Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Kinetics and Mechanistic Aspects of the Iodine Transfer Copolymerization of Vinylidene Fluoride with 2,3,3,3-Tetrafluoro-1-propene and Functionalization into ω-Hydroxy Fluorinated Copolymer

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Determination of reactivity ratios of VDF and 1234yf

Copolymer compositions were determined by measuring VDF and 1234yf conversions by ^{19}F NMR spectroscopies using equations 2 and 3, described in the main manuscript.

The following equation was used:

$$G = r_{VDF} - r_{1234yf}$$

$$\text{where, } G = x(X-1) / X.$$

$$H = x^2/X.$$

where $x = f_{VDF}/f_{1234yf}$, and f_{VDF} and f_{1234yf} stand for the initial molar fractions of VDF and 1234yf, respectively.

$X = F_{VDF}/F_{1234yf}$, where F_{VDF} and F_{1234yf} stand for the VDF and 1234yf molar fractions, respectively, in the obtained copolymer.

In the Kelen-Tüdös laws, the following equation was used:

$$\eta = (r_{VDF} + r_{1234yf}/\alpha)\zeta - r_{1234yf}/\alpha$$

$$\text{where, } \eta = G/(\alpha + H)$$

$$\zeta = H/(\alpha + H)$$

$$\alpha = (H_{min} \times H_{max})1/2$$

To calculate the parameters for extended Kelen-Tüdös plot,

$$H = x/Z^2 \text{ and } G = (x-1)/Z$$

$$\text{where } Z = \log(1-\xi_1)/\log(1-\xi_2).$$

ξ_2 and ξ_1 partial molar conversions of VDF and 1234yf are defined as follows:

$\xi_2 = w\ (\mu+F) / (\mu+f)$ and $\xi_1 = \xi 2\ (f/F)$, respectively;

w is the weight conversion

Table S1 Parameters for extended Kelen-Tüdös plot for the determination of VDF and 1234yf's reactivity ratios in the free radical copolymerization of these comonomers

f_{VDF}	f_{1234yf}	x	F_{VDF}	F_{1234yf}	X	G	H	η	ξ
0	1.00	0	0	1	0	--	--	--	--
0.55	0.45	1.222	0.19	0.81	0.235	-3.988	6.368	0.838	-0.597
0.85	0.15	5.667	0.62	0.38	1.632	2.193	19.681	0.489	0.358
0.90	0.10	9.000	0.82	0.18	4.556	7.024	17.780	0.239	0.891
0.95	0.05	19.000	0.94	0.06	15.667	17.787	23.042	0.162	1.466
1.00	0	--	1.00	0	--	--	--	--	--

*   symbol represents undefined values

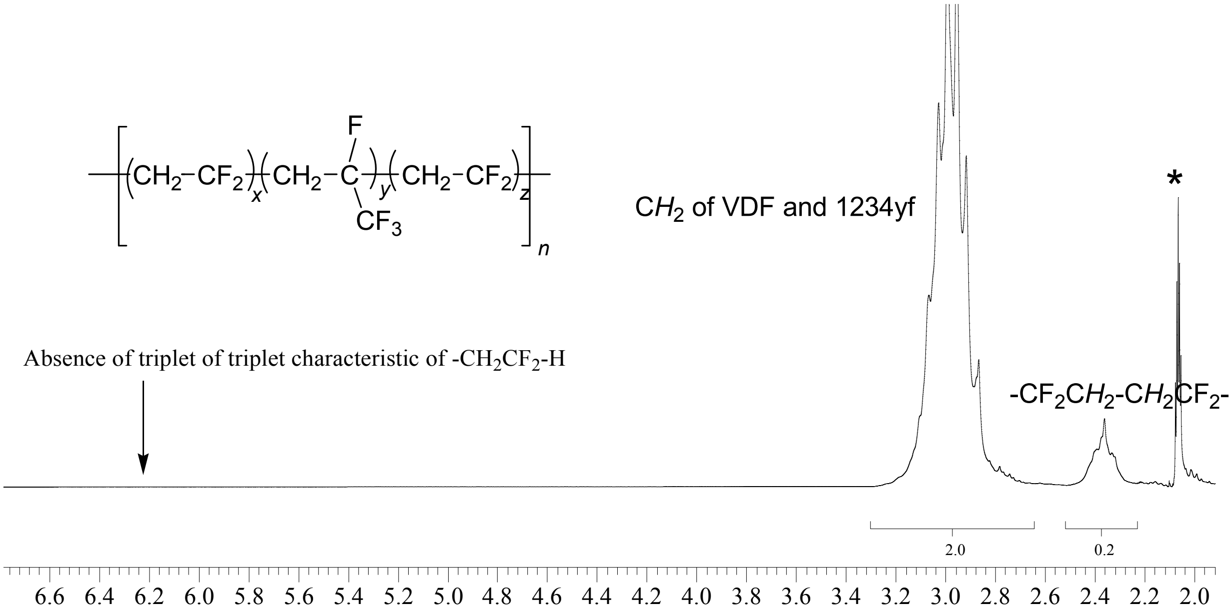

Fig. S1 Representative ^1H NMR spectrum of poly(VDF-*co*-1234yf) copolymer prepared by free radical copolymerization of VDF and 1234yf using *tert*-butyl peroxypivalate (TBPPi) in 1,1,1,3,3-pentafluorobutane (PFB) at 74 °C (P4, Table 1), recorded in acetone-d_6 at 20 °C. (* Solvent (acetone) peak).

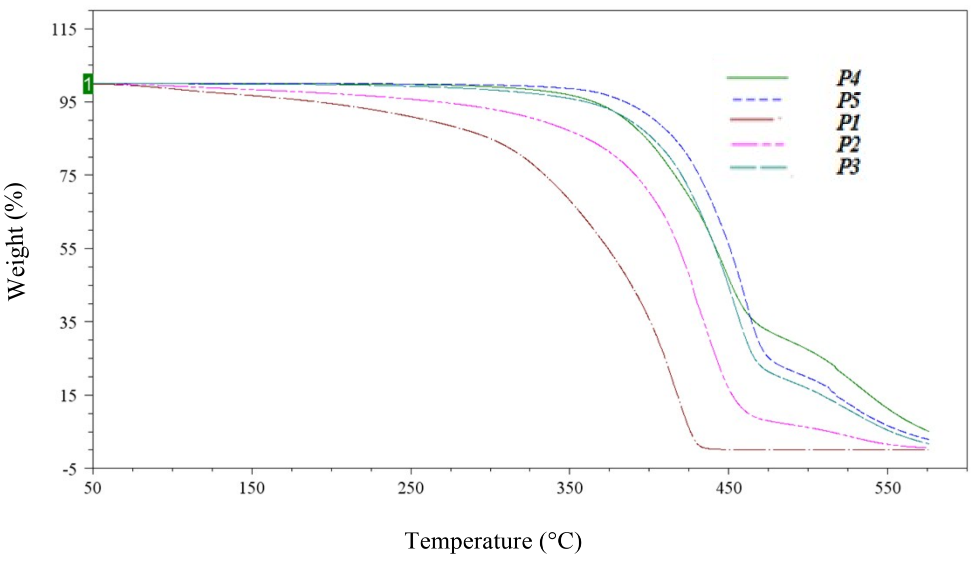

Fig. S2 TGA thermograms of poly(VDF-*co*-1234yf) copolymers (P1-P5, Table 1), heated at 10 °C min^{-1} under air.

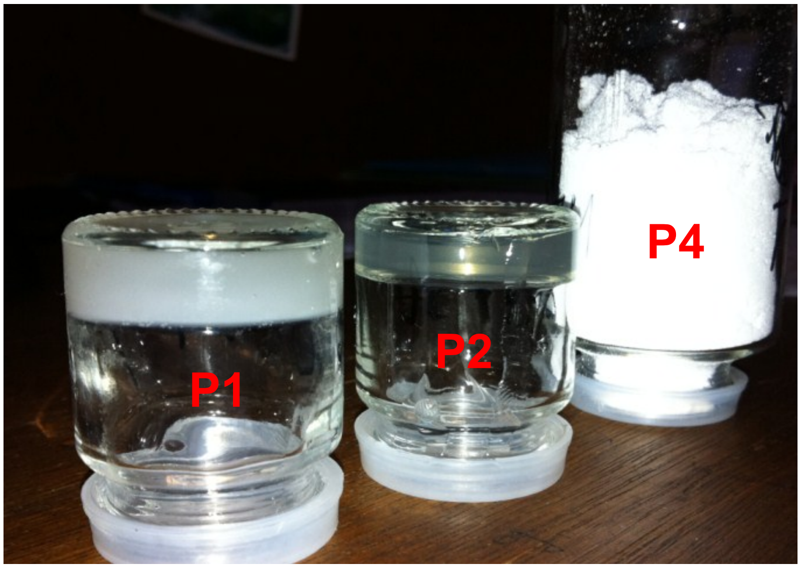

Fig. S3 Pictures of flasks containing poly(VDF-*co*-1234yf) copolymers: from left to right: P1, P2, and P4 copolymers (see Table 1 for the polymerization conditions and characterization data).

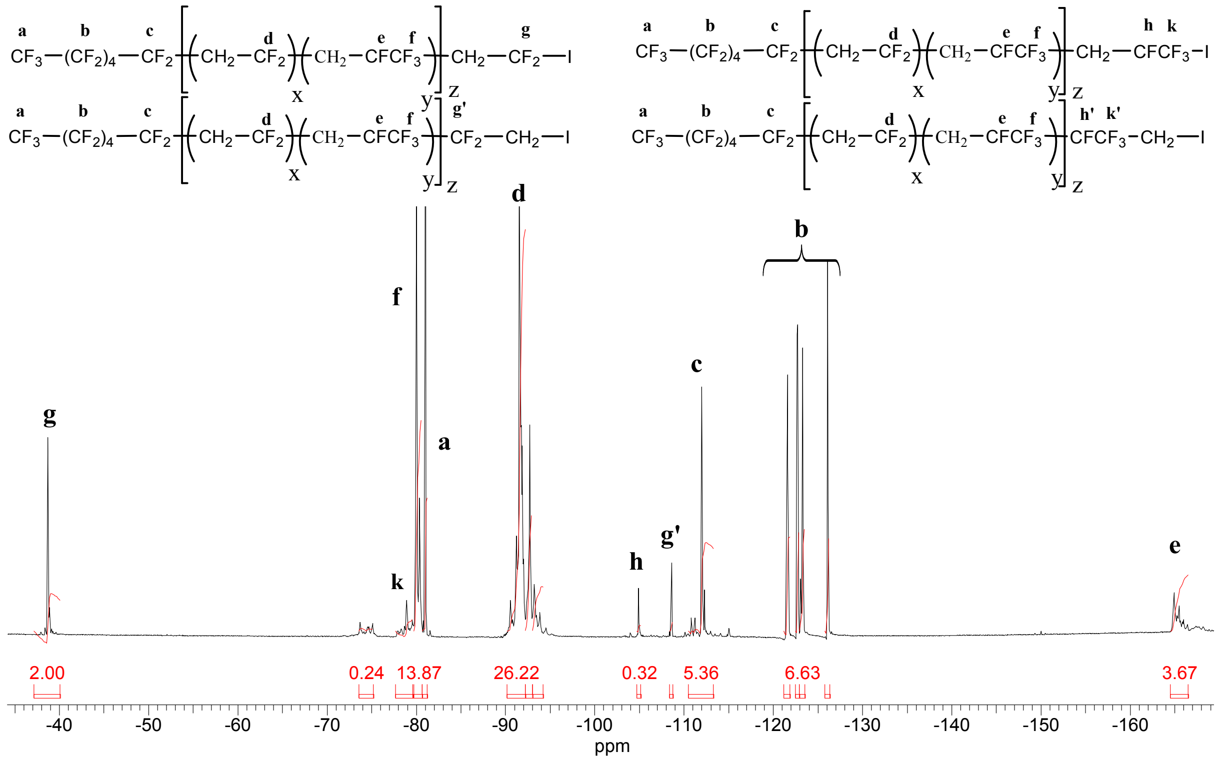

Fig. S4 ^{19}F NMR spectrum (recorded in acetone-*d_6* at 20 °C) of C_6F_{13}poly(VDF-*co*-1234yf)-I copolymers (**P10**, Table 2).

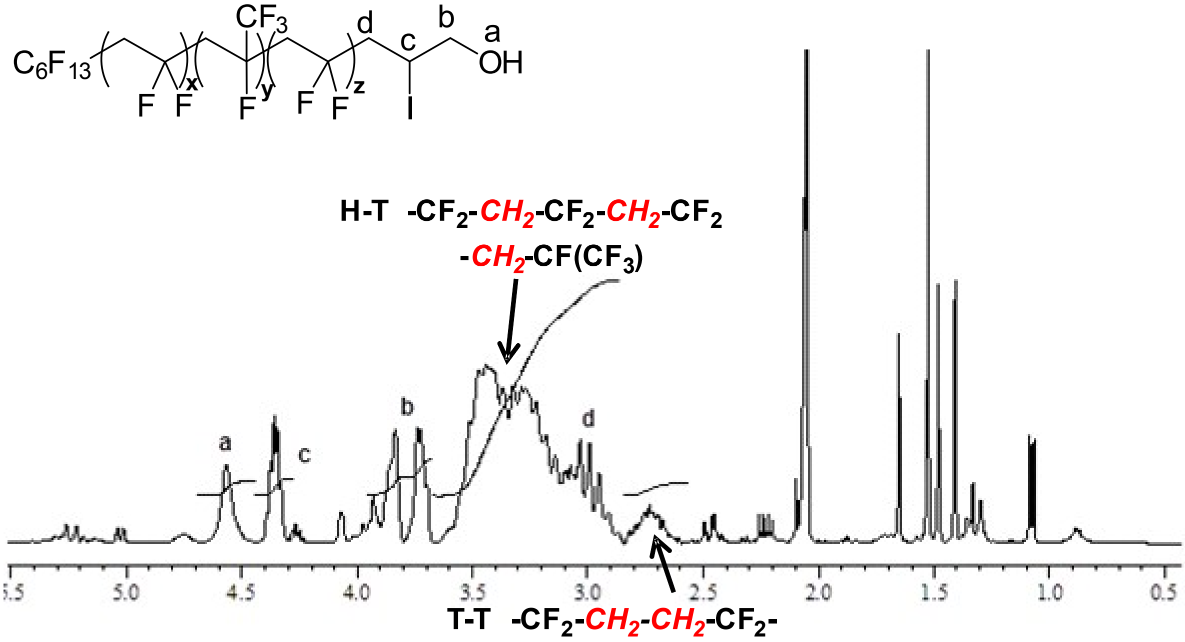

Fig. S5 ^{1}H NMR spectrum (recorded in acetone-d_6 at 20 °C) of P11 copolymer produced after radical addition of iodo poly(VDF-*co*-1234) P10 onto allyl alcohol.

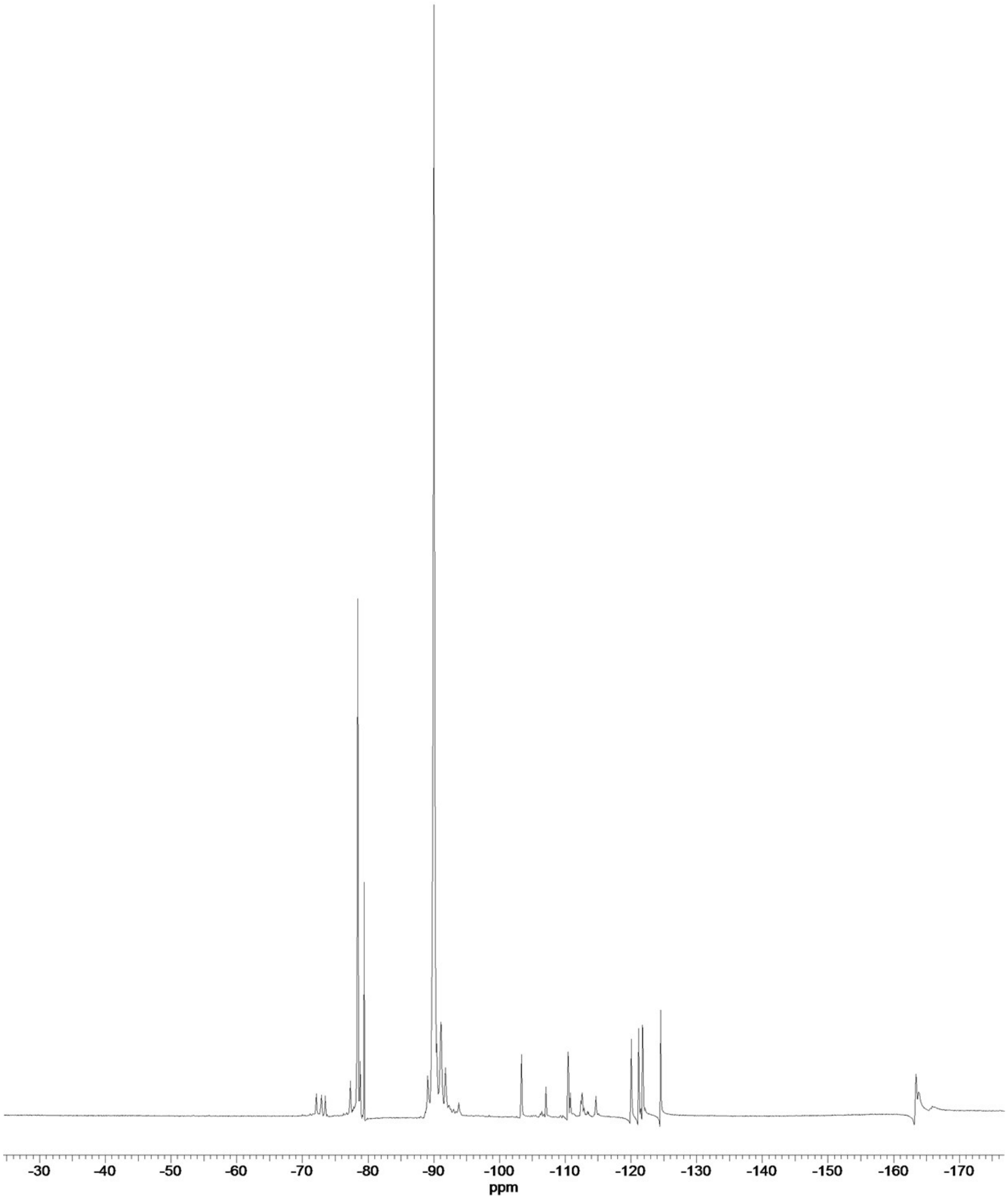

Fig. S6 ^{19}F NMR spectrum (recorded in acetone-d_6 at 20 °C) of P11 copolymer achieved after the radical addition of iodo poly(VDF-*co*-1234) P10 onto allyl alcohol (with uncorrected chemical shifts of ca. 3 ppm).

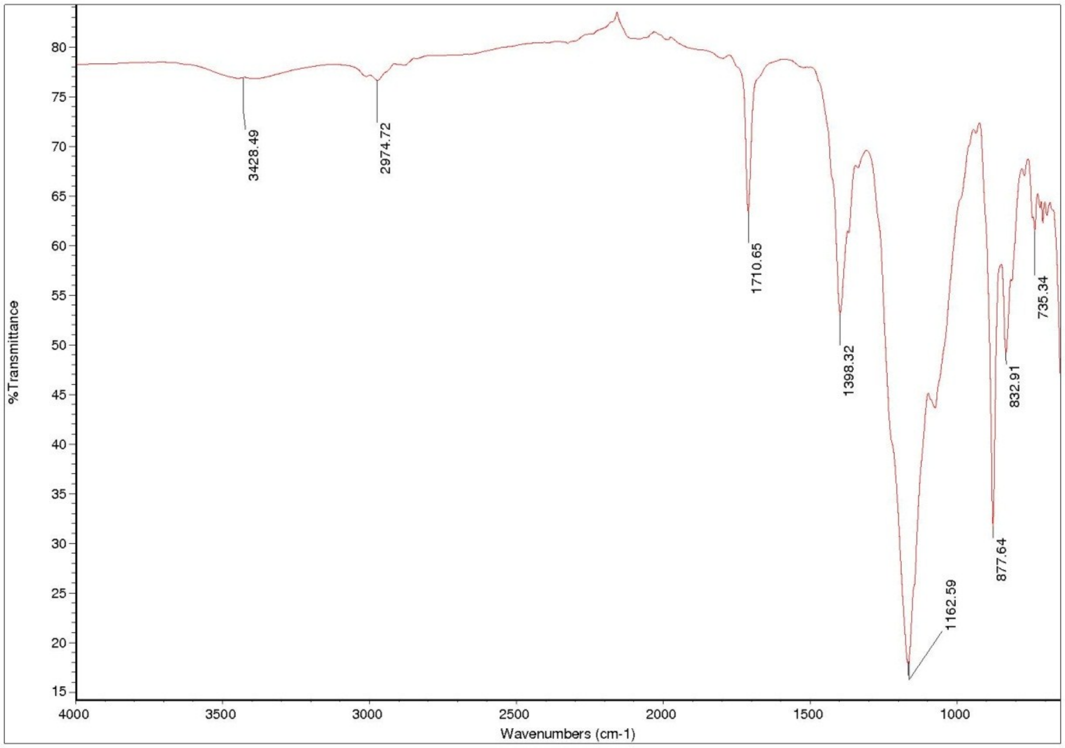

Fig. S7 FTIR spectrum (KBr at 20 °C) of P11 copolymer produced after radical addition of iodo poly(VDF-*co*-1234) cooligomer P10 onto allyl alcohol (frequency at 1710 cm^{-1} is assigned to unevaporated of acetone).

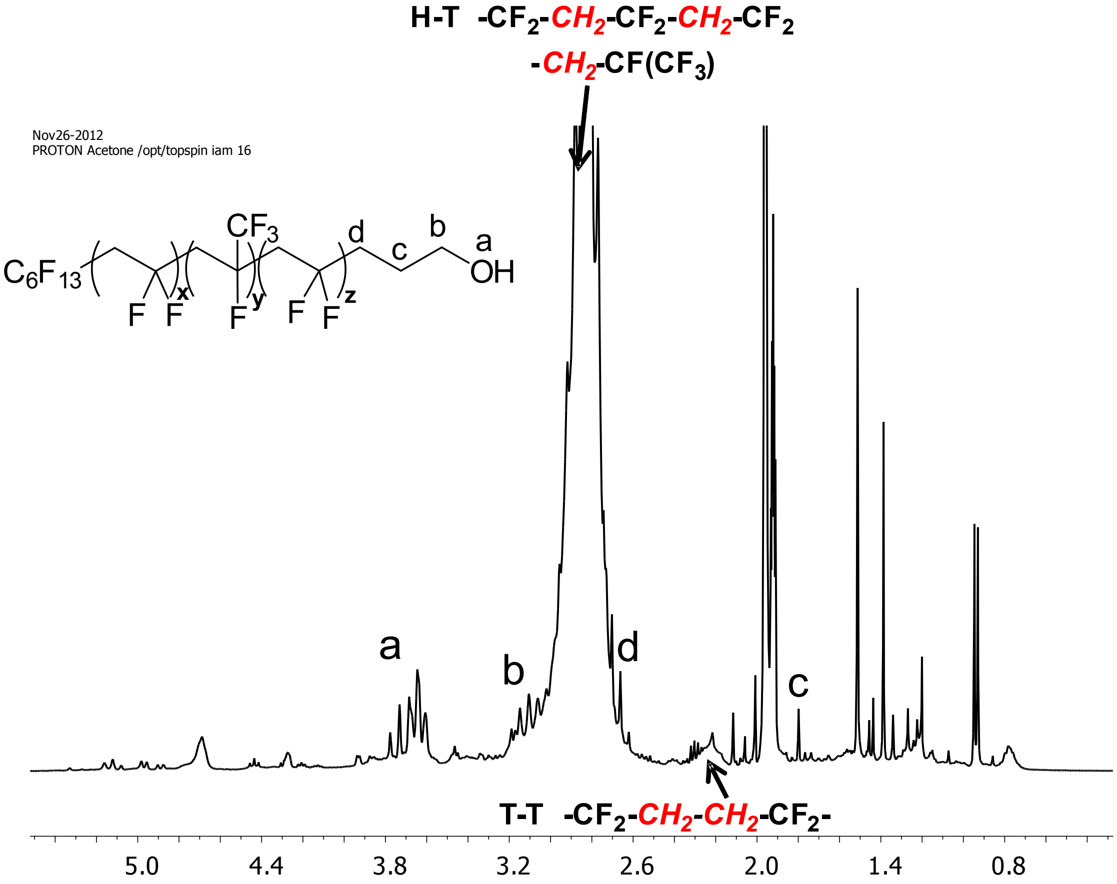

Fig. S8 ^{1}H NMR spectrum (recorded in acetone-d_6 at 20 °C) of hydroxyl poly(VDF-*co*-1234) cooligomer P12 achieved after reduction of iodhydrin P11.

ca. 3 ppm).

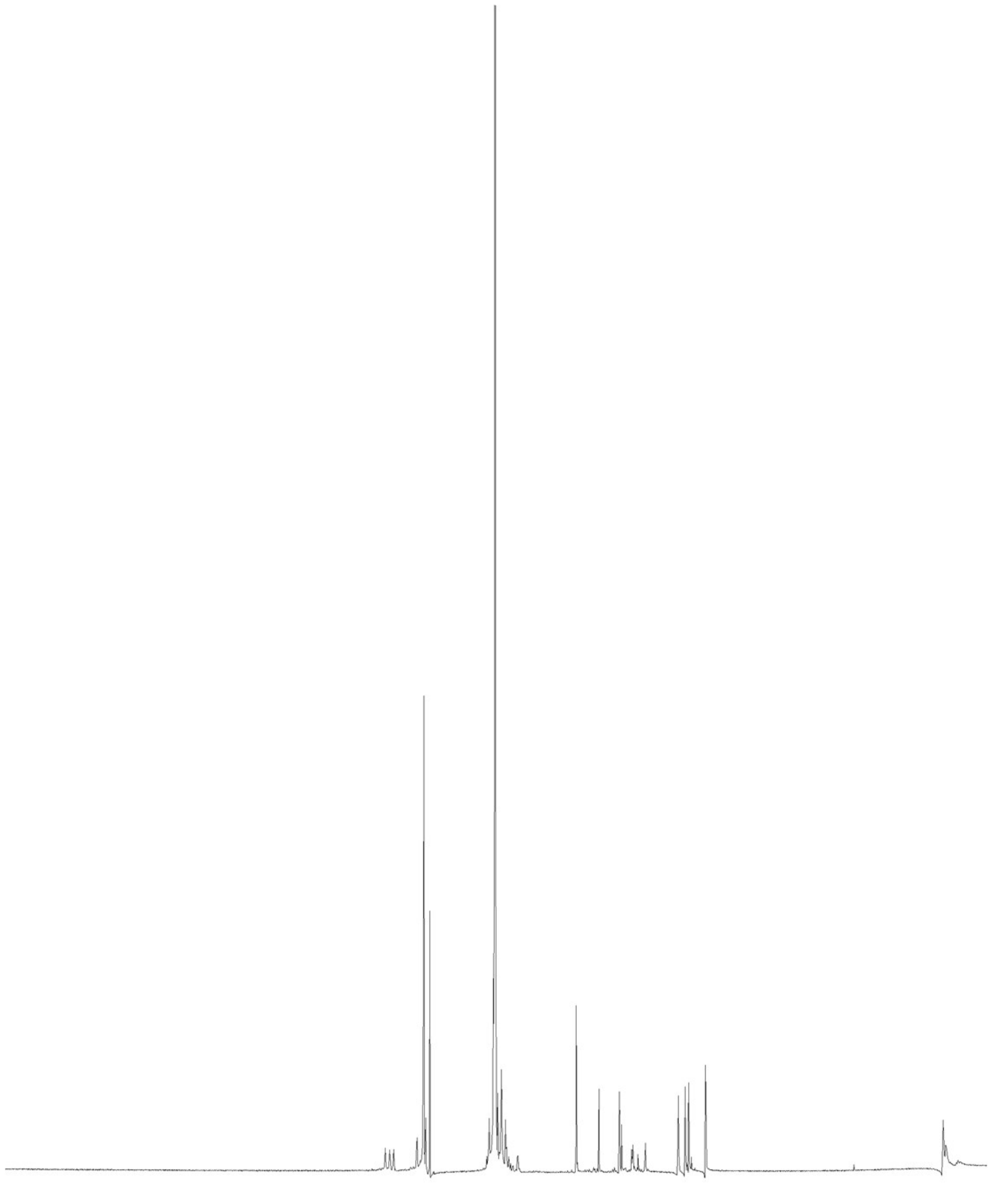

Fig. S9 ^{19}F NMR spectrum (recorded in acetone-d_6 at 20 °C) of hydroxyl poly(VDF-*co*-1234) cooligomer P12 achieved after reduction of iodhydrin P11 (with uncorrected chemical shifts of ca. 3 ppm).

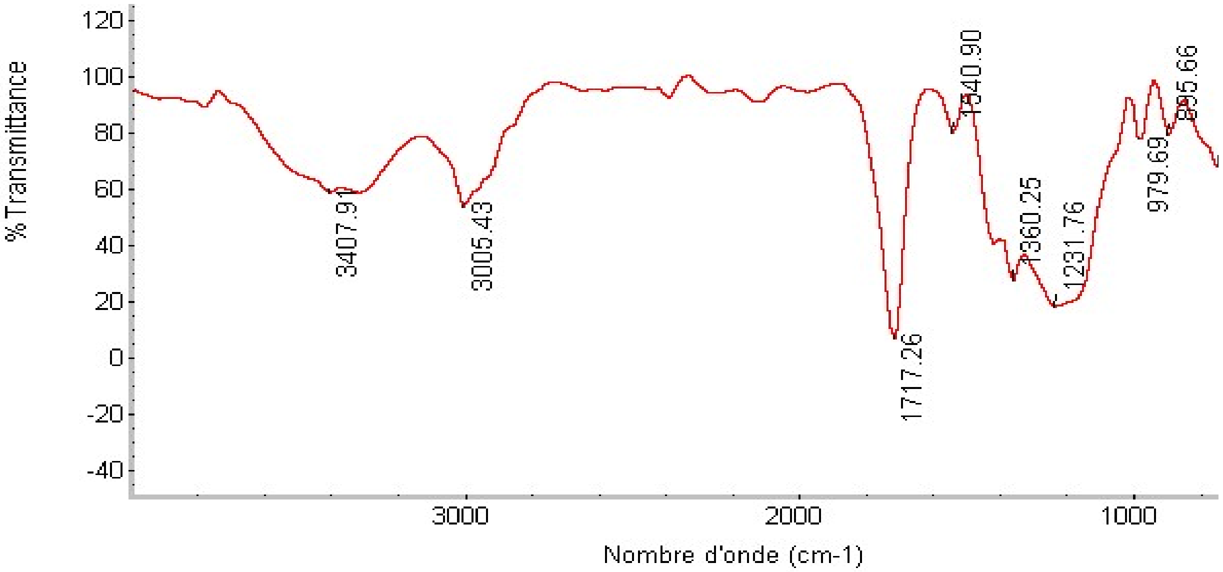

Fig. S10 FTIR spectrum of hydroxyl poly(VDF-*co*-1234) final product (P12) achieved after reduction of iodhydrin P11 (frequency at 1717 cm^{-1} is assigned to acetone).