In-situ formation of crosslinked core-corona polymeric nanoparticles from a novel hyperbranched core

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SUPPORTING INFORMATION

$^1$H NMR spectrum for hyperbranched polyDVB core (Fig. S1) and calculation of branching ratio (Eq. S1). The kinetic study and initiation efficiency of homopolymerization of styrene and methyl methacrylate with DE-ATRP approach (Table S1). Composition data of CCC nanogel by $^1$H NMR spectroscopy (Table S2). AFM topology image for CCC nanogel deposited on silica substrate (Fig. S2).

![PolyDVB core](image)

**Figure S1.** The $^1$H NMR spectrum for a hyperbranched polyDVB core (Entry 1, Table 1). The calculation of branching ratio was given in Eq.S1.

\[
Branching \ ratio = \frac{\text{Branched DVB units}}{\text{Linear DVB units}} = \frac{\left[\text{integral of (d + e)} - 3\times\text{integral of b}\right]}{\text{integral of b}} \quad (\text{Eq. S1})
\]
**Table S1.** Homopolymerisation of styrene and methyl methacrylate with DE-ATRP approach. The initiation efficiency was calculated from the kinetic study.

<table>
<thead>
<tr>
<th>Reaction Time (hrs)</th>
<th>Conv(^{c})</th>
<th>(M_\text{n}) (g.mol(^{-1}))(^{d})</th>
<th>PDI (^{d})</th>
<th>(M_\text{theo}) (g.mol(^{-1}))(^{e})</th>
<th>Initiation Efficient(^{f})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Styrene(^{a})</td>
<td>9</td>
<td>21%</td>
<td>4630</td>
<td>1.12</td>
<td>4541</td>
</tr>
<tr>
<td>2. MMA(^{b})</td>
<td>6</td>
<td>24.2%</td>
<td>5210</td>
<td>1.1</td>
<td>5011</td>
</tr>
</tbody>
</table>

[a]. Polymerisation condition: [Styrene]/[EBriB]/CuBr/CuBr\(_2\)/bpy =200:1:0.4:0.133:1.06 [Sty]=3M in toluene, T=90 °C  
[b]. Polymerisation condition: [MMA]/[EBriB]/CuBr/CuBr\(_2\)/bpy =200:1:0.4:0.133:1.06 [MMA]=3M in butanone, T=60 °C  
[c]. Monomer conversion is determined by \(^1\)H NMR  
[d]. \(M_\text{n}\) and PDI is determined by GPC-RI detector with linear PMMA standard  
[e]. Theoretical molecular weight= 200 x FW\(_\text{monomer}\) x Conv+FW\(_\text{initiator}\)  
[f]. Initiation Efficiency=\(M_\text{theo}\)/\(M_\text{n}\)

**Table S2.** Characterization composition of DVB and MMA units for hyperbranched core (entry 1) and crosslinked core-corona nanogel (entry 2-4) formed using DE-ATRP. The compositions were calculated by comparing the integrals of different resonance of protons from DVB and MMA in the \(^1\)H NMR spectra (see Eq. 2 and Fig.5 in main text). It worth noting that the ratio of MMA to DVB could be an underestimate due to the presence of solvent (CDCl\(_3\)) peak at 7.26 ppm.

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>DVB: MMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>-</td>
</tr>
<tr>
<td>Core-Crosslinked Corona (CCC)</td>
<td>0.5:2.3</td>
</tr>
<tr>
<td></td>
<td>2:4.1</td>
</tr>
<tr>
<td></td>
<td>10:5.2</td>
</tr>
</tbody>
</table>
Figure S2 AFM topology image for CCC microgel deposited on silica substrate. The samples are prepared in a dilute solution (10 μg/L) in THF and dropped on silica substrate by spin coating (1000 rpm). The enlarged image (right) clearly shows the core-shell like molecule was formed during the reaction. The core-shell polymer is displayed as a ‘fried egg’ shape on the dry silica substrate.