Supporting Information for:

In situ synthesis of the self-assembled AB/B blend of poly(ethylene glycol)-*b*-polystyrene/polystyrene by dispersion RAFT polymerization

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1. Synthesis of the PEG_{45}-*b*-PS_{282} nano-assemblies

The PEG_{45}-*b*-PS_{282} nano-assemblies were synthesized by dispersion RAFT polymerization of styrene in the methanol/water mixture (80/20 w/w) at 70 ℃ with the weight ratio of the styrene monomer to the solvent at 15% under $[St]_0$:$[PEG_{45}\text{-TTC}]_0$: $[AIBN]_0$ =300:1:1/3. Into a 25 mL Schlenk flask with a magnetic bar, PEG_{45}-TTC (0.075 g, 0.0320 mmol), St (1.00 g, 9.60 mmol), and AIBN (1.76 mg, 0.0107 mmol) were dissolved in the methanol/water mixture (80/20 w/w, 6.67 g). And then the mixture was degassed with nitrogen at 0 ℃. The polymerization was started by immersing the flask into a preheated oil bath at 70 ℃. After 24 h, the polymerization was quenched by immersing the flask in iced water and the polymerization solution was exposed to air. The monomer conversion, molecular weight, polydispersity index, $M_{n,GPC}$ and ^{1}H NMR of PEG_{45}-*b*-PS_{282} were determined by the same characterization techniques of the PEG-*b*-PS/PS self-assembled blend.

2. Synthesis of the PS_{280} homopolymer particles

The PS_{280} homopolymer particles were synthesized by dispersion RAFT polymerization under $[St]_0$:$[DDMAT]_0$: $[AIBN]_0$ = 300:1:1/3 in the presence of the PVP stabilizer with the weight ratio of the styrene monomer to the solvent at 15%. Into a 25 mL Schlenk flask with a magnetic bar, DDMAT (0.012 g, 0.0328 mmol), St (1.00 g, 9.60 mmol), AIBN (1.76 mg, 0.0107 mmol) and stabilizer PVP (0.30 g) dissolved in the methanol/water mixture (80/20 w/w, 6.67 g) were added, and then the mixture was degassed with nitrogen at 0 ℃. The polymerization was started by immersing the flask into a preheated oil bath at 70 ℃. After 25 h, the polymerization was quenched by immersing the flask in iced water and the polymerization solution was exposed to air. The monomer conversion was determined by ^{1}H NMR, and the morphology of the PS_{280} homopolymer particles was checked by TEM. To collect the PS_{280} homopolymer for GPC and ^{1}H NMR analysis, the particles were separated by centrifugation (10000 rpm, 3 min), washed with methanol, dissolved in DCM, precipitated into methanol, collected by three precipitation/filtration cycles, and finally dried under vacuum at room temperature.

3. Equations

$$\text{Degree of polymerization (DP)} = \text{monomer conversion (\%)} \times \frac{[St]_0}{\sum[\text{RAFT agent}]} \quad \text{(S1)}$$

The equation for the calculation of DP based on monomer conversion, where $[St]_0$ denotes the initial concentration of St monomer, and $\sum$[RAFT agent] is the total concentration of RAFT agents.

4. Figures

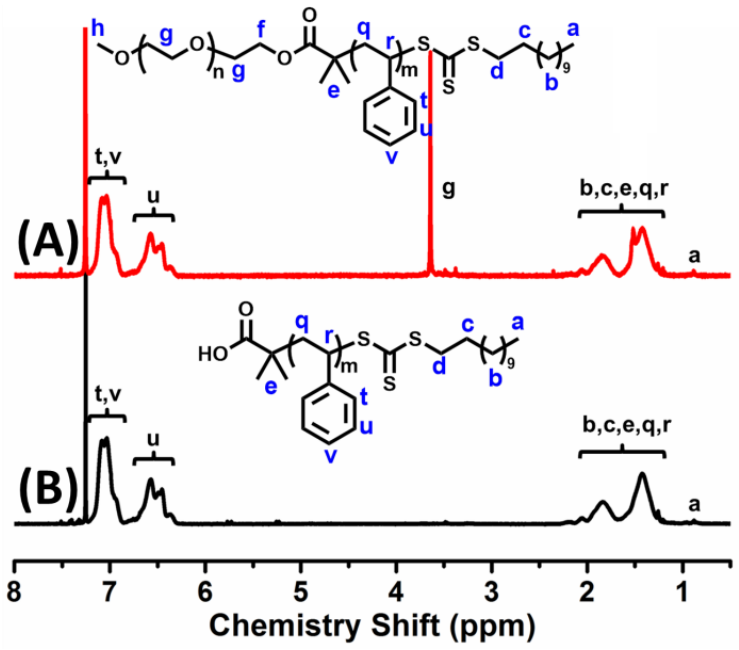

Figure S1. ^{1}H NMR spectra of PEG_{45}-*b*-PS_{282} (A) and PS_{280} (B) prepared by dispersion RAFT polymerization.

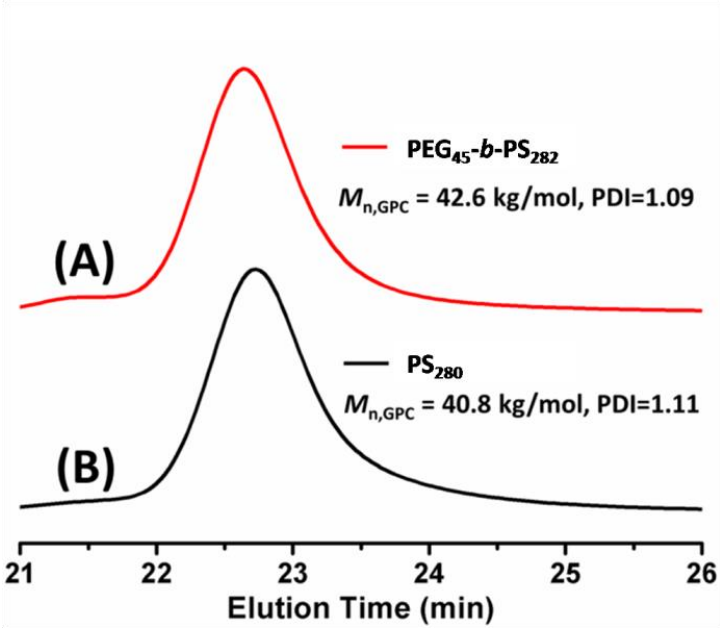

Figure S2. GPC traces of PEG_{45}-*b*-PS_{282} (A) and PS_{280} (B).

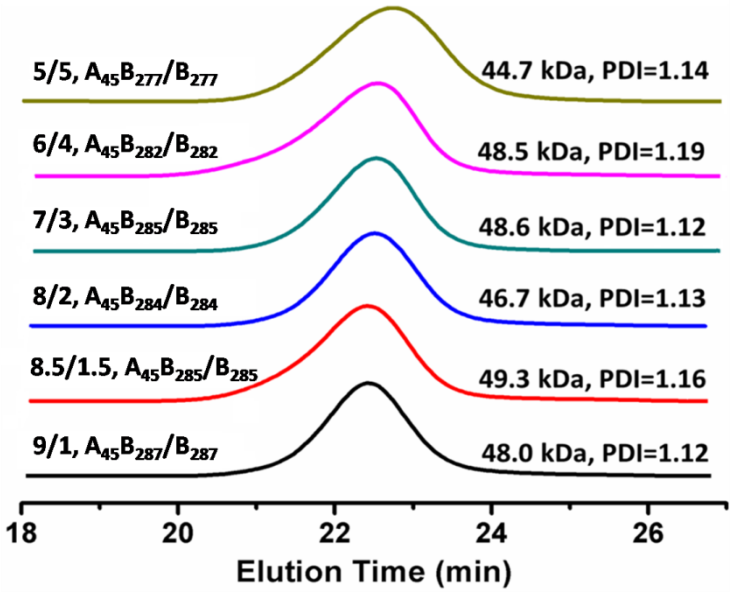

Figure S3. The GPC graces of the PEG-*b*-PS/PS self-assembled blend synthesized through dispersion RAFT polymerization at the polymerization time of 25 h under $[St]_0$:$[RAFT]_0$:$[AIBN]_0$ = 300:1:1/3, with the PEG_{45}-TTC/DDMAT molar ratio at 9/1, 8.5/1.5, 8/2, 7/3, 6/4, and 5/5.