Supplementary Information for

Investigation on the fluorescence-(stimulus-response) properties of linear and star PVBCz-b-PDMAEMA block copolymers synthesized via ATRP

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Synthetic procedures

Synthesis of monomer (VBCz)

VBCz was synthesized according to the reference\(^1\). A mixture of carbazole (5.00 g, 30.0 mmol), sodium hydroxide (1.20 g, 37.5 mmol) and tetra-\(n\)-butylammonium bromide (TBAB) (200 mg, 0.62 mmol) in DMF (100 mL) was stirred for 2 h. Then 1-(chloromethyl)-4-ethenyl-benzen (5.50 g, 36.0 mmol) was added dropwise, and the reaction mixture was continually stirred for 20 h at ambient temperature (scheme 1). The resulting mixture was precipitated in deionized water. The resultant white precipitate was filtered and dried under vacuum at 70°C. The crude product was purified by recrystallization from acetone to give 5.40 g of white crystals with a yield of 63.5%. \(^1\)H-NMR(400 MHz, CDCl\(_3\), \(\delta\), ppm): 5.18-5.20 (d, 1H, CH\(_2\)=C), 5.65 (s, 2H, N-CH\(_2\)), 5.71-5.76 (d, 1H, CH\(_2\)=C), 6.61-6.68 (m, 1H, CH\(_2\)=CH), 7.13-7.15 (d, 2H, ArH), 7.21-7.64 (m, 8H, ArH), 8.17-8.19 (d, 2H, ArH). Anal.Calcd for C\(_{21}\)H\(_{17}\)N: C 89.01, H 6.05, N 4.94; Found: C 88.92, H 5.97, N 4.86.
Synthesis of the monomer (VBCz).

**Scheme S1.** Synthesis of the monomer (VBCz).

**Synthesis of multi-functional initiators**

**4-arm initiator** Pentaerythritol (3.29g, 24.2mmol) (2.79, 50.0mmol), TEA (15.2mL, 108.7mmol) were added into a Schlenk flask along with anhydrous THF (100 mL) by syringe under argon. Cooling the mixture to -18 °C, and 2-Bromo-iso-butyryl bromide (BiBB) (13.5mL, 108.7mmol) dissolved in anhydrous THF (40 mL) was added dropwise (Scheme 1b). The reaction solution was subjected to continuous stirring for 24 h at room temperature and then diluted with CH$_2$Cl$_2$. The resulting organic extracts were washed twice with 200 mL HCl (2 M), twice with 200 mL saturated NaHCO$_3$, and twice with 200mL saturated NaCl in turn. The solution was then dried with anhydrous MgSO$_4$. (Scheme 2). The resultant mixture was filtered, concentrated, recrystallized from hot methanol and filtered to afford 11.5g (yield: 65%) of 4-arm initiator as a colorless crystalline solid. $^1$H-NMR(400 MHz, CDCl$_3$, δ, ppm): 1.88 (s, 24H, 8C$_3$H$_3$), 4.27 (s, 8H, 4C$_2$H$_2$). $^{13}$C-NMR(100 MHz, CDCl$_3$, δ, ppm): 29.7 (8C$_3$H$_3$), 42.9 (C(CH$_2$O)$_4$), 54.3 (4CBr), 61.8 (4CH$_2$O), 169.8 (4C=O). (Scheme S2)

**6-arm initiator** The procedure was the same as discussed in the previous section except that dipentaerythritol (2.20g, 7.85mmol) was used instead of ethylene glycol. TEA (10.0mL, 71.5mmol), anhydrous THF (100 mL) and 2-bromo-2-methylpropanoyl bromide (8.8mL, 70.9mmol) dissolved in anhydrous THF (20 mL) was added sequentially in this reaction (Scheme 2). This procedure afforded 5.1g (yield: 52%) of 6-arm initiator as a colourless crystalline solid. $^1$H-NMR(400 MHz, CDCl$_3$, δ, ppm): 1.94 (s, 36H, 12CH$_3$), 3.60 (s, 4H, CH$_2$OCH$_2$), 4.29 (s, 12H,
6CH2O). 13C-NMR(100MHz, CDCl3, δ, ppm): 30.6 (12CH3), 43.9 (2C(CH2)4), 55.2 (6CBr), 63.2 (6CH2O), 69.3 (CH2OCH2), 170.6 (6C=O). (Scheme S2)

Scheme S2. Synthesis of the multi-functional initiators

Table S1 Reaction conditions of the star PVBCz

<table>
<thead>
<tr>
<th>Sample</th>
<th>VBCz (mmol)</th>
<th>Initiator (mmol)</th>
<th>CuBr (mmol)</th>
<th>PMDETA (mmol)</th>
<th>[M]/[I]</th>
<th>Cyclohexanone (mL)</th>
<th>Reaction Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-arm PVBCz</td>
<td>8.00</td>
<td>0.80</td>
<td>0.80</td>
<td>1.60</td>
<td>10</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>4-arm PVBCz</td>
<td>8.00</td>
<td>0.27</td>
<td>0.27</td>
<td>0.54</td>
<td>30</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>6-arm PVBCz</td>
<td>8.00</td>
<td>0.16</td>
<td>0.16</td>
<td>0.32</td>
<td>50</td>
<td>10</td>
<td>2</td>
</tr>
</tbody>
</table>

(a) [CDCl3, 1H-NMR spectra of (a) VBCz and 4-arm PVBCz. (b) the PVBCz linear and star polymers.](image)

(b) [CDCl3, 1H-NMR spectra of (a) VBCz and 4-arm PVBCz. (b) the PVBCz linear and star polymers.](image)
Table 2 Polymerization conditions and molecular weight parameters of the 6-arm PVBCz-b-PDMAEMA block copolymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>feed ratio&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Reaction Time (h)</th>
<th>$M_n$&lt;sup&gt;b&lt;/sup&gt; ($\times 10^4$ g·mol&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>$M_w$&lt;sup&gt;b&lt;/sup&gt; ($\times 10^4$ g·mol&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>PDI&lt;sup&gt;c&lt;/sup&gt;</th>
<th>$D_P_{arm}$&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Ratio&lt;sub&gt;arm,GPC&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Ratio&lt;sub&gt;arm,NMR&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>L6-1</td>
<td>100</td>
<td>2</td>
<td>4.17</td>
<td>5.80</td>
<td>1.39</td>
<td>8±30</td>
<td>1 : 3.8</td>
<td>1 : 4.4</td>
</tr>
<tr>
<td>L6-2</td>
<td>500</td>
<td>5</td>
<td>8.41</td>
<td>11.86</td>
<td>1.41</td>
<td>8±75</td>
<td>1 : 9.4</td>
<td>1 : 11.9</td>
</tr>
<tr>
<td>L6-3</td>
<td>800</td>
<td>7</td>
<td>13.33</td>
<td>15.86</td>
<td>1.19</td>
<td>8±106</td>
<td>1 : 13.3</td>
<td>1 : 12.4</td>
</tr>
</tbody>
</table>

<sup>a</sup> feed ratio is the ratio of VBCz to the initiator.  
<sup>b</sup> Determined by GPC.  
<sup>c</sup> DP, the number-average degree of polymerization of PVBCz;  
<sup>d</sup> $D_P_{arm}$, the number-average degree of polymerization of PVBCz on every arm.  
<sup>d</sup> Ratio<sub>arm,GPC</sub>, the block ratios of PVBCz to PDMAEMA calculated according to the GPC results;  
<sup>d</sup> Ratio<sub>arm,NMR</sub>, the block ratios calculated according to the $^1$H-NMR spectra.

Fig. S2 $^1$H-NMR spectra (a) and GPC traces (b) of the 1- and 6-arm PVBCz-b-PDMAEMA.
Notes and references


