Supporting information

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

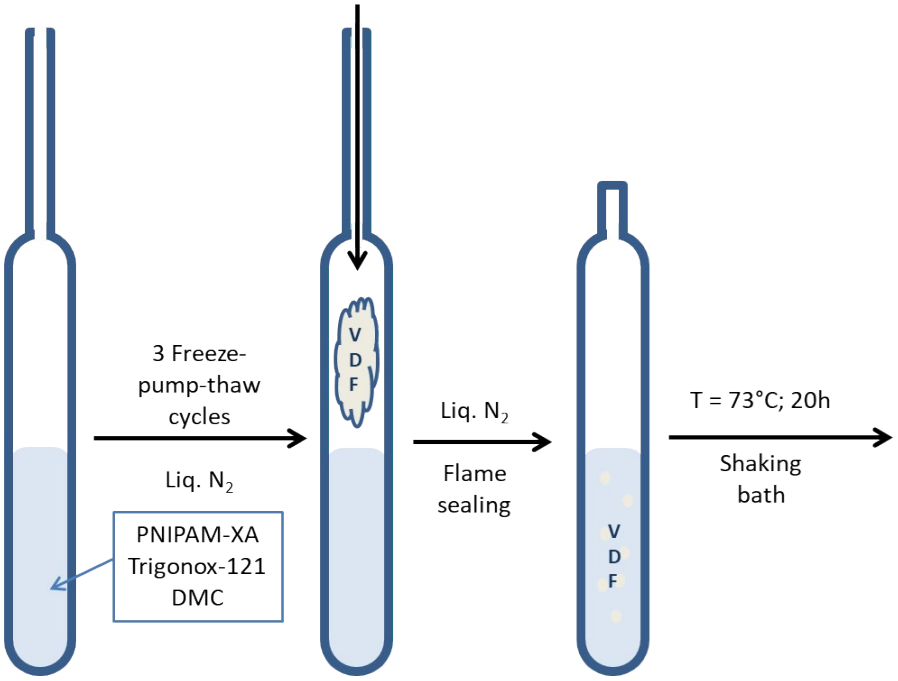
Enrique Folgado,[a,b] Matthias Mayor,[b] Didier Cot,[b] Michel Ramonda,[c] Franck Godiard,[d] Vincent Ladmiral,[b*] Mona Semsarilar[a*]

[a]*Institut Charles Gerhardt de Montpellier, ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France.*

[b]*Institut Européen des Membranes, IEM, Univ Montpellier, CNRS, ENSCM, Montpellier, France.*

[c]*Centre de technologie de Montpellier, CTM, Université de Montpellier, Bât. 5, cc007 Campus Saint Priest - France*

[d]*Service de Microscopie Electronique, Université Montpellier, Place Eugene Bataillon, 34095 Montpellier Cedex 5, France.*



Scheme S1. Schematic representation of the synthesis protocol of PVDF BCPs in carius tubes using PNIPAM macroCTAs.

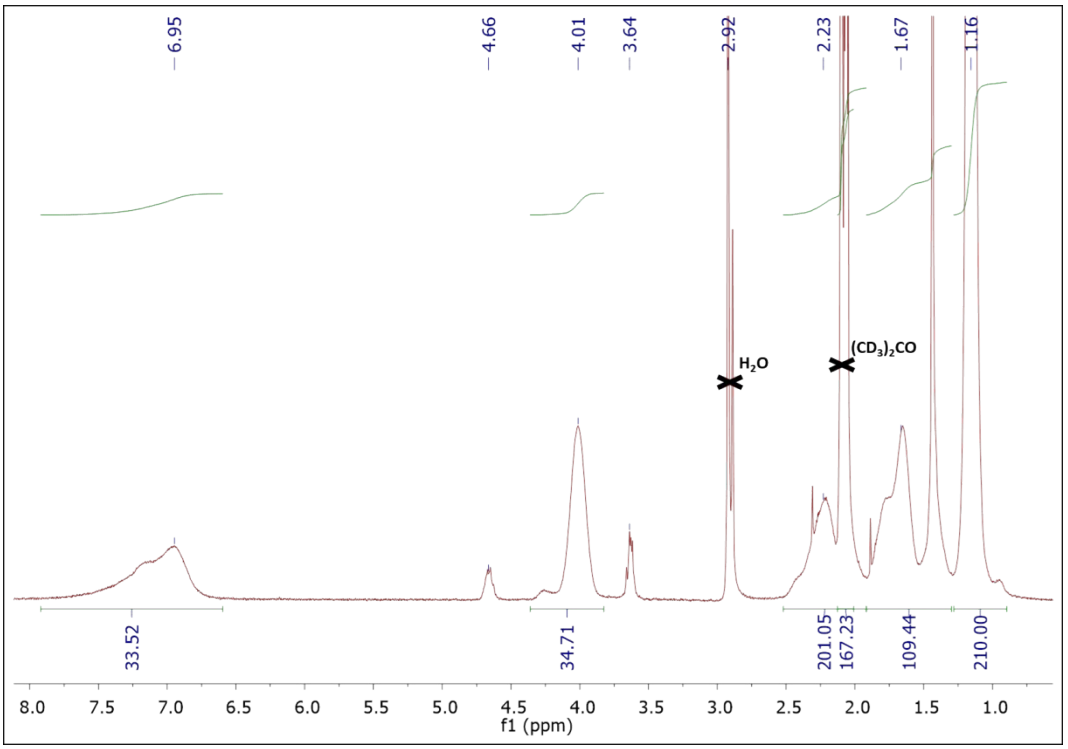


Figure S1. ^{1}H NMR (400 MHz) spectrum PNIPAM$_{35}$-XA in $(CD_3)_2CO$.

S2. DP and Mn calculations using NMR.

The calculation of the degree of polymerization of the PNIPAM macro-CTA was done using the following equation:

$$DP_{PNIPAAm-XA} = \frac{\frac{1}{6}\int_{0.9}^{1.28} \text{-NH-CH}(CH_3)_2 + \frac{1}{2}\int_{1.28}^{1.90} \text{-CH}_2\text{-CH(C=O)} + \int_{1.90}^{2.50} \text{-CH}_2\text{-CH(C=O)} + \int_{3.95}^{4.25} \text{-NH-CH}(CH_3)_2 + \int_{6.50}^{8.00} \text{-NH-CH}(CH_3)_2}{\frac{5}{2}\int_{4.5}^{4.76} \text{-CH}_2CH_3(CTA)}$$

(Equation 2)

$$M_{n,\,theo} = \frac{[NIPAAm]_0}{[CTA]_0} \times Yield \times M_{n,\,NIPAAm} + M_{n,\,CTA-XA}$$

(Equation 3)

$$M_{n,\,PNIPAAm-XA} = M_{n,\,CTA-XA} + DP_{PNIPAAm-XA} \times M_{n,\,NIPAAm}$$

(Equation 4)

With $M_{n,\,NIPAAm-XA}$= 113.16 g.mol^{-1}, and $M_{n,\,CTA-XA}$= 208.29 g.mol^{-1}.

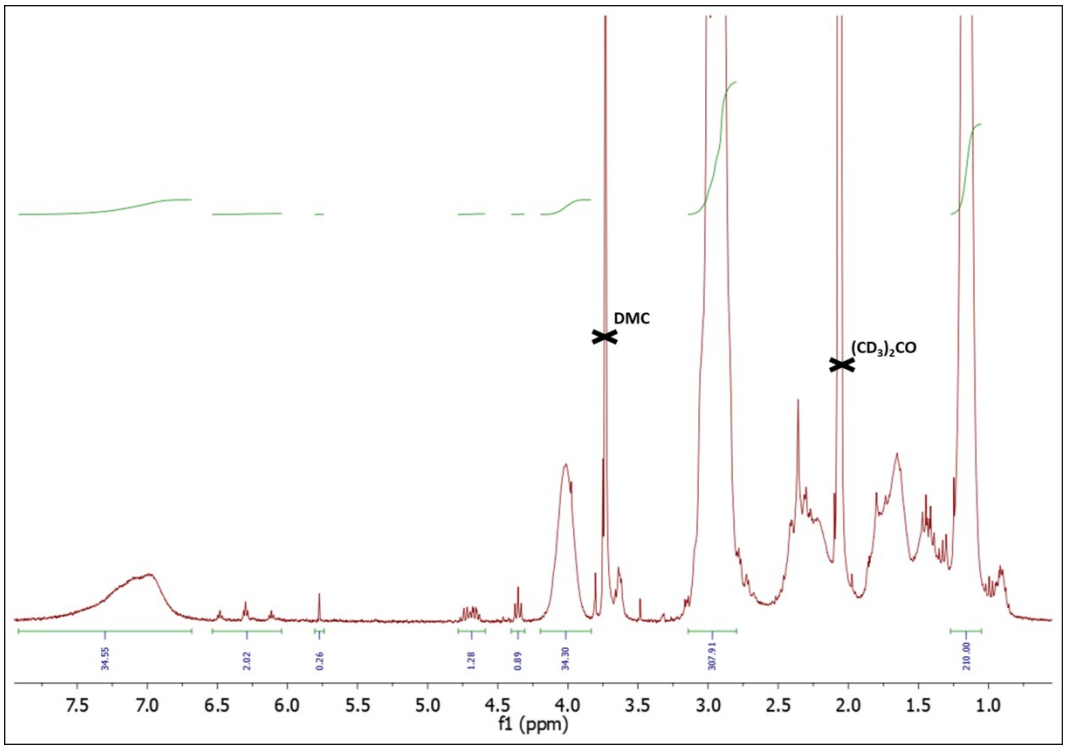


Figure S3a. ^{1}H NMR (400 MHz) spectrum of the crude PNIPAM$_{35}$-*b*-PVDF$_{150}$ in $(CD_3)_2CO$.

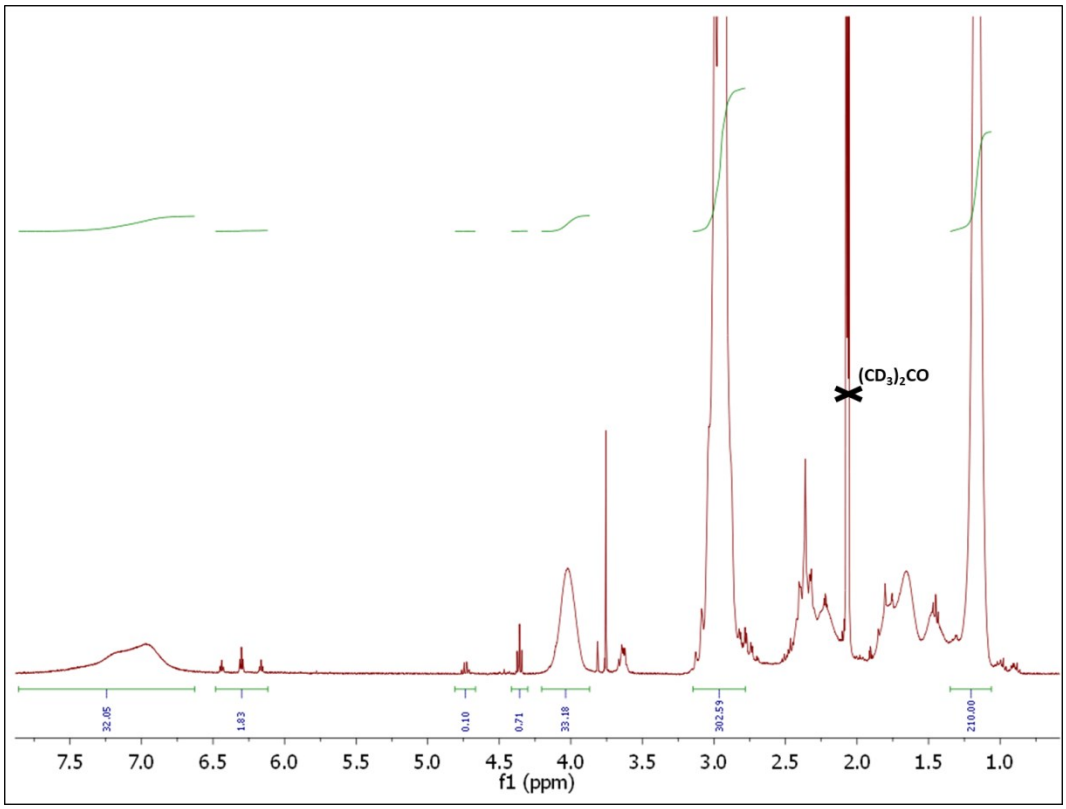


Figure S3b. ^{1}H NMR (400 MHz) spectrum of the purified PNIPAM$_{35}$-*b*-PVDF$_{150}$ in $(CD_3)_2CO$.

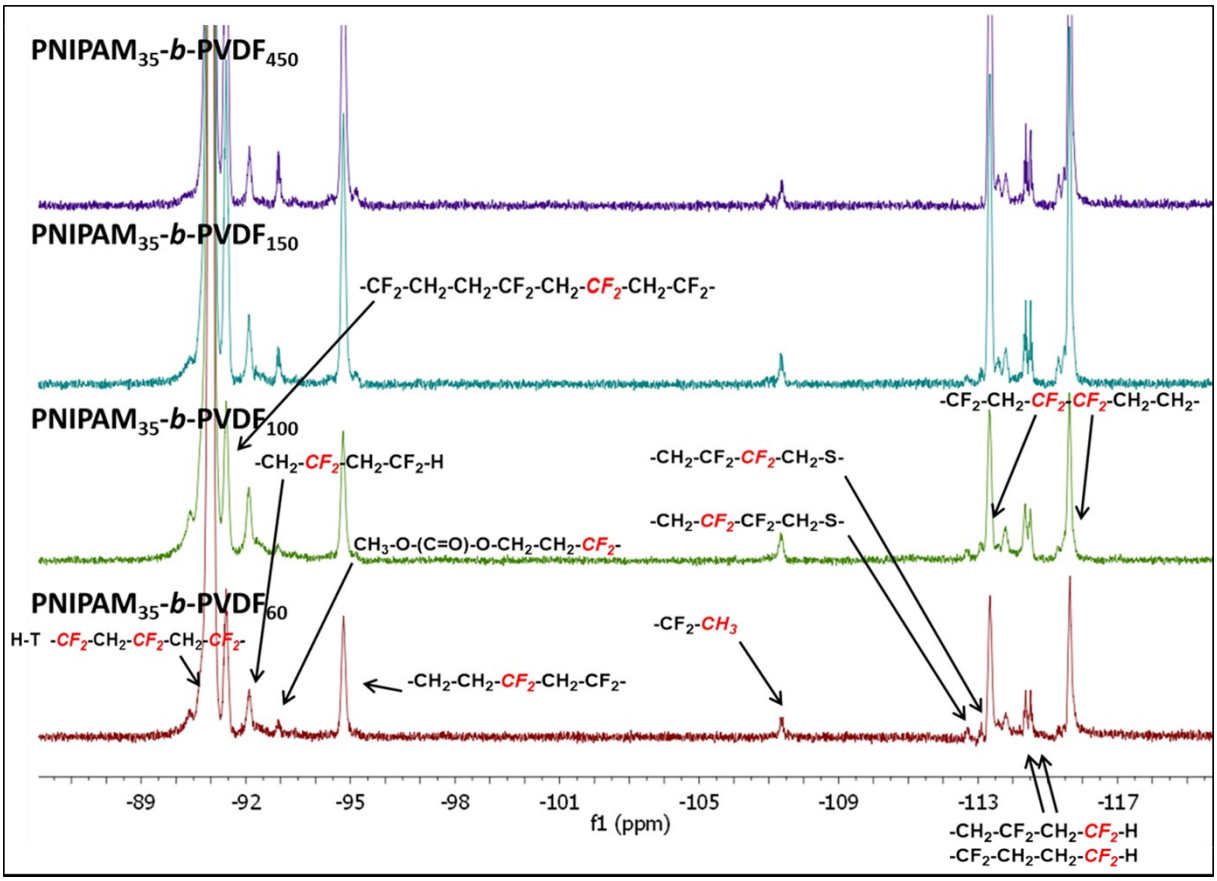


Figure S4. PNIPAM$_m$-*b*-PVDF$_n$ ^{19}F NMR spectra in $(CD_3)_2CO$

S5. Chain end functionality estimation derived from ^{19}F NMR spectra

$$(\%) - CH_2 - CF_2H = \frac{\int_{-91.7}^{-92.4} -CH_2\text{-}CF_2H}{\int_{-106.7}^{-107.7} -CF_2\text{-}CH_3 + \int_{-112.0}^{-113.2} -CF_2\text{-}CF_2\text{-}CH_2\text{-}XA \int_{-91.7}^{-92.4} -CH_2\text{-}CF_2H}$$

-CH_2CF_2H(PVDF$_{450}$) = 83.2 %
-CH_2CF_2H(PVDF$_{150}$) = 81.7 %
-CH_2CF_2H(PVDF$_{100}$) = 78.0 %
-CH_2CF_2H(PVDF$_{60}$)= 66.3 %

$$(\%) - CF_2\text{-}CH_3 = \frac{\int_{-106.7}^{-107.7} -CF_2\text{-}CH_3}{\int_{-106.7}^{-107.7} -CF_2\text{-}CH_3 + \int_{-112.0}^{-113.2} -CF_2\text{-}CF_2\text{-}CH_2\text{-}XA \int_{-91.7}^{-92.4} -CH_2\text{-}CF_2H}$$

-CF_2CH_3($PVDF_{450}$) = 15.4 %
-CF_2CH_3($PVDF_{150}$) = 16.0 %
-CF_2CH_3($PVDF_{100}$) = 16.6 %
-CF_2CH_3($PVDF_{60}$) = 14.5 %
In consequence by difference the remaining -CH_2-XA chain end functionality are:

-CH_2-XA($PVDF_{450}$) = 1.4 %
-CH_2-XA($PVDF_{150}$) = 2.3 %
-CH_2-XA($PVDF_{100}$) = 5.4 %
-CH_2-XA($PVDF_{60}$) = 19.2 %

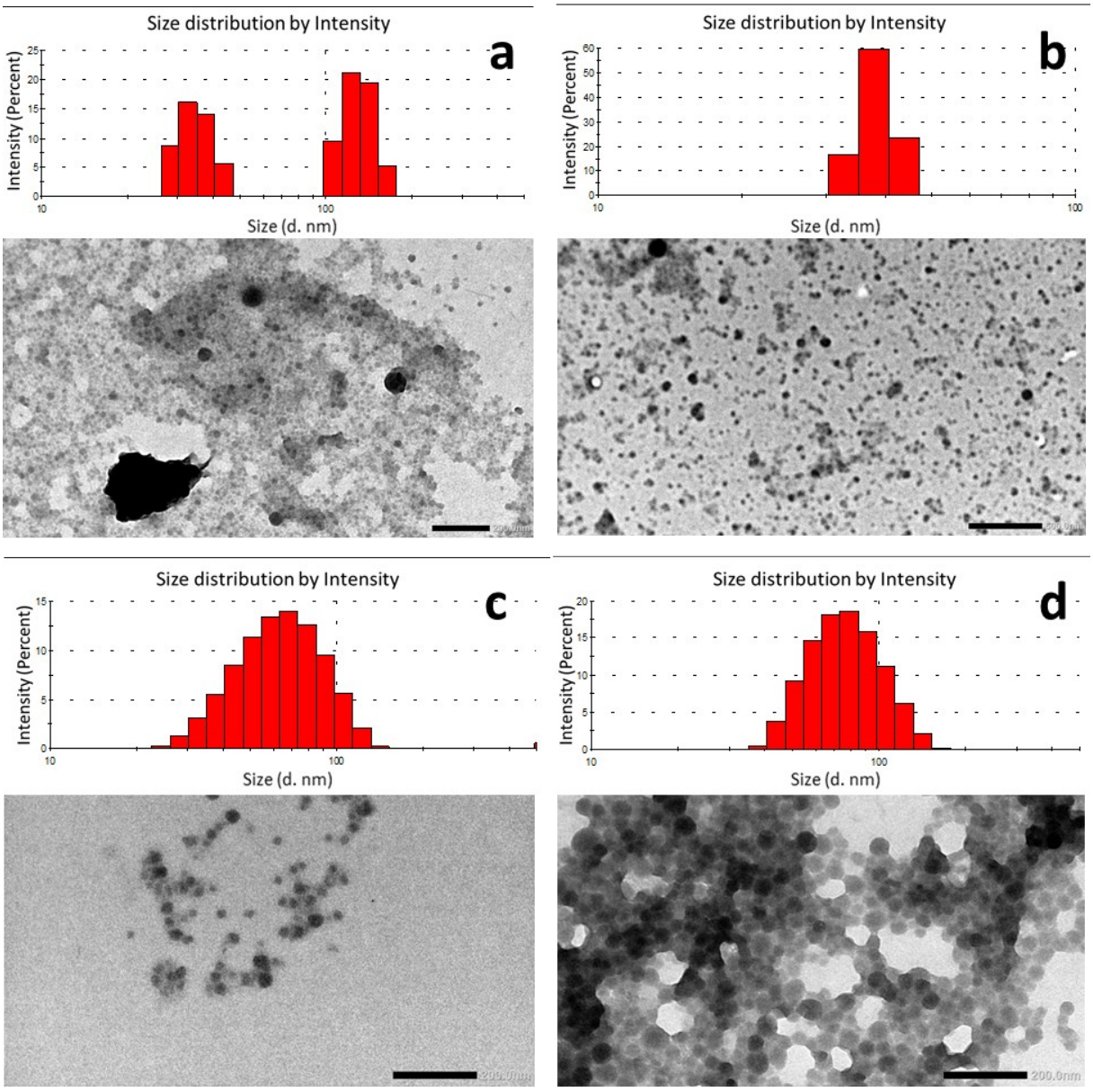


Figure S6. TEM images of spherical micelles prepared from (a) $PNIPAM_{35}$-*b*-$PVDF_{60}$, (b) $PNIPAM_{35}$-*b*-$PVDF_{100}$, (c) $PNIPAM_{35}$-*b*-$PVDF_{150}$ and (d) $PNIPAM_{35}$-*b*-$PVDF_{450}$. All samples were prepared by

nanoprecipitation in water from polymer 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. Insets correspond to the intensity DLS data for each sample.

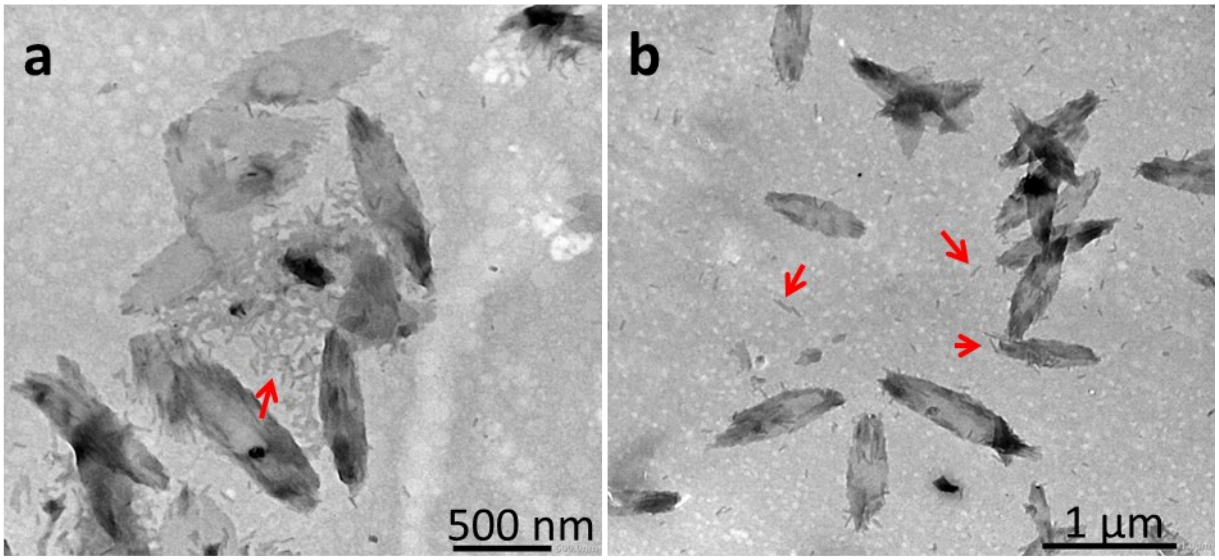


Figure S7. TEM images of 2D lenticular aggregates obtained by micellization protocol of $PNIPAM_{25}$-*b*-$PVDF_{35}$ (a- b). Initial polymer concentration in acetone = 2 mg mL^{-1}. Final concentration = 0.5 mg mL^{-1} in acetone: water (1:3) mixture (for a) and 0.4 mg mL^{-1} in acetone: water (1:4) mixture (for b). water addition rate = 4 mL h^{-1}. Red arrows indicate some of the observed short 1D aggregates.

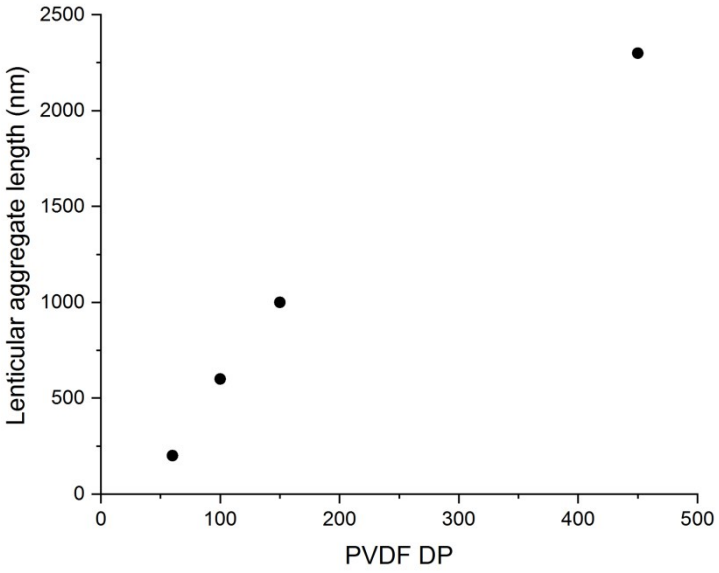


Figure S8. Plot of PVDF degree of polymerization *vs.* length of lenticular aggregates.

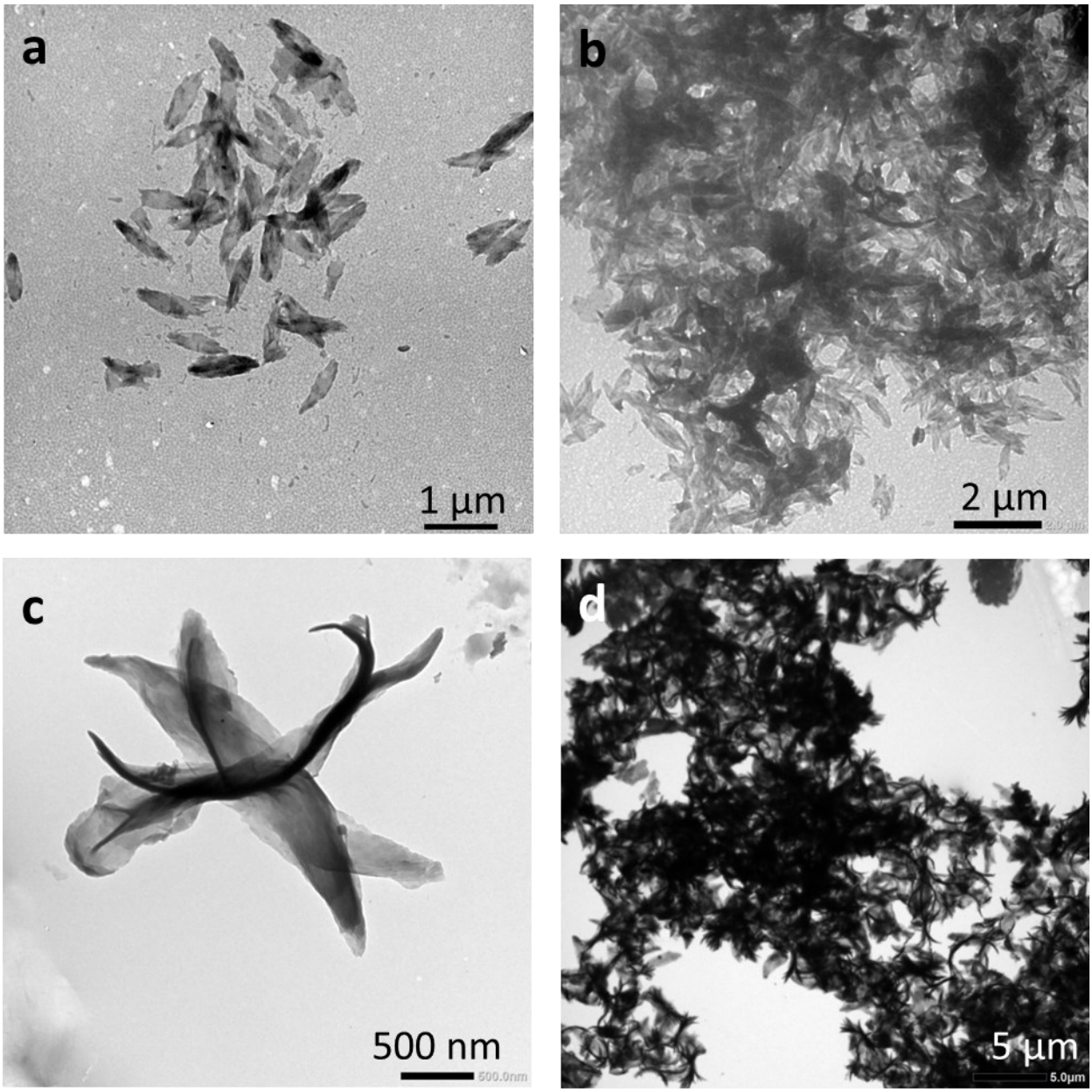


Figure S9. Self-assembled structures prepared by micellization using water as selective solvent and: a) 1 mg mL^{-1} acetone stock solutions of $PNIPAM_{25}$-*b*-$PVDF_{35}$, b) 4 mg mL^{-1} acetone stock solutions of $PNIPAM_{25}$-*b*-$PVDF_{35}$, c) 1 mg mL^{-1} acetone stock solutions of $PNIPAM_{35}$-*b*-$PVDF_{450}$, and d) 4 mg mL^{-1} acetone stock solutions of $PNIPAM_{35}$-*b*-$PVDF_{450}$. Final acetone: water ratio = 1:4. Water addition rate = 4 mL h^{-1}.

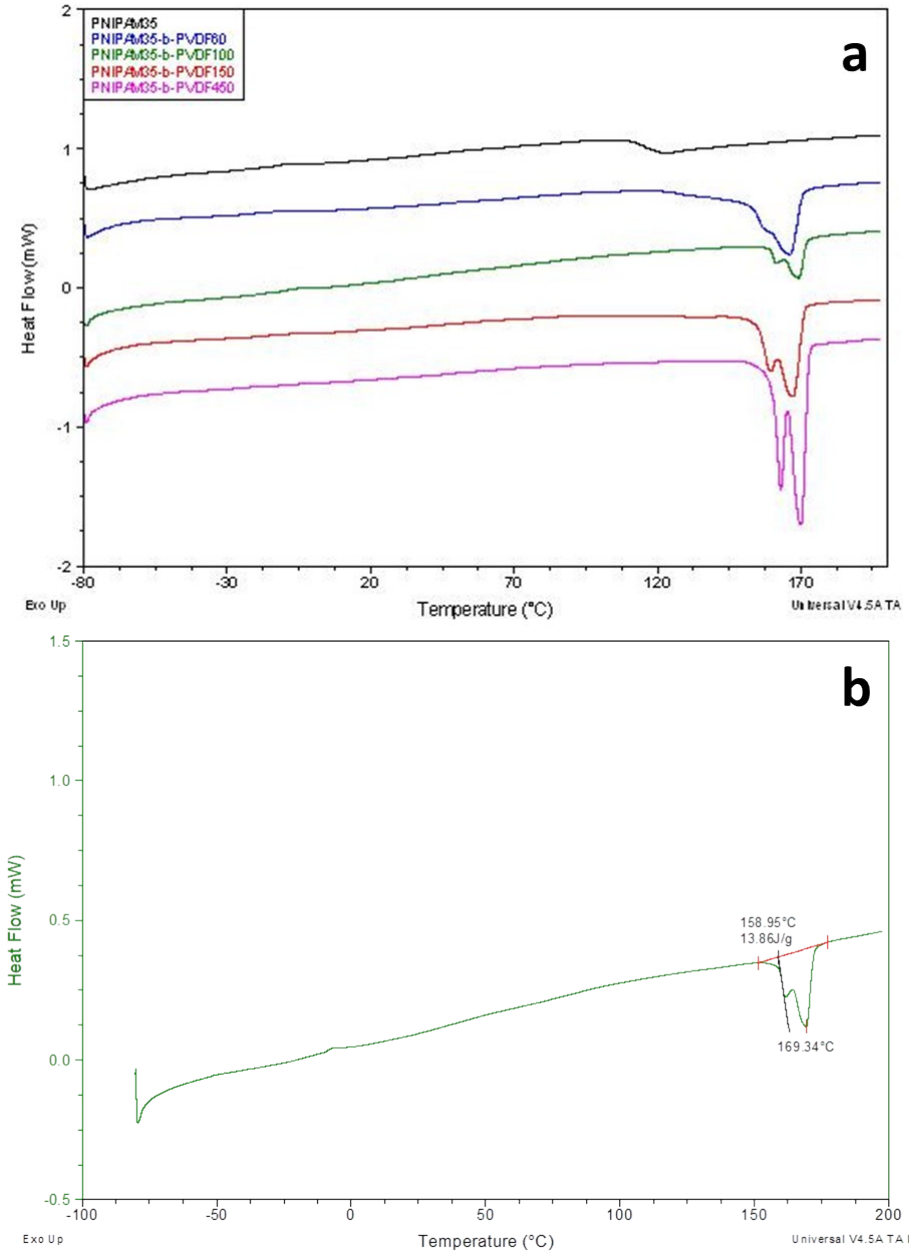


Figure S10. DSC thermograms of PNIPAM$_m$-*b*-PVDF$_n$ (a). DSC thermogram of PNIPAM$_{35}$-*b*-PVDF$_{150}$ and calculation of ΔH_f for the PVDF block (b).

$$\chi_c(\%) = \frac{\Delta H_f}{\Delta H_f^\circ \Phi_m} \times 100$$

Where ΔH_f is heat of melting (extracted from the DSC trace) and ΔH_f° is a reference value and represents the heat of melting if the polymer were 100% crystalline (both in J/g). $\Phi_m$is the weight fraction of the different block forming the diblock copolymer.

ΔH_f° of PVDF is 104.7 J·g^{-1}.

The molar mass of the block copolymer PNIPAM$_{35}$-*b*-PVDF$_{150}$ (deduced from NMR) is 13,700 g·mol^{-1} and the weight fraction of the PVDF and PNIPAM blocks (Φ_m) are 0.68 and 0.32 respectively.

χ_{cPVDF}= (13.86/(104.7·0.68))x100= 19.5%

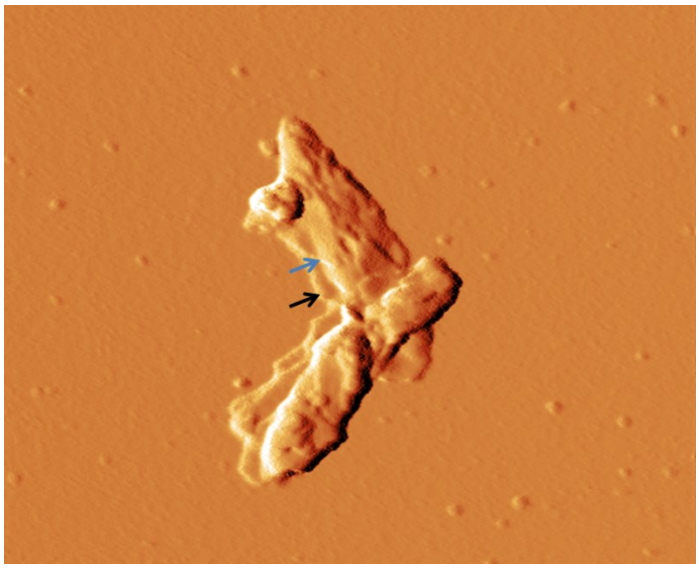


Figure S11. AFM amplitude image of PNIPAMm$_{35}$-*b*-PVDF$_{100}$ lenticular aggregates. Arrows indicate two stacked lenticular aggregates.

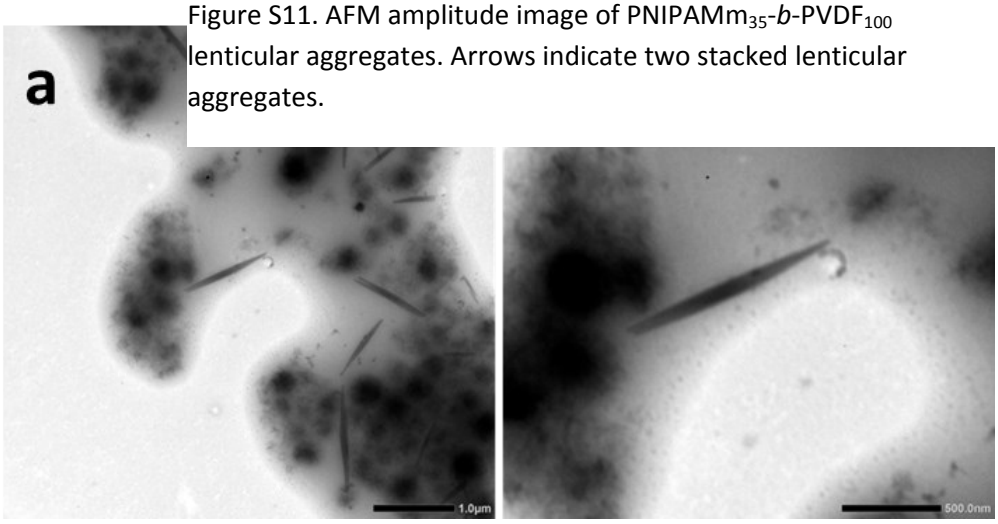


Figure S12. TEM images of crystalline structures prepared from a 5 mg mL^{-1} PNIPAM$_{25}$-*b*-PVDF$_{35}$ solution in DMF by micellization. DMF: water (1:1) solvent mixture. Water addition rate = 4 mL h^{-1}. Solution heated at 90°C for 30 min then cooled down to room temperature. Scale bars are 1 µm (a) and 500 nm (b).

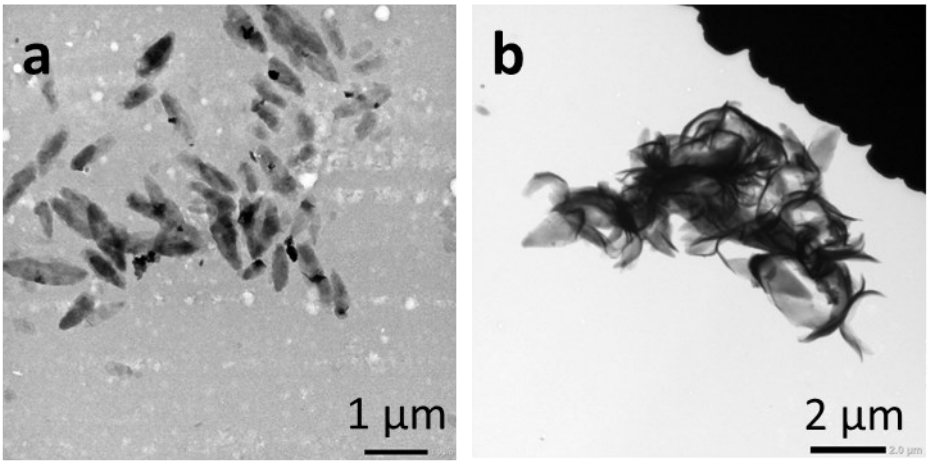


Figure S13. TEM images of self-assembled 2D lenticular morphologies prepared from (a) $PNIPAM_{35}$-*b*-$PVDF_{150}$ and (b) $PNIPAM_{35}$-*b*-$PVDF_{450}$ via micellization in acetone : water mixture after acetone removal by rotary evaporation at room temperature.