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ARTICLE

Preparation of well-defined 2D-lenticular aggregates by self-assembly of PNIPAM-*b*-PVDF amphiphilic diblock copolymers in solution

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PNIPAM-*b*-PVDF (poly(*N*-isopropylacrylamide)-*b*-poly(vinylidene fluoride) amphiphilic block copolymers (BCPs) were synthesized via RAFT polymerization from PNIPAM macromolecular chain transfer agents (macro-CTA). PNIPAM was used as it is one of the few hydrophilic polymers soluble in dimethyl carbonate (DMC) and which can be synthesized using xanthate CTA with relatively good control. The polymerizations were conducted at 73 °C in DMC using two PNIPAM macro-CTAs of different molar masses and targeting various DPs for the PVDF block. The RAFT polymerization of VDF resulted in relatively well-defined BCPs ($\bar{D} \leq 1.50$). These amphiphilic BCPs were able to self-assemble into various morphologies such as spherical, crumpled, lamellar and lenticular 2D aggregates by changing the common solvent or the self-assembly protocol. The size of the aggregates could be controlled by varying the DP of the PVDF block. The polymers were characterized by ¹H and ¹⁹F NMR, SEC, TGA, DSC, and the assembled structures were studied by TEM, SEM and AFM. The thermosensitive behavior of the 2D lenticular aggregates was also examined.

Introduction

Poly(vinylidene fluoride) (PVDF), despite its remarkable properties such as piezoelectricity, ferroelectricity, chemical inertness, and biocompatibility^{1,2} has not received as much attention as other polymers in fields such as macromolecular engineering and polymer self-assembly. This is likely due to the synthesis constraints inherent to the peculiar reactivity of VDF. In addition, since VDF is a gaseous monomer, its polymerization usually requires the use of high-pressure vessel, not commonly available in every laboratories. However, in recent years the use of reversible-deactivation radical polymerization techniques to prepare PVDF and PVDF-based BCP have been investigated with some success.^{3–6}

RAFT polymerization and iodine-transfer polymerization of VDF lead to the accumulation of VDF tail-terminated chains (–CF₂CF₂CH₂–X, X = xanthate or iodine).⁷ These chains are not easily reactivated which hinders the preparation of PVDF-based block copolymers. So far, only PVDF-*b*-PVAc block copolymers (VAc = vinyl acetate) could be synthesized by chain extension of CF₂–CH₂–XA-terminated-PVDF (XA = xanthate) prepared by RAFT polymerization.⁸ Cobalt-mediated radical polymerization was shown to largely mitigate this end-group reactivity issue, and is arguably the best RDRP technique for VDF.^{4,9} However, it requires the use of air-sensitive organometallic compounds and is thus not easy to implement. Although, coupling strategies using click chemistry (CuAAC, or thia-Michael addition for example)^{10–13} are efficient, they may require the preparation of functional RAFT agents, and often lead to mixtures of block copolymers and homopolymers which are not easy to separate. Perhaps the most straightforward solution is the chain extension of RAFT macromolecular chain transfer agents (macro-CTAs) with PVDF.

To date, only four reports describe the preparation of PVDF-based block copolymers from RAFT macro-CTAs using sequential addition of VDF. Kostov et al. described the synthesis of PVAc-*b*-P(VDF-*co*-TFP) block copolymers (TFP = trifluoropropene).¹⁴ Girard et al. reported the preparation of PDMA-*b*-PVDF and PDMA-*b*-P(VDF-*co*-PMVE) by chain extension of a PDMA macro-CTA (DMA = dimethylacrylamide, PMVE = perfluorinated methyl vinyl ether).¹⁵ Guerre et al. reported the preparation of PEVE-*b*-PVDF (EVE = ethyl vinyl ether) block copolymers via the sequential combination of cationic RAFT polymerization of vinyl ethers and

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radical RAFT polymerization of VDF.¹⁶ Guerre et al. also reported the polymerization-induced self-assembly (PISA) of PVAc-*b*-PVDF block copolymers.¹⁷ VAc units were then hydrolyzed to prepare PVA-*b*-PVDF amphiphilic BCP (VA = vinyl alcohol).¹⁸ Only PDMA- and PVA-based PVDF-containing amphiphilic block copolymers have been prepared by sequential addition of VDF.

PVDF is a semi-crystalline fluorinated polymer, which as such, is appealing for the preparation of self-assembled block copolymer morphologies through crystallization-driven self-assembly (CDSA) in selective solvents. The self-assembly of non-crystalline (coil-coil) BCPs in solution is well-established.¹⁹ However, the complexity of the self-assembly process increases when one block of the BCP can crystallize. The formation of semi-crystalline BCP self-assembled structures can be viewed as a two-step process. The structures will first form by minimizing the unfavourable contacts between the solvophobic block and the solvent, and the semi-crystalline block will then start to crystallize in a second step, leading to the final structure. As crystallization takes place in the insoluble core, the initial morphology is either preserved or a morphological transformation into a novel structure is triggered.²⁰ Diverse polymeric architectures have been obtained by the crystallization-driven self-assembly (CDSA) approach. Arno et al. reported recently the preparation of PCL-*b*-PMMA-*b*-PDMA (CL = ϵ -caprolactone, MMA = methyl methacrylate) biocompatible and biodegradable 1D cylindrical and 2D platelet micelles via CDSA. Interestingly, they were able to control the dimensions and dispersity of the self-assembled nanostructures.²¹ Li et al. have reported a poly(L-lactide)-based diblock glycopolymer that assembled into 1D cylinders and 2D diamond-shaped platelets.²² Qiu and Gao et al. have reported the preparation of rectangular and hollow structures from polymer blends.²³

To date, most reported coil-crystalline self-assembled aggregates with control over their size were prepared via CDSA, requiring heating and aging steps. The most common crystalline blocks in these assembled structures are PEO (poly(ethylene oxide)),²⁴ PCL,^{21,25} PE (poly(ethylene)),²⁶ and PFS (poly(ferrocenyldimethylsilane)).^{21,27–30} Only a few studies describe the self-assembly in solution of BCPs containing a fluoropolymer block,^{10,12,18,31} and even fewer are dealing with the CDSA behavior of these fluorinated BCPs.^{10,17}

Dimethyl carbonate (DMC) was shown to be the solvent of choice for the RAFT polymerization of VDF as it allows relatively fast polymerization and acceptable level of transfer reactions.^{3,6} However, one major limitation of the chain extension with PVDF approach to prepare amphiphilic PVDF-based BCPs is the rather low solubility of hydrophilic macro-CTAs in DMC.

PNIPAM is hydrophilic and soluble in DMC at the required temperature for VDF polymerization (ca. 73 °C). PNIPAM features a near body lower critical solution temperature (LCST = 32 °C), and biocompatibility, and is thus very appealing for biomedical applications.^{32–36} So far the reports mentioning both PVDF and PNIPAM only describe polymer blends for the preparation of electrospun fibers or flat membranes, or the grafting of PNIPAM

on PVDF membranes.³⁷ To date, the preparation of PNIPAM-*b*-PVDF block copolymers (BCPs) and the study of their self-assembly in selective solvents have not been reported.

The present study recounts the synthesis via RAFT sequential addition of VDF, characterization and self-assembly in solution of amphiphilic PNIPAM-*b*-PVDF diblock copolymers. The self-assembly of these BCPs in water led to a wide range of morphologies such as spherical, crumpled-spherical, lamellar and well-defined 2D lenticular aggregates without the need for thermal annealing. The formation and molecular arrangement of these self-assembled structures are discussed, and the thermoresponsive behaviour of the PNIPAM-containing aggregates in water was also examined.

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-methoxycarbonyl) ethyldithiocarbonate (CTA_{XA}) was prepared according to the method described by Liu et al.³⁸ *tert*-Amyl peroxy-2-ethylhexanoate (Trigonox 121, purity 95%) was purchased from AkzoNobel (Chalons-en-Champagne, France). Ethanol (EtOH), dimethyl carbonate (DMC), diethyl ether, toluene, laboratory reagent grade hexane (purity >95%), *N*-isopropylacrylamide (NIPAM, purity 97%) were purchased from Sigma Aldrich. All deuterated solvents were purchased from Eurisotop. NIPAM was recrystallized twice from hexane/toluene (10/1, v/v).

Measurements

Nuclear Magnetic Resonance (NMR). The NMR spectra were recorded on a Bruker AV III HD Spectrometer (400 MHz for ¹H and 376 MHz for ¹⁹F).

Coupling constants and chemical shifts are given in hertz (Hz) and parts per million (ppm), respectively. The experimental conditions for recording ¹H and ¹⁹F NMR spectra were as follows: flip angle, 30°; acquisition time, 4 s (2 s for ¹⁹F NMR); pulse delay, 1 s (2 s for ¹⁹F NMR); number of scans, 16; and pulse widths of 9.25 and 11.4 μ s for ¹H and ¹⁹F NMR, respectively.

Size-Exclusion Chromatography (SEC). Size exclusion chromatograms were recorded using a Triple detection GPC system from Agilent Technologies with its corresponding Agilent software, dedicated to multi-detector GPC calculation. The system used two ResiPore 3 μ m 300 x 7.5 mm columns with DMF as the eluent with a flow rate of 1 mL/min and toluene as flow rate marker. The detectors used were a PL0390-06034 capillary viscometer and a 390-LC PL0390-0601 refractive index detector. The entire SEC-HPLC system was thermostated at 35 °C. Low dispersity PMMA standards were used for the calibration. Typical sample concentration was 10 mg/mL.

Differential Scanning Calorimetry (DSC). DSC measurements were performed on 2–3 mg samples on a TA Instruments DSC Q20 equipped with an RCS90 cooling system. For all measurements, the following heating / cooling cycle was employed: cooling from 40 °C to –73 °C, isotherm at –73 °C for 5 min, first heating ramp from –73 °C to 200 °C at 10 °C/min, isotherm at 200 °C for 5 min, cooling stage from 200 °C to –73 °C at 10 °C/min, isotherm plateau at –73 °C for 1 min, second heating ramp from –73 °C to 200 °C at 10 °C/min, isotherm at 200 °C for 1 min, and last cooling stage from 200 °C to 40 °C. Calibration of the instrument was performed with noble metals and checked before analysis with an indium sample. Melting points were determined at the maximum of the enthalpy peaks.

Thermogravimetric analysis (TGA). TGA analyses were carried out with a TA Instruments TGA G500 from 20 °C to 800 °C. A heating rate of 10 °C min^{–1} was used under air atmosphere with a flow rate of 60 mL min^{–1}. Dry sample weight of 3 mg was used.

Dynamic light scattering (DLS). DLS measurements of polymer solutions were carried out in a Malvern ZEN1600 using a quartz cuvette. Refractive indices of solvent mixtures were determined using the following equation:

$$\frac{n_m^2 - 1}{n_m^2 + 2} = y_1 \frac{n_1^2 - 1}{n_1^2 + 2} + y_2 \frac{n_2^2 - 1}{n_2^2 + 2} \quad (\text{Equation 1})$$

Where n_1, n_2, n_m are the solvent 1, solvent 2 and, mixture refractive indices at a certain temperature, and y_1, y_2 are solvent 1 and solvent 2 volume fractions. Viscosities of solvent mixtures were extracted from scientific publications^{39,40} and online resource.⁴¹

Transmission electron microscopy (TEM). TEM studies were conducted using a JEOL 1400+ instrument equipped with a numerical camera, operating with a 120 kV acceleration voltage at 25 °C. To prepare TEM samples, a drop (10.0 µL) of micellar solution was placed onto a Formvar/carbon coated copper grid for 60 s, blotted with filter paper and dried under ambient conditions. All TEM grids were prepared from self-assembly solutions without further dilution.

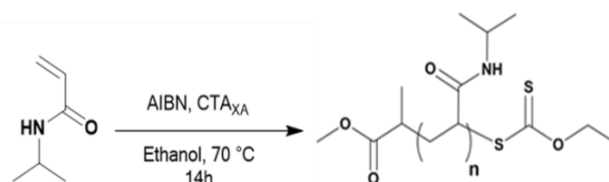
Scanning electron microscopy (SEM). SEM analyses were conducted using a Hitachi S-4500 instrument operating at spatial resolution of 1.50 nm at 15 kV energy. The samples were folded on a 45° SEM Mount after being coated with an ultrathin layer of electrically conducting Platinum deposited by high-vacuum evaporation.

Atomic force microscopy (AFM). AFM images were obtained using a Nanoman V from Bruker Instrument employing repulsive-Tapping mode, and a tip Nanosensors PPP NCL freq = 158 kHz Q factor = 350, $k \sim 14 \text{ N/m}$, $R_{\text{tip}} \sim 5 \text{ nm}$.

X-Ray diffraction (XRD). XRD powder patterns were carried out on a Philips X'pert Pro MPD diffractometer by using Ni-filtered CuKα1 radiation ($\lambda = 1.5406 \text{ \AA}$) in Bragg–Brentano scanning mode with a 2θ angle range from 5–60°, and a time per step of 50 s.

Synthesis

PNIPAM-XA synthesis.

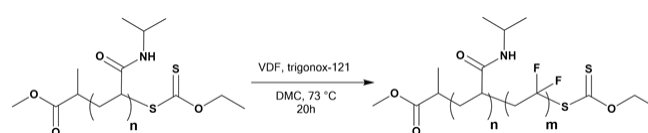


Scheme 1. RAFT/MADIX synthesis of PolyNIPAM macro CTA.

A typical polymerization (Entry 1 in Table 1) of NIPAM was performed as follows: NIPAM (6 g, 53.02 10^{-3} mmol), AIBN (25 mg, 0.15 10^{-3} mmol) and CTA_{XA} (315 mg 1.51 10^{-3} mmol) were dissolved in ethanol (9 mL) in a round bottom flask, under magnetic stirring at 20 °C. The solution was degassed by N₂ bubbling for 20 min. Then, the flask was placed in an oil bath at 70 °C for 14 h. The reaction was followed by ¹H NMR and was stopped at NIPAM conversion > 99 %. The polymer was isolated by precipitation in chilled ether and centrifugation and was dried overnight under vacuum at 30 °C.

¹H NMR (400 MHz, (CD₃)₂CO, δ (ppm), Figure S1): 0.9 – 1.28 (m, –NH–CH(CH₃)₂–; –CH(CH₃)(C=O)–), 1.28 – 1.90 (m, –CH₂–CH–(C=O)–; CH₃–CH₂–O–), 1.90 – 2.50 (m, –CH₂–CH–(C=O)–), 3.64 (–O–CH₃, (R CTA)) 3.95 – 4.25 (m, –NH–CH(CH₃)₂), 4.50 – 4.76 (O–CH₂–CH₃ (Z CTA)), 6.50 – 8.00 (m, –NH–CH(CH₃)₂).

PNIPAM-*b*-PVDF synthesis.



Scheme 2. RAFT/MADIX synthesis of PNIPAM-*b*-PVDF block copolymers using PNIPAM macro CTA.

Typical polymerization of PNIPAM-*b*-PVDF block copolymers was performed as follow: A thick 8 mL Carius tube containing PNIPAM-XA macroCTA (Table 1, entry 3) (658 mg, 2.34 10^{-4} mmol), DMC (5 mL) and the initiator (Trigonox-121) (11 mg, 4.68 10^{-5} mmol) were sonicated for 5 min or until complete dissolution of PNIPAM-XA. Then, the tubes were degassed with three freeze–pump–thaw cycles to remove oxygen. The gaseous VDF monomer (1.5 g, 23.42 10^{-3} mmol) was transferred into the Carius tubes and condensed in the tube using a liquid nitrogen bath. The tubes were then sealed, before being placed horizontally in a shaking water bath thermostated at 73 °C (see Scheme S1). After 20 hours, the tube was placed into a liquid nitrogen bath and the opened. After return to room temperature, the crude sample was precipitated twice in a

tenfold excess of chilled pentane. The PNIPAM-*b*-PVDF block copolymers were recovered by centrifugation at 4000 rpm for 5 min in 50 mL conical centrifuge tubes. The polymers were dried overnight under vacuum at 25 °C. Polymerization yields were determined gravimetrically (mass of dried precipitated polymers / mass of monomer introduced in the Carius tube).

¹H NMR (400 MHz, (CD₃)₂CO, δ (ppm), Figure S2): 0.90 - 1.26 (m, -NH-CH(CH₃)₂-), 1.28 - 1.90 (m, -CH₂-CH-NIPAM), 1.90 - 2.50 (m, -CH₂-CH-NIPAM), 2.16 - 2.37 (t, -CF₂-CH₂-CH₂-CF₂-, VDF-VDF HH reverse addition), 2.66 - 3.01 (t, -CF₂-CH₂-CF₂-, VDF-VDF HT regular addition), 3.8 (s, CH₃-O-(C=O)-(CH₃)CH-), 3.95 - 4.25 (m, -NH-CH(CH₃)₂), 4.40 (t, CH₂-CF₂-CF₂-CH₂-S-), 4.60 - 4.78 (q, -S(C=S)OCH₂-CH₃, ³J_{HH} = 7.1 Hz), 6.09 - 6.50 (tt, -CH₂-CF₂-H, ²J_{HF} = 55.6 Hz, ³J_{HH} = 4.7 Hz), 6.50 - 8.00 (m, -NH-CH(CH₃)₂).

¹⁹F NMR (376 MHz, (CD₃)₂CO, δ (ppm), Figure S3): -115.64 (-CH₂-CF₂-CF₂-CH₂-CH₂-, VDF-VDF HH reverse addition), -114.45- (-CH₂-CF₂-H), -113.36 (-CH₂-CF₂-CF₂-CH₂-CH₂-, HH reverse addition), -113.09 (CH₂-CF₂-CF₂-CH₂-S-), -112.69 (-CH₂-CF₂-CF₂-CH₂-S-), -107.40 (-CF₂-CH₃) -94.81 (-CH₂-CH₂-CF₂-CH₂-, TT reverse addition), -93.00 (CH₃-O-(C=O)-O-CH₂-CH₂-CF₂-, DMC-initiated PVDF), -92.50 (PNIPAM-CH₂-CF₂-), 92.06 (-CH₂-CF₂-CH₂-CF₂-H), -91.43 (-CH₂-CH₂-CF₂-CH₂-CF₂-CH₂-CF₂-, regular VDF-VDF HT addition), -91.00 (-CH₂-CF₂-CH₂-, regular VDF-VDF HT addition).

The degree of polymerization (DP) of the PNIPAM block were calculated from the ¹H NMR spectrum of the purified BCP using the equation found in the supporting information (See S2, Eq. 2). DP values were then used for the determination of the experimental M_n (S2, Eq. 4). The degree of polymerization (DP) of the PVDF block was determined using equation 5 from the integral of the signals (at 0.9 – 1.28 ppm) corresponding to the methyl groups (-CH₃) of the NIPAM units, used as reference, and the integral of the signals of the -CH₂- group of the normal (HT) VDF additions (at 2.70–3.19 ppm). The signal of the -CH₃ of the NIPAM unit is the only signal visible for BCP with a DP higher than 150. Regarding the reverse (TT) VDF additions, the average number of monomer additions occurring per chain between two degenerative transfers increases with increasing [VDF]₀/[CTA]₀. However, the total amount of TT (or HH) VDF additions (intra-chain + chain-end) stabilizes to identical proportion (ca. 4.1%) for PVDF homopolymerization as previously reported by our group.⁷ As the signals assigned to these inversions overlap with signals of the PNIPAM macro-CTA, a 1.041 multiplying factor was employed for the determination of the DP of PVDF.

$$DP_{PVDF} = \frac{\frac{1}{2} \int_{2.70}^{3.19} -CH_2 (HT \text{ VDF additions})}{\frac{1}{6} \int_{0.9}^{1.28} -NH-CH(CH_3)_2} \times 1.041 \quad (\text{Equation 5})$$

Molar masses were then calculated using equation (6) (with M_{n,PNIPAM-XA} calculated using eqn (4) and (2)):

$$M_{n,NMR} = M_{n,PNIPAM-XA} + DP_{PVDF} \times M_{n,VDF} \quad (\text{Equation 6})$$

Theoretical molar masses were calculated using equation (6) with yield = conversion and the [VDF]₀/[PNIPAM-XA]₀ ratios listed in Table 1.

$$M_{n,theo} = \frac{[VDF]_0}{[PNIPAM-XA]_0} \times Yield \times M_{n,VDF} + M_{n,PNIPAM-XA} \quad (\text{Equation 7})$$

With M_{n,VDF} = 64.03 g mol⁻¹.

Self-assembly

Preparation of block copolymer solutions

Stock solutions of 2 mg mL⁻¹ of block copolymer were prepared in DMF, acetone or THF at room temperature using magnetic stirring until full solubilisation.

Nanoprecipitation

Glass vials containing 2 mL of non-solvent and a magnetic bar were placed on a stirring plate. To each vial 0.1 mL of block copolymer solution (2 mg mL⁻¹) in DMF were added dropwise. After 1h of stirring, samples were analysed by DLS and TEM. Final concentration of the block copolymer was 0.1 mg mL⁻¹ in DMF: water (1:20).

Note: Difference between precipitation and nanoprecipitation.

-Polymer precipitation refers to a polymer purification technique in which a solution of the polymer is cast dropwise into a non solvent. Upon contact between the two miscible solvents, the polymer crashes out of solution while the impurities remained in the solvent phase. In the case of block copolymers, for an efficient precipitation the different blocks must be insoluble in the non-solvent.

-In contrast, polymer nanoprecipitation refers to a BCP self-assembly technique in which a polymer solution is cast dropwise into a solvent selective for one of the blocks. The insoluble block forms the core of the self-assembled structure while the soluble block act as a steric stabilizer of the polymer morphology.

Solvent switch

Vials containing 0.5 mL of the stock solution (2 mg mL⁻¹) in different solvents (THF, DMF and acetone) were placed on a stirring plate. Water (2, 3 or 4 mL) was added dropwise using a syringe pump at a fixed rate of (4 mL h⁻¹). 10 μL were taken to prepare TEM samples at 1:4, 1:6 and 1:8 solvent:non-solvent ratios.

Thermally-induced Crystallisation-Driven Self-assembly (Ti-CDSA)

A 5 mg mL⁻¹ PNIPAM₂₅-*b*-PVDF₃₅ solution in DMF was self-assembled by adding water to a 1:1 solvent: non-solvent ratio, and this solution was then heated at 90°C for 30 min and slowly cooled down to room temperature.

Results and discussion

PNIPAM-XA macro-CTAs were synthesized by RAFT polymerization using CTA_{XA} following protocols described previously by Sistach *et al.*⁴² The reactions were stopped when the NIPAM conversion

reached at least 99%. After purification by precipitation, ^1H NMR spectroscopy of the resulting PNIPAM-XA macro-CTAs was employed to determine their molar masses and degrees of polymerization (DP). Amphiphilic PVDF-based block copolymers with PVDF of different DPs were prepared from these PNIPAM macro-CTAs (see Table 1) by chain extension with VDF in DMC (a common solvent for PNIPAM and PVDF allowing relatively high VDF polymerization rate) using Trigonox 121 as the radical initiator.

^{19}F NMR spectroscopy of the resulting polymers showed the successful chain extension of PVDF from the PNIPAM macro-CTAs. The presence of the signals of $-\text{CF}_2-\text{CF}_2-\text{CH}_2-\text{XA}$ at $\delta = -113.09$ ppm and -112.69 ppm and of $-\text{CH}_2-\text{XA}$ at $\delta = 4.45$ ppm and $-\text{CH}_2-\text{SC(S)-O}-\text{CH}_2-$ at $\delta = 4.72$ ppm in the ^{19}F NMR and ^1H NMR spectra respectively (Figure S4 and S3b), indicates the formation of the diblock copolymers.

As expected, the polymerization of VDF was accompanied by a non-negligible amount of transfer to DMC. The characteristic signals of these transfer reactions can be observed in the ^1H NMR spectrum (Figure S3a and S3b) as a triplet of triplets at 6.3 ppm corresponding

to the $-\text{CF}_2\text{H}$ chain-end, and in the ^{19}F NMR spectrum (Figure S4) as a doublet of triplet at -114.45 ppm ($-\text{CF}_2\text{H}$) and a multiplet at -107.3 ppm corresponding to the CF_2CH_3 chain end. The ^1H NMR spectrum also shows: a singlet at 5.77 ppm assigned to the DMC-xanthate adduct ($\text{CH}_3\text{O}(\text{C}=\text{O})\text{O}-\text{CH}_2-\text{XA}$, Figure S3a), eliminated by the precipitation step (Figure S3b); and a well-defined triplet at 4.35 ppm and a singlet at 3.73 ppm assigned to the $-\text{CH}_2-$ and $-\text{CH}_3$ groups of the DMC moieties of the DMC-initiated-PVDF chains, respectively. The RAFT polymerization of VDF is accompanied by a progressive loss of chain-end functionality (loss of xanthate group).⁶⁻⁷ This phenomenon has previously been reported for the synthesis of PVAc-*b*-PVDF BCPs.¹⁷ This loss of functionality can be very extensive. Here the remaining molar fraction of xanthate-functionalized chain end derived from the ^{19}F NMR spectra (Figure S4 and calculations S5) were 19.2, 5.4, 2.3 and 1.4 % for the PNIPAM₃₅-*b*-PVDF₆₀, PNIPAM₃₅-*b*-PVDF₁₀₀, PNIPAM₃₅-*b*-PVDF₁₅₀, and PNIPAM₃₅-*b*-PVDF₄₅₀ copolymers respectively.

Table 1. Synthesis and characterization of PNIPAM macro-CTA, and PNIPAM-*b*-PVDF block copolymers prepared by RAFT polymerization of VDF in DMC at 73 °C.

Entry	CTA	M	$[\text{M}]_0/[\text{CTA}]_0$	Reaction time (h), Solvent	yield(%)	$\text{DP}_{(\text{NMR})}(\text{R})$	$\text{M}_{\text{n}(\text{theo})}^{\text{d}}$ (g/mol)	$\text{M}_{\text{n}(\text{NMR})}(\text{R})^{\text{e}}$ (g/mol)	$\text{M}_{\text{nSEC}}^{\text{f}}$ (g/mol)	Đ^{f}
1	CTA _{XA}	NIPAM	25	14, EtOH	>99	25 ^a	3000	3000	3200	1.30
2	PNIPAM ₂₅ -XA	VDF	50	20, DMC	60 ^b	35 ^c	4900	5300	6700	1.38
3	CTA _{XA}	NIPAM	35	14, EtOH	>99	35 ^a	4100	4200	4400	1.19
4	PNIPAM ₃₅ -XA	VDF	100	20, DMC	60 ^b	60 ^c	8000	8000	7500	1.29
5	PNIPAM ₃₅ -XA	VDF	150	20, DMC	61 ^b	100 ^c	10000	10600	9200	1.36
6	PNIPAM ₃₅ -XA	VDF	200	20, DMC	62 ^b	150 ^c	12100	13800	9800	1.43
7	PNIPAM ₃₅ -XA	VDF	600	20, DMC	61 ^b	450 ^c	27600	33000	25500	1.50

Reactions conditions: (i) (entry 1 and 3) NIPAM homopolymerization: $[\text{I}]/[\text{CTA}_{\text{XA}}] = 0.1$ with $\text{I} = \text{AIBN}$ and $\text{CTA}_{\text{XA}} = O\text{-ethyl-}S\text{-(1-methoxycarbonyl)ethylthiocarbonate}$, $T = 70$ °C; (ii) (entries 2 and 4-7) chain extension of PNIPAM₃₅-XA: $[\text{I}]/[\text{CTA}_{\text{XA}}] = 0.2$ with $\text{I} = \text{Trigonox 121}$, $T = 73$ °C.

^aDetermined by ^1H NMR using equation (2). ^bDetermined gravimetrically. ^cDetermined by ^1H NMR using equation (5). ^dCalculated using yield as conversion and equations (3) for PNIPAM and (7) for the BCP. ^eCalculated from DP_{NMR} using equations (4) for PNIPAM and (6) for PVDF. ^fDetermined by SEC (RI detector).

Despite these transfer reactions and loss of functionality, the chain extension of PNIPAM macro-CTAs with PVDF produced relatively well-defined BCP with dispersity below 1.50 and monomodal SEC traces without shoulders or significant tailing (Figure 1). These SEC traces also show a clear shift towards higher molar masses with the increasing DP of PVDF.

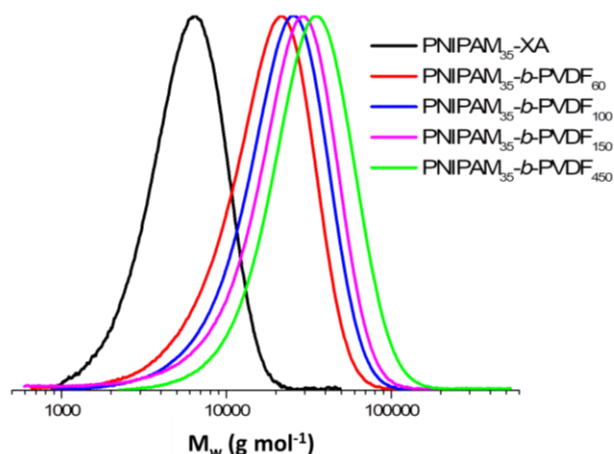


Figure 1. Normalized SEC traces (viscometric detector) of: PNIPAM₃₅-XA (black trace), PNIPAM₃₅-*b*-PVDF₆₀ (red trace), PNIPAM₃₅-*b*-PVDF₁₀₀ (blue trace), PNIPAM₃₅-*b*-PVDF₁₅₀ (green trace) and PNIPAM₃₅-*b*-PVDF₄₅₀ (pink trace) after purification by precipitation in chilled ether for PNIPAM or cold pentane for the BCPs.

These amphiphilic block copolymers were then used to prepare self-assembled morphologies in different solvents.

Note on solvents: in the following self-assembly study, three solvents were used as good solvents for both the PNIPAM and the PVDF segments: Acetone, THF and DMF. All of these solvents are good solvents of PNIPAM. Bottino et al.⁴³ investigated the solubility of a 450,000 g mol⁻¹ PVDF in 46 liquids and concluded that DMF is a solvent of PVDF, while acetone and THF are good swelling agents. The PVDF blocks synthesized here have much lower molar mass (a PVDF with a DP = 450 would have a Mn of 28,800 g mol⁻¹), it is thus not surprising that THF and acetone behave as good solvents especially considering the low concentrations used (2 mg mL⁻¹, whereas Bottino et al. aimed at preparing 100 mg mL⁻¹ solutions). In addition, the self-assembly described and discussed below concerns PNIPAM-*b*-PVDF block copolymers which solubility would be enhanced by the PNIPAM block. These copolymers indeed readily dissolved in acetone, and in THF although gentle heating of the solution was necessary for the latter.

Self-assembly of amphiphilic BCP using rapid solvent exchange, usually lead to the formation of colloidal objects via microphase separation. The final structure of these block copolymer colloids is primarily dictated by the volume fraction of the blocks and by the interfacial surface tensions. A feature of the nanoprecipitation process (which consists in the dropwise addition of the BCP solution into a selective solvent under vigorous stirring) is the ability to access kinetically trapped morphologies in nonequilibrium states due to short mixing time. This kinetic trapping is even more pronounced in the case of semicrystalline polymer such as PVDF. In such case, the PVDF segments often crystallize before the polymer chains can reach the equilibrium morphology during phase separation.

The self-assembly of the PNIPAM-*b*-PVDF block copolymers was achieved via nanoprecipitation in water from a dilute DMF BCP solution. After stirring for 1h, samples were analyzed by DLS and

TEM. This approach led to the formation of spherical aggregates of roughly 20 to 60 nm in diameter (Figure 2).

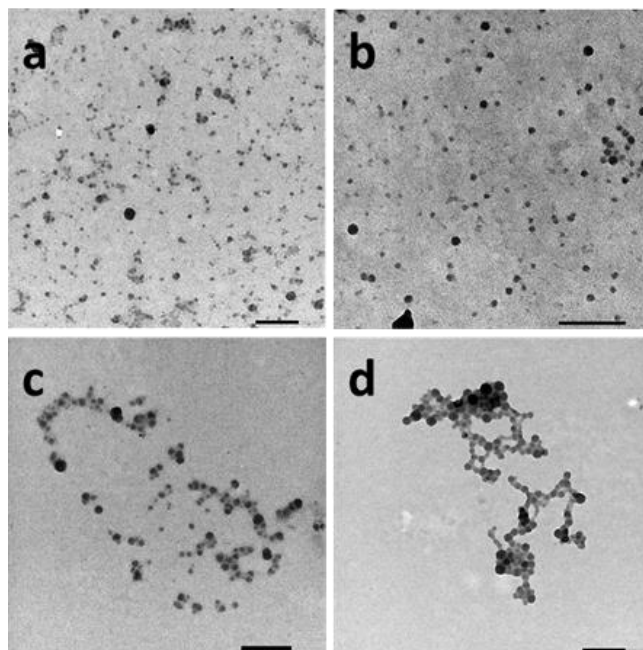


Figure 2. TEM images of spherical aggregates prepared from (a) PNIPAM₃₅-*b*-PVDF₆₀, (b) PNIPAM₃₅-*b*-PVDF₁₀₀, (c) PNIPAM₃₅-*b*-PVDF₁₅₀ and (d) PNIPAM₃₅-*b*-PVDF₄₅₀. All samples were prepared by nanoprecipitation in water from BCP solutions in DMF at 2 mg mL⁻¹ (final concentration = 0.1 mg mL⁻¹ in DMF: water (1:20)). Scale bars correspond to 200 nm.

The particle sizes measured by TEM were in good agreement with the average hydrodynamic diameters measured by DLS (Figure S6) ranging between 30 and 80 nm and increasing with the DP of the core-forming PVDF block.

Solvent switch experiments (slow addition of water into a solution of PNIPAM₃₅-*b*-PVDF_x in DMF, THF or acetone) were also performed using three (1:4, 1:6 and 1:8) solvent: non-solvent ratios.

When DMF was employed as common solvent and water as selective solvent for the PNIPAM block, irregular crumpled spherical aggregates were obtained with all the solvent: non-solvent ratios tested (Figure 3). CDSA self-assembled polymers are thought to favor the formation of aggregates with low interfacial curvature.⁴⁴ These morphologies may be due to a co-nonsolvency of PNIPAM blocks when DMF molar fraction changes in the solvent mixture, provoking the collapse of the metastable aggregates before attaining the spherical morphology obtained by nanoprecipitation. A reversible collapse-swelling behavior has already been observed in PNIPAM latexes in water-DMF mixtures.⁴⁵ When DMF molar fraction was between 0.02 and 0.25, the latex volume was smaller from that observed in pure water.

When THF was used as the good solvent for both blocks, solvent switch protocols led to formation of flat sheet morphologies, presumably 2D bilayer aggregates (Figure 4).

When acetone was used as the good solvent, well-defined flat 2D lenticular morphologies with relatively low dispersity and good dimensional control were obtained (Figures 5-7).

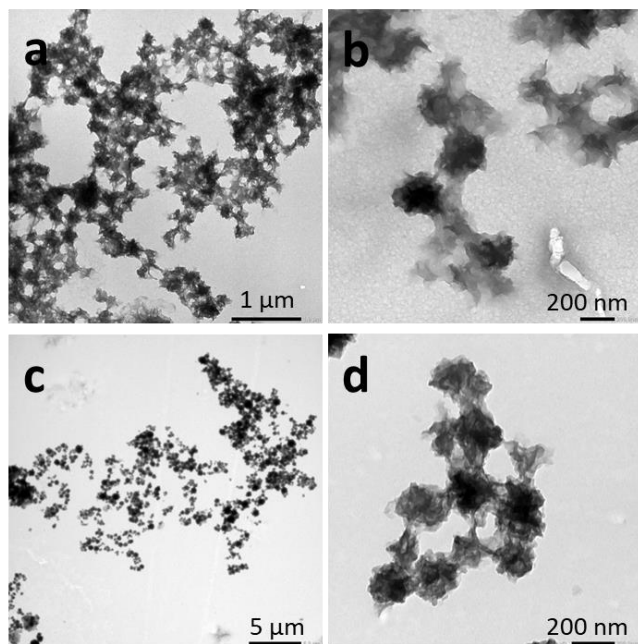


Figure 3. TEM images of crumpled aggregates obtained by solvent switch of (a and b) PNIPAM₂₅-*b*-PVDF₃₅, and (b and c) PNIPAM₃₅-*b*-PVDF₄₅₀ in DMF at 2 mg mL⁻¹. Final concentration = 0.4 mg mL⁻¹ in DMF: water (1:4) mixture.

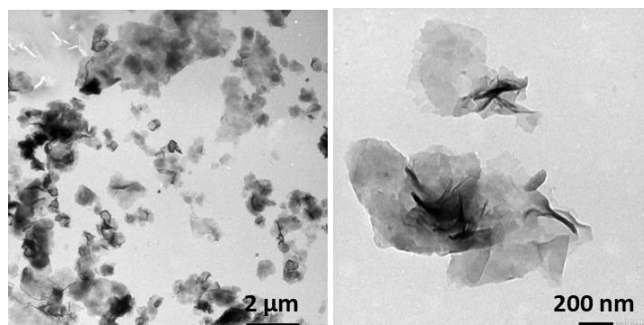


Figure 4. TEM images of the bilayer aggregates obtained by solvent switch of PNIPAM₃₅-*b*-PVDF₄₅₀. Initial polymer concentration in THF = 2 mg mL⁻¹. Final concentration = 0.4 mg mL⁻¹ in THF: water (1:4) mixture. Water addition rate was 4 mL h⁻¹.

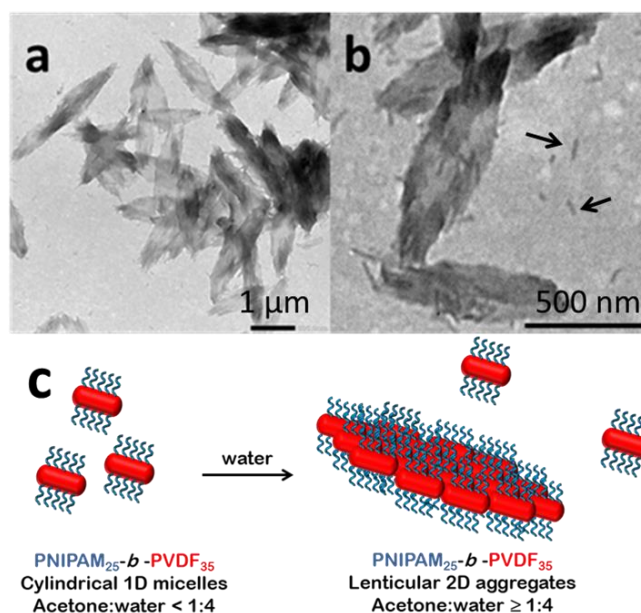


Figure 5. TEM images of 2D lenticular micelles obtained by self-assembly via solvent switch protocol of PNIPAM₂₅-*b*-PVDF₃₅ (a - b). Initial BCP concentration in acetone = 2 mg mL⁻¹. Final concentration = 0.4 mg mL⁻¹ in acetone: water (1:4) mixture. Non-solvent addition rate was 4 mL h⁻¹. Arrows indicate the isolated 1D micelles. Schematic representation of the proposed mechanism of formation of PNIPAM₂₅-*b*-PVDF₃₅ lenticular aggregates from short 1D rod-like micelles (c).

In the case of the PNIPAM₂₅-*b*-PVDF₃₅ BCP these lenticular objects had an average length and width of 600 nm and 250 nm respectively, and ragged edges that seemed to be formed by aggregation of smaller 1D rod-like aggregates (Figure 5b and S7). Crystallization-induced aggregation of micelles has already been observed for PB-*b*-PEO BCPs.⁴⁶ These short 1D micelles have an average length and width of 98 and 19 nm, respectively.

In contrast, the PNIPAM-*b*-PVDF BCP prepared from the PNIPAM₃₅ macro-CTA self-assembled into lenticular objects with much smoother-looking edges with average lengths of 200, 600, 1000 and 2300 nm and average widths of 90, 250, 400 and 850 nm for PVDF DPs of 60, 100, 150 and 450 (Figure 6).

The length and width of the lenticular 2D micelles showed a linear dependence to the degree of polymerization of PVDF up to 150 (Figure S7). The loss of linearity observed for the PVDF₄₅₀ BCP may be due to the poor accuracy on the DP value calculated from weak NMR signals. The real DP of this PVDF block might be closer to 300 than the calculated 450.

Due to their relatively large size (in the micrometric range), these morphologies were not colloidally stable and sedimented over time (ca. 14h). However, they were easily redispersed by simple shaking.

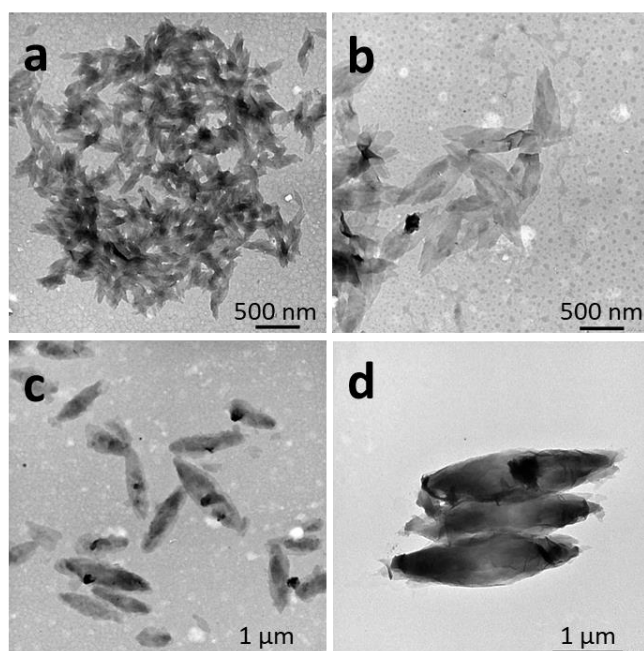


Figure 6. TEM images of representative self-assembled 2D lenticular morphologies prepared from (a) PNIPAM₃₅-*b*-PVDF₆₀, (b) PNIPAM₃₅-*b*-PVDF₁₀₀, (c) PNIPAM₃₅-*b*-PVDF₁₅₀ and (d) PNIPAM₃₅-*b*-PVDF₄₅₀. All samples were prepared via solvent switch in acetone: water mixtures. Initial polymer concentration in acetone = 2 mg mL⁻¹. Final concentration = 0.4 mg mL⁻¹ in acetone: water (1:4) mixture. Water addition rate = 4 mL h⁻¹.

The shape and size of these morphologies were not affected by the concentration of the initial BCP solutions over the concentration range studied (Figure S9). In addition, once the self-assembled structures were formed in acetone: water mixture (1:4) they did not evolve within the 2-week observation time, they thus seem to be kinetically trapped. Increasing the water content of the self-assembly media or decreasing the acetone content (by evaporation) of the solvent mixture only affected the aggregation rate. However, the lenticular shape of these assemblies was strongly affected by the ratio of the length of the hydrophobic and hydrophilic blocks. The morphologies were rather patchy with sharp edges for the PNIPAM₂₅-*b*-PVDF₃₅ (Figure 5), while better-defined objects were found for PNIPAM₃₅-*b*-PVDF_n BCPs with $n > 60$ (Figure 6). Better defined lenticular objects were obtained as higher DPs of the PVDF were targeted.

The PVDF fraction of these BCP was crystalline as determined from DSC thermograms (Figure S10). However, the PVDF crystallinity could not be observed on these self-assembled structures by electron diffraction during TEM analysis. This was ascribed to the thinness of these lenticular objects, undergoing fast amorphisation under the electron beam.

Nevertheless, the XRD diffraction pattern (Figure 8) obtained from freeze-dried 2D aggregates formed via self-assembly of a 2 mg mL⁻¹ solution of PNIPAM₃₅-*b*-PVDF₁₀₀ BCP in acetone:water (1:4) suggests that the PVDF phase of these aggregates was indeed crystalline and in the α -form with characteristic 2θ peaks at 17.6 (100), 18.5 (020), 19.8 (110), 26.5 (021), 36.1 (200) and 39 (002).⁴⁷ The α -crystal phase

is hexagonal, with aligned polymer chains anti-parallel to each other, in the conformation of *trans*-gauche-*trans*-gauche' (TG₂GTG'). α -form is the most common and spontaneously forming crystalline form of PVDF.^{48, 49}

SEM images of the lenticular objects (Figure 7) suggest that they can fold and twist to an extent, and are often stacked on top of each other, making their characterization quite difficult. AFM images (Figure 9) confirmed the stacking of the objects but also revealed the increase of their thickness with the increase of the DP of the PVDF block.

The presence of short cylindrical 1D micelles (Figure 6b) suggests that the lenticular morphologies may form by aggregation these smaller structures. In addition, the thickness of the lenticular aggregates seems to be related to the length and folding of the PVDF segments. As the degree of polymerization of the PVDF core-forming block increased, the thickness of the aggregates increased.

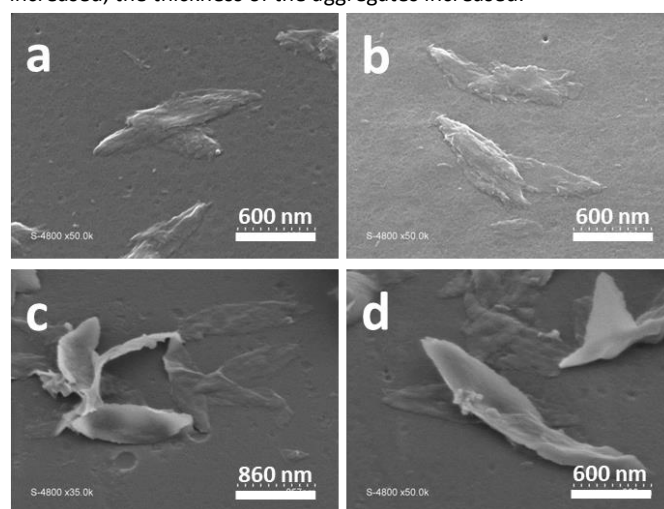


Figure 7. SEM images of 2D lenticular objects prepared from: PNIPAM₂₅-*b*-PVDF₃₅ (a, b), PNIPAM₃₅-*b*-PVDF₄₅₀ (c, d).

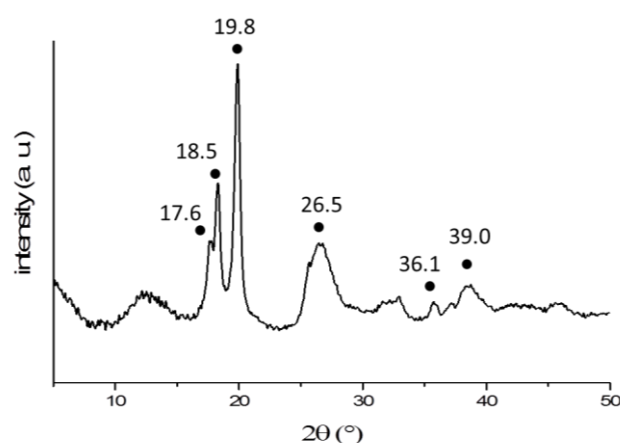


Figure 8. X-Ray diffraction pattern of freeze-dried 2D lenticular aggregates obtained from PNIPAM₃₅-*b*-PVDF₁₀₀ BCP. Black dots indicate the characteristic peaks of α -phase of PVDF.

Since the PVDF in these aggregates is crystallized in the α -form, the number of folding of the PVDF chains can be estimated. In α -form

crystal, 0.462 nm is the dimensions of 2.5 VDF units in that specific conformation.⁵⁰ Crystallized PVDF chains of DP 60, 100, 150 and 450 would thus extend over 11.1, 18.5, 27.7 and 83.2 nm, respectively in α -form. The thicknesses of the lenticular objects derived from the AFM topographic images shown in Figure 9 are in agreement with these calculations for PVDF₆₀, PVDF₁₀₀ and PVDF₁₅₀. Figure 9a, corresponding to PNIPAM₃₅-*b*-PVDF₆₀, shows a thickness of 10-15 nm. Figure 9b and Figure S11, corresponding to PNIPAM₃₅-*b*-PVDF₁₀₀ give a thickness of about 40 nm. This value is roughly twice the calculated length of the PVDF₁₀₀ (18.5 nm). This is because the AFM images in Figure 9b show two aggregates stacked on top of each other. The thickness measured for the PNIPAM₃₅-*b*-PVDF₁₅₀ in Figure

9c is 30 nm which also is in agreement with the corresponding calculated value of 27.7 nm. In the case of the PNIPAM₃₅-*b*-PVDF₄₅₀ BCP, the calculated thickness of 83.2 nm does not match the thickness of 10 nm measured on Figure 9d. This discrepancy may be explained by considering that in this case the crystallized PVDF chains are folded rather than extended. Indeed, the calculated and measured values can be reconciled if the PVDF₄₅₀ chains were folded 7 times (or 5 times if the real DP is actually 300 as mentioned above). This explanation is also consistent with the observation of larger aggregates for higher PVDF degree of polymerization.

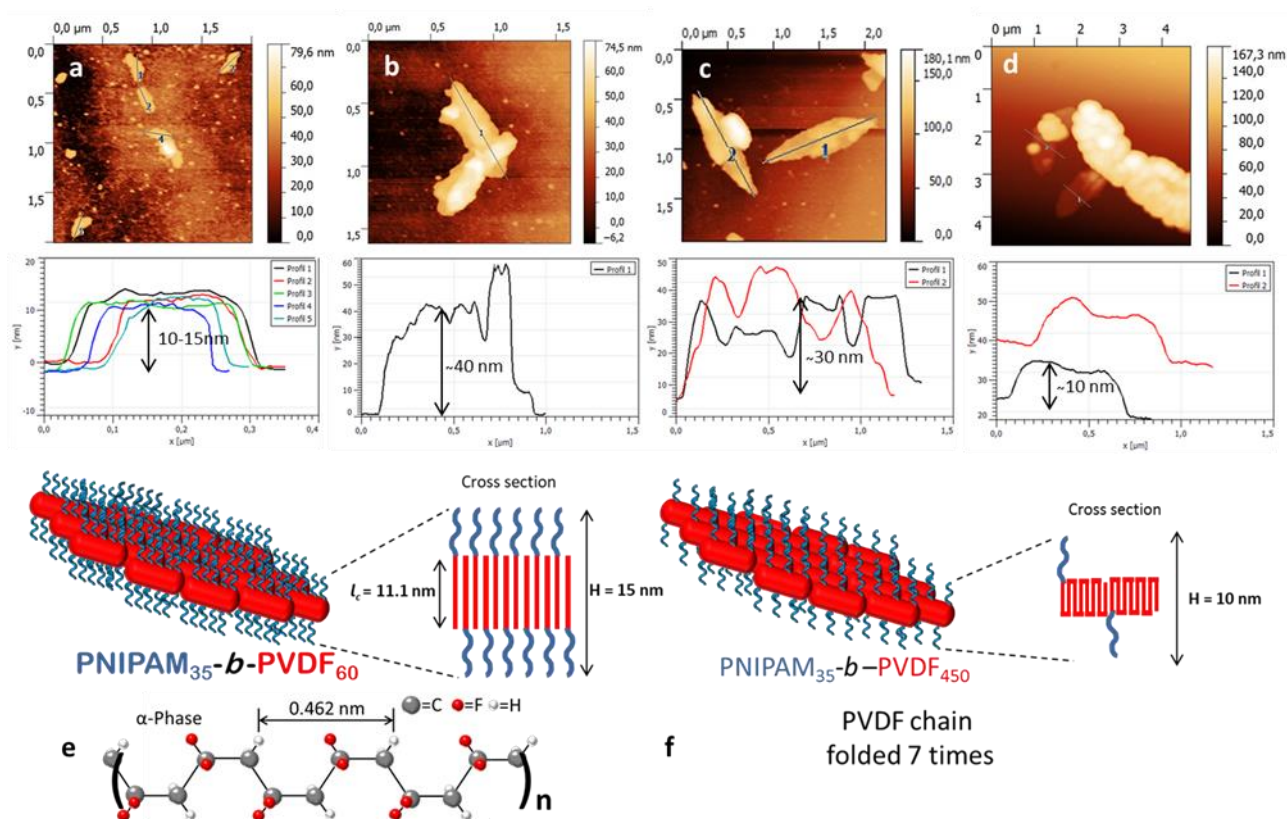


Figure 9. AFM images of 2D lenticular aggregates prepared from: (a) PNIPAM₃₅-*b*-PVDF₆₀, (b) PNIPAM₃₅-*b*-PVDF₁₀₀, (c) PNIPAM₃₅-*b*-PVDF₁₅₀, and (d) PNIPAM₃₅-*b*-PVDF₄₅₀. (e and f) Schematic representation and suggested molecular arrangement of the 2D lenticular aggregates formed by assembly of PNIPAM₃₅-*b*-PVDF₆₀ and PNIPAM₃₅-*b*-PVDF₄₅₀ respectively.

Table 2. Shape of self-assembled aggregates for the different polymer systems and protocols.

BCP	NP DMF: H ₂ O	SS DMF: H ₂ O	SS THF: H ₂ O	SS Acetone: H ₂ O	SS + TI-CDSA DMF: H ₂ O
PNIPAM ₂₅ - <i>b</i> -PVDF ₃₅	spherical	Crumpled spherical	flat sheet	lenticular*	spindle
PNIPAM ₃₅ - <i>b</i> -PVDF ₆₀	spherical	-	-	lenticular	-
PNIPAM ₃₅ - <i>b</i> -PVDF ₁₀₀	spherical	-	-	lenticular	-
PNIPAM ₃₅ - <i>b</i> -PVDF ₁₅₀	spherical	-	-	lenticular	-
PNIPAM ₃₅ - <i>b</i> -PVDF ₄₅₀	spherical	Crumpled spherical	flat sheet	lenticular	-

NP, SS and TI-CDSA stands for nanoprecipitation, solvent switch and temperature-induced crystallization-driven self-assembly protocols respectively. *(sharp edges). In all PNIPAM₃₅-*b*-PVDF_m systems examined, the size of the nanoaggregates increased with increasing DP of PVDF block. Initial concentration for

nanoprecipitation and solvent switch protocols was 2 mg mL^{-1} (5 mg mL^{-1} in the case of the sample used for TI-CDSA). Rate of selective solvent addition was 4 mL h^{-1} for the solvent switch protocol and dropwise added in the case of Nanoprecipitation. TI-CDSA sample was placed 30 min in an oil bath at 90°C and slowly cooled down after that time.

As PVDF chains fold more, the repulsion between the PNIPAM hydrophilic chains decrease, allowing the formation of larger but thinner 2D aggregates.

Since the degree of crystallinity can be modified via temperature annealing, a heating and cooling treatment was applied to the crumpled structures (Figure 3 obtained by self-assembly from DMF solution). In addition, at higher temperature the solubility of PVDF in DMF/water mixture increases. A 5 mg mL^{-1} PNIPAM₂₅-*b*-PVDF₃₅ BCP solution in DMF was self-assembled by adding water to reach a 1:1 solvent: non-solvent ratio; then this solution was heated at 90°C for 30 min and slowly cooled down to room temperature. Figure S12 shows that this temperature treatment led to a mixture of ill-defined aggregates and spindle-shape morphologies with lengths ranging from 300 nm to 1 μm . The crumpled sphere to spindle morphology transition is thought to proceed via temperature-induced crystallization-driven self-assembly (TI-CDSA) due to the degradation of the solvent quality for the crystallisable block caused by the slow cooling.²⁰

To sum up, five different morphologies were observed by self-assembly of these PNIPAM-*b*-PVDF BCPs as depicted in Table 2.

Without surprise, the solvents used and the self-assembly protocol played a crucial role in the resulting BCP structures. The same DMF/water binary mixture of solvents afforded three distinct morphologies depending on the self-assembly process used. Spherical nanoparticles were obtained when nanoprecipitation was used while a solvent switch protocol led to the formation of crumpled spheres. These crumpled spheres evolved into spindle-like aggregates when a TI-CDSA protocol was applied. Solvent switch protocol produced 2D lamellar aggregates in the case of THF/water and well-defined lenticular shape aggregates of increasing length and width with increasing DP of the PVDF block in acetone/water binary mixture.

Thermoresponse of PNIPAM-*b*-PVDF lenticular nanoparticles

The thermoresponsiveness of the PNIPAM-*b*-PVDF lenticular aggregates were also investigated. The usual turbidity test could not be used due to the poor colloidal stability of the BCP aggregates even at room temperature. Since the LCST of PNIPAM is affected by the presence of organic solvents, acetone was completely removed from the PNIPAM-*b*-PVDF BCP suspensions under reduced pressure using a rotary evaporator at room temperature to prepare an aqueous suspension of the self-assembled morphologies. TEM analysis of this suspension (Figure S13) showed that the size and shape of the assemblies were not affected by the removal of acetone.

The samples were heated at 50°C under gentle stirring for a period of 30 min then cooled down to room temperature.

Figure 10 shows the effect of temperature on the aqueous PNIPAM-*b*-PVDF BCP morphologies. The lenticular objects partly lost their well-defined shape, crumpled to an extent and also broke into smaller flat sheet aggregates. The change of

conformation of the PNIPAM blocks provoked by the decrease of the PNIPAM solubility in water at $T > \text{LCST}_{\text{PNIPAM}}$ is thought to be responsible for the aggregates to irreversibly break or evolve into the observed crumpled morphologies.

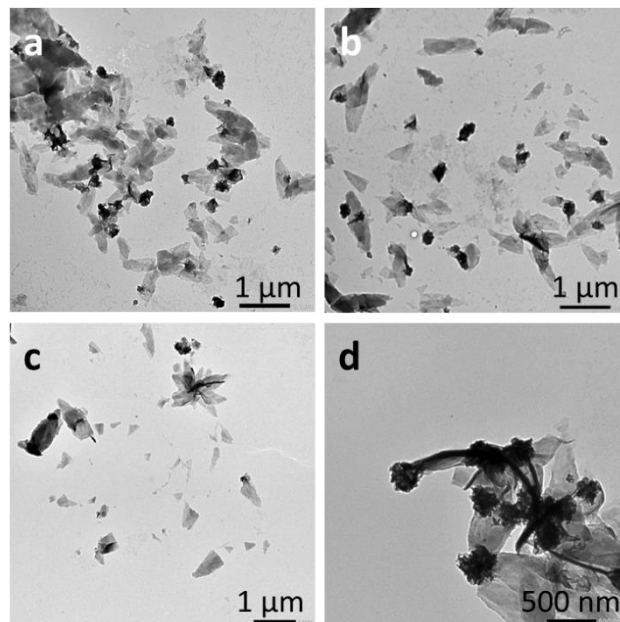


Figure 10. TEM images of representative samples of 2D lenticular aggregates prepared from: (a, b) PNIPAM₃₅-*b*-PVDF₁₅₀ BCP, (c, d) PNIPAM₃₅-*b*-PVDF₄₅₀ BCP in pure water after being heated at 45°C for 30 min.

Conclusions

A series of relatively well-defined PNIPAM-*b*-PVDF semicrystalline amphiphilic diblock copolymers was successfully synthesized by RAFT polymerization using PNIPAM macro-CTAs. These diblock copolymers were fully characterized by ^1H and ^{19}F NMR spectroscopy, TGA, DSC and SEC. Despite the loss of xanthate functionality observed when DPs of PVDF higher than 50 were targeted, BCPs with relatively low dispersity ($\text{Đ} < 1.50$) were achieved. Due to their amphiphilic nature, these BCPs had the ability to self-assemble in aqueous solutions. The self-assembled structures were characterized by TEM, SEM and AFM microscopies. The final structures were strongly affected by the choice of common solvents and self-assembly protocol used. Five types of morphologies were obtained depending on the common solvent and the self-assembly protocol. Surprisingly self-assembly from acetone solutions led to the formation of well-defined 2D lenticular aggregates which dimensions increased with the degree of polymerization of PVDF, reaching lengths of $2.3 \mu\text{m}$ for the longest PVDF synthesized. These aggregates were morphologically stable over time and accessible even at higher

concentrations. A formation pathway and a possible molecular arrangement of these 2D lenticular aggregates was proposed.

Conflicts of interest

There are no conflicts to declare.

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