Supplementary information

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

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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), DMA (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 \(^\circ\)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 1 h. After the reaction proceeded under stirring at 25 \(^\circ\)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 \(^\circ\)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 \(^\circ\)C. For kinetic studies, aliquots were taken under N\(_2\) at different time intervals for analysis by \(^3\)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 N₂ at different time intervals for analysis by ¹H NMR and GPC characterizations.

4 Synthesis of PHEA₃₆-BTPA and PDMA₆₀-BTPA macro-RAFT agents

The PHEA₃₆-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 PHEA₃₆-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 PHEA₃₆-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-TTC¹.

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 PDMA₆₀-BTPA. The molecular weight M_{n,GPC} of PDMA₆₀-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}.

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M_{n,th} = \left[\text{monomer}\right]_0 \times M_{monomer} \times \text{conversion} + M_{RAFT} \quad (1)
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Fig.S1 ¹H NMR spectra of BTPA (A) in D₆-DMSO, mPEG₁₁₃-OH (B), and mPEG₁₁₃-BTPA (C) in CDCl₃.
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-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-PS 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]:[macro-RAFT]:[AIBN]=1200:3:1, solids content=15%, methanol-water mixture (80/20, w/w). (A) polymerization kinetics plot, (B) molecular weight and dispersity of PDMA_{60}-b-PS diblock copolymer vs monomer conversion, and (C) evolution of GPC traces of PDMA_{60}-b-PSt diblock copolymer vs monomer conversion.

Notes and references