## **Electronic Supplementary Information**

## Towards New Strategies for the Synthesis of Functional Vinylidene

## Fluoride-based Copolymers with Tunable Wettability

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Bis[4-(tert-butyl)cyclohexyl)] peroxydicarbonate (BTBCP)



Perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent perfluoroalkyl branched radical (PPFR)



Tert-amyl peroxy-2-ethylhexanoate (Trogonox 121)

↓<sup>N</sup>×<sub>N</sub>↑ ~0 `0

2,2'-azo-bis(4-methoxy-2,4-dimethyl valeronitrile) (V-70)

Scheme S1. Chemical Structures of the Initiators



**Figure S1.** Stack plot of <sup>1</sup>H NMR spectra of  $[MAF + D_2O]$  at every 22-23 minutes up to 16 h 18 min at 48 °C in D<sub>2</sub>O.



**Figure S2.** Stack plots of <sup>19</sup>F NMR spectra of  $[MAF + D_2O]$  at every 22-23 min up to 16 h 18 min at 48 °C in D<sub>2</sub>O.



**Figure S3.** Comparison of <sup>1</sup>H NMR spectra, recorded in  $D_2O$  at 20 °C, of the product obtained by reaction of MAF with  $D_2O$  (upper spectrum) and  $H_2O$  (lower spectrum).



**Figure S4.** Representative <sup>1</sup>H NMR spectrum of poly(VDF-*co*-MAF) copolymer prepared by free radical copolymerization of VDF and MAF using bis(4-*tert*-butyl cyclohexyl) peroxydicarbonate (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 <sup>19</sup>F NMR spectrum of poly(VDF-*co*-MAF) copolymer prepared by free radical copolymerization of VDF and MAF using bis(4-*tert*-butyl cyclohexyl) peroxydicarbonate (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.** <sup>1</sup>H NMR spectra of MAF-TBE and [MAF-TBE + H<sub>2</sub>O] (MAF-TBE: H<sub>2</sub>O = 1:57) after heating at 74 °C for 24 h, recorded in acetone- $d_6$  at 20 °C. (\*) Solvent (acetone) peak.



**Figure S7.** <sup>19</sup>F NMR spectra of MAF-TBE and [MAF-TBE + H<sub>2</sub>O] (MAF-TBE: H<sub>2</sub>O = 1:57) after heating at 74 °C for 24 h, recorded in acetone- $d_6$  at 20 °C.



**Figure S8.** <sup>1</sup>H NMR spectra of APFO and [MAF-TBE + APFO + H<sub>2</sub>O] (MAF-TBE: H<sub>2</sub>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.** <sup>19</sup>F NMR spectra of APFO and [MAF-TBE + APFO + H<sub>2</sub>O] (MAF-TBE: H<sub>2</sub>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 <sup>1</sup>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-3pentyl 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 <sup>19</sup>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.** <sup>1</sup>H NMR spectra showing the effect of water, with respect to the solvent mixture (at various dimethyl carbonate (DMC)/H<sub>2</sub>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.** <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectrum of poly(VDF-*co*-MAF-TBE) copolymer, recorded in acetone- $d_6$  at 20 °C. The correlation of -CH<sub>2</sub> methylene group in MAF-TBE is highlighted with the black lines and the -CH<sub>3</sub> of reinitiating dimethyl carbonate radical is evidenced by the dashed line.



**Figure S15.** <sup>1</sup>H-<sup>13</sup>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<sub>3</sub> with C=O of reinitiating dimethyl carbonate radical is evidenced by the dashed line.



**Figure S16**. <sup>1</sup>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<sup>-1</sup> characteristic of the all-trans conformation of the  $\beta$ -phase of PVDF crystals and arrow (pointing up) highlight the presence at 1380 cm<sup>-1</sup> of a vibration band characteristic of the  $\alpha$ -phase of PVDF crystals.