Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary information

Z-type and R-type macro-RAFT agent in RAFT dispersion polymerization - another mechanism perspective for PISA

Mingguang Yu[a], Jianbo Tan[b], Jianwen Yang[a], Zhaohua Zeng*[a]

[a] Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, and Key Laboratory of Designed Synthesis and Application of Polymer Material, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China. E-mail: ceszzh@mail.sysu.edu.cn

[b] Department of Polymeric Materials and Engineering, School of Materials and Energy, Guangdong University of Technology Guangzhou 510006, China

1. Synthesis of $mPEG_{113}$-DDMAT Macro-RAFT Agent

The $mPEG_{113}$-DDMAT macro-RAFT agent was synthesized according to the reported procedures with some modification. For the $mPEG_{113}$-DDMAT macro-RAFT agent, the $mPEG_{113}$-OH (10.0 g, 2 mmol), DDMAT (1.45 g, 4 mmol), DMAP (0.05 g, 0.4 mmol) were dissolved in 120 mL dry DCM in a dry flask. After the reaction mixture was cooling to 0 ^{o}C in an ice-water bath, the DCC (0.83 g, 4.0 mmol) diluted in dry DCM (30 mL) was added dropwise over 30 min, and still proceed in the ice-water bath for about 1h. After the reaction proceeded under stirring at 25 ^{o}C for 48 h, the reaction mixture was filtered to remove insoluble salts, concentrated, and precipitated into cold mixture of n-hexane and diethyl ether (v/v = 1:1) to yield a yellowish powder. In order to increase the grating rate of hydroxyl-terminated mPEG and ensure it complete esterification, 2-fold excess of RAFT agents (DDMAT or BTPA) were added. And then the product was purified by silica column chromatography, using chloroform and methanol (v/v = 95:5) as mobile phase, to removed the excess of small molecule RAFT agents and N,N'-dicyclohexylcarbodiimide (DCC).

2 RAFT dispersion polymerization of styrene with $mPEG_{113}$-DDMAT macro-RAFT agent in methanol–water mixture

RAFT dispersion polymerization of St was performed in methanol-water (80/20, w/w) at 70 °C. The total solid was controlled at 15%, and the molar ratio of [St]:[$mPEG_{113}$-TTC]:[AIBN] was 1200:3:1. In a typical experiment, St (1.25 g, 12 mmol), $mPEG_{113}$-DDMAT (0.16 g, 0.03 mmol), and AIBN (1.64 mg, 0.01 mmol) were dissolved in the methanol-water mixture (80/20, w/w, 8.0 g). The reaction mixture was purged with nitrogen for 30 min, sealed, and then immersed into a preheated oil bath at 70 °C. For kinetic studies, aliquots were taken under N_2 at different time intervals for analysis by ^{1}H NMR and GPC characterizations.

3 RAFT solution polymerization of styrene with $mPEG_{113}$-DDMAT macro-RAFT agent

Synthesis of $mPEG_{113}$-PSt diblock copolymer was via RAFT solution polymerization at 1200:3:1 molar ratios of [St]:[$mPEG_{113}$-TTC]:[AIBN] in 1,4-dioxane at 70 °C. In a typical experiment, St (2.50 g, 24 mmol), $mPEG_{113}$-DDMAT (0.32 g, 0.06 mmol), and AIBN (3.28 mg, 0.02 mmol) were dissolved in 1,4-dioxane (2.82 g). The reaction mixture was purged with nitrogen for 30 min, sealed, and then immersed into a preheated oil bath at 70 °C. For kinetic studies, aliquots were taken under N_2 at different time intervals for analysis by ^{1}H NMR and GPC characterizations.

4 Synthesis of $PHEA_{36}$-BTPA and $PDMA_{60}$-BTPA macro-RAFT agents

The PHEA-BTPA macro-RAFT agent was synthesized by RAFT solution polymerization in 1,4-dioxane at [HEA]:[BTPA]:[AIBN]=45:1:0.1. The monomer conversion of HEA was quenched at 79.6% after 2 h polymerization. The theoretical molecular weight ($M_{n,\,th}$) of PHEA-BTPA is 4.46Kg/mol, labeled as $PHEA_{36}$-BTPA, in which the polymerization degree (DP) of 36 is calculated according to eq (1) based on theoretical molecular weight ($M_{n,\,th}$). The GPC molecular weight $M_{n,GPC}$ of $PHEA_{36}$-BTPA analyzed by THF-based GPC is 2.18Kg/mol with M_w/M_n value of 1.07 (Fig. S4). The obtained $M_{n,GPC}$ value is obviously lower than $M_{n,\,th}$, which is possibly due to the polar differences between non-polar polystyrene standard and the polar PHEA-TTC[1].

The PDMA-BTPA macro-RAFT agent was synthesized by RAFT solution polymerization in 1,4-dioxane at [DMA]:[BTPA]:[AIBN]=60:1:0.1. The monomer conversion of DMA was quenched at about 100% after 2 h polymerization. The theoretical molecular weight ($M_{n,\,th}$) of PDMA-BTPA is 6.22Kg/mol, labeled as $PDMA_{60}$-BTPA. The molecular weight $M_{n,GPC}$ of $PDMA_{60}$-BTPA analyzed by THF-based GPC is 2.60Kg/mol with M_w/M_n value of 1.11 (Fig. 4B). Similarly, the obtained $M_{n,GPC}$ value is obviously lower than $M_{n,\,th}$.

$$M_{n,\,th} = \frac{[\text{monomer}]_0 \times M_{monomer}}{[\text{RAFT}]_0} \times \text{conversion} + M_{\text{RAFT}} \quad (1)$$

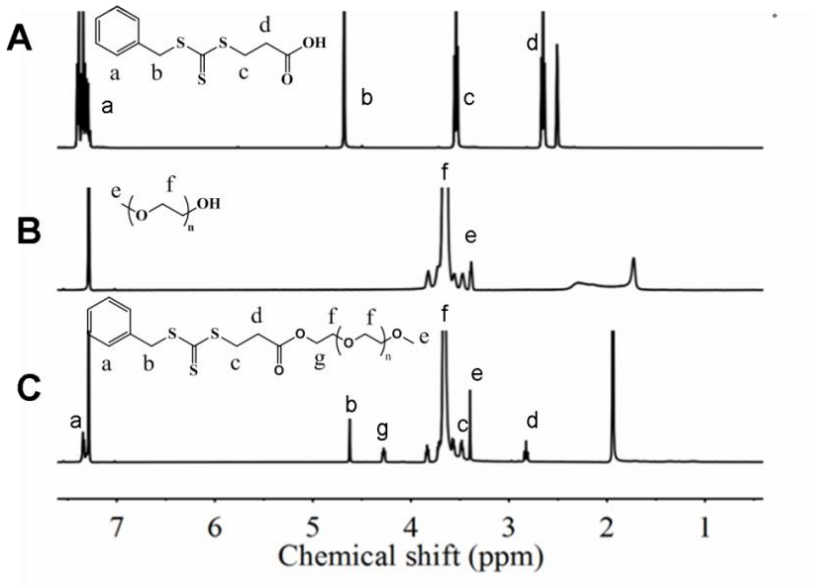

Fig.S1 ^{1}H NMR spectra of BTPA (A) in D_6-DMSO, $mPEG_{113}$-OH (B), and $mPEG_{113}$-BTPA (C) in $CDCl_3$.

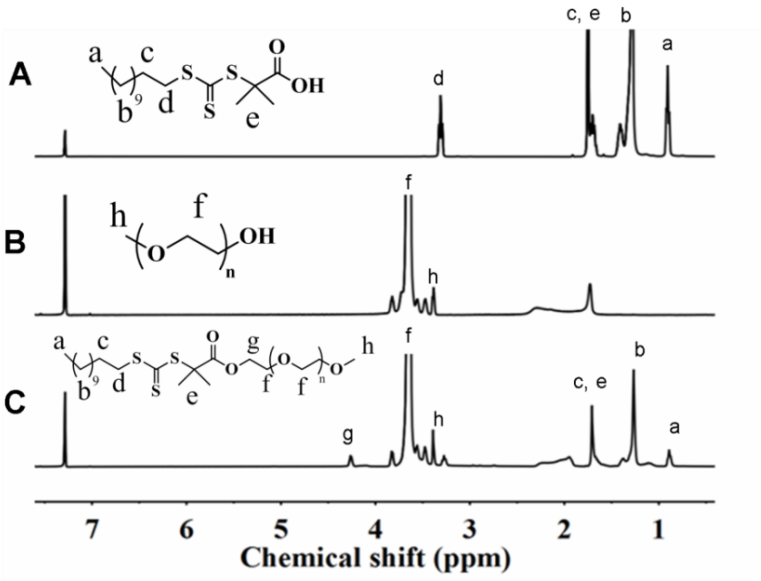

Fig.S2 ^{1}H NMR spectra of DDMAT (A), mPEG$_{113}$-OH (B), and mPEG$_{113}$-DDMAT(C) in $CDCl_3$.

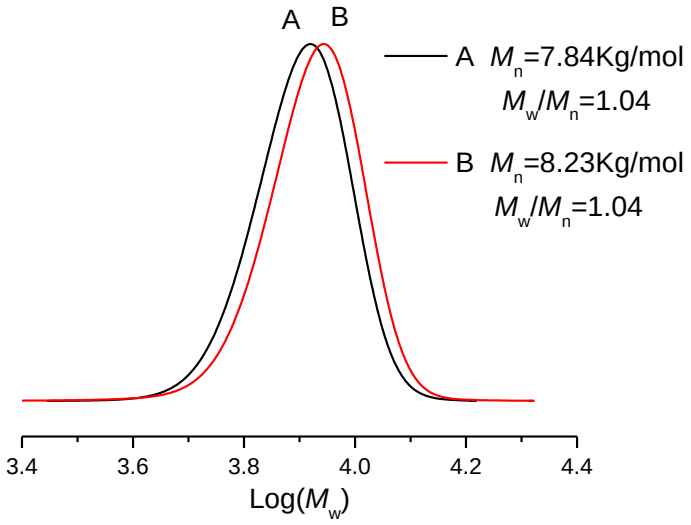

Fig. S3 GPC traces of mPEG$_{113}$-DDMAT (A) and mPEG$_{113}$-BTPA (B).

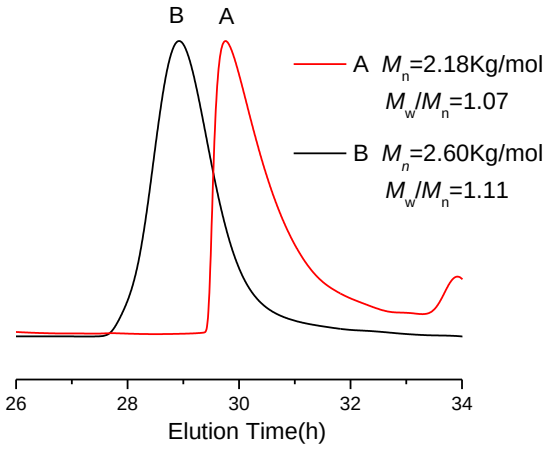

Fig. S4 GPC traces of $PHEA_{36}$-BTPA (A) and $PDMA_{60}$-BTPA (B).

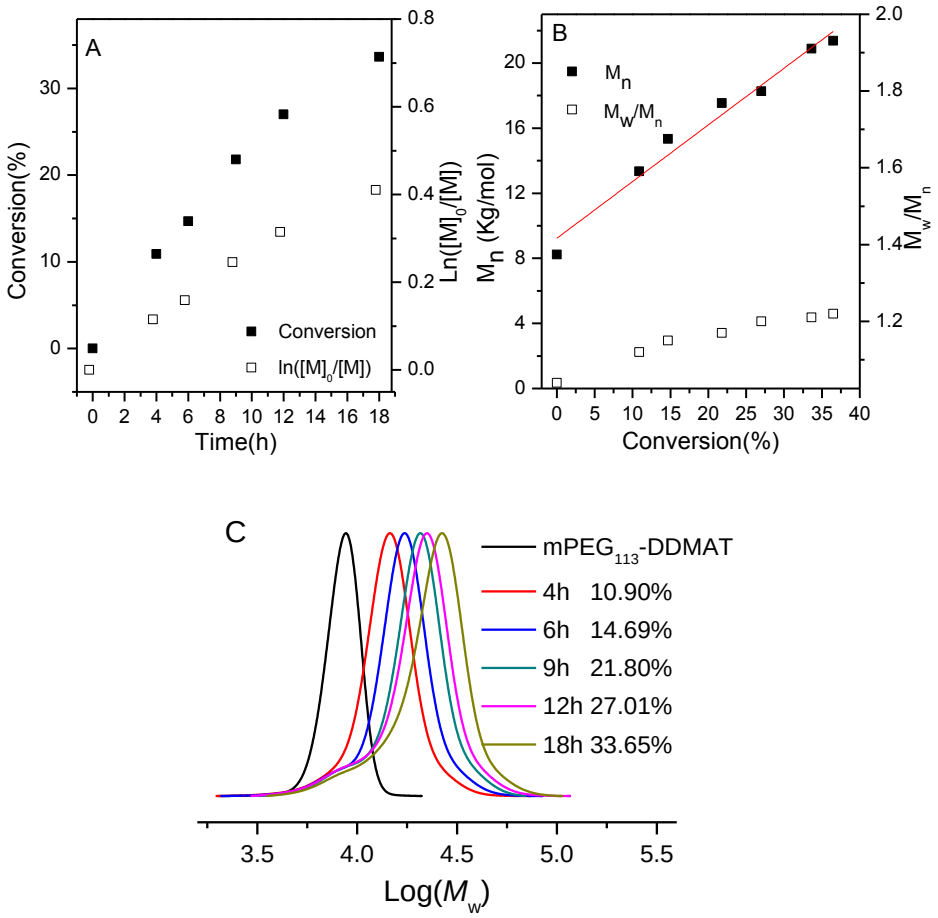

Fig. S5 RAFT solution polymerization of St using $mPEG_{113}$-DDMAT macro-RAFT agent at 70°C, $[St]_0$:$[macro\text{-}RAFT]_0$:$[AIBN]_0$=1200:3:1, solids content=50%, 1,4-dioxane. (A) polymerization kinetics plot, (B) molecular weight and dispersity of $mPEG_{113}$-*b*-PSt diblock copolymer vs monomer conversion, and (C) evolution of GPC traces of $mPEG_{113}$-b-PS diblock copolymer vs monomer conversion.

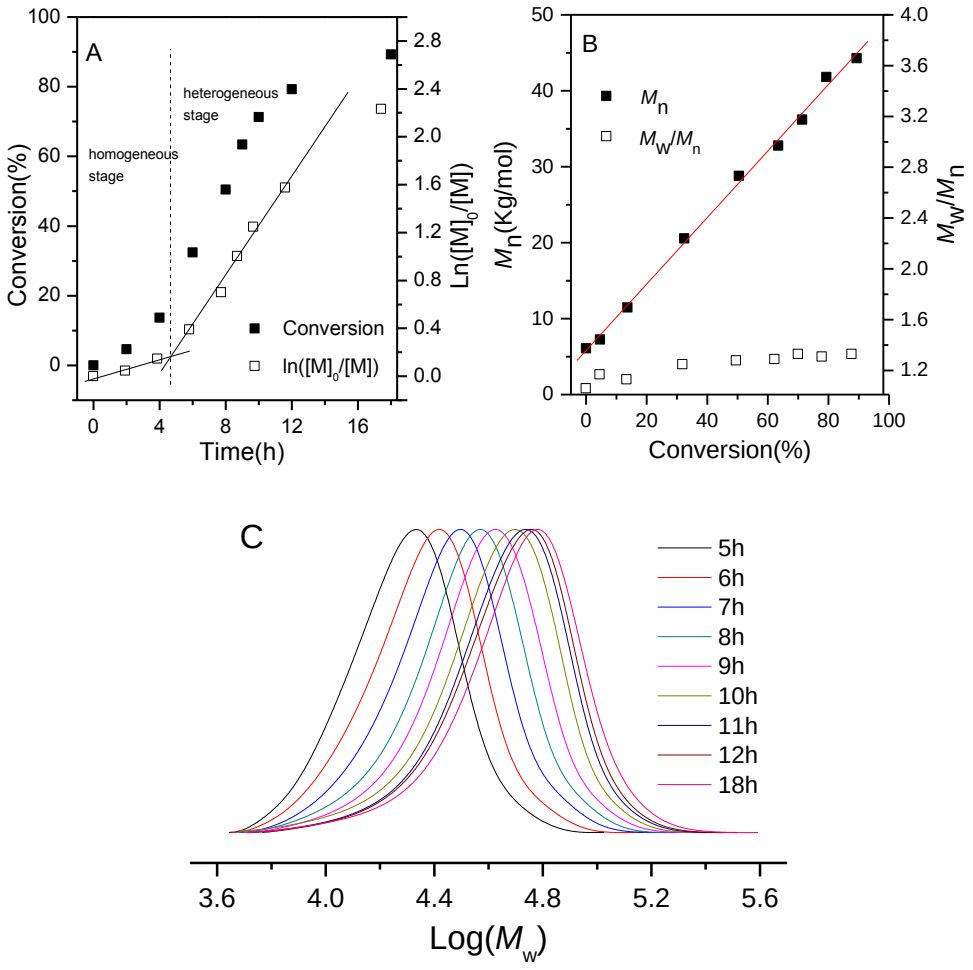

Fig. S6 RAFT dispersion polymerization of St using $PDMA_{60}$-BTPA macro-RAFT agent at 70°C, $[St]_0$:$[macro\text{-}RAFT]_0$:$[AIBN]_0$=1200:3:1, solids content=15%, methanol-water mixture (80/20, w/w). (A) polymerization kinetics plot, (BB) molecular weight and dispersity of $PDMA_{60}$-*b*-PSt diblock copolymer vs monomer conversion, and (C) evolution of GPC traces of $PDMA_{60}$-*b*-PSt diblock copolymer vs monomer conversion.

Notes and references

1 A. P. Narrainen, A. Pascual and D. M. Haddleton, J. Polym. Sci., Part A: Polym. Chem., 2002, 40, 439–450.