Supporting information for:

PMMA based soluble polymeric temperature sensors based on UCST transition and solvatochromic dyes

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Experimental Part

Materials
Methyl methacrylate (MMA) was purchased from Sigma-Aldrich and was purified with an inhibitor-remover before use. Disperse red 1 and pyrene-1-methanol were purchased from Sigma-Aldrich and were used without purification. Azobis(isobutyronitrile) (AIBN, Aldrich) was recrystallized from methanol. 2-Cyano-2-butyl dithiobenzoate (CBDB) was prepared according to a literature procedure for a related compound.[1]
All analytical grade solvents were purchased from Biosolve Ltd or Fluka. Column chromatography was carried out on either standardized aluminium oxide 90 or silica gel purchased from Merck. The deuterated solvents (CDCl$_3$ or CD$_2$Cl$_2$) for NMR spectroscopy were obtained from Cambridge Isotope Laboratories.

Instrumentation
Size-exclusion chromatography (SEC) was performed on a Shimadzu system equipped with a SCL-10A system controller, a LC-10AD pump, a RID-10A refractive index detector and a PSS SDV column with chloroform:triethylamine:2-propanol (94:4:2) as eluent and the column oven was set to 50 °C. PMMA calibration standards were used.
Nuclear magnetic resonance spectra were recorded on a Varian Mercury 400 MHz spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm) calibrated to an internal standard, tetramethylsilane (TMS) in deuterated solvents (CDCl$_3$ or CD$_2$Cl$_2$).
UV/vis spectra were recorded on a Perkin-Elmer Lamda-45 UV/vis spectrophotometer equipped with a PTP-6 Peltier system to heat or cool the cuvette. For fluorescence measurements a Perkin-Elmer Luminescence Spectrometer LS 50B with a PTP-1 Peltier Temperature Programmer were used. For the temperature measurements on these spectrophotometers a temperature profile with a temperature rate of 0.5 °C/min was used.
Elemental analyses were carried out on a EuroVector EuroEA300 elemental analyzer for CHNS–O. The cloud point measurements for the identification of the UCST behavior were performed by heating the polymer (1.0 mg/mL) in ethanol or ethanol/water mixtures from 10 to 70 °C with a heating rate of 1.0 °C per minute followed by cooling to 10 °C at a cooling rate of 1.0 °C per minute after keeping it 10 minutes at 70 °C. This cycle was repeated three times. During these controlled cycles the transmission through the solutions was monitored in a Crystal16™ from Avantium Technologies. The cloud points are reported as the 50% transmittance temperature in the third heating run.
Synthesis of monomer 3a, DR1-MA:

(2-{N-Ethyl-N-[4-(4-nitrophenylazo)phenyl]amino}ethyl methacrylate)\(^{[2]}\)

A solution of 1.0 g (3.2 mmol) disperse red 1 (DR1) and 1.46 mL of triethylamine (10.5 mmol) in 50 mL of anhydrous THF was prepared followed by dropwise addition of methacryloyl chloride (0.92 mL, 9.5 mmol) under stirring at 0 °C. The resulting mixture was stirred at 0 °C and allowed to warm to room temperature during 24 hours. Subsequently, the solvent was evaporated under reduced pressure and the solid residue was dissolved in diethyl ether and washed with water. After evaporation of the diethyl ether, the crude product DR1-methacrylate was purified by silica gel chromatography eluting with \( n \)-hexane/methylene chloride (1:5).

**GC-MS:** \( m/z \) (%) = 382 (20) [M\(^+\)], 283 (100) [M\(^+\) - C\(_5\)H\(_7\)O\(_2\)], 237 (16) [283 – NO\(_2\)].

**\( ^1\)H-NMR (400 MHz, CDCl\(_3\)):** \( \delta \) = 8.33 (d, \( ^3J = 8.4 \) Hz, 2H, H\(_1\)), 7.91 (dd, \( ^3J = 8.8 \) Hz, 4H, H\(_2,3\)), 6.81 (d, \( ^3J = 8.4 \) Hz, 2H, H\(_4\)), 6.14 (s, 1H, H\(_9\)), 5.59 (s, 1H, H\(_8\)), 4.37 (t, \( ^3J = 6.4 \) Hz, 2H, H\(_8\)), 3.73 (t, \( ^3J = 6 \) Hz, 2H, H\(_7\)), 3.56 (q, \( ^3J = 7.2 \) Hz, 2H, H\(_5\)), 1.94 (s, 3H, H\(_10\)), 1.26 (s, 3H, H\(_6\)) ppm. **Elemental analysis:** C\(_{20}\)H\(_{22}\)N\(_4\)O\(_4\) (382.41): cal.: C 62.82% H 5.80% N 14.65%; found: C 62.49% H 5.82% N 14.60%.

**UV/vis (ethanol):** \( \lambda_{\text{max}}/\text{nm} \ (\varepsilon/(\text{M}^{-1}\cdot\text{cm}^{-1})) \): 284 (10,360), 470 (31,980).
Synthesis of monomer 3b, (PyMMA): Pyrene-1-ylmethyl-methacrylate\[^{[3,4]}\]

![Pyrene-1-ylmethyl-methacrylate](image)

A solution of triethylamine (1.80 mL, 12.8 mmol) and 1.0 g of pyrene-1-ylmethanol (4.3 mmol) in 50 mL of anhydrous THF was prepared followed by dropwise addition of methacryloyl chloride (1.24 mL, 12.8 mmol) under stirring at 0 °C. The reaction was then stirred and allowed to warm to room temperature overnight (24 hours). Subsequently, the reaction medium was filtered and the solvent was evaporated under reduced pressure. Afterwards the solid residue was dissolved in diethyl ether and washed with water. After evaporation of the diethyl ether, the crude monomer has been purified by recrystallization from ethanol at 40 °C.

**GC-MS:** \( m/z \) (%): 300 (38) [M\(^{+}\)], 215 (100) [M\(^{+}\) - C\(_6\)H\(_{10}\) + H\(^{+}\)], 189 (8), 107 (5), 94 (9), 41 (10) [all aromatic fragmentation].

**\(^{1}\)H-NMR** (400 MHz, CDCl\(_3\)): \( \delta \) = 8.32-8.00 (m, 9H, aromatic H\(_{2-10}\)), 6.16 (s, 1H, H\(_{12}\)), 5.91 (s, 2H, H\(_{11}\)), 5.57 (s, 1H, H\(_{12}\)), 1.98 (s, 3H, H\(_{13}\)) ppm.

**\(^{13}\)C-NMR** (100 MHz, CDCl\(_3\)): \( \delta \) = 167.4 (C=O), 136.2, 131.7, 131.2, 130.7, 129.5, 129.0, 128.1, 127.8, 127.6, 127.3, 126.1, 126.0, 125.5, 125.4, 124.9, 124.6, 124.5, 122.9 (16 aromatic C and -C=CH\(_2\)), 65.0 (CH\(_2\)-O), 18.4 (-CH\(_3\)) ppm. **Elemental analysis:** C\(_{21}\)H\(_{16}\)O\(_2\) (300.35): cal.: C 83.98% H 5.37%; found: C 84.08% H 5.64%.

**UV/vis** (n-heptane): \( \lambda \text{max}/\text{nm} \) (\( \varepsilon/(\text{M} \cdot \text{cm}) \)): 201 (16.120), 233 (26.060), 242 (46.680), 265 (16.350), 276 (31.270), 312 (7.760), 326 (20.210), 342 (32.520).

**Fluorescence** (THF): \( \lambda \text{max}/\text{nm} \): 377, 394, 416 (shoulder), 435 (shoulder).
Synthesis of copolymer 5a: Poly(MMA-stat-DR1-MA)

Poly(MMA-stat-DR1-MA) was prepared in a closed reaction vessel with a [MMA]:[DR1-MA]:[CBDB]:[AIBN] ratio of 97:3:1:0.25. The polymerization mixture was prepared with 0.41 mL MMA (3.88 mmol), 1.59 mL toluene, 1.64 mg of AIBN (0.01 mmol), 45.9 mg of DR1-MA (0.12 mmol) and 9.41 mg CBDB (0.04 mmol). Before the polymerization, the solution was degassed by bubbling with argon for at least 30 min. Subsequently, the reaction mixture was heated to 70 °C for 12 hours. Afterwards the polymer mixture was diluted with dichloromethane and precipitated twice in ice-cold methanol resulting in a red powder.

UV/vis (1,4-dioxane): \( \lambda_{\text{max}}/\text{nm} \left( \varepsilon/(\text{M}^{-1} \cdot \text{cm}^{-1}) \right) : 288 (44,440), 468 (92,610).

**Table S1:** Characterization of the precipitated poly(MMA-stat-DR1-MA).

<table>
<thead>
<tr>
<th>sample</th>
<th>[MMA]/[DR1-MA]</th>
<th>( M_n \left[ \text{g mol}^{-1} \right]^{a} ) SEC</th>
<th>PDI(^a)</th>
<th>DP(_{SEC}^{a})</th>
<th>( M_n \left[ \text{g mol}^{-1} \right]^{b} ) (^1)H NMR</th>
<th>DP(_{NMR}^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>95/5</td>
<td>10,500</td>
<td>1.08</td>
<td>97</td>
<td>14,000</td>
<td>134</td>
</tr>
</tbody>
</table>

\(^a\) Obtained from SEC with CHCl\(_3\) as eluent and PMMA standards.

\(^b\) Obtained from the integrals of the RAFT end group and the polymer backbone in the \(^1\)H-NMR spectrum (400 MHz, CD\(_2\)Cl\(_2\)).

**Table S2:** Composition of poly(MMA-stat-DR1-MA).

<table>
<thead>
<tr>
<th>sample</th>
<th>theor. ratio MMA/DR1-MA</th>
<th>Composition(^a) (^1)H NMR</th>
<th>Composition(^b) UV/vis DRI [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>97/3</td>
<td>95/2.6</td>
<td>2.9</td>
</tr>
</tbody>
</table>

\(^a\) Obtained from the integrals of the DR1 and the polymer backbone in the \(^1\)H NMR spectrum.

\(^b\) Obtained from the \( \varepsilon \) of the UV/vis spectrum using the Lambert-Beer-Law and \( M_n \) of SEC.
Synthesis of copolymer 5b: Poly(MMA-stat-PyMMA)

Poly(MMA-stat-PyMMA) was prepared in a closed reaction vessel with a [MMA]:[PyMMA]:[CBDB]:[AIBN] ratio of 95:5:1:0.25. The polymerization mixture was prepared by dissolving 1.64 mg of AIBN (0.01 mmol), 60.1 mg of PyMMA (0.2 mmol) and 9.41 mg CBDB (0.04 mmol) in 0.40 mL MMA (3.8 mmol) and 1.60 mL toluene. Before the polymerization, the solutions were degassed by bubbling with argon for at least 30 min. Subsequently, the reaction mixture was heated to 70 °C for 12 hours. Afterwards the polymer mixture was diluted with dichloromethane and precipitated twice in ice-cold methanol resulting in a pink powder.

UV/vis (1,4-dioxane): $\lambda_{\text{max}}$/nm ($\varepsilon$(M$^{-1}$·cm$^{-1}$): 244 (211,340), 266 (120,160), 277 (216,290), 314 (66,970), 328 (141,960), 342 (204,470). Fluorescence (ethanol/water [80/20]): $\lambda_{\text{max}}$/nm: 395, 453.

**Table S3: Characterization of the precipitated poly(MMA-stat-PyMMA).**

<table>
<thead>
<tr>
<th>sample</th>
<th>[MMA]/[PyMMA]</th>
<th>$M_n$ [g mol$^{-1}$]$^a$ SEC</th>
<th>PDI$^a$</th>
<th>DP$^a$ SEC</th>
<th>$M_n$ [g mol$^{-1}$]$^b$ $^1$H NMR</th>
<th>DP$^b$ NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>5b</td>
<td>95/5</td>
<td>9,100</td>
<td>1.16</td>
<td>82</td>
<td>13,100</td>
<td>117</td>
</tr>
</tbody>
</table>

$^a$ Obtained from SEC with CHCl$_3$ as eluent and PMMA standards.

$^b$ Obtained from the integrals of the RAFT end group and the polymer backbone in the $^1$H-NMR spectrum (400 MHz, CD$_2$Cl$_2$).

**Table S4: Composition of poly(MMA-stat-PyMMA).**

<table>
<thead>
<tr>
<th>sample</th>
<th>theor. ratio MMA/PyMMA</th>
<th>Composition$^a$ $^1$H NMR</th>
<th>Composition$^b$ UV/vis pyrene[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5b</td>
<td>95/5</td>
<td>95/5.3</td>
<td>4.9</td>
</tr>
</tbody>
</table>

$^a$ Obtained from the integrals of the pyrene and the polymer backbone in the $^1$H-NMR spectrum.

$^b$ Obtained from the $\varepsilon$ of the UV/vis spectrum using the Lambert-Beer-Law and $M_n$ of SEC.
Figure S1. UV-vis spectra at different temperatures to demonstrate the temperature dependence of 1a, DR1 in ethanol (2.4 $10^{-4}$ mol L$^{-1}$).

Figure S2. SEC traces of copolymers 5a (left) and 5b (right). The $M_n$ and PDI values were determined from the RI traces with PMMA standards.
Figure S3. Cloud point measurements for the identification of the UCST behavior of copolymer 5a (1.0 mg mL⁻¹).

Table S5 Observed solvatochromic shifts of 1a and copolymer 5a in various solvents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>E_r(30) [kcal mol⁻¹][5]</th>
<th>λ_max [nm][a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>cyclohexene</td>
<td>30.9</td>
<td>449</td>
</tr>
<tr>
<td>1a</td>
<td>1,4-dioxane</td>
<td>36.0</td>
<td>474</td>
</tr>
<tr>
<td>1a</td>
<td>ethyl acetate</td>
<td>38.1</td>
<td>481</td>
</tr>
<tr>
<td>1a</td>
<td>DMF</td>
<td>43.2</td>
<td>502</td>
</tr>
<tr>
<td>1a</td>
<td>ethanol</td>
<td>51.9</td>
<td>482</td>
</tr>
<tr>
<td>1a</td>
<td>1 M HCl</td>
<td>63.1</td>
<td>515</td>
</tr>
<tr>
<td>5a</td>
<td>1,4-dioxane</td>
<td>36.0</td>
<td>468</td>
</tr>
<tr>
<td>5a</td>
<td>ethyl acetate</td>
<td>38.1</td>
<td>472</td>
</tr>
<tr>
<td>5a</td>
<td>DMF</td>
<td>43.2</td>
<td>491</td>
</tr>
<tr>
<td>5a</td>
<td>ethanol 7 °C (globule, PMMA)</td>
<td>---</td>
<td>480</td>
</tr>
<tr>
<td>5a</td>
<td>ethanol 60 °C (coil)</td>
<td>---</td>
<td>470</td>
</tr>
</tbody>
</table>

[a] Recorded λ_max-values of the π*←π transition in the respective solution of 1a or 5a.

References