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.

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

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>% of Acetonitrile</th>
<th>% of Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>1.3</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>28</td>
<td>72</td>
</tr>
<tr>
<td>11</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>11.5</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>12</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>12.5</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>17</td>
<td>10</td>
<td>90</td>
</tr>
</tbody>
</table>

Nuclear Magnetic Resonance spectometry (H-NMR) analyses.

The final product of triblock copolymers was dissolved in deuterium oxide to determine the structure by $^1$H-NMR on a Bruker Avance III 400 MHz Nuclear Magnetic Resonance (NMR) spectrometer. The measured $^1$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$_{25}$-PEO$_{230}$-PSPMA$_{25}$.
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 $1_6$ is estimated using $\phi = \pi a d^2/4$ [2], where $a = 0.48$ nm, and $d = 7$ nm are the length per monomer and diameter of $1_6$, respectively. The number density of $1_6$ is estimated using $\rho = cN_A$, where $c = 0.63$ mole/m$^3$ the $1_6$ concentration, and $N_A = 6.02 \times 10^{23}$ Avogadro’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 $L_e \approx (L_P)^{1/5} (a \rho)^{-2/5}$ [3] with $L_P = 1.5$ µm the measured persistence length. This gives $L_e \approx 135$ nm.

References


Figure S2: $^1$H-NMR-spectrum of the negatively charged triblock copolymer.