Electronic Supplementary Material (ESI) for Polymer Chemistry

Cyclic Polystyrene Topologies via RAFT and CuAAC.

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Table S1: Summary of kinetic analysis data for the synthesis of 2-arm cPSTY under three different conditions at 25 ^{o}C. Reactants; cPSTY-N_3 (**7**) + propagyl ether.

CuBr/PMDETA		**CuBr/DMF**		**CuBr/triazole**	
Time (hours)	% of dicyclic	Time (hours)	% of dicyclic	Time (hours)	% of dicyclic
0.167	79	0.167	87	0.167	27
0.5	75	0.75	87	2.5	85
1	67	3	87	5	87
3	42	7	86	12	89
7	28	14	85	24	88
24	5	24	81		

Table S2: Summary of kinetic analysis data for the synthesis of 3-arm cPSTY under three different conditions at 25 ^{o}C. Reactants; cPSTY-N_3 (**7**) + tripropagylamine.

CuBr/PMDETA			**CuBr/DMF**			**CuBr/triazole**		
Time	dicyclic	tricyclic	**Time**	dicyclic	tricyclic	**Time**	dicyclic	tricyclic
10 m	7	71	10m	5	47	10 m	12	19
30m	12	60	45m	6	55	2.5 h	7	78
1h	17	50	3h	6	54	5h	6	82
2h	16	43	7h	5	56	12h	4	89
5h	8	29	14h	6	58	24h	5	88
24h	2	3	24h	6	58	--	--	--

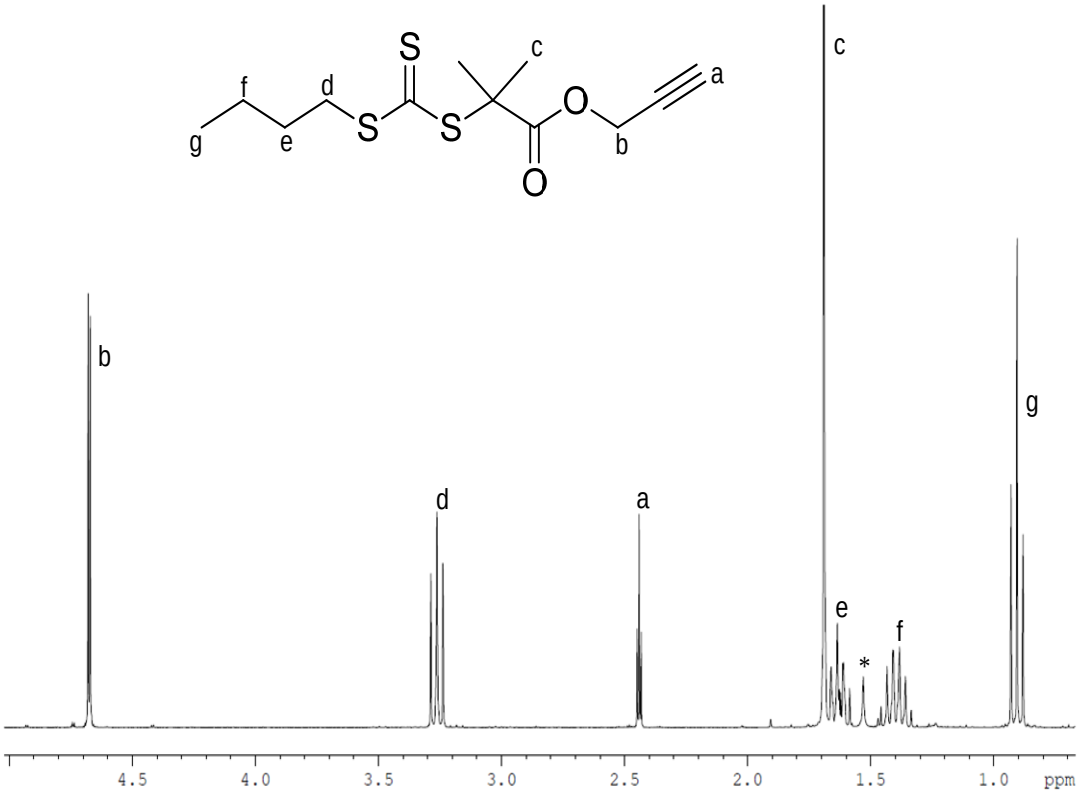

Figure S1. Prop-2-ynyl-2-(butylthiocarbonothioylthio)-2-methylpropanoate alkyne RAFT, chain transfer agent **1** in $CDCl_3$ (* H_2O).

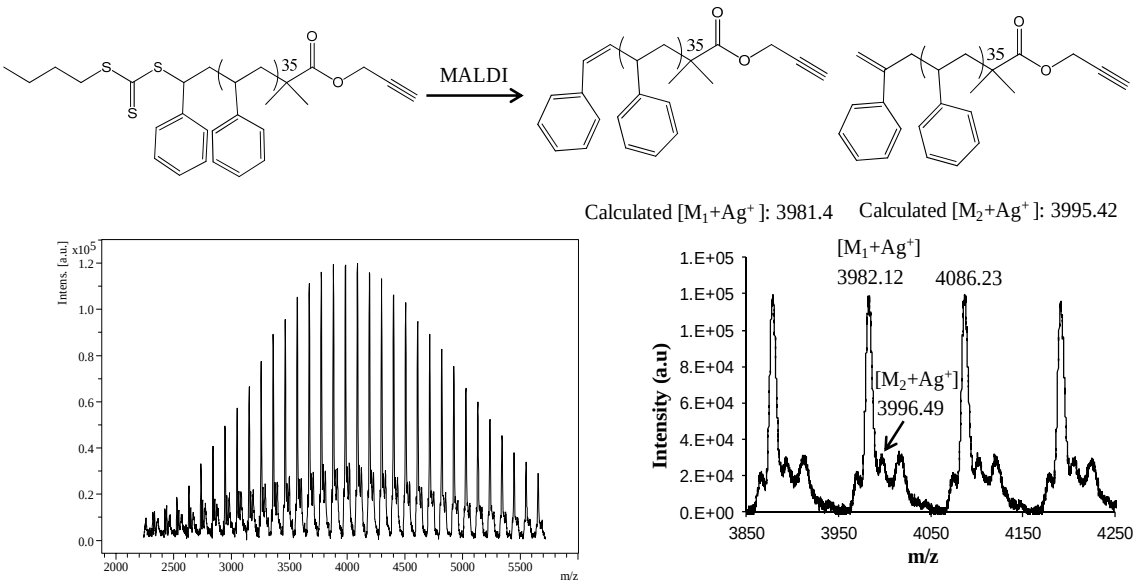

Figure S2: MALDI-ToF mass spectrum acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to RAFT-PSTY-Alk **2** ; calculated [M+Ag^+] = 3981.4 for the fragmentation of RAFT polymer , DP_n = 36.

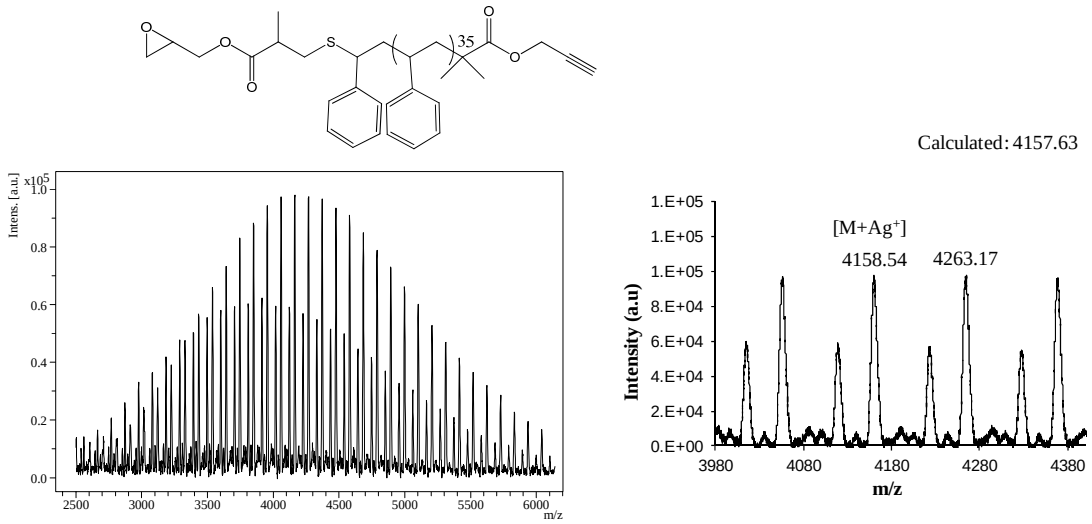

Figure S3: MALDI-ToF mass spectrum acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to Epo-PSTY-Alk **3** ; calculated [M+Ag^+] = 4157.63, DP_n = 36. The another fragmentation peak was unknown.

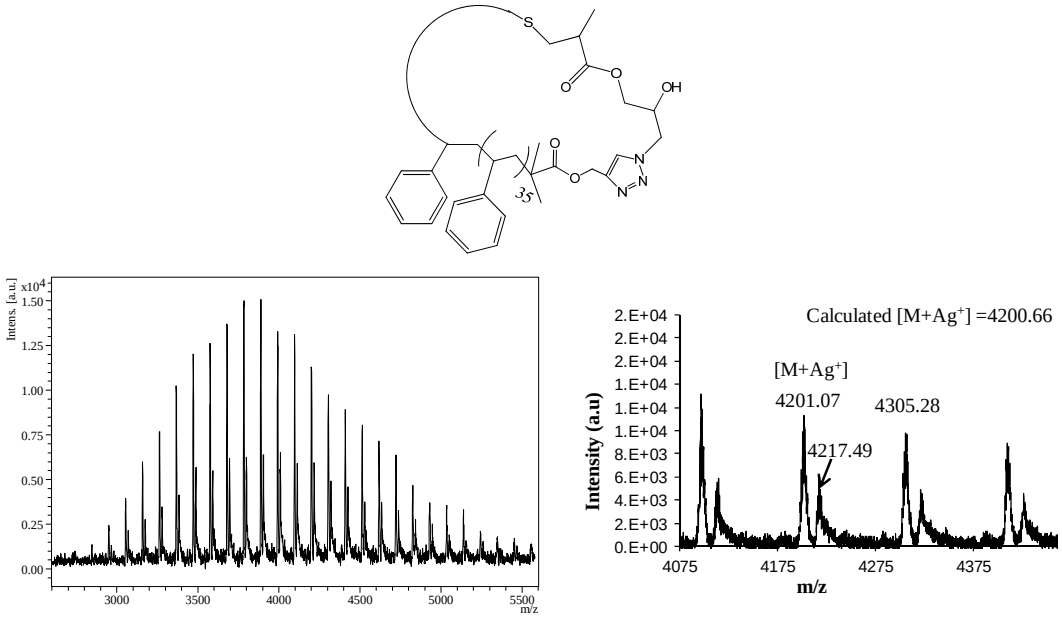

Figure S4: MALDI-ToF mass spectrum acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to cPSTY-OH **5** ; calculated $[M+Ag^+]$ = 4200.66, DP_n = 36.

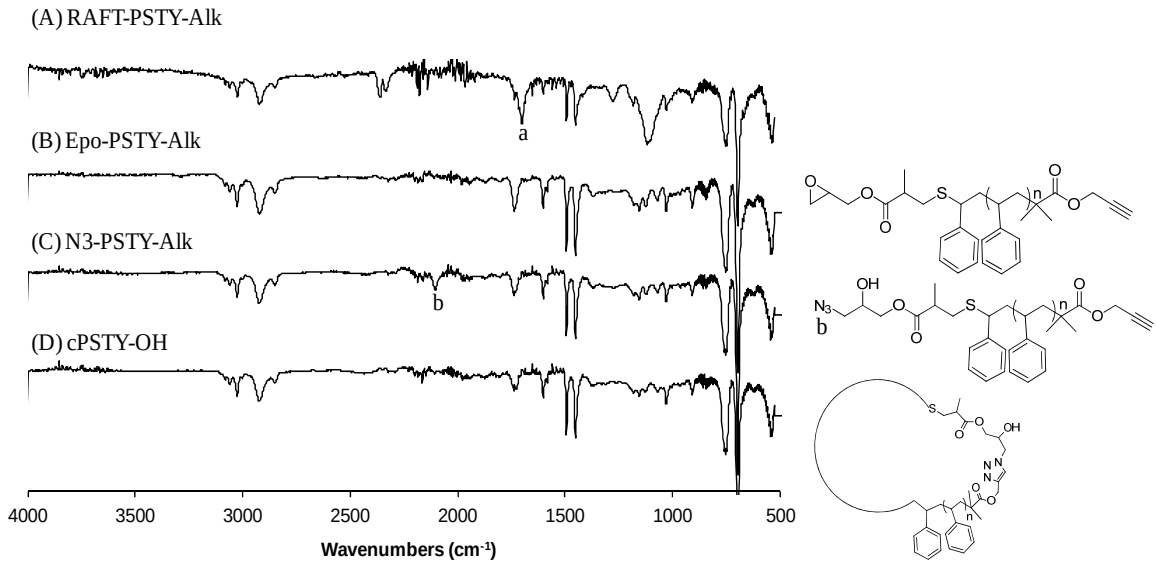

Figure S5. ATR-FTIR analysis of (A) RAFT-PSTY-Alk **2** (B) Epo-PSTY-Alk **3** (C) N_3-PSTY-Alk **4** and (D) cPSTY-OH **5**.

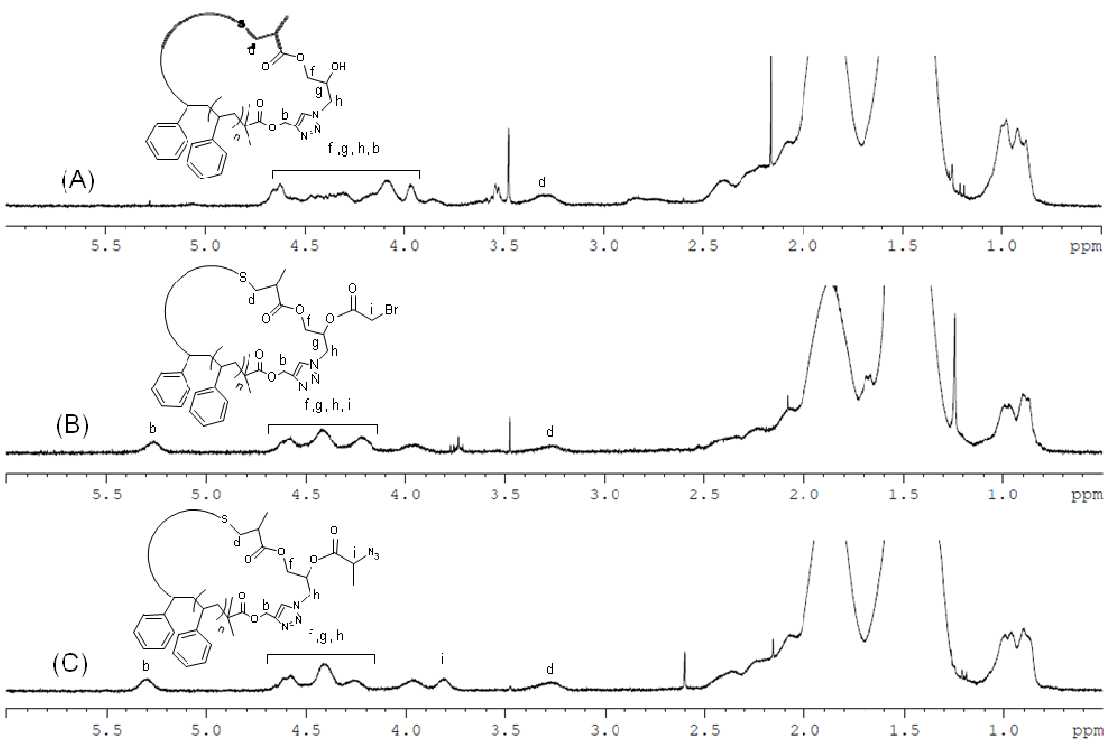

Figure S6: 500 MHz ^{1}H 1D DOSY NMR spectra of (A) cPSTY-OH **5** (B) cPSTY-Br **6** and (C) cPSTY-N_3 **7** (*methanol).

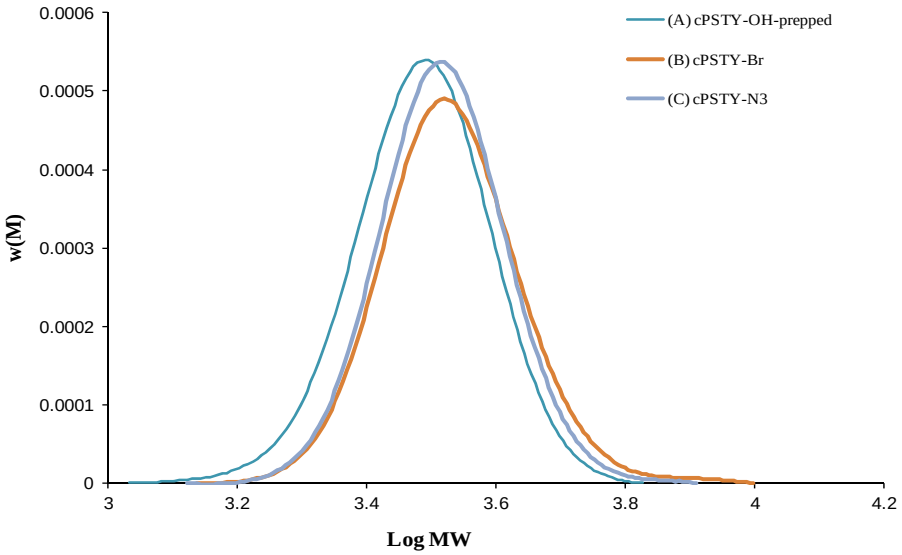

Figure S7: SEC chromatograms for cyclization of (A) cPSTY-OH –prepped purified **5 (**B) cPSTY-Br **6** and (C) cPSTY-N_3 **7**. SEC analysis based on polystyrene calibration curve.

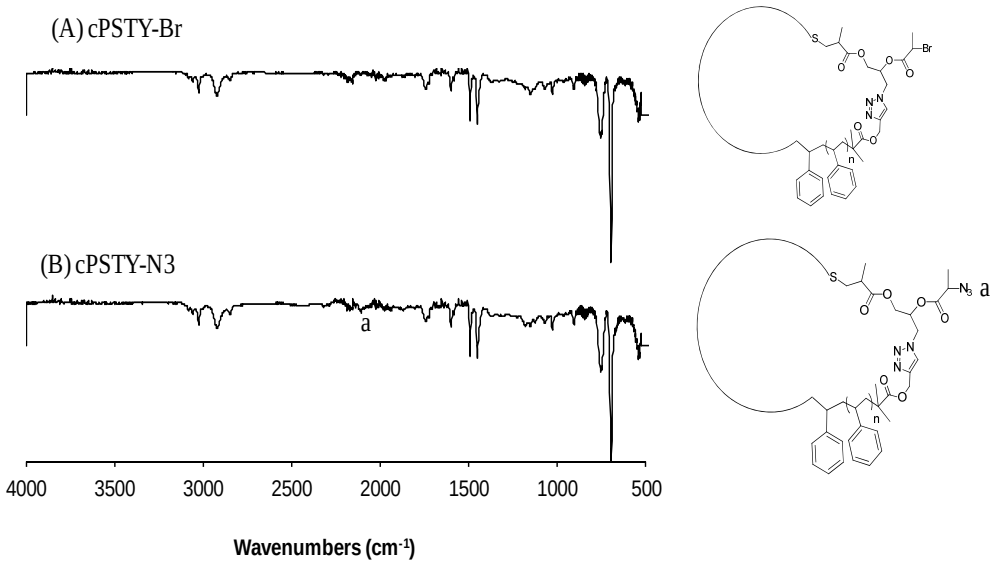

Figure S8. ATR-FTIR analysis of (A) cPSTY-Br **6** (B) cPSTY-N_3 **7**.

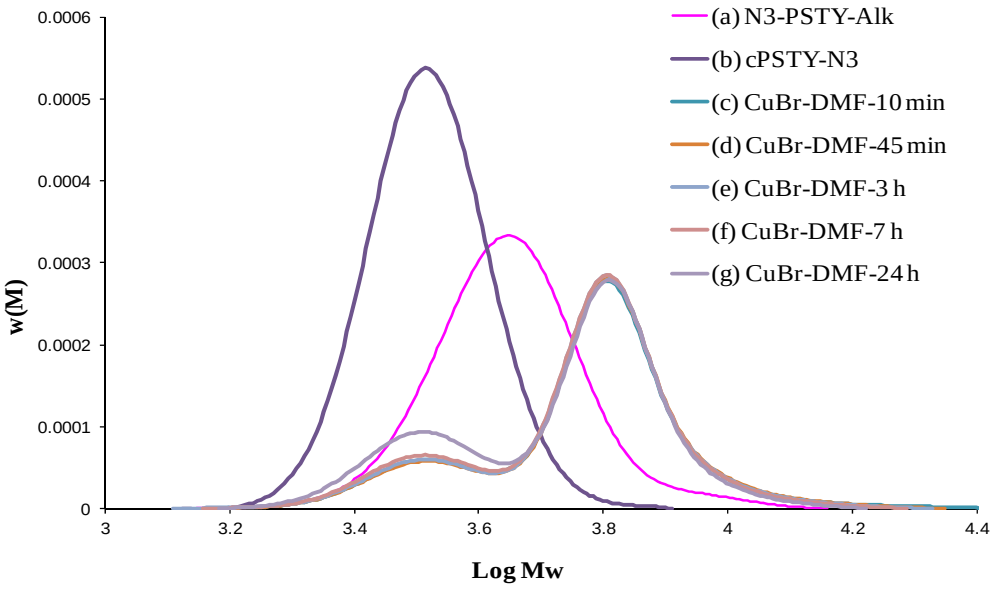

Figure S9: SEC chromatograms for the degradation studies in the synthesis of di-cyclic PSTY by one pot using CuBr/DMF; (a) N_3-PSTY-Alk 4 (b) cPSTY-N_3 7; degradation after (c) 10 min (d) 45 min (e) 3 h (f) 7 h and (h) 24 h.

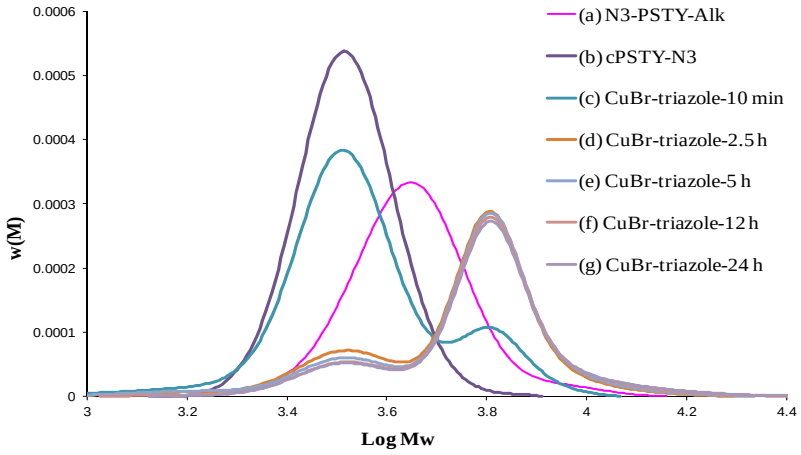

Figure S12: SEC chromatograms for the degradation studies in the synthesis of di-cyclic PSTY by one pot using CuBr/triazole in toluene; (a) N_3-PSTY-Alk **4 (**b) cPSTY-N_3 **7**; degradation after (c) 10 min (d) 2.5 h (e) 5h (f) 12 h and (g) 24 h.

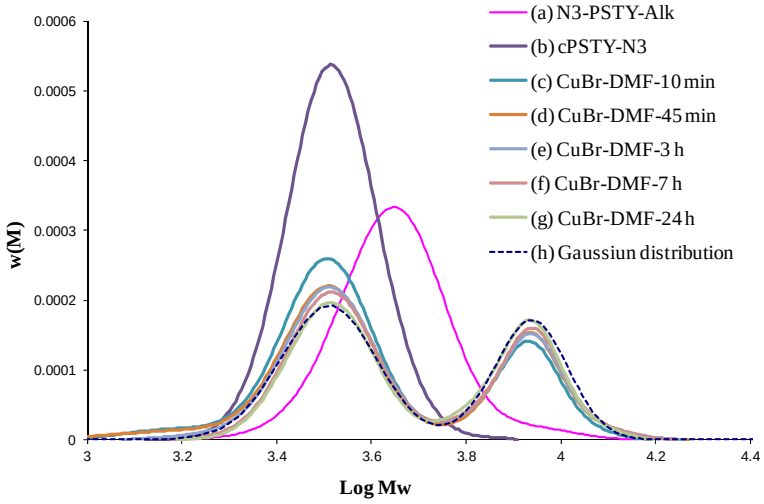

Figure S13: SEC chromatograms for the degradation studies in the synthesis of tri-cyclic PSTY by one pot using CuBr/DMF; (a) N3-PSTY-Alk **4** (b) cPSTY-N_3 **7**; degradation after (c) 10 min (d) 45 min (e) 3h (f) 7 h and (g) 24 h.

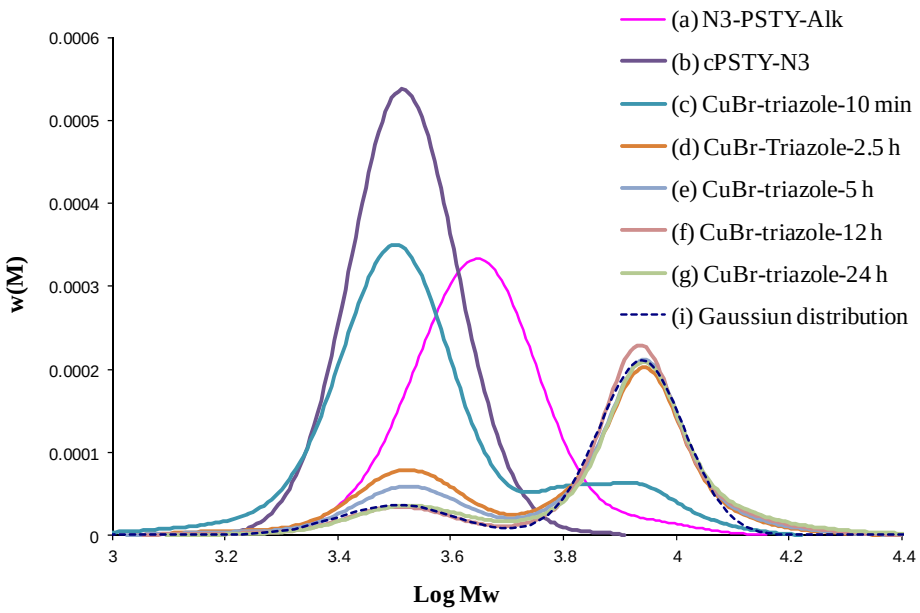

Figure S14: SEC chromatograms for the degradation studies in the synthesis of tri-cyclic PSTY by one pot using CuBr/triazole in toluene; (a) N_3-PSTY-Alk **4**, (b) cPSTY-N_3 7; degradation after (c) 10 min (d) 2.5 h (e) 5 h (f) 12 h and (g) 24 h.

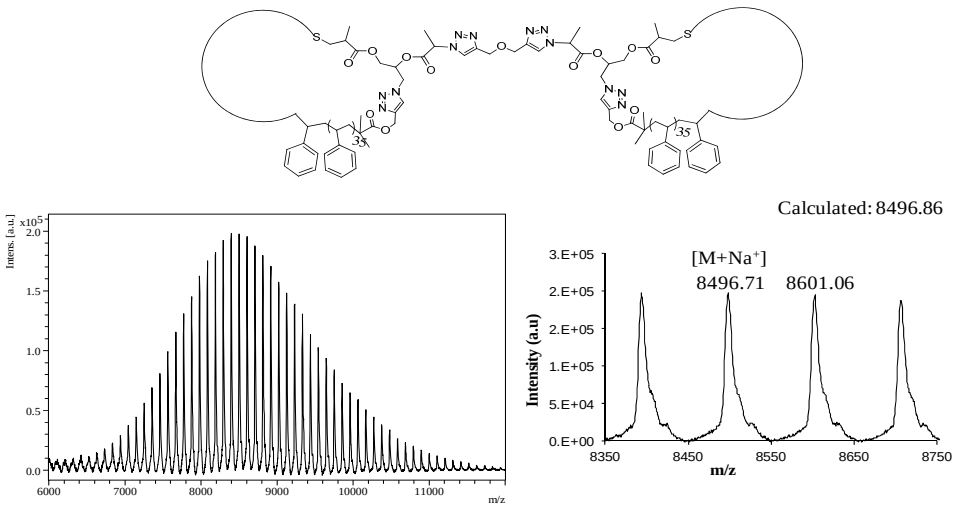

Figure S15: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to $(cPSTY)_2$ **8** ; calculated $[M+Na^+]$ = 8496.86, DP_n = 72.

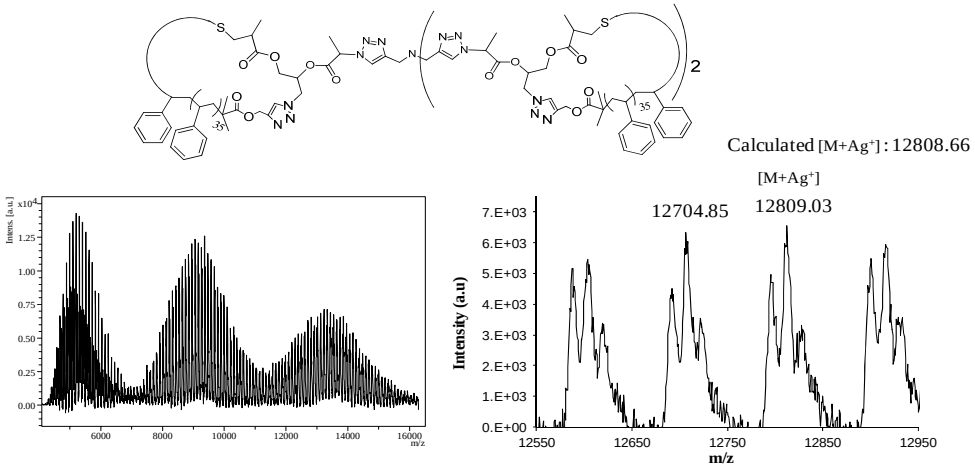

Figure S16: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to $(cPSTY)_3$ **9**; calculated $[M+Ag^+]$ = 12808.66, DP_n = 108.

Reference:

1. C. A. Bell, Z. Jia, S. Perrier, M. J. Monteiro, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, 49, 4539–4548