Supporting Information for:

Synthesis of star thermoresponsive amphiphilic block copolymer nano-assemblies and topology effect on thermoresponse

Mengjiao Cao,[a] Huijun Nie,[a] Yuwen Hou,[a] Guang Han*,[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.

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

1. Equations

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

$$\frac{n_1}{n_3} = \frac{M_3}{M_1} \times \frac{M_{n,PS_1}\, {D_3}^3}{M_{n,PS_3}\, {D_1}^3} \qquad \text{(S2)}$$

2. Table

Table S1. Summary of linear and star block copolymers of (PNIPAM-*b*-PS)$_n$ with shorter PS blocks.

(PNIPAM-*b*-PS)$_n$	$[St]_0$:$[CTA]_0$:$[I]_0$	Time (h)	Conv.[a] (%)	M_n (kg/mol)			$Đ$[e]
				$M_{n,th}$[b]	$M_{n,GPC}$[c]	$M_{n,NMR}$[d]	
$PNIPAM_{150}$-*b*-PS_{20}	100:1:0.2	9	20	19.3	19.6	20.1	1.20
$(PNIPAM_{140}$-*b*-$PS_{15})_2$	200:1:0.4	12	15	35.2	29.2	37.5	1.24
$(PNIPAM_{150}$-*b*-$PS_{18})_3$	300:1:0.6	10	18	57.1	40.4	58.9	1.26
$(PNIPAM_{136}$-*b*-$PS_{20})_4$	400:1:0.8	10	20	70.7	51.3	72.8	1.24

[a] Monomer conversion determined by UV-vis. [b] Theoretical molecular weight determined by monomer conversion according to eq. S1. [c] Molecular weight determined by GPC. [d] Molecular weight determined by ^{1}H NMR. [e] $Đ$ (M_w/M_n) determined by GPC.

3. Figures

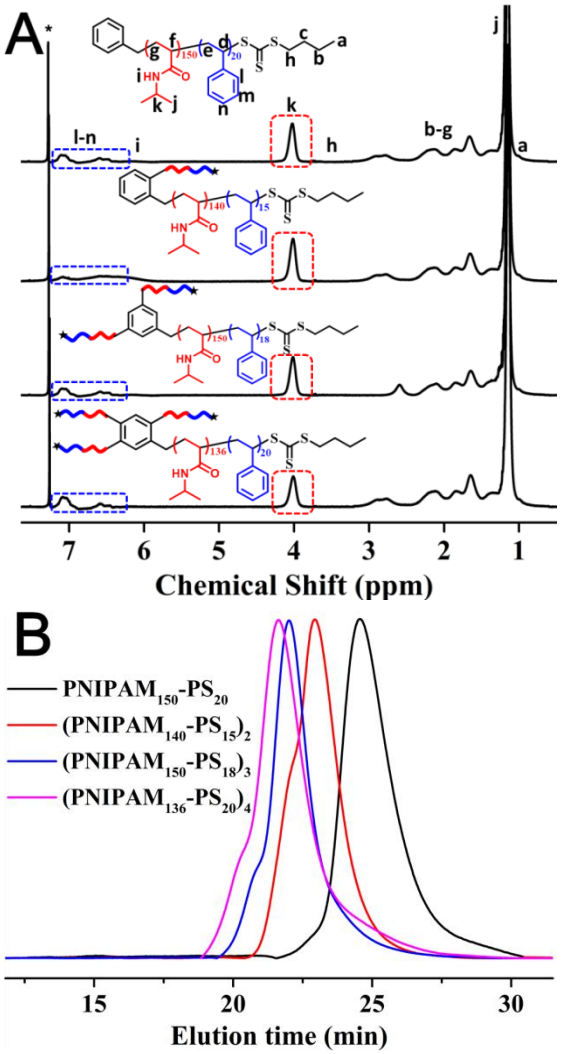

Figure S1. The ^{1}H NMR spectra (A) and GPC traces (B) of PNIPAM$_{150}$-*b*-PS$_{20}$, (PNIPAM$_{140}$-*b*-PS$_{15}$)$_2$, (PNIPAM$_{150}$-*b*-PS$_{18}$)$_3$ and (PNIPAM$_{136}$-*b*-PS$_{20}$)$_4$.

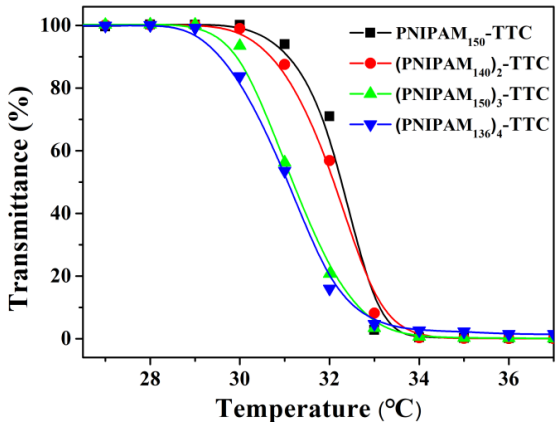

Figure S2. Temperature-dependent transmittance of 0.20 wt% solution of the PNIPAM$_{150}$-TTC, (PNIPAM$_{140}$-TTC)$_2$, (PNIPAM$_{150}$-TTC)$_3$, (PNIPAM$_{136}$-TTC)$_4$.

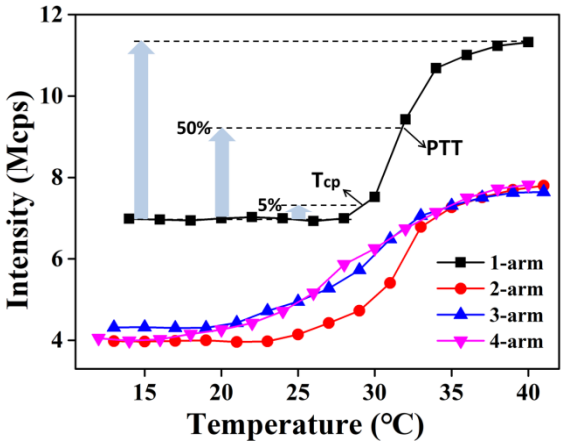

Figure S3. The evolution of scattering intensity with temperature of 0.20 wt% aqueous dispersions of PNIPAM$_{150}$-*b*-PS$_{90}$, (PNIPAM$_{140}$-*b*-PS$_{147}$)$_2$, (PNIPAM$_{150}$-*b*-PS$_{108}$)$_3$ and (PNIPAM$_{136}$-*b*-PS$_{84}$)$_4$.

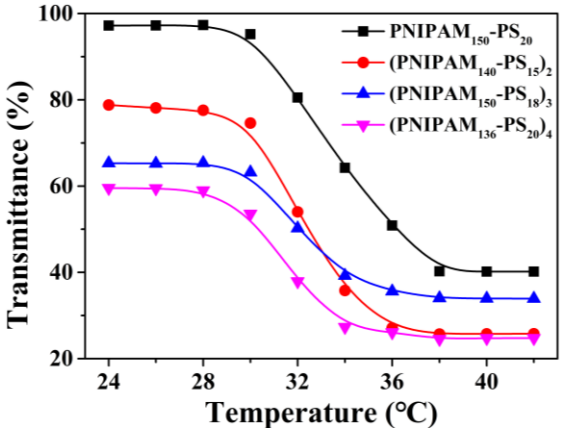

Figure S4. Temperature-dependent transmittance of 0.01 wt% aqueous dispersions of linear PNIPAM$_{150}$-*b*-PS$_{20}$, 2-arm (PNIPAM$_{140}$-*b*-PS$_{15}$)$_2$, 3-arm (PNIPAM$_{150}$-*b*-PS$_{18}$)$_3$, and 4-arm (PNIPAM$_{136}$-*b*-PS$_{20}$)$_4$.