Poly(vinylidene fluoride)/polymethylene-based block co/terpolymers

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ABSTRACT: Dual crystalline diblock copolymers consisting of polymethylene (PM) and poly(vinylidene fluoride) (PVDF) blocks as well as triblock terpolymers with polystyrene (PS) as middle block were synthesized. For the synthesis, two/three different polymerization methods such as polyhomologation, atom transfer radical polymerization (ATRP) and iodine transfer polymerization (ITP) along with chain-end post-polymerization reactions were employed. Solid-state NMR spectroscopy revealed the characteristic peaks of all constituent blocks while gel permeation chromatography (GPC) results demonstrated the controlling/living nature of all implemented polymerization methods. The analysis of crystallization behavior based on differential scanning calorimetry (DSC) indicates the presence of different PVDF crystalline phases (α , β , and γ) upon the incorporation of PM and PS blocks. Further analysis with X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopies revealed the co-existence of α - and β - phases in diblock and β - and γ - phases in triblock terpolymer. An initial study on self-assembly in DMF, a selective solvent for PVDF and PS, was performed by dynamic light scattering (DLS) and atomic force microscopy (AFM).

1. INTRODUCTION

Fluoropolymers, and especially PVDF, have attracted considerable attention both in academia and industry due to their outstanding properties and uses.¹⁻⁴ In particular, the high dielectric constant and electroactive response including piezo-, pyro- and ferro-electrical effects of PVDF offer a wide range of applications in energy generation and storage, capacitors, sensors, etc. PVDF has five different crystalline phases (α , β , γ , δ and ϵ) associated with several dielectric properties, due to the coexistence of both fluoro and hydrocarbon segments.⁵⁻⁷ Among them, α -, β - and γ -phases exhibit better dielectric properties.⁷ Since perfluorinated polymers are not miscible or compatible with hydrogenated ones, the synthesis of PVDF/polyhydrocarbon-based block copolymers (BCPs) would potentially improve or even introduce novel unprecedented properties. In addition, it can serve as a compatibilizer between PVDF and hydrocarbon polymers.⁸

Despite the extensive use of PVDF in industry (second largest production among the fluoropolymers), the number of studies dealing with well-defined PVDF-based BCPs is limited and nonexistent for PVDF/hydrocarbon-based BCPs.⁹ This is due to the fact that PVDF cannot be readily polymerized, as other vinyl monomers, by controlled/living radical polymerization techniques, such as ATRP; reversible addition-fragmentation transfer (RAFT) and nitroxide mediated polymerization (NMP).^{7,9} Among the polymerization methods reporting the controlled radical polymerization of vinylidene fluoride (VDF) (telomerization¹⁰ and degenerative chain transfer process involving xanthates, referred to as MADIX¹¹), ITP is the only industrial technique for PVDF synthesis.^{12,13} For a typical ITP process fluorinated iodocompounds are used as efficient chain transfer agents since the weak alkyl-iodide bond (dissociation energy equal to 45 kJ mol⁻¹) can be easily cleaved.

Beyond the recognized impact of polyethylene (PE) in the industry as the most commodity polymer, synthesis of well-defined PE-based BCPs is still of high demand.¹⁴ Polyhomologation (C1 polymerization), an alkylborane-initiated polymerization of dimethyl sulfoxonium methylide is an attractive method for the synthesis of linear, well-defined PM (PM is equivalent to PE).¹⁵ PM synthesized by polyhomologation bears high end-group fidelity such as hydroxyl group, which enables

the combination with several polymerization methods, to obtain a plethora of well-defined PE-based homo/copolymers of different macromolecular architectures.¹⁶⁻²⁴

In virtue of PM and PVDF properties, the combination of the corresponding polymer constitutes an appealing objective in material design. However, synthesis of well-defined PM-*b*-PVDF block copolymers is challenging and to the best of our knowledge, no data have been reported. Ma and coworkers reported the only study combining polyhomologation and ITP, up to date. In more details, visible light-induced activation of iodo-functionalized PM was employed as macro-chain transfer agent (macro-CTA) for the synthesis of PM-*b*-poly(vinyl acetate) diblock copolymers.²⁵ Recently, our group used a combination of ATRP-ITP chain-extension strategy and copper-catalyzed azide-alkyne cycloaddition (CuAAC) to synthesize (PVDF-*b*-PS)₂(PEG)₂ 4-miktoarm star terpolymers.²⁶ We consider that most bromide ATRP initiators can be seen as masked ITP initiators after Br → I exchange. Adopting this methodology, PM-based precursors bearing iodine end group may be used as a macro-CTA for the subsequent polymerization of fluorinated-olefin monomer such as VDF.

Herein, built upon our previous work we expand the range of ITP to PM-based materials after appropriate post-polymerization exchange reactions. PM-OH is used as a precursor of one/two subsequent polymerization methods towards the synthesis of PM-*b*-PVDF and PM-*b*-PS-*b*-PVDF co/terpolymers.

2. EXPERIMENT

Styrene (Sigma, 99.5%) was purified from the added inhibitor by passing it through a short plug of silica or basic alumina before use. Toluene (VWR) and tetrahydrofuran (VWR) were refluxed over sodium/benzophenone before use. Triethylborane solution in hexane (1 M), 2,2-bromoisobutyryl bromide (98%), trimethylsulfoxonium iodide (≥98%), benzyltributylammonium chloride (Sigma, 98%), sodium iodide (≥99.5%), Bis(*t*-butyl peroxy)cyclohexane and trimethylamine-*N*-oxide dihydrate (TAO•2H₂O, ≥99%) were purified by Sigma and used without any further purification. 1,1-vinylidene fluoride (Apollo received from Scientific, ≥98%). Copper (I) bromide (99.999%) and N,N,N',N'',N''-

Pentamethyldiethylenetriamine (PMDETA, 99%) purchased also from Sigma. Dimethylsulfoxonium methyllide was prepared according to Corey's method followed by switching the solvent from THF to toluene.²⁷

2.1. Synthesis of the PM-OH. For the synthesis of ylide (dimethylsulfoxonium methyllide) and the PM-based precursors, all manipulations involving air- and/or moisture sensitive compounds were carried out in the Schlenk line.²⁷ In a typical process, 13.6 g (0.56 mol) of NaH (after its filtration to remove the mineral oil) was introduced into a two-necked flask connected with a condenser and argon/vacuum line and three air-argon circles took place. 200 mL of freshly distilled THF is added, followed by the addition of 40.0 g (0.38 mol) of dry trimethylsulfoxonium chloride. The mixture was heated and refluxed at 75 °C until the gas ceased (4-5 h). The THF was removed under low pressure followed by transferring 50 mL of dry toluene into the flask and stirred for 0.5 h. The resulting turbid solution was filtered through a dry Celite® 545 column. A clear and transparent solution with a light yellow color was obtained. All the operations were performed under argon. The concentration of ylide was determined by titration with a standard hydrochloric acid aqueous solution (1.05 mmol/mL yield: 72%).

The produced ylide solution inserted into a two-neck 1000 ml flask and kept under stirring for 30 min. Then, 0.45 ml of triethylborane (0.45 mmol) injected into the flask to initiate the polymerization and the solution left for 30 min under stirring. 10-time excess (4.5 mmol, 0.5 g) of trimethylamine-N-oxide dehydrate (TAO•2H₂O) was used for the oxidation/hydrolysis of tris-organoborane at 80 °C in order to obtain PM-OH quantitatively. After 24 h, the reaction was stopped by cooling in an ice-bath. The reaction mixture was poured into cold methanol (500 mL) under stirring. The polymer was filtered, washed with methanol, dried under vacuum and characterized by ¹H NMR and HT-GPC (Figure S1, SI). ¹H-NMR (**Figure S3a**, SI, 600 MHz, 1,2-dichlorobenzene-*d*₄, 80 °C): δ=3.60 (t, 2H, CH₂-OH), 1.10–1.45 (s, m, -CH₂CH₂-), 0.75 (t, 3H, CH₃).

2.2. Synthesis of the PM-Br macroinitiator. 1.7 g of PM-OH macroinitiator (0.53 mmol), 1.0 ml pyridine (12.4 mmol) and 80 mL of dry toluene (100 °C) were added in a two-neck flask (250 mL)

while the temperature was raised up to 100 °C. Then, 0.66 mL of 2-bromoisobutyryl bromide (5.3 mmol) was inserted to the flask dropwise and the solution was left under stirring for 24 h. The reaction mixture was cooled to room temperature and poured into 400 mL of acidic methanol (containing 30 mL of 1 M aqueous HCl). The polymer was filtered, washed successively with methanol (2 × 20 mL), 1 M aqueous HCl (2 × 10 mL), methanol (2 × 20 mL) and dried at 50 °C for 3 h in vacuum to give an off-white solid.

¹H-NMR (**Figure S3b**, SI, 600 MHz, 1,2-dichlorobenzene-*d*₄, 80 °C): δ=4.18 (t, 2H, -CH₂O), 1.70 (6H, (CH₃)₂), 1.13–1.48 (s, m, -CH₂CH₂-), 0.77 (t, 3H, CH₃).

2.3. Synthesis of the PM-I macro-CTA. PM-I was synthesized via a typical nucleophilic substitution reaction. NaI (0.51 g, 3.40 mmol) was added to a stirred solution of PM-Br (0.9 g, 0.28 mmol) in 20 mL of dry acetone and 20 mL dry toluene. The reaction mixture was stirred for 48 h under argon at 70 °C. The reaction mixture was cooled down to room temperature and precipitated twice into methanol), recovered by vacuum filtration and washed extensively with methanol. The polymer was dried under vacuum for 24 h at 25 °C obtained as white powder.

2.4. Synthesis of PM-*b*-PS-Br diblock copolymer. In a typical ATRP polymerization the PM-Br macroinitiator (0.35 g, 0.053 mmol, N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA, 0.156 mL, 0.318 mol) and toluene (5 mL) were placed in a 50-mL Schlenk flask under nitrogen. The mixture was allowed to warm up to 100 °C to dissolve the macroinitiator. After the dissolution, the mixture was cooled to room temperature and then styrene (1.65 g, 15.9 mmol) was added and the mixture was degassed through three freeze–pump–thaw cycles. CuBr (23 mg, 0.16 mmol) was added to the mixture under a nitrogen flow and then degassed again through a freeze–pump–thaw cycle. The mixture was heated to 100 °C and the polymerization was left to proceed for 18 h. The resulting polymerization mixture was poured into methanol, and the precipitated polymer was filtered, washed with methanol and dried in vacuum at 25 °C for 24 h. Further purification took place by dissolving the polymer in toluene and precipitated in methanol to obtain white powder which dried in vacuum at 25 °C for 24 h.

^1H NMR (**Figure S3c**, SI) (600 MHz, 1,2-dichlorobenzene- d_4 , δ , ppm): 6.95-6.5 (Ar, 5H, PS), 4.41 (2H, PS-Br), 3.37 (2H, $-\text{OCH}_2$), 1.84-1.43 ($-\text{CH}$ and $-\text{CH}_2$ backbone of PS), 1.56 (m, 2H, PE), 1.24 (6H, $-(\text{CH}_3)_2$).

2.5. Synthesis of PM-*b*-PS-I macro-CTA. PM-*b*-PS-I was synthesized via a typical nucleophilic substitution reaction. NaI (0.164 g, 1.2 mmol) was added to a stirred solution of PE-Br (1.4 g, 0.096 mmol) in the mixture of the dry solvents acetone (20 mL) and toluene (15 mL). The reaction mixture was stirred for 48 h under argon atmosphere at 75 °C. After the reaction time, the solution was concentrated by rotary evaporation, precipitated in methanol, recovered by vacuum filtration and washed extensively with water and methanol. The polymer was dried under vacuum for 24 h at 40 °C and obtained as white powder.

2.6. Synthesis of PM-*b*-PVDF-I diblock copolymer. Parr autoclave was filled with PM-I as the macro-CTA (0.45 g, 0.068 mmol) and 1,1-bis(tert-butylperoxy)cyclohexane as the initiator (4 mg, 0.015 mmol) dissolved in dimethyl carbonate (75 mL). The reactor was cooled in a liquid nitrogen bath to condense VDF gas (1.1 g, 171 mmol) into the autoclave under weight control. It was then heated gradually up to 80 °C and the evolutions of pressure and temperature were recorded. The pressure was increased up to 12 bars, and a decrease was observed to 7 bars during the reaction. The reaction was stopped after 24 h and the autoclave cooled to room temperature and then placed in an ice bath. After purging the non-reacted monomer, the reactor was opened and a colorless liquid was obtained. The solution was concentrated by rotary evaporation, precipitated in hexane, dried under vacuum for 24 h at 40 °C and obtained as a colorless powder.

^1H NMR (**Figure S5-S6**, SI) (500 MHz, Toluene- d_8 + DMF- d_7 , δ , ppm): 4.34 (t, 2H, $-\text{CF}_2\text{CH}_2\text{I}$), 3.56 (2H, $-\text{OCH}_2$), 2.87 (m, $-\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2$, normal addition of PVDF, H-T), 2.28 (m, $-\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2$, reverse addition of PVDF, T-T), 1.86 (m, $-\text{CH}_2$ of PE), 1.58 (6H, $-(\text{CH}_3)_2$).

^{19}F NMR (**Figure S12-S13**, SI) (500 MHz, Toluene- d_8 + DMF- d_7 , δ , ppm) -92 to -96 (m, 2F, normal addition of VDF, $\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2$, H-T), -109 (2F, $\text{CF}_2\text{CH}_2\text{I}$), -114 to -117 (m, 2F, reverse addition of VDF, $\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2$, H-H).

2.7. Synthesis of PM-*b*-PS-*b*-PVDF-I triblock terpolymer. Parr autoclave was filled with PM-*b*-PS-I as the macroinitiator (13 g, 0.09 mmol), and 1,1-bis(*tert*-butylperoxy)cyclohexane as the initiator (4 mg, 0.01 mmol) dissolved in dimethyl carbonate (75 mL). The reactor was cooled in a liquid nitrogen bath to condense VDF gas (10.0 g, 156 mmol) into the autoclave under weight control. The rest procedure was similar as described above. A light-yellow liquid was obtained. The solution was concentrated by rotary evaporation, the product precipitated in hexane, dried under vacuum for 24 h at 40 °C and obtained as a light yellow color powder.

¹H NMR (**Figure S7-S9**, SI) (500 MHz, Toluene-*d*₈ + DMF-*d*₇, δ , ppm): 6.4-6.9 (m, 5H, Ar-PS), 4.34 (t, 2H, -CF₂CH₂I), 3.56 (2H, -OCH₂), 2.88 (m, 2H, -CF₂CH₂CF₂CH₂, normal addition of PVDF, H-T), 2.22 (m, 2H, -CF₂CH₂CH₂CF₂, reverse addition of PVDF, T-T), 1.86 (m, 2H, -CH₂ of PE), 1.5-1.3 (m, -CH and -CH₂ backbone of PS), 1.13 (6H, -(CH₃)₂).

¹⁹F NMR (**Figure S14-S16**, SI) (500 MHz, Toluene-*d*₈ + DMF-*d*₇, δ , ppm) -92 to -96 (m, 2F, normal addition of VDF, CH₂CF₂CH₂CF₂, H-T), -109 (2F, CF₂CH₂I), -114 to -116 (2F, reverse addition of VDF, CH₂CF₂CF₂CH₂, H-H).

2.8. Polymer cleavage by hydrolysis. In a 100 mL round-bottomed flask, 100 mg of the PM₄₇₁-*b*-PVDF₃₄₄ sample was dispersed in 40 mL solution of toluene/DMF (1/1 v/v) and sonicated for 30 min. Then, a condenser was fitted in the flask and placed in an oil bath at 90 °C. 5 mL of 1 M NaOH solution in methanol was then added to the polymer solution and the mixture was refluxed for 24 h. Then, the solution was centrifuged and the supernatant (PVDF block) was poured in water. The solid was isolated, dried in a vacuum oven overnight and characterized by GPC with DMF as eluent ($M_{n,PVDF}$ = 7000, $\bar{D}$ =1.29). A similar procedure was followed for the cleavage of PM₄₇₁-*b*-PS₁₂₅-*b*-PVDF₃₂₈ sample ($M_{n,PS-b-PVDF}$ = 16000, $\bar{D}$ =1.38).

2.9. Synthesis of 1-Phenylethyl Iodide. The synthetic procedure of 1-phenylethyl iodide initiator was adopted from the literature.²⁸ Hexadecyltributylammonium bromide (0.1 equiv) was added under stirring the biphasic mixture of styrene (1 equiv) and 47% hydroiodic acid (3-4 equiv). The solution was kept under stirring for 12 h at 40 °C. As the reaction proceeded, the organic layer remained colorless

and above the aqueous layer turned into dark red and eventually was inverted as the lower layer with the aqueous layer above. The mixture was then separated and the aqueous layer washed with 3 x 25 mL of CH_2Cl_2 . The organic layers were then combined and washed with the following: 25 mL of H_2O , 3 x 25 mL of saturated Na_2CO_3 , 3 x 25 mL of H_2O . The organic layers were then combined and dried over sodium sulfate and subsequently evaporated to leave a dark red oil. This was purified by flash chromatography with hexanes through silica gel to give a pale yellow solution. Evaporation of hexane gave a yellow oil, which was found to be light sensitive and stored in the dark at below 0 °C.

^1H NMR (**Figure S10**, SI) (500 MHz, CDCl_3 , δ , ppm) 7.4-7.15 (m, 5H, Ar), 5.4 (quint, 1H), 2.2 (d, 3H).

3.0. Synthesis of PVDF homopolymer by 1-phenylethyl iodide CTA. Parr autoclave was filled with 1-Phenylethyl Iodide CTA (85 mg, 0.37 mmol), and 1,1-bis(*tert*-butylperoxy)cyclohexane as the initiator (10 mg, 0.037 mmol) dissolved in dimethyl carbonate (75 mL). The reactor was cooled in a liquid nitrogen bath to condense VDF gas (11.0 g, 185 mmol) into the autoclave under weight control. The rest procedure was similar as described above. A yellow liquid was obtained. The solution was concentrated by rotary evaporation, the product precipitated in hexane, dried under vacuum for 24 h at 40 °C and obtained as a yellow color powder.

^1H NMR (**Figure S11**, SI) (500 MHz, acetone- d_6 , δ , ppm): 7.5-7.2 (5H, Ar of CTA), 4.3 (1H, $-\text{CH}-\text{PVDF}$ in normal addition H-T), 3.7 (2H, $-\text{CF}_2\text{CH}_2\text{I}$), 3.47 (1H, $-\text{CH}-\text{PVDF}$ in reverse addition T-T), 2.91 (2H, $-\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2$, normal addition of PVDF, H-T), 2.28 (2H, $-\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2$, reverse addition of PVDF, tail-tail), 2.2 (3H, $-\text{CH}_3$ of CTA).

^{19}F NMR (**Figure S17**, SI) (500 MHz, acetone- d_6 , δ , ppm) -92 to -96 (2F, normal addition of VDF, $\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2$, H-T), -109 (2F, $\text{CF}_2\text{CH}_2\text{I}$), -114 to -117 (2F, reverse addition of VDF, $\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2$, H-H).

3.1. Characterizations. Liquid state ^1H and ^{19}F NMR spectra were obtained at 298 K using a Bruker AVQ 500 MHz instrument. Chemical shifts are reported as δ (ppm) values, using either TMS or residual solvent peaks as an internal standard, and coupling constants (J) as Hz values. For PM-based

samples, ^1H -NMR (Bruker ADVANCE III-600 MHz spectrometer) spectra were recorded in 1,2-dichlorobenzene- d_4 at 80 °C. One-dimensional ^1H MAS solid-state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 600 MHz resonance frequencies. Experiments employed a conventional 3.2 mm HCN triple-resonance probe. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external references TMS and adamantane. The delay between the scans was set to 5 s to allow the complete relaxation of the ^1H nuclei, and the number of scans was 32. ^1H - ^1H Multiple-Quantum Spectroscopy: Two-dimensional double-quantum (DQ) experiments were recorded on a Bruker AVANCE III spectrometer operating at 600 MHz with a conventional double-resonance 3.2 mm CP/MAS probe, according to the following general scheme: excitation of DQ coherences, t_1 evolution, z filter, and detection. The spectra were recorded in a rotor synchronized fashion in t_1 by setting the t_1 increment equal to one rotor period (45.45 μs). One cycle of the standard back-to-back (BABA) recoupling sequences was used for the excitation and reconversion period. Quadrature detection in w_1 was achieved using the States-TPPI method. An MAS frequency of 22 kHz was used. The 90° proton pulse length was 2.5 μs , while a recycle delay of 5 s was used. A total of 128 t_1 increments with 32 scans per each increment were recorded. The DQ frequency in the w_1 dimension corresponds to the sum of two single-quantum (SQ) frequencies of the two coupled protons and correlates in the w_2 dimension with the two corresponding proton resonances. Conversely, groups of less than two equivalent spins will not give rise to diagonal signals in this spectrum. The molecular weight and the molecular weight distribution (Đ) of PM and PM-*b*-PS precursors were determined by high temperature gel permeation chromatography (HT-GPC) with 1,2,4-trichlorobenzene (TCB) as eluent (1 mL/min, 145 °C) by a Viscotek HT-GPC Module 350 with DRI detector. Calibration for DRI was based on PS standards. The molecular weight and the molecular weight distribution (Đ) of the cleaved PVDF and PS-*b*-PVDF polymers were determined by an Agilent liquid chromatography system fitted with refractive index (RID) and UV-Vis detectors, using two identical PLgel columns (5 μm , MIXED-C) in connected series with DMF as the mobile phase (1 mL/min). The column and flow path were temperature controlled at

35 °C. DSC measurements were conducted using a Perkin-Elmer Pyris 1 apparatus. Scans were recorded at a heating and cooling rate of 10 °C·min⁻¹ from -60 to +200 °C. XRD analysis conducted at Brucker D2 Phaser (K α ₁, λ =1.5405600 Å) by using Cu K α radiation. Morphological observation of the final polymers was performed by the Dynamic light scattering (DLS) measurements using a Malvern Zetasizer Nano ZS instrument equipped with a 632.8 nm He-Ne laser. The measurement angle was 173°. For each analysis, micellar dispersions were prepared via dispersion in DMF. The cells were temperature-controlled at 20 ± 0.1. By adjusting the strength of the tapping mode-AFM, height images of the spin coated films (DMF solution onto silicon wafer substrates) were used to visualize and evaluate the di- and triblock copolymer aggregates. AFM measurements were performed on an Agilent 5400 SPM instrument with AAC mode and K (spring constant) equal to 2-6 N/m.

3. RESULTS AND DISCUSSION

Two PM-*b*-PVDF diblock copolymers and three PM-*b*-PS-*b*-PVDF triblock co/terpolymers were synthesized starting from the same PM precursor, for comparison reasons (**Scheme 1**). The synthesis of PM-I macro-CTA involves the three following steps: (a) polyhomologation of dimethylsulfoxonium methylide²⁶ using triethylborane as initiator followed by oxidation/hydrolysis to afford hydroxyl-terminated linear PM, PM-OH, (b) esterification of the OH group with 2,2-bromoisobutyryl bromide to introduce bromide at the ω -chain end, and (c) subsequent halide exchange (Br $\rightarrow$ I) using sodium iodine. HT-GPC confirmed the synthesis of two well-defined PM samples (run 1, **Table 1**, **Table S1**) with narrow molecular weight distribution ($\mathcal{D}$) (**Figure 1a** and **Figure S1**, SI). After the completion of ylide polymerization, oxidation/hydrolysis with trimethylamine *N*-oxide dihydrate (TAO·2H₂O) of tris-polymethylene (C-B bonds) took place. The ¹H NMR spectrum of PM-OH revealed a triplet peak (δ =3.55 ppm) assigned to methylene protons adjacent to the hydroxyl group (-CH₂-OH) (**Figure S3a**, SI). The observed chemical shift at δ =1.4 ppm corresponds to the aliphatic protons (-CH₂- two protons for each methylene unit). The integrated ratio of the above-mentioned chemical shifts was used to determine the number average molecular weight of both PM-OH samples by end-group analysis.

Scheme 1. Synthesis of PM-*b*-PVDF diblock copolymer and PM-*b*-PS-*b*-PVDF triblock terpolymer by subsequent polyhomologation and ITP or polyhomologation, ATRP and ITP techniques, respectively.

To initiate ITP of VDF, the terminal OH group was converted to bromide by esterification reaction and subsequently to iodide by nucleophilic substitution reaction yielding the ITP macro-CTA (**Scheme 1**). In more details, ten equivalents of 2,2-bromo isobutyryl-bromide and pyridine with respect to hydroxyl groups was a sufficient excess for the completion of esterification in toluene at 100 °C to obtain PM-Br. Upon increasing the molar mass of macroinitiator, higher excess of 2-bromoisobutyryl bromide and pyridine compared to hydroxyl group as well as higher reaction times to achieve quantitative conversion are required.

After esterification, the characteristic chemical shift of the protons adjacent to the hydroxyl groups ($-CH_2-OH$ $\delta=3.55$ ppm) disappeared and a new peak at $\delta = 4.15$ ppm of the $-CH_2-$ connected to the ester group appeared (**Figure S3b**, SI), indicating the formation of PM-Br. As a next step, the bromide end groups are converted to iodide groups by adding an excess of sodium iodide. Since acetone favors the exchange reaction (S_N2 mechanism) and PM is not soluble in acetone, a mixture of acetone/toluene (2/1 volume ratio) was used at 75 °C and the reaction left to proceed for 48 h.

Table 1. Molecular characterization data for PM-*b*-PVDF and PM-*b*-PS-*b*-PVDF polymers

Run	Polymer Sample ^a	M _n (kg/mol) ^a				Đ ^b
		PM	PS	PVDF	Total	
1	PM ₄₇₁ -I	6.6	-	-	-	1.12
2	PM ₄₇₁ - <i>b</i> -PVDF ₃₄₄	6.6	-	22	28.6	-
3	PM ₄₇₁ - <i>b</i> -PS ₁₂₅ -I	6.6	13	-	19.6	1.18
4	PM ₄₇₁ - <i>b</i> -PS ₁₂₅ - <i>b</i> -PVDF ₃₂₈	6.6	13	21	40.6	-

^a DP and M_n estimated from ¹H NMR. ^b from HT-GPC (TCB as eluent, 145 °C).

The aforementioned macro-CTA was employed as an ITP initiator of VDF to yield PM-*b*-PVDF diblock copolymer (run 2, **Table 1**). The characterization of the diblock copolymers in solution (GPC, NMR) was a challenging task due to the difficulty in finding a common solvent for both blocks. This problem was overcome, by performing GPC measurements of the isolated PVDF block after hydrolysis (NaOH in methanol/toluene/DMF mixture) of the in-chain ester group. The GPC chromatograph (DMF as eluent at 35 °C) of the cleaved PVDF block displayed a monomodal peak with narrow molecular weight distribution (Đ=1.29), confirming the controlled nature of the ITP process (**Figure 1b**). The PM block trace was similar with the one of PM-OH precursor. Likewise, liquid NMR analysis was feasible only when the diblock copolymer was dissolved in a mixture of solvents (Toluene-*d*₈ and DMF-*d*₇). The ¹H NMR spectra of PM-*b*-PVDF supports the results of GPC indicating the successful polymerization of VDF to PVDF. Signals at δ = 4.34 ppm, 2.87 ppm and 2.28 ppm correspond respectively to the chain end (-CF₂CH₂I), normal (-CF₂CH₂-CF₂CH₂) and reverse addition of PVDF chain (-CF₂CH₂-CH₂CF₂) (**Figure S5-S6**, SI). Additionally, the presence of signals from the macro-CTA (3.56 ppm, 1.86 ppm and 1.58 ppm, ascribing to -OCH₂, PM (-CH₂) and -(CH₃)₂, respectively) confirms the polymerization initiated by the macro-CTA chain end. The degree of polymerization (DP) of PVDF was determined by comparing the integral of the peak at δ = 2.87 ppm and the peak at δ = 4.34 ppm. ¹⁹F NMR spectrum is in agreement with ¹H NMR and showed the characteristics signals at -92 to -96 ppm, -109 ppm and -114

to -117 ppm due to the normal addition of $(-\text{CF}_2\text{CH}_2-\text{CF}_2\text{CH}_2)$, chain-end $(-\text{CF}_2\text{CH}_2\text{I})$ and reverse addition of PVDF $(-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CH}_2$ and $-\text{CF}_2\text{CH}_2-\text{CH}_2\text{CF}_2)$, respectively (**Figure S12-S13**, SI).

Figure 1. GPC traces of (a) PM₄₇₁ homopolymer (TCB at 145 °C), (inverted for better visualization) (b) PVDF block after hydrolysis of PM₄₇₁-*b*-PVDF₃₄₄ (DMF at 35 °C), (c) PM₄₇₁-*b*-PS₁₂₅ diblock copolymer (TCB at 145 °C) and (d) PS-*b*-PVDF after hydrolysis of PM₄₇₁-*b*-PS₁₂₅-*b*-PVDF₃₂₈ (DMF at 35 °C).

Solid-state NMR (SS-NMR) analyses were performed to further confirm the formation of the diblock copolymers. Analogous to the results by liquid state NMR, the ¹H-MAS NMR spectra displays all characteristic signals attributed to each constituent blocks and chain-end at X and Y ppm respectively (**Figure 2a**). The signals at 2.7 and 1.3 ppm auto-correlate at the diagonal in 2D double-quantum (DQ) assigned to PVDF and PM, respectively (**Figure 2a**). Furthermore, a correlation in the DQ/SQ spectrum between the PVDF peak at 2.7 ppm and at 3.6 ppm confirms the nearby distance between these two protons attributed to the chain end of the polymer ($\text{CH}_2\text{-I}$). In order to confirm that VDF polymerization took place by ITP and not by a typical free radical polymerization, comparison of the SS-NMR spectra between PVDF + PM homopolymers blend and PM-*b*-PVDF diblock copolymer was carried out (**Figure S18**, SI). The SS-NMR of the blend showed the narrow shapes of all peaks compared to their diblock copolymer formation (broad resonances) as well as the absence of ¹H-¹H correlation which

provides clear insight into the high dynamics motion, indicating that the polymerization was initiated by the macro-CTA. In addition, a marked difference between characteristic signals also noticed in both blend and diblock copolymer SS-NMRs.

Figure 2. Solid State NMR spectra of (a) PM₄₇₁-*b*-PVDF₃₄₄ diblock copolymer and (b) PM₄₇₁-*b*-PS₁₂₅-*b*-PVDF₃₂₈ triblock terpolymer.

We took advantage of the efficient transformation reaction from hydroxyl (PM-OH) to α -haloester (PM-Br) not only for the subsequent halogen exchange (Br $\rightarrow$ I) but also to use PM-Br as a macroinitiator for ATRP of styrene, in order to incorporate the amorphous PS between the two crystalline (PM and PVDF) blocks. The ATRP of styrene was conducted with CuBr/PMDETA as catalyst/ligand at 100 °C in toluene.^{29,30} After 18 hours, the polymer was precipitated in methanol and dried under vacuum. HT-GPC results of the PM-*b*-PS diblock copolymer (run 3, **Table 1**) showed narrow polydispersity indexes ($\bar{D}$ = 1.15–1.3) and the M_n of the constituent blocks ranged from 15000 to 19000 g/mol (**Figure 1c** and **Figure S1**, SI). Although HT-GPC does not provide any information about the absolute molar mass, a clear shift of the precursor peak to the higher molecular weight area was evidenced.

The molecular weights and the composition of the constituent blocks were determined by ¹H-NMR (**Figure S3c-S4**, SI). We calculated the degree of polymerization via comparison of the integration of the relevant peaks. Here, the appearance of two new broaden peaks, which is attributed to aromatic

protons (*-phenyl-* δ =6.50–7.20 ppm, **d+ d'**) and aliphatic protons (*-CH₂-CH-phenyl*, δ =1.96–2.50 ppm, **f+g**) of PS block, confirms the formation of PM-*b*-PS diblock copolymer.

Before the synthesis of triblock terpolymer, we performed a model polymerization of VDF using 1-phenylethyl iodide as a CTA (**Scheme S1**, SI). Both ¹H (**Figure S11**, SI) and ¹⁹F NMR (**Figure S17**, SI) evidenced that the polymerization was initiated through the methylbenzyl iodide initiator. For the synthesis of triblock terpolymers, PM-*b*-PS-I was used as macro-CTA for the polymerization of VDF (run 4, **Table 1**). The successful synthesis was indirectly confirmed by GPC measurement of the cleaved PS-*b*-PVDF, following the same cleavage protocol as mentioned above. The GPC trace showed monomodal peak with relatively narrow molecular weight distribution ($\mathcal{D}$ =1.38) (**Figure 1d**). The triblock formation was also confirmed by ¹H NMR exhibiting signals at δ = 6.4-6.9 (m, 5H, Ar-PS), 4.34 ppm, 2.88 ppm and 2.22 ppm due to the chain end (-CF₂CH₂I), normal addition of PVDF (-CF₂CH₂-CF₂CH₂) and reverse addition of PVDF (-CF₂CH₂-CH₂CF₂), respectively, 1.86 ppm (m, 2H, PM), signals from macro-CTA (3.56 ppm and 1.13 ppm ascribed to -OCH₂ and -(CH₃)₂, respectively) and 1.5-1.3 (m, -CH and -CH₂ backbone of PS) (**Figure S7-S9**, SI). The DP of PS and PVDF was determined by comparing the integral of the peak at δ =6.34, 2.87 ppm and peak at δ = 4.34 ppm. ¹⁹F NMR spectrum showed characteristics signals of PVDF similar to the block copolymers mentioned above (**Figure S14-S16**, SI). The ¹H MAS NMR signals of PM-*b*-PS-*b*-PVDF triblock terpolymer at 6.9, 2.6 and 1.2 ppm auto-correlate at the diagonal in 2D DQ NMR spectrum which assigned to PS, PVDF and PM, respectively (**Figure 2b**). In addition, the PS peak at 6.9 ppm has a correlation with the peak at 0.6 ppm which is attributed to the backbone protons of PS (-CH and -CH₂) while PVDF peak at 2.6 ppm has a correlation with the peak at 3.6 ppm which is attributed to the polymer chain end (CH₂-I). DSC measurements were performed to investigate the phase behavior and the crystallization properties of the PVDF-based co/terpolymers. PVDF homopolymer with a melting peak at 145 °C was measured as a reference (**Figure 3a**). The thermograms of PM-*b*-PVDF diblock copolymer (**Figure 3a**) reveal the PM (112 °C) and PVDF (145 and 155 °C) melting temperatures, indicating that the two constituent blocks are separated and behave as independent phases upon crystallization of PVDF.³¹ We observed

that the different block compositions did not affect significantly the melting temperature of diblock copolymers (**Figure S19**, SI). The double melting peaks, observed for PVDF block, correspond to either the melting-recrystallization phenomenon^{32,33} or to the presence of two different crystalline phases. Due to the fact that the characteristic DSC PVDF peaks depend on the crystallization phases as well as on the morphology (chain defects, crystalline size, etc.), the melting temperature cannot be defined as a sharp peak but as a temperature range.⁵ The DSC thermogram of PM-*b*-PS-*b*-PVDF triblock terpolymer showed that the addition of an amorphous block (PS) slightly increases the melting temperature of each blocks as compared to diblock copolymer. Similarly to diblock copolymers, the heat flow curve (**Figure 3a**) indicate melting temperatures at 116 °C for PM and 156, 166 °C for PVDF. As previously reported, the glass transition temperature of PS block is hidden by the melting trace of PM block and the melting temperature of PM block decreased as its M_n decreasing (**Figure S20**, SI).^{16,22} Concerning the higher melting temperatures observed in triblock terpolymer, we presume that the crystalline phases are different compared to diblock copolymers. However, the exact melting temperature for different crystalline phases are still controversial, but it is well-documented in the literature that the melting temperature increases from α -phase to β - phase to γ -phase.³³⁻³⁵ According to that, we assume the existence of α -phase in PVDF, α - and β -phase in diblock copolymer and β - and γ -phase in triblock terpolymer.

To further investigate the crystalline phases of PVDF-based BCPs, XRD measurements were also carried out. For comparison, a PVDF homopolymer synthesized by ITP was used as a reference (**Figure 21**, SI). Here, the homo- PVDF XRD pattern indicates peaks at 2θ values of 17.70, 18.32, 20.04 and a weaker one at 26.56 corresponding to α -phase (**Figure S21**, SI).⁵ For PM-*b*-PVDF, the XRD pattern shows a superposition at $2\theta = 20.33$ which is a clear indication of β -phase. However, the existence of two additional peaks at $2\theta = 18.30$ and 26.56 indicates also the formation of α -phase (**Figure 3b**). The addition of PM block next to PVDF seems to promote the formation of β -phase in PVDF. Therefore, the DSC data of diblock copolymer is consistent with XRD result. Taking into account that no additional treatments (mechanical strength, annealing etc.) were applied to the triblock terpolymer, PS block

prohibited the formation of α -phase. Nevertheless, three peaks at $2\theta = 18.50$, 20.04 and a weaker at 26.8 , exclusively associated to γ -phase appears (**Figure 3b**).^{36,37} Moreover, a single weaker peak at 20.8 confirms the fraction of β -phase. Among all the possible chain conformations that are attributed to different PVDF phases, first β -phase and then γ -phase are the most beneficiary for electroactive properties.^{36,37}

Figure 3. (a) DSC spectra of PM₄₇₁ and PVDF₂₃₄ homopolymers and PM₄₇₁-b-PVDF₃₄₄ diblock copolymer and PM₄₇₁-b-PS₁₂₅-b-PVDF₃₂₈ triblock terpolymer, (b) XRD pattern of PM₄₇₁ homopolymer, PM₄₇₁-b-PVDF₃₄₄ diblock copolymer and PM₄₇₁-b-PS₁₂₅-b-PVDF₃₂₈ triblock terpolymer and (c) FTIR spectra of PVDF₂₃₄ homopolymer and PM₄₇₁-b-PVDF₃₄₄ diblock copolymer and PM₄₇₁-b-PS₁₂₅-b-PVDF₃₂₈ triblock terpolymer.

FTIR was also used as a complementary technique to identify the crystalline forms of PVDF (**Figure 3c**). The PVDF homopolymer showed the absorption bands at 409 , 534 , 616 , 769 , 796 , 855 and 977 cm⁻¹ which are exclusive of the α -phase.⁵ The FTIR spectrum of PM-b-PVDF diblock copolymer clearly reveals the formation of β -phase having the presence of absorption bands at 511 , 840 and 1281 cm⁻¹.^{5,38,39} This result is in agreement with the results from DSC and XRD were covalently linked PM to PVDF block led to the formation of β -phase. For the PM-b-PS-b-PVDF triblock terpolymer, bands obtained at 432 , 513 , 776 , 840 and 1235 cm⁻¹ can be assigned to γ -phase as similarly indicated by DSC and XRD data.^{5,38,39}

In order to study the self-assembly of the PM-b-PVDF diblock copolymer and of PM-b-PS-b-PVDF triblock terpolymer in solution (runs 2,4, **Table 1**) the samples were poured in DMF (1 mg/mL) and kept under ultrasound bath until the solution becomes cloudy and homogeneous (1 h). DMF is a selective solvent for PS and PVDF blocks. The mean size and size distribution of the formed particles

were measured by DLS at room temperature. The hydrodynamic diameter of the particles for the diblock was measured 410 nm, while for the triblock 490 nm, suggesting the formation of large aggregates, probably due to the DMF-phobic PM block. The polydispersity value is relatively high for the diblock (PDI=0.521), while for the triblock is 0.387 (**Figure 4a**). The formation of aggregated particles was also visualized by Atomic Force Microscopy (AFM) where height images indicate an average size of non-spherical particles about 190 nm and 220 nm for diblock and triblock, respectively (**Figure 4b and 4c**). The difference in the measured sizes between DLS and AFM can be attributed to the fact that the former method measures the mobility of the particles in solution, while the latter reveals the direct imaging of the dry particles.

Figure 4. (a) DLS curves for PM₄₇₁-*b*-PVDF₃₄₄ diblock copolymer and PM₄₇₁-*b*-PS₁₂₅-*b*-PVDF₃₂₈ triblock terpolymer in DMF solution (1mg/mL), (b) AFM height images for PM₄₇₁-*b*-PVDF₃₄₄ diblock copolymer and (c) AFM of PM₄₇₁-*b*-PS₁₂₅-*b*-PVDF₃₂₈ triblock terpolymer.

4. CONCLUSIONS

A series of PVDF-based diblock and triblock co/terpolymers containing crystalline PM and amorphous PS blocks were synthesized via a combination of two/three different polymerization techniques. PM-I obtained from polyhomologation and PM-*b*-PS-I from polyhomologation and subsequent ATRP were proved as efficient macro-CTAs for the ITP polymerization of VDF. Two separated crystallization peaks for PVDF and one for PE component indicates the sequential crystallization of covalently linked blocks for both co/terpolymer. XRD measurements showed superpositions which indicate fractions of the

electroactive β - phase but also non electroactive α - phase for the diblock copolymer while β - and γ - phase for triblock terpolymers. Furthermore, according to DSC, XRD and IR results, the presence of a PS intermediate block between PM and PVDF led to the formation of mainly γ -phase. Efforts to extend the synthesis of a variety of semi-fluorinated polymers, as well as to gain additional insights into their morphology, self-assembly, and dispersive properties are currently underway in our laboratory. These type of PVDF-based copolymer could be potentially used as polymer binders for lithium-ion batteries optimizing properties like adhesion strength and flexibility. Finally, this study opens new horizons towards the synthesis of PM-*b*-PVDF-based complex macromolecular architectures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Additional experimental details, procedure, materials, GPC traces, XRD, DSC data, ^1H , ^{19}F liquid state NMR and ^1H SS NMR (PDF).

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