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 ends¹ provided that the counter-anion, here the nucleophilic chloride anion, is quite mobile in the medium.¹² 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.

<table>
<thead>
<tr>
<th>#</th>
<th>Copolypeptide</th>
<th>Expected DP (PBLG)</th>
<th>DP PBLG (1H NMR)</th>
<th>$\overline{M}_n$ (1H NMR) (g.mol$^{-1}$)</th>
<th>$f$ (%)</th>
<th>$\overline{M}_n$ SEC* (g.mol$^{-1}$)</th>
<th>$D$</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>ELP</td>
<td>-</td>
<td>-</td>
<td>17,000</td>
<td>-</td>
<td>18,000</td>
<td>1.03</td>
<td>-</td>
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<tr>
<td>1</td>
<td>PBLG$_{21}$-b-ELP</td>
<td>52</td>
<td>21</td>
<td>21,600</td>
<td>79</td>
<td>24,900</td>
<td>1.03</td>
<td>73</td>
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<td>2</td>
<td>PBLG$_{33}$-b-ELP</td>
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<td>33</td>
<td>24,300</td>
<td>70</td>
<td>30,200</td>
<td>1.06</td>
<td>80</td>
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<td>3</td>
<td>PBLG$_{61}$-b-ELP</td>
<td>117</td>
<td>61</td>
<td>30,400</td>
<td>56</td>
<td>37,100</td>
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<td>4</td>
<td>PBLG$_{110}$-b-ELP</td>
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<td>110</td>
<td>41,200</td>
<td>41</td>
<td>44,800</td>
<td>1.20</td>
<td>70</td>
</tr>
</tbody>
</table>

*$f$: 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 PBLG25-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:H₂O by microfluidics is 70:30.
(1) Dimitrov, I.; Schlaad, H. Chemical Communications 2003, 2944-2945.