SUPPORTING INFORMATION

Injectable Hydrogel: Amplifying the pH Sensitivity of a Triblock Copolypeptide by Conjugating the N-termini via Dynamic Covalent Bonding

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1. pH responsiveness by ^{1}H NMR.

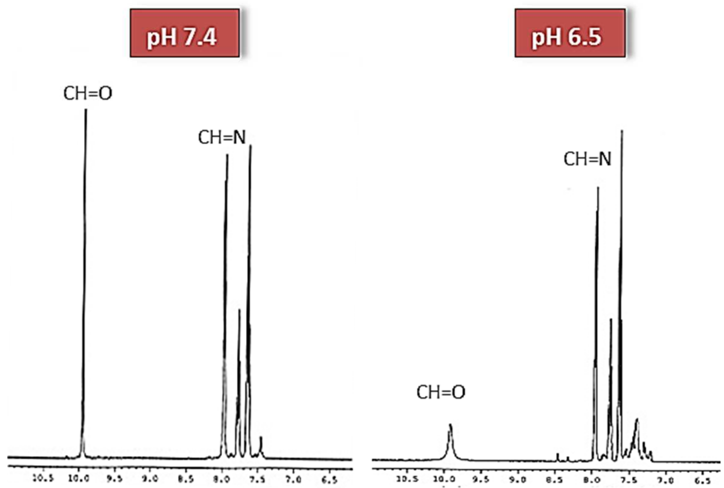

Figure S1. ^{1}H NMR spectra of Bz-$A_5E_{11}A_5$-Bz in D_2O at pD 7.4 and 6.5.

2. Polymersome preparation

The polymersomes were prepared using PCL-PEO-P2VP-PEO-PCL pentablock terpolymers. Details of the synthesis and characterization are reported elsewhere.[S1] The molecular characteristics of the terpolymers are gathered in Table S1.

Table S1. Molecular characteristics of the terpolymers.

POLYMER	M_W[a]	PDI[b]	PEO[c] wt%	P2VP[c] wt%	QP2VP[d] wt%	QP2VP[d] mol%	PCL[c] wt%
PCL_{46}-PEO_{199}-$P2VP_{598}$-PEO_{199}-PCL_{46} (P5b)	90 950	1.14	19.4	69	-	-	11.6
PCL_{46}-PEO_{199}-P(2VP-*co*-2VP$_q$)$_{598}$-PEO_{199}-PCL_{46} (Q5b)	108 840	1.14	16	45.5	29.9	19	8.6

[a] by LS and ^{1}H NMR, [b] by GPC, [c] by ^{1}H NMR, [d] by titration

3. Gelation threshold

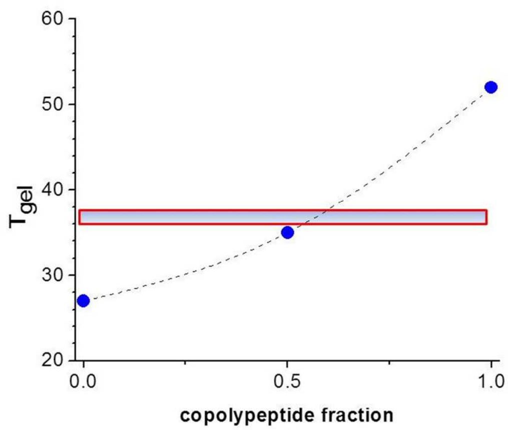

Figure S2 Gelation threshold, T_{gel} as a function of the copolypeptide ($A_5E_{11}A_5$) fraction of the $A_5E_{11}A_5$/Bz-$A_5E_{11}A_5$-Bz blend. The physiological temperature window is marked with red area.

From the above plot, the gelation threshold T_{gel} can be regulated as to cover the physiological region (36-37 ^oC) by a $A_5E_{11}A_5$/Bz-$A_5E_{11}A_5$-Bz blend slightly rich with the bare $A_5E_{11}A_5$ copolypeptide, i.e 60/40 $A_5E_{11}A_5$/Bz-$A_5E_{11}A_5$-Bz mass ratio.

References

S1. Popescu, M.-T.; Korogianaki, M. ; Marikou, K. ; Tsitsilianis, C. CBABC Terpolymer-based Nanostructured Vesicles with Tunable Membrane Permeability as Potential Hydrophilic Drug Nanocarriers. *Polymer*, **2014**, 55, 2943-2951.