Morphological Evolution of Poly(glycerol monomethacrylate-stat-Glycine-Phenylalanine-Phenylalanine-methacrylamide-b-Poly(2-hydroxypropylmethacrylate)

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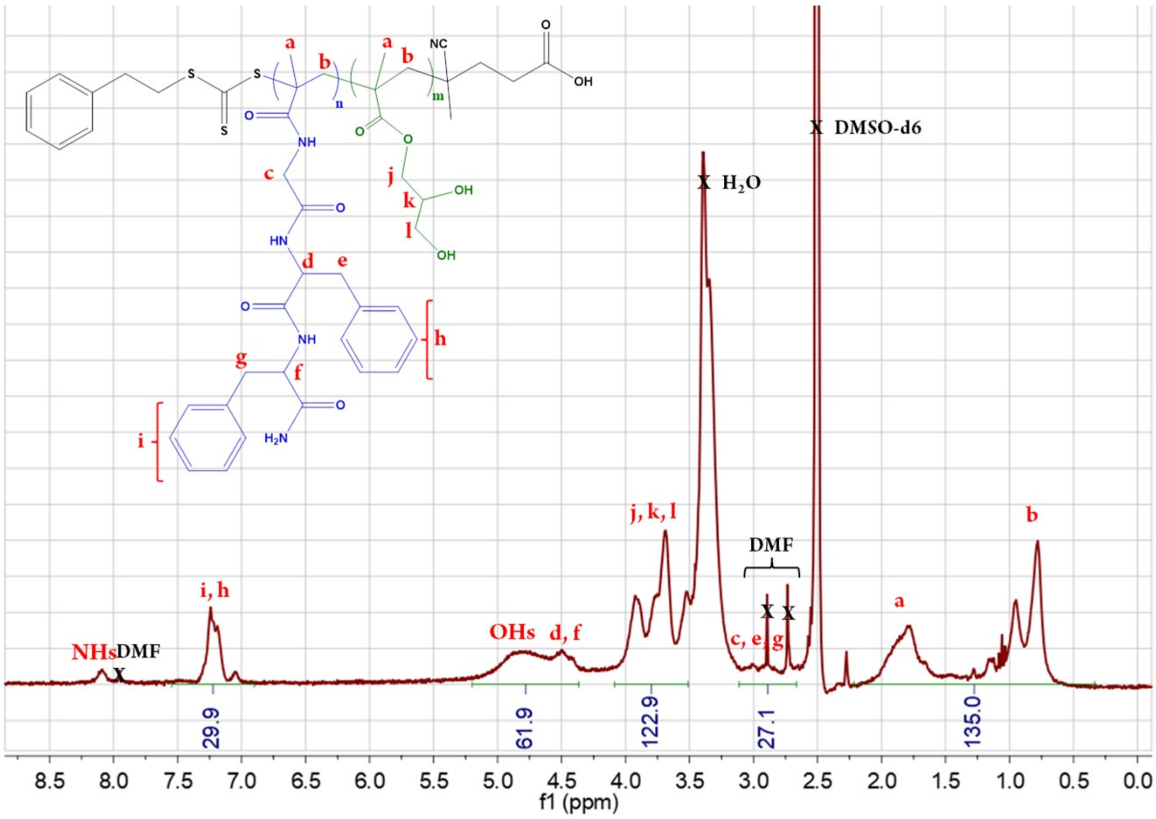
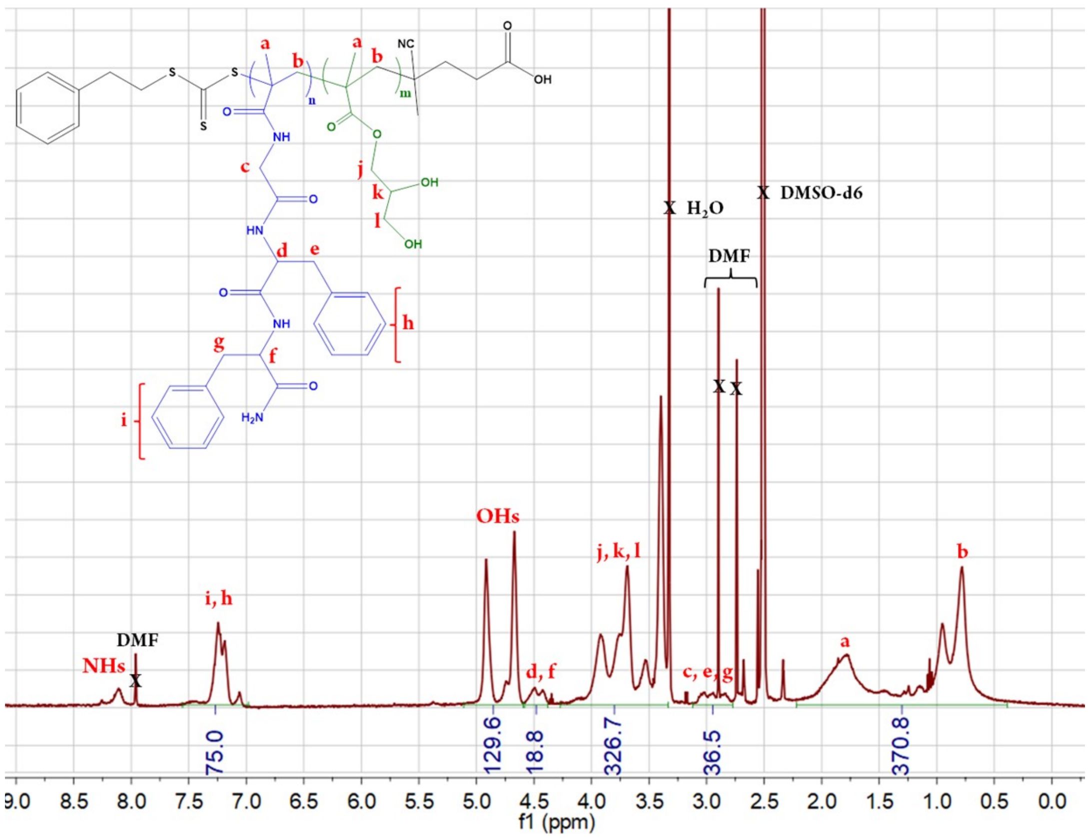
SUPPORTING INFORMATION

(a)



(b)



(c)

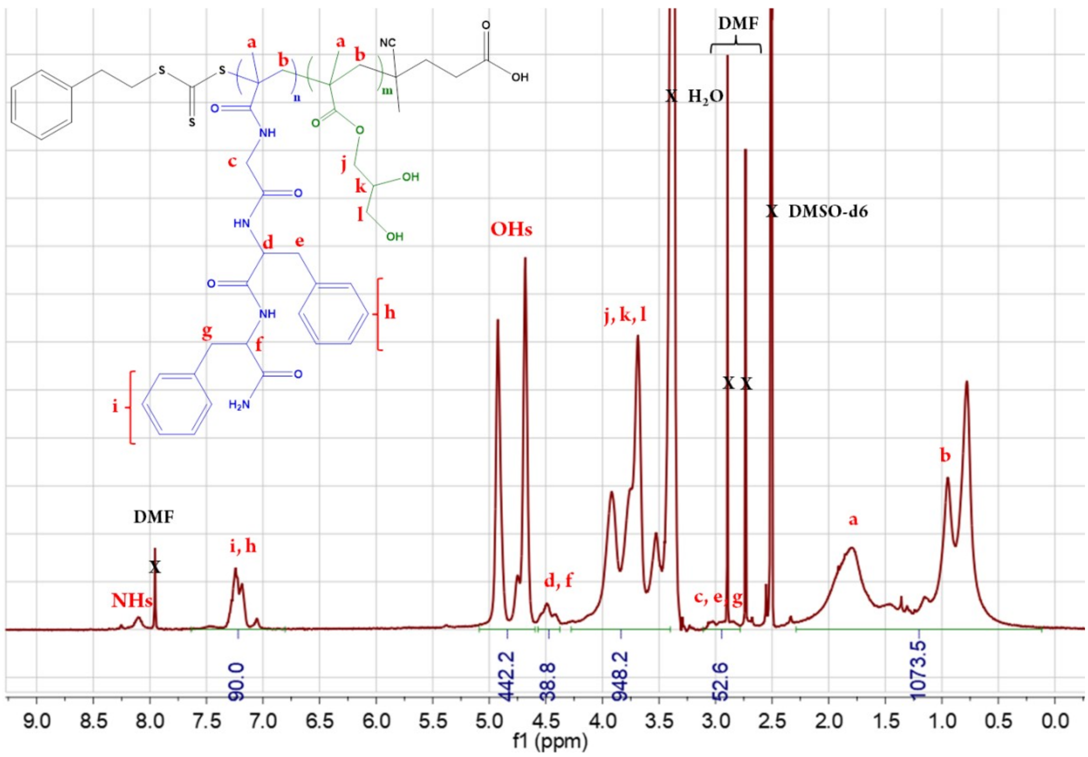


Figure S1. Chemical structure and ^{1}H NMR spectrum in DMSO-d6 of (a) P(GMA$_{24}$-*stat*-(MAm-GFF)$_{3}$) (mCTA **1**), (b) P(GMA$_{65}$-*stat*-(MAm-GFF)$_{7}$) (mCTA **2**) and (c) P(GMA$_{200}$-*stat*-(MAm-GFF)$_{9}$) (mCTA **3**).

Determination of the mCTA DP and composition

The DP and composition of the mCTA were calculated from the GMA and MAM-GFF conversions determined by ^{1}H NMR spectroscopy and the target DP of each monomers, as described in *Macromolecules* **2020**, 53, 16, 7034–7043.

$DP_{MAM\text{-}GFF} = [MAM\text{-}GFF]_0 / [PETTC]_0 \times \alpha_{MAM\text{-}GFF}$ and $DP_{GMA} = [GMA]_0 / [PETTC]_0 \times \alpha_{GMA}$, where $\alpha_{MAM\text{-}GFF}$ and α_{GMA} are the conversions in MAM-GFF and GMA respectively.

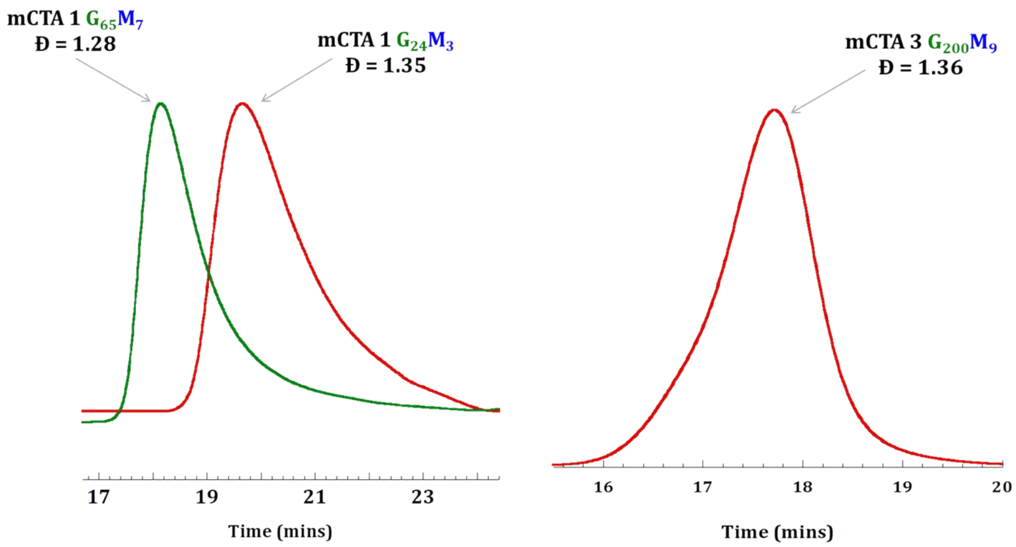


Figure S2. DMF SEC data of P(GMA$_{24}$-*stat*-(MAm-GFF)$_3$) (mCTA **1**), P(GMA$_{65}$-*stat*-(MAm-GFF)$_7$) (mCTA **2**) and DMAc SEC data P(GMA$_{200}$-*stat*-(MAm-GFF)$_9$) (mCTA **3**).

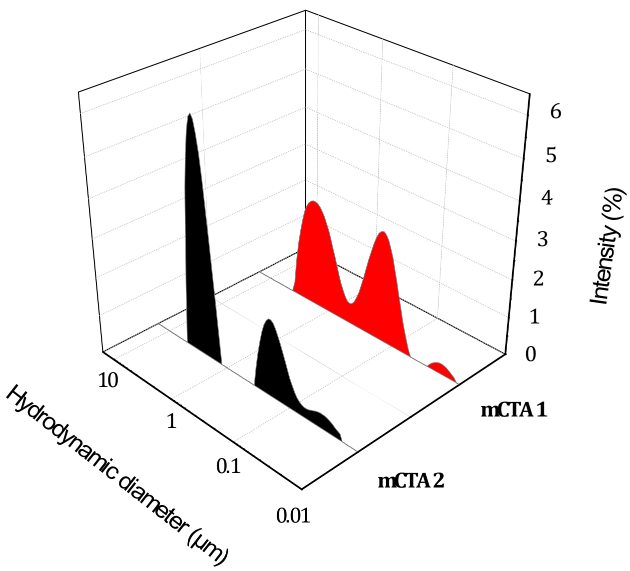


Figure S3. Intensity-average hydrodynamic diameter distributions of P(GMA_{24}-*stat*-(MAm-GFF)$_3$) (mCTA 1) and P(GMA_{65}-*stat*-(MAm-GFF)$_7$) (mCTA 2) in MilliQ water at 0.1 % w/w at 30°C.

Table S1. Molecular characterization (SEC in DMF) of P(GMA-*stat*-(MAm-GFF)) macro-CTAs and P(GMA-*stat*-(MAm-GFF))-*b*-PHPMA synthesized at 10% w/w solids via RAFT dispersion polymerization of HPMA in water and water-ethanol mixtures at 70 °C.

No.	Composition	Solvent	Mn (g/mol)	Mw (g/mol)	Đ
1	G_{24} M_3	DMF	6600	8900	1.35
2	G_{24} M_3 $\mathbf{H_{14}}$	H_2O	10200	13300	1.31
3	G_{24} M_3 $\mathbf{H_{29}}$	H_2O	13700	16590	1.23
4	G_{24} M_3 $\mathbf{H_{58}}$	H_2O	18100	21800	1.21
5	G_{24} M_3 $\mathbf{H_{108}}$	H_2O	37400	46000	1.23
6	G_{65} M_7	DMF	13300	17000	1.28
7	G_{65} M_7 $\mathbf{H_{42}}$	H_2O	23100	29000	1.26
8	G_{65} M_7 $\mathbf{H_{54}}$	H_2O	27000	33600	1.24
9	G_{65} M_7 $\mathbf{H_{63}}$	H_2O	33700	42000	1.25
10	G_{65} M_7 $\mathbf{H_{200}}$	H_2O	60000	74700	1.25
11	G_{65} M_7 $\mathbf{H_{66}}$	1 H_2O : 1 EtOH	34200	43000	1.24
12	G_{65} M_7 $\mathbf{H_{66}}$	1.2 H_2O : 0.8 EtOH	34000	43000	1.26
13	G_{65} M_7 $\mathbf{H_{66}}$	1.6 H_2O : 0.4 EtOH	33900	42000	1.24
14	G_{200} M_9	DMF	32100	44000	1.36
15	G_{200} M_9 $\mathbf{H_{51}}$	H_2O	80300	107000	1.33
16	G_{200} M_9 $\mathbf{H_{102}}$	H_2O	130400	172000	1.33
17	G_{200} M_9 $\mathbf{H_{250}}$	H_2O	241000	309500	1.28
18	G_{200} M_9 $\mathbf{H_{510}}$	H_2O	524700	645400	1.23