

Nano-assemblies with Core-Forming Hydrophobic Polypeptide *via* Polymerization-Induced Self-Assembly (PISA)

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SUPPORTING INFORMATION

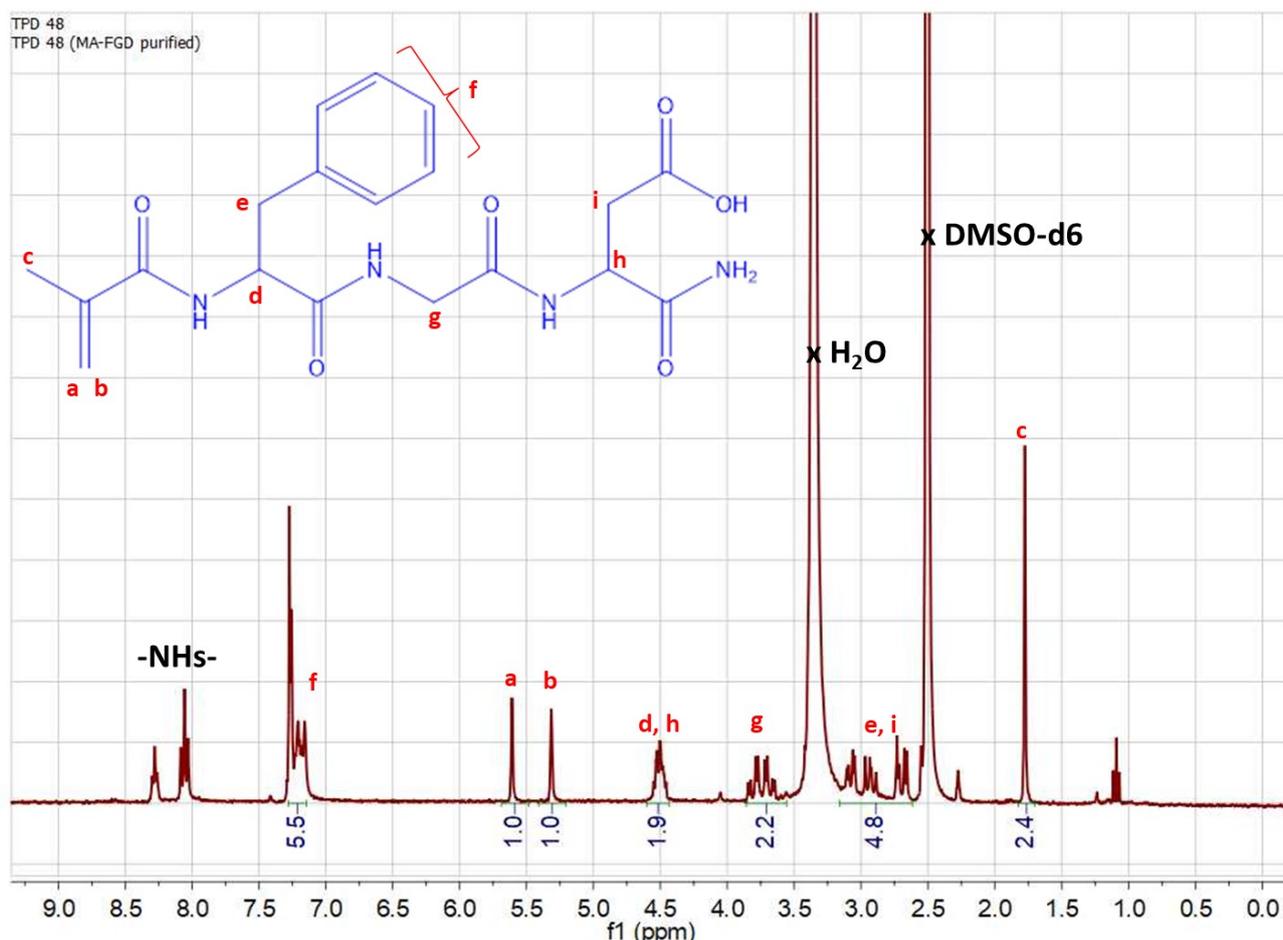
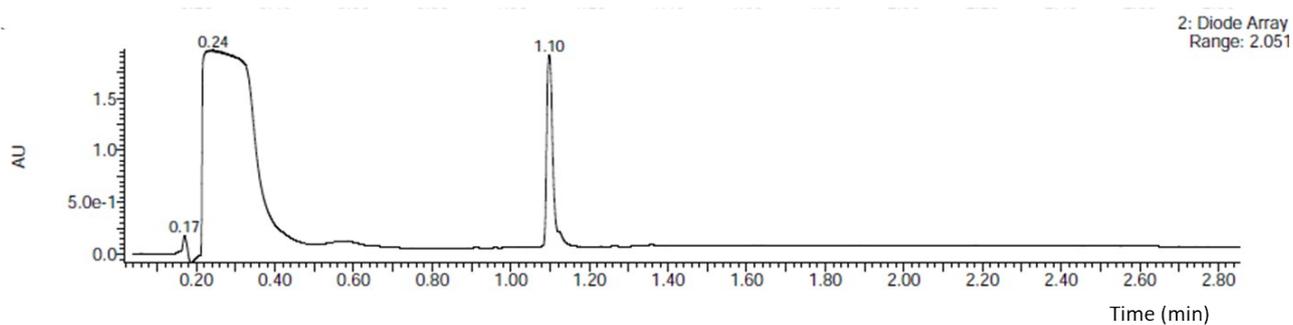


Figure S1. Chemical structure and ¹H NMR spectrum in DMSO-d₆ of MA-FGD



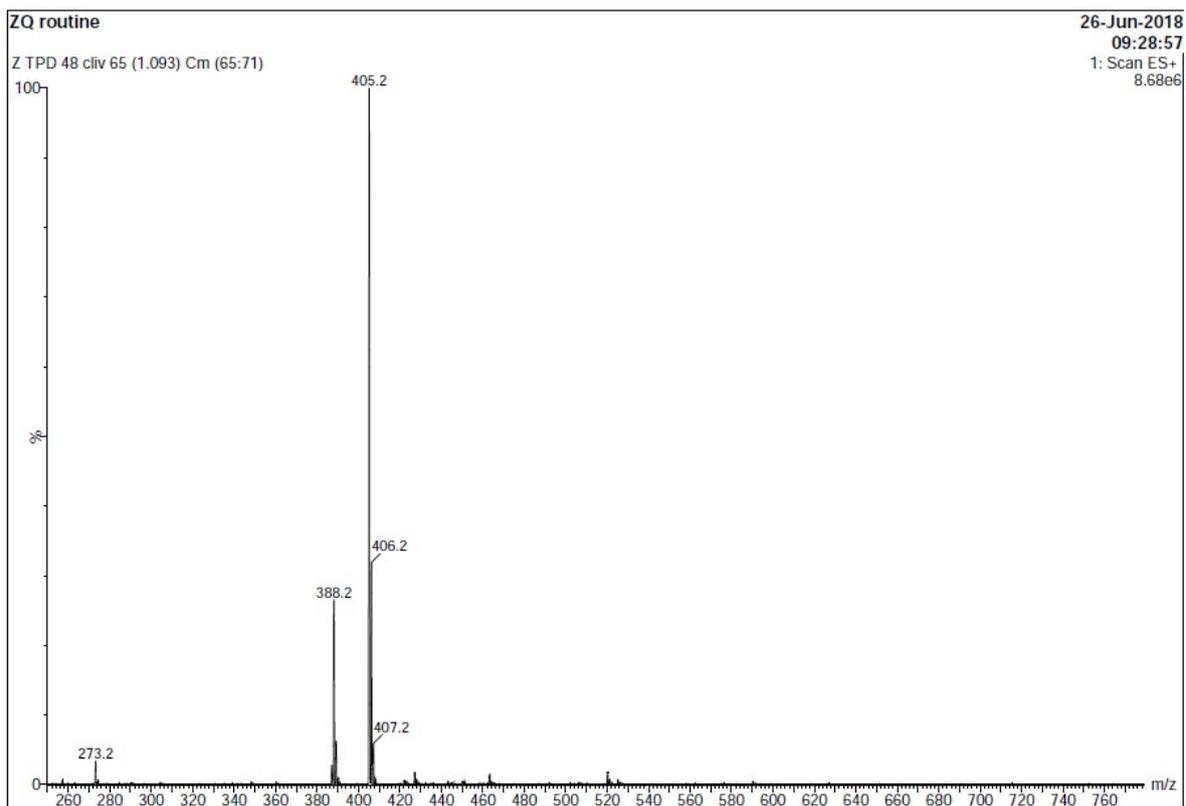


Figure S2. HPLC profiles and ESI-MS of MAm-FGD ($t_R = 1.10$ min, m/z 405.2 ($[M+H]^+$))

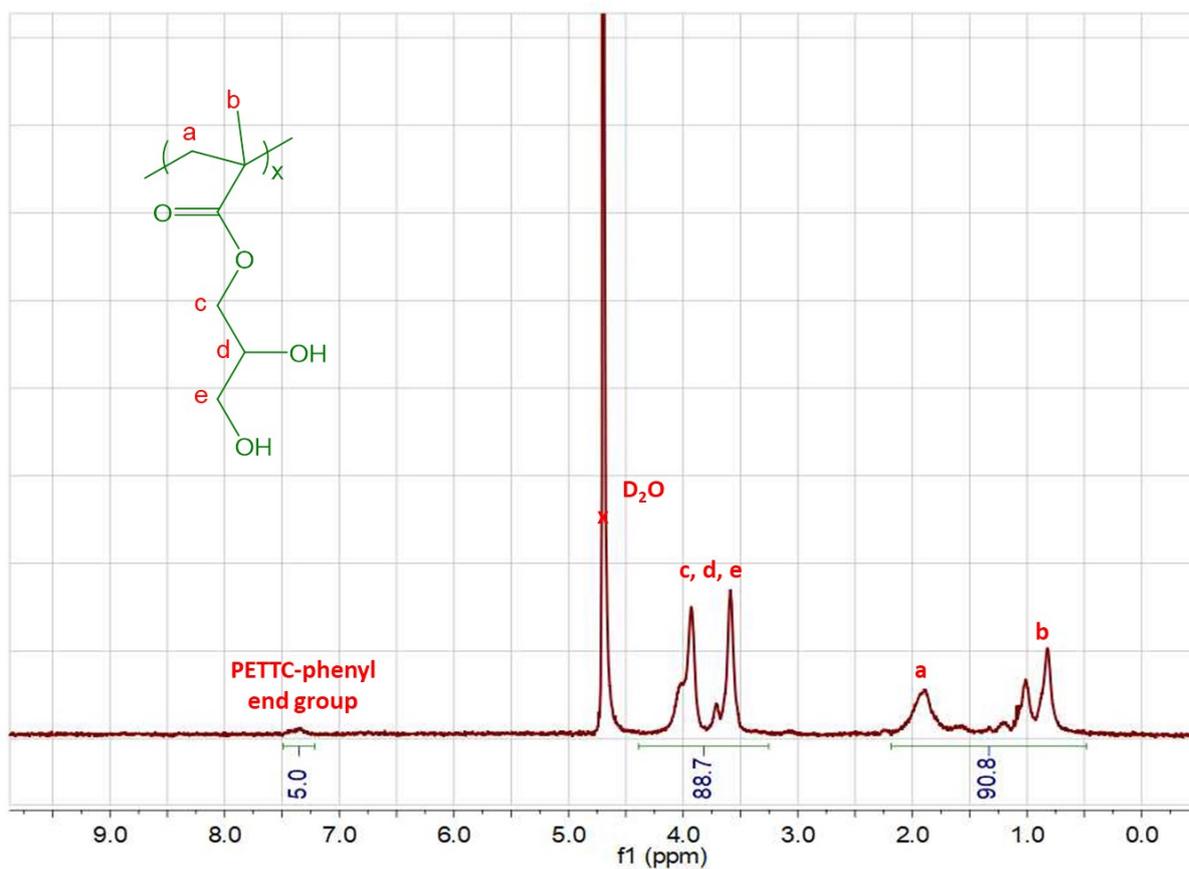


Figure S3. Chemical structure and ^1H NMR spectrum in D_2O of PGMA_{18} mCTA (mCTA 1)

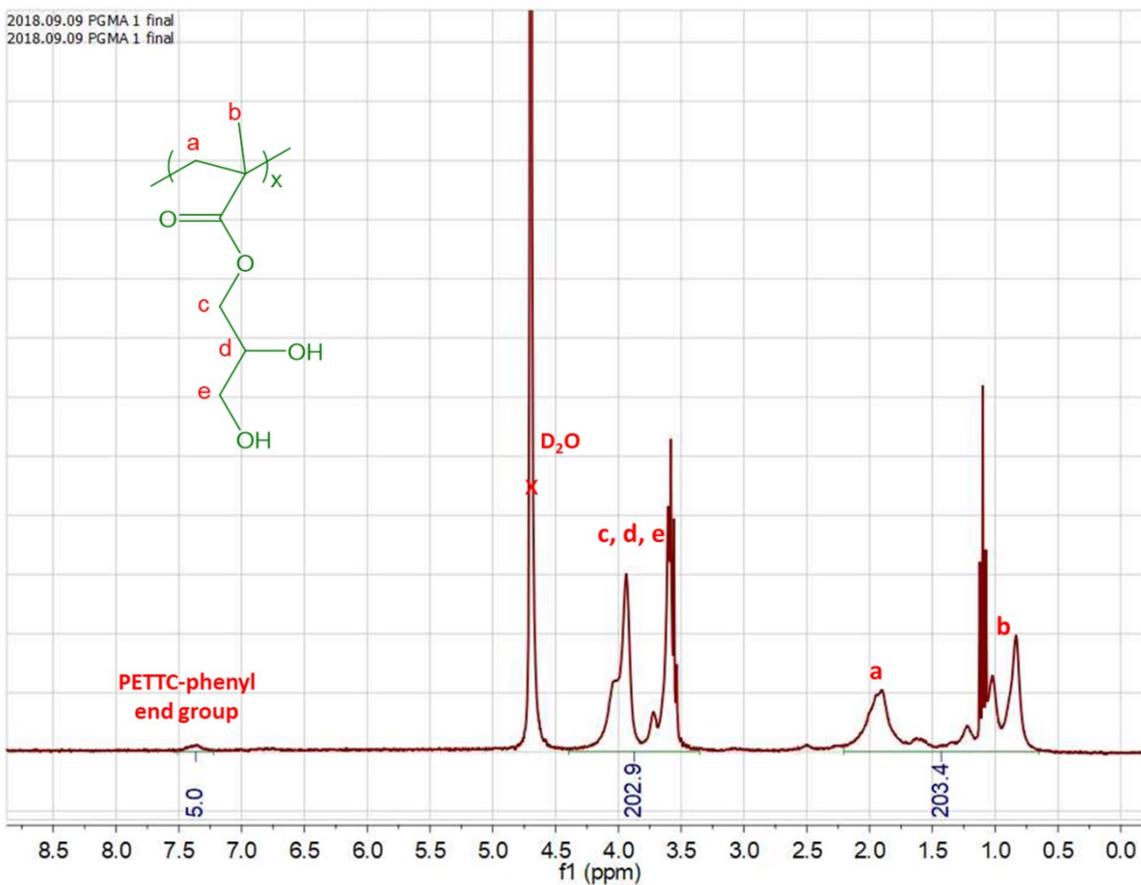


Figure S4. Chemical structure and 1H NMR spectrum in D_2O of $PGMA_{40}$ mCTA (mCTA 2)

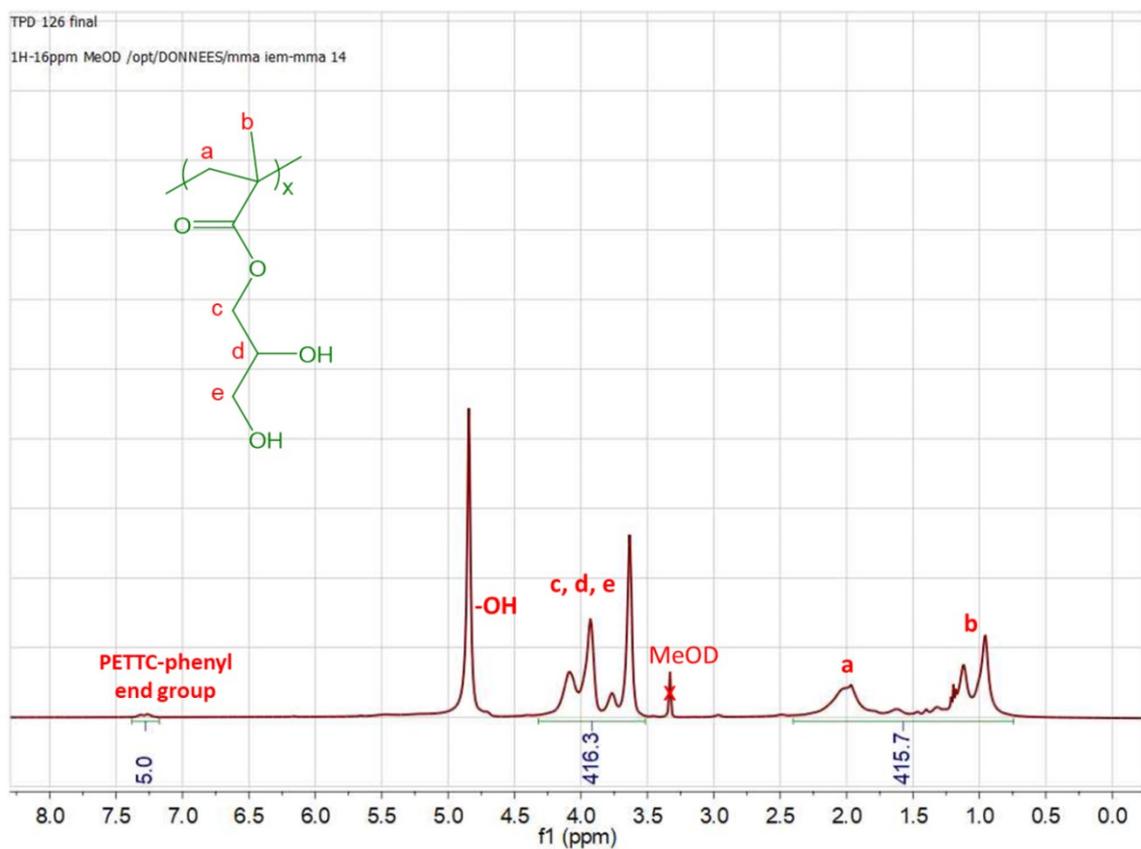


Figure S5. Chemical structure and 1H NMR spectrum in Methanol- d_4 of $PGMA_{83}$ mCTA (mCTA 3)

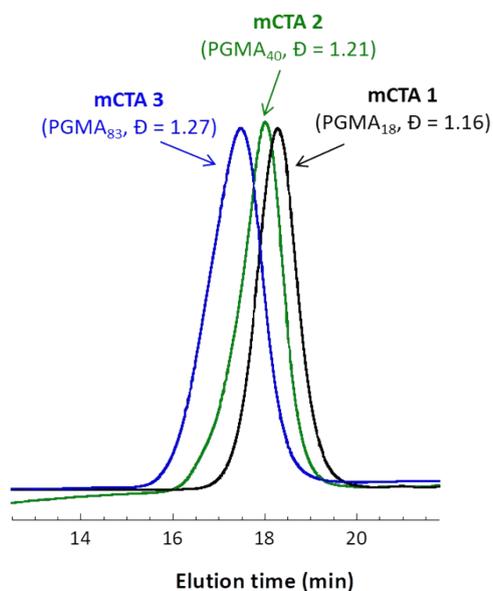


Figure S6. DMAc SEC data (refractive index detector) for the PGMA macro-CTAs

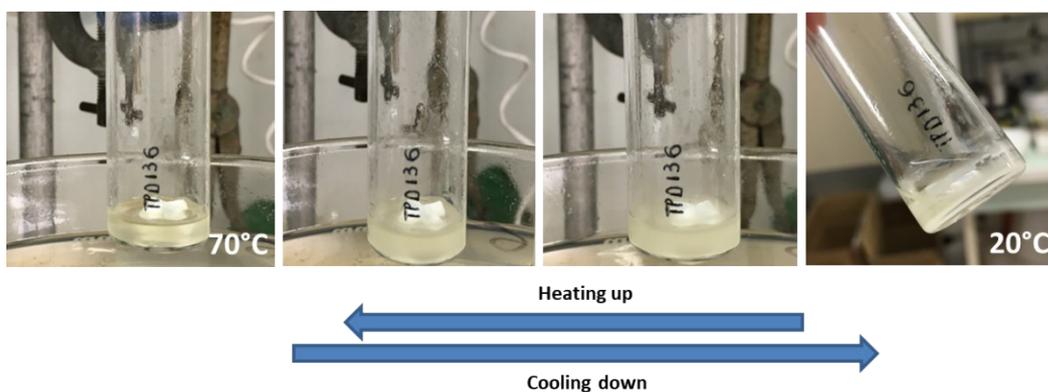


Figure S7. Photos taken for diblock copolymer $\text{PGMA}_{18}\text{-}b\text{-P}(\text{MAm-GFF})_4$ obtained by PISA carried out at 11.2 % w/w in ethanol at 70°C and when cooling down to ambient temperature (ca. 20°C)

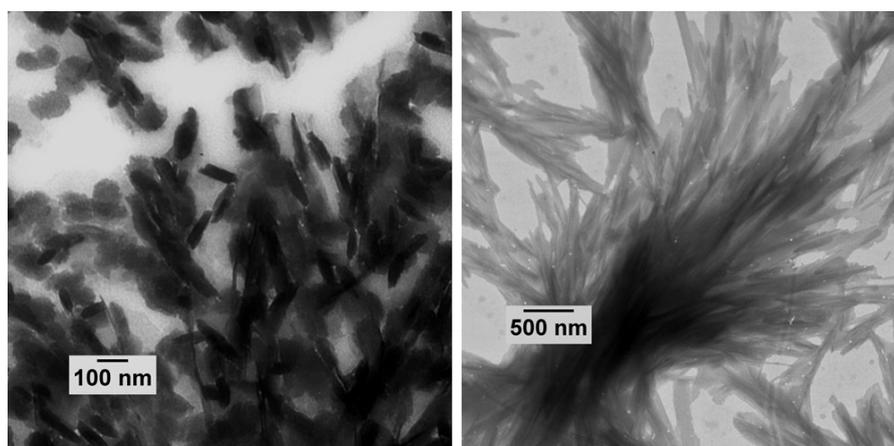


Figure S8. Representative TEM images of $\text{PGMA}_{18}\text{-}b\text{-P}(\text{MAm-GFF})_4$ (left) and $\text{PGMA}_{18}\text{-}b\text{-P}(\text{MAm-GFF})_9$ (right) suspension in ethanol at 70°C (0.1% w/w). the TEM grids were prepared at 70°C.

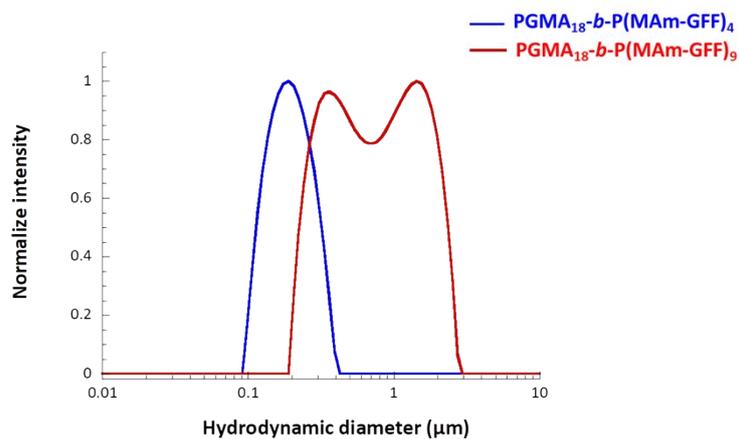


Figure S9. Intensity-average hydrodynamic diameter distribution of $\text{PGMA}_{18}\text{-}b\text{-P}(\text{MAm-GFF})_4$ and $\text{PGMA}_{18}\text{-}b\text{-P}(\text{MAm-GFF})_9$ suspension in ethanol at 0.112 % w/w and 0.125 % w/w respectively

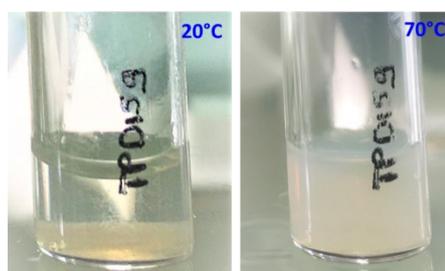


Figure S10. Diblock copolymer $\text{PGMA}_{18}\text{-}b\text{-P}((\text{MAm-GFF})_9\text{-}co\text{-GMA}_{48})$ obtained by PISA carried out at 15% w/w in ethanol at 70°C: on the left: after cooling from 70°C to 20°C and on the right: heating it up again from 20°C to 70°C (right)

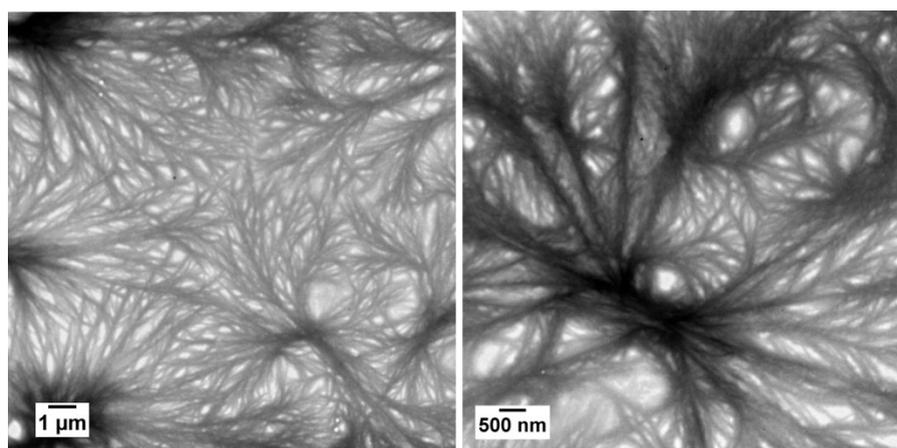


Figure S11. TEM images of $\text{PGMA}_{18}\text{-}b\text{-P}((\text{MAm-GFF})_9\text{-}co\text{-GMA}_{48})$ diblock copolymer diluted at 70°C.

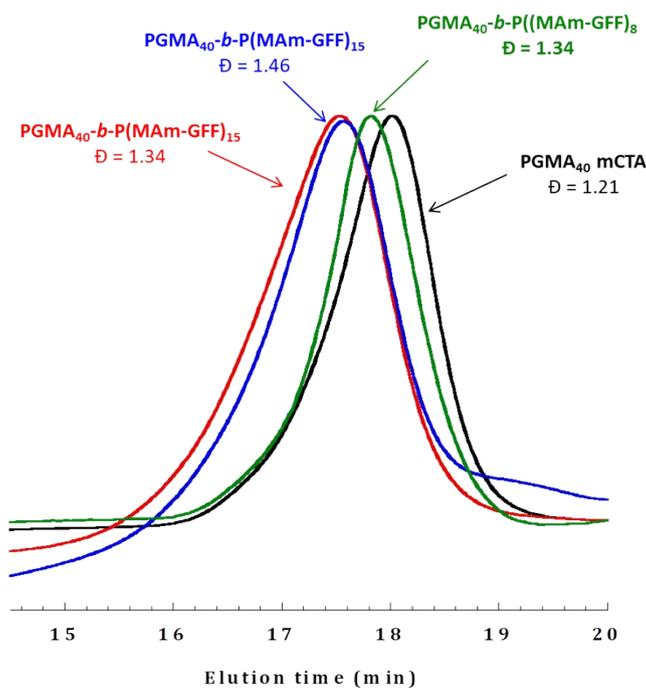


Figure S12. DMAC SEC chromatograms (refractive index detector) of mCTA **2** (PGMA_{40}) (black) and the diblock copolymers: $\text{PGMA}_{40}\text{-}b\text{-P}(\text{MAm-GFF})_8$ prepared *via* RAFT-mediated PISA in ethanol (green), $\text{PGMA}_{40}\text{-}b\text{-P}(\text{MAm-GFF})_{15}$ prepared *via* RAFT-mediated PISA in 1/1 v/v and 1/2 v/v water/acetonitrile mixtures (red and blue respectively)

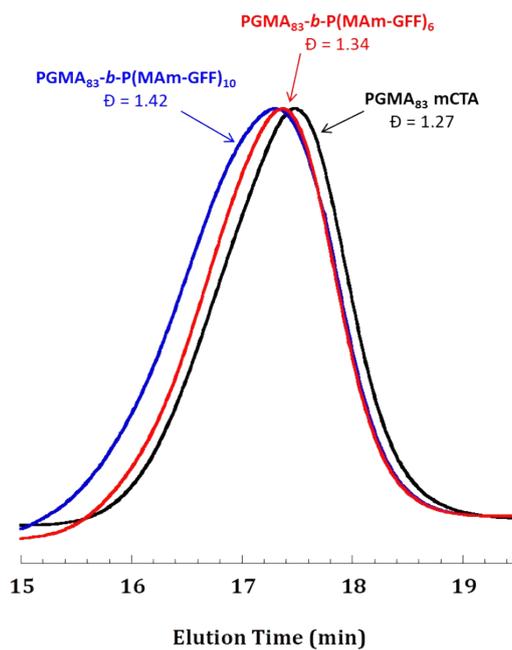


Figure S13. DMAC SEC chromatograms (refractive index detector) of mCTA **3** (PGMA_{83}) and diblock copolymers $\text{PGMA}_{83}\text{-}b\text{-P}(\text{MAm-GFF})_6$ (red) and $\text{PGMA}_{83}\text{-}b\text{-P}(\text{MAm-GFF})_{10}$ (blue) prepared *via* RAFT-mediated PISA in ethanol

Table S1. Summary of the RAFT –PISA syntheses conditions and results of the diblock copolymers.

Products	Solvent	Visual aspect at starting time of PISA (at 70°C)	Solids content (%)	Initial ratio [mCTA] ₀ : [peptide] ₀ : [GMA] ₀ or [mCTA] ₀ : [peptide] ₀ : [HPMA] ₀	Monomer peptide conversion (%)	M _n GPC (DMAC)	Đ _{GPC} (DMAC)	Visual aspect at ending time of PISA (at 70°C)
Macro-CTA 1: PGMA₁₈	-	-	-	-	-	20 500	1.16	-
PGMA ₁₈ - <i>b</i> -P(MAm-GFF) ₄	Ethanol	Solution	5%	1 : 5	45%	-	-	Clear solution
PGMA ₁₈ - <i>b</i> -P(MAm-GFF) ₄	Ethanol	Emulsion	11.2 %	1 : 5	87%	22 900	1.17	Turbid suspension
PGMA ₁₈ - <i>b</i> -P(MAm-GFF) ₉	Ethanol	Emulsion	12.5 %	1 : 10	92%	24 300	1.28	Turbid suspension
PGMA ₁₈ - <i>b</i> -P((MAm-GFF) ₉ -CO- GMA ₄₈)	Ethanol	Emulsion	15%	1 : 10 : 48	90%	38 300	1.33	Turbid suspension
PGMA ₁₈ - <i>b</i> -P((MAm-GFF) ₉ -CO- HPMA ₆₁)	Ethanol	Emulsion	15%	1 : 10 : 61	90%	45 400	1.34	Clear dispersion
PGMA ₁₈ - <i>b</i> -P((MAm-GFF) ₁₉ -CO-HPMA ₅₀)	Ethanol	Emulsion	15%	1 : 20 : 50	95%	51 400	1.32	Clear dispersion
PGMA ₁₈ - <i>b</i> -P(MAm-FGD) ₁₀	Water	Solution	10%	1 : 10	100%	25 900	1.24	Turbid suspension
Macro-CTA 2: PGMA₄₀	-	-	-	-	-	23 400	1.21	-
PGMA ₄₀ - <i>b</i> -PMAGFF ₈	Ethanol	Emulsion	12%	1 : 10	86%	31 000	1.34	Turbid suspension
PGMA ₄₀ - <i>b</i> -PMAGFF ₁₅	H ₂ O/ACN 1/1 v/v	Solution	10%	1 : 20	69%	42 600	1.34	Clear dispersion
PGMA ₄₀ - <i>b</i> -PMAGFF ₁₅	H ₂ O/ACN 1/2 v/v	Solution	10%	1 : 20	72%	40 100	1.46	Clear dispersion
PGMA ₄₀ - <i>b</i> -P(MAm-FGD) ₂₀	Water	Solution	10%	1 : 20	100%	33 000	1.24	Turbid suspension
Macro-CTA 3: PGMA₈₃	-	-	-	-	-	45 300	1.27	-
PGMA ₈₃ - <i>b</i> -PMAGFF ₆	Ethanol	Emulsion	12%	1 : 6	90%	46 100	1.34	Turbid suspension
PGMA ₈₃ - <i>b</i> -PMAGFF ₁₀	Ethanol	Emulsion	12%	1 : 10	95%	51 000	1.42	Turbid suspension
PGMA ₈₃ - <i>b</i> -P(MAm-FGD) ₂₀	Water	Solution	10%	1 : 20	100%	53 500	1.32	Clear dispersion

Note: The ratio of mCTA and ACVA initiator used was 0.2 in all the reactions.