Electronic Supplementary Material (ESI) for Polymer Chemistry.

Amphiphilic poly(vinylidene fluoride)-*b*-poly(vinyl alcohol) block copolymer: Synthesis and self-Assembly in water

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SUPPORTING INFORMATION

EXPERIMENTAL SECTION

Material

All reagents were used as received unless stated otherwise. 1,1-Difluoroethylene (vinylidene fluoride, VDF) was kindly supplied by Arkema (Pierre-Benite, France). *O*-ethyl-*S*-*(*1-methoxycarbonyl)ethyldithiocarbonate (CTA_{XA}) was synthesized according to the method described by Liu et al.[1] *Tert*-amyl peroxy-2-ethylhexanoate (Trigonox 121, purity 95%) was purchased from AkzoNobel (Chalons-sur-Marne, France). ReagentPlus grade (purity > 99%) Poly(vinyl alcohol) M_w= 89000 – 98000 g/mol 99+% hydrolyzed, 2,2-azoisobutyronitrile (AIBN), vinyl acetate (VAc), dimethyl carbonate (DMC), dimethylformamide (DMF), tetrahydrofuran, (THF), ethanol (EtOH), potassium carbonate (K_2CO_3) and laboratory reagent grade hexane (purity > 95%) were purchased from Sigma Aldrich and used as received. AIBN was purified by recrystallization from methanol twice before use.

Characterization

Nuclear Magnetic Resonance

The Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AC 400 instrument. Deuterated acetone was used as the solvent in each sample. Coupling constants and chemical shifts are given in Hertz (Hz) and parts per million (ppm), respectively. The experimental conditions for recording ^{1}H and ^{19}F NMR spectra were as follows: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 2 s), number of scans 128 (or 512), and a pulse width of 5 μs for ^{19}F NMR. *In situ* NMR experiments were recorded with a pulse delay of 1 s, acquisition times of 4 s and 0.87 s, and 8 and 16 scans for ^{1}H and ^{19}F NMR, respectively.

Size Exclusion Chromatography

Size exclusion chromatograms (SEC) were recorded using a triple detection GPC from Agilent Technologies with its corresponding Agilent software, dedicated to multi-detector GPC calculation. The system used two PL1113-6300 ResiPore 300 x 7.5 mm columns with DMF (containing 0.1 wt % of LiCl) as the eluent with a flow rate of 0.8 $mL.min^{-1}$ and toluene as flow rate marker. The detector suite comprised a PL0390-0605390 LC light scattering detector with 2 diffusion angles (15° and 90°), a PL0390-06034 capillary viscosimeter, and a 390-LC PL0390-0601 refractive index detector. The entire SEC-HPLC system was thermostated at 35°C. PMMA standards were used for the calibration. The typical sample concentration was 10 mg/mL.

Fourier Transform Infrared

FTIR analyses were performed using a PerkinElmer Spectrum 1000 in ATR mode, with an accuracy of ±2 cm−1.

Dynamic Light Scattering

Dynamic Light Scattering (DLS) experiments were performed at 25 °C on a Malvern instrument Nano-ZS equipped with a He-Ne laser as the light source ($\lambda = 633$ nm). The scattered light was detected at the scattering angle of $\nu = 173°$. Samples of water solutions of blocks copolymers (3 mg mL^{-1}) were introduced into cells (pathway, 10 mm) without filtration.

Cryogenic-temperature transmission electron microscopy(Cryo-TEM).

Vitrified specimens were prepared in a controlled environment vitrification system (CEVS)35 at 25 °C and 100% relative humidity. A drop (~3 μL) of the sample was placed ona perforated carbon film-coated copper grid, blotted with filterpaper, and plunged into liquid ethane at its freezing point. The vitrified specimens were transferred to a 626 Gatan cryoholderand observed at 120 kV acceleration voltage in an FEITecnai T12 G2 transmission electron microscope at about −175 °C in the low-dose imaging mode to minimize electron beam radiation damage. Images were digitally recorded with a Gatan US1000 high-resolution CCD camera

Autoclave

The polymerizations of VDF were performed in a 100 mL Hastelloy Parr autoclave systems (HC 276), equipped with a mechanical Hastelloy stirring system, a rupture disk (3000 PSI), inlet and outlet valves, and a Parr electronic controller to regulate the stirring speed and the heating. Prior to reaction, the autoclave was pressurized with 30 bars of nitrogen to check for leaks. The autoclave was then put under vacuum ($20 \cdot 10^{-3}$ bar) for 30 minutes to remove any trace of oxygen. A degassed solution of initiator and CTA_{XA} was introduced via a funnel under vacuum. The reactor was then cooled using a liquid nitrogen bath and VDF was transferred by double weighing (*i.e.* mass difference before and after filling the autoclave with VDF). After warming to ambient temperature, the autoclave was heated to the target temperature under mechanical stirring.

Syntheses

RAFT Homopolymerization of VDF

Using the experimental setup described above, the polymerization of VDF was performed as follows: A solution of Trigonox 121 (158 mg, 6.87 10^{-4} mol) and CTA_{XA} (1.30 g, 6.25 10^{-3} mol) in DMC (60 mL), was degassed by N_2 bubbling during 30 min. This homogenous solution was introduced into the autoclave using a funnel, VDF gas (21.0 g, 2.97 10^{-1} mol) was transferred in the autoclave at low temperature, and the reactor was gradually heated to 73 °C. The reaction was stopped after 18 h. During the reaction, the pressure increased to a maximum of 25 bars and then decreased to 10 bars after 18 h. The autoclave was cooled down to room temperature (ca. 20 °C), purged from the residual monomers and DMC was removed under vacuum. The crude product was dissolved in 30 mL of warm THF (ca. 40 °C), and left under vigorous stirring for 30 minutes. This polymer solution was then precipitated from 400 mL of chilled hexane. The precipitated polymer (white powder) was filtered through a filter funnel and dried under vacuum ($15 \cdot 10^{-3}$ bar) for two hours at 50 °C. The polymerization yield (65 %) was determined gravimetrically (mass of dried precipitated polymers / mass of monomer introduced in the pressure reactor). Yields were used as conversion, since conversion is very difficult to measure accurately for VDF or other gaseous monomers.

DP and $M_{n(NMR)}$ calculations:

The degree of polymerization (DP) of PVDF can be calculated according to equations (1) and (2):

$$(1)\quad DP = \frac{\int_{2.70}^{3.19} \mathrm{CH_2\ (HT)} + \int_{2.28}^{2.43} \mathrm{CH_2(TT)} + \int_{4.02}^{4.17} \mathrm{CH_2(End-group)}}{2/3 \times \int_{1.19}^{1.24} \mathrm{CH_3\ (R-CTA_{XA})}}$$

$$(2)\quad M_{n,NMR}(\mathrm{R}) = M_{n,CTA} + (DP \times M_{n,VDF})$$

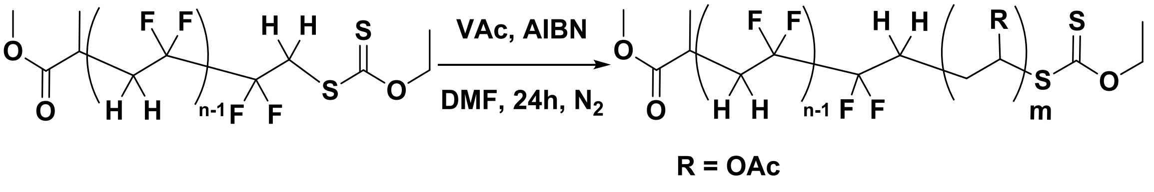
Where $M_{n\,CTA}$ = 208.3 g.mol^{-1} and $M_{n\,VDF}$= 64.04 g.mol^{-1}

^{1}H NMR (400 MHz $(CD_3)_2CO$, δ (ppm), Figure S1) : 1.19-1.24 (d, -CH(C**H$_3$**)(C=O)-, $^3J_{HH}$ = 7.1 Hz), 1.40-1.46 (t, -S(C=S)O-CH$_2$-C**H$_3$**, $^3J_{HH}$ = 7.2 Hz), 2.28-2.43 (m,-CF$_2$-C**H$_2$**-C**H$_2$**-CF$_2$-, VDF-VDF TT reverse addition), 2.70-3.19 (t, -CF$_2$-C**H$_2$**-CF$_2$-, VDF-VDF HT regular addition), 3.60-3.69 (s, -(C=O)-O-C**H$_3$**), 4.02-4.17 (t, -CF$_2$-C**H$_2$**-S(C=S)OEt, $^3J_{HF}$ = 18 Hz), 4.67-4.77 (q, (-S(C=S)O-C**H$_2$**-CH$_3$, $^3J_{HH}$ = 7.2 Hz), 6.05-6.45 (tt, $^2J_{HF}$ = 55 Hz , $^3J_{HH}$ = 4.6 Hz -CH$_2$-CF$_2$-**H**).

^{19}F NMR (376 MHz $(CD_3)_2CO$, δ (ppm), Figure S2) : -115.63 (-CH$_2$-CF$_2$-C**F$_2$**-CH$_2$-CH$_2$-, VDF-VDF HH reverse addition), -114.29 ($^2J_{HF}$ = 55 Hz, -CH$_2$-C**F$_2$**-H), -113.34 (-CH$_2$-C**F$_2$**-CF$_2$-CH$_2$-CH$_2$-, HH reverse addition), -113.09 (CH$_2$-CF$_2$-**CF$_2$**-CH$_2$-S-), -112.69 (-CH$_2$-**CF$_2$**-CF$_2$-CH$_2$-S-), -94.79 (-CH$_2$-CH$_2$-C**F$_2$**-CH$_2$-, TT reverse addition), -93.50 (-CH$_2$-C**F$_2$**-CH$_2$-CH(CH$_3$)(C=O)-), -92.12 (-CH$_2$-C**F$_2$**-CH$_2$-CF$_2$H), -91.44 (-CH$_2$-CH$_2$-CF$_2$-CH$_2$-**CF$_2$**-CH$_2$-CF$_2$-, regular VDF-VDF HT addition), -91.00 (-CH$_2$-C**F$_2$**-CH$_2$-, regular VDF-VDF HT addition)

Synthesis of PVDF-*b*-PVAc block copolymers using PVDF-XA as MacroCTA

The synthesis of a PVDF-*b*-PVAc block copolymer was performed as follows (Scheme 1): PVDF-XA macroCTA (0.500 g, 1.364·10^{-4} mol) and AIBN (4.5 mg, 2.728·10^{-5} mol) were dissolved in 5 mL of DMF. The solution was stirred and bubbled with N_2 for 20 min, and a degassed solution of VAc (1.76 g, 2.05·10^{-2} mol) was injected. The septum was carefully replaced by a glass stopper and firmly closed with a keck joint clip.



Scheme 1. Schematic synthetic procedure for the PVDF-*b*-PVAc block copolymer.

The solution was then stirred and heated at 70 °C for 24 h. The viscous reaction was diluted with 5 mL of acetone and precipitated in a large excess of hexane. The resulting solid was dried until constant weight under vacuum at 40 °C (Yield = 88 %)

DP and $M_{n(NMR)}$ calculations:

The degree of polymerization (DP) can be calculated from ^{1}H NMR using the integrals of the signals corresponding to: the methyl group of the CTA R-group (1.19-1.24 ppm), the CH of PVAc backbone (4.76-5.14 ppm) and the CH_2 group end capped with xanthate moieties of the reverse VAc additions (HH, 3.22-3.46 ppm). However, as reported in a previous work, the PVDF-XA chains initiated by R-radicals from the CTA were not all terminated by a CTA Z-group. Transfer to the DMC occurred in the course of the polymerization, leading to around 14 % of dead chains terminated by a $-CF_2H$ group. Therefore, a correction factor (α= 0.86) was introduced in equation (3) to calculate a more accurate DP and molar mass for the PVAc block.

$$(3) \quad DP = \frac{\int_{4.76}^{5.14} \mathrm{CH} \; + 1/2 \int_{3.22}^{3.46} \mathrm{CH_2(HH\ End-group)}}{\frac{\alpha}{3} \times \int_{1.19}^{1.24} \mathrm{CH_3\ (R-CTA_{XA})}}$$

The molar mass was then calculated using equation (2):

$$(4) \quad M_{n,NMR}(\mathrm{R}) = M_{n,PVDF51-XA} + (DP \times M_{n,VAc})$$

where $M_{n\ PVDF51\text{-}XA}$ = 3400 g.mol^{-1}, and $M_{n\ VAc}$= 86.09 g.mol^{-1}.

^{1}H NMR (400 MHz $(CD_3)_2CO$, δ (ppm), Figure S3) : 1.19-1.24 (d, $-CH(C\mathbf{H_3})(C{=}O)-$, $^3J_{HH}$ = 7.1 Hz), 1.40-1.46 (t, ($-S(C{=}S)O-CH_2-C\mathbf{H_3}$), 1.63-1.92 (m, $-CH(OAc)-C\mathbf{H_2}-CH(OAc)-$, VAc), 1.92-2.03 (m, -CH(O**Ac)**-, VAc), 2.28-2.43 (m,$-CF_2-C\mathbf{H_2}-C\mathbf{H_2}-CF_2-$, VDF-VDF TT reverse addition), 2.70-3.19 (t, $-CF_2-C\mathbf{H_2}-CF_2-$, regular VDF-VDF HT addition), 3.21-3.42 (m, $-CH(OAc)-C\mathbf{H_2}-S(C{=}S)OEt$, VAc HH reverse addition), 3.60-3.69 (s, $-(C{=}O)-O-C\mathbf{H_3}$), 3.95-4.13

(-CH_2-C$\mathbf{H_2}$(OAc), VAc), 4.63-4.72 (q, (-S(C=S)O-C$\mathbf{H_2}$-CH_3, $^3J_{HH}$ = 7.2 Hz), 4.76-5.14 (-CH_2-C**H(**OAc)-CH_2-), 6.05-6.45 (tt, $^2J_{HF}$ = 55 Hz , $^3J_{HH}$ = 4.6 Hz -CH_2-CF_2-**H**).

^{19}F NMR (376 MHz $(CD_3)_2CO$, δ (ppm), Figure S4) : -115.63 (-CH_2-CF_2-C$\mathbf{F_2}$-CH_2-CH_2-, VDF-VDF HH reverse addition), -115.43 (-CH_2-CF_2-$\mathbf{CF_2}$-CH_2-CH_2-CH(OAc)-), -114.29 ($^2J_{HF}$ = 55 Hz, -CH_2-C$\mathbf{F_2}$-H), -113.34 (-CH_2-C$\mathbf{F_2}$-CF_2-CH_2-CH_2-, HH reverse addition), -94.79 (-CH_2-CH_2-C$\mathbf{F_2}$-CH_2-, TT reverse addition), -93.50 (-CH_2-C$\mathbf{F_2}$-CH_2-CH(CH_3)(C=O)-), -92.12 (-CH_2-C$\mathbf{F_2}$-CH_2-CF_2H), -91.44 (-CH_2-CH_2-CF_2-CH_2-$\mathbf{CF_2}$-CH_2-CF_2-, regular VDF-VDF HT addition), -91.00 (-CH_2-C$\mathbf{F_2}$-CH_2-, regular VDF-VDF HT addition).

Saponification of PVDF-*b*-PVAc precursor

$PVDF_{51}$-*b*-PVA_{172} (300 mg, $2.8\cdot10^{-3}$ eq/mol of ester function) block copolymer was dissolved in 1 g of DMF, then 4 mL of an alcoholic-water mixture (75:25) solution of K_2CO_3 at 0.723 mol/ was added and left under stirring at 60 °C for 3 days. The precipitated PVDF-*b*-PVA amphiphilic polymer was recovered by filtration and dried until constant weight.

Exactly same conditions were used for the PVDF treatment necessary to the quantification of deshydrofluoration reactions.

Typical procedure for the preparation of self-assembled objects

$PVDF_{51}$-*b*-PVA_{172} (20 mg) block copolymer was dissolved in 10 g of DMSO for 16 hours at 80 °C. The solution was then filtered on 0.45 µm filter, transferred into dialysis tubing (MWCO = 1000 Da) and dialyzed against deionized nanopure water for 4 days, leading to 17.30 g of solution with a polymer concentration of 1.16 g/L.

Run	**$M_{n,NMR}$ (g/mol)**	**$M_{n,GPC}$ (g/mol)**	Đ	wt % VDF/VAc/VA	mol % VDF/VAc/VA
PVDF$_{51}$-*XA*	3,400	8,300	1.40	100/0/0	100/0/0
PVDF$_{51}$-*b*-PVAc$_{172}$	18,300	17,500	1.34	18/82/0	23/77/0
***PVDF$_{51}$-*b*-PVA$_{172}$**	*11,000	n.a.	n.a.	30/0/70	23//77

Table S1. Molar mass, dispersity, weight and molar fractions of the PVDF-XA, PVDF-*b*-PVAc and PVDF-*b*-PVA BCPs.

Note: * The composition of the PVDF-*b*-PVA diblock copolymer has been determined on the parent copolymer PVDF-*b*-PVAc, because after hydrolysis the resulting copolymer is not sufficiently soluble in any solvents to provide sufficiently accurate spectra. Thus, the corresponding NMR molar mass was calculated using equation S5.

$$(5) \quad M_{n,NMR} = M_{n,PVDF51-XA} + (DP_{PVA} \times M_{n,VA})$$

Where $M_{n\ PVDF51\text{-}XA}$ = 3,400 g.mol^{-1}, M_{nVA} = 44.05 g.mol^{-1}, DP_{PVA} = 172.

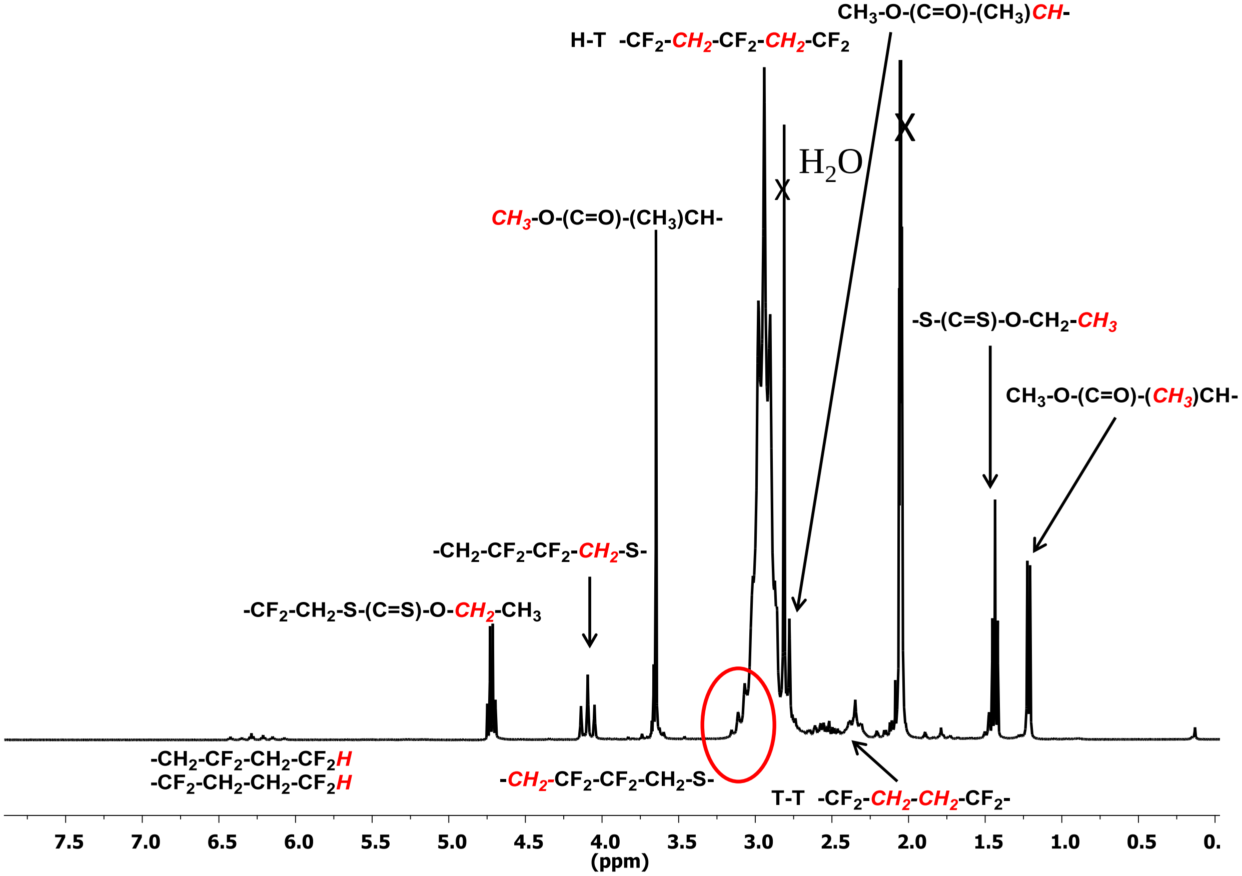


Figure S1. Expansion region from 0 to 7.8 ppm of ^1H NMR spectrum of $PVDF_{51}$-XA in $(CD_3)_2CO$.

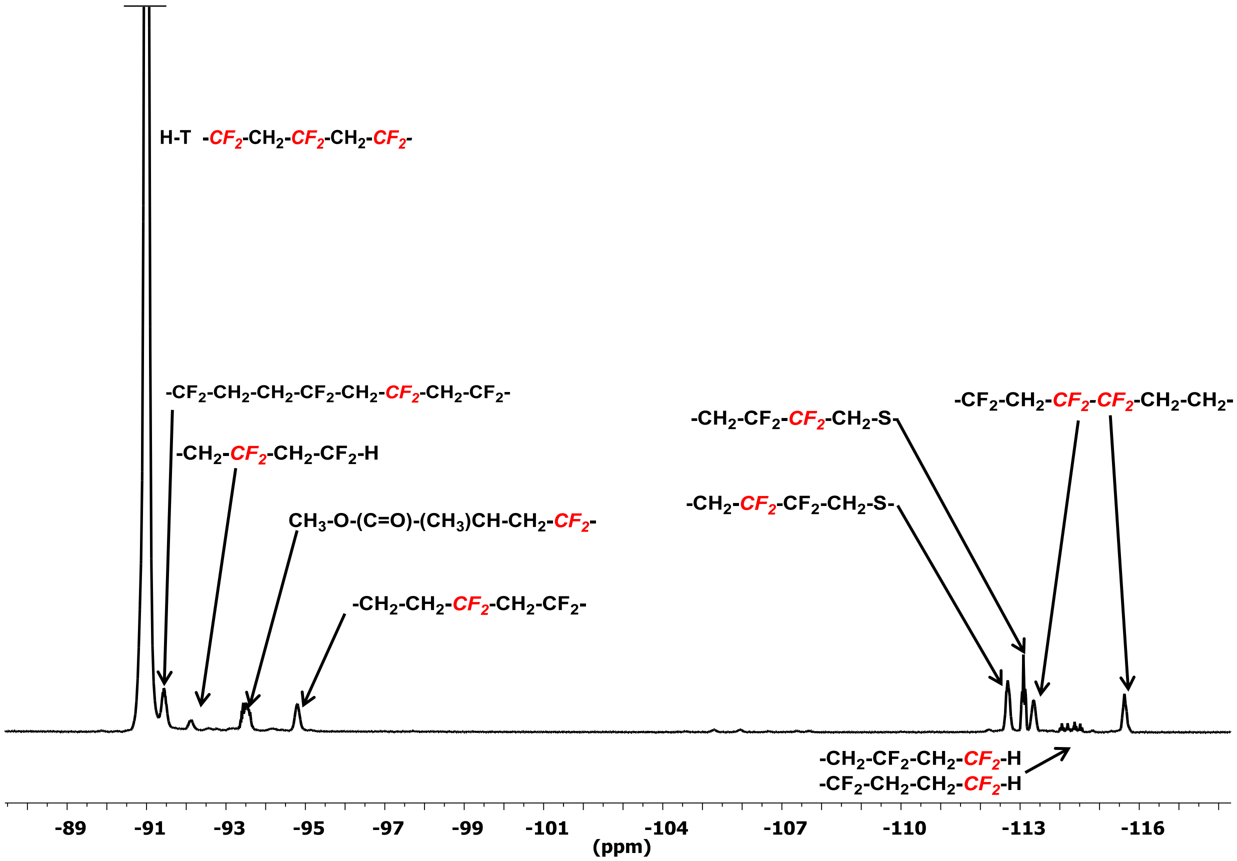


Figure S2. Expansion region from -87.5 to -118 ppm of ^{19}F NMR spectrum of PVDF$_{51}$-XA in $(CD_3)_2CO$.

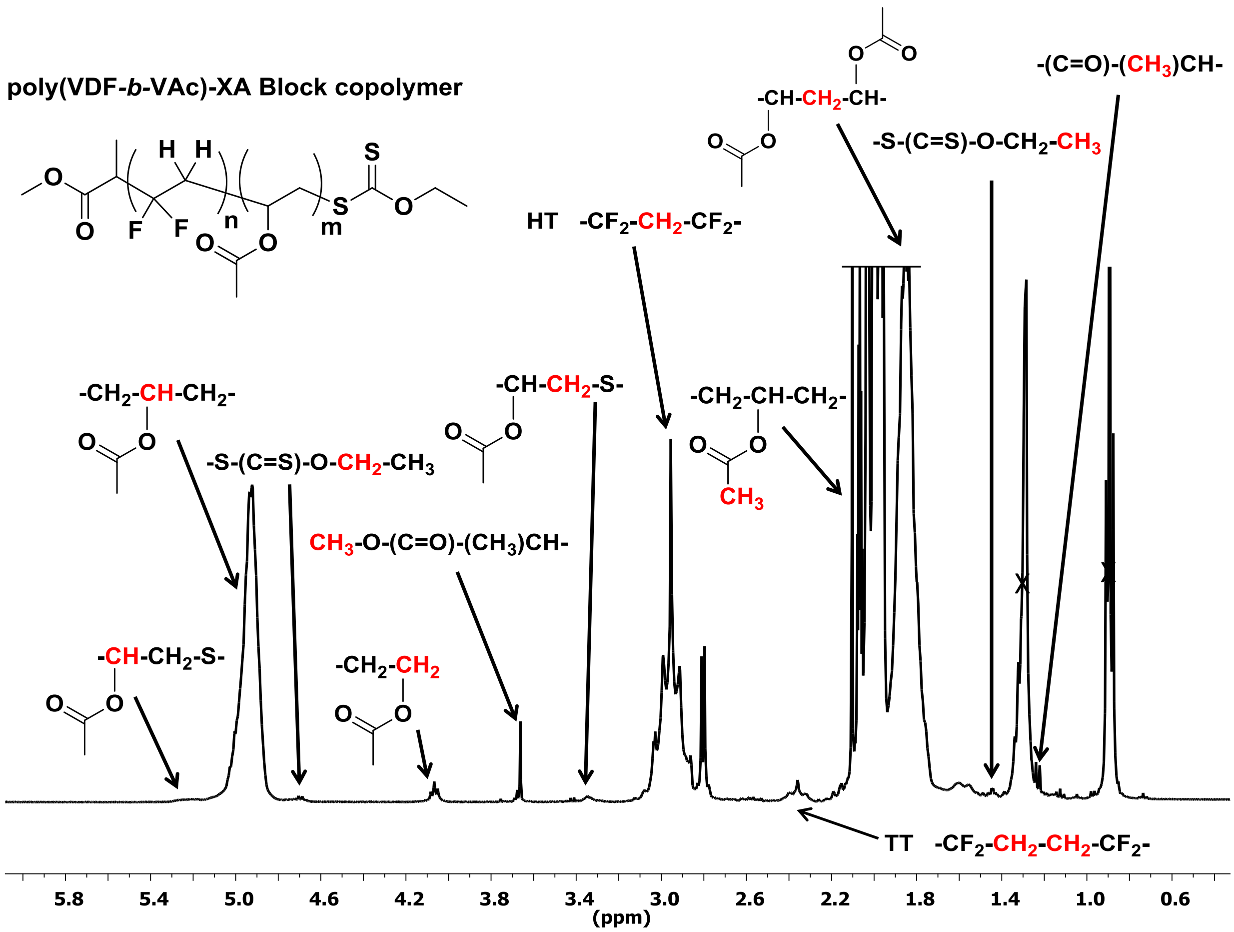


Figure S3. Expansion region from 0 to 6.1 ppm of ^{1}H NMR spectrum of $PVDF_{51}$-*b*-$PVAc_{172}$ in $(CD_3)_2CO$.

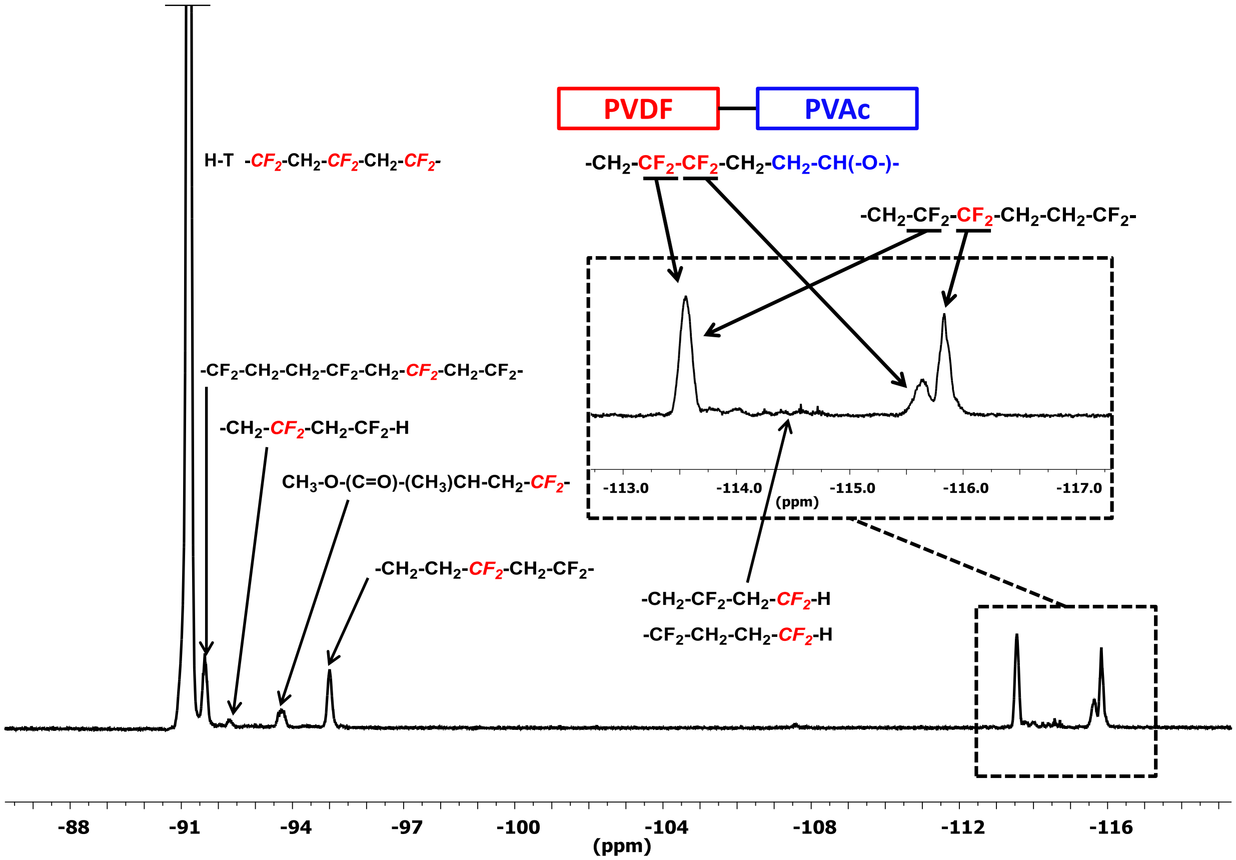


Figure S4. Expansion region from -87 to -120 ppm of ^{19}F NMR spectrum of PVDF$_{51}$-*b*-PVAc$_{172}$ in $(CD_3)_2CO$.

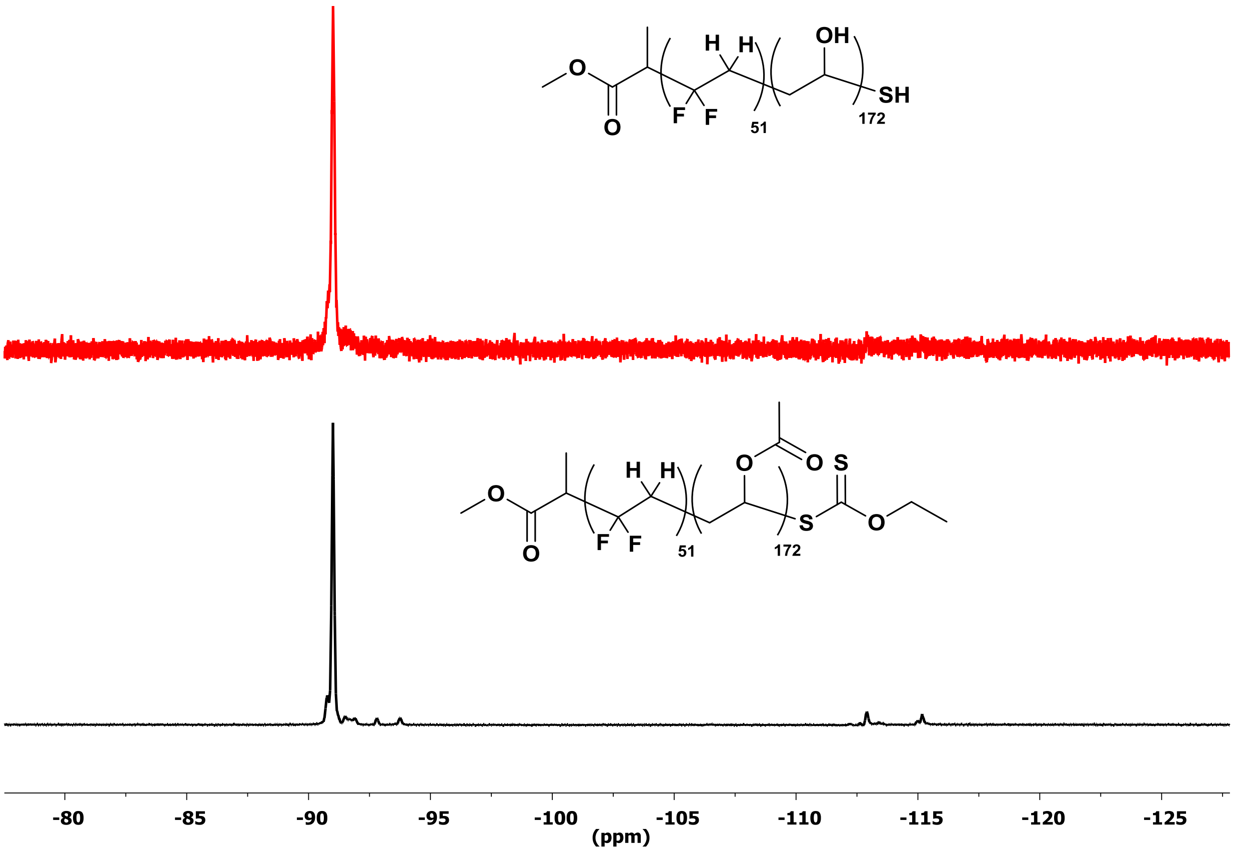


Figure S5. Expansion region from -78 to -127.5 ppm of ^{19}F NMR spectrum of PVDF$_{51}$-*b*-PVAc$_{172}$ (bottom) and PVDF$_{51}$-*b*-PVA$_{172}$ (top) in DMSO-d$_6$

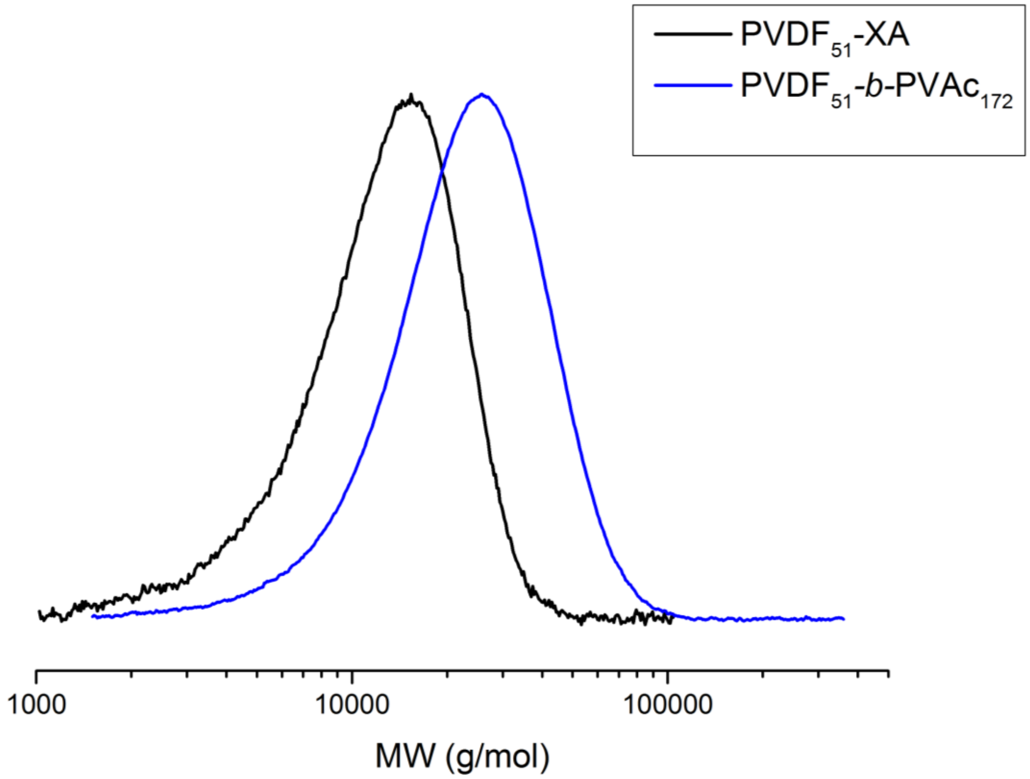


Figure S6. SEC chromatogram of $PVDF_{51}$ and $PVDF_{51}$-*b*-$PVAc_{172}$ block copolymer before hydrolysis.

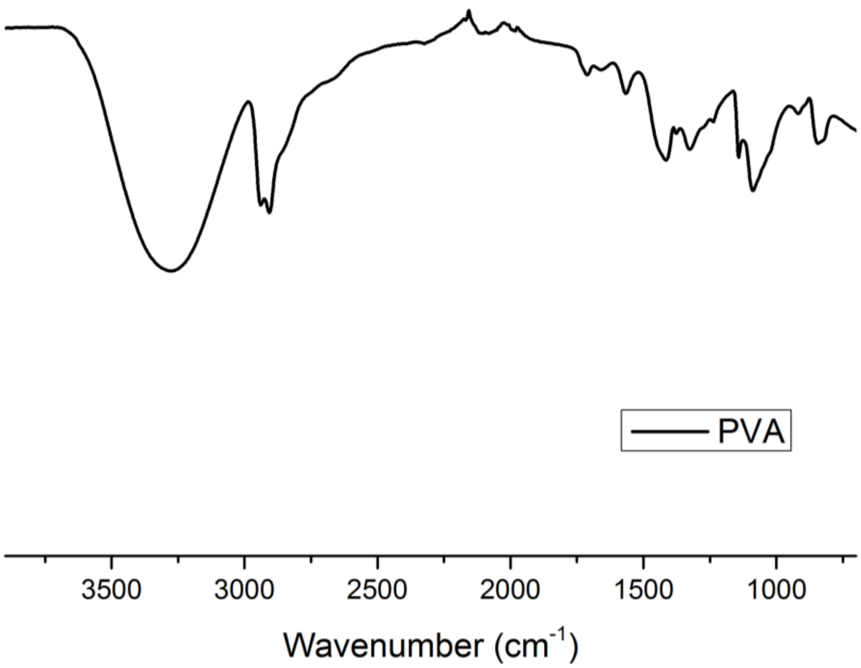


Figure S7. FTIR spectrum of commercial poly(vinyl alcohol) (>99 % of acetate hydrolysis).

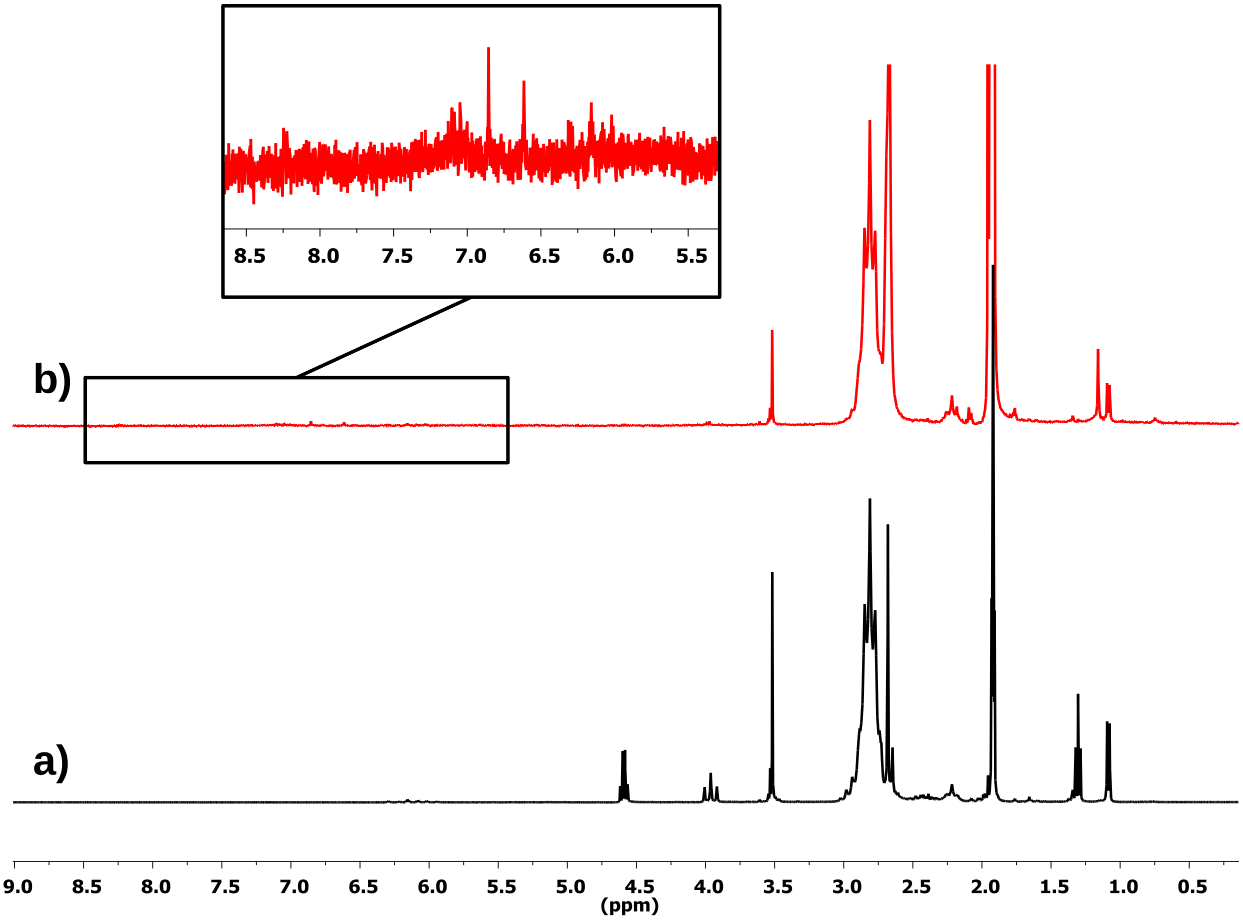


Figure S8. ^{1}H NMR spectrum of a) PVDF-XA and b) PVDF after treatment with a water/alcoholic solution of K_2CO_3 in $(CD_3)_2CO$.

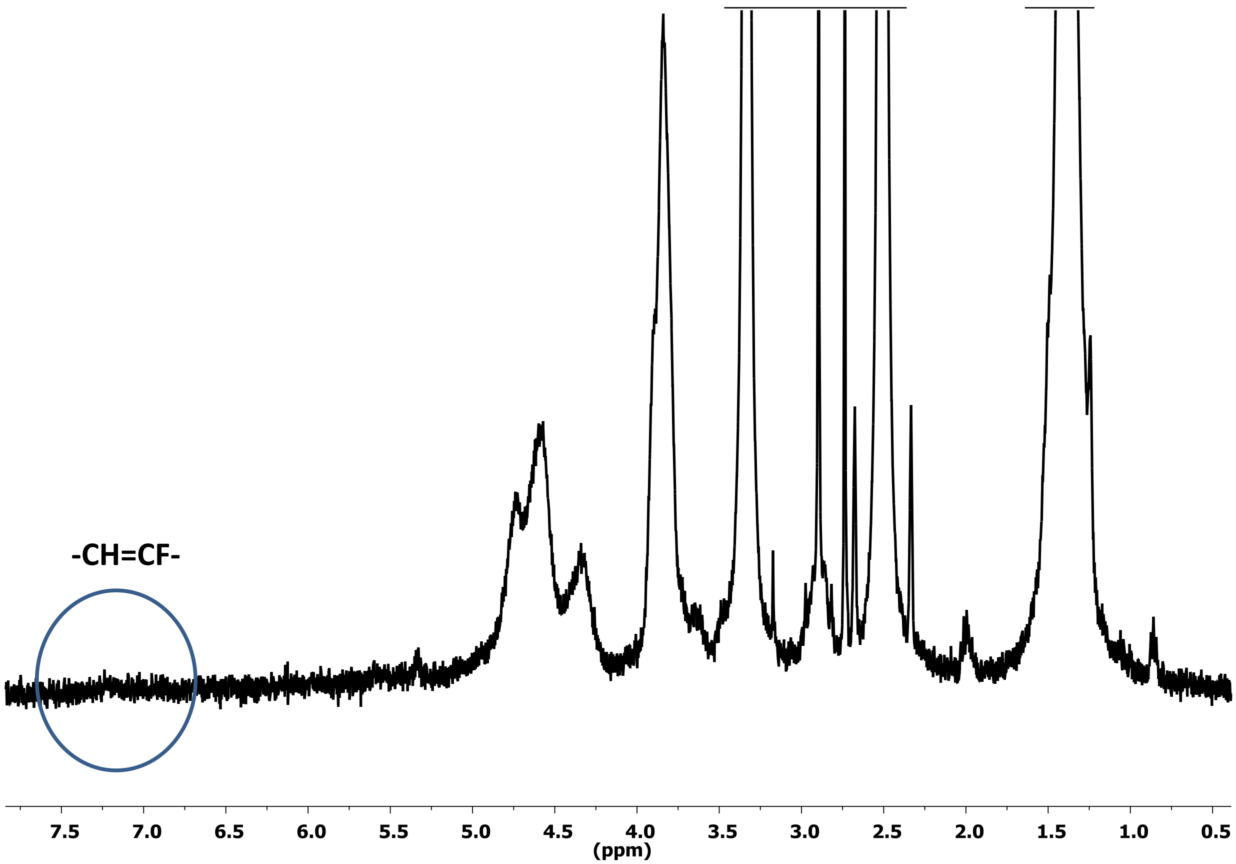


Figure S9. ^{1}H NMR spectrum of PVDF-*b*-PVA block copolymer in *d6*-DMSO. Circled zone shows the potential –CH=CF- double bonds assigned to the dehydrofluorination reactions.

References:

(1) Liu, X.; Coutelier, O.; Harrisson, S.; Tassaing, T.; Marty, J.-D.; Destarac, M., *ACS Macro Lett.*, **4**, 89-93.