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Direct Synthesis of Vinylidene Fluoride-Based Amphiphilic Diblock Copolymers by RAFT/MADIX Polymerization

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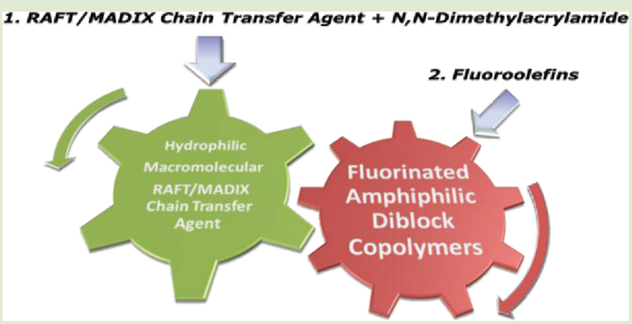
Supporting Information



ABSTRACT: We herein report the synthesis of original vinylidene fluoride (VDF)-based amphiphilic block copolymers by RAFT/MADIX polymerization. The controlled polymerization of VDF could be successfully mediated by a xanthate chain transfer agent as evidenced by size exclusion chromatography (SEC), ^{19}F NMR, and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis. Copolymers of VDF and perfluoro(methyl vinyl ether) (PMVE) of varying controlled chain lengths were also obtained. Finally, the direct synthesis of main-chain fluorinated amphiphilic block copolymers was performed from hydrophilic poly(*N*,*N*-dimethylacrylamide) macro-RAFT agents. It is expected that this finding will open interesting perspectives for the development of new class of polymeric surfactants for the stabilization of emulsions based on water and supercritical carbon dioxide media.

Fluoropolymers possess unique properties of resistance to thermal aging or weather aggressions and excellent inertness to a wide range of chemical environments.[1] However, their low solubility in most organic solvents except chlorofluorocarbons represents a major concern for the industrial scale production of these materials in homogeneous processes. To circumvent the use of such environmentally harsh solvents, DeSimone and co-workers first reported the solution radical polymerization of fluoroacrylate monomers in supercritical carbon dioxide (sc-CO_2).[2] Indeed, polyfluoroacrylates feature quadrupolar interactions with CO_2 and low self-interactions, which made them readily soluble in sc-CO_2 even at high molecular weight and under low pressure conditions (ca. 170 bar).[3] In contrast, poly(vinylidene fluoride) (PVDF), a specialty fluoropolymer with widespread use in industry,[4] exhibits lower solubility in sc-CO_2,[5] because of its semicrystalline character. Actually, only VDF oligomers possess high partition coefficients in sc-CO_2 at 150 bar and 338 K.[6,7] Consequently, high molecular weight PVDF can only be synthesized by dispersion[8] or precipitation[9,10] polymerization in sc-CO_2. This heterogeneous process can be also switched to a solution polymerization under extremely high pressures (ca. 1500 bar)[11] or via a copolymerization of vinylidene fluoride (VDF) with vinyl acetate[12] or hexafluoropropylene[13] under milder pressure conditions.

Hence, polyfluoroacrylates and low molecular weight polyfluoroolefins are natural candidates as CO_2-philic building blocks for the design of CO_2-philic block copolymers.[14,15] To this end, macromolecular engineering by reversible-deactivation radical polymerization (RDRP)[16,17] technologies is a resourceful toolbox for the synthesis of amphiphilic copolymers. Thus, original well-defined amphiphilic block copolymers were synthesized with fluorinated styrenic and methacrylate monomers[18] whose polymerization could be easily implemented and controlled by RDRP techniques. In contrast, examples of fluorinated amphiphilic copolymers that incorporate polyfluoroolefin blocks are scarce in the literature. In fact, RDRP techniques with the exceptions of (reverse) iodine transfer polymerization ((R)ITP)[19−22] and some alkylborane/oxygen couples[23] have so far failed to control the radical polymerization of fluoroolefins and VDF in particular. First examples came from derivative strategies using VDF telomers[24,25] or VDF/8-bromo-1*H*,1*H*,2*H*-perfluorooct-1-ene copolymers[26] as atom transfer radical polymerization macroinitiators for the formation of block and graft copolymers, respectively. For its part, ITP allowed the direct synthesis of PVDF−polystyrene block copolymers from iodoperfluoralkane chain transfer agents.[27] However, (R)ITP polymerization has been only successfully applied to hydrophobic monomers including styrenics, (meth)acrylates, and to a lesser extent, vinyl acetate (VAc).[28]

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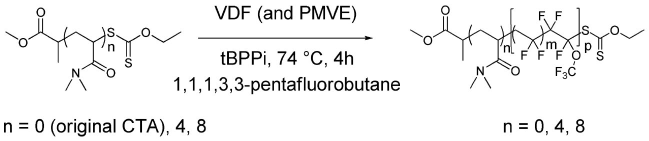
Considering these limitations, the RAFT[29−31]/MADIX[32] process offers greater perspectives for the generation of fluorinated amphiphilic copolymers due to its well-established applicability to a broad range of hydrophilic monomers.[32,33] Interestingly, recent works have highlighted the relevance of RAFT/MADIX technology in the radical polymerization of fluoroolefins. Liu et al.[34] successfully demonstrated the living/controlled character of statistical copolymers of chlorotrifluoroethylene and butyl vinyl ether synthesized at room temperature under ^{60}Co γ-ray irradiation in the presence of *S*-benzyl *O*-ethyl dithiocarbonate. Kostov et al.[35] synthesized copolymers of VDF and 3,3,3-trifluoropropene in the presence of a fluorinated xanthate, whose livingness could be assessed via a chain extension with VAc. Thus, amphiphilic block copolymers that are potentially nonbioaccumulative could be subsequently obtained after an additional hydrolysis step of the PVAc block. Therefore, it appears that RAFT/MADIX polymerization has an unrevealed great potential for the synthesis of new CO_2-philic (co)polymers based on fluoroolefins with well-defined macromolecular characteristics, architectures, and functionalities. Consequently, this communication describes the direct synthesis of novel VDF-based amphiphilic copolymers via RAFT/MADIX polymerization (see Scheme 1).

Scheme 1. Synthetic Procedure for the Direct Synthesis of VDF-Based (Co)polymers by RAFT/MADIX Polymerization



The RAFT/MADIX homopolymerization of VDF was first investigated using the industrially available Rhodixan A1 chain transfer agent (namely, 2-mercaptopropionic acid methyl ester *O*-ethyl dithiocarbonate). As both 2,2′-azobis(2-methylpropionitrile) (AIBN) and bis(4-*tert*-butylcyclohexyl) peroxydicarbonate-initiated VDF polymerizations only achieved very low conversions, *tert*-butyl peroxypivalate (tBPPi), whose effectiveness and decomposition mechanisms have been previously investigated for the free-radical polymerization of VDF,[36] was selected for the RAFT/MADIX study. The molar ratio of chain transfer agent (CTA) to tBPPi ($[CTA]_0/[tBPPi]_0$) was gradually decreased from 10 to 1 until high conversions of VDF were obtained at 74 °C (see runs 1−3 of Table 1). Then, different number-average molecular weights (M_n) were targeted to assess the mediation of the polymerization with Rhodixan A1. Experimental M_n were higher than the theoretical ones, which was attributed to the known difference of hydrodynamic volumes between PVDF samples and poly(methyl methacrylate) standards in dimethylformamide (DMF). Interestingly, dispersities ($Đ = M_w/M_n$)[37] were moderate ($1.30 < Đ < 1.60$) while increasing with M_n. This may be related to the formation of an increasing amount of head-to-head VDF adducts with increasing chain length (see Table S1 in the Supporting Information), as noticed during the ITP of VDF.[19,21] Furthermore, SEC-RI-UV analysis, with the wavelength set at the maximum absorption of the dithiocarbonate group (290 nm), furnished convincing evidence that M_n increased with time due to reversible transfer of the *O*-ethyl xanthate group between dormant and growing PVDF chains (see Figure 1a and Figure S2 in the Supporting Information), thereby proving the controlled character of the RAFT/MADIX polymerization of VDF.

The ability to mediate the polymerization of VDF with Rhodixan A1 could be further demonstrated by ^{19}F NMR. Indeed, all ^{19}F NMR spectra of low conversion samples exhibited a complex signal around −72 ppm, which was assigned to PVDF chains end-capped with a xanthate moiety (see Figure 2). Thus, the first VDF-xanthate adduct was properly evidenced by a characteristic NMR chemical shift centered at −72.5 ppm and considered as a doublet of doublets of doublets. Longer VDF oligomers end-capped with a xanthate group exhibited a slightly upshielded signal at −71 ppm. Interestingly, the formation of inverted VDF-xanthate adducts was also observed with a signal around −117 ppm (assigned from a $HCF_2CF_2CH_2S(C{=}S)OCH_2CH_3$ model compound, see the Supporting Information). This type of terminal defect, which was previously observed in ITP of VDF,[19] is thought to be far less reactive than a classical VDF-xanthate chain end and

Table 1. Experimental Results for the Direct Synthesis of VDF-Based (Co)polymers by RAFT/MADIX Polymerization

				feed ratio (mol %)		copolymer composition (mol %)[b]						
run	CTA	$[CTA]_0/[tBPPi]_0$[a]	$M_{n,targeted}$ (g·mol^{-1})	VDF	PMVE	VDF	PMVE	yield[c] (%)	$M_{n,theo}$ (g·mol^{-1})	$M_{n,SEC}$[d] (g·mol^{-1}) (Đ)	T_m (°C)	T_m (°C)
1	Rhodixan A1	10	4200	100		100		<5		n.d.[e]	n.o.[f]	92.7
2	Rhodixan A1	2.5	4200	100		100		20	1000	5200 (1.15)	n.o.	104.1
3	Rhodixan A1	1	4200	100		100		82	3400	8700 (1.60)	n.o.	142.4
4	Rhodixan A1	1	2100	100		100		80	1750	6200 (1.33)	n.o.	130.9
5	Rhodixan A1	1	2400	65	35	63	37	85	1850	3700 (1.26)[g]	−36.6	
6	Rhodixan A1	1	4200	70	30	74	26	71	3000	6000 (1.58)[g]	−41.4	
7	Rhodixan A1	1	6000	70	30	71	29	81	4850	8900 (1.63)[g]	−39.5	
8	$PDMA_{0.4k}$-Xa	1	3800	100		100		45	1650	n.d.	−6.8	118.8
9	$PDMA_{0.8k}$-Xa	0.5	3700	100		100		30	1800	n.d.	13.3	115.7
10	$PDMA_{0.4k}$-Xa	1	4600	70	30	69	31	75	3500	5900 (1.74)	−21.6	
11	$PDMA_{0.8k}$-Xa	1	5500	70	30	68	32	75	4200	7400 (1.53)	−4.1	

[a] See Table S1 in the Supporting Information for values of concentration. [b] Determined by ^{19}F NMR. [c] Measured by gravimetry. [d] Determined by SEC in DMF + 10 mM LiBr with PMMA standards. [e] n.d.: not determined due to nearly isorefractive response. [f] Not observed. [g] Determined by SEC in THF with PS standards.

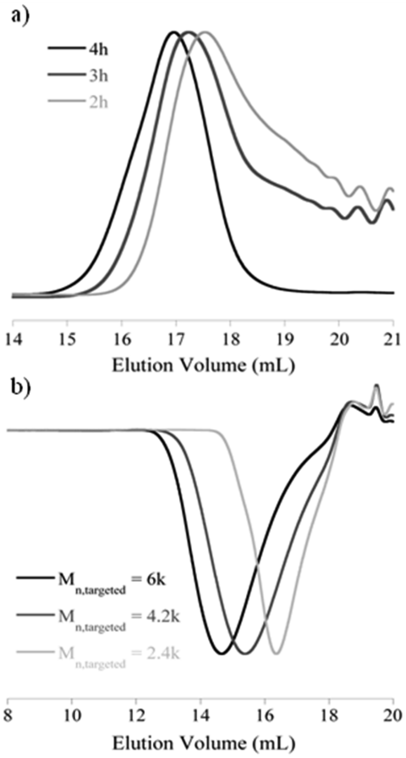


Figure 1. Overlays of SEC chromatograms for (a) the RAFT/MADIX polymerization of VDF (run 4, UV detection, in DMF) and (b) RAFT/MADIX polymerization of VDF and PMVE (runs 5−7 of Table 1, $M_{\mathrm{n,targeted}}$, RI detection, in THF) with 5.5, 2.6, and 1.8 mmol of CTA, respectively.

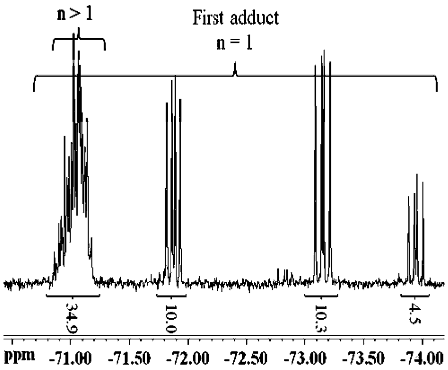


Figure 2. Expansion of the −70 to −74 ppm zone in the ^{19}F NMR spectrum of a PVDF obtained by RAFT/MADIX polymerization (run 2 of Table 1).

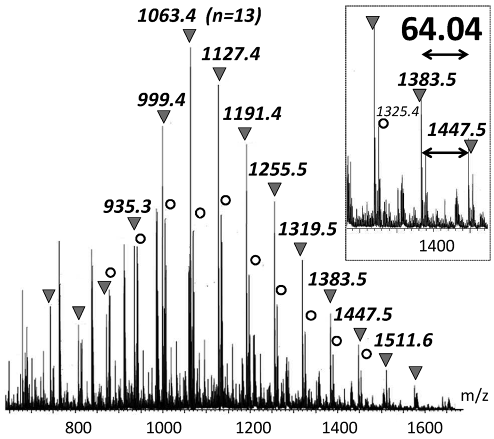


Figure 3. MALDI-TOF mass spectrum of a PVDF polymer synthesized in the presence of the Rhodixan A1 RAFT/MADIX agent (run 1 of Table 1). (▼) $CH_3CH(CO_2CH_3)-(C_2H_2F_2)_n-S(C{=}S)OCH_2CH_3$. (○) $CH_3CH(CO_2CH_3)-(C_2H_2F_2)_{n-1}-CH{=}CF_2$.

responsible to some extent for the broadening of molecular weight distribution when M_n increases. Ultimately, MALDI-TOF mass spectrometry was considered although it has been scarcely used for the characterization of PVDF.[19,38] The MALDI-TOF spectrum of a low molecular weight PDVF (see Figure 3) confirmed xanthate-capped PVDF as the main population of polymer chains (▼) and also revealed another population corresponding to PVDF chains terminated by a $-CH{=}CF_2$ group (○). The latter was attributed to the degradation products possibly arising from the laser beam.[39]

The main population was centered at m/z = 1063.4, corresponding to a PVDF chain of 13 monomer units bearing the two xanthate fragments at both ends. This perfectly matched the DP_n value of 12.7 calculated by ^{19}F NMR (see Figure S3 in Supporting Information).

The same methodology was then applied to the RAFT/MADIX copolymerization of VDF and perfluoro(methyl vinyl ether) (PMVE). Indeed, the incorporation of PMVE units in PVDF chains leads to completely amorphous copolymers that exhibit extremely low glass transition temperature (T_g) values (∼−40 °C, see entries 5−7 of Table 1),[22,40] which render them potentially CO_2-philic materials. A 70:30 molar feed ratio was selected to obtain completely amorphous polymers, and three different molecular weights were targeted to assess the control on the copolymerization of VDF with PMVE by Rhodixan A1. SEC measurements (see Figure 1b) revealed that M_n is inversely proportional to xanthate concentration. In addition, well-defined molecular weight distributions with relatively low dispersity values were obtained ($1.26 < Đ < 1.63$).

At this stage, the competitive advantage of RAFT/MADIX polymerization may mainly lie in the direct synthesis of main-chain fluorinated amphiphilic block copolymers. Indeed, these materials would be of particular interest as they are potentially original CO_2-philic/CO_2-phobic copolymers like the recently reported poly(*N*,*N*-dimethylacrylamide)-*block*-poly(vinyl acetate).[15] A solution process could be implemented with low molecular weight hydrophilic poly(*N*,*N*-dimethylacrylamide) (PDMA) polymers[15] that were synthesized by RAFT/MADIX polymerization and featured excellent solubility in 1,1,1,3,3-pentafluorobutane. They were used as RAFT/MADIX macromolecular agents to produce either amphiphilic PDMA-*block*-PVDF (runs 8 and 9, Table 1, and Figure 4a) or PDMA-*block*-(PVDF-*co*-PMVE) (runs 10 and 11, Table 1, and Figure 4b) copolymers. The efficiency of the reinitiation of the first block and the subsequent formation of the block copolymers were again proven by SEC analysis (Figure 4). However, in the specific case of PVDF, lower conversions were observed in comparison with the polymerizations ran with Rhodixan A1. Finally, these PDMA-*b*-poly(VDF-*co*-PMVE) copolymers exhibited a single T_g value comprised between those of both homopolymers taken separately, as values of T_g for $PDMA_{0.4k}$-Xa and $PDMA_{0.8k}$-Xa homopolymers were respectively −6.8 and 13.3 °C.[15]

Herein, we proposed several successful strategies to synthesize VDF-based controlled homopolymers and copolymers through RAFT/MADIX polymerization with an *O*-ethyl

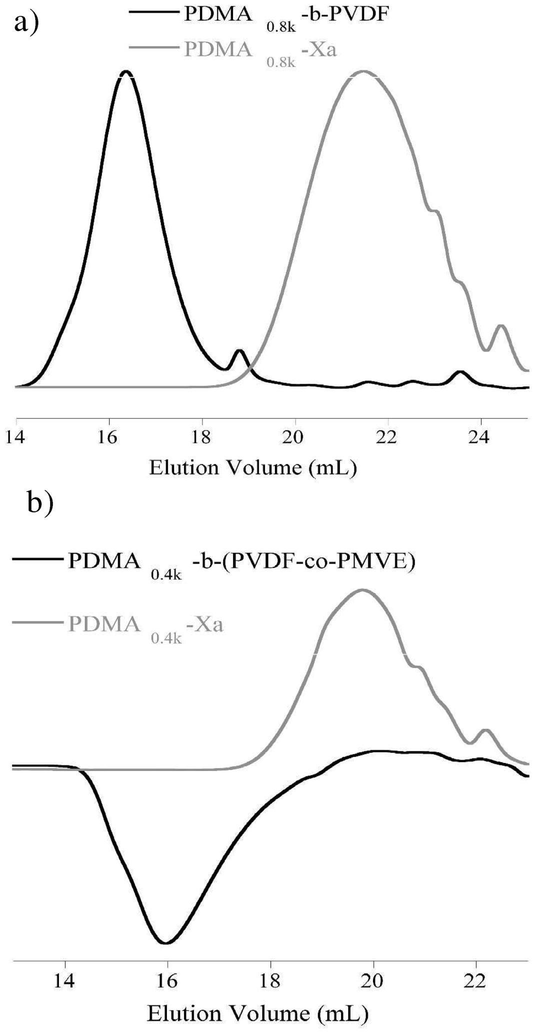


Figure 4. Overlays of SEC chromatograms for the RAFT/MADIX polymerization of (a) VDF from a PDMA$_{0.8k}$ macromolecular agent (run 9, UV detection, in DMF) and (b) VDF and PMVE from a PDMA$_{0.4k}$ macromolecular agent (run 10, RI detection, in DMF).

xanthate transfer agent. Excellent control was also achieved over the homopolymerization of VDF and its copolymerization with PMVE, offering new possibilities to finely tune macromolecular and glass transition characteristics of these copolymers. By means of hydrophilic macromolecular RAFT/MADIX agents, postpolymerization modification steps could be circumvented to obtain main-chain fluorinated amphiphilic block copolymers in a straightforward manner. Ultimately, the versatility of the RAFT/MADIX technology offers great perspectives for engineered polyfluoroolefins, with a huge application potential in fields where they could act like partners or substitutes for low molar mass fluorosurfactants. Thus, their evaluation as new CO$_2$-philic materials and polymer surfactants is currently under investigation.

■ EXPERIMENTAL METHODS

The following general procedure was applied. A solution of *tert*-butyl peroxypivalate and the (macromolecular) chain transfer agent in 1,1,1,3,3-pentafluorobutane (65 mL) was degassed with N$_2$ for 20 min and transferred into a 100 mL Hastelloy autoclave under vacuum. The autoclave was cooled down to −65 °C with acetone ice. VDF was introduced. When required, PMVE was condensed in the autoclave before VDF. The total amount of monomer introduced was estimated by double weighing. Then, the autoclave was progressively heated to 74 °C, while a pressure rise (typically from 7 to 16 bar) was observed. After 4 h of reaction, the autoclave was placed in an ice bath for 60 min, and unreacted monomers were progressively released. After opening the autoclave, 1,1,1,3,3-pentafluorobutane was evaporated with a rotary vacuum evaporator, and the sample was dried under vacuum. A gravimetric yield was then determined. The sample was finally characterized by ^{19}F and ^{1}H NMR spectroscopy in DMF-d_7 or acetone-d_6 and by SEC in DMF or THF.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, SEC chromatograms of PVDF, and calculations of chain defects and DP$_n$ by ^{19}F NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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