

One-pot Synthesis of Poly(Vinylidene Fluoride)Methacrylate Macromonomer via *thia-* Michael addition

Marc Guerre,^a Bruno Ameduri,^a Vincent LADMIRAL^{t,}*

SUPPORTING INFORMATION

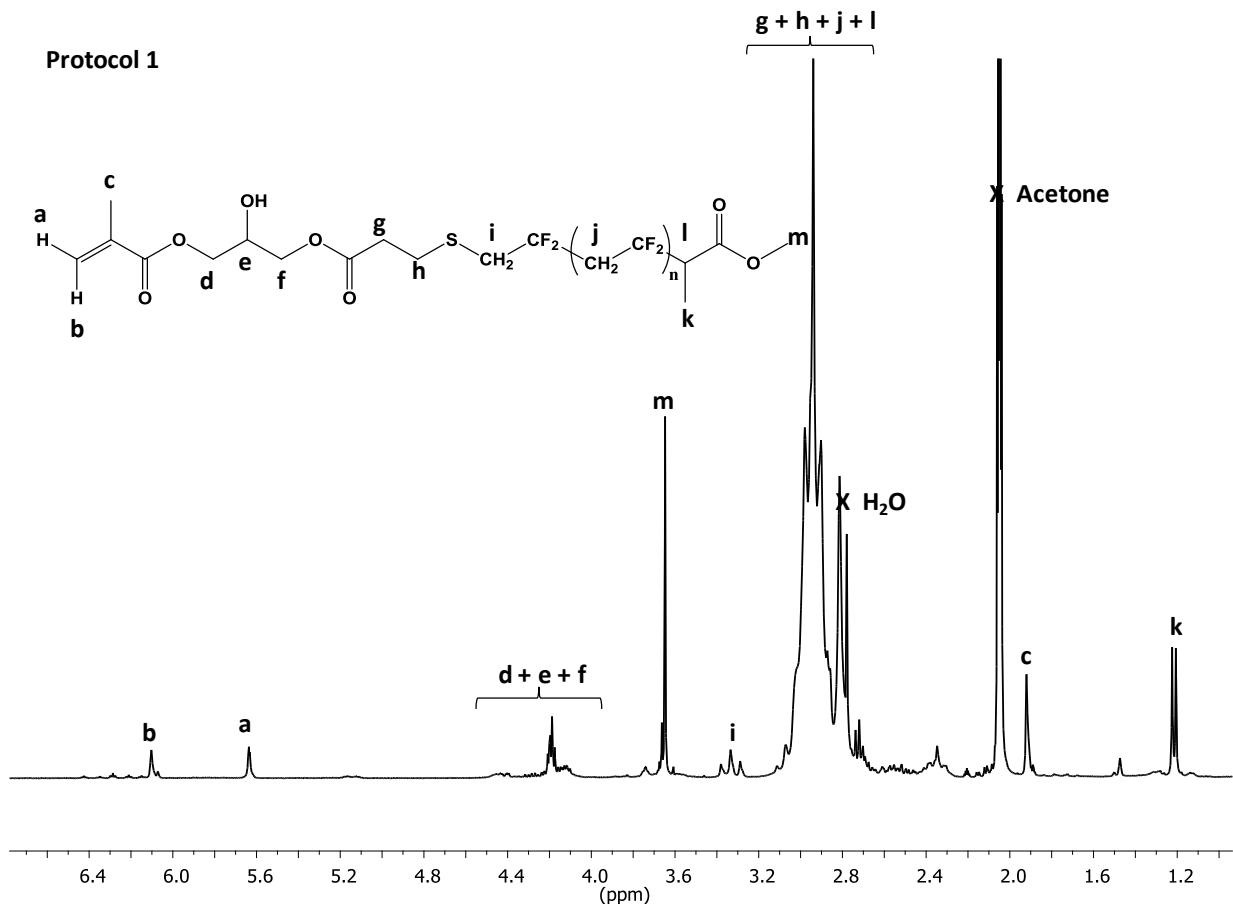


Figure S1. ^1H NMR spectrum (with signal assignment) in $(\text{CD}_3)_2\text{CO}$ of PVDF-MA macromonomer synthesized using protocol 1.

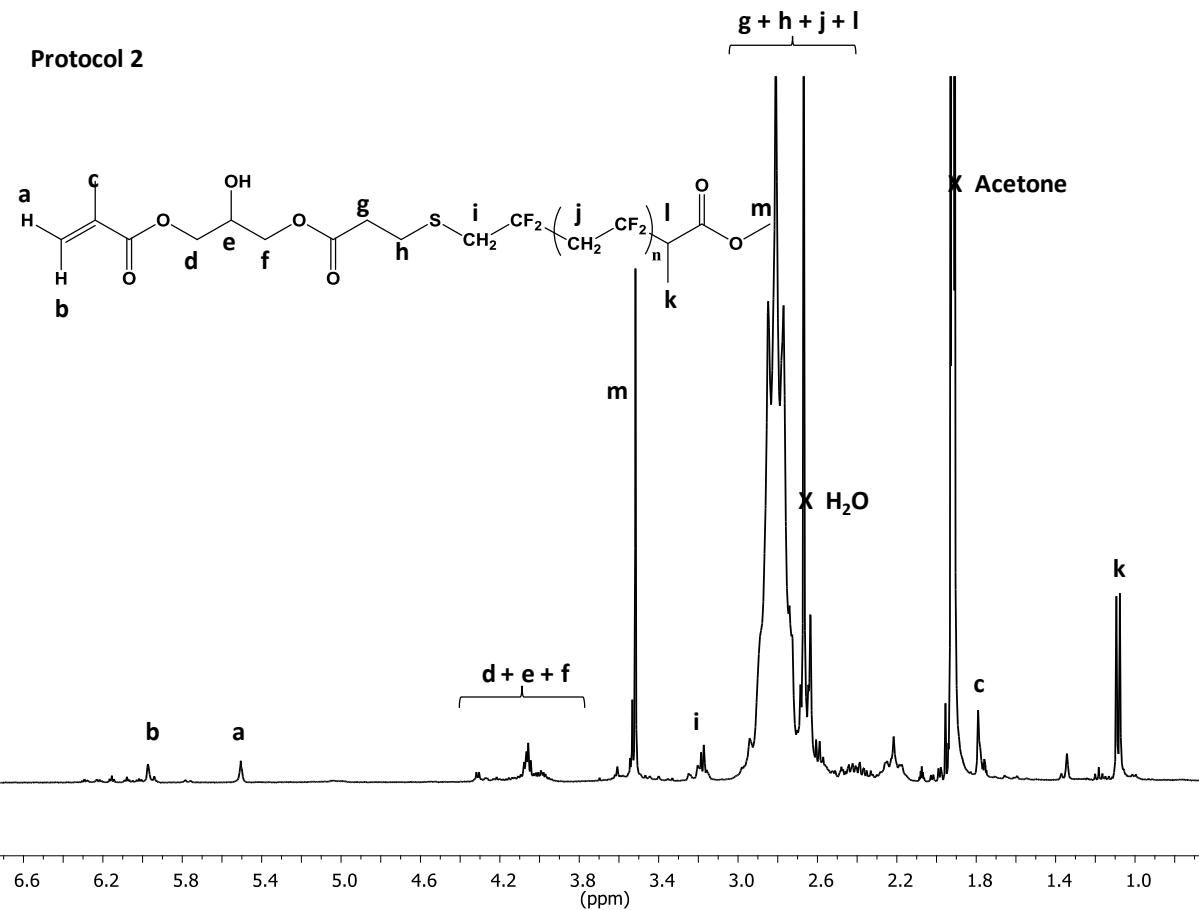


Figure S2. ^1H NMR spectrum (with signal assignments) in $(\text{CD}_3)_2\text{CO}$ the PVDF-MA macromonomer synthesized using protocol 2.

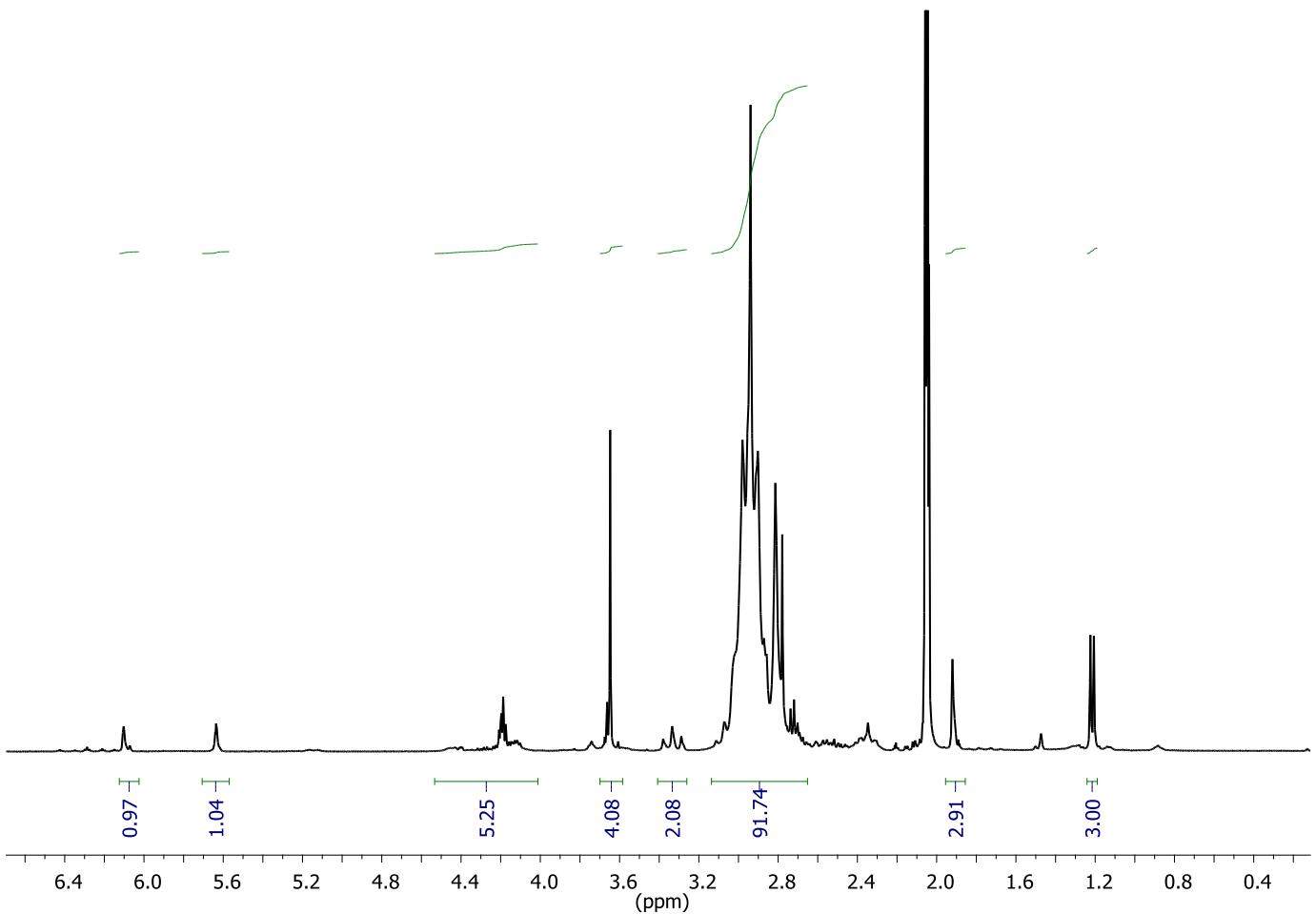


Figure S3. Integration of the ^1H NMR spectrum signals of the PVDF-MA synthesized using protocol 1.

$$\begin{aligned}
 \text{Assessment of Functionality (\%)} &= \frac{\int_{6.04}^{6.13}(\text{H}) + \int_{5.56}^{5.68}(\text{H}) + \int_{1.86}^{1.96}(\text{CH}_3)}{\frac{5}{3} \int_{1.18}^{1.25}(\text{CH}_3)} \times \alpha \\
 &= \frac{0.97 + 1.04 + 2.91}{\frac{5}{3} \times 3.00} \times 0.86 = 85\%
 \end{aligned}$$

$$\begin{aligned}
 \text{Determination of Coupling efficiency (\%)} &= \frac{\int_{6.04}^{6.13}(\text{H}) + \int_{5.56}^{5.68}(\text{H}) + \int_{1.86}^{1.96}(\text{CH}_3)}{\frac{5}{3} \int_{1.18}^{1.25}(\text{CH}_3)} \\
 &= \frac{0.97 + 1.04 + 2.91}{\frac{5}{3} \times 3.00} = 99\%
 \end{aligned}$$

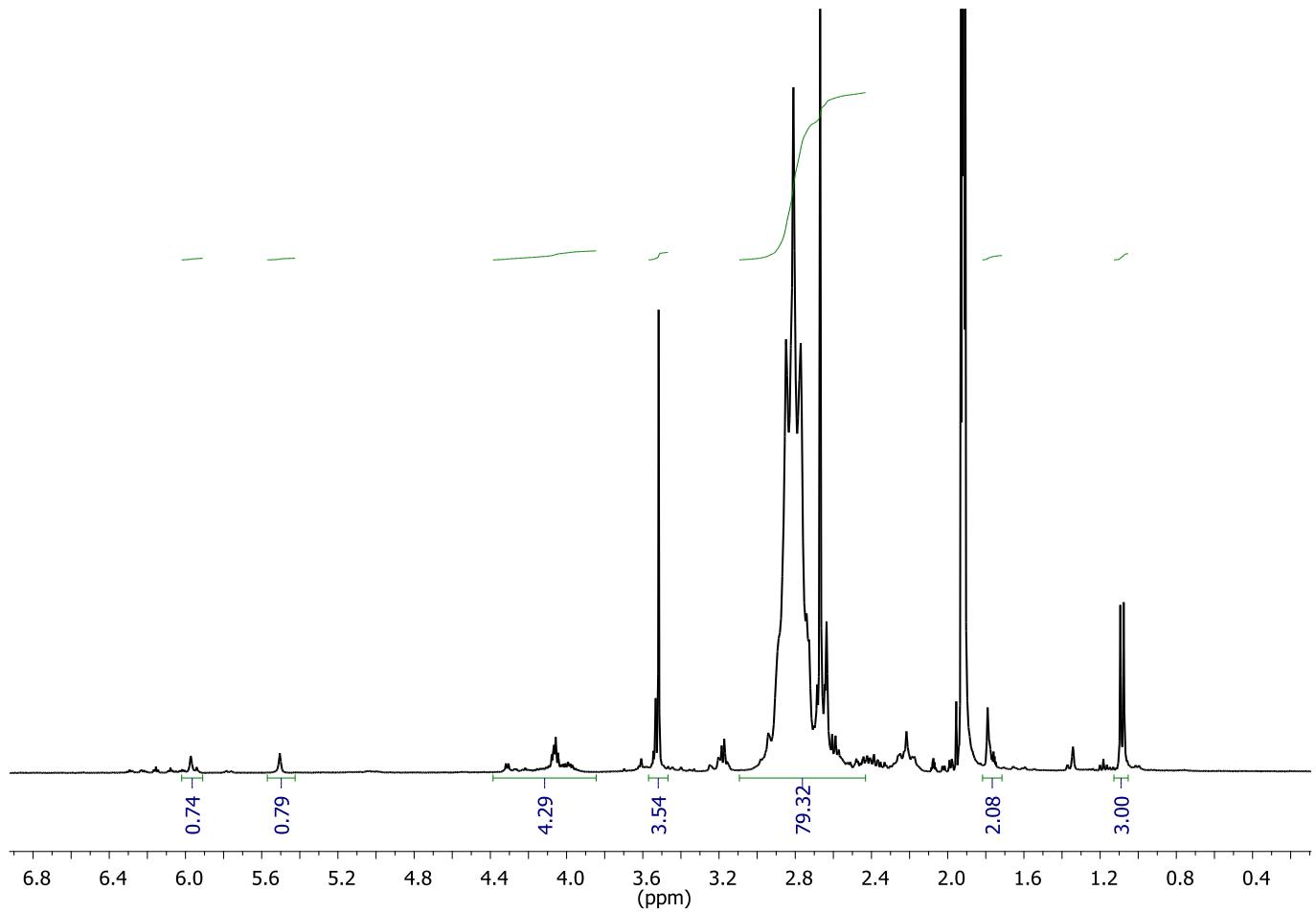


Figure S4. Integration of the ^1H NMR spectrum signals of the PVDF-MA synthesized using protocol 2.

$$\text{Assessment of Functionality (\%)} = \frac{\int_{6.04}^{6.13}(\text{H}) + \int_{5.56}^{5.68}(\text{H}) + \int_{1.86}^{1.96}(\text{CH}_3)}{\frac{5}{3} \int_{1.18}^{1.25}(\text{CH}_3)} \times \alpha$$

$$= \frac{0.74 + 0.79 + 2.08}{\frac{5}{3} \times 3.00} \times 0.86 = 62 \%$$

$$\begin{aligned} \text{Determination of Coupling efficiency (\%)} &= \frac{\int_{6.04}^{6.13}(\text{H}) + \int_{5.56}^{5.68}(\text{H}) + \int_{1.86}^{1.96}(\text{CH}_3)}{\frac{5}{3} \int_{1.18}^{1.25}(\text{CH}_3)} \\ &= \frac{0.74 + 0.79 + 2.08}{\frac{5}{3} \times 3.00} \times 0.86 = 72 \% \end{aligned}$$

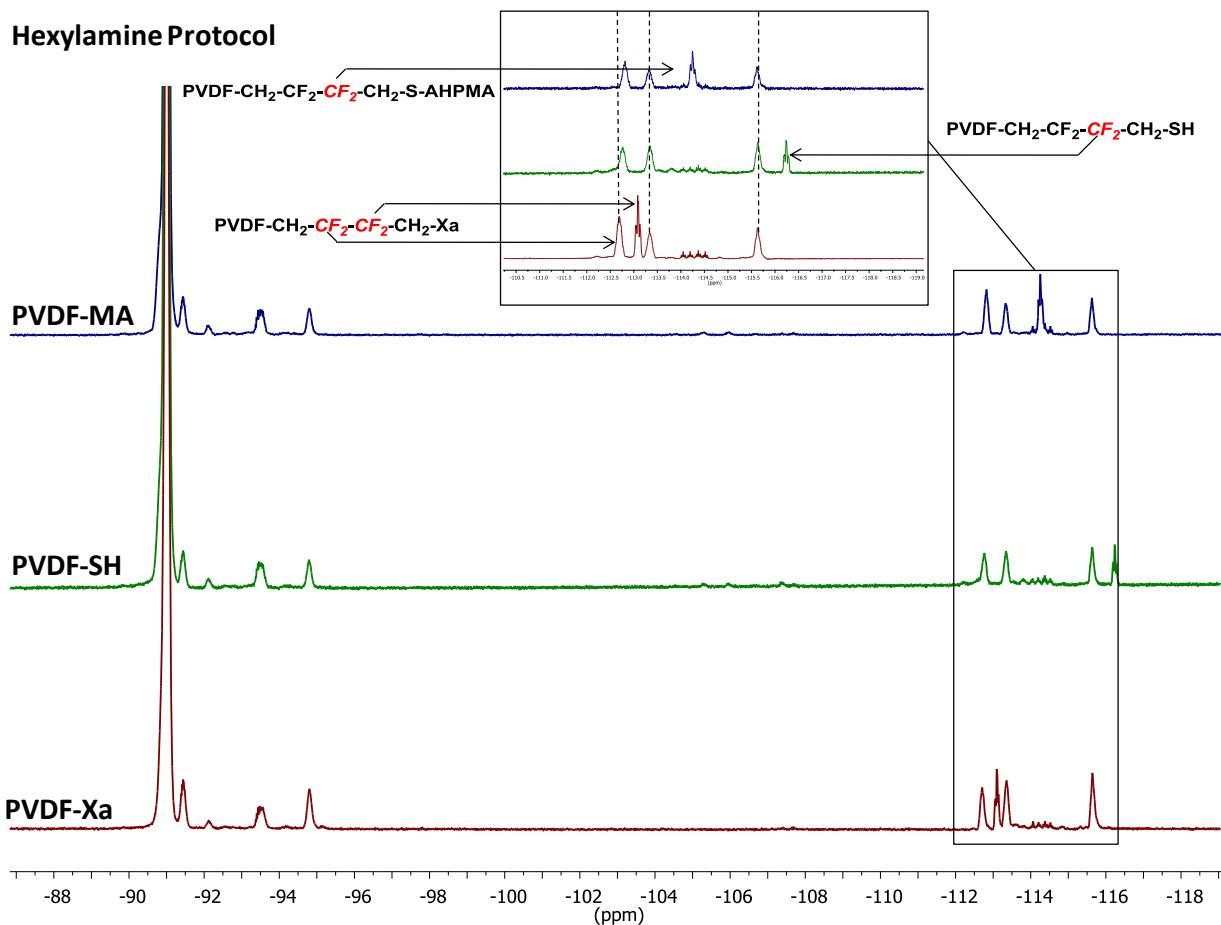


Figure S5. ^{19}F NMR spectra in $(\text{CD}_3)_2\text{CO}$ of: PVDF-XA, PVDF-SH synthesized via aminolysis using hexylamine, and of PVDF-MA prepared following protocol 1.

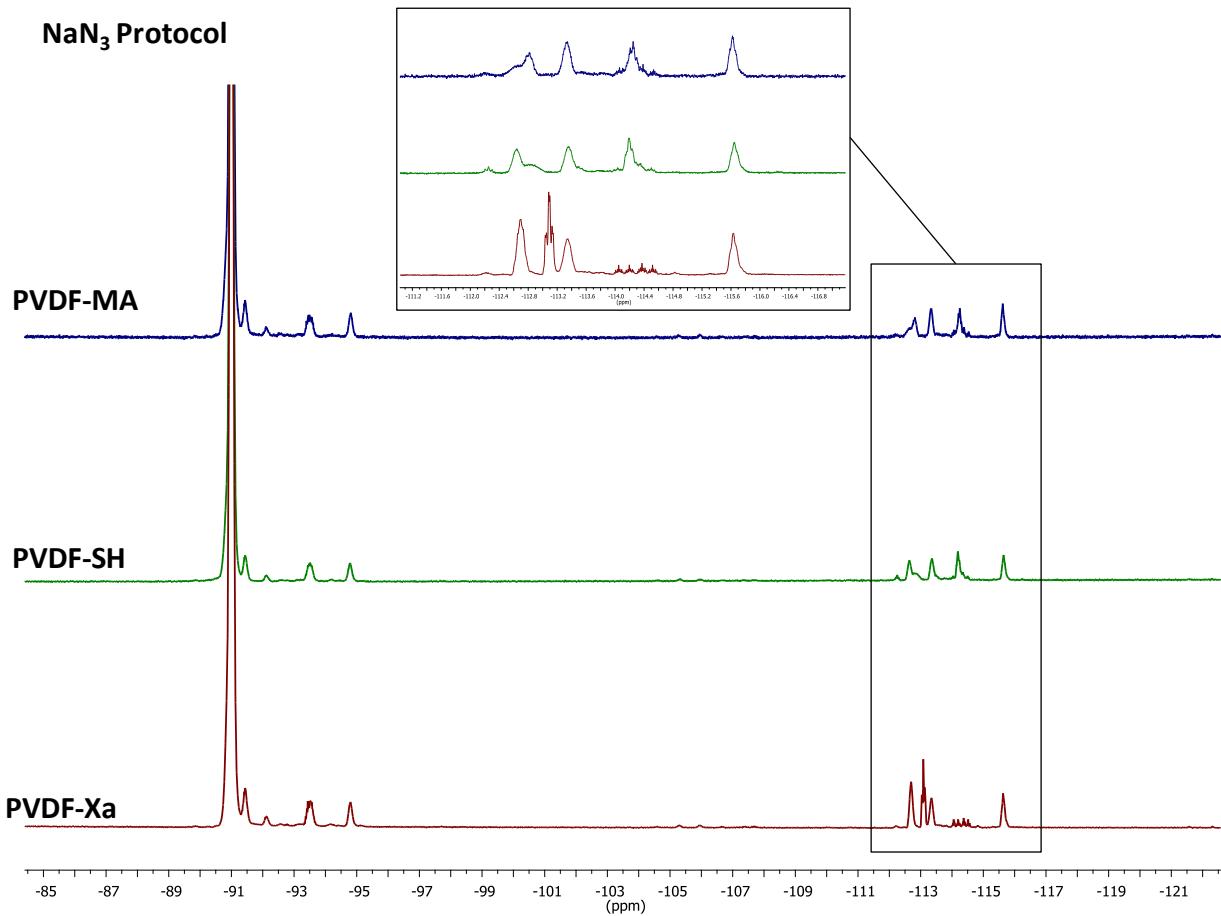


Figure S6. ¹⁹F NMR spectra in (CD₃)CO of: PVDF-XA, PVDF-SH synthesized using NaN₃ as end-group removal agent, and of PVDF-MA prepared following protocol 2.

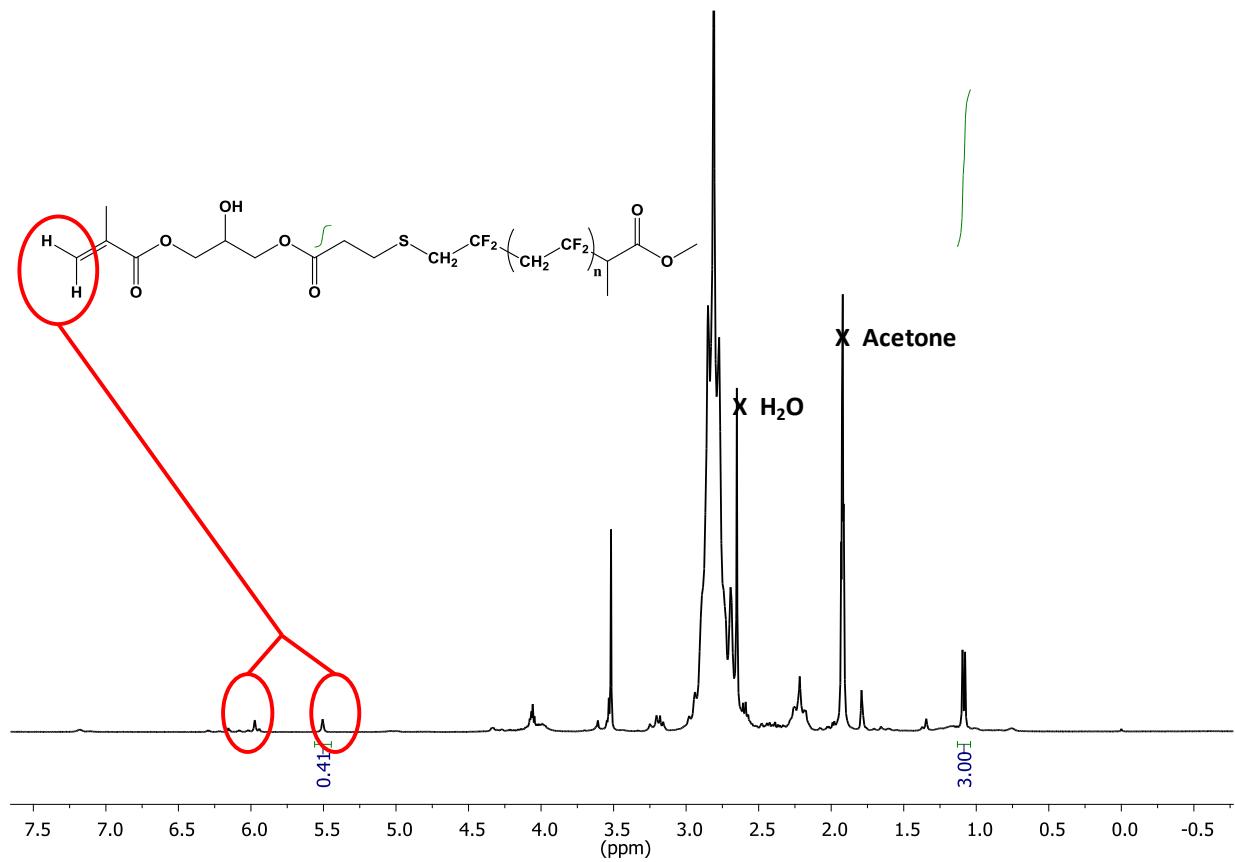


Figure S7. ^1H NMR spectrum in $(\text{CD}_3)_2\text{CO}$ of PVDF-MA homopolymer prepared by RAFT polymerization.

$$\text{Conversion} = 1 - \frac{\int_{5.60}^{5.68} \text{HCH}=\text{C(CH}_3\text{)} \text{ Methacrylate end group}}{\frac{1}{3} \times \int_{1.19}^{1.24} \text{CH}_3-\text{CH R CTA end group}} = 1 - \frac{0.41}{\frac{1}{3} \times 3.00} = 59 \%$$

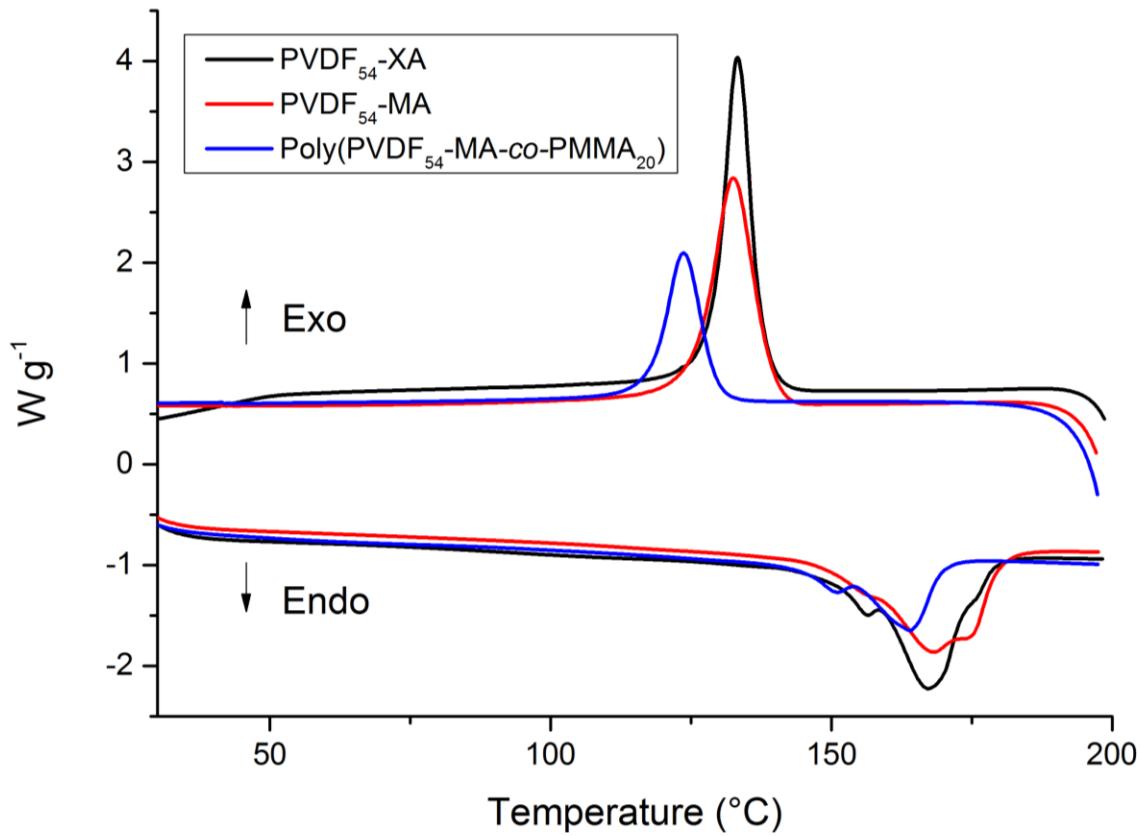


Figure S8. DSC thermogram for PVDF-XA, PVDF-MA synthesized using Protocol 1 and poly(PVDF-MA-*co*-MMA) copolymer.