Efficient synthesis of snowman- and dumbbell-like silica/polymer anisotropic heterodimers through emulsion polymerization using a surface-anchored cationic initiator

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**Monomers**

Styrene

Methyl methacrylate

**Initiators**

ADIBA

VA86

**Surfactants**

NP30

SDS

*Figure S1.* Chemical structures of the main chemicals used in this study.
ADIBA adsorption isotherm

The Langmuir coefficients for the linearized Langmuir equation were obtained by plotting Ce/Qe versus Ce (mg.L⁻¹) according to:

\[
\frac{Ce}{Qe} = \frac{1}{Q_{\text{max}} K_L} + \frac{Ce}{Q_{\text{max}}} \tag{S1}
\]

where \(K_L \text{ (L.mg}^{-1}\) is the Langmuir sorption constant related to the adsorption energy and \(Q_{\text{max}} \text{ (mg/g)} is the maximum sorption capacity of the solid. The isotherm was found to be linear over the entire concentration range studied with a good square correlation coefficient showing that the data correctly fit the Langmuir relation. An example of linearized isotherm for an initial silica concentration of 50 g.L⁻¹ is given in Figure S3. The Langmuir constants determined from the slope of the line (1/Q_{\text{max}}) and the intercept (1/Q_{\text{max}}K_L) are summarized in Table S1.

Figure S2. TEM image and particle size histogram of the colloidal silica sol used in this study.
Figure S3. Linearized Langmuir isotherm for ADIBA adsorption onto the silica sol in water at pH = 9.1 and 25°C for a fixed silica concentration of 50 g.L\(^{-1}\).

Table S1. Langmuir constants and correlation coefficient for adsorption of ADIBA onto silica in water at pH = 9.1 and 25°C for different silica concentrations

<table>
<thead>
<tr>
<th>Silica (g.L(^{-1}))</th>
<th>Slope (1/Q(_{\text{max}}))</th>
<th>Intercept (1/Q(<em>{\text{max}})K(</em>{\text{L}}))</th>
<th>Q(_{\text{max}}) (mg.g(^{-1}))</th>
<th>K(_{\text{L}}) (L.mg(^{-1}))</th>
<th>Correlation coefficient R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.23</td>
<td>0.44</td>
<td>4.29</td>
<td>0.53</td>
<td>0.9987</td>
</tr>
<tr>
<td>30</td>
<td>0.24</td>
<td>0.59</td>
<td>4.12</td>
<td>0.41</td>
<td>0.9992</td>
</tr>
<tr>
<td>50</td>
<td>0.25</td>
<td>1.43</td>
<td>3.98</td>
<td>0.18</td>
<td>0.9998</td>
</tr>
</tbody>
</table>
Figure S4. Effect of SDS concentration on the morphology of silica/PMMA composite latexes (Table 2). a) 1 wt% SDS, $N_{\text{Latex}}/N_{\text{Silica}} = 0.60$ (entry 4), b) 2 wt% SDS, $N_{\text{Latex}}/N_{\text{Silica}} = 0.85$ (entry 2) and c) 3 wt% SDS, $N_{\text{Latex}}/N_{\text{Silica}} = 0.90$ (entry 5). $[\text{SiO}_2] = 50 \text{ g.L}^{-1}$. $[\text{ADIBA}] = 0.1 \text{ g.L}^{-1}$. 
Figure S5. Effect of silica concentration on the morphology of the silica/PMMA nanocomposite latexes (Table 2). a) [SiO$_2$] = 10 g.L$^{-1}$; 14 % conversion; N$_{\text{Latex}}$/N$_{\text{Silica}}$ = 2.6 (entry 7). b) [SiO$_2$] = 10 g.L$^{-1}$; 88 % conversion; N$_{\text{Latex}}$/N$_{\text{Silica}}$ = 3.0 (entry 7). c) [SiO$_2$] = 40 g.L$^{-1}$; 99% conversion; N$_{\text{Latex}}$/N$_{\text{Silica}}$ = 0.98 (entry 9) and d) [SiO$_2$] = 90 g.L$^{-1}$; 60 % conversion; N$_{\text{Latex}}$/N$_{\text{Silica}}$ = 0.55 (entry 10). [Surfactant] = 3 g.L$^{-1}$ and NP30/SDS/ (wt/wt) = 98/2.
Figure S6. Cryo-TEM images of dissymmetrical silica/PMMA heterodimers with a $N_{\text{Latex}}/N_{\text{Silica}}$ ratio of 0.96. $[\text{SiO}_2] = 40 \text{ g.L}^{-1}$ and NP30/SDS = 98/2 (entry 9 in Table 2). On the right side, the dumbbells are represented by a line joining the silica and the PMMA particle, the trimers by two lines converging on silica, and the tetramers by three lines. Isolated silica particles were encircled to make them distinct from the hybrid particles.
Figure S7. Cryo-TEM images illustrating the evolution of particle morphology with conversion during the synthesis of dissymmetrical silica/PMMA heterodimers. a) 5 % conversion, b) 22 % conversion, c) 54 % conversion and d) 68 % conversion. [SiO$_2$] = 40 g.L$^{-1}$ and NP30/SDS = 98/2 (entry 8 in Table 2).