Supporting Information

Loop-stabilized BAB block copolymer morphologies by PISA in water

Pauline Biais, Patricia Beaunier, François Stoffelbach, Jutta Rieger

P. Biais, Dr. F. Stoffelbach, Dr. J. Rieger
Sorbonne Université, CNRS, UMR 8232, Institut Parisien de Chimie Moléculaire (IPCM)
Polymer Chemistry Team, 4 Place Jussieu, 75252 Paris Cedex 05, France
E-mail: jutta.rieger@upmc.fr; francois.stoffelbach@upmc.fr

Dr. P. Beaunier
Sorbonne Université, CNRS, UMR 7197, Laboratoire de Réactivité de Surface (LRS)
4 Place Jussieu, 75252 Paris Cedex 05, France
Synthesis of (C₄-TTC-PDMAc)₂-EG MacroRAFT agent and (C₄-TTC-PDAAm-b-PDMAc)₂-EG Block Copolymers

The macroRAFT agent (C₄-TTC-PDMAc)₂-EG (Table S1, entry C) has been synthesized following the same protocol as for the macroRAFT agents A and B (see experimental section in the main article) using (C₄-TTC)₂-EG as a RAFT agent synthesized as previously reported.¹

The RAFT dispersion polymerizations of DAAm in presence of the macroRAFT agent were performed following the protocol described in the experimental section and using the conditions detailed in Table S2.

Table S1. Polymerization Conditions and Characteristics of the Poly(N,N-dimethylacrylamide) MacroRAFT Agents Prepared by Solution Polymerization of DMAc in DMF at 70 °C⁷

<table>
<thead>
<tr>
<th>Entry</th>
<th>RAFT agent</th>
<th>time (min)</th>
<th>conv. b (%)</th>
<th>DPₙ,th c (kg mol⁻¹)</th>
<th>Mₙ,th c (kg mol⁻¹)</th>
<th>Mₙ,LS d (kg mol⁻¹)</th>
<th>Mₙ,PMMA f (kg mol⁻¹)</th>
<th>Mₙ,RMN d (kg mol⁻¹)</th>
<th>η f</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(C₁₂-TTC)₂-BA</td>
<td>133</td>
<td>75</td>
<td>86</td>
<td>9.3</td>
<td>9.5</td>
<td>9.6</td>
<td>6.0</td>
<td>1.21</td>
</tr>
<tr>
<td>B</td>
<td>(C₄-TTC)₂-BA</td>
<td>129</td>
<td>73</td>
<td>84</td>
<td>8.9</td>
<td>9.0</td>
<td>10.0</td>
<td>5.4</td>
<td>1.21</td>
</tr>
<tr>
<td>C</td>
<td>(C₄-TTC)₂-EG</td>
<td>135</td>
<td>74</td>
<td>85</td>
<td>8.9</td>
<td>8.4</td>
<td>10.0</td>
<td>6.7</td>
<td>1.13</td>
</tr>
</tbody>
</table>

⁷ [DMAc]₀ = 2 M, [RAFT agent]₀/[AIBN]₀ = 10. b Monomer conversion determined by ¹H NMR. c Theoretical number-average molar mass, Mₙ,th, and number-average degree of polymerization, DPₙ,th, calculated using the experimental conversion. d Number-average molar mass Mₙ,LS, determined by ¹H NMR. e Number-average molar mass Mₙ,LS determined by SEC in DMF (+ LiBr 1g L⁻¹) with light scattering (LS) detector (dn/dc = 0.081 mL g⁻¹). f Number-average molar mass Mₙ,PMMA and dispersity D determined by SEC in DMF (+ LiBr 1g L⁻¹) with a PMMA calibration.

Table S2. Experimental Conditions and Results for the Dispersion Polymerizations of DAAm in the Presence of the MacroRAFT Agent (C₄-TTC-PDMAc)₂-EG in Water at 70 °C⁸

<table>
<thead>
<tr>
<th>Entry</th>
<th>[DAAm]₀ (wt%)</th>
<th>[ACPA]₀ (mmol L⁻¹)</th>
<th>[RAFT]₀ (mmol L⁻¹)</th>
<th>[RAFT]₀/[ACPA]₀</th>
<th>pH</th>
<th>time (min)</th>
<th>conv. b (%)</th>
<th>DPₙ,th c (PDAAm)</th>
<th>Mₙ,th c (kg mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>19</td>
<td>1.45</td>
<td>7.4</td>
<td>5.1</td>
<td>5.7</td>
<td>125</td>
<td>95</td>
<td>203</td>
<td>44.9</td>
</tr>
<tr>
<td>C-2</td>
<td>7</td>
<td>0.90</td>
<td>2.2</td>
<td>2.4</td>
<td>5.1</td>
<td>279</td>
<td>94</td>
<td>203</td>
<td>44.4</td>
</tr>
</tbody>
</table>

⁸ Mₙ,LS (macroRAFT agent C) = 10.0 kg mol⁻¹. b Monomer conversion determined by ¹H NMR. c Theoretical number-average degree of polymerization, DPₙ,th (PDAAm), and number-average molar mass, Mₙ,th calculated using the experimental conversion.
Figure S1. (A) Evolution of DMAc conversion versus time in presence of the RAFT agents \((C_{12}-\text{TTC})_2\)-BA and \((C_{4}-\text{TTC})_2\)-BA. (B) Semilogarithmic kinetic curve for RAFT polymerizations of DMAc in presence of the RAFT agents \((C_{12}-\text{TTC})_2\)-BA and \((C_{4}-\text{TTC})_2\)-BA. (C) Evolution of the \(M_n\) (square and trend line) (derived from a PMMA calibration) and \(D\) (triangle) with monomer conversion for the polymerization of DMAc with the RAFT agent \((C_{12}-\text{TTC})_2\)-BA. (D) SEC chromatograms in DMF of the macroRAFT agents A and B (Table S1) (D).

Scheme S1. Self-assembly of PDAAm-\(b\)-PDMAc-\(b\)-PDAAm block copolymer via PISA in water showing the formation of flower-like micelles and bridged micelles/aggregates.
Figure S2. (A) Acid titration curve to determine the pKa of a (C_{12}-TTC-PDMAc)_2-BA macroRAFT agent ($M_{n,RMN} = 5.0$ kg mol$^{-1}$) with a NaOH solution (0.01 M). (B) pKa determination using the Gran method (see Equation 1 in the main article).

Figure S3. SEC chromatograms for block copolymers A-4, A-5 and A-6 (A) (Table 1) and B-4, B-5 and B-7 (B) prepared by dispersion polymerization of DAAm in water at 70 °C, at pH = 4.2 with the macroRAFT agents A and B respectively.
Figure S4. TEM images and macroscopic aspects for samples B-1 to B-5 and macroscopic aspect for the heterogeneous sample B-7 prepared by the dispersion polymerization of DAAm with the macroRAFT agent B (C₄-TTC-PDMAc)₂-BA at pH = 5.0 and pH = 4.2.
Figure S5. SEC chromatograms and macroscopic aspects for block copolymers C-1 and C-2 (Table S2) prepared by dispersion polymerization of DAAm in water at 70 °C with the macroRAFT agent (C₄-TTC-PDMAc)₂-EG.

References