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First Amphiphilic Poly(vinylidene fluoride-*co*-3,3,3-trifluoropropene)-*b*-oligo(vinyl alcohol) Block Copolymers as Potential Nonpersistent Fluorosurfactants from Radical Polymerization Controlled by Xanthate

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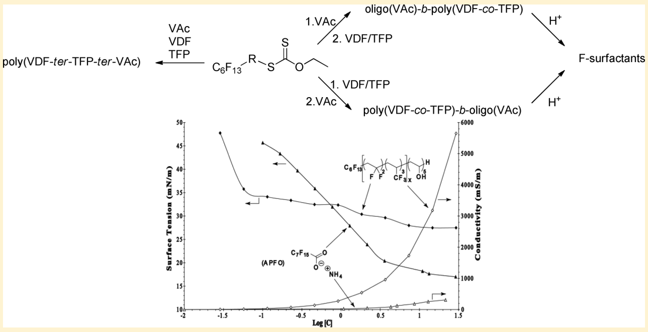
S *Supporting Information*



ABSTRACT: The synthesis of poly(vinylidene fluoride-*co*-3,3,3-trifluoropropene)-*b*-oligo(vinyl alcohol) block copolymers by sequential controlled radical copolymerization of vinylidene fluoride (VDF) and 3,3,3-trifluoropropene (TFP) and of vinyl acetate in the presence of xanthate and their use as original surfactants are presented. First, a fluorinated xanthate $C_6F_{13}C_2H_4OC(O)CH(CH_3)SC(S)OC_2H_5$ was prepared in two steps from 1*H*,1*H*,2*H*,2*H*-perfluorooctanol in 67% overall yield. Then, it was successfully involved as a chain transfer agent for the macromolecular design via the interchange of xanthates (MADIX) polymerization of vinyl acetate in a fluorinated solvent in 71% yield, and a good agreement was noted between targeted and experimental molecular weights of poly(vinyl acetate). This fluorinated xanthate was also successfully used in the radical copolymerization of VDF and TFP. Then, these poly(VDF-*co*-TFP) copolymers bearing a xanthate end group were involved in the controlled radical polymerization of vinyl acetate (VAc) leading to poly(VDF-*co*-TFP)-*b*-oligo(VAc) block copolymers. All the structures of the obtained intermediates and copolymers were characterized by NMR spectroscopy and size exclusion chromatography to assess the molar contents of VDF, TFP, and VAc and the molecular weights and polydispersity indices. The results show, particularly in the case of the direct radical terpolymerization, that VAc and VDF are the most and the least reactive monomers, respectively. The acidic hydrolysis of poly(VAc) sequences of the block copolymers into oligo(vinyl alcohol) led to original water-soluble surfactant, the surface tension of which (27 mN m^{-1} at 7.2 g L^{-1}) was comparable to that of ammonium perfluorooctanoate (APFO) and thus appears as potential alternative to APFO surfactant.

■ INTRODUCTION

Fluorinated surfactants[1,2] are amphiphilic molecules based on hydrophobic/hydrophilic counterparts. They are involved in more than 200 applications that range from emulsifiers for aqueous polymerization of hydrophobic monomers (and especially fluoromonomers), to antimisting agents, surface agents, firefighting foams, pressure-sensitive adhesives, paint additives, coatings, and to cosmetics.[3−5] They have found much interest because they exhibit very low critical micellar concentration values.[1] Fluorinated surfactants (i.e., containing a fluorinated hydrophobic part) are known to be more efficient than their hydrogenated homologues.[1]

Various commercially available compounds have been marketed by Asahi Glass, Atofina, Daikin, Clariant, and DuPont, under the Surlyn, Forafac, Unidyne, Fluowet, and Zonyl trade names, respectively. However, recent toxicological surveys have reported that compounds containing perfluorinated chain longer than six or seven carbon atoms are regarded as too stable and hence induce bioaccumulation (perfluorooctanesulfonic acid's half-life is ca. 3.26 years in human blood[6,7]).[8−10] Among these bioaccumulable compounds are the well-known perfluorooctanoic acid ($C_7F_{15}CO_2H$, PFOA), ammonium perfluorooctanoate ($C_7F_{15}CO_2NH_4$, APFO), and perfluorooctanesulfonic acid ($C_8F_{17}SO_3H$, PFOS), for which C_7F_{15} and C_8F_{17} are too stable

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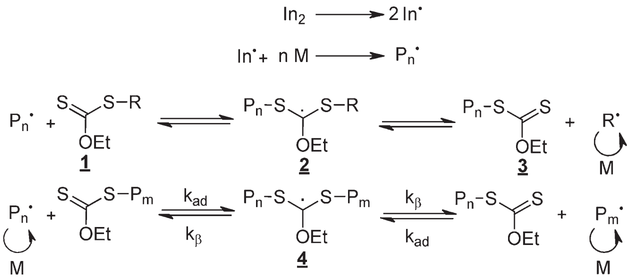
and responsible for the long half-lives of these surfactants. Indeed, the Stewardship program[11] involving eight major industrial chemical industrial companies in organofluorine and macromolecular fluorine chemistries are trying to find alternatives to prepare efficient fluorinated surfactants that do not exhibit these three aforementioned drawbacks. For example, 3M reported the synthesis of surfactants containing a C_4F_9 end group.[12] Recently, Arkema Company[13] has claimed the synthesis of $C_2F_5(VDF)_2-CH_2CO_2H$ prepared in four steps from the radical telomerization of vinylidene fluoride (VDF) with C_2F_5I. On the other hand, fluorinated surfactants based on oligo(hexafluoropropylene oxide) have shown good surface properties and can be biodegraded.[14,15] Besides these exotic surfactants, it is urgent to find new chemicals with highly surface active properties that can be degraded during biological or metabolic processes. To fulfill that challenge, it is worth synthesizing fluorinated surfactants containing a hydrogenofluorinated hydrophobic counterpart. As in the above case, fluorinated chains based on VDF units may undergo possible degradation by the action of enzymes or in a metabolic process. Thus, we prepared surfactants based on 3,3,3-trifluoropropene (TFP). This monomer is interesting since it can be telomerized or copolymerized to be incorporated in long chain compounds, which has the concomitant advantages to bear CF_3 side groups (favoring better surface properties and regarded as the hydrophobic part) and to possess methylene groups (which enable the degradation). In contrast to perfluorinated compounds, hydrofluorinated molecules can be degraded by first, elimination of HF, yielding a double bond that can be oxidized and cleaved.[16] This degradation can be advantageously achieved by the methylene and methyne protons brought by each TFP unit. The hydrophilic counterpart can be brought by a polar group or by a polar block.

To the best of our knowledge, none of these products containing TFP are available in the market, and the literature reports only one survey[17] in which this olefin can be polymerized under controlled radical polymerization. That strategy offers a wide range of polymeric architectures and especially block copolymers suitable as novel materials. For a more efficient copolymerization or cotelomerization of TFP, vinylidene fluoride (VDF)[18] was inserted in the media as recently achieved, either by iodine transfer copolymerization (ITP)[19] or by stepwise cotelomerization[20,21] of both above-mentioned fluoroolefins, leading to poly(VDF-*co*-TFP) cotelomers or copolymers.

However, the insertion of a polar group in the produced poly(VDF-*co*-TFP)-I copolymer was achieved in low to fair yield. Hence, it was of interest to find out another process. Although discovered in the late 1970s by Tatemoto (ITP),[22,23] the controlled radical polymerization (CRP) has drawn a lot of attention since the mid-1990s.[24−28] CRP is based on the fast exchange between active and dormant species.[29] The active species is able to propagate as in traditional free radical polymerization. This equilibrium induces a linear growth of the chains (and hence of the molar masses versus the monomer conversion) and therefore a good control over the reaction. A precise control of the molecular weight (M_n) or degree of polymerization (DP_n) and a narrow polydispersity (PDI) are obtained when the polymerization has a controlled character (no dead chains) together with a rapid consumption of the initiator (concurrent growth of the chains) and a sufficient speed of exchange between the active and dormant species (at least as fast as the propagation).

Several techniques of CRP have been developed such as nitroxide-mediated polymerization (NMP),[30,31] atom transfer radical polymerization (ATRP),[32,33] reversible addition−fragmentation transfer (RAFT),[34−36] (reversible) iodine transfer polymerization ((R)ITP),[37] and the macromolecular design for interchange of xanthates (MADIX).[38] MADIX polymerization proceeds over a degenerative chain transfer mechanism in which two equilibria are included (Scheme 1). The controlled character is caused by the reversible addition−fragmentation mechanism in the pre-equilibrium as well as the main equilibrium, which is obtained by stabilizing the intermediate (inducing an elevated exchange constant).[39] For example, the incorporation of electron-withdrawing groups in the Z group (OEt in Scheme 1) could increase the rate of the equilibrium, leading to better control and i.e. lower polydispersities. For MADIX, dithioagent 1 is always a dithiocarbonate (xanthate) while any other dithioesters or trithiocarbonates[40] are related to RAFT polymerizations.[25,27,34,35]

Scheme 1. Mechanism of Reversible Addition−Fragmentation Chain-Transfer Polymerization (RAFT)/Macromolecular Design via the Interchange of Xanthates (MADIX)[a]



[a] In, M, P_n, and P_m represent the initiator, the monomer, and the polymers, respectively.

As specific agents may not be used universally for all monomers, the dithioagent has to be well chosen. RAFT agents do work well for styrenic monomers, acrylates (even fluoroacrylates that led to amphiphilic block copolymers[40]), and only a few RAFT agents works with methacrylates.[41] In contrast, MADIX[42] process is efficient for the controlled polymerization of vinyl acetate (VAc) which is usually difficult to control (though iodine transfer polymerization was reported by Iovu and Matyjaszewski[43] and Koumura et al.[44]) but has never been attempted with fluorinated olefins.

Hence, the objective of this article deals with the synthesis of well-defined fluorinated copolymers obtained by CRP in the presence of xanthate. In addition, as the polymerization of vinyl acetate can be achieved by MADIX, poly(VDF-*co*-TFP) copolymers terminated by xanthate can further be used to obtain poly(VDF-*co*-TFP)-*b*-oligo(VAc) block copolymers. The hydrolysis of the oligo(VAc) block into oligo(vinyl alcohol) makes the resulting amphiphilic block copolymer an original surfactant.

■ EXPERIMENTAL SECTION

Materials. All reagents were used as received unless stated otherwise.

3,3,3-Trifluoropropene (TFP) was kindly supplied by the Great Lakes Chemical Corp. (now Chemtura Co., West Lafayette, IN). 1,1-Difluoroethylene (vinylidene fluoride, VDF) and 1,1,1,3,3-pentafluorobutane (Solkane 365mfc) were kindly supplied by Solvay S.A. (Tavaux, France). *tert*-Butyl peroxypivalate in solution of isododecane (Trigonox 25-C75, TBPPi) (purity 75 wt %), 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Trigonox 101) (purity 92 wt %), and azobis(isobutyronitrile) (AIBN) were gifts from Akzo Nobel (Chalons sur Marne, France). 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-ol was kindly

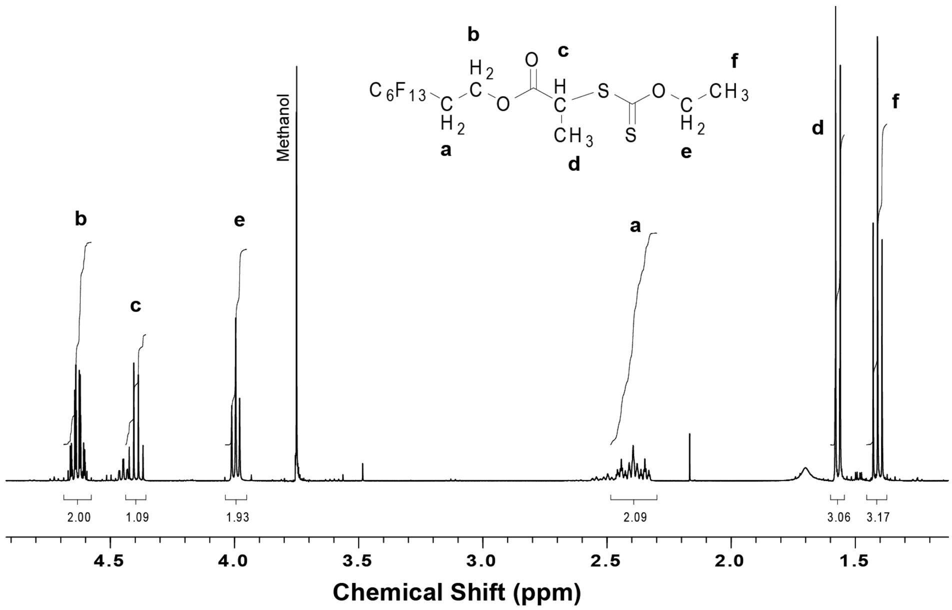


Figure 1. ^{1}H NMR spectrum (recorded in $CDCl_3$) of xanthate **9**.

supplied by Atofina (now Arkema, Paris, France). Ammonium perfluorooctanoate (APFO) was kindly supplied by Solexis (Italy). Vinyl acetate (VAc), sulfuric acid (puriss. 96%), *o*-ethylxanthic acid potassium salt (puriss. 96%), 2-bromopropionic acid (purum, 99%), and all other chemicals were purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France). Vinyl acetate was freshly distilled over calcium hydride before use. Deuterated solvents (chloroform and acetone) used for the NMR spectroscopy were purchased from Euroiso-top (Grenoble, France) (purity >99.8%).

Characterization. *NMR.* The NMR spectra were recorded on Bruker AC 400 instruments, using deuterated chloroform or acetone, as the solvent and tetramethylsilane (TMS) (or $CFCl_3$) as the references for ^{1}H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in hertz (Hz) and parts per million (ppm), respectively. The experimental conditions for recording ^{1}H [or ^{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 5 s], number of scans 36 [or 64], and a pulse width of 5 μs for ^{19}F NMR.

SEC. Size exclusion chromatography (SEC) was carried out in tetrahydrofuran at 30 °C, at a flow rate of 0.8 mL/min, by means of a Spectra Physics Winner Station, a Waters Associate R 401 differential refractometer, and a set of four columns connected in series: Styragel (Waters) HR4 5 m, HR3 analyses 5 m, PL Gel (Polymer Laboratories) 5 m 100 Å. Monodispersed (PMMA) standards were used for calibration. Aliquots were sampled from the reaction medium, diluted with tetrahydrofuran up to a known concentration ($C_{p,t}$) ca. 4 wt %, filtered through a 20 mm PTFE Chromafil membrane, and finally analyzed by SEC under the conditions described above.

FTIR. IR spectra were recorded on a Nicolet 510P Fourier transform infrared (FTIR) spectrometer from KBr pellets (10 wt %), and the intensities of the absorption bands (cm^{-1}) were labeled strong (s), medium (m), or weak (w). The accuracy was ±2 cm^{-1}.

TGA. Thermogravimetric analyses (TGA) were performed with a TGA 51 apparatus from TA Instruments, under air, at the heating rate of 5 °C min^{-1} from room temperature up to a maximum of 580 °C. The sample size vary between 10 and 15 mg.

DSC. Differential scanning calorimetry (DSC) measurements were conducted using a Perfkin Elmer Pyris 1 apparatus. Scans were recorded at a heating rate of 20 °C min^{-1} from -100 to $+100$ °C, and the cooling rate was 20 °C min^{-1}. A second scan was required for the assessment of the T_g, defined as the inflection point in the heat capacity jump. The sample size is about 10 mg.

Tensiometry. Surface tensions of the amphiphilic poly(VDF-*co*-TFP)-*b*-oligo(VA) copolymers and of APFO were measured at different concentrations to assess the critical micellar concentration (cmc) of the surfactant in water at 25 °C. The surface tension was measured with a Dataphysics DCAT 21 tensiometer using the Wilhemy plate method. Each concentration was prepared at least 24 h prior to measurement. The solution was allowed to equilibrate in the apparatus, and the surface tension was considered stable when the difference is less than 0.03 mN m^{-1}. The value for the surface tension was determined as the average of the last 50 points. The critical micellar concentration (cmc) was calculated as the intersection between the two straight lines emerging from high and low concentrations.

Conductimetry. It is also possible to assess the critical micellar concentration by conductimetry, where an inflection point can be seen on the curve of the conductivity versus the concentration. Conductivity was measured on a CDM210 conductimeter from MeterLab equipped with a two-pole conductivity cell (CDC745-9 from Radiometer Analytical).

Autoclave. The radical copolymerizations of VDF and TFP were performed in a 160 mL Hastelloy autoclave Parr system (HC 276) equipped with a manometer, a mechanical Hastelloy anchor, a rupture disk (3000 PSI), inlet and outlet valves. An electronic device regulated and controlled both the stirring and heating of the autoclave. Prior to reaction, the autoclave was pressurized with 30 bar of nitrogen for 1 h to check for leaks. The autoclave was then conditioned for the reaction with several nitrogen/vacuum cycles (10^{-2} mbar) to remove any trace of oxygen. The liquid and dissolved solid phases were introduced via a funnel tightly connected to the autoclave, and then the gases were introduced by double weighing (i.e., the difference of weight before and after filling the autoclave with the gases).

Synthesis. *Synthesis of the Fluorinated Xanthate.* The preparation of the fluorinated xanthate follows the path displayed in Scheme 3.

First step: preparation of ester **7** (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-2-bromopropanoate). In a 500 mL flask, 2-bromopropionic acid, **6** (30.1 g, 0.196 mol), and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane-1-ol, **5** (68.1 g, 0.187 mol), were dissolved in toluene (300 mL), *p*-toluenesulfonic acid was added in a catalytic amount (0.3 g, 1 mass % vs 2-bromopropionic acid), and the solution was refluxed at 120 °C. The

Table 1. Experimental Conditions and Results of the Radical Homopolymerization of VAc or Copolymerization of VDF and TFP or Terpolymerization of VDF, TFP, and VDF for the Preparation of the First Block in the Presence of the Fluorinated Xanthate[a]

		composition															
		feed			copolymer												
run no.	Xa (%)	VDF (%)	TFP (%)	VAc (%)	VDF (%)	TFP (%)	VAc (%)	initiator type	%	T (°C)	t_R (h)	ΔP (bar)	yield (%)	M_n (g/mol)	PDI	$T_{d,10\%}$
1		49	51		25	75		TBPPi	2.0	75	16	2	42		2.55	
2	5			100			100	AIBN	2.0	82	16		60	1960	1.43	230
3	10	59	41		48	52		TBPPi	2.1	75	16	27	59			
4	7	60	40		51	49		TBPPi	2.0	75	55	0				
5	10	65	35		50	50		TBPPi	4.0	75	48	8	47			
6	5	62	38		47	53		TBPPi	1.0	75	60	0	28			
7	1.5	62	38		51	49		Trig101	0.8	130	48	4	47	1940	1.39	290
8	10	66	34	50	52	48		AIBN	2.0	82	60	1	<15			
9	7	47	35	18	27	24	49	TBPPi	2.0	75	48	6	53	1050	1.20	

[a] Solvent used: $C_4F_5H_5$, 80 mL. All molar ratios are towards monomers. All percentages regarding the composition are molar percentages. Copolymer compositions were assessed by NMR. T: reaction temperature; ΔP: pressure drop observed in the autoclave during the reaction; t_R: reaction time (h); τ_{conv}: conversion based on the consumption of gaseous monomers; M_n: molecular weight determined by SEC calibrated with PMMA standards; VDF: vinylidene fluoride; TFP: 3,3,3-trifluoropropene; VAc: vinyl acetate; TBPPi: *tert*-butyl peroxypivalate; AIBN: azobis(isobutyronitrile); Trig 101: Trigonox 101, i.e., 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane.

produced water (50−60 mL) was collected in a Dean−Stark water separator. After 14 h, the reaction was completed and the solvent was removed. The mixture was washed with a $NaHCO_3$ solution (pH = 8) to neutral state. The organic phase was separated, and the aqueous phase was twice extracted with diethyl ether (200 mL). The collected organic phases were dried over Na_2SO_4, the solvent was evaporated, and the esterification product **7** was dried under vacuum (10^{-2} bar). The reaction led to a good yield (92%). ^{1}H and ^{19}F NMR spectra are given in the Supporting Information (Figures S1 and S2). ^{1}H NMR ($CDCl_3$, Figure S1 in Supporting Information) δ (ppm): 1.82 (d, $^3J_{HH}$ = 7.2 Hz, $\mathbf{CH_3}$, 3H); 2.51 (tt, $^3J_{HF}$ = 18 Hz, $^3J_{HH}$ = 6.4 Hz, $C_6F_{13}\mathbf{CH_2}$, 2H); 4.37 (q, $^3J_{HH}$ = 7.2 Hz, $\mathbf{CH}$Br, 1H); 4.47 (dt, $^3J_{HH}$ = 6.4 Hz, $^4J_{HF}$ = 1.6 Hz, $\mathbf{CH_2}$O, 2H). ^{19}F NMR ($CDCl_3$, Figure S2 in Supporting Information) δ (ppm): −126.2 (s, $CF_3\mathbf{CF_2}$, 2F); −123.6 (s, $C_2F_5\mathbf{CF_2}$, 2F); −122.9 (s, $C_3F_7\mathbf{CF_2}$, 2F); −122.0 (s, $C_4F_9\mathbf{CF_2}$, 2F); −113.7 (s, $\mathbf{CF_2}CH_2$, 2F); −80.9 (s, $\mathbf{CF_3}$, 3F).

Second step: preparation of xanthate **9** (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-2-((ethoxycarbonothioyl)thio)propanoate) from ester **7**. In a 500 mL round-bottom flask equipped with a dropping funnel, ester **7** produced above (45 g, 0.09 mol) was dissolved in methanol (170 mL). The dropping funnel was charged with methanol (50 mL) and xanthate **8** ($EtO-CS_2^-,K^+$, 21.7 g, 0.135 mol). This xanthate salt was added dropwise over 3 h at 0 °C. The mixture was stirred overnight and warmed to room temperature. After removing the solvent, the resulting thick material was dropped into chilled ether. While the salt precipitated, product **9** could easily be separated. The solvent was evaporated, and fluorinated xanthate **9** was dried under vacuum (10^{-2} bar). The overall yield over both steps was 67% (yellow liquid). ^{1}H NMR ($CDCl_3$, Figure 1) δ (ppm): 1.41 (t, $^3J_{HH}$ = 7.2 Hz, $\mathbf{CH_3}CH_2O$, 3H); 1.57 (d, $^3J_{HH}$ = 7.6 Hz, $\mathbf{CH_3}$CHS, 3H); 2.40 (ttt, $^3J_{HF}$ = 18.8 Hz, $^3J_{HH}$ = 6.4 Hz, $^4J_{HF}$ = 1.6 Hz, $C_6F_{13}\mathbf{CH_2}$, 2H); 4.00 (t, $^3J_{HH}$ = 6.4, $CH_3\mathbf{CH_2}O$, 2H), 4.40 (q, $^3J_{HH}$ = 7.6, C$\mathbf{H}$S, 1H); 4.63 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HF}$ = 1.6, $C_6F_{13}CH_2\mathbf{CH_2O}$, 2H). ^{19}F NMR ($CDCl_3$, Figure S3 in Supporting Information) δ (ppm): −126.1 (s, $CF_3\mathbf{CF_2}$, 2F), −123.7 (s, $C_2F_5\mathbf{CF_2}$, 2F), −122.9 (s, $C_3F_7\mathbf{CF_2}$, 2F), −121.9 (s, $C_4F_9\mathbf{CF_2}$, 2F); −113.5 (m, $\mathbf{CF_2}CH_2$, 2F); −80.8 (tt, $^3J_{FF}$ = 8 Hz, $^4J_{FF}$ = 2.8 Hz, $\mathbf{CF_3}$, 3F).

Radical Homopolymerization of VAc in the Presence of Fluorinated Xanthate ***9*** *(Run 2 in Table 1).* Xanthate **9** (10.0 g, 0.0185 mol), freshly distilled VAc (31.9 g, 0.37 mol), and AIBN as the initiator (1.22 g, 0.0074 mol) were dissolved in 1,1,1,3,3-pentafluorobutane ($C_4F_5H_5$, 80 mL) and purged with nitrogen for 15 min. All reactants were introduced in the autoclave under vacuum. The autoclave was then heated to 82 °C in an oil bath for 16 h. After stopping the reaction, the autoclave was cooled to room temperature and the weight was checked. The solvent and nonreacted VAc were removed under reduced pressure (2.5 × 10^{-2} bar) at 40 °C. The reaction mixture was precipitated in chilled *n*-pentane and dried under vacuum (10^{-2} bar, 40 °C). Bright amber flakes amorphous product (yield = 71%) was obtained soluble in acetone, ethanol, methanol, tetrahydrofuran, and chloroform. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.4 (t, $^3J_{HH}$ = 7.1 Hz, $\mathbf{CH_3}CH_2O$, 3H); 1.52 ($-\mathbf{CH_2}CH(OCOCH_3)-$ 2nH); 1.6 (d, $^3J_{HH}$ = 7.5 Hz, $-CH(\mathbf{CH_3})-S-$, 3H); 2.04 ($-CH_2CH(OCO\mathbf{CH_3})-$ 3nH); 2.2 ($R_F\mathbf{CH_2}-$, 2H); 4.0 (m, $^3J_{HH}$ = 6.50 Hz, $CH_3-\mathbf{CH_2}$, 2H); 4.34 ($-CH_2\mathbf{CH}(OCOCH_3)-$ 1nH); 4.4 (m, $\mathbf{CH}$, 1H); 4.6 (t, $^3J_{HH}$ = 6.9 Hz, $C_6F_{13}-CH_2-\mathbf{CH_2}$, 2H). ^{19}F NMR ($CDCl_3$) δ (ppm): −81.16 ($\mathbf{CF_3}$, 3F), −114.09 ($\mathbf{CF_2}CH_2$ 2F), −122.34 (2F), −123.31 (2F), −124.04 (2F), −126.56 (2F). FTIR (cm^{-1}): 2975, 2862 (s, C−H), 1743 (s, C═O of acetate), 1242 (m, $O-CH_2$), 1069 (s, C−F). GPC: M_n = 1960 g mol^{-1}; M_w = 2800 g mol^{-1}; PDI = 1.43.

Radical Copolymerization of VDF and TFP in the Presence of the Fluorinated Xanthate To Yield Poly(VDF-co-TFP) Copolymer as a First Block (Run 7 in Table 1). The autoclave was filled under vacuum with fluorinated xanthate **9** (2.0 g, 3.6 × 10^{-3} mol) and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane as the initiator (Trigonox 101) (0.7 g, 2 × 10^{-3} mol) both dissolved in $C_4F_5H_5$ (80 mL). The reactor was cooled in an acetone/liquid nitrogen bath to condense the fluorinated gases: First, TFP (9.0 g, 9.4 × 10^{-2} mol) and then VDF (10.0 g, 1.56 × 10^{-1} mol) into the autoclave under weight control. The reactor was heated gradually up to 130 °C, and the evolution of pressure and temperature were recorded. An increase of the pressure to 37.5 bar and a decrease to 34 bar during the reaction were observed. The reaction was stopped after 48 h and the autoclave cooled to room temperature and then placed in an ice bath. After purging the nonreacted monomer, the conversion of gaseous monomers was determined by double weighing (55%). A yellow-light brown liquid was obtained (75.6 g). The solvent was completely removed by distillation. The product was precipitated in chilled pentane and then dried under vacuum (10^{-2} bar, 40 °C). The poly(VDF-*co*-TFP) fluorinated copolymer, a brownish gum, was characterized by ^{1}H and ^{19}F NMR spectroscopy. The calculated yield was 47 wt %. ^{1}H NMR ($CDCl_3$) δ (ppm) (Figure 3): 1.4 (t, $^3J_{HH}$ = 7.1 Hz, CH_3CH_2O, 3H); 1.6 (d, $^3J_{HH}$ = 7.5 Hz, $\mathbf{CH_3}$, 3H); 1.43 (t, $^3J_{HH}$ = 7.0 Hz,

Table 2. Experimental Conditions and Results for the Preparation of the Second Block in the Presence of the Fluorinated Xanthate (First Block from Table *1*)[a]

			composition													
	xanthate block		feed			copolymer										
run no.	name	%	VDF (%)	TFP (%)	VAc (%)	VDF (%)	TFP (%)	VAc(%)	initiator type	%	T (°C)	t_R (h)	yield (%)	M_n (g/mol)	PDI	$T_{d,10\%}$
10	3	50			50	29	34	37	none		75	24	45			102
11	2	50	58	42					none		82	65	<15			250
12	4				50	12	10	78	none		82	60	51			
13	2	50	65	35		23	18	59	TBPPi	1	75	16	60	2270	1.57	245
14	6	50			50	31	26	43	TBPPi	1	75	48	43			
15	7	50			50	22	21	57	TBPPi	1	75	48	87	2520	1.2	283

[a] Solvent used: $C_4F_5H_5$, 80 mL. All molar ratios are towards monomers. All percentages regarding the composition are molar percentages. T: reaction temperature. The variation of the pressure (ΔP) observed in the autoclave was ≤ 1 bar. t_R: reaction time (h); τ_{conv}: conversion based on the consumption of gaseous monomers; M_n: molecular weight determined by SEC calibrated with PS standards; VDF: vinylidene fluoride; TFP: 3,3,3-trifluoropropene; VAc: vinyl acetate; TBPPi: *tert*-butyl peroxypivalate.

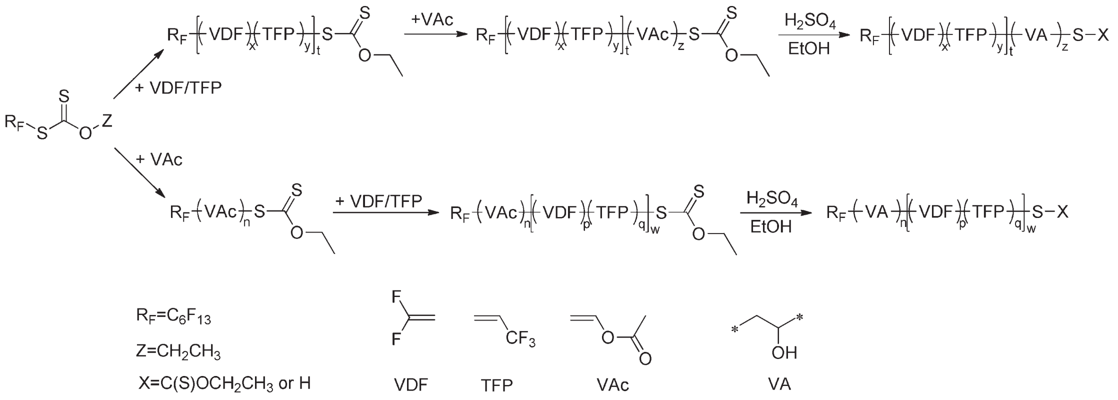
CH_3, 3H); 2.2 (tt, $^3J_{HF}$ = 19.45 Hz, $^3J_{HH}$ = 6.42 Hz, $\mathbf{CH_2}$, 2H a); 1.8−2.8 ($\mathbf{CH_2}$ in TFP and VDF, 6H e + g + l); 4.0 (m, $^3J_{HH}$ = 6.50 Hz, $CH_3-\mathbf{CH_2}$, 2H); 4.4 (m, **CH**, 5H c + f + k); 4.6 (t, $^3J_{HH}$ = 6.9 Hz, $C_6F_{13}-CH_2-\mathbf{CH_2}$, 2H b). ^{19}F NMR ($CDCl_3$) δ (ppm): −126.5 (s, 2F); −124.0 (s, 2F); −123.3 (s, 2F); −122.2 (s, 2F); −113.9 (q, 2F); −98.6 (h, CF_2 of VDF in VDF-TFP diad); −90 to −96 (h, $\mathbf{CF_2}$ of VDF, norm, 2F); −81.2 (s, CF_3 in C_6F_{13}, 3F); −71.5 (g, $\mathbf{CF_3}$ in TFP, 3F); −71 (h′, $-CH_2-\mathbf{CF_2}S-$, 2F); −64.5 to −67.2 (g′ $-CH_2-C(\mathbf{CF_3})-S-C(S)-OEt$, 3F). GPC: M_n = 1940 g mol^{-1}, M_w = 2700 g mol^{-1}, PDI = 1.39. TGA (under air, 10 °C min^{-1}): $T_{d,10\%}$ = 290 °C.

*Direct Radical Terpolymerization of VDF, TFP, and VAc Mediated by Fluorinated Xanthate **9** (Run 9 in Table 1).* The same procedure as above was used to prepare the autoclave. It was filled under vacuum with fluorinated xanthate **9** (20.0 g, 3.6 × 10^{-2} mol), freshly distilled VAc (8.0 g, 9.3 × 10^{-2} mol), and TBPPi initiator (0.15 g, 7.2 × 10^{-4} mol) both dissolved in $C_4F_5H_5$ (80 mL). The reactor was cooled in an acetone/liquid nitrogen bath to condense TFP (18.0 g, 1.9 × 10^{-1} mol) and VDF (16.0 g, 2.5 × 10^{-1} mol). The autoclave was heated gradually to 75 °C, and the evolution of pressure and temperature were recorded. An increase of the pressure to 20 bar and a decrease to 14 bar during the reaction were observed. The reaction was stopped after 48 h; the reactor was cooled to room temperature and then placed in an ice bath. After purging the nonreacted monomers, the conversion of gaseous monomers was determined by double weighing (29%). A yellow-light brown liquid was obtained. The solvent was completely removed by distillation. The product was precipitated in chilled pentane and dried under vacuum (10^{-2} bar, 40 °C). The fluorinated poly(VDF-*ter*-TFP-*ter*-VAc) copolymer, a yellow viscous liquid, was characterized by ^{1}H NMR and ^{19}F NMR. The yield was 53 wt %. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.80−5.20 ($R_FCH_2\mathbf{CH_2}-$, 2H b); 4.6−4.8 (CH in TFP and VAc, 1H c + f + k); 4.2−4.3 (m, $CH_3\mathbf{CH_2}O$, 2H); 2.4−3.1 ($\mathbf{CH_2}$ in TFP and VDF, 2H e+g); 2.2 ($R_F\mathbf{CH_2}-$, 2H a); 1.96 (s, $-CH_2CH(OCO\mathbf{CH_3})-$, 3H), 1.7 ($-\mathbf{CH_2}CH(OCOCH_3)-$ 2H), signals of TFP overlap with broad signals of PVAc block; 1.3 ($-CH(\mathbf{CH_3})S-$, 3H); 1.1 ($\mathbf{CH_3}CH_2O-$, 3H). ^{19}F NMR ($CDCl_3$) δ (ppm): −126.1 (s, 2F, xanthate); −123.6 (s, 2F, xanthate); −122.9 (s, 2F, xanthate); −121.9 (s, 2F, xanthate); −113.6 (s, 2F, xanthate); −80.8 (s, 3F, xanthate) −68.9 to −73.6 ($-CH_2-CH(CF_3)-$ of TFP and $-CH_2-CF_2-S-$ of VDF), −66.7 (reverse addition of TFP); −62.3 ($-CH_2-CH(CF_3)-S-$, traces). GPC: M_n = 1050 g mol^{-1}, M_w = 1260 g mol^{-1}, PDI = 1.2. FTIR (cm^{-1}): 2975, 2863 (s, C−H), 1743 (s, C═O), 1245−1062 (s, C−F), 1040 (s, C═S).

Radical Polymerization of VAc as a Second Block in the Presence of Poly(VDF-co-TFP) Xanthate (Run 15 in Table 2). In a 100 mL two-necked round-bottom flask, the poly(VDF-*co*-TFP) copolymer bearing a xanthate end group (2.0 g, 2 × 10^{-4} mol) was introduced in the flask with TBPPi (2.3 g, 1.3 × 10^{-2} mol) as well as the solvent ($C_4F_5H_5$, 50 mL). Then, VAc (2.0 g, 2.3 × 10^{-2} mol) was added, and the temperature was increased to 75 °C. The reaction was stopped after 16 h, and the reaction mixture was cooled down to room temperature. The solvent was evaporated, and the product precipitated in chilled pentane. The produced block copolymer was dried under vacuum (10^{-2} bar, 40 °C) and then analyzed. The yield was 88 wt %. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.80 ($R_FCH_2\mathbf{CH_2}-$, 2H, b); 4.6−4.8 (CH in TFP and VAc, 1H c + f + k); 4.1 (m, $CH_3\mathbf{CH_2}O$, 2H); 2.4 to 2.9 ($\mathbf{CH_2}$ in TFP and VDF, 2H e + g); 2.2 ($R_F\mathbf{CH_2}-$, 2H a); 1.96 (s, $-CH_2CH(OCO\mathbf{CH_3})-$, 3H), 1.69 ($-\mathbf{CH_2}CH(OCOCH_3)-$ 2H), signals of TFP overlap with broad signals of PVAc block; 1.3 ($\mathbf{CH_3}$ of xanthate, 3H d); 1.1 ($\mathbf{CH_3}$-CH_2O, 3H n). ^{19}F NMR ($CDCl_3$) δ (ppm): −126.1 (s, 2F, xanthate); −123.6 (s, 2F, xanthate); −122.9 (s, 2F, xanthate); −121.9 (s, 2F, xanthate); −113.6 (s, 2F, xanthate); −91.9 to −103.4 (7F, $-CH_2-CF_2-$ of VDF); −80.8 (s, 3F, xanthate) −68.9 to −73.6 (28 F, $-CH_2-CH(CF_3)-$ of TFP and $-CH_2-CF_2-S-$ of VDF), −66.7 (12F, reverse addition of TFP); −62.3 (5F, $-CH_2-CH(CF_3)-S-$ of TFP). GPC: M_n = 2520 g mol^{-1}, M_w = 3024 g mol^{-1}, PDI = 1.2. FTIR (cm^{-1}): 2975, 2863 (s, C−H), 1743 (s, C═O), 1245−1062 (s, C−F), 908 (s, C═S). TGA (under air, 10 °C min^{-1}): $T_{d,10\%}$ = 283 °C. DSC: T_g = 10 °C.

Radical Copolymerization of VDF and TFP in the Presence of Poly(VAc)-xanthate To Insert Hydrophobic Poly(VDF-co-TFP) Block as the Second Block (Run 13 in Table 2). The autoclave was prepared as described above. The PVAc-xanthate synthesized in Run 2 (16.1 g, 1.27 × 10^{-2} mol) was introduced in the reactor with TBPPi (0.23 g, 1.3 × 10^{-3} mol) and $C_4F_5H_5$ (50 mL). TFP (5 g, 5.2 × 10^{-2} mol) and VDF (7 g, 1.09 × 10^{-1} mol) were condensed into the autoclave, which was further heated to 75 °C. A small decrease of the pressure was observed (from 15 to 14 bar). After 16 h, the reaction was stopped, the autoclave placed into an ice bath for 30 min, and unreacted gases were removed. The solvent was evaporated, and the product precipitated in chilled pentane. The product was dried under vacuum (10^{-2} bar, 40 °C) and analyzed (yield = 60 wt %). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.69 ($-\mathbf{CH_2}CH(OCOCH_3)-$, 2nH); 1.96 ($-CH_2CH(OCO\mathbf{CH_3})-$, 3nH); 4.80 ($-CH_2\mathbf{CH}(OCOCH_3)-$, 1nH); signals of TFP overlap with broad signals of PVAc block. ^{19}F NMR ($CDCl_3$) δ (ppm): −126.1 (s, $CF_3-\mathbf{CF_2}-$, 2F, xanthate); −123.6 (s, $C_2F_5-\mathbf{CF_2}-$, 2F, xanthate); −122.9 (s, $C_3F_7-\mathbf{CF_2}-$, 2F, xanthate); −121.9 (s, $C_4F_9-\mathbf{CF_2}-$, 2F, xanthate); - 113.6 (s, $C_5F_{11}-\mathbf{CF_2}-$, 2F, xanthate); −91.9 to −103.4 (7F, $-CH_2-\mathbf{CF_2}-$ of VDF); −80.8 (s, $\mathbf{CF_3}-C_5F_{10}-$, 3F, xanthate) −73.6 to 73.6 (28 F, $-CH_2-CH(CF_3)-$ of TFP and $-CH_2-CF_2-S-$ of VDF), −66.7 (12F, $-CH_2-CH(CF_3)-$ reverse

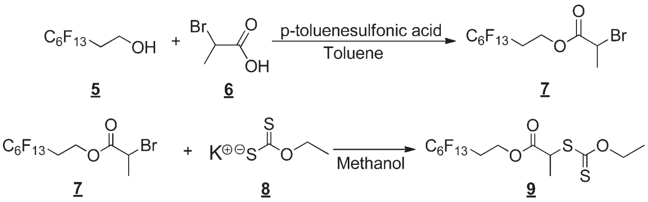
Scheme 2. Strategies for the Preparation of Amphiphilic Block Copolymers Based on Vinylidene Fluoride (VDF), 3,3,3-Trifluoropropene (TFP), Vinyl Acetate (VAc), and Vinyl Alcohol (VA) Controlled by R$_F$-SC(S)OZ Xanthate



addition of TFP, 3F); −62.3 (5F, −CH$_2$−CH(CF$_3$)−S− of TFP). FTIR (cm^{-1}): 2983 (s, C−H), 2849 (s, C−H), 1743 (s, C=O), 1062 (s, C−F), 910 (s, C=S). GPC: M_n = 2270 g mol^{-1}, M_w = 3570 g mol^{-1}, PDI = 1.57. TGA (under air, 10 °C min^{-1}): $T_{d,10\%}$ = 245 °C.

Hydrolysis of Poly(VDF-co-TFP)-b-poly(VAc) Diblock Copolymer (Run 19 in Table 3). In a 250 mL two-necked round-bottom flask equipped with magnetic stirring bar, condenser, and rubber septum, the diblock copolymer from the previous section with the chain transfer agent end group (4.0 g) were dissolved in ethanol (150 mL). The mixture was gently purged for 15 min with nitrogen, and then water (3.0 g) and sulfuric acid (1 mL) were added and the temperature was increased gradually up to 80 °C. The solution was stirred for 3 days and checked periodically after 12, 24, 36, 48, and 72 h by FTIR spectroscopy to monitor the decrease of $\nu_{C=O}$ at 1742 cm^{-1} and the increase of ν_{O-H} from 3300 to 3500 cm^{-1}. The reaction was stopped, the solvent was evaporated, and the product was precipitated in chilled pentane and dried under vacuum (10^{-2} bar, 40 °C). Yield = 68 wt %. The hydrolyzed product was soluble in polar solvents, methanol and diethyl ether. ^{1}H NMR (CDCl$_3$) δ (ppm): 4.80 (b, R$_F$CH$_2$CH$_2$, 2H); 4.6−4.8 (c + f + k, **CH** in TFP and VAc, 2H); 4.1 (q, CH$_3$**CH$_2$**O, $^3J_{HH}$ = 7.0 Hz, 2H); 2.4−2.9 (e + g, **CH$_2$** in TFP and VDF, 4H); 2.2 (a, R$_F$**CH$_2$**, 2H); 1.69 (−**CH$_2$**CH(OH)−), signals of TFP overlap with broad signals of PVA block, 2H); 1.2 (d, **CH$_3$**CHCO$_2$, 3H); 1.1(t, **CH$_3$**CH$_2$, $^3J_{HH}$ = 7.0 Hz, 3H). ^{19}F NMR (CDCl$_3$) δ (ppm): −126.1 (s, CF$_3$−**CF$_2$**−, 2F, xanthate); −123.6 (s, C$_2$F$_5$−**CF$_2$**−, 2F, xanthate); −122.9 (s, C$_3$F$_7$−**CF$_2$**−, 2F, xanthate); −121.9 (s, C$_4$F$_9$−**CF$_2$**−, 2F, xanthate); −113.6 (s, C$_5$F$_{11}$−**CF$_2$**−CH$_2$−, 2F, xanthate); −91.9 to −103.4 (−CH$_2$−**CF$_2$**− of VDF, 2F); −80.8 (s, **CF$_3$**−(CF$_2$)$_5$−CH$_2$−, 3F, xanthate) −68.9 to −73.6 (−CH$_2$−CH(**CF$_3$**)− of TFP and −**CF$_2$**−S− of VDF, 2F), −66.7 (**CF$_3$** reverse addition of TFP, 3F); −62.3 (−CH$_2$−CH(**CF$_3$**)−S− of TFP, 3F). GPC: M_n = 3700 g mol^{-1}, M_w = 4400 g mol^{-1}, PDI = 1.2. FTIR (cm^{-1}): 3700−3500 (s, O−H), 2975 (s, C−H), 2863 (s, C−H), 1743 (w, C=O), 1245−1062 (s, C−F), 908 (s, C=S). TGA (under air, 10 °C min^{-1}): $T_{d,10\%}$ = 115 °C. DSC: T_g = 4 °C.

Scheme 3. Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl-2-((ethoxycarbonothioyl)thio)propanoate (Fluorinated Xanthate 9)



RESULTS AND DISCUSSION

To the best of our knowledge, only a couple of xanthates (see formula in Scheme 1) bearing a fluorinated group have been synthesized yet. However, in all cases, the fluorinated chain (CF$_3$,[45] C$_3$F$_7$,[46,47] and C$_6$F$_{13}$[46,47]) was inserted in the Z group (see formula in Scheme 2) to enhance the reactivity of the xanthate. It was worth synthesizing a xanthate with a long fluorinated group in the R$_F$ position (see formula in Scheme 1) both to enhance the solubility of the transfer agent in the fluoroorganic medium and to use it as a useful labeling agent for the ^{19}F NMR spectroscopy by analogy to some ATRP initiator bearing a R$_F$ group.[48,49] Hence, a new fluorinated xanthate has been prepared for further use as chain transfer agent to control the radical copolymerization of 3,3,3-trifluoropropene (TFP) and vinylidene fluoride (VDF). This process, named macromolecular design via interchange of xanthate (MADIX), is also the most successful means for the controlled radical copolymerization of vinyl acetate (VAc).[46,50−52] Hence, a second block of poly(VAc) was inserted. In the final step, the poly(VAc) block of the copolymer was chemically modified into poly(vinyl alcohol) via acid hydrolysis to achieve a poly(VDF-*co*-TFP)-*b*-poly(VAc)-Xa amphiphilic block copolymer. The reverse path was investigated as well leading to poly(VAc)-*b*-poly(VDF-*co*-TFP)-Xa diblock copolymer. Both strategies are summarized in Scheme 2.

Preparation of the Xanthate. The synthesis of fluorinated xanthate **9** was carried out in a two step-reaction (Scheme 3). The first step concerns the esterification of the commercially available fluorinated alcohol **5** with 2-bromopropionic acid **6**. In the second step, the obtained fluorinated 2-bromopropanoate **7** reacts in a nucleophilic substitution with the potassium salt of the xanthate **8**.

Ester **7** was obtained in good yield (92%). It was characterized by ^{1}H and ^{19}F NMR spectroscopies which both showed the four characteristic signals of the expected structure (Supporting Information, Figures S1 and S2).

The second step deals with the nucleophilic substitution of the bromine atom on **7** by xanthate salt **8**. Figure 1 shows the ^{1}H NMR spectrum of xanthate **9**.

The ^{19}F NMR spectrum exhibits all the characteristic signals already noted in the spectrum of ester **7** (see Figure S2 in the Supporting Information).

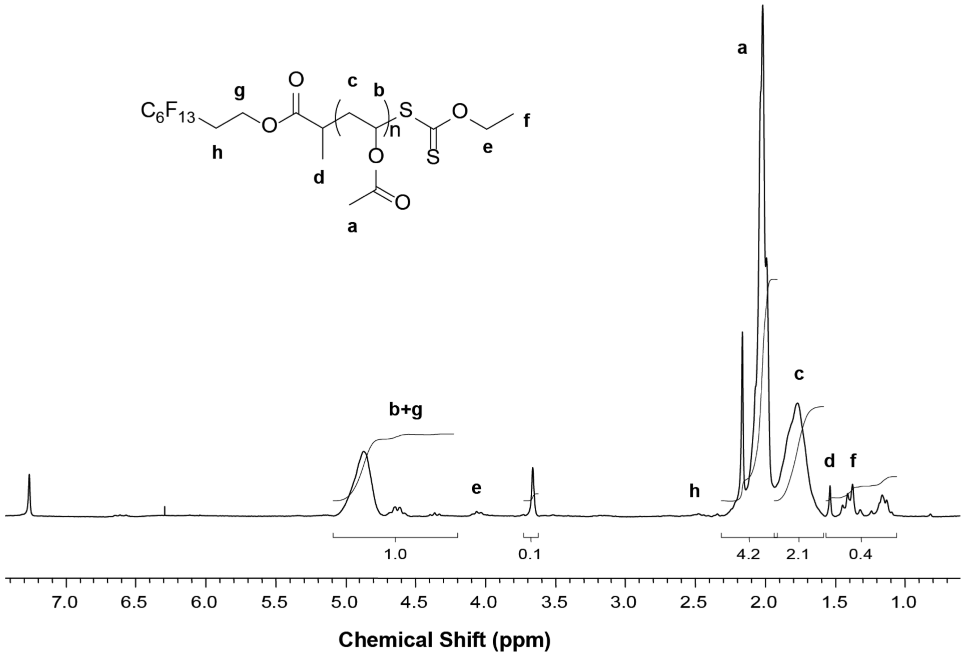


Figure 2. ^1H NMR spectrum of poly(vinyl acetate) prepared by MADIX process (run 2 in Table 1) from xanthate **9** (recorded in deuterated chloroform).

Preparation of the First Block. Two pathways to prepare block copolymers based on vinyl acetate and oligo(TFP-*co*-VDF) are proposed (Scheme 2).

*Preparation of Poly(VAc) Homopolymer Controlled by Fluorinated Xanthate **9** via MADIX Process (Run 2 in Table 1).* Azobis(isobutyronitrile) (AIBN) was chosen as the initiator, and the initial chain transfer agent/monomer molar ratio was R_0 = 0.05 to target an average degree of polymerization of 20. This reaction was carried out under a slight pressure and in a fluorinated solvent ($CF_3CH_2CF_2CH_3$) contrarily to other procedures[42,51,53,54] where the polymerization of VAc was carried out in hexafluoroisopropanol.[44] This enabled us to check if the pressure has an influence on the reaction and to use similar conditions as those for the radical copolymerization of vinylidene fluoride with 3,3,3-trifluoropropene. The reaction mixture was heated to 82 °C for 16 h. After reaction and purification, the resulting product was characterized by ^1H and ^{19}F NMR and FTIR spectroscopies. The ^1H NMR spectrum (Figure 2) shows the three broad signals characteristic of poly(vinyl acetate). The ^{19}F NMR spectrum exhibits the same characteristic signals as that of the fluorinated xanthate.

The Fourier transformed infrared spectrum (FTIR) shows the characteristic carbonyl band at 1742 cm^{-1} of the carbonyl function of the acetate (top spectrum in Figure 7). Frequencies at 2974 and 2862 cm^{-1} were attributed to the C—H vibration. Another strong band at 1069 cm^{-1} was attributed to C—C vibration. Although FTIR spectra of the PVAc and the xanthate do not lead to the same band data, a huge difference in the intensity of the C—F stretching vibration can be seen as a hint for the success of this polymerization step.

In the ^1H NMR spectrum (Figure 2), a signal of the xanthate (2H at 4.62 ppm) could be used as a reference and showed a number of VAc units of 30. This number of units was assessed by the following relation

$$2 \times \frac{\int_{2.05} -\mathrm{CH(OCOCH_3)}-}{\int_{4.62} \mathrm{R_FCH_2CH_2}-}$$

where $\int -\mathrm{CH(OCOCH_3)}-$ and $\int \mathrm{R_FCH_2CH_2}-$ represent the intensities of the signals assigned to acetate and the methylene reference. However, as a result of background noise, this value is estimated to be faulty and is much over the rough calculated DP_n of 20 (R_0 = 5%). Size exclusion chromatography (SEC) (Figure 5, curve 1) showed an average molecular weight M_n of ca. 2000 g mol^{-1} and a narrow molecular weight distribution (PDI = 1.45). The DP_n can be calculated by the following formula

$$\mathrm{DP_n} = \frac{M_n - M(\mathrm{Xa})}{M(\mathrm{VAc})} \times \alpha(\mathrm{VAc})$$

where M_n, M(Xa), M(VAc), and α(VAc) stand for the average molecular weights of the polymer measured by SEC, of the xanthate, of a vinyl acetate unit in the polymer, and the VAc monomer conversion, respectively. A DP_n of 17 was then calculated showing a good agreement with the targeted DP_n (18) considering a VAc conversion of ca. 90% since the yield of the VAc homopolymerization is 71% after purification. This indicates that the presence of the C_6F_{13} end groups in the xanthate and 1,1,1,3,3-pentafluorobutane as the solvent do not disturb the controlled radical polymerization of vinyl acetate. Indeed, this fluorinated solvent has not been tested for the polymerization of VAc as reported by Koumura et al.,[44] who used other fluorinated solvents (fluorinated alcohols, mainly) for the ITP of VAc in the presence of R_FI.

Preparation of Poly(TFP-co-VDF) Copolymers via MADIX (Run 3 in Table 1). In an initial step, copolymers were prepared with a low content of both comonomers to obtain model compounds. For the preparation of a statistical copolymer based on 3,3,3-trifluoropropene (TFP) and vinylidene fluoride (VDF), the copolymerizations were carried out under pressure in high-pressure autoclaves since these fluoroolefins are gases. The VDF:TFP molar ratio was about 60:40, with a 10-fold excess of fluoromonomer compared to the xanthate. The reaction mixture was then heated and stirred for about 48 h. During the reaction, an increase of pressure with temperature and a decrease of ΔP = 27 bar were observed.

The ^{19}F NMR spectrum (Figure 3) shows the characteristic peaks for C_6F_{13} group and those of TFP and VDF units. An

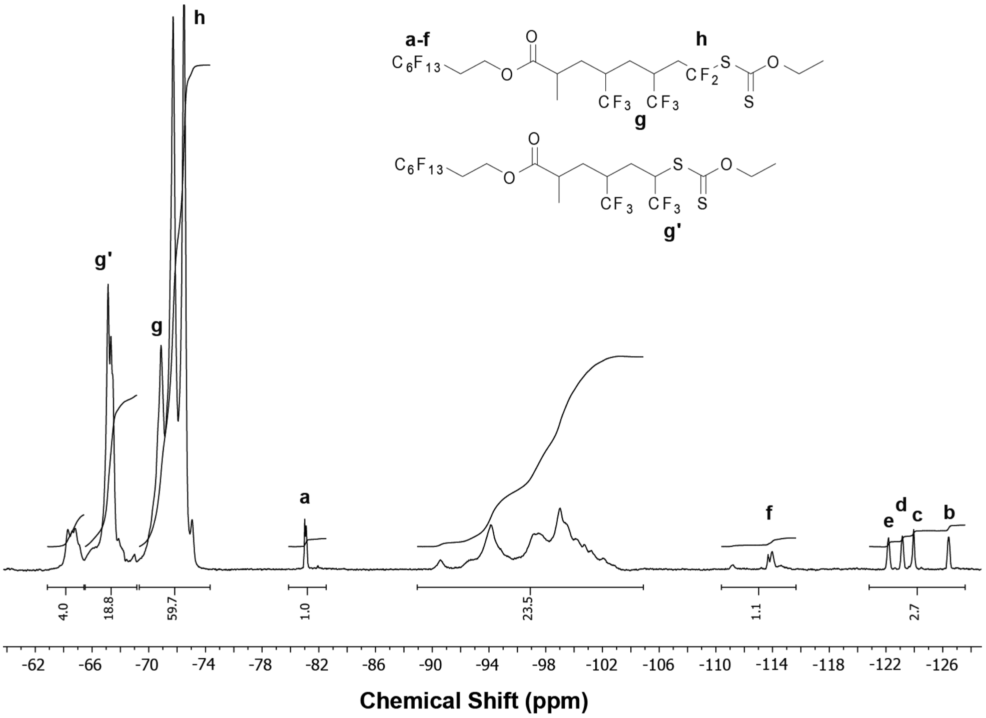


Figure 3. ^{19}F NMR spectrum (recorded in $CDCl_3$) of the fluorinated first block based on TFP and VDF (run 3 in Table 1).

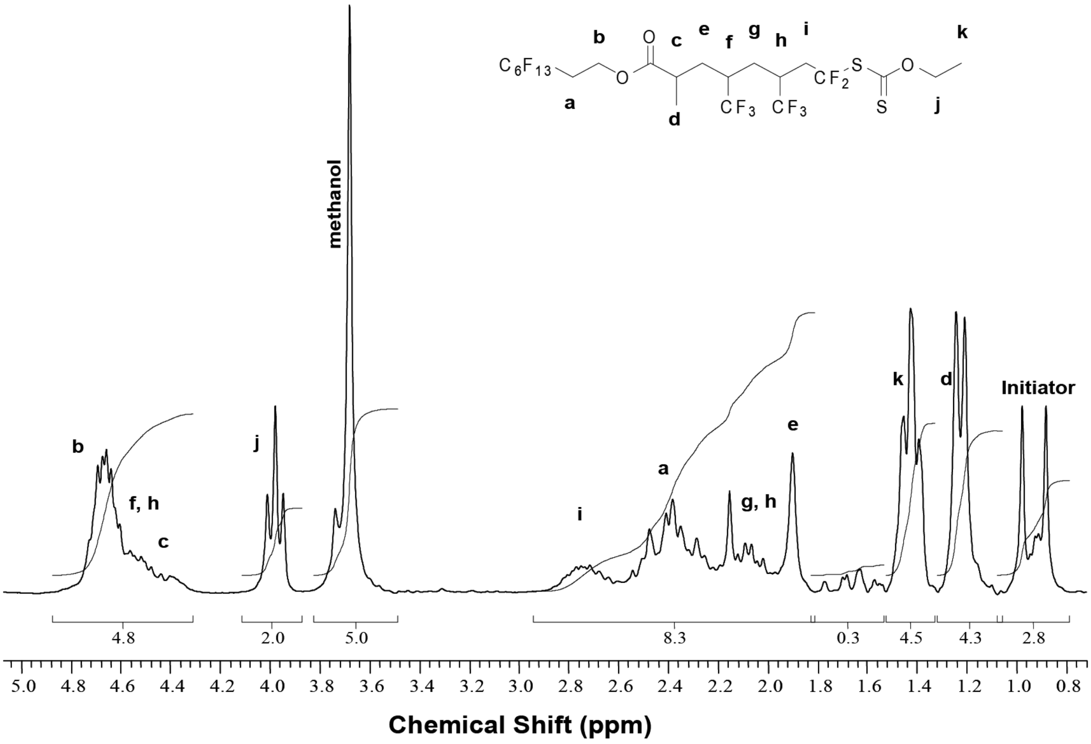


Figure 4. ^1H NMR spectrum (recorded in $CDCl_3$) of the fluorinated poly(TFP-*co*-VDF) xanthate (run 3 in Table 1).

overlapping between the CF_3 of TFP and CF_2 of VDF next to the sulfur atom of the dithioester may be observed at −70.9 ppm ($-CH_2-CF_2-S-$).[55−58] The DP_n was calculated from the integral of these above signals in ^{19}F NMR, and it was found that the oligomer contained two TFP units and one VDF unit. The numbers of TFP and VDF units were assessed from the following equations (where $\int_{-i}$ stands for the integral of the chemical shift centered at $-i$ ppm in the ^{19}F NMR spectrum):

$$\mathrm{TFP} = \frac{\int_{-71.2}^{-72.5} \mathrm{CF_3 \ in \ TFP}}{\int_{-81} \mathrm{CF_3 \ in \ C_6}F_{13}}$$

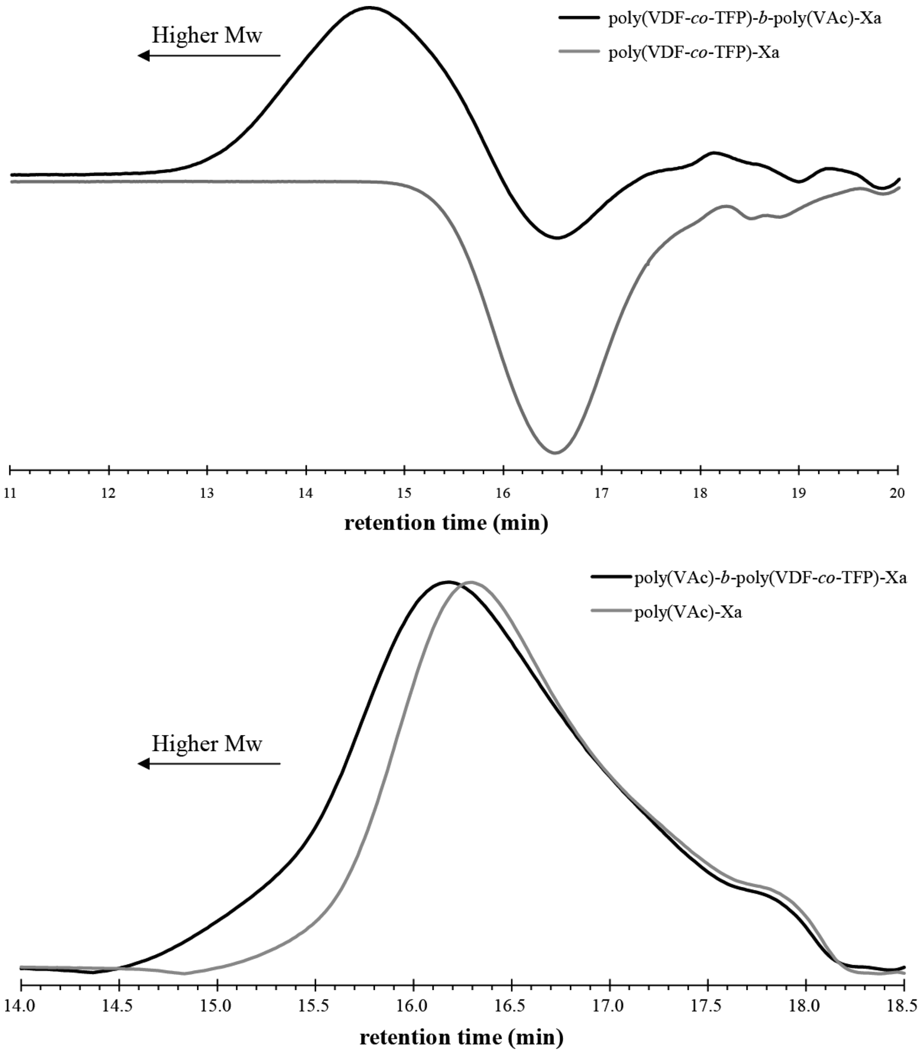


Figure 5. Size exclusion chromatograms of poly(VDF-*co*-TFP) (run 7 in Table 1, gray line in upper spectrum) and its diblock copolymer with VAc (run 15 in Table 2, black line in upper spectrum) and PVAc homopolymer (run 2 in Table 1, gray line in lower spectrum) and its fluorinated diblock copolymer (run 13 in Table 2, black line in lower spectrum).

$$\mathrm{VDF} = \frac{\int_{-97}^{-102} \mathrm{CF_2\ in\ VDF}/2}{\int_{-81} \mathrm{CF_3\ in\ C_6}F_{13}/3}$$

In ^{1}H NMR spectrum (Figure 4), all signals assigned to the xanthate can be found (peaks labeled a, b, c, d, j, k).The signals from TFP (e, f, g, h) are also observed though they overlap with a, b, and c protons. A peak of relatively small intensity assigned to VDF (peak labeled i) appears at 2.75 ppm, in agreement with previous work.[59−61]

These results are in good agreement with those observed for the iodine transfer copolymerization of VDF and TFP in the presence of perfluoroalkyl iodide showing that TFP is more reactive than VDF.[21] This also confirms that the presence of xanthate does not disturb the TFP and VDF reactivity.

Direct cotelomerization of TFP, VDF, and VAc was carried out in the presence of xanthate **9**. Though azobis(isobutyronitrile) (AIBN) was not a good initiator, direct cotelomerization was successful with *tert*-butylperoxypivalate (TBPPi) (run 9). This experiment obtained in a moderate yield (50%) showed the higher reactivity of vinyl acetate with respect to TFP and VDF.

For sample run 4, no values for yield and conversion were taken as it was used without any purification for polymerization of the second block.

Preparation of the Second Block. As shown in Scheme 2, the objective of the second step deals with the insertion of the second block. Two strategies have been chosen and compared: (i) the radical copolymerization of TFP and VDF in the presence of poly(VAc)-xanthate and (ii) the radical polymerization of VAc in the presence of poly(VDF-*co*-TFP)-xanthate. For these polymerizations, the analyzed reaction mixtures from the first step were charged into the autoclave. The corresponding monomer and the required amount of initiator (1 mol % regarding the monomer quantity) were added with a fluorinated solvent.

Polymerization of VAc in the Presence of poly(TFP-co-VDF)-Xa Copolymer. As can be seen from Tables 1 and 2, best conditions for the initiation of the fluorinated block copolymerization were found when TBPPi and especially 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane were used as the initiators in

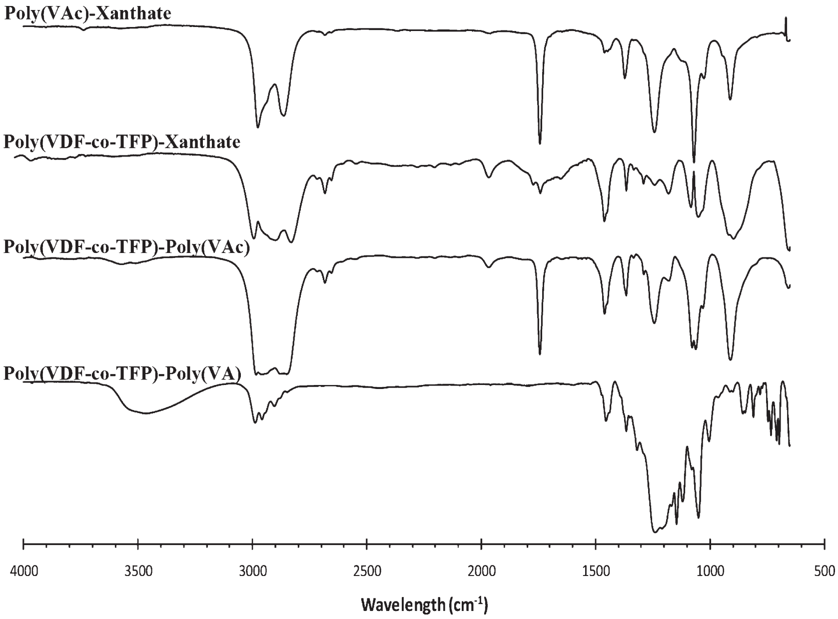


Figure 6. FTIR spectra of PVAc (upper spectrum), fluorinated poly(VDF-*co*-TFP)-xanthate (second spectrum from the top), poly(VDF-*co*-TFP)-*b*-poly(VAc), (second spectrum from the bottom), and poly(VDF-*co*-TFP)-*b*-poly(VA) (lower spectrum) copolymers synthesized with MADIX technology, where VAc, VDF, and TFP stand for vinyl acetate, vinylidene fluoride, and 3,3,3-trifluoropropene, respectively.

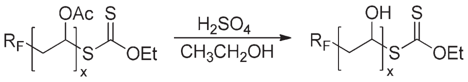
a molar ratio of 1% with respect to the monomers. For the formation of the PVAc block, AIBN is considered as the best initiator. A smaller molar ratio even led to better yields which are in contrast to the expected lower polymerization rate. The initial $[\mathrm{CTA}]_0/[\mathrm{initiator}]_0$ molar ratios were chosen between 1.5 and 10. A higher ratio induced a lower polydispersity. A dependence on the molar ratio could however not be observed.

Maximum yields both for polymerization of PVAc block and fluorinated block as a second block were 60%. For the polymerization of the statistic fluorinated copolymer only small monomer conversion up to 20% and yields up to 47% were obtained. On the other hand, using 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane as an initiator led to the best results to insert an oligo(VDF-*co*-TFP) block. In this case, first a poly(VDF-*co*-TFP) fluorinated block was synthesized in good yield (63 wt %). Then, the second poly(VAc) block was added using TBPPi as the initiator with 88 wt % yield. The experimental conditions are shown in Table 1 (runs 7 and 15) while analyses such as ^{19}F and ^{1}H NMR spectra are depicted in Figures 7 and 8.

Radical Copolymerization of VDF and TFP in the Presence of Poly(VAc)-Xa Polymer. The gaseous monomers (TFP, VDF) were condensed into the autoclave already filled with the poly(VAc)-Xa, the initiator, and 1,1,1,3,3-pentafluorobutane. The autoclave was then heated at the required temperature (see Table 2 for experimental conditions). In both cases (runs 11 and 13 in Table 2), a slight decrease of pressure was observed showing the incorporation of gaseous monomers into the copolymer.

As we started with an increased proportion of fluoroolefins, a higher amount of TFP and VDF units in the polymer was noted. From the ^{19}F NMR spectrum (Figure 7, upper spectrum), the numbers of TFP and VDF units in the polymer were found to be 19 and 11, respectively (hence confirming the higher reactivity of TFP with respect to VDF as reported in a previous study[21]).

Scheme 4. Acid Hydrolysis of PVAc Block into Oligo(vinyl alcohol) for the Preparation of Fluorosurfactants Based on Poly(VDF-*co*-TFP)-*b*-oligo(VA) Block Copolymers



The formation of block copolymers was evidenced by Figure 5 which displays the size exclusion chromatography (SEC) traces of both first and diblock copolymers obtained from both strategies (Scheme 2). In the case where the fluorinated block was obtained first, a negative RI trace was observed (upper part of Figure 5). This was expected since fluoropolymers are known to exhibit low-refractive indices, and thus a negative RI signal in SEC, as already noted for poly(VDF)-*g*-polystyrene,[62] poly(VDF)-*b*-polystyrene,[63,64] poly(VDF-*co*-chlorotrifluoroethylene)-*g*-polystyrene,[65] and poly(chlorotrifluoroethylene-*alt*-vinyl ether)-*g*-polystyrene.[66] Upon polymerization of VAc, a strong shift toward high molecular weights is noted on the chromatogram (Figure 5, upper trace), indicating that the polymerization of VAc occurred well, also evidenced by the chromatogram's flip (decrease of the fluorine content).

When PVAc was used as the first block (Figure 5, bottom chromatograms), only a small shift toward higher molecular weights was observed. In such a case, while the homopolymer's molar mass is 1960 g mol^{-1}, that of the fluorinated diblock copolymer was higher (2300 g mol^{-1}), and the PDI increased from 1.45 to 1.57, which is in agreement with the presence of the second block. The incorporation of the fluorinated block was not enough to flip the SEC trace, indicating that the VAc polymerized better that VDF and TFP.

Among the different results, it was more suitable to insert the oligo(VAc) sequence first and then to insert the poly(VDF-*co*-TFP) as the second block. This may be due to a better stabilization

Table 3. Hydrolysis and Yield of Poly(VDF-*co*-TFP)-*b*-poly(VAc) Diblock Copolymers[a]

run no.	diblock copolymer name	diblock copolymer m (g)	EtOH (mL)	H_2O (g)	H_2SO_4 (mL)	T (°C)	t_R (h)	yield (%)
16	2	4	150	4	1	80	96	60
17	13	5	150	3	1	80	40	72
18	13	4	100	3	1	80	48	72
19	15	4	100	3	1	80	72	68

[a] T: reaction temperature; t_R: reaction time (h).

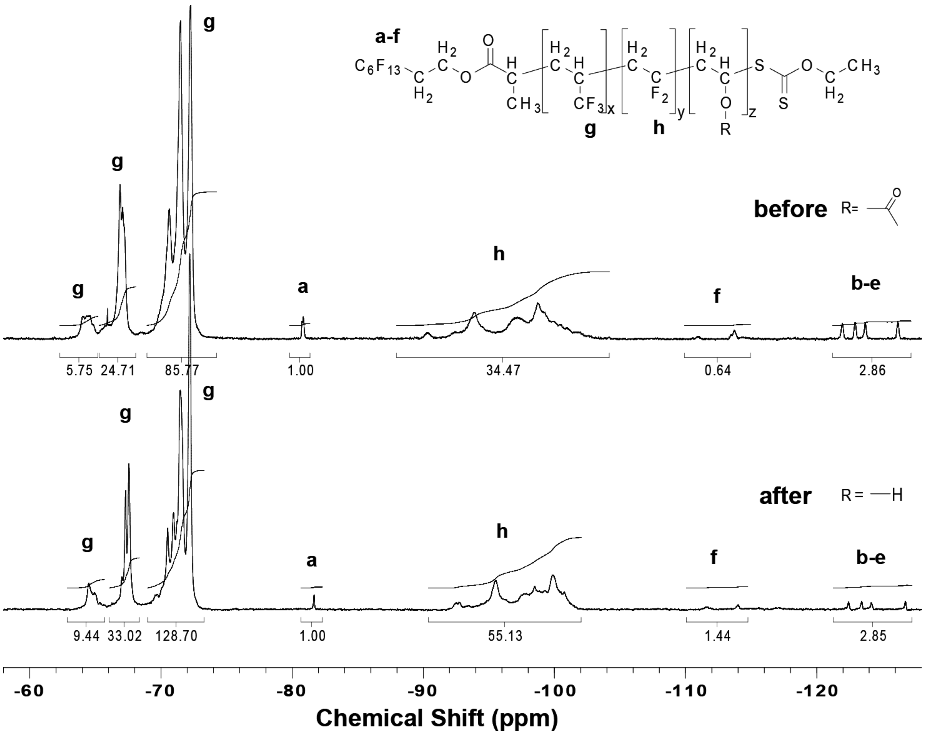


Figure 7. ^{19}F NMR spectra of the poly(VDF-*co*-TFP)-*b*-PVAc diblock copolymer before (recorded in $CDCl_3$) and after hydrolysis (recorded in $(CD_3)_2C{=}O$) into poly(VDF-*co*-TFP)-*b*-PVA (runs 15 and 19 in Tables 2 and 3, respectively), where VAc, VDF, and TFP stand for vinyl acetate, vinylidene fluoride, and 3,3,3-trifluoropropene, respectively.

of the radical formed by the macroCTA of the PVAc block. The secondary radical with an electron-withdrawing group is much more stable than a radical formed of the fluorinated block with VDF addition to the xanthate. The fragmentation of the CTA is therefore favored for this strategy. Thus, the second way in Scheme 2 favors better results as demonstrated by SEC (Figure 5).

Hydrolysis of Poly(VAc) Block. To obtain potential surfactants, the hydrolysis of the PVAc block was achieved under acidic condition (since VDF units are base sensitive, an alkaline hydrolysis must be avoided), as shown in Scheme 4. First, the hydrolysis, in the presence of H_2SO_4 and water in catalytic amounts, was attempted on a homopolymer of VAc as a model reaction, and then that strategy was adopted for the oligo(VAc) sequence in the fluorinated diblock copolymer. The results are displayed in Table 3.

The FTIR spectra enabled to monitor such a hydrolysis. They showed a continuous decreasing of the frequencies at 1743 cm^{-1}, assigned to both the carbonyl function of the poly(vinyl acetate) and the thiocarbonyl functions of the xanthate (Figure 6). The IR spectrum of the resulting product shows characteristic frequencies for the formed alcohol (Figure 6) as evidenced by the OH vibration band at 3478 cm^{-1}. The band for the carbonyl group almost disappeared (1743 cm^{-1}). The band between 3000 and 2900 cm^{-1} was attributed to the C—H stretch.

That hydrolysis was also confirmed by NMR spectroscopy. ^{19}F NMR (Figure 7) did not show any modification of the poly(VDF-*co*-TFP) block. In fact, no possible dehydrofluorination was observed while the C_6F_{13} end group remained unchanged. ^1H NMR (Figure 8) exhibits both the remaining OEt (though possible SH group resulting from the degradation of the xanthate identified by a triplet centered at 1.2 ppm can be expected) and the vanishing of acetoxy group at 1.8 ppm.

At the end, the hydrolysis of diblock copolymer forms poly(vinyl alcohol) block in 68% yield (Figures 7 and 8, lower spectra). Hence, the overall yield of poly(VDF-*co*-TFP)-*b*-oligo(vinyl alcohol) block copolymer was ca. 40%.

Thermostability. The thermal analysis of the (co)polymers by TGA revealed no major difference in the thermal stability under oxygen atmosphere (Figure 9). This may be due to the low molecular weight oligomers containing few VDF and TFP units.

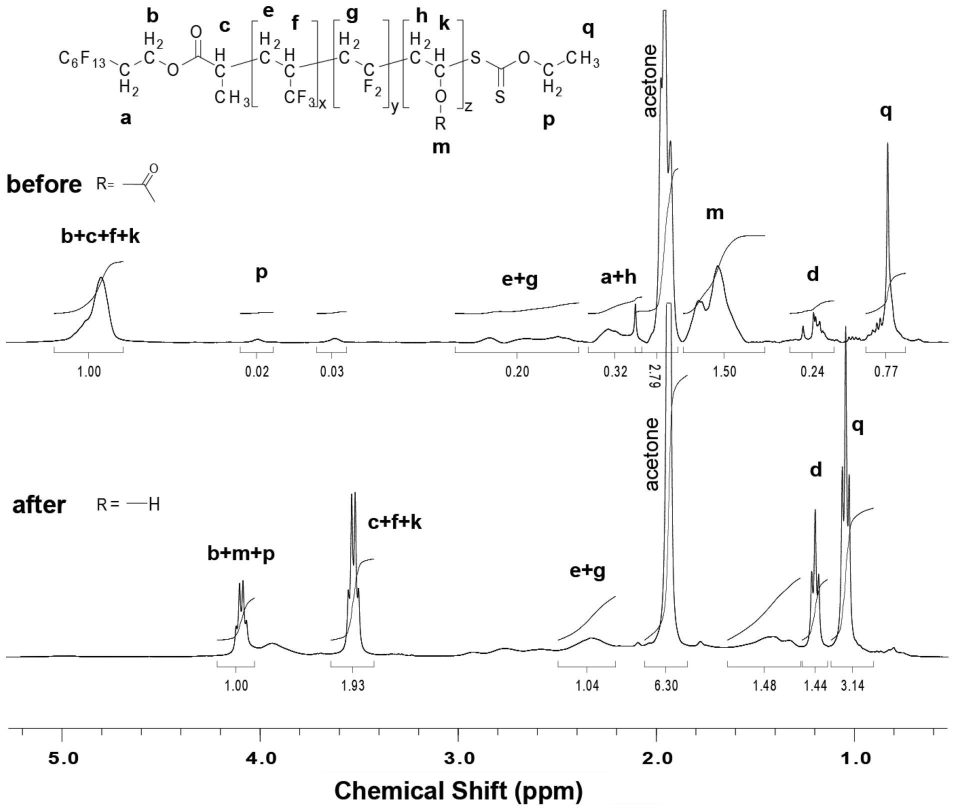


Figure 8. ^{1}H NMR spectra of the poly(VDF-*co*-TFP)-*b*-PVAc diblock copolymer before (recorded in $CDCl_3$) and after hydrolysis (recorded $(CD_3)_2CO$) into poly(VDF-*co*-TFP)-*b*-PVA (runs 15 and 19 in Tables 2 and 3, respectively), where VAc, VDF, and TFP stand for vinyl acetate, vinylidene fluoride, and 3,3,3-trifluoropropene, respectively.

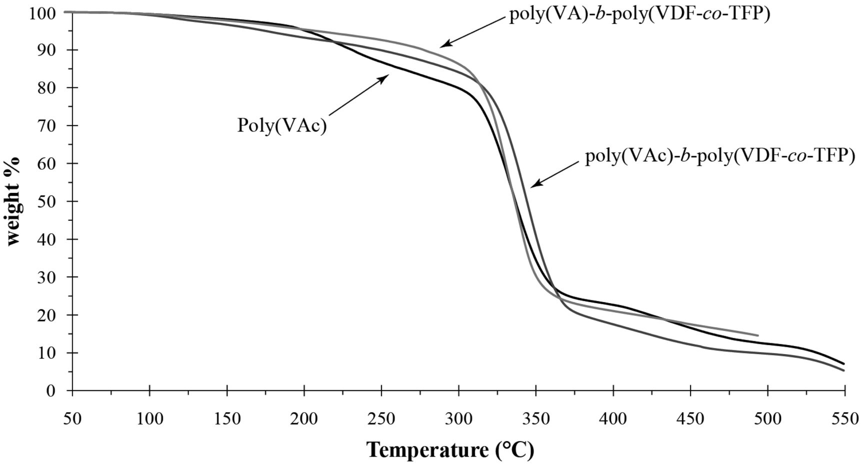


Figure 9. Thermograms of PVAc homopolymer (Run 2 in Table 1) and fluorinated diblock copolymer (Run 11 in Table 2) under oxygen atmosphere, where VAc, VDF, and TFP stand for vinyl acetate, vinylidene fluoride, and 3,3,3-trifluoropropene, respectively.

These compounds with a high content of fluorine are volatile. As it is the fluorinated part that induces thermal stability, the difference in the thermal behavior between the homopolymer and the diblock copolymer may arise from the presence of TFP and VDF units that polymerized in the second step. The aimed ratio of 50% of fluorinated monomers in the polymer should shift the decomposition toward higher temperatures. The decomposition of PVAc is known to take place in the region below 300 °C,[67] in good agreement with the observed decomposition for both diblock copolymer and poly(VAc) homopolymer. However, only a small increase of the stability was noted in the case of the diblock copolymer and is explained by the fact that the poly(VAc) homopolymer already contains the fluorinated C_6F_{13} leaving group.

Evaluation of the Surfactant Properties. The surfactant properties of the poly(VDF-*co*-TFP)-*b*-PVA (run 18) were assessed by means of tensiometry and conductimetry (Figure 10). By means of comparison, the surface tension of the ammonium

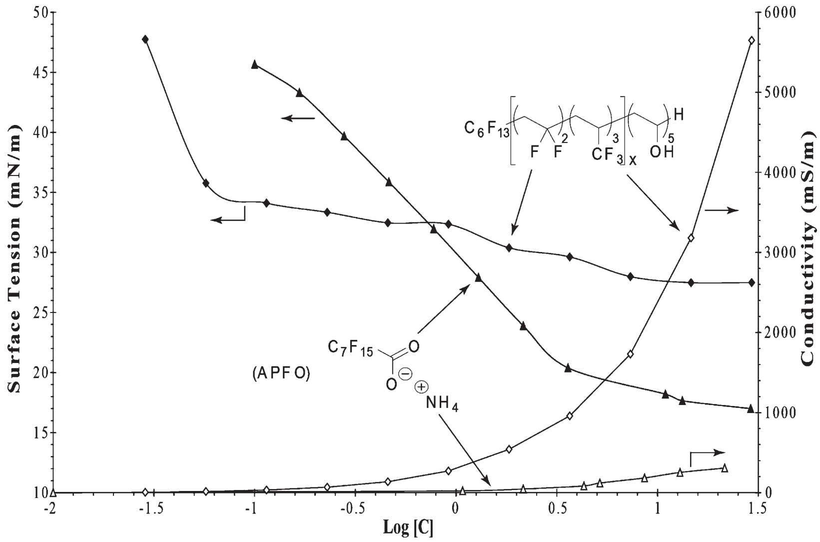


Figure 10. Surface tensions and conductimetries vs concentration of poly(VDF-*co*-TFP)-*b*-oligo(VA) surfactant (run 18, black) compared to those of APFO (white), where APFO, VA, VDF, and TFP stand for ammonium perfluorooctanoate, vinyl alcohol, vinylidene fluoride, and 3,3,3-trifluoropropene, respectively.

perfluorooctanoate (APFO), a commonly used surfactant, was also assessed. It can be seen that the poly(VDF-*co*-TFP)-*b*-oligo(vinyl alcohol) block copolymer shows a decrease of the surface tension (about 27 mN m^{-1} at 7.2 g L^{-1}). However, the reduction of the surface tension is not in the same order as that of APFO, but in the low concentration range, poly(VDF-*co*-TFP)-*b*-oligo(vinyl alcohol) block copolymer performs better than APFO does. However, the former exhibits a much lower critical micellar concentration (cmc) compared to APFO (0.06 vs 4.0 g L^{-1}) and thus outperforms APFO in the 0.06−0.8 g L^{-1} concentration range. Conductimetry is often used to assess the cmc of surfactants. In Figure 10 and for run 18, the cmc value determined by conductimetry does not correlate well with that achieved from tensiometry. However, there is a good agreement in the case of APFO. This is attributed to the fact that poly(VDF-*co*-TFP)-*b*-PVA (run 18), in contrast to APFO, is a nonionic surfactant and thus nonconducting. Hence, conductimetry is not a valid method for the assessment of critical micellar concentrations for such nonionic surfactants.[1]

CONCLUSIONS

A new fluorinated xanthate was synthesized and was involved in radical (co)polymerizations of vinyl acetate and of fluoroalkenes. Though the molar masses−monomer conversion linear dependence was not investigated, original fluorinated block copolymers based on vinylidene fluoride (VDF) and 3,3,3-trifluoropropene (TFP), poly(VDF-*co*-TFP), and oligo(vinyl alcohol) sequences were synthesized by radical polymerization controlled by the presence of that fluorinated xanthate. The microstructures of the resulting poly(VAc)-*b*-poly(VDF-*co*-TFP) and poly(VDF-*co*-TFP)-*b*-poly(VAc) block copolymers were characterized by different spectrometric and chromatographic techniques. First, the polymerization of VAc carried out in a fluorinated solvent and controlled by this xanthate offered oligo(VAc) in high yields, and interestingly, the experimental and targeted DP_n values were in good agreement. The radical copolymerization of vinylidene fluoride and 3,3,3-trifluoropropene, controlled by the above-mentioned fluorinated xanthate, was successfully achieved, and to the best of our knowledge, this is the first time that fluorinated alkenes have been polymerized by such a strategy. Second, diblock structures were obtained by reinitiating the terminal xanthate of the first block in the presence of the other monomer(s). Thus, the radical copolymerization of VDF and TFP via MADIX technology in the presence of poly(VAc) bearing xanthate end group yielded poly(VAc)-*b*-poly(VDF-*co*-TFP) block copolymers. In contrast to *tert*-butylperoxypivalate and azobis(isobutyronitrile) initiators that led to fluorinated block oligomers in a low DP_n value, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane yielded higher molecular weight-oligomers (M_n reaching 10 000 g mol^{-1}) in good yields (>60 wt %). Reversely, the polymerization of VAc was explored from the fluorinated poly(VDF-*co*-TFP)-xanthate and led to poly(VDF-*co*-TFP)-*b*-poly(VAc) block copolymers in good yields. The former route gave better results than the latter one for preparing poly(VAc)-*b*-poly(VDF-*co*-TFP) diblock copolymers. In addition, direct terpolymerization of VDF, TFP, and VAc was also successfully achieved producing poly(VDF-*ter*-TFP-*ter*-VAc) terpolymers. When *tert*-butyl peroxypivalate was used as initiator, a terpolymer was obtained in good yield (53%) and revealed the higher reactivity of VAc over TFP and VDF.

Hydrolysis under acidic conditions of poly(VAc) block took place in a satisfactory yield. The resulting poly(VDF-*co*-TFP)-*b*-poly(vinyl alcohol) block copolymer showed a good solubility in water and exhibited a comparable surface tension as that of ammonium perfluorooctaonate. Hence, original surfactants have been synthesized, the degradations of which are under investigation.

ASSOCIATED CONTENT

S Supporting Information. Experimental procedures for the polymerization VDF and TFP in the presence of xanthate; the radical copolymerization of VAc in the presence of poly(VDF-*co*-TFP)-Xa and its hydrolysis; ^1H and ^{19}F NMR spectra of various compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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