Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Ferroelectric Fluorinated Copolymers with Improved Adhesion Properties

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KEYWORDS: Adhesion, Ferroelectricity, Fluorinated copolymer, Piezoelectricity, Trifluoroethylene, 2-(trifluoromethyl)acrylic acid, Vinylidene fluoride.

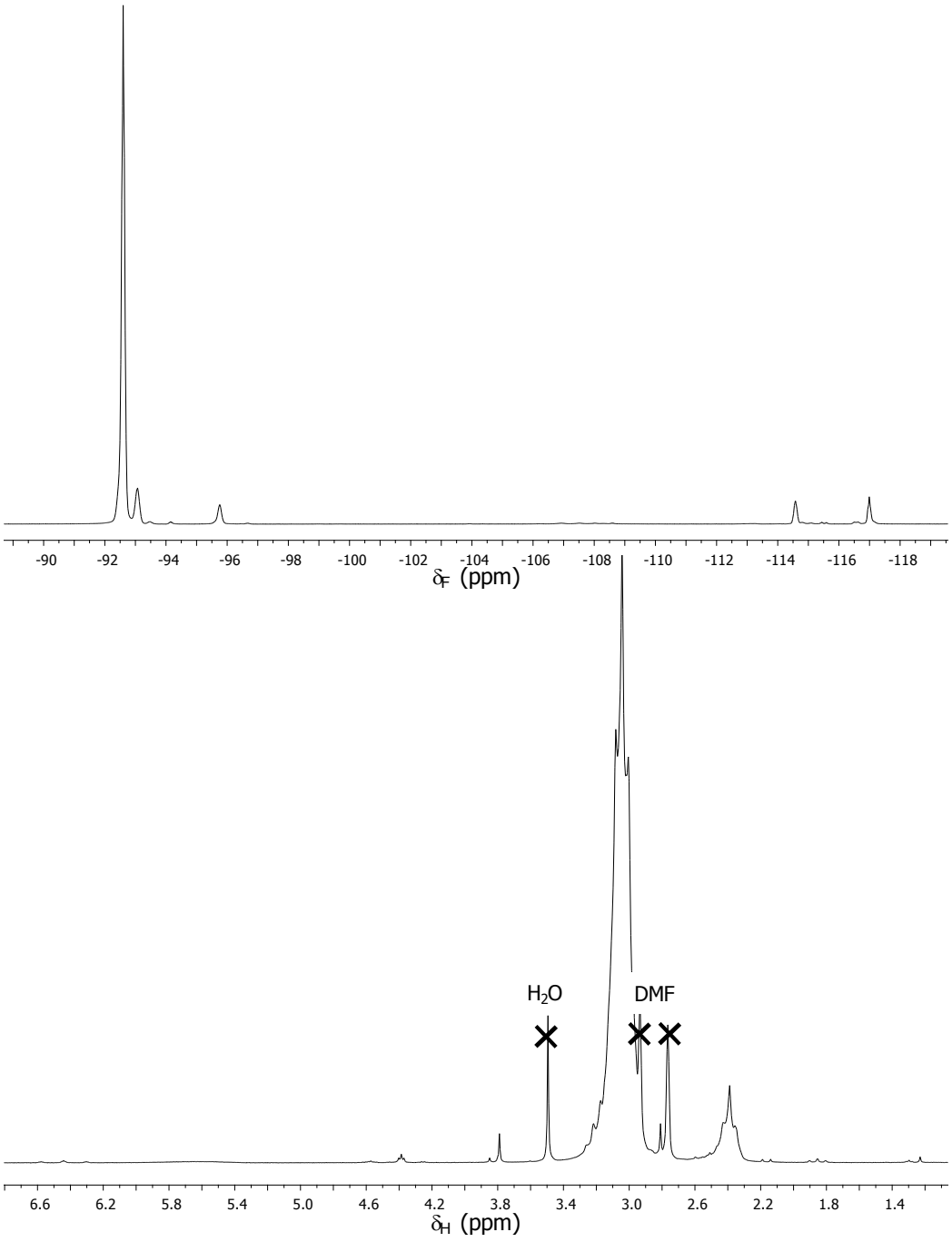

Figure S1. ^{19}F (top) and ^{1}H (bottom) NMR spectra in $DCON(CD_3)_2$ of a PVDF homopolymer (Run 1, Table 1).

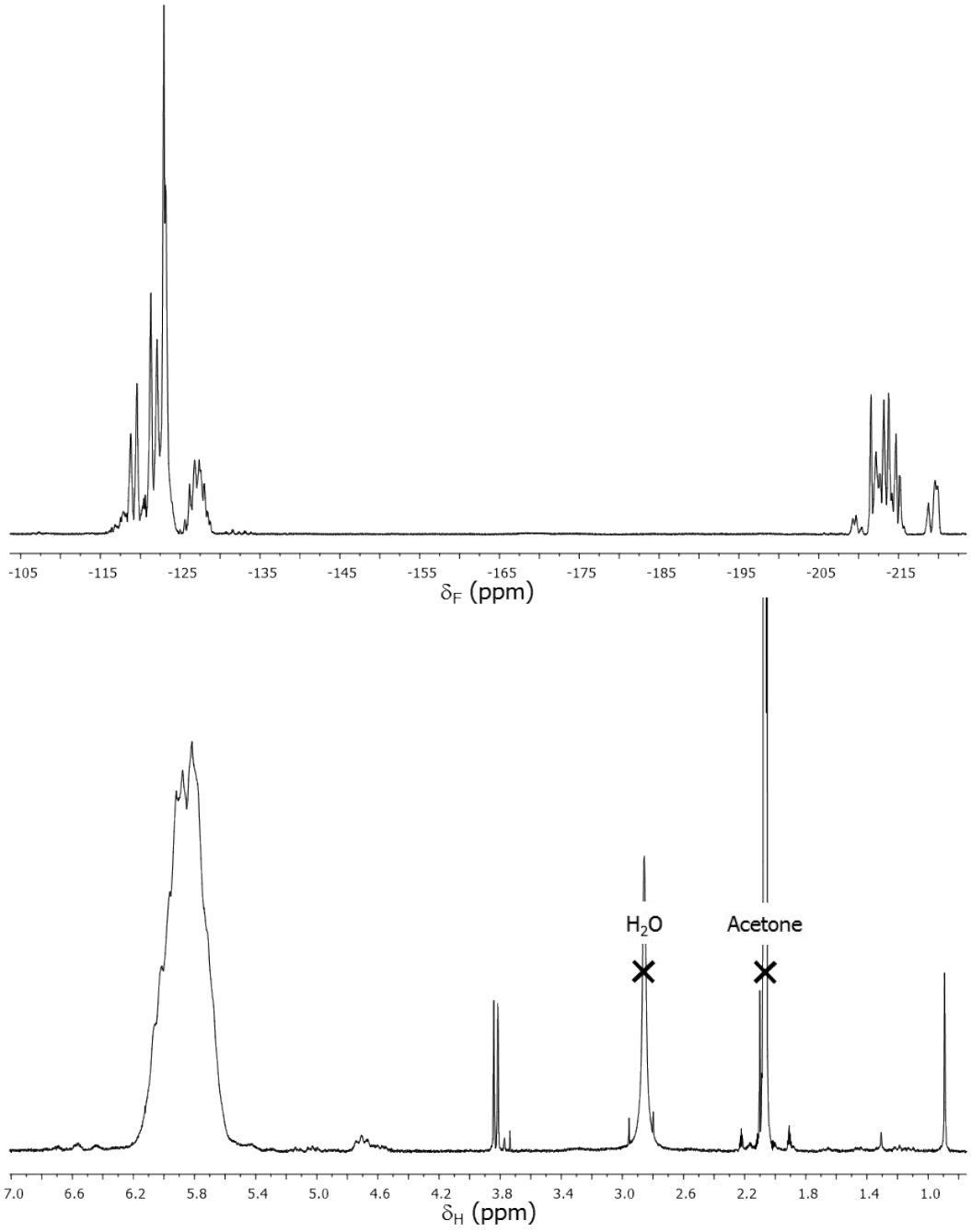

Figure S2. ^{19}F (top) and ^{1}H (bottom) NMR spectra in $(CD_3)_2CO$ of a PTrFE homopolymer (Run 2, Table 1).

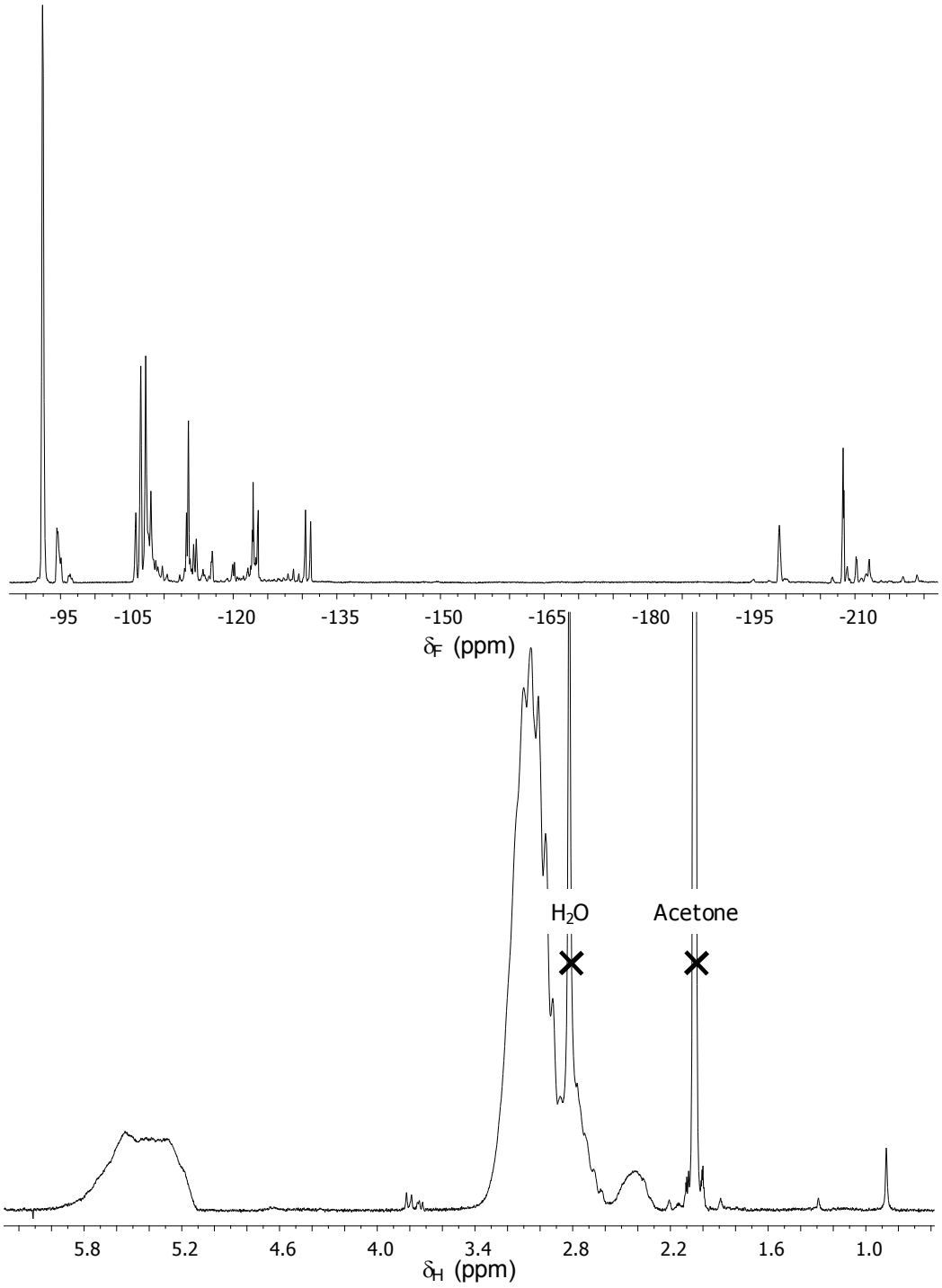

Figure S3. ^{19}F (top) and ^{1}H (bottom) NMR spectra in $(CD_3)_2CO$ of a poly(VDF_{69}-*co*-$TrFE_{31}$) copolymer (Run 4, Table 1).

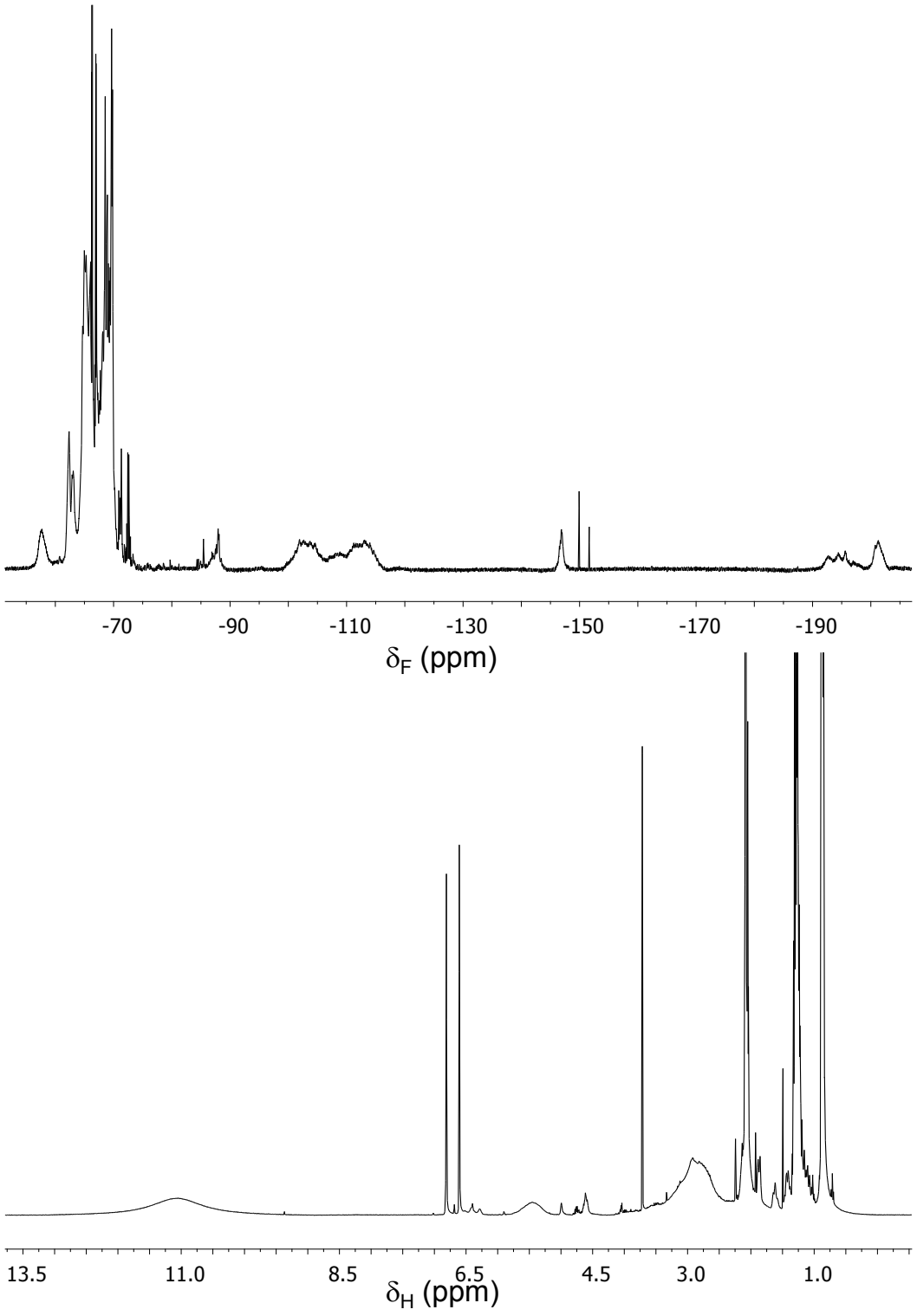

Figure S4. ^{19}F (top) and ^{1}H (bottom) NMR spectra in $(CD_3)_2CO$ of a poly(TrFE-*co*-MAF) copolymer (Run 4, Table 1).

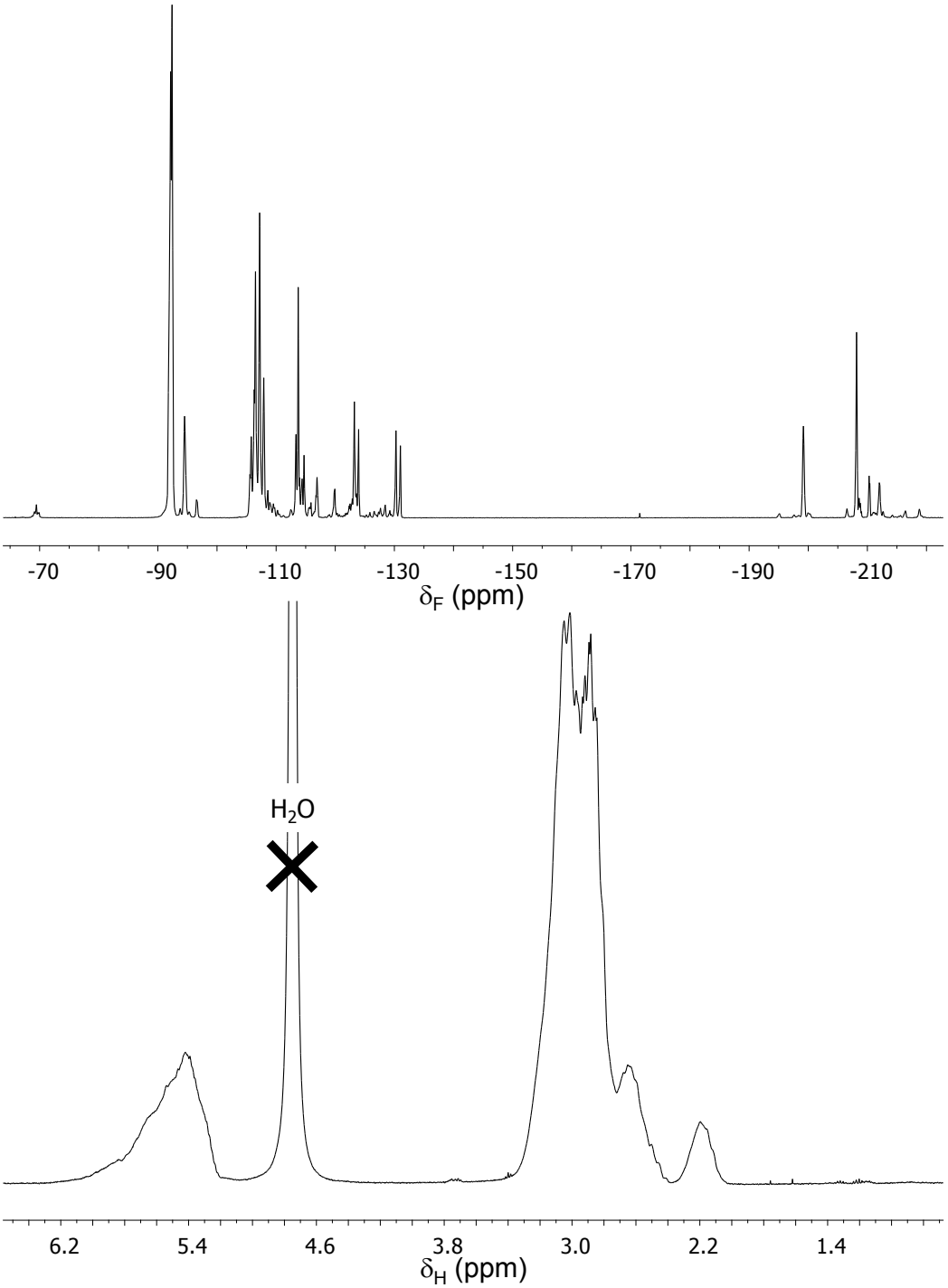

Figure S5. ^{19}F (top) and ^{1}H (bottom) NMR spectra in C_5D_5N of a poly(VDF_{69}-*ter*-$TrFE_{30}$-*ter*-MAF_1) terpolymer prepared by aqueous suspension polymerization (Run 11, Table 1).

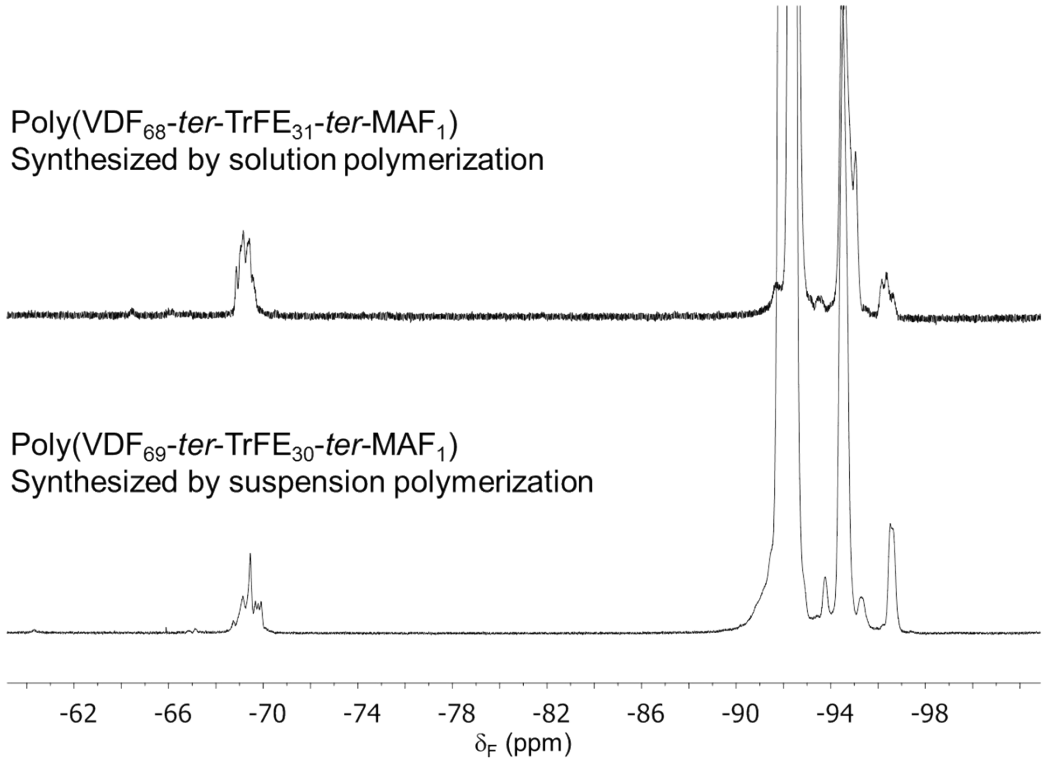

Figure S6. Comparision of the ^{19}F NMR spectra (Expansion of the -59 to -103 ppm region), of two poly(VDF-*ter*-TrFE-*ter*-MAF) terpolymers prepared by solution polymerization in DMC (Top) and aqueous suspension polymerization (Bottom)

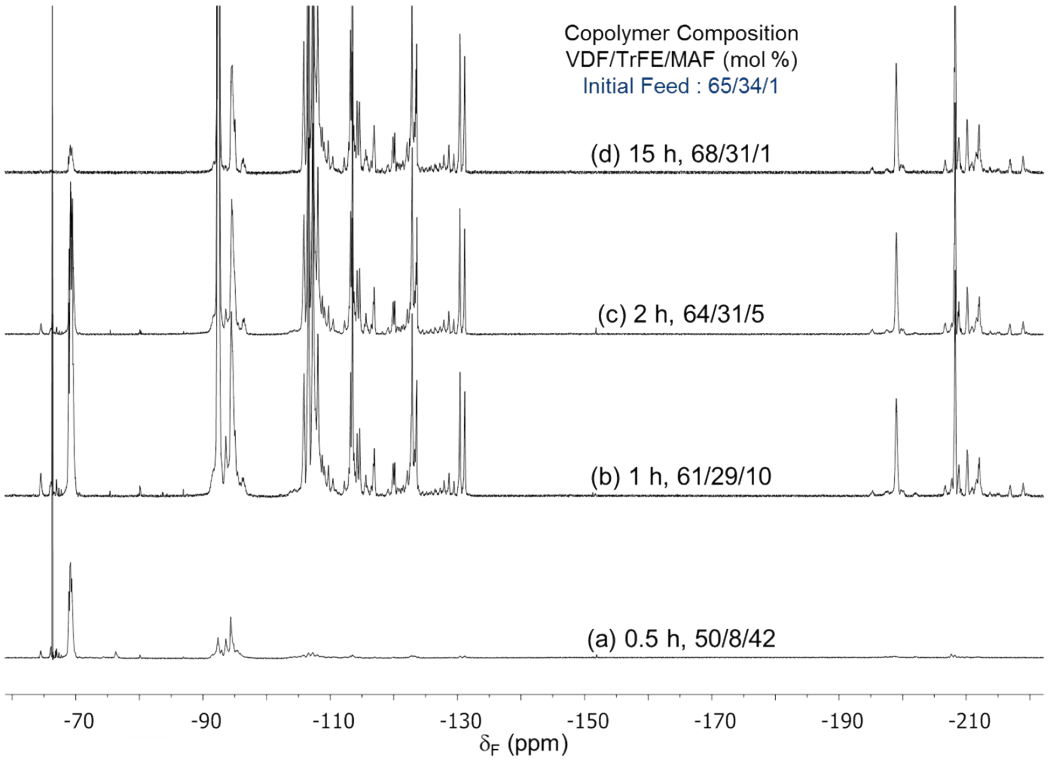

Figure S7. ^{19}F NMR spectra, recorded in $(CD_3)_2CO$, of poly(VDF-*ter*-TrFE-*ter*-MAF) samples taken from Run 5 (Table 1) at: (a) 0.5 h, (b) 1 h, (c) 1.5 h and (d) 14 h. Initial VDF/TrFE/MAF monomer composition in mol %: 65/34/1. Terpolymers VDF/TrFE/MAF compositions in mol %: (a) 50/8/42, (b) 61/29/10, (c) 64/31/5, (d) 68/31/1.

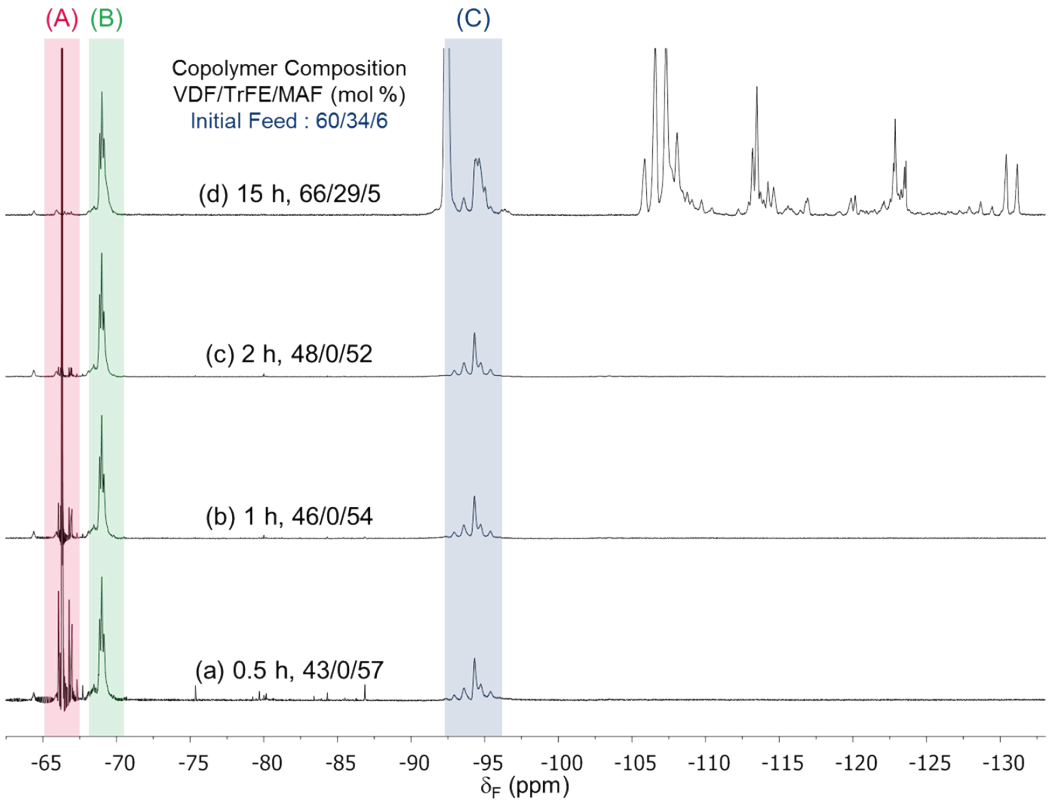

Figure S8. ^{19}F NMR spectra, recorded in $(CD_3)_2CO$, of poly(VDF-*ter*-TrFE-*ter*-MAF) samples taken from Run 8 (Table 1) at: (a) 0.5 h, (b) 1 h, (c) 2 h and (d) 15 h. C**F**$_3$ of residual MAF monomer, C**F**$_3$ of copolymerized MAF, C**F**$_2$ of VDF in VDF-MAF alternating structure are highlighted in red (A), green (B) and blue (C), respectively. Initial VDF/TrFE/MAF monomer composition in mol %: 60/34/6. Terpolymers VDF/TrFE/MAF compositions in mol %: (a) 43/0/57, (b) 46/0/54, (c) 48/0/52, (d) 66/29/5. The corresponding pressure profile is represented in Figure S7.

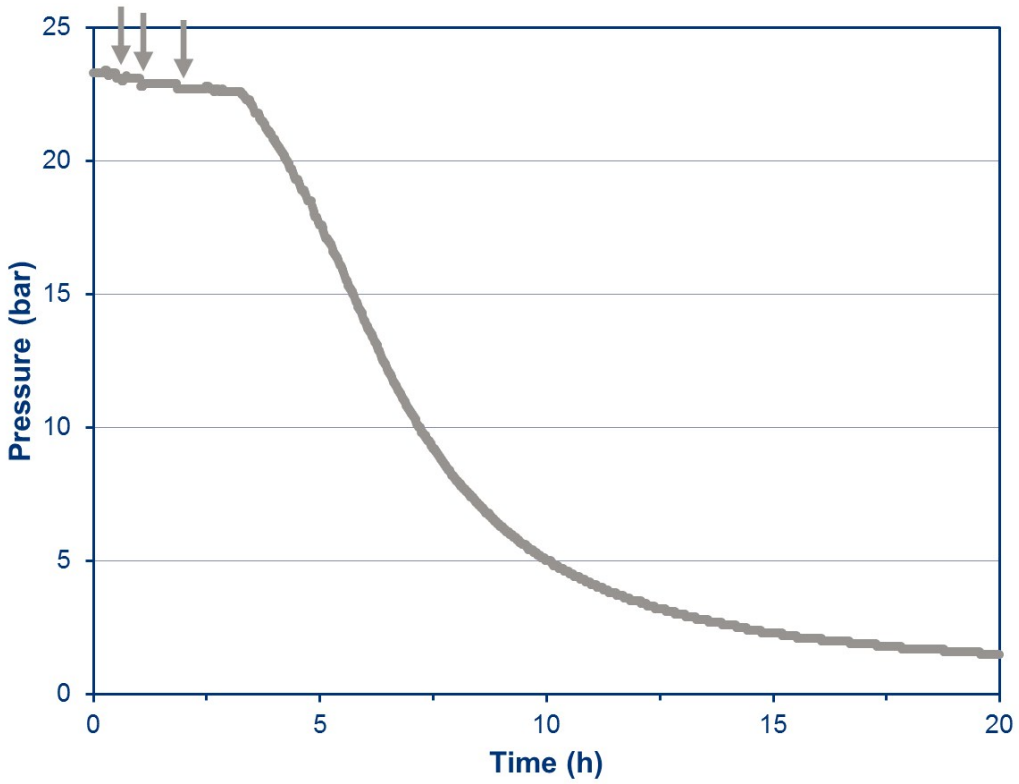

Figure S9. Pressure evolution *versus* reaction time during the radical terpolymerization of VDF, TrFE and MAF starting from a 64/34/6 mol % initial monomer feed (Run 8, Table 1). Arrows indicate when samples were taken off the reaction solution to determine the terpolymers' compositions by ^{19}F NMR spectroscopy.

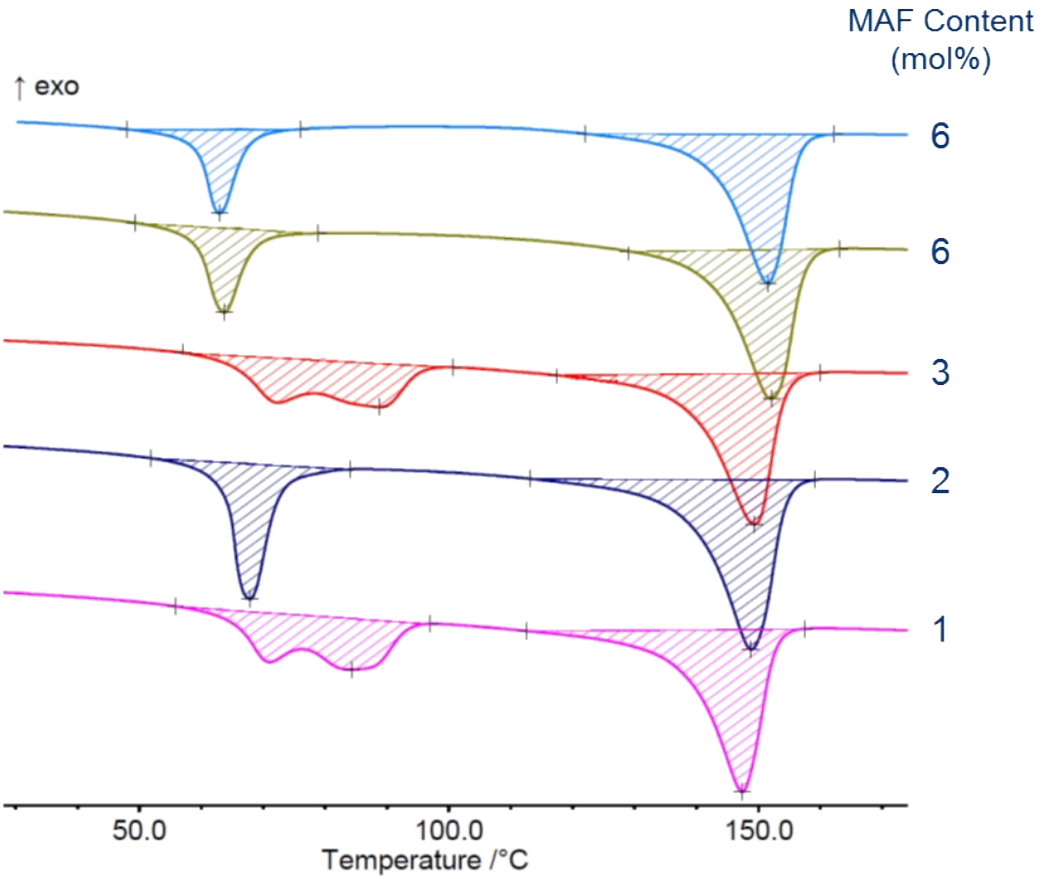

Figure S10. Second heating DSC thermograms of poly(VDF-*ter*-TrFE-*ter*-MAF) terpolymers prepared by batch solution polymerization with increasing MAF content ranging from 1 to 6 mol % (Runs 5-7, 9 and 10; Table 1)