Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information to

Quantitative end-group functionalization of PNIPAM from aqueous SET-LRP via in situ reduction of Cu(II) with $NaBH_4$.

*Mikhail Gavrilov,[1] Zhongfan Jia, [1] Virgil Percec[2] and Michael J. Monteiro[1,]**

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

2. Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 190104-6323, United States

*author to whom correspondence should be sent:

e-mail: m.monteiro@uq.edu.au

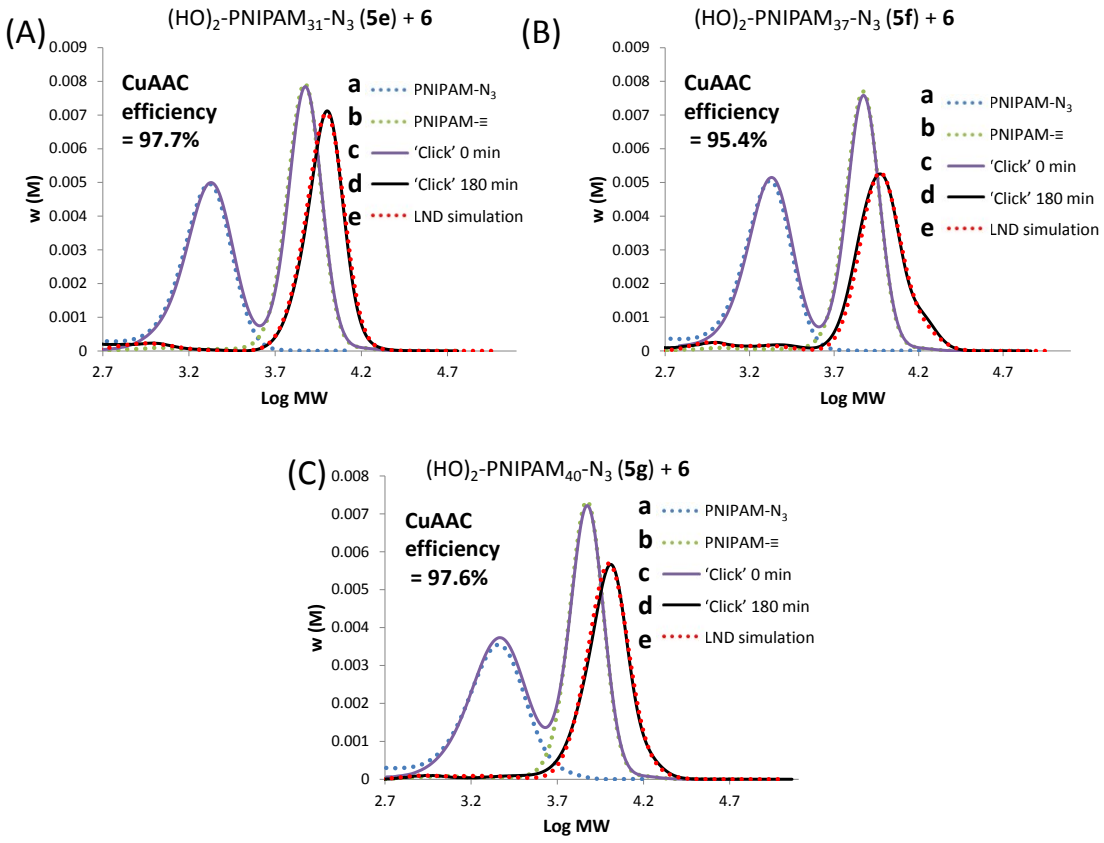

Figure S1. Size exclusion chromatograms for the CuAAC 'click' reaction between **5** and **6**. (A) Polymer **5e** + **6**, (B) Polymer **5f** + **6**, (C) Polymer **5g** + **6**. Curves (a) **5**, (b) **6**, (c) at time = 0 min for CuAAC, (d) at time = 180 min for CuAAC, and (e) LND model simulation of curve d.

Table S1. Weight fractions of components after the CuAAC reaction determined by LND model simulation of SEC curves.

CuAAC	PNIPAM-N_3 (**5**), %	PNIPAM-≡ (**6**), %	PNIPAM-PNIPAM (**7**), %	Alk-Alk coupling (**8**), %	Unknown 1, %	Unknown 2, %
6+**5a**	0.14	8.59	65.67	25.60		
6+**5b**	0.00	10.77	67.97	21.26		
6+**5c**	0.38	13.13	70.93	15.56		
6+**5d**	0.64	10.70	71.92	16.73		
6+**5e**	0.00	15.66	82.77	1.12	0.00	0.45
6+**5f**	0.53	5.01	80.18	13.78	0.25	0.25
6+**5g**	0.25	12.77	80.53	6.14	0.25	0.07

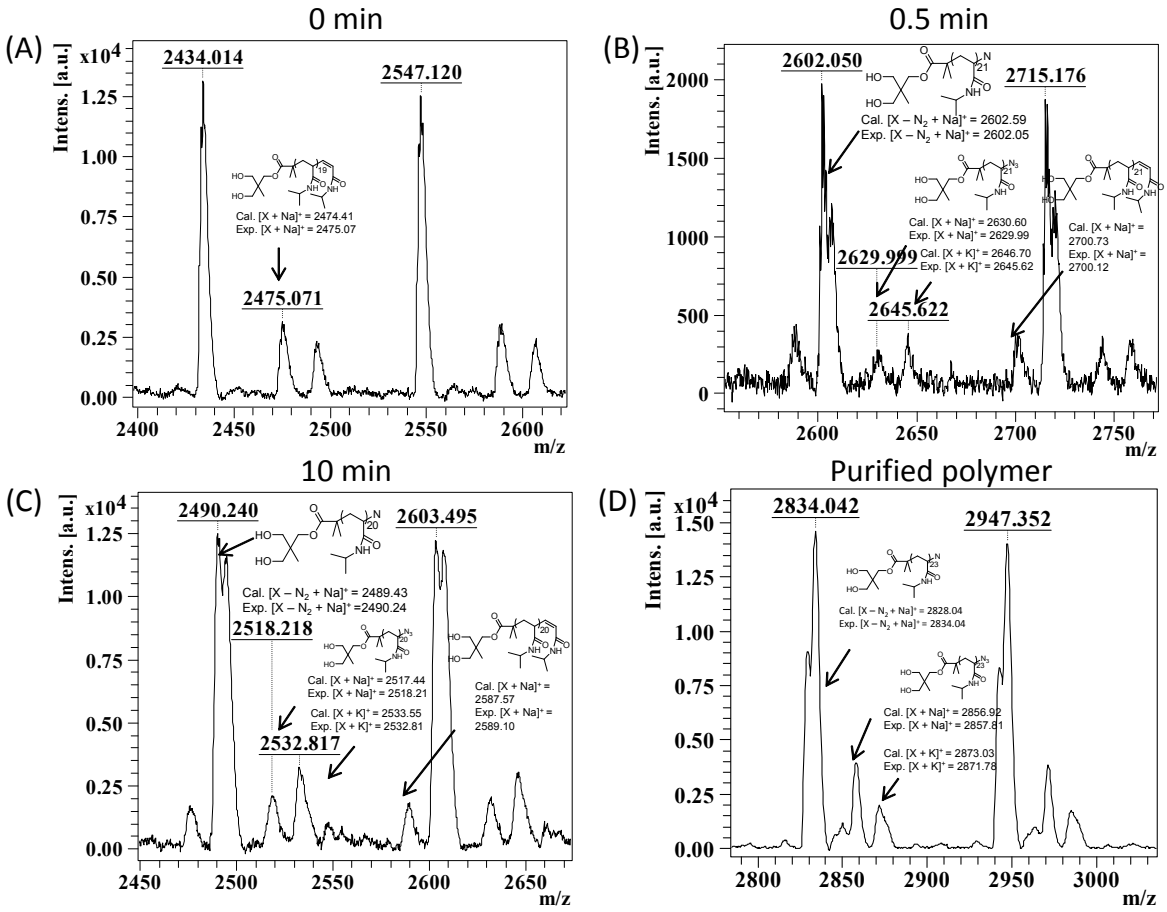

Figure S2. Kinetics of in situ azidation of $(HO)_2$-PNIPAM$_n$-Br (**2a**) after 120 min of aqueous SET-LRP at 0°C. MALDI-ToF spectra of (A) at 0 min, (B) 0.5 min, (C) 10min and (D) of purified **5a**.

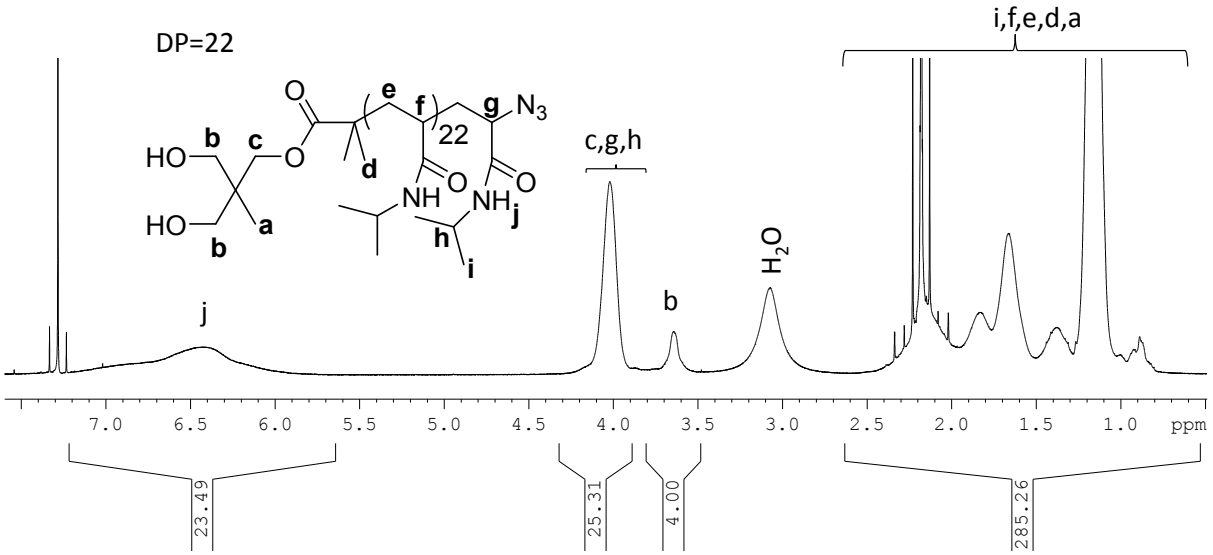

Figure S3. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{22}$-N_3 (**5a**) recorded in $CDCl_3$ at 298K (400 MHz).

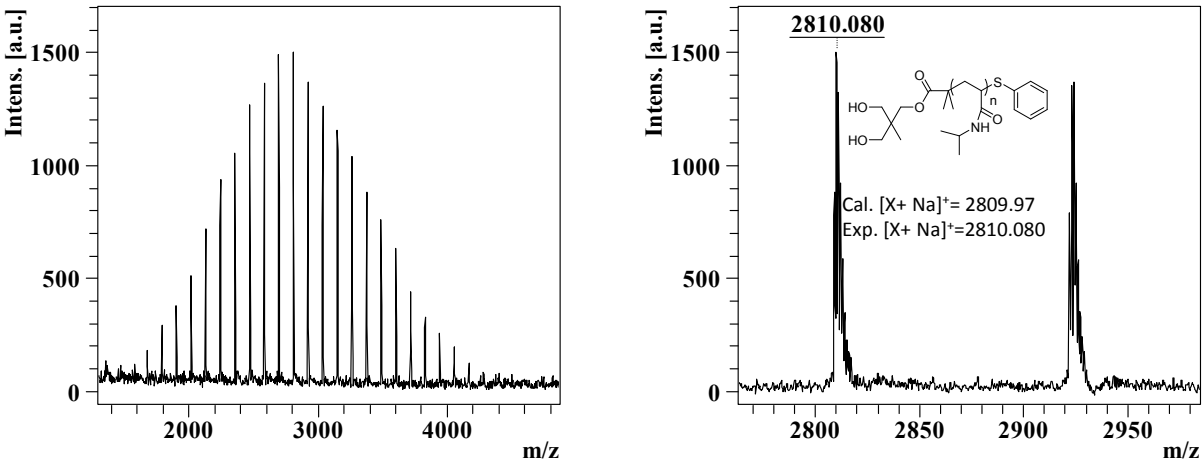

Figure S4. Full and expanded MALDI-ToF spectra of $(HO)_2$-$PNIPAM_{24}$-S-Ph (**4a)** acquired in reflectron mode with Na salt as cationizing agent and DCTB matrix.

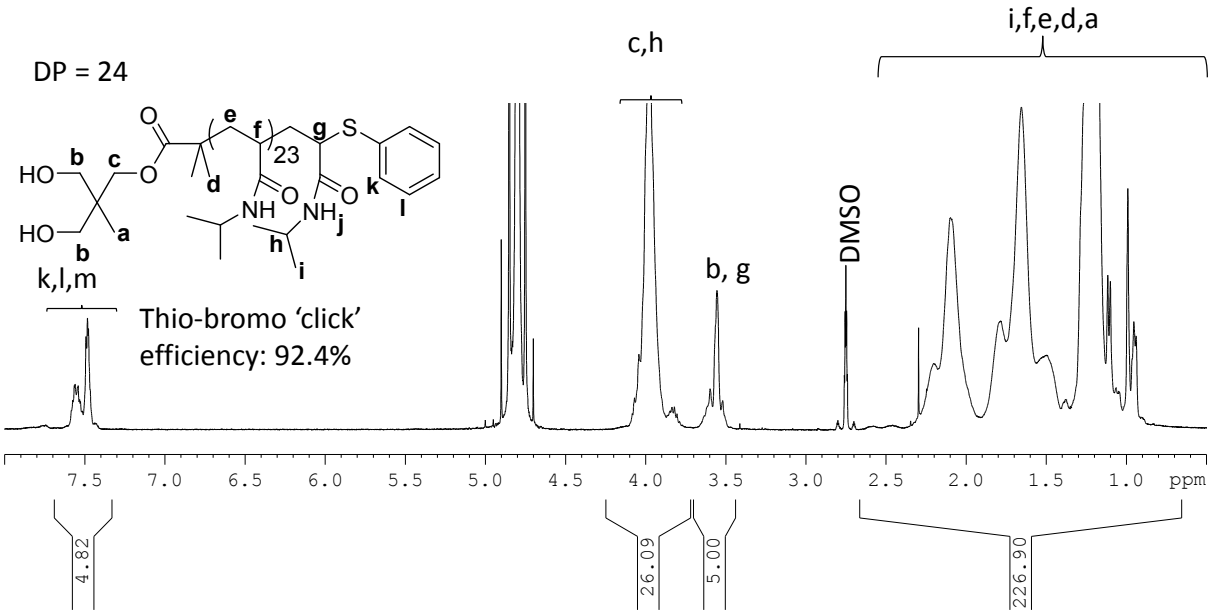

Figure S5. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{24}$-S-Ph (**4a**) recorded in D_2O (0.6 mL) + DMSO-d_6 (0.1mL) at 298K (400 MHz).

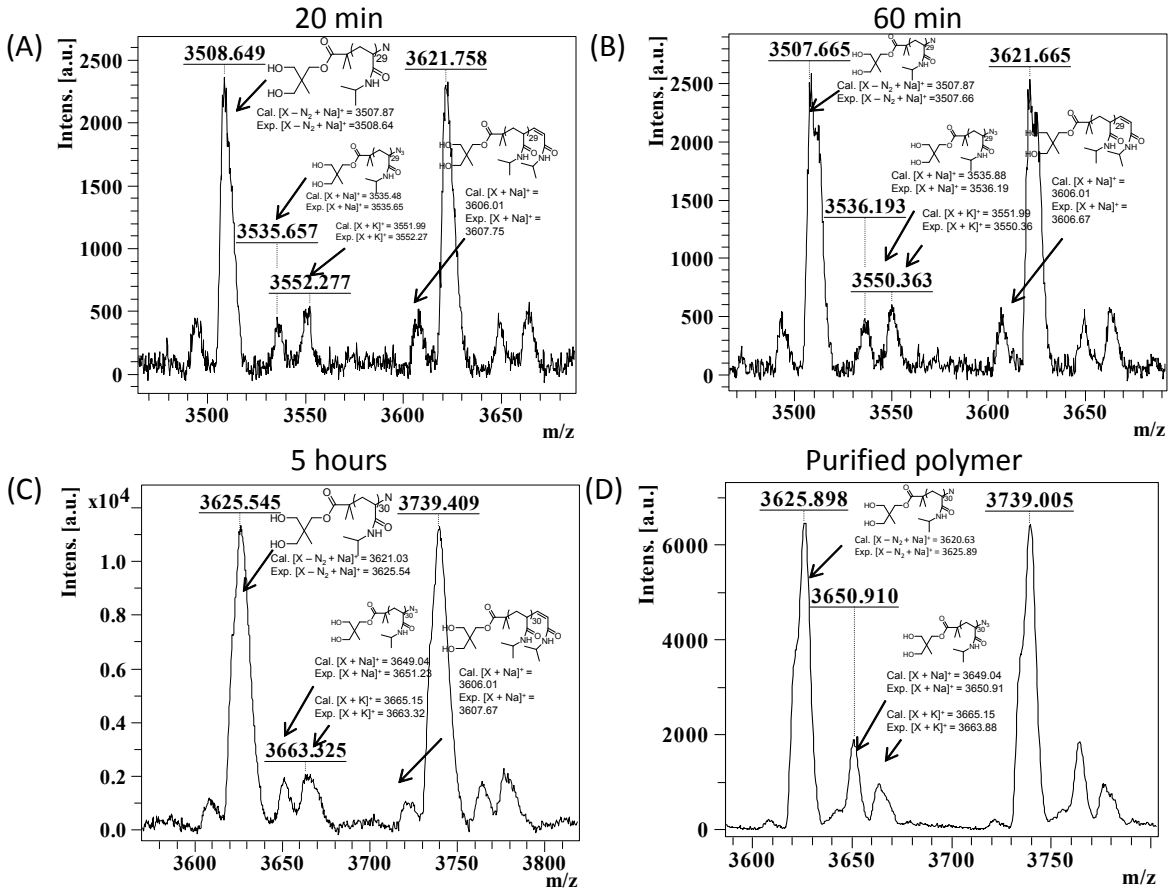

Figure S6. Kinetics of in situ azidation of $(HO)_2$-PNIPAM$_n$-Br (**2b**) after 120 min of aqueous SET-LRP at 0°C. MALDI-ToF spectra of (A) at 20 min, (B) 60 min, (C) 5 hours and (D) of purified **5b**.

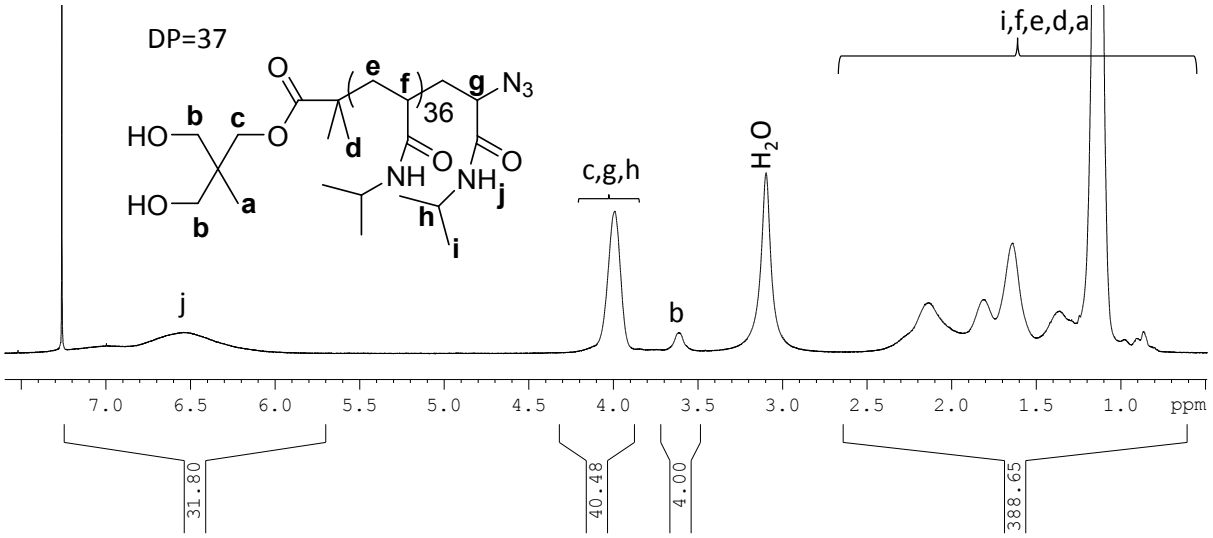

Figure S7. ^{1}H NMR spectrum of $(HO)_2$-$PNIPAM_{37}$-N_3, **5b** recorded in $CDCl_3$ at 298K (400 MHz).

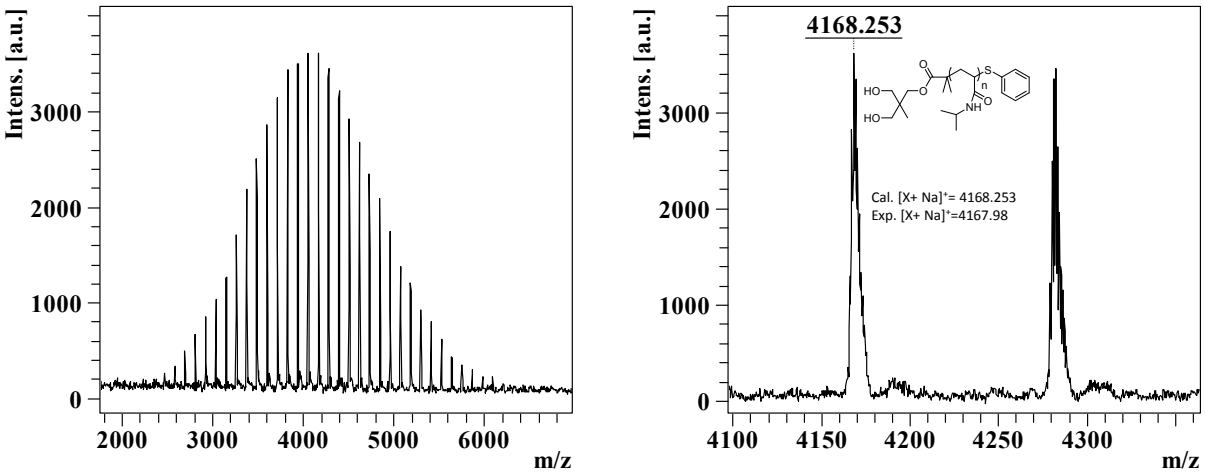

Figure S8. Full and expanded MALDI-ToF spectra of $(HO)_2$-$PNIPAM_{36}$-S-Ph (**4b)** acquired in reflectron mode with Na salt as cationizing agent and DCTB matrix.

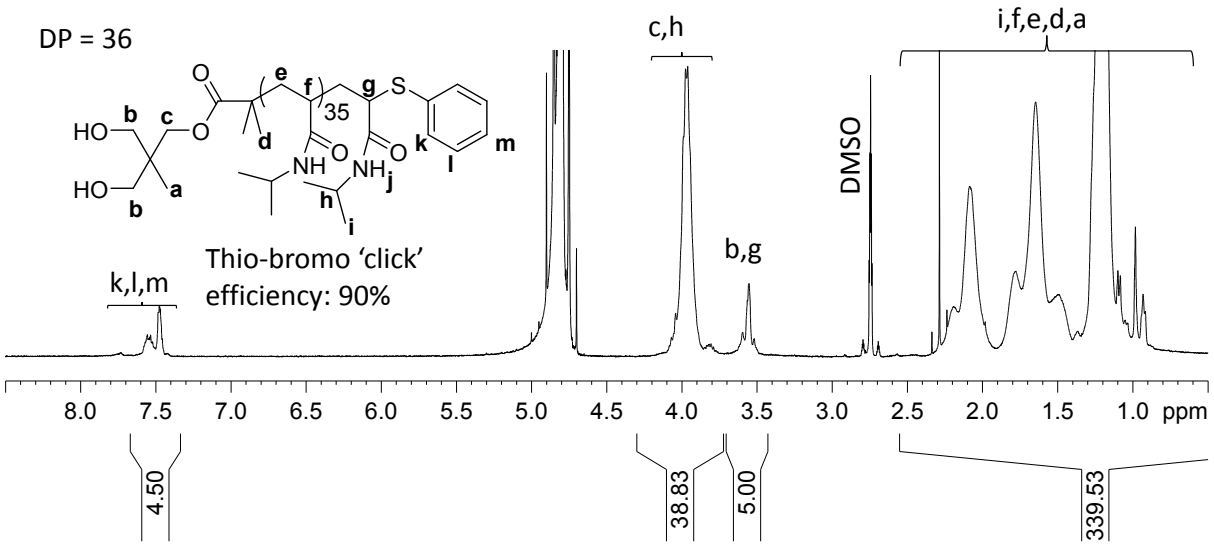

Figure S9. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{36}$-S-Ph, **4b** recorded in D_2O (0.6 mL) + DMSO-d_6 (0.1mL) at 298K (400 MHz).

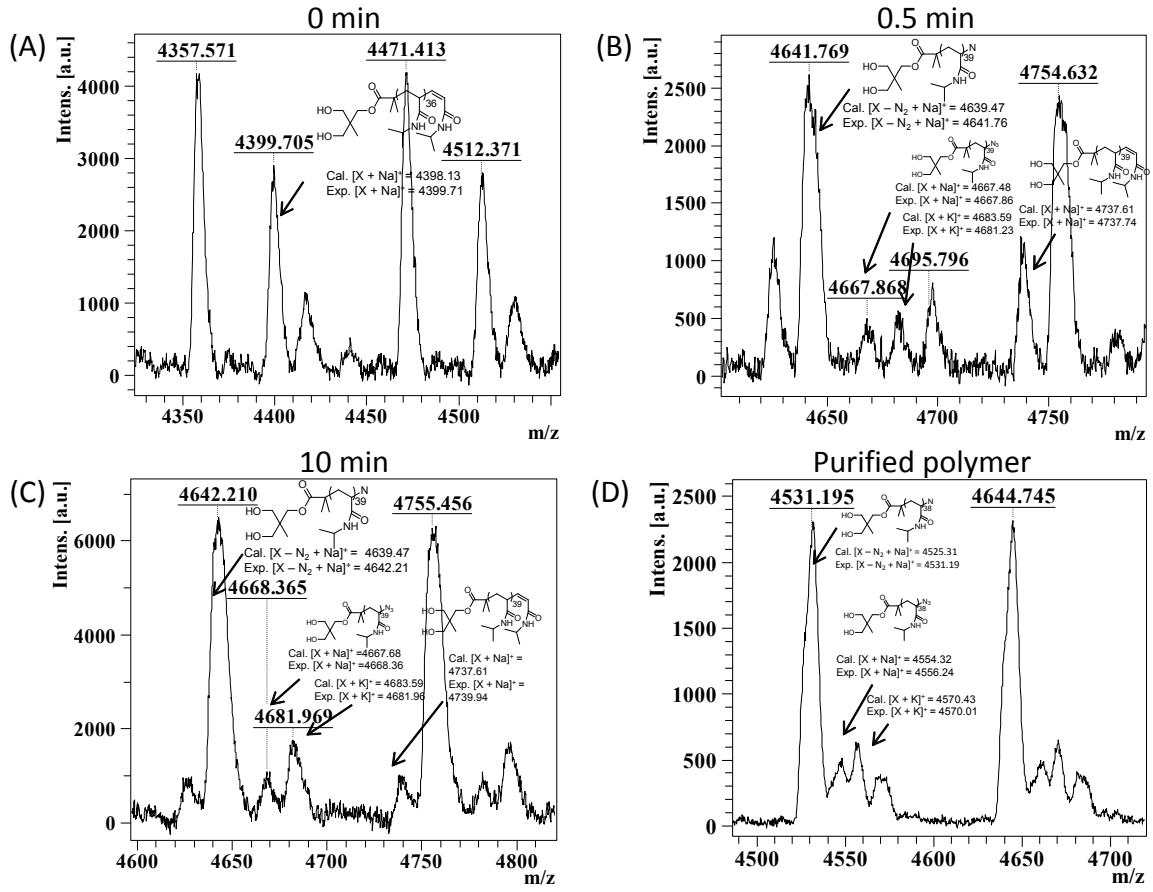

Figure S10. Kinetics of in situ azidation of $(HO)_2$-PNIPAM$_n$-Br (**2c**) after 120 min of aqueous SET-LRP at 0°C. MALDI-ToF spectra of (A) at 0 min, (B) 0.5 min, (C) 10min and (D) of purified **5c**.

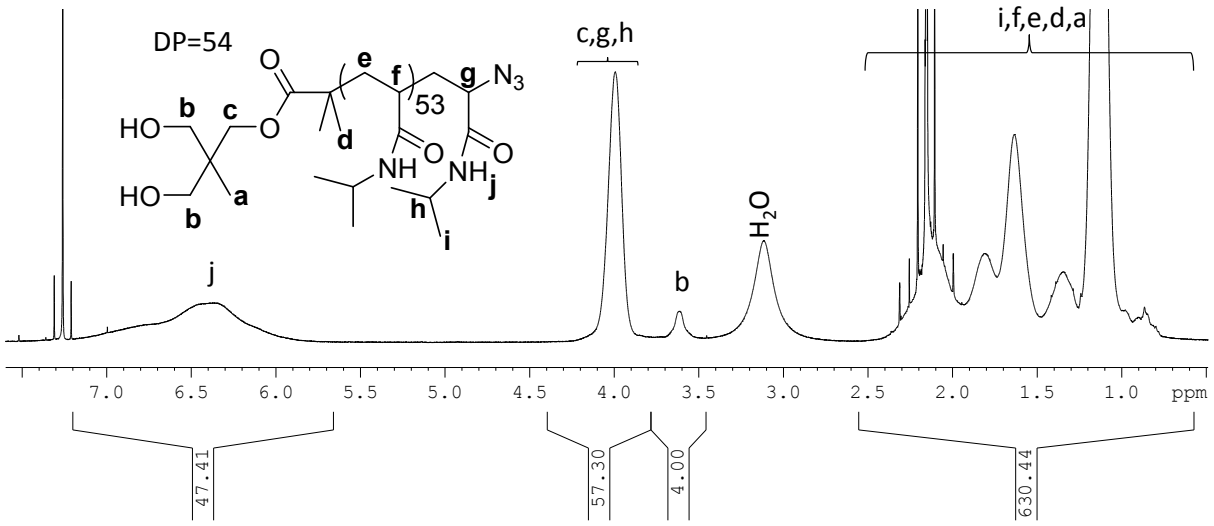

Figure S11. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{54}$-N_3, **5c** recorded in $CDCl_3$ at 298K (400 MHz).

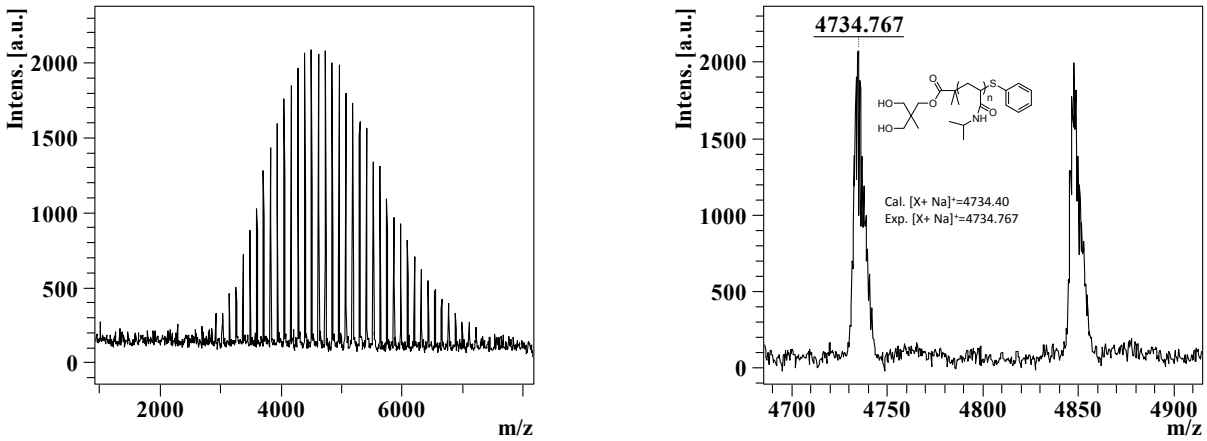

Figure S12. Full and expanded MALDI-ToF spectra of $(HO)_2$-$PNIPAM_{44}$-S-Ph (**4c)** acquired in reflectron mode with Na salt as cationizing agent and DCTB matrix.

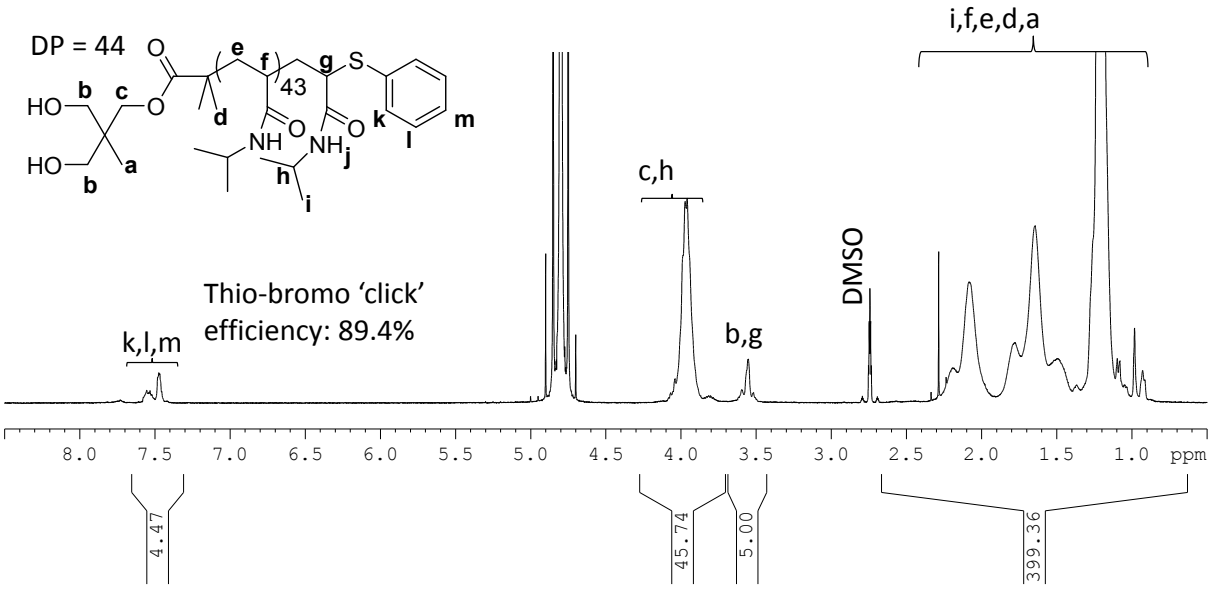

Figure S13. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{44}$-S-Ph, **4c** recorded in D_2O (0.6 mL) + DMSO-d_6 (0.1mL) at 298K (400 MHz).

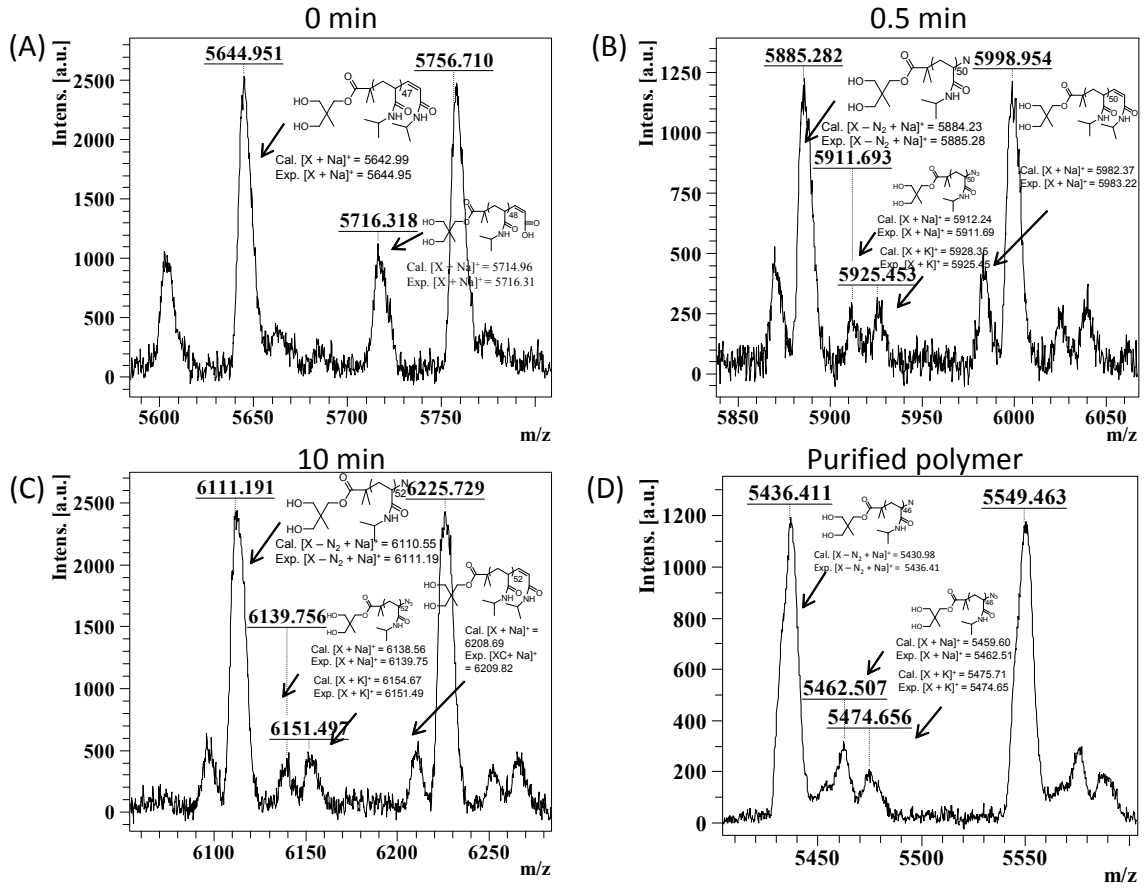

Figure S14. Kinetics of in situ azidation of $(HO)_2$-PNIPAM$_n$-Br (**2d**) after 120 min of aqueous SET-LRP at 0°C. MALDI-ToF spectra of (A) at 0 min, (B) 0.5 min, (C) 10min and (D) of purified **5d.**

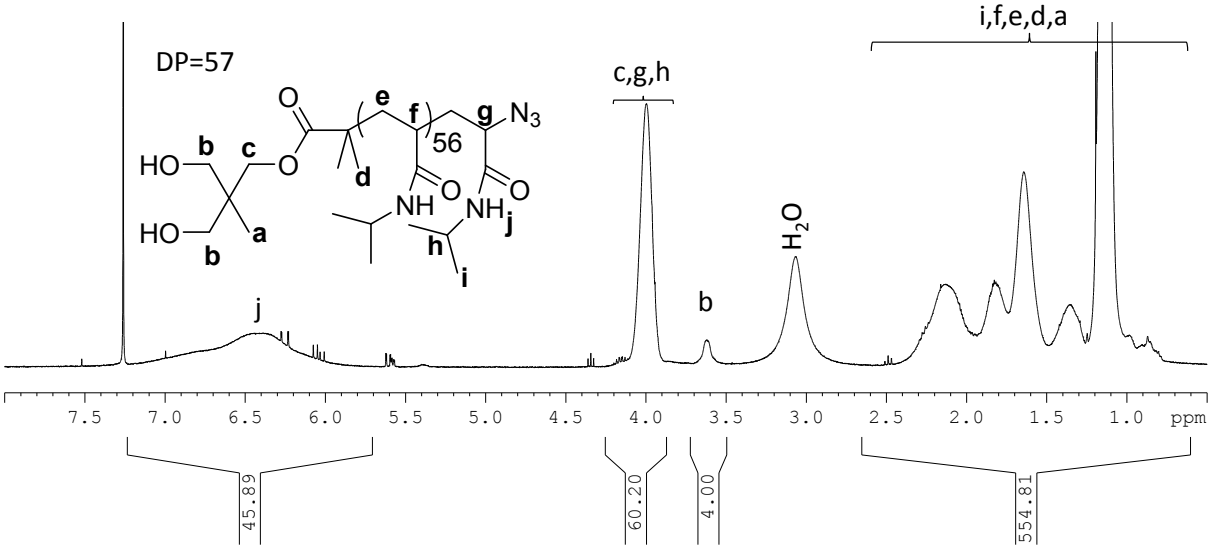

Figure S15. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{57}$-N_3, **5d** recorded in $CDCl_3$ at 298K (400 MHz).

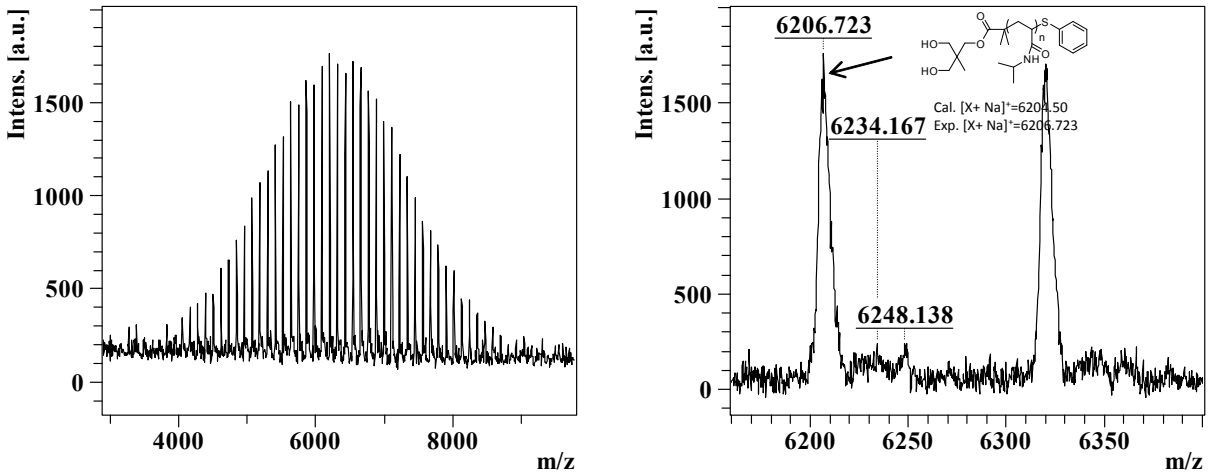

Figure S16. Full and expanded MALDI-ToF spectra of $(HO)_2$-$PNIPAM_{55}$-S-Ph (**4d)** acquired in reflectron mode with Na salt as cationizing agent and DCTB matrix.

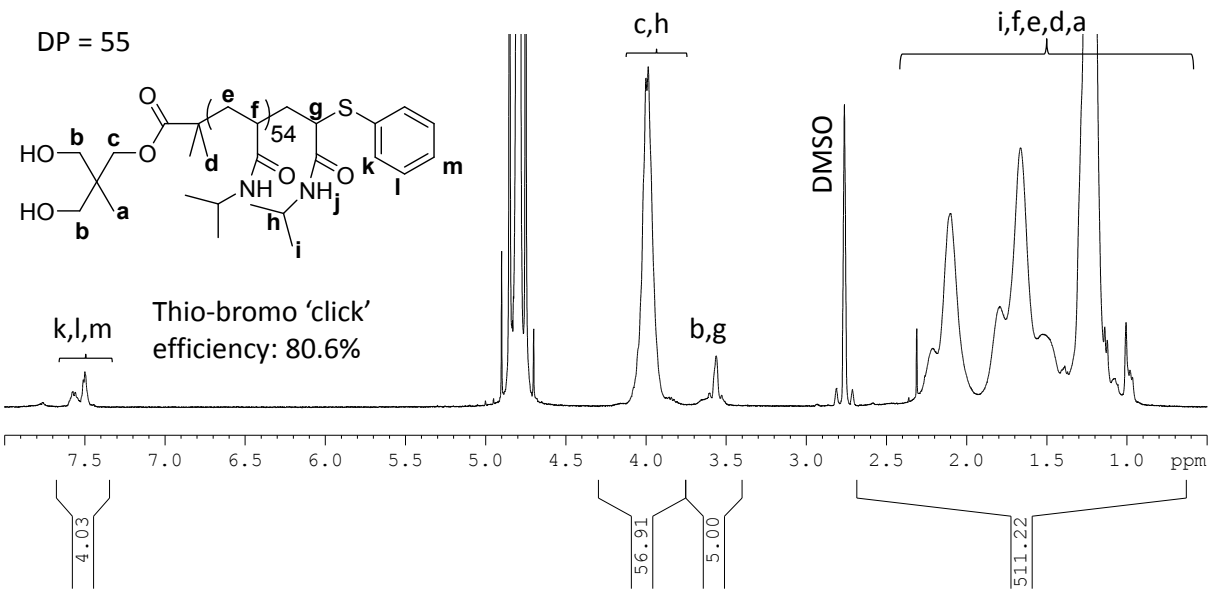

Figure S17. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{55}$-S-Ph, **4d** recorded in D_2O (0.6 mL) + DMSO-d_6 (0.1mL) at 298K (400 MHz).

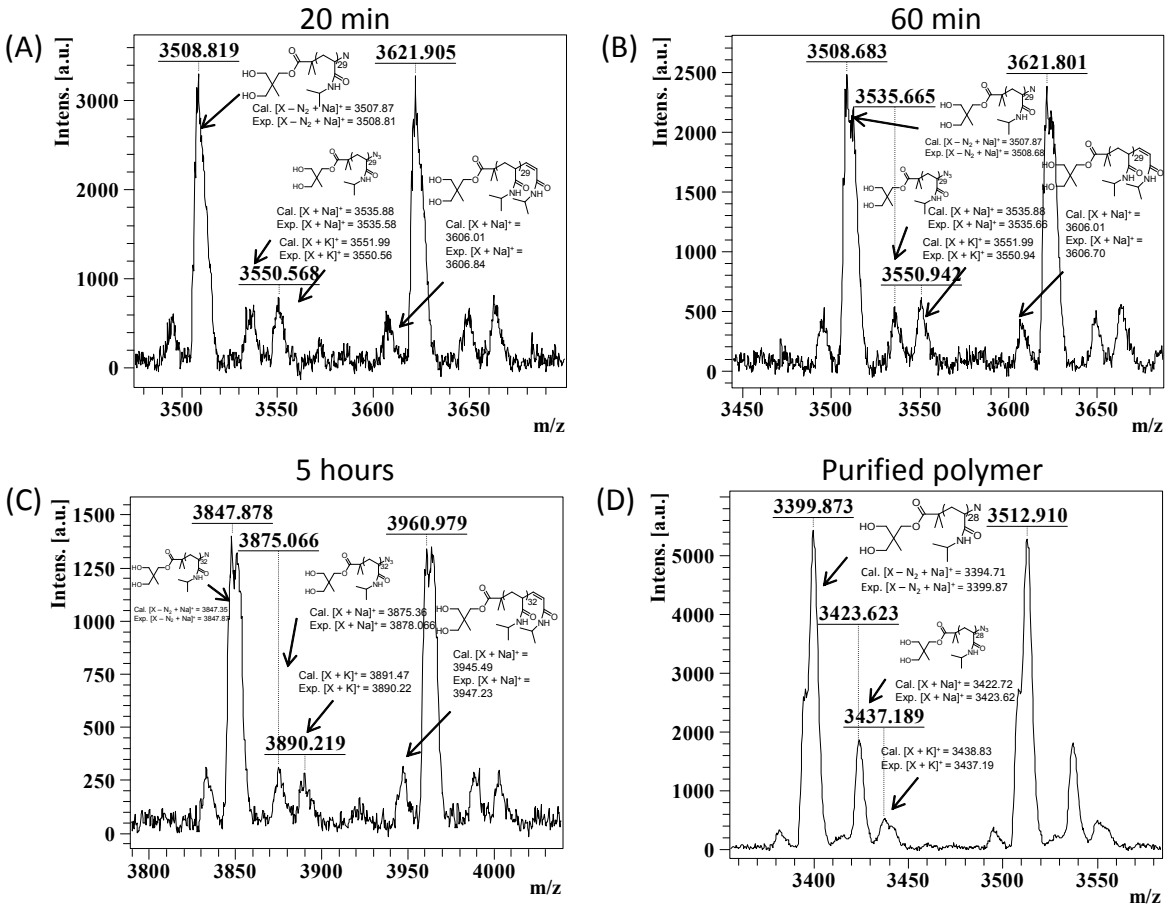

Figure S18. Kinetics of in situ azidation of $(HO)_2$-PNIPAM$_n$-Br (**2e**) after 120 min of aqueous SET-LRP at 0°C. MALDI-ToF spectra of (A) at 20 min, (B) 60 min, (C) 5 hours and (D) of purified **5e**.

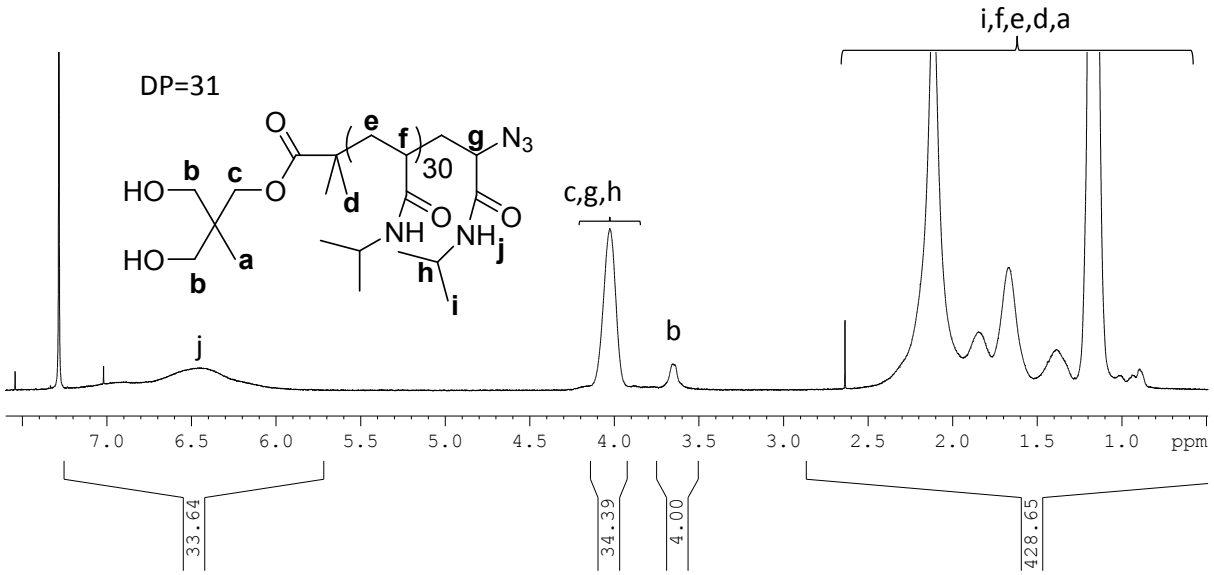

Figure S19. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{31}$-N_3 (**5e**) recorded in $CDCl_3$ at 298K (400 MHz).

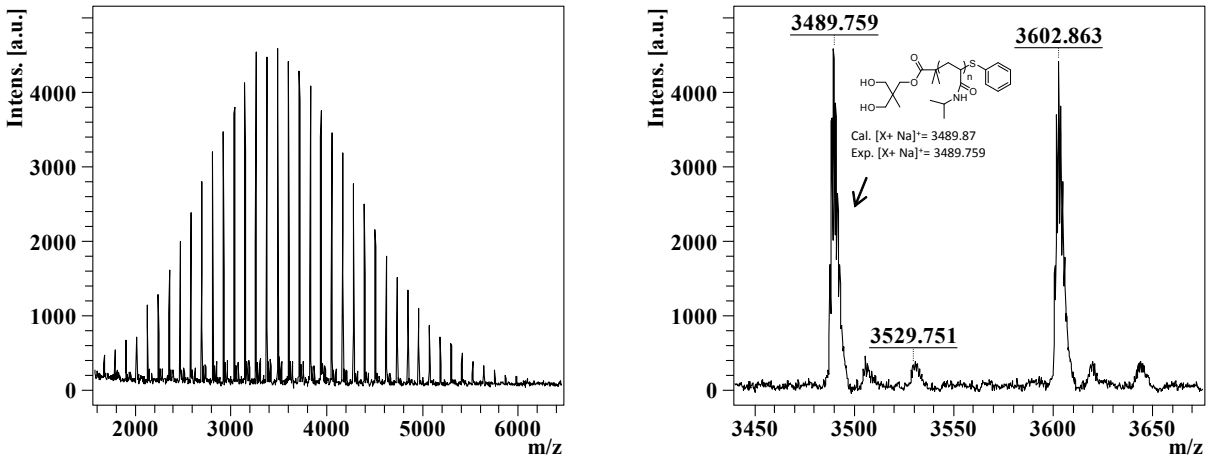

Figure S20. Full and expanded MALDI-ToF spectra of $(HO)_2$-$PNIPAM_{34}$-S-Ph (**4e)** acquired in reflectron mode with Na salt as cationizing agent and DCTB matrix.

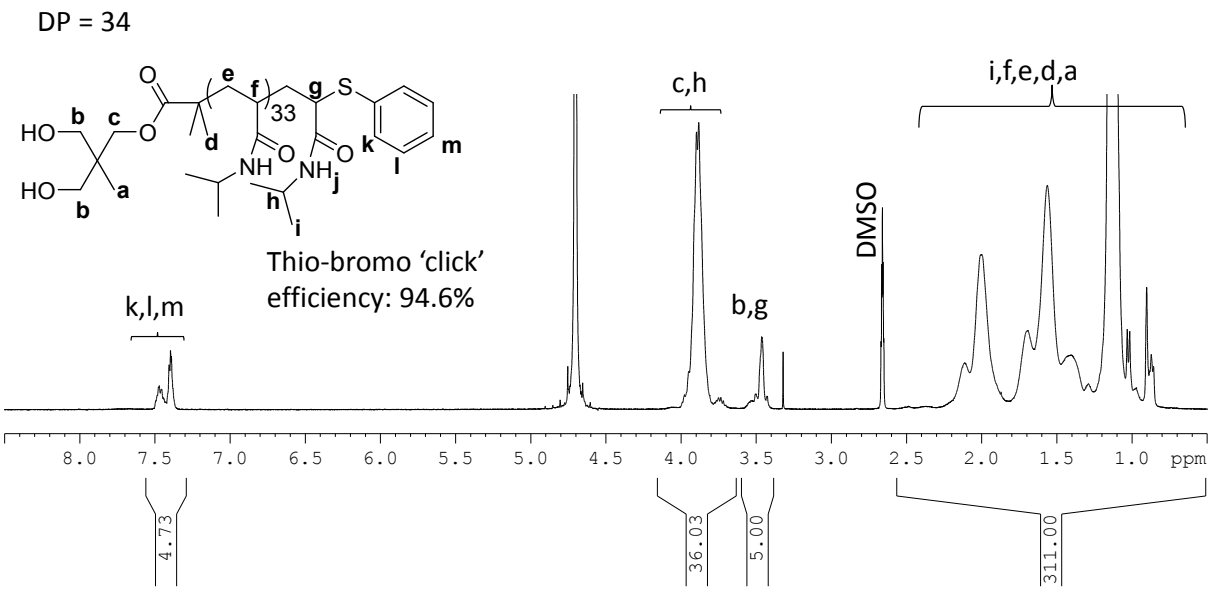

Figure S21. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{34}$-S-Ph (**4e**) recorded in D_2O (0.6 mL) + DMSO-d_6 (0.1mL) at 298K (400 MHz).

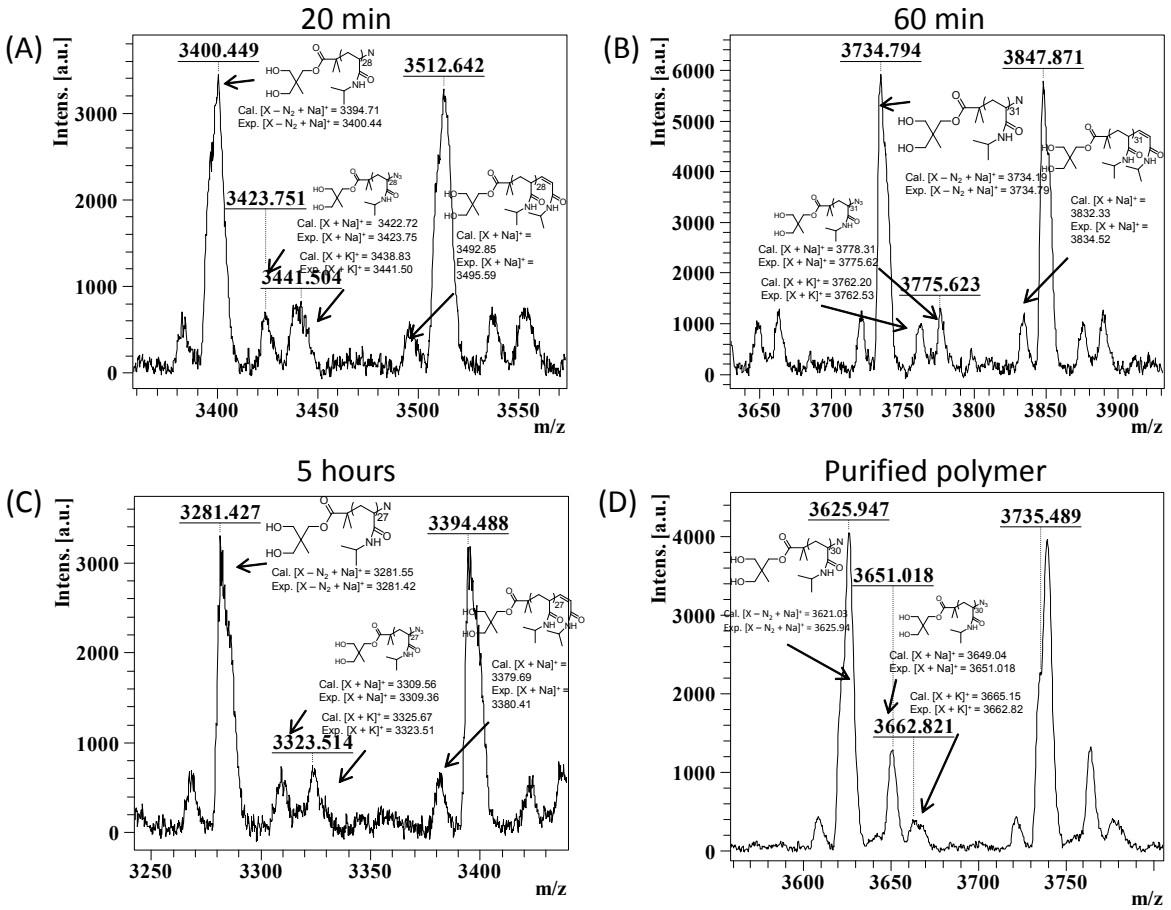

Figure S22. Kinetics of in situ azidation of $(HO)_2$-PNIPAM$_n$-Br (**2f**) after 120 min of aqueous SET-LRP at 0°C. MALDI-ToF spectra of (A) at 20 min, (B) 60 min, (C) 5 hours and (D) of purified **5f**.

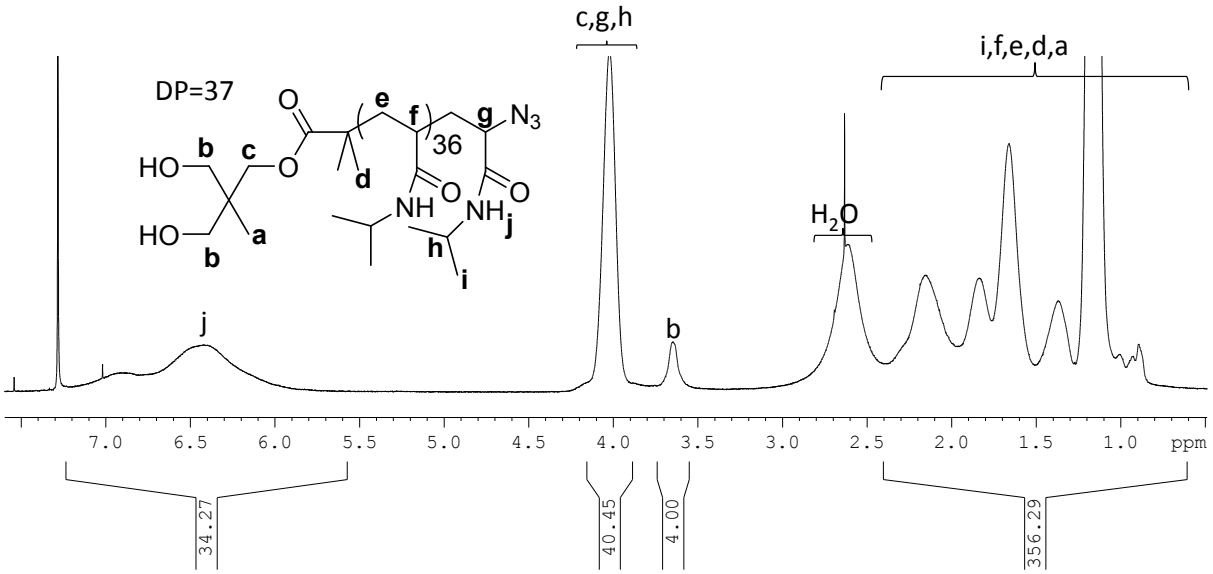

Figure S23. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{37}$-N_3 (**5f**) recorded in $CDCl_3$ at 298K (400 MHz).

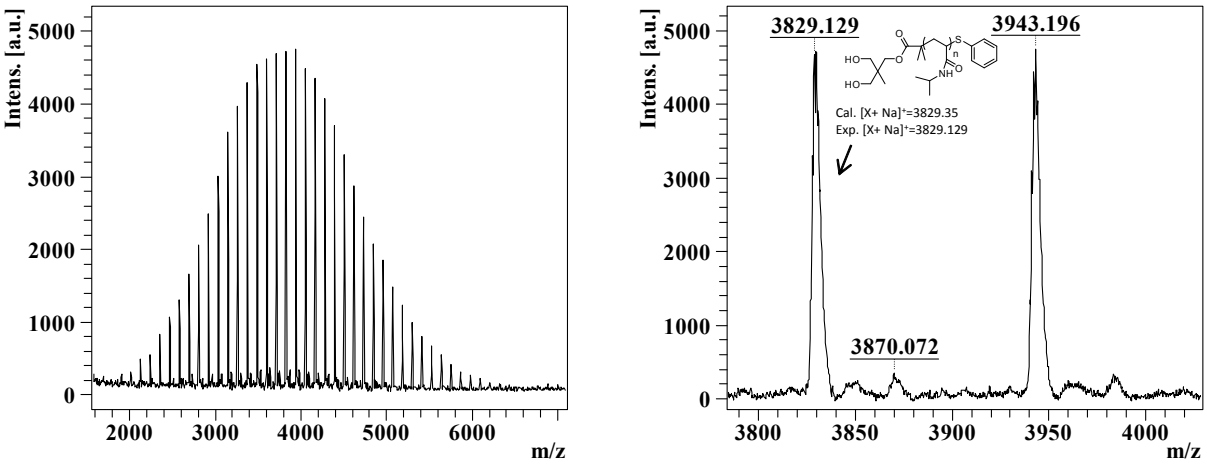

Figure S24. Full and expanded MALDI-ToF spectra of $(HO)_2$-$PNIPAM_{31}$-S-Ph (**4f)** acquired in reflectron mode with Na salt as cationizing agent and DCTB matrix.

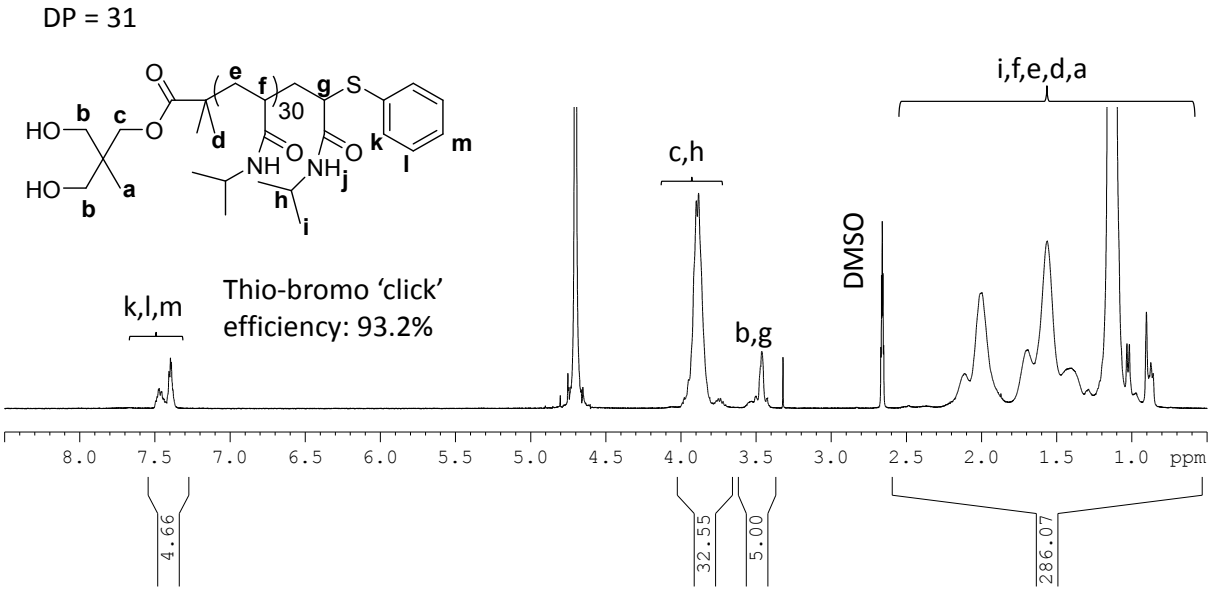

Figure S25. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{31}$-S-Ph (**4f**) recorded in D_2O (0.6 mL) + DMSO-d_6 (0.1mL) at 298K (400 MHz).

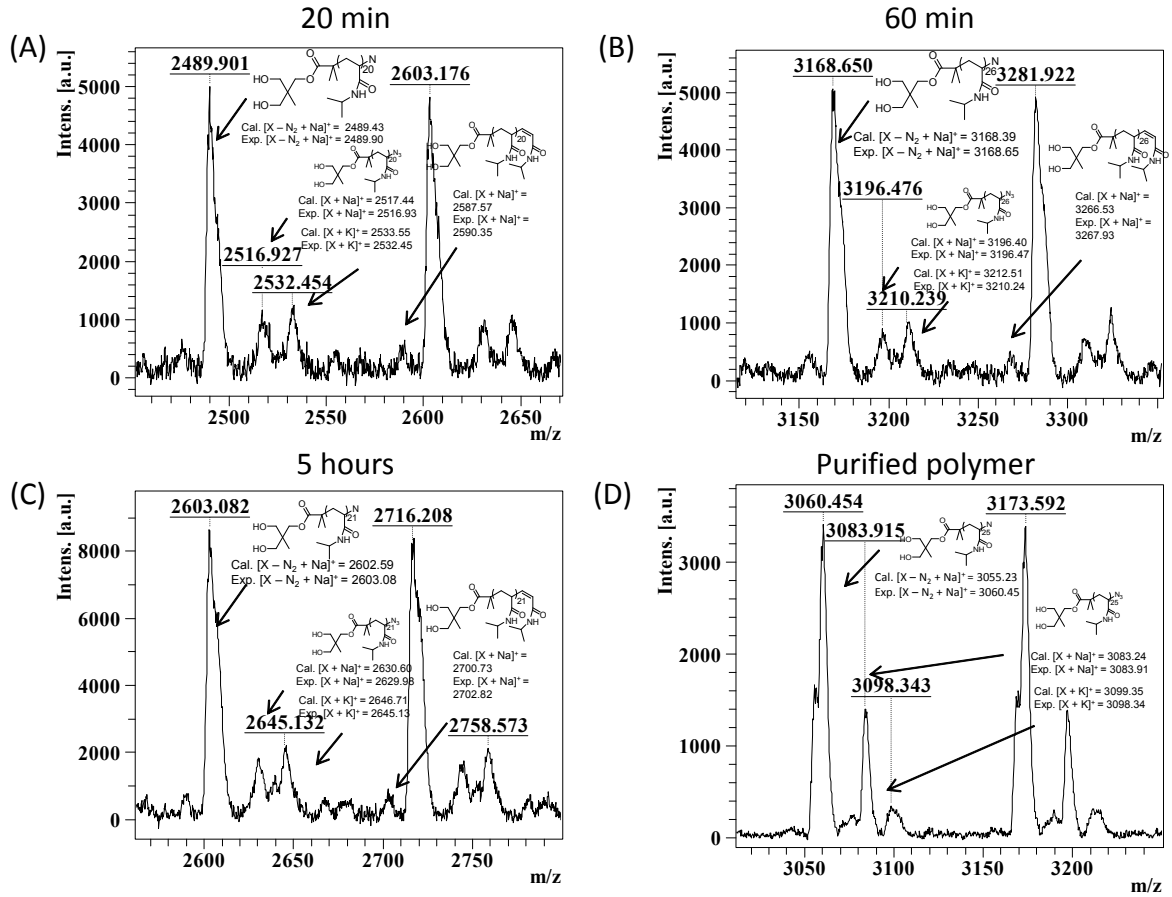

Figure S26. Kinetics of in situ azidation of $(HO)_2$-PNIPAM$_n$-Br (**2g**) after 120 min of aqueous SET-LRP at 0°C. MALDI-ToF spectra of (A) at 20 min, (B) 60 min, (C) 5 hours and (D) of purified **5g**.

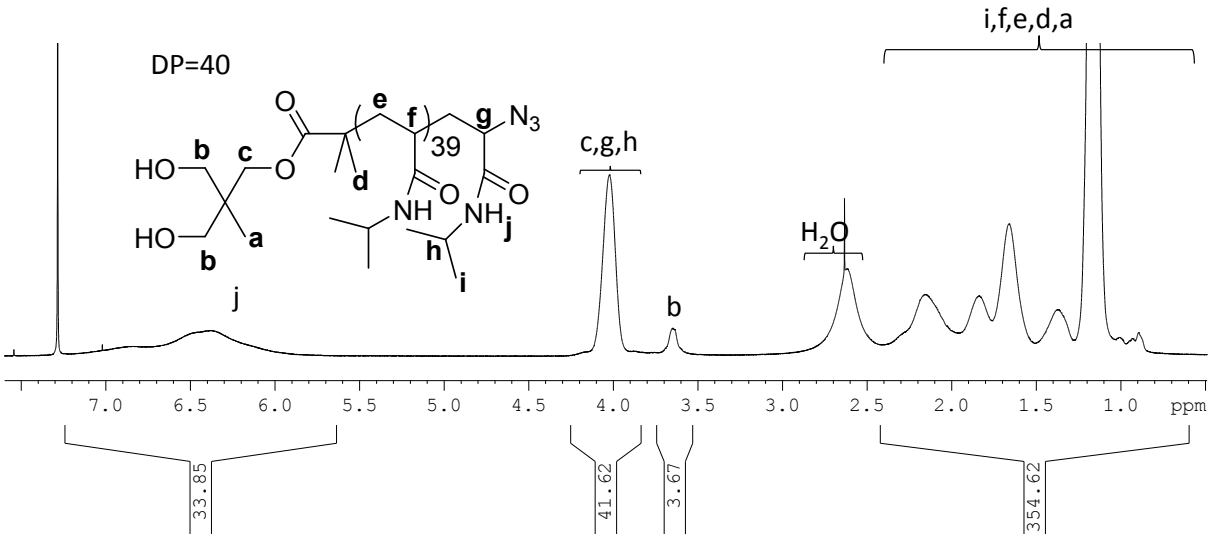

Figure S27. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{40}$-N_3 (**5g**) recorded in $CDCl_3$ at 298K (400 MHz).

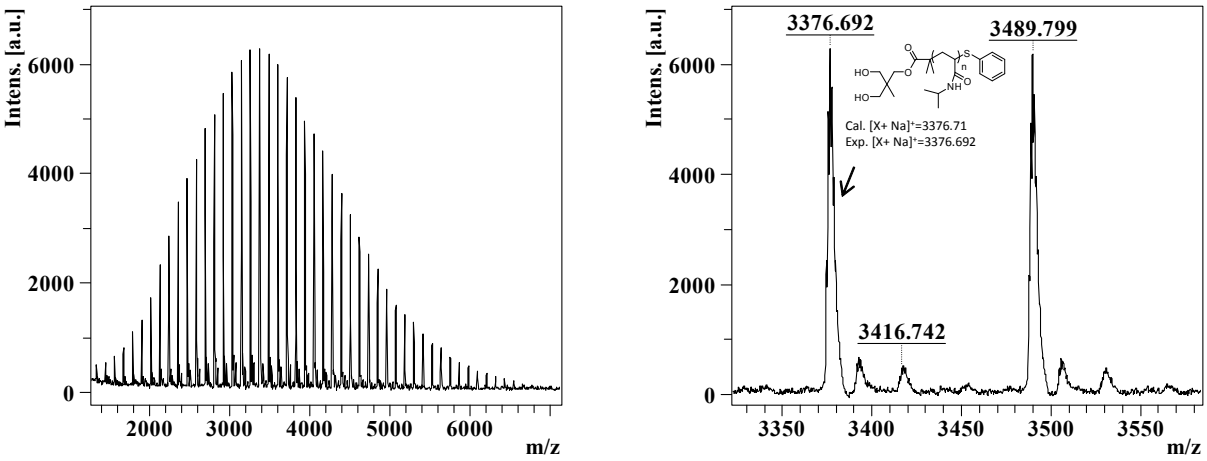

Figure S28. Full and expanded MALDI-ToF spectra of $(HO)_2$-$PNIPAM_{34}$-S-Ph (**4g)** acquired in reflectron mode with Na salt as cationizing agent and DCTB matrix.

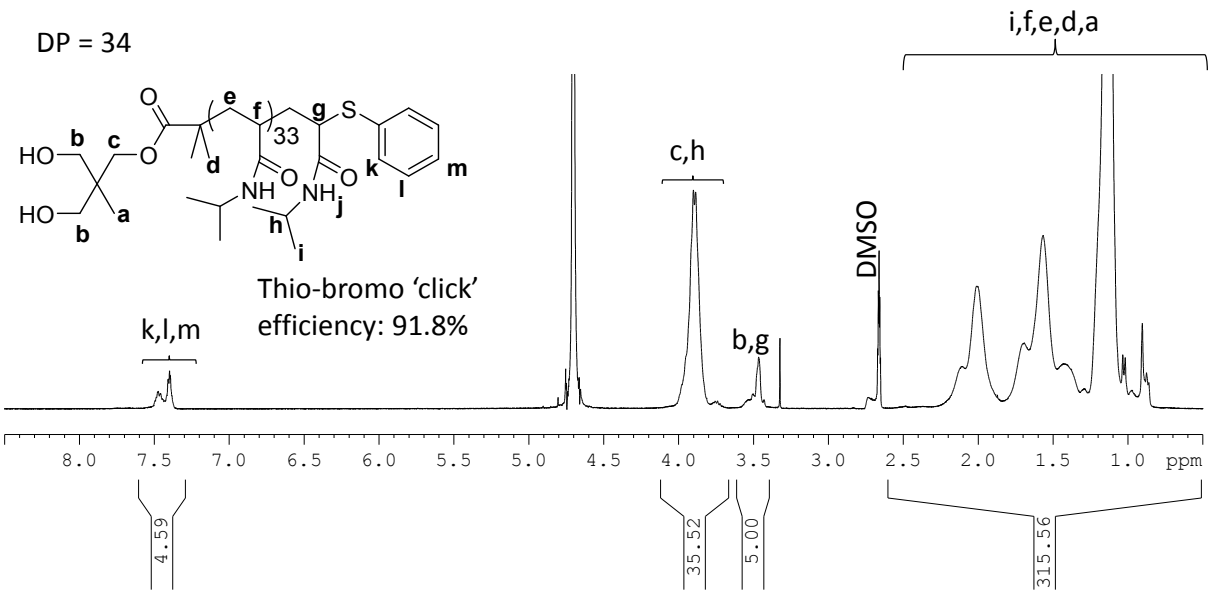

Figure S29. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{34}$-S-Ph (**4g**) recorded in D_2O (0.6 mL) + DMSO-d_6 (0.1mL) at 298K (400 MHz).

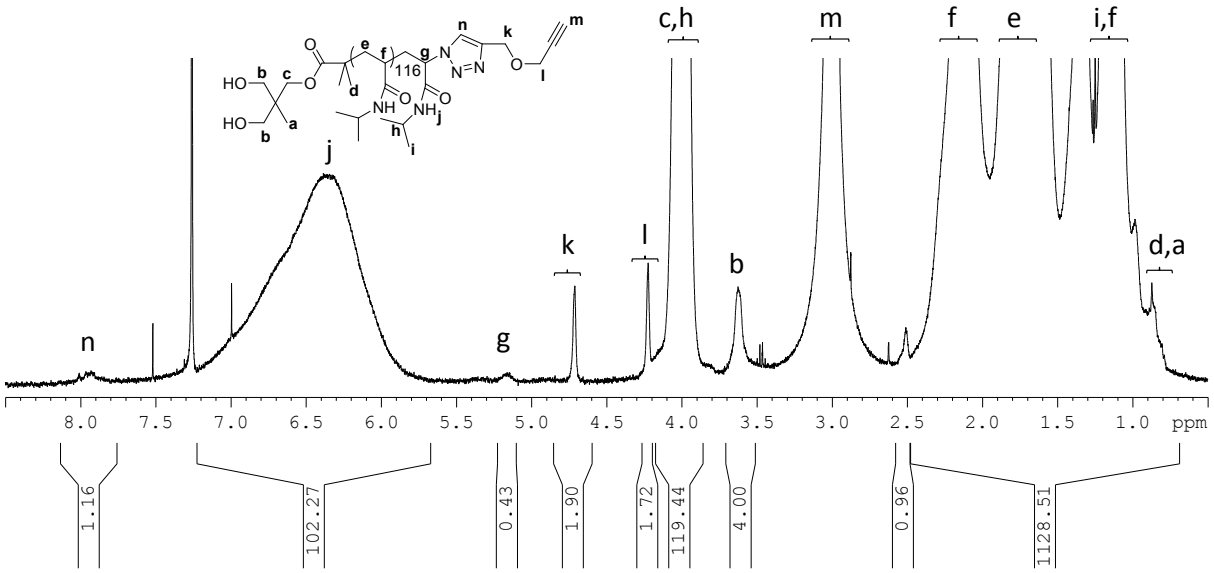

Figure S30. ^{1}H NMR spectrum of $(HO)_2$-PNIPAM$_{117}$-≡ (**5**) recorded in $CDCl_3$ at 298K (400 MHz).

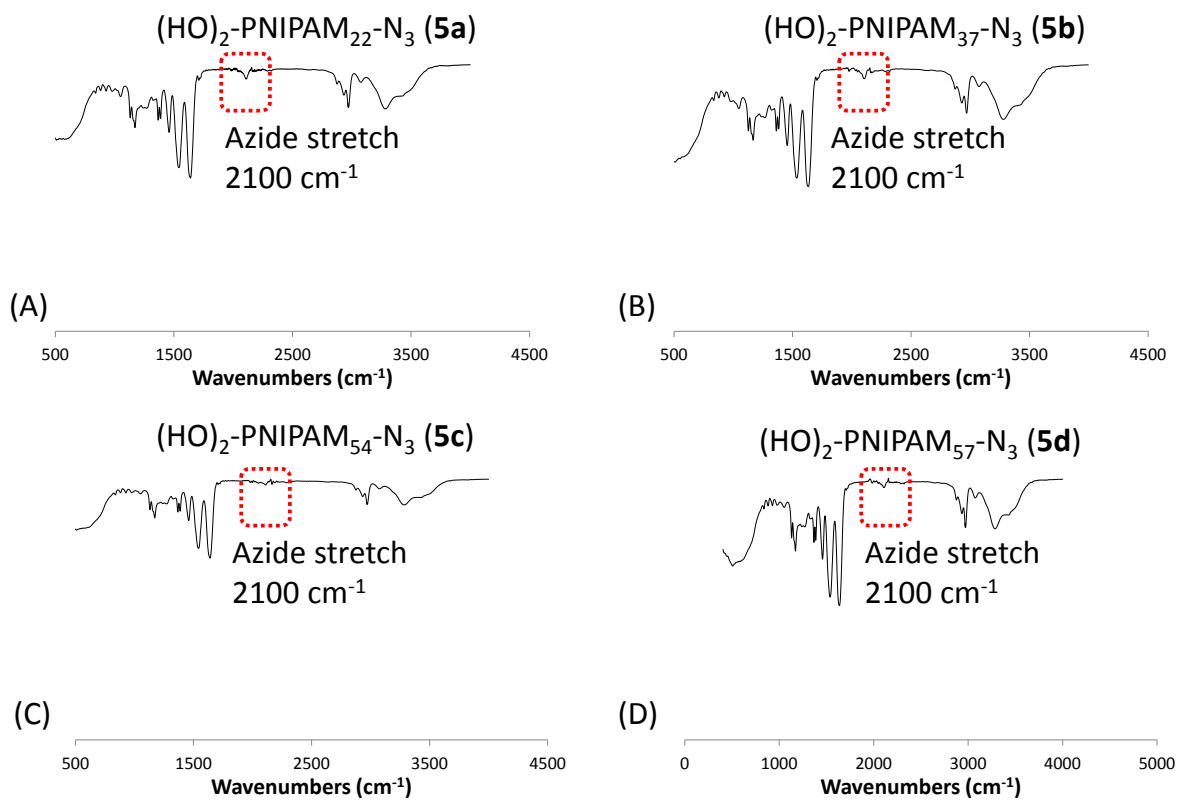

Figure S31: ATR-FTIR of spectra of (A) $(HO)_2$-$PNIPAM_{22}$-N_3 (**5a**), (B) $(HO)_2$-$PNIPAM_{37}$-N_3 (**5b**), (C) $(HO)_2$-$PNIPAM_{54}$-N_3 (**5c**) and (D) $(HO)_2$-$PNIPAM_{57}$-N_3 (**5d**).

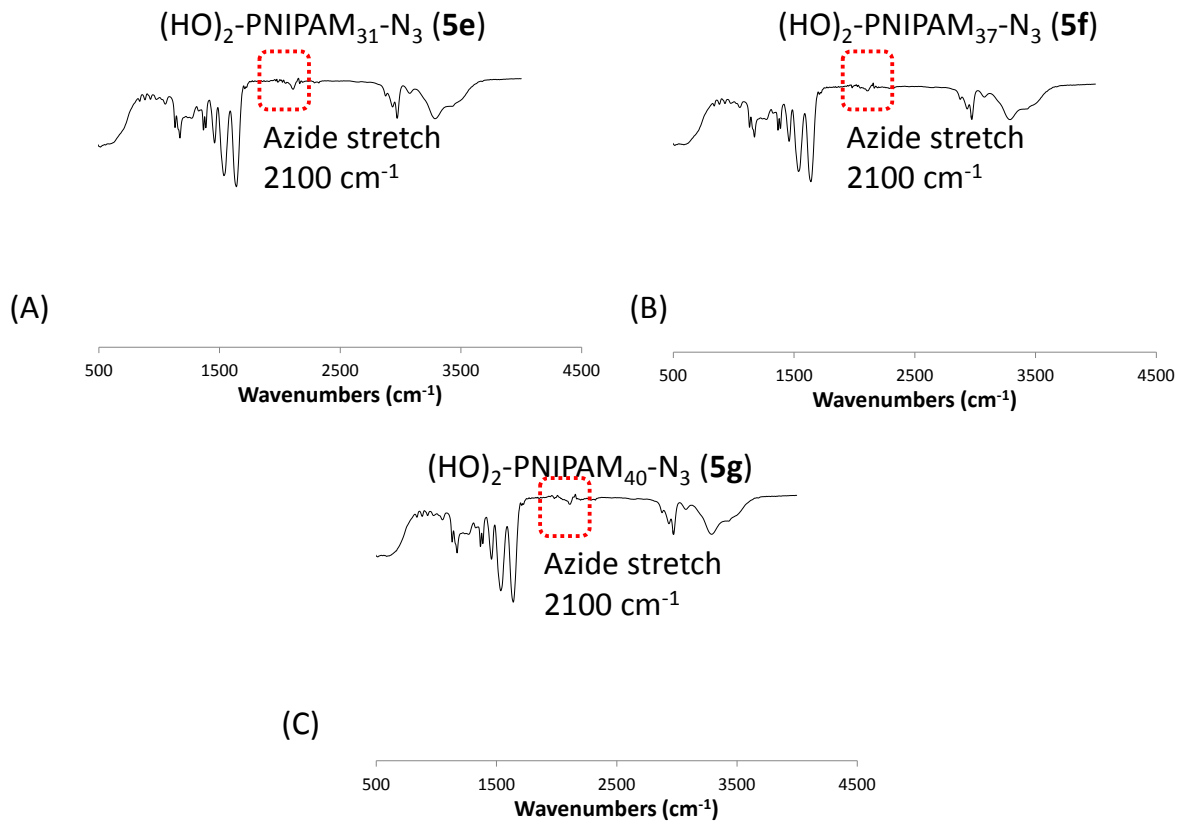

Figure S32: ATR-FTIR of spectra of (A) $(HO)_2$-$PNIPAM_{31}$-N_3 (**5e**), (B) $(HO)_2$-$PNIPAM_{37}$-N_3 (**5f**) and (C) $(HO)_2$-$PNIPAM_{40}$-N_3 (**5g**).