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**“One-Pot” Aminolysis/Thia-Michael Addition preparation of well-defined amphiphilic PVDF-b-PEG-b-PVDF triblock copolymers: Self-assembly behaviour in mixed solvents**

Enrique Folgado, a,b Marc Guerre, ab Antonio Da Costa, a Anthony Ferri, c Ahmed Addad, d Vincent Ladimair, d* and Mona Semsarilar b c d e

Polyvinylidene fluoride- (PVDF) containing block copolymers are scarce and difficult to prepare. Amphiphilic block copolymers containing PVDF have been rarely reported. In consequence, few studies of the self-assembly of PVDF-based block copolymers exist. Here a new synthetic route to prepare poly(vinylidene fluoride)-block-poly(ethylene glycol)-block-poly(vinylidene fluoride) (PVDF-b-PEG-b-PVDF) ABA triblock copolymer is presented. The synthesis relies on the efficient coupling of a PVDF prepared by RAFT and a PEG diacrylate in one pot via aminolysis of the xanthate moiety and subsequent thia-Michael addition. The novel amphiphilic triblock copolymer was fully characterized by 1H and 13C NMR spectroscopy, TGA, DSC, DLS and XRD; and its self-assembly in water and ethanol was studied. Micellization (addition of a selective solvent for PVDF to a solution of the triblock) and nanoprecipitation (addition of a solution of the triblock into a non solvent of PVDF) protocols led to the formation of micelles and vesicles. Surprisingly, under nanoprecipitation conditions (in THF/ethanol), well-defined crystalline micrometric structures were obtained.

**Introduction**

ABA triblock copolymers are important materials which have found high added value applications. SBS (polystyrene-b-polybutadiene-b-polystyrene) are crucial thermoplastic elastomers for the tyre industry for example, and Pluronics® are used in numerous fields as dispersants, emulsifiers, thickeners, antifoaming or wetting agent.  

Amphiphilic ABA triblock copolymers are indeed very interesting polymer architectures. When the A and B blocks are incompatible, these triblock copolymers readily self-assemble from the melt into well-ordered nanostructures. In selective solvents, the self-assembly of such ABA triblock copolymers can generate a variety of morphologies, such as spherical micelles, wormlike micelles, vesicles or more complex structures such as toroids. In aqueous media, and when the B block is hydrophilic, these triblocks readily form self-assembled micelles comprising a hydrophobic core constituted of the A segments, and a stabilizing hydrophilic corona made of the hydrophilic B blocks. These micelles, sometimes named flower-like micelles, may connect to each other via intermicellar bridges. The formation of these bridges depends on several factors such as micelle concentration, size and nature of A and B blocks and interchain interactions for example.

The formation of such bridges is favoured when the hydrophobic core-forming block is smaller than the stabilizing corona segments. If the hydrophobic block is too short, the conformational energy will not be favourable to the formation of loops. There must be a compromise between inter-chain interactions, increasing with the length of the hydrophilic block, and the formation of loops, also favored by longer chains. Finally, if the system is too diluted, the intermicellar interactions will be too rare for bridges to form.

In industry most ABA triblock copolymers are prepared by anionic polymerization. However, progress in Reversible Deactivation Radical Polymerization (RDRP) techniques, such as RAFT (Reversible Addition-Fragmentation chain Transfer), ATRP (Atom-Transfer Radical Polymerization) or CMRP (Cobalt-Mediated Radical Polymerization) for example, have enabled the facile synthesis of ABA triblock copolymers. Numerous acrylates-, methacrylates- or styrenics-based ABA triblock copolymers have been described and...
reported by academic research groups. Singh et al. reported the use of ATRP for the preparation of an ABA PDCPMA-b-PHEA-b-PDCPMA (DCPMA = dicyclopentadiene methylacrylate, EHA = 2-ethylhexylacrylate) triblock copolymer using a Br-PEHA-Br difunctional macroinitiator.24 Xie et al. synthesised via activator generated by electron transfer (AGET) ATRP, a poly(n-butylacrylate) homopolymer and a polystyrene-b-poly(n-butylacrylate)-b-polystyrene (PS-PnBA-PS) triblock copolymer from ethylene bis(2-bromoisobutyrate).25 Following a similar approach and using a difunctional triiodohomocysteate RAFT agent, Semsaril et al. synthesised a polystyrene-b-poly(sodium 4-styrenesulfonate)-b-polystyrene (PS-b-PNaSS-b-PS) ABA triblock.9 Shipp et al. employed a difunctional polydimethylsiloxane xanthate macro RAFT agents to polymerize N-vinylpyrrolidone (NVP) and prepare a PVP-b-PDMS-b-PVP ABA triblock copolymer.26 CMRP is particularly well-adapted to prepare ABA triblock copolymers from LAMs (less-activated monomers) such as vinyl acetate for example.27 It is arguably the most efficient method to control the polymerization of LAMs and to prepare well-defined copolymers from these type of monomers.27 ABA triblock copolymers are also very easily synthesized by CMRP from diblock copolymers using a very efficient radical coupling cobalt-catalyzed chemistry.23,28–31

Fluorinated polymers bearing fluorine atoms on the main chain such as PTFE (polytetrafluoroethylene) or PVDF (poly(vinylidene fluoride)) are valuable specialty polymers endowed with remarkable properties. PVDF in particular displays high resistance to weathering and chemical aggressions as well as unusual electroactivity. Copolymers of VDF, trifluoroethylene and chlorotrifluoroethylene for example are outstanding relaxor ferroelectrics.32–34 Copolymers of VDF and TrFE possess high sensitivity and wide frequency responses to electric fields, are relatively flexible, and easy to produce. These copolymers have a great potential for emerging applications such as haptics, sensors, artificial muscles, etc.35

Only few references describe the self-assembly of PVDF block copolymers in solution, probably because well-defined PVDF-containing block copolymers are difficult to synthesize.36–38 Qian et al. studied the self-assembly of PVDF-b-PS block copolymers in DMF-containing mixtures of solvents. The presence of DMF was necessary to give sufficient mobility to the PVDF segments and gain access to non-spherical self-assembled structures.39 Rodionov et al. prepared interesting 4-nitroanil star copolymers containing 2 PVDF-b-PS arms and 2 PEG arms via the combination of ATRP, Iodine Transfer Polymerization (ITP) and copper-catalyzed azide-alkyne cycloaddition (CuAAC); and studied their self-assembly in organic solvents and water.40 Over the last two years we developed the RAFT polymerization of VDF,41 and prepared some PVDF-containing block copolymers,42 which self-assembled in water and organic solvents. PVDF-b-PVA (PVA = poly(vinyl alcohol)) formed spherical particles in water,43 PVDF-b-PDMAEMA (PDMAEMA = poly (2-dimethylaminoethyl methacrylate) in water displayed spherical aggregates and rigid rods which are thought to be generated via crystallisation-driven self-assembly;44 and PVAc-b-PVDF (PVAc = poly(vinyl acetate)) readily self-assembled in dimethyl carbonate under polymerization-induced self-assembly conditions into highly crystalline micrometric structures.45 The synthesis of PVDF-based BCPs by RAFT (or ITP) and sequential addition of monomers is difficult due to the fast accumulation of much less reactive inversely-terminated PVDF chains (-CH2-xanthate-terminated chains). For example, in spite of what was recently wrongly reported,46 well-defined PVDF-b-PNVP (PNVP = poly N-vinyl pyrrolidone) cannot be synthesized by polymerization of NVP starting from a PVDF macroRAFT agent since only -CF2-xanthate-terminated chains (which disappear entirely from the reaction medium quickly) can be reinitiated with PNVP radicals.37 Synthesis strategies based on the coupling of two or more homopolymers may afford better-defined block copolymers provided the coupling reaction is efficient enough, although complete removal of the residual homopolymers is often difficult or requires tedious purification steps. Huck et al., for example, purified a PFTBT-b-P3HT diblock copolymer (P3HT = poly(3-hexylthiophene) and PFTBT = poly(9,9-dioctyfluorene)-2,7-diyl-alt-[4,7-bis(3hexylthienyl-5-yl)-1,3-benzothiadiazole]-2′,2″-diyl)) via preparative GPC to remove the excess of P3HT homopolymer.43 This strategy has been successfully implemented with the copper-catalyzed coupling of azides and alkynes (CuAAC) to prepare PVDF-block copolymers45 and PEG-b-PFPE-b-PEG (PEG = polyethylene glycol, PFPE = perfluoropolyether) ABA triblock copolymers.7 CuAAC is a powerful click chemistry technique, but the removal of copper is often tedious. In contrast, the thia-Michael addition does not use copper, and is very well-suited to polymers made by RAFT.48,49 It does not require functionalRAFT agents and can be conducted in one pot.50,51

In this paper, we report the synthesis using RAFT polymerization and a one-pot thia-Michael addition procedure, the characterization of a novel amphiphilic PVDF-based ABA triblock copolymer (PVDF0-0-b-PPEG0-b-PVDF0), its self-assembly in NMP/water, THF/ethanol and THF/water mixtures and the characterization of the obtained structures using TEM and AFM.

Experimental section

Materials
All reagents were used as received unless otherwise stated. 1,1-Difluoroethylene (vinylidene fluoride, VDF) was supplied by Arkema (Pierre-Bénite, France). O-Ethyl-S-(1-methoxy carbonyl) ethylidithiocarbonate was synthesized according to the method described by Liu et al.52 Tert- Amyl peroxide-2-ethylhexanoate (Trigonox 121, purity 95%) was purchased from AkzoNobel (Chalons-sur-Marne, France). PEG6000, acetonitrile (ACN),
ethanol (EtOH), dimethyl carbonate (DMC), hexylamine, N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), triethylamine (NEt₃) and laboratory reagent grade hexane (purity >95%) were purchased from Sigma-Aldrich.
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ARTICLE

1) PVDF-XA synthesis

![Diagram of PVDF-XA synthesis]

2) Acrylation

![Diagram of Acrylation]

3) Aminolysis + Michael Addition

![Diagram of Aminolysis + Michael Addition]

4) Self-Assembly

![Diagram of Self-Assembly]

Scheme 1. Synthesis and self-assembly of the amphiphilic PVDF-b-PEG-b-PVDF ABA triblock copolymer. 1) Synthesis of PVDF-XA by RAFT. 2) PEG diacrylate (PEGDA) synthesis in dichloromethane using acryloyl chloride. 3) One-pot synthesis of the triblock copolymer by aminolysis of the xanthate groups and thia-Michael addition of the resulting PVDF-HT to PEGDA. 4) Self-assembly into expected flower-like micelles of the ABA triblock copolymer (nanoprecipitation or micellization).

temperature (ca. 20 °C), purged from the residual monomers, and DMC 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 was then precipitated from 400 mL of chilled hexane. The precipitated polymer (white powder) was filtered through a filter funnel and dried under vacuum (15∙10⁻³ mbar) for two hours at 50°C. The polymerization yield (65%) was determined gravimetrically (mass of dried precipitated polymers / mass of monomer introduced in the pressure reactor).

¹H NMR (400 MHz (CD₃)₂CO, δ (ppm), Figure S1): 1.09 (d, -CH(CH₃)(C=O), JHH = 7.1 Hz), 1.31 (t, -S(C=O)-O-CH₂-CH₂-, JHH = 7.1 Hz), 2.13-2.31 (m,-CF₂-CH₂-CH₂-CH₃C₃F₇, VDF-VDF TT reverse addition), 2.66-3.01 (t, -CF₂-CH₂-CH₂-, VDF-VDF HT regular addition), 3.48-3.57 (s, -(C=O)-O-CH₃), 3.97 (t, -CF₂-CH₂-S(C=O)OEt, JHH = 17.7 Hz), 4.59 (q, -(S(C=O)OCH₂-CH₂-, JHH = 7.0 Hz), 6.05-6.45 (tt, JHH = 55 Hz, JHH = 4.6 Hz · CH₂-CF₂-H).

¹³C NMR (376 MHz (CD₃)₂CO, δ (ppm), Figure S2): -115.64 (-CH₃-CH₂-CF₂-CH₂-CH₂-, VDF-VDF HH reverse addition), -114.29 (JHH = 55 Hz, -CH₂-CF₂-H), -113.35 (-CH₂-CF₂-CH₂-CH₂-CH₂-ChH reverse addition), -113.09 (CH₂-CF₂-CH₂-S-), -112.69 (-CH₂-CF₂-CH₂-CH₂-S-), -94.79 (-CH₂-CH₂-CF₂-CH₂-CF₂-CF₂-CH₂-CF₂-, TT reverse addition), -93.50 (-CH₂-CH₂-CF₂-CH₂-CH₂-CH₂-CH₂-CH₂-CF₂-, regular VDF-VDF HT addition), -91.43 (-CH₂-CH₂-CF₂-CH₂-CH₂-CH₂-CF₂-, regular VDF-VDF HT addition).

The degree of polymerization (DP) and number average molar mass of PVDF were calculated from the ¹H NMR spectrum using the following equations:

\[
DP = \frac{\int_{2.31}^{3.11} CH₂(HT) + \int_{2.13}^{2.83} CH₂(TT) + \int_{6.06}^{4.99} CH₂(End-group)}{2/3 \times \int_{5.9}^{6.1} CH₂(R-CTA₂ₙ)}
\]

\[
Mₙ,NMR(R) = Mₙ,CTA + (DP \times Mₙ,VDF)
\]

Where \(Mₙ,CTA = 208.3 \text{ g.mol}^{-1}\) and \(Mₙ,VDF = 64.04 \text{ g.mol}^{-1}\).

PEGDA₁₃₆ synthesis. PEG diacrylates were obtained from commercial PEG₆₀₀₀ as follows: polyethylene glycol (PEG₆₀₀₀; 7 g; 1.17 mmol; 1 eq.) and acryloyl chloride (0.95 mL; 11.7 mmol; 10 eq.) were dissolved in dichloromethane (DCM, 48 mL) in a
round bottom flask under magnetic stirring at room temperature (25°C). After 10 min, triethylamine (TEA, 0.47 g, 4.68 mmol, 4 eq) was added dropwise. The reaction was monitored by 1H NMR. After 60 h, the precipitate was filtered off on Celite, and the target polymer was precipitated in cold diethyl ether and then dried under vacuum.

1H NMR (400 MHz, (CD3)2SO, δ (ppm), Figure S4): 6.43 (d, J = 17.3 Hz, 2H, -CH=CH2), 6.16 (dd, J = 17.4 Hz and 10.4 Hz, 2H, -C=CH-C=O), 5.85 (d, J = 10.4 Hz, 2H, -CH=CH2), 4.23 (m, 2H, (C=O)-O-CH2-CH2-O), 3.4-3.8 (m, -CH2-CH2-O).

**PVDF-b-PcEg-PcDv trifile synthesis.** PVDF-50-XA (5.000 g, 1.47 mmol) and PEGDA,236 (4.410 g, 0.735 mmol) were dissolved in DMF (115 mL). The mixture was degassed with N2 (5.000 g, 1.47 mmol) and PEGDA (1.2 mmol) in DMF was injected into the reaction mixture. N2 was bubbled for another 10 min. The mixture was stirred 16 h until the reaction was complete and no unreacted acrylate could be detected by 1H NMR. The product was then precipitated twice in cold diethyl ether.

1H NMR (400 MHz (CD3)2SO, δ (ppm), Figure S5) : 1.15-1.20 -CH(CH3)(C=O)-, 2.16–2.38 (m, -CF2-CH2-CF2-CF2-, VDF-VDF TT reverse addition), 2.62-2.71 (m, -S-CH2-CH2(C=O)), 2.71-3.05 (t, -CF2-CH2-CF2-, VDF-VDF HT regular addition), 3.07-3.14 (m, CF2-CH2-S), 3.42-3.60 (m, -O-(CH2-CH2)), 3.60-3.69 (s, -O-(CH2-CH2)), 3.72-3.81 (m, -C(CH3)=O-CH2-CH2), 4.13-4.23 (-C(CH3)=O-CH2-CH2). 13C NMR (377 MHz, (CD3)2SO δ (ppm), Figure S6): 113.16 (-CH2-CF2-CF2-CH2-CF2-), -113.77 (-CH2-CF2-CF2-CH2-CH2-), -112.87 (-CH2-CF2-CF2-CH2-Si), -112.25 (-CH2-CF2-CF2-CH2-Si), -93.75 (-CH2-CF2-CF2-CH2-Si), -92.76 (CH3=O-(C=O)-(CH2=CH2-CF2-CF2), -91.82 (-CH2-CF2-CF2-CH2-H), -91.46 (CH2=CH2-CF2-CF2-CH2-CF2-CF2), -91.00 (-CH2-CF2-CF2-CH2-CF2), regular VDF-VDF HT addition).

**Self-assembly**

**Preparation of the solution**

A 5% w/w triblock copolymer solution in NMP (60 mg of triblock copolymer in 1.2 mL of solvent) and another solution in THF at 1% w/w (24 mg of triblock copolymer in 2.4 mL of solvent) were prepared in glass vials and heated to 70°C in the case of NMP and to 60°C in the case of THF for at least 24 h.

**Micellization protocol**

To different glass vials placed in a stirring plate and equipped with magnetic bars were added 0.2 mL of triblock solution (5% w/w in NMP or 1% w/w in THF). To each vial a non-solvent for PVDF was added dropwise to reach different solvent/non-solvent ratios (i.e. 0.4 mL for 1:2 ratio; 0.8 mL for 1:4 ratio; 1.2 mL for 1:6 ratio). Only water was used as non-solvent in the case of NMP triblock copolymer solutions.

**Nanoprecipitation protocol**

To different glass vials placed in a stirring plate and equipped with magnetic bars was added 1.2 mL of non-solvent. To each vial an adequate triblock solution volume (5% w/w in NMP or 1% w/w in THF) was added dropwise to reach different solvent/non-solvent ratios (i.e. 0.6 mL for the 1:2 ratio; 0.3 mL for the 1:4 ratio; 0.15 mL for the 1:6 ratio).

In all micellization and nanoprecipitation samples cloudy solutions were obtained. At the end 18 vials containing micellar solutions were obtained. Three of each protocols in the case of NMP samples and six of each protocol in the case of THF (three used water as non-solvent and three ethanol).

**Preparation of AFM samples**

Self-assembled structures were deposited on silicon wafers by spin-coating of suspension of triblock copolymer in THF/ethanol (or NMP/water). The suspension was spin-coated (SPS Spin 150 spin coater) onto a clean silicon wafer at 1000 rpm for 120 s (or 300 s) with a speed ramp of 100 rpm s⁻¹. The AFM analyses were performed directly on the silicon wafer.

**Results and discussion**

The amphiphilic ABA triblock copolymer was prepared by a one pot aminolysis/thia-Michael addition involving a mono-functional PVDF-Xanthate (PVDF-XA) and a difunctional PEG acrylate (PEGDA) (Scheme 1). The PVDF-50-XA was synthesized by RAFT polymerization following an already established protocol.46 The PEG diacrylate (PEGDA) was prepared by simple acrylation of a commercial dihydroxylated PEG (Figure S3). The acrylation reaction resulted in quantitative functionalization of the commercial PEG (Figure S4). Then, the targeted PVDF-b-PcEg-b-PcDv ABA triblock copolymer was synthesized in relatively high yield (86%) by coupling reaction using relative stoichiometric equivalents of PVDF and PEG. The conversion of the coupling reaction was followed by 1H NMR and was evidenced by the disappearance of both signals of the xanthate groups at δ = 1.40-1.46 ppm and δ = 4.67-4.77 ppm (conversion of the xanthate end-groups into thiol via aminolysis), and signals of the acrylate groups at δ = 5.85, 6.16 and 6.43 ppm (thia-Michael addition) (Figure S5). The success of the thia-Michael addition was also confirmed by 19F NMR spectroscopy with a up shifted flight of the fluorine signals of the –CF3 unit directly bonded to the xanthate moiety from δ = -113.09 to δ = -113.77 ppm (Figure S6). The formation of the triblock copolymers was further confirmed by SEC-HPLC. Figure 1 shows the SEC chromatograms of the two homopolymer precursors and of the resulting ABA triblock. These chromatograms confirm the successful coupling reaction with a clear shift of the triblock copolymer trace towards shorter retention time (higher molar masses). However, a small shoulder at lower retention time reveals the presence of small amounts of residual PVDF precursors that were not removed by precipitation. This residual PVDF is likely the non-functional PVDF-H chains (10 mol %) formed by transfer reactions (estimation made from 1H NMR data (Figure 1), PVDF-H signals at 6.05 ~ 6.45 ppm). Indeed, the starting PVDF was composed of 90 mol. % of chains terminated by a head-to-head addition (-CH2-CF2-CF2-CH2-XXA) and 10 mol. % of chains terminated by a hydrogen atom (-CF3-H et -CH3) resulting transfer reaction.

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diffusion-ordered spectroscopy (DOSY) NMR experiments were also carried out to further characterize the ABA triblock copolymer. These DOSY experiments provide 2D correlation maps showing chemical shifts and diffusion coefficients on the horizontal and vertical axes, respectively.

The $^1$H DOSY map of the PVDF$_{20}$-b-PEG$_{1350}$-b-PVDF$_{50}$ triblock copolymer (Figure 2 and S7) shows that all $^1$H NMR signals correlate with a single diffusion coefficient ($2.8 \times 10^{-5}$ m$^2$ s$^{-1}$). In comparison DOSY experiments carried out on PVDF-XA and PEGDA provided diffusion coefficients of 9.1 $\times$ $10^{-5}$ m$^2$ s$^{-1}$ and 7.5 $\times$ $10^{-5}$ m$^2$ s$^{-1}$ respectively. These results suggest quantitative coupling reactions without contamination of residual homopolymers.

The discrepancy between the SEC and $^1$H DOSY NMR results are likely due to the higher lower detection limit of $^1$H DOSY NMR compared to SEC. Nevertheless these analyses indicate that the protocol used here led to a relatively well defined PVDF-b-PEG-b-PVDF triblock copolymer ($D<1.3$).

Thermogravimetric analyses (under air) (Figure 3) revealed that the PVDF$_{20}$-b-PEG$_{1350}$-b-PVDF$_{50}$ triblock copolymer displayed a thermal behaviour relatively similar to those of its precursors. No significant weight loss was observed before 348 °C (TD$_{5\%}$ of the triblock) close to the degradation temperature of the PEGDA (TD$_{5\%}$ = 360 °C), while PVDF-XA started to degrade at marginally higher T (TD$_{5\%}$ = 365 °C, TD$_{10\%}$ = 389 °C). Differential scanning calorimetry (DSC) of the PVDF$_{20}$-b-PEG$_{1350}$-b-PVDF$_{50}$ triblock copolymer revealed the characteristic exothermic and endothermic peaks corresponding to the crystallization and melting transitions at 40.3 and 56 °C for PEG and at 139.5 and 178.3 °C for PVDF, respectively (Figure S13, and Figure 4). These values are in good agreement with those obtained for PEGDA (T$_c$ = 42°C and T$_m$ = 58°C) (Figure S12) and PVDF-XA homopolymers (T$_c$ = 140°C and T$_m$ = 168.7°C) (Figure. S11). In addition, the DSC thermogram of the triblock (Figure 4 and Figure S13) displayed two distinct glass transition temperatures corresponding to VDF (-34 °C) and PEG (-10 °C), confirming the bulk incompatibility of these two polymers. The DSC thermograms were also used to quantify the degree of crystallinity of the PVDF (47.1%) and of the PEG (53.8%) in the triblock copolymer (See S14 for details on these calculations).

The self-assembly in solution of the new PVDF-based amphiphilic triblock copolymer was then studied.
Among the various methods used to promote the self-assembly of amphiphilic block copolymer in solution, we selected the two most common techniques used so far: (i) Direct dissolution of the polymer in a selective solvent for one of the blocks, and (ii) Dissolution of the block copolymer in a good solvent for both blocks, followed by slow addition of a selective solvent for one of the blocks.\textsuperscript{53} 

The first method, often called nanoprecipitation, is an easy and direct way to provoke self-assembly and is well-suited for block copolymers with relatively low molar masses and relatively short insoluble block.\textsuperscript{53} Given the high hydrophobicity and crystallinity of PVDF, the second method (called here micellization), although more time-consuming, is probably more suitable to the present PVDF-b-PEG-b-PVDF triblock copolymer. Indeed, under nanoprecipitation conditions, self-assembly occurs very fast and generally leads to frozen morphologies. A slower self-assembling process such as the micellization method is more likely to deliver thermodynamically more stable self-assembled structures. Note that due to the non-ergodicity of amphiphilic block copolymer systems, both methods likely lead to kinetically trapped structures.\textsuperscript{54} 

Two solutions of the triblock copolymers were prepared: One solution in NMP at 5\% w/w, and one solution in THF at 1\% w/w. Complete dissolution of the triblock copolymers was achieved only after heating for prolonged time (24 h at 60 °C for THF and at 70 °C for NMP). The molecular dissolution of the triblock was confirmed by DLS (Figure S15). Only 1\% w/w solution could be prepared in THF due to the poor solubility of PVDF in THF. The solutions in NMP at 5\% w/w and in THF at 1\% w/w were then used to investigate the self-assembly of the triblock copolymer via nanoprecipitation and micellization. 

Transmission electron microscopy and atomic force microscopy revealed that the nanoprecipitation protocol led to the formation of small roughly spherical aggregates for the 1:6 NMP: water systems (Figure 5, and S16). These small aggregates with size ranging from 20 to 75 nm displayed relatively rough surfaces and were not perfectly spherical. This is likely caused by the high crystallinity of PVDF and the fast solvent de-mixing times, not leading the BCP to reach kinetically stable morphologies.\textsuperscript{44} 

When micellar solutions at 1:2 and 1:4 NMP: water ratios were analysed by TEM, only large micrometric aggregates were observed (Figure S16). The concentration of non-solvent was probably not enough at these stages, and the observed non-defined aggregates are due to non-self-assembled BCP. 

In the case of the THF: water solvent: non-solvent system, both self-assembly protocols produced vesicles of around 300 nm (Figure 6a, 6b and S16). Higher THF: water ratios led to larger aggregates (Figure S16). As above, better defined particles were obtained at lower solvent: non-solvent ratios. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{DSC Thermograms of PVDF-b-PEG-b-PVDF triblock copolymer. a) Area highlighting the glass transitions of PVDF and PEG. b) Area presenting the two endothermic signals corresponding to the melting points of PEG and PVDF.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{a) and b) TEM images of PVDF-b-PEG-b-PVDF aggregates obtained from a 5\% w/w solution in NMP by nanoprecipitation (NMP:water (1:6)). c) AFM topographic image of these aggregates deposited by spin-coating on a silicon wafer.}
\end{figure}
In the nanoprecipitation experiments, higher solvent/non-solvent ratios, likely lead to instability of the vesicles and thus, big aggregates of non-assembled polymer are also observed.

In contrast, nanoprecipitation of the THF solution in ethanol using 1:6 (Figure 7b, and S16) lead to the formation of crystalline structures with ovoidal shape and using 1:4 THF:ethanol ratio a mixture of ovoidal, crystalline shard like structures and spheres of various size were observed (Figure 7a, 7c, and S16). Ovoidal crystalline structures have already been reported in our group from PVAc-b-PVDF diblock copolymers. In the latter case the corona forming block was not crystalline so the objects observed by TEM should not differ from the ones in solution (i.e. the corona-forming block does not crystallize when the solvent evaporates). Similar structures have been also described by Wang et al. for self-assembled PEG-b-PPDO, by Wang J. et al. in the case of a (MPEG)(PCL)(PPE) 3-miktoarm star terpolymer, by Chen et al. for PCL-b-PDMAEMA and PCL-b-PAAM block copolymers and by Rizis et al. for PEG-b-PCL. These structures are thought to be formed by crystallisation-driven self-assembly (CDSA). The crystallinity of those structures was highlighted by the analysis of the SAED patterns recorded during TEM analysis and compared to the XRD diffraction pattern (Figure 8). From XRD measurement, the two diffraction peaks observed at 2θ = 19.8 and 26.5° are found to be characteristic of the PVDF phase. In addition, the specific peak at 26.5° unambiguously evidences the α-crystal phase (no existence of the β- and γ-crystal phases). The XRD pattern also shows two peak at 2θ = 19.2 and 23.4° attributed to the crystalline structure of the PEG (see S18).

Moreover, the symmetrical Bragg spots of (110)\textsubscript{PVDF} and (021)\textsubscript{PVDF} can be clearly observed from the SAED pattern, indicating that the ovoidal structures may be considered to be single crystals of PVDF (the entire object analysed was inside the selected area). In addition, the symmetrical spots of (032)\textsubscript{PEG} indicate that the PEG is crystalline too. According to previous reports preparation of single-crystals is complicated and time-consuming (self-seeding method) and it has never been reported for PVDF-based block copolymers.
Conclusions

An ABA PVDF-b-PEG-b-PVDF amphiphilic triblock copolymer was synthesized using an efficient one-pot aminolysis / thia-Michael addition of a PVDF prepared by RAFT and PEG diacrylate. This novel PVDF-based ABA triblock copolymer was thoroughly characterised by $^{1}H$, $^{13}C$ DOSY and $^{19}F$-NMR spectroscopies, GPC as well as TGA, DSC and XRD. These characterizations proved the coupling strategy efficient and revealed a relatively well-defined (low D) triblock copolymer. As expected, the triblock copolymer had thermal resistance close to that of PEG and inferior to that of PVDF and both blocks present the inherent crystallinity of these materials. The self-assembly of this amphiphilic triblock copolymer was performed using nanoprecipitation and micellization protocols using NMP or THF as good solvents and water or ethanol as the block selective solvents. In most cases, the self-assembly experiments led to roughly spherical aggregates with size ranging from 20 to 75 nm and vesicles up to 300 nm. However, when THF solutions were used under nanoprecipitation protocols in ethanol, micrometric crystalline oval morphologies were obtained. The crystallinity of both α-PVDF and PEG in those structures was confirmed by SAED patterns recorded during TEM analysis and identified by XRD measurement. These original triblock copolymers and self-assembled morphologies may offer new opportunities to design electroactive structures at the nano- and micrometric scales.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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J. Name., 2013, 00, 1-3 | 10


37 R. Guerre, Marc; Wahidur Rahaman, S. M.; Améduri, Bruno; Poli and V. Ladmiral, Polym. Chem., 2016, \(7\), 6918–6933.


56 Y. Yuan and J. Wang, Colloids Surfaces B Biointerfaces, 2011, \(85\), 81–85.


