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## Supporting Information for: Multi-step control over self-assembled hydrogels of peptide-derived building blocks and a polymeric cross-linker

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### Ultra performance liquid chromatography (UPLC) analyses.

UPLC analyses were performed on a Waters Acquity H-class machine equipped with diode array UV/Vis detector. The eluents, acetonitrile and water contained 0.1% of TFA. The peptide solutions were eluted with a gradient as shown in detail in Table S1 and Fig. S1.

Time (min)	% of Acetonitrile	% of Water
0	10	90
1	10	90
1.3	25	75
3	28	72
11	40	60
11.5	95	5
12	95	5
12.5	10	90
17	10	90

Table S1: Solution components eluted using acetonitrile and water containing 0.1~% of TFA

# Nuclear Magnetic Resonance spectometry (H-NMR) analyses.

The final product of triblock copolymers was dissolved in deuterium oxide to determine the structure by <sup>1</sup>H-NMR on a Bruker Avance III 400 MHz Nuclear Magnetic Resonance (NMR) spectrometer. The measured <sup>1</sup>H-NMR spectrum of the triblock copolymer is shown in Fig. S2. Following Lemmers *et al.* [1], we determine the degree of polymerization (DP) by the ratio of the integrals of peak 1 to the one of PEG, taking into account the number of protons in a PEG monomer and group 1 of the triblock copolymer:  $DP = 2I_1N_{PEG}/I_{PEG} = 50$ , with  $I_1$  the integral surface of the group 1-peak (see [1] for details),  $I_{PEG}$  the surface of the PEG-peak, and  $N_{PEG}$  the number of PEG-monomers in each chain. Hence we end up with a triblock with a neutral mid-block and two negatively charged end-blocks: PSPMA<sub>25</sub>-PEO<sub>230</sub>-PSPMA<sub>25</sub>.



Figure S1: **UPLC traces for:** (a) pre-formed hexamer seed, (b) 3.8 mM solution of **1** after oxidation by sodium perborate solution, (c) 1 day and (d) 2 days after 20 % seeding by hexamer seed.

### Volume fraction and entanglement length estimations

Volume fraction of  $\mathbf{1}_6$  is estimated using  $\phi = \pi \rho a d^2/4$  [2], where a = 0.48 nm, and d = 7 nm are the length per monomer and diameter of  $\mathbf{1}_6$ , respectively. The number density of  $\mathbf{1}_6 \rho = 3.8 \times 10^{23} \text{ m}^{-3}$  is estimated using  $\rho = cN_A$ , where c = 0.63 mole/m<sup>3</sup> the  $\mathbf{1}_6$  concentration, and  $N_A = 6.02 \times 10^{23}$  Avodgadro's number. Inserting these numbers to the above equation, we obtain  $\phi = 6.7 \times 10^{-3}$ .

From this, we obtain the entanglement length as  $L_e \simeq (L_P)^{1/5} (a\rho)^{-2/5}$  [3] with  $L_P = 1.5 \ \mu \text{m}$  the measured persistence length. This gives  $L_e \simeq 135 \ \text{nm}$ .

### References

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Figure S2:  $^1\mathrm{H}\text{-}\mathrm{NMR}\text{-}\mathrm{spectrum}$  of the negatively charged triblock copolymer.