SUPPORTING INFORMATION:

Design and self-assembly of PBLG-*b*-ELP hybrid diblock copolymers based on synthetic and elastin-like polypeptides

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Synthesis mechanism hypothesis

Because the purification of ELP involves the use of sodium chloride, we can reasonably assume the polymerization to be initiated by the *N*-terminal ammonium group of the ELP with the chloride Cl^- as counter-anion. Consequently, the block copolypeptides poly(γ-benzyl-*L*-glutamate)-*block*-ELP were synthesized by ROP of the γ-BLG NCA initiated by the primary ammonium end group of the ELP.

It was previously postulated by Schlaad et *al.* that the ammonium-mediated ROP mechanism may lead to a controlled propagation comparable to nitroxyde-mediated radical or living cationic polymerizations involving an equilibrium between dormant (ammonium) and active (amine) chain ends[1] provided that the counter-anion, here the nucleophilic chloride anion, is quite mobile in the medium.[1,2] The ammonium salt in addition is suspected to suppress the activated monomer mechanism (AMM) due to protonation of the NCA anions.[1]

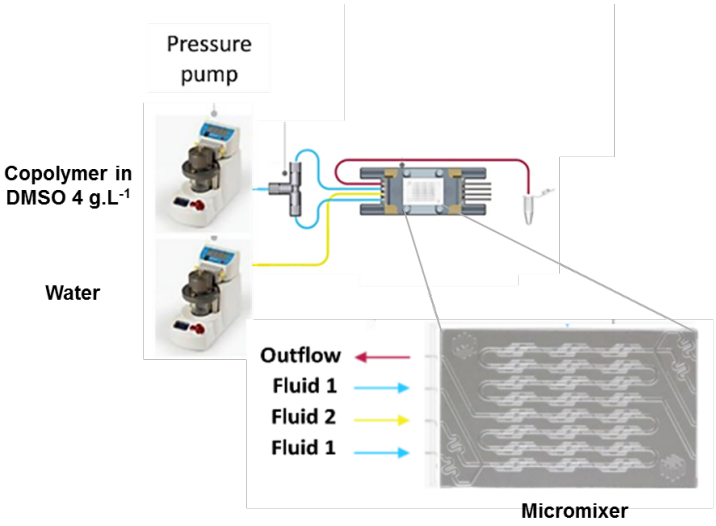
Interestingly, in the present case of the polymerization of γ-BLG NCA, we suspect the ELP macroinitiator to afford sufficient polarity to the medium to allow an excellent control of ammonium-mediated ROP with the chloride counterion. We additionally presume the formation of hydrogen bonds between the polypeptide chain amide groups and the γ-BLG NCA, stabilizing the latter and limiting the AMM mechanism, and consequently favoring the normal NAM amine mechanism.

Table S1. Molecular characteristics of ELP and hybrid diblock copolypeptides PBLG-*b*-ELP obtained by ROP of γ-BLG NCA at 25 °C.

#	Copolypeptide	Expected DP (PBLG)	DP PBLG (^{1}H NMR)	$\overline{M_n}$ ^{1}H NMR (g.mol^{-1})	*f* (%) ^{1}H NMR	$\overline{M_n}$ SEC* (g.mol^{-1})	*Đ* SEC*	Yield (%)
-	**ELP**	-	-	17,000	-	18,000	1.03	-
1	**PBLG$_{21}$-*b*-ELP**	52	21	21,600	79	24,900	1.03	73
2	**PBLG$_{33}$-*b*-ELP**	78	33	24,300	70	30,200	1.06	80
3	**PBLG$_{61}$-*b*-ELP**	117	61	30,400	56	37,100	1.15	77
4	**PBLG$_{110}$-*b*-ELP**	181	110	41,200	41	44,800	1.20	70

**f*: hydrophilic weight fraction determined from the $\overline{M_n}$ calculated by ^{1}H NMR

****SEC in DMF (0.8 mL.min^{-1}) at 50 °C in the presence of LiBr (1 g.L^{-1}) with RI detector and polystyrene used as standard.



Scheme S1. Schematic representation of the microfluidics device used.

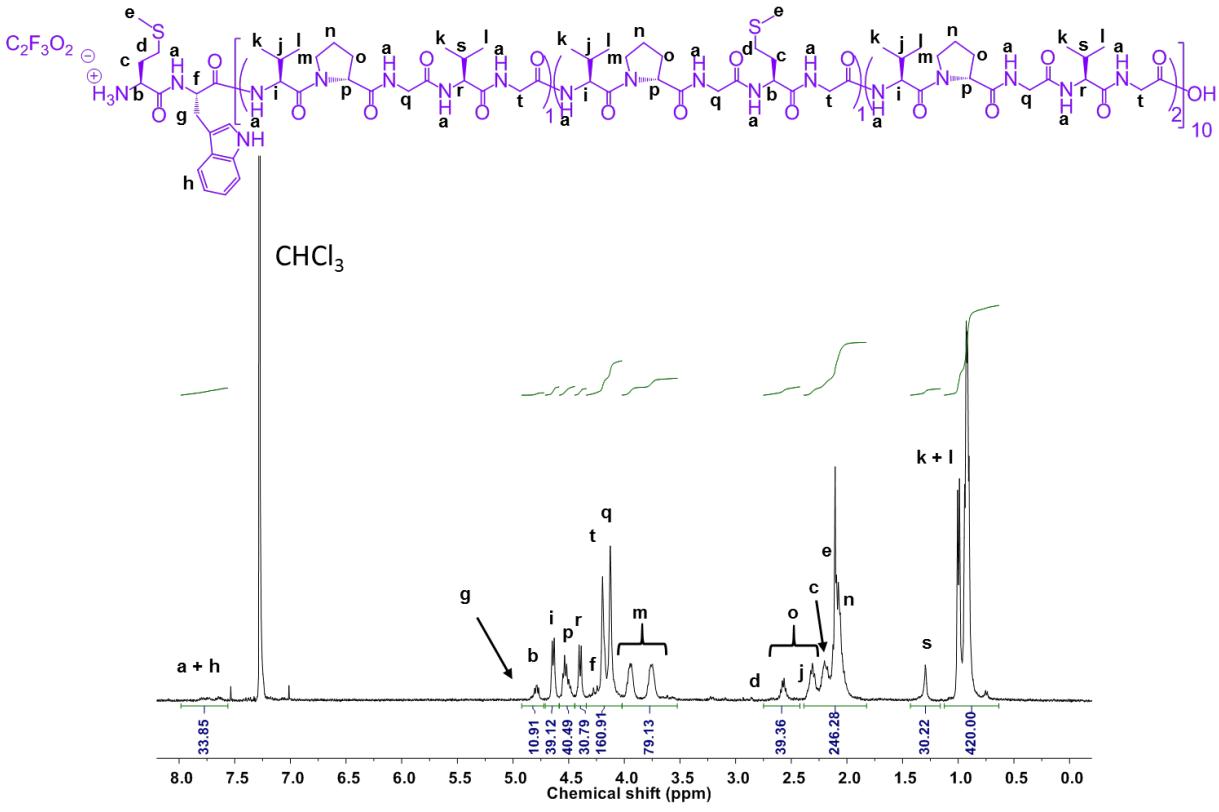


Figure S1. ^{1}H NMR spectrum of ELP in $CDCl_3$ containing 15 % trifluoroacetic acid (TFA).

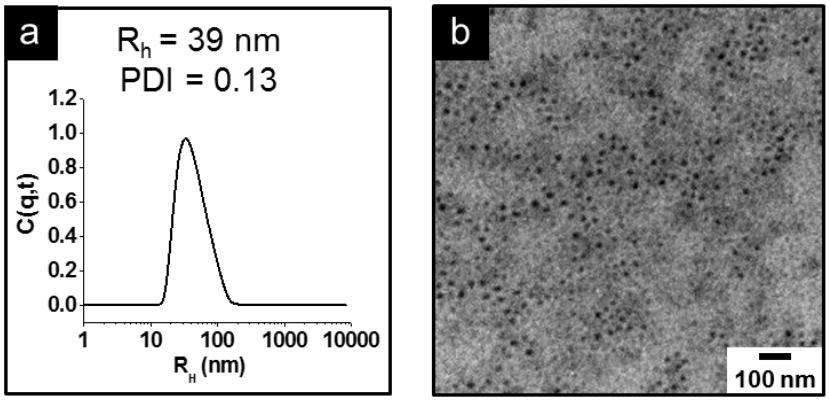


Figure S2. (a) Size distribution of nano-particles by DLS.(b) TEM micrographs of nano-particles obtained from $PBLG_{25}$-*b*-ELP by direct solubilization.

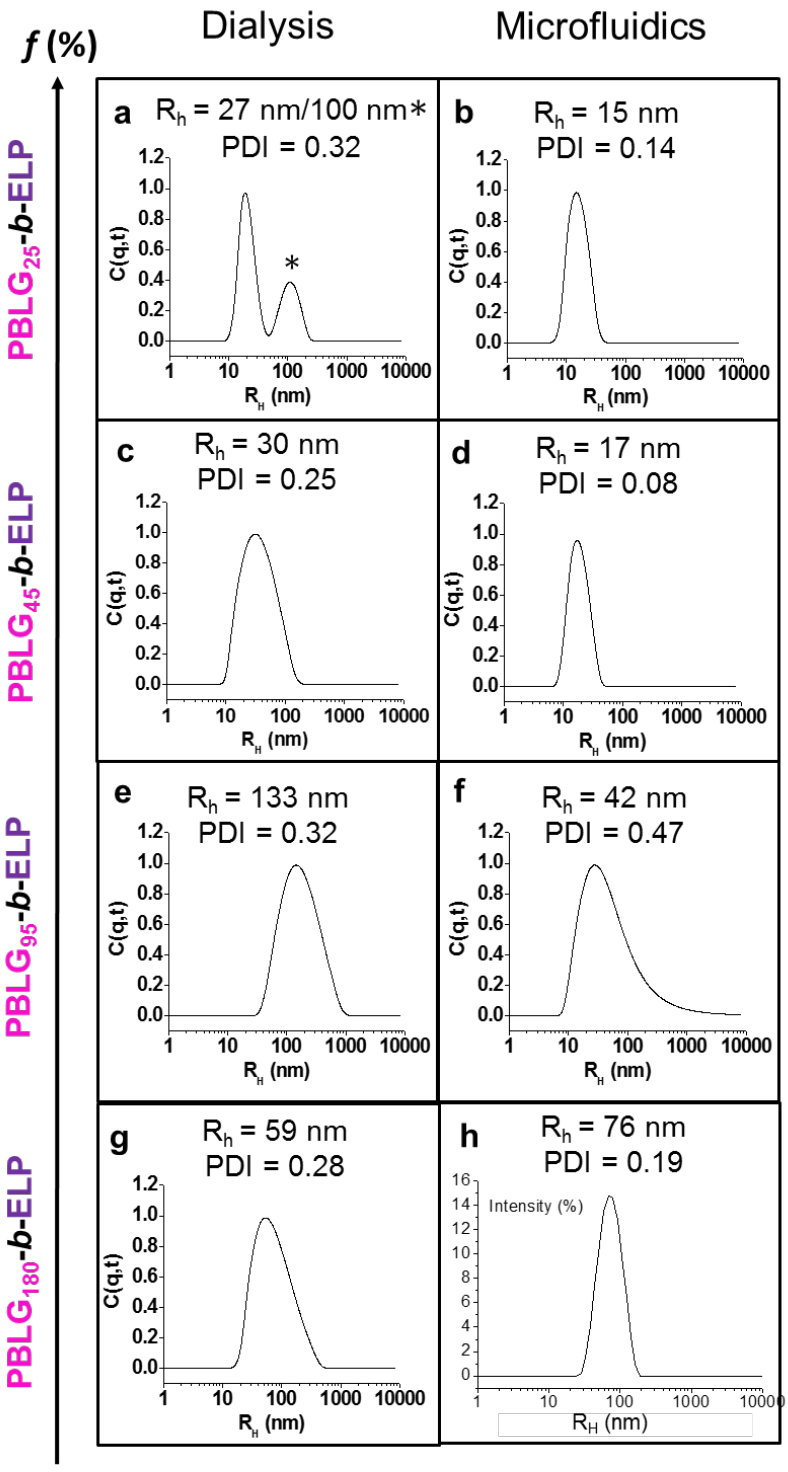


Figure S3. Size distribution of nano-particles by DLS depending on the technique of self-assembly process. (i) Characterized directly after the formation of nano-objects. Ratio DMSO:H_2O by microfluidics is 70:30.

(1) Dimitrov, I.; Schlaad, H. *Chemical Communications* **2003**, 2944-2945.
(2) Lutz, J. F.; Schütt, D.; Kubowicz, S. *Macromolecular rapid communications* **2005**, *26*, 23-28.