Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Core-Crosslinked Worm-like Micelles from Polyether-based Diblock Terpolymers

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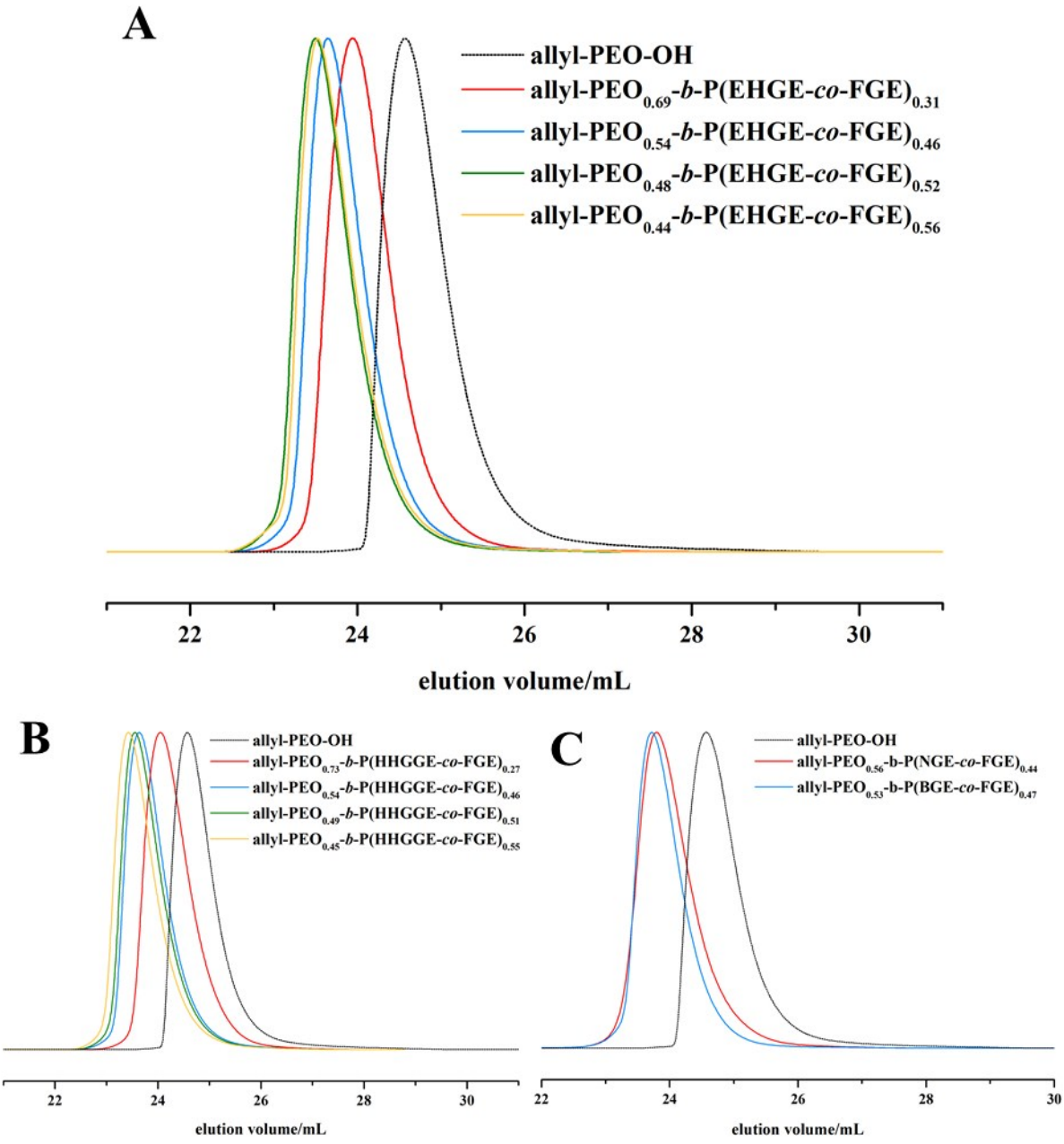

Figure S1: SEC traces of diblock terpolymers containing EHGE (**A**), HHGGE (**B**) and NGE or BGE (**C**) as hydrophobic comonomer.

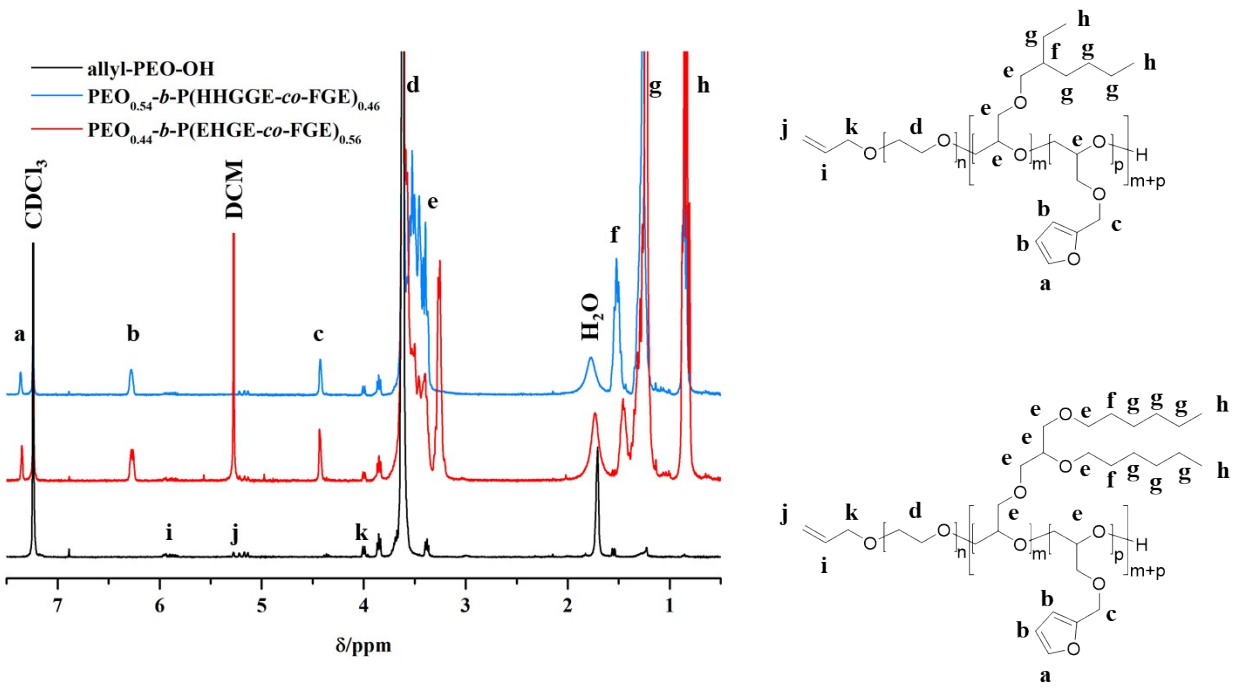

Figure S2: [1]H NMR spectra of the allyl-PEO-OH macroinitiator before (black) and after block extension with EHGE (red) or HHGGE (blue) and FGE.

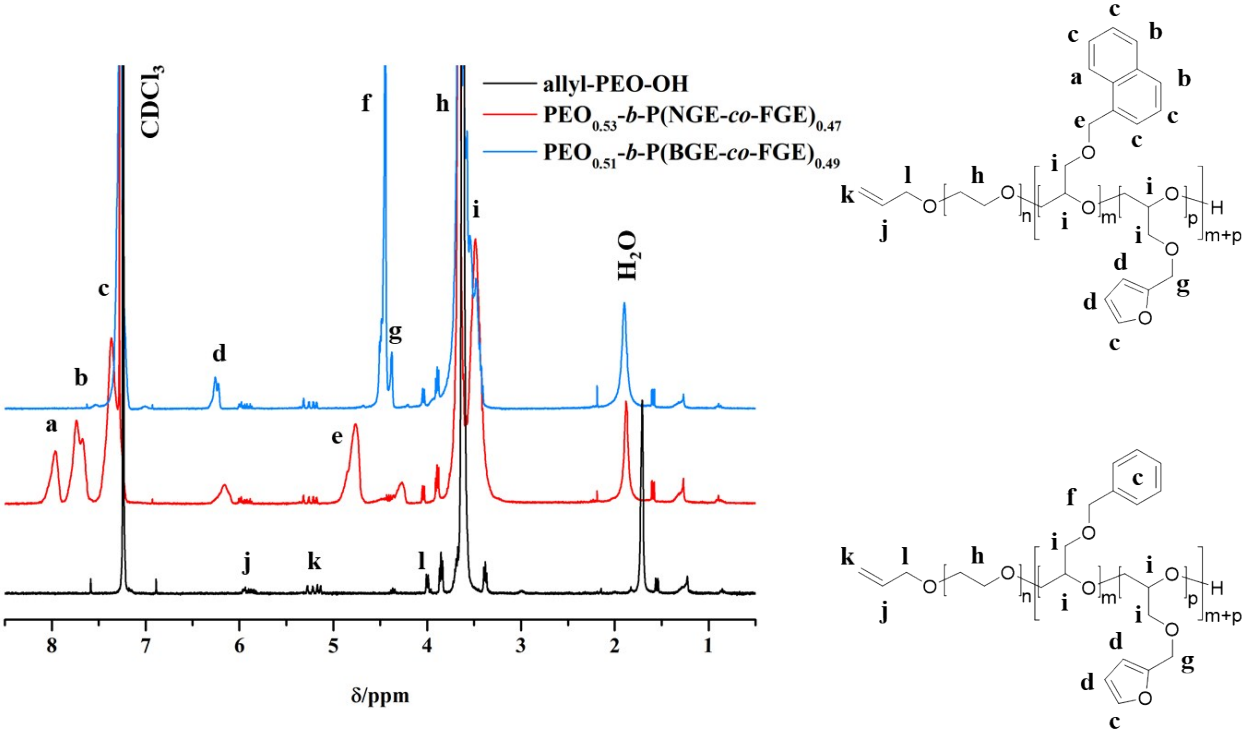

Figure S3: [1]H NMR spectra of the allyl-PEO-OH macroinitiator before (black) and after block extension with NGE (red) or BGE (blue) and FGE.

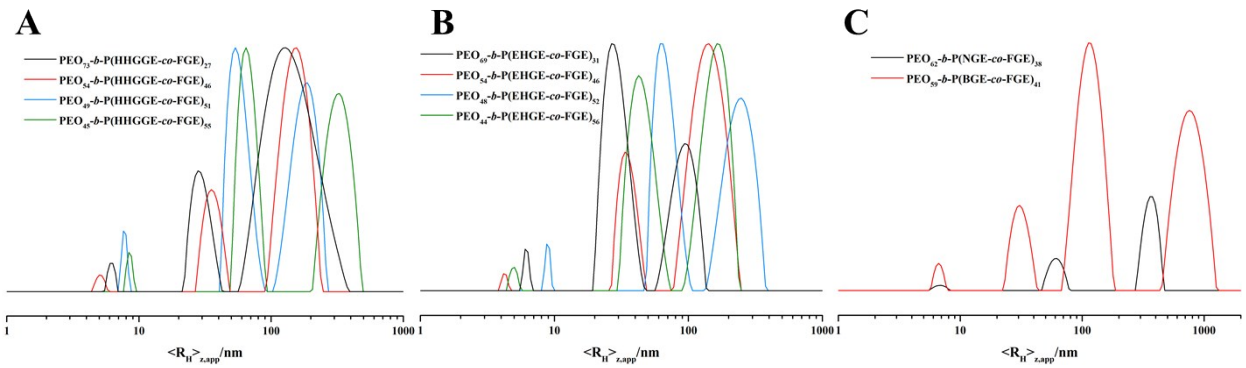

Figure S4: Intensity-weighted DLS CONTIN plots of micellar solutions (1 mg mL^{-1}) of different amphiphilic diblock terpolymers also listed in Table 1.

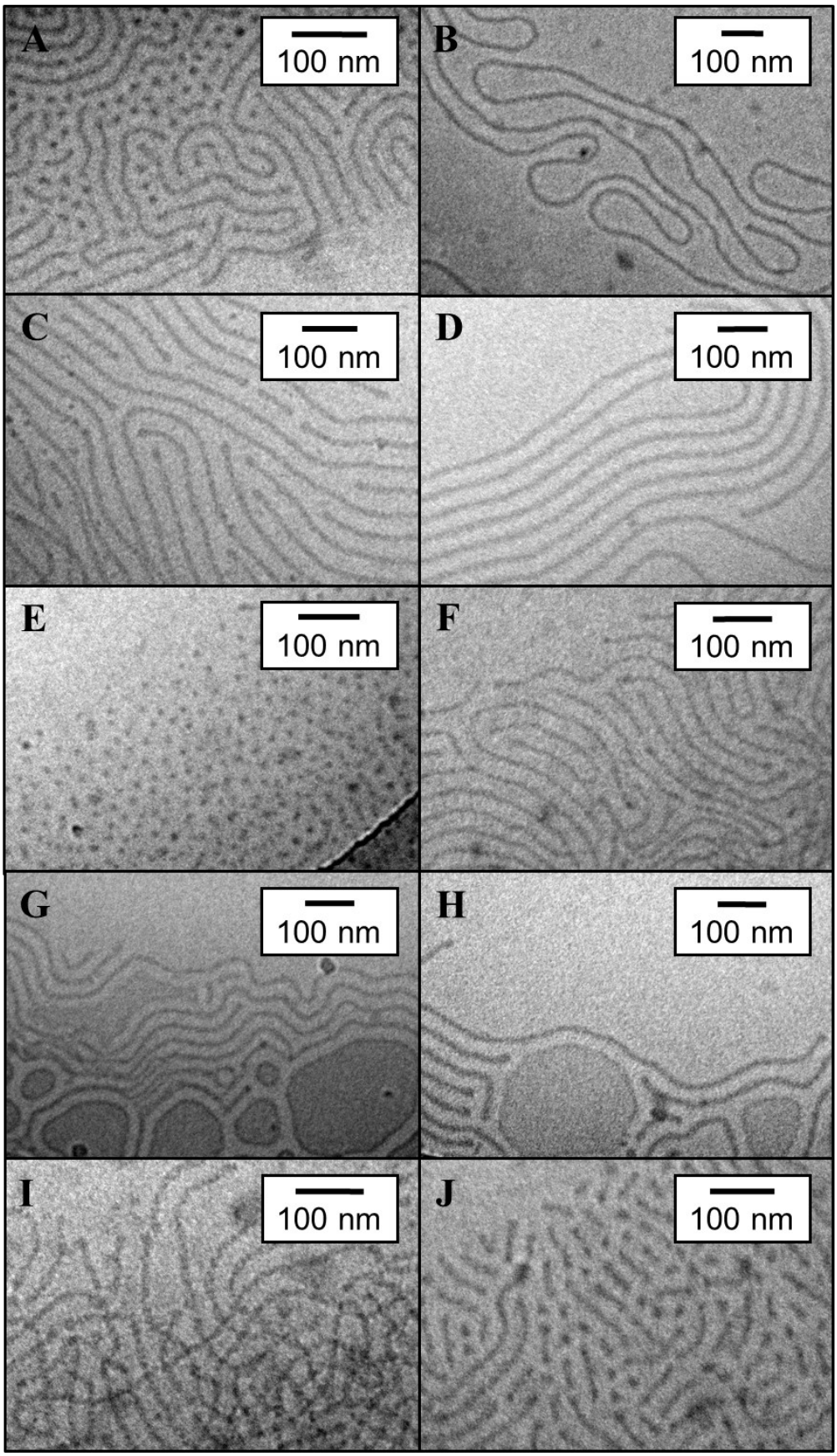
A
100 nm
B
100 nm
C
100 nm
D
100 nm
E
100 nm
F
100 nm
G
100 nm
H
100 nm
I
100 nm
J
100 nm

Figure S5: Representative selection of cryo-TEM micrographs for each micellar system investigated in this study. **A**: PEO_{69}-*b*-P(EHGE-*co*-FGE)$_{31}$, **B**: PEO_{54}-*b*-P(EHGE-*co*-FGE)$_{46}$, **C**: PEO_{48}-*b*-P(EHGE-*co*-FGE)$_{52}$, **D**: PEO_{44}-*b*-P(EHGE-*co*-FGE)$_{56}$, **E**: PEO_{73}-*b*-P(HHGGE-*co*-FGE)$_{27}$, **F**: PEO_{54}-*b*-P(HHGGE-*co*-FGE)$_{46}$, **G**: PEO_{49}-*b*-P(HHGGE-*co*-FGE)$_{51}$, **H**: PEO_{45}-*b*-P(HHGGE-*co*-FGE)$_{55}$, **I**: PEO_{62}-*b*-P(NGE-*co*-FGE)$_{38}$, **J**: PEO_{59}-*b*-P(BGE-*co*-FGE)$_{41}$. Concentration of aqueous solutions: 1 mg mL-1 diblock terpolymer.

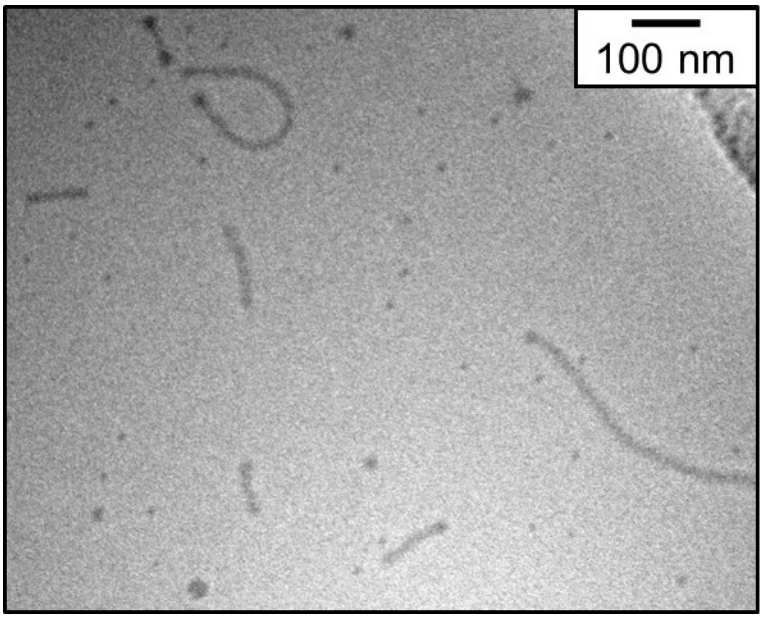

Figure S6: Cryo-TEM micrograph of micelles prepared from PEO_{44}-*b*-P(EHGE-*co*-FGE)$_{56}$ via the solvent switch method. The diblock terpolymer was dissolved in THF at a concentration of 10 mg mL^{-1} and the solution was added dropwise to micropure water. THF was allowed to evaporate by stirring the solution in an open vial. The final concentration of the polymer in micropure water was 1 mg mL^{-1}. Lowering the diblock terpolymer concentration of the THF solution to 1.6 mg mL^{-1} or adding water to the THF solution instead did not lead to different results here.

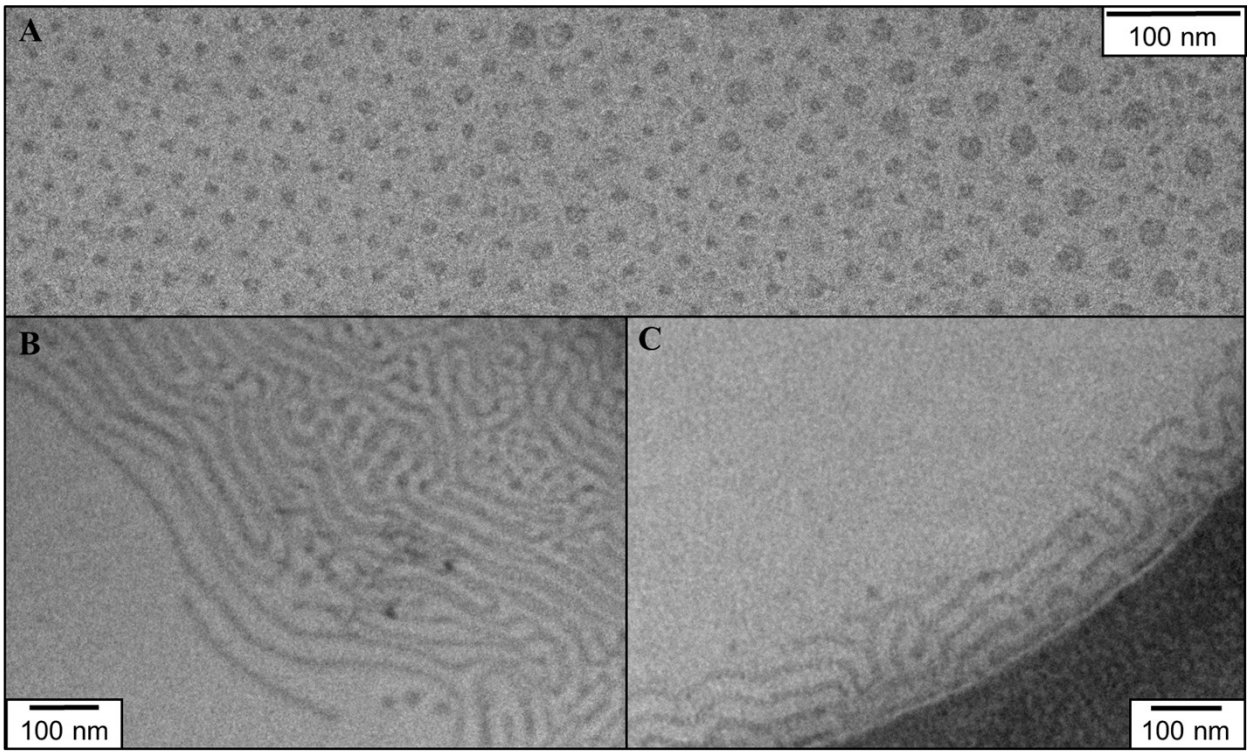

Figure S7: Cryo-TEM micrographs of a mixture of 20wt% PEO_{50}-*b*-P(*t*BGE-*co*-FGE)$_{50}$ (M_n(NMR): 8 100 g mol^{-1}, FGE content: 4.7%, Đ: 1.07, $<R_H>_{z,app}$: 13.5 nm, r: 5.1 ± 0.7 nm, **A**) and 80wt% PEO_{48}-*b*-P(EHGE-*co*-FGE)$_{52}$. The diblock terpolymer species were mixed before (**B**) or after (**C**) direct dissolution and self-assembly in micropure water for three days.

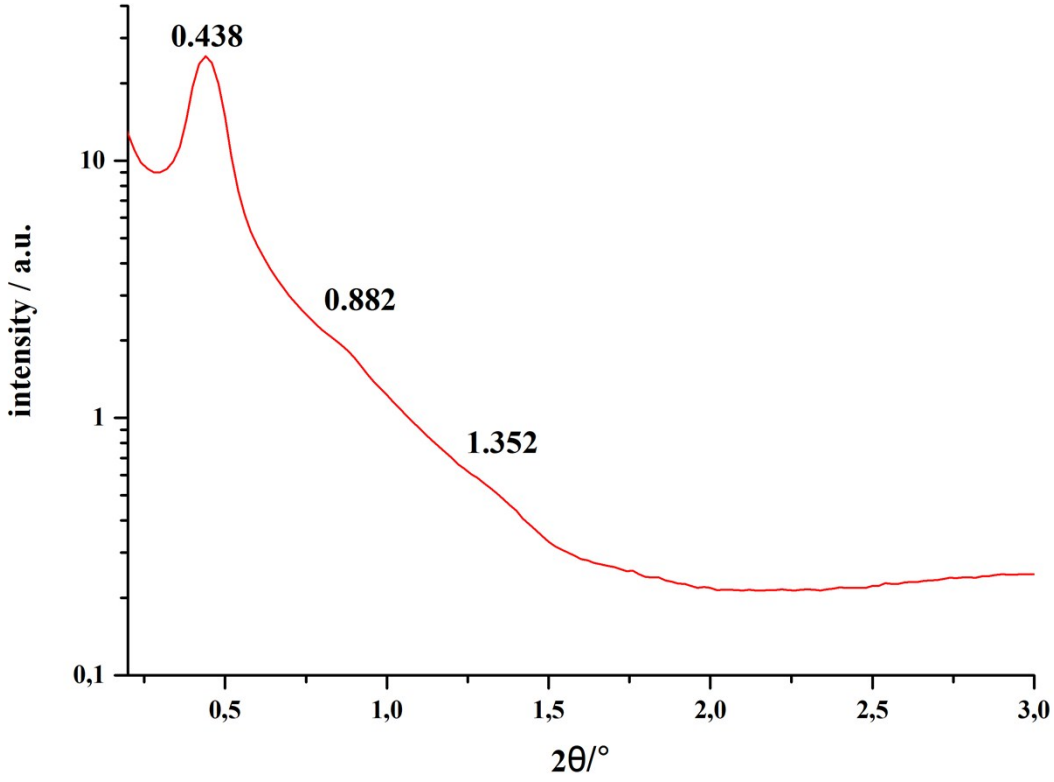

Figure S8: SAXS pattern of a thin film of PEO_{44}-*b*-P(EHGE-*co*-FGE)$_{56}$ and the bismaleimide crosslinker used for film rehydration and micelle formation. The reflexes highlighted indicate a lamellar structure of the diblock terpolymer film.

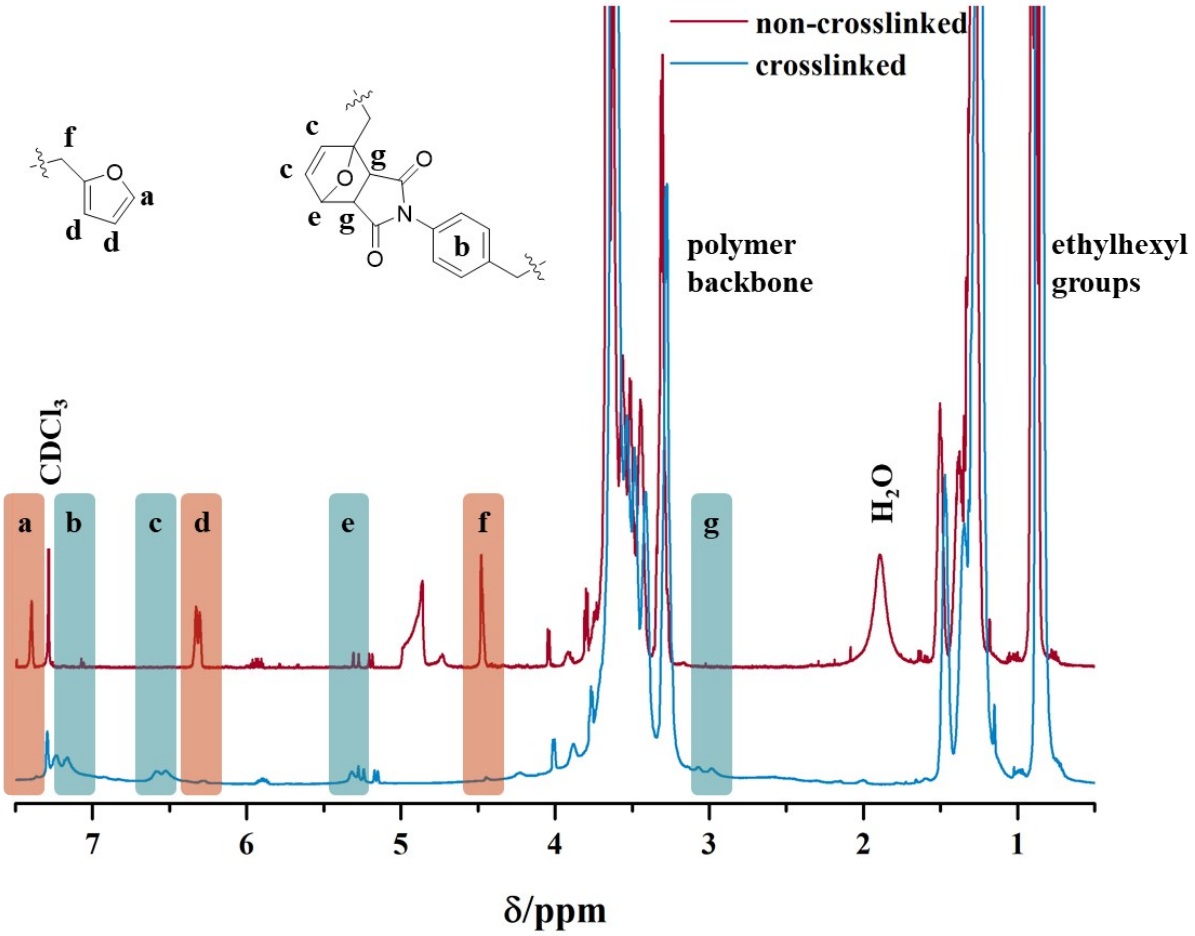

Figure S9: HR-MAS ^{1}H NMR spectra of crosslinked and non-crosslinked micelles prepared from PEO_{44}-*b*-P(FGE-*co*-EHGE)$_{56}$. Integration of the corresponding signals results in a degree of crosslinking of approximately 80%.

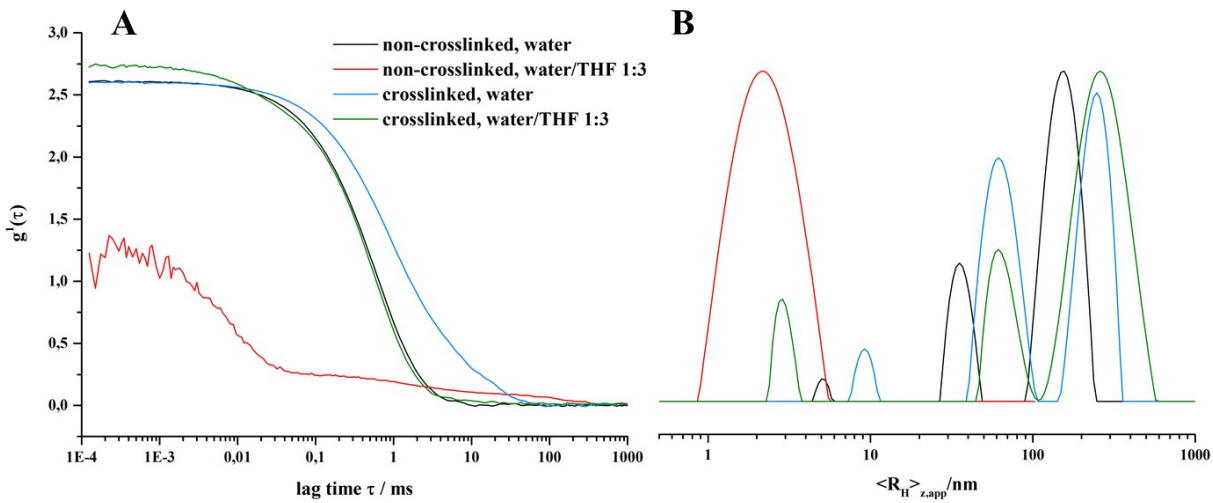

Figure S10: DLS correlation functions (**A**) and DLS intensity-weighted CONTIN plots (**B**) of crosslinked and non-crosslinked micelles formed from PEO_{44}-*b*-P(FGE-*co*-EHGE)$_{56}$ before dilution with THF (diblock terpolymer concentration 1 mg mL^{-1}) and after dilution with THF (diblock terpolymer concentration 0.25 mg mL^{-1}). Comparable results were found for micelles formed from other polymeric species investigated in this study, except for PEO_{69}-*b*-P(EHGE-*co*-FGE)$_{31}$ and PEO_{73}-*b*-P(HHGGE-*co*-FGE)$_{27}$.