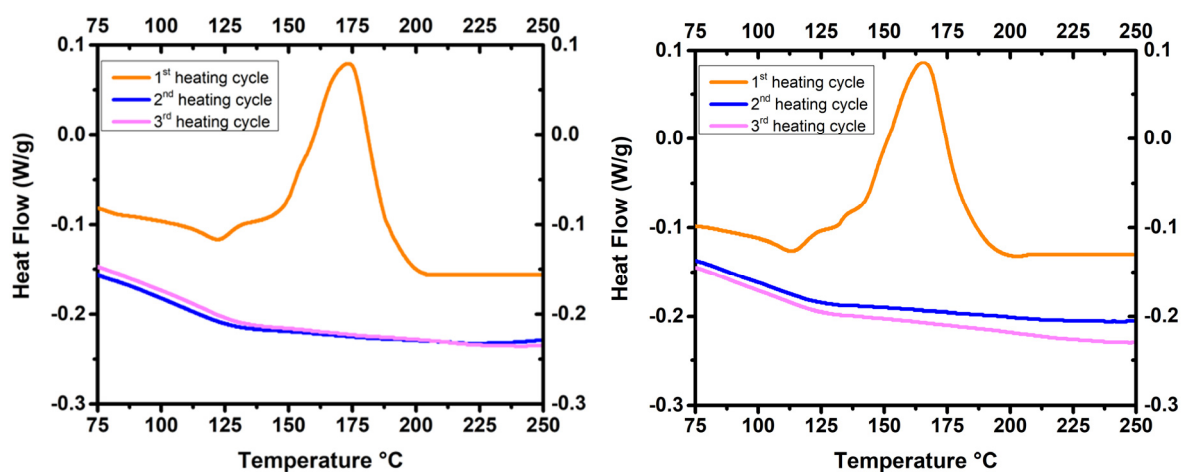


Figure S13. DSC analysis (10 °C/min in N_2) of *poly(1-co-4)A* (Left) and *poly(1-co-4)AF* (Right).

S4. ^1H NMR, GPC, and ATR-FTIR Data of *poly(2-co-4)A/AF* Copolymers

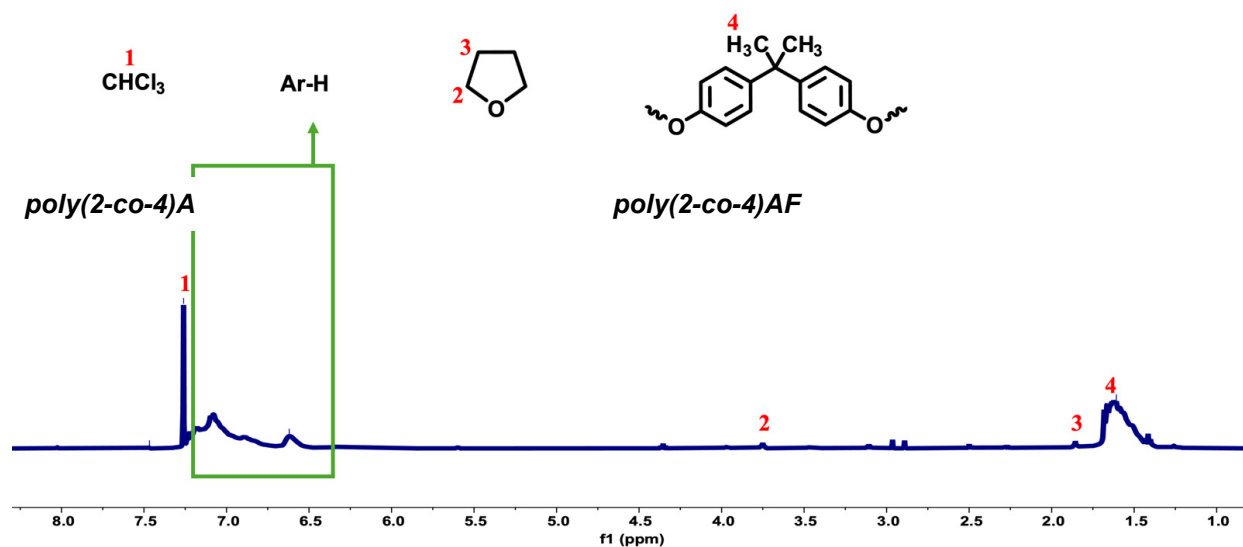


Figure S14. ^1H NMR (500 MHz, CDCl_3) of isolated copolymer *poly(2-co-4)A*.

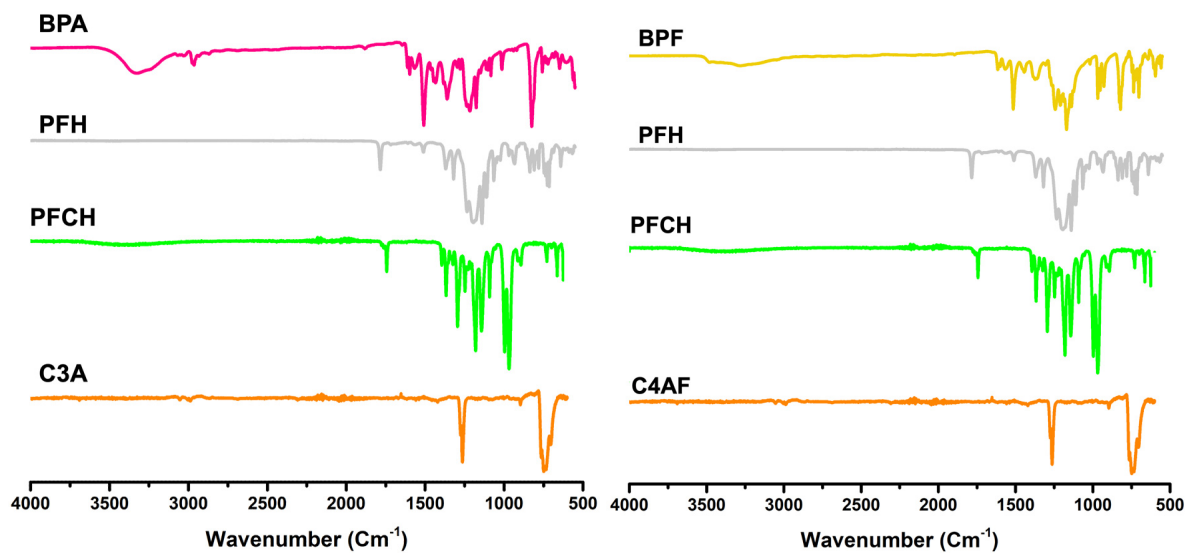


Figure S15. Stacked ATR-FTIR of starting materials and isolated copolymers *poly(2-co-4)A* (right) and *poly(2-co-4)AF* (left).

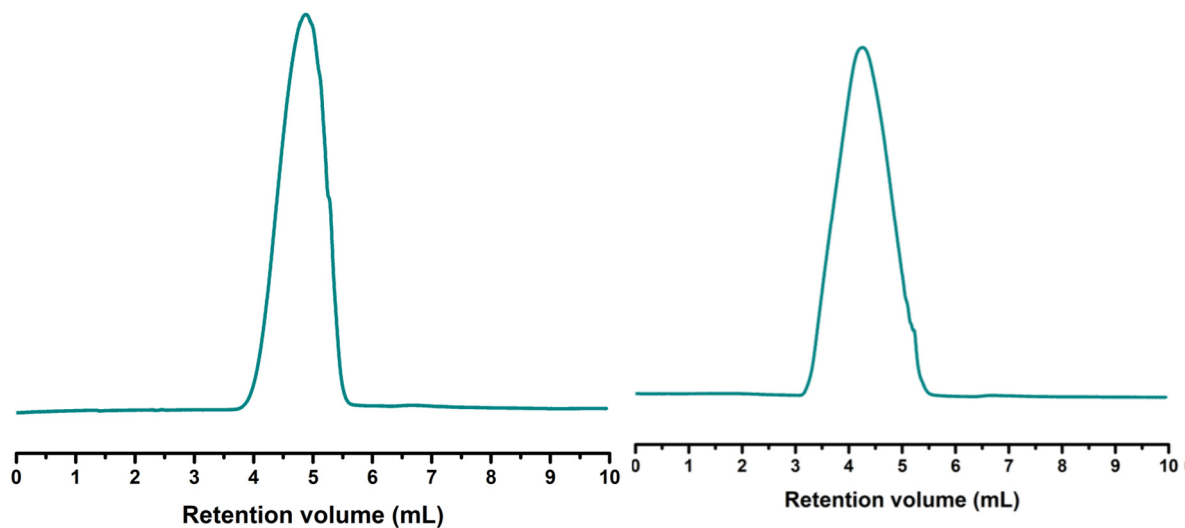


Figure S16. Copolymer *poly(2-co-4)A* (right) and *poly(2-co-4)AF* (left) GPC (THF) with $M_n = 15.2$ and 13.4 kDa and PDI (M_w/M_n) = 1.1, 1.5, respectively.

S5. ^{19}F NMR, GPC, Thermal Analysis (TGA /DSC), and ATR-FTIR Data of *poly(1-co-3)AF*

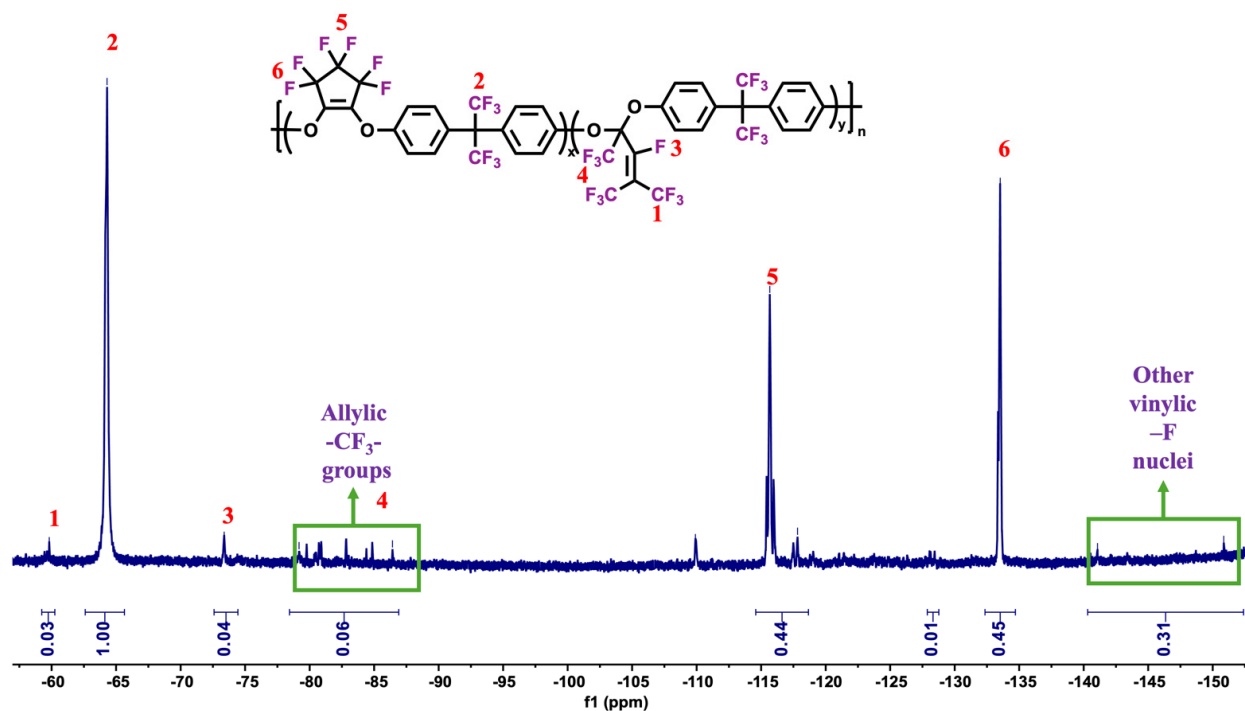


Figure S17. ^{19}F NMR (470 MHz, CDCl_3) analysis of *poly(1-co-3)AF* copolymer.

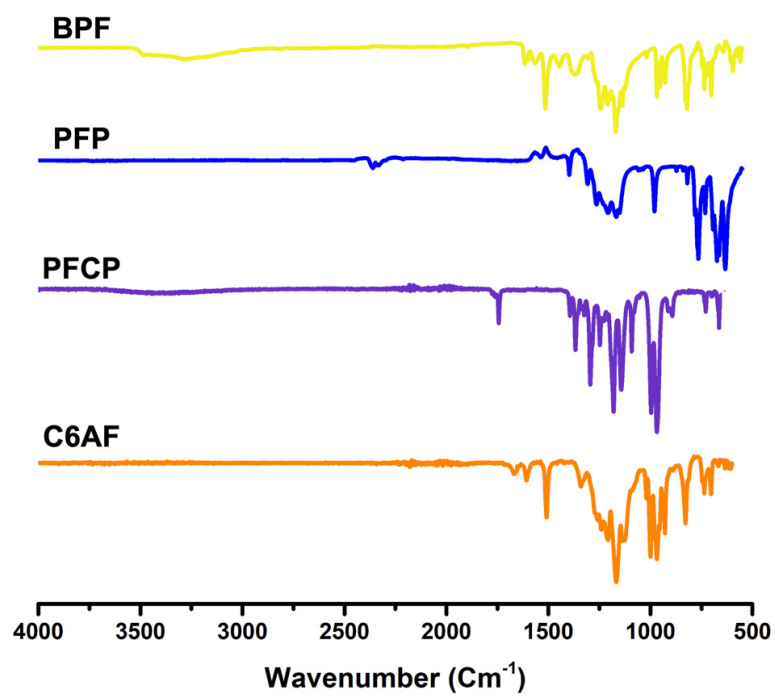


Figure S18. Stacked ATR-FTIR of starting materials and isolated copolymer *poly(1-co-3)AF*.

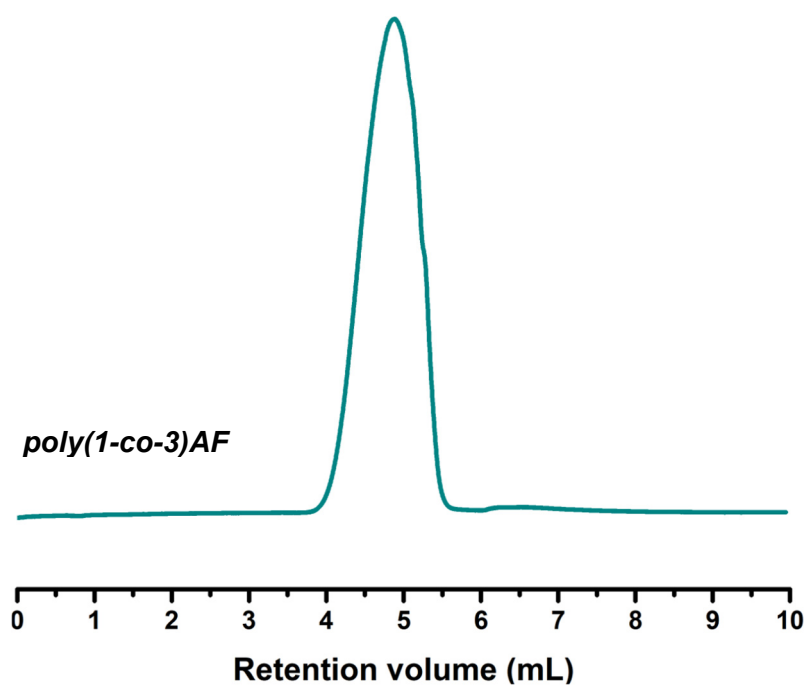


Figure S19. Copolymer *poly(1-co-3)AF* GPC (THF) with $M_n = 13.0$ kDa and PDI (M_w/M_n) = 1.3, respectively.

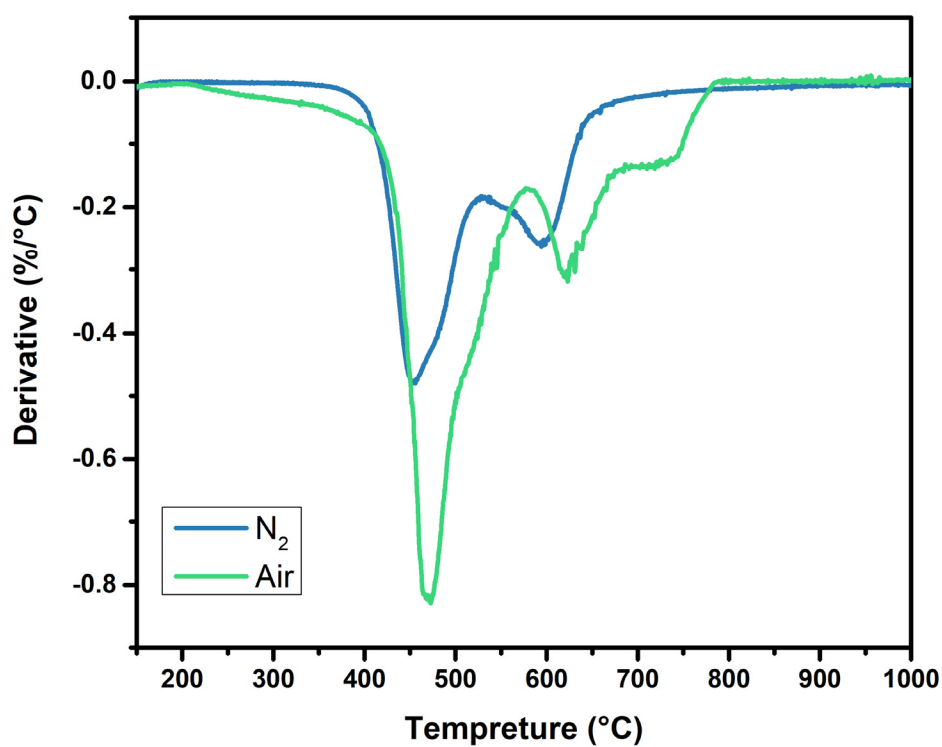
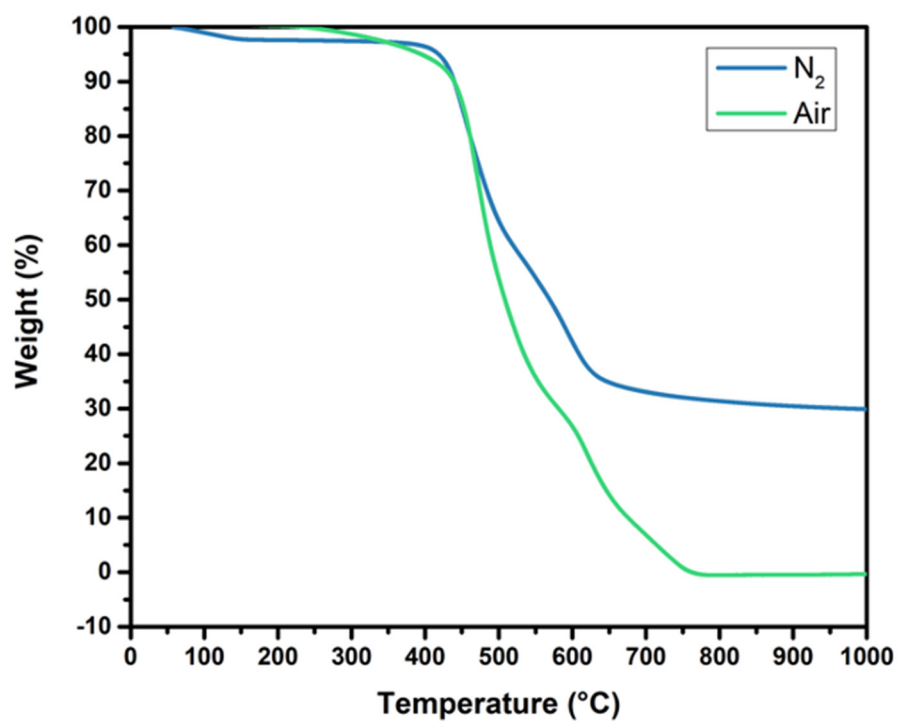


Figure S20. TGA (10 °C/min) of *poly(1-co-3)AF*(Top), and DTG of *poly(1-co-3)AF*(Bottom).

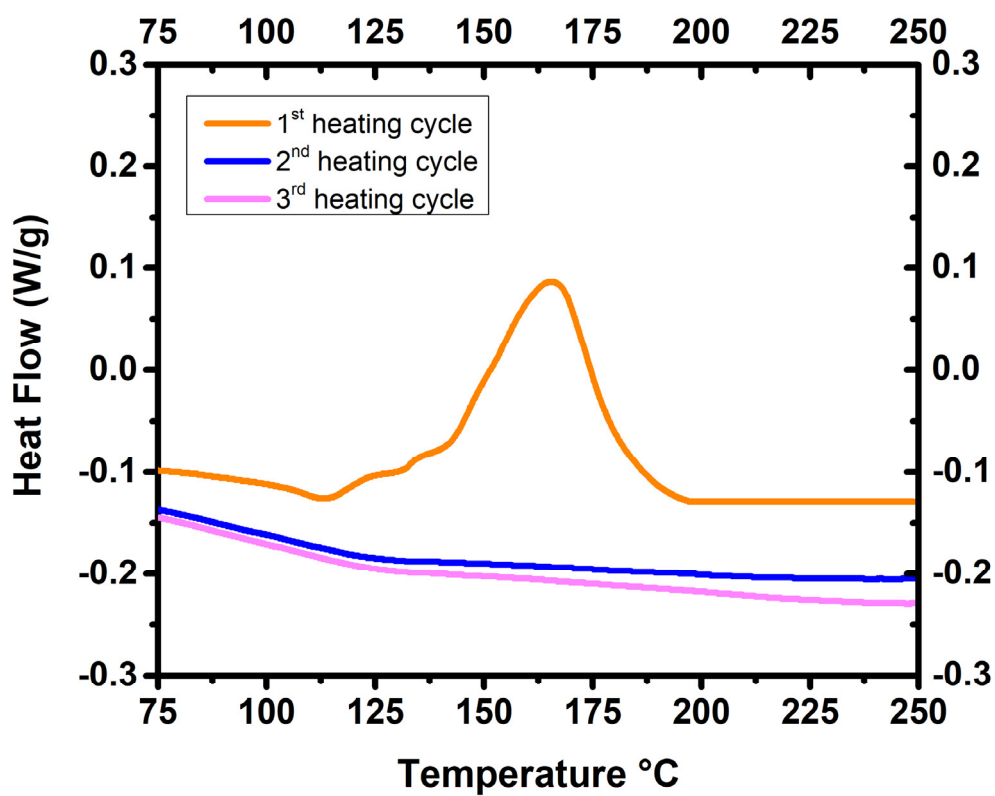


Figure S21. DSC analysis (10 °C/min in N₂) of *poly(1-co-3)AF*.

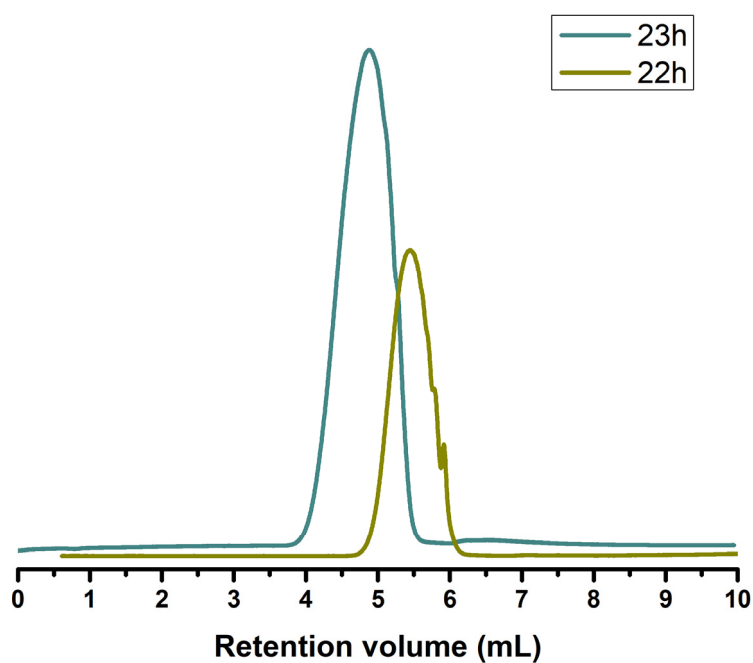


Figure S22. Comparative GPC of *poly(1-co-3)AF*.