Supporting Information

The Effect of Comb Architecture on Complex Coacervation

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Table S1. Polymerization data, and monomer:catalyst ratios used to synthesize LK5SB-X (X = mol% SB)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Target mol% SB</th>
<th>[M]-[I]</th>
<th>[M] (M)</th>
<th>Conversion (%)</th>
<th>Incorporated mol% SB</th>
<th>Mn,theo a (g/mol)</th>
<th>Mw b (g/mol)</th>
<th>Poly b</th>
<th>Yield c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LK5SB-26</td>
<td>20</td>
<td>62.5</td>
<td>0.09</td>
<td>73</td>
<td>26</td>
<td>38600</td>
<td>42900</td>
<td>1.35</td>
<td>48</td>
</tr>
<tr>
<td>LK5SB-44</td>
<td>40</td>
<td>83.3</td>
<td>0.12</td>
<td>77</td>
<td>44</td>
<td>50500</td>
<td>44500</td>
<td>1.45</td>
<td>47</td>
</tr>
<tr>
<td>LK5SB-65</td>
<td>60</td>
<td>125</td>
<td>0.5</td>
<td>88</td>
<td>65</td>
<td>68500</td>
<td>43900</td>
<td>1.52</td>
<td>24</td>
</tr>
<tr>
<td>LK5SB-88</td>
<td>80</td>
<td>250</td>
<td>0.5</td>
<td>N/A</td>
<td>88</td>
<td>126500</td>
<td>126000</td>
<td>1.77</td>
<td>22</td>
</tr>
</tbody>
</table>

aMn,theo = ([monomer]:[initiator])*conversion*(molecular weight per repeat unit), assuming 100% conversion for LKSB-88
bEstimated relative to PMMA standards by SEC eluting in TFE with 0.02 M sodium trifluoroacetate
cYield = (conversion)*(mixture of monomer and polymer used in deprotection, g)*(average MW per repeat unit deprotected polymers, g/mol)/(average MW per repeat unit Boc-protected polymers, g/mol)
Figure S1. $^1$H NMR spectrum (500 MHz) of LE5-COE in DMSO-d$_6$

Figure S2. $^1$H NMR spectrum (300 MHz) of LK5SB-44 in D$_2$O
Figure S3. $^1$H NMR spectrum (300 MHz) of LK5 in D$_2$O

Figure S4. $^1$H NMR spectrum (500 MHz) of LE5 in D$_2$O
Figure S5. SEC-MALS trace of LE5 in aqueous solution with 5% ammonium phosphate and 3% acetonitrile
Figure S6. Plot of turbidity as a function of the mole fraction of cationic monomer comparing orders of addition during complex formation (polycation into polyanion or polyanion into polycation)