Supporting Information

A degradable fluorinated surfactant for emulsion polymerization of vinylidene fluoride

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1- Materials. All reagents were used as received unless stated otherwise. 2-Trifluoromethyl acrylic acid (MAF) was kindly offered by Tosoh Fine Chemicals (Shunan, Japan). 1,1-Difluoroethylene (vinylidene fluoride, VDF) was kindly supplied by Arkema (Pierre Benite, France). Potassium persulfate (KPS, 99.99%), and laboratory reagent grade pentane (purity >95%) were purchased from Sigma-Aldrich and used as received. Deuterated acetone (acetone-d_6) used for NMR spectroscopy was supplied from Euroiso-top (Grenoble, France) (purity >99.8%).

2- Experimental Procedures.

2.1. Synthesis of 3-hydroxy-2-(trifluoromethyl)propanoic acid (MAF-OH).

The fluorinated surfactant (MAF-OH) was obtained from the addition of H_2O onto MAF and characterized by a previously reported procedure.[1]

2.2. Decomposition of MAF-OH in Pressurized Hot Water (PHW).

Decomposition of MAF-OH in PHW with either argon or O_2 atmosphere was carried out in a stainless steel high pressure reactor (31 mL volume) equipped with a thermocouple and a stainless steel screw cap. The screw cap was connected to a pressure gauge for monitoring pressure in the reactor and also connected to a gas sampling port through a needle valve. A gold vessel was fitted into the reactor to eliminate the possibility of contamination from the reactor metal. In a typical run using argon gas, an argon-saturated aqueous (Milli-Q) solution (10 mL) of MAF-OH (59.5 μmol, 5.95 mM) was poured into the gold vessel, and the reactor was pressurized with argon gas up to 0.60 MPa and then sealed. The reactor was placed in an oven, and was heated to the desired temperature (150–250 ºC) at a rate of ca. 10 ºC min^{-1}, and was kept constant for 6 h. Then, the reactor was quickly cooled to room temperature by an electric fan and ice water. Reactions using O_2 gas instead of argon were also carried out. After cooling, a gas sampling bag was connected to the gas sampling port in the screw cap of the reactor, and the gas in the reactor was transferred into the sampling bag through the port by opening the needle valve. The collected gas was analyzed by gas chromatography (GC) and GC-mass spectrometry (GC/MS). On the other hand, the reaction solution in the reactor was subjected to ion chromatography, total organic carbon (TOC) measurement, electrospray ionization mass spectrometry (ESI-MS), and HPLC.

2.3. Radical emulsion polymerization of VDF in water in the presence of MAF-OH as a surfactant. A typical radical emulsion polymerization of VDF (P2, Table 1) was performed in a 100 mL Hastelloy autoclave Parr system (HC 276) equipped with a manometer, a mechanical Hastelloy anchor, a rupture disk (3000 PSI), and inlet and outlet valves. An electronic device regulated and controlled both stirring and heating of the reaction mixture inside the autoclave. Before the reaction, the autoclave was pressurized with 30 bars of nitrogen for 1 h to check for leaks. Then, the autoclave was conditioned for the reaction with several nitrogen/vacuum cycles (10^{-2} mbar) to remove the last trace of oxygen. It was then filled under vacuum with a solution containing the initiator (KPS, 442 mg, 1.635 mmol), the surfactant, MAF-OH (675 mg, 4.270 mmol, 71 mM) and solvent (deionized water; 60 mL). The surfactant solution containing MAF-OH, KPS and water was purged with nitrogen for 20 mins before transferring into the autoclave. The surfactant has been added in such a way that its concentration exceeds the critical micelle concentration. The vessel was then cooled in an acetone/liquid nitrogen bath and the fluorinated gas, VDF (7.0 g, 109 mmol) was transferred into the autoclave under weight control. Then, after warming up to room temperature, the reactor was stirred and gradually heated up to 70 °C. The evolutions of pressure and temperature were recorded during the polymerization. The reaction was stopped by putting the autoclave in an ice bath. The unreacted monomer was purged off and the autoclave was emptied to obtain a stable white dispersion in water. This dispersion was frozen and thawed to coagulate (precipitate). The obtained crude was filtered, washed with water and methanol and then dried under vacuum (20×10^{-3} bar, 70 °C) for 16 h.

The yield of the polymerization was determined gravimetrically (mass of polymers obtained/mass of monomer transferred into the pressure reactor) (yield = 61%). The obtained PVDF white powder was characterized by ^{1}H and ^{19}F NMR spectroscopy.

The rate of inversion to VDF was calculated using the following equations:

$$^{1}H\%\ inversion = \left[\left(\frac{\int_{2.0}^{2.4} I}{\int_{2.0}^{2.4} I + \int_{2.7}^{3.3} I}\right)/2\right] \times 100 \qquad (S1)$$

$$^{19}F\%\ inversion = \frac{\int_{-116}^{-116.5} I}{\int_{-90}^{-95} I + \int_{-113.5}^{-114} I + \int_{-116}^{-116.5} I} \times 100 \qquad (S2)$$

3- Characterization.

3.1. Analysis of MAF-OH Decomposition. The F$^-$ ions in the reaction solutions were quantified by means of an ion-chromatograph equipment (Tosoh IC-2001) consisted of an automatic sample injector (injection volume was 30 μL), analytical column (Tosoh TSKgel Super IC-Anion), and mobile phase consisting of an aqueous solution containing $Na_2B_4O_7$ (6 mM), H_3BO_3 (15 mM), and $NaHCO_3$ (0.2 mM). TOC concentration in the reaction solutions was measured by means of a TOC analyzer (N/C 3100 BU, Analytik Jena) equipped with a halogen-removing column. The TOC concentration was obtained by subtracting inorganic carbon concentration from total carbon concentration. ESI-MS was employed to identify the products in the reaction solutions, using a Shimadzu LCMS-2010 EV instrument and the analyses were performed in negative ion mode. Reaction solution was delivered to the electrospray probe using a mixture of acetonitrile and pure water (20 : 80, by volume) as a mobile phase at a flow rate of 0.2 mL min^{-1}. An HPLC system (Infinity 1200, Agilent) consisting of an automatic sample injector (injection volume was 20 μL), a separation column (Tosoh TSKgel ODS-100V), a column oven and an UV detector (detection wavelength, 210 nm) was also used to identify the products in the reaction solutions. The mobile phase was an aqueous solution containing acetonitrile (0.38 M) and H_3PO_4 (15 mM).

A GC system (GC 323, GL Sciences) consisting of an injector (150 ºC), a column oven (110 ºC), an active carbon column (60/80 mesh, 2.17-mm i.d., 2-m length), and a thermal conductivity detector (130 ºC) was used to quantify CO_2 in the gas phase after reactions. The carrier gas was argon. The gas phase was also analyzed by GC/MS equipment (Shimadzu GCMS-QP2010SE) with a fused silica capillary column (Restek Rt-Q-Bond, 0.32 nm i.d., 30 m length). The carrier gas was helium, and the column oven temperature was programmed from 30 ºC (5 min) to 200 ºC at a rate of 20 ºC min^{-1}, which was held for 20 min. The measurements were performed in full-scan mode (m/z 2.0–200).

3.2. Determination of CMC of MAF-OH using pyrene as a fluorescent probe. The method used followed closely that described by Kalyanasundaram and Thomas in an earlier report.[2] Fluorescence measurements were carried out on a Shimadzu RF 5301 PC Fluorescence Spectrometer with excitation wavelength of 334 nm and the emission spectrum was recorded from 350 to 450 nm. Before each measurement, 1.5 μL of 0.2 mM pyrene solution in ethanol was added into 1 mL surfactant sample, mixed by vortexing, and the fluorescence spectrum recorded immediately. The fluorescence intensities of the peaks at ~372 nm (I_1) and ~383 (I_3) were extracted from the spectra, and the I_3/I_1 value vs. surfactant, MAF-OH concentration was used for CMC determination. One inflection points was observed (Figure S2B) which was selected as the CMC.

3.3. Photoluminescence (PL) Measurements. Photoluminescence (PL) spectra of the aqueous solution of MAF-OH were recorded using a Shimadzu RF 5301 PC Fluorescence Spectrometer.

3.4. Nuclear Magnetic Resonance (NMR) Spectroscopy. The microstructures of the copolymers were determined by ^{1}H, ^{13}C and ^{19}F NMR spectroscopies, recorded on a Bruker AC 400 Spectrometer (400 MHz for ^{1}H and 376 MHz for ^{19}F). Coupling constants and chemical shifts are given in Hertz (Hz) and parts per million (ppm), respectively. The experimental conditions for recording ^{1}H [or ^{13}C or ^{19}F] NMR spectra were as follows: flip angle 90 ° [or 90 °or 30 °], acquisition time 4.5 s [or 0.3 s or 0.7 s], pulse delay 2 s [or 1 or 5 s], number of scans 32 [or 8192 or 64], and a pulse width of 12.5, 9.5 and 10.4 μs for ^{1}H, ^{13}C and ^{19}F NMR, respectively.

3.5. Size Exclusion Chromatography (SEC) Measurements. Molecular weights (M_ns) and dispersities (*Đ*s) of the (co)polymers were assessed from size exclusion chromatography (SEC) with triple-detection GPC from Agilent Technologies using a PL0390-0605390 LC light scattering detector with two diffusion angles (15° and 90°), a PL0390-06034 capillary viscometer, and a 390-LC PL0390-0601 refractive index detector and two PL1113-6300 ResiPore 300 × 7.5 mm columns. DMF (containing 0.1 wt % of LiCl) was used as the eluent at a flow rate of 0.8 mL min^{-1} and toluene as the flow rate marker. The entire SEC-HPLC system was thermostated at 35 °C. Poly(methyl methacrylate) standards were used for calibrating the SEC instrument and the results were processed using the corresponding Agilent software.

3.6. Thermogravimetric Analysis (TGA). The thermogravimetric analysis of the purified and dried polymer samples were performed under air using a TGA 51 apparatus from TA Instruments at a heating rate of 10 °C min^{-1} from room temperature to 580 °C.

3.7. Differential Scanning Calorimetry (DSC). DSC analyses of the (co)polymers were carried out using a Netzsch DSC 200 F3 instrument under N_2 atmosphere. The DSC instrument was calibrated with noble metals and checked before analysis with an indium sample (T_m = 156.6 °C). The heating or cooling range was from -100 °C to 200 °C at a scanning rate of 10 °C min^{-1}. After its insertion into the DSC apparatus, the sample was initially stabilized at 20 °C for 10 min. Then the first scan was made at a heating rate of 10 °C min^{-1} up to 200 °C. It was then cooled to -100 °C. Finally, a second scan was performed at a heating rate of 10 °C min^{-1} up to 200 °C. Melting points (T_ms) were evaluated from the second heating, taken at the maximum of the enthalpy peaks and its area determined the melting enthalpy (ΔH_m). This ensured elimination of the thermal history of the polymers during the first heating.

The degrees of crystallinity of the copolymers were determined using the following eqn:

$$Degree\ of\ crystallinity\ (\chi) = \frac{\Delta H_m}{\Delta H_c} \times 100 \qquad (S3)$$

where ΔH_c (104.5 J g^{-1}) and ΔH_m correspond to the enthalpy of melting of a 100% crystalline PVDF[3] and the heat of fusion of the copolymer (determined by DSC in J g^{-1}), respectively.

3.8. Cryogenic Temperature Electron Microscopy (Cryo-TEM). Cryo-TEM specimens were prepared by applying a drop (ca. 3 µL) of the sample on a perforated carbon film supported on a copper TEM grid (lacey Formvar/carbon films on 200 mesh Cu grids, from Ted Pella, Redding, CA, USA), held by tweezers inside a controlled environment vitrification system (CEVS),[4] kept at 25 °C and 100% relative humidity. Excess liquid was removed by blotting with filter-paper supported on a metal strip. The specimens, about 200-400 nm thick, were vitrified by plunging into liquid ethane at its freezing point of -183°C. The specimens were examined with an FEI Talos 200C field-emission-gun equipped high-resolution TEM at an accelerating voltage of 200 kV, using a Gatan 626 cryo-holder kept at about -180 °C. Images were recorded digitally by a 4k x 4k pixels FEI Falcon II direct-imaging camera, using the low-dose imaging mode to minimize electron-beam radiation-damage.

4- Supplementary tables.

Table S1. Decomposition of MAF-OH and related chemicals in PHW.[a]

Entry	Substrate [initial amt/μmol]	Coexisiting gas	*T*/ °C	*P*/MPa	F^-/μmol [yield /%]	CO_2/μmol [yield /%]	TOC/μmol [remaining ratio/%]
1	MAF-OH [59.5]	Ar	150	1.2	158±7 [89±1]	37.2±1.4 [16]	175±2 [74±2]
2	MAF-OH [59.5]	Ar	200	1.9	159±1 [89±1]	32.7±2.4 [14±1]	173±0.5 [73]
3	MAF-OH [59.5]	Ar	230	2.9	158±0.05 [89]	37.9±2.9 [16±1]	182±5 [76±3]
4	MAF-OH [59.5]	Ar	250	4.1	171±3 [96±2]	49.2±8.8 [21±3]	170±19 [71±8]
5	MAF-OH [59.5]	O_2	150	1.2	161±5 [90±3]	38.1±1.7 [16±1]	162±8 [68±3]
6	MAF-OH [59.5]	O_2	200	2.0	167±11 [93±6]	89.0±3.3 [37±1]	99±14 [42±6]
7	MAF-OH [59.5]	O_2	230	3.0	159±3 [89±2]	111±17 [47±7]	8±3 [3±2]
8	MAF-OH [59.5]	O_2	250	4.0	155±3 [87±2]	118±6 [50±3]	54±26 [23±11]
9[b]	PFOS [3.72]	Ar	350	–	0.10 [0.16]	–	–
10[c]	PFOA [3.86]	Ar	350	–	1.09 [1.88]	–	–

[a] Reaction time was 6 h. [b] Taken from H. Hori, Y. Nagaoka, A. Yamamoto, T. Sano, N. Yamashita, S. Taniyasu, S. Kutsuna, I. Osaka, R. Arakawa, *Environ. Sci. Technol*, 2006, 40, 1049-1054. Potassium salt of PFOS was used. In this reaction, the gas phase was not monitored. [c] Performed under the same reaction conditions with entry 9, except that PFOA was used. Both PFOS and PFOA were very little mineralized to F^- in pure subcritical water under argon even at high temperature, 350 °C.

Formation of F^- ions in the reaction solution and formation of CO_2 in the gas phase were observed (Table S1). When the reaction was carried out at 150 °C, 158 μmol of F^- was detected in the reaction solution (entry 1), which corresponds to the F^- yield of 89%. Although MAF-OH has a CF_3 group, no CF_3H was detected in the gas phase.

The total organic carbon (TOC) measurement enabled to evaluate the organic compounds present in the reaction solution. When the reaction was performed at 150 °C, the amount of TOC was 175 μmol (entry 1), 74% of the carbon atoms in the initial MAF-OH remained in the reaction solution as component of organic compounds. This result revealed that carbon atoms in MAF-OH were not well mineralized in pure PHW at those temperatures. At 250 °C, the TOC amount was 170 μmol (entry 4), indicating that 71% of the carbon atoms involved in initial MAF-OH remained in organic compounds. At this temperature, the sum of amounts of TOC (170 μmol) and CO_2 (49.2 μmol) were calculated to be 219 μmol, which is 92% of the carbon atoms in initial MAF-OH.

Table S2 CMC of different F-surfactants

Entry	Surfactant	CMC	Reference
1	Tivada	0.2 wt%	[5]
2	PFOA	9 mM	[6]
		38 mM	[7]
		25 mM	[8]
3	PFOS	8.9 mM	[7]
		8 mM	[9]
4	MAF-OH	2.3 mM	Present study

Table S3. Experimental conditions and results for the emulsion polymerization of VDF, initiated by KPS in presence of MAF-OH.[a]

entry	MAF-OH (wt%)	Yield (%)	M_n[b] (g/mol)	$Đ$[b]	*Defects*[c] *(%)*	$D_{h,DLS}$ *(nm)*[d]	$T_{d10\%}$[e] (°C)	T_m[f] (°C)	χ[f] (%)
P1	0	51	2100	1.72	3.45	297	435	161	56
P2	0.1	55	2600	1.69	2.55	260	427	165	54
P3	0.5	64	2400	1.64	2.45	176	414	162	49
P4	1.0	67	2900	1.65	2.35	178	394	164	45
P5	1.5	70	3100	1.70	2.35	148	367	161	45
P6	2.0	73	3200	1.68	2.3	123	319	163	39

Acronyms: VDF: vinylidene fluoride; MAF-OH : 3-hydroxy-2-(trifluoromethyl)propanoic acid ; KPS: potassium persulfate. [a]Conditions: Volume of solvent, water = 60 mL. [b]Molar masses (M_n)s and dispersities ($Đ$) of the original PVDF, determined by SEC in DMF, from PMMA standard. [c]Defects (%) were assessed by by ^{1}H (T-T) and ^{19}F (H-H) NMR spectroscopy using eqn (S1-S2). [c]Determined by DLS. [e]Assessed by thermogravimetric analysis (TGA), under air at 10 °C min^{-1}. [f]Determined by differential scanning calorimetry (DSC); χ: crystallinity determined from eqn (S3).

5- Supplementary figures.

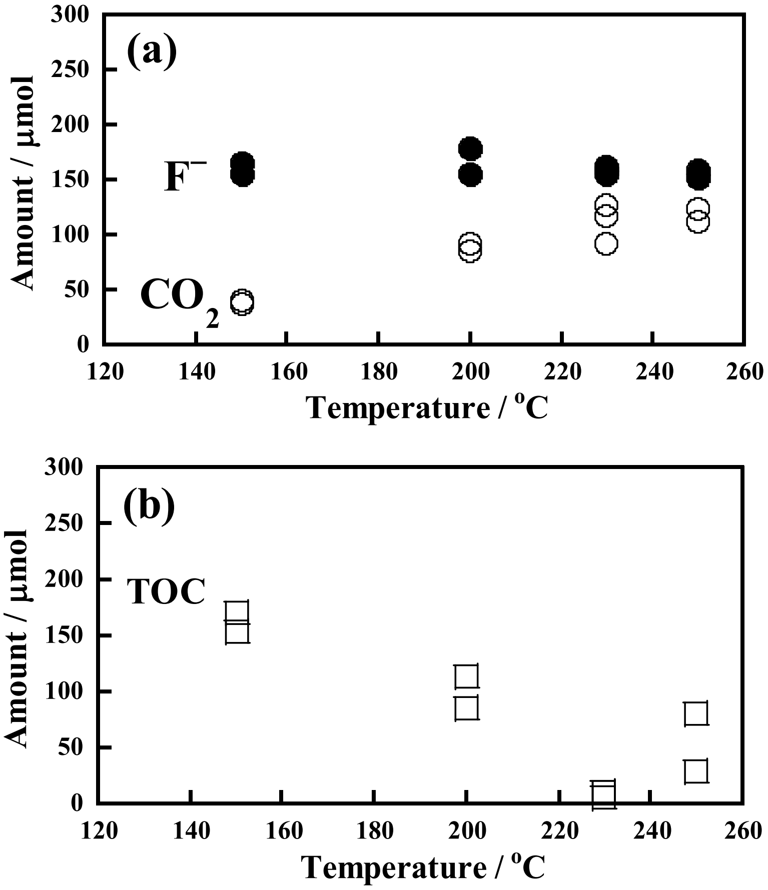
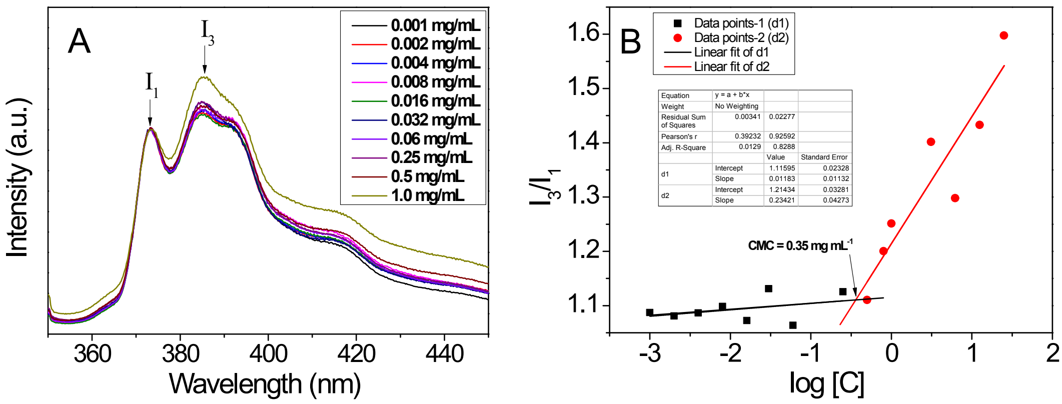


Fig. S1. Temperature dependence of decomposition of MAF-OH in PHW performed under O_2: (a) amounts of F^- in the reaction solution and CO_2 in the gas phase, and (b) amount of TOC in the reaction solution. Aqueous solution (10 mL) of MAF-OH (59.5 µmol, 5.95 mM) was heated at 150–250 °C for 6 h under O_2. Two or three reactions were performed under the same conditions. The corresponding data listed in Table S1 (entries 5-8) represent the average values.

Reactions in the presence of O_2 were also carried out. The formation amounts of F^- and CO_2 are listed in entries 5–8 in Table S1. In accordance with the reactions under argon, fluorine atoms in the initial MAF-OH were well mineralized to F^-. When the reaction was carried out at 150 °C, the F^- amount was 161 µmol, which indicates the F^- yield was 90%. Likewise, reaction performed at 250 °C led to a F^- amount of 155 µmol, indicating a F^- yield of 87%. Very similarly, F^- values were obtained at all tested temperatures, and result was similar to that observed for reactions under argon. In contrast, CO_2 formation in the reactions in the presence of O_2 showed different tendency from those achieved under argon. At 150 ºC, the CO_2 amount was 38.1 μmol, indicating a CO_2 yield of 16% (entry 5). This value was the same as that obtained under argon (16%, entry 1). However, in contrast to the reactions under argon, increasing reaction temperature clearly enhanced CO_2 formation. For reaction was performed at 250 ºC, the CO_2 amount became 118 μmol, which corresponds to a CO_2 yield of 50% (entry 8). Increasing reaction temperature decreased the TOC amount. A reaction performed at 250 ºC led to TOC amount of 54 μmol (entry 8). This value corresponds to 23% of the amount of carbon atoms in initial MAF-OH. The sum of amounts of TOC (54 μmol) and CO_2 (118 μmol) was 172 μmol, which corresponds to 72% of the carbon atoms in initial MAF-OH. Such a lower value than that under argon (92%) suggests that some carbon containing species other than CO_2 released to the gas phase in the reaction with O_2. In fact, GCMS measurement evidenced the presence of some hydrocarbons in the gas phase. Only C_2H_4 could be quantified, in trace amount (~0.1 μmol).



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.00341	0.02277	
Pearson's r	0.39232	0.92592	
Adj. R-Square	0.0129	0.8288	
		Value	Standard Error
d1	Intercept	1.11595	0.02328
	Slope	0.01183	0.01132
d2	Intercept	1.21434	0.03281
	Slope	0.23421	0.04273

Fig. S2. A) Surfactant concentration dependent vibronic band intensities of pyrene fluorescence: [pyrene] = 2 pM; λ_{excit} = 334 nm. B) Determination of critical micellar concentration (CMC) of MAF-OH. Any physical property of a surfactant solution changes sharply at the onset of cmc formation.

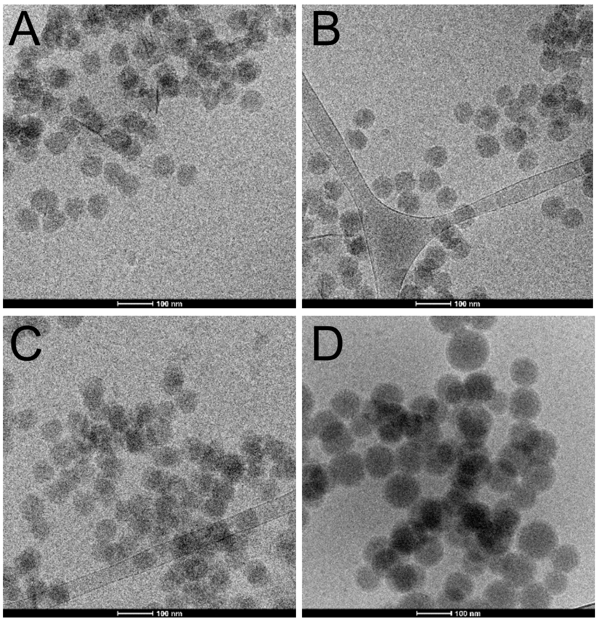


Fig. S3 cryo-TEM images of PVDF latex prepared by radical polymerization of VDF in presence of different MAF-OH concentrations (A: entry P2; B: entry P4; C: entry P5; D: entry P6 of Table S2).

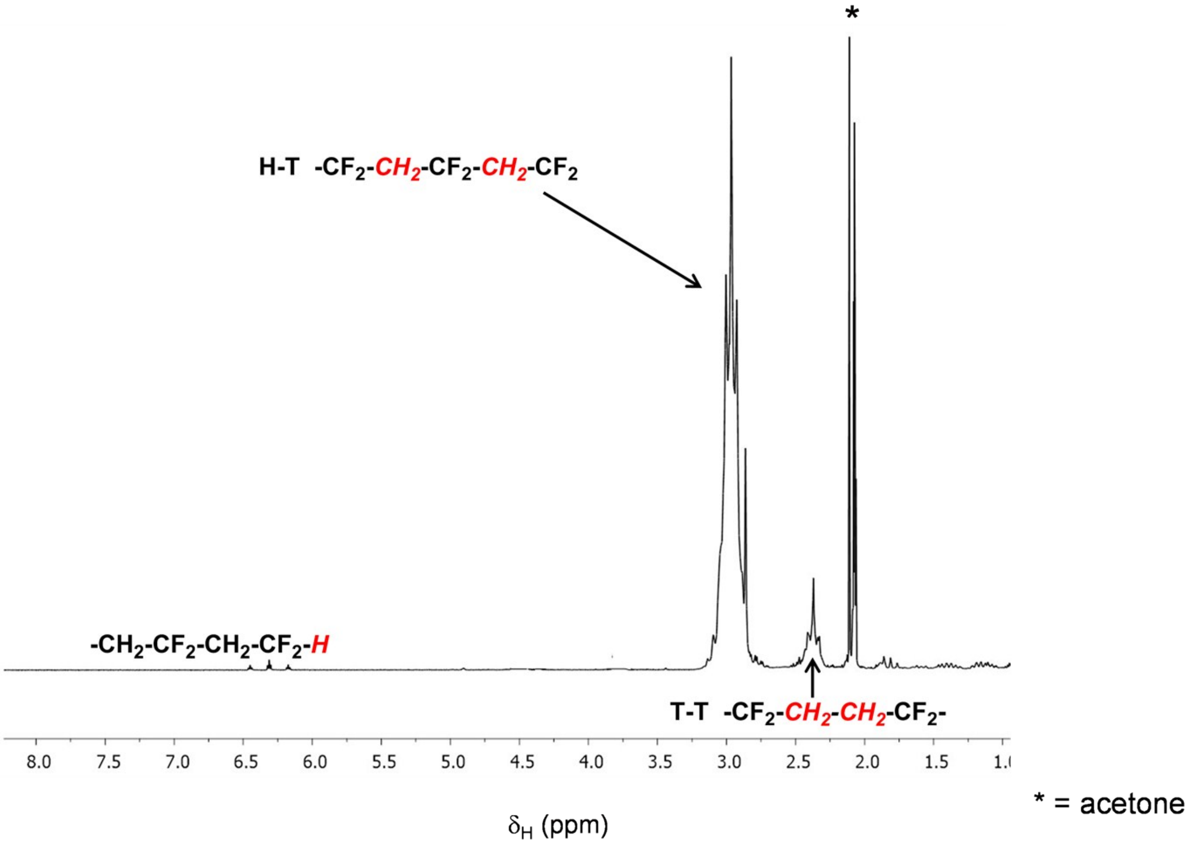


Fig. S4 Representative ^{1}H NMR spectrum of PVDF (P3, Table S1) prepared by radical polymerization using KPS in presence of MAF-OH, recorded in acetone-d_6 at 20 °C. (*) Solvent (acetone) peak.

The ^{1}H NMR spectrum of the PVDF homopolymer (Fig. S3). reveals the characteristic signal of the -$CF_2C\underline{H_2}$-$C\underline{H_2}CF_2$- reverse T-T VDF-VDF dyad addition (m, 2.35 to 2.50 ppm), -$C\underline{H_2}CF_2$-$C\underline{H_2}CF_2$-, normal H-T VDF-VDF dyad addition (m, 2.60 to 3.20 ppm), and a small triplet of triplets corresponding to the -CH_2CF_2-$\underline{H}$ end-group caused either by the transfer to the solvent or polymer or from the backbiting[10] (in the range of 6.05 to 6.45 ppm, $^2J_{HF}$ = 55 Hz, $^3J_{HH}$ = 6-7 Hz).

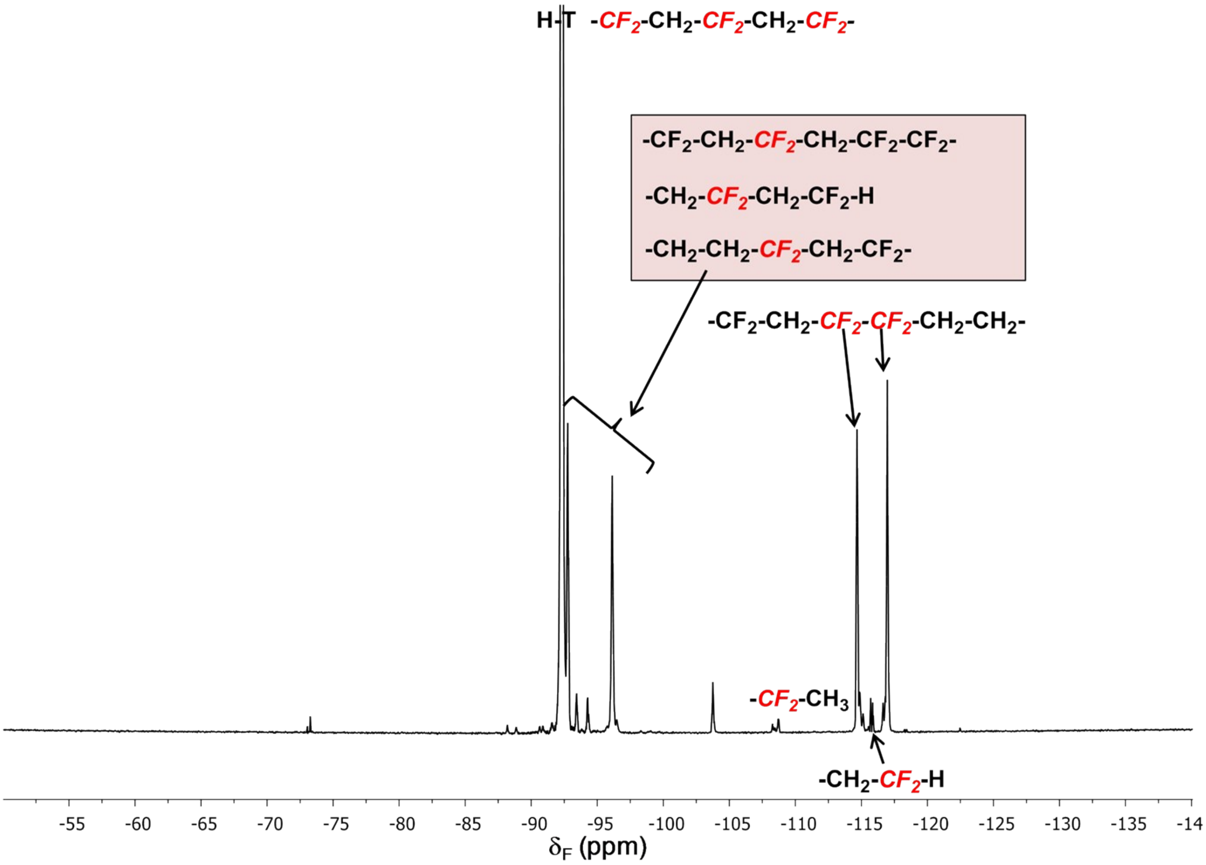


Fig. S5 Representative ^{19}F NMR spectrum of PVDF (P1, Table S1) prepared by radical polymerization of VDF using KPS in presence of MAF-OH, recorded in acetone-d6 at 20 °C.

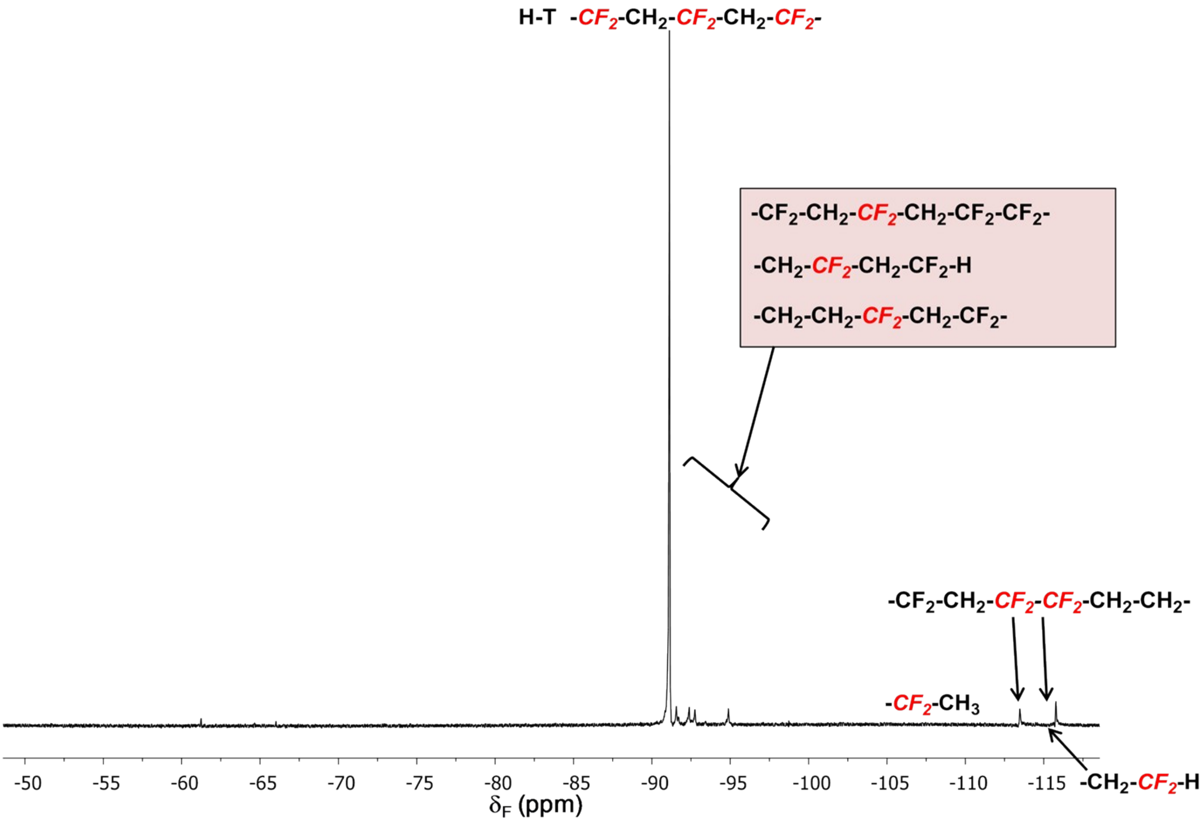


Fig. S6 Representative ^{19}F NMR spectrum of PVDF (P2, Table S1) prepared by radical polymerization of VDF using KPS in presence of MAF-OH, recorded in acetone-d6 at 20 °C.

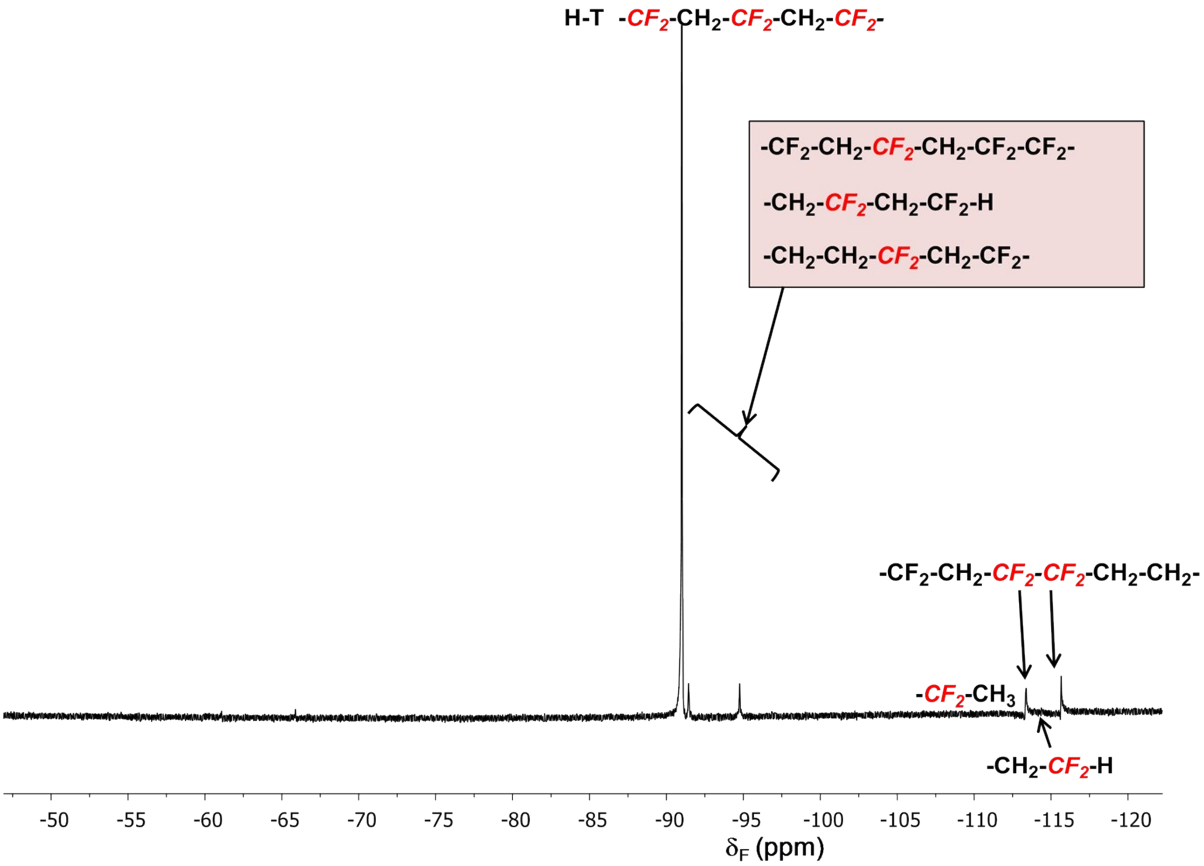


Fig. S7 Representative ^{19}F NMR spectrum of PVDF (P4, Table S1) prepared by radical polymerization of VDF using KPS in presence of MAF-OH, recorded in acetone-d6 at 20 °C.

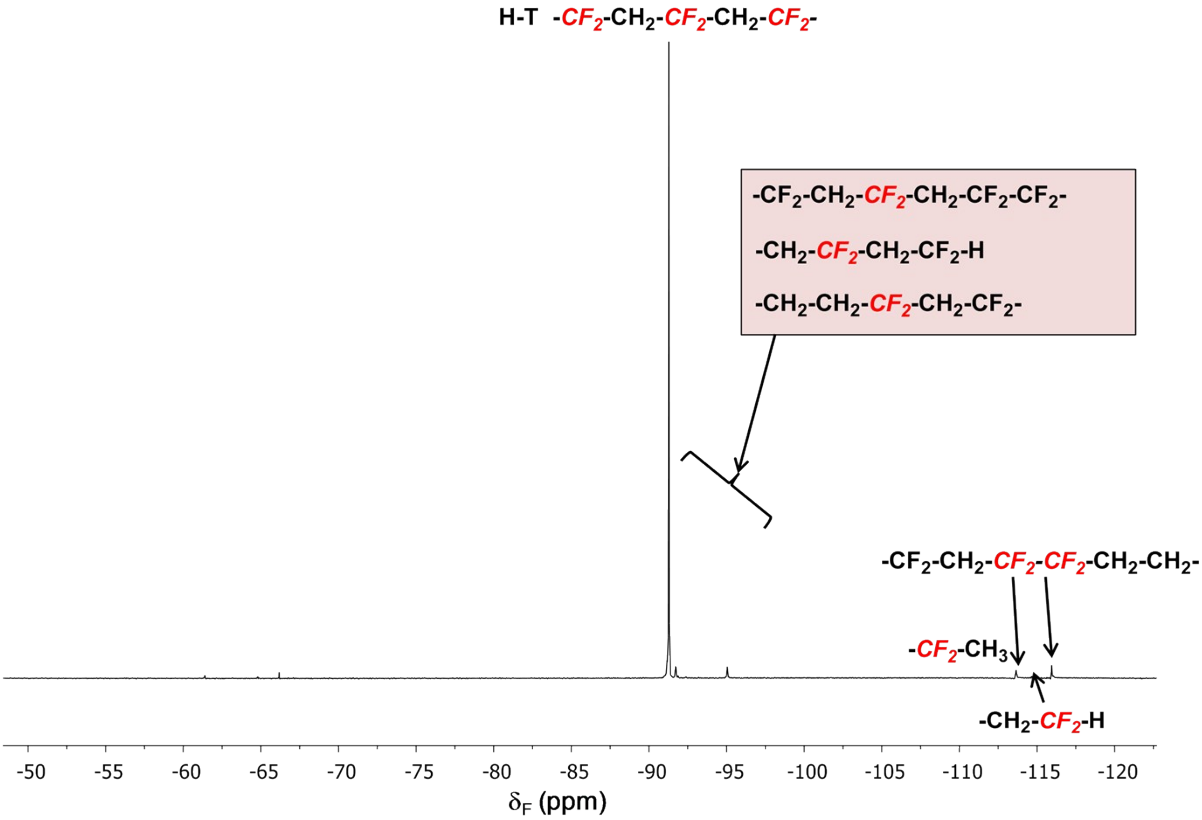


Fig. S8 Representative ^{19}F NMR spectrum of PVDF (P5, Table S1) prepared by radical polymerization of VDF using KPS in presence of MAF-OH, recorded in acetone-d6 at 20 °C.

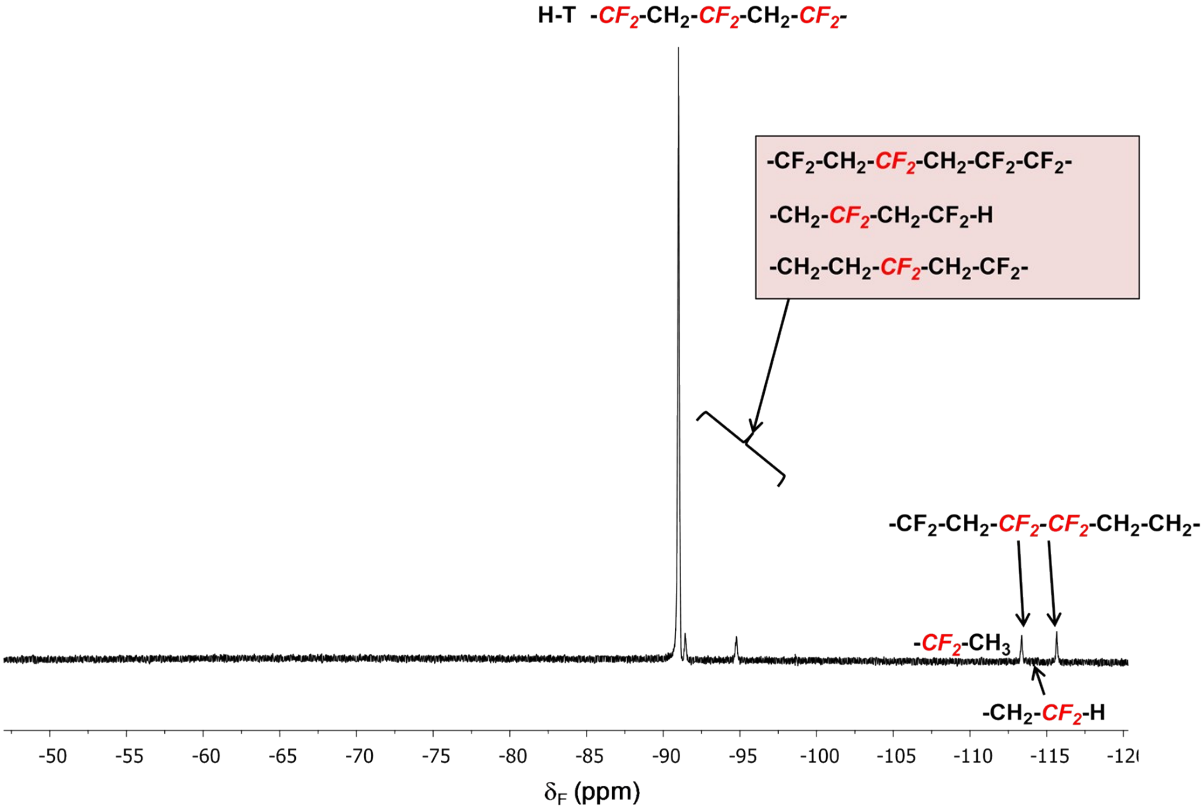


Fig. S9 Representative ^{19}F NMR spectrum of PVDF (P6, Table S1) prepared by radical polymerization of VDF using KPS in presence of MAF-OH, recorded in acetone-d6 at 20 °C.

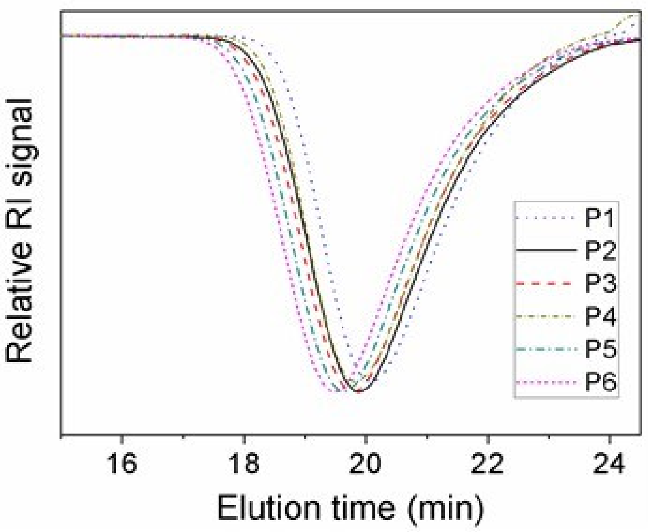


Fig. S10 SEC traces of PVDF samples synthesized via emulsion polymerization of VDF, stabilized by different wt% of MAF-OH surfactant (entries P1-P6, Table S2). Because PVDF have lower refractive indices (RIs) compared to the eluent and the detector is RI, the SEC signals are negative.

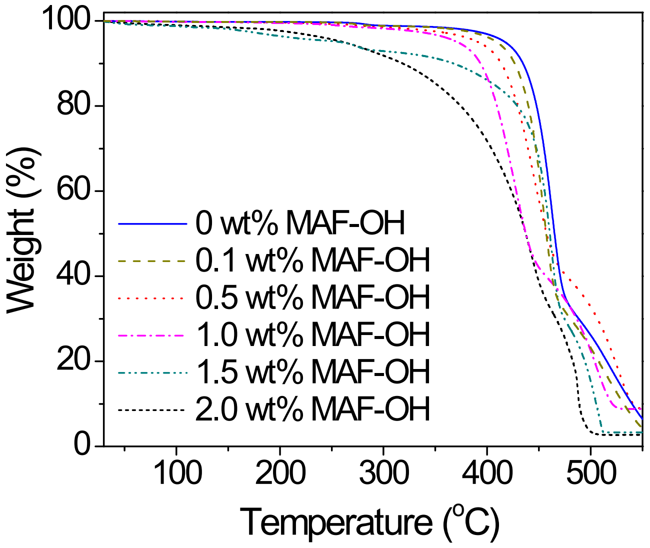


Fig. S11 TGA thermograms of PVDF samples synthesized via emulsion polymerization of VDF, stabilized by different wt% of MAF-OH surfactant (entries P1-P6, Table S2), heated at 10 °C min^{-1} under air.

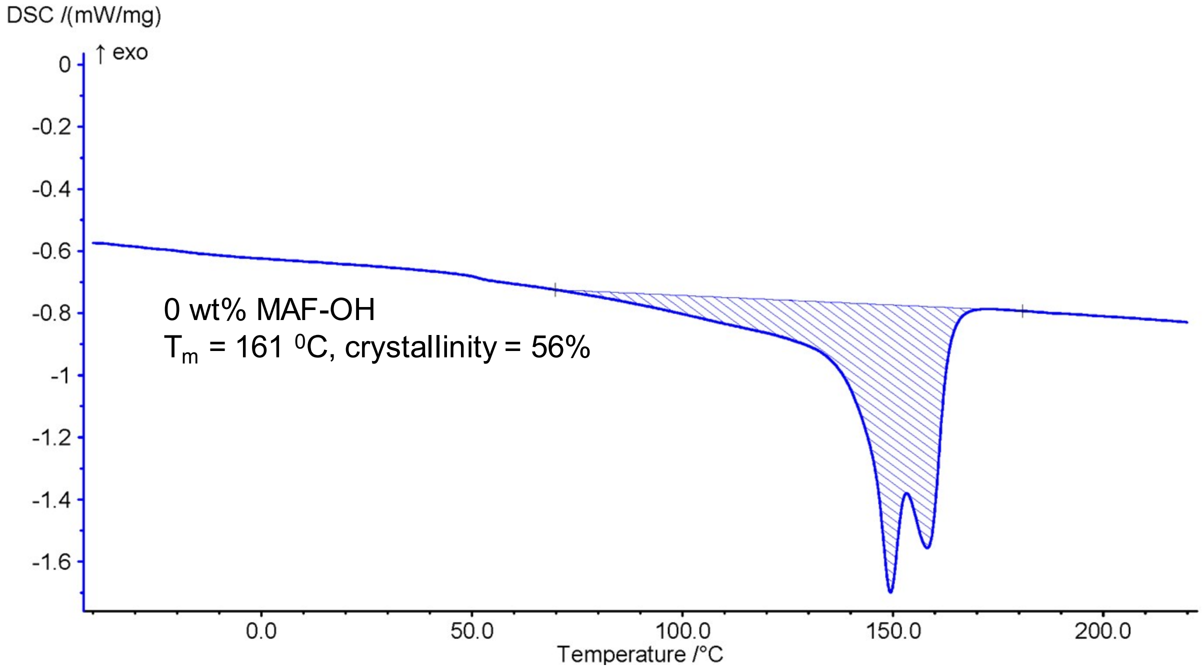


Fig. S12 DSC thermogram of PVDF sample, synthesized via emulsion polymerization of VDF, in absence of MAF-OH surfactant (entry P1, Table S2).

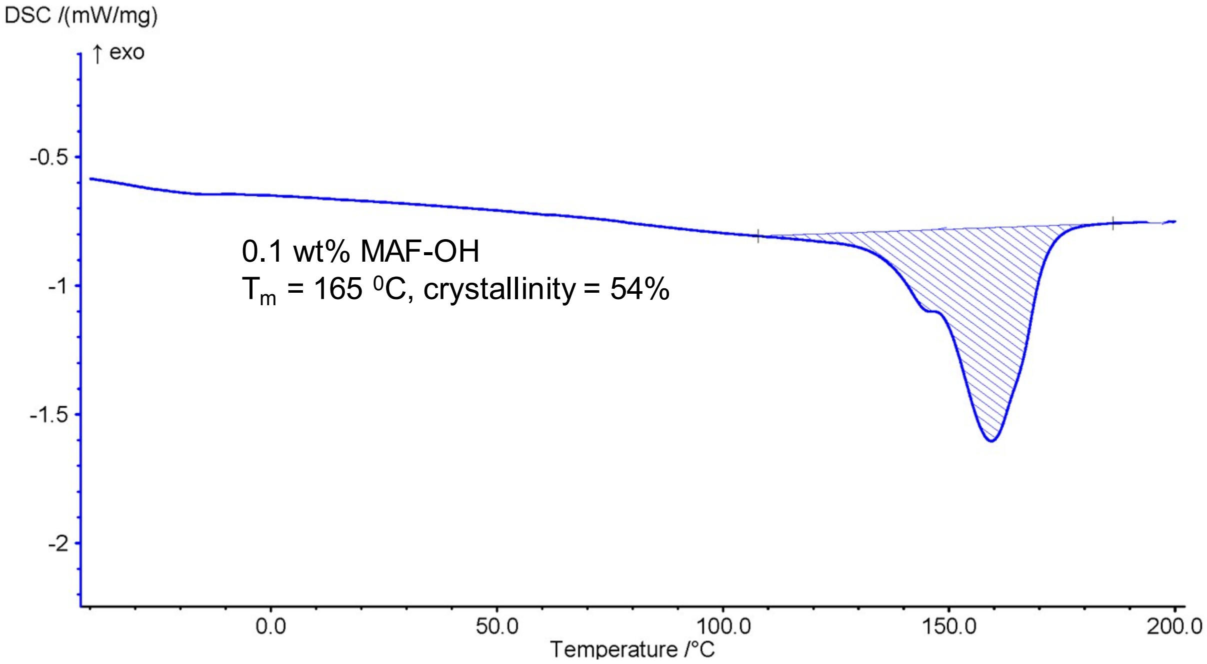


Fig. S13 DSC thermogram of PVDF sample, synthesized via emulsion polymerization of VDF, stabilized by 0.1 wt% MAF-OH surfactant (entry P2, Table S2).

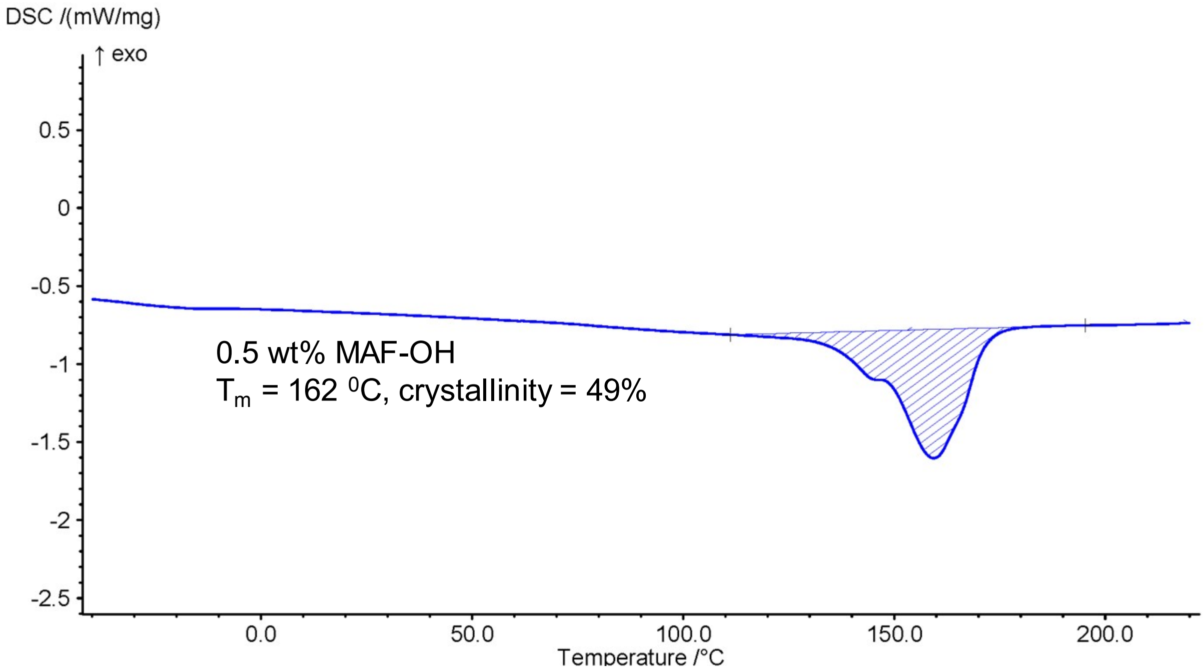


Fig. S14 DSC thermogram of PVDF sample, synthesized via emulsion polymerization of VDF, stabilized by 0.5 wt% MAF-OH surfactant (entry P3, Table S2).

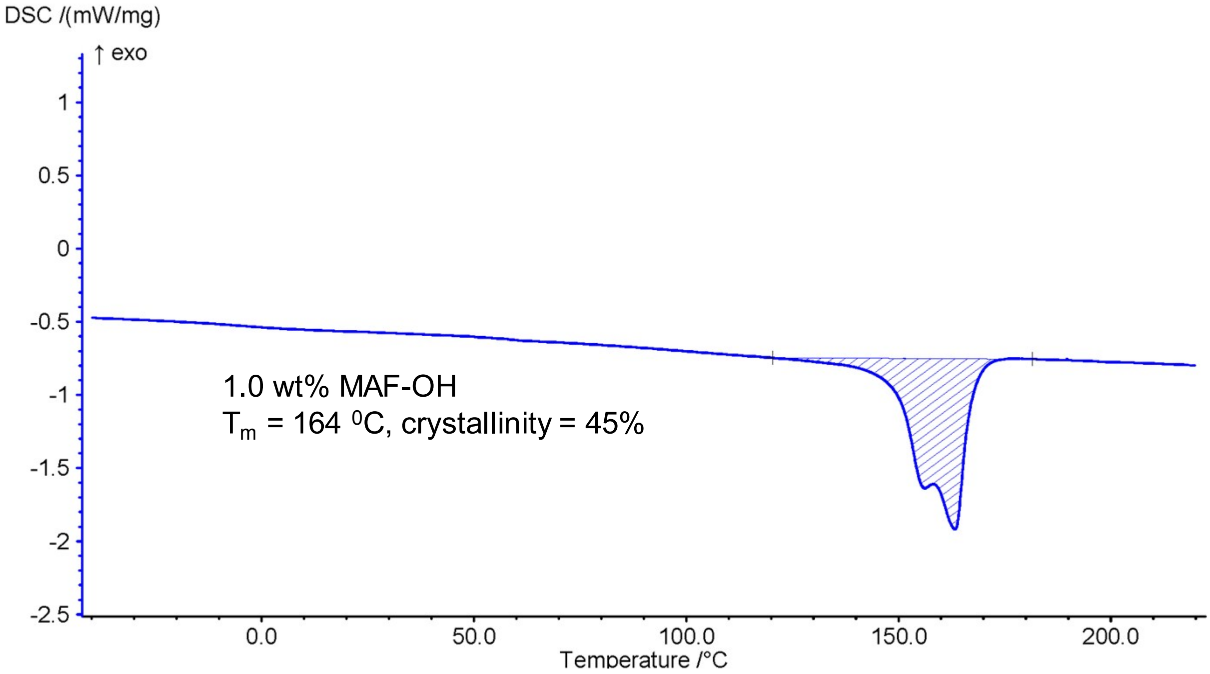


Fig. S15 DSC thermogram of PVDF sample, synthesized via emulsion polymerization of VDF, stabilized by 1.0 wt% MAF-OH surfactant (entry P4, Table S2).

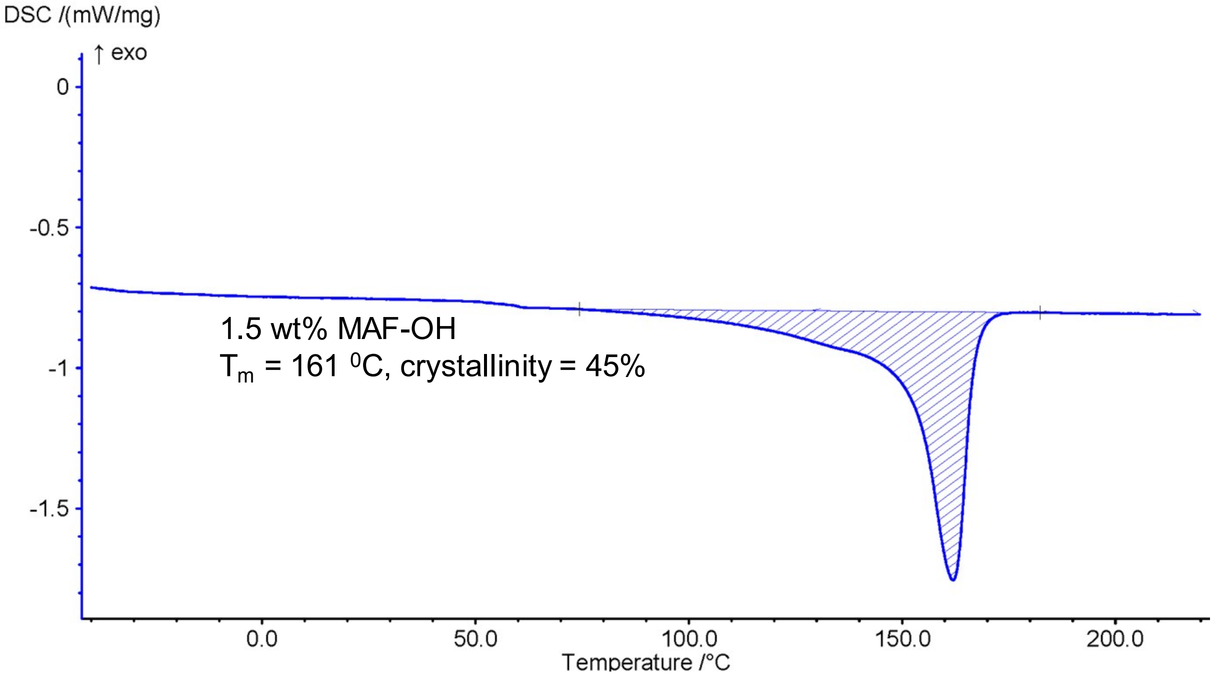


Fig. S16 DSC thermogram of PVDF sample, synthesized via emulsion polymerization of VDF, stabilized by 1.5 wt% MAF-OH surfactant (entry P5, Table S2).

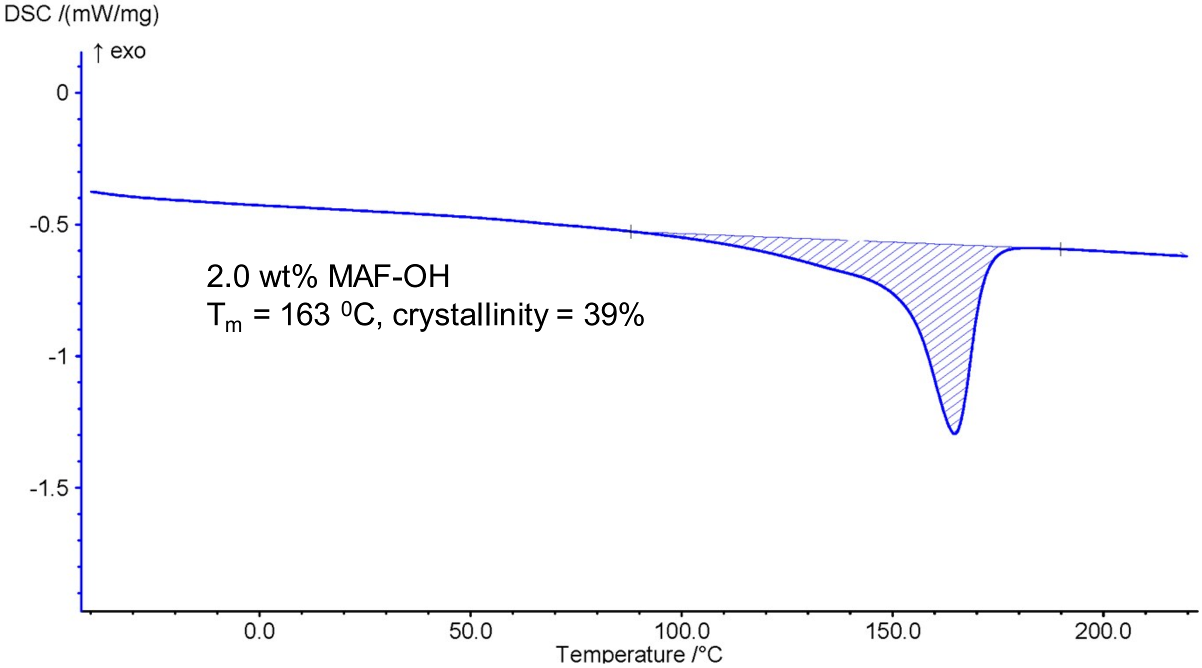


Fig. S17 DSC thermogram of PVDF sample, synthesized via emulsion polymerization of VDF, stabilized by 2.0 wt% MAF-OH surfactant (entry P6, Table S2).

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