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An amphiphilic poly(vinylidene fluoride)-*b*-poly(vinyl alcohol) block copolymer: synthesis and self-assembly in water†

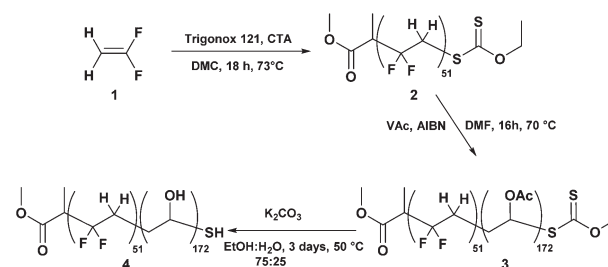
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This study is the first report of the synthesis and self-assembly in water of an amphiphilic PVDF-*b*-PVA block copolymer. The block copolymer was prepared by sequential RAFT polymerization of VDF and VAc followed by saponification of the PVAc block and was characterized by ¹H NMR and FTIR. The self-assembled nanoparticles were characterized by DLS and cryo-TEM.

Poly(vinylidene fluoride) (PVDF) is the second most produced fluoropolymers. It possesses remarkable thermal, chemical and electroactive properties.^{1–4} In industry, it is prepared by radical polymerization of VDF in dispersed aqueous media. Although PVDF is a relatively well-known polymer, well-defined architectures such as block, or graft copolymers for example, have been very rarely reported^{5–13} in comparison to other vinyl polymers. The reversible deactivation radical polymerization (RDRP) of VDF is indeed more challenging than that of (meth)acrylates or styrenics, for example, because of the formation and accumulation of much less reactive PVDF chains resulting from VDF head-to-head (HH) addition.¹⁴ We recently reported a detailed study on the RAFT polymerization of VDF which highlights the generation of these less reactive PVDF chains.^{14,15} In previous articles, we also showed how RAFT polymerization can be used to prepare PVDF-methacrylate macromonomers,¹⁶ or fluorinated dendrimers,¹⁷ and reported a comprehensive study of the effect of these less reactive chains (PVDF_T-XA, chains terminated with a -CF₂-CH₂-XA end-sequence, where XA represents the xanthate moiety) on the mechanism of the RAFT polymerization of VDF.¹⁸ This latter work also showed how relatively high molar mass PVDF with high end-group functionality could be synthesized. These PVDF chains, thought to be unreactive, were indeed experimentally observed to be involved in the RAFT polymerization

of VDF and to react *via* degenerative and non-degenerative transfer reactions with PVDF[•] radicals, albeit at a much slower rate than their highly reactive regularly terminated counterparts, PVDF_H-XA (chains terminated with a -CH₂-CF₂-XA end-sequence). This behaviour was rationalized using DFT calculations.¹⁸ The resulting accumulation of these PVDF_T-XA chains results in the gradual broadening of the molar mass distribution of the PVDF, and eventually to a degradation of the control of the polymerization, when all PVDF chains have been converted into PVDF_T-XA, which are mediocre chain transfer agents. These studies provide a much better understanding of the RAFT of VDF, and allow the preparation of a well-defined PVDF with high chain end fidelity and a relatively high degree of polymerization.¹⁸ Building on this improved understanding, PVDF-based diblock copolymers^{19–21} were synthesized by sequential addition of monomers using PVDF macroCTAs.²² We recently showed that PVDF_H-XA can readily be reactivated by poly(*N*-vinyl pyrrolidone) and poly(vinyl acetate) (PVAc) radicals, while PVDF_T-XA only reacted with PVAc[•], and prepared unprecedented well-defined PVDF-*b*-PVAc diblock copolymers.²² The present Communication reports the preparation of a PVDF-*b*-PVA (where VA stands for vinyl alcohol) amphiphilic diblock copolymer and its self-assembly in water.

This novel amphiphilic PVDF-*b*-PVA diblock copolymer was prepared from a PVDF-*b*-PVAc precursor by the hydrolysis of the ester groups of the VAc units (Scheme 1). The hydrophobic



Scheme 1 Schematic representation of the synthesis of the PVDF-*b*-PVA block copolymer.

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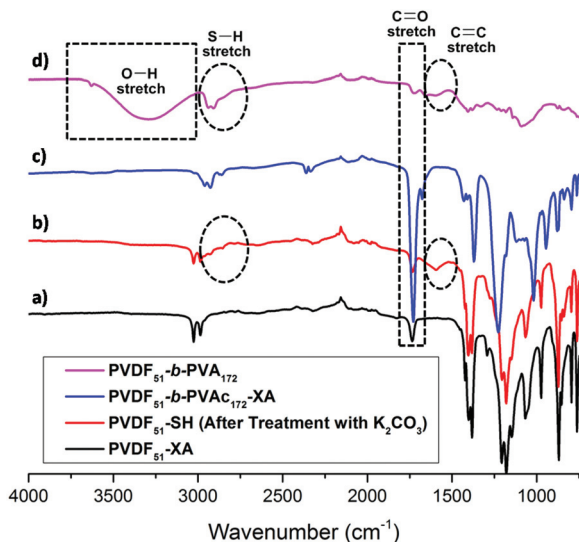


Fig. 1 FTIR spectra of: (a) the PVDF₅₁-XA (black), (b) PVDF₅₁-SH after K₂CO₃ treatment (red), (c) PVDF₅₁-b-PVAc₁₇₂ (blue), (d) PVDF₅₁-b-PVA₁₇₂ (pink) copolymers.

PVDF macroCTA (**2**) was synthesized by RAFT polymerization of VDF (**1**) following a procedure published previously.¹⁴ This polymerization afforded a well-defined PVDF (**2**) ($D = 1.40$, DP = 51) with high functionality (86% of PVDF_T-XA active end-group and 14% of -CF₂H dead chains). The PVDF-*b*-PVAc (**3**) block copolymer was prepared by chain extension of this PVDF macroCTA using RAFT polymerization of VAc.²² The resulting

well-defined PVDF₅₁-*b*-PVAc₁₇₂ diblock copolymer (**3**) ($D = 1.34$, Fig. S3†) was then dispersed in an ethanol solution and the PVAc block was hydrolyzed into PVA by basic hydrolysis using an aqueous/alcoholic solution of K₂CO₃.^{23,24}

The FTIR spectra of the PVDF₅₁-*b*-PVA₁₇₂ block copolymer and of its precursor (Fig. 1) show the quantitative hydrolysis of the ester bonds of the VAc units (complete disappearance of the carbonyl signal of PVAc at 1735 cm⁻¹). The spectrum of the amphiphilic diblock copolymer displays the characteristic stretching bands of PVA^{25,26} (Fig. 1d and S7,† OH vibration band at 3293 cm⁻¹ and C-H signal at 1396 cm⁻¹), as well as a broad stretching band at 2590 cm⁻¹ corresponding to the S-H bonds formed by the hydrolysis of the xanthate group.^{27,28} The disappearance of the vibration assigned to the C=S band (1000–1200 cm⁻¹) was, however, difficult to see. Chain-chain coupling *via* disulfide bond formation may occur, but it could not be seen on the FTIR spectrum, as it falls outside of the analysis window (400–500 cm⁻¹). However, disulfide linkage formation was not observed in previous studies on the hydrolysis of PVAc-XA.^{23,24} As expected, a small signal assigned to the -CH=CF- double bond at 1630 cm⁻¹ appeared after basic treatment.^{29–32} PVDF is relatively prone to dehydrofluorination in the presence of bases.² The hydrolysis of PVAc was thus accompanied by some dehydrofluorination, which generated internal carbon-carbon double bonds within the PVDF backbone, and gave a dark color to the resulting material.^{16,33}

The hydrolysis of the PVAc block was also confirmed by ¹H NMR spectroscopy (Fig. 2). The signals corresponding to the CH₂ (signal **b**, in Fig. 2) and to the CH (signal **c** in Fig. 2) of the PVAc backbone were, as expected, quantitatively shifted

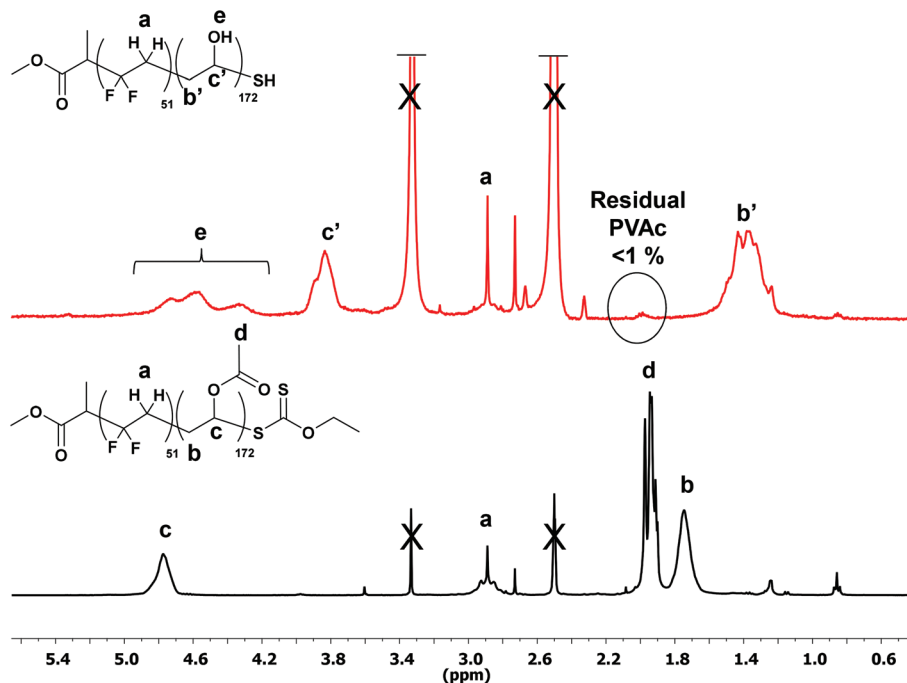


Fig. 2 Expansion of the 0.4–5.7 ppm region of the ¹H NMR spectra of PVDF-*b*-PVAc-XA (bottom) and PVDF-*b*-PVA (top) block copolymers recorded in DMSO-*d*₆. The crossed-out signals are those of water (3.33 ppm) and DMSO (2.5 ppm).

from 1.74 and 4.77 ppm to 1.37 and 3.83 ppm, respectively, upon hydrolysis of the acetate groups. The signal centered at 1.94 ppm (signal **d** in Fig. 2), assigned to the CH₃ of the acetate of the VAc units, almost entirely disappeared (only 1% of the original signal remained), and a new broad signal (probably caused, in part, by the tacticity of the PVA segments) corresponding to the hydroxyl groups of PVA appeared around 4.5 ppm (**e**, in Fig. 2). The signals of the PVDF segments remained untouched at 2.89 ppm.^{13,15,18} It is however important to note that although DMSO efficiently solubilizes the PVA block, it is only a moderately good solvent of PVDF (compared to acetone for example). This solubility difference can be easily seen on the PVDF NMR signal at 2.89 ppm in acetone, (PVDF-*b*-PVAc, Fig. S3†) and in DMSO (PVDF-*b*-PVAc bottom and PVDF-*b*-PVA top, Fig. 2). Consequently, in DMSO, the amphiphilic block copolymer is probably not entirely soluble, and could be already somewhat self-assembled into loose nano-objects with a PVDF core and a PVA corona (the ratio of the integrals of the signals of the PVDF and PVAc blocks is 0.22 in the PVDF-*b*-PVAc copolymers, whereas the PVDF/PVA integral ratio is estimated to be 0.16 in the amphiphilic copolymer). The signals of the *O*-ethyl xanthate end-group at 1.63 and 4.63 ppm overlapped with the signals of the CH and OH of PVA, respectively. The complete end-group removal thus cannot be confirmed by NMR spectroscopy on the PVDF-*b*-PVA NMR spectrum. On the other hand, the *O*-ethyl xanthate end-chain signals have totally disappeared from the ¹H NMR spectrum of treated PVDF (PVDF having undergone the same PVDF-*b*-PVAc hydrolysis conditions) (Fig. S8†). This indirectly proves the ω chain-end elimination after hydrolysis. In addition, the C=C double bonds arising from the dehydrofluorination reaction and barely identifiable in FTIR (1630 cm⁻¹, Fig. 1) could not be seen by ¹H or ¹⁹F NMR spectroscopy (Fig. S8 and S9†). To the best of our knowledge such NMR signals (caused by dehydrofluorination of PVDF) have never been reported anywhere.^{30,33,34} In the case of the diblock copolymer studied here, this may also be explained by the reduced solubility of the PVDF block in DMSO, by the small quantity of these double bonds, and the sensitivity limits of NMR spectroscopy. Therefore, a PVDF homopolymer was treated under the same conditions as the PVDF-*b*-PVAc block copolymer, and subsequently analyzed by FTIR, ¹H and ¹⁹F NMR in deuterated acetone (good solvent for PVDF, Fig. S9†). After treatment with K₂CO₃, a new weak and broad signal appeared around 7 ppm on the ¹H NMR spectrum. However, this signal was not intense enough to quantify accurately the extent of the dehydrofluorination reactions caused by the base. These results suggest that the extent of dehydrofluorination of the PVDF-*b*-PVA diblock copolymer is not significant.

To study the self-assembly behaviour in the solution of the new PVDF-*b*-PVA amphiphilic fluorinated block copolymer, a good solvent for both blocks was required. However, due to the large difference of solubility of each block, and the high crystallinity of PVDF and PVA, the PVDF-*b*-PVA copolymer was particularly difficult to solubilize in any solvent. PVDF is usually

solubilized in polar solvents such as DMF, DMAc, NMP, acetone or to a lesser extent DMSO, while PVA is only soluble in hot water or DMSO. The diblock copolymer was thus dissolved in hot DMSO (80 °C) at a concentration of 2.2 g L⁻¹ to improve the solubility of the PVDF block. The resulting polymer solution was then filtered (using 0.45 μm filters) and self-assembled in water using the dialysis method^{35,36} with a final concentration of 1.16 g L⁻¹. The dispersion of the self-assembled objects was analyzed by dynamic light scattering and cryo-TEM. The intensity-average hydrodynamic diameter distribution displayed in Fig. 3 shows an almost monomodal peak centered at 147 nm. A few larger objects (2 populations with a hydrodynamic diameter ranging from 500 nm to 1 μm and around 7 μm) were also detected. These larger aggregates may be caused by aggregation of a minor fraction of the self-assembled nano-objects. The smaller PVDF-*b*-PVA self-assembled nano-objects were spherical and displayed a relatively large diameter distribution (from 70 nm to 350 nm), as observed both by DLS and cryo-TEM (Fig. 3b–e).

In this Communication we have described the synthesis of the first PVDF-*b*-PVA block copolymer *via* sequential RAFT polymerization and basic hydrolysis, and the self-assembly of this original amphiphilic fluorinated block copolymer in water. The first PVDF block was prepared by RAFT polymerization of VDF in the presence of xanthate. Chain extension with VAc was then successfully performed, leading to a PVDF-*b*-PVAc block copolymer. The acetate groups of this copolymer were finally hydrolysed with K₂CO₃ to form the unprecedented PVDF-*b*-PVA amphiphilic fluorinated block copolymer. This amphiphilic block copolymer was subsequently self-assembled in water using the dialysis method. The quantitative hydrolysis was confirmed by FTIR and ¹H NMR spectroscopies. Although dehydrofluorination of the PVDF backbone caused by the basic treatment could be seen on the FTIR spectrum and from the polymer colour change (from white to dark brown), NMR

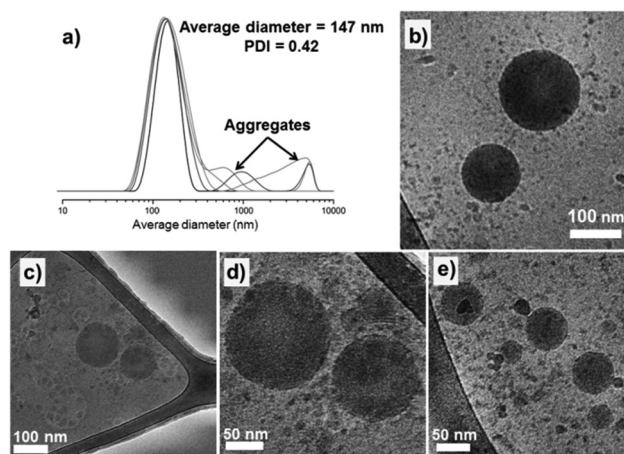


Fig. 3 (a) Intensity-average hydrodynamic diameter distribution of PVDF₅₁-*b*-PVA₁₇₂ amphiphilic block copolymers self-assembled in water ($c = 1.16 \text{ mg mL}^{-1}$) measured by DLS. (b, c, d, and e) Cryo-TEM micrographs of the PVDF₅₁-*b*-PVA₁₇₂ nano-objects self-assembled in water.

spectroscopy failed to detect clearly the expected CF=CH double bonds. This is likely due to the very small extent of the dehydrofluorination reaction under the conditions used here for the hydrolysis of PVAc. The self-assembly of the diblock copolymer in water, which was studied by DLS and cryo-TEM, led to the formation of a major population of spherical nano-objects constituted of a PVDF core and a PVA shell with diameters centered around 147 nm. Minor particle aggregation was also observed. This first foray into the synthesis and self-assembly of fluorinated amphiphilic PVDF- and PVA-containing block copolymers opens new opportunities in the study of fluorinated colloids.

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