

Synthesis and Post-Polymerization Modification of Star-Shaped Poly(ethylene glycol)-*block*-Poly (dehydroalanine) Block Copolymers: A Versatile Template for Designing Multifunctional Polymers

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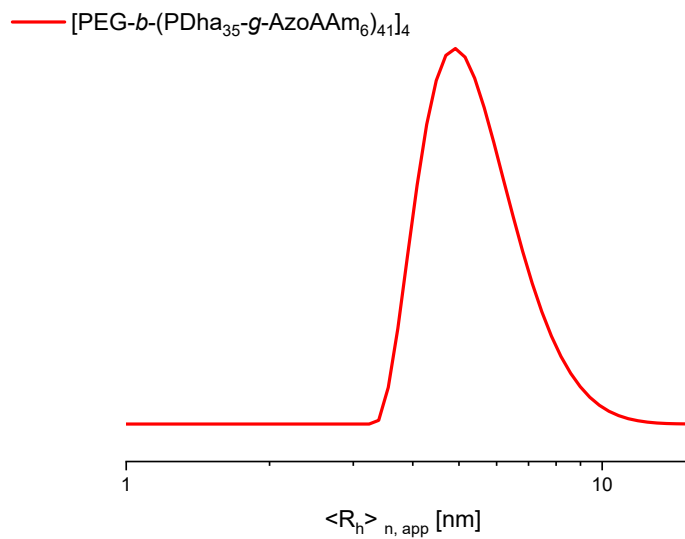

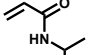
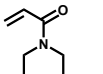
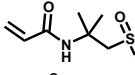
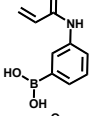
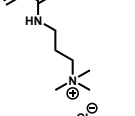
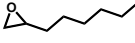
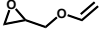
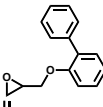
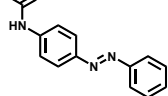


Figure S1: Number-weighted DLS CONTIN plot of [PEG₂₇-*b*-(PDha₃₅-g-AzoAAm₆)₄₁]₄ using 2mg/mL with deionized water as solvent.

Table S1: Summary of synthesized [PEG₂₇-*b*-(PDha-*g*-X)₄₁]₄ graft copolymers and their characterization *via* ¹H-NMR and SEC.

Modifier	Modifier	Eq modifier per PDha	Solvent\ Base	Polymer concentration	DoF [%] ^a	<i>M_n</i> [g/mol]	[<i>D</i>]
	PEG-LOM	10	3	6.25 mg/mL	7	-	-
	NiPAAm	30	1	12.5 mg/mL	63	8 600 ^b	1.8 ^b
	DEA	30	1	12.5 mg/mL	92	7 200 ^b	1.7 ^b
	AMPS	30	1	12.5 mg/mL	30	1 * 10 ⁶ ^c	3.4 ^c
	AAPBA	10	2	10 mg/mL	17	-	-
	AMTC	30	1	12.5 mg/mL	170	9 100 ^c	1.6 ^c
	EOcT	30	3	10 mg/mL	74	16 400 ^b	1.7 ^b
	AGE	15	1	12.5 mg/mL	99	9 000 ^b	1.8 ^b
	BpyOM	30	3	6.25 mg/mL	13	11 700 ^b	1.7 ^b
	AzoAAm	0.2	3	6.25 mg/mL	13	10 000 ^b	1.7 ^b

^aDetermined by ¹H-NMR spectroscopy. ^bDetermined SEC (eluent: DMSO/LiBr [99.79/0.21], 4-arm star PEG calibration) ^c Determined SEC (eluent: water and 0.3% TFA/ 0.1 M NaCl [pH < 2], polyvinyl pyridine calibration).

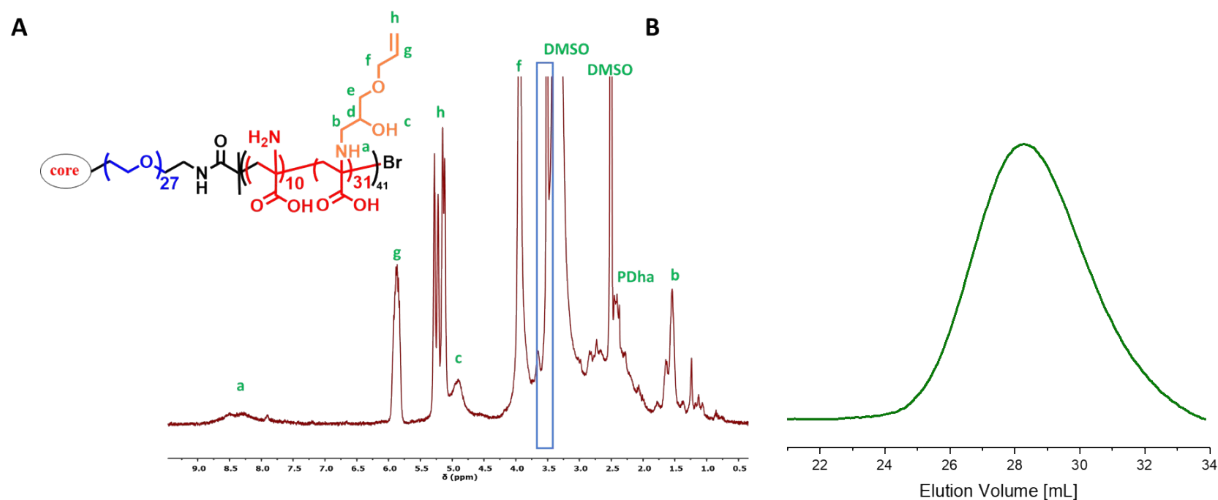


Figure S2A: Exemplary $^1\text{H-NMR}$ spectrum of successful post polymerization reaction of $[\text{PEG}_{27}\text{-}b\text{-PDha}_{41}]_4$ with AGE as modifier (DMSO) **B:** SEC-traces of post polymerization reaction of $[\text{PEG}_{27}\text{-}b\text{-PDha}_{41}]_4$ with AGE as modifier (eluent: DMSO\LiCl [99.79/0.21], 4-arm star PEG calibration).

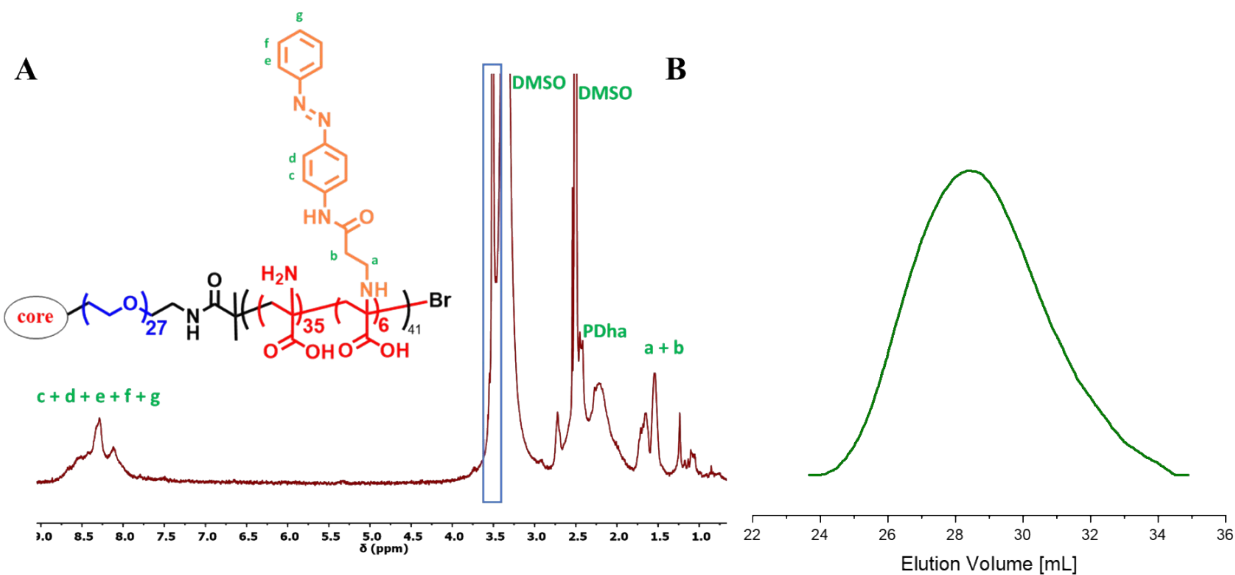


Figure S3: A: Exemplary $^1\text{H-NMR}$ spectrum of successful post polymerization reaction of $[\text{PEG}_{27}\text{-}b\text{-PDha}_{41}]_4$ with AzoAAM as modifier (DMSO) **B:** SEC-traces of post polymerization reaction of $[\text{PEG}_{27}\text{-}b\text{-PDha}_{41}]_4$ with AzoAAM as modifier (eluent: DMSO\LiCl [99.79/0.21], 4-arm star PEG calibration).

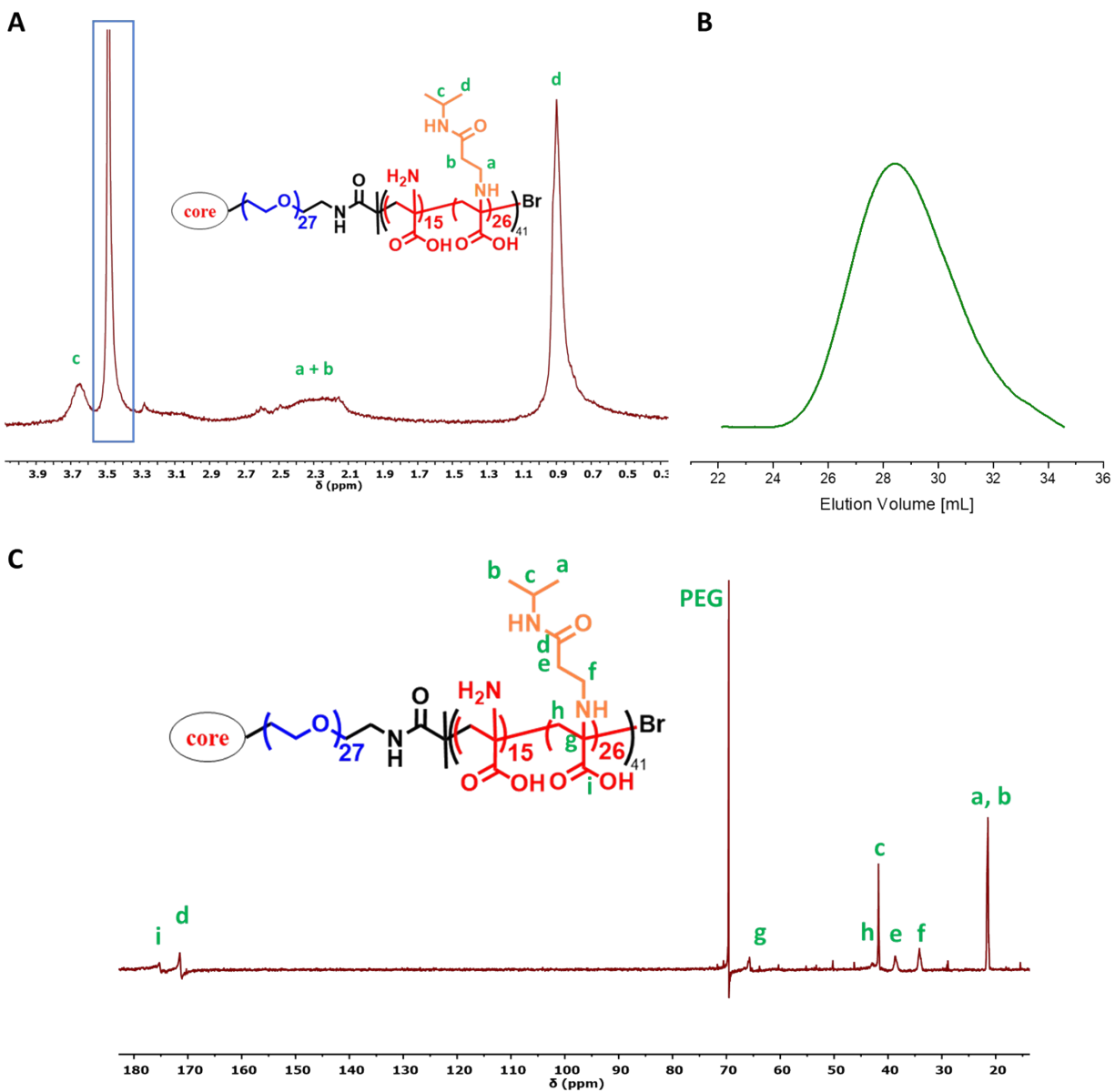


Figure S4: Exemplary $^1\text{H-NMR}$ spectrum of successful post polymerization reaction of $[\text{PEG}_{27}\text{-}b\text{-PDha}_{41}]_4$ with NiPAAm as modifier (D_2O) B: SEC-traces of post polymerization reaction of $[\text{PEG}_{27}\text{-}b\text{-PDha}_{41}]_4$ with NiPAAm as modifier (eluent: $\text{DMSO}\backslash\text{LiCl}$ [99.79/0.21], 4-arm star PEG calibration) C: Exemplary $^{13}\text{C-NMR}$ spectrum of successful post polymerization reaction of $[\text{PEG}_{27}\text{-}b\text{-PDha}_{41}]_4$ with NiPAAm as modifier (D_2O).

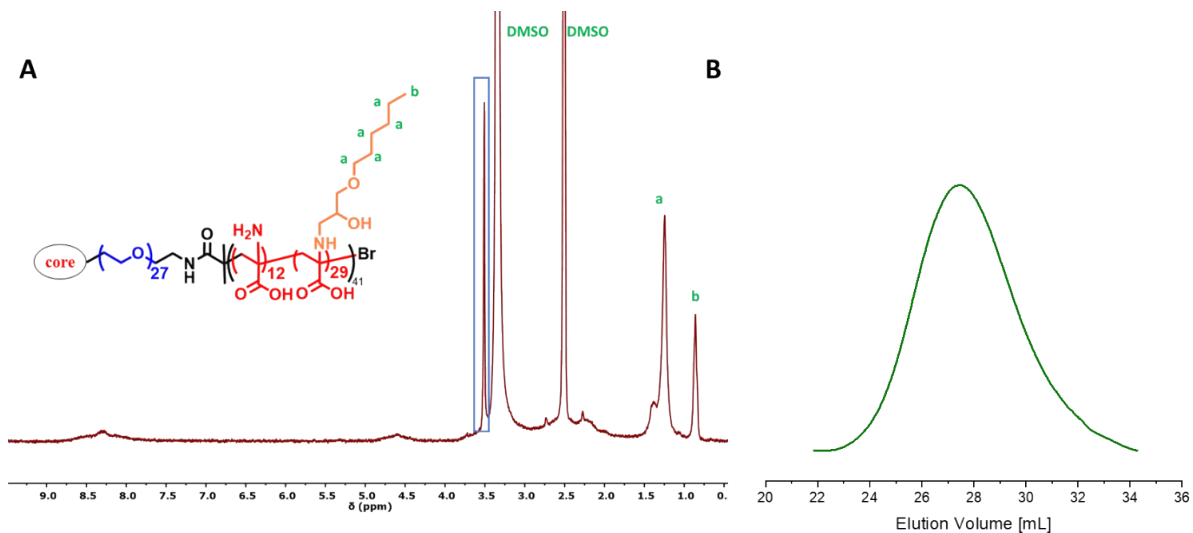


Figure S5: Exemplary $^1\text{H-NMR}$ spectrum of successful post polymerization reaction of $[\text{PEG}_{27}\text{-}b\text{-PDha}_{41}]_4$ with EOct as modifier (DMSO) B: SEC-traces of post polymerization reaction of $[\text{PEG}_{27}\text{-}b\text{-PDha}_{41}]_4$ with EOct as modifier (eluent: DMSO/LiCl [99.79/0.21], 4-arm star PEG calibration).

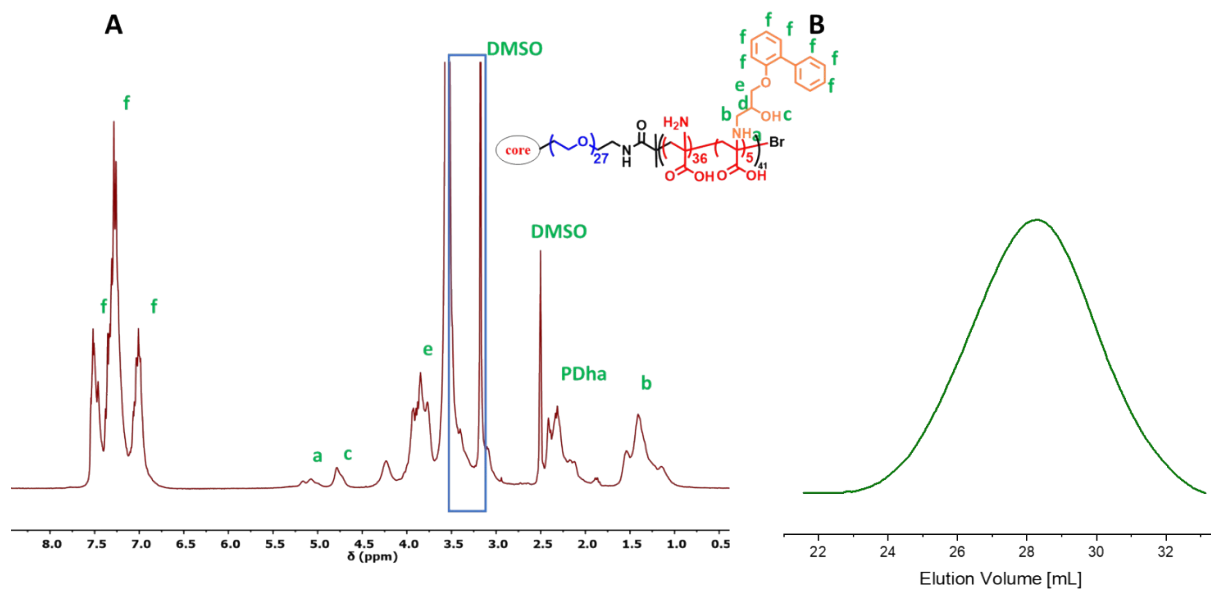


Figure S6: Exemplary $^1\text{H-NMR}$ spectrum of successful post polymerization reaction of $[\text{PEG}_{27}\text{-}b\text{-PDha}_{41}]_4$ with BpyOM as modifier (DMSO) B: SEC-traces of post polymerization reaction of $[\text{PEG}_{27}\text{-}b\text{-PDha}_{41}]_4$ with BpyOM as modifier (eluent: DMSO/LiCl [99.79/0.21], 4-arm star PEG calibration).

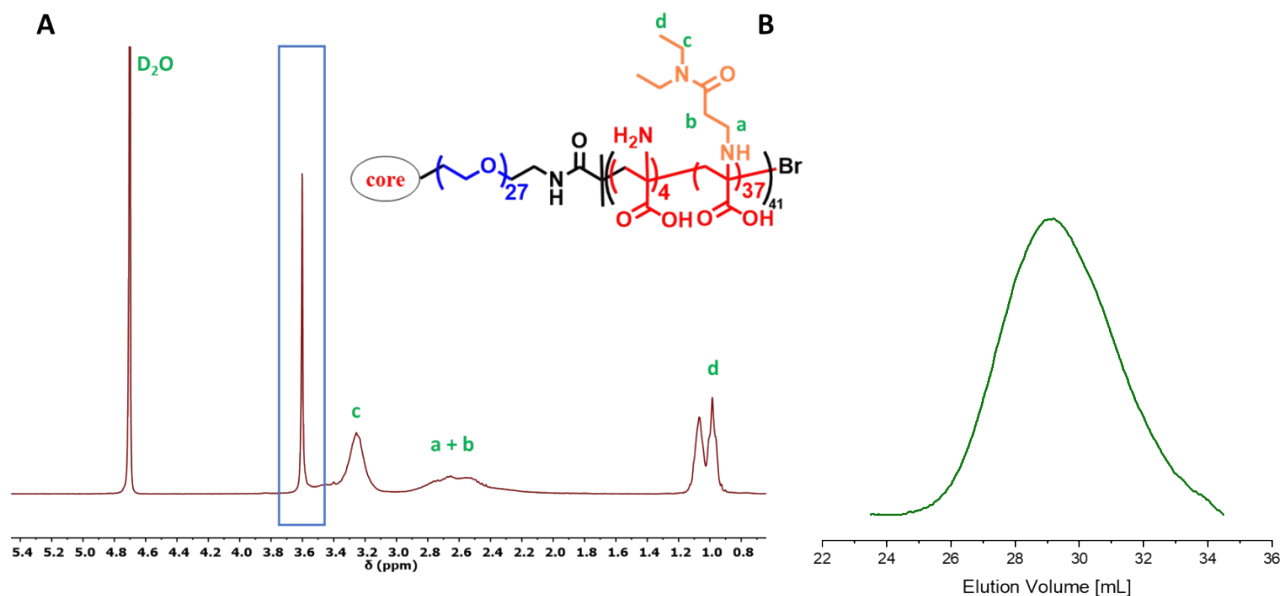


Figure S7: Exemplary ¹H-NMR spectrum of successful post polymerization reaction of [PEG₂₇-b-PDha₄₁]₄ with DEA as modifier (D₂O) B: SEC-traces of post polymerization reaction of [PEG₂₇-b-PDha₄₁]₄ with DEA as modifier (eluent: DMSO/LiCl [99.79/0.21], 4-arm star PEG calibration).

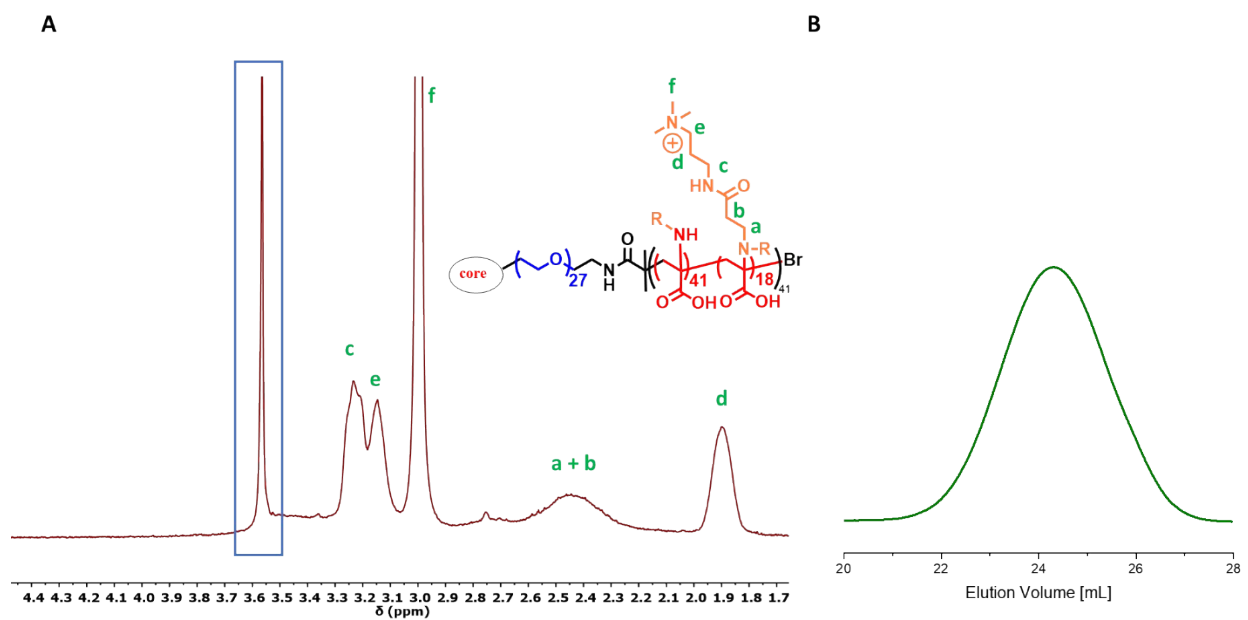


Figure S8: Exemplary ¹H-NMR spectrum of successful post polymerization reaction of [PEG₂₇-b-PDha₄₁]₄ with AMTC as modifier (DMSO) B: SEC-traces of post polymerization reaction of [PEG₂₇-b-PDha₄₁]₄ with AMTC as (eluent: water and 0.3% TFA/ 0.1 M NaCl [pH < 2], poly(vinyl pyridine) calibration).

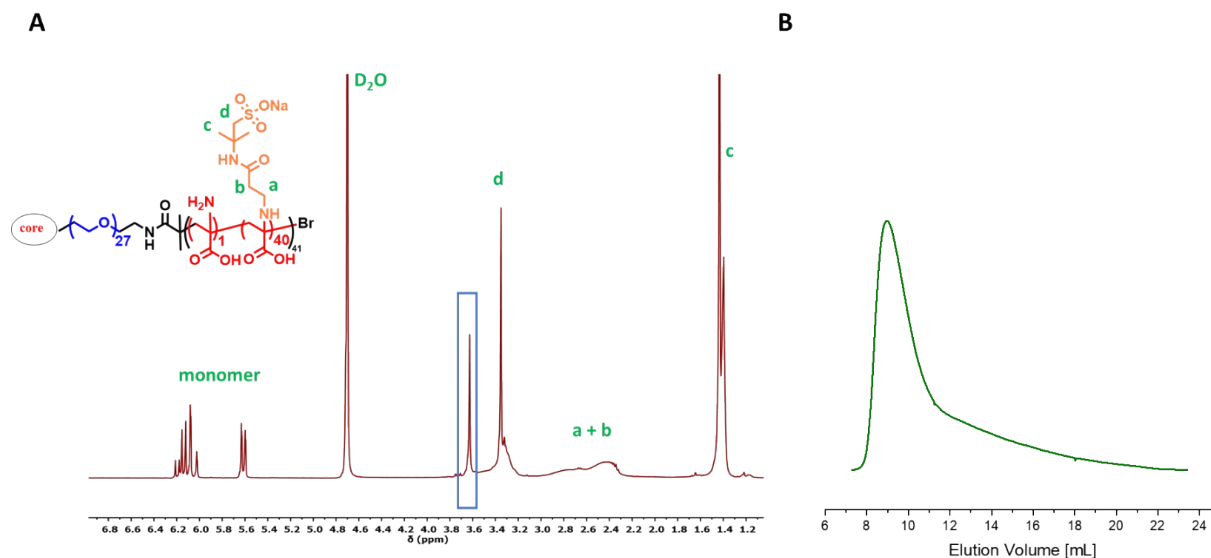


Figure S9: Exemplary ¹H-NMR spectrum of successful post polymerization reaction of [PEG₂₇-*b*-PDha₄₁]₄ with AMPS as modifier (D₂O) B: SEC-traces of post polymerization reaction of [PEG₂₇-*b*-PDha₄₁]₄ with AMPS as (eluent: water and 0.3% TFA/ 0.1 M NaCl [pH < 2], poly(vinyl pyridine) calibration).

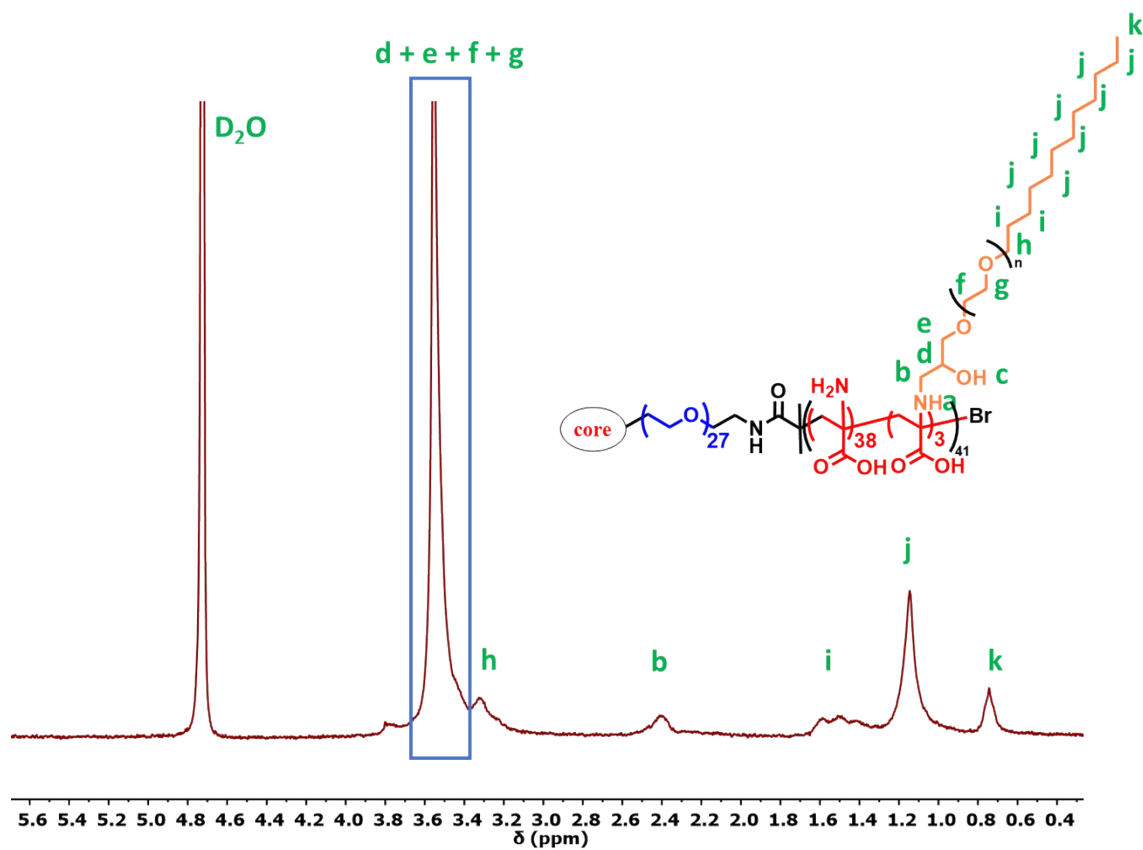


Figure S10: A: Exemplary ¹H-NMR spectrum of successful post polymerization reaction of [PEG₂₇-*b*-PDha₄₁]₄ with PEG-LOM as modifier (D₂O)

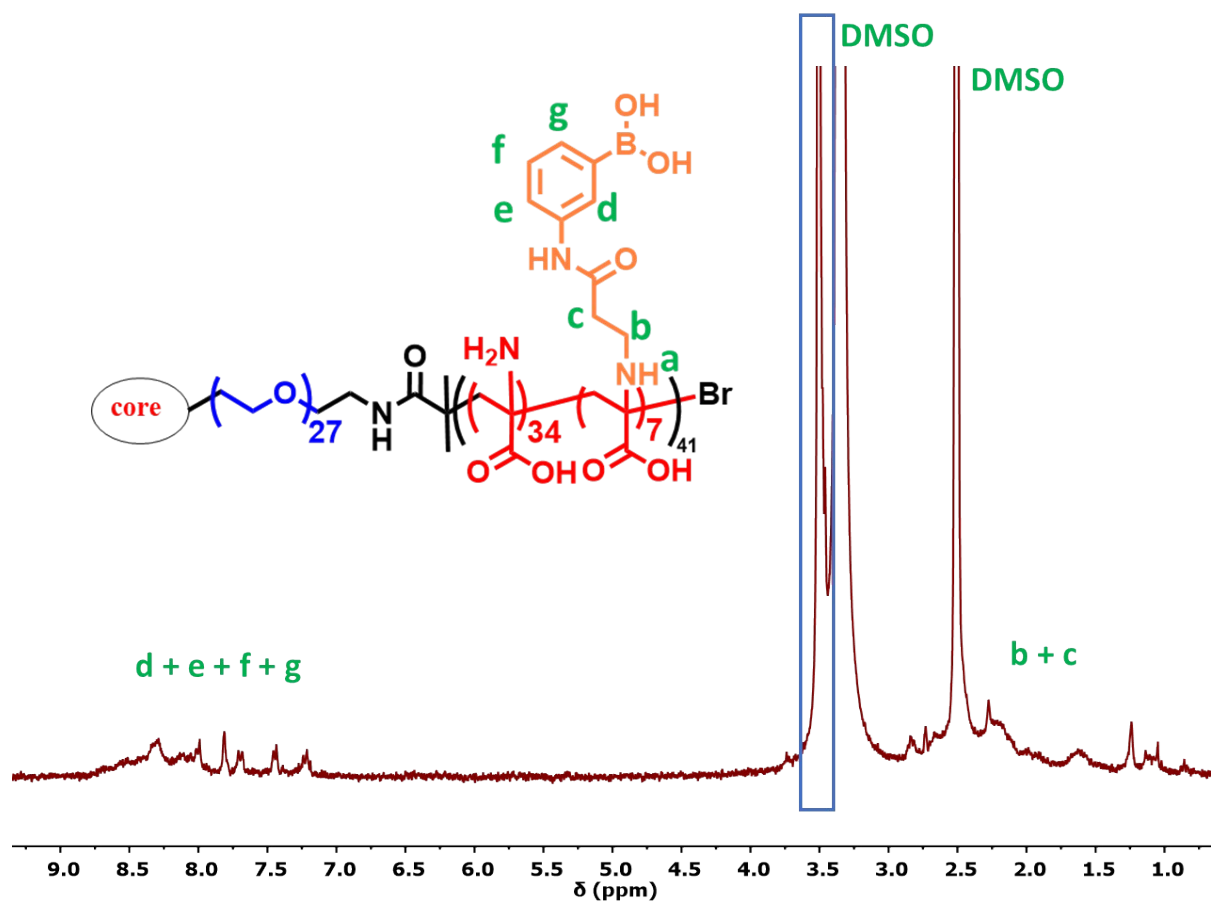


Figure S11: Exemplary ¹H-NMR spectrum of successful post polymerization reaction of [PEG₂₇-*b*-PDha₄₁]₄ with AAPBA as modifier (DMSO).