Supporting Information for

Ambient Temperature Polymer Modification by
In-situ Phototriggered Deprotection and Thiol-Ene
Chemistry

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Study on the concentrations influence of DMPP during photodeprotection

Figure S1. SEC/ESI-MS spectra of 2 after UV irradiation in presence of 0.5 eq. (a), 0.2 eq. (b) and 0.01 eq. (c) of DMPP (with respect to thiol-protected functionality).
**In Situ photodeprotection and radical photo-initiated thiol-ene reaction**

2 (3.0 mg) was dissolved in DCM (4 mL) and aliquoted into headspace vials (Pyrex, diameter 20 mm), which were crimped air-tight employing SBR seals with PTFE inner liner. The solution was deoxygenated by purging with nitrogen for 10 min and 10 eq. of a degassed solution of ethyl vinyl ether were added. The flasks were subsequently irradiated for 16 hours by revolving around a compact low-pressure fluorescent lamp (Arimed B6, Cosmedico GmbH, Stuttgart, Germany) emitting at 320 nm (± 30 nm) at a distance of 40–50 mm in a custom-built photoreactor, whose setup has previously been described (see also Fig. S10). The solvent was evaporated after the reaction, THF (2 mL) was added and the slightly yellow solution was analyzed immediately via SEC/ESI-MS.

![SEC/ESI-MS spectra](image)

**Figure S2.** SEC/ESI-MS spectra of 2 after UV irradiation in presence of 10 eq. of ethyl vinyl ether. As expected, longer irradiation times decreased 3 and increased 3’, but major side product formation could not be avoided in any case.
NMR of 3-((2-nitrobenzyl)thio)propanoic acid 1

Figure S3. $^1$H NMR spectrum of 3-((2-nitrobenzyl)thio)propanoic acid in DMSO-d$_6$. Note that the singlet at 2.50 ppm is associated with the DMSO solvent and the minor (broad) peak at 3.35 ppm is caused by water.
NMR of photomonomer 2-((3-((2-nitrobenzyl)thio)propanoyl)oxy)ethyl methacrylate 3

Figure S4. $^1$H NMR spectrum of 2-((3-((2-nitrobenzyl)thio)propanoyl)oxy) ethyl methacrylate 3 in CDCl$_3$. 
**Figure S5.** SEC trace for the ATRP polymer 5a of monomer 3 in anisole (33 wt.%) at 80°C for 15 hours. ([3]/[CuBr]/[EBiB]/[PMDETA] = 200:1:1:1).

**Figure S6.** SEC trace for the ATRP polymer 5b of monomer 3 in anisole (50 wt.%) at 80°C for 8.5 hours. ([3]/[CuBr]/[EBiB]/[PMDETA] = 100:1:1.2:1.2).
ESI-MS analysis of Photopolymer 5c

Figure S7 depicts the ESI-MS spectra of the bromine-terminated polymer 5c alongside with by-products formed either during ATRP or during ESI-MS ionization. Indeed thermal rearrangement (most likely during ESI-MS ionization) of 5c resulted in the formation of lactone functionality 5c’, which occurrence has been previously reported during ESI-MS analysis of PMMA.\textsuperscript{2,3} Nucleophilic substitution of bromine-terminated species formed the hydroxyl-capped polymer 5c’’. In addition, the formation of disproportionation products was observed (species 6 and 7). Importantly, all found species differ only in their polymeric end group, implying that the lateral photodegradable groups are still fully intact.
Figure S7. SEC/ESI-MS spectra of the polymer 5c obtained by ATRP in anisole (50 wt.%) at 80 °C ([4]/[CuBr]/[EBiB]/[PMDETA] = 100:1:1.2:1.2). Note the isotopic pattern of the bromine terminated species 5c.
Figure S8. Evolution of GPC traces of the ATRP polymerization in anisole (50 wt.%) at 80 °C ([4]/[CuBr]/[EBiB]/[PMDETA] = 100:1:1.2:1.2).

Figure S9. $^1$H NMR spectrum of 9 in CDCl$_3$. 9 was prepared according to a previously reported procedure.$^4$
### Theoretical and experimental values for ESI-MS measurements

**Table S1.** Experimental and theoretical $m/z$ values for the first peak in the isotopic distribution of Figure 1 in the $m/z$ range between 1810 and 1855.

<table>
<thead>
<tr>
<th>$m/z_{expt}$</th>
<th>ion assignment</th>
<th>formula</th>
<th>$m/z_{theor}$</th>
<th>$\Delta m/z$</th>
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<tbody>
<tr>
<td>1818.9</td>
<td>$2_{(n=35)} + Na^+$</td>
<td>$[C_{81}H_{153}NNaO_{39}S]^+$</td>
<td>1819.0</td>
<td>0.1</td>
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<tr>
<td>1816.0</td>
<td>$3_{(n=38)} + Na^+$</td>
<td>$[C_{80}H_{160}NaO_{40}S]^+$</td>
<td>1816.0</td>
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**Table S2.** Experimental and theoretical $m/z$ values for the first peak in the isotopic distribution of Figure 4 in the $m/z$ range between 1500 and 1800.

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<th>formula</th>
<th>$m/z_{theor}$</th>
<th>$\Delta m/z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1549.5</td>
<td>$6_{(n=5)} + Na^+$</td>
<td>$[C_{70}H_{88}N_4NaO_{26}S_4]^+$</td>
<td>1549.4</td>
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<tr>
<td>1551.5</td>
<td>$7_{(n=4)} + Na^+$</td>
<td>$[C_{70}H_{70}N_4NaO_{26}S_4]^+$</td>
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<tr>
<td>1567.5</td>
<td>$5c´´_{(n=4)} + Na^+$</td>
<td>$[C_{70}H_{88}N_4NaO_{27}S_4]^+$</td>
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<td>1629.3</td>
<td>$5c_{(n=4)} + Na^+$</td>
<td>$[C_{70}H_{78}BrN_4NaO_{26}S_4]^+$</td>
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<td>1635.5</td>
<td>$5c´_{(n=5)} + Na^+$</td>
<td>$[C_{74}H_{92}N_4NaO_{28}S_4]^+$</td>
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**Table S3.** Experimental and theoretical $m/z$ values for the first peak in the isotopic distribution of Figure S2 in the $m/z$ range between 1750 and 1780.

<table>
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<th>$m/z_{theor}$</th>
<th>$\Delta m/z$</th>
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<tr>
<td>1772.0</td>
<td>$3_{(n=37)} + Na^+$</td>
<td>$[C_{78}H_{156}NaO_{36}S]^+$</td>
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<tr>
<td>1756.0</td>
<td>$3´_{(n=35)} + Na^+$</td>
<td>$[C_{78}H_{156}NaO_{38}S]^+$</td>
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Figure S10. Drawing of the custom-built photoreactor employed in the current study.
**Figure S11.** Emission spectrum of the employed compact low-pressure fluorescent lamp (36 W, Arimed B6, $\lambda_{\text{max}} = 320$ nm).

**References**


