Supporting Information for:

Synthesis of multi-arm star thermo-responsive polymers and topology effect on phase transition

Mengjiao Cao,[a] Guang Han,[b] Wenfeng Duan,*[,b] and Wangqing Zhang*,[a,c]

[a] Key Laboratory of Functional Polymer Materials of the Ministry of Education, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China. E-mail: wqzhang@nankai.edu.cn, Fax: 86-22-23503510.

[b] State Key Laboratory of Special Functional Waterproof Materials, Beijing Oriental Yuhong Waterproof Technology Co., Ltd, Beijing 100123, China. E-mail: duanwf@yuhong.com.cn.

[c] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China.

1. Synthesis of the monomer of *N*-acryloylsarcosine methyl ester (NASME)

Into a flask with a magnetic bar, sarcosine methyl ester hydrochloride (13.96 g, 100 mmol), CH_2Cl_2 (150.0 mL) and Et_3N (50.0 mL) were added and magnetically stirred to form a turbid suspension, and then the flask was kept at 0 ^oC in iced water. Subsequently, acryloyl chloride (9.50 g, 105 mmol) dissolved in CH_2Cl_2 (10.0 mL) was added dropwise over 2 h. After the complete addition of acryloyl chloride, the reaction was performed for another 1 h at 25 ^0C. The reaction solution was washed with cold ether (150 mL) for three times and then the precipitated triethylamine hydrochloride was removed by filtration. The collected filtrate was concentrated by rotary evaporation under reduced pressure to afford the crude product. Further purification was achieved via flash chromatography on a silica gel eluting with ethyl acetate to give pale yellow liquid of NASME (14.13 g, 90% yield).

2. Equations

$$M_{n,th} = \frac{[\text{monomer}]_0 \times M_{\text{monomer}}}{[\text{RAFT}]_0} \times conversion + M_{\text{RAFT}} \qquad \text{(S1)}$$

3. Figures

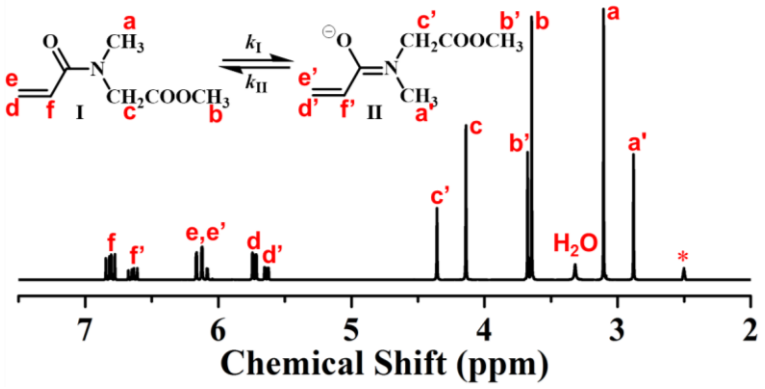

Figure S1. ^{1}H NMR spectra of two isomers of NASME in d_6-DMSO.

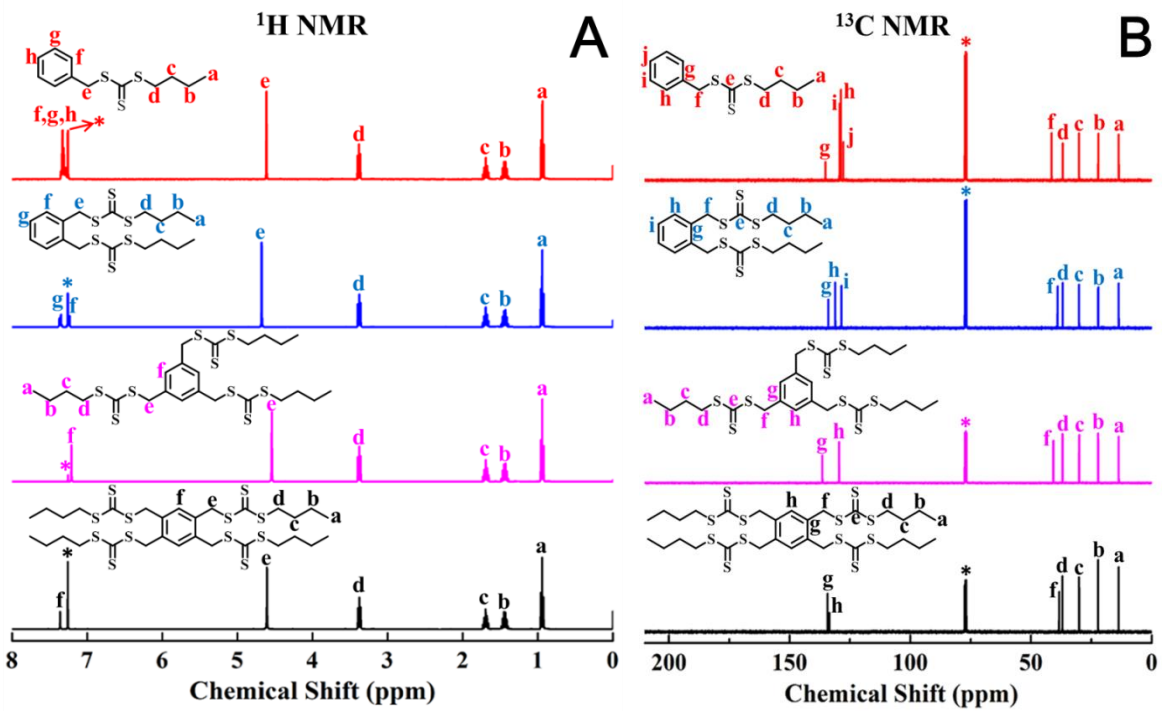

Figure S2. ^{1}H NMR spectra (A) and ^{13}C NMR spectra (B) of the four kinds of RAFT agents. Note: **e** peak at 220 ppm in ^{13}C NMR spectra is out the range of test.

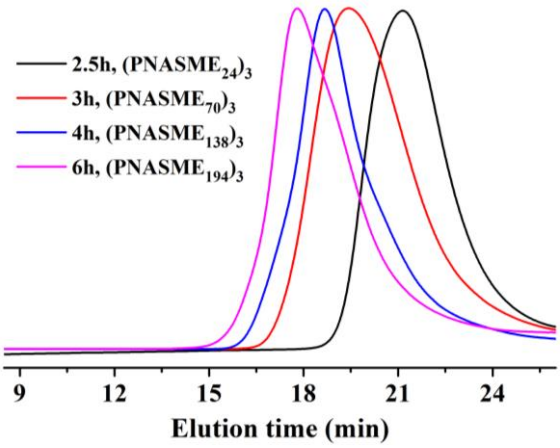

Figure S3. The GPC traces of the 3-arm star $(PNASME)_3$ employing DMF as eluent.

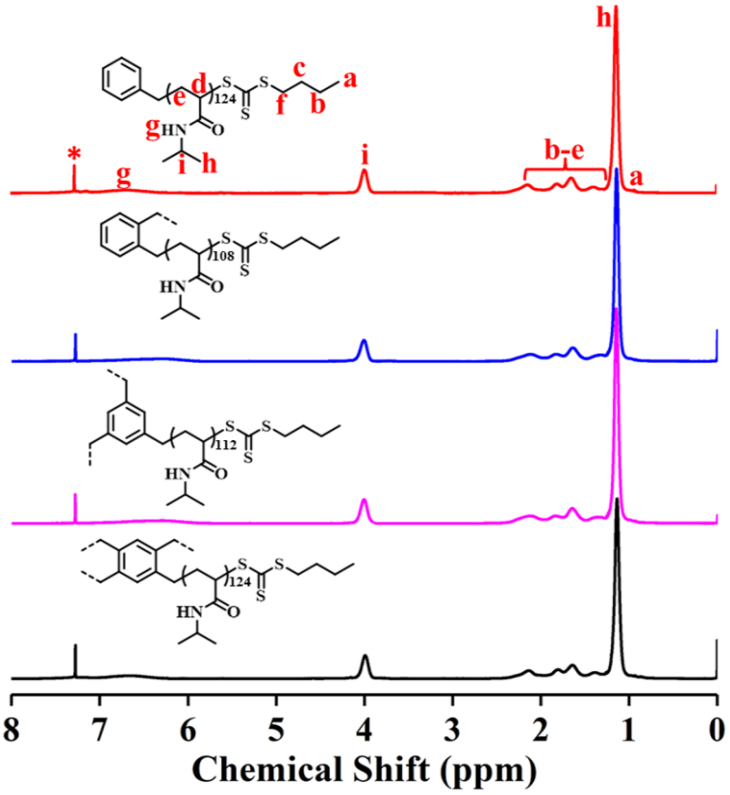

Figure S4. ^{1}H NMR spectra of the linear and star $(PNIPAM)_n$.

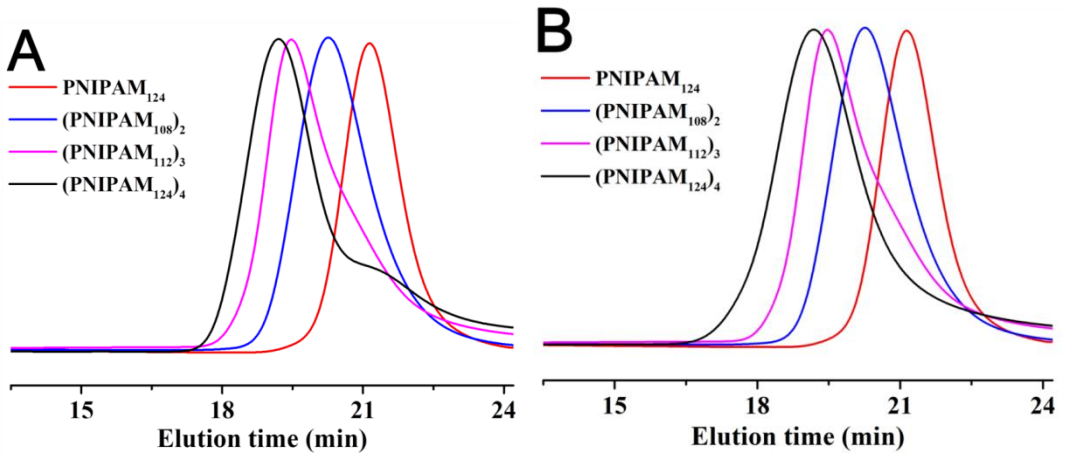

Figure S5. The GPC traces of $(PNIPAM)_n$ employing THF (A) and DMF (B) as eluent.

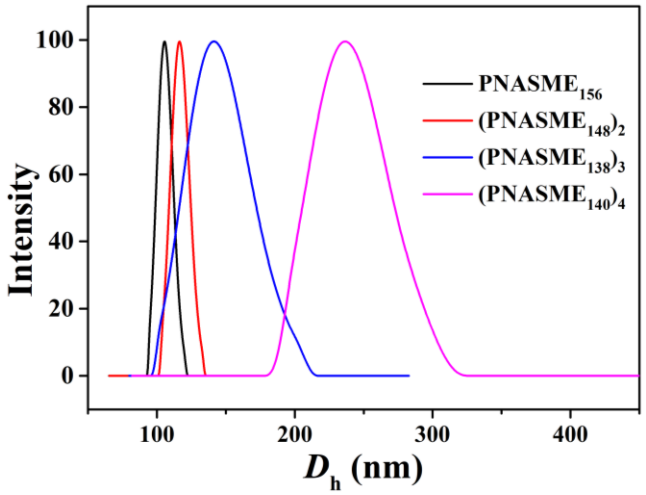

Figure S6. The hydrodynamic diameter D_h of the 0.50% aqueous solution of $(PNIPAM)_n$ at 60 ^oC.