Supplementary Information

Biodegradable Core Crosslinked Star Polymer Nanoparticles as\n$^{19}$F MRI Contrast Agents for Selective Imaging

Kewei Wang, Hui Peng, Kristofer J. Thurecht, Simon Puttick and Andrew K. Whittaker*

Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, St Lucia, 4072, Australia

E-mail: a.whittaker@uq.edu.au

Fig. S1 RAFT polymerisation of PEGMA using alkyne-CTA. (A) Pseudo-first-order kinetic plot of the polymerisation. (B) Dependence of number-average molecular weight ($M_n$, determined by GPC) and molar-mass dispersity ($D_M$) on monomer conversion. (C) GPC traces during the polymerisation.
Fig. S2 Digital photo of the samples withdrawn at different time intervals during the synthesis of CCS polymer by RAFT dispersion polymerisation. The samples were at room temperature (~25 oC).

Fig. S3 DLS results of the samples at different polymerisation time before and after filtration using 450 μm syringe filters. Each size was the average of five measurements at 25 oC.
Fig. S4 GPC traces of CCS polymers synthesised at (A) different water/ethanol ratios, (B) with or without spacer and (C) different EGDMA/arm ratios. Conditions: (A) [Arm-1]/[EGDMA]/[BMA]/[ACVA] = 1/5/5/0.2, [arm-1] = 5 mM, 70 °C, 1 h. (B) [Arm-1]/[EGDMA]/[Spacer]/[ACVA] = 1/10/10/0.2, [arm-1] = 5 mM, water/ethanol (50/50, v/v), 70 °C, 1 h. (C) [Arm-1]/[ACVA] = 1/0.2, [arm-1] = 5 mM, water/ethanol (50/50, v/v), 70 °C, 1 h. (D) [Arm-1]/[EGDMA] = 1/10, [arm-1] = 5 mM, water/ethanol (50/50, v/v), 70 °C.
Fig. S5 (A), (B) and (C) 1H NMR spectra of macro-CTA, Arm-1, filtrate-1 and CCS-1. ‘c’ represents the two protons of the CH$_2$ adjacent to –COO$^-$ in PEGMA. (D) 13C NMR spectrum of CCS-1.

Fig. S6 GPC traces of the polymers related to the synthesis of CCS-2 and CCS-3
Fig. S7 GPC traces during the degradation of CCS-1 using DTT in THF. [DTT] = 50 mM, [CCS-1] = 1.15 × 10^{-3} mM.

Fig. S8 Zeta potential of CCS-1 and CCS-2 at different pH in PBS.
Calculation of arm number

The arm number can be calculated according to the previously published methods. 

First, the weight fractional of arms in CCS polymer can be calculated based on the Eq. (1)

\[ WF_{\text{arm}} = \frac{m_{\text{arm}} \times X_{\text{arm}}}{m_{\text{arm}} + m_{\text{CL}} \times X_{\text{CL}}} \]  

where \( WF_{\text{arm}} \) is the weight fractional of arms in CCS polymer, \( m_{\text{arm}} \) is the mass of arms, \( X_{\text{arm}} \) is the conversion of arms that are incorporated into CCS polymer, \( m_{\text{CL}} \) is the mass of crosslinker, and \( X_{\text{CL}} \) is the conversion of crosslinker. We assume that the conversion of crosslinker is 100% because of the high polymerisation rate in a RAFT dispersion polymerisation.

Then the arm number can be obtained using the Eq. (2)

\[ f = \frac{M_{\text{w(CCS)}} \times WF_{\text{arm}}}{M_{\text{w(arm)}}} \]  

where \( f \) is arm number, \( M_{\text{w(CCS)}} \) is weight-average molecular weight of CCS polymer and \( M_{\text{w(arm)}} \) is weight-average molecular weight of arms.

The details are listed in the following table.

**Table S1** Details for the calculation of arm numbers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( m_{\text{arm}} ) (g)</th>
<th>( X_{\text{arm}} )</th>
<th>( m_{\text{CL}} )</th>
<th>( X_{\text{CL}} )</th>
<th>( M_{\text{w(CCS)}} )</th>
<th>( M_{\text{w(arm)}}^* )</th>
<th>( WF_{\text{arm}} )</th>
<th>( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCS-1</td>
<td>2.16</td>
<td>0.74</td>
<td>0.58</td>
<td>1</td>
<td>764400</td>
<td>10500</td>
<td>0.734</td>
<td>53</td>
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<tr>
<td>CCS-2</td>
<td>0.39</td>
<td>0.65</td>
<td>0.1</td>
<td>1</td>
<td>516300</td>
<td>11300</td>
<td>0.717</td>
<td>33</td>
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<tr>
<td>CCS-3</td>
<td>0.53</td>
<td>0.6</td>
<td>0.139</td>
<td>1</td>
<td>785500</td>
<td>11700</td>
<td>0.713</td>
<td>49</td>
</tr>
</tbody>
</table>

\( M_n \) (\(^{1}H\) NMR) was used for \( M_{\text{w(arm)}} \)

**References**