Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

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

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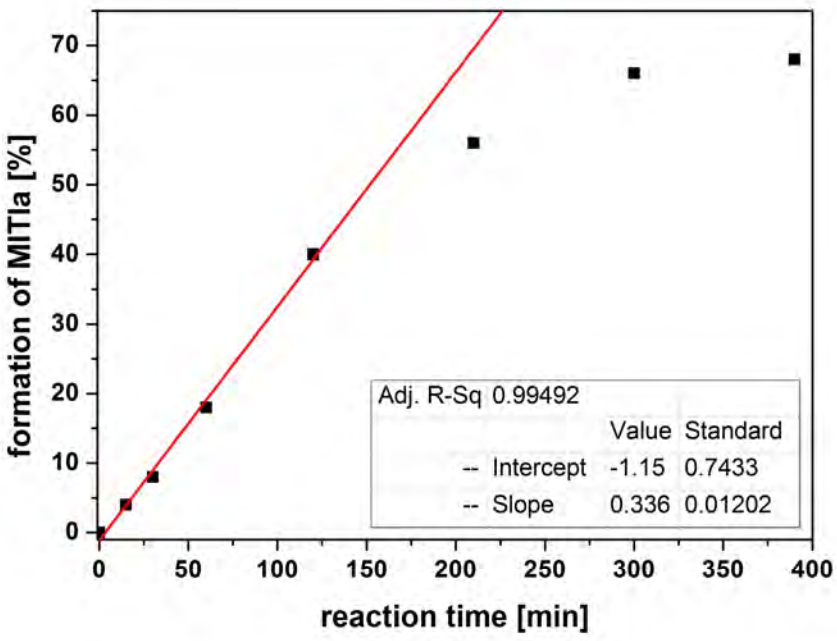

Figure S1: Kinetic investigation of the synthesis of MITla comparing the newly formed thiolactone signal at 4.95 ppm (DMSO-d_6) to trioxane as internal standard at 70 °C.

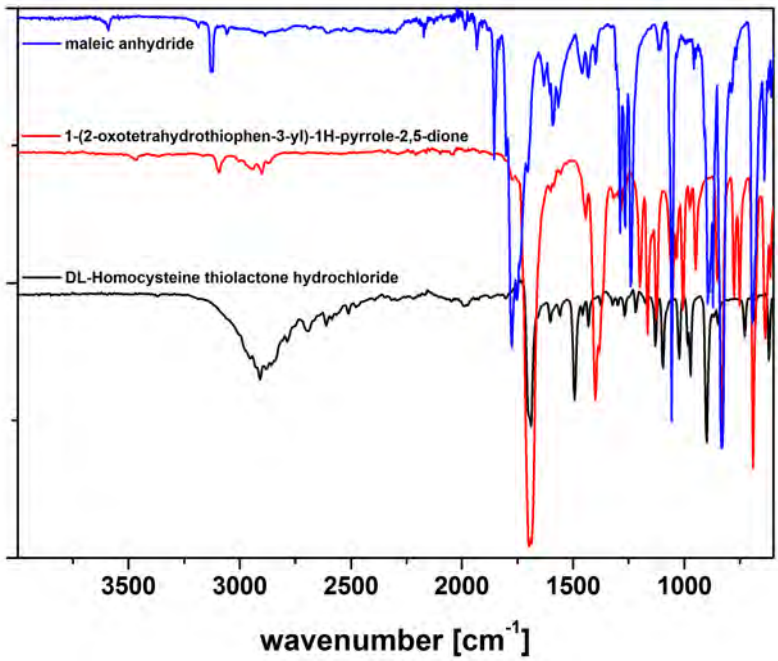

Figure S2: Comparison of FT-IR spectra for maleic anhydride (blue trace-), D,L-homocysteine thiolactone hydrochloride (black trace), and the desired maleimide thiolactone (IUPAC: 1-(2-oxotetrahdrothiophen-3-yl)-1H-pyrrole-2,5-dione; MITla, red trace).

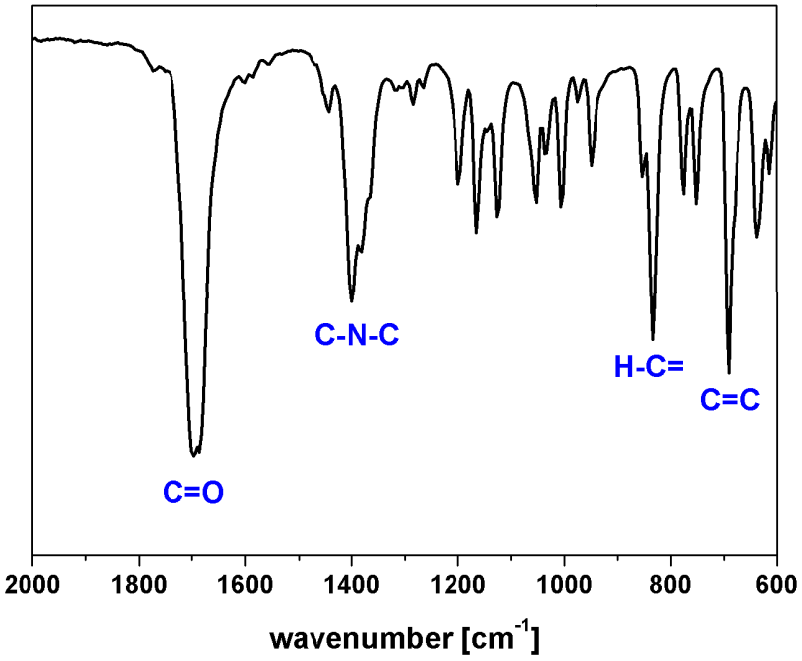

Figure S3: Enlarged FT-IR spectrum for MITla and the important signals for: carbonyls at 1689, C-N-C at 1400, and the maleimide double bond at 830 and 690 cm^{-1}.

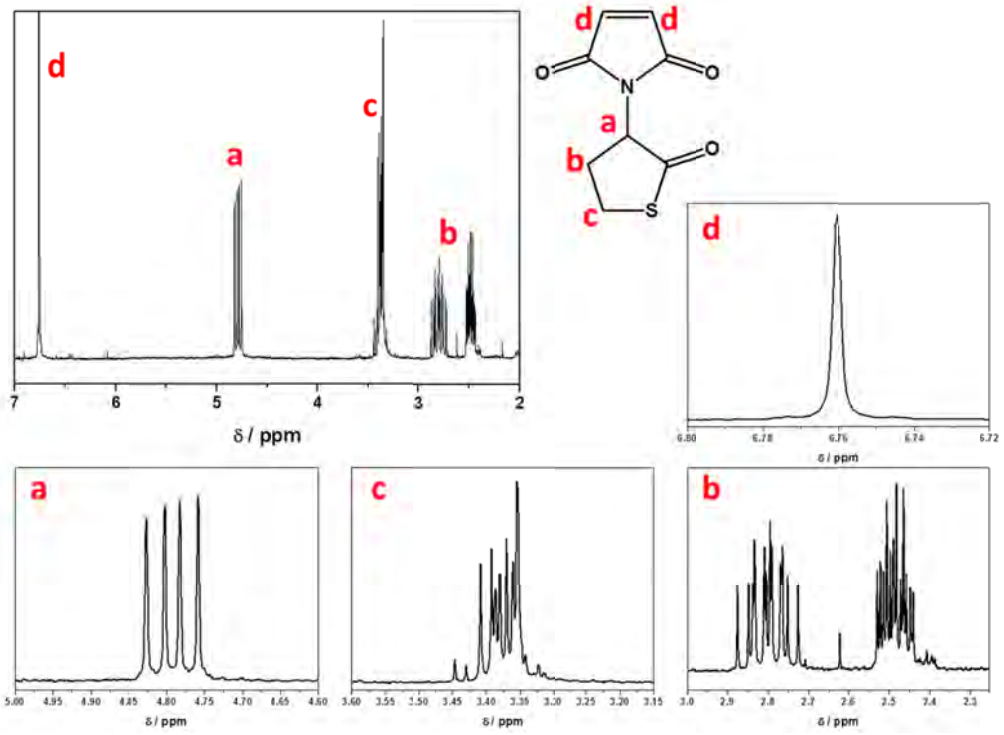

Figure S4: ^{1}H-NMR spectra of maleimide thiolactone (MITla) and peak assignment ($CDCl_3$, 300 MHz).

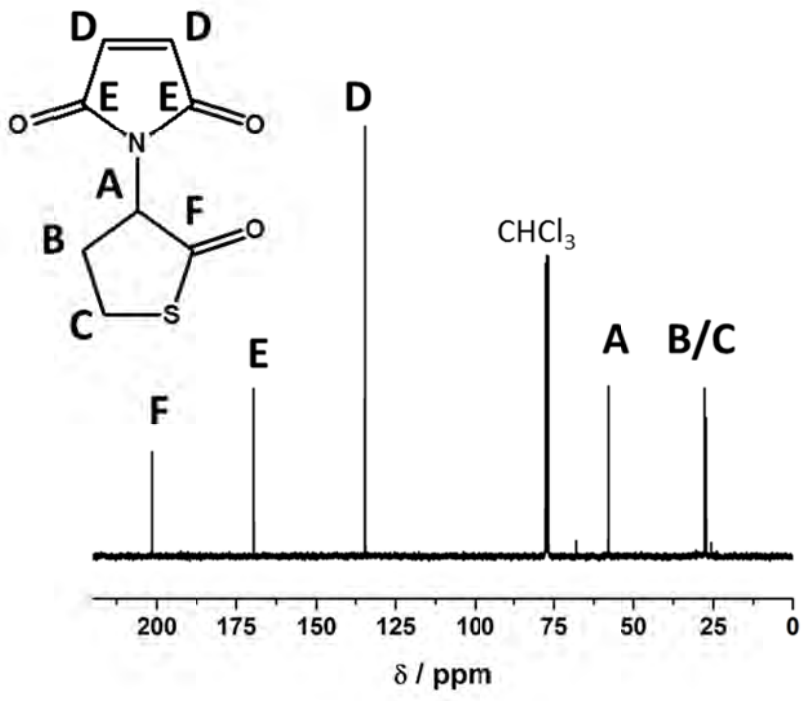

Figure S5: ^{13}C-NMR spectrum of maleimide thiolactone (MITla) ($CDCl_3$, 75 MHz).

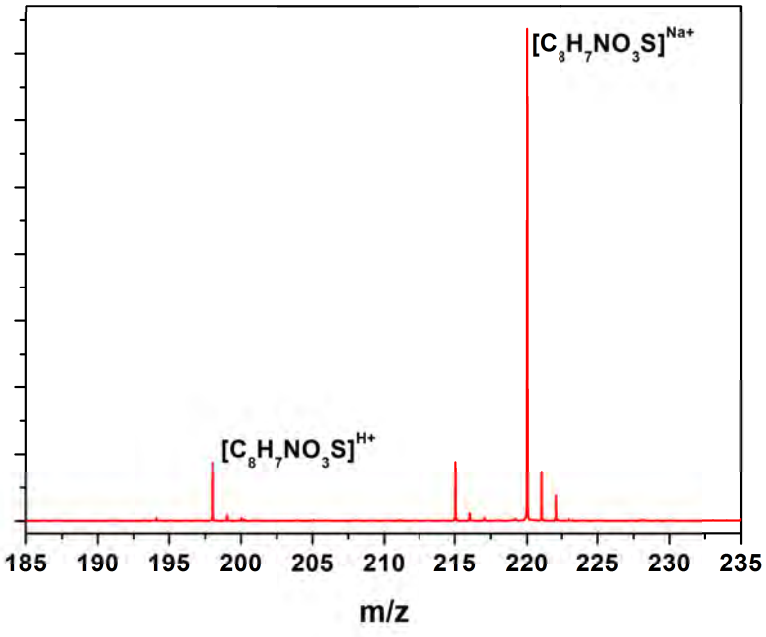

Figure S6: ESI-MS spectrum for MITla.

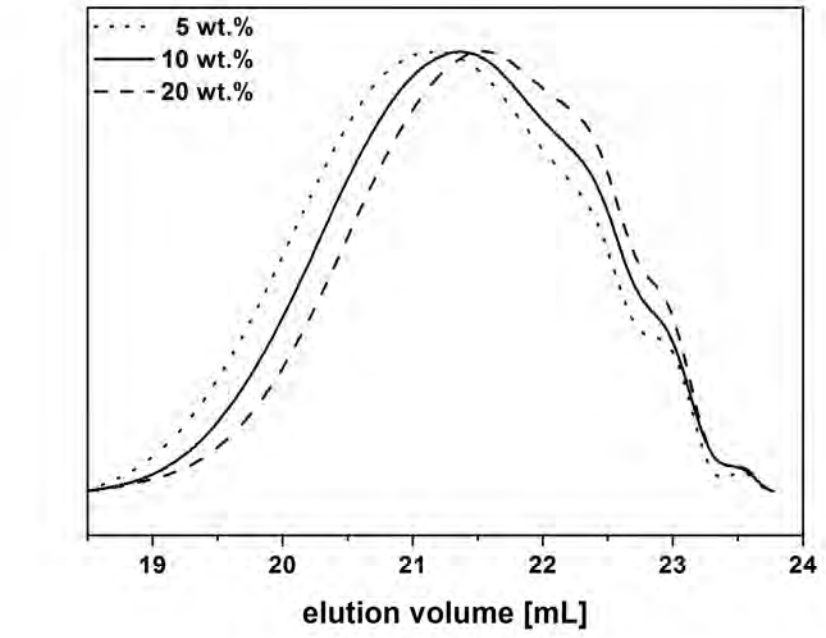

Figure S7: Comparison of SEC traces for the homopolymerization of MITla initiated by different amounts of TPO in solution (100 mg mL^{-1} DCM): 5 wt.% (dotted line), 10 wt.% (straight line), and 20 wt.% (dashed line).

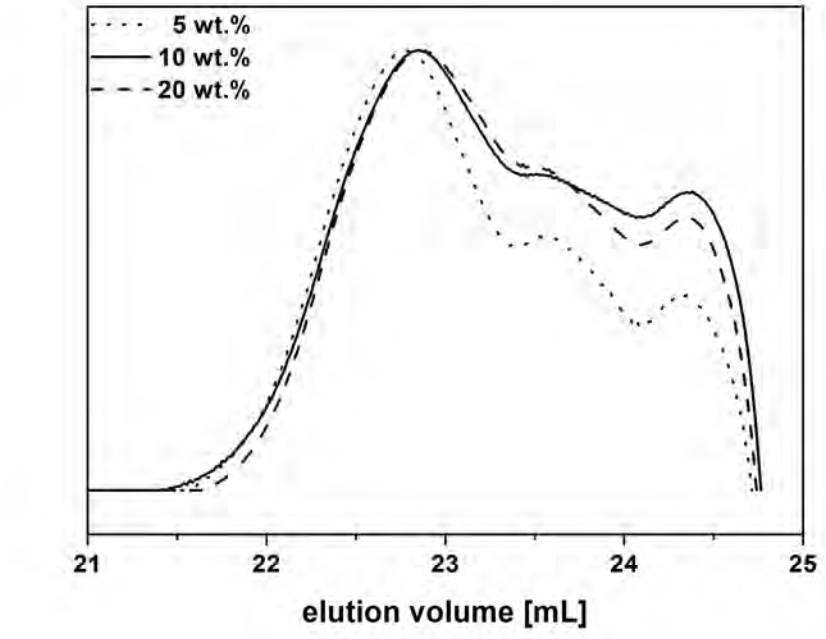

Figure S8: Comparison of SEC traces for the homopolymerization of MITla initiated by different amounts of AIBN in solution (100 mg mL^{-1} THF): 5 wt.% (dotted line), 10 wt.% (straight line), and 20 wt.% (dashed line).

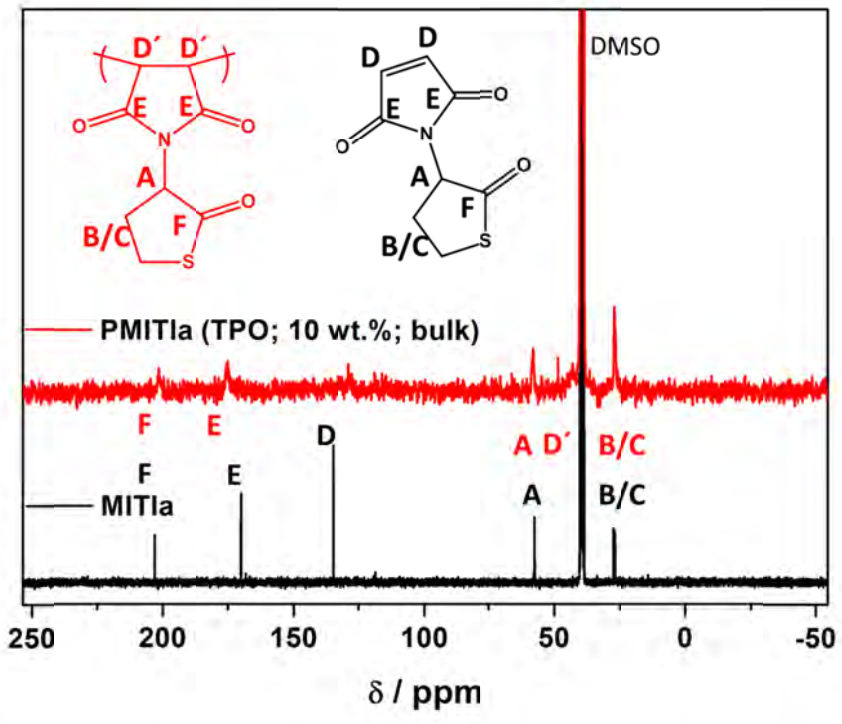

Figure S9: Comparison of ^{13}C-NMR traces for MITla (black trace) and PMITla (10 wt.% TPO, bulk; red trace) (DMSO-d_6 , 75 MHz).

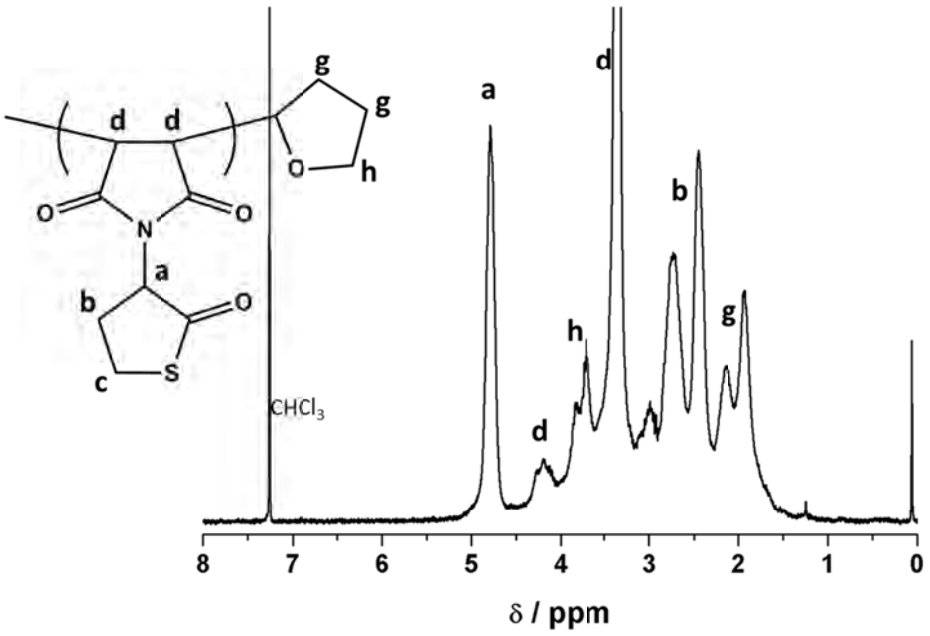

Figure S10: NMR spectrum for PMITla^{AIBN} initiated by AIBN in THF ($CDCl_3$, 300 MHz).

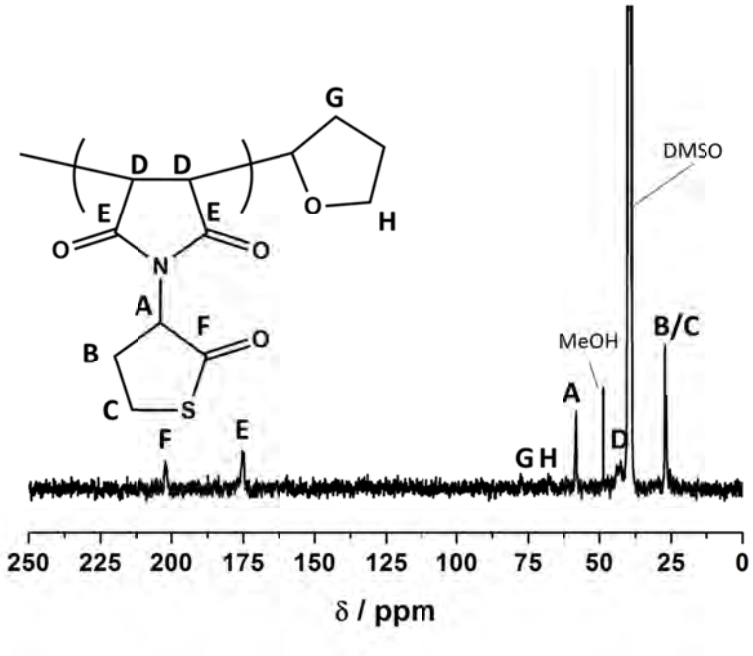

Figure S11: ^{13}C-NMR spectrum for PMITla^{AIBN} (DMSO-d_6 , 75 MHz).

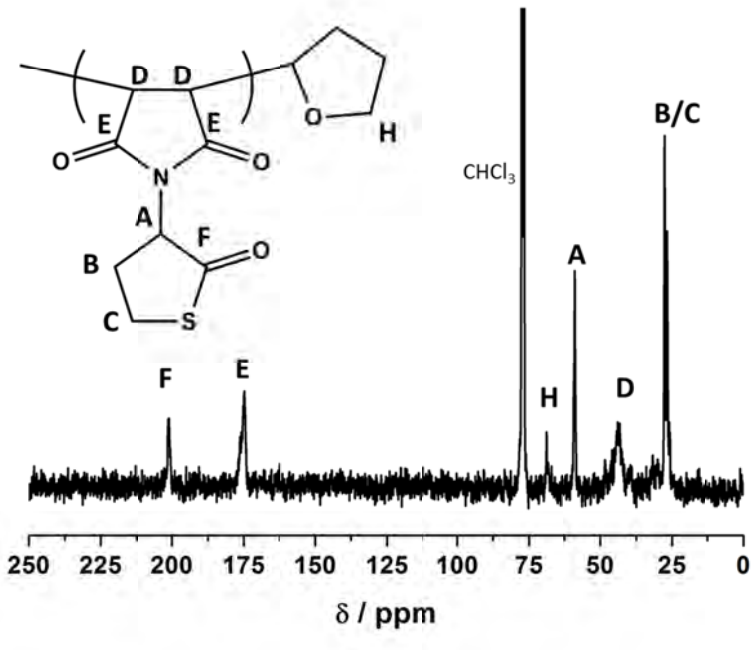

Figure S12: ^{13}C-NMR spectrum for PMITla^{AIBN} ($CDCl_3$, 75 MHz).

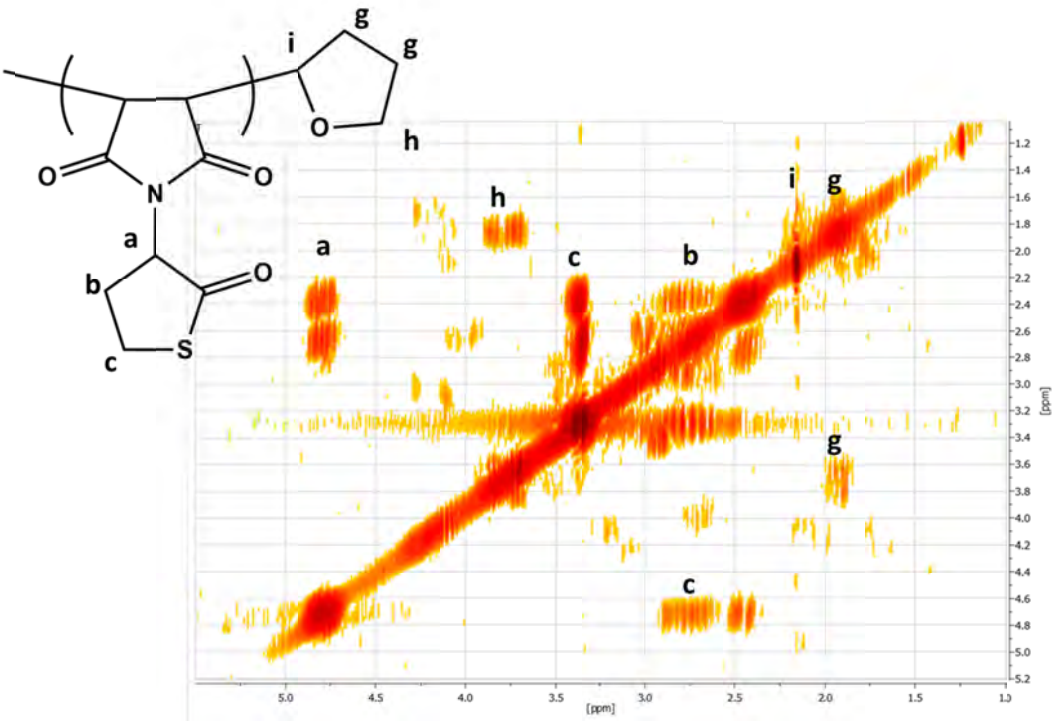

Figure S13: COSY spectrum for PMITla^{AIBN} initiated *via* AIBN in THF (300 MHz; $CDCl_3$).

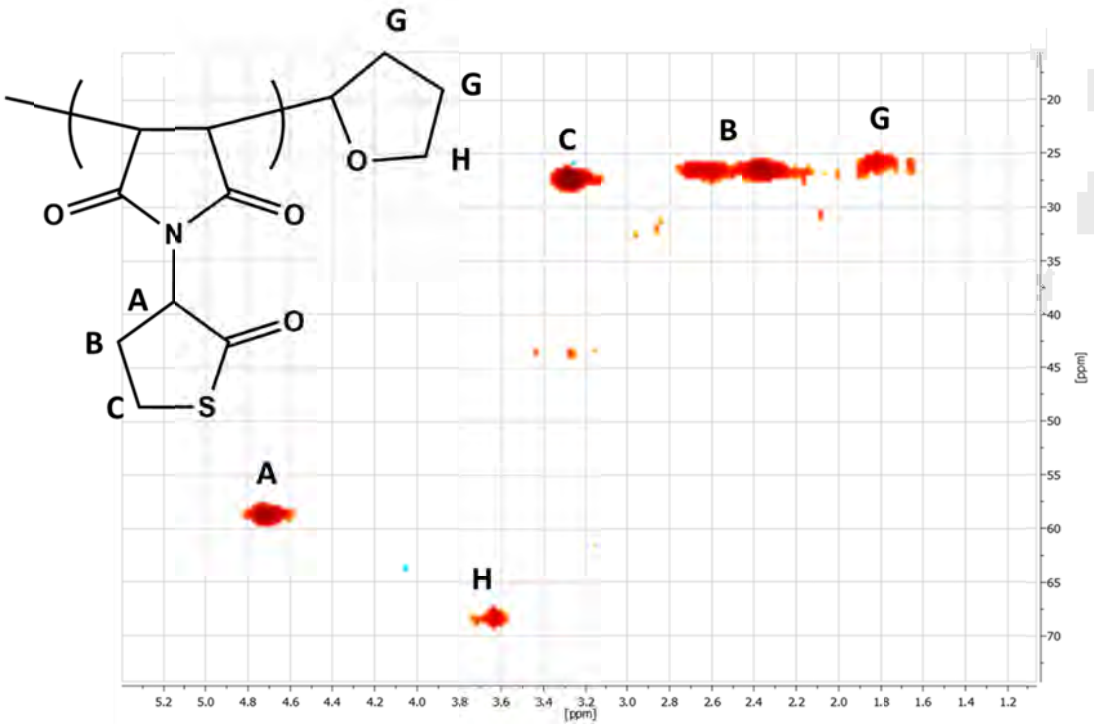

Figure S14: HSQC NMR spectrum for PMITla^{AIBN} initiated *via* AIBN in THF (300 MHz; $CDCl_3$).

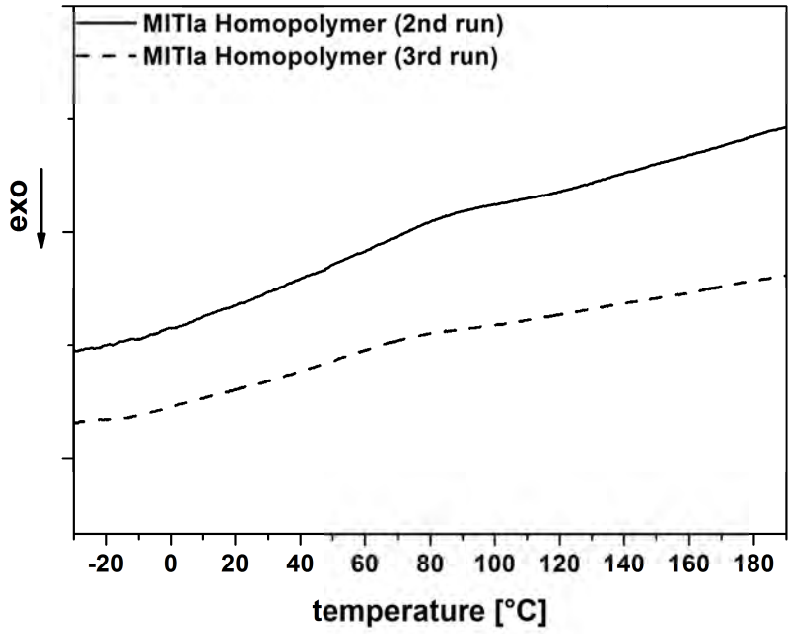

Figure S15: DSC thermogram for PMITla^{TPO} in the temperature range of -30 to 200°C.

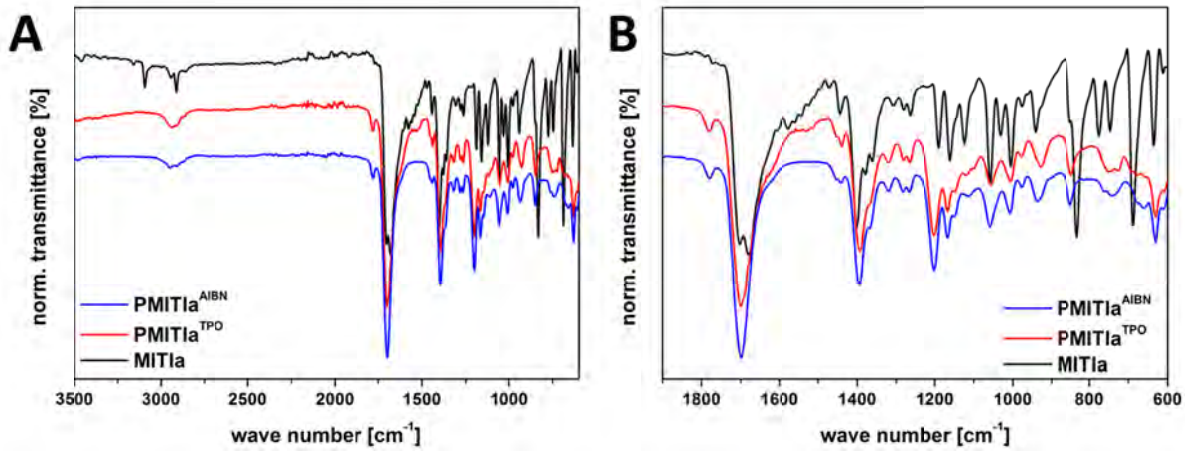

Figure S16: Comparison of FT-IR traces for PMITla^{AIBN} (red trace) and PMITla^{TPO} (black trace) (A) and an enlargement of the fingerprint region (B).

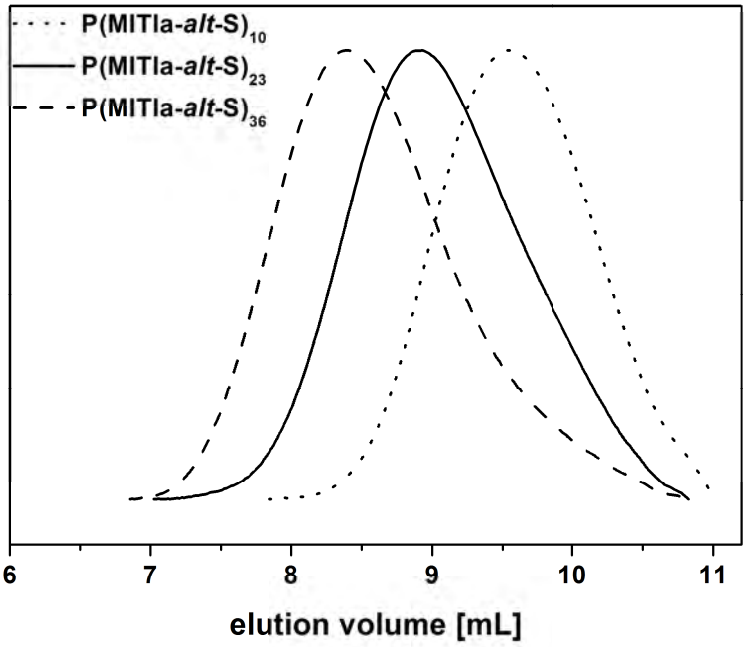

Figure S17: Comparison of SEC traces for P(MITla-*alt*-S)$_{10}$ (dotted line), P(MITla-*alt*-S)$_{23}$ (straight line), and P(MITla-*alt*-S)$_{36}$ (dashed line).

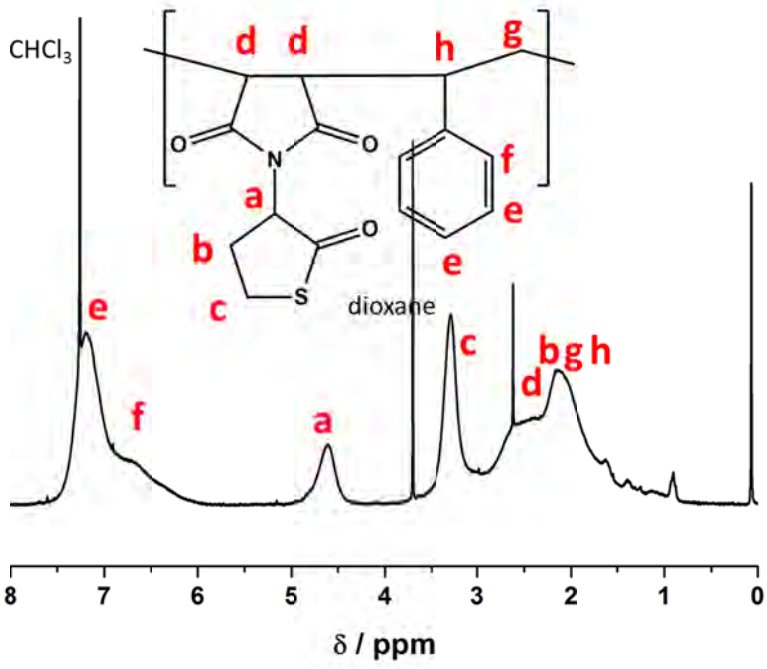

Figure S18: ^{1}H-NMR spectrum for P(MITla-*alt*-S)$_{23}$ and peak assignment (300 MHz; $CDCl_3$).

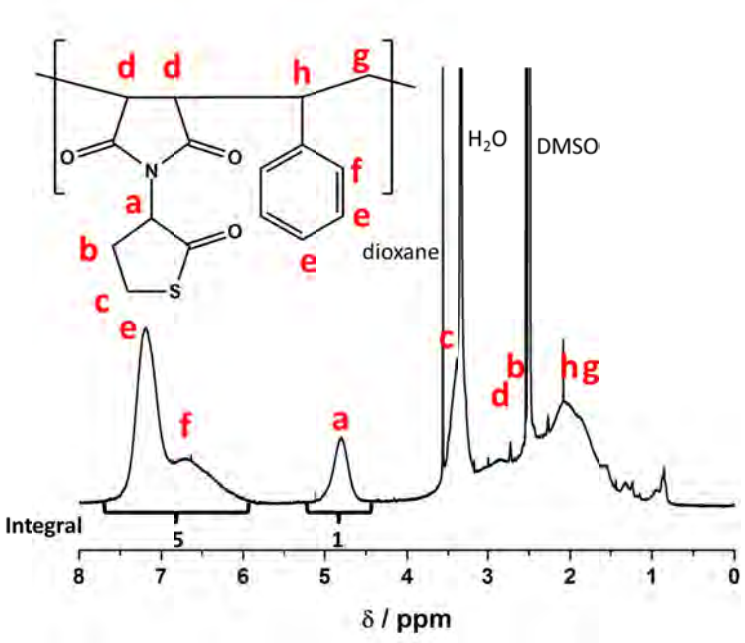

Figure S19: ^{1}H-NMR spectrum for P(MITla-*alt*-S)$_{23}$ and peak assignment (300 MHz; DMSO-d_6).

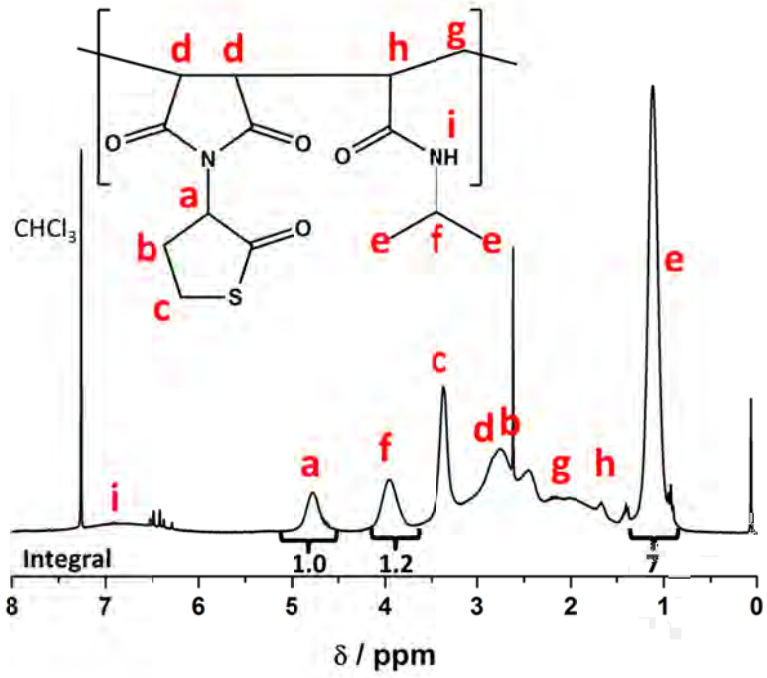

Figure S20: ^{1}H-NMR spectrum for P(MITla-*co*-NIPAAm)$_{23}$ and peak assignment (300 MHz; $CDCl_3$).

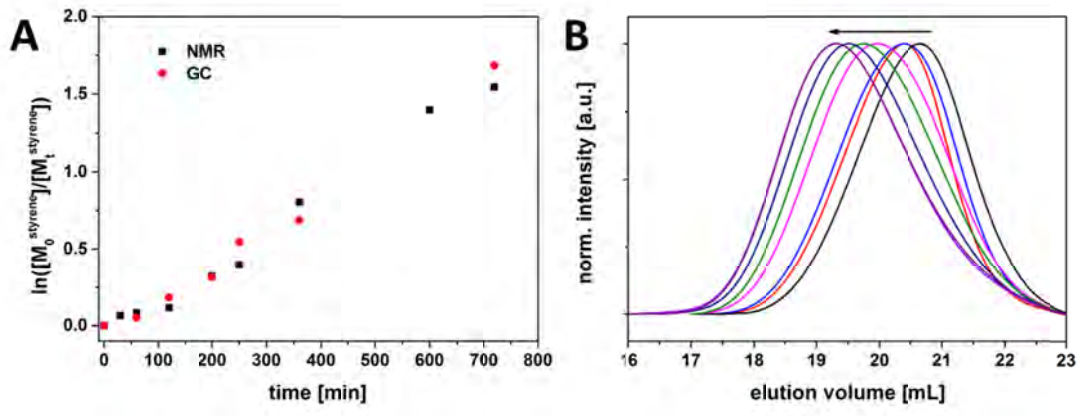

Figure S21: A) Time vs. styrene monomer conversion plot determined by NMR (black square) and GC (red dot) for the copolymerization of MITla and styrene; B) comparison of SEC traces for the kinetic investigation of the copolymerization of MITla and styrene using RAFT.

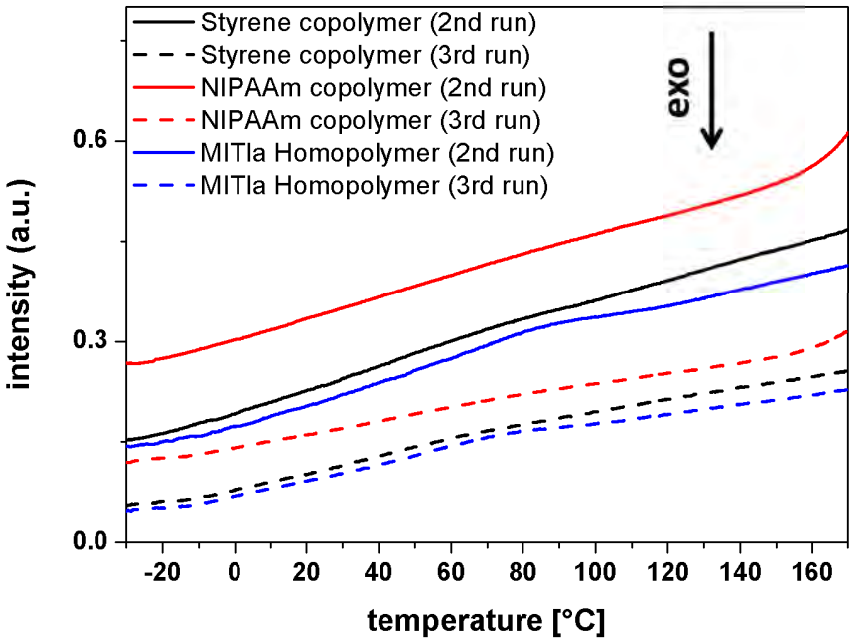

Figure S22: Comparison of DSC traces for P(MITla-*alt*-S)$_{23}$ (black lines), P(MITla-*co*-NIPAAm)$_{23}$ (red lines) and PMITla^{TPO} (blue lines) in the second (straight lines) and third (dashed lines) heating run.

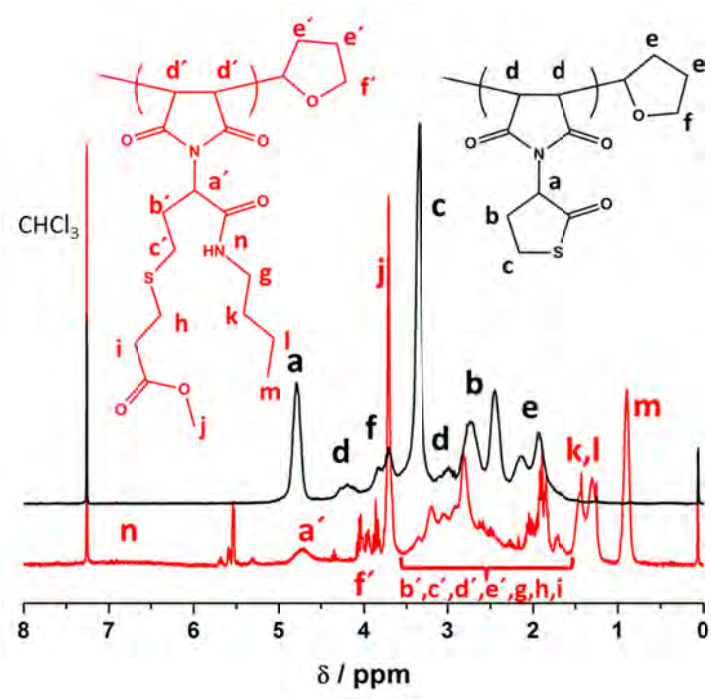

Figure S23: Comparison of NMR spectra for PMITla^{AIBN} before (black trace) and after (red trace) double modification *via n*-butylamine and methyl acrylate (300 MHz; $CDCl_3$).

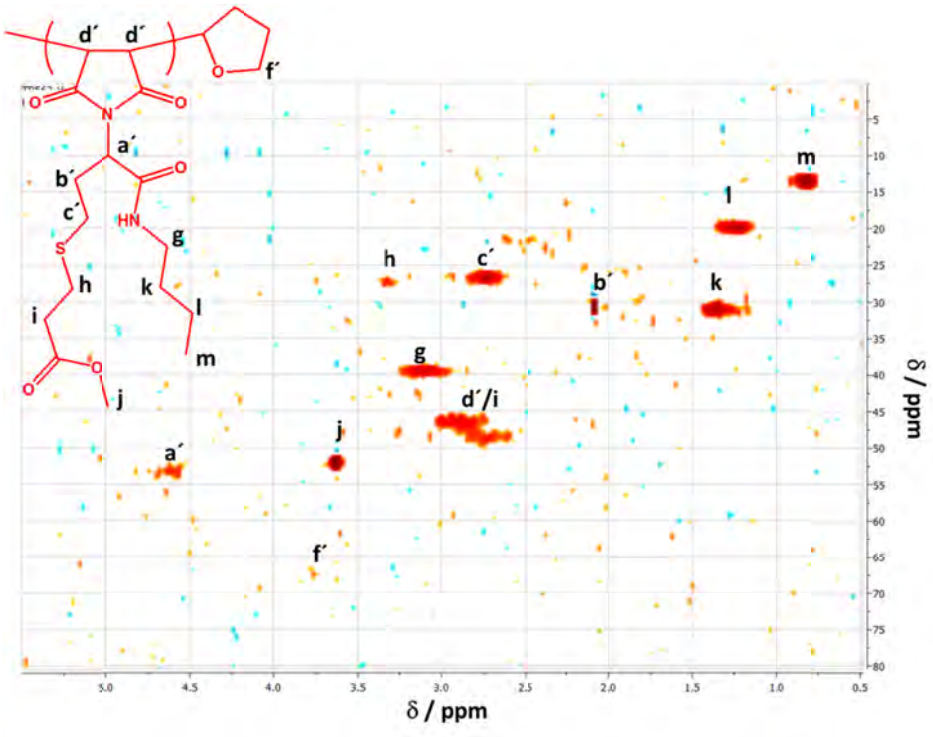

Figure S24: HSQC NMR spectra for PMITla^{AIBN,DM} initiated *via* AIBN in $CHCl_3$ by methyl acrylate and *n*-butylamine and peak assignment (300 MHz; $CDCl_3$).

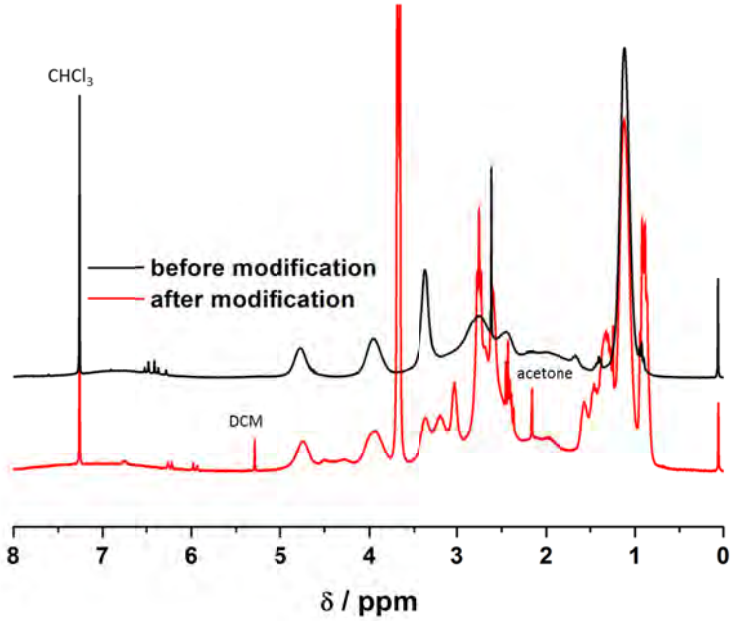

Figure S25: Comparison of NMR traces for P(MITla-*co*-NIPAAm)$_{23}$ before (black trace) and after (red trace) double modification *via n*-butylamine and methyl acrylate (300 MHz; $CDCl_3$).

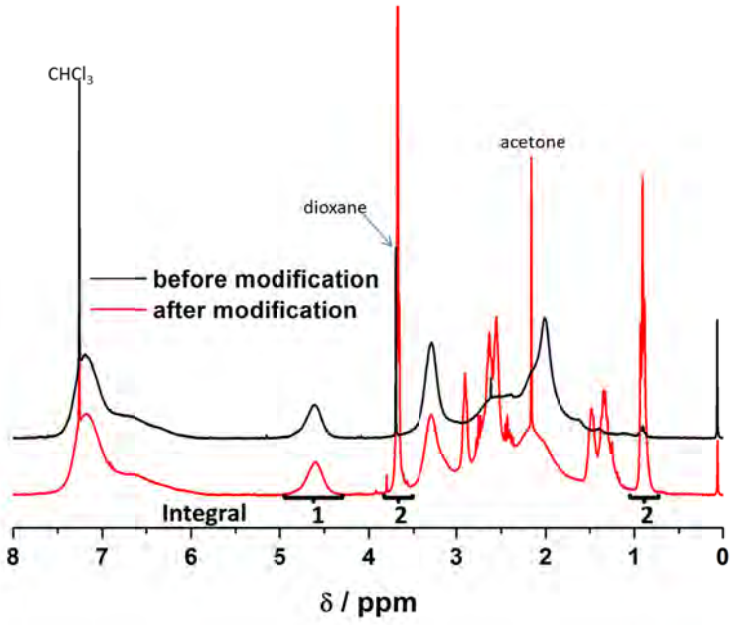

Figure S26: Comparison of NMR traces for P(MITla-*alt*-S)$_{36}$ before (black trace) and after (red trace) double modification *via n*-butylamine and methyl acrylate (300 MHz; $CDCl_3$).

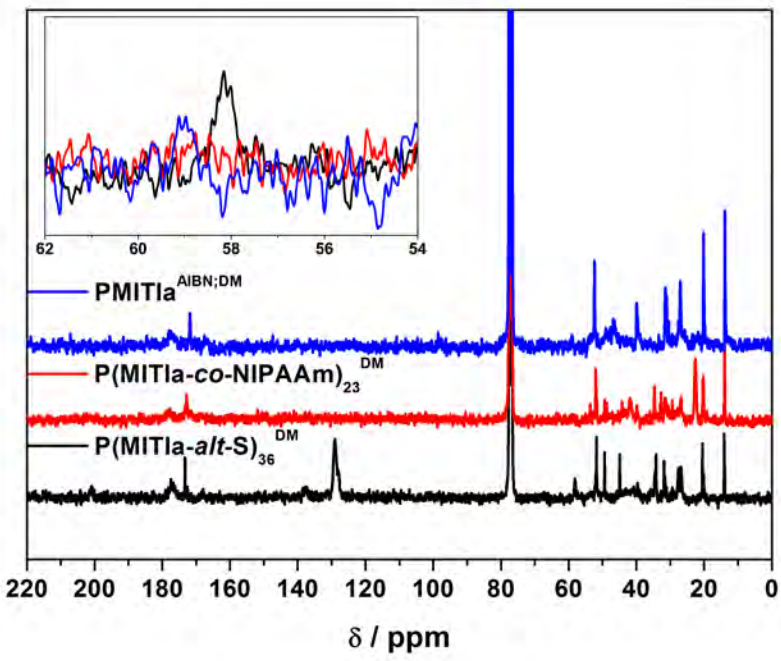

Figure S27: Comparison of ^{13}C-NMR traces for PMITIa^{AIBN,DM} (blue trace), P(MITIa-*co*-NIPAAm)$_{23}^{DM}$ (red trace), and P(MITIa-*alt*-S)$_{36}^{DM}$ (black trace); inset shows the signal at 58 ppm.

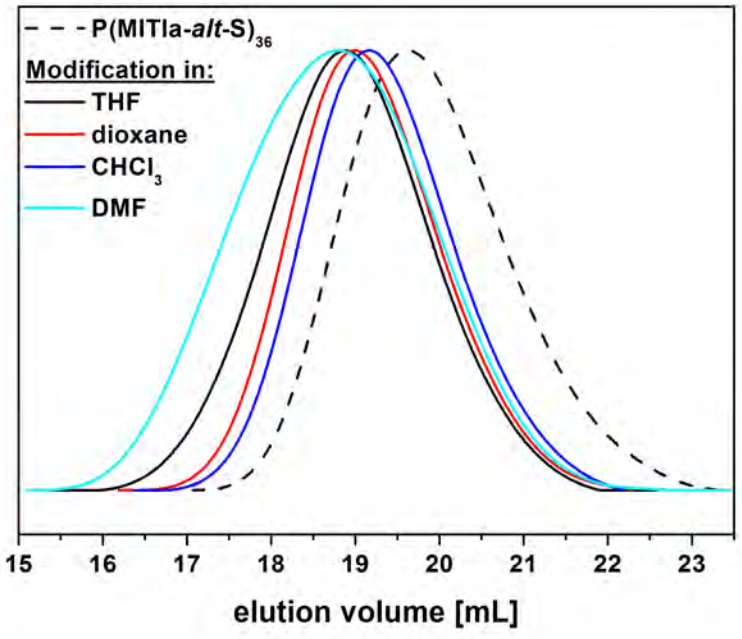

Figure S28: Comparison of SEC traces for the double modification by methyl acrylate and *n*-butylamine for P(MITIa-*alt*-S)$_{36}$ in different solvents: pristine P(MITIa-*alt*-S)$_{36}$ (dashed line), in THF (black line), in dioxane (red line), chloroform (blue line), DMF (blue line).

Table S1: Double modification of P(MITla-*co*-S)$_{36}$ by *n*-butylamine and methyl acrylate at different conditions (25 mg mL^{-1}).

Solvent	Reaction Time [h]	Further educt addition after	Estimated degree of functionalization [%][a]	M_n[b] [g mol^{-1}]	Đ[b]
DMF	48	24 h	40	19 600	1.55
THF	48	24 h	60	18 600	1.37
Dioxane	48	24 h	50	16 600	1.30
Chloroform	48	24 h	60	15 000	1.29

a) Degree of functionalization is estimated *via* ^{1}H-NMR (300 MHz; $CDCl_3$)
b) SEC (DMAC/LiCl): PS-calib.

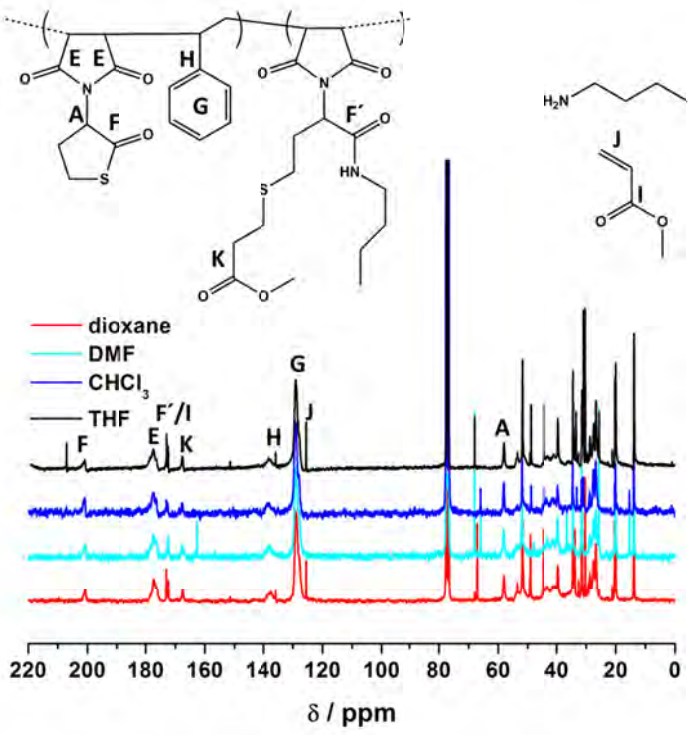

Figure S29: Comparison of ^{13}C-NMR spectra for double modification by methyl acrylate and *n*-butylamine for P(MITla-*alt*-S)$_{36}$ in different solvents: in THF (black line), in dioxane (red line), chloroform (blue line), DMF (blue line) (75 MHz; $CDCl_3$); (As polymers were only precipitated once before measuring NMR, educt signals are still observed).

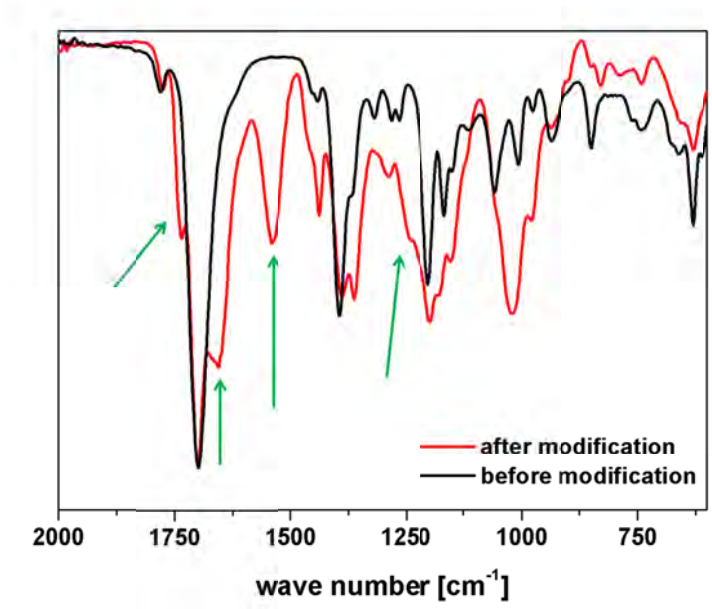

Figure S30: Comparison of FT-IR spectra for PMITla^{AIBN} before (black trace) and after (red trace) modification by methyl acrylate and *n*-butylamine.

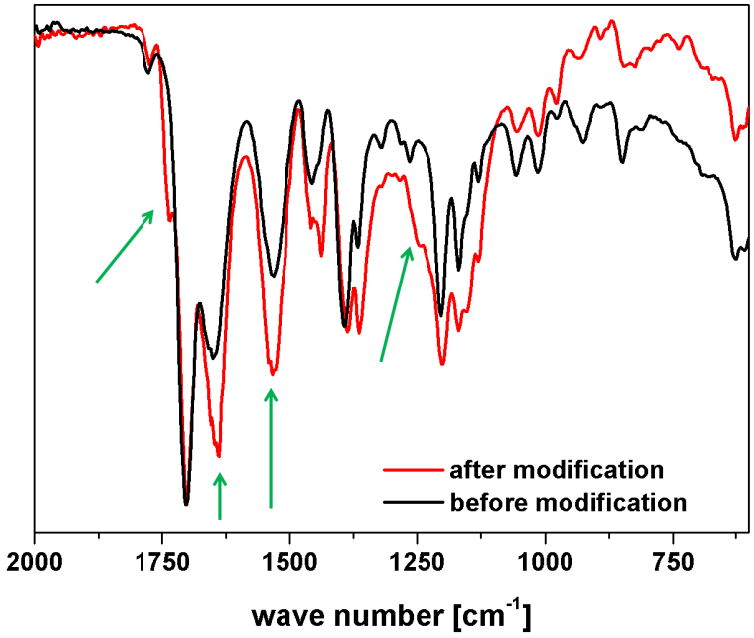

Figure S31: Comparison of FT-IR spectra for P(MITla-*co*-NIPAAm)$_{23}$ before (black trace) and after (red trace) modification by methyl acrylate and *n*-butylamine.

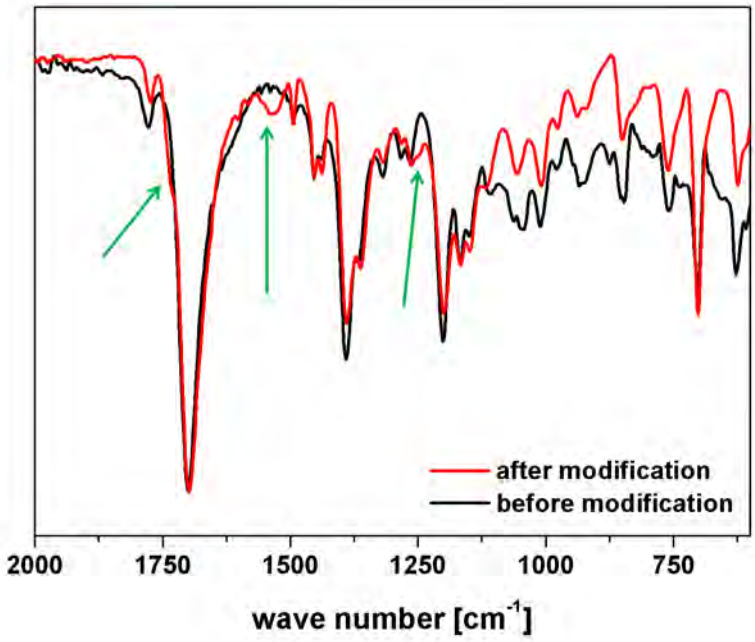

Figure S32: Comparison of FT-IR spectra for P(MITla-*co*-S)$_{36}$ before (black trace) and after (red trace) modification by methyl acrylate and *n*-butylamine.