Electronic Supplementary Information

Towards New Strategies for the Synthesis of Functional Vinylidene Fluoride-based Copolymers with Tunable Wettability

Sanjib Banerjee, Thibaut Soulestin, Yogesh Patil, Vincent Ladmiral and Bruno Ameduri*

Ingénierie et Architectures Macromoléculaires, Institut Charles Gerhardt, UMR 5253 CNRS, UM, ENSCM, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

*Corresponding Author: E-mail: Bruno.ameduri@enscm.fr (B. Ameduri)
Scheme S1. Chemical Structures of the Initiators
Figure S1. Stack plot of $^1$H NMR spectra of [MAF + D$_2$O] at every 22-23 minutes up to 16 h 18 min at 48 °C in D$_2$O.
Figure S2. Stack plots of $^{19}$F NMR spectra of [MAF + D$_2$O] at every 22-23 min up to 16 h 18 min at 48 °C in D$_2$O.
Figure S3. Comparison of $^1$H NMR spectra, recorded in $\text{D}_2\text{O}$ at 20 °C, of the product obtained by reaction of MAF with $\text{D}_2\text{O}$ (upper spectrum) and $\text{H}_2\text{O}$ (lower spectrum).
**Figure S4.** Representative $^1$H NMR spectrum of poly(VDF-co-MAF) copolymer prepared by free radical copolymerization of VDF and MAF using bis(4-tert-butyl cyclohexyl) peroxycarbonate (BTBCP) in 1,1,1,3,3-pentafluorobutane/actonitrile (50:50) at 60 °C (entry 1, Table 1), recorded in acetone-$d_6$ at 20 °C. (*) Solvent (acetone) peak.
Figure S5. Representative $^{19}$F NMR spectrum of poly(VDF-$co$-MAF) copolymer prepared by free radical copolymerization of VDF and MAF using bis(4-tert-butyl cyclohexyl) peroxycarbonate (BTBCP) in 1,1,1,3,3-pentafluorobutane/actonitrile (50:50) at 60 °C (entry 1, Table 1), recorded in acetone-$d_6$ at 20 °C.
Figure S6. $^1$H NMR spectra of MAF-TBE and [MAF-TBE + H$_2$O] (MAF-TBE: H$_2$O = 1:57) after heating at 74 °C for 24 h, recorded in acetone-$d_6$ at 20 °C. (*) Solvent (acetone) peak.
Figure S7. $^{19}$F NMR spectra of MAF-TBE and [MAF-TBE + H$_2$O] (MAF-TBE: H$_2$O = 1:57) after heating at 74 °C for 24 h, recorded in acetone-$d_6$ at 20 °C.
Figure S8. $^1$H NMR spectra of APFO and [MAF-TBE + APFO + H$_2$O] (MAF-TBE: H$_2$O = 1:57, using 2% aqueous solution of APFO) after heating at 74 °C for 60 h, recorded in acetone-$d_6$ at 20 °C. (*) Solvent (acetone) peak.
Figure S9. $^{19}$F NMR spectra of APFO and [MAF-TBE + APFO + H$_2$O] (MAF-TBE: H$_2$O = 1:57, using 2% aqueous solution of APFO) after heating at 74 °C for 60 h, recorded in acetone-$d_6$ at 20 °C.
Figure S10. SEC traces of poly(VDF-co-MAF-TBE) copolymers prepared by free radical copolymerization of VDF and MAF-TBE (see entries 9-15, Table 1 for polymerization conditions and molecular characterization data). As the detector is refractive index (RI) and because fluoropolymer has lower RI compared to the eluent, the SEC signal is negative.
Figure S11. Representative $^1$H NMR spectrum of poly(VDF-$co$-MAF-TBE) copolymer prepared by free radical copolymerization of VDF and MAF-TBE using perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical (PPFR) in dimethyl carbonate at 90 °C (entry 14, Table 1), recorded in acetone-$d_6$ 20 °C. (*) Solvent (acetone) peak.
Figure S12. Representative $^{19}$F NMR spectrum of poly(VDF-co-MAF-TBE) copolymer prepared by free radical copolymerization of VDF and MAF-TBE using perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical (PPFR) in dimethyl carbonate at 90 °C (entry 14, Table 1), recorded in acetone-$d_6$ at 20 °C.
Figure S13. $^1$H NMR spectra showing the effect of water, with respect to the solvent mixture (at various dimethyl carbonate (DMC)/H$_2$O ratio), on the chain transfer to DMC (see entries 11-13, Table 1 for the polymerization conditions), recorded in acetone-$d_6$ at 20 °C. The signals were normalized with respect to t-Bu signal of MAF-TBE in the copolymer, considering the fact that these three copolymers have the same VDF content.
Figure S14. $^1$H-$^{13}$C HSQC NMR spectrum of poly(VDF-co-MAF-TBE) copolymer, recorded in acetone-$d_6$ at 20 °C. The correlation of -CH$_2$ methylene group in MAF-TBE is highlighted with the black lines and the -CH$_3$ of reinitiating dimethyl carbonate radical is evidenced by the dashed line.
Figure S15. $^1$H-$^{13}$C HMBC NMR spectrum of poly(VDF-$co$-MAF-TBE) copolymer, recorded in acetone-$d_6$ at 20 °C. The methylene group correlations of MAF-TBE are highlighted with the black lines and the correlation of -CH$_3$ with C=O of reinitiating dimethyl carbonate radical is evidenced by the dashed line.
Figure S16. $^1$H NMR spectra of poly(VDF-co-MAF-TBE) copolymer (entry 10, Table 1) before and after hydrolysis, recorded in acetone-$d_6$ at 20 °C. The evolution of the signal attributed to the tert-butyl ester groups is highlighted. (*) Solvent (acetone) peak.
Figure S17. DSC thermogram of poly(VDF-co-MAF-TBE) copolymer (entry 10, Table 1).
Figure S18. ATR-IR spectra of pure PVDF (black line), poly(VDF-co-MAF-TBE) copolymer before hydrolysis (red line) and poly(VDF-co-MAF-TBE) copolymer after hydrolysis 92% (blue line). ATR-IR spectra of pure PVDF (black line), poly(VDF-co-MAF-TBE) copolymer before hydrolysis (red line) and poly(VDF-co-MAF-TBE) copolymer after hydrolysis (blue line). The square regions highlight the absence of sharp vibrations bands at 850 and 1290 cm\(^{-1}\) characteristic of the all-trans conformation of the \(\beta\)-phase of PVDF crystals and arrow (pointing up) highlight the presence at 1380 cm\(^{-1}\) of a vibration band characteristic of the \(\alpha\)-phase of PVDF crystals.