

Supplementary Information for
**Replacing Cu(II)Br₂ with Me₆-TREN in Biphasic Cu(0)/TREN Catalyzed
SET-LRP Reveals the Mixed-Ligand Effect**

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1. Kinetic Plots, Molecular Weight and Polydispersity Evolution for the SET-LRP of MA

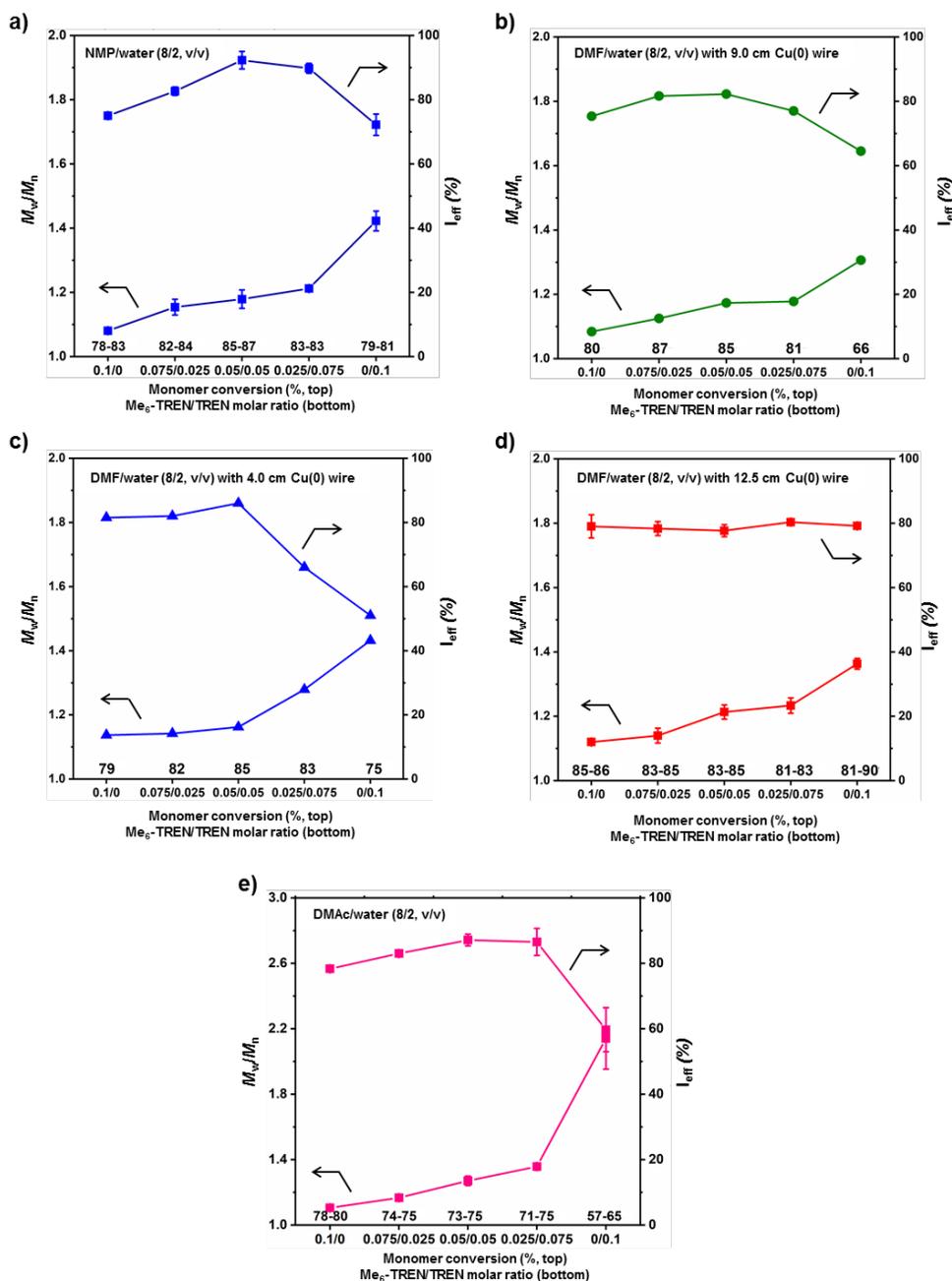


Figure S1. Evolution of M_w/M_n and I_{eff} for the SET-LRP of MA initiated with BPE in various “programmed” biphasic reaction mixtures at 25 °C. (a) NMP/water mixture (8/2, v/v) using 9.0 cm nonactivated Cu(0) wire as catalyst. (b) DMF/water mixture (8/2, v/v) using 9.0 cm of nonactivated Cu(0) wire as catalyst. (c) DMF/water mixture (8/2, v/v) using 4.0 cm of nonactivated Cu(0) wire as catalyst. (d) DMF/water mixture (8/2, v/v) using 12.5 cm of nonactivated Cu(0) wire as catalyst. (e) DMAC/water mixture (8/2, v/v) using 9.0 cm of nonactivated Cu(0) wire as catalyst. Reaction conditions: MA = 1 mL, organic solvent = 0.4 mL, water = 0.1 mL, and $[MA]_0/[BPE]_0/[L]_0 = 222/1/0.1$.

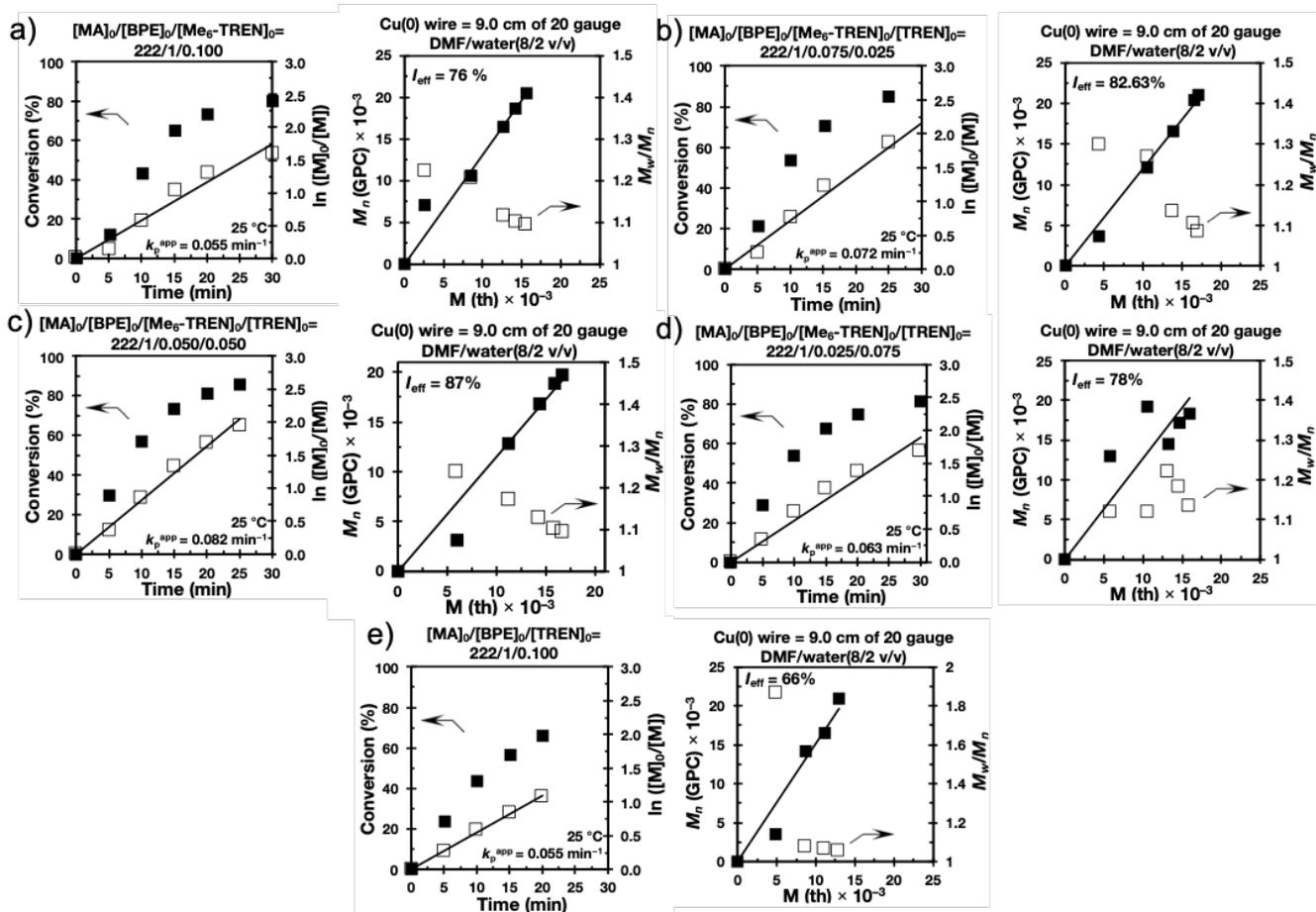


Figure S2. Kinetic plots, molecular weight and polydispersity evolution for the SET-LRP of MA in DMF/water mixture (8/2, v/v) initiated with BPE and catalyzed by 9.0 cm nonactivated Cu(0) wire at 25 °C. Experimental data in different colors were obtained from different kinetics experiments sometimes performed by different researches. k_p^{app} and I_{eff} are the average values of three experiments. Reaction conditions: MA = 1 mL, DMF = 0.4 mL, water = 0.1 mL, $[MA]_0/[BPE]_0/[L]_0 = 222/1/0.1$.

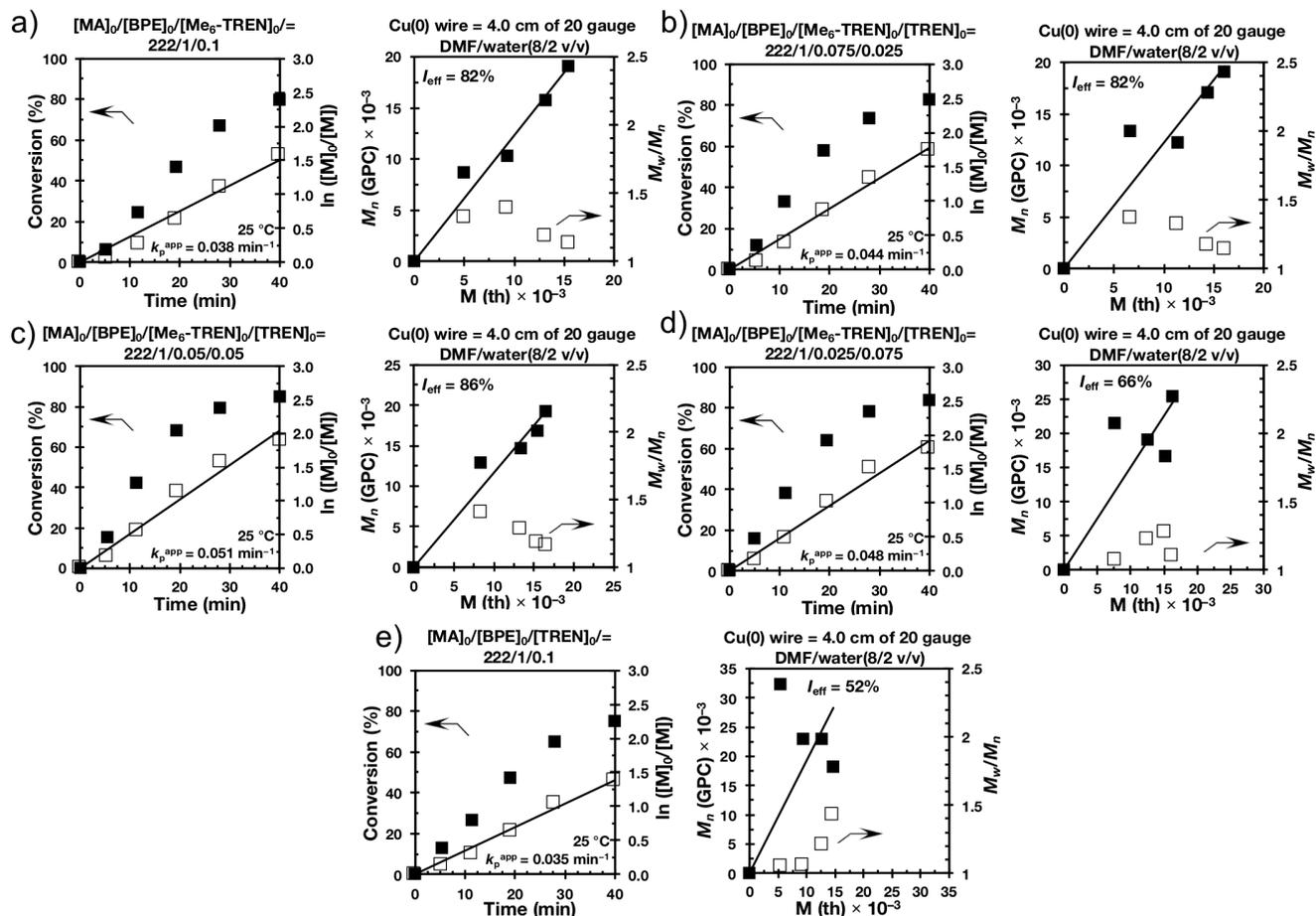


Figure S3. Kinetic plots, molecular weight and polydispersity evolution for the SET-LRP of MA in DMF/water mixture (8/2, v/v) initiated with BPE and catalyzed by 4.0 cm nonactivated Cu(0) wire at 25 °C. Experimental data in different colors were obtained from different kinetics experiments sometimes performed by different researches. k_p^{app} and I_{eff} are the average values of three experiments. Reaction conditions: MA = 1 mL, DMF = 0.4 mL, water = 0.1 mL, $[MA]_0/[BPE]_0/[L]_0 = 222/1/0.1$.

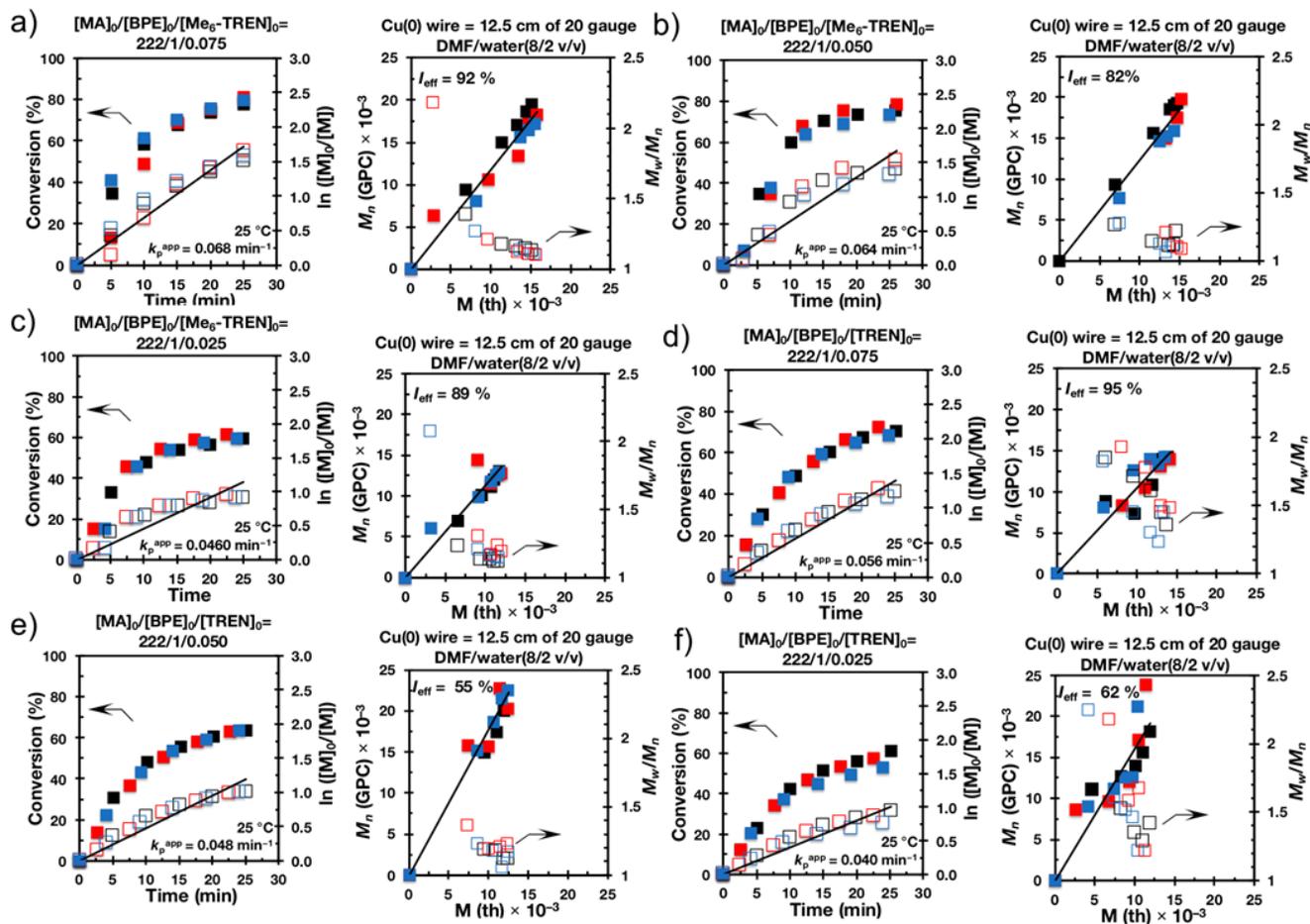


Figure S5. Kinetic plots, molecular weight and polydispersity evolution for the SET-LRP of MA in DMF/water mixture (8/2, v/v) initiated with BPE and catalyzed by the 12.5 cm nonactivated Cu(0) wire at 25 °C. Experimental data in different colors were obtained from different kinetics experiments sometimes performed by different researches. k_p^{app} and I_{eff} are the average values of three experiments. Reaction conditions: MA = 1 mL, DMF = 0.4 mL, water = 0.1 mL, $[MA]_0/[BPE]_0/[L]_0 = 222/1/0.075$ (panels a,d), $[MA]_0/[BPE]_0/[L]_0 = 222/1/0.05$ (panels b,e), $[MA]_0/[BPE]_0/[L]_0 = 222/1/0.025$ (panels c,f).

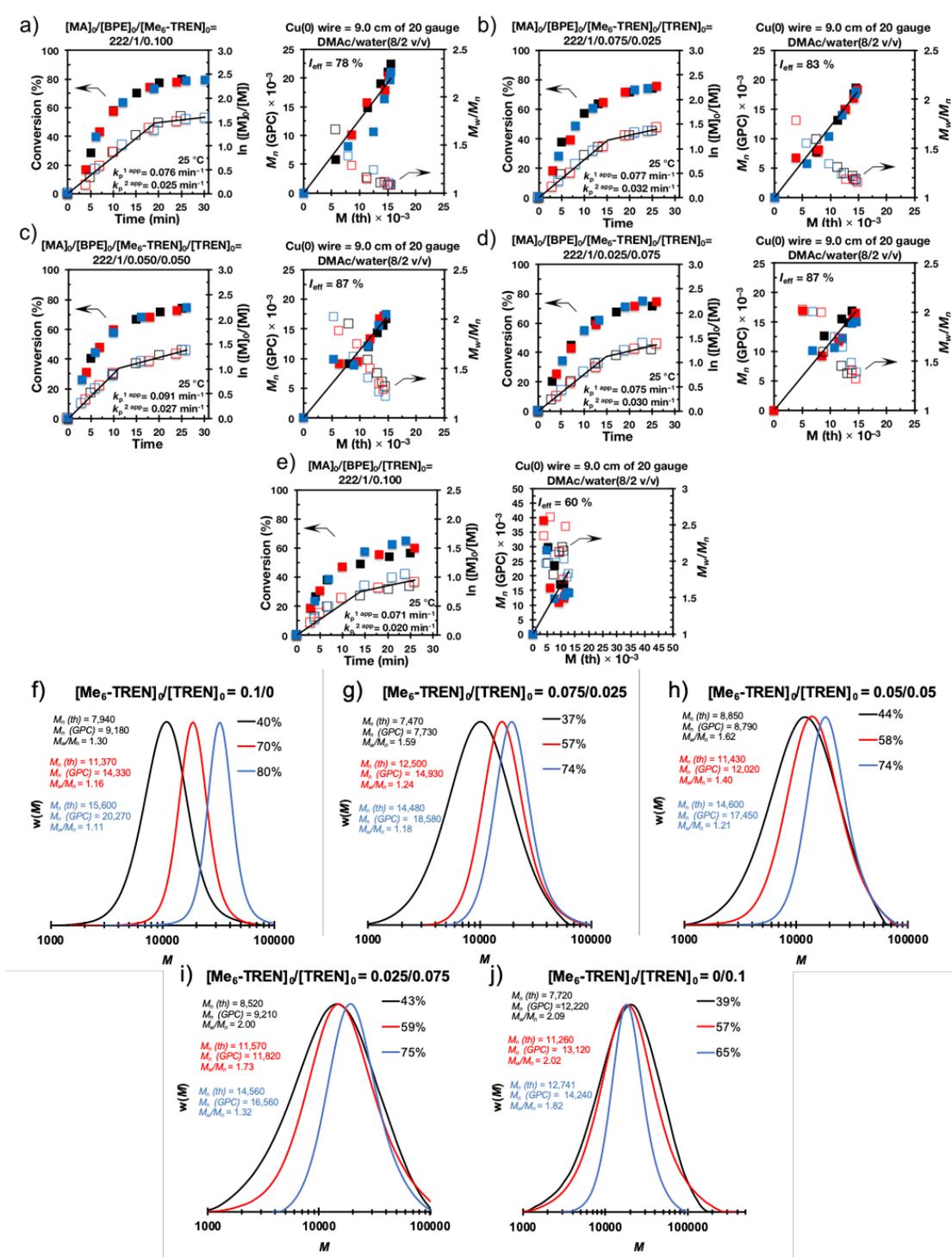


Figure S6. Kinetic plots, molecular weight, polydispersity evolution and representative GPC traces of the evolution of molecular weight as a function of conversion for the SET-LRP of MA in DMAc/water mixture (8/2, v/v) initiated with BPE and catalyzed by 9.0 cm nonactivated Cu(0) wire at 25 °C. Experimental data in different colors were obtained from different kinetics experiments sometimes performed by different researches. k_p^{app} and I_{eff} are the average values of three experiments. Reaction conditions: MA = 1 mL, DMAc = 0.4 mL, water = 0.1 mL, $[MA]_0/[BPE]_0/[L]_0 = 222/1/0.1$.

2. Digital Images of Control Experiments

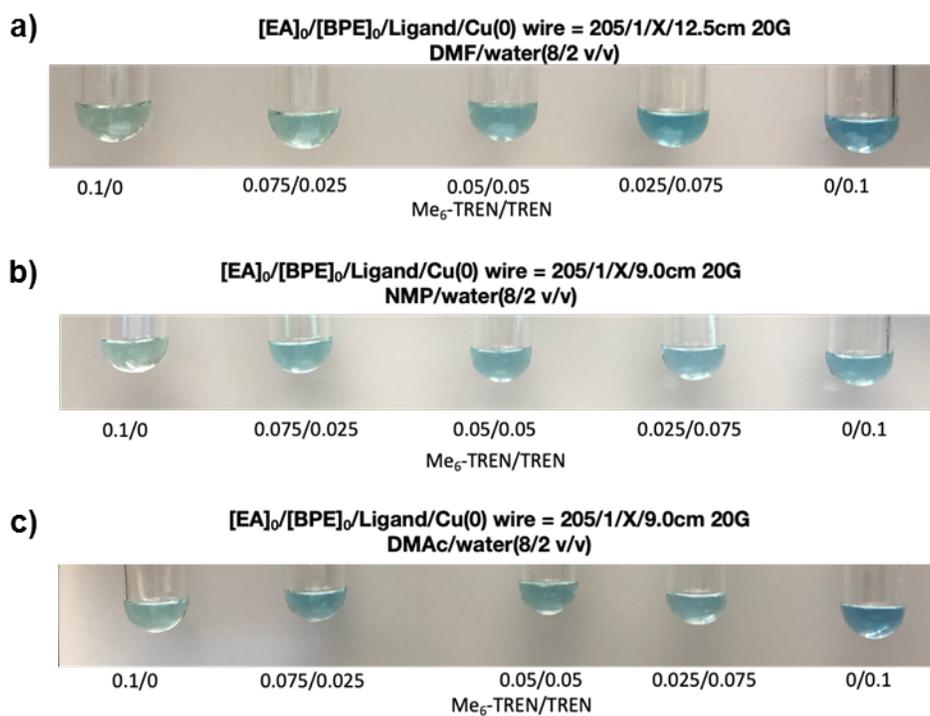


Figure S7. Visualization of the reaction mixture for the control experiments performed under the conditions placed at the top of each series of experiments. EA is the short name used for ethyl acetate employed to mimic an inert compound resembling methyl acrylate (MA).

3. ¹H NMR and MALDI-TOF MS of PMA after SET-LRP

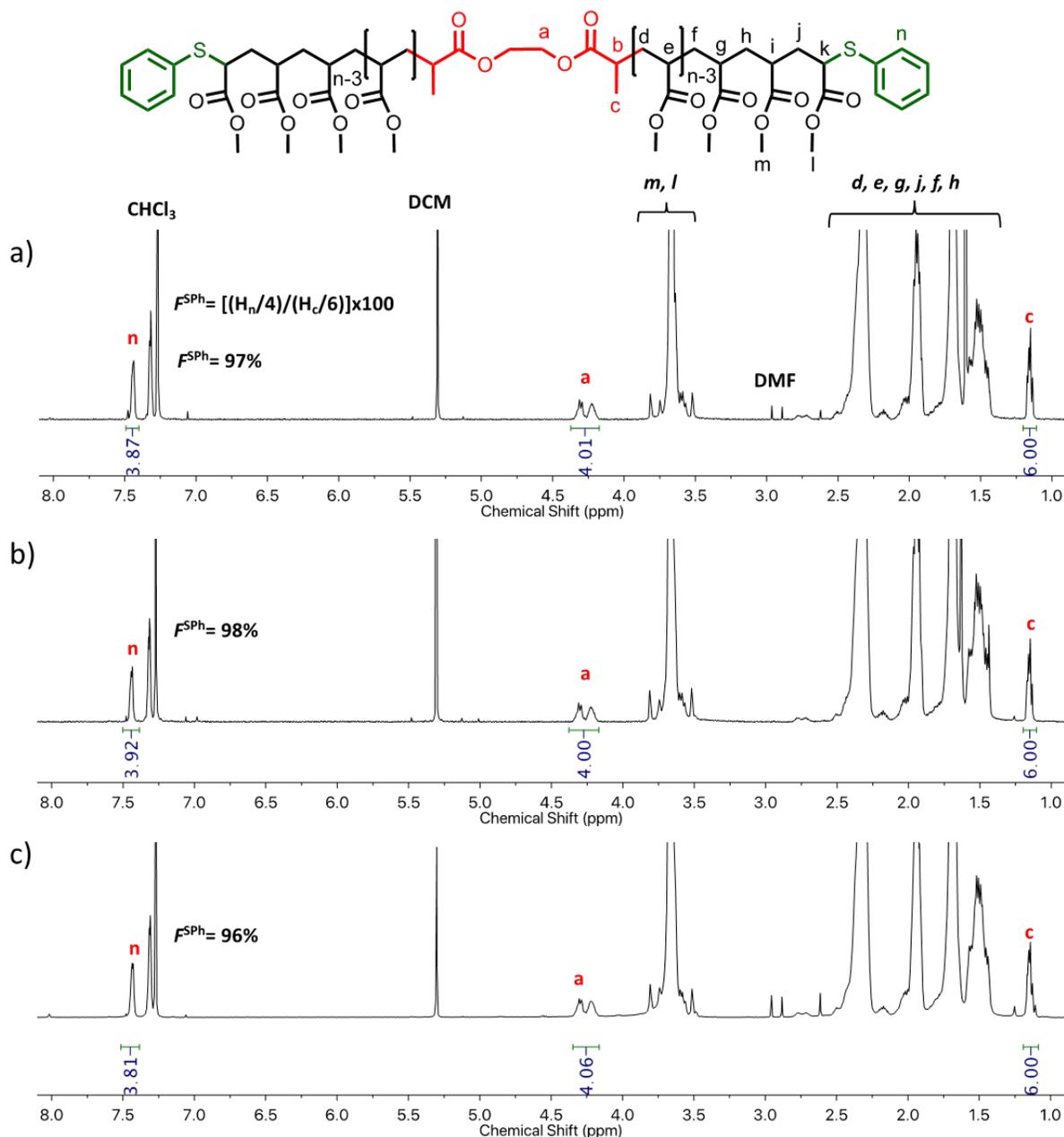
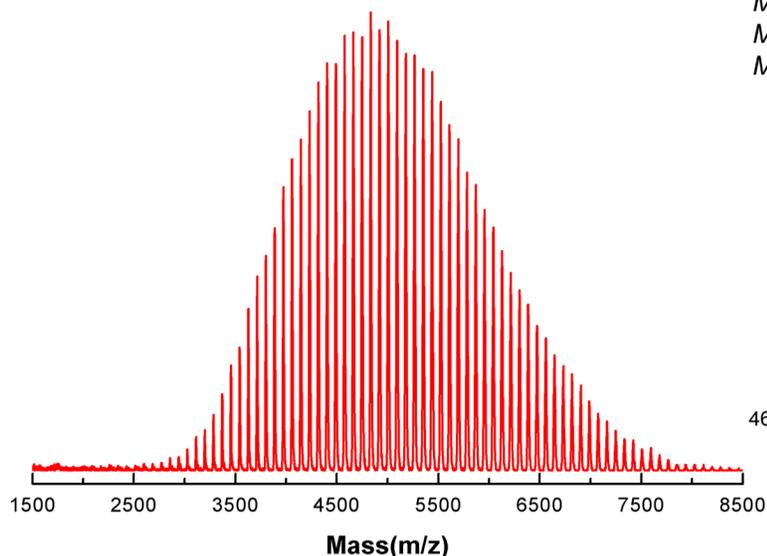
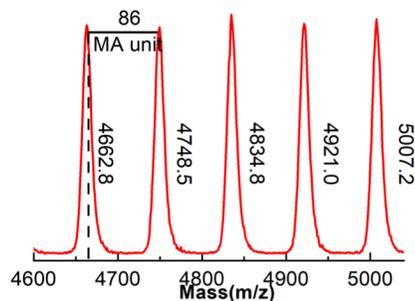


Figure S8. ¹H NMR spectra at 400 MHz of α,ω -di(phenylthio)PMA at (a) 93% monomer conversion ($M_n = 7,420$ and $M_w/M_n = 1.15$) ($[MA]_0/[BPE]_0/[Me_6-TREN]_0 = 60/1/0.1$); (b) 91% monomer conversion ($M_n = 8,260$ and $M_w/M_n = 1.17$) ($[MA]_0/[BPE]_0/[Me_6-TREN]_0/[TREN]_0 = 60/1/0.05/0.05$); (c) 94% monomer conversion ($M_n = 6,090$ and $M_w/M_n = 1.34$) ($[MA]_0/[BPE]_0/[TREN]_0 = 60/1/0.1$). Polymerization conditions: MA = 1 mL, DMF = 0.4 mL, water = 0.1 ml using 12.5 cm of nonactivated Cu(0) wire 20-gauge wire. The signals at 7.26 ppm and 5.30 ppm are due to partially nondeuterated residue of CDCl₃ and dichloromethane, respectively.

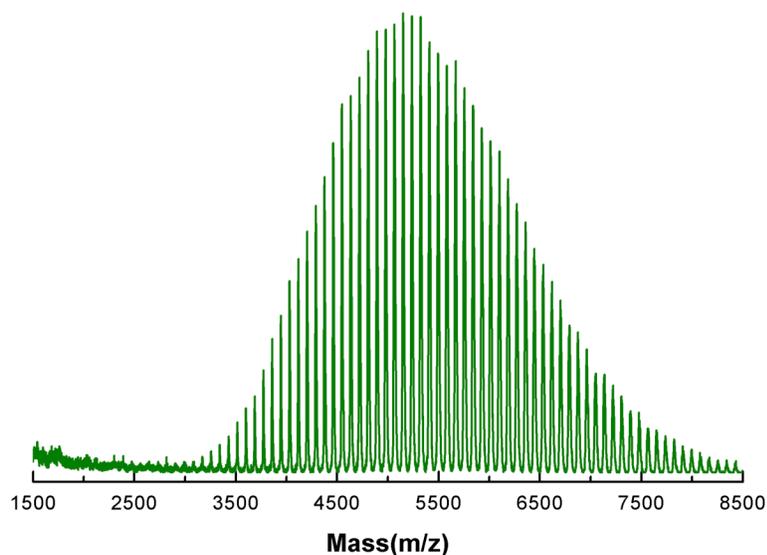
a) PMA before thioetherification



Conversion = 93%
 $M_{th} = 5,130$
 $M_{n,GPC} = 6,480$; $M_w/M_n = 1.14$
 $M_{n,MALDI} = 5,050$; $M_w/M_n = 1.04$



b) PMA after thioetherification



Conversion = 93%
 $M_{th} = 5,130$
 $M_{n,GPC} = 7,420$; $M_w/M_n = 1.15$
 $M_{n,MALDI} = 5,410$; $M_w/M_n = 1.04$

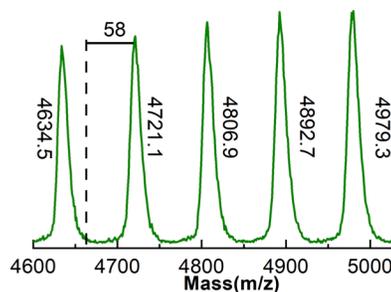


Figure S9. MALDI-TOF of α,ω -di(bromo)PMA isolated at 93% monomer conversion from SET-LRP of MA in DMF/water (8/2, v/v) mixture initiated with BPE and catalyzed by nonactivated Cu(0) wire at 25 °C: (a) before and (b) after “thio-bromo “click”. Polymerization conditions: MA = 1 mL, DMF = 0.4 mL, water = 0.1 mL using 12.5 cm of nonactivated Cu(0) wire 20-gauge wire ($[MA]_0/[BPE]_0/[Me_6-TREN]_0 = 60/1/0.1$). The dotted line in expansion after thioetherification shows the original peak from before thioetherification, while 58 represents the increase in molar mass after thioetherification i.e., $2x[SPh(109.2) - Br(79.9)] = 58.57$ for each chain end.

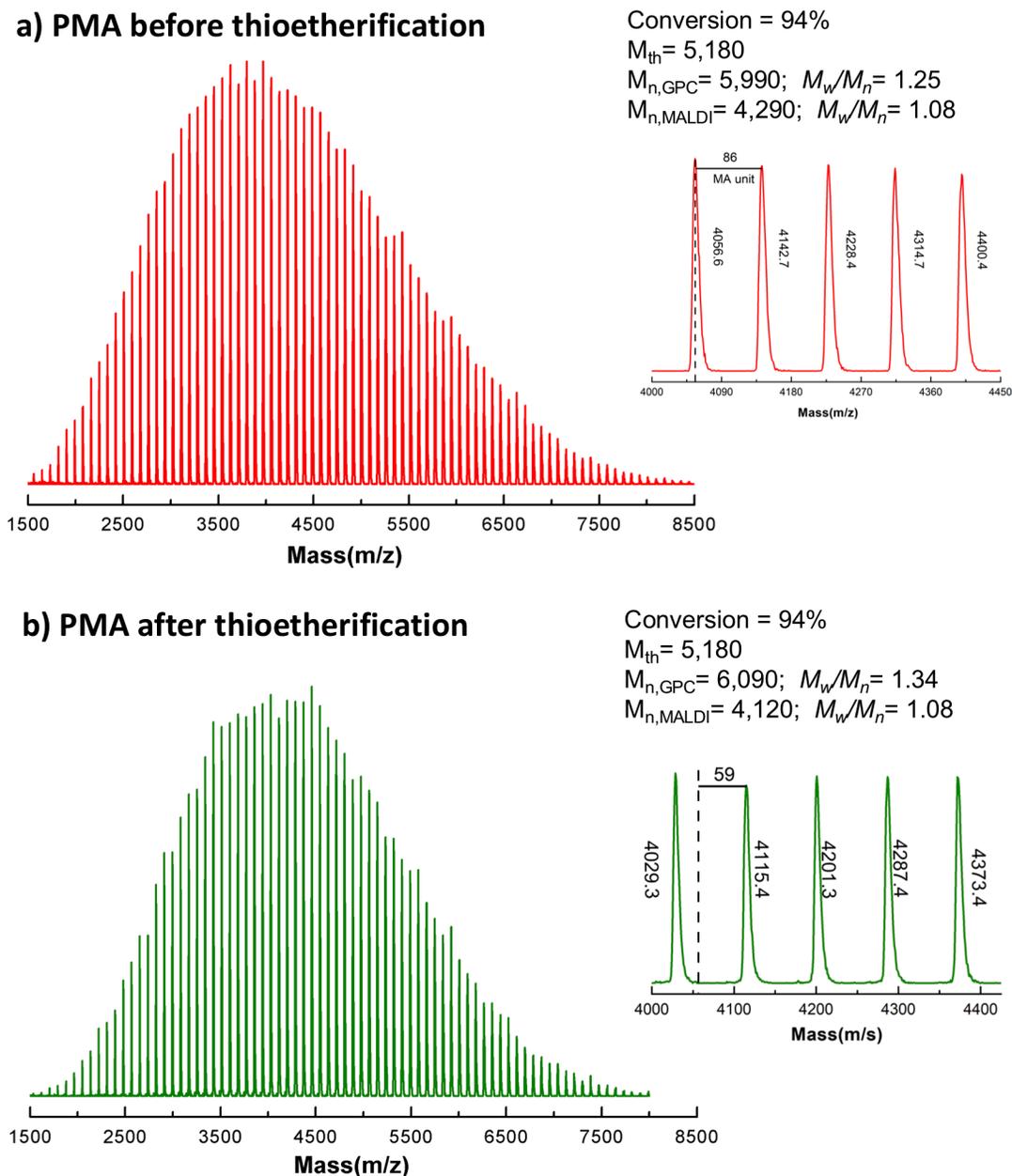


Figure S10. MALDI-TOF of α,ω -di(bromo)PMA isolated at 94% monomer conversion from SET-LRP of MA in DMF/water (8/2, v/v) mixture initiated with BPE and catalyzed by nonactivated Cu(0) wire at 25 °C: (a) before and (b) after “thio-bromo “click”. Polymerization conditions: MA = 1 mL, DMF = 0.4 mL, water = 0.1 ml using 12.5 cm of nonactivated Cu(0) wire 20-gauge wire ($[MA]_0/[BPE]_0/[TREN]_0 = 60/1/0.1$). The dotted line in expansion after thioetherification shows the original peak from before thioetherification, while 58 represents the increase in molar mass after thioetherification i.e., $2x[SPH(109.2) - Br(79.9)] = 58.57$ for each chain end.

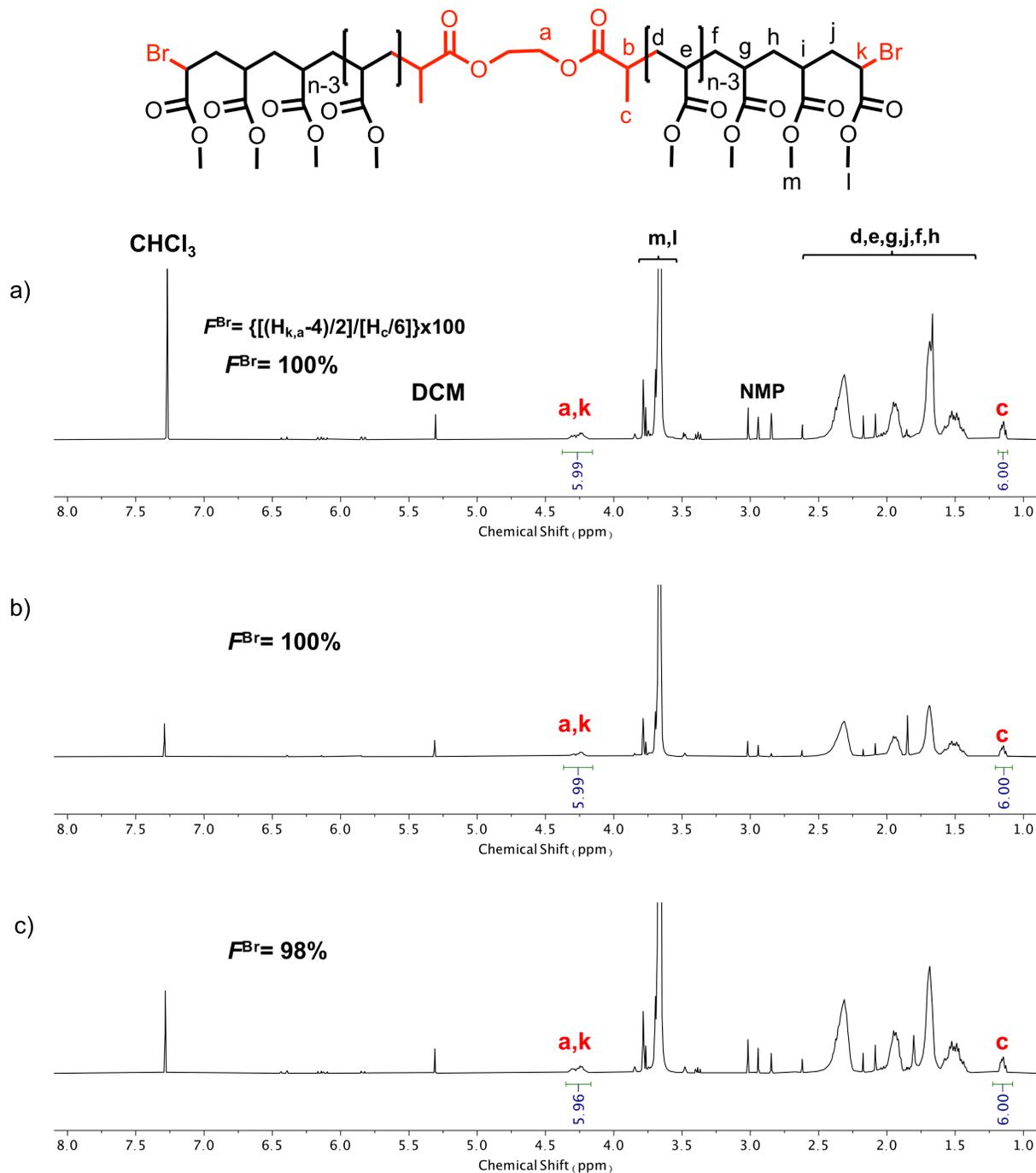


Figure S11. ^1H NMR spectra at 400 MHz of α,ω -di(bromo)PMA at (a) 98% monomer conversion ($M_n = 6,850$ and $M_w/M_n = 1.17$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0 = 60/1/0.1$); (b) 98% monomer conversion ($M_n = 4,750$ and $M_w/M_n = 1.25$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0/[\text{TREN}]_0 = 60/1/0.05/0.05$); (c) 99% monomer conversion ($M_n = 6,470$ and $M_w/M_n = 1.33$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{TREN}]_0 = 60/1/0.1$). Polymerization conditions: MA = 1 mL, NMP = 0.4 mL, water = 0.1 ml using 9.0 cm of nonactivated Cu(0) wire 20-

gauge wire. The signals at 7.26 ppm and 5.30 ppm are due to partially nondeuterated residue of CDCl_3 and dichloromethane, respectively.

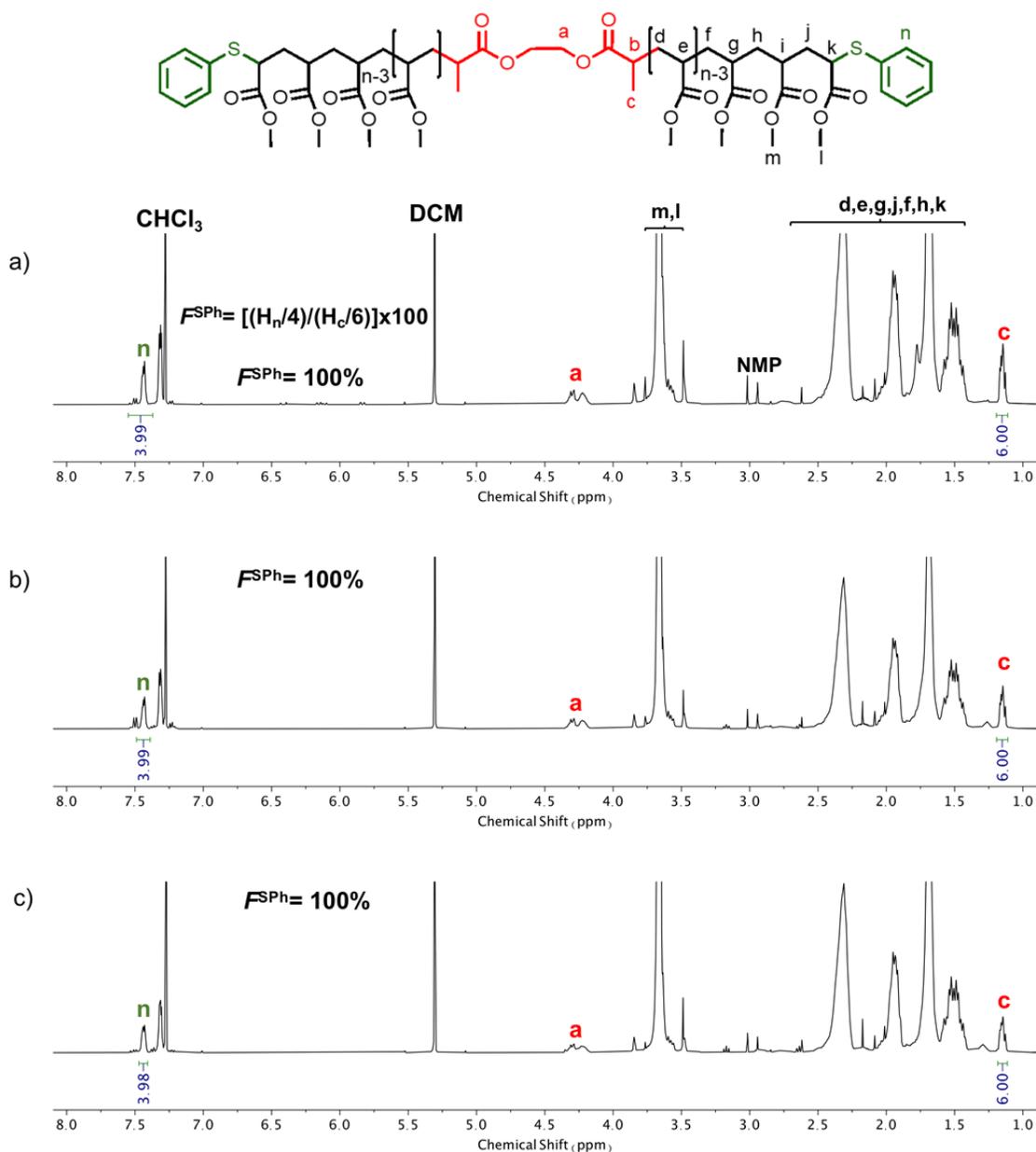
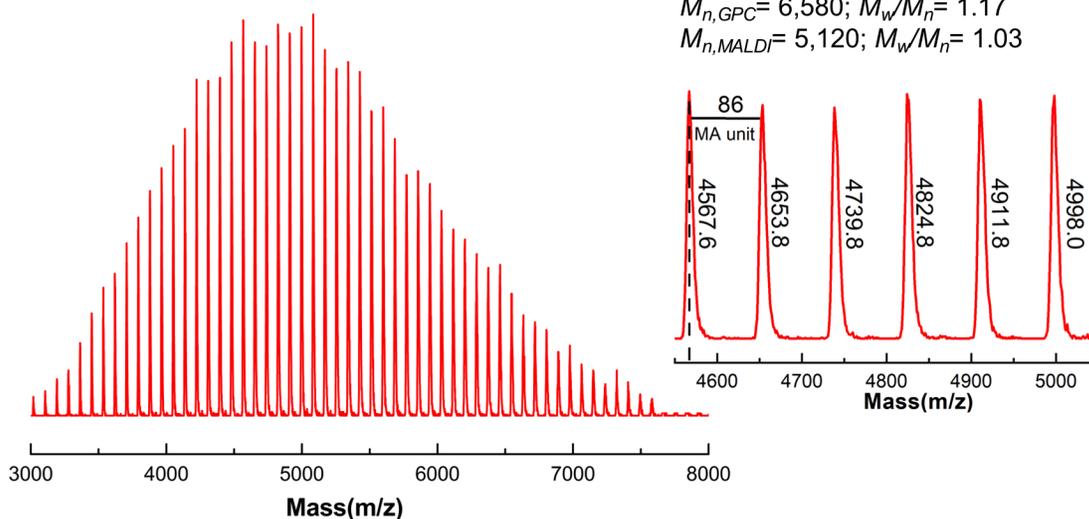


Figure S12. ^1H NMR spectra at 400 MHz of α,ω -di(phenylthio)PMA at (a) 98% monomer conversion ($M_n = 7,340$ and $M_w/M_n = 1.17$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0 = 60/1/0.1$); (b) 98% monomer conversion ($M_n = 5,890$ and $M_w/M_n = 1.29$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0/[\text{TREN}]_0 = 60/1/0.05/0.05$); (c) 99% monomer conversion ($M_n = 7,400$ and $M_w/M_n = 1.35$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{TREN}]_0 = 60/1/0.1$). Polymerization conditions: MA = 1 mL, NMP = 0.4 mL, water = 0.1 ml using 9.0 cm of nonactivated Cu(0) wire 20-gauge wire. The signals at 7.26 ppm and 5.30 ppm are due to partially nondeuterated residue of CDCl_3 and dichloromethane, respectively.

a) PMA before thioetherification

Conversion = 98%
 $M_{th} = 5,390$
 $M_{n,GPC} = 6,580$; $M_w/M_n = 1.17$
 $M_{n,MALDI} = 5,120$; $M_w/M_n = 1.03$



b) PMA after thioetherification

Conversion = 98 %
 $M_{th} = 5,390$
 $M_{n,GPC} = 7,340$; $M_w/M_n = 1.17$
 $M_{n,MALDI} = 5,390$; $M_w/M_n = 1.03$

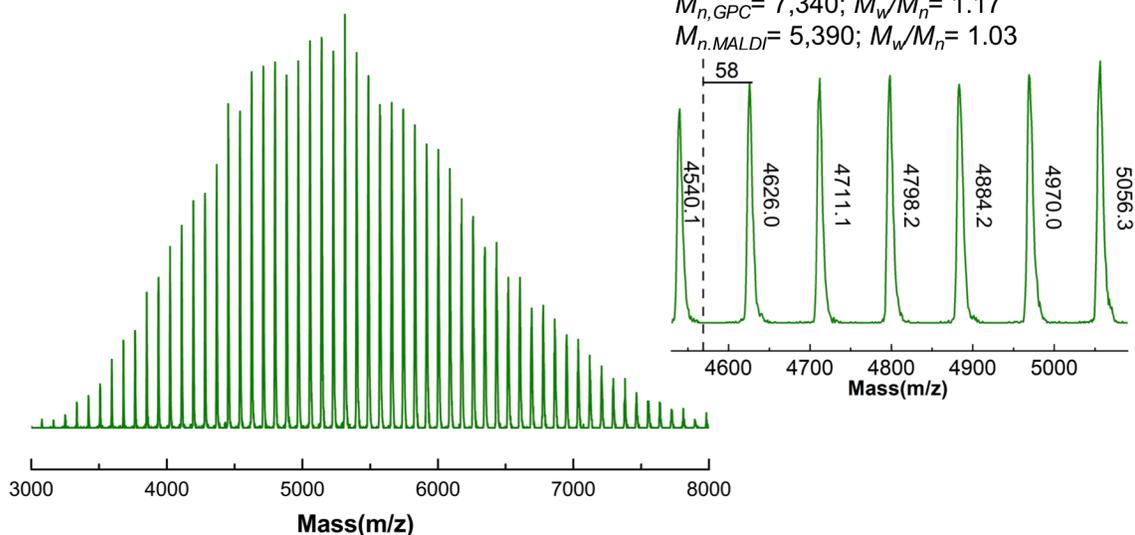


Figure S13. MALDI-TOF of α,ω -di(bromo)PMA isolated at 98% monomer conversion from SET-LRP of MA in NMP/water (8/2, v/v) mixture initiated with BPE and catalyzed by nonactivated Cu(0) wire at 25 °C: (a) before and (b) after “thio-bromo “click”. Polymerization conditions: MA = 1 mL, NMP = 0.4 mL, water = 0.1 ml using 9.0 cm of nonactivated Cu(0) wire 20-gauge wire ($[MA]_0/[BPE]_0/[Me_6-TREN]_0 = 60/1/0.1$). The dotted line in expansion after thioetherification shows the original peak from before thioetherification, while 58 represents the increase in molar mass after thioetherification i.e., $2x[SPh (109.2) - Br (79.9)] = 58.57$ for each chain end.

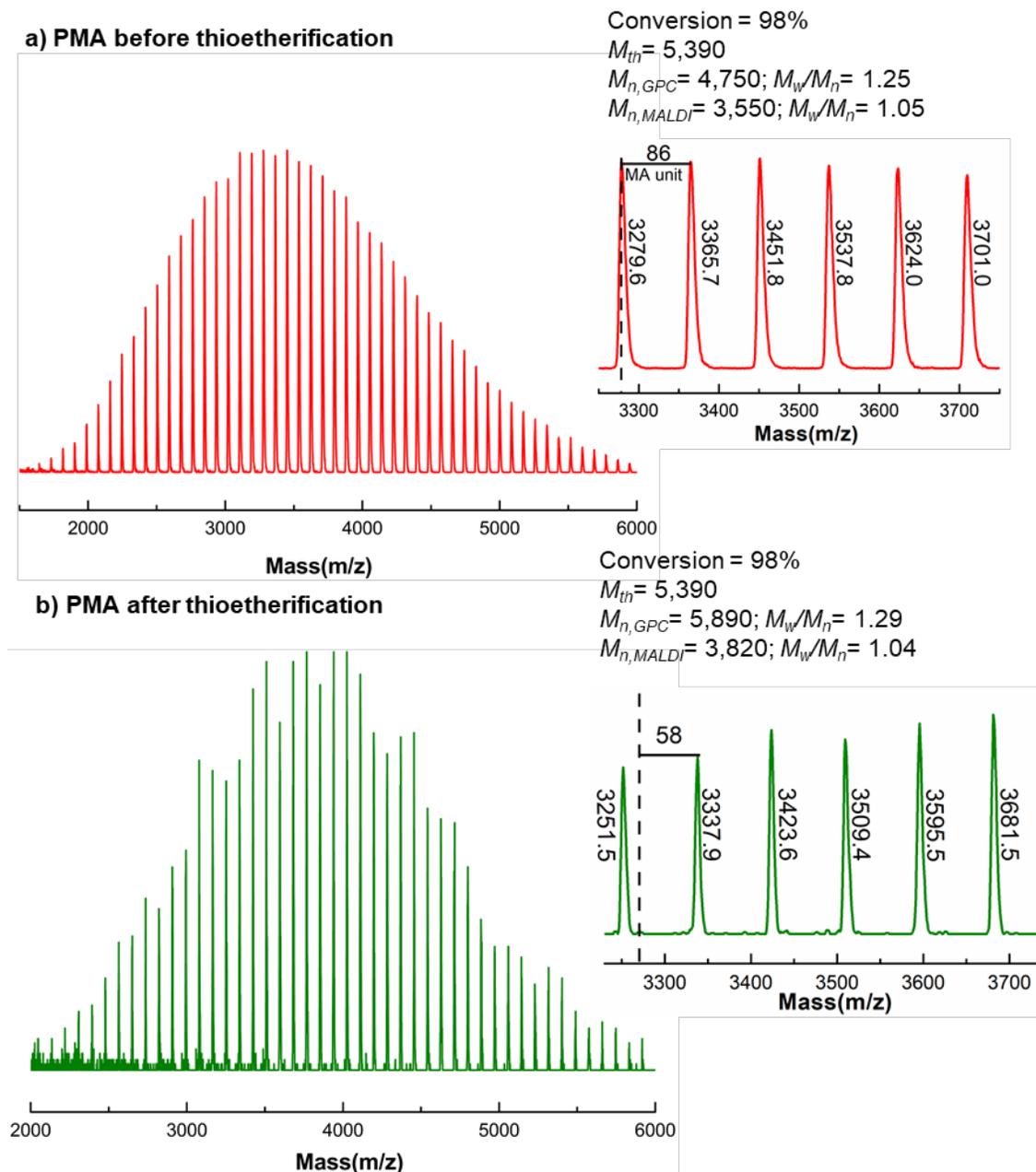


Figure S14. MALDI-TOF of α,ω -di(bromo)PMA isolated at 98% monomer conversion from SET-LRP of MA in NMP/water (8/2, v/v) mixture initiated with BPE and catalyzed by nonactivated Cu(0) wire at 25 °C: (a) before and (b) after “thio-bromo “click”. Polymerization conditions: MA = 1 mL, NMP = 0.4 mL, water = 0.1 ml using 9.0 cm of nonactivated Cu(0) wire 20-gauge wire ($[MA]_0/[BPE]_0/[Me_6-TREN]_0/[TREN]_0 = 60/1/0.05/0.05$). The dotted line in expansion after thioetherification shows the original peak from before thioetherification, while 58 represents the increase in molar mass after thioetherification i.e., $2 \times [SPh (109.2) - Br (79.9)] = 58.57$ for each chain end.

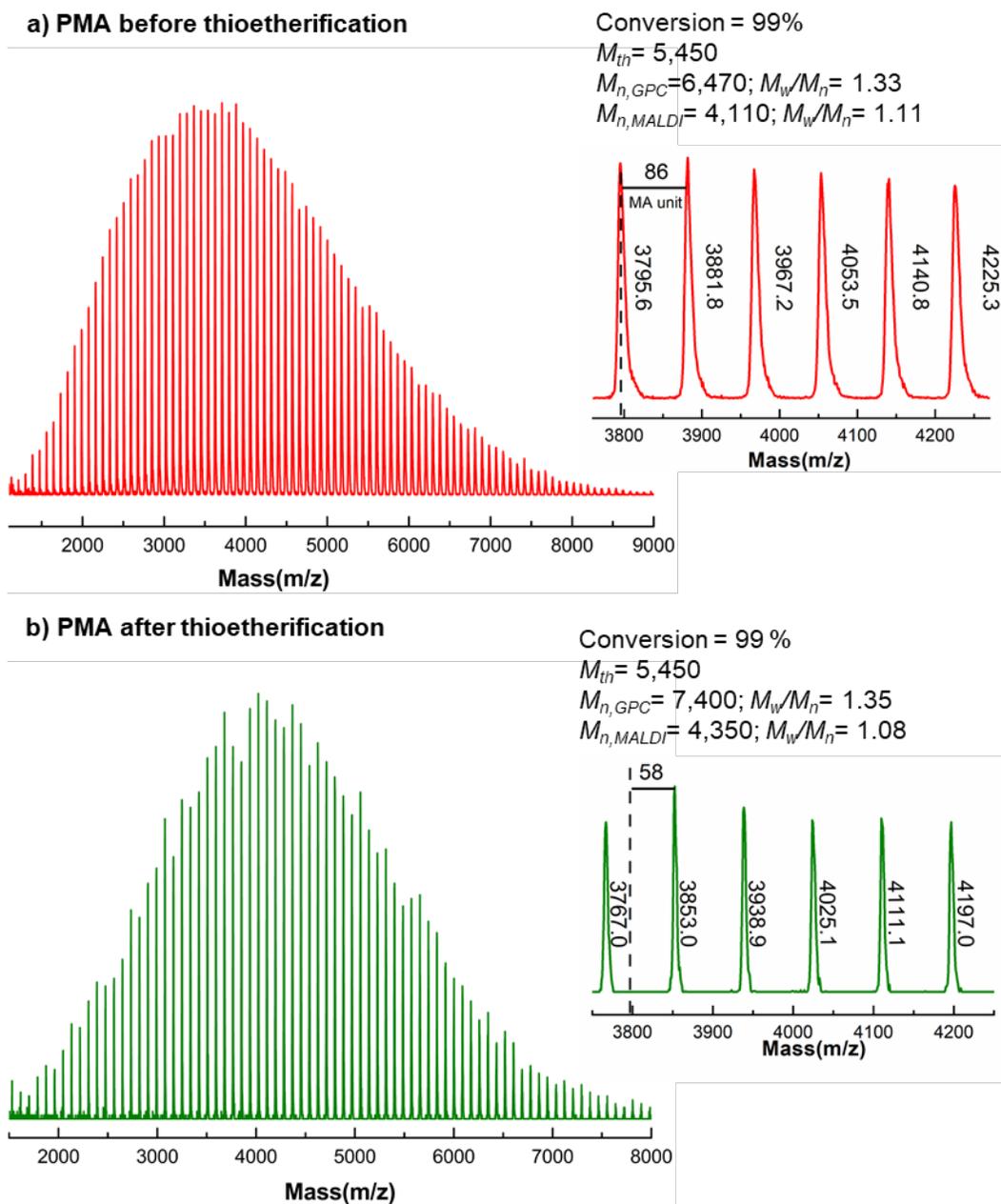


Figure S15. MALDI-TOF of α,ω -di(bromo)PMA isolated at 99% monomer conversion from SET-LRP of MA in NMP/water (8/2, v/v) mixture initiated with BPE and catalyzed by nonactivated Cu(0) wire at 25 °C: (a) before and (b) after “thio-bromo “click”. Polymerization conditions: MA = 1 mL, NMP = 0.4 mL, water = 0.1 ml using 9.0 cm of nonactivated Cu(0) wire 20-gauge wire ($[MA]_0/[BPE]_0/[TREN]_0 = 60/1/0.1$). The dotted line in expansion after thioetherification shows the original peak from before thioetherification, while 58 represents the increase in molar mass after thioetherification i.e., $2x[SPH (109.2) - Br (79.9)] = 58.57$ for each chain end.

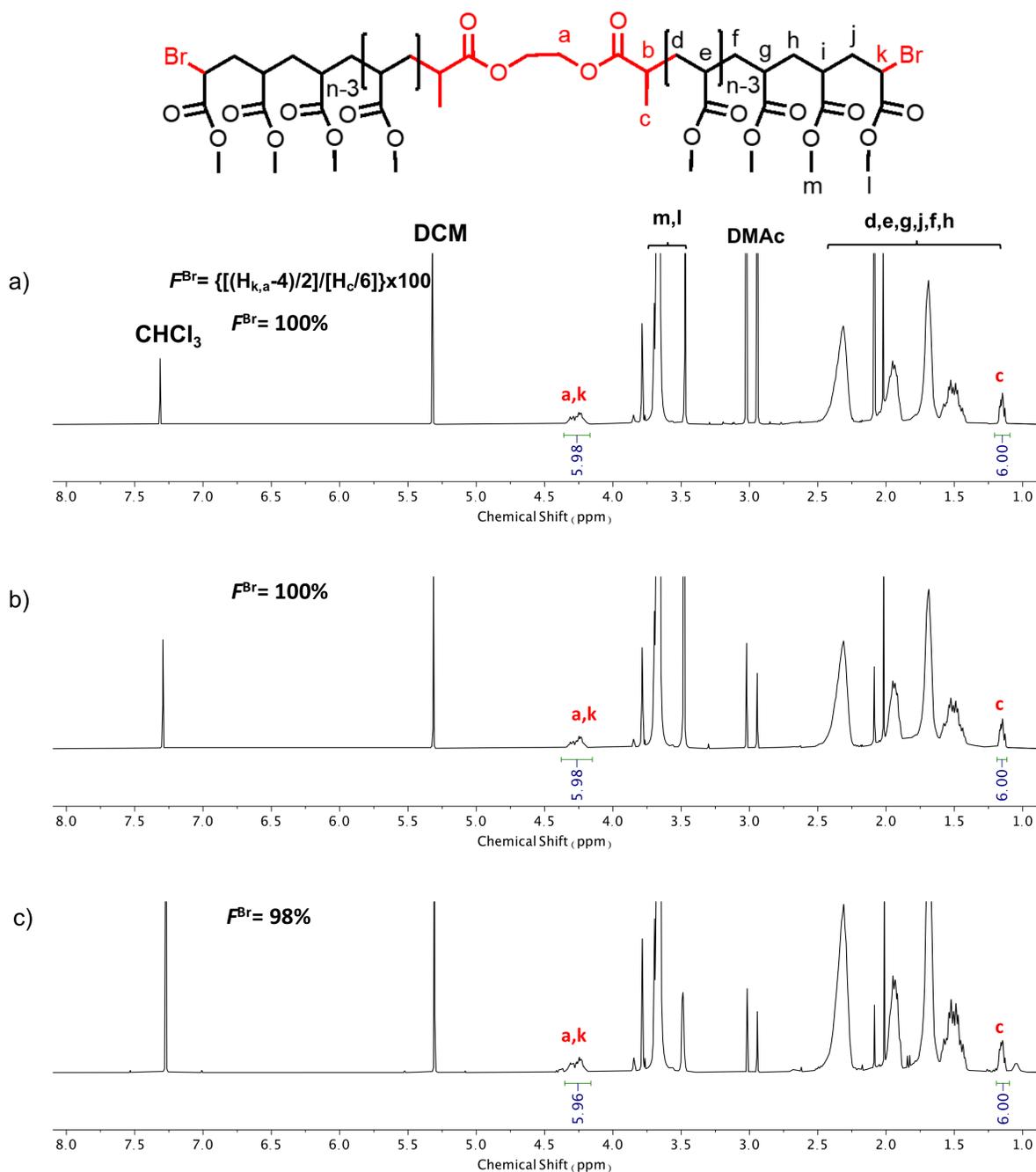


Figure S16. ^1H NMR spectra at 400 MHz of α,ω -di(bromo)PMA at (a) 96% monomer conversion ($M_n = 6,280$ and $M_w/M_n = 1.16$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0 = 60/1/0.1$); (b) 98% monomer conversion ($M_n = 6,150$ and $M_w/M_n = 1.29$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0/[\text{TREN}]_0 = 60/1/0.05/0.05$); (c) 83% monomer conversion ($M_n = 4,870$ and $M_w/M_n = 1.95$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{TREN}]_0 = 60/1/0.1$). Polymerization conditions: MA = 1 mL, DMAc = 0.4 mL, water = 0.1 ml using 9.0 cm of nonactivated Cu(0) wire 20-gauge wire. The signals at 7.26 ppm and 5.30 ppm are due to partially nondeuterated residue of CDCl_3 and dichloromethane, respectively.

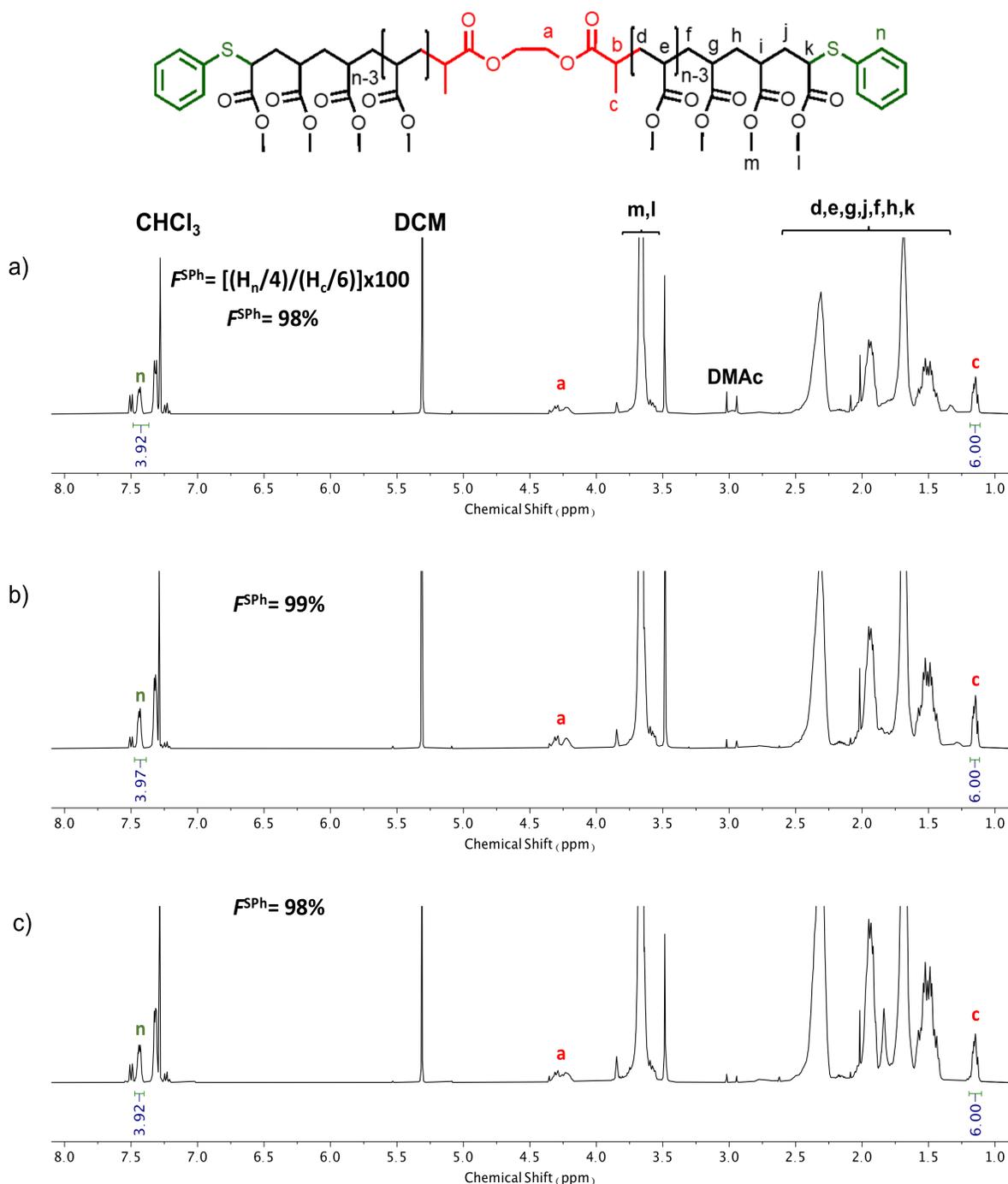


Figure S17. ^1H NMR spectra at 400 MHz of α,ω -di(phenylthio)PMA at (a) 96% monomer conversion ($M_n = 6,460$ and $M_w/M_n = 1.17$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0 = 60/1/0.1$); (b) 98% monomer conversion ($M_n = 6,560$ and $M_w/M_n = 1.30$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0/[\text{TREN}]_0 = 60/1/0.05/0.05$); (c) 83% monomer conversion ($M_n = 7,380$ and $M_w/M_n = 1.69$) ($[\text{MA}]_0/[\text{BPE}]_0/[\text{TREN}]_0 = 60/1/0.1$). Polymerization conditions: MA = 1 mL, DMAc = 0.4 mL, water = 0.1 ml using 9.0 cm of nonactivated Cu(0) wire 20-gauge wire. The signals at 7.26 ppm and 5.30 ppm are due to partially nondeuterated residue of CDCl_3 and dichloromethane, respectively.

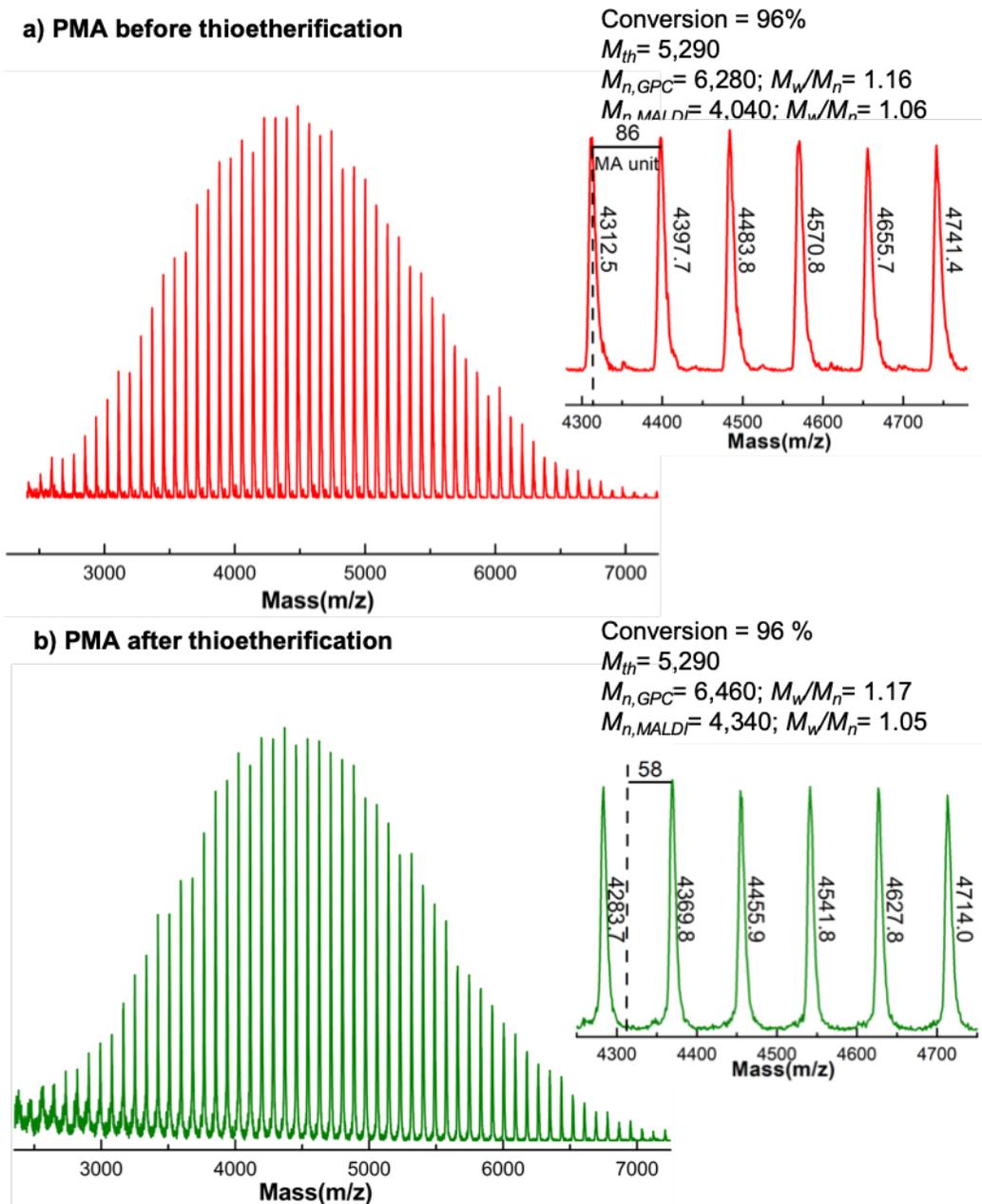


Figure S18. MALDI-TOF of α,ω -di(bromo)PMA isolated at 96% monomer conversion from SET-LRP of MA in DMAc/water (8/2, v/v) mixture initiated with BPE and catalyzed by nonactivated Cu(0) wire at 25 °C: (a) before and (b) after “thio-bromo “click”. Polymerization conditions: MA = 1 mL, DMAc = 0.4 mL, water = 0.1 ml using 9.0 cm of nonactivated Cu(0) wire 20-gauge wire ($[MA]_0/[BPE]_0/[Me_6-TREN]_0 = 60/1/0.1$). The dotted line in expansion after thioetherification shows the original peak from before thioetherification, while 58 represents the increase in molar mass after thioetherification i.e., $2x[SPh (109.2) - Br (79.9)] = 58.57$ for each chain end.

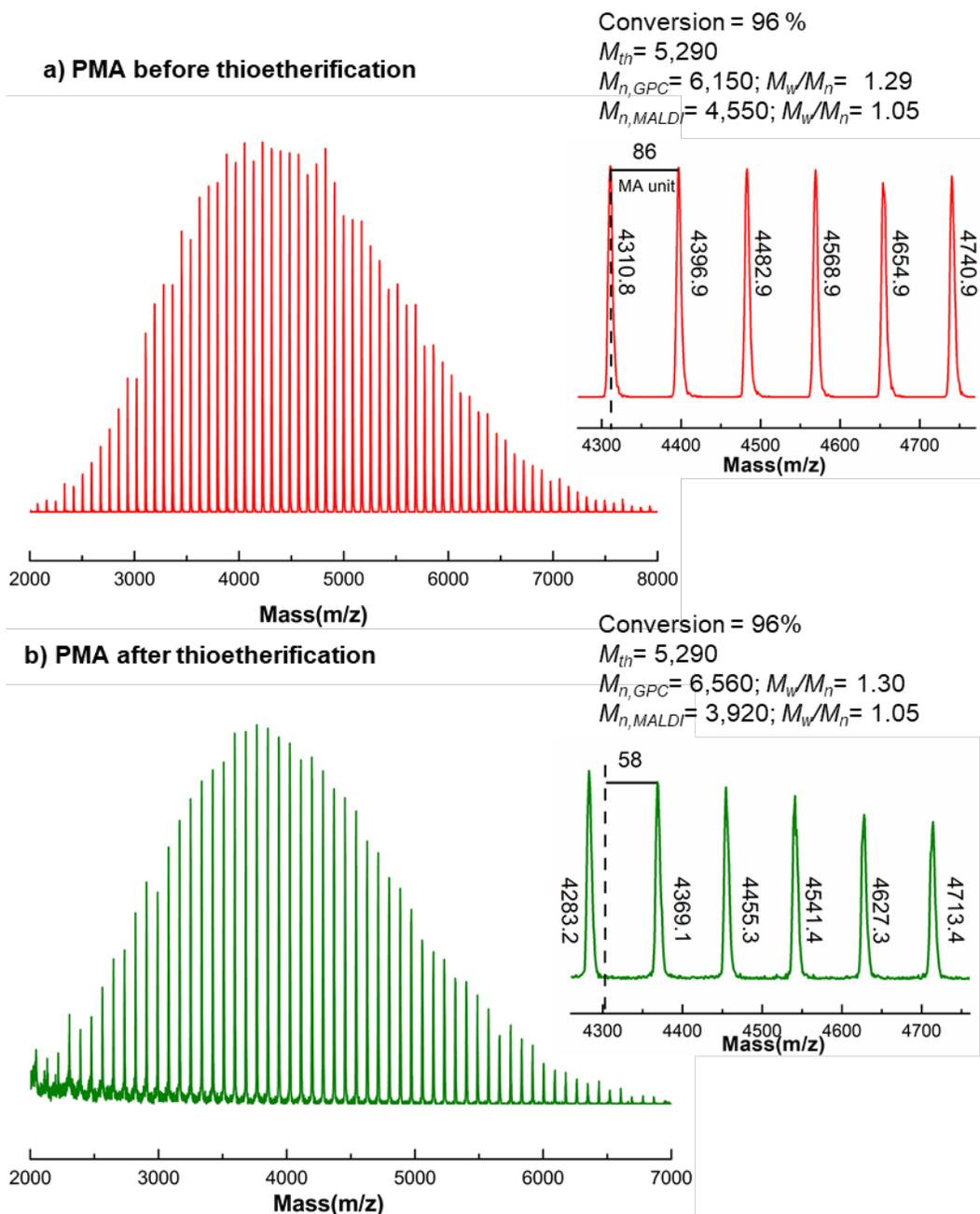


Figure S19. MALDI-TOF of α,ω -di(bromo)PMA isolated at 96% monomer conversion from SET-LRP of MA in DMAc/water (8/2, v/v) mixture initiated with BPE and catalyzed by nonactivated Cu(0) wire at 25 °C: (a) before and (b) after “thio-bromo “click”. Polymerization conditions: MA = 1 mL, DMAc = 0.4 mL, water = 0.1 ml using 9.0 cm of nonactivated Cu(0) wire 20-gauge wire ($[MA]_0/[BPE]_0/[Me_6-TREN]_0/[TREN]_0 = 60/1/0.05/0.05$). The dotted line in expansion after thioetherification shows the original peak from before thioetherification, while 58 represents the increase in molar mass after thioetherification i.e., $2x[SPh (109.2) - Br (79.9)] = 58.57$ for each chain end.

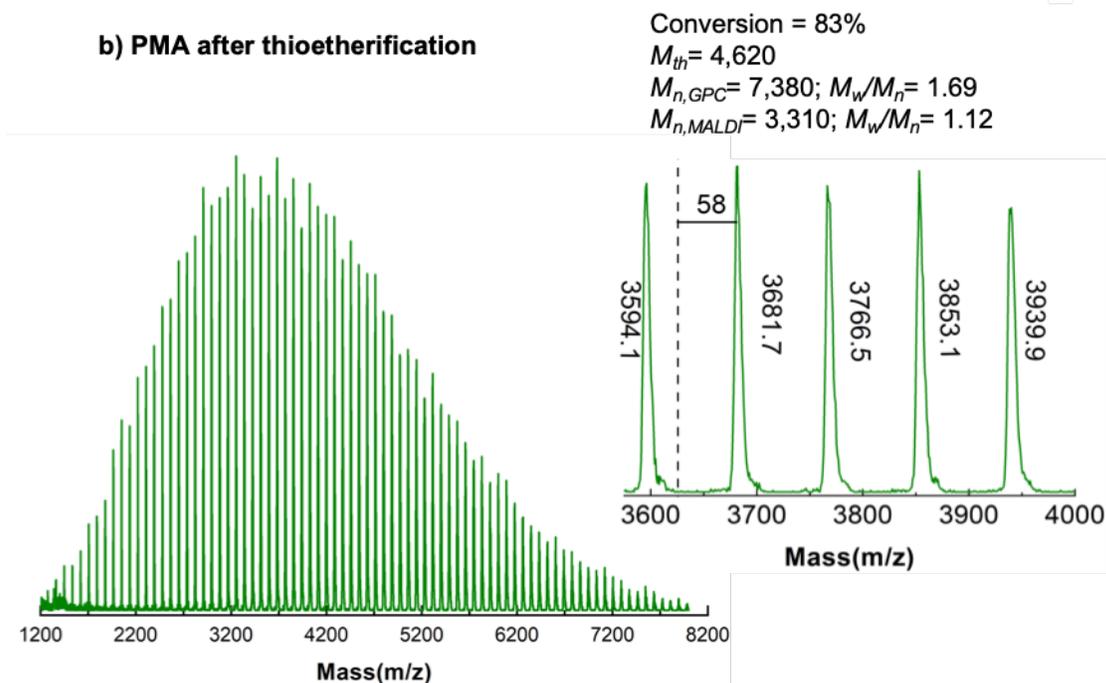
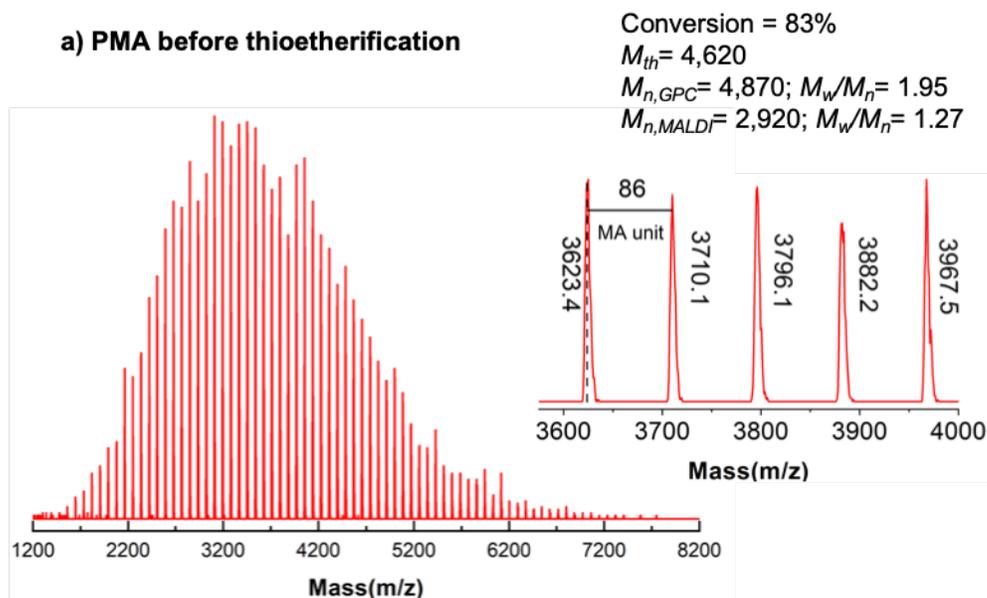


Figure S20. MALDI-TOF of α,ω -di(bromo)PMA isolated at 83% monomer conversion from SET-LRP of MA in DMAc/water (8/2, v/v) mixture initiated with BPE and catalyzed by nonactivated Cu(0) wire at 25 °C: (a) before and (b) after “thio-bromo “click”. Polymerization conditions: MA = 1 mL, DMAc = 0.4 mL, water = 0.1 ml using 9.0 cm of nonactivated Cu(0) wire 20-gauge wire ($[MA]_0/[BPE]_0/[Me_6-TREN]_0 = 60/1/0.1$). The dotted line in expansion after thioetherification shows the original peak from before thioetherification, while 58 represents the increase in molar mass after thioetherification i.e., $2x[SPh(109.2) - Br(79.9)] = 58.57$ for each chain end.

4. Summary of SET-LRP of MA

Table S1. Dependence of k_p^{app} on the Dimension of the Cu(0) Wire in the SET-LRP of MA Initiated with BPE in DMF/water(8/2,v/v) at 25 °C^a

entry	Wire length (cm)	Reaction conditions	k_p^{app} (min ⁻¹)	$k_p^{app}/k_p^{app}(\text{TREN})$	M_w/M_n	$I_{eff}(\%)$
1	12.5	[MA]/[BPE]/[Me ₆ -TREN] 222/1/0.1	0.079	1.4	1.12	79
2	12.5	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.075/0.025	0.086	1.5	1.14	78
3	12.5	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.05/0.05	0.095	1.6	1.21	78
4	12.5	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.025/0.075	0.084	1.4	1.23	80
5	12.5	[[MA]/[BPE]/[TREN] 222/1/0.1	0.058	1.0	1.36	79
6	9.0	[MA]/[BPE]/[Me ₆ -TREN] 222/1/0.1	0.055	1.0	1.09	76
7	9.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.075/0.025	0.057	1.0	1.08	82
8	9.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.05/0.05	0.082	1.5	1.09	87
9	9.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.025/0.075	0.063	1.1	1.13	78
10	9.0	[[MA]/[BPE]/[TREN] 222/1/0.1	0.055	1.0	1.25	66
11	4.0	[MA]/[BPE]/[Me ₆ -TREN] 222/1/0.1	0.038	1.1	1.14	81
12	4.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.075/0.025	0.044	1.3	1.14	82
13	4.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.05/0.05	0.051	1.4	1.16	86
14	4.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.025/0.075	0.048	1.4	1.28	66
15	4.0	[[MA]/[BPE]/[TREN] 222/1/0.1	0.035	1.0	1.40	51

^aReaction conditions: monomer = 1 mL; solvent + water = 0.5 mL. The v/v ratio must be multiplied by 10 to obtain % solvent/% water. The value of v + v must be divided by 20 to obtain the total volume of solvents, 0.5 mL.

Table S2. Dependence of k_p^{app} on the Dimension of the Cu(0) Wire in the SET-LRP of MA Initiated with BPE in NMP/water(8/2,v/v) at 25 °C^a

entry	Wire length (cm) 20G	Reaction conditions	k_p^{app} (min ⁻¹)	$k_p^{\text{app}}/k_p^{\text{app}}(\text{TREN})$	M_w/M_n	$I_{\text{eff}}(\%)$
1	9.0	[MA]/[BPE]/[Me ₆ -TREN] 222/1/0.1	0.068	1.1	1.08	75
2	9.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.075/0.025	0.078	1.3	1.15	87
3	9.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.05/0.05	0.080	1.3	1.18	85
4	9.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.025/0.075	0.076	1.3	1.21	96
5	9.0	[[MA]/[BPE]/[TREN] 222/1/0.1	0.060	1.0	1.42	77

^aReaction conditions: monomer = 1 mL; solvent + water = 0.5 mL. The v/v ratio must be multiplied by 10 to obtain % solvent/% water. The value of v + v must be divided by 20 to obtain the total volume of solvents, 0.5 mL.

Table S3. Dependence of k_p^{app} on the Dimension of the Cu(0) Wire in the SET-LRP of MA Initiated with BPE in DMAc/water(8/2,v/v) at 25 °C^a

entry	Wire length (cm)	Reaction conditions	k_p^{app} (min ⁻¹)	$k_p^{\text{app}}/k_p^{\text{app}}(\text{TREN})$	M_w/M_n	$I_{\text{eff}}(\%)$
1	9.0	[MA]/[BPE]/[Me ₆ -TREN] 222/1/0.1	0.076	1.1	1.11	78
2	9.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.075/0.025	0.077	1.1	1.16	83
3	9.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.05/0.05	0.091	1.3	1.29	87
4	9.0	[MA]/[BPE]/[Me ₆ -TREN]/[TREN] 222/1/0.025/0.075	0.075	1.0	1.36	87
5	9.0	[[MA]/[BPE]/[TREN] 222/1/0.1	0.071	1.0	2.14	60

^aReaction conditions: monomer = 1 mL; solvent + water = 0.5 mL. The v/v ratio must be multiplied by 10 to obtain % solvent/% water. The value of v + v must be divided by 20 to obtain the total volume of solvents, 0.5 mL.