Supporting Information for:

The synthesis of thermoresponsive POSS-based eight-arm star poly(*N*-isopropylacrylamide): A comparison between Z-RAFT and R-RAFT strategies

Bo Pang,[a] Rui Liu,[a] Guang Han,*[,b] Wei Wang*[,c] and Wangqing Zhang*[,a,d]

[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, Tel: 86-22-23509794, 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: hanguang@yuhong.com.cn.

[c] School of Chemistry & Material Science, Langfang Normal University, Langfang, 065000, China. E-mail: wangwei@lfnu.edu.cn.

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

1. Synthesis of R-Type eight-trithiocarbonate functionalized POSS (POSS-TTC-R)

Into a flask with a magnetic stirrer under argon atmosphere, DDMAT (1.75 g, 4.8 mmol) and CH_2Cl_2 (20 mL) were added, and then $(COCl)_2$ (1.7 mL, 20.0 mmol) dissolved in CH_2Cl_2 (20 mL) was added dropwise into the flask at room temperature, and the mixture was stirred for 6 h. The remaining $(COCl)_2$ and CH_2Cl_2 were removed by rotary evaporation under vacuum. Into the above-mentioned flask, POSS-OH (0.412 g, 0.30 mmol) dissolved in THF (20 mL) was poured, and the mixture was stirred for 24 h at room temperature under argon atmosphere. After removal of THF, the crude product was purified by silica gel column chromatography employing the ethyl acetate/n-hexane mixture (1:10 by volume) to afford R-Type eight-trithiocarbonate functionalized POSS (POSS-TTC-R, 64% yield). Fig. S1 shows the ^1H NMR spectra of POSS-TTC-R as well as DDMAT.
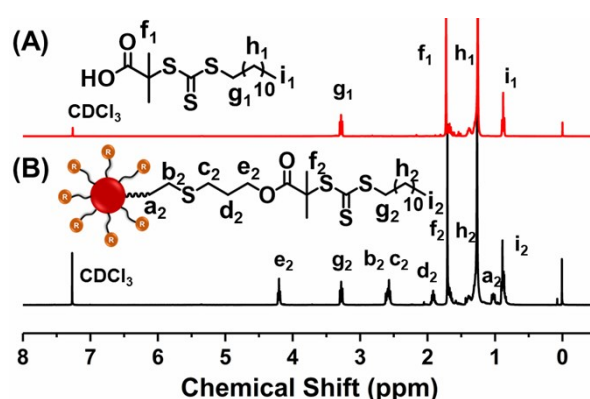

Fig. S1. The ^1H NMR spectra of DDMAT (A), and POSS-TTC-R (B).

2. Synthesis of POSS-(PNIPAM)$_8$-Z

In the synthesis of POSS-(PNIPAM)$_8$-Z, the monomer conversion of NIPAM was detected by NMR. Fig. S2 shows the typical ^1H NMR spectra of raw polymer solution of POSS-(PNIPAM$_{72}$)$_8$-Z in the presence of 1,3,5-trioxane as the internal standard. By comparing the signals at 5.15 ppm (1,3,5-trioxane) and 5.60 ppm (NIPAM), the monomer conversion was obtained.
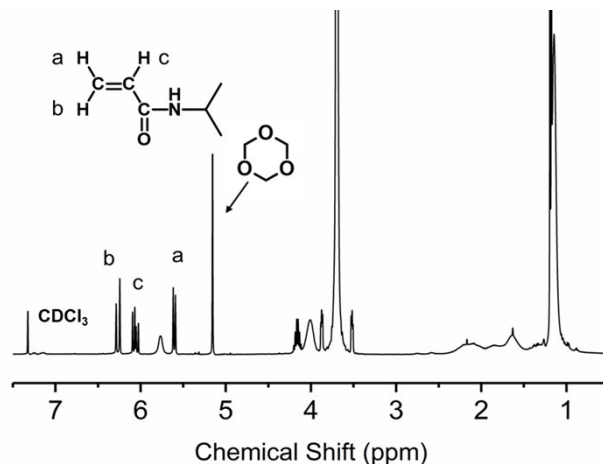
Fig. S2. The ^{1}H NMR spectra of raw polymer solution of POSS-(PNIPAM$_{72}$)$_8$-Z.

Table S1 summarizes the star POSS-(PNIPAM)$_8$-Z synthesized by solution RAFT polymerization under different conditions, in which theoretical molecular weight of POSS-(PNIPAM)$_8$-Z was determined by eqn S1. And more, the GPC traces of the synthesized POSS-(PNIPAM)$_8$-Z are shown in Fig. S3.

$$M_{n,th} = \frac{[monomer]_0 \times M_{monomer}}{[CTA]_0} \times Conversion + M_{n,CTA}$$

(S1)

Table S1. Summary of star POSS-(PNIPAM)$_8$-Z synthesized by solution RAFT polymerization.

Samples	Initiator [I]	[NIPAM]$_0$:[CTA]$_0$:[I]$_0$	Temperature (°C)	Time (h)	Conv.^{a} (%)	$M_{n,th}{}^b$	$M_{n,GPC}{}^c$	Đ^d
S1	AIBN	1600:1:2	70	1	90	166.1	59.1	1.96
S2	AIBN	1600:1:2	65	1	78	144.4	78.9	1.78
S3	ABVN	1600:1:1	50	1	73	135.3	110.8	1.41
S4	ABVN	1600:1:1	45	1	35	66.7	109.8	1.08
S5	ABVN	1600:1:2	45	1	49	92.0	120.3	1.06

^{a} The monomer conversion determined by ^{1}H NMR. ^{b} The theoretical molecular weight determined by monomer conversion according to eqn S1. ^{c} The molecular weight determined by DMF GPC. ^{d} The Đ (M_w/M_n) values determined by GPC.
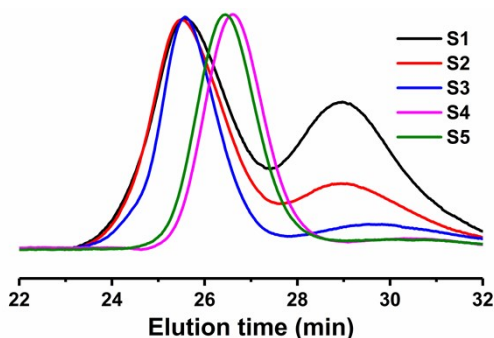
Fig. S3. The GPC traces of star POSS-(PNIPAM)$_8$-Z synthesized by solution RAFT polymerization.

Under the optimized conditions, the RAFT polymerization employing the POSS-TTC-Z was performed and the polymerization kinetics was explored, the results are shown in Table S2.

**Table S2.** Summary of the star POSS-(PNIPAM)$_8$-Z synthesized at different monomer conversions.

Polymers	[NIPAM]$_0$:[CTA]$_0$:[ABVN]$_0$	Time (min)	Conv.^{a}(%)	$M_{n,th}$^{b}	$M_{n,GPC}$^{c}	$Đ^d$
				M_n(Kg/mol)		
POSS-(PNIPAM$_{39}$)$_8$-Z	2400:1:2	30	13	38.6	78.9	1.09
POSS-(PNIPAM$_{51}$)$_8$-Z	2400:1:2	40	17	49.5	106.3	1.06
POSS-(PNIPAM$_{75}$)$_8$-Z	2400:1:2	50	25	71.2	122.3	1.09
POSS-(PNIPAM$_{96}$)$_8$-Z	2400:1:2	60	32	90.2	162.5	1.14
POSS-(PNIPAM$_{153}$)$_8$-Z	2400:1:2	70	51	141.7	235.7	1.08
POSS-(PNIPAM$_{195}$)$_8$-Z	2400:1:2	80	65	179.7	288.3	1.08
POSS-(PNIPAM$_{240}$)$_8$-Z	2400:1:2	100	80	220.4	180.2	1.66

^{a} The monomer conversion determined by ^{1}H NMR. ^{b} The theoretical molecular weight determined by monomer conversion according to eqn S1. ^{c} The molecular weight determined by DMF GPC. ^{d} The Đ (M_w/M_n) values determined by GPC.

3. Cutting off PNIPAM arms from POSS-(PNIPAM)$_8$-Z

Cutting off PNIPAM arms from POSS-(PNIPAM)$_8$-Z is shown in Scheme S1. Typically, into a flask with a magnetic stirrer, POSS-(PNIPAM$_{188}$)$_8$-Z (1.00 g, 0.0058 mmol), 1-propylamine (5.50 mg 0.093 mmol) and CH$_2$Cl$_2$ (4 mL) were added, and then the mixture was stirred for 24 h at room temperature. The leached PNIPAM was precipitated in iced diethyl ether, collected by three precipitation/filtration cycles,

followed by dried under vacuum at room temperature. The GPC traces of the leached PNIPAM and POSS-(PNIPAM$_{188}$)$_8$-Z are shown in Figure S4.
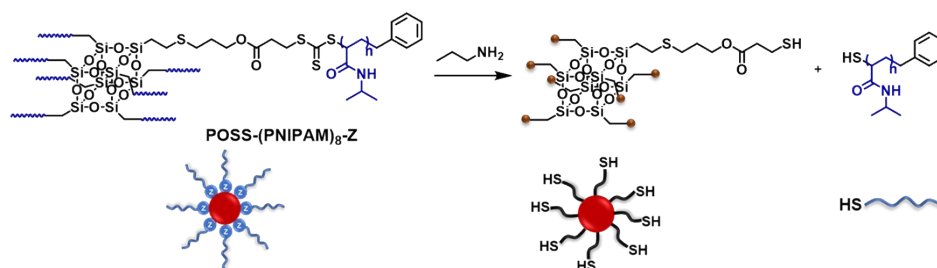
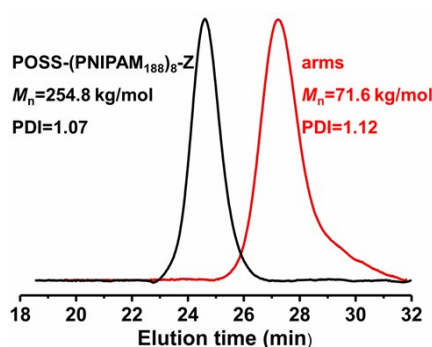**Scheme S1.** Schematic of cutting PNIPAM arms from the star POSS-(PNIPAM)$_8$-Z.

POSS-(PNIPAM$_{188}$)$_8$-Z
M_n=254.8 kg/mol
PDI=1.07

arms
M_n=71.6 kg/mol
PDI=1.12

Fig. S4. The GPC traces of POSS-(PNIPAM$_{188}$)$_8$-Z and the leached PNIPAM$_{188.}$

4. Synthesis of POSS-(PNIPAM)$_8$-R

POSS-(PNIPAM)$_8$-R was prepared by solution RAFT polymerization using ABVN as initiator and POSS-TTC-R as CTA and the details are summarized in Table 1. Here is a typical synthesis of star POSS-(PNIPAM$_{70}$)$_8$-R under [NIPAM]$_0$:[POSS-TTC-R]$_0$:[ABVN]$_0$ = 800:1:2. Into a Schlenk flask, NIPAM (2.00 g, 17.6 mmol), POSS-TTC-R (91.0 mg, 0.022 mmol) and ABVN (11.0 mg, 0.044 mmol) dissolved in 1,4-dioxane (8.0 g) were added. The oxygen in the flask was removed by argon purging and the reaction was performed at 45 °C for 80 min. The 70% monomer conversion of NIPAM was detected by ^{1}H NMR analysis using 1,3,5-trioxane as internal standard. The synthesized POSS-(PNIPAM$_{70}$)$_8$-R was precipitated in iced diethyl ether, collected by three precipitation/filtration cycles, followed by dried under

vacuum at room temperature.

5. Comparison between the GPC traces of POSS-(PNIPAM$_{37}$)$_8$-Z and POSS-(PNIPAM$_{35}$)$_8$-R

To make comparison, the GPC traces of POSS-(PNIPAM$_{37}$)$_8$-Z and POSS-(PNIPAM$_{35}$)$_8$-R are shown in Fig. S5.
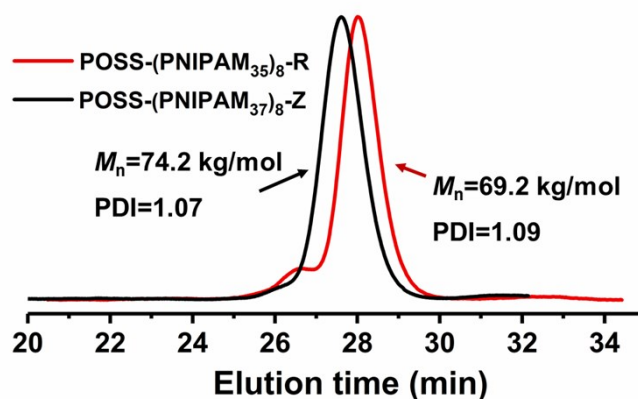
Fig. S5. The GPC traces of POSS-(PNIPAM$_{37}$)$_8$-Z and POSS-(PNIPAM$_{35}$)$_8$-R

6. Summary of PTT and D_h of star POSS-(PNIPAM)$_8$ and linear PNIPAM

Table S3. Summary of PTT and D_h of star and linear samples.

Polymers	PTT$_{(\%T)}$[a] (^{o}C)	PTT$_{(NMR)}$[b] (^{o}C)	D_h[c](nm)	PDI[d]
POSS-(PNIPAM$_{72}$)$_8$-Z	29.5	31.3	74	0.125
POSS-(PNIPAM$_{150}$)$_8$-Z	30.4	32.4	86	0.080
POSS-(PNIPAM$_{188}$)$_8$-Z	30.5	32.5	98	0.053
POSS-(PNIPAM$_{360}$)$_8$-Z	31.2	33.0	110	0.036
PNIPAM$_{141}$-Z	30.6	33.3	272	0.037

[a] The phase transition temperatures (PTT) determined by Temperature-dependent transmittance of 1.0 wt% aqueous solution of star and linear polymers. [b] The PTTs determined by variable temperature ^{1}H NMR spectra of the 1.0 wt% star and linear polymers solution of D$_2$O. [c] Hydrodynamic diameter distribution f (D_h) of 0.05 wt% aqueous solution of star and linear polymers at 40 ^{o}C. [d] Polydispersity index (PDI) of D_h.
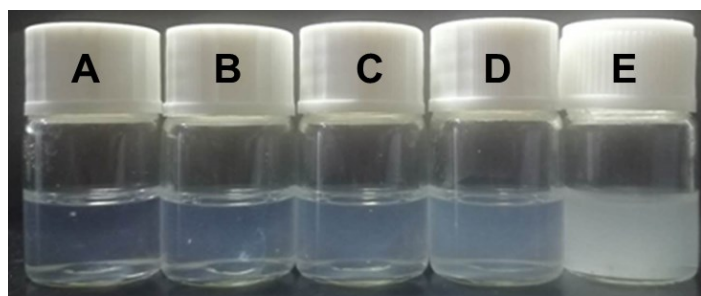
Fig. S6. Images of 0.05 wt% aqueous solution of star POSS-(PNIPAM$_{72}$)$_8$-Z (A), star POSS-(PNIPAM$_{150}$)$_8$-Z (B), star POSS-(PNIPA$_{188}$)$_8$-Z (C), star POSS-(PNIPAM$_{360}$)$_8$-Z (D) and linear PNIPAM$_{141}$-Z (E) at 40 °C.

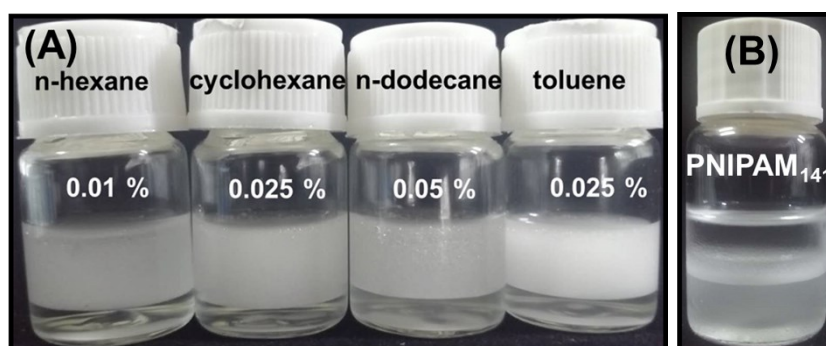## 7. On the emulsion stabilized by POSS-(PNIPAM)$_8$

Fig. S7. Images of oil-in-water emulsions using POSS-(PNIPAM$_{72}$)$_8$-Z as emulsifier (A) and images of toluene-in-water emulsion stabilized by 0.10 wt% PNIPAM$_{141}$-Z (B).
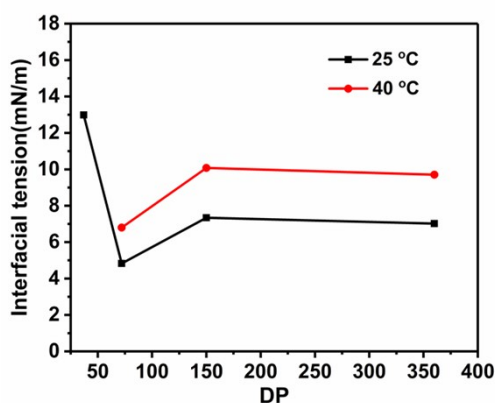

Fig. S8. The toluene/water interfacial tension in the presence of 0.10 wt% of POSS-(PNIPAM$_{37}$)$_8$-Z POSS-(PNIPAM$_{72}$)$_8$-Z, POSS-(PNIPAM$_{150}$)$_8$-Z and POSS-(PNIPAM$_{360}$)$_8$-Z at 25 °C and 40 °C. Note: the toluene/water interfacial tension in the presence of 0.10 wt% of POSS-(PNIPAM$_{37}$)$_8$-Z at 40 °C is not shown, since it is out of the analysis due to it becoming milky at this temperature.