Supporting information

Poly(thiolactone) Homo- and Copolymers from Maleimide Thiolactone: Synthesis and Functionalization

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Figure S1: Kinetic investigation of the synthesis of MITla comparing the newly formed thiolactone signal at 4.95 ppm (DMSO- $d_6$) to trioxane as internal standard at 70 °C.

Figure S2: Comparison of FT-IR spectra for maleic anhydride (blue trace-), d,l-homocysteine thiolactone hydrochloride (black trace), and the desired maleimide thiolactone (IUPAC: 1-(2-oxotetrahydrothiophen-3-yl)-1H-pyrrole-2,5-dione; MITla, red trace).
Figure S3: Enlarged FT-IR spectrum for MITlα and the important signals for: carbonyls at 1689, C-N-C at 1400, and the maleimide double bond at 830 and 690 cm⁻¹.

Figure S4: ¹H-NMR spectra of maleimide thiolactone (MITlα) and peak assignment (CDCl₃, 300 MHz).
Figure S5: $^{13}$C-NMR spectrum of maleimide thiolactone (MIT1a) (CDCl$_3$, 75 MHz).

Figure S6: ESI-MS spectrum for MIT1a.
Figure S7: Comparison of SEC traces for the homopolymerization of MITla initiated by different amounts of TPO in solution (100 mg mL⁻¹ DCM): 5 wt.% (dotted line), 10 wt.% (straight line), and 20 wt.% (dashed line).

Figure S8: Comparison of SEC traces for the homopolymerization of MITla initiated by different amounts of AIBN in solution (100 mg mL⁻¹ THF): 5 wt.% (dotted line), 10 wt.% (straight line), and 20 wt.% (dashed line).
Figure S9: Comparison of $^{13}$C-NMR traces for MITla (black trace) and PMITla (10 wt.% TPO, bulk; red trace) (DMSO-$d_6$, 75 MHz).

Figure S10: NMR spectrum for PMITla$^{\text{thms}}$ initiated by AIBN in THF (CDCl$_3$, 300 MHz).
Figure S11: $^{13}$C-NMR spectrum for PMITla$^{\text{AIBN}}$ (DMSO-$d_6$, 75 MHz).

Figure S12: $^{13}$C-NMR spectrum for PMITla$^{\text{AIBN}}$ (CDCl$_3$, 75 MHz).
Figure S13: COSY spectrum for PMITlαAIBN initiated via AIBN in THF (300 MHz; CDCl₃).

Figure S14: HSQC NMR spectrum for PMITlαAIBN initiated via AIBN in THF (300 MHz; CDCl₃).
Figure S15: DSC thermogram for PMITlα^{TPO} in the temperature range of -30 to 200°C.

Figure S16: Comparison of FT-IR traces for PMITlα^{AIBN} (red trace) and PMITlα^{TPO} (black trace) (A) and an enlargement of the fingerprint region (B).
Figure S17: Comparison of SEC traces for P(MITla-alt-S)_{10} (dotted line), P(MITla-alt-S)_{23} (straight line), and P(MITla-alt-S)_{50} (dashed line).

Figure S18: $^1$H-NMR spectrum for P(MITla-alt-S)_{23} and peak assignment (300 MHz; CDCl$_3$).
Figure S19: $^1$H-NMR spectrum for P(MITla-alt-S)$_{23}$ and peak assignment (300 MHz; DMSO-$d_6$).

Figure S20: $^1$H-NMR spectrum for P(MITla-co-NIPAAm)$_{23}$ and peak assignment (300 MHz; CDCl$_3$).
Figure S21: A) Time vs. styrene monomer conversion plot determined by NMR (black square) and GC (red dot) for the copolymerization of MITla and styrene; B) comparison of SEC traces for the kinetic investigation of the copolymerization of MITla and styrene using RAFT.

Figure S22: Comparison of DSC traces for P(MITla-alt-S)$_{32}$ (black lines), P(MITla-co-NIPAAm)$_{32}$ (red lines) and PMITla$^{TP}$ (blue lines) in the second (straight lines) and third (dashed lines) heating run.
Figure S23: Comparison of NMR spectra for PMITla<sub>ABN</sub> before (black trace) and after (red trace) double modification via <i>n</i>-butylamine and methyl acrylate (300 MHz; CDCl₃).

Figure S24: HSQC NMR spectra for PMITla<sub>ABN,DM</sub> initiated via AIBN in CHCl₃ by methyl acrylate and <i>n</i>-butylamine and peak assignment (300 MHz; CDCl₃).
Figure S25: Comparison of NMR traces for P(MITIa-co-NIPAAm)\textsubscript{23} before (black trace) and after (red trace) double modification via \textit{n}-butylamine and methyl acrylate (300 MHz; CDCl\textsubscript{3}).

Figure S26: Comparison of NMR traces for P(MITIa-alt-S)\textsubscript{28} before (black trace) and after (red trace) double modification via \textit{n}-butylamine and methyl acrylate (300 MHz; CDCl\textsubscript{3}).
Figure S27: Comparison of $^{13}$C-NMR traces for PMITla$_{ABN,DM}$ (blue trace), P(MITla-co-NIPAAm)$_{23}^{DM}$ (red trace), and P(MITla-alt-S)$_{36}^{DM}$ (black trace); inset shows the signal at 58 ppm.

Figure S28: Comparison of SEC traces for the double modification by methyl acrylate and $\alpha$-butylamine for P(MITla-alt-S)$_{36}$ in different solvents: pristine P(MITla-alt-S)$_{36}$ (dashed line), in THF (black line), in dioxane (red line), chloroform (blue line), DMF (blue line).
Table S1: Double modification of P(MITla-co-S)₃₈ by n-butylamine and methyl acrylate at different conditions (25 mg mL⁻¹).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Reaction Time [h]</th>
<th>Further educt addition after</th>
<th>Estimated degree of functionalization [%]ᵃ</th>
<th>Mₙ [g mol⁻¹]</th>
<th>Dᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>48</td>
<td>24 h</td>
<td>40</td>
<td>19 600</td>
<td>1.55</td>
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<tr>
<td>THF</td>
<td>48</td>
<td>24 h</td>
<td>60</td>
<td>18 600</td>
<td>1.37</td>
</tr>
<tr>
<td>Dioxane</td>
<td>48</td>
<td>24 h</td>
<td>50</td>
<td>16 600</td>
<td>1.30</td>
</tr>
<tr>
<td>Chloroform</td>
<td>48</td>
<td>24 h</td>
<td>60</td>
<td>15 000</td>
<td>1.29</td>
</tr>
</tbody>
</table>

ᵃ) Degree of functionalization is estimated via ¹H-NMR (300 MHz; CDCl₃)
ᵇ) SEC (DMAC/LiCl): PS-calib.

Figure S29: Comparison of ¹³C-NMR spectra for double modification by methyl acrylate and n-butylamine for P(MITla-alt-S)₃₈ in different solvents: in THF (black line), in dioxane (red line), chloroform (blue line), DMF (blue line) (75 MHz; CDCl₃); (As polymers were only precipitated once before measuring NMR, educt signals are still observed).
Figure S30: Comparison of FT-IR spectra for PMITlaN before (black trace) and after (red trace) modification by methyl acrylate and \textit{n}-butylamine.

Figure S31: Comparison of FT-IR spectra for P(MITla-co-NIPAAm)$_{23}$ before (black trace) and after (red trace) modification by methyl acrylate and \textit{n}-butylamine.
Figure S32: Comparison of FT-IR spectra for P(MITla-co-S)$_{36}$ before (black trace) and after (red trace) modification by methyl acrylate and $n$-butylamine.