

Supporting Information for

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

*Thomas Pauloehrl,<sup>1</sup> Guillaume Delaittre,<sup>1,2</sup> Martin Bastmeyer<sup>2,3</sup> and*

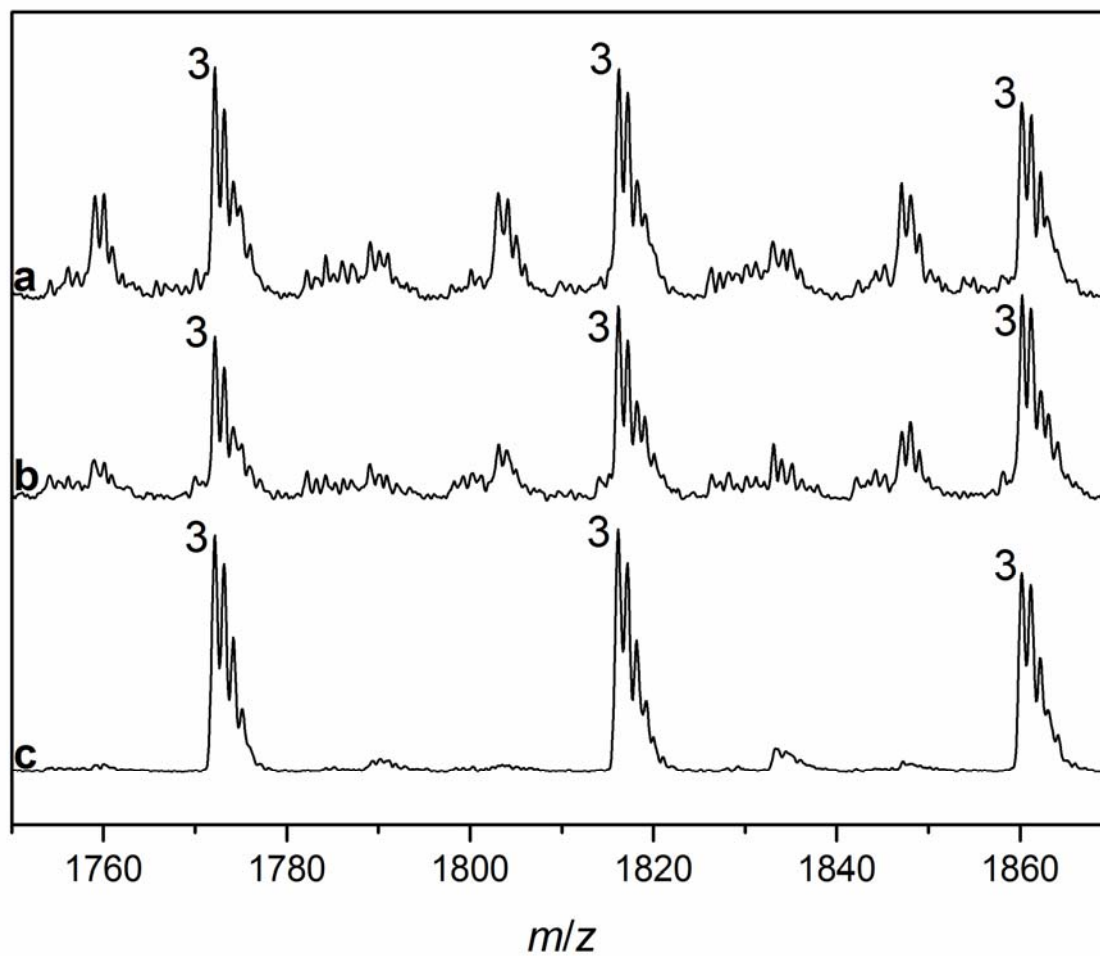
*Christopher Barner-Kowollik<sup>1,3\*</sup>*

<sup>1</sup>Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany, christopher.barner-kowollik@kit.edu; Phone: (+49) 721 608 45741, Fax: (+49) 721 608 45740.

<sup>2</sup>Zoologisches Institut, Zell- und NeurobiologieKarlsruher Institut für Technologie (KIT), Haid-und-Neu-Straße 9, 76131 Karlsruhe Germany.

<sup>3</sup>Center for Functional Nanostructures, Karlsruher Institut für Technologie (KIT), Wolfgang-Gaede-Str. 1a, 76131 Karlsruhe, Germany

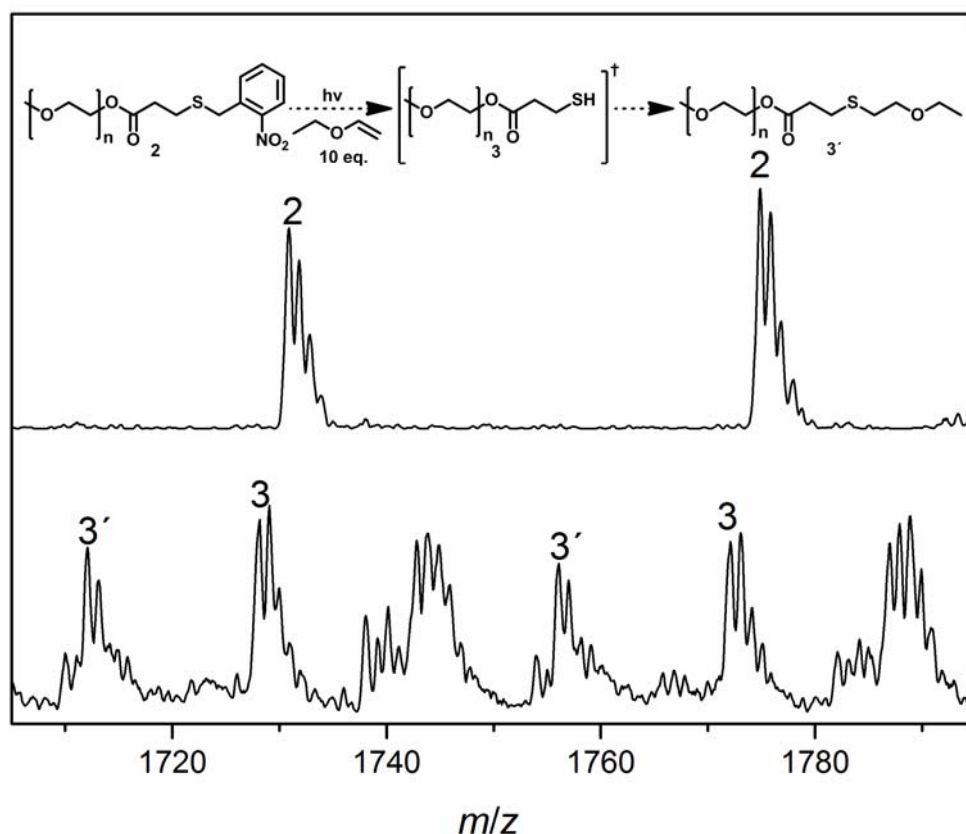
### Study on the concentrations influence of DMPP during photodeprotection



**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).

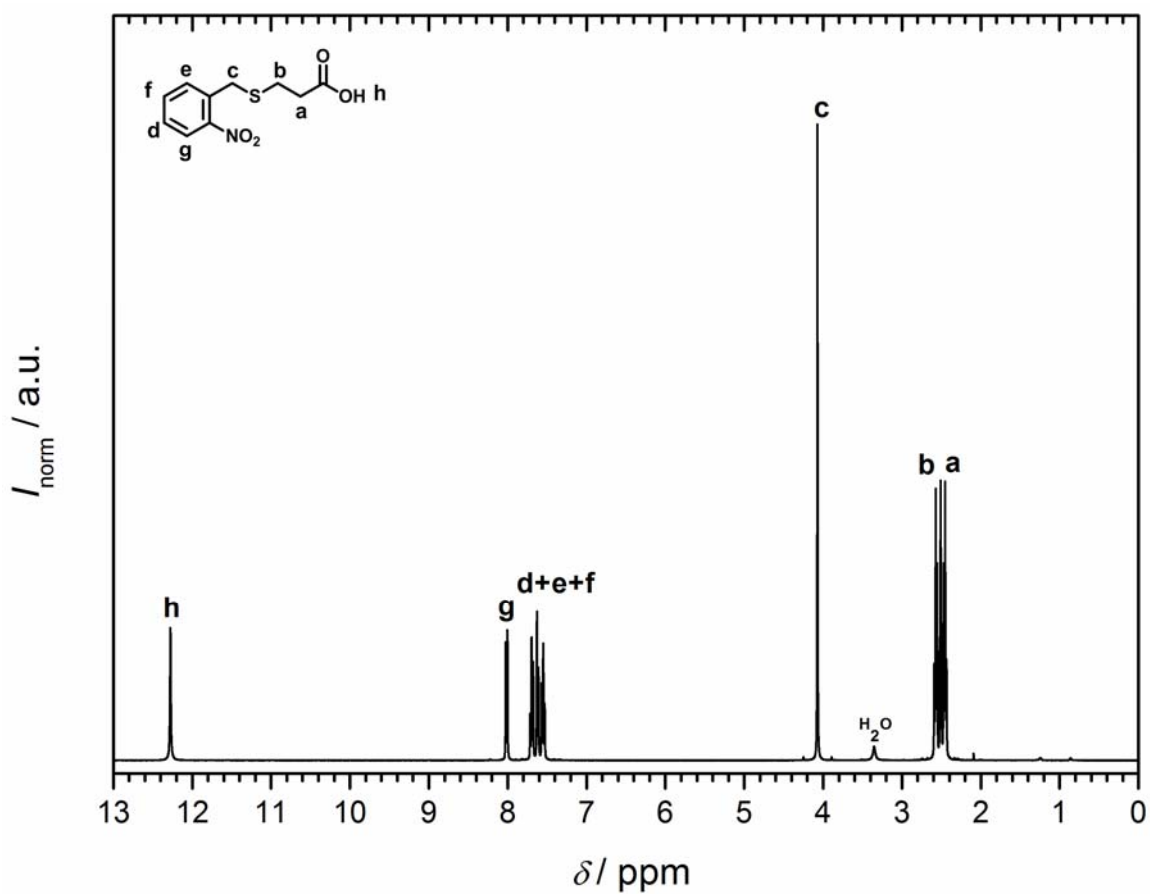
### In Situ photodeprotection and radical photo-initiated thiol-ene reaction

**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 ( $\pm 30$  nm) at a distance of 40–50 mm in a custom-built photoreactor, whose setup has previously been described (see also Fig. S10).<sup>1</sup> The solvent was evaporated after the reaction, THF (2 mL) was added and the slightly yellow solution was analyzed immediately via SEC/ESI-MS.



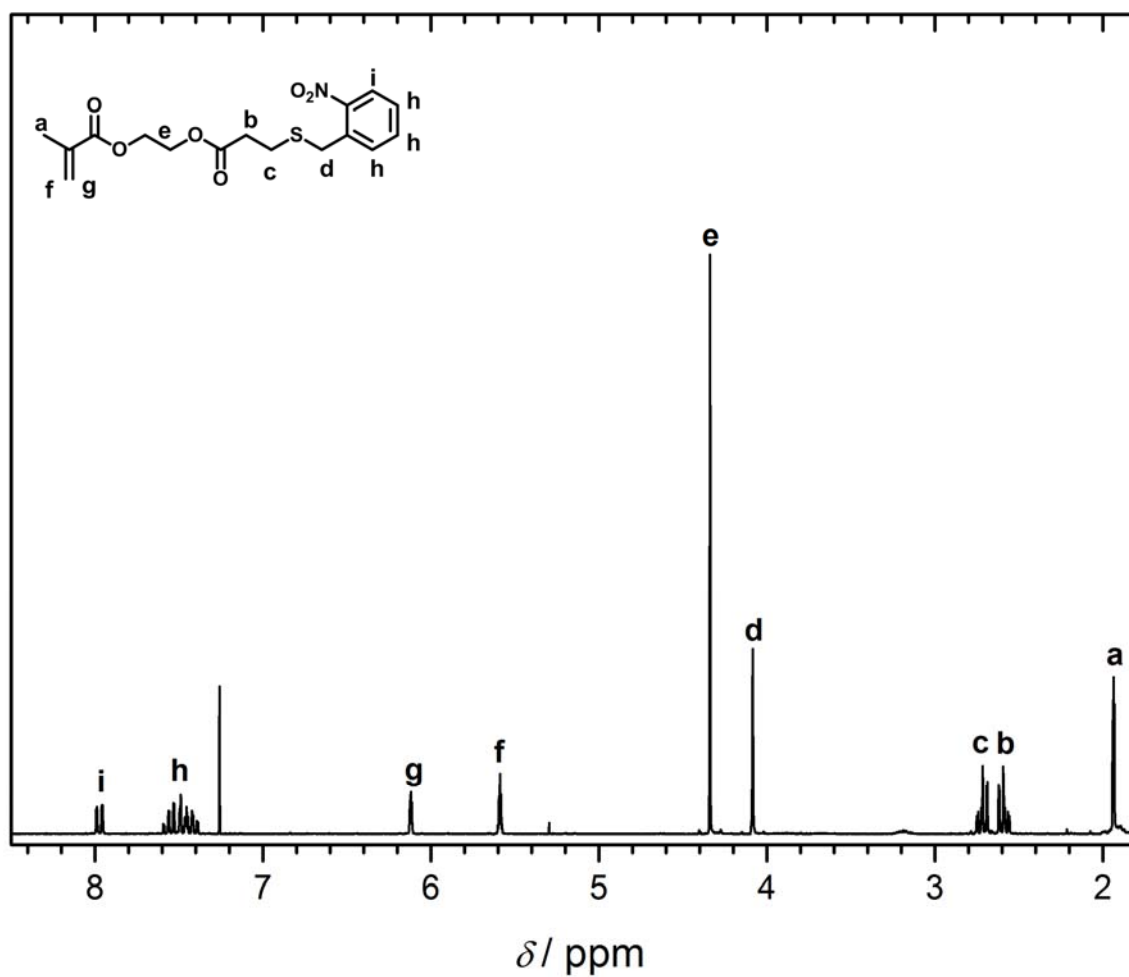
**Figure S2.** SEC/ESI-MS spectra of **2** after UV irradiation in presence of 10 eq. of ethyl vinyl ether. As expected, longer irradiation times decreased **3** and increased **3'**, but major side product formation could not be avoided in any case.

### NMR of 3-((2-nitrobenzyl)thio)propanoic acid 1

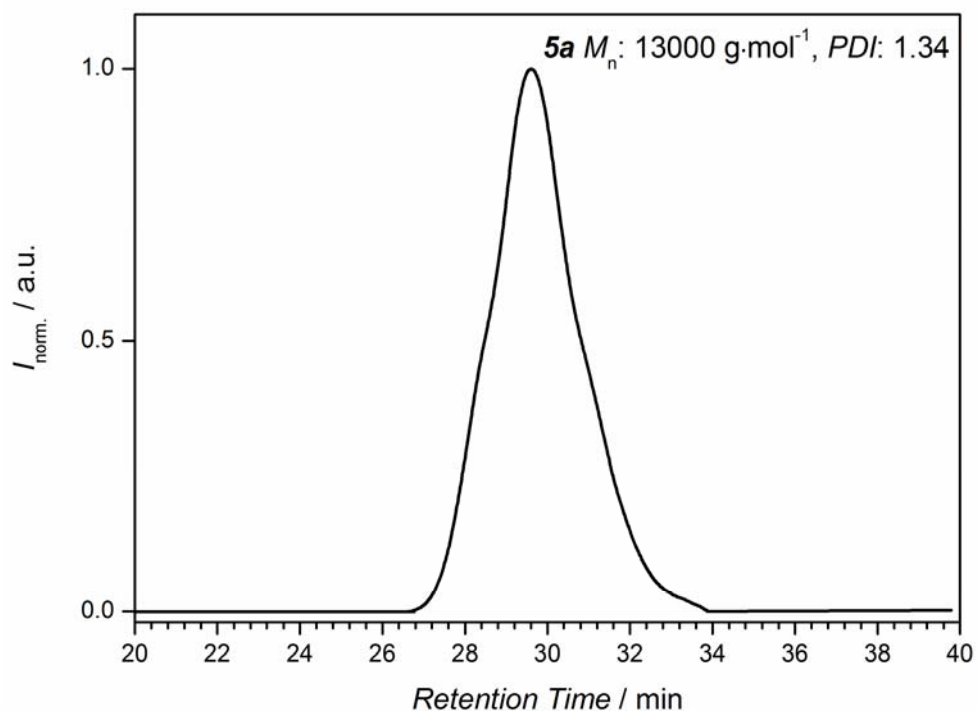


**Figure S3.** <sup>1</sup>H NMR spectrum of 3-((2-nitrobenzyl)thio)propanoic acid in DMSO-d<sup>6</sup>. Note that the singlet at 2.50 ppm is associated with the DMSO solvent and the minor (broad) peak at 3.35 ppm is caused by water.

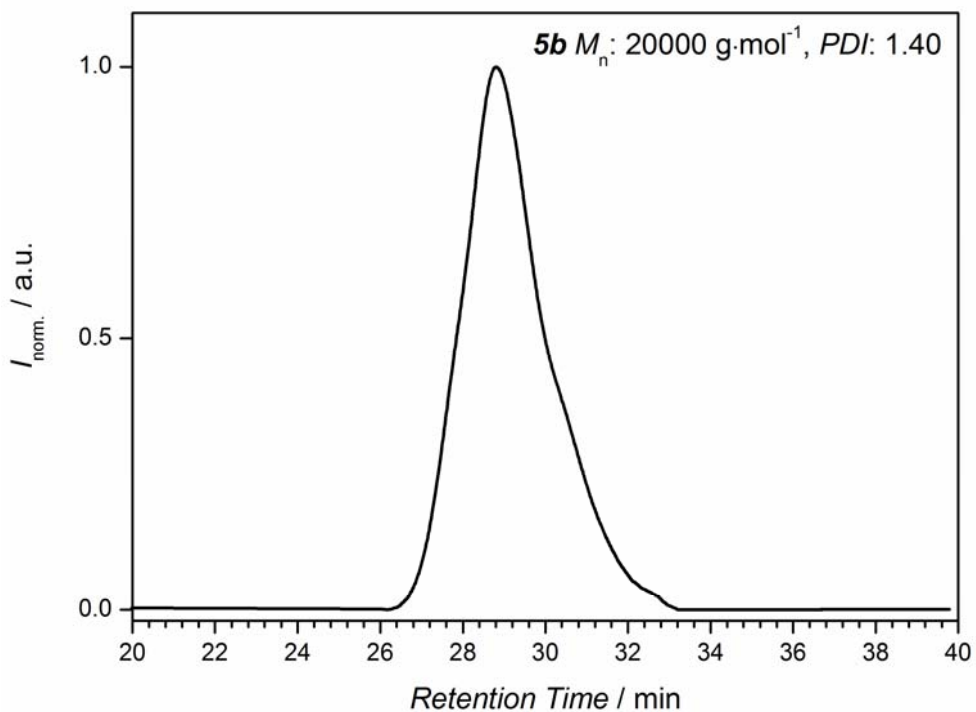
### NMR of photomonomer 2-((3-((2-nitrobenzyl)thio)propanoyl)oxy)ethyl methacrylate **3**



**Figure S4.** <sup>1</sup>H NMR spectrum of 2-((3-((2-nitrobenzyl)thio)propanoyl)oxy)ethyl methacrylate **3** in CDCl<sub>3</sub>.



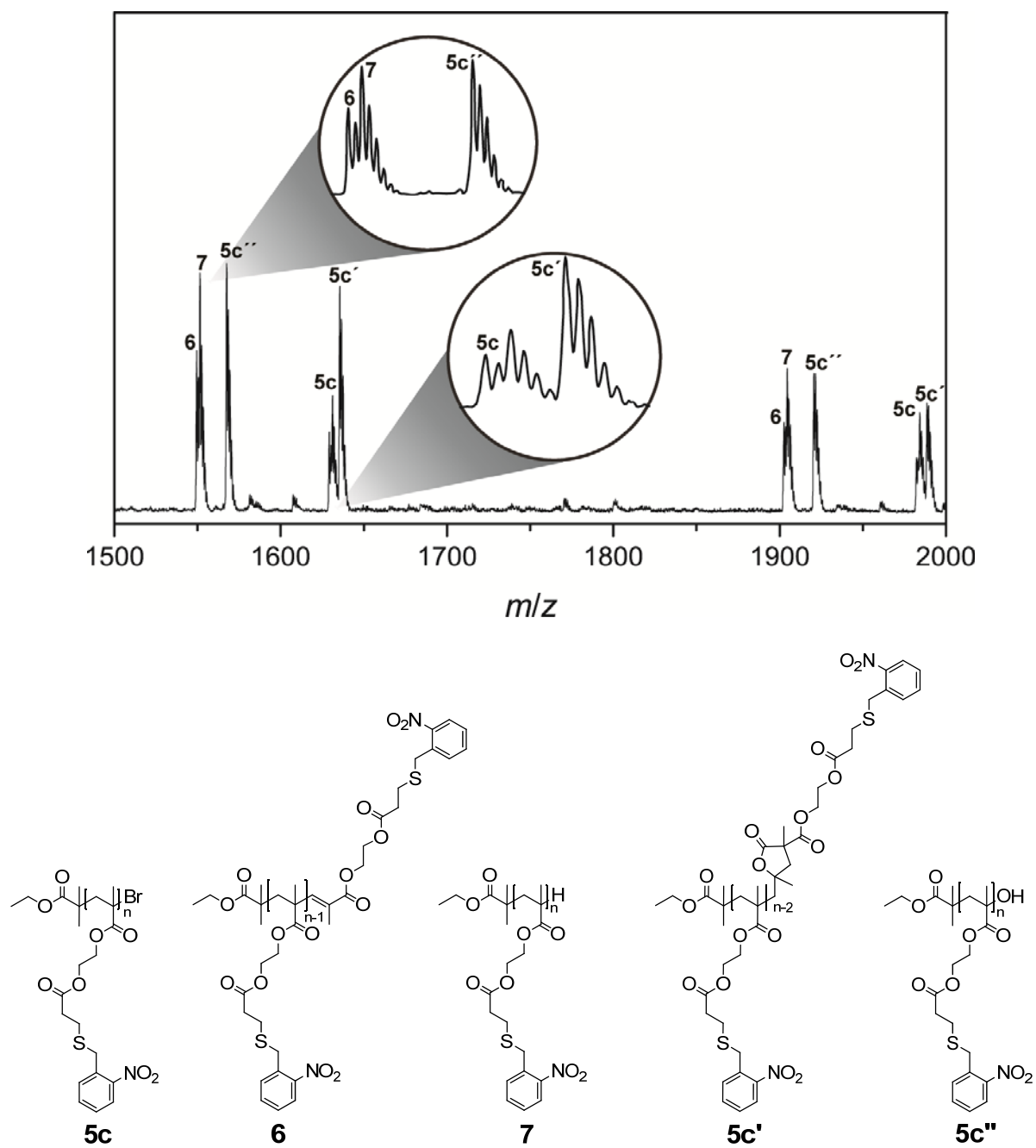
**Figure S5.** SEC trace for the ATRP polymer **5a** of monomer **3** in anisole (33 wt.%) at 80°C for 15 hours. ( $[\mathbf{3}]/[\text{CuBr}]/[\text{EBiB}]/[\text{PMDETA}] = 200:1:1:1$ ).



**Figure S6.** SEC trace for the ATRP polymer **5b** of monomer **3** in anisole (50 wt.%) at 80°C for 8.5 hours. ( $[\mathbf{3}]/[\text{CuBr}]/[\text{EBiB}]/[\text{PMDETA}] = 100:1:1.2:1.2$ ).

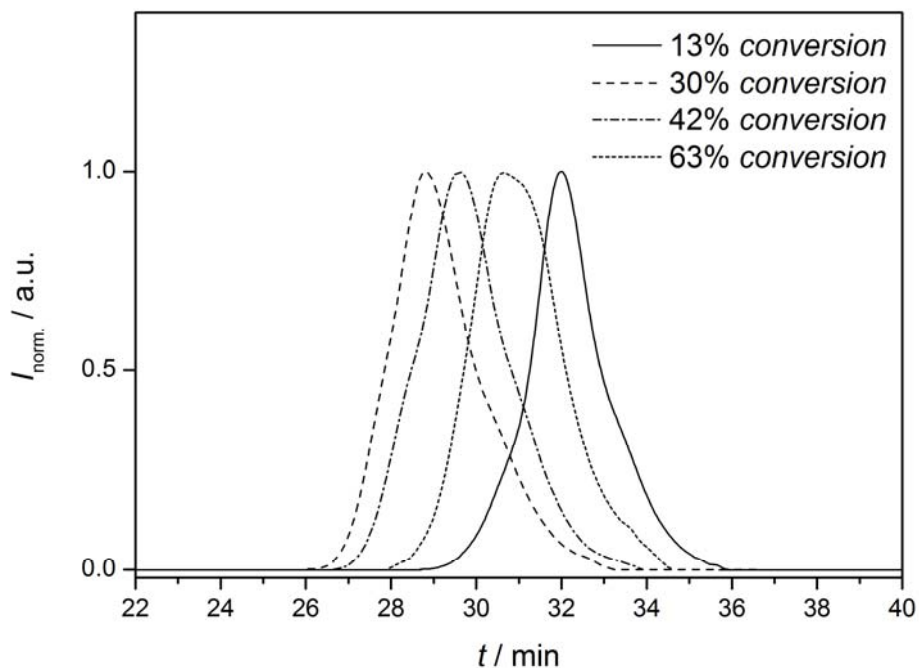
### ESI-MS analysis of Photopolymer **5c**

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.<sup>2,3</sup> 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.

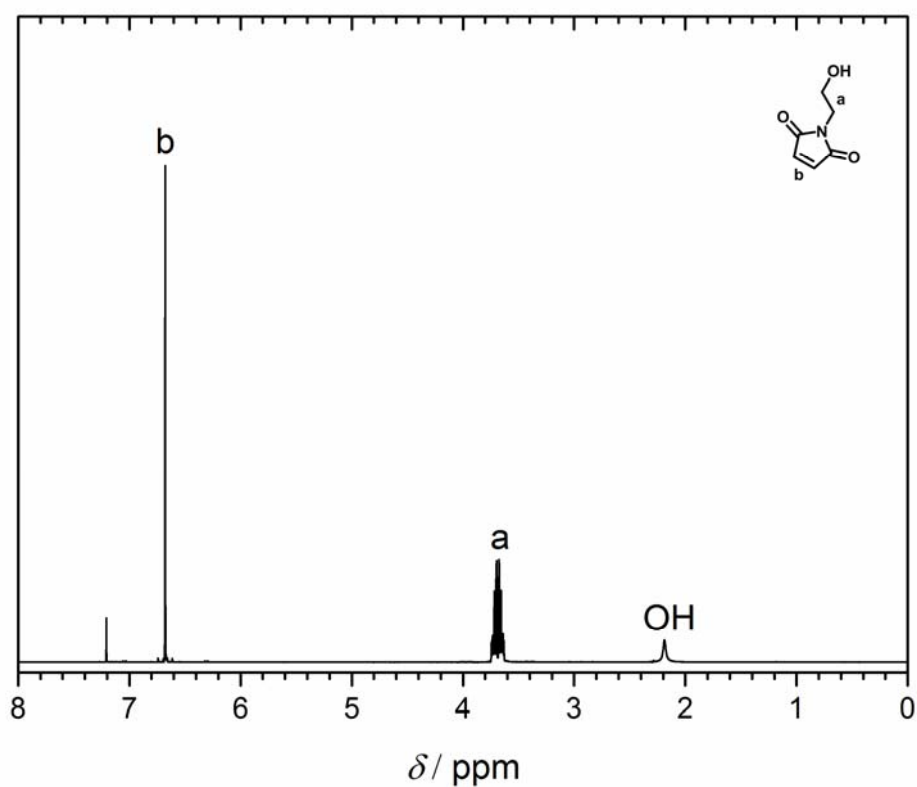


**Figure S7.** SEC/ESI-MS spectra of the polymer **5c** obtained by ATRP in anisole (50 wt.%) at 80 °C ( $[4]/[CuBr]/[EBiB]/[PMDETA] = 100:1:1.2:1.2$ ). Note the isotopic pattern of the bromine terminated species **5c**.





**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.**  $^1\text{H}$  NMR spectrum of **9** in  $\text{CDCl}_3$ . **9** was prepared according to a previously reported procedure.<sup>4</sup>

### 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.

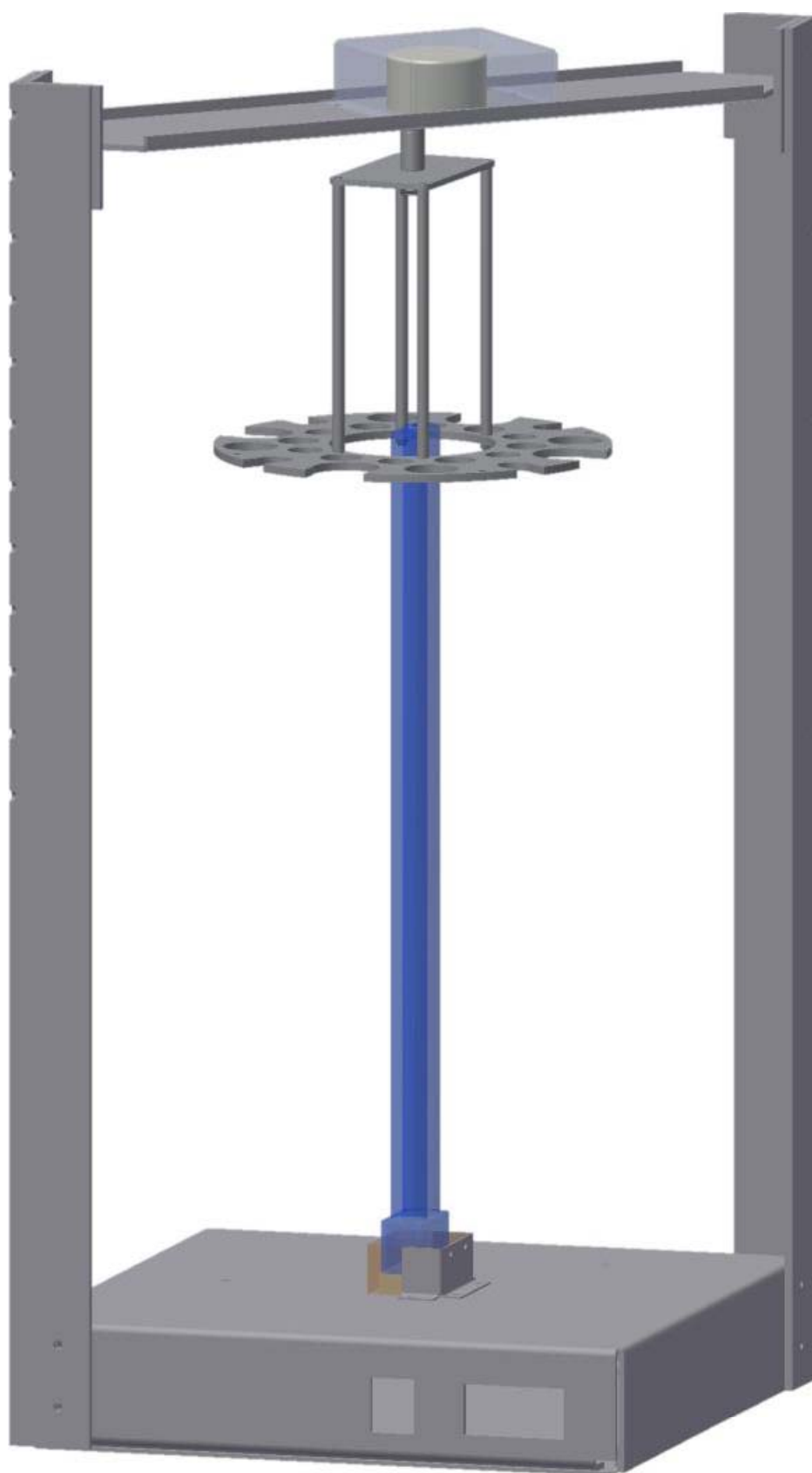
$m/z_{\text{expt}}$	ion assignment	formula	$m/z_{\text{theor}}$	$\Delta m/z$
1818.9	$2_{(n=35)} + \text{Na}^+$	$[\text{C}_{81}\text{H}_{153}\text{NNaO}_{39}\text{S}]^+$	1819.0	0.1
1816.0	$3_{(n=38)} + \text{Na}^+$	$[\text{C}_{80}\text{H}_{160}\text{NaO}_{40}\text{S}]^+$	1816.0	0.0

**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.

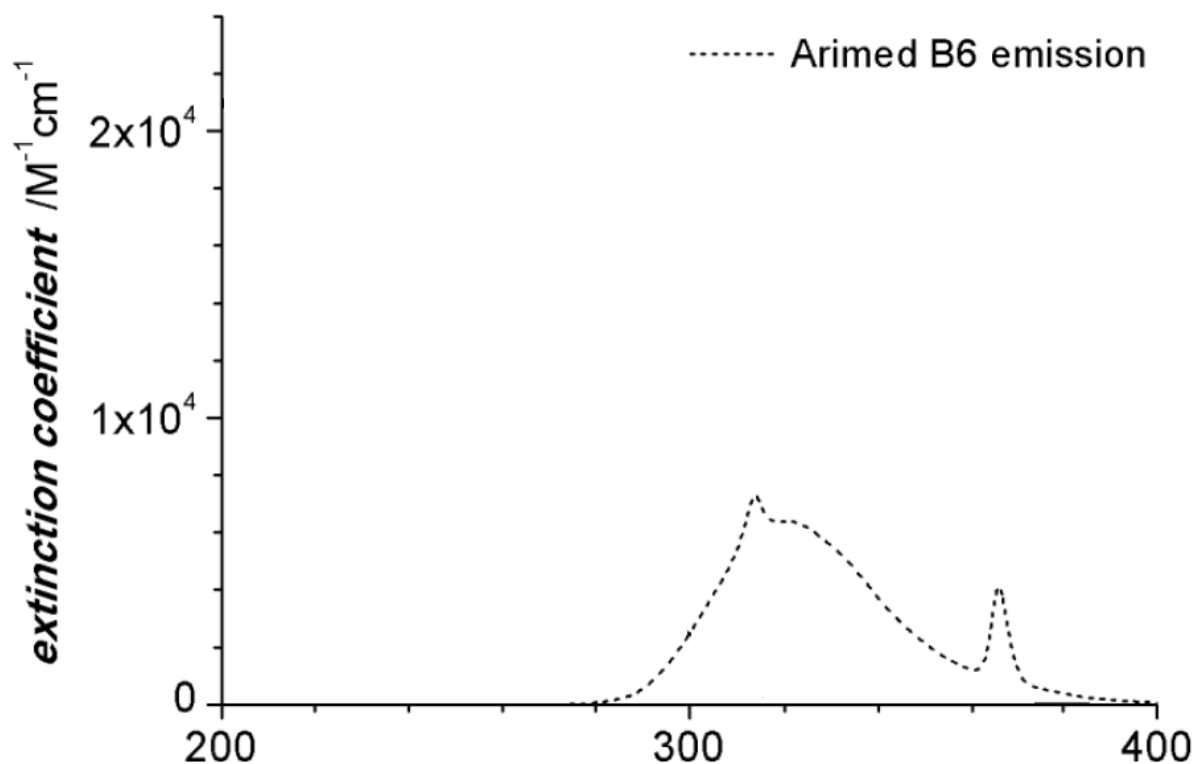
$m/z_{\text{expt}}$	ion assignment	formula	$m/z_{\text{theor}}$	$\Delta m/z$
1549.5	$6_{(n=5)} + \text{Na}^+$	$[\text{C}_{70}\text{H}_{88}\text{N}_4\text{NaO}_{26}\text{S}_4]^+$	1549.4	0.1
1551.5	$7_{(n=4)} + \text{Na}^+$	$[\text{C}_{70}\text{H}_{70}\text{N}_4\text{NaO}_{26}\text{S}_4]^+$	1551.4	0.1
1567.5	$5c''_{(n=4)} + \text{Na}^+$	$[\text{C}_{70}\text{H}_{88}\text{N}_4\text{NaO}_{27}\text{S}_4]^+$	1567.4	0.1
1629.3	$5c_{(n=4)} + \text{Na}^+$	$[\text{C}_{70}\text{H}_{87}\text{BrN}_4\text{NaO}_{26}\text{S}_4]^+$	1629.4	0.1
1635.5	$5c'_{(n=5)} + \text{Na}^+$	$[\text{C}_{74}\text{H}_{92}\text{N}_4\text{NaO}_{28}\text{S}_4]^+$	1635.5	0.0

**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.

$m/z_{\text{expt}}$	ion assignment	formula	$m/z_{\text{theor}}$	$\Delta m/z$
1772.0	$3_{(n=37)} + \text{Na}^+$	$[\text{C}_{78}\text{H}_{156}\text{NaO}_{39}\text{S}]^+$	1772.1	0.1
1756.0	$3'_{(n=35)} + \text{Na}^+$	$[\text{C}_{78}\text{H}_{156}\text{NaO}_{38}\text{S}]^+$	1756.1	0.0



**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,  $\lambda_{max} = 320$  nm).

## References

- (1) Gruending, T.; Oehlenschlaeger, K. K.; Frick, E.; Glassner, M.; Schmid, C.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2011**, *32*, 807.
- (2) Borman, C. D.; Jackson, A. T.; Bunn, A.; Cutter, A. L.; Irvine, D. J. *Polymer* **2000**, *41*, 6015.
- (3) Jackson, A. T.; Bunn, A.; Priestnall, I. M.; Borman, C. D.; Irvine, D. J. *Polymer* **2006**, *47*, 1044.
- (4) Gramlich, W. M.; Robertson, M. L.; Hillmyer, M. A. *Macromolecules* **2010**, *43*, 2313.