Supporting Information

Dispersion RAFT polymerization: comparison between the monofunctional and bifunctional macromolecular RAFT agents

Chengqiang Gao, Shentong Li, Quanlong Li, Pengfei Shi, Sayyar Ali Shah and Wangqing Zhang*

Key Laboratory of Functional Polymer Materials of the Ministry of Education, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Institute of Polymer Chemistry, Nankai University, Tianjin 300071, China.

* To whom correspondence should be addressed. E-mail: wqzhang@nankai.edu.cn, Tel: 86-22-23509794, Fax: 86-22-23503510.

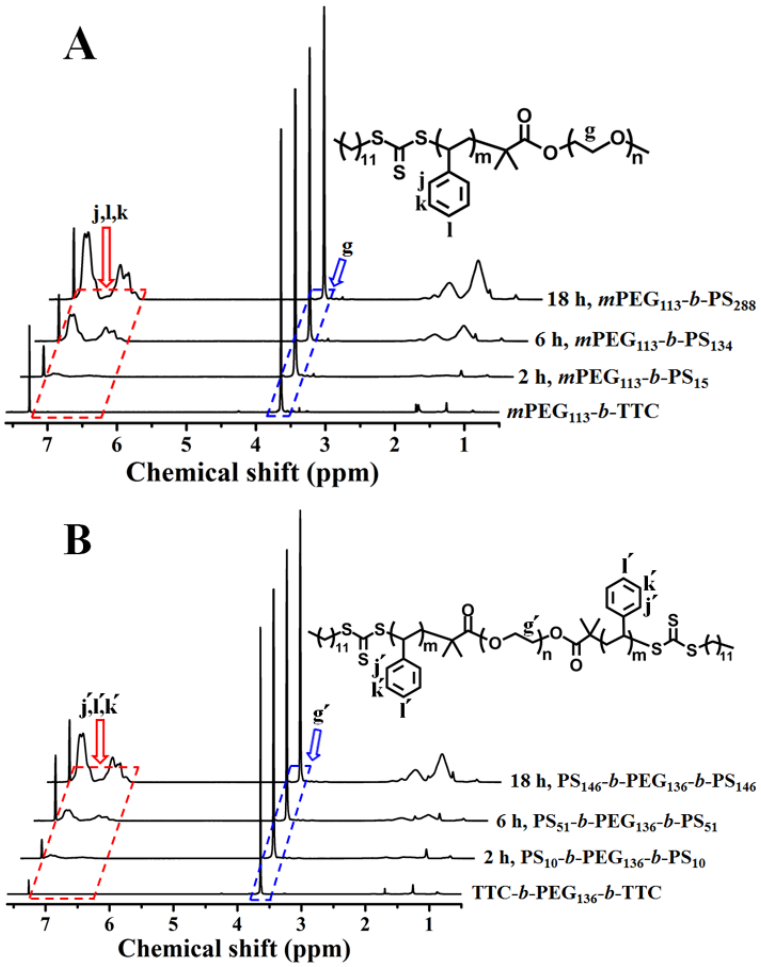

Figure S1. The ^{1}H NMR spectra of the *m*PEG$_{113}$-*b*-PS diblock copolymers (A) and the PS-*b*-PEG$_{136}$-*b*-PS triblock copolymers (B) synthesized at different polymerization times.

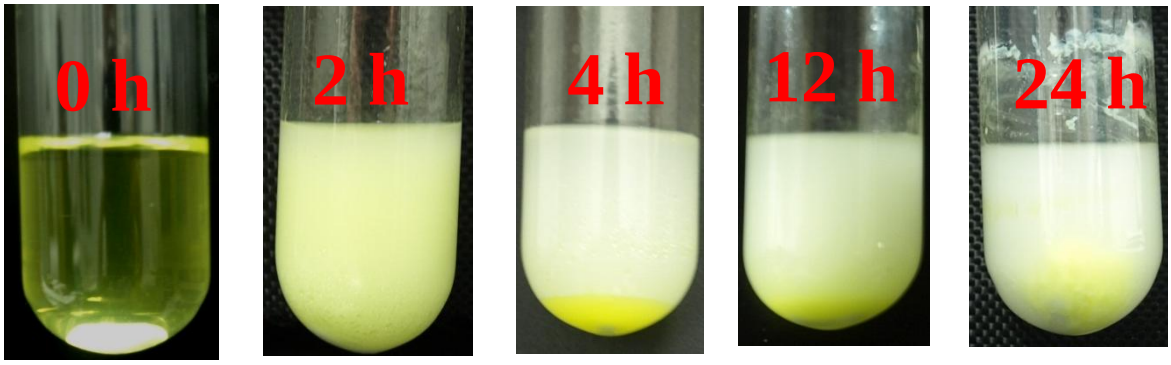

Figure S2. Optical photos of the polymerization solution of the dispersion polymerization in the presence of the bifunctional TTC-PEG$_{45}$-TTC macro-RAFT agent at different polymerization time.

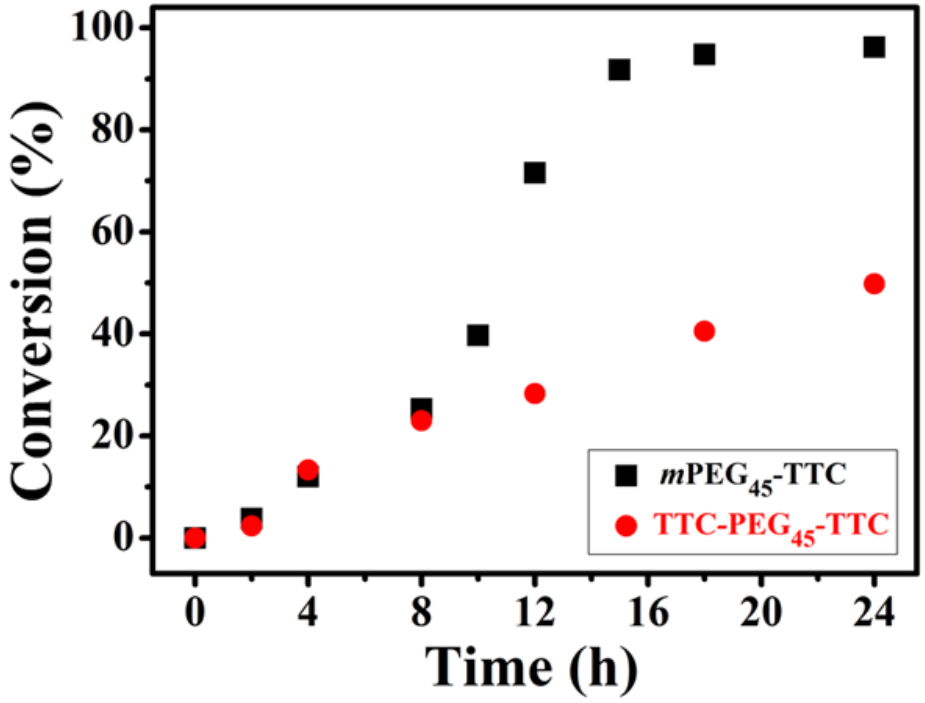

Figure S3. The monomer conversion-time plots for the dispersion RAFT polymerization of St mediated with the macro-RAFT agent of *m*PEG$_{45}$-TTC or TTC-PEG$_{45}$-TTC. Polymerization conditions: St (1.00 g, 9.60 mmol), the methanol/water mixture (6.69 g, 80/20 by weight), [St]$_0$:[*m*PEG$_{45}$-TTC]$_0$:[AIBN]$_0$ = 900:3:1 or [St]$_0$:[TTC-PEG$_{45}$-TTC]$_0$:[AIBN]$_0$ = 900:3:2, 70 ^{o}C.

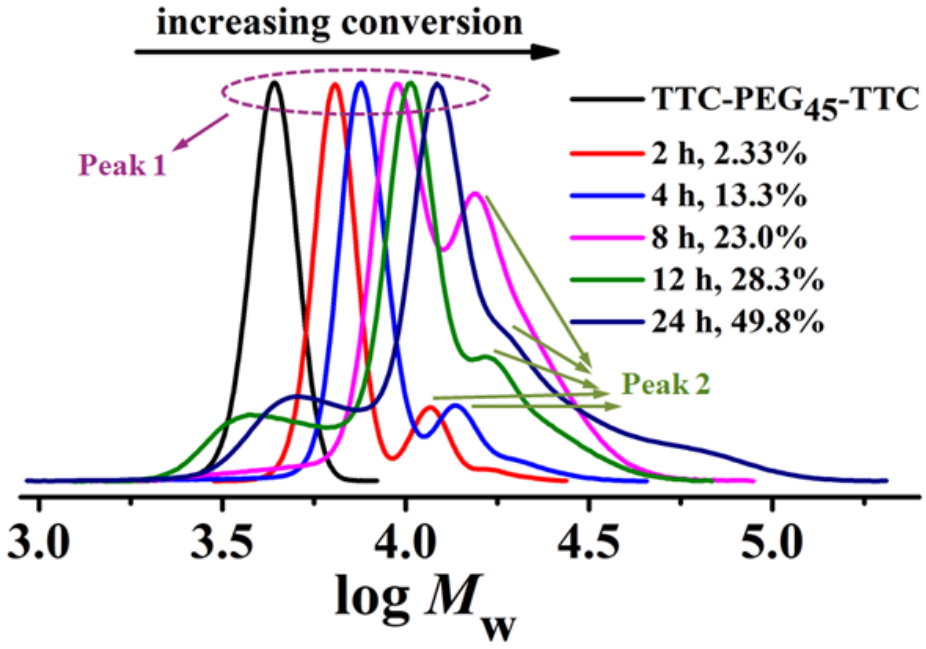

Figure S4. The GPC traces of the PS-*b*-PEG$_{45}$-*b*-PS triblock copolymers synthesized through dispersion polymerization of St mediated with the TTC-PEG$_{45}$-TTC macro-RAFT agent.

Table S1. Summary of the GPC analysis of the PS-*b*-PEG$_{45}$-*b*-PS triblock copolymers.

Time (h)	[a]$M_{peak\ 1}$ (kg/mol)	[b]$M_{peak\ 2}$ (kg/mol)	[c]$M_{n,GPC}$ (kg/mol)	[d]PDI
0	4.1		4.0	1.02
2	6.2	11.7	6.9	1.09
4	7.4	13.4	8.2	1.13
8	9.4	14.1	11.8	1.24
12	10.0	16.8	8.7	1.38
24	12.2	18.8	10.9	1.64

[a]The molecular weight of peak 1 determined by GPC analysis. [b]The molecular weight of peak 2 determined by GPC analysis. [c]The molecular weight determined by GPC analysis. [d]The PDI (M_w/M_n) value determined by GPC analysis.

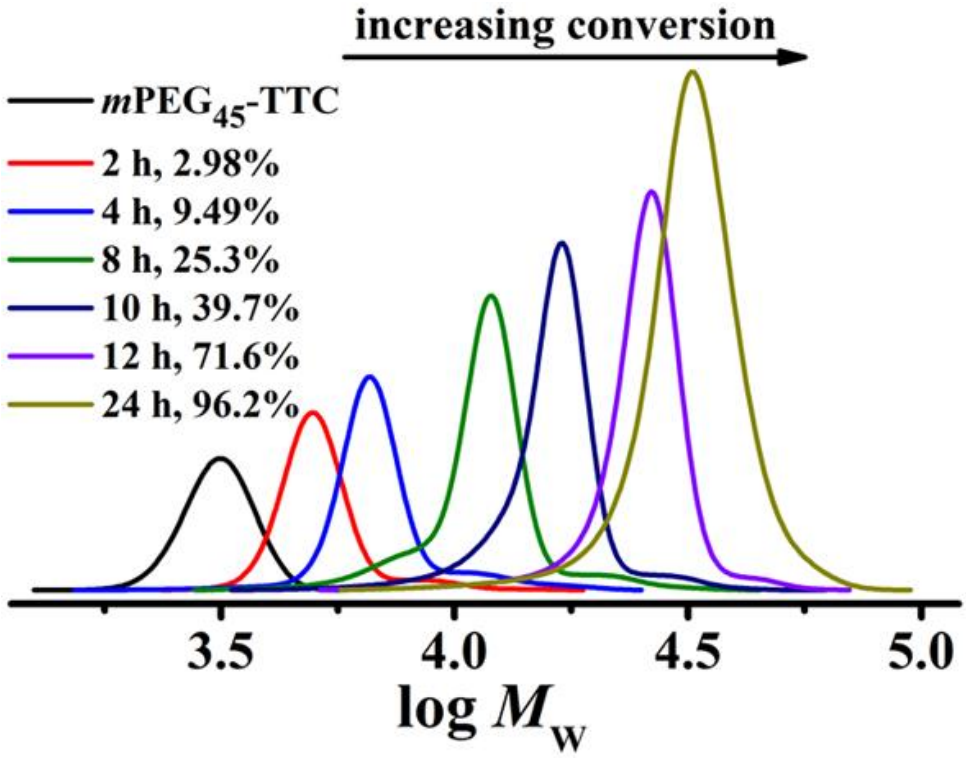

Figure S5. The GPC traces of the *m*PEG$_{45}$-*b*-PS diblock copolymers synthesized through dispersion polymerization of St mediated with the *m*PEG$_{45}$-TTC macro-RAFT agent.

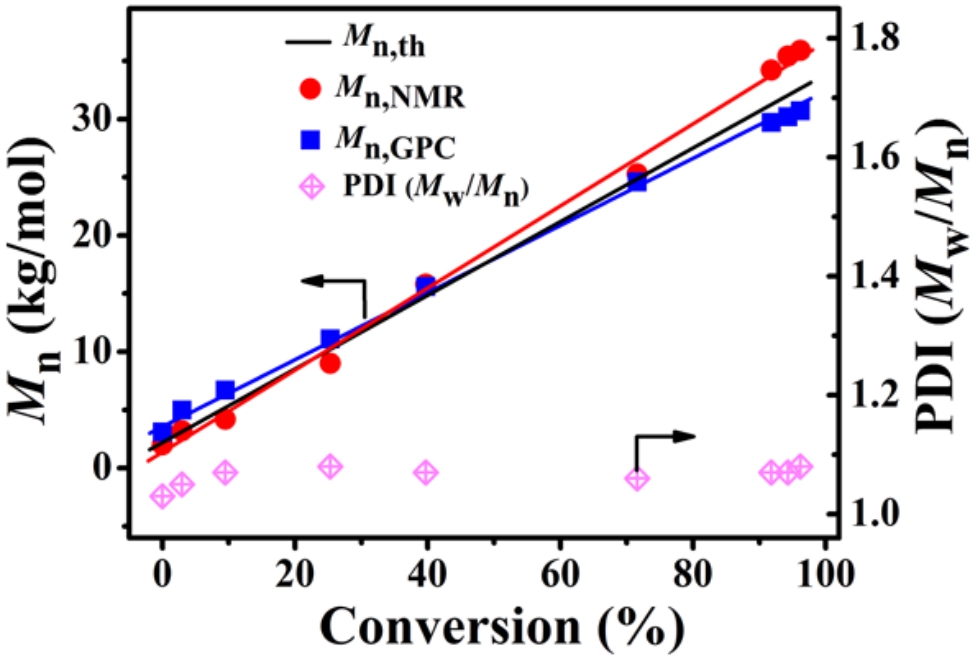

Figure S6. The evolution of the molecular weight and the PDI (M_w/M_n) values of the *m*PEG$_{45}$-*b*-PS diblock copolymers synthesized through dispersion polymerization of St mediated with the *m*PEG$_{45}$-TTC macro-RAFT agent.

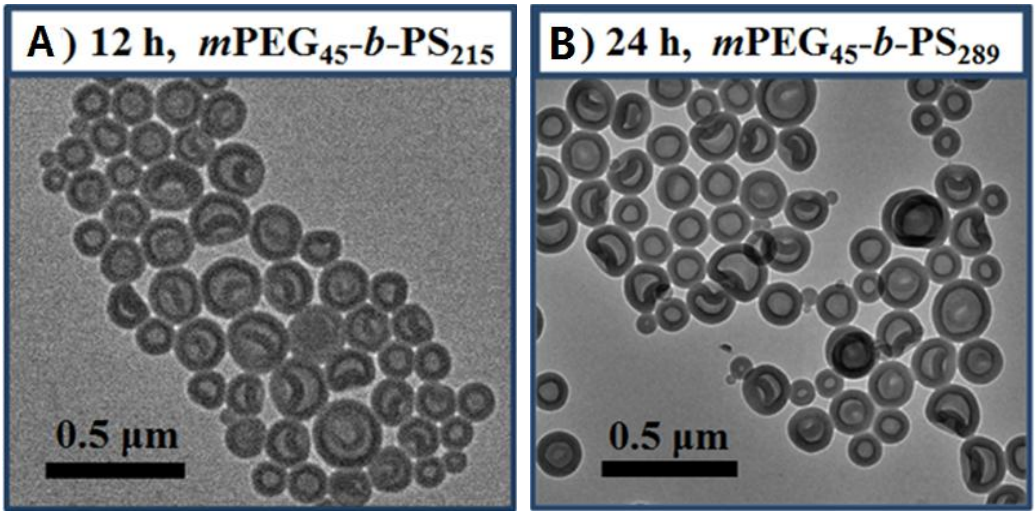

Figure S7. TEM images of the *m*PEG$_{45}$-*b*-PS diblock copolymer nanoparticles prepared through the monofunctional *m*PEG$_{45}$-TTC macro-RAFT agent mediated dispersion polymerization at the polymerization time of 12 h (A) and 24 h (B).