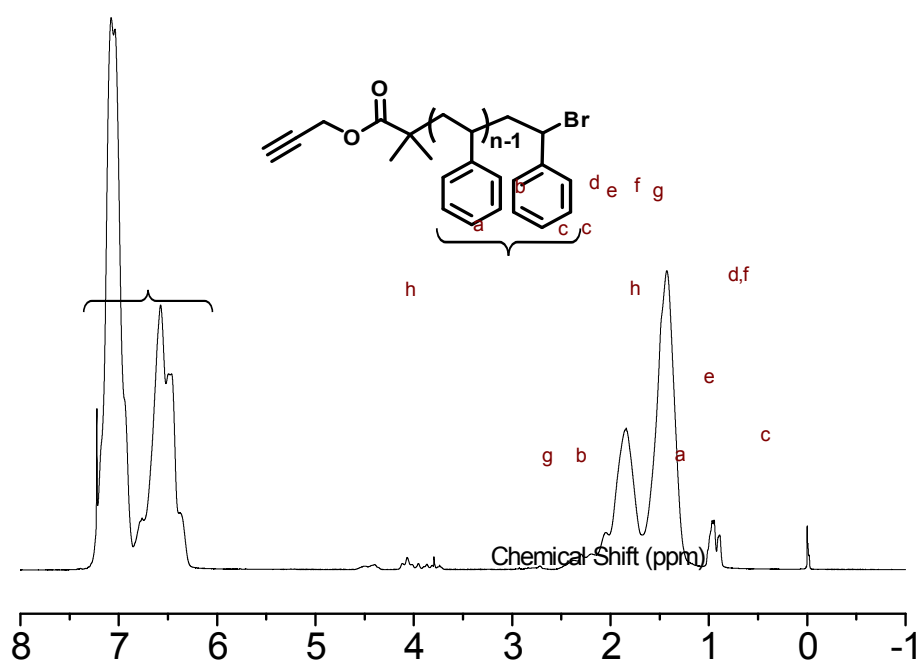
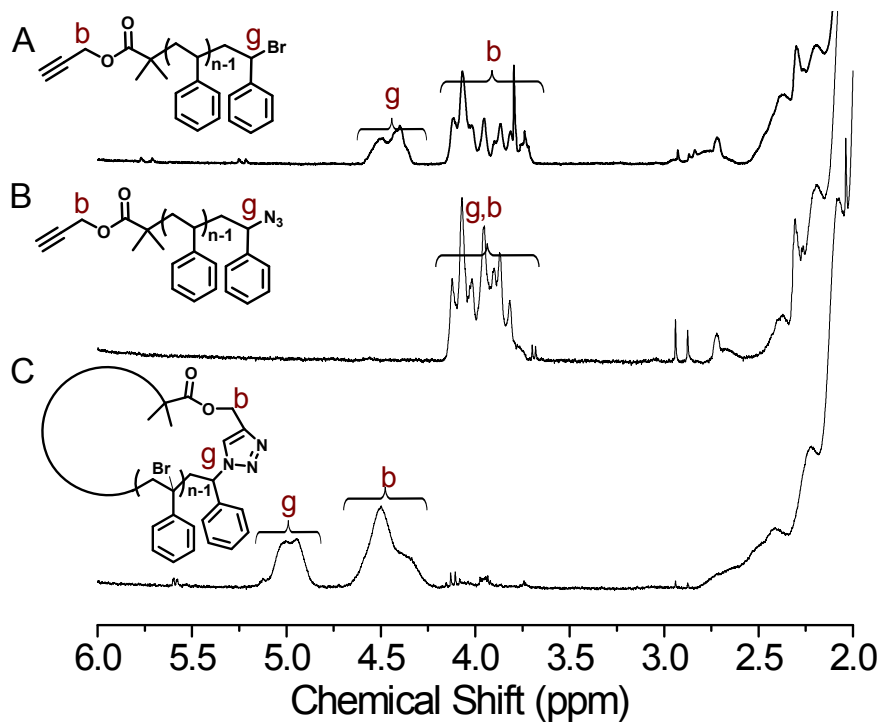


**Supporting Information for**  
**Synthesis of Diverse Cyclic-Brush Polymers with Cyclic Polystyrene**  
**as Universal Template *via* Grafting-from Approach**

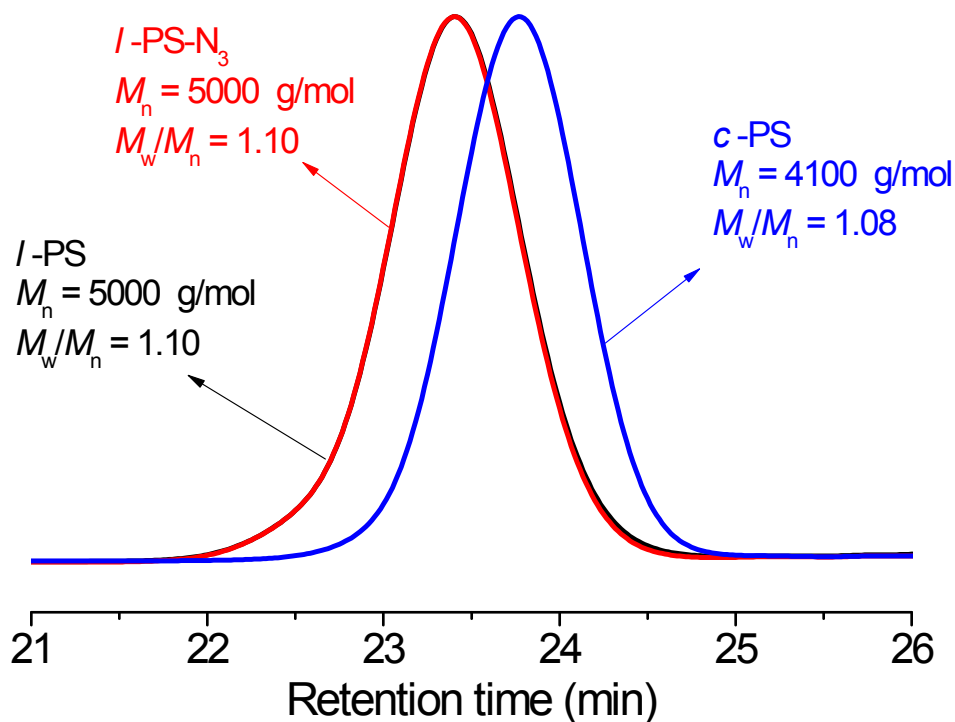
*Shuangshuang Zhang, Lu Yin, Wei Zhang\*, Zhengbiao Zhang\* and Xiulin Zhu\**



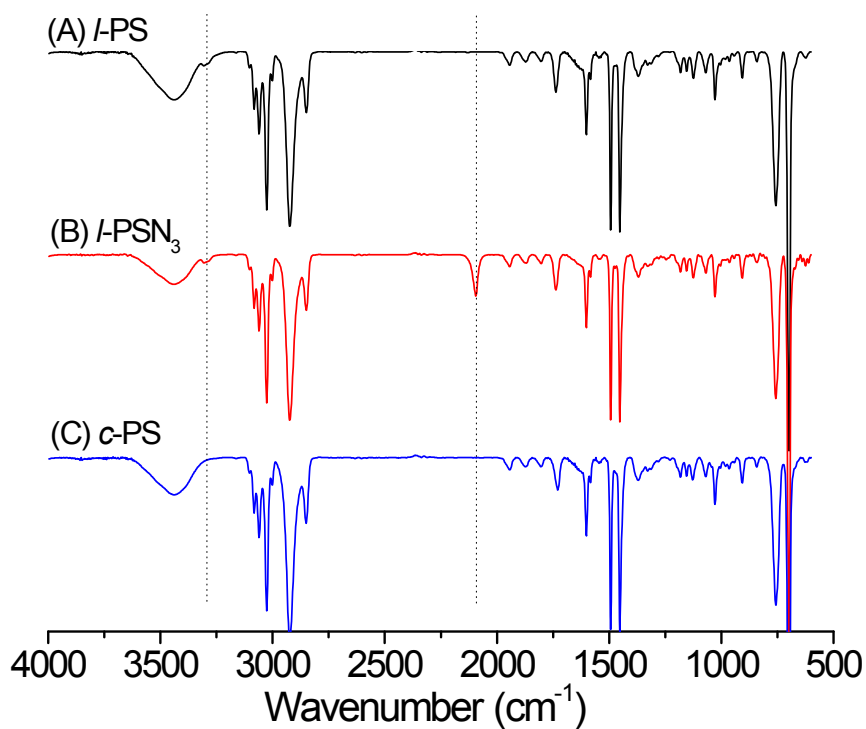
**Fig. S1.** Full <sup>1</sup>H NMR (300 MHz) spectrum of linear polystyrene (*l*-PS) precursor in CDCl<sub>3</sub>.



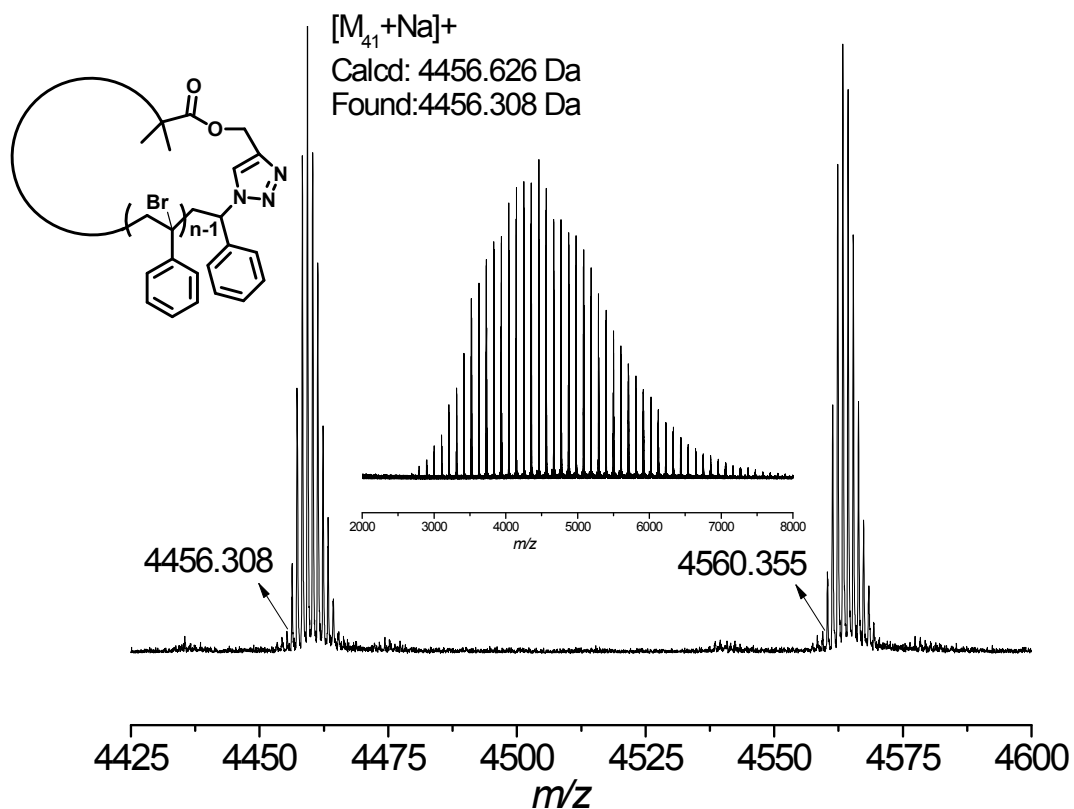
**Fig. S2.** Expanded <sup>1</sup>H NMR (300 MHz) spectra of (A) *l*-PS, (B) *l*-PS-N<sub>3</sub> and (C) purified *c*-PS in CDCl<sub>3</sub>.



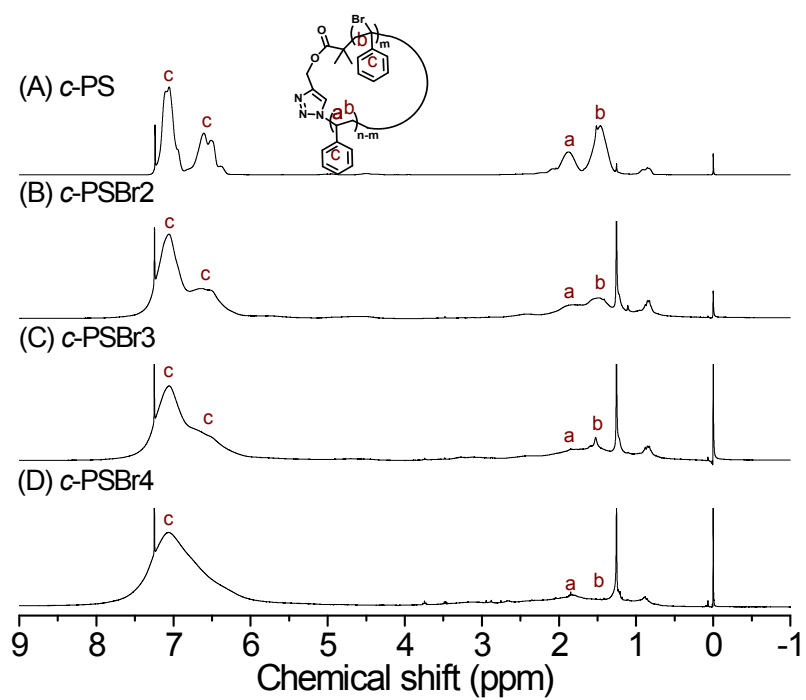
**Fig. S3.** GPC traces of *l*-PS, *l*-PS-N<sub>3</sub> and purified *c*-PS. DMF as the eluent and calibration with PS standards.



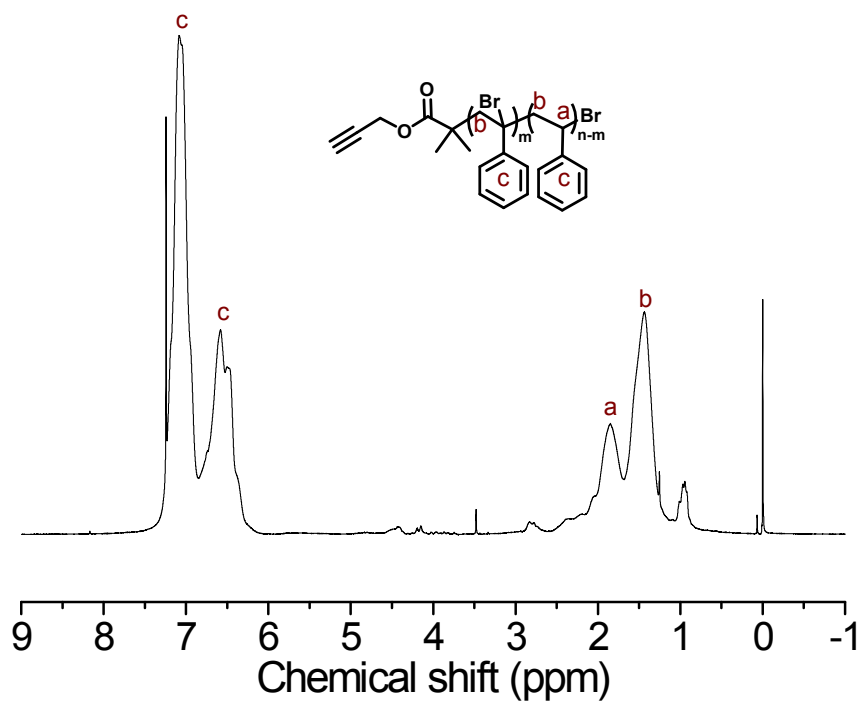
**Fig. S4.** FT-IR spectra of *l*-PS, *l*-PS-N<sub>3</sub> and purified *c*-PS.



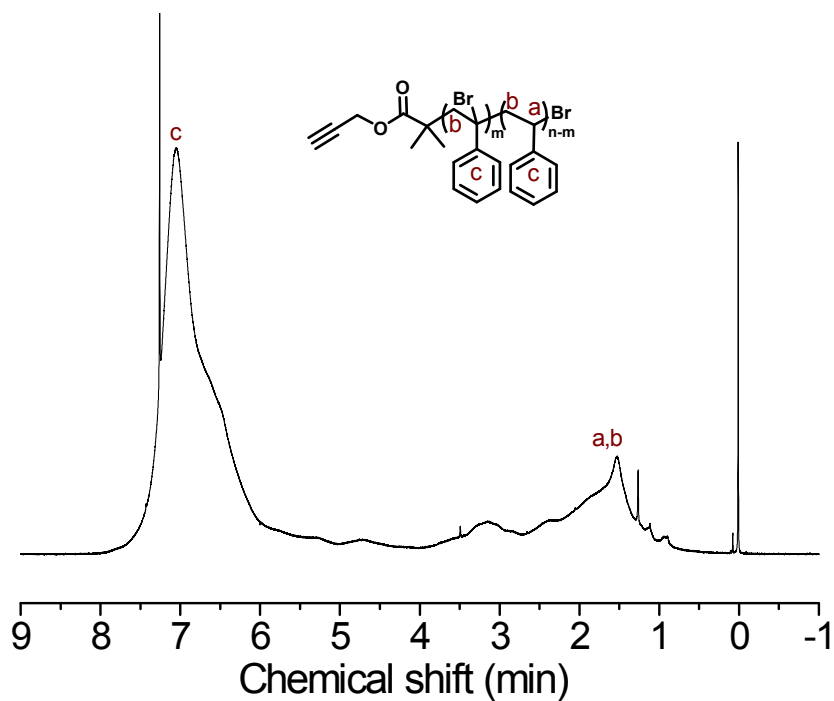
**Fig. S5.** Expanded MALDI-TOF mass spectra of purified cyclic polystyrene (*c*-PS) with the inserted full spectra.



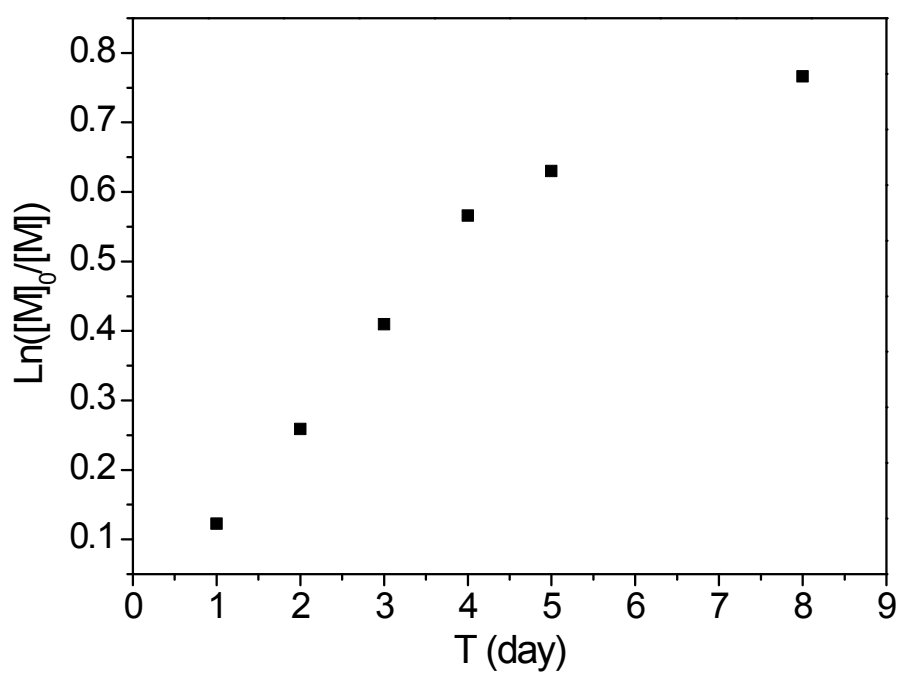
**Fig. S6.**  $^1\text{H}$  NMR (300 MHz) spectra of (A) *c*-PS, (B) *c*-PSBr<sub>2</sub>, (C) *c*-PSBr<sub>3</sub> and (D) *c*-PSBr<sub>4</sub> ( $\text{CDCl}_3$ ).



**Fig. S7.**  $^1\text{H}$  NMR (300 MHz) spectra of *l*-PSBr (Br mol % < 10%) at 55 °C ( $\text{CDCl}_3$ ).



**Fig. S8.** <sup>1</sup>H NMR (600 MHz) spectra of *l*-PSBr (Br mol %  $\approx$  50%) (CDCl<sub>3</sub>).

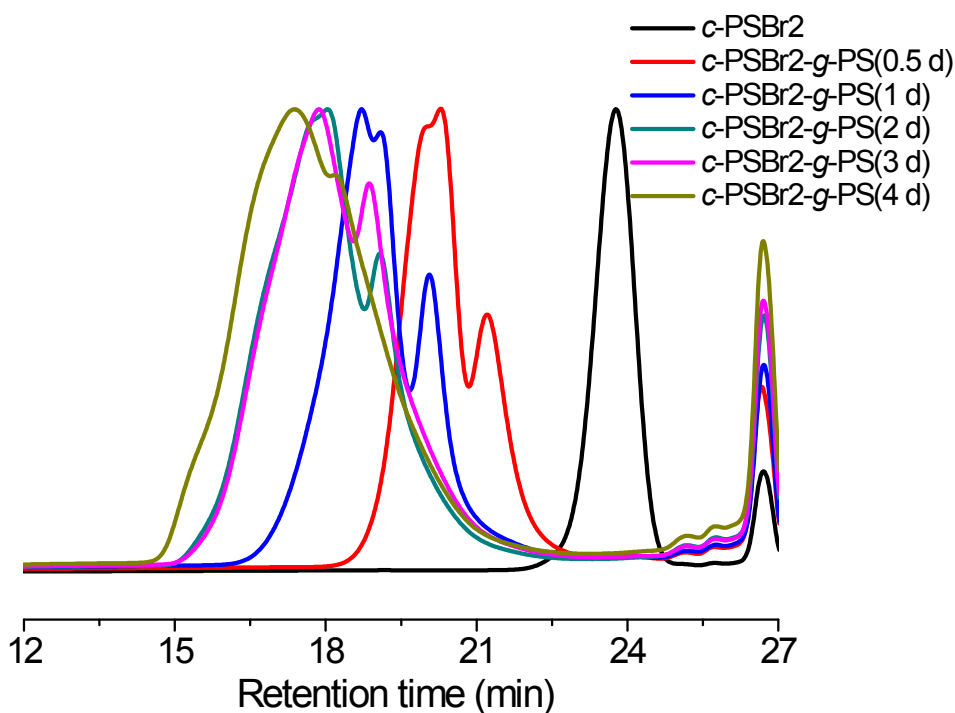


**Fig. S9.**  $\ln([M]_0/[M])$  vs polymerization time for grafting polymerization of St with *c*-PSBr1 as ATRP macroinitiator at 90 °C.

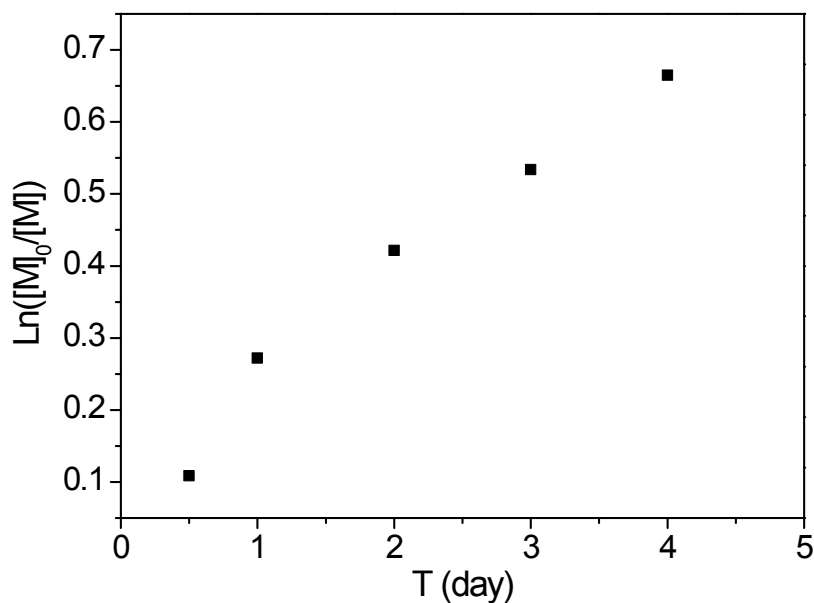
**Table S1.** Experimental results from graft polymerization of St with *c*-PSBr2 as macroinitiator, using CuBr/PMDETA as catalyst system at 90 °C under different time.

Entry	t (day)	$M_{n, \text{GPC}}$ (g/mol) <sup>a</sup>	$M_w/M_n^a$	Conv. <sup>b</sup> (%)	$T_g$ (°C)
1	0.5	21100	1.08	10.30	105.78
		56300	1.12		
2	1	151600	1.26	23.82	106.13
		42000	1.18		
3	2	330600	1.39	34.39	106.93
		71400	1.28		
4	3	273800	1.49	41.36	107.80
		55300	1.30		
5	4	190800	2.56	48.57	106.83

$[c\text{-PSBr}_2]_0 : [\text{St}]_0 : [\text{CuBr}]_0 : [\text{PMDETA}]_0 = 1 : 100 : 1 : 1$ ; *c*-PSBr2 (25.3 mol%Br)  
 Calculated by elementary analysis; <sup>a</sup>From GPC measurement calibrated by PS standards; <sup>b</sup>Conversion calculated by gravimetric method.



**Fig. S10.** GPC curves of *c*-PSBr2 (25.3%) and a series of cyclic-brush polymers prepared with *c*-PSBr2 as macroinitiator. THF as the eluent and calibration with PS standards.



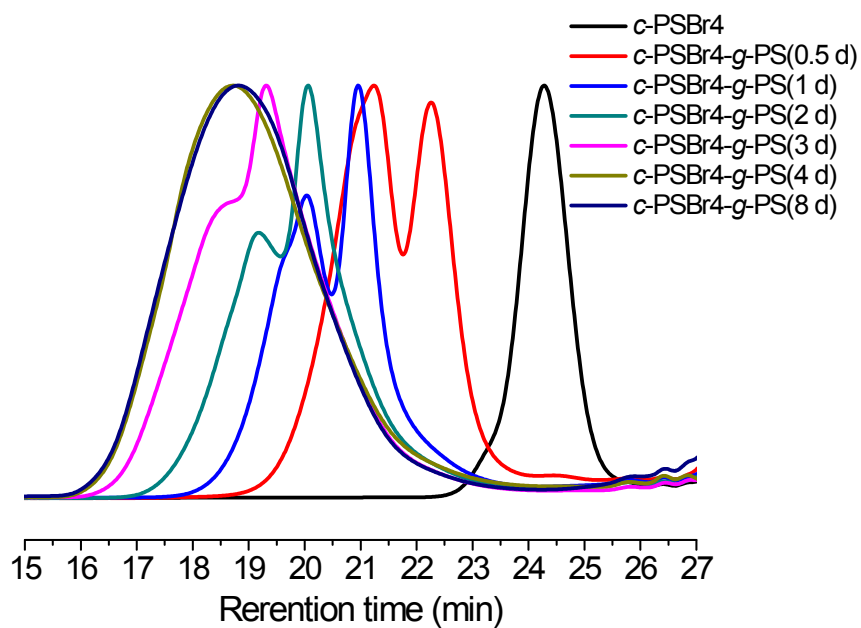
**Fig. S11.** Ln ( $[M_0]/ [M]$ ) vs polymerization time for grafting polymerization of St with *c*-PSBr2 as macroinitiator at 90 °C.

**Table S2.** Experimental results from the graft polymerization of St with *c*-PSBr4 as macroinitiator, using CuBr/PMDETA as catalyst system at 90 °C under different time.

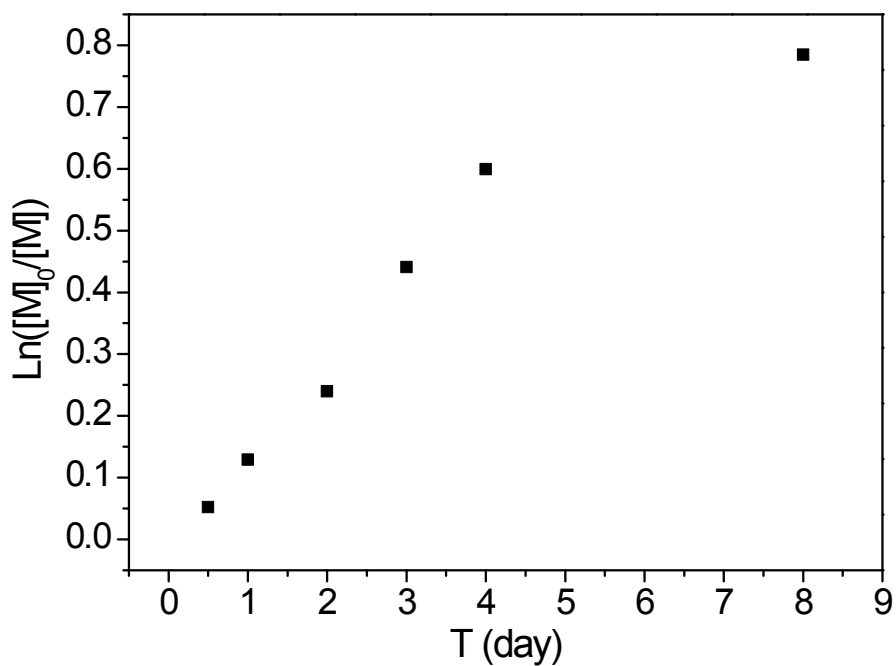
Entry	t (day)	$M_{n, GPC}$ (g/mol) <sup>a</sup>	$M_w/M_n$ <sup>a</sup>	Conv. <sup>b</sup> (%)	$T_g$ (°C)																														
1	0.5	44200	1.16	5.08	104.02																														
		16100	1.08			2	1	106900	1.16	12.10	101.68	34400	1.19	3	2	208400	1.18	21.31	105.49	53200	1.34	4	3	104100	2.24	35.66	105.28	5	4	116000	2.49	45.09	105.40	6	8
2	1	106900	1.16	12.10	101.68																														
		34400	1.19			3	2	208400	1.18	21.31	105.49	53200	1.34	4	3	104100	2.24	35.66	105.28	5	4	116000	2.49	45.09	105.40	6	8	124200	2.37	54.38	105.23				
3	2	208400	1.18	21.31	105.49																														
		53200	1.34			4	3	104100	2.24	35.66	105.28	5	4	116000	2.49	45.09	105.40	6	8	124200	2.37	54.38	105.23												
4	3	104100	2.24	35.66	105.28																														
5	4	116000	2.49	45.09	105.40																														
6	8	124200	2.37	54.38	105.23																														

$[c\text{-PSBr4}]_0 : [St]_0 : [CuBr]_0 : [PMDETA]_0 = 1 : 100 : 1 : 1$ ; *c*-PSBr2 (50.3 mol%Br)

Calculated by elementary analysis; <sup>a</sup>From GPC measurement calibrated by PS standard; <sup>b</sup>Conversion calculated by gravimetric method.

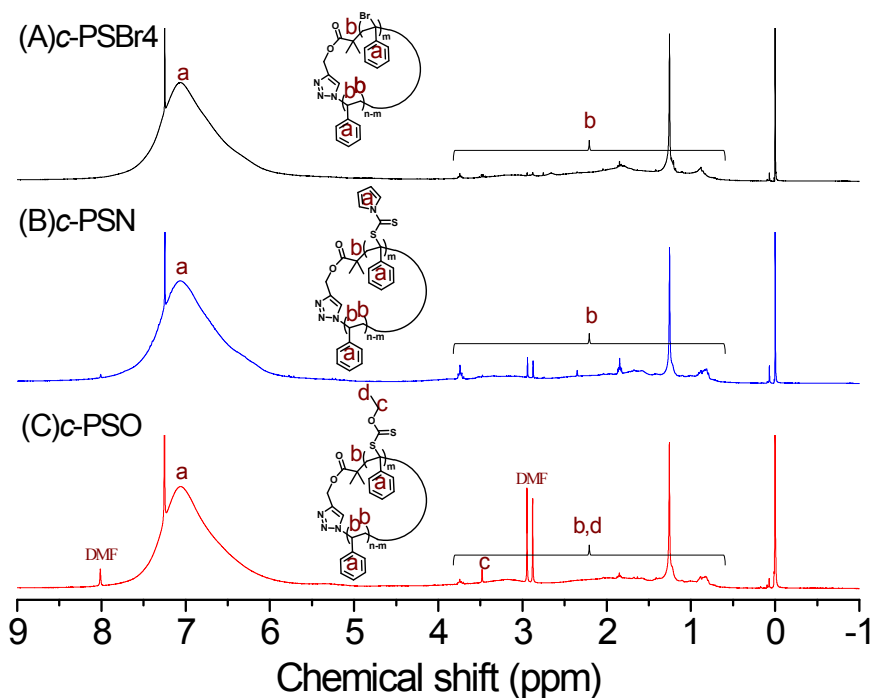


**Fig. S12.** GPC curves of *c*-PSBr4 (50.3%) and a series of cyclic-brush polymers prepared with *c*-PSBr4 as macroinitiator. THF as the eluent and calibration with PS standards.



**Fig. S13.**  $\ln([M]_0/[M])$  vs polymerization time for grafting polymerization of St with *c*-PSBr4 as macroinitiator at 90 °C.



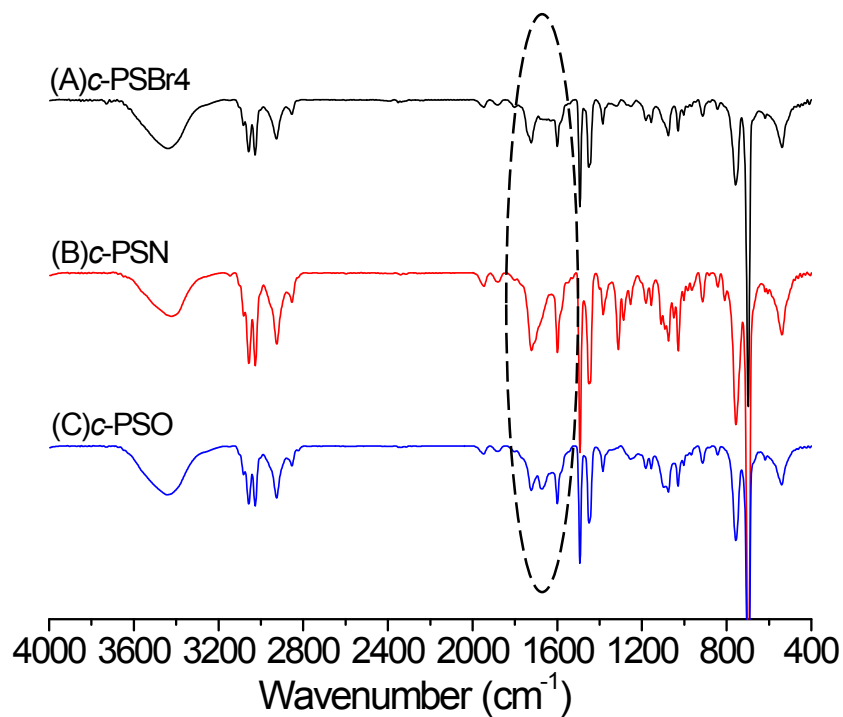


**Fig. S14.**  $^1\text{H}$  NMR (300 MHz) spectra of (A) *c*-PSBr<sub>4</sub>, (B) *c*-PSN and (C) *c*-PSO in  $\text{CDCl}_3$ .

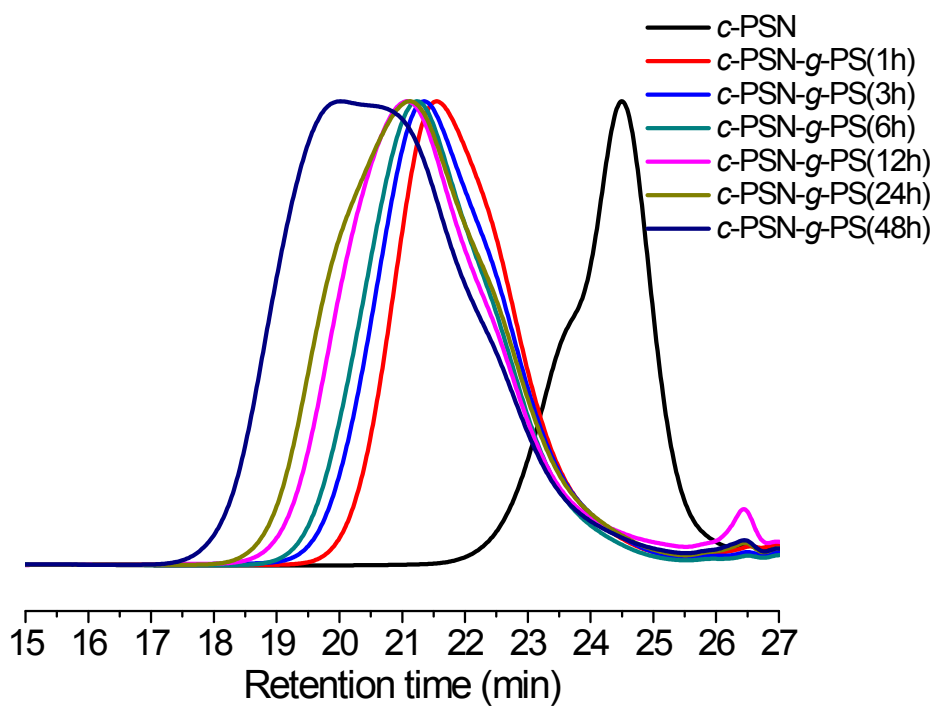
**Table S3.** Experimental results from the graft polymerization of St with *c*-PSN/AIBN/toluene system at 90 °C under different time.

Entry	t (h)	$M_{n,\text{GPC}}$ (g/mol) <sup>a</sup>	$M_{w,\text{GPC}}$ (g/mol) <sup>a</sup>	$M_w/M_n^a$	Conv. <sup>b</sup> (%)
1	1	19200	29400	1.53	22.70
2	3	21100	35300	1.67	37.96
3	6	23700	40400	1.70	40.14
4	12	30300	54800	1.81	47.80
5	24	29200	59800	2.05	52.03
6	48	40200	97600	2.43	67.45

$[c\text{-PSN}]_0 : [\text{St}]_0 : [\text{AIBN}]_0 = 1 : 200 : 0.5$ ; <sup>a</sup>From GPC measurement calibrated by standard PS; <sup>b</sup>Conversion calculated by gravimetric method.



**Fig. S15.** FT-IR spectra of (A) *c*-PSBr<sub>4</sub>, (B) *c*-PSN and (C) *c*-PSO.

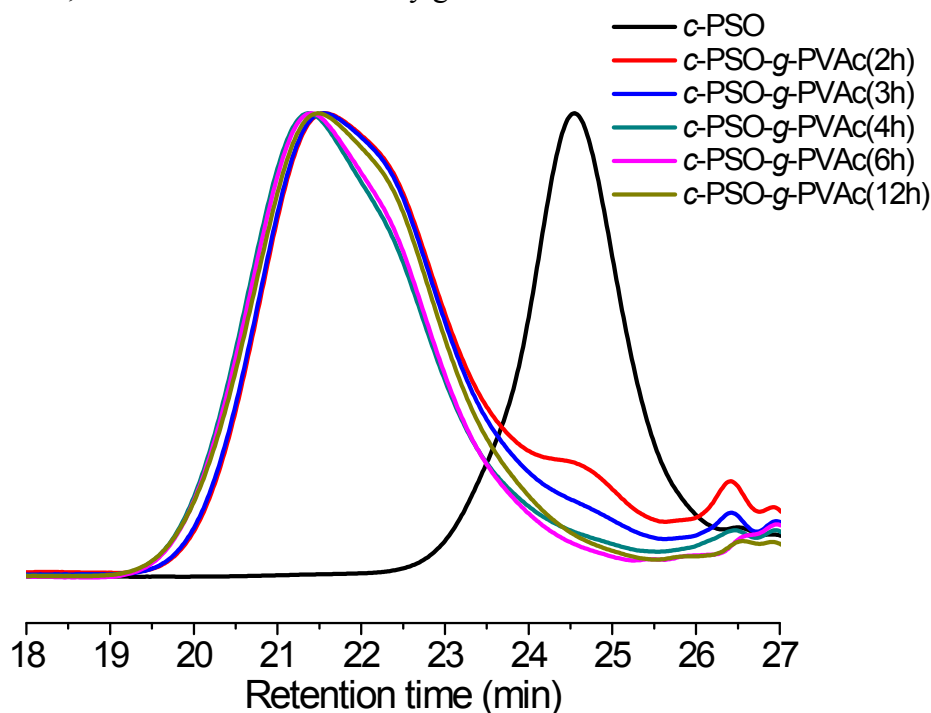


**Fig. S16.** GPC curves of *c*-PSBr<sub>N</sub> and a series of cyclic-brush polymers prepared with *c*-PSBr<sub>N</sub> as macro-RAFT agent. THF as the eluent and calibration with PS standards.

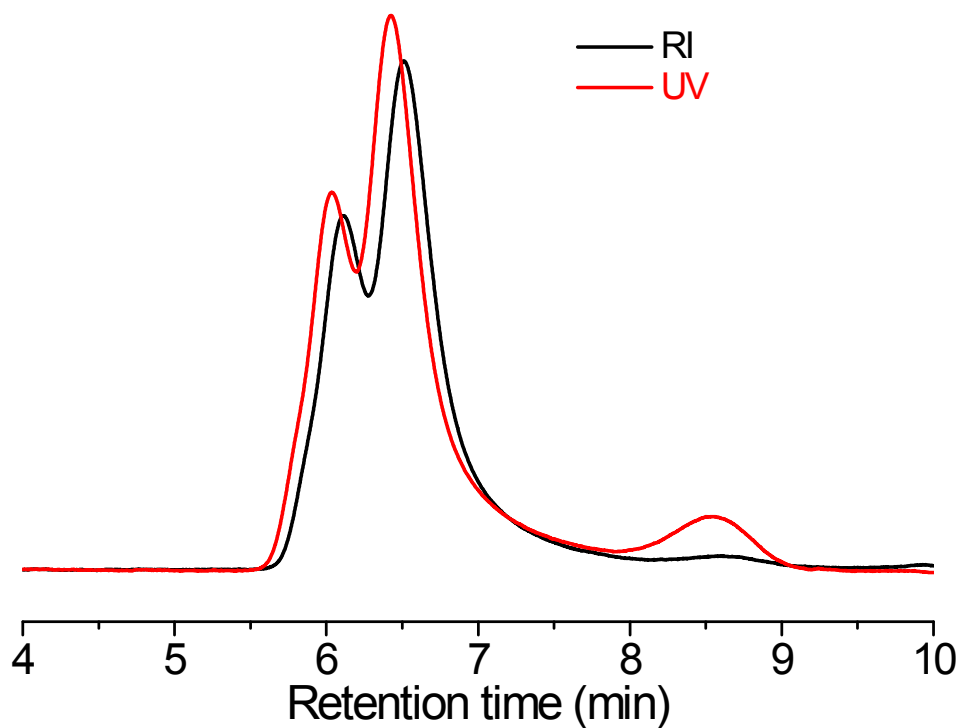
**Table S4.** Experimental results from the graft polymerization of VAc with *c*-PSO/AIBN/1, 4-dioxane system at 70 °C under different time.

Entry	t (h)	$M_{n, \text{GPC}}$ (g/mol) <sup>a</sup>	$M_{w, \text{GPC}}$ (g/mol) <sup>a</sup>	$M_w/M_n^a$	Conv. <sup>b</sup> (%)
1	2	15000	27900	1.85	11.96
2	3	16500	28900	1.75	31.70
3	4	20000	33600	1.68	36.94
4	6	20300	33300	1.64	53.46
5	12	18600	31600	1.71	70.11

$[c\text{-PSO}]_0 : [\text{VAc}]_0 : [\text{AIBN}]_0 = 1 : 200 : 0.5$ ; <sup>a</sup>From GPC measurement calibrated by standard PS; <sup>b</sup> Conversion calculated by gravimetric method.



**Fig. S17.** GPC curves of *c*-PSO and a series of cyclic-brush polymers prepared with *c*-PSO as macro-RAFT agent. THF as the eluent and calibration with PS standards.



**Fig. S18.** GPC curves of *c*-PSBr1-g-PS (polymerization time 24 h) gained by GPC dual detection (RI/UV) technique.