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ARTICLE

One-pot Synthesis of Poly(Vinylidene Fluoride) Methacrylate Macromonomer via *thia*-Michael addition

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This study presents a new synthetic route to prepare original PVDF macromonomer and PVDF-based architectures. A poly(vinylidene fluoride) polymer, PVDF, synthesized using MADIX controlled polymerization in the presence of O-ethyl-S-(1-methoxycarbonyl)ethyldithiocarbonate was chemically modified via two strategies and fully characterized. Using a one-pot procedure, the xanthate end-groups of the PVDF were converted into thiols which were immediately added onto the acrylate moieties of 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHPMA) via regioselective *thia*-Michael addition to form new PVDF-MA macromonomers. Two methods of elimination of the thiocarbonylthio group were tested and compared : aminolysis, and elimination using sodium azide. These reactions were thoroughly examined via ^{1}H and ^{19}F NMR spectroscopies and SEC-HPLC. The aminolysis procedure was shown to give better coupling efficiency and better-defined macromonomers. The PVDF-MA macromonomers with a highest functionality were further polymerized by RAFT. The RAFT homopolymerization of PVDF-MA revealed that a non-negligible amount of macromonomer did not react. In contrast RAFT copolymerization of PVDF-MA and MMA resulted in the total conversion of the macromonomer and allowed the synthesis of novel methacrylic copolymers and block copolymers.

Introduction

PVDF-based materials have found many applications as paints and coatings, materials for packaging, high performance elastomers and separators in Lithium batteries[1]. Since the late 1970s, and Tatemoto's[2] pioneering work on the iodine transfer polymerization (ITP) of fluoroalkenes, the study of the controlled radical polymerization of fluorine-containing monomers was reported in a number of articles. Many studies deal with the controlled radical polymerization (CRP) of fluorinated styrene,[3] (meth)acrylate monomers,[4-6] and vinyl esters[7] but only few articles describe convincingly the CRP of fluoroalkenes (alkenes bearing fluorine atoms directly on the vinylic carbons).[8-17] Fluorinated block copolymer have recently been synthesised[18] by ATRP,[19-24] RAFT/MADIX polymerization,[10-13] photomediated ITP,[14-16] or via the use of the combination of CRP[25] or of functional initiator[26] and Click Chemistry. These developments represent significant progress towards the synthesis of well-defined PVDF with predetermined molecular weights, narrow molecular weight distributions, sophisticated architectures, and useful end-functionalities. Nonetheless, the synthesis of VDF-based polymers with perfect end-group fidelity is still very difficult, and so far only moderately well-defined block and copolymers have been prepared. The synthesis of PVDF-based macromonomers has been scarcely reported.[27] In 2004, Ameduri *et al.*[28] achieved the synthesis of a PVDF-based acrylate bearing from 1 to 8 VDF units via the combination of VDF telomerisation, and end group modification. Huang *et al.*[29] revisited this procedure and synthesized monoacrylates containing one or two VDF units. However, for all its merits, this method yielded PVDF macromonomers with only few VDF units and requires several synthetic steps.

Our recent work[14] on the RAFT/MADIX homopolymerization of VDF opens new opportunities to prepare PVDF macromonomers, by harnessing the chemistry of the xanthate chain end-group. The end-group removal and modification of RAFT polymers, has been well studied over the 10 last years.[30,31] Indeed, the sulphur-containing end-group could lead to unwanted colouring, or odors (caused by decomposition), and undesirable residual chemical reactivity. To achieve this goal, several ways have been studied: thermolysis,[32-34] radical induced end-group removal,[35] hetero-Diels Alder chemistry,[36,37] reduction,[38] and nucleophilic substitution usually using primary amines[39]. This latter technique does not remove the terminal sulphur atom from the polymer. This remaining terminal thiol or thiolate can nonetheless be very useful for further chemical modification owing to the rich chemistry of thiols and their derivatives.

Thiol-ene and thiol-yne reactions for example have been very successfully used to prepare a range of functional polymers.[40-45] Another attractive reaction, is the thia-Michael addition which can be considered as an example of click chemistry. This reaction efficiently catalysed by phosphines[46-48] allows the introduction of functional group, and to synthesize uncommon architecture, using mild conditions. For example, Lowe *et al.*[47] reported the synthesis of star polymers using *thia*-Michael addition of a polyacrylamide synthesized by RAFT on a tri acrylate core. The same team[46] also described the post-functionalization of polyacrylamides into allyl and propargyl function using the same method. This *thia*-Michael addition

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was shown to be a very facile and powerful method to synthesize monomers[49-51] and macromonomers[52] using 3-(Acryloyloxy)-2-hydroxypropylmethacrylate (AHPMA) a dissymmetric telechelic molecule featuring both a methacrylate and an acrylate functional group. Thiols add with total regioselectivity onto the acrylate group to form a new methacrylate (macro)monomer.

The main goal of this work was to develop a robust and facile method to synthesise PVDF macromonomers. Two one-pot strategies of PVDF macromonomer synthesis have thus been investigated and compared: *Protocol 1:* Using hexylamine to remove xanthate end-groups, and *Protocol 2:* using sodium azide as a nucleophile. The PVDF macromonomers obtained by the most efficient method were homopolymerized and copolymerized with MMA by RAFT polymerization.

Experimental

Materials and methods

4-Cyano-4-(2-phenylethanesulfanylthiocarbonyl)sulfanyl pentanoicacid (PETTC) CTA was synthesized according to the method described by Semsarilar *et al.*[53] 2,2'-Azobis-isobutyronitrile (AIBN) purchased from Sigma Aldrich was recrystallized in methanol prior to use. All other reagents were used as received unless stated otherwise. 1,1-Difluoroethylene (vinylidene fluoride, VDF) was kindly supplied by Arkema (Pierre-Benite, France). O-ethyl-S-(1-methoxycarbonyl)ethyldithiocarbonate, was kindly provided by Solvay SA. *Tert*-Amyl peroxy-2-ethylhexanoate (purity 95%, Trigonox 121) and 4,4'-azobis-4-cyanopentanoic acid (ACVA, >98%) and azobisisobutyronitrile (AIBN > 98%) were purchased from AkzoNobel (Chalons-sur-Marne,France). ReagentPlus grade (purity >99%) dimethyl carbonate (DMC), 2-phenylethanethiol, dimethylformamide (DMF), 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHPMA), sodium Azide (NaN_3), dimethylphenylphosphine (DMPP), triethylamine (TEA), hexylamine, methyl methacrylate (MMA), methanol (MeOH), tetrahydrofuran (THF), ethyl acetate and laboratory reagent grade Hexane and diethyl ether (purity > 95%) were purchased from Sigma Aldrich.

Nuclear Magnetic Resonance (NMR)

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

Size Exclusion Chromatography (SEC)

Size exclusion chromatograms were recorded using a Triple detection GPC from Agilent Technologies with its corresponding Agilent software, dedicated to multi-detector GPC calculation. The system used two PL1113-6300 ResiPore 300 x 7.5 mm columns (all range of Mw) with DMF as the eluent with a flow rate of 0.8 mL/min and Toluene as flow rate marker. The detector suite comprised a PL0390-0605390 LC light scattering detector with 2 diffusion angles (15° and 90°), a PL0390-06034 capillary viscometer, and a 390-LC PL0390-0601 refractive index detector. The entire SEC-HPLC system was thermostated at 35°C. PMMA narrow standards were used for the calibration. Typical sample concentration was 10 mg/mL.

Autoclave

The radical polymerizations of VDF were performed in a 100 mL Hastelloy Parr autoclave systems (HC 276), equipped with a mechanical Hastelloy stirring system, a rupture disk (3000 PSI), inlet and outlet valves, and a Parr electronic controller to regulate the stirring speed and the heating. Prior to reaction, the autoclave was pressurized with 30 bars of nitrogen to check for leaks. The autoclave was then put under vacuum (20.10^{-3} bar) for 30 minutes to remove any trace of oxygen. A degassed solution of solvent, initiator and Xanthate CTA was introduced via a funnel. The reactor was then cooled down in liquid nitrogen to about -80°C, and the desired quantity of VDF was transferred by double weighing (i.e. the difference of weight before and after filling the autoclave with VDF). After warming up to ambient temperature (*ca.* 20 °C), the autoclave was heated to the targeted temperature under mechanical stirring.

Thermogravimetric Analysis (TGA)

TGA analyses were carried out on 10-15 mg samples on a TGA Q50 apparatus from TA Instruments from 20 °C to 580 °C, in platinum pans, at a heating rate of 10 °C min^{-1}, under air

Synthetic procedures

Madix Homopolymerization of Vinylidene fluoride (VDF)

Using the experimental setup described above, a typical polymerization of VDF was performed as follows: A solution of *tert*-amyl peroxy-2-ethylhexanoate (158 mg, 6.87 10^{-4}mol) and *O*-Ethyl-*S*-(1-methoxycarbonyl)ethyldithiocarbonate (1.30 g, 6.25 10^{-3} mol) in dimethylcarbonate (DMC, 60 mL), was degassed by N_2 bubbling during 30 min. This homogenous solution was introduced in the autoclave using a funnel, VDF gas (19 g, 2.97 10^{-1} mol) was transferred into the autoclave at low temperature, and the reactor was gradually heated to 73 °C. The reaction was stopped after 24 h. During the reaction, the pressure increased to a maximum of 25 bar and then decreased to 10 bar over 24h. The autoclave was cooled down to room temperature (*ca.* 20 °C), purged from the residual monomers, and dimethylcarbonate was removed under vacuum. The crude product was dissolved in 30 mL of warm THF (ca. 40 °C), and left under vigorous stirring for 30 minutes. This polymer solution in THF was then precipitated dropwise into 400 mL of chilled hexane. The polymer (white powder) was filtered through a filter funnel and dried under vacuum (15 10^{-3} bar) for two hours at 50 °C. The polymerization yield (yield = 65 %) was determined by gravimetry (mass of polymers obtained / mass of monomer introduced in the

pressure reactor). Yields were used as conversion, since conversion is very difficult to measure accurately for VDF and other gaseous monomers.

The degree of polymerization (DP) can be calculated from ^{1}H NMR using the integrals of the signals corresponding to: the methyl of the CTA R-group (1.19-1.24 ppm), the CH_2 of the regular VDF additions (Head-to-Tail, HT, 2.70-3.19 ppm),the CH_2 of the reverse VDF additions (Tail-to-Tail, TT, 2.28-2.43 ppm), and the CH_2 of the terminal VDF units (4.02-4.17 ppm), according to equation (1):

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

Molecular weight was then calculated using equation (2):

$$M_{nNMR}(\mathrm{R}) = M_n CTA + (DP \times M_n VDF) \quad (2)$$

Where M_nCTA = 208.30 gmol^{-1} and M_nVDF= 64.04 gmol^{-1}

^{1}H NMR (400 MHz $(CD_3)_2CO$, δ (ppm)) Figure 1a:
1.19-1.24 (d, -CH(**CH_3**)(C=O)-, $^3J_{HH}$= 7.1 Hz), 1.40-1.46 (t, **CH_3**-CH_2-O-, $^3J_{HH}$= 7.2 Hz), 2.28-2.43 (m,-CF_2-**CH_2-CH_2**-CF_2-, VDF-VDF TT reverse addition), 2.70-3.19 (t, -CF_2-**CH_2**-CF_2-, VDF-VDF HT normal addition), 3.60-3.69 (s, -(C=O)-O-**CH_3**), 4.02-4.17 (t, -(C=S)-S-**CH_2**-CF_2-, $^3J_{HF}$ = 18 Hz), 4.67-4.77 (q, CH_3-**CH_2**-O-, $^3J_{HH}$= 7.2 Hz), 6.05-6.45 (tt, $^2J_{HF}$ = 55 Hz , $^3J_{HH}$= 4.5 Hz -CH_2-CF_2-**H,** about 14 mol %)

^{19}F NMR (376 MHz $(CD_3)_2CO$, δ (ppm)) Figure S5 : -115.63 (-CH_2-CF_2-**CF_2**-CH_2-CH_2-, VDF-VDF HH reverse addition), -114.29 (-CH_2-CF_2-**H**), -113.34 (-CH_2-**CF_2**-CF_2-CH_2-CH_2-, HH reverse addition), -113.09 (-S-CH_2-**CF_2**-CF_2-CH_2-), -112.69 (-S-CH_2-CF_2-**CF_2**-CH_2-), -94.79 (-CH_2-CH_2-**CF_2**-CH_2-, TT reverse addition), -93.50 (-CH_2-**CF_2**-CH_2-CH(CH_3)(C=O)-), -92.12 (-CH_2-**CF_2**-CH_2-CF_2H), -91.44 (-CH_2-**CF_2**-CH_2-CF_2-CH_2-CH_2-, regular VDF-VDF HT addition), -91.00 (-CH_2-**CF_2**-CH_2-, regular VDF-VDF HT addition).
HH, HT and TT stand for head-to-head, head-to-tail, and tail-to-tail, respectively.
(Mn_{SEC} = 5100 g.mol^{-1}, Đ = 1.34, Mn_{NMR} = 3000 g.mol^{-1})

Macromonomers Synthesis (PVDF-MA)

Hexylamine protocol

The aminolysis and subsequent Michael addition were conducted using a one-pot protocol described by McKee et al.[52] In a typical reaction $PVDF_{54}$–XA, where XA represent the ethylxanthate group, (1.00 g, 3.33 10^{-4} mol) and 3-(Acryloyloxy)-2-hydroxypropyl methacrylate, AHPMA, (0.214 g, 1.00 10^{-3} mol) were dissolved in DMF (23 mL). The solution was degassed by nitrogen bubbling for 10 min and a degassed mixture of *n*-hexylamine (0.135 g, 1.33 10^{-3} mol), triethylamine (0.056 g, 5.00 10^{-4} mol) and 0.1 mL of DMPP in 1 mL of DMF were injected in to the reaction mixture. Nitrogen bubbling was continued for a further 10 min and the reaction solution was then stirred at 25°C for 16h. The dark solution was precipitated twice from chilled methanol, and the resulting solid was filtered through a filter funnel and dried under high vacuum at 70°C until constant weight to remove traces of DMF. (Yield = 76%)

^{1}H NMR (400 MHz $(CD_3)_2CO$, δ (ppm)) Figure 1d : 1.19-1.24 (d, -CH(**CH_3**)(C=O)-, $^3J_{HH}$= 7.1 Hz), 1.85-1.96 (s, H_2C=C(**CH_3**)), 2.28-2.43 (m,-CF_2-**CH_2-CH_2**-CF_2-, VDF-VDF TT reverse addition), 2-.70-3.19 (t, -CF_2-**CH_2**-CF_2-, VDF-VDF HT normal addition), 3.25-3.40 (t, -CF_2-CF_2-**CH_2**-S-, $^3J_{HF}$ = 18 Hz), 3.60-3.69 (s, -(C=O)-O-**CH_3**), 4.00-4.55 (m, -O-**CH_2-CH**(OH)-**CH_2**-O-), 5.60-5.68 (s, **H**-CH=C(CH_3)-), 6.05-6.14 (s, **H**-CH=C(CH_3)-), 6.05-6.45 (tt, $^2J_{HF}$ = 55 Hz , $^3J_{HH}$= 4.5 Hz -CH_2-CF_2-**H,** about 14 mol %)

^{19}F NMR (376 MHz $(CD_3)_2CO$, δ (ppm)) Figure 2d : -115.63 (-CH_2-CF_2-**CF_2**-CH_2-CH_2-, VDF-VDF HH reverse addition), -114.29 (-CH_2-CF_2-**H**), -114.24 (-CH_2-CF_2-**CF_2**-CH_2-S-), -113.34 (-CH_2-**CF_2**-CF_2-CH_2-CH_2-, HH reverse addition), -112.83 (-CH_2-**CF_2**-CF_2-CH_2-S-),-94.79 (-CH_2-CH_2-**CF_2**-CH_2-, TT reverse addition), -93.50 (-CH_2-**CF_2**-CH_2-CH(CH_3)(C=O)-), -92.12 (-CH_2-**CF_2**-CH_2-CF_2H), -91.44 (-CH_2-**CF_2**-CH_2-CF_2-CH_2-CH_2-, regular VDF-VDF HT addition), -91.00 (-CH_2-**CF_2**-CH_2-, regular VDF-VDF HT addition).
(Mn_{SEC} = 6000 gmol^{-1}, Đ = 1.22, Mn_{NMR} = 3000 gmol^{-1})

NaN_3 protocol

As above, the conversion of xanthate end-group and the Michael addition were conducted using a one-pot protocol. The removal of the xanthate group was perfomed using NaN_3 instead of amines as described by Wu et al.[58]
In a typical reaction, $PVDF_{54}$–XA (1.00 g, 3.33 10^{-4} mol) and 3-(Acryloyloxy)-2-hydroxypropyl methacrylate, AHPMA, (0.214 g, 1.00 10^{-3} mol) were dissolved in DMF (23 mL). The solution was degassed by nitrogen bubbling for 10 min and a degassed solution of NaN_3 (0.130 g, 2.00 10^{-3} mol) and 0.1 mL of DMPP in a mixture of 1 mL of DMF and 1 mL of distilled water was injected into the reaction mixture. Nitrogen bubbling was continued for a further 10 min and the reaction solution was then stirred at 25°C for 16h. The red solution was precipitated twice from chilled methanol, and the resulting solid was filtered through a filter funnel and dried under high vacuum at 70°C until constant weight to remove traces of DMF. (Yield = 80%)
(Mn_{SEC} = 8800 gmol^{-1}, Đ = 1.41, Mn_{NMR} = 3000 gmol^{-1})

RAFT homopolymerization of PVDF-MA macromonomer

In a typical reaction, $PVDF_{54}$-MA (1.00 g, 2.78 10^{-4} mol), AIBN (1.2 mg, 7.3 10^{-6} mol) and PETTC (9.55 mg, 2.81 10^{-5} mol) were dissolved in 5 mL of DMF. The solution was degassed by nitrogen bubbling for 15 min and left under stirring at 70°C for 24h. The crude reaction was precipitated in a large excess of methanol and the resulting solid was dried under vacuum at 70°C until constant weight. (Yield = 95 %)

RAFT copolymerization of PVDF-MA macromonomer and Methyl methacrylate

A mixture of $PVDF_{54}$-MA (0.10 g, 2.78 10^{-5} mol), MMA (136 mg, 1.36 10^{-3} mol), PETTC (9.40 mg, 2.70 10^{-5} mol), and AIBN (1.00 mg, 5.60 10^{-6} mol) was dissolved in 2 mL of DMF. The solution

was degassed by N_2 bubbling for 15 min and left under stirring at 70°C for 24h. The crude reaction was precipitated in a large excess of methanol and the resulting solid was dried under vacuum at 70°C until constant weight. (Yield = 85 %)

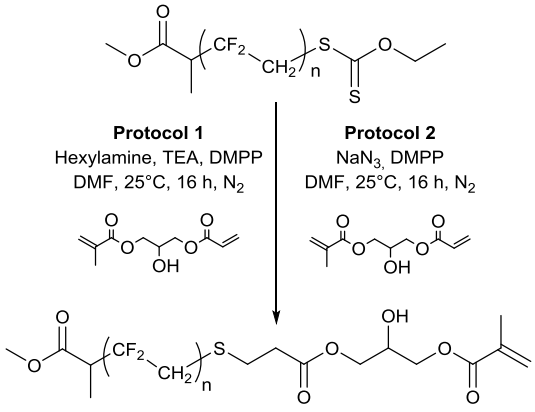
Synthesis of Poly(PVDF-MA – *co* – MMA) – *b* – PMMA block copolymer

Poly(PVDF-MA – *co* – MMA) copolymer (20 mg, 4.0 10^{-6} mol), MMA (80 mg, 8.0 10^{-4} mol) and AIBN (0.15 mg, 9.1 10^{-7} mol) were dissolved in 0.5 mL of DMF. The solution was degassed by N_2 bubbling for 15 min and left under stirring at 70°C for 24h. The crude reaction was precipitated in a large excess of methanol and the resulting solid was dried under vacuum at 70 °C until constant weight. (Yield = 51 %)

Results and discussion

Comparison of Methods

Special care was paid to the thiocarbonylthio group removal step. Indeed, PVDF is relatively sensitive to bases which can cause dehydrofluorination.[54-56] This sensitivity may be a significant limitation to PVDF chemical modification strategies. In the presence of a base, PVDF solutions readily turn black as a consequence of dehydrofluorination reaction creating conjugated C=C bonds within the PVDF backbone. However, it has been shown that only 0.1% of dehydrofluorination is sufficient to cause a deep black coloration of PVDF.[54] This undesired reaction was partially investigated with several alkaline compounds, and should also occur with primary amine.[56] However, the very fast and quantitative reaction of primary amines with xanthate groups and the mild conditions used (low temperature, short reaction time, amine/xanthate group molar ratios) should limit this phenomenon. Furthermore, the conjugated C=C bonds in dehydrofluorinated PVDF can be easily assigned in ^{1}H NMR as a distinctive signals at 6 ppm.[56,58] Using sodium azide[59] instead of amine could be an efficient way to prepare thiol-terminated PVDF while avoiding the undesired dehydrofluorination reaction. The synthesis of the PDVF macromonomer was achieved using the experimental protocols depicted in Scheme 1. In these reactions, NaN_3 and Hexylamine played the role of nucleophilic thiocarbonylthio-group removal agent, while DMPP was used as catalyst, TEA as proton sponge for the thia-Michael addition, and AHPMA as a Michael acceptor. Protocol 1 yielded black polymers while protocol 2 delivered reddish polymers. These observations suggest that dehydrofluorination probably occurred in parallel to the xanthate removal. However, this dehydrofluorination could not be detected by either ^{1}H or ^{19}F NMR (vide infra). The extent of the dehydrofluorination is thus likely negligible. Figure 1 displays the ^{1}H NMR spectra of: a) xanthate-functionalized PVDF (PVDF-XA) synthesized by MADIX polymerization, b) the thiol-functionalized PDVF (PVDF-SH) formed by aminolysis of PVDF-XA using hexylamine, *c)* the thiol-functionalized PDVF (PVDF-SH) formed via NaN_3 elimination, d) the PVDF Methacrylate macromonomer (PVDF-MA) synthesized using protocol 1 (Scheme 1) and e) the PVDF



Scheme 1. Synthesis of PVDF-MA macromonomer from PVDF-XA according two strategies

Methacrylate macromonomer (PVDF-MA) synthesized using protocol 2 (Scheme 1). As reported previously,[14] the ^{1}H NMR spectrum of the PVDF-XA (Figure 1a) shows the characteristic signals of the O-ethyl xanthate terminal group (a triplet at 1.4 ppm (CH_3 of the O-ethyl xanthate) and a quartet at 4.7 ppm (-CH_2-O-of the O-ethyl xanthate)), and a well-defined triplet centered at 4.1 ppm corresponding to the CH_2 group of last VDF unit connected to the O-ethyl xanthate moiety (-CF_2-CH_2-S-). Indeed, MADIX polymerization of VDF leads to an accumulation of PVDF chains terminated by -CF_2-CH_2-XA moieties.[14] The PVDF used here was exclusively composed of such -CF_2-CH_2-XA-terminated chains.

After aminolysis, the ^{1}H NMR spectrum of the PVDF-SH (Figure 1b) shows the elimination of the ω-chain end group (complete disappearance of the triplet and quartet of the O-ethyl Xanthate at 1.4 and 4.7 ppm, respectively); and the formation of the thiol end-group revealed by the shift of the signal of the methylene of the terminal VDF unit from 4.1 ppm to 3.3 ppm. This signal is also split into a doublet of triplets (with a coupling constant $^3J_{HH}$ = 8.2 Hz) in agreement with a -CH_2-SH motif. After the Michael addition, this coupling between the proton of the thiol and the CH_2 of the terminal VDF unit disappears (Figure 1d). Instead, a triplet can be seen at 3.3 ppm on the ^{1}H NMR spectrum of the polymer isolated after reaction following the one-pot aminolysis and thia-Michael addition protocol, thus confirming the synthesis of PDVF methacrylate macromonomer. The ^{1}H NMR spectra of the PVDF-SH (Figure 1c) obtained using NaN_3 as nucleophile and of PVDF-MA (Figure 1e) prepared via protocol 2 (one-pot reaction using sodium azide in the presence of AHPMA and DMPP) are very different from the corresponding PVDF-SH (Figure 1c) and PVDF-MA (Figure 1d) prepared using hexylamine and protocol 1 respectively. The well-resolved triplet observed at 3.3 ppm on the ^{1}H NMR spectrum of the PVDF-MA synthesized via protocol 1 (Figure 1d), appears as a multiplet in the case of the PVDF-MA synthesized using protocol 2 (Figure 1e). This difference suggests that the thia-Michael addition did not proceed quantitatively in protocol 2 or that it is accompanied by undesired side reactions. The comparison of the intensity of the signals of the methacrylic protons (at 5.63, 6.10, and 1.90 ppm, in Figure 1d and 1e) to that of the (-CH-**CH_3**) signal at 1.2 ppm (Figure 1a) or that of the ((C=O)-O-**CH_3**) signal at 3.6 ppm

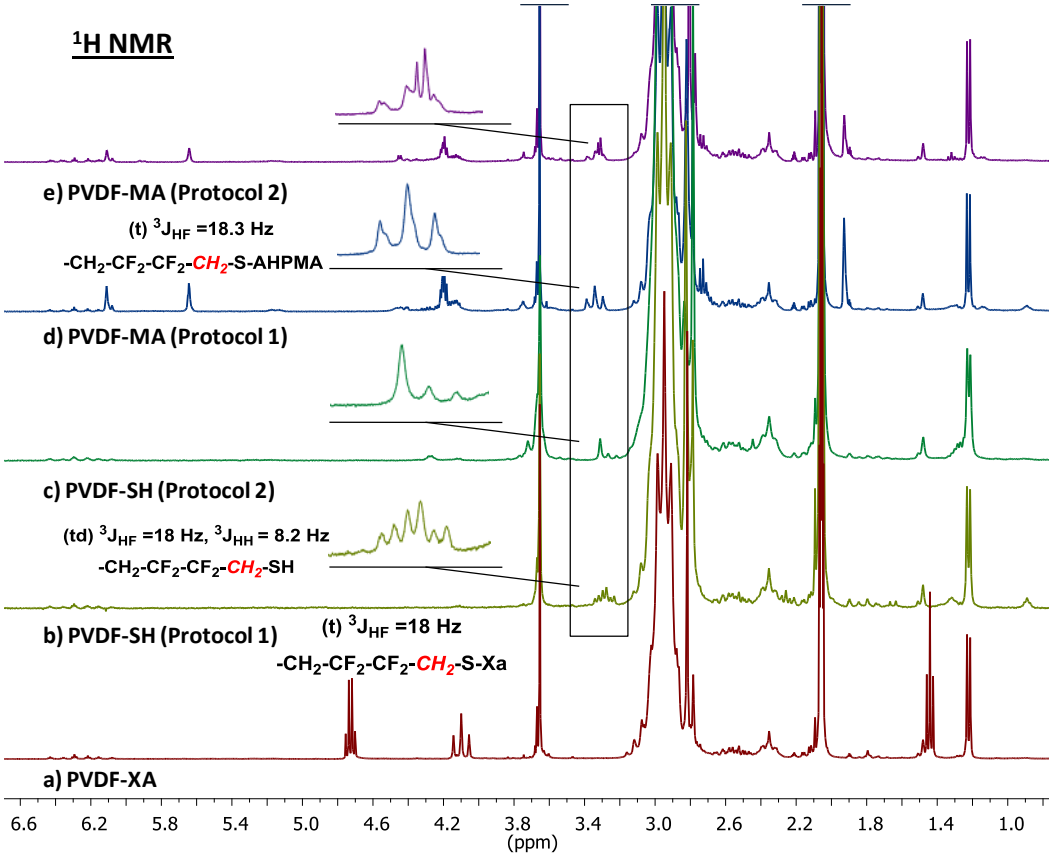


Figure 1.[1]H NMR spectra in $(CD_3)_2CO$ of: a) PVDF-XA, b)PVDF-SH prepared using Hexylamine (protocol 1), c)PVDF-SH prepared using sodium azide (protocol 2),d) PVDF-MA Methacrylic macromonomer prepared using protocol 1, and e)PVDF-MA Methacrylic macromonomer prepared using protocol 2.

(Figure 1a) of the MADIX CTA R-group at the α-end of the PVDF chain, allows the calculation of the extent of the replacement of xanthate moiety into methacrylate (see equation 3 below). However, as reported in a previous work[14], the PVDF-XA chains initiated by R radicals from the CTA were not totally terminated by xanthate Z group. Transfer to the DMC occurred in the course of the polymerisation, leading to around 14 % of the dead chains terminated by a $-CF_2H$ group. Therefore, a correction factor (α= 0.86) was introduced in equation (3) in order to have a real percentage of end group functionality.

$$\text{Functionality (\%)} = \frac{\int_{6.04}^{6.13}(\text{H}) + \int_{5.56}^{5.68}(\text{H}) + \int_{1.86}^{1.96}(\text{CH}_3)}{\frac{5}{3}\int_{1.18}^{1.25}(\text{CH}_3)} \times \alpha \quad (3)$$

This calculation shows a total functionality of 85% and 62 % with a coupling efficiency of 99% and 72 % for protocol 1 and protocol 2, respectively (See Figures S3 and S4 for details). The aminolysis-Michael addition method is thus confirmed to be more efficient that the method utilizing sodium azide.

The same comparative study was carried out using ^{19}F NMR Spectroscopy. Figure 2 presents the -111.5 to -117 ppm region of the ^{19}F NMR spectra of: a) PVDF-XA b) PVDF-SH, formed by aminolysis of PVDF-XA using hexylamine *c)* PVDF-SH, formed via NaN_3 elimination d) PVDF-MA synthesized using protocol 1 e) PVDF-MA synthesized using protocol 2. (Full NMR spectra are provided in Figures S5 and S6). The effect of the aminolysis can easily be seen by monitoring the -112 ppm -117 ppm region where the signals corresponding to the ultimate and penultimate VDF unit appear ($-CH_2-CF_2-\mathbf{CF_2}-CH_2-S-$: -113.09 ppm, and $-CH_2-\mathbf{CF_2}-CF_2-CH_2-S-$: -112.69 ppm). On the spectrum of PVDF-SH (Figure 2b) a surprising highfield shift of the signal of the CF_2 terminal VDF unit from -113.09 ppm to -116.4 was observed following aminolysis. This shielding was caused by the removal of the xanthate group. This end-group removal also had a small influence on the CF_2 of the penultimate VDF unit, (which shifted from -112.69 to -112.77 ppm). Similarly to what was observed by ^1H NMR Spectroscopy, ^{19}F NMR also shows that the end-group removal by aminolysis was quantitative. The spectrum of PVDF-MA prepared via protocol 1 (Figure 2d) shows the deshielding of the signals of the CF_2 of the ultimate VDF unit from -116.4 ppm in PVDF-SH to -114.24 ppm and the shielding of the signal of the CF_2 of the penultimate VDF unit from -112.77 ppm (in PVDF-SH) to -112.83 ppm. The complete shifts of these ^{19}F NMR signals confirms the quantitative coupling of the AHPMA onto the ω-end of the PVDF chains. The study of the ^{19}F NMR spectra of the product obtained using protocol 2 revealed significant differences (Figure 2c,e). For PVDF-SH, the signal of the CF_2 of the ultimate VDF unit shifted from -113.09 to -114.19 ppm and the peak assigned to the CF_2 of the penultimate VDF unit observed at -112.73 in PVDF-XA was split into two distinctive peaks at -112.66 ppm and -112.84 ppm after treatment with

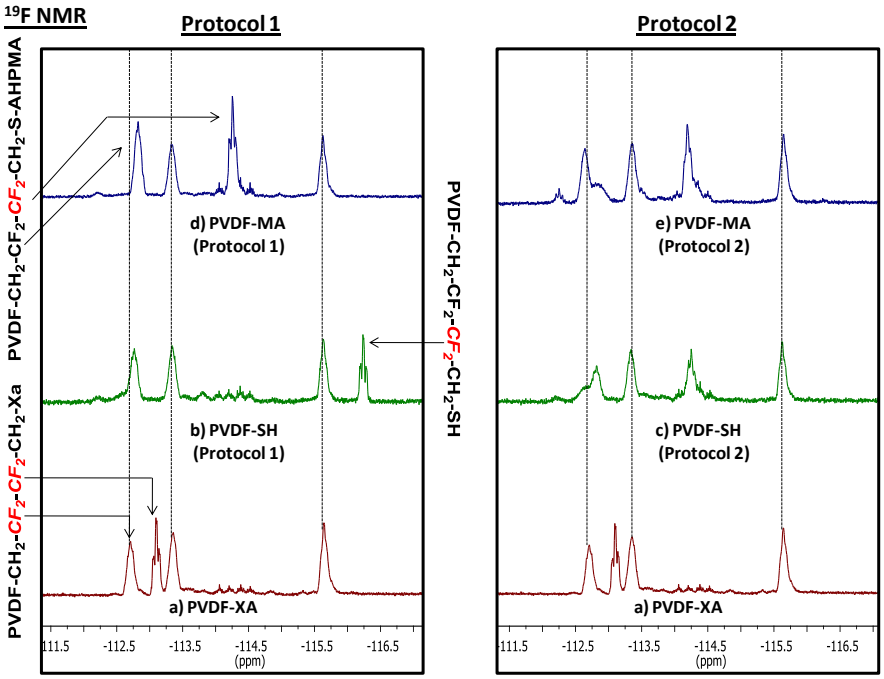


Figure 2. Expansion of the -111.5 - -117 ppm region of the ^{19}F NMR spectra in $(CD_3)_2CO$ of : a) PVDF-XA, b) PVDF-SH prepared by aminolysis, c) PVDF-SH prepared by action of NaN_3, d) PVDF-MA prepared following protocol 1 and e) PVDF-MA prepared following protocol 2

NaN_3 (Figure 2c). This feature can also be seen in the ^{19}F NMR spectrum of PVDF-MA prepared using protocol 2 (Figure 2e). This difference may be ascribed to differences in the xanthate group removal reaction. The mechanism of the reaction involving NaN_3 was proposed by Zhu *et al*.[58] and this reaction was reported to be extremely fast (quantitative in 3-5 min). The formation of disulfide linkages was readily observed by by Zhu *et al.* in their study. In the case of PVDF-XA, the reaction was also observed to be very fast and the GPC traces (Figure 3) of PVDF-SH and of PVDF-MA also suggest the formation of substantial amounts of PVDF-S-S-PVDF, even when the reaction was carried out in the presence of a reducing agent such as DMPP.

McKee et al.[52] showed that the reaction rate of the thia-Michael additions was faster than that of the aminolysis reaction. Consequently, as soon as a thiol was formed by aminolysis, it reacted immediately on the Michael acceptor. This one pot reaction (Aminolysis/thia-Michael addition) is an efficient method to decrease the thiol concentration in the reaction medium, which in turn impairs the formation of disulfide bond.

The lower efficiency of protocol 2 compared to protocol 1 may lie in the large difference of reaction rate between the thia-Michael additions and the xanthate end-group removal effected by sodium azide. Indeed, this reaction is very fast. The hypothesis is that it releases, in a very short time, a large quantity of thiols which are not immediately consumed by thia Michael addition, but form disulfide bond instead. If this hypothesis is true, then protocol 2 may, in a way, be considered as a two-step process where PVDF-XA are first converted into PVDF-SH which can then react either on themselves to form disulfides or on AHPMA to yield PVDF-MA. In conclusion, protocol 1 is a better method to efficiently synthesise PDVF Methacrylates with high chain-end functionality.

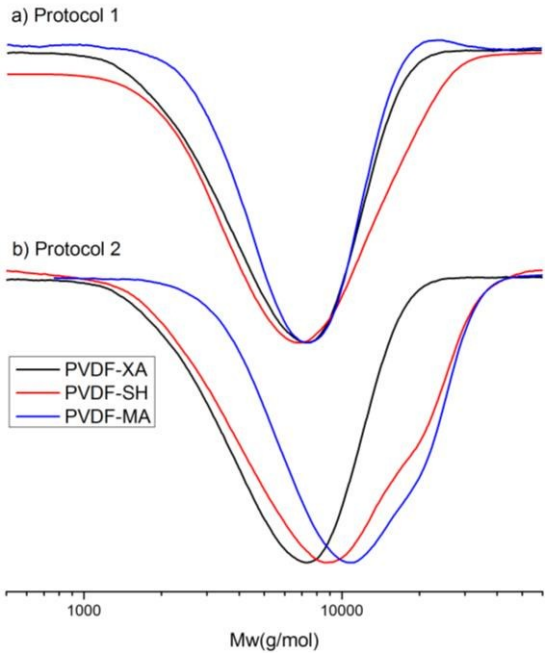
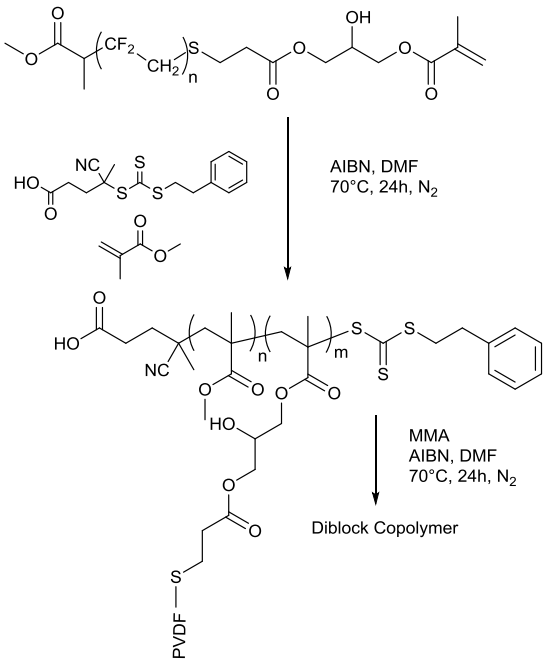


Figure 3.RI GPC traces of: a) PVDF-XA, PVDF-SH prepared by aminolysis, and PVDF-MA prepared following protocol 1; b) PVDF-XA, PVDF-SH prepared by action of NaN_3 and PVDF-MA prepared following protocol

RAFT homopolymerization and copolymerization of PVDF-MA macromonomer with Methyl methacrylate

Typical polymerizations of PVDF-MA macromonomer and synthetic procedure of copolymerization with methyl methacrylate are summarized and depicted in Table 1 and Scheme 2. The RAFT homopolymerization of the PVDF-MA macromonomer (run 1, Table 1) did not reach high conversion (59 % only in 24h), probably due to the lack of reactivity of the methacrylate group of PVDF-MA caused by steric hindrance and lack of chain mobility. In addition, the purification of the oligo (PVDF-MA) obtained (elimination of the excess macromonomer) was quite difficult. The GPC traces (Figure 4a) of the PVDF-MA and of the oligo(PVDF-MA) obtained after 24 hours of polymerization clearly show that a significant amount of PVDF-MA did not react. However, when RAFT polymerization was carried out on a 50/1 mixture of MMA/PVDF-MA, total conversion of the PVDF-MA was achieved (Table 1, Run 2 and Figure 5). The GPC trace of the corresponding copolymer of PVDF-MA and MMA is displayed in Figure 4b (red chromatogram).



Scheme 2. RAFT copolymerization of PDVF-MA macromonomer

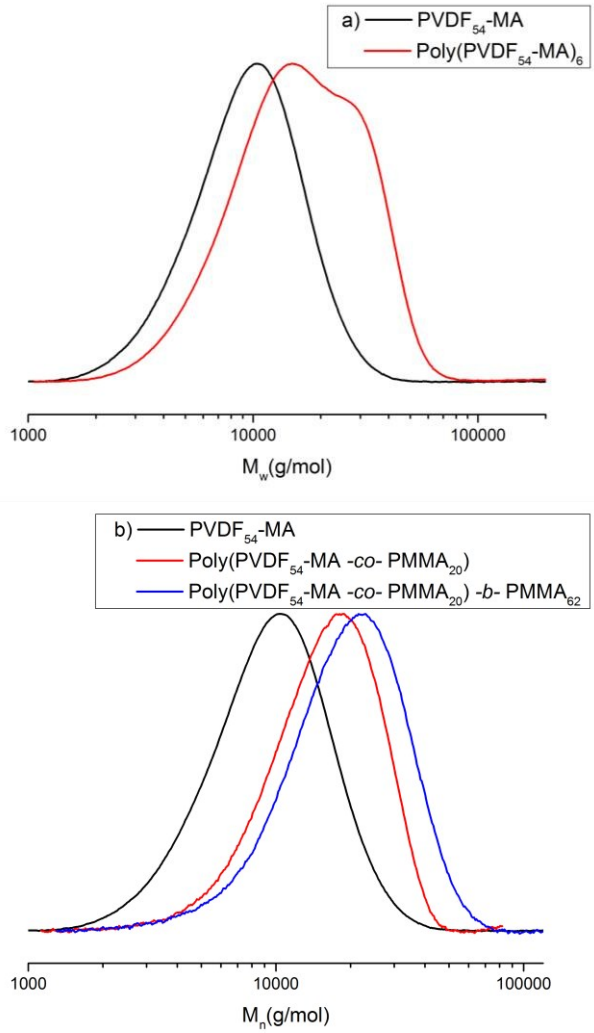


Figure 4. a) GPC traces (viscometric detector) of $PVDF_{54}$-MA (black trace) and poly$(PVDF_{54}\text{-MA})_6$ (red trace) prepared by RAFT polymerization. b) GPC traces (viscometric detector) of PVDF-MA (black trace), Poly($PVDF_{54}$-MA-co-MMA_{20}) (red trace) and of [Poly($PVDF_{54}$-MA-co-MMA_{20})]-*b*-$PMMA_{62}$(blue trace)

[a] Measured by ^{1}H NMR (Figure S8). [b] Measured by gravimetry. [c]Mntheo = ($[M]_0/[CTA]_0$ x $M_w$monomer x conversion)/100. [d]Calculated from the degree of polymerization determined by ^{1}H NMR. [e] SEC data based on PMMA narrow standard calibration (solvent: DMF). * Poly($PVDF_{54}$-MA-co-MMA_{20}) (Run 2) used as MacroCTA. Reaction conditions : [I]/[CTA] = 0.2, T = 70 °C, with : CTA = 4-Cyano-4-(2-phenylethanesulfanylthiocarbonyl)sulfanylpentanoicacid, Initiator = AIBN, Solvent = DMF

Run	$[PVDF\text{-}MA]_0$ / $[CTA]_0$	$[MMA]_0$ / $[CTA]_0$	Conversion PVDF-MA[a] (%)	Conversion MMA[b] (%)	$M_n$theo[c] (g/mol)	M_nNMR[d] (g/mol)	M_nSEC[e] (g/mol)	Đ[e]
1	10	0	59	0	18300	21000	9700	1.48
2	1	49	100	52	5600	5000	9800	1.33
3	1*	200	0	45	12000	9500	14100	1.35

Table 1.Experimental conditions for the RAFT (co)polymerization of PVDF-MA macromonomer

The significant shift of the GPC trace towards higher molecular weights suggests that the copolymerization proceeded under good control.

The ^{1}H NMR spectrum of the poly(PVDF-MA-*co*-MMA) copolymer (Figure 5) attests the complete conversion of the PVDF-MA (complete disappearance of the methacrylic protons in the 5.6 to 6.1 ppm range). The chain extension of the poly(PVDF-MA-*co*-MMA) with methyl methacrylate was also carried out (Run 3, Table 1). This polymerization reached 45 % conversion. The GPC trace of the resulting poly[(PVDF-MA-*co*-MMA)-*b*-PMMA] (Figure 4b, blue chromatogram) suggests the efficient chain extension of the copolymers with a PMMA block.

Thermal stability

The thermal stabilities of PVDF-XA, PVDF-MA and poly(PVDF-MA-co-MMA) copolymer were determined by thermogravimetric analysis under air (Figure 6). As expected, PDVF polymers (PVDF-MA and PVDF-XA) exhibited good thermal stabilities[1] with no significant weight loss until 336 °C and 350 °C, respectively. The superior thermal stability of PVDF-MA is most likely due to the higher stability of the methacrylate group, compared to thiocarbonylthio end group.[60] Above 380 °C, decomposition of the PVDF via dehydrofluorination is rapidly observed.

The TGA profile of the poly(PVDF-MA-co-MMA) copolymer showed several weight loss stages, indicating a complex thermal decomposition mechanism.[61] The first decomposition stage (occurring at about 200 °C) is due to the scissions of the head-to-head linkages in the PMMA segments. The second decomposition stage (occurring at 330 °C) is caused by unzipping depolymerization from vinylidene ends (both PMMA and PVDF chains) and dehydrofluorination of the PVDF segments, and the third stage (500 °C) corresponds to random scissions within the polymethacrylic and PDVF backbones.

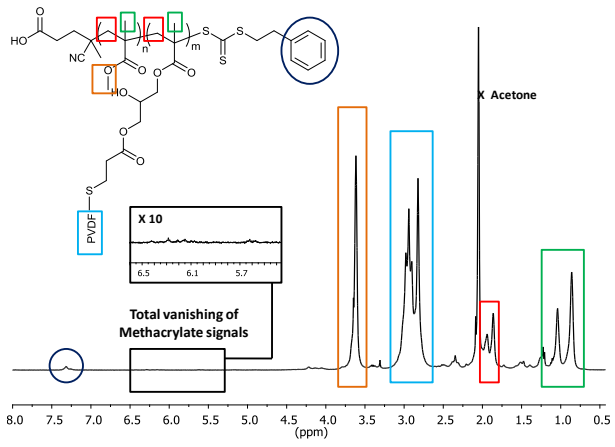


Figure 5. ^{1}H NMR spectrum of the RAFT copolymerization of MMA with PVDF-MA in $(CD_3)_2CO$

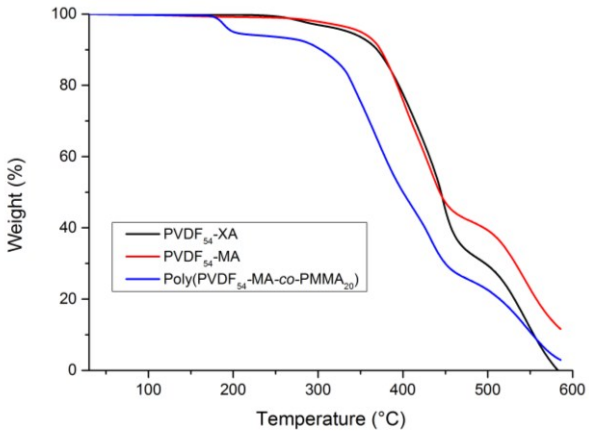


Figure 6. Thermogravimetric analysis under air of PVDF-XA, PVDF-MA, and Poly(PVDF-MA-co-MMA) copolymer

Conclusion

This article presents and compares two one-pot methods to prepare well-defined PVDF-based methacrylate macromonomers prepared from PVDF (synthesized by MADIX homopolymerization of VDF) and 3-(Acryloyloxy)-2-hydroxypropyl methacrylate (AHPMA). The aminolysis/thia Michael addition combination (protocol 1) proved to be very efficient to afford well-defined PVDF-MA macromonomers and to be superior to the sodium azide treatment/thia Michael addition combination (protocol 2). Indeed, protocol 2 did not provide total functionalization of the polymer end-group in contrast to protocol 1 which allowed the transformation of 99% of the xanthate chain-ends into methacrylate for a total polymer functionality of 85% as shown by detailed ^{1}H and ^{19}F NMR characterizations. The PVDF-MA macromonomer prepared were black, due to some dehydrofluorination caused by attack of the PVDF by the primary amine. The extent of this dehydrofluorination was nonetheless not detected either by ^{1}H or ^{19}F NMR and was not detrimental to either the macromonomer synthesis or its polymerization. RAFT homopolymerization of PVDF-MA did not proceed with high conversion but well-defined poly(PVDF-MA-*co*-MMA) copolymer and poly[(PVDF-MA-*co*-MMA)-*b*-PMMA] block copolymer were easily synthesized by RAFT polymerization. The aminolysis/thia Michael addition one-pot protocol is thus very efficient to prepare well-defined PVDF methacrylate macromonomers. These novel macromonomers open the way to the synthesis of new PVDF-based architectures such as block copolymers, graft copolymers and bottle brush copolymers for example.

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Notes and references

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Electronic Supplementary Information (ESI) available:[details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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Graphical Abstract