Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information to

SET-LRP of NIPAM in Water via In Situ Reduction of Cu(II) to Cu(0) with $NaBH_4$.

*Mikhail Gavrilov[1], Timothy J. Zerk[2], Paul V. Bernhardt[2], Virgil Percec[3] and Michael J. Monteiro[1,]**

[1.] Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, St Lucia, Brisbane QLD 4072, Australia.

[2]. School of Chemistry and Molecular Biosciences, The University of Queensland, St Lucia, Brisbane QLD 4072, Australia.

[3]. Roy ans Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 190104-6323.

* To whom correspondence should be addressed. m.monteiro@uq.edu.au

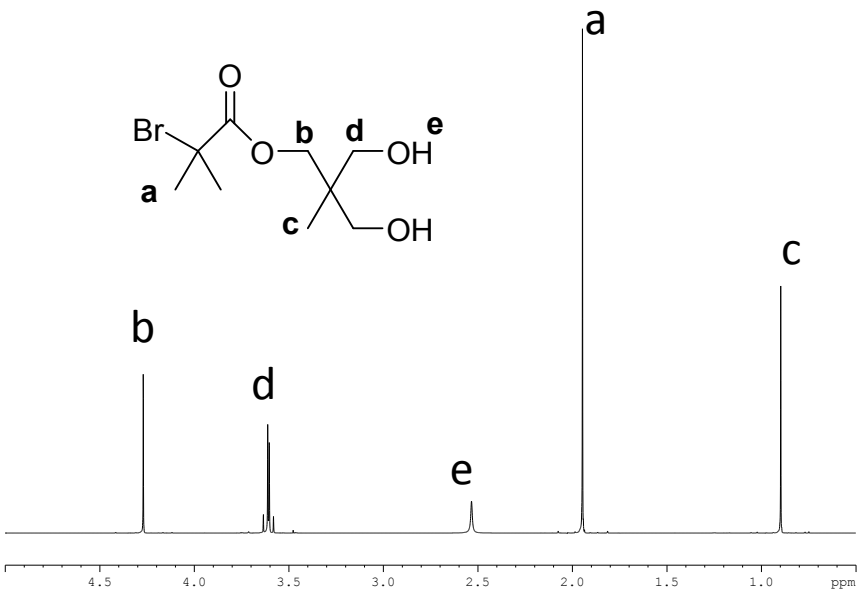

Figure S1. ^{1}H NMR of **11** at 298K (500 MHz), recorded in $CDCl_3$.

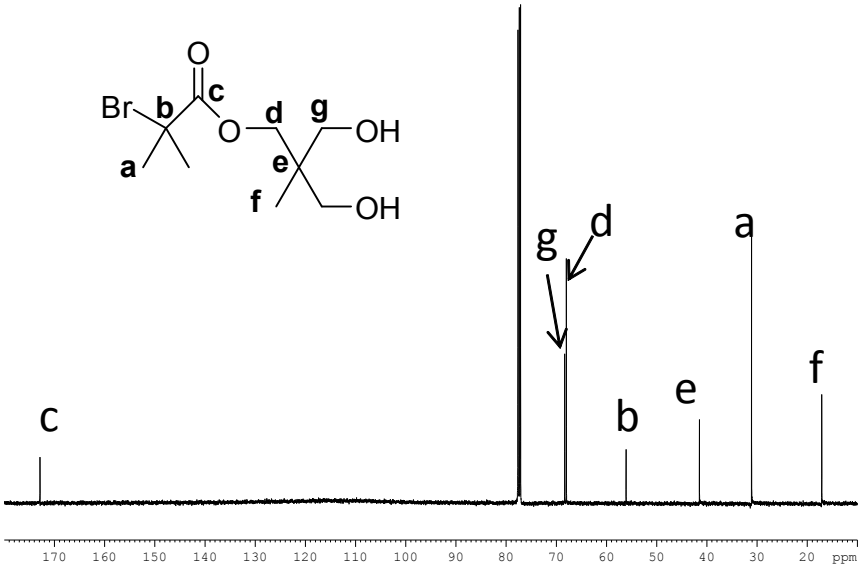

Figure S2. ^{13}C NMR of **11** at 298K (500 MHz), recorded in $CDCl_3$.

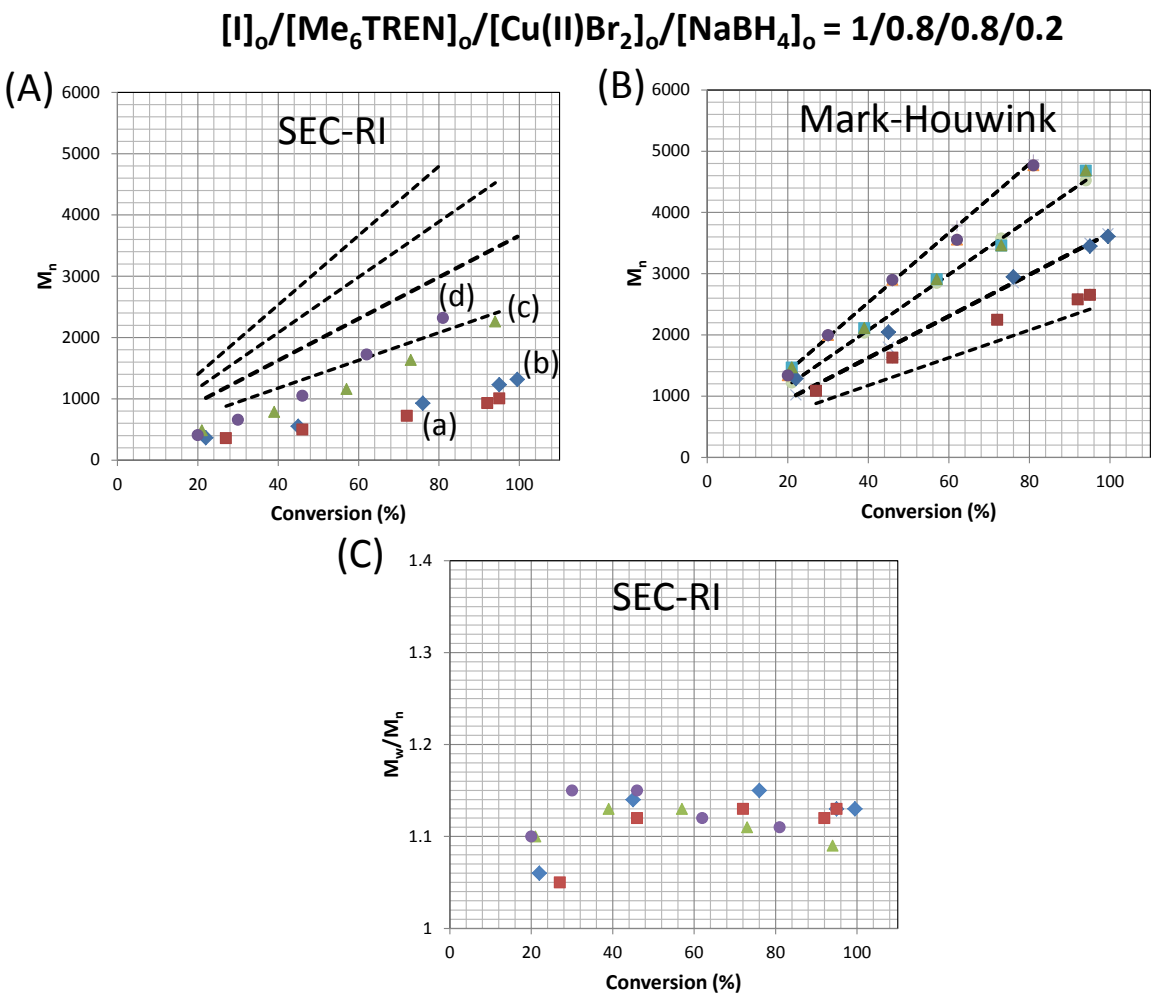

Figure S3. Aqueous SET-LRP of NIPAM catalyzed by the *in situ* generation of Cu(0) from $NaBH_4$ by varying $[NIPAM]_o/[I]_o$ from (a) 20/1 ■, (b) 30/1 ♦, (c) 40/1 ▲, (d) 50/1 ●. (A) M_n determined from SEC using RI and polystyrene standards (dashed lines represent theoretical M_n values). (B) M_n calculated using the Mark-Houwink equation from correlation between SEC and MALDI M_n's, and (C) M_w/M_n values after re-calculation using the Mark-Houwink equation . Reaction conditions: $[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 1/0.8/0.8/0.2. [I]=0.0267 M in 3.48 mL of water.

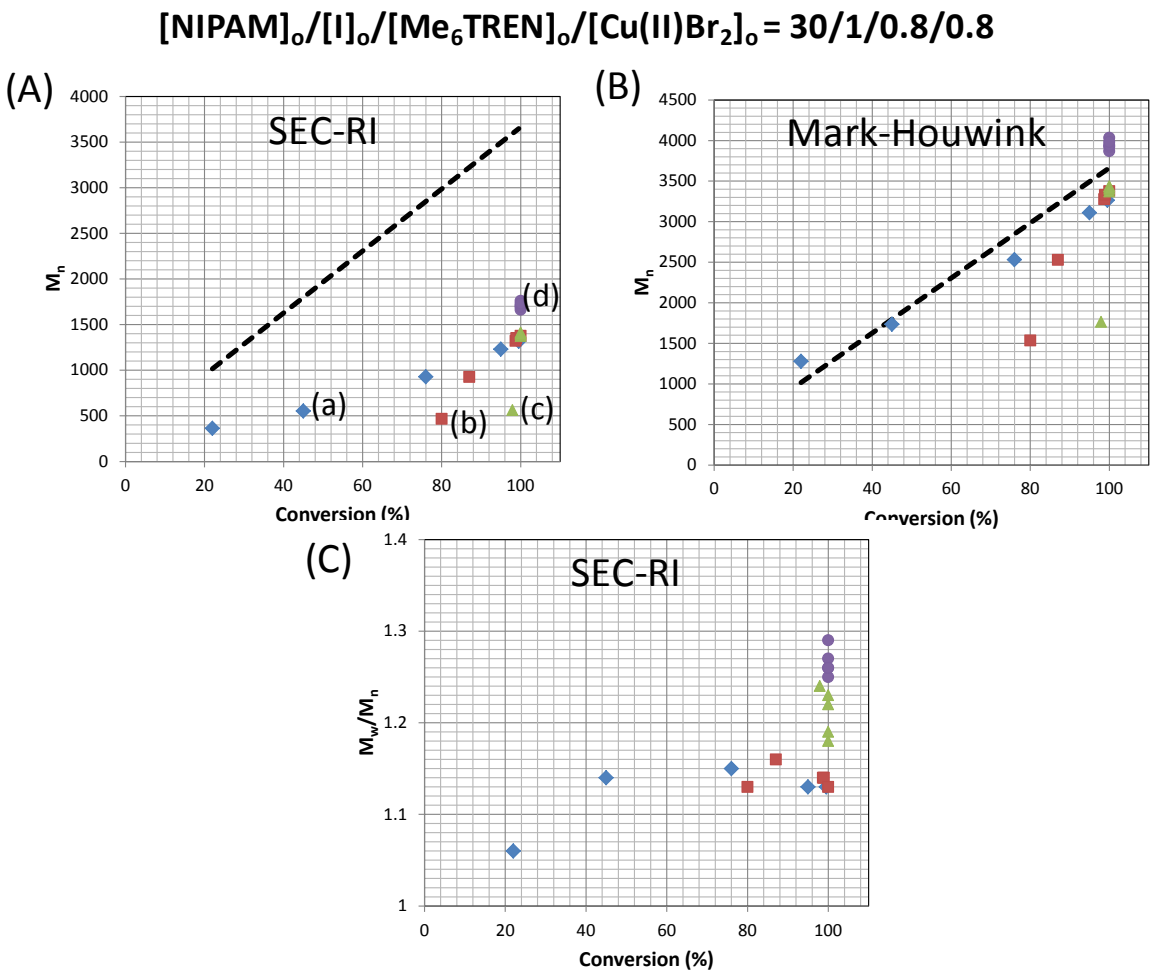

Figure S4. Aqueous SET-LRP of NIPAM catalyzed by the *in situ* generation of Cu(0) from $NaBH_4$ at $[NIPAM]_o/[I]_o = 30$ and varying $[CuBr_2]_o/[NaBH_4]_o$ from (a) 0.8/0.2 ♦, (b) 0.8/0.4 ■, (c) 0.8/0.6 ▲, (d) 0.8/0.8 ●. (A) M_n determined from SEC using RI and polystyrene standards (dashed lines represent theoretical M_n values), (B) M_n calculated using the Mark-Houwink equation and (C) M_w/M_n values from SEC using the Mark-Houwink equation. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o$ = 30/1/0.8/0.8. [I]=0.0267 M in 3.48 mL of water.

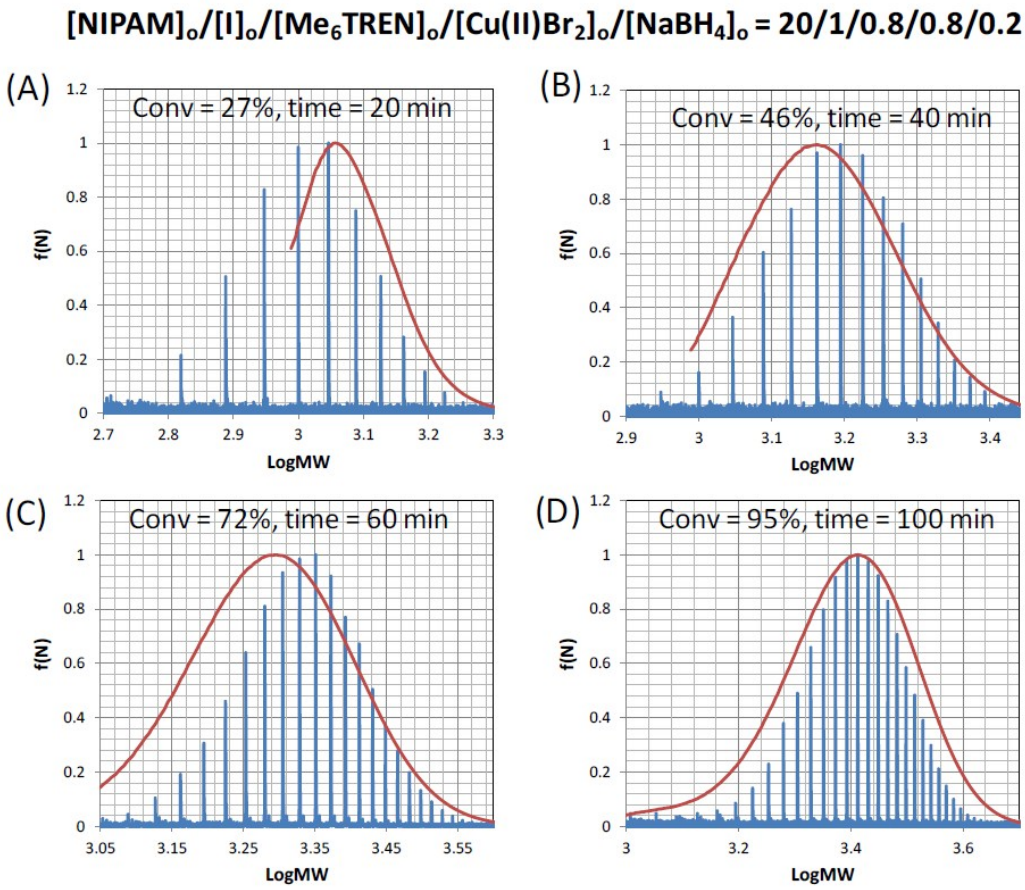

Figure S5. MALDI-ToF and SEC (RI using polystyrene standards, red line) for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 20/1/0.8/0.8/0.2. [I]=0.0267 M in 3.48 mL of water.

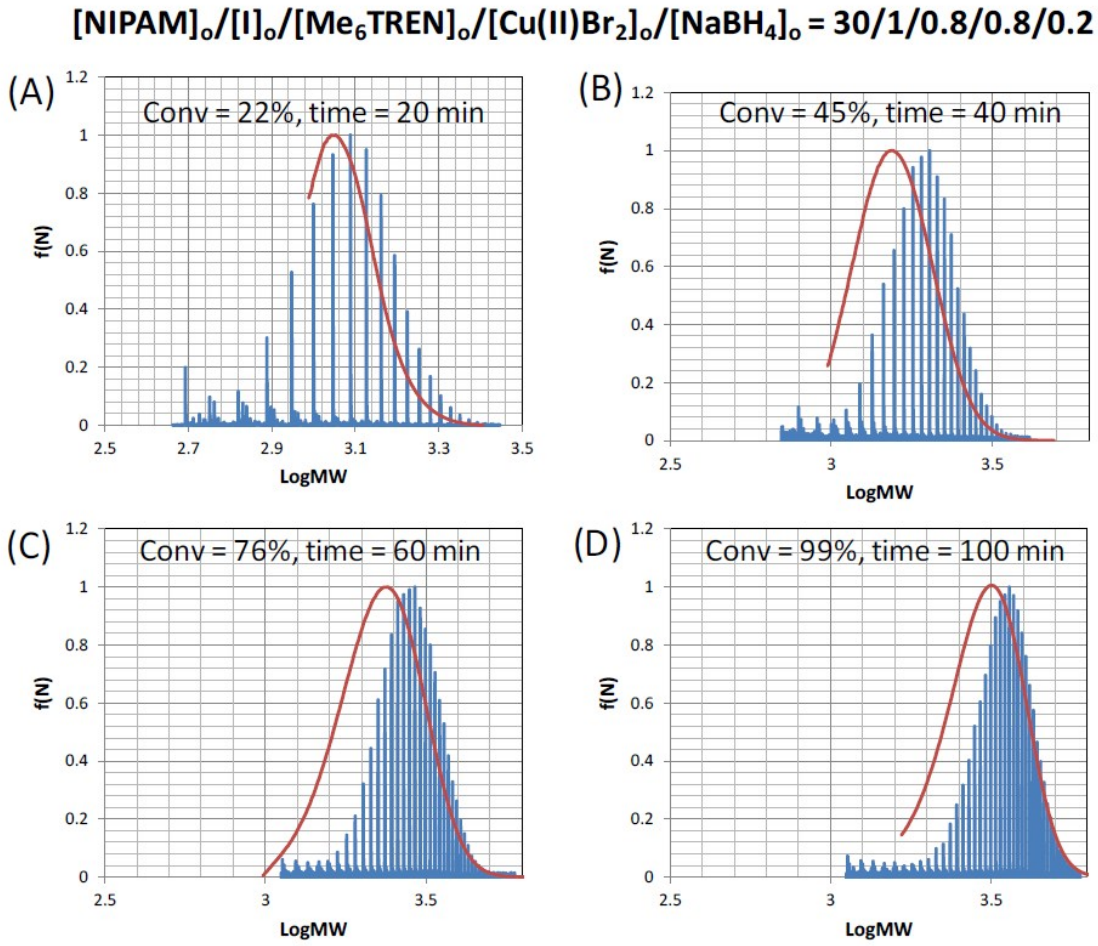

Figure S6. MALDI-ToF and SEC (RI using polystyrene standards, red line) for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 30/1/0.8/0.8/0.2. [I]=0.0267 M in 3.48 mL of water.

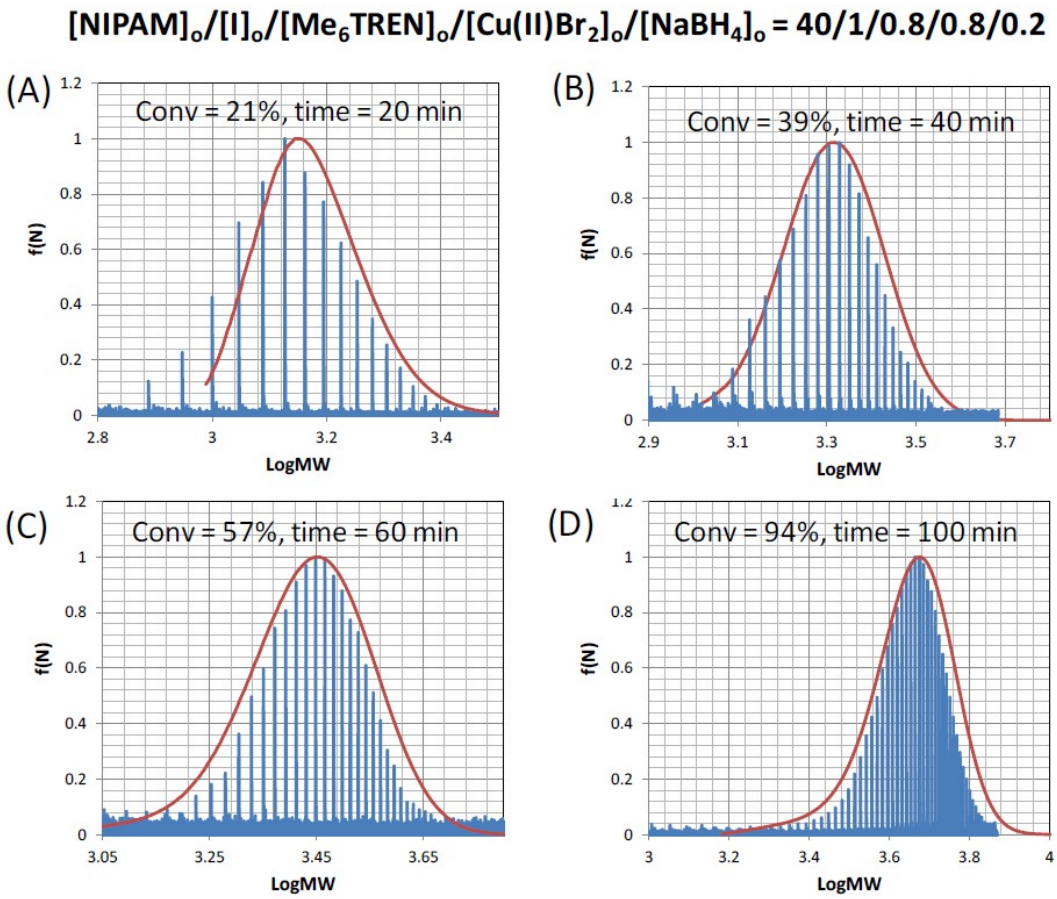

Figure S7. MALDI-ToF and SEC (RI using polystyrene standards, red line) for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 40/1/0.8/0.8/0.2. [I]=0.0267 M in 3.48 mL of water.

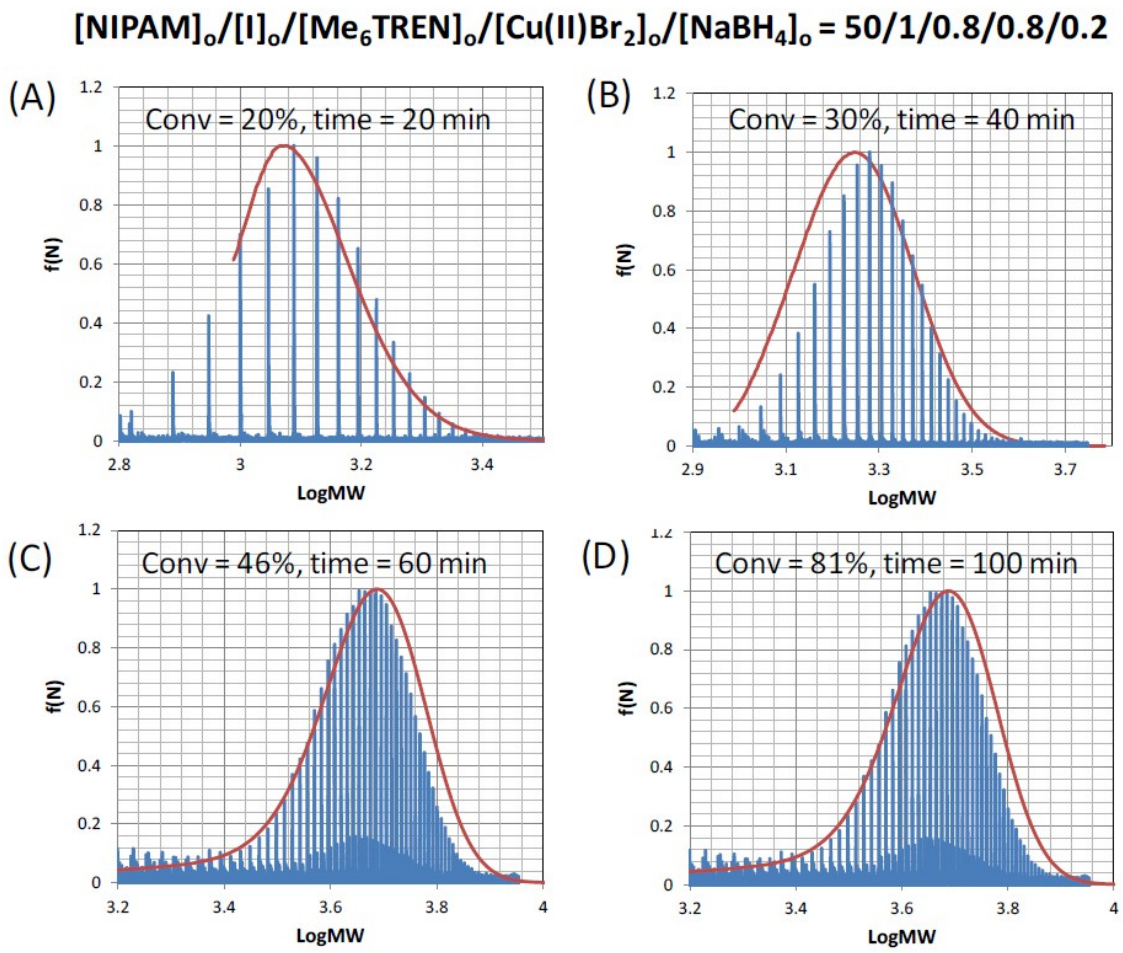

Figure S8. MALDI-ToF and SEC (RI using polystyrene standards, red line) for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 50/1/0.8/0.8/0.2. [I]=0.0267 M in 3.48 mL of water.

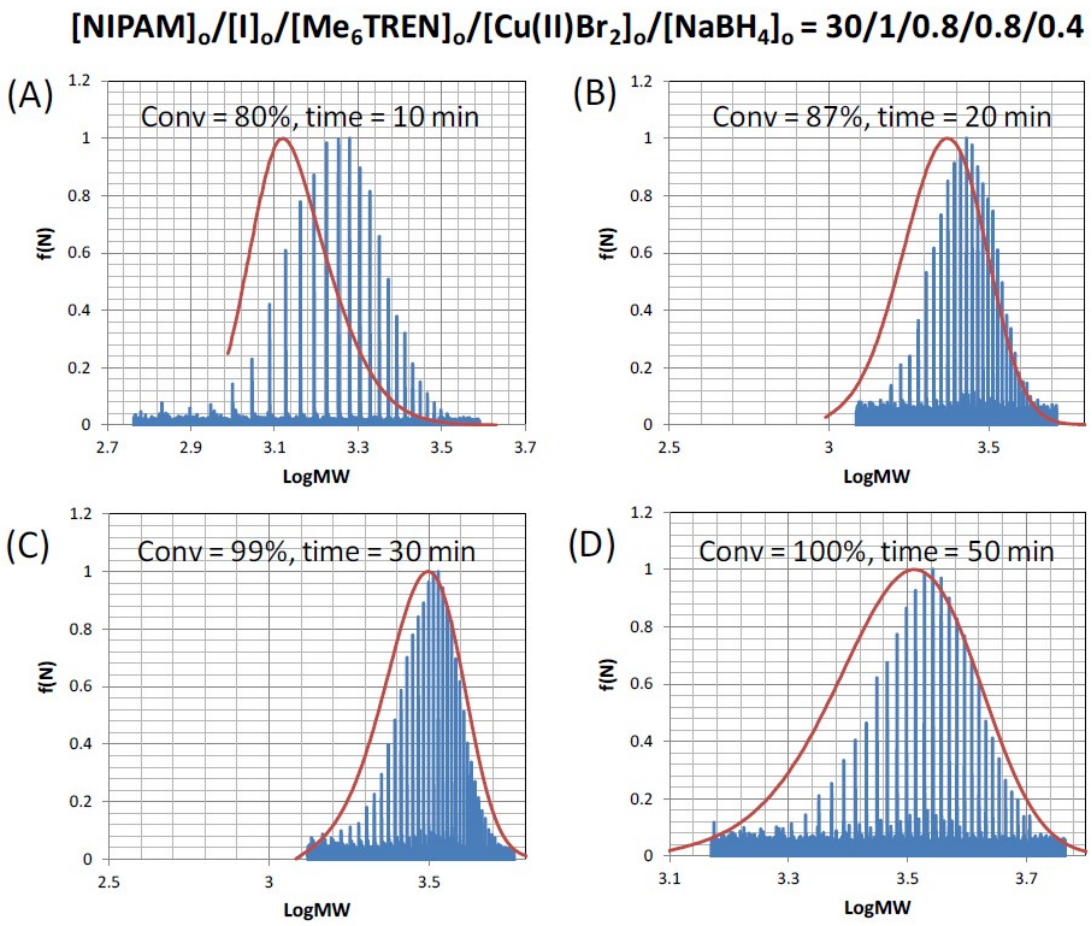

Figure S9. MALDI-ToF and SEC (RI using polystyrene standards, red line) for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 30/1/0.8/0.8/0.4. [I]=0.0267 M in 3.48 mL of water.

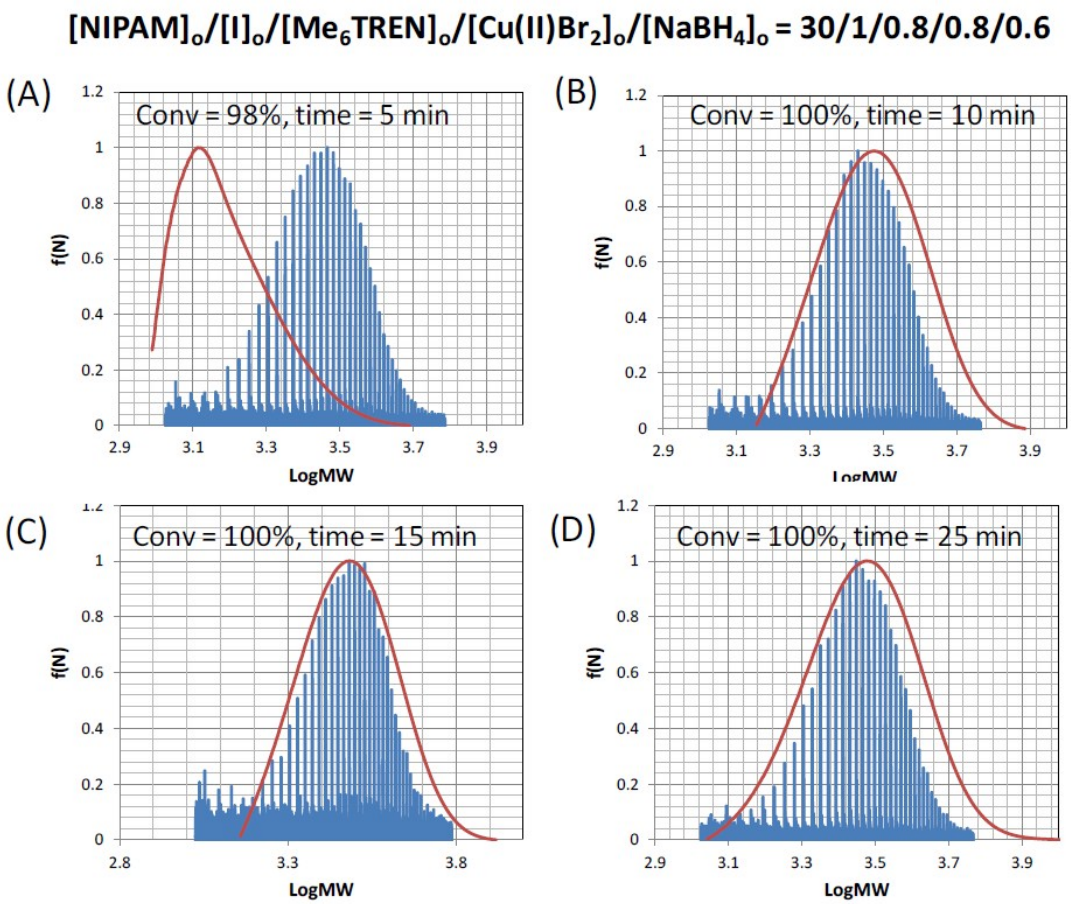

Figure S10. MALDI-ToF and SEC (RI using polystyrene standards, red line) for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 30/1/0.8/0.8/0.6. [I]=0.0267 M in 3.48 mL of water.

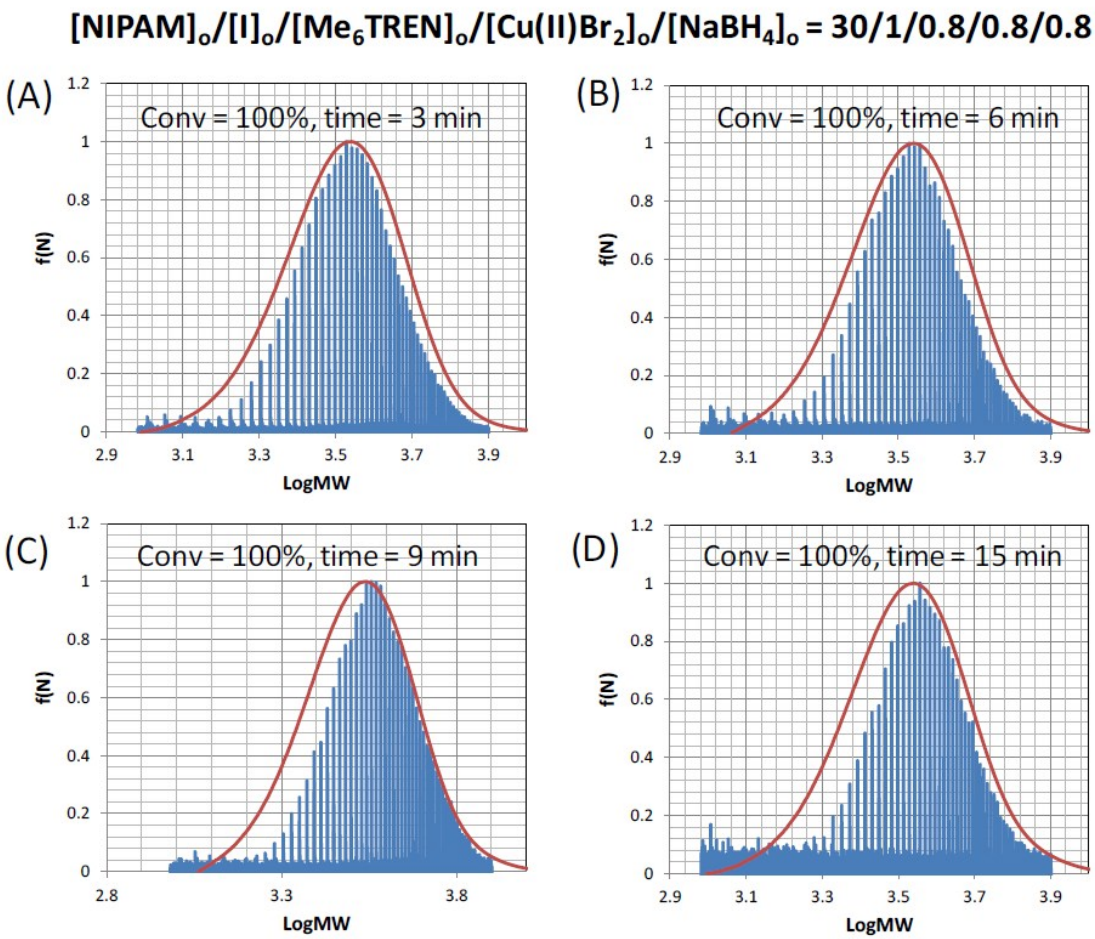

Figure S11. MALDI-ToF and SEC (RI using polystyrene standards, red line) for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 30/1/0.8/0.8/0.8. [I]=0.0267 M in 3.48 mL of water.

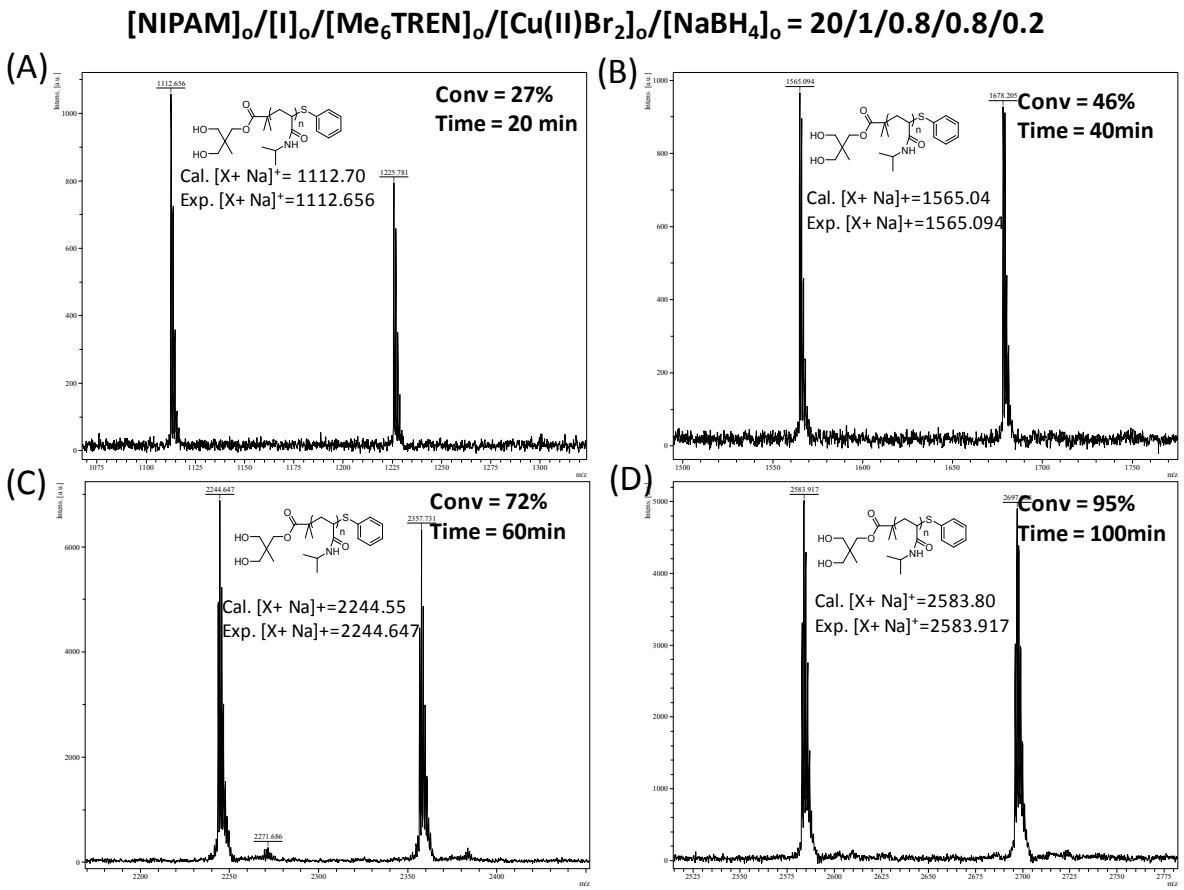

Figure S12. MALDI-ToF for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 20/1/0.8/0.8/0.2. [I]=0.0267 M in 3.48 mL of water.

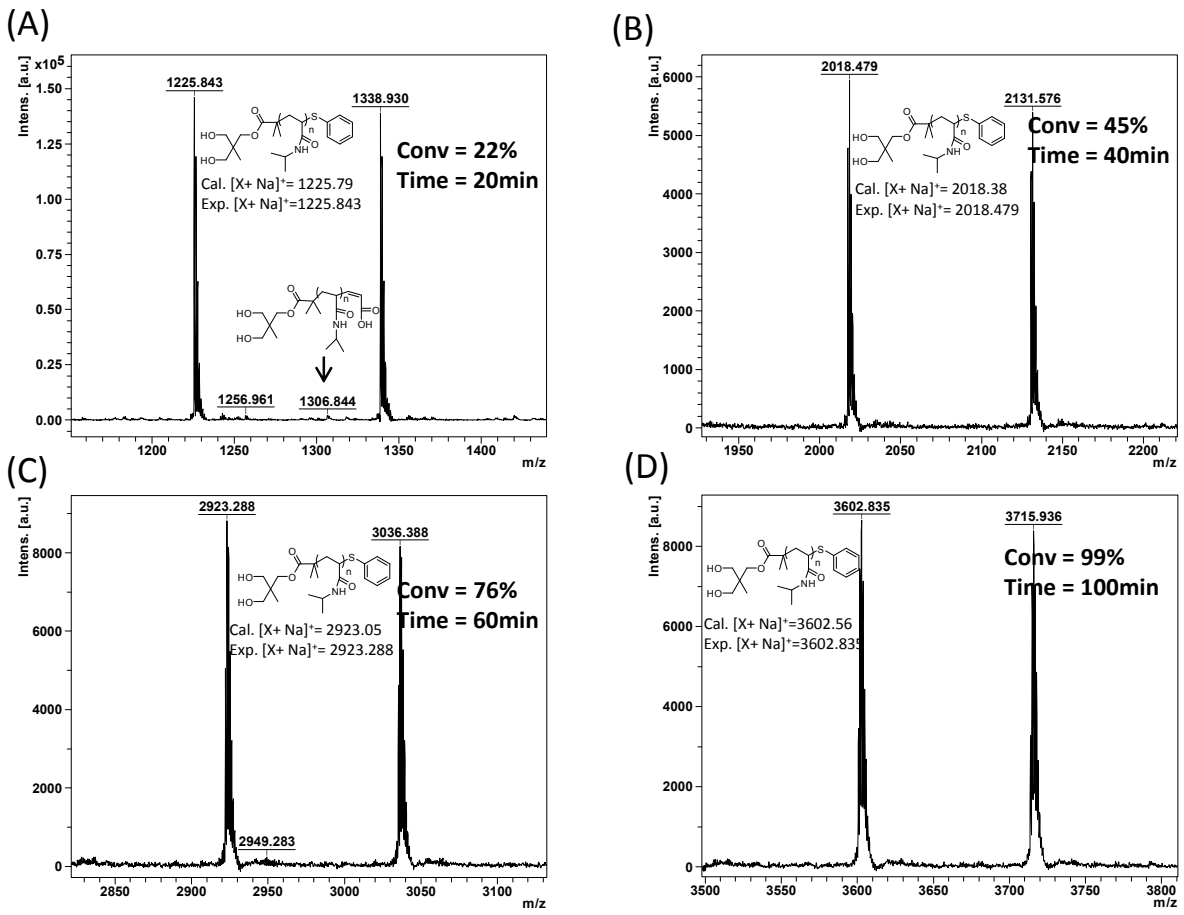

Figure S13. MALDI-ToF for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 30/1/0.8/0.8/0.2. [I]=0.0267 M in 3.48 mL of water.

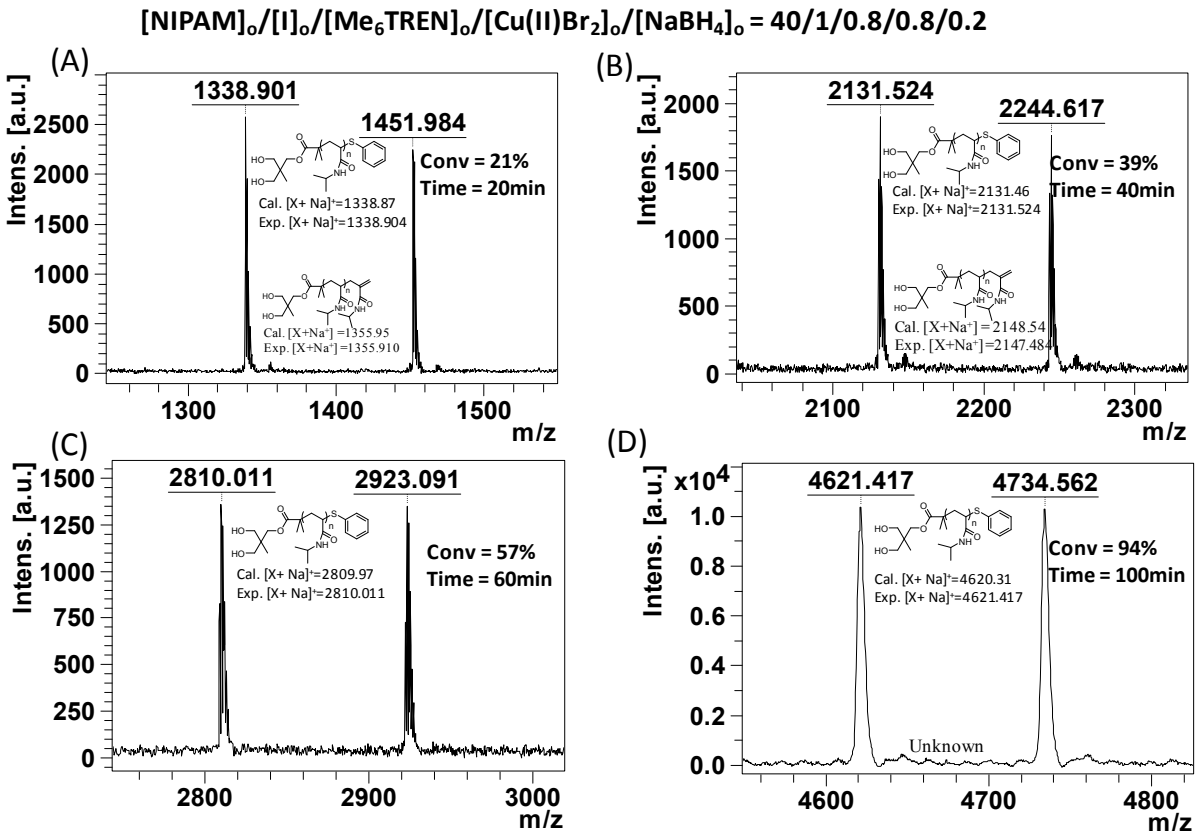

Figure S14. MALDI-ToF for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 40/1/0.8/0.8/0.2. [I]=0.0267 M in 3.48 mL of water.

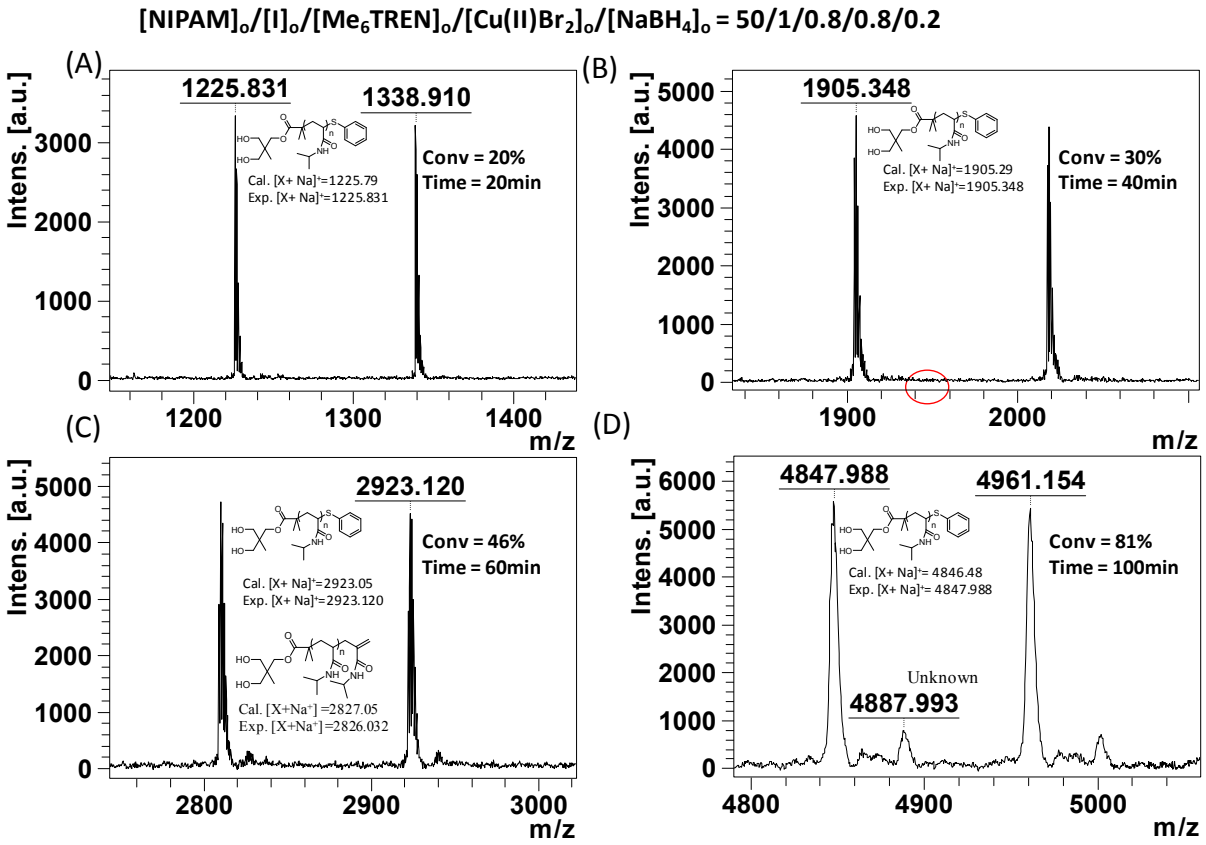

Figure S15. MALDI-ToF for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 50/1/0.8/0.8/0.2. [I]=0.0267 M in 3.48 mL of water.

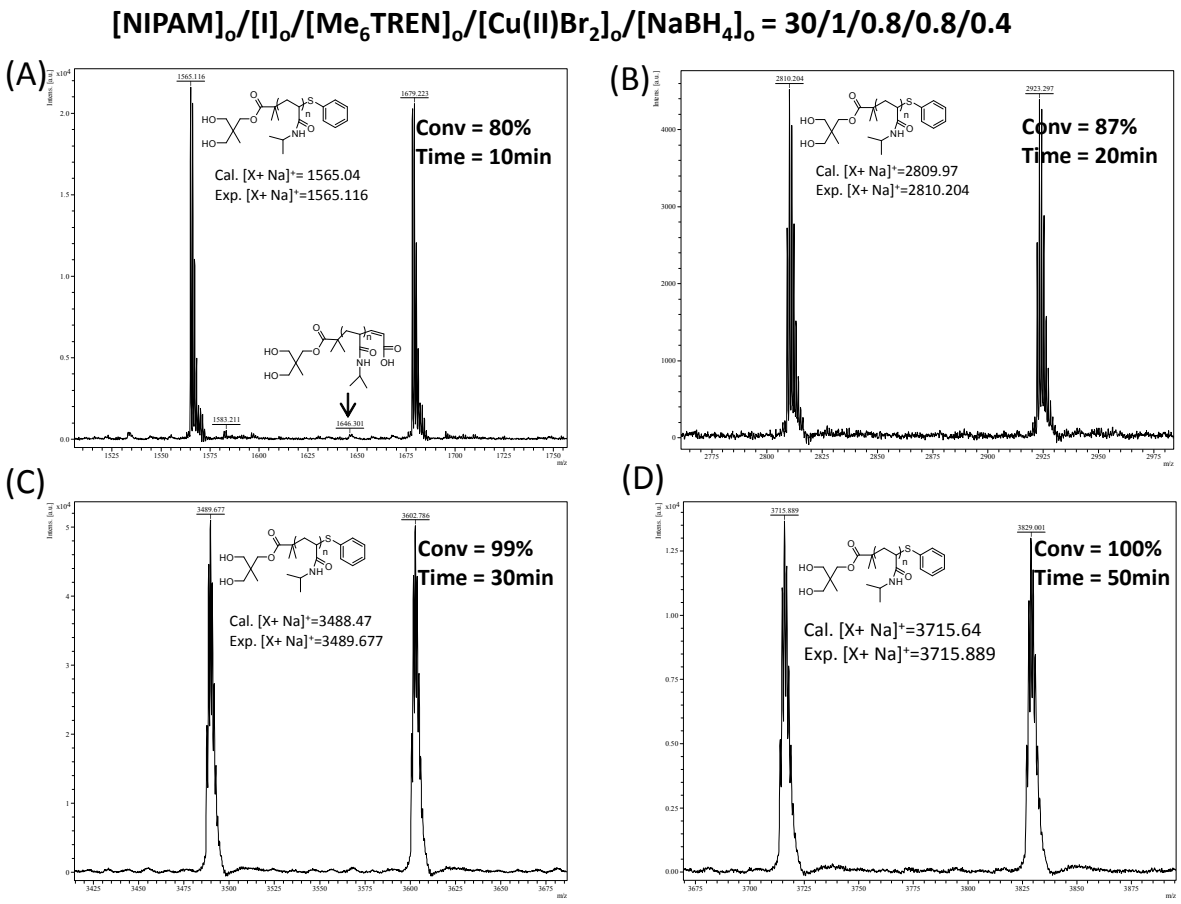

Figure S16. MALDI-ToF for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 30/1/0.8/0.8/0.4. [I]=0.0267 M in 3.48 mL of water.

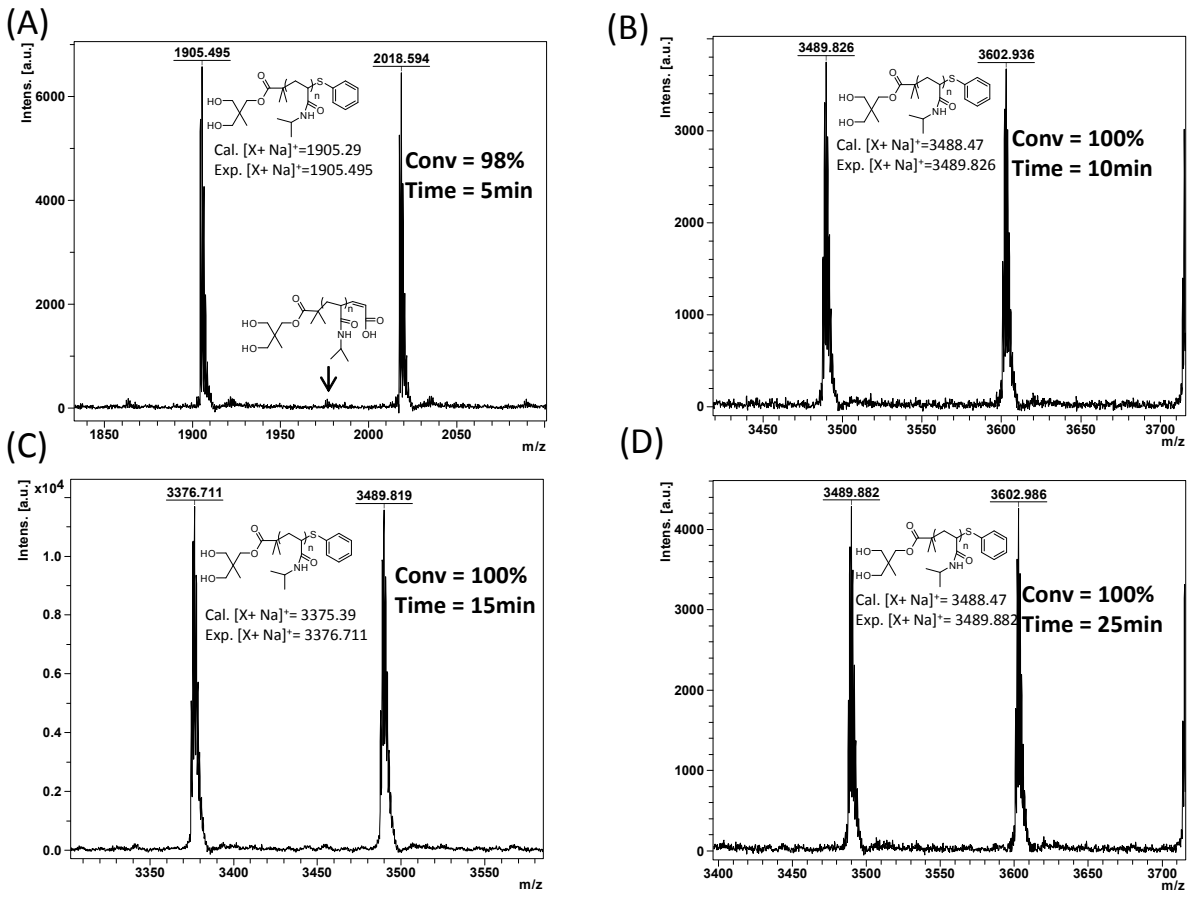

Figure S17. MALDI-ToF for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 30/1/0.8/0.8/0.6. [I]=0.0267 M in 3.48 mL of water.

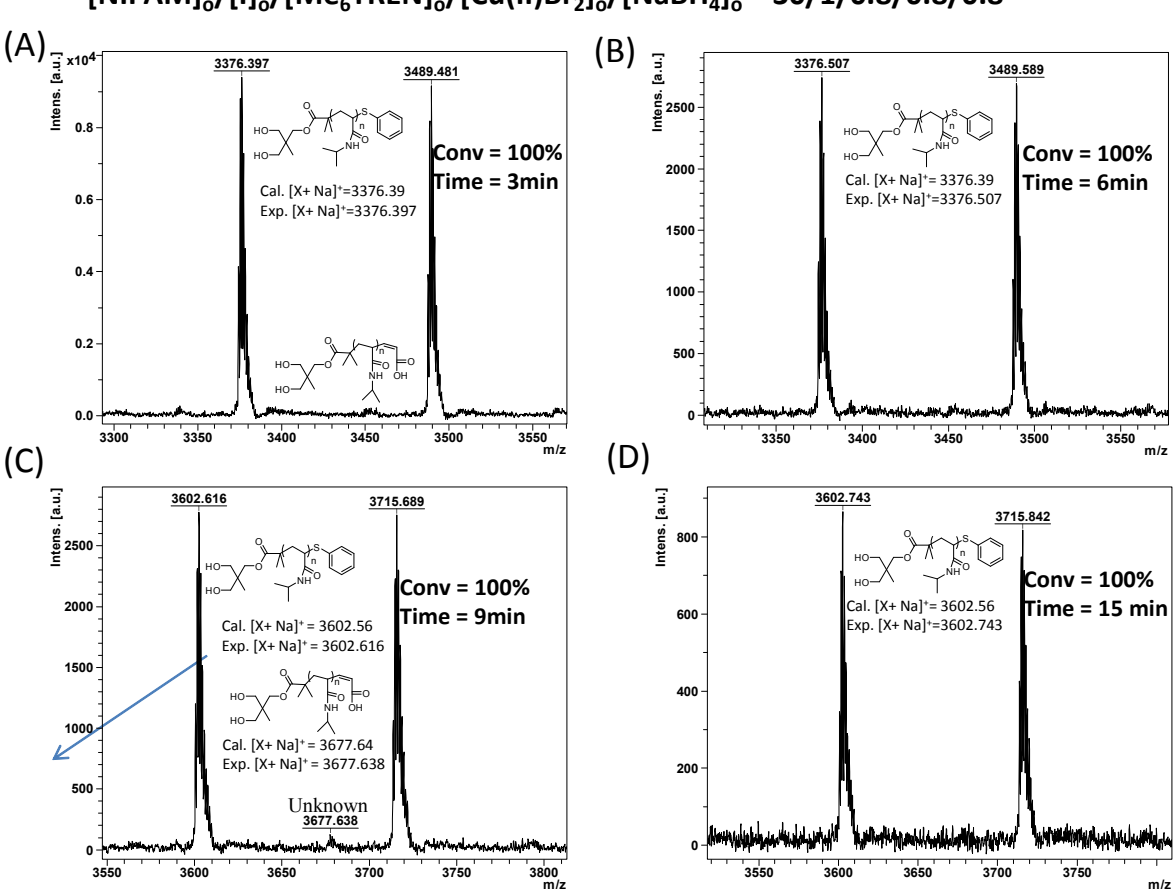

Figure S18. MALDI-ToF for the aqueous SET-LRP of NIPAM over the conversion range. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 30/1/0.8/0.8/0.8. [I]=0.0267 M in 3.48 mL of water.

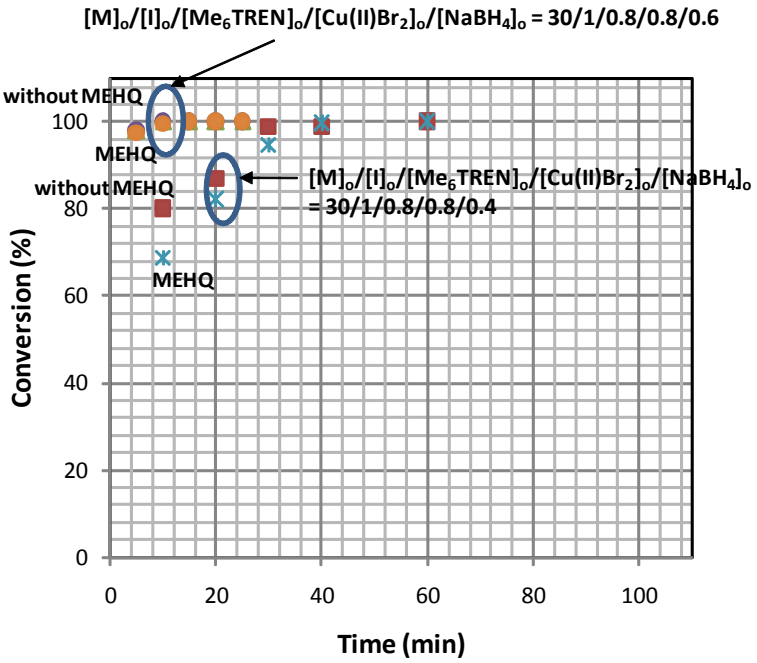

Figure S19. Aqueous SET-LRP of NIPAM catalyzed by the *in situ* generation of Cu(0) from $NaBH_4$ at $[NIPAM]_o/[I]_o$ = 30 in the absence and presence of inhibitor MEHQ added to the polymerization mixture after sampling, and varying $[CuBr_2]_o/[NaBH_4]_o$ from (a) 0.8/0.6 ● without MEHQ, (b) 0.8/0.6 ● with MEHQ, (c) 0.8/0.4 ■ without MEHQ, (d) 0.8/0.4 *. Reaction conditions: $[NIPAM]_o/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o$ = 30/1/0.8/0.8. [I]=0.0267 M in 3.48 mL of water.

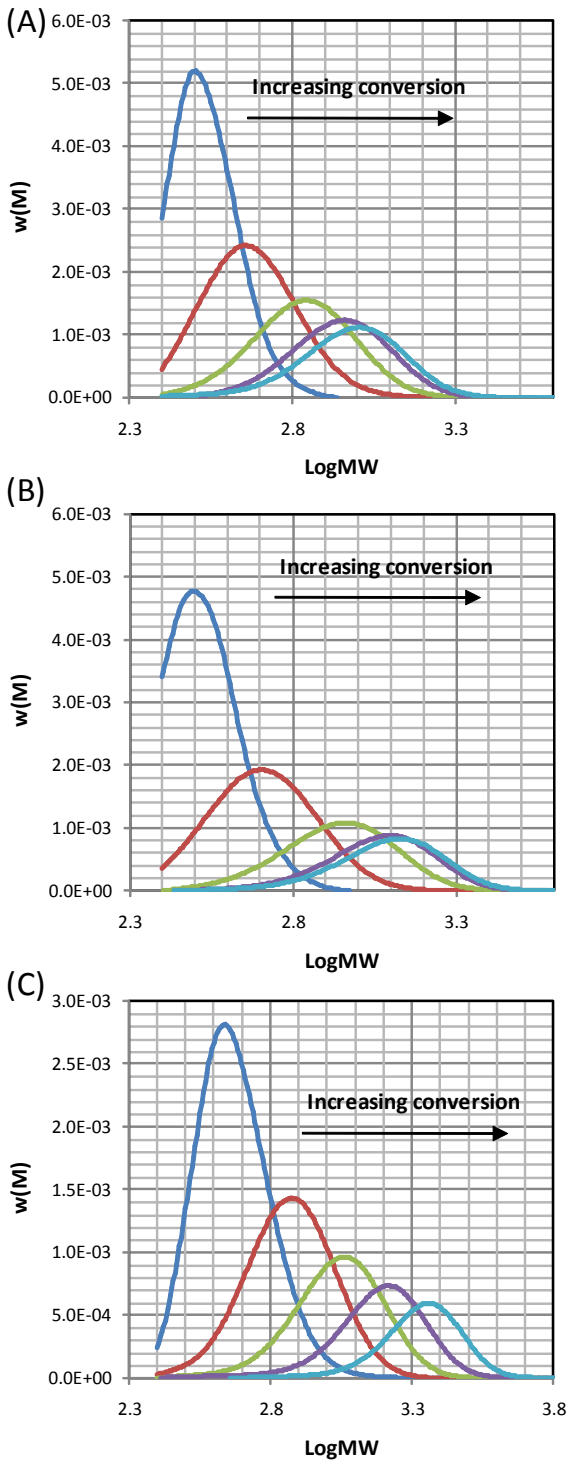

Figure S20. SEC chromatograms from aqueous SET-LRP of NIPAM catalyzed by the *in situ* generation of Cu(0) from $NaBH_4$ by varying $[NIPAM]_o/[I]_o$ from (A) 20/1 , (B) 30/1 , and (C) 40/1. Reaction conditions: $[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 1/0.8/0.8/0.2. [I]=0.0267 M in 3.48 mL of water. These SEC chromatograms are based on a polystyrene calibration curve and have not been adjusted using the Mark-Houwink parameters.

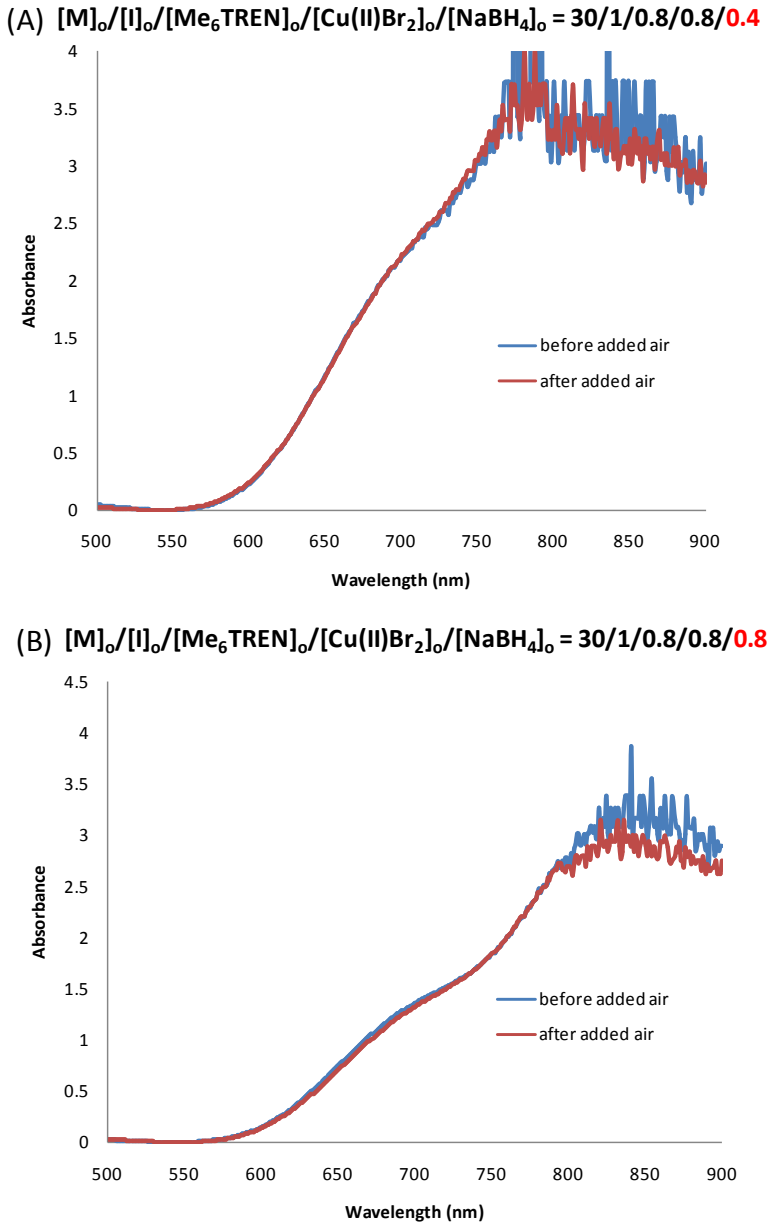

Figure S21. UV-vis spectra (measured in the 500-900 nm range) at the end of the aqueous SET-LRP of NIPAM polymerization before and after opening and bubbling with air for 1 min. (A) $[M]_0/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 30/1/0.8/0.8/0.4, and (B) $[M]_0/[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 30/1/0.8/0.8/0.8. Reaction conditions: $[I]_o/[Me_6TREN]_o/[Cu(II)Br_2]_o/[NaBH_4]_o$ = 1/0.8/0.8/0.2. [I]=0.0267 M in 3.48 mL of water.