Adding Solvophilic Comonomer to Polymerization-Induced Self-Assembly of Block Copolymer and Homopolymer: A Cooperative Strategy for preparing Large Compound Vesicles

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The $^1$H NMR spectrum of the polymerization solution and the equations

Figure S1. The $^1$H NMR spectrum of the polymerization solution after the RAFT dispersion polymerization of 4VP and St mediated by mPEG$_{45}$-DDMAT and DDMAT in CDCl$_3$.

\[
\text{Conversion}_{4VP} \% = \frac{l_{7.9 \sim 8.4}}{l_{7.9 \sim 8.4} + l_{5.97 \sim 6.06} + l_{5.65 \sim 5.82}} \times 100\% \quad \text{(S1)}
\]

\[
\text{Conversion}_{St} \% = \frac{l_{6.4 \sim 6.85} - l_{7.9 \sim 8.4} - l_{5.97 \sim 6.06} - l_{5.65 \sim 5.82}}{l_{6.4 \sim 6.85} - l_{7.9 \sim 8.4} - l_{5.97 \sim 6.06} + l_{5.65 \sim 5.82}} \times 100\% \quad \text{(S2)}
\]

\[
\text{Conversion}_{St/4VP} \% = \frac{n_{St} \times \text{Conversion}_{St} + n_{4VP} \times \text{Conversion}_{4VP}}{n_{St} + n_{4VP}} \times 100\% \quad \text{(S3)}
\]

in which, $n_{St}$ and $n_{4VP}$ are the initial molar quantity of the feeding styrene and 4-vinylpyridine, respectively.
Table S1. Summary of GPC data obtained for polymer nano-objects synthesized at 15% w/w solids via RAFT dispersion polymerization of St and 4VP in methanol/water (80/20, w/w) at 70 °C with [mPEG_{45}-DDMAT]/[DDMAT] =1/1 at different [St]₀/[4VP]₀ ratios (DP of 200).

<table>
<thead>
<tr>
<th>Exp.</th>
<th>[St]₀/[4VP]₀</th>
<th>final compositions</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6/1</td>
<td>mPEG_{45}-P(St_{133}-co-4VP_{18})/P(St_{133}-co-4VP_{18})</td>
<td>13.6</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>5/1</td>
<td>mPEG_{45}-P(St_{124}-co-4VP_{20})/P(St_{124}-co-4VP_{20})</td>
<td>12.0</td>
<td>1.10</td>
</tr>
<tr>
<td>3</td>
<td>4/1</td>
<td>mPEG_{45}-P(St_{108}-co-4VP_{24})/P(St_{108}-co-4VP_{24})</td>
<td>11.1</td>
<td>1.12</td>
</tr>
<tr>
<td>4</td>
<td>3/1</td>
<td>mPEG_{45}-P(St_{93}-co-4VP_{31})/P(St_{93}-co-4VP_{31})</td>
<td>10.6</td>
<td>1.13</td>
</tr>
<tr>
<td>5</td>
<td>2/1</td>
<td>mPEG_{45}-P(St_{96}-co-4VP_{49})/P(St_{96}-co-4VP_{49})</td>
<td>12.0</td>
<td>1.14</td>
</tr>
</tbody>
</table>

Figure S2. $^1$H NMR spectra of mPEG_{45}-P(St-co-4VP)/ P(St-co-4VP) assemblies prepared via RAFT dispersion polymerization of St and 4VP with [mPEG_{45}-DDMAT]/[DDMAT] = 1/1 at different [St]₀/[4VP]₀ molar ratios in CDCl₃.
Figure S3. TEM images of polymer nano-objects prepared via RAFT dispersion polymerization of St and 4VP in methanol/water (80/20, w/w) at 70 °C mediated by mPEG45-DDMAT at different [St]/[4VP] ratios (target DP of 200).