

Supporting information

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

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Figure S1. PVDF-XA homopolymer ¹H NMR (400 MHz (CD₃)₂CO).

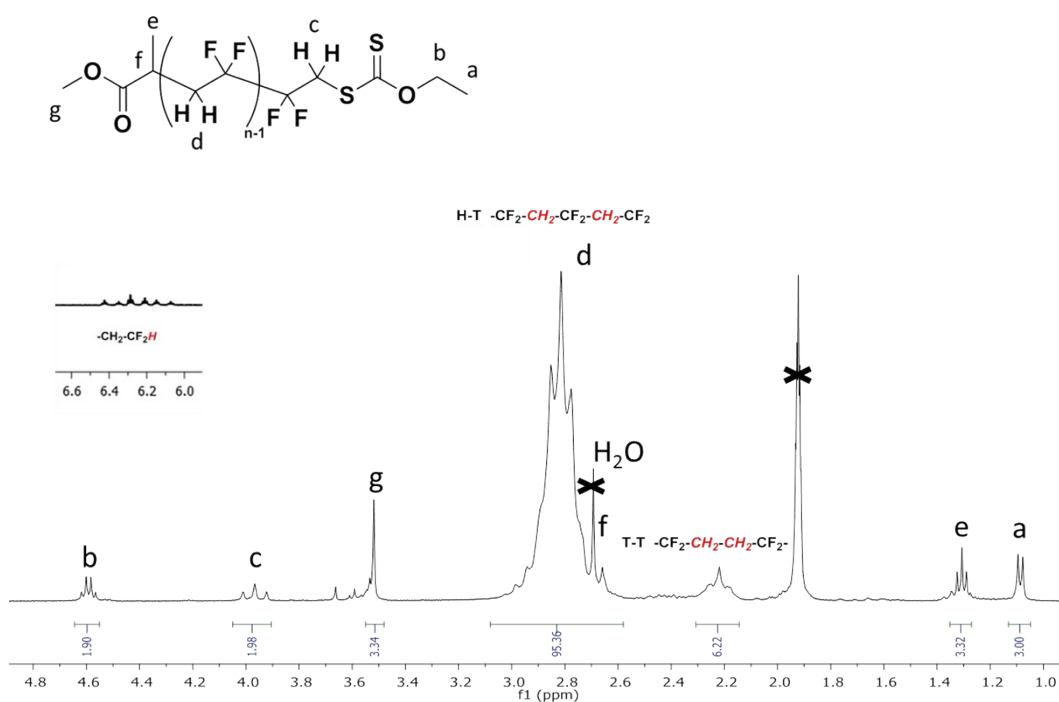


Figure S2. PVDF-XA homopolymer ^{19}F NMR (376 MHz, $(\text{CD}_3)_2\text{CO}$).

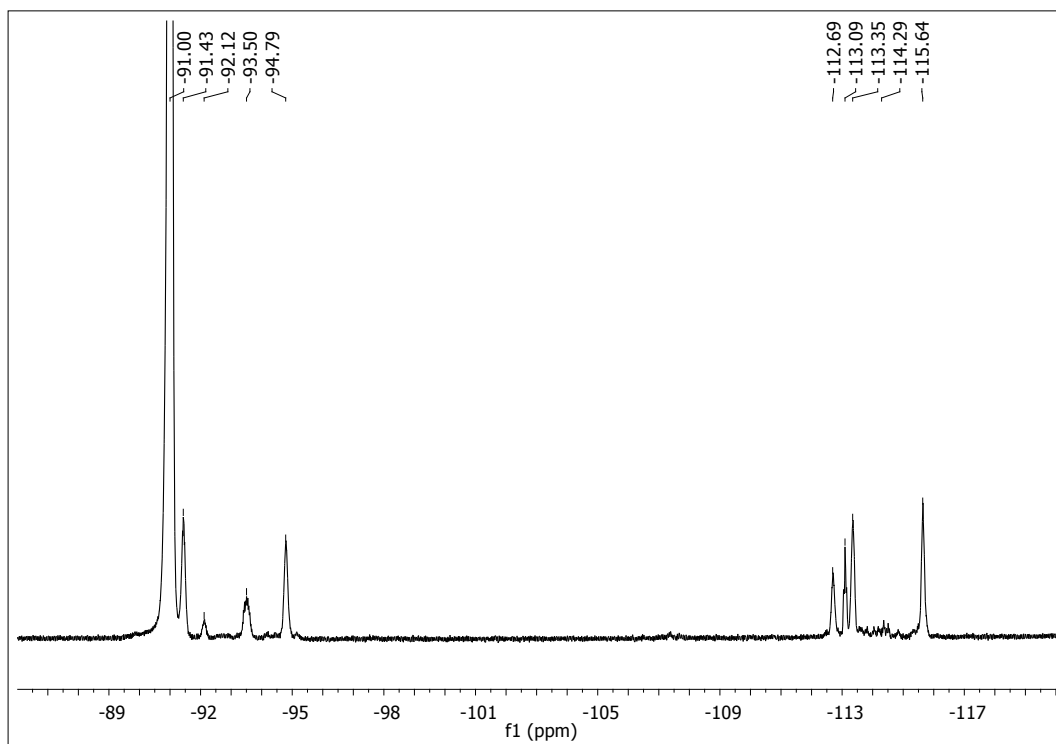


Figure S3. PEG₆₀₀₀ commercial polymer ^1H NMR (400 MHz, CDCl_3).

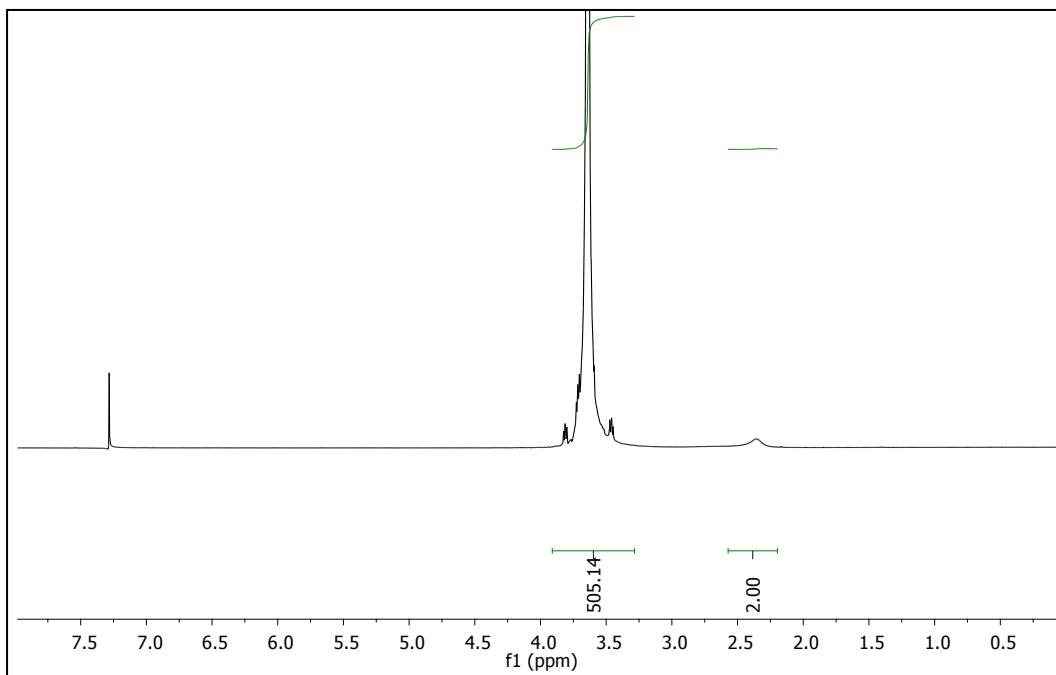
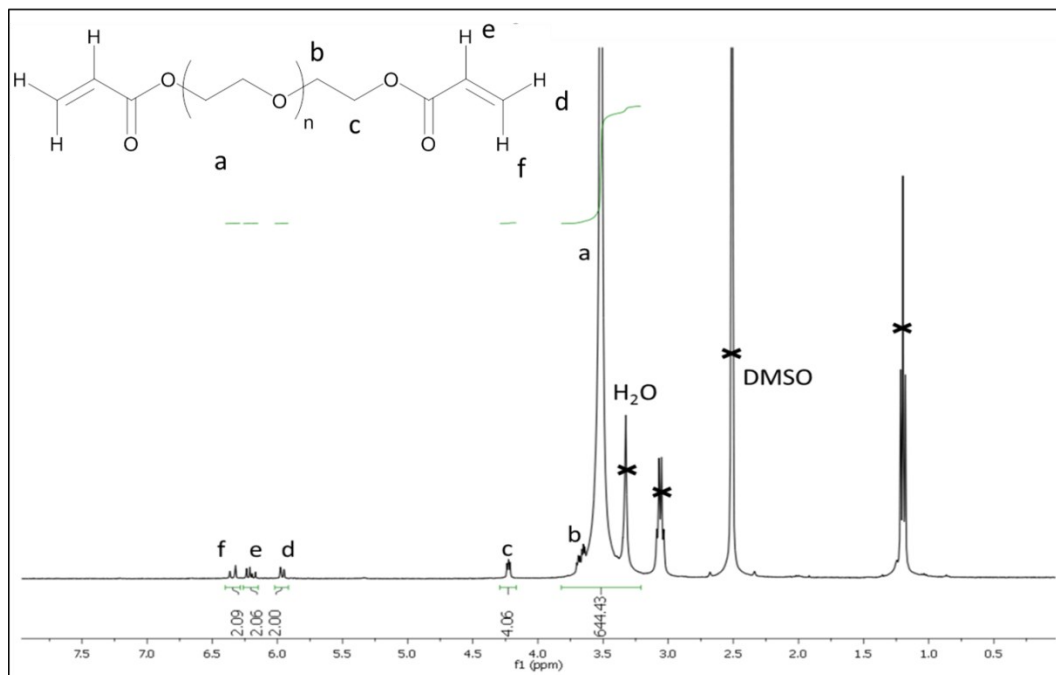


Figure S4. PEG diacrylate homopolymer ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$).



Note: the peaks at 1.20 and 3.07 ppm are assigned to residual triethylammonium chloride.

Figure S5. PVDF-*b*-PEG-*b*-PVDF ¹H NMR (400 MHz, (CD₃)₂SO), recorded at 60 °C).

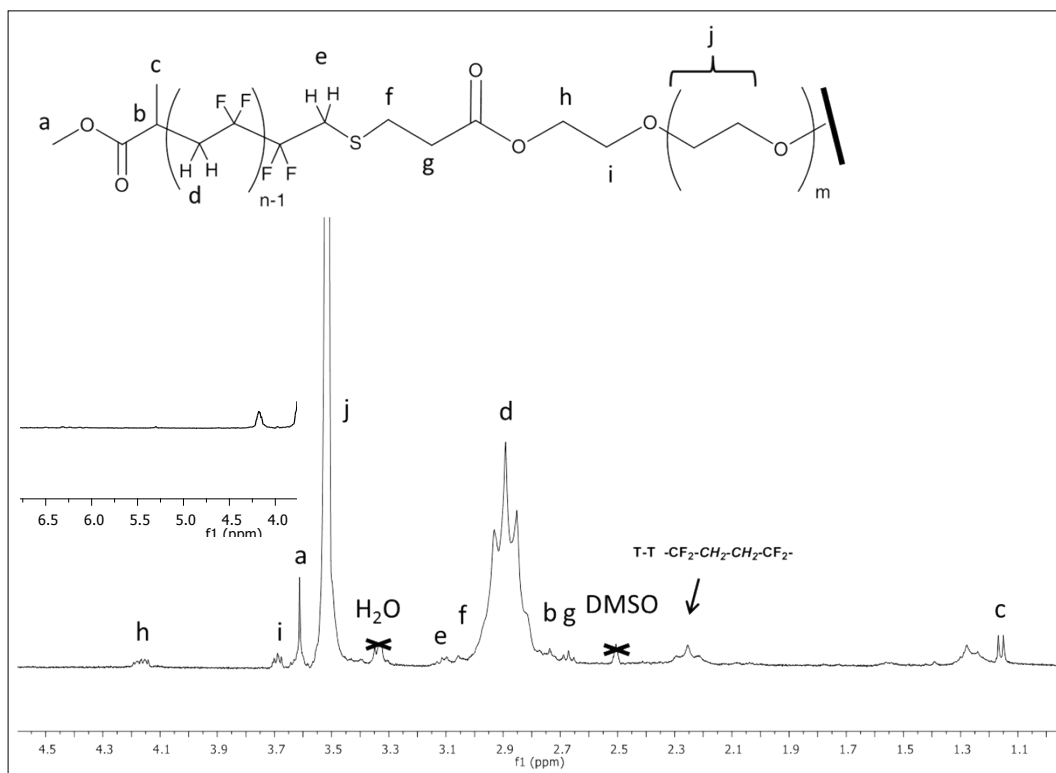


Figure S6. PVDF-*b*-PEG-*b*-PVDF ¹⁹F NMR (376 MHz, (CD₃)₂SO).

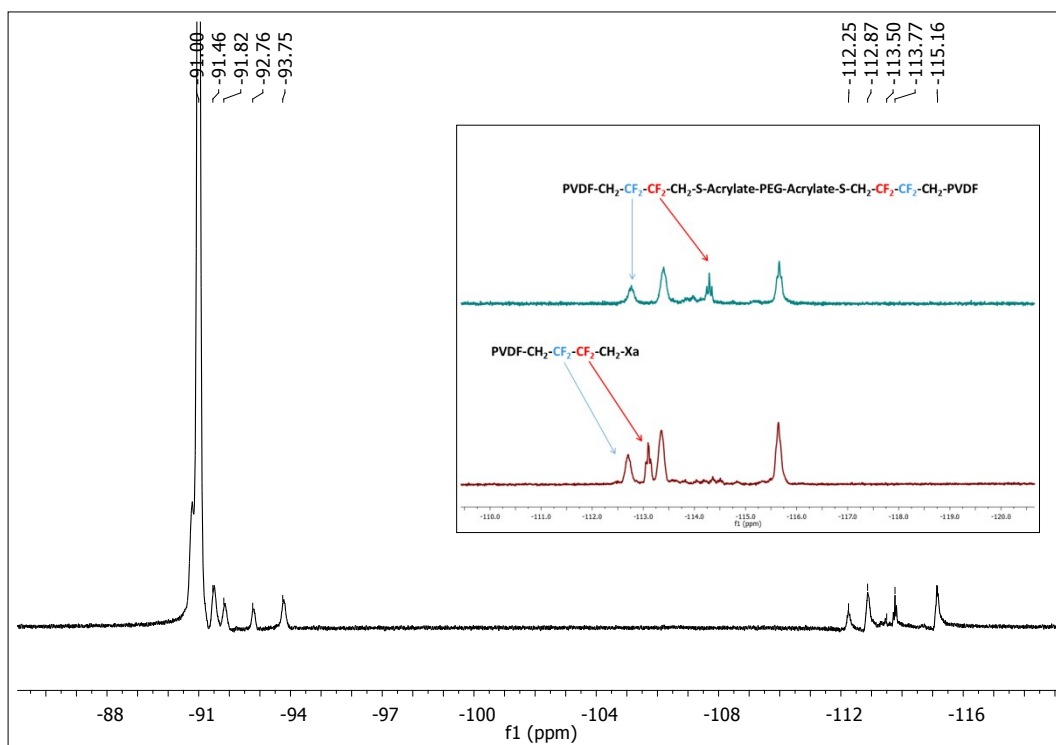


Figure S7. ^1H DOSY-NMR experiments recorded in $(\text{CD}_3)_2\text{SO}$ at $60\text{ }^\circ\text{C}$ of PVDF-XA homopolymer.

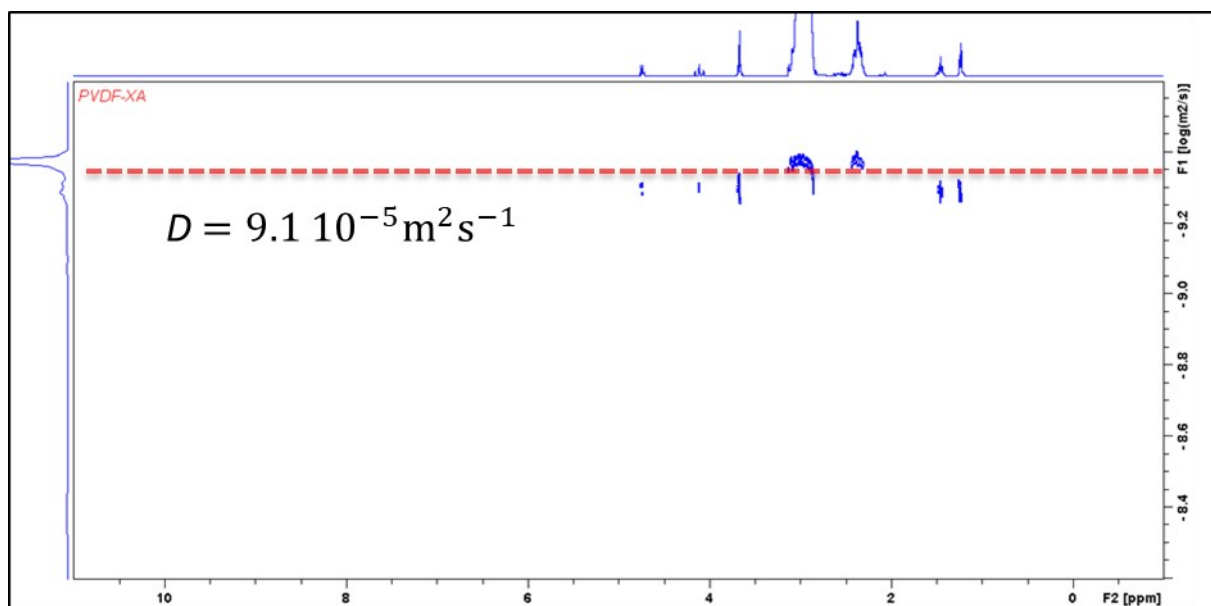


Figure S8. ^1H DOSY-NMR experiments recorded in $(\text{CD}_3)_2\text{SO}$ at $60\text{ }^\circ\text{C}$ of PEGDA homopolymer.

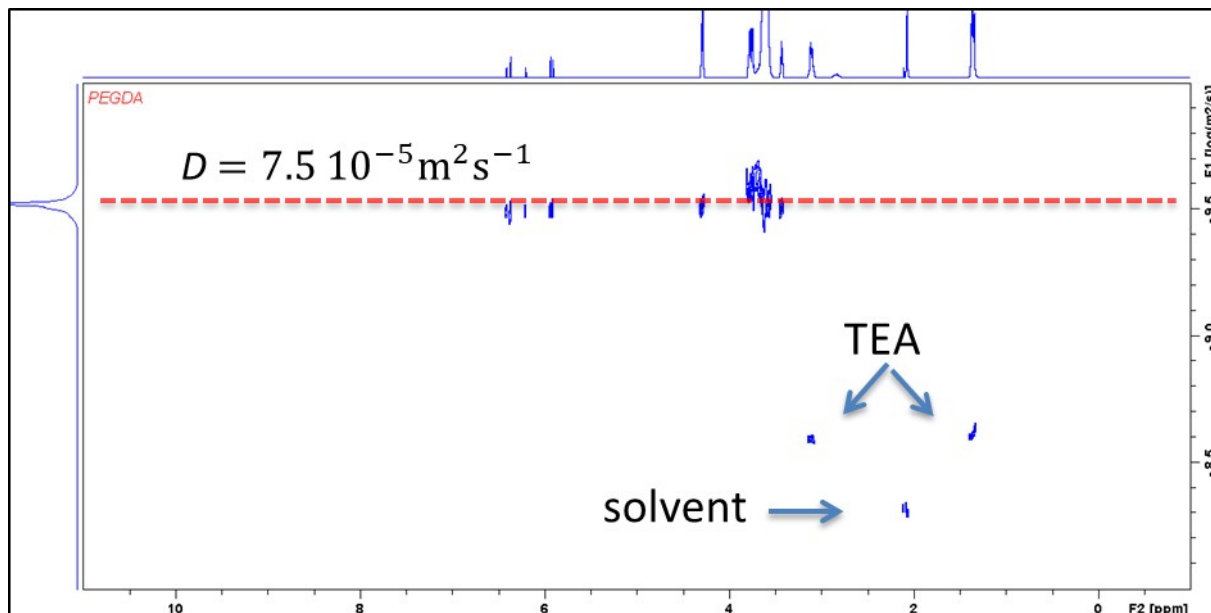


Figure S9. ^1H DOSY-NMR experiments recorded in $(\text{CD}_3)_2\text{SO}$ at 60°C of PVDF-*b*-PEG-*b*-PVDF triblock copolymer.

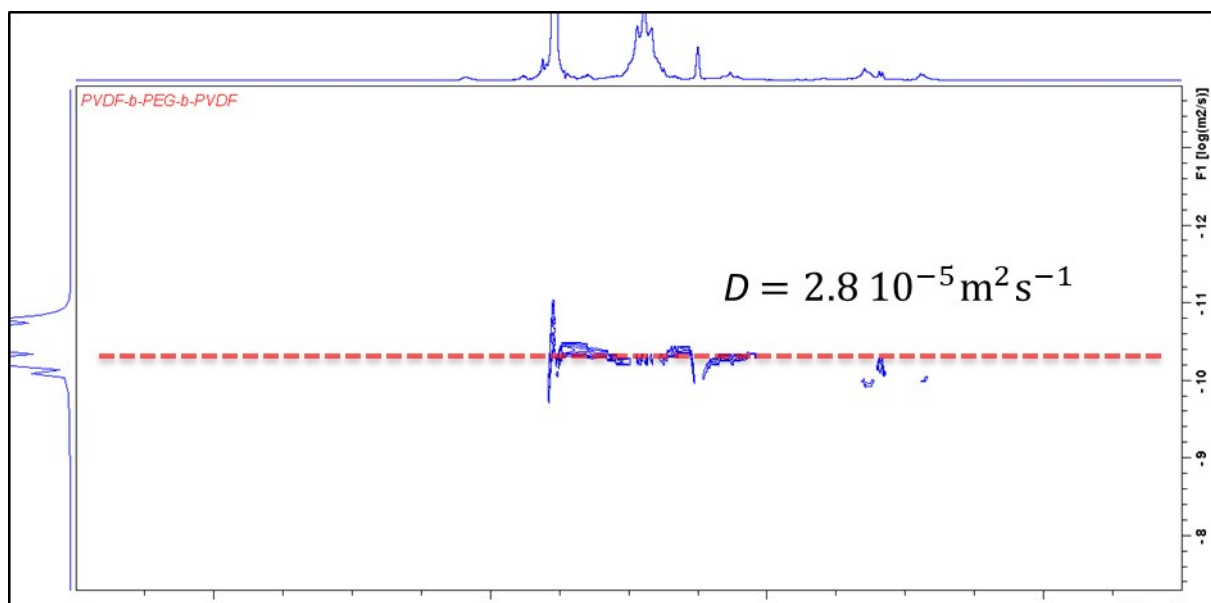


Figure S10. Thermogravimetric analysis (TGA). Weight derivative traces of the PVDF-XA and PEGDA homopolymers and of the PVDF₅₀-*b*-PEG₁₃₆-*b*-PVDF₅₀ triblock copolymer.

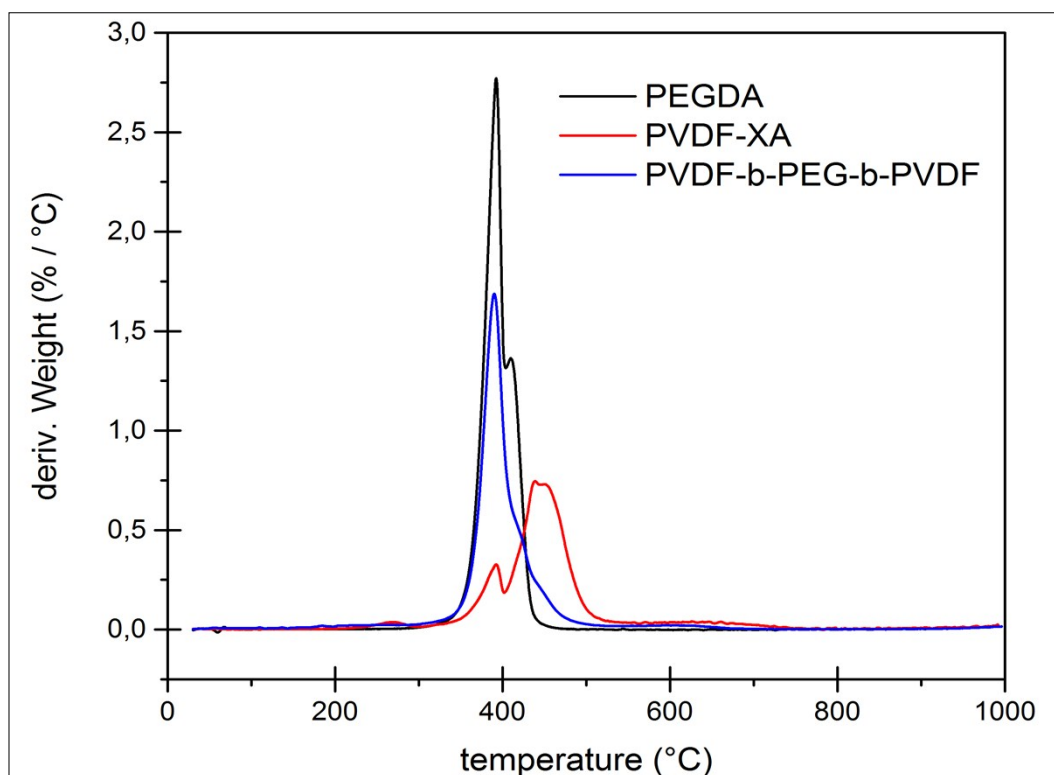


Figure S11. Differential scanning calorimetry (DSC) thermogram of PVDF-XA homopolymer.

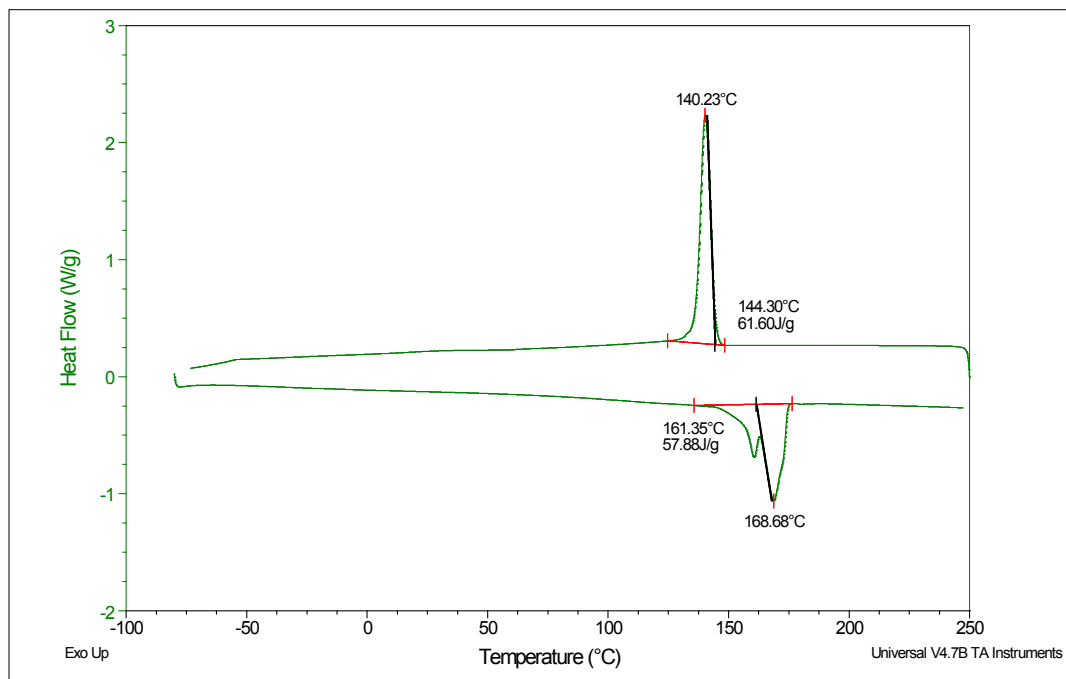


Figure S12. Differential scanning calorimetry (DSC) thermogram of PEGDA homopolymer.

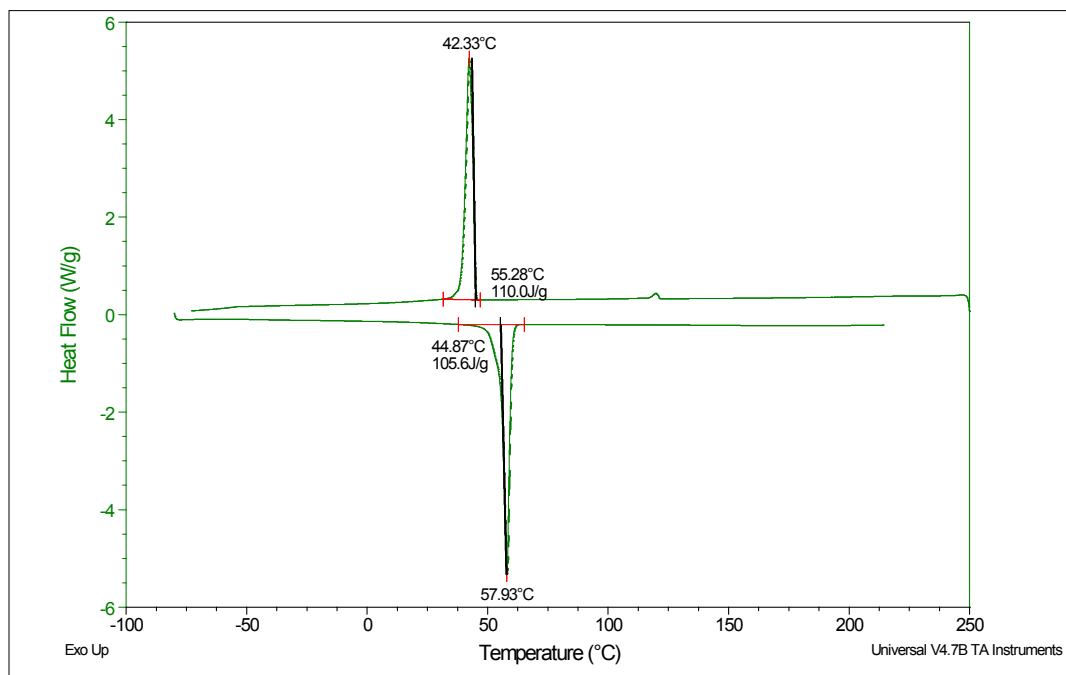
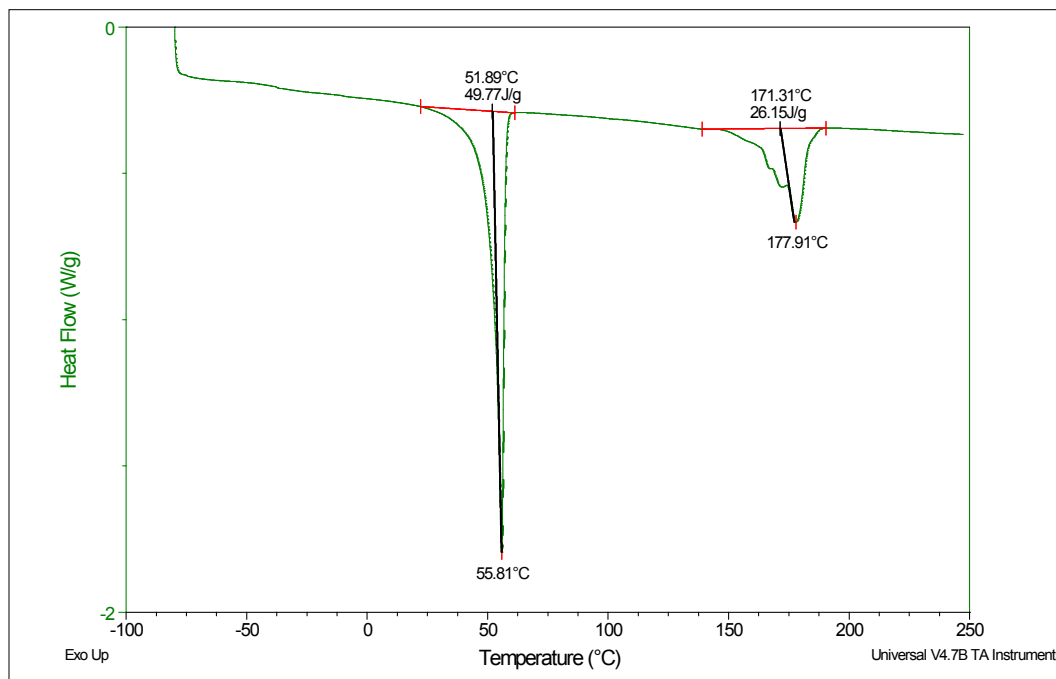


Figure S13. Differential scanning calorimetry (DSC) thermogram of PVDF-*b*-PEG-*b*-PVDF triblock copolymer.



S14. Calculation of the degrees of crystallinity

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

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). Φ_m is the weight fraction of the different polymer forming the triblock copolymer.

ΔH_f° of PVDF and PEG were extracted from the literature as $104.7 \text{ J}\cdot\text{g}^{-1}$ and $196.8 \text{ J}\cdot\text{g}^{-1}$ respectively.^{1,2}

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

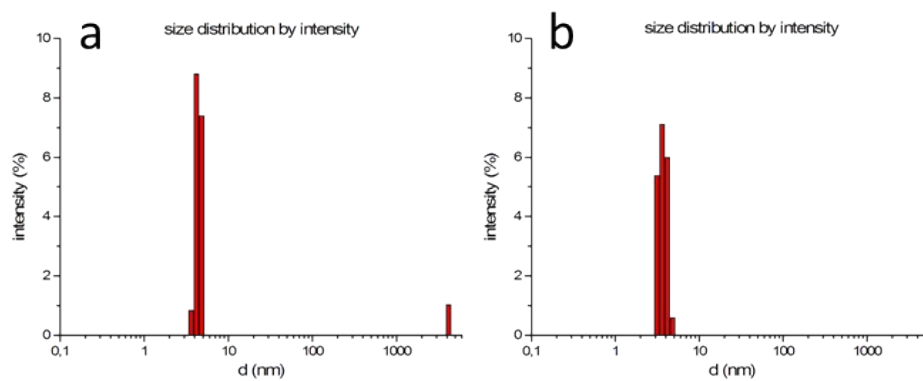
$$\chi_c \text{ PVDF} = (26.15 / (104.7 \cdot 0.53)) \times 100 = 47.1\%$$

$$\chi_c \text{ PEG} = (49.77 / (196.8 \cdot 0.47)) \times 100 = 53.8\%$$

1 S. Hietala, S. Holmberg, M. Karjalainen, J. Na, M. Paronen and R. Serimaa, *J. Mater. Chem.*, 1997, **7**, 721–726.

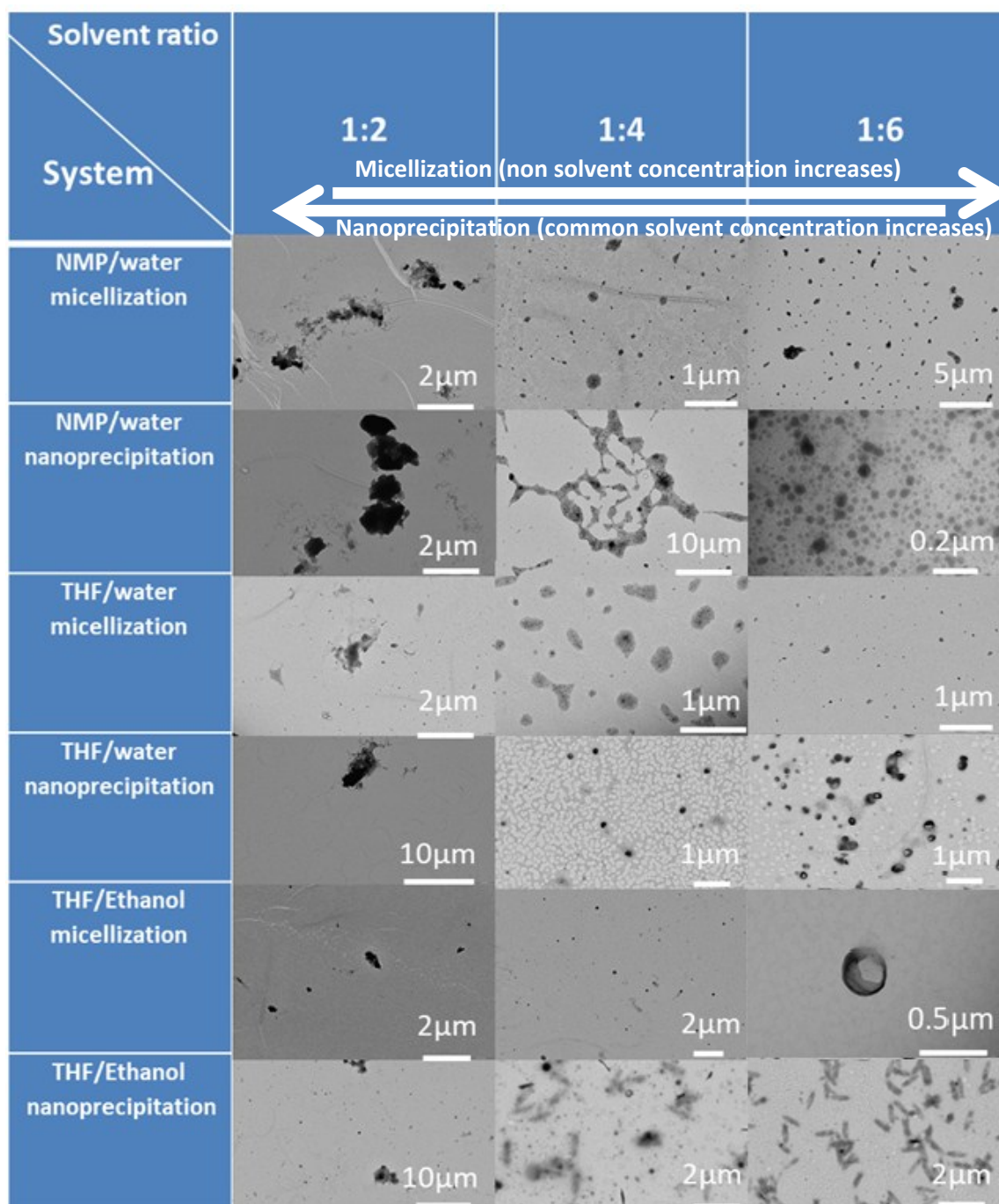
2 K. Pielichowska, J. Bieda and P. Szatkowski, *Renew. Energy*, 2016, **91**, 456–465.

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

Figure S16. TEM images of the self-assembly experiments.



- 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)

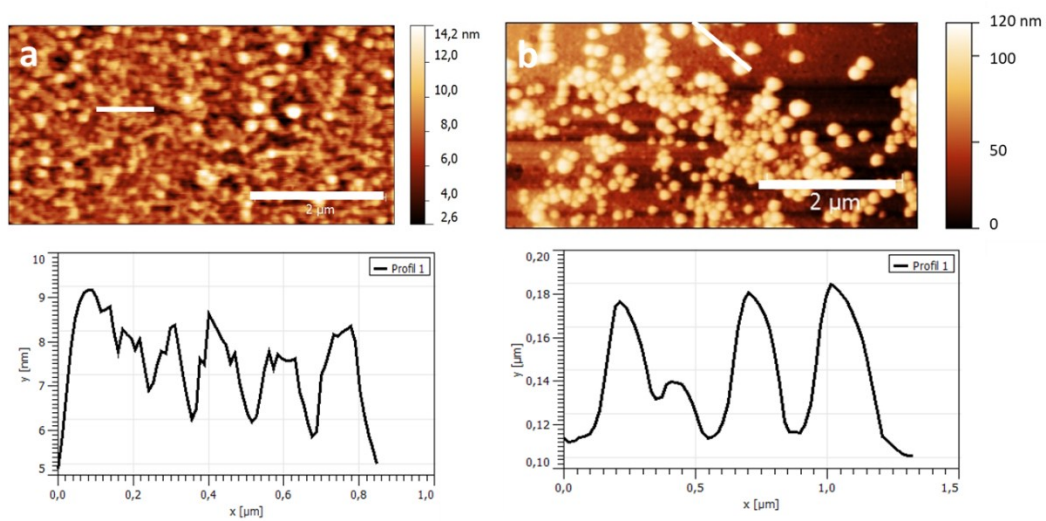


Figure S18. XRD pattern of PEG₆₀₀₀.

