Supporting

Experimental section

Materials:

Acrylic acid (AA, 99%, Tianjin fuchen chemical plant) was distilled under reduced pressure prior to use. Styrene (St, 99%, Tianjin fuchen chemical plant) was distilled under reduced pressure and stored in a freezer before use. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. S-1-Dodecyl-S′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (DDMAT) was synthesized as discussed elsewhere. The ^{1}H NMR spectrum of DDMAT is shown in Fig. S10. PEG (Alfa, M_n of 400, 1000 or 2000 g·mol^{-1}, abbreviated as PEG400, PEG600, PEG800, PEG1000 or PEG2000, respectively) was used as received. Trimethylsilyldiazomethane (2 M solution in hexanes, Alfa) was used as received. Deionized water was used in the present study.

Synthesis of poly(acrylic acid) trithiocarbonate (PAA-TTC) macro-CTA

A solution of AA (2.565 g, 3.563 × 10^{-2} mol), DDMAT (0.5187 g, 1.425 × 10^{-3} mol), ethanol (10 g) and AIBN (0.0467 g, 2.85 × 10^{-4} mol) with the molar ratio of [AA] /[DDMAT]/[AIBN] = 25 : 1 : 0.2 were added into a 25 mL round bottomed flask equipped with a magnetic bar. The reaction medium was purged with argon for 30 min at 0 °C to remove oxygen. After five freeze-thaw-pump cycles, the flask was sealed and placed in an oil bath at 70 °C. After 8 h, the flask was cooled to room temperature with ice-water. The final monomer conversion was determined to be above 97% by ^{1}H NMR analysis. The resulting mixture was used directly without further purification for the next step polymerization. ^{1}H NMR was used to characterize the resultant PAA-TTC and the number-average degree of polymerization (DP_n) of this PAA-TTC macro-CTA (determined by the area ratio of the signal at δ = 2.21 ppm of AA units to that of the RAFT terminal group at δ = 0.88 ppm) was bout 25 (formulated as PAA_{25}-TTC)

Dispersion RAFT polymerization of St with PAA_{25}-TTC macro-CTA in the presence of PEG

The PAA_{25}-TTC macro-RAFT agent mediated dispersion polymerization of St was

carried out in ethanol/water/PEG mixtures at 70 °C. A typical dispersion RAFT polymerization with [PAA_{25}-TTC]/[St]/[AIBN] = 1 : 300 : 0.2 in 70/30/10 w/w/w ethanol/water/PEG2000 mixtures was as follows: St (14.82 g, 0.14 mol), AIBN (0.0156 g, 9.5×10^{-5} mol), ethanol (34.24 g), water (16.10 g) and PEG2000 (5.37 g) were added into a 100 mL round bottomed flask equipped with a magnetic bar. The mixtures were purged with argon for 30 min at 0 °C. Then the as-prepared PAA_{25}-TTC solution was injected under argon into the reaction flask. After five freeze–thaw–pump cycles, the polymerization was initiated by immersing the flask in a preheated oil bath at 70 °C. After a given time interval, the polymerization was quenched by immersing the flask in iced water. The conversion of St was determined gravimetrically. The resulting polymer was washed with methanol/water (80/20, w/w), and then collected by three precipitation/filtration cycles. The product was then dried under vacuum at room temperature for ^{1}H NMR and gel permeation chromatography (GPC) analysis. The morphology and size of the resulting colloids were observed using transmission electron microscopy (TEM) and dynamic light scattering (DLS).

Characterization

The molar mass and molar mass distributions (PDI = M_w/M_n) of the synthesized polymers were measured by GPC using a TOSOH HLC-8320 instrument, which was consisted of a solvent delivery system, a column set with two TSK gel Super Multipore HZ-M columns, and a differential refractometer index (RI) detector. The eluent was THF at a flow rate of 0.35 mL min^{-1} at 40 °C and narrow distributed PSt was used as calibration standard. Before analysis, the carboxylic acid groups of the resulting polymers were methylated using trimethylsilyldiazomethane[1]. ^{1}H NMR spectra were obtained on a Bruker AV400-MHz spectrometer at room temperature. The PAA-TTC was dissolved in DMSO-d_6 and the PAA-*b*-PSt was dissolved in $CDCl_3$. Tetramethylsilane (TMS) was used as an internal reference. The PAA-TTC was precipitated into cold diethyl ether, collected by three precipitation/filtration cycles, and then dried at room temperature under vacuum. The PAA-*b*-PSt was washed with methanol/water, and then collected by three precipitation/filtration cycles. The product was then dried under vacuum at room temperature. Transmission electron

microscope (TEM) observation was performed using a Hitachi HT7700 electron microscope at an accelerating voltage of 120 KV. During the TEM samples preparation, the colloidal dispersion was first diluted with ethanol/water mixed solvent. A drop of the diluted dispersion was then deposited on a copper grid and dried at room temperature under vacuum. Dynamic laser scattering (DLS) was measured using a BI-200SM (Brookhaven, USA) at 25 °C with 532 nm laser after diluted with ethanol/water mixed solvent.

Tables and Figures

Table S1 The summary table of the synthesis of PAA_{25}-*b*-PSt diblock copolymer with different ratio of [AA]:[St] in the presence of PEG1000

Entry	Solvent composition(w/w/w)	[AA]:[St]	Time (h)/Conv.	Morphplogy	D_{TEM}(nm)	D_{DLS}(nm) (PDI)
1	ethanol/water=70:30	25:200	13 (93.0%)	Lacunal nanospheres	110±13	133±23(0.055)
2	ethanol/water=70:30	25:300	21 (98.0%)	Lacunal nanospheres	151±21	229±31(0.172)
3	ethanol/water/PEG1000=70:30:30	25:200	13 (96.1%)	spheres	46±6	56±8(0.005)
4	ethanol/water/PEG1000=70:30:30	25:300	23 (99.8%)	Lacunal nanospheres	131±17	144±21(0.060)
5	ethanol/water/PEG1000=70:30:30	25:350	22 (99.8%)	Lacunal nanospheres	141±19	151±25(0.009)

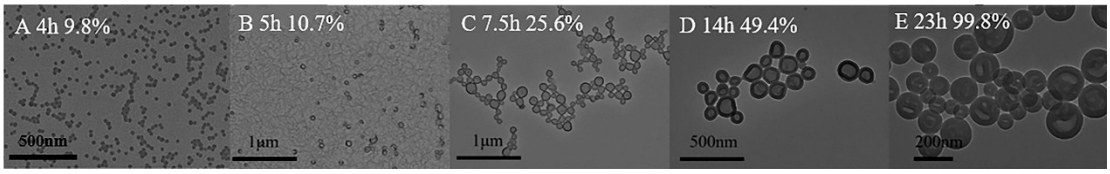

Fig. S1 The morphological transition of PAA_{25}-*b*-PSt block copolymer obtained by dispersion RAFT polymerization of St. Polymerization conditions: [PAA_{25}-TTC]/[St]/[AIBN]=1:300:0.2; St (14.82 g, 0.14 mol); ethanol/water (53.675 g, 70/30 w/w); 70 °C.

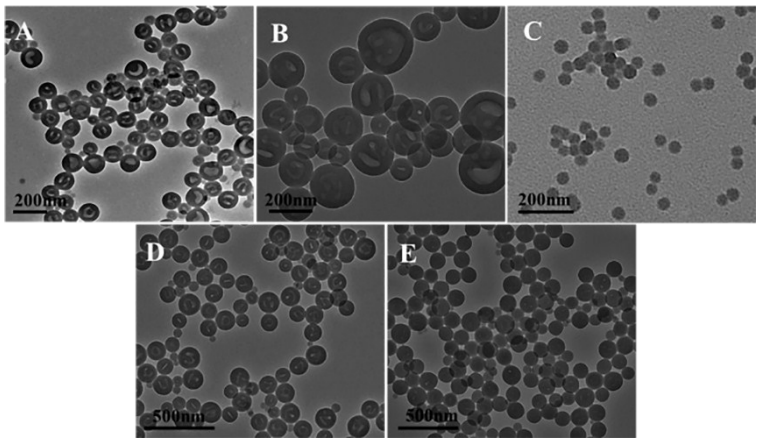

Fig. S2 The final morphology of PAA-*b*-PSt block copolymer obtained in different polymerization conditions. (A) ethanol/water=70:30 w/w; [PAA_{25}-TTC]:[St]=1:200; (B) ethanol/water=70:30 w/w; [PAA_{25}-TTC]:[St]=1:300; (C) ethanol/water/PEG1000=70:30:30 w/w/w; [PAA_{25}-TTC]:[St]=1:200; (D) ethanol/water/PEG1000=70:30:30 w/w/w; [PAA_{25}-TTC]:[St]=1:300; (E) ethanol/water/PEG1000=70:30:30 w/w/w; [PAA_{25}-TTC]:[St]=1:350.

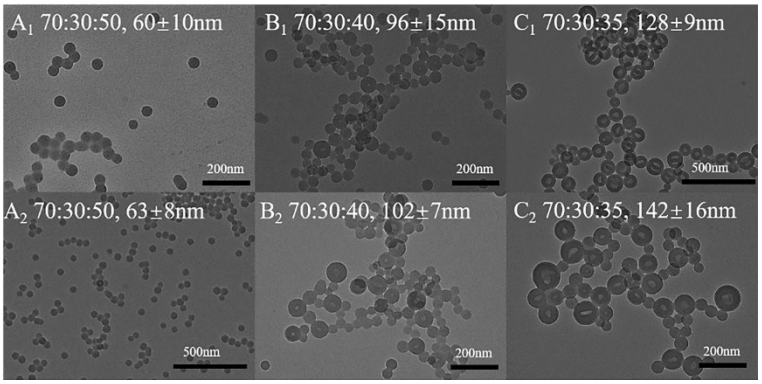

Fig. S3 TEM images of nanoassemblies with different amount of PEG (Ethanol/water/PEG=70:30:50, 70:30:40, 70:30:35). A_1-C_1: PEG 600, A_2-C_2: PEG 1000

Table S2 The summary table of the polymer GPC data for different amounts of PEG2000 [a]

Polymer	Solvent composition (w/w/w)	Time (h)/Conv.	$M_{n,th}$[b](g·mol^{-1})	$M_{n,GPC}$(g·mol^{-1})	M_w /M_n
PAA_{25}-*b*-PSt_{300}	ethanol/water/PEG2000 = 70:30:50	13 (99.9%)	33100	34900	1.13
PAA_{25}-*b*-PSt_{297}	ethanol/water/PEG2000 = 70:30:30	23 (99.0%)	33100	32900	1.19
PAA_{25}-*b*-PSt_{297}	ethanol/water/PEG2000 = 70:30:10	23 (99.1%)	33100	33300	1.19
PAA_{25}-*b*-PSt_{296}	ethanol/water/PEG2000 = 70:30:5	23 (98.8%)	32100	31800	1.25
PAA_{25}-*b*-PSt_{296}	ethanol/water/PEG2000 = 70:30:1.77	23 (98.6%)	33100	32300	1.21
PAA_{25}-*b*-PSt_{294}	ethanol/water = 70:30	21 (98.0%)	32700	33100	1.22

[a] Polymerization conditions can be found in the caption for **Table 2**. [b]$M_{n,th}$ is calculated by

Equation S1 $$M_{n,th} = \frac{[St]0 \times MSt}{[RAFT]0} \times \text{conversion} + M_{PAA\text{-}TTC}$$

Table S3 The effects of the PEG2000 amount on the polymerization rate and the morphologies of the synthesized diblock copolymer nano-objects after 13 h [a]

Entry	Solvent composition (w/w/w)	Time (h)/Conv.	Morphplogy	D_{TEM} (nm)	D_{DLS}(nm) (PDI)
1	ethanol/water/PEG2000 = 70:30:50	13 (99.0%)	spheres	55±5	60±11(0.057)
2	ethanol/water/PEG2000 = 70:30:30	13 (62.5%)	vesicles	145±17	149±24(0.031)
3	ethanol/water/PEG2000 = 70:30:10	13 (47.4%)	vesicles	121±20	123±15(0.076)
4	ethanol/water/PEG2000 = 70:30:5	13 (45.8%)	vesicles	111±14	130±16(0.005)
5	ethanol/water/PEG2000 =70:30:1.77	13 (40.1%)	vesicles	125±17	202±37(0.167)
6	ethanol/water = 70:30	13 (38.9%)	vesicles	121±24	210±32(0.175)

[a] Polymerization conditions: [PAA_{25}-TTC]/[St]/[AIBN]=1:300:0.2; St (14.82g, 0.14mol); either ethanol/water (53.675 g) or various ethanol/water/PEG mixtures (54.625-80.512 g); 13 h; 70 °C.

Table S4 The summary table of the polymer GPC data with different molecular weight PEG[a]

Polymer	Solvent composition (w/w/w)	Time (h)/Conv.	$M_{n,th}$[b] (g·mol^{-1})	$M_{n,GPC}$ (g·mol^{-1})	M_w /M_n
PAA_{25}-*b*-PSt_{284}	ethanol/water/PEG400 = 70:30:30	14 (94.8%)	31400	31700	1.19
PAA_{25}-*b*-PSt_{299}	ethanol/water/PEG600 = 70:30:30	23 (99.5%)	32900	33700	1.17
PAA_{25}-*b*-PSt_{299}	ethanol/water/PEG800 = 70:30:30	23 (99.7%)	33000	32100	1.20
PAA_{25}-*b*-PSt_{299}	ethanol/water/PEG1000 =70:30:30	23 (99.8%)	33000	32500	1.18
PAA_{25}-*b*-PSt_{297}	ethanol/water/PEG2000 =70:30:30	23 (99.0%)	33100	32900	1.19
PAA_{25}-*b*-PSt_{294}	ethanol/water=70:30	21 (98.0%)	32700	33100	1.22

[a] Polymerization conditions can be found in the caption for **Table 1**. [b]$M_{n,th}$ is calculated by Equation S1

$$M_{n,th} = \frac{[St]0 \times MSt}{[RAFT]0} \times \text{conversion} + M_{PAA\text{-}TTC}$$

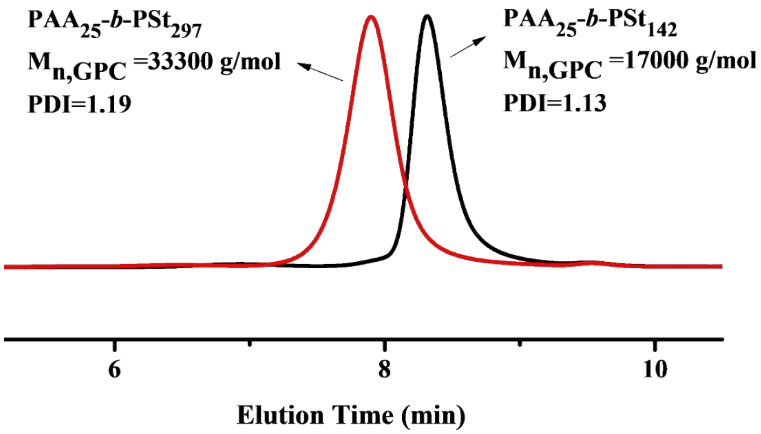

Fig. S4 The typical GPC traces of PAA_{25}-b-PSt_{142} and PAA_{25}-b-PSt_{297}. Polymerization conditions: [PAA_{25}-TTC]/[St]/[AIBN]=1:300:0.2; ethanol/water/PEG2000 (70:30:10 w/w/w); 70 °C.

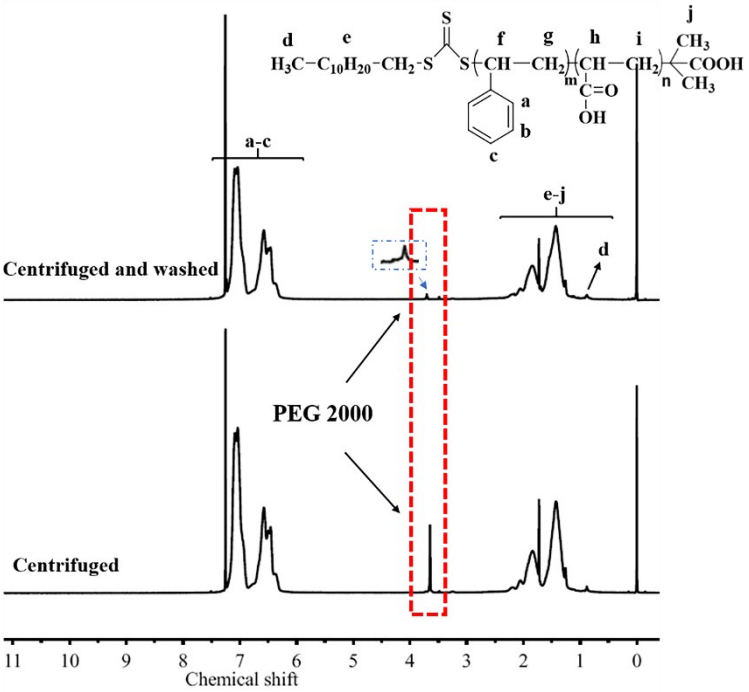

Fig. S5 The ^{1}H NMR spectra of PAA_{25}-*b*-PSt_{296} prepared in the presence of PEG2000 (Ethanol/water/PEG 2000=70:30:30) .

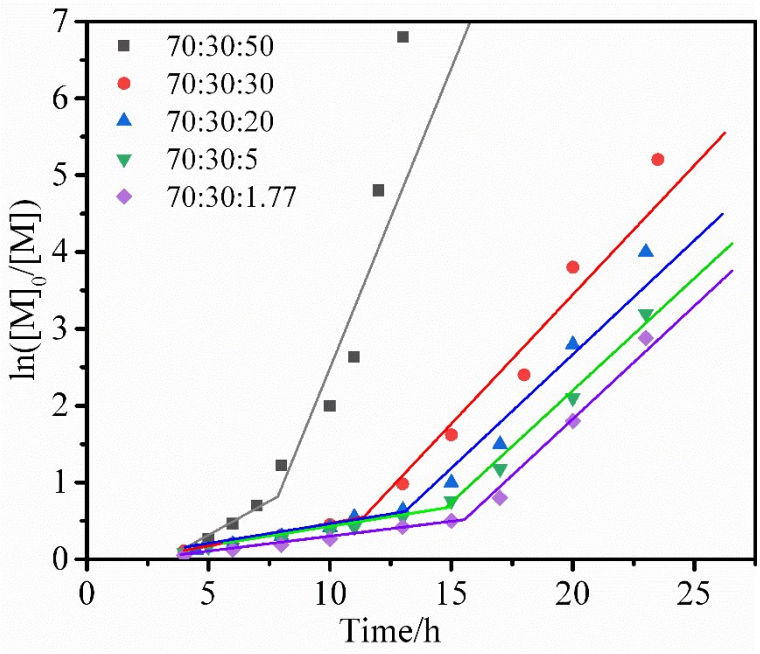

Fig. S6 The kinetics curve of the polymerization with different amount of PEG2000

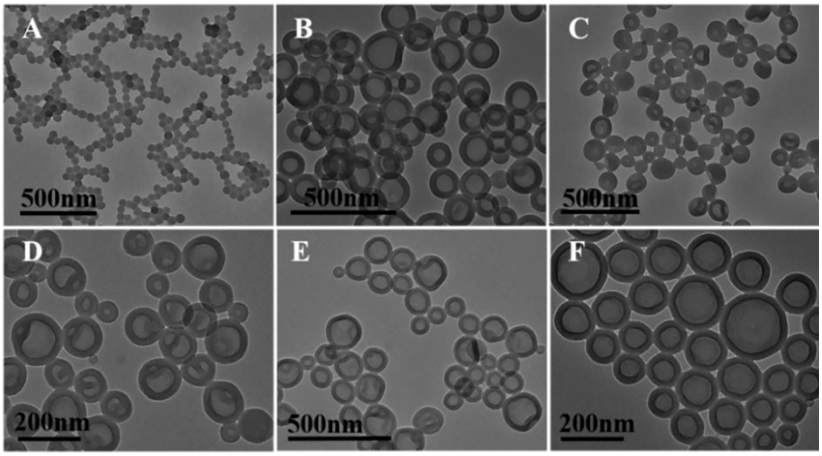

Fig. S7 The TEM images of block copolymer nano-objects after 13 h in the presence of different amount of PEG2000. Ethanol/water/PEG2000 = (A) 70:30:50 w/w/w; (B) 70:30:30 w/w/w; (C) 70:30:10 w/w/w; (D) 70:30:5 w/w/w; (E) 70:30:1.77 w/w/w; (F) 70:30:0 w/w/w

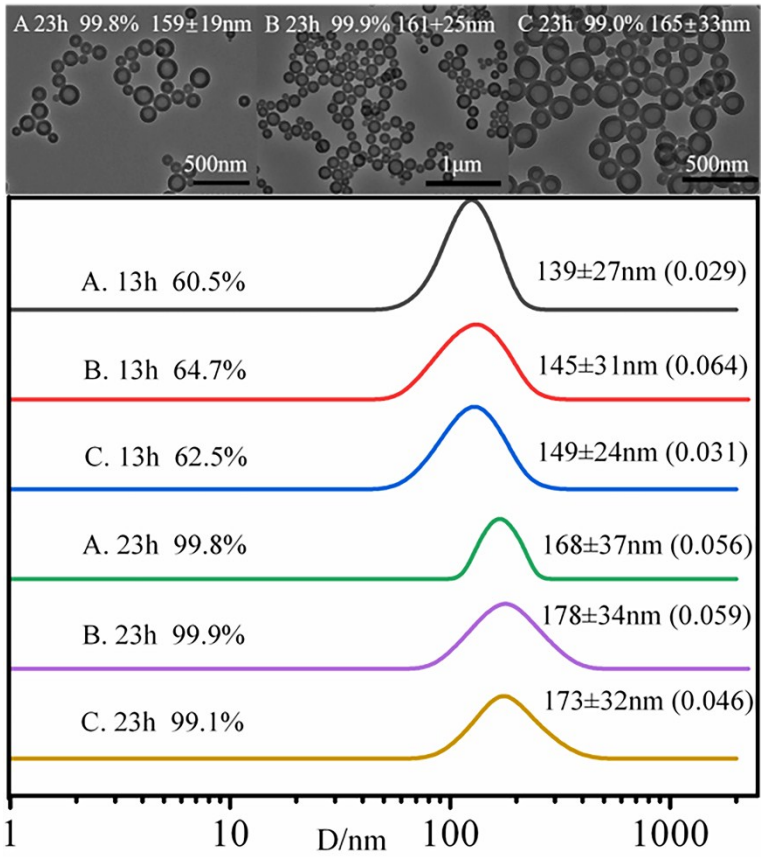

Fig. S8 The TEM images and DLS data of final nanoassemblies with PEG2000 (ethanol/water/PEG2000=70:30:30). A: samples of the second time; B: samples of the third time; C: samples in the original manuscript.

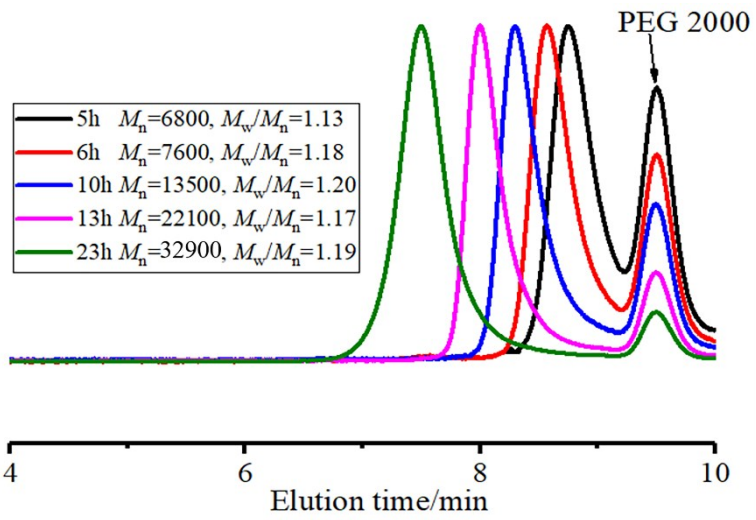

Fig. S9 GPC trace of PAA-b-PSt with PEG 2000 (Ethanol/water/PEG 2000=70:30:30)

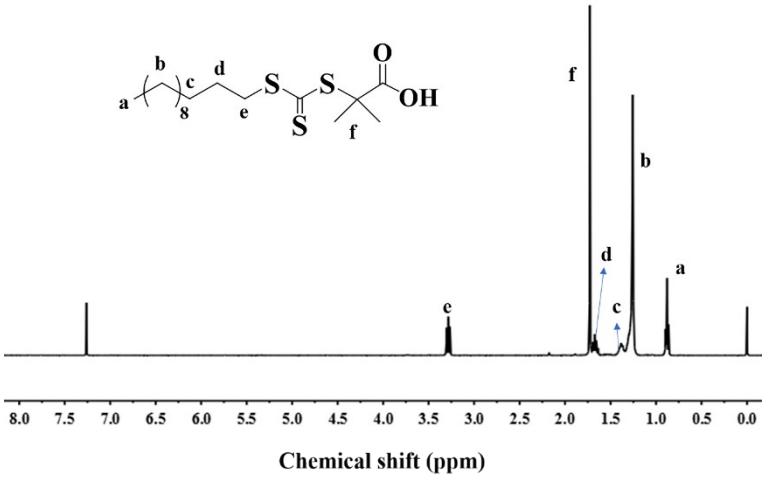

Figure S10 The ^{1}H NMR spectroscopy of DDMAT in $CDCl_3$

Reference

1 Couvreur L, Lefay C, Belleney J, Charleux B, Guerret O, Magnet S. *Macromolecules*. 2003, **36**, 8260.