

## Supporting Information

### Double modular modification of thiolactone-containing polymers: towards polythiols and derived structures

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#### LC-MS analysis of the St-TLa monomer

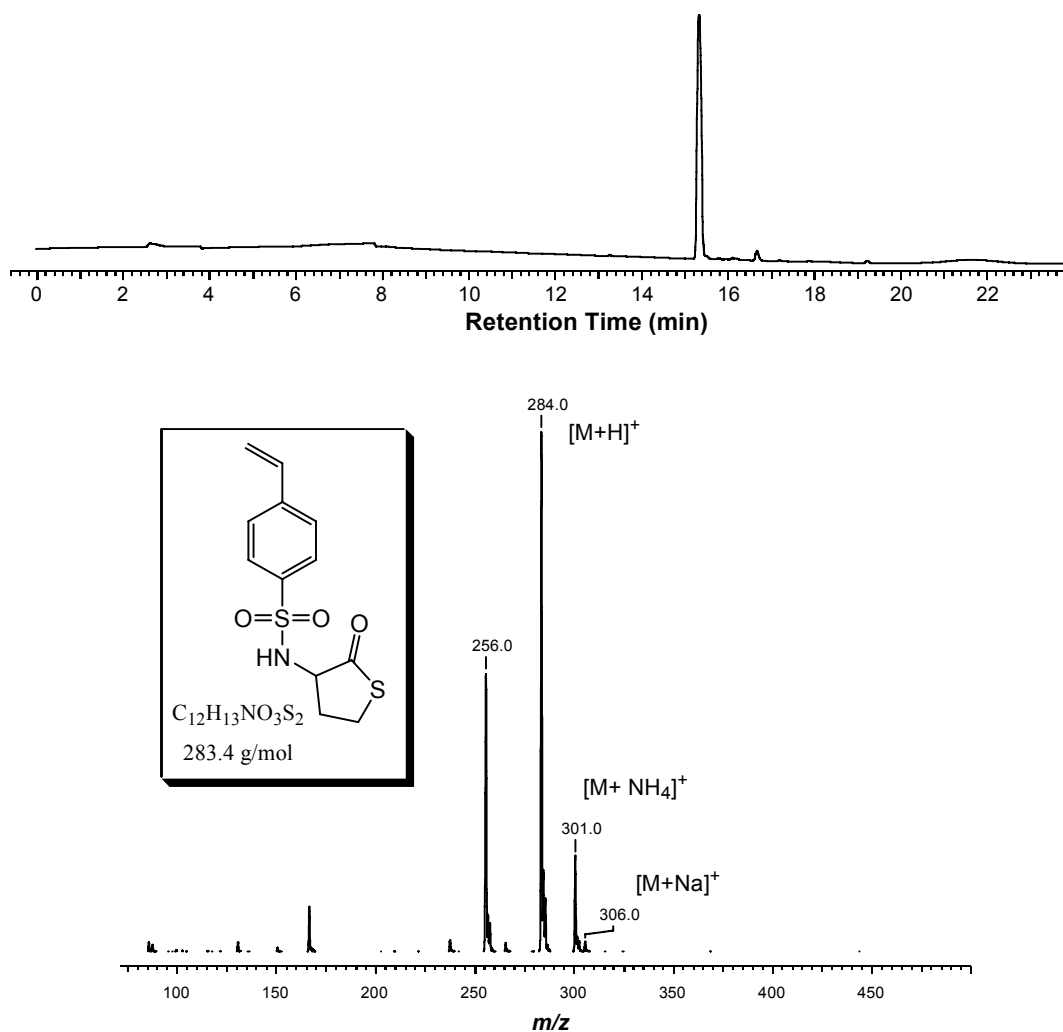
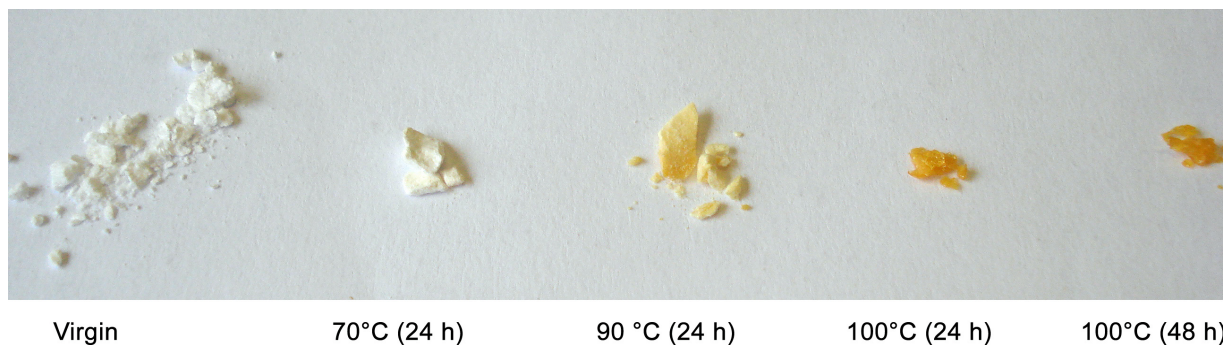


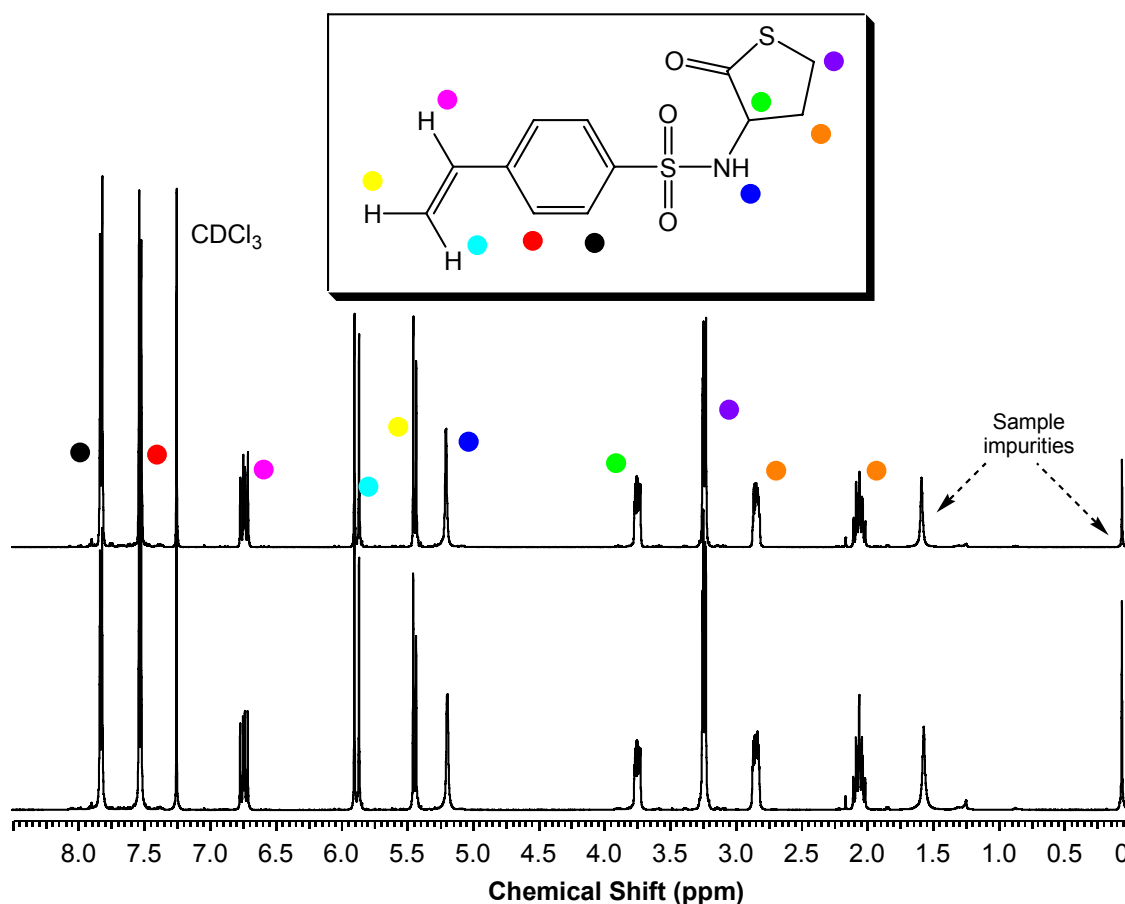
Figure S 1 - LC-MS analysis of the purified St-TLa monomer: LC trace (top) and ESI-MS spectrum with assignment of relevant peaks (bottom).

### Stability of the St-TLa monomer

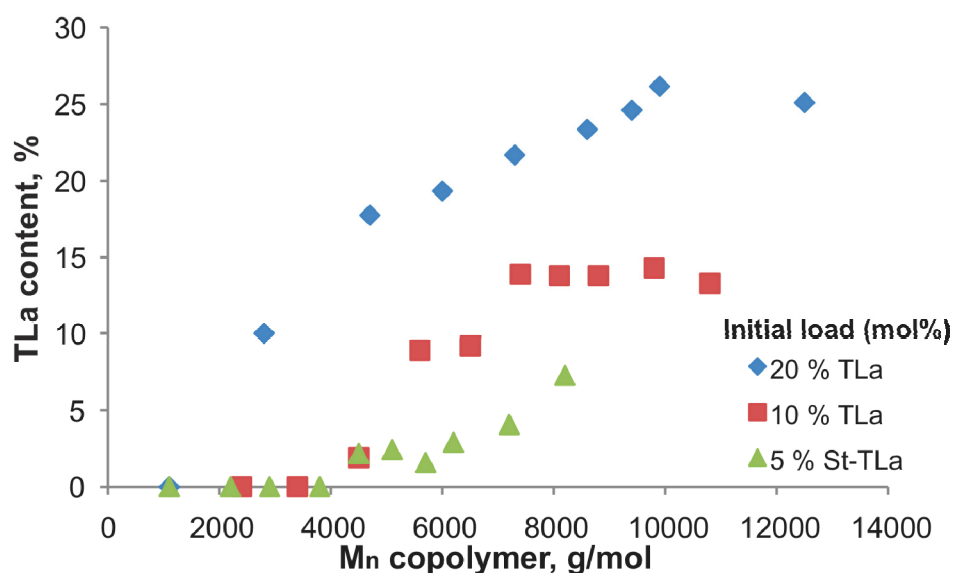
A neat solid sample of the St-TLa monomer was heated in an oven. The details are mentioned below the sample pictures (Figure S 2). The virgin and the “70 °C” sample were analyzed with  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ , Figure S 3). After heating at 90 °C or 100 °C, the samples were colored and insoluble in  $\text{CDCl}_3$ , demonstrating degradation.



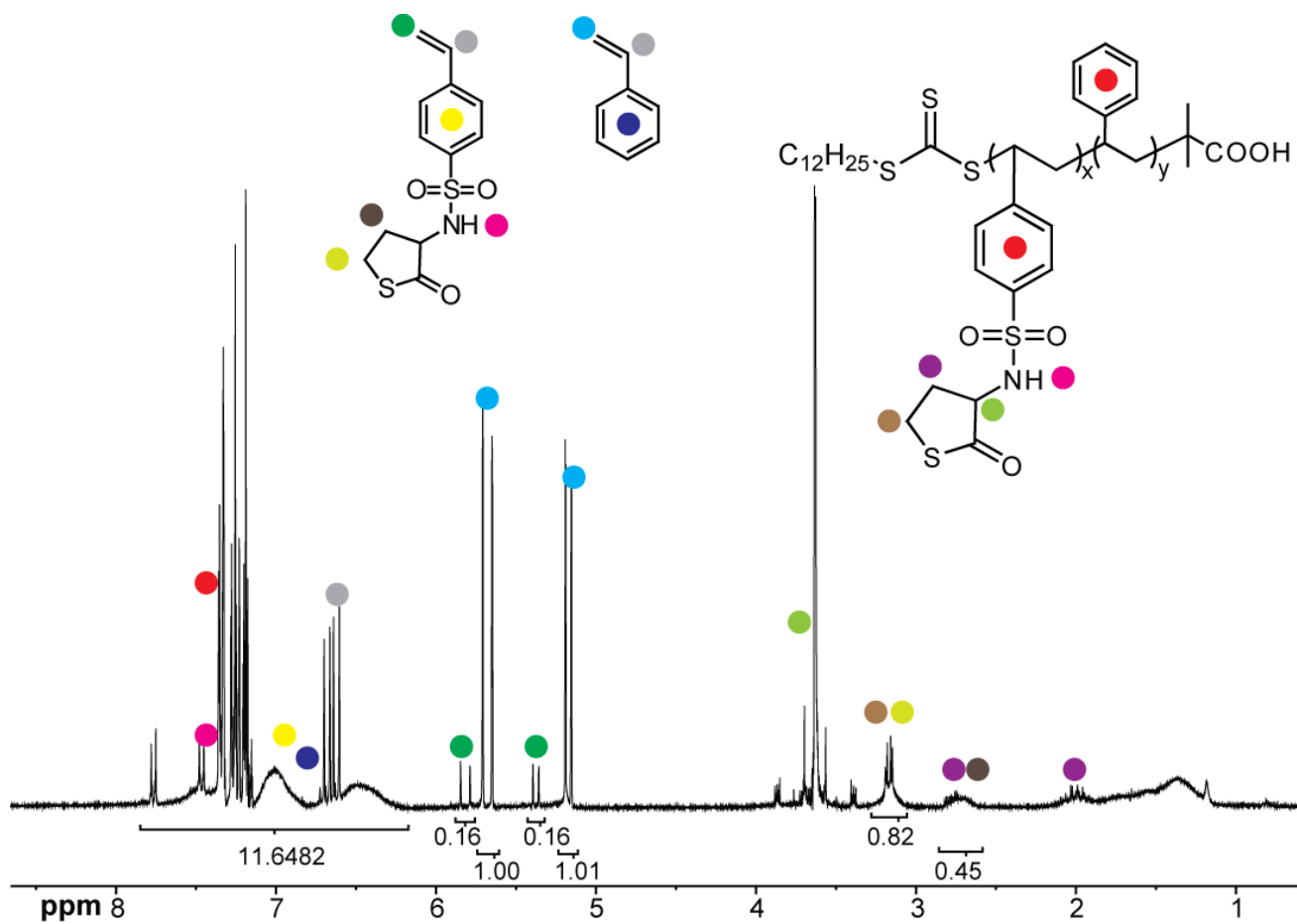
**Figure S 2** – Heat treatment of St-TLa monomer to demonstrate (thermal) stability. A neat solid sample of the St-TLa monomer was heated in an oven. Times and temperatures are mentioned below the samples.



**Figure S 3** -  $^1\text{H-NMR}$  analysis (500 MHz,  $\text{CDCl}_3$ ) of a virgin sample of St TLa monomer with peak assignment (top) and of a sample after heat treatment (70 °C for 24 h) in an oven.



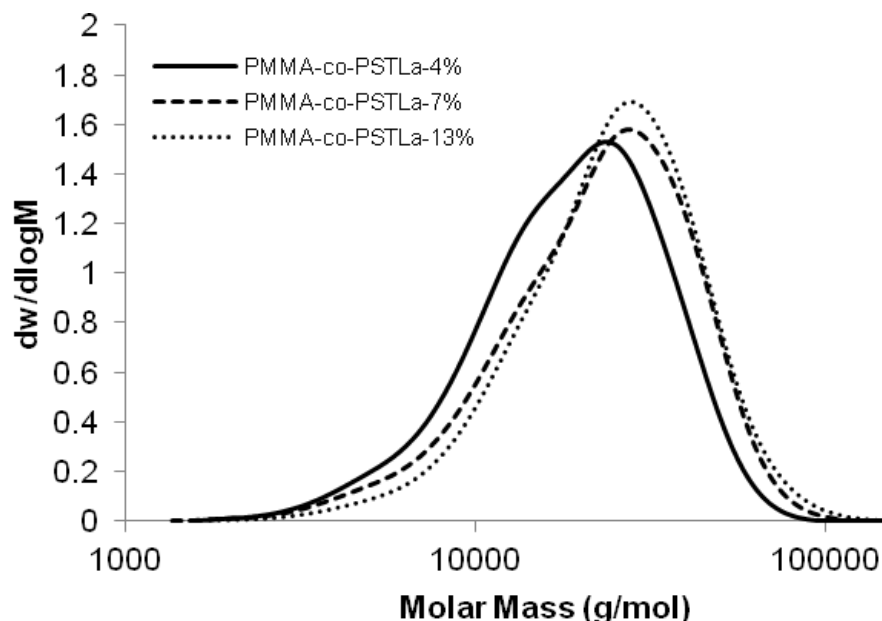
**Figure S 4** – Thiolactone content versus  $M_n$  of copolymer for all initial loads of St-TLa e.g. 20, 10 and 5 mol %



**Figure S 5** -  $^1\text{H-NMR}$  analysis (300 MHz,  $\text{CDCl}_3$ ) of an aliquot of copolymerization of St and St-TLa, taken at 12 h of polymerization (Table 1, Entry 4). The indicated assigned signal values were used for individual monomer conversion.

### Monomer conversion of St and St-TLa

Off-line  $^1\text{H-NMR}$  was employed to evaluate the kinetics of the RAFT copolymerization of styrene and St-TLa. In the case of St-TLa, the peak integrals ratio of the monomer vinylic protons (5.82 and 5.38 ppm) to the thiolactone ring corresponding protons (3.17 and 2.72 ppm) was used to calculate the St-TLa monomer conversion. The styrene conversion was calculated based on the signal integrals of the styrenic double bond protons (5.18 and 5.68 ppm), benzene ring protons (6.20 – 7.80 ppm) and St-TLa corresponding protons (e.g. amine, benzene ring), as they overlap with styrene related protons.



**Figure S 6** - Overlay of the molar mass distribution plots for PMMA-*co*-PS-TLa-4% (dotted line), PMMA-*co*-PS-TLa-7% (dashed line) and PMMA-*co*-PS-TLa S-TLa-13% (solid line)

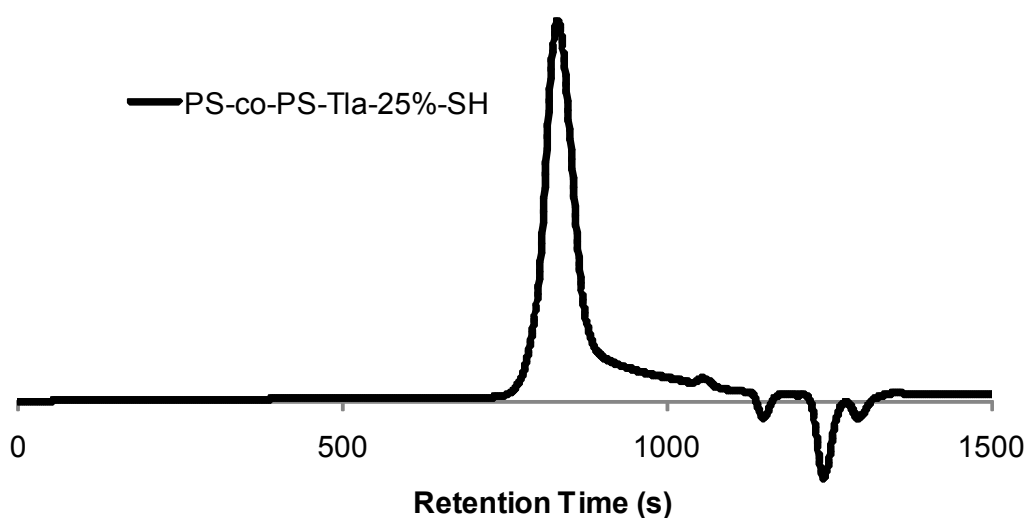
### RAFT copolymerization of methyl methacrylate and styrene-thiolactone (St-TLa)

St-TLa (0.68 g, 2.4 mmol), methyl methacrylate (2 ml, 18.6 mmol), 4-cyanopentanoic acid dithiobenzoate (0.03 g,  $1.1 \times 10^{-4}$  mol), AIBN (1.8 mg,  $1.1 \times 10^{-5}$  mol) as thermal initiator ( $[\text{M}_{\text{MMA}+\text{St-TLa}}]_0/[\text{CTA}]_0/[\text{AIBN}]_0 = 200/1/0.1$ ) and 1,4-dioxane as solvent were introduced in a Schlenk tube, which was degassed by three freeze-pump-thaw cycles, backfilled with nitrogen, sealed, and heated in an oil bath at 65 °C. The final crude solution was precipitated in 10-fold excess of cold methanol, filtered, and dried under reduced pressure overnight, yielding the copolymer of methyl methacrylate and St-TLa (PMMA-*co*-PS TLa-*x*%), a pink fine powder.

**Table S 1** - Reaction conditions and results of the copolymerization of MMA and St-TLa.

Entry	$[M]_0/[CTA]_0/[AIBN]_0$	St-TLa/MMA Initial molar ratio	Solvent	Time, h	$^aM_n^{exp}$ , g.mol <sup>-1</sup>	$^aPDI$	St-TLa initial load, mol %	$^b$ St-TLa incorporated, mol %
1	200/1/0.1	0/100	Dio <sup>c</sup> ,50 vol%	8	12000	1.05	0	0
2	200/1/0.1	10/90	Dio,50 vol%	8	16000	1.28	10	ca. 20

<sup>a</sup> SEC, THF as eluent, PMMA standards; <sup>b</sup> estimated from the initial mol% load and conversion via NMR; <sup>c</sup> Dio: 1,4-dioxane

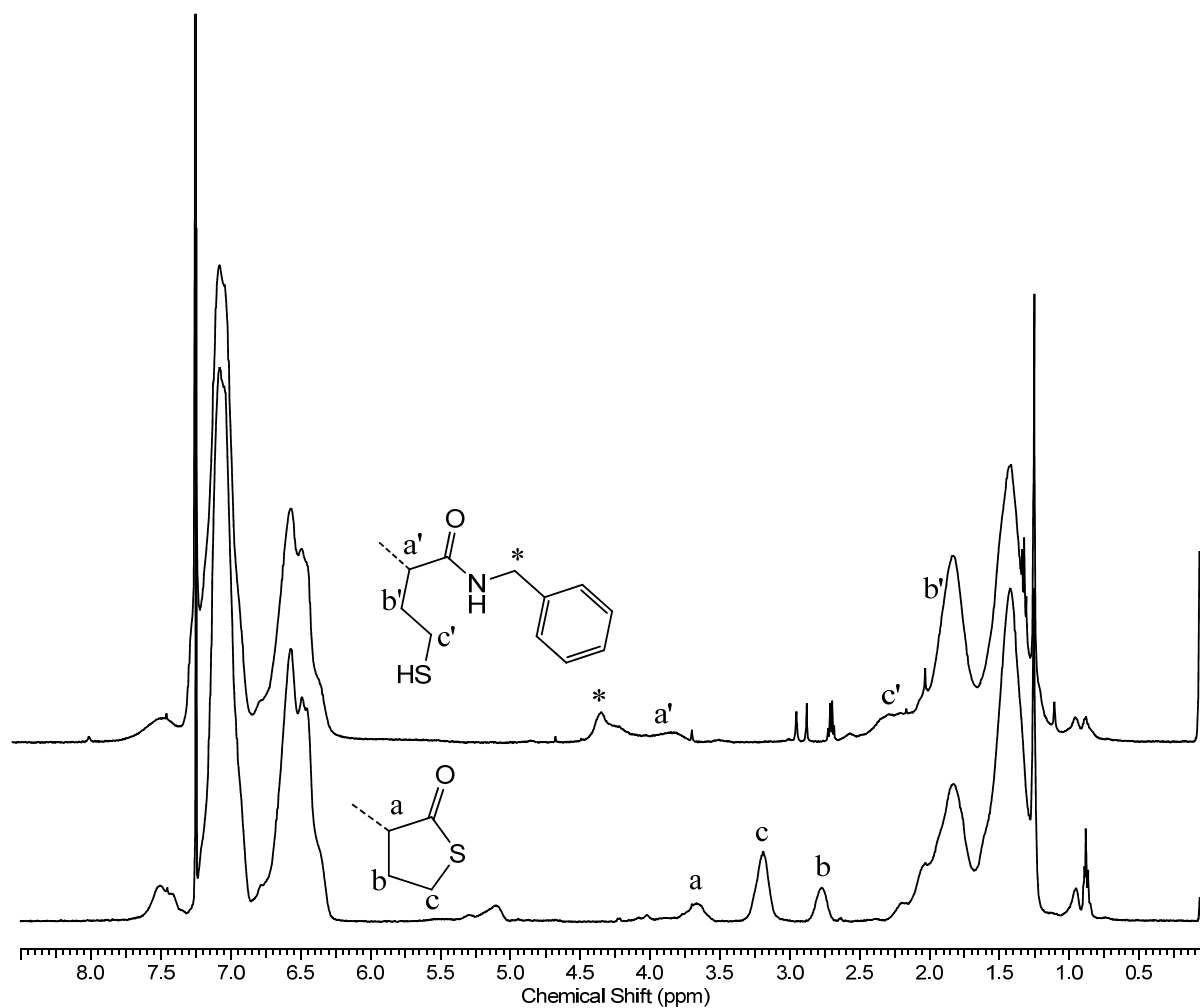


**Figure S 7** – SEC trace of PS-co-PS-TLa-25%-SH reveals tailing at the low molecular weight range (beyond the exclusion limit), compromising integration of the peak and thus adequate determination of the molar mass values.

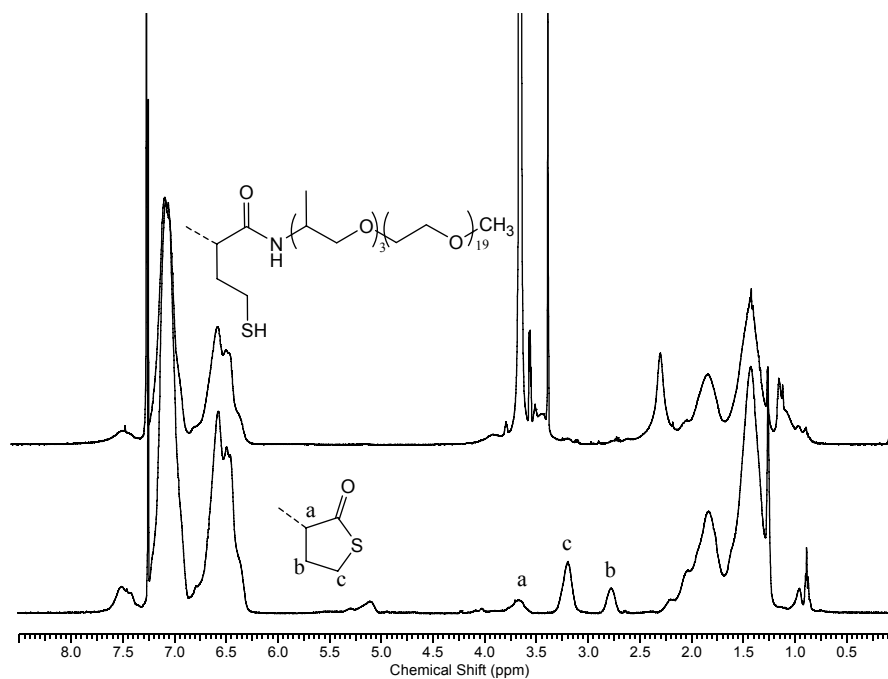
**Table S 2** - SEC results obtained after modification of different batches of PS-co-PS-TLa, using propylamine as nucleophile

Entry	$M_n$ (g.mol <sup>-1</sup> )	$M_w$ (g.mol <sup>-1</sup> )	PDI
PS-co-PS-TLa-9%	7600	8500	1.11
PS-SH-4	7700	8700	1.12
PS-co-PS-TLa-13%	11300	12600	1.12
PS-SH-5 <sup>a</sup>	10800	12200	1.13
PS-co-PS-TLa-25%	12000	14200	1.19
PS-SH-6 <sup>a</sup>	11200	12600	1.12

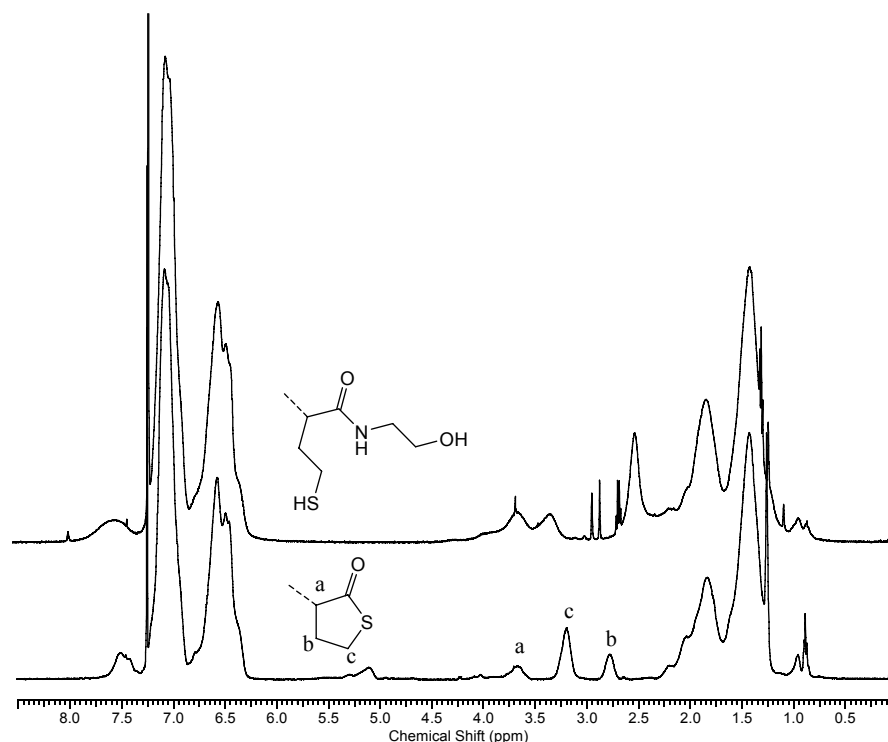
<sup>a</sup> Tailing is observed and values obtained for  $M_n$ ,  $M_w$  and PDI are thus not accurate.



**Figure S 8** - Overlay of the NMR spectra (300 MHz,  $\text{CDCl}_3$ ) of PS-co-PS-TLa-9% (bottom) and PS-SH-1 (benzylamine) (top). Only thiolactone unit as side chain functional handle and its derivative are shown.

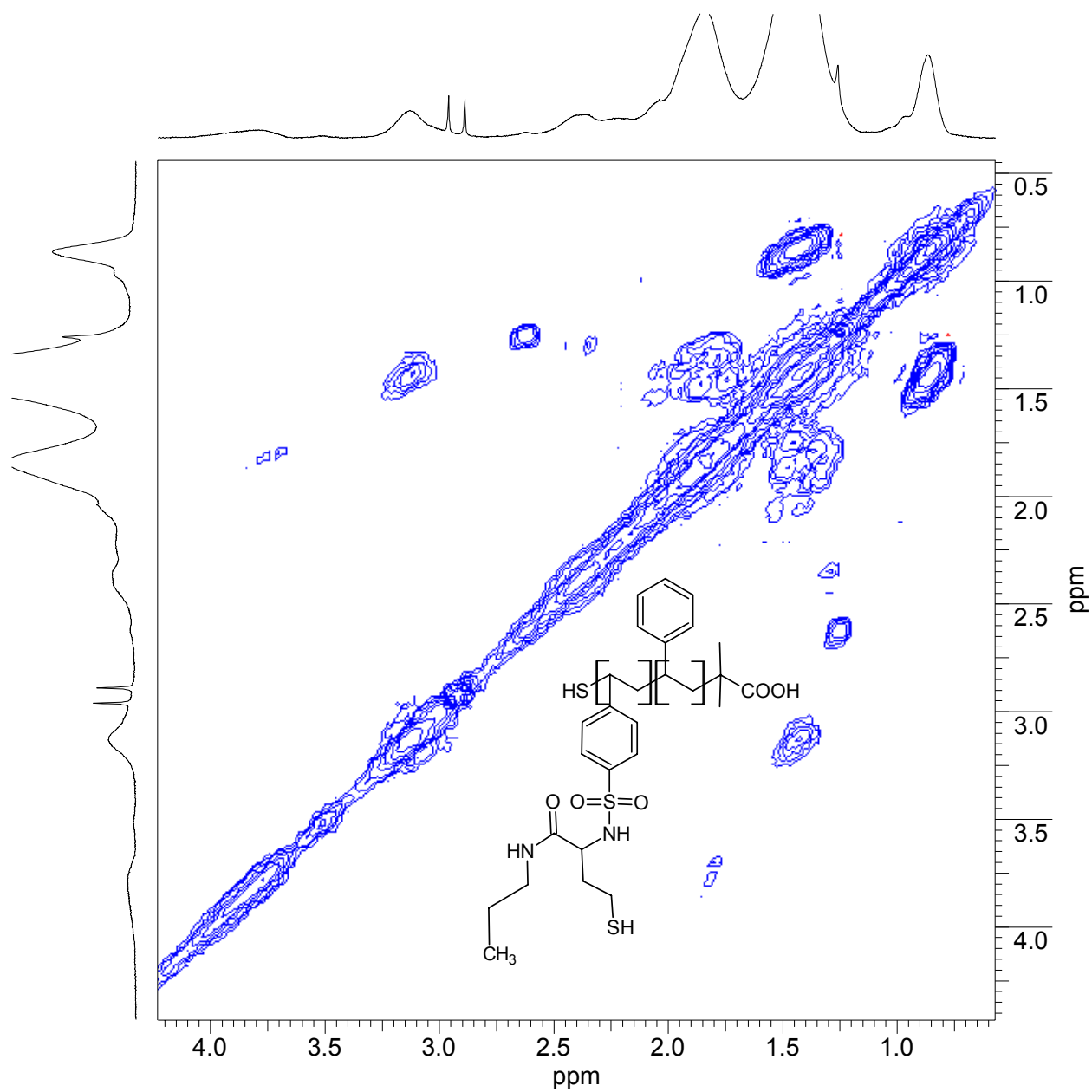


**Figure S 9** - Overlay of NMR spectra (500 MHz,  $\text{CDCl}_3$ ) of PS-co-PS-TLa-9% (bottom) and PS-SH-2 (Jeffamine M-1000) (top). Only thiolactone unit as side chain functional handle and its derivative are shown.



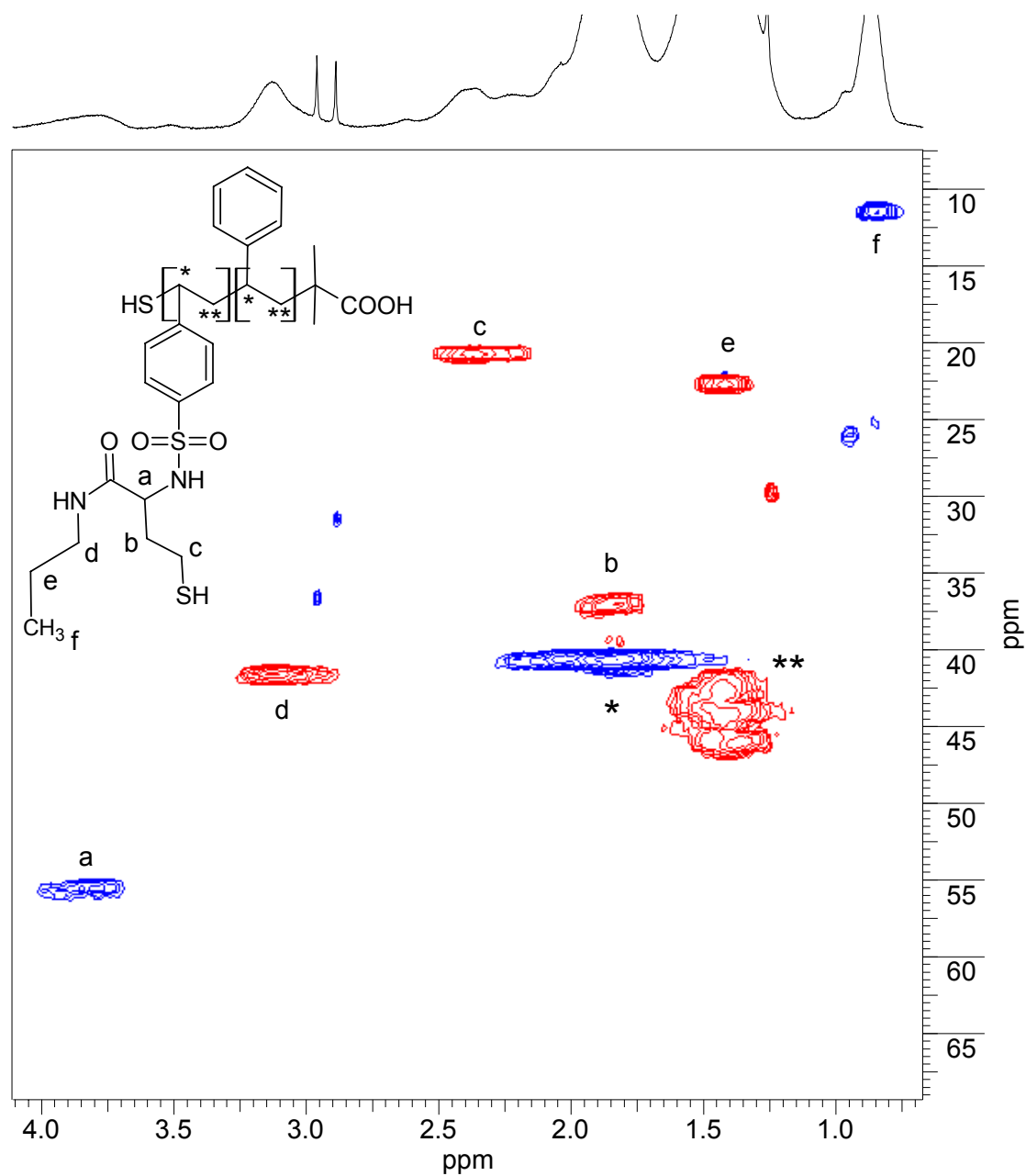
**Figure S 10** - Overlay of NMR spectra (500 MHz,  $\text{CDCl}_3$ ) of PS-co-PS-TLa-9% (bottom) and PS-SH-3 (ethanolamine) (top). Only thiolactone unit as side chain functional handle and its derivative are shown.

From Figure S 8, S 9 and S 10, it is seen that the signals (a,b,c) allocated to the thiolactone, clearly shift to other ppm values after reaction with the amine (benzylamine, Jeffamine M-1000 and ethanolamine) as indicated. This implies a complete consumption of thiolactone moieties in all cases.

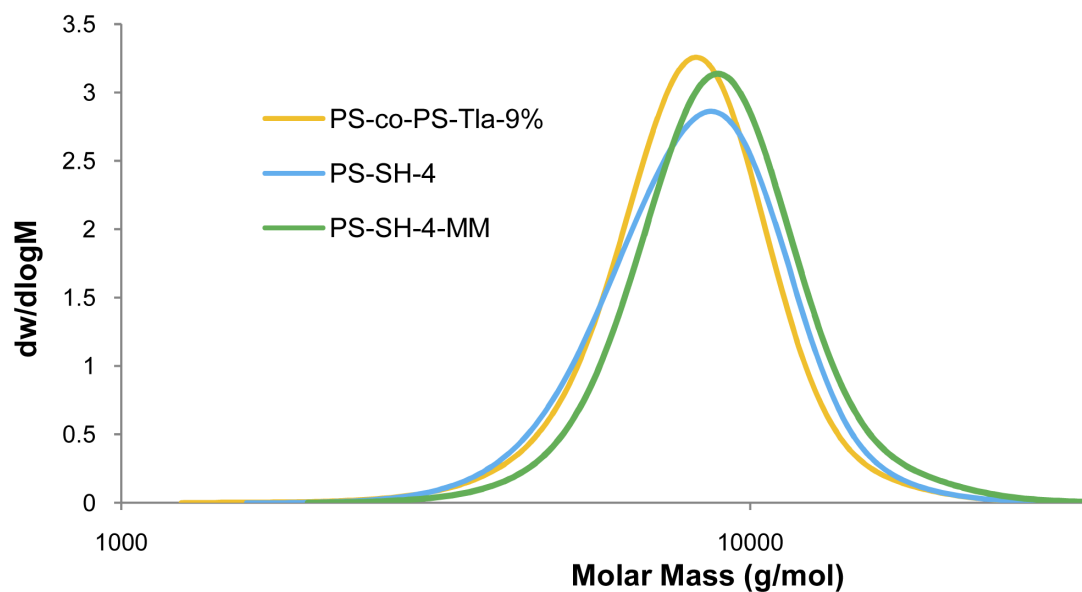


**Figure S 11** – Detail of the COSY spectrum (500 MHz, CDCl<sub>3</sub>) of PS-co-PS-co-TLA-9%-SH (after ring-opening with propylamine)

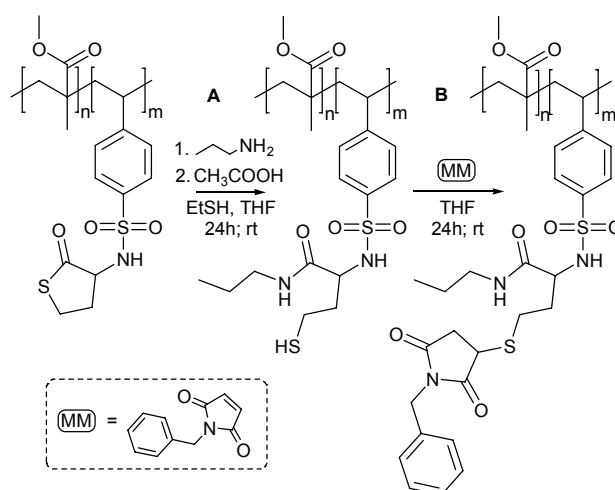




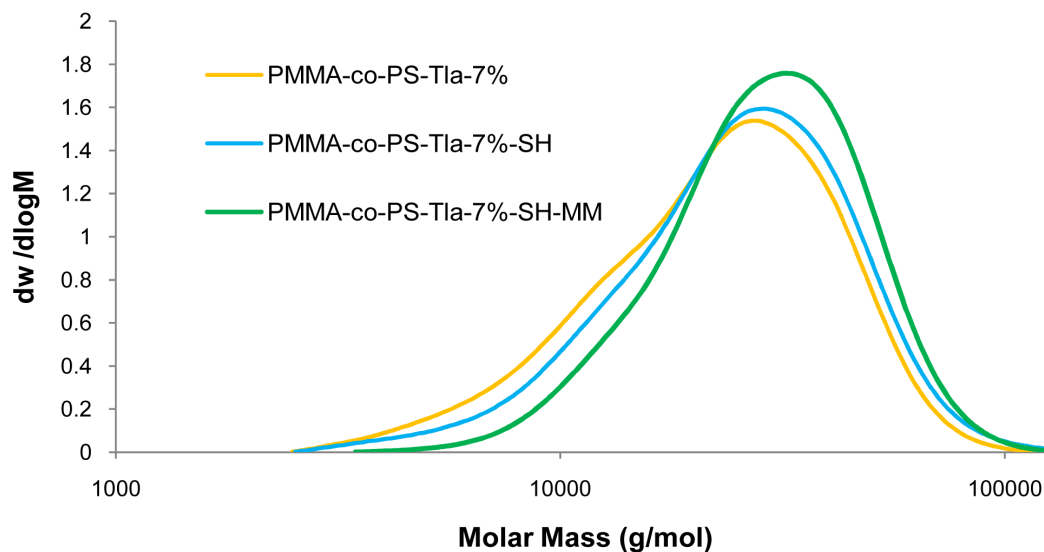
**Figure S 12** – Detail of the HSQC spectrum (500 MHz,  $\text{CDCl}_3$ ) of PS-co-PS-TLa-9%-SH (ring-opening with propylamine) with peak assignment of side chain (a - f) and backbone (\* and \*\*) non-aromatic atoms. Cross-peaks in red represent methylene ( $\text{CH}_2$ ) units, while the blue ones represent methine (CH) or methyl ( $\text{CH}_3$ ) units.



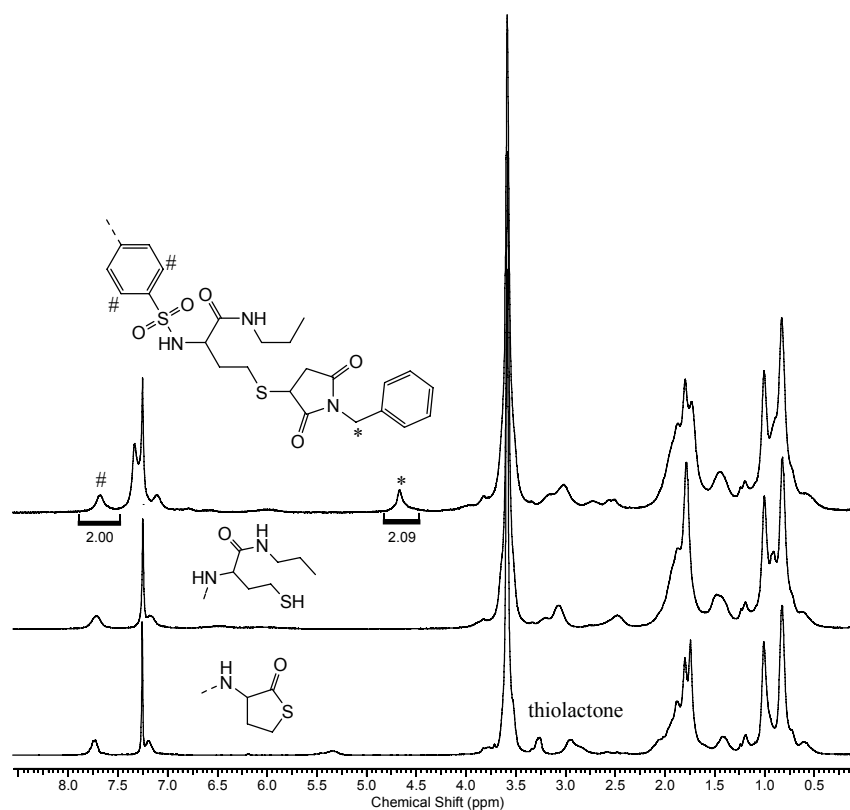
**Figure S 13** - Overlay of the molecular weight distribution plots of PS-co-PS-TLa-9%, PS-SH-4 and PS-SH-4-MM (SEC). With every modification step, an increase in molecular weight is observed, while PDI's remain low.



**Scheme S 1** - Double modification of PMMA-co-PS-TLa. **A**. Nucleophilic ring-opening of thiolactone groups on the polymer backbone. **B**. Subsequent thiol-ene modification with *N*-benzylmaleimide



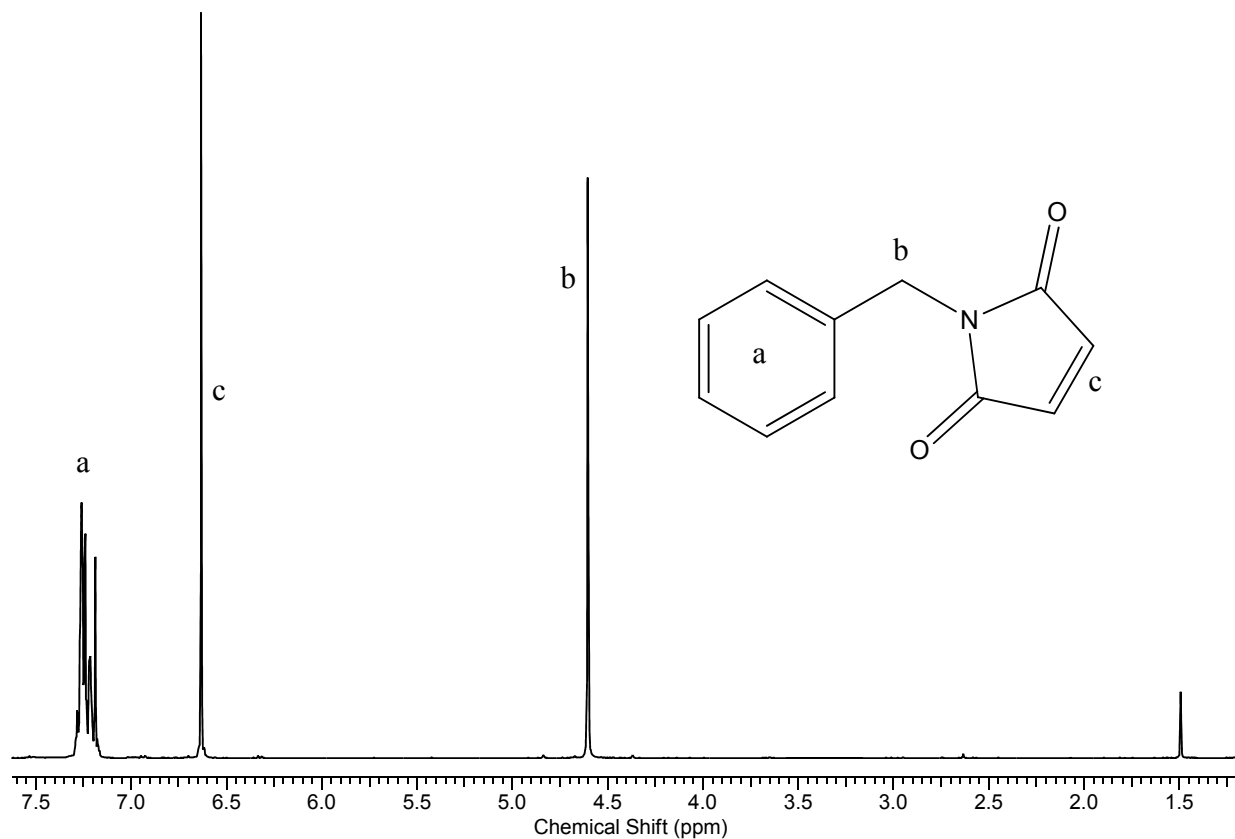
**Figure S 14** - Overlay of SEC chromatograms of PMMA-co-PS-TLa-7% before modification, after modification with propylamine and after consecutive modification with *N*-benzylmaleimide.



**Figure S 15** - Overlay of  $^1\text{H-NMR}$  spectra (300 MHz,  $\text{CDCl}_3$ ) of PMMA-co-PS-TLa-7% (bottom), PMMA-co-PS-TLa-7%-SH (middle) and PMMA-co-PS-TLa-7%-SH-MM (top). Only thiolactone unit as side chain functional handle and its derivatives are shown.

From Figure S 15, it is clear that after reaction with propylamine, the signals assigned to the thiolactone moieties disappear. After reaction with benzylmaleimide, a signal from the benzylic protons becomes visible.

From integration it was concluded that the reaction was near quantitative. The integration was performed relative to the aromatic protons at 7.75 ppm (originating from St-TLa). The excess of benzylmaleimide is removed by precipitation, since it is soluble in MeOH. The benzylic protons at 4.5 ppm are originating from maleimide attached to the polymer backbone: this is concluded by the absence of double bond protons (6.75 ppm) in the spectrum (Figure S 15). In Figure S 16, the  $^1\text{H-NMR}$  spectrum of benzylmaleimide is depicted as reference.



**Figure S 16** -  $^1\text{H-NMR}$  spectrum (300 MHz,  $\text{CDCl}_3$ ) of benzylmaleimide.