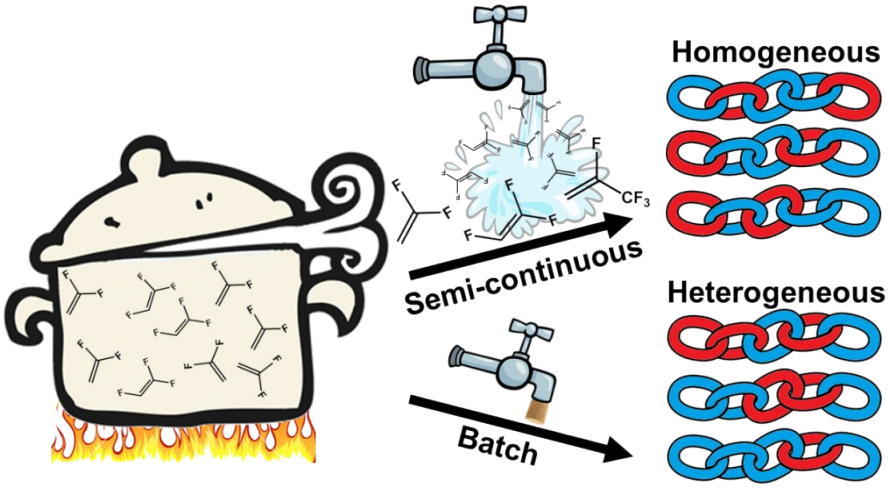
Differences in Electroactive Terpolymers Based on VDF, TrFE and 2,3,3,3-tetrafluoropropene Prepared by Batch Solution and Semi-continuous Aqueous Suspension Polymerizations.

Thibaut Soulestin,[a, b] *Vincent Ladmiral,*[a] *Thierry Lannuzel,*[b] *Fabrice Domingues Dos Santos,*[b] *Bruno Améduri*[a]*

[a]Institut Charles Gerhardt, UMR 5253 CNRS, ENSCM, UM. Ingénierie et Architectures Macromoléculaires (IAM). 8, rue de l'Ecole Normale, 34296 Montpellier, Cedex 5, France.

[b]Piezotech S.A.S., Arkema - CRRA, rue Henri-Moissan, 69493 Pierre-Bénite, Cedex, France.



For Table of Contents use only

Table S1. Assignments of ^{19}F NMR signals for poly(VDF-*ter*-TrFE-*ter*-1234yf) terpolymers. The CF_2 groups of VDF and TrFE, and the $CF(CF_3)$ group of 1234yf are labelled as the head (H). The CHF groups of TrFE, and the CH_2 groups of VDF and 1234yf are labelled as the tail (T)

Unit	3C Sequence	5C Sequence	Designation	Chemical Shift (ppm)
$\mathbf{CF_3}$	$CH_2CF(\mathbf{CF_3})CH_2$		1234yf-1234yf, H-T	-74 to -83
	$CH_2CF(\mathbf{CF_3})CHF$		1234yf-TrFE, H-T	
	$CH_2CF(\mathbf{CF_3})CH_2$		1234yf-VDF, H-T	-65 to -72
	$CH_2CF(\mathbf{CF_3})CF_2$		1234yf-VDF, H-H	
$\mathbf{CF_2}$	$CH_2\mathbf{CF_2}CH_2$	$CF_2CH_2\mathbf{CF_2}CH_2CF_2$	VDF-VDF, H-T	-92.4
		$CF_2CH_2\mathbf{CF_2}CH_2CF(CF_3)$	VDF-VDF-1234yf, H-T / H-T	-91.4 to -93.7
		$CH_2CH_2\mathbf{CF_2}CH_2CF_2$	VDF-VDF-VDF, T-T / H-T	-94.9 to -97.1
		$CHFCH_2\mathbf{CF_2}CH_2CF_2$	TrFE-VDF-VDF, H-T / H-T	-93.8 to -94.9
	$CH_2\mathbf{CF_2}CHF$	$CF(CF_3)CH_2\mathbf{CF_2}CHFCF_2$	1234yf-TrFE-TrFE, H-T / H-T	-103 to -112
		$CF_2CH_2\mathbf{CF_2}CHFCF_2$	VDF-TrFE H-T	-107.0
	$CH_2\mathbf{CF_2}CF_2$	$CH_2CH_2\mathbf{CF_2}CF_2CH_2$	VDF-VDF-VDF, T-T / H-H	-116.6
		$CF_2CH_2\mathbf{CF_2}CF_2CH_2$	VDF-VDF-VDF, H-T / H-H	-120.4
		$CF_2CH_2\mathbf{CF_2}CF_2CHF$	VDF-VDF-TrFE, H-T / H-H	-113.5
	$CHF\mathbf{CF_2}CHF$	$CF_2CHF\mathbf{CF_2}CHFCF_2$	TrFE-TrFE, H-T	-122.9
		$CH_2CHF\mathbf{CF_2}CHFCF_2$	VDF-TrFE-TrFE, T-T / H-T	-123.7
	$CHF\mathbf{CF_2}CF_2$	$CH_2CHF\mathbf{CF_2}CF_2CH_2$	TrFE-VDF, H-H	-130.4
$\mathbf{CF(CF_3)}$	$CH_2\mathbf{CF}(CF_3)CF_2$		1234yf-VDF	-163 to -172
	$CH_2\mathbf{CF}(CF_3)CH_2$			
	$CH_2\mathbf{CF}(CF_3)CHF$		1234yf-TrFE	-165 to -187
	$CH_2\mathbf{CF}(CF_3)CH_2$	$CF(CF_3)CH_2\mathbf{CF}(CF_3)CH_2CF(CF_3)$	1234yf-1234yf-1234yf, H-T / H-T	-171 to -180
$\mathbf{CHF}$	$CF(CF_3)\mathbf{CHF}CF_2$		1234yf-TrFE, H-T	-202 to -213
		$CHFCF_2\mathbf{CHF}CF_2CHF$	TrFE-TrFE, T-H	-210.1 to -212.1
	$CF_2\mathbf{CHF}CF_2$	$CF_2CF_2\mathbf{CHF}CF_2CHF$	TrFE-TrFE, H-H / T-H	-199.0
		$CH_2CF_2\mathbf{CHF}CF_2CH_2$	TrFE-VDF, T-H	-200.3
	$CF_2\mathbf{CHF}CHF$	$CF_2CF_2\mathbf{CHF}CHFCF_2$	VDF-TrFE-TrFE, H-H / T-T	-216.9 to -218.9

Reactivity Ratios Section

The **Mayo-Lewis law**[1] (ML) uses the following equation:

$$F_1 = \frac{r_1 f_1^2 + f_1(1-f_1)}{r_1 f_1^2 + 2f_1(1-f_1) + r_2(1-f_1)^2}$$

where, f_1 and F_1 are the instantaneous composition in monomer 1 in the feed and in the copolymer, respectively.

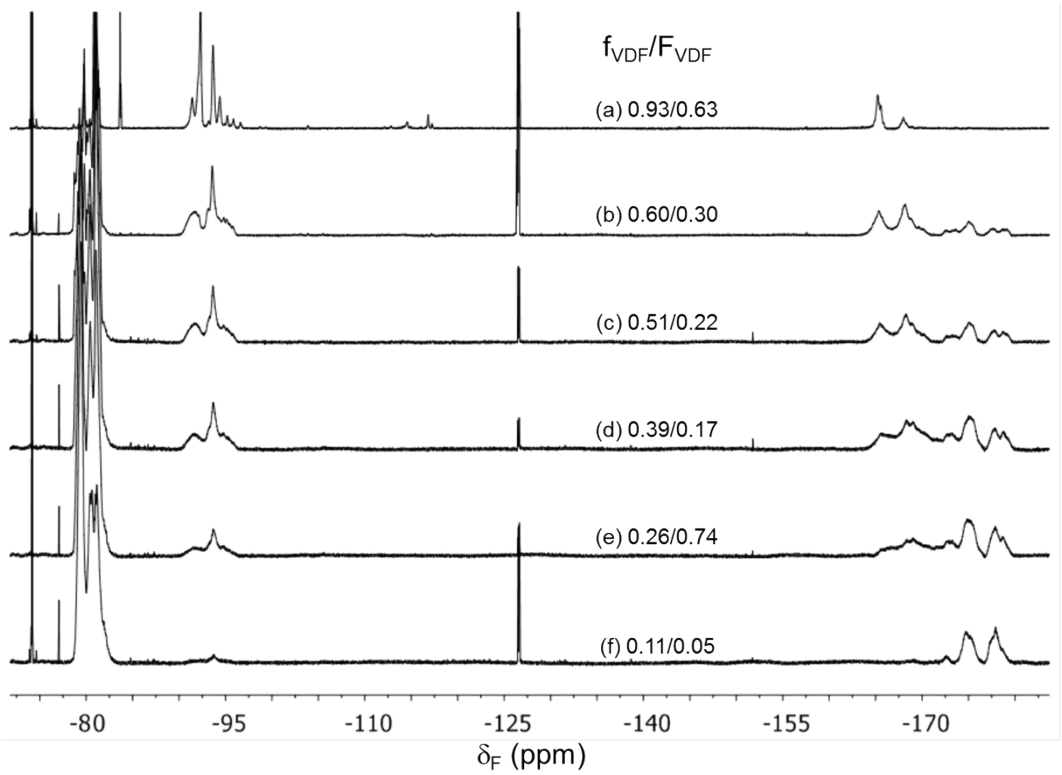


Figure S1. ^{19}F NMR spectra recorded at 25 °C in $(CD_3)_2CO$ of six poly(VDF-*co*-1234yf) copolymers. The polymerizations were stopped at low monomer conversion (<10 %) .

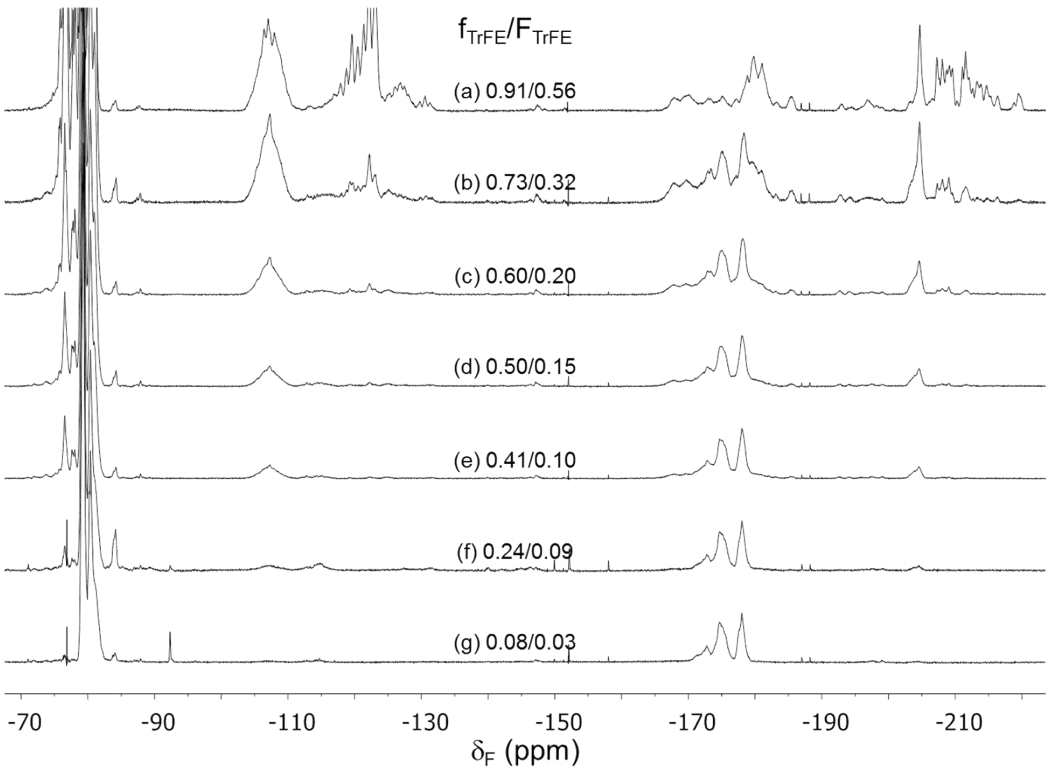


Figure S2. ^{19}F NMR spectra recorded at 25 °C in $(CD_3)_2CO$ of seven poly(TrFE-*co*-1234yf) copolymers. The polymerization were stopped at low monomer conversion (<10 %).

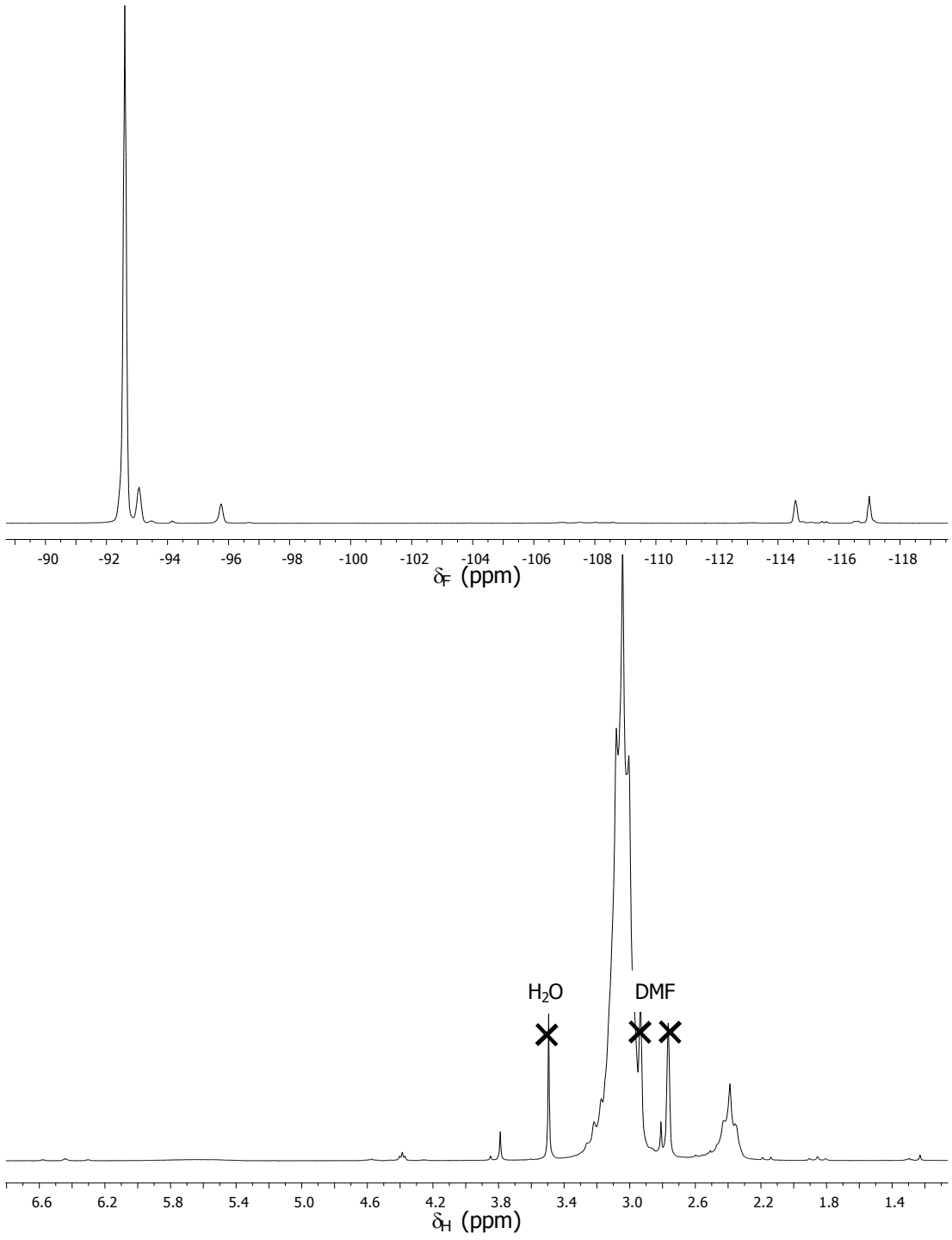


Figure S3. ^{19}F (top) and ^{1}H (bottom) NMR spectra in $DCON(CD_3)_2$ of a PVDF homopolymer (Run 1, Table 2).

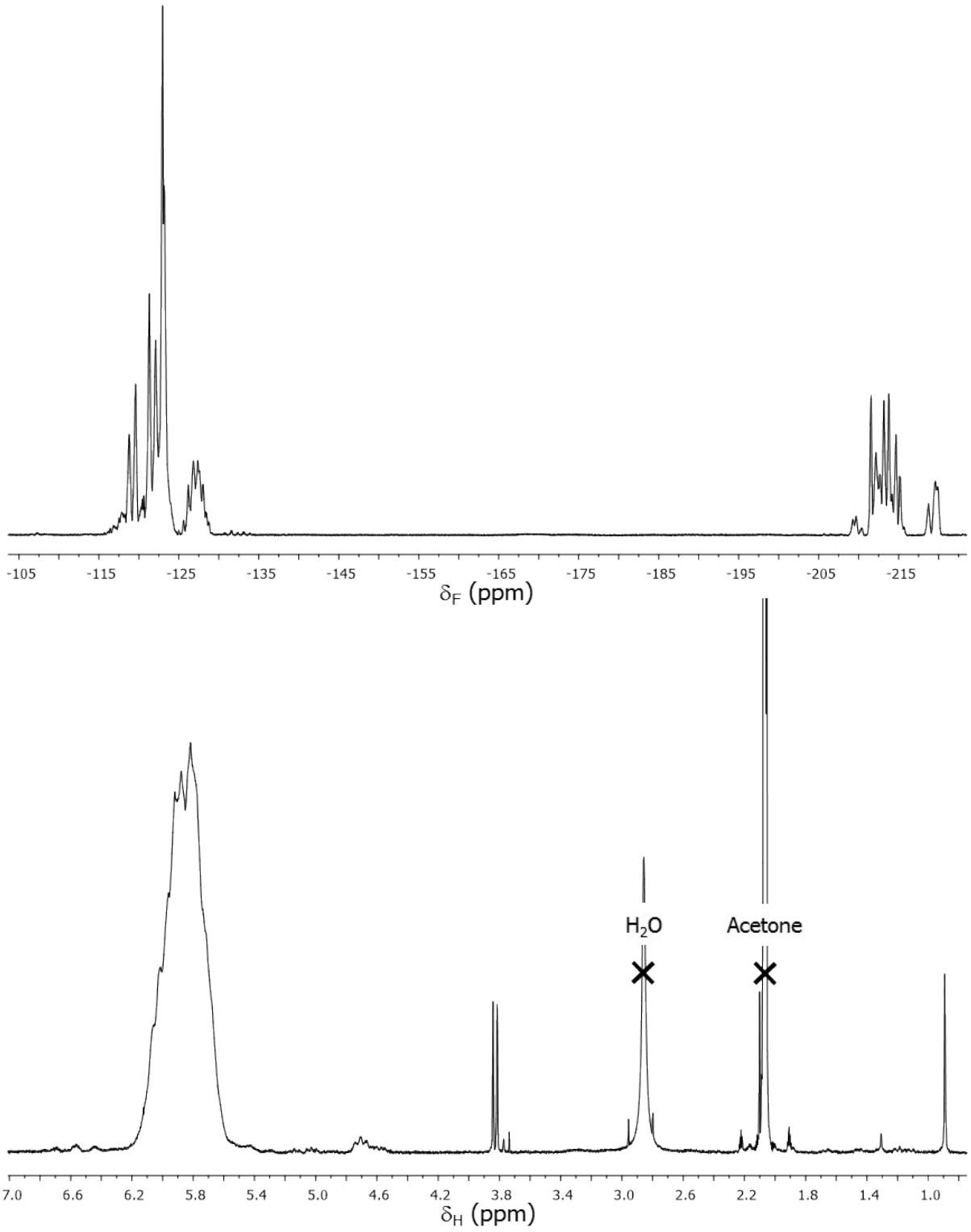


Figure S4. ^{19}F (top) and ^{1}H (bottom) NMR spectra in $(CD_3)_2CO$ of a PTrFE homopolymer (Run 2, Table 2).

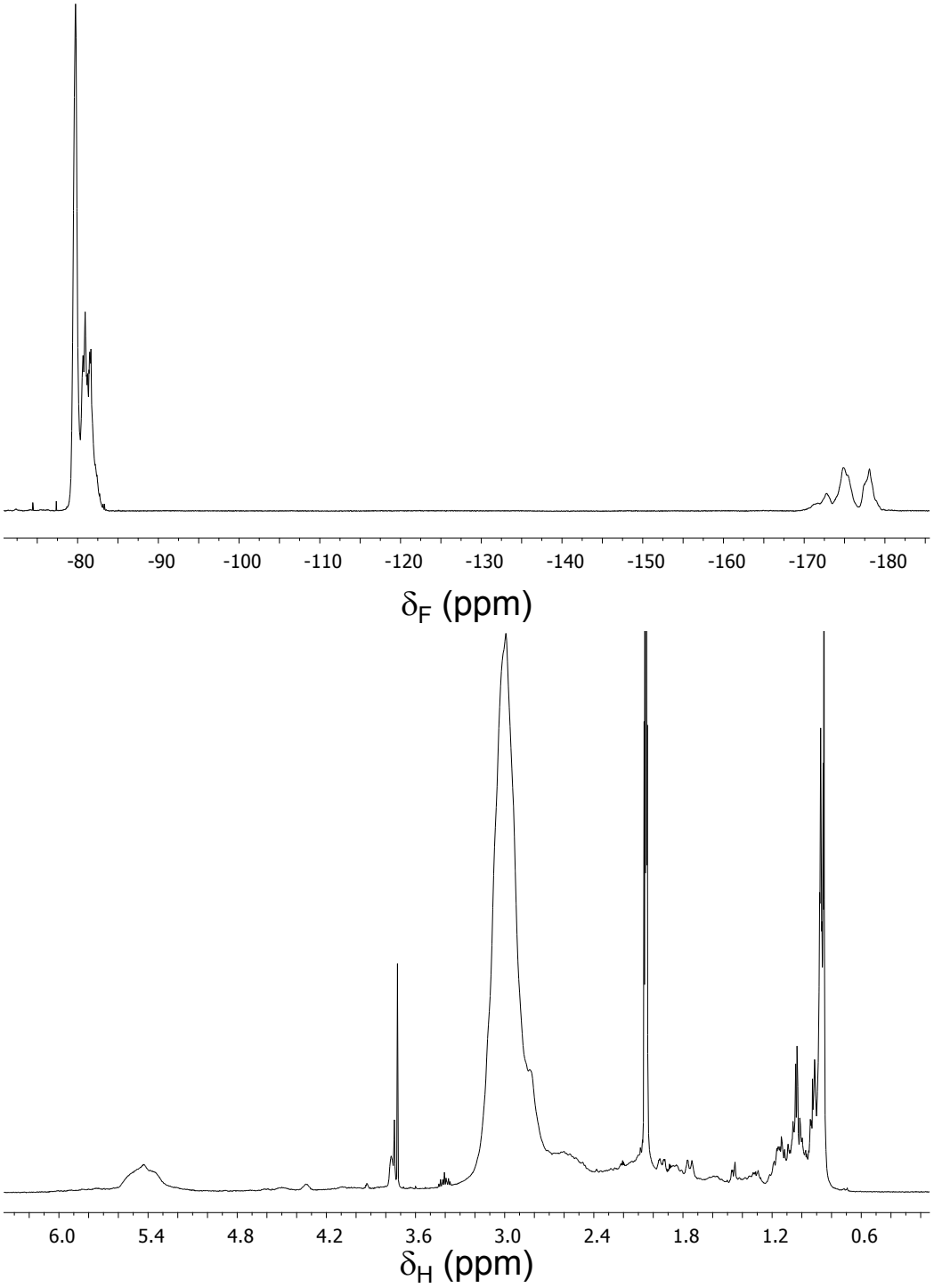


Figure S5. ^{19}F (top) and ^{1}H (bottom) NMR spectra in $(CD_3)_2CO$ of a P1234yf homopolymer (Run 3, Table 2).

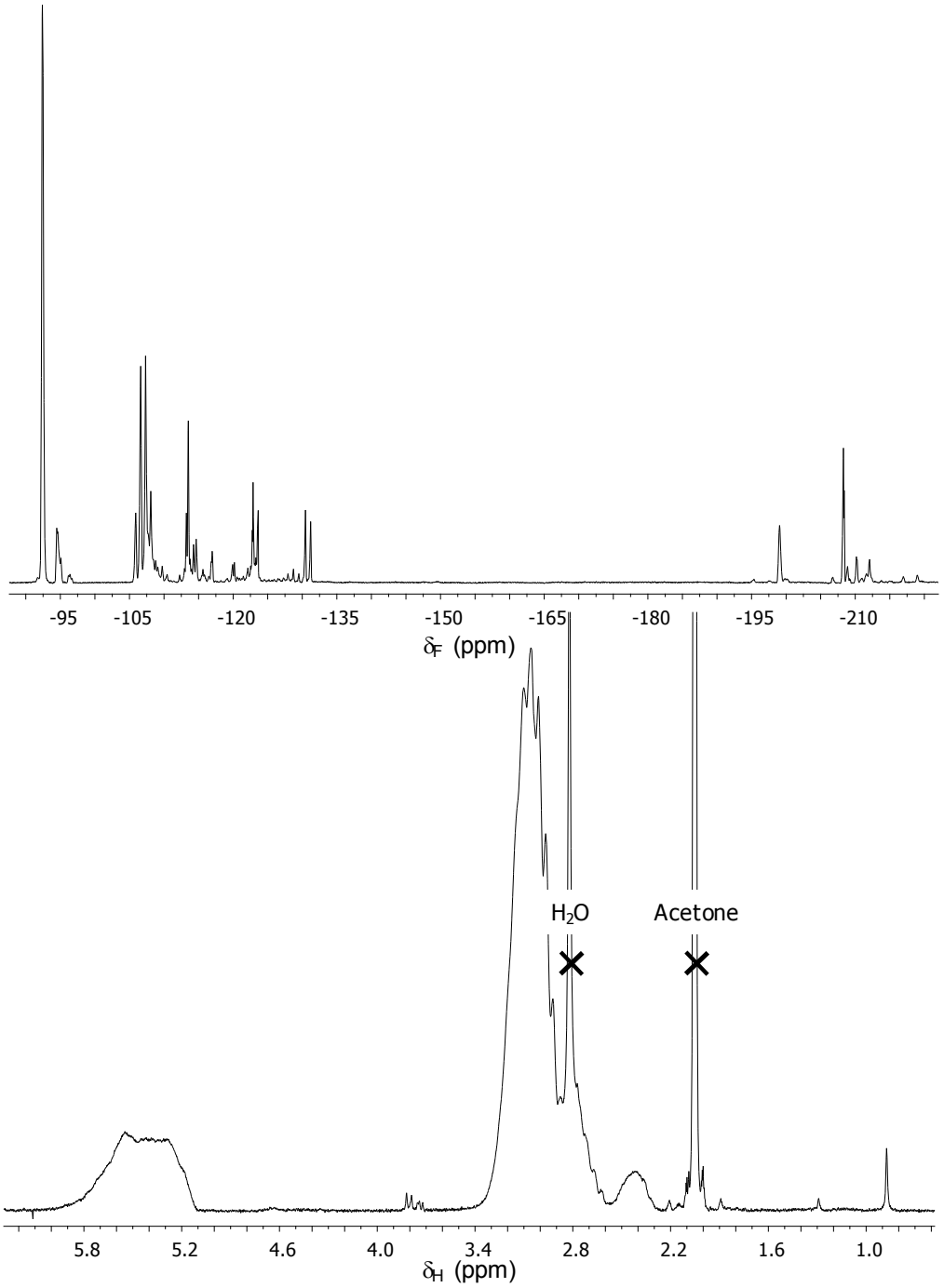


Figure S6. ^{19}F (top) and ^{1}H (bottom) NMR spectra in $(CD_3)_2CO$ of a poly(VDF_{69}-*co*-$TrFE_{31}$) copolymer (Run 5, Table 2).

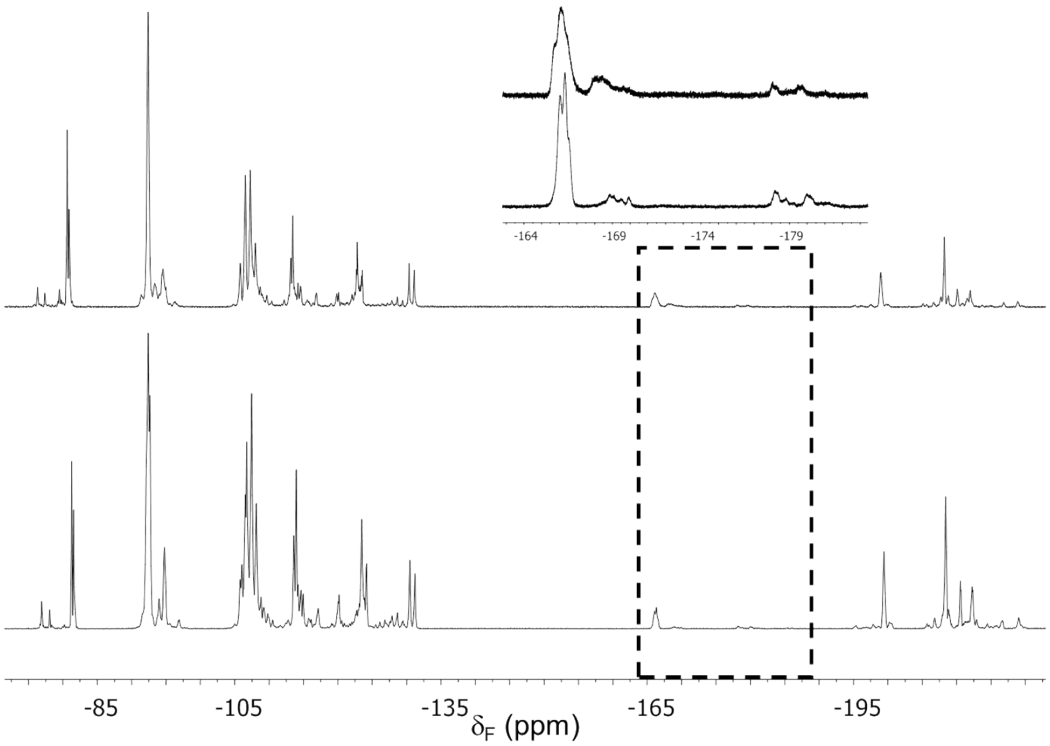


Figure S7. Comparison of ^{19}F NMR spectra of two poly(VDF-*ter*-TrFE-*ter*-1234yf) terpolymers prepared by batch solution polymerization (Top; Molar composition: 65/27/8; Run 8, Table 2) and semi-continuous aqueous suspension polymerization (Bottom, Molar composition: 59/36/5; Run 11 Table).

Equations for Addition Probabilities[2]

$$p_{11} = \frac{[M_1]}{[M_1] + {[M_2]}/{r_{12}} + {[M_3]}/{r_{13}}} \quad (ES1)$$

$$p_{12} = \frac{[M_2]}{[M_1]r_{12} + [M_2] + {[M_3]}^{r_{12}}/{r_{13}}} \quad (ES2)$$

$$p_{13} = \frac{[M_3]}{[M_1]r_{13} + {[M_2]}^{r_{13}}/{r_{12}} + [M_3]} \quad (ES3)$$

$$p_{21} = \frac{[M_1]}{[M_1] + [M_2]r_{21} + {[M_3]}^{r_{21}}/{r_{23}}} \quad (ES4)$$

$$p_{22} = \frac{[M_2]}{{[M_1]}/{r_{21}} + [M_2] + {[M_3]}/{r_{23}}} \quad (ES5)$$

$$p_{23} = \frac{[M_3]}{{[M_1]}^{r_{23}}/{r_{21}} + [M_2]r_{23} + [M_3]} \quad (ES6)$$

$$p_{31} = \frac{[M_1]}{[M_1] + {[M_2]}^{r_{31}}/{r_{32}} + [M_3]r_{31}} \quad (ES7)$$

$$p_{32} = \frac{[M_2]}{{[M_1]}^{r_{32}}/{r_{31}} + [M_2] + [M_3]r_{32}} \quad (ES8)$$

$$p_{33} = \frac{[M_3]}{{[M_1]}/{r_{31}} + {[M_2]}/{r_{32}} + [M_3]} \quad (ES9)$$

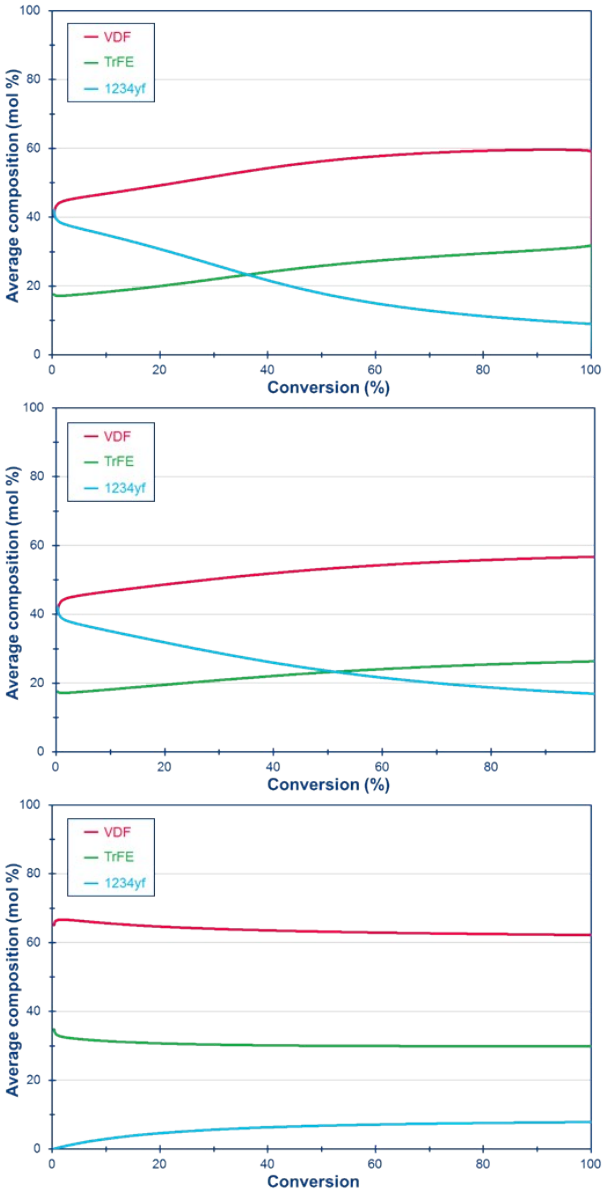


Figure S8. Simulation of the evolutions of the average composition of poly(VDF-*ter*-TrFE-*ter*-1234yf) terpolymers: (A) synthesized by batch polymerization from a 59/32/9 initial feed. (B) synthesized by semi-continuous polymerization from a 59/32/9 initial feed and a 59/32/9 secondary mixture. (C) synthesized by semi-continuous polymerization from a 65/35/0 initial feed and a 59/32/9 secondary mixture. Initial and secondary feed contain the same molar amount of monomers. The total conversion is calculated from the amount of monomers in the initial mixture. Secondary mixtures are constantly fed over the course of the polymerization. The monomer ratios are given in mol %.

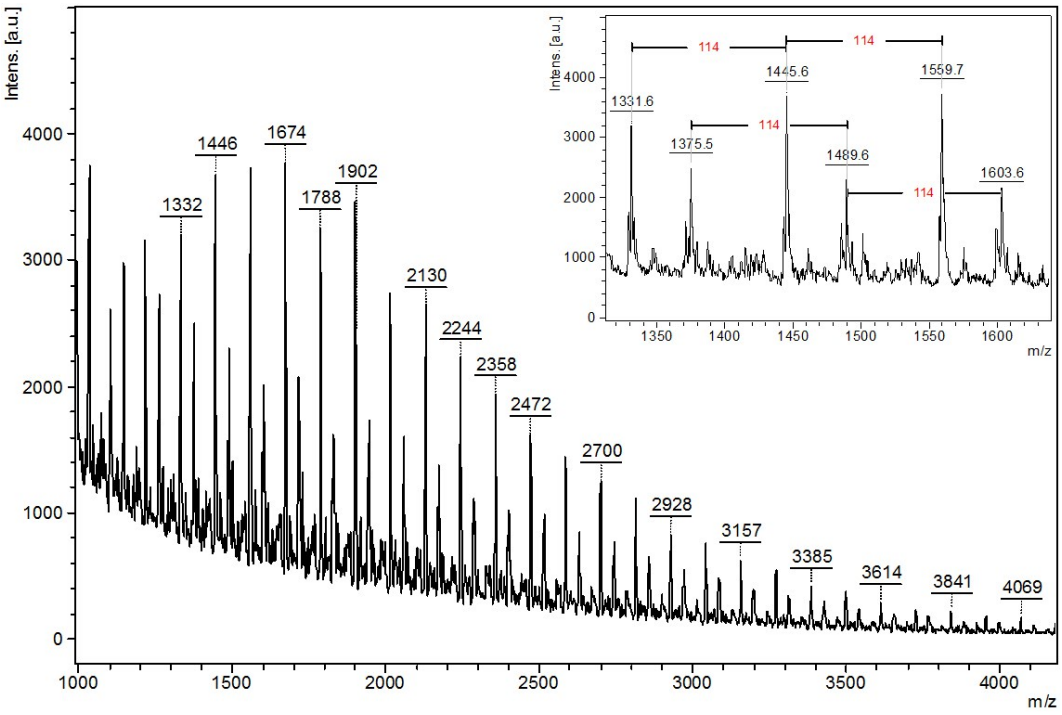


Figure S9. Negative ion MALDI-TOF mass spectrum of P1234yf homopolymer, synthesized by radical solution polymerization at 48 °C in dimethylcarbonate (DMC) and initiated by di(*tert*-butylcyclohexyl) peroxydicarbonate (DTBCPC) (Run 3, Table 2), with DCTB as matrix and LiCl as the cationic agent.

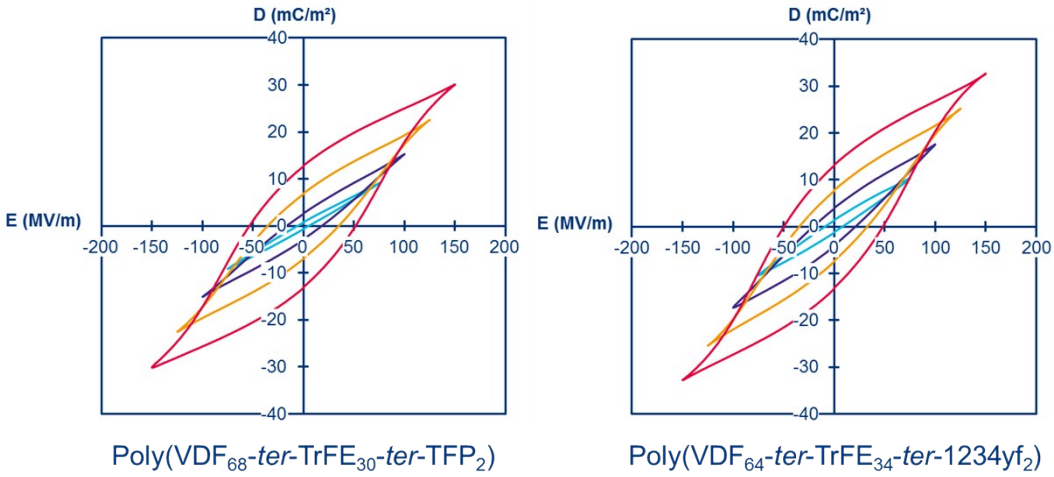


Figure S10. Comparison of bipolar D-E loops of a poly(VDF_{68}-*ter*-$TrFE_{30}$-*ter*-TFP_2)[3] (left Figure) terpolymer with a poly(VDF_{64}-*ter*-$TrFE_{34}$-*ter*-$1234yf_2$) terpolymer (right Figure). The terpolymers were prepared in batch solution in DMC by free radical polymerization. TFP stands for 3,3,3-trifluoropropene.

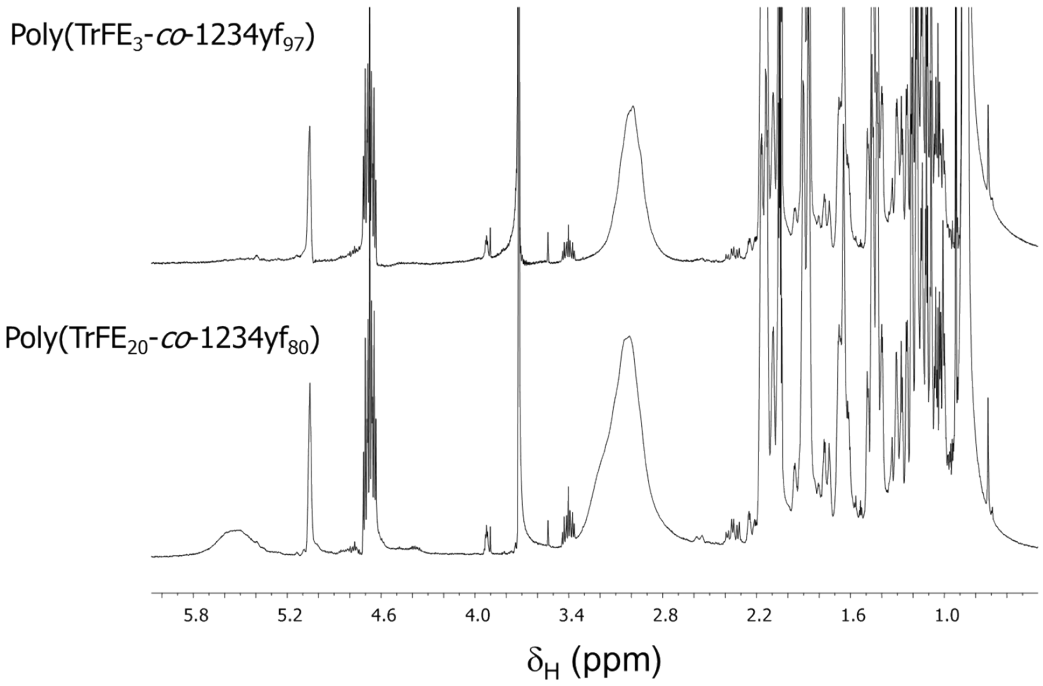


Figure S11. ^{1}H NMR spectra, recorded in recorded in $(CD_3)_2CO$, of two unpurified poly(TrFE-*co*-1234yf) copolymers.

References

(1) Mayo, F. R.; Lewis, F. M. Copolymerization. I. A Basis for Comparing the Behavior of Monomers in Copolymerization; The Copolymerization of Styrene and Methyl Methacrylate. *Journal of the American Chemical Society* **1944,** *66*, 1594-1601.
(2) Odian, G., Chain Copolymerization. In *Principles of Polymerization*, Odian, G., Ed. John Wiley & Sons, Inc.: Hoboken, New Jersey, 2004; pp 464-543.
(3) Soulestin, T.; Ladmiral, V.; Lannuzel, T.; Domingues Dos Santos, F.; Ameduri, B. Importance of Microstructure Control for Designing New Electroactive Terpolymers Based on Vinylidene Fluoride and Trifluoroethylene. *Macromolecules* **2015,** *48*, 7861-7871.