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

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Figure S1. PVDF-XA homopolymer \textsuperscript{1}H NMR (400 MHz (CD\textsubscript{3})\textsubscript{2}CO).
Figure S2. PVDF-XA homopolymer $^{19}$F NMR (376 MHz, (CD$_3$)$_2$CO).

Figure S3. PEG$_{6000}$ commercial polymer $^1$H NMR (400 MHz, CDCl$_3$).
Figure S4. PEG diacrylate homopolymer $^1$H NMR (400 MHz, (CD$_3$)$_2$SO).

Note: the peaks at 1.20 and 3.07 ppm are assigned to residual triethylammonium chloride.
Figure S5. PVDF-\textit{b}-PEG-\textit{b}-PVDF $^1$H NMR (400 MHz, (CD$_3$)$_2$SO), recorded at 60 °C).

Figure S6. PVDF-\textit{b}-PEG-\textit{b}-PVDF $^{19}$F NMR (376 MHz, (CD$_3$)$_2$SO).
Figure S7. $^1$H DOSY-NMR experiments recorded in (CD$_3$)$_2$SO at 60 °C of PVDF-XA homopolymer.

$D = 9.1 \times 10^{-5} \text{m}^2 \text{s}^{-1}$

Figure S8. $^1$H DOSY-NMR experiments recorded in (CD$_3$)$_2$SO at 60 °C of PEGDA homopolymer.

$D = 7.5 \times 10^{-5} \text{m}^2 \text{s}^{-1}$
Figure S9. $^1$H DOSY-NMR experiments recorded in (CD$_3$)$_2$SO) at 60 °C of PVDF-$b$-PEG-$b$-PVDF triblock copolymer.

\[ D = 2.8 \times 10^{-5} \text{ m}^2\text{s}^{-1} \]

Figure S10. Thermogravimetric analysis (TGA). Weight derivative traces of the PVDF-XA and PEGDA homopolymers and of the PVDF$_{50}$-$b$-PEG$_{136}$-$b$-PVDF$_{50}$ triblock copolymer.
Figure S11. Differential scanning calorimetry (DSC) thermogram of PVDF-XA homopolymer.

Figure S12. Differential scanning calorimetry (DSC) thermogram of PEGDA homopolymer.
Figure S13. Differential scanning calorimetry (DSC) thermogram of PVDF-b-PEG-b-PVDF triblock copolymer.

S14. Calculation of the degrees of crystallinity

\[ \chi_c(\%) = \frac{\Delta H_f}{\Delta H_f^o \cdot \Phi_m} \times 100 \]

Where \( \Delta H_f \) is heat of melting (extracted from the DSC trace) and \( \Delta H_f^o \) 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 polymer forming the triblock copolymer.

\( \Delta H_f^o \) of PVDF and PEG were extracted from the literature as 104.7 J·g\(^{-1}\) and 196.8 J·g\(^{-1}\) respectively.\(^{1,2}\)

The molar mass of the triblock copolymer (deduced from NMR) is 12800 g·mol\(^{-1}\) and the weight fraction of the PVDF and PEG blocks (\( \Phi_m \)) are 0.53 and 0.47 respectively.

\[ \chi_c \text{ PVDF} = \frac{26.15}{(104.7\cdot0.53)}\times100 = 47.1\% \]

\[ \chi_c \text{ PEG} = \frac{49.77}{(196.8\cdot0.47)}\times100 = 53.8\% \]
Figure S15. Size distribution measured by DLS of block copolymer stock solutions. (a) 1% w/w solution in THF (b) 5% w/w solution in NMP.

- Solvents were filtered. Polymer solutions were not filtered
The micellization protocol leads to the formation of micelles and vesicles when solvent:non-solvent ratios of at least 1:4 are reached (THF/ethanol).

The nanoprecipitation protocol allowed the rapid formation of micelles, vesicles and crystalline aggregates at 1:6 solvent: non-solvent ratios employing NMP/water, THF/water and THF/ethanol respectively. Addition of more common solvent (containing BCP) leads to destabilization of the BCP assemblies and ill-defined or mixtures of structures were observed by TEM analysis.
Figure S17. AFM topographic images and height profiles of micelles (a) and vesicles (b)

Figure S18. XRD pattern of PEG₆₀₀₀₀.