Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

of

Dual associations of toothbrush-like double hydrophilic block copolymers

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1. Materials and Experimental section

Oligo(ethylene glycol) monomethyl ether methacrylate (OEGMA, M_n=300, OEGMA300, Sigma-Aldrich) was purified by passing through a basic Al_2O_3 column to remove the inhibitor. Poly(ethylene glycol) methyl ether methacrylate (POEGMA, M_n=480, OEGMA480, Sigma-Aldrich) was used as received. *N*-isopropyl acrylamide (J&K, 99%) was purified twice by recrystallization from n-hexane (Rionlon (Tianjin), 97%), *N*-(2-hydroxypropyl) methacryamide (HPMA) was prepared according to literature[1], 2,2'-Azoisobuthylacetamide (J&K, 99%) was recrystallized twice from ethanol (Rionlon (Tianjin), 95%). 1,4-dioxane (Rionlon(Tianjin), 99.5%) was distilled under reduced pressure to remove the inhibitor. 4-cyanopentanoic acid dithiobenzate (CPADB, Aldrich, 97%), *N*,*N*-dimethylacetamide (DMAc, Adrich, anhydrous, 99.8%), tetrahydrofuran (THF, Rionlon (Tianjin), 99%), anhydrous ethyl ether (Rionlon (Tianjin), 99.0%) , anhydrous methanol (Rionlon (Tianjin), 99.5%), *N*,*N*-Dimethylformamide (DMF, Rionlon (Tianjin), 99.5%) and other chemicals were used as received.

RAFT synthesis of P (OEGMA300)$_{17}$ using CPADB as a CTA

P(OEGMA300) was prepared according to the reported procedure[2]. In a typical procedure, CPADB (0.0576 g, 0.2 mmol), OEGMA300 (3 g, 0.2 mmol), and AIBN (0.01117 g, 0.067 mmol) were dissolved in 10 ml of DMAc. The solution was purged with N_2 for 10 min and then immersed in an oil bath preheated at 70 ^oC. After 103 min, the polymerization was quenched by freezing in the liquid nitrogen. After thawing, the polymer solution was diluted with THF and the product was precipitated in ice-cold n-hexane. The product was purified by extensive dialysis (MWCO, 3500) against distilled water to remove any unreacted monomers, and harvested by freeze-drying to yield red-oil product. Yield=34.2%.

RAFT synthesis of PNIPAAm$_{133}$-*b*-P(OEGMA300)$_{17}$ using P (OEGMA300)$_{17}$ as a macro-CTA

NIPAAm (0.23094 g, 2 mmol), P(OEGMA300) macro-CTA (0.05 g, 0.01 mmol), AIBN (0.00056 g, 0.0033 mmol), and 1,4-dioxane (1600 µl) were introduced into a 10 ml Schlenk flask. The solution was deoxygenated by three freeze-pump-thaw cycles, and then immersed in an oil bath preheated at 70 ^{o}C. After 4.5 h, the polymerization was quenched by immersing the flask in the liquid nitrogen. After thawing, the polymer solution was diluted with THF, and precipitated in anhydrous ethyl ether to yield light pink power. The product was further purified by dissolving in DMF followed by extensive dialysis (MWCO, 3500) against distill water. The final product was harvested by freeze-drying. Yield=40.7%.

RAFT synthesis of P (OEGMA480)$_9$ using CPADB as a CTA

CPADB (0.0288 g, 0.1 mmol), OEGMA480 (2.4 g, 5 mmol), and AIBN (0.00559 g, 0.033 mmol) were dissolved in 5 ml of DMAc. The solution was deoxygenated by three freeze-pump-thaw cycles, and then immersed in an oil bath preheated at 70 ^{o}C. After 138 min, polymerization was quenched by immersing the flask in the liquid nitrogen. After thawing, the polymer solution was diluted with THF, and precipitated in n-hexane to yield red-oil product. The product was purified by extensive dialysis (MWCO, 10000) against distilled water to remove any unreacted monomers, and harvested by freeze-drying. Yield=8.8%.

RAFT synthesis of P(NIPAAm)$_{133}$-*b*-P(OEGMA480)$_9$ using P(OEGMA480)$_9$ as a macro-CTA

NIPAAm (0.23094 g, 2 mmol), P(OEGMA480) macro-CTA (0.02 g, 0.004 mmol), AIBN (0.00022 g, 0.0013 mmol), and 1, 4-dioxane (1600 µl) were introduced into a 10 ml Schlenk flask. The solution was deoxygenated by three freeze-pump-thaw cycles, and then immersed in an oil bath preheated at 70 ^{o}C. After 184 min, polymerization was quenched by immersing the flask in the liquid nitrogen. After thawing, the polymer solution was diluted with THF, and precipitated in anhydrous ethyl ether to yield light pink power. The product was further purified by dissolving in

DMF followed by extensive dialysis (MWCO, 3500) against distill water. The final product was harvested by freeze-drying. Yield=19.7%.

RAFT synthesis of P (HPMA)$_{31}$ using CPADB as a CTA

CPADB (0.0144 g, 0.05 mmol), HPMA (1.42875 g, 10 mmol), AIBN (0.00279 g, 0.0167 mmol) and a mixture of methanol/1,4-dioxane (10 mL, 1/2 (V/V)) were introduced into a 50 ml Schlenk flask. The solution was deoxygenated by three freeze-pump-thaw cycles, and then immersed in an oil bath preheated at 70 ^{o}C. After 305 min, polymerization was quenched by immersing the flask in the liquid nitrogen. After thawing, the polymer solution was diluted with methanol, and precipitated in diethyl ether to yield pink powder. The product was purified by extensive dialysis (MWCO, 10000) against distilled water to remove any unreacted monomers, and harvested by freeze-drying. Yield=14.8%.

RAFT synthesis of P(NIPAAm)$_{129}$-*b*-P(HPMA)$_{31}$ using P(HPMA)$_{31}$ as a macro-CTA

NIPAAm monomer (0.27713 g, 2.4 mmol), P(HPMA) macro-CTA (0.02 g, 0.004 mmol), AIBN (0.00022 g, 0.0013 mmol), and a mixture of methanol/1,4-dioxane (1920µl, 1/2.5 (V/V)) were introduced into a 10 ml Schlenk flask. The solution was deoxygenated by three freeze-pump-thaw cycles, and then immersed in an oil bath preheated at 70 ^{o}C. After 165 min, polymerization was quenched by immersing the flask in the liquid nitrogen. After thawing, the polymer solution was diluted with THF, and precipitated in anhydrous ethyl ether to yield light pink power. The product was further purified by dissolving in DMF followed by extensive dialysis (MWCO, 3500) against distill water. The final product was harvested by freeze-drying. Yield=18.7%.

Polymer characterizations

^{1}H NMR spectra were recorded on a JNM-ECS spectrometer at 400 MHZ using $CDCl_3$, D_2O and *d*-DMSO as the solvents, respectively. Specifically, $CDCl_3$ was used

for P(OEGMA300)$_{17}$, P(OEGMA480)$_9$, and P(NIPAAm)$_{133}$-*b*-P(OEGMA480)$_9$. D_2O was used for P(NIPAAm)$_{133}$-*b*-P(OEGMA300)$_{17}$ at different temperatures of 25, 38 and 41 ^oC. d_6-DMSO was used for P(NIPAAm)$_{133}$-*b*-P(OEGMA300)$_{17}$, P(HPMA)$_{31}$, P(NIPAAm)$_{129}$-*b*-P(HPMA)$_{31}$, P(NIPAAm)$_{92}$-*b*-P(OEGMA300)$_{17,}$ and P(NIPAAm)$_{229}$-*b*-P(OEGMA300)$_{17}$. Optical absorbance of polymer solutions at various temperatures was measured at 500 nm with a Lambda 35 UV-Vis spectrometer (Perkin-Elmer). The average hydrodynamic diameter (D_h) at various temperatures was measured by dynamic light scattering (DLS) on a BI-200SM (Brookhaven, USA) instrument. The scattering angle was fixed at 90 ^oC. The size-exclusion chromatography and multi-angle laser light scattering (SEC-MALLS) was carried out to determine the molecular weight and molecular weight distribution of the polymers. SEC using HPLC-grade DMF containing 0.1 wt% LiBr at 60 ^oC as the eluent at a flow rate of 1 ml/min Tosoh TSK-GEL R-3000 and R-4000 columns (Tosoh Bioscience) were connected in series to a Agilent 1260 series (Agilent Technologies), an interferometric refractometer (Optilab-rEX, Wyatt Technology) and a MALLS device (DAWN EOS, Wyatt Technology). The MALLS detector was operated at a laser wavelength of 690.0 nm. TEM measurements were carried out on a JNM-2010 instrument operating at an acceleration voltage of 200 keV. The polymer solution (1 mg/ml) was thermostatted at certain temperature for 3 h prior to sample preparation. The TEM samples were made by dropping 10 μl of the solution onto a carbon-coated copper grid for 5 min, and the excess solution was slightly blotted up by a filter paper. Thereafter, one drop of phosphotungstic acid solution (PTA, 1%, pH 6.5) was added onto the copper grid and kept for 5 min for staining. The final grid was dried overnight under ambient environment. SEM measurements was conducted on a JSM-5600LV scanning electron microscopy (SEM, Japan). The P(NIPAAm)$_{133}$-*b*-P(OEGMA300)$_{17}$ aqueous solution (1 mg/ml) was thermostatted at 38 ^oC for 3 h prior to sample preparation. The sample was fixed on aluminum stubs and coated with gold prior to SEM observation.

2. Discussion about using phosphotungstic acid to stain polymer for TEM observation

Phosphotungstic acid was used as a staining reagent to provide sufficient contrast for TEM observation of polymeric nanoparticles composed of only light atoms, such as C, H, O, N. Although Phosphotungstic acid is believed to produce a negative staining effect, *i.e.*, staining of the background to highlight the objects, we did observe positive staining, *i.e.*, staining of the particles in our study. Similar results have been reported in our previous study as well.[3]

3. Possible explanations for the disappearance of characteristic signals attributed to the dithiobenzoate moiety of RAFT group in the ^{1}H NMR spectra of block copolymers

For RAFT-synthesized homopolymers of P(OEGMA300), P(OEGMA480), and P(HPMA) with MWs all around 5.0 kDa, the characteristic signals of RAFT group, *i.e.*, the dithiobenzoate moiety are readily recorded in the ^{1}H NMR spectra (Figure S2, S8, S10), however, further chain extention with NIPAAm using these homopolymers as macro-CTAs generates DHBCs with MW reaching ~20.0 kDa, leading to much weaker signals of ternminal RAFT group compared to the strong signals from polymer block. The signal of the dithiobenzoate moiety is thus not clearly shown in the ^{1}H NMR spectra of DHBCs (Figure S3, S9, S11, S14, S17).

References

1. Y. J. Pan, D. Li, S. Jin, C. Wei, K. Y. Wu, J. Guo, and C. C. Wang, *Polymer Chemistry*, 2013, **4**, 3545-3553.

2. H. Wei, J. A. Pahang, and S. H. Pun, *Biomacromolecules*, 2013, **14**, 275-284.

3. H. Wei, S. Perrier, S. Dehn, R. Ravarian, and F. Dehghani, *Soft Matter*, 2012, **8**, 9526-9528.

Table S1. Summary of P(OEGMA300) prepared at different polymerization time using CPADB as a RAFT CTA.

	No.	Time (min)	Conv. (%) by ^{1}H NMR	DP determined by ^{1}H NMR	M_n (^{1}H NMR, kDa)	Theoretical M_n [a] (kDa)
[M]:[CTA]:[AIBN]	1	46	8	4	1.48	1.48
=50:1:0.33,	2	52	13	6	2.08	2.23
target M_n=5.3 kDa,	3	105	31	15	4.78	4.93
[M]=1.0 M, T=70 °C,	4	130	40	20	6.28	6.28
DMAc	5	180	51	25	7.78	7.93

[a] $M_n\,(\text{theor}) = \frac{[M]}{[CTA]} \times M_{\text{monomer}} \times \text{conversion} + M_{\text{CTA.}}$

Table S2. Summary of PNIPAAm-*b*-P(OEGMA300)$_{17}$ prepared at different polymerization time using P(OEGMA300)$_{17}$ as a macro-CTA.

	No.	Time (min)	Conv (%) by ^{1}H NMR	DP determined by ^{1}H NMR	M_n (^{1}H NMR, kDa)	Theoretical M_n [a] (kDa)
[M]:[macro-CTA]:[AIBN]	1	210	36	70	13.3	13.5
=200:1:0.33,	2	240	43	82	14.7	15.1
target M_n =20.4 kDa, [M]=1.25 M,	3	270	68	133	20.4	20.8
T=70 °C, 1,4-dioxane	4	480	81	158	23.3	23.8

[a] $M_n\,(\text{theor}) = \frac{[M]}{[macro\text{ - }CTA]} \times M_{\text{monomer}} \times \text{conversion} + M_{\text{macro-CTA}}$

Table S3. Summary of P(OEGMA480) prepared at different polymerization time using CPADB as a RAFT CTA.

	No.	Time (min)	Conv (%) by ^{1}H NMR	DP determined by ^{1}H NMR	M_n (^{1}H NMR, kDa)	Theoretical M_n [a] (kDa)
[M]:[CTA]:[AIBN] =50:1:0.33, target M_n =5.3 kDa, [M]=1.25M,T=70℃, DMAc	1	135	12	6.0	3.19	3.19
	2	138	21	10.0	5.08	5.32
	3	150	37	18.4	9.15	9.14

[a] M_n (theor) = $\frac{[M]}{[CTA]} \times M_{monomer} \times$ conversion + M_{CTA}

Table S4. Summary of P(NIPAAm)-*b*-P(OEGMA480)$_9$ prepared at different polymerization time using P (OEGMA480)$_9$ as a macro-CTA.

	No.	Time (min)	Conv (%) by ^{1}H NMR	DP determined by ^{1}H NMR	M_n (^{1}H NMR, kDa)	Theoretical M_n [a] (kDa)
[M]:[macro-CTA]:[AIBN] =500:1:0.33, target M_n =19.6 kDa, [M]=1.25 M, T=70℃, 1,4-dioxane	1	130	15	68.6	12.8	13.0
	2	160	21	98.7	16.2	16.5
	3	184	28	133.3	20.1	20.4
	4	197	31	149.4	21.9	22.4

[a] M_n(theor) = $\frac{[M]}{[macro\text{ - }CTA]} \times M_{monomer} \times$ conversion + $M_{macro\text{-}CTA}$

Table S5. Summary of P (HPMA) prepared at different polymerization time using CPADB as a RAFT CTA.

	No.	Time (min)	Conv (%) by ^{1}H NMR	DP determined by ^{1}H NMR	M_n (^{1}H NMR, kDa)	Theoretical M_n (kDa)
[M]:[CTA]:[AIBN] =200:1:0.33, target M_n =5.3 kDa, [M]=1.25M,T=70℃, methanol/1,4-dioxane=1/2	1	150	10	20	3.14	3.14
	2	205	16	31	4.72	4.86
	3	300	31	61	9.01	9.16

[a] $M_n(\text{theor}) = \frac{[M]}{[CTA]} \times M_{\text{monomer}} \times \text{conversion} + M_{\text{CTA}}$

Table S6. Summary of P(NIPAAm)-*b*-P(HPMA)$_{31}$ prepared at different polymerization time using P (HPMA)$_{31}$ as a macro-CTA.

	No.	Time (min)	Conv (%) By ^{1}H NMR	DP determined by ^{1}H NMR	M_n (^{1}H NMR, kDa)	Theoretical M_n [a] (kDa)
[M]:[macro-CTA]:[AIBN] =600:1:0.33, target M_n =19.8 kDa, [M]=1.25 M, T=70℃, methanol/1,4-dioxane=1/2.5	1	140	16	91	15.0	15.3
	2	165	22	129	19.3	19.7
	3	180	37	218	29.4	30.0
	4	250	67	395	49.4	50.5

[a] $M_n(\text{theor}) = \frac{[M]}{[macro\text{-}CTA]} \times M_{\text{monomer}} \times \text{conversion} + M_{\text{macro-CTA}}$

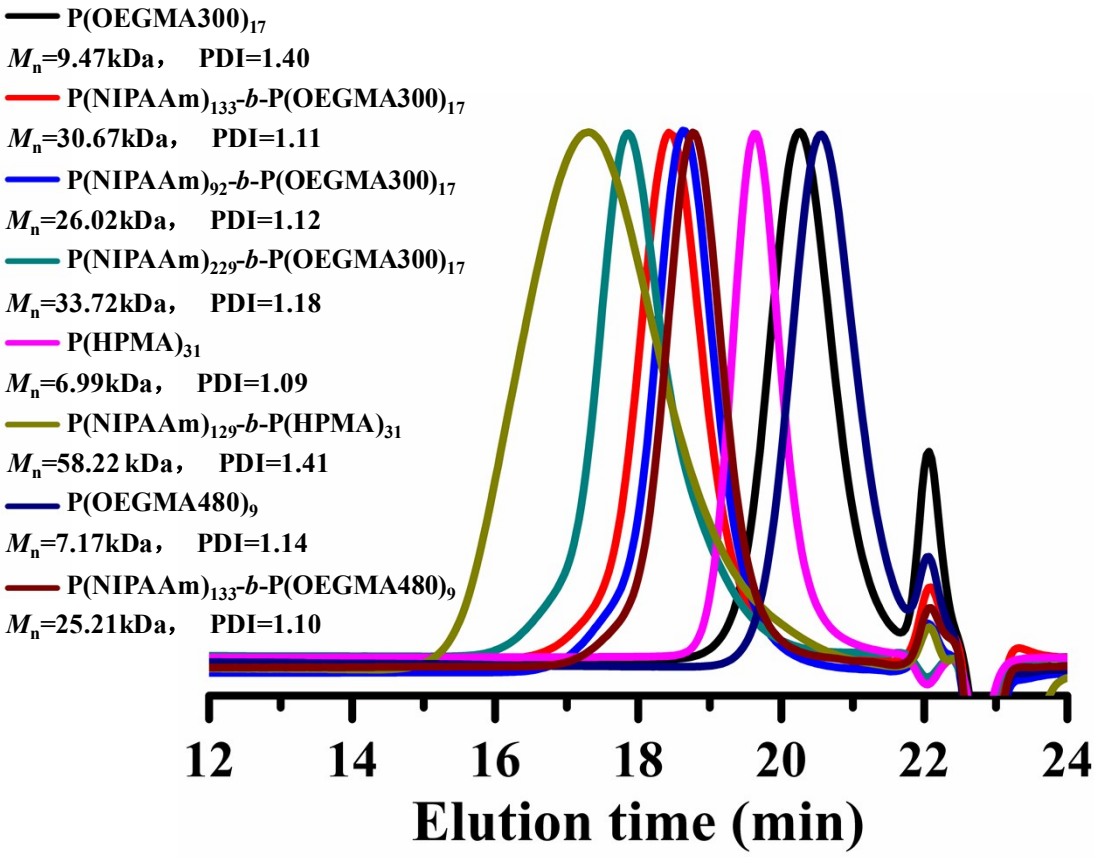

Figure S1. SEC elution traces of $P(OEGMA300)_{17}$, $P(NIPAAm)_{133}$-*b*-$P(OEGMA300)_{17}$, $P(NIPAAm)_{92}$-*b*-$P(OEGMA300)_{17,}$ $P(NIPAAm)_{229}$-*b*-$P(OEGMA300)_{17,}$ $P(HPMA)_{31}$, $P(NIPAAm)_{129}$-*b*-$P(HPMA)_{31}$, $P(OEGMA480)_9$ and $P(NIPAAm)_{133}$-*b*-$P(OEGMA480)_9$ using DMF as an eluent.

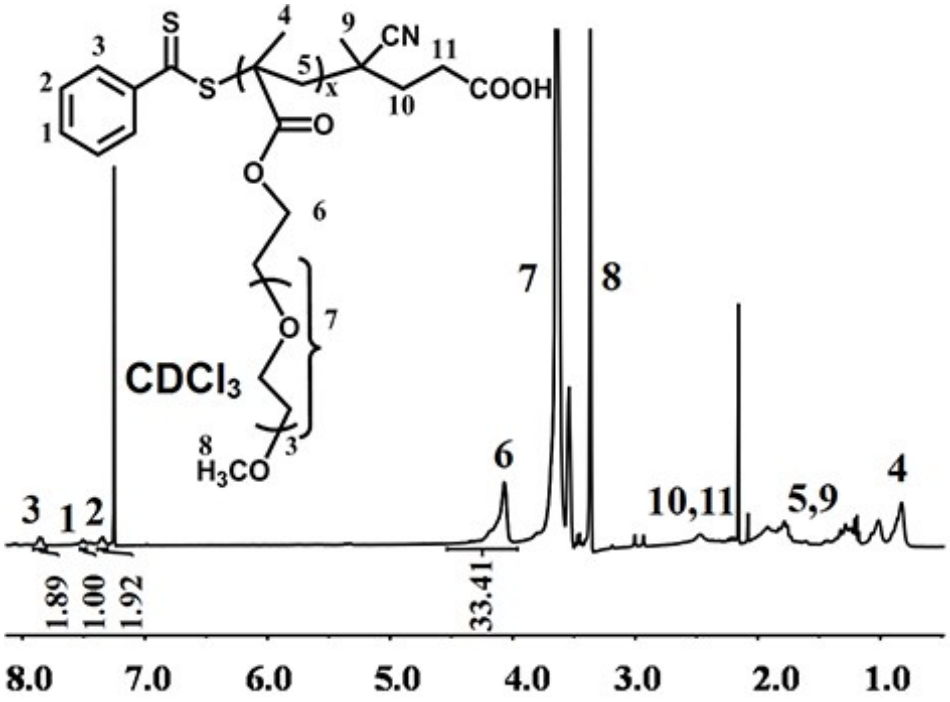

Figure S2. ^{1}H NMR spectrum of P(OEGMA300)$_{17}$ in $CDCl_3$.

The DP (n) of P(OEGMA300) synthesized at 103 min was determined by NMR chain-end analysis based on the integral ratio of peak 6 and peak (1,2,3) in the ^{1}H NMR spectrum of the polymer (Figure S2) as follows,

$$\frac{2n}{5} = \frac{integral\ of\ signal\ 6}{integral\ of\ signals(1,2,3)}$$

$$\Rightarrow \quad n = \frac{integral\ of\ signal\ 6}{integral\ of\ signals(1,2,3)} \times \frac{5}{2}$$

The DP of P(OEGMA300) was calculated to be ~17.

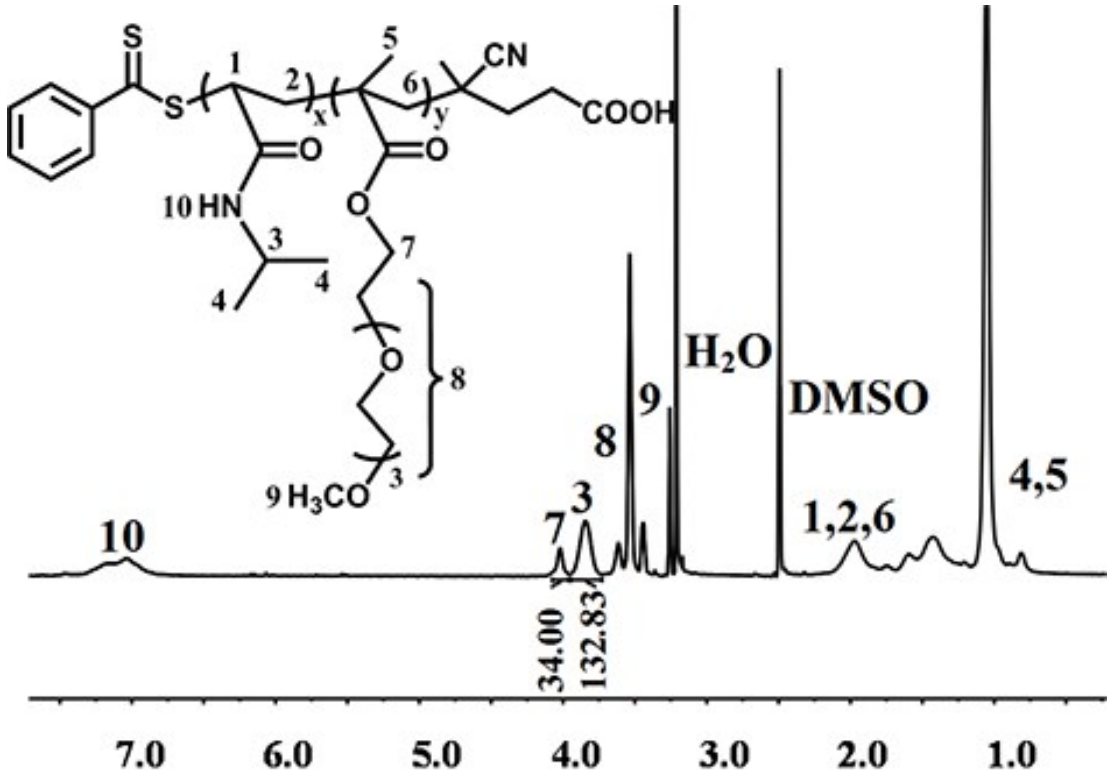

Figure S3. ^{1}H NMR spectrum of P(NIPAAm)$_{133}$-*b*-P(OEGMA300)$_{17}$ in d_6-DMSO.

The DP (n) of PNIPAAm was determined by comparing integral intensity of peak 3 and peak 7 in the ^{1}H NMR spectrum of the polymer (Figure S3) as follows,

$$\frac{DP(PNIPAAm)}{2 \times DP(P(OEGMA300))} = \frac{integral\ of\ signal\ 3}{integral\ of\ signal\ 7}$$

$$\Rightarrow \quad DP(PNIPAAm) = \frac{integral\ of\ signal\ 3}{integral\ of\ signal\ 7} \times 2 \times DP(P(OEGMA300))$$

The DP of PNIPAAm was calculated to be 133.

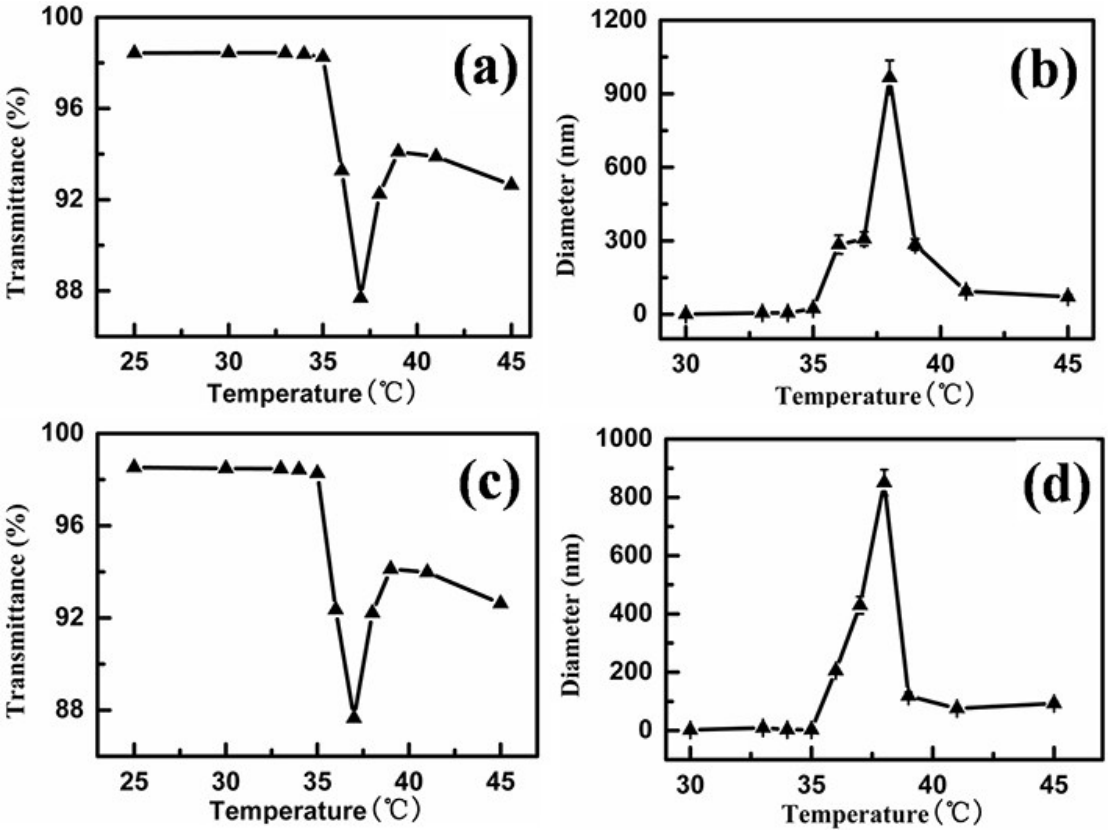

Figure S4. The first (a & b) and second (c & d) measurements of both optical transmittance and size variations with increasing temperature. Polymer solution of $P(NIPAAm)_{133}$-*b*-$P(OEGMA300)_{17}$ (1 mg/ml) thermostatted at a high temperature was placed into a freezer set at -4^{o}C for the second test immediately when the first measurements was completed.

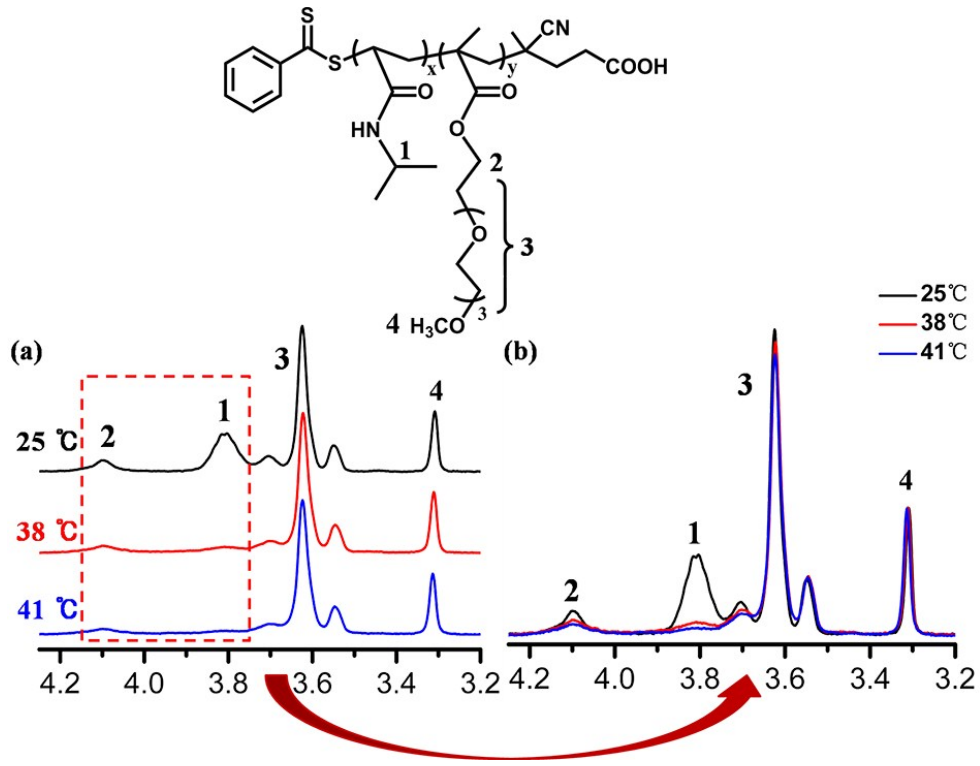

Figure S5. ^{1}H NMR spectra (a) of P(NIPAAm)$_{133}$-*b*-P(OEGMA300)$_{17}$ in D_2O recorded at different temperatures of 25, 38, and 41 ^{o}C, andamplified spectra (b) of characteristics signals 1, 2, 3, and 4 in Figure S5(a).

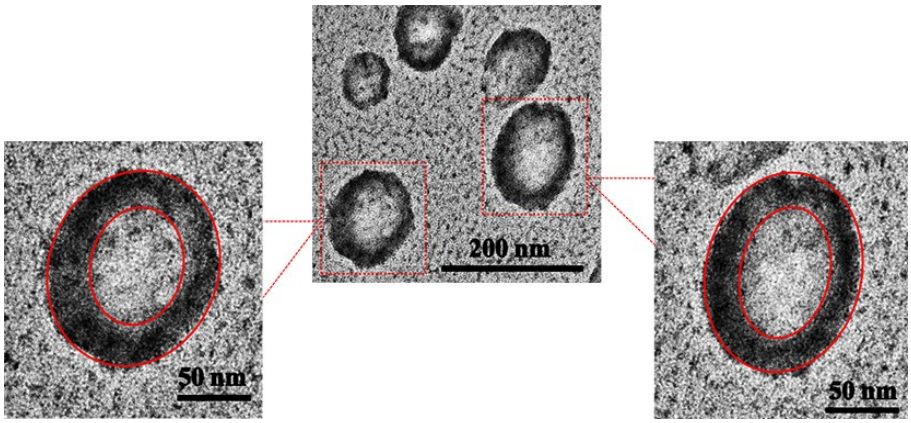

Figure S6. TEM images of $P(NIPAAm)_{133}$-*b*-$P(OEGMA300)_{17}$ aqueous solution (1 mg/ml) at 38 °C.

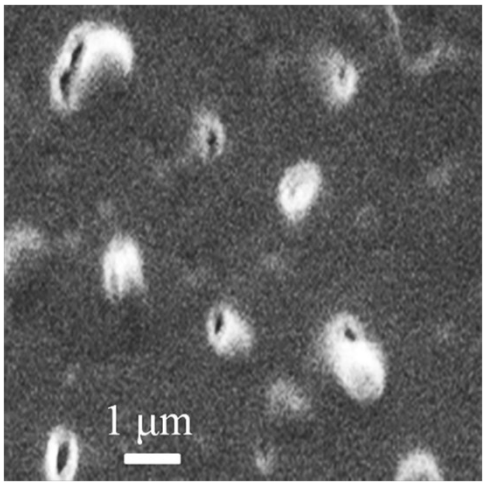

Figure S7. SEM image of $P(NIPAAm)_{133}$-*b*-$P(OEGMA300)_{17}$ aqueous solution (1 mg/ml) at 38 °C.

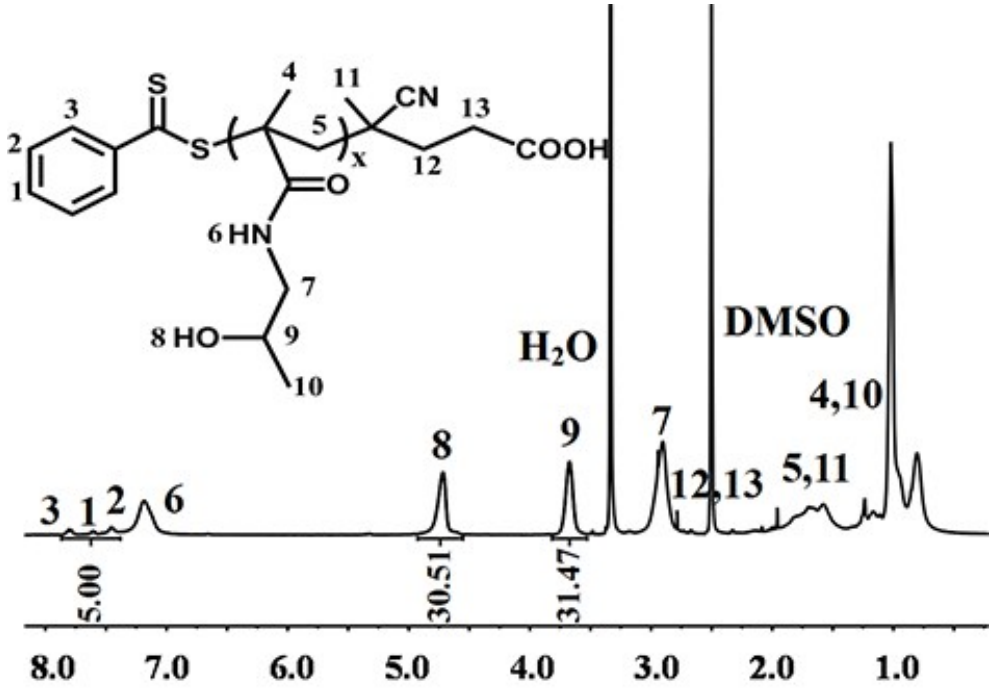

Figure S8. ^{1}H NMR spectrum of P(HPMA)$_{31}$ in d_6-DMSO.

The DP (n) of P(HPMA) synthesized at 305 min was determined by NMR chain-end analysis based on the integral ratio of peak 9 and peak (1,2,3) in the ^{1}H NMR spectrum of the polymer (Figure S8) as follows,

$$\frac{n}{5} = \frac{integral\ of\ signal\ 9}{integral\ of\ signals(1,2,3)}$$

$$\Rightarrow \quad n = \frac{integral\ of\ signal\ 9}{integral\ of\ signals(1,2,3)} \times 5$$

The DP was calculated to be ~31.

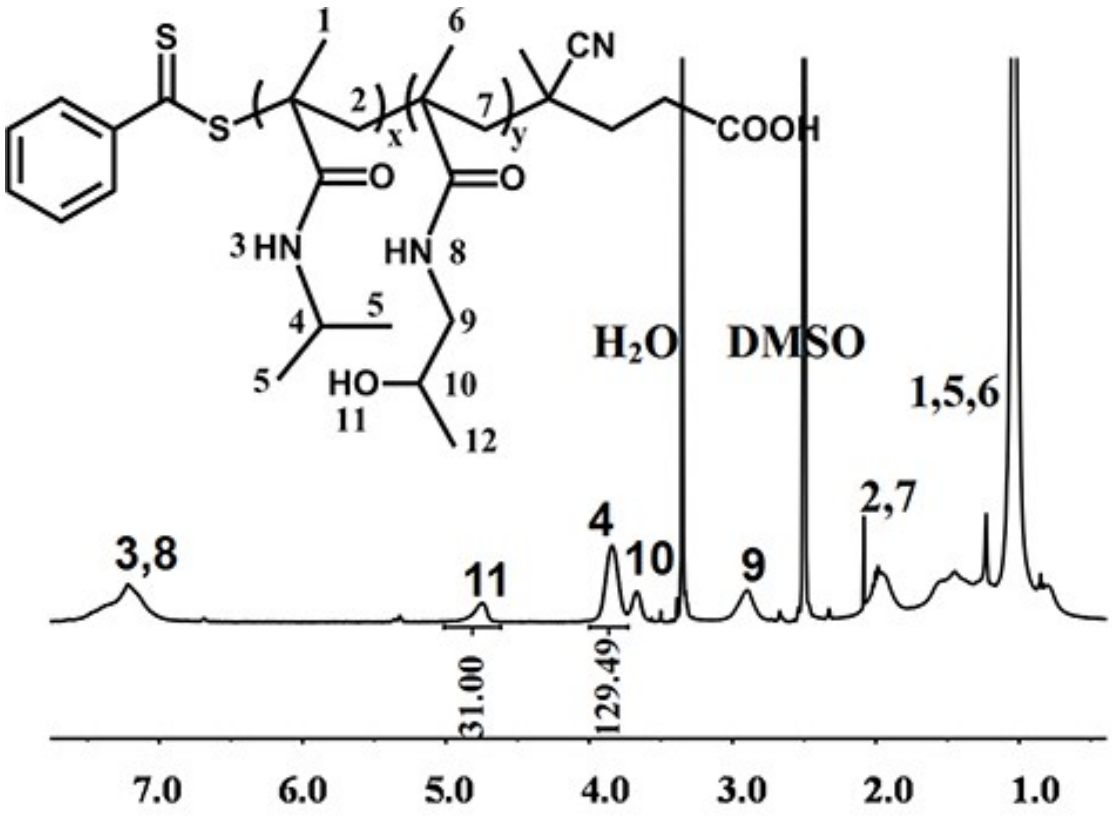

Figure S9. ^{1}H NMR spectrum of P(NIPAAm)$_{129}$-*b*-P(HPMA)$_{31}$ in d_6-DMSO.

The DP (n) of PNIPAAm was determined by comparing integral intensity of peak 4 and peak 11 in the ^{1}H NMR spectrum of the polymer (Figure S9) as follows,

$$\frac{DP(PNIPAAm)}{DP(P(HPMA))} = \frac{integral\ of\ signal\ 4}{integral\ of\ signal\ 11}$$

$$\Rightarrow \quad DP(PNIPAAm) = \frac{integral\ of\ signal\ 4}{integral\ of\ signal\ 11} \times DP(P(HPMA))$$

The DP of PNIPAAm was calculated to be 129.

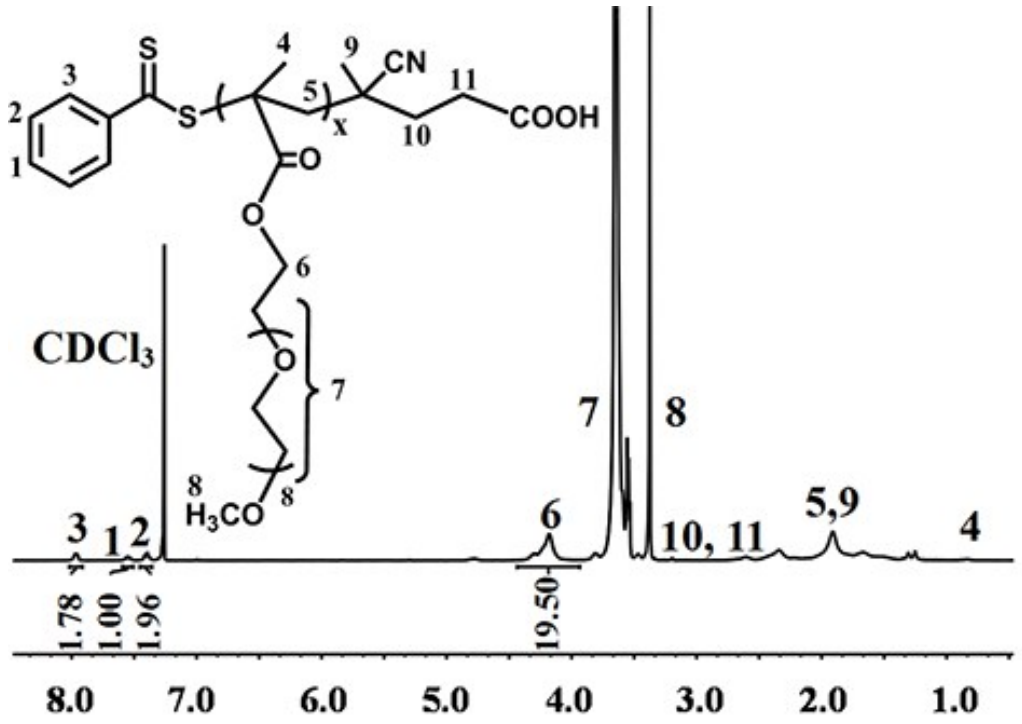

Figure S10. ^{1}H NMR spectrum of P(OEGMA480)$_9$ in $CDCl_3$.

The DP (n) of P(OEGMA480) synthesized at 138 min was determined by NMR chain-end analysis based on the integral ratio of peak 6 and peak (1,2,3) in the ^{1}H NMR spectrum of the polymer (Figure S10) as follows,

$$\frac{2n}{5} = \frac{integral\ of\ signal\ 6}{integral\ of\ signals(1,2,3)}$$

$$\Rightarrow \quad n = \frac{integral\ of\ signal\ 6}{integral\ of\ signals(1,2,3)} \times \frac{5}{2}$$

The DP was calculated to be ~9.

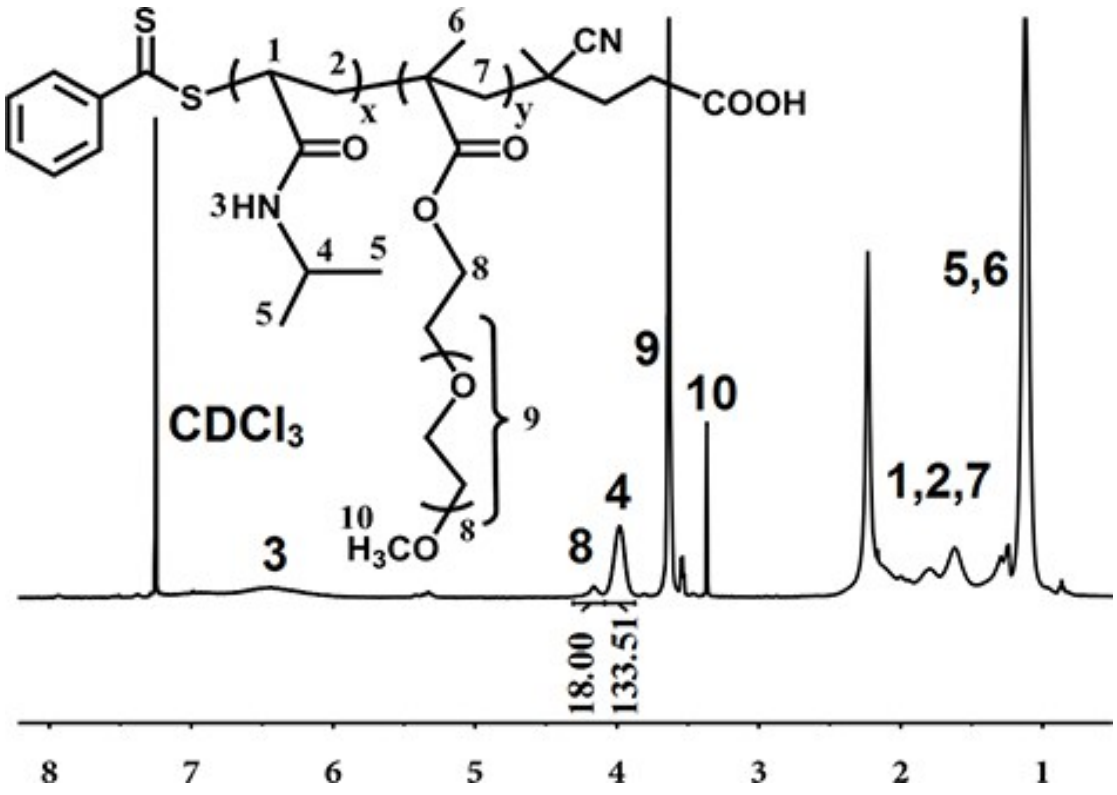

Figure S11. ^{1}H NMR spectrum of P(NIPAAm)$_{133}$-*b*-P(OEGMA480)$_{9}$ in $CDCl_3$.

The DP (n) of PNIPAAm was determined by comparing integral intensity of peak 4 and peak 8 in the ^{1}H NMR spectrum of the polymer (Figure S11) as follows,

$$\frac{DP(PNIPAAm)}{2 \times DP(P(OEGMA480))} = \frac{integral\ of\ signal\ 4}{integral\ of\ signal\ 8}$$

$$\Rightarrow \quad \mathrm{DP}(P\mathrm{NIPAAm}) = \frac{\text{integral of signal 4}}{\text{integral of signal 8}} \times 2 \times \mathrm{DP(P(OEGMA480))}$$

The DP of PNIPAAm was calculated to be 133.

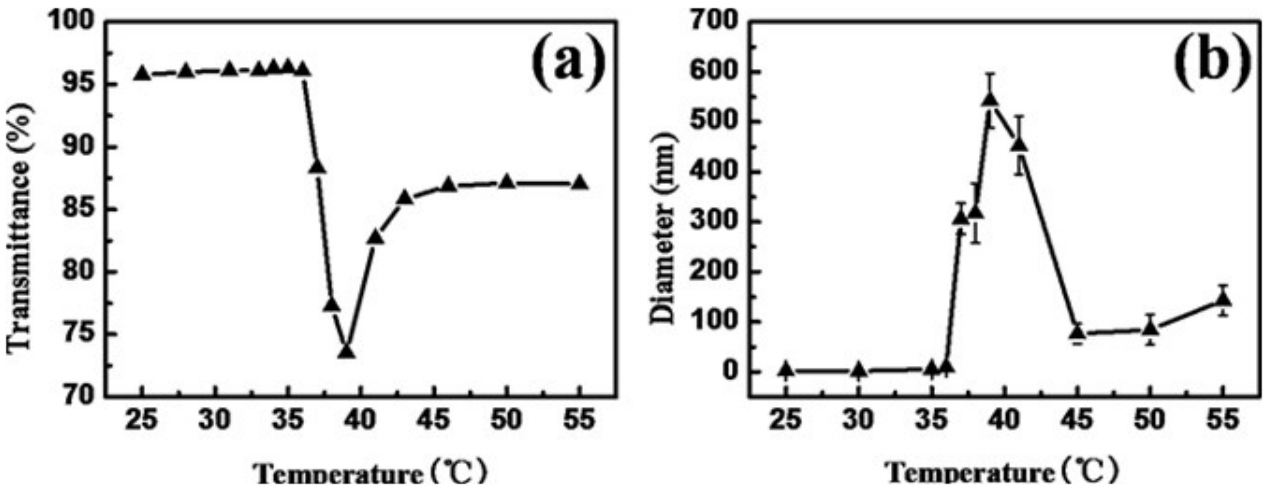

Figure S12. Temperature-dependent optical transmittance at 500 nm (a) and average size (b) of P(NIPAAm)$_{133}$-*b*-P(OEGMA480)$_9$ ([polymer] =1 mg/ml).

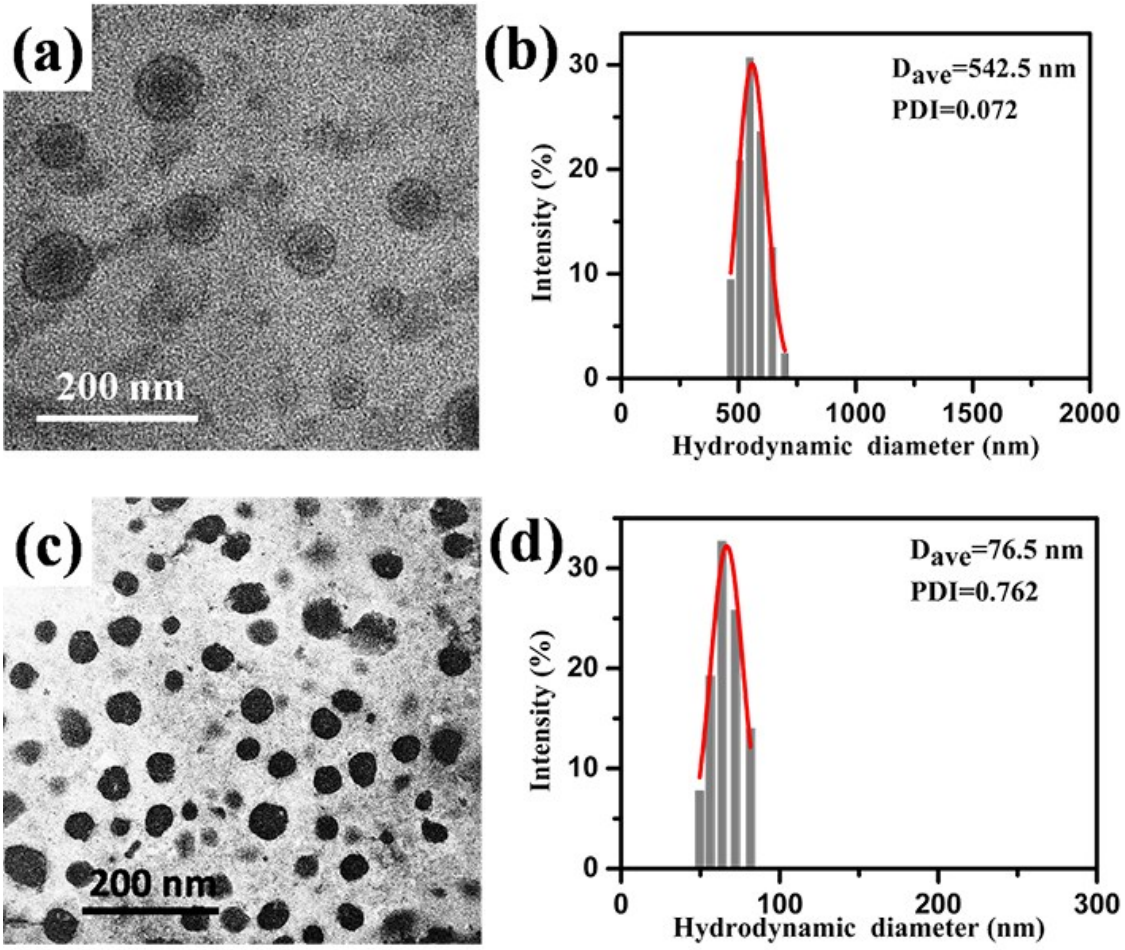

Figure S13. TEM images and size distributions of $P(NIPAAm)_{133}$-*b*-$P(OEGMA480)_9$ aqueous solution (1 mg/ml) at 39 °C (a & b) and 45 °C (c & d).

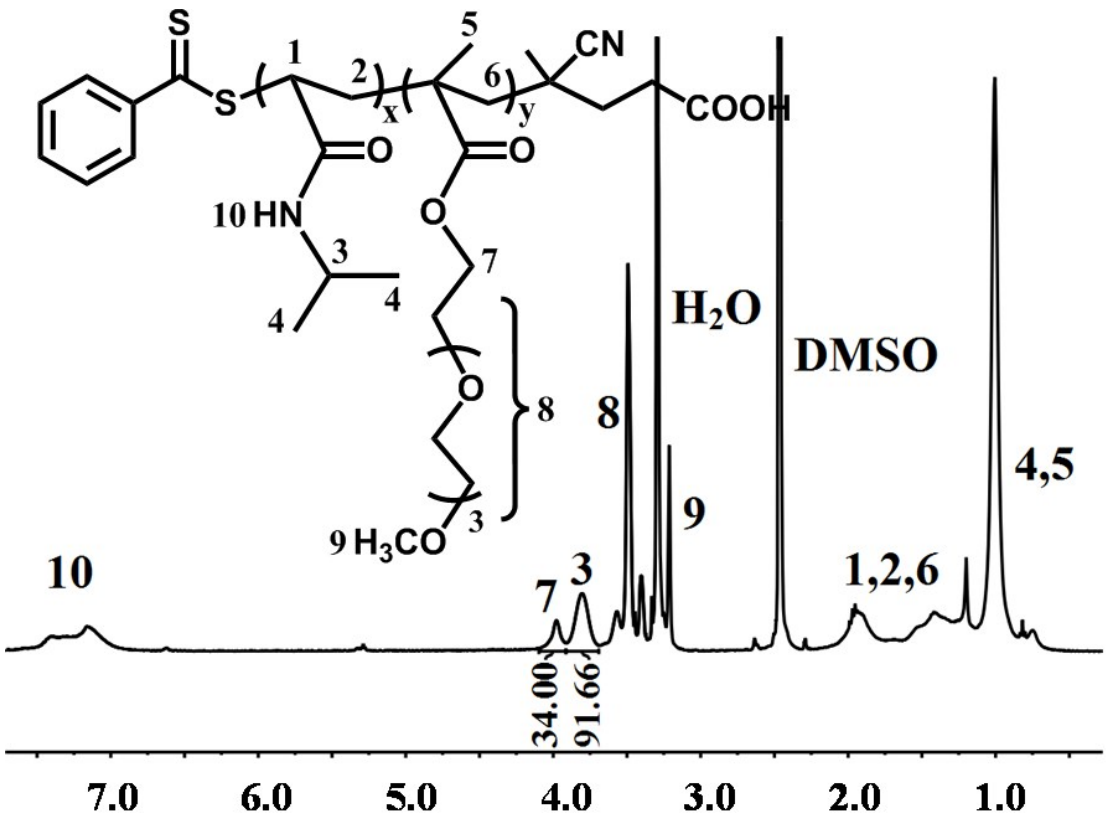

Figure S14. ^{1}H NMR spectrum of P(NIPAAm)$_{92}$-*b*-P(OEGMA300)$_{17}$ in d_6-DMSO.

The DP (n) of PNIPAAm was determined by comparing integral intensity of peak 3 and peak 7 in the ^{1}H NMR spectrum of the polymer (Figure S14) as follows,

$$\frac{DP(PNIPAAm)}{2 \times DP(P(OEGMA300))} = \frac{integral\ of\ signal\ 3}{integral\ of\ signal\ 7}$$

$$\Rightarrow \quad DP(PNIPAAm) = \frac{integral\ of\ signal\ 3}{integral\ of\ signal\ 7} \times 2 \times DP(P(OEGMA300))$$

The DP of PNIPAAm was calculated to be 92.

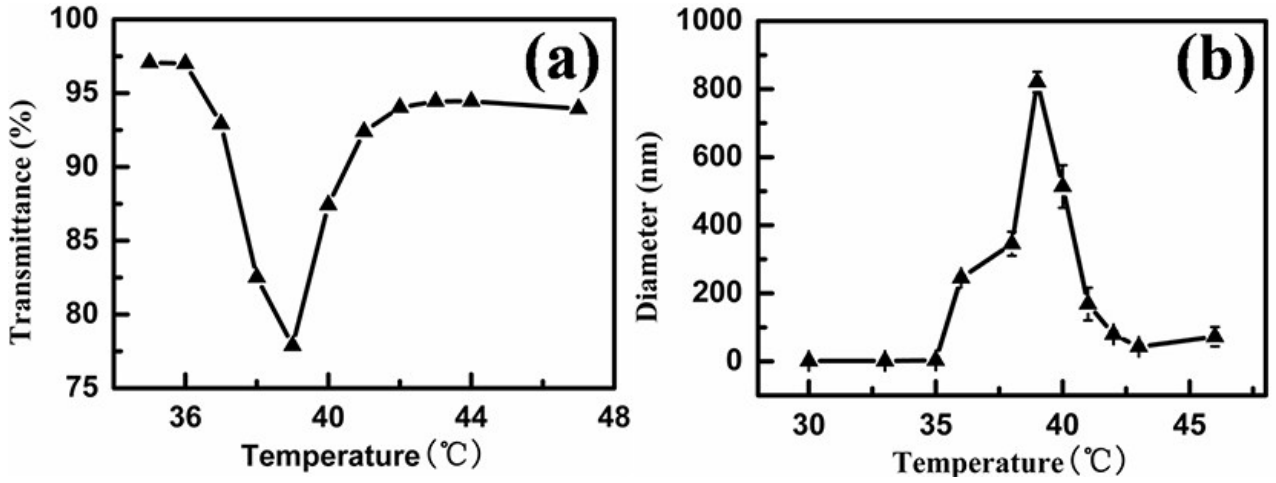

Figure S15. Temperature-dependent optical transmittance at 500 nm (a) and average size (b) of $P(NIPAAm)_{92}$-*b*-$P(OEGMA300)_{17}$ ([polymer] =1 mg/ml).

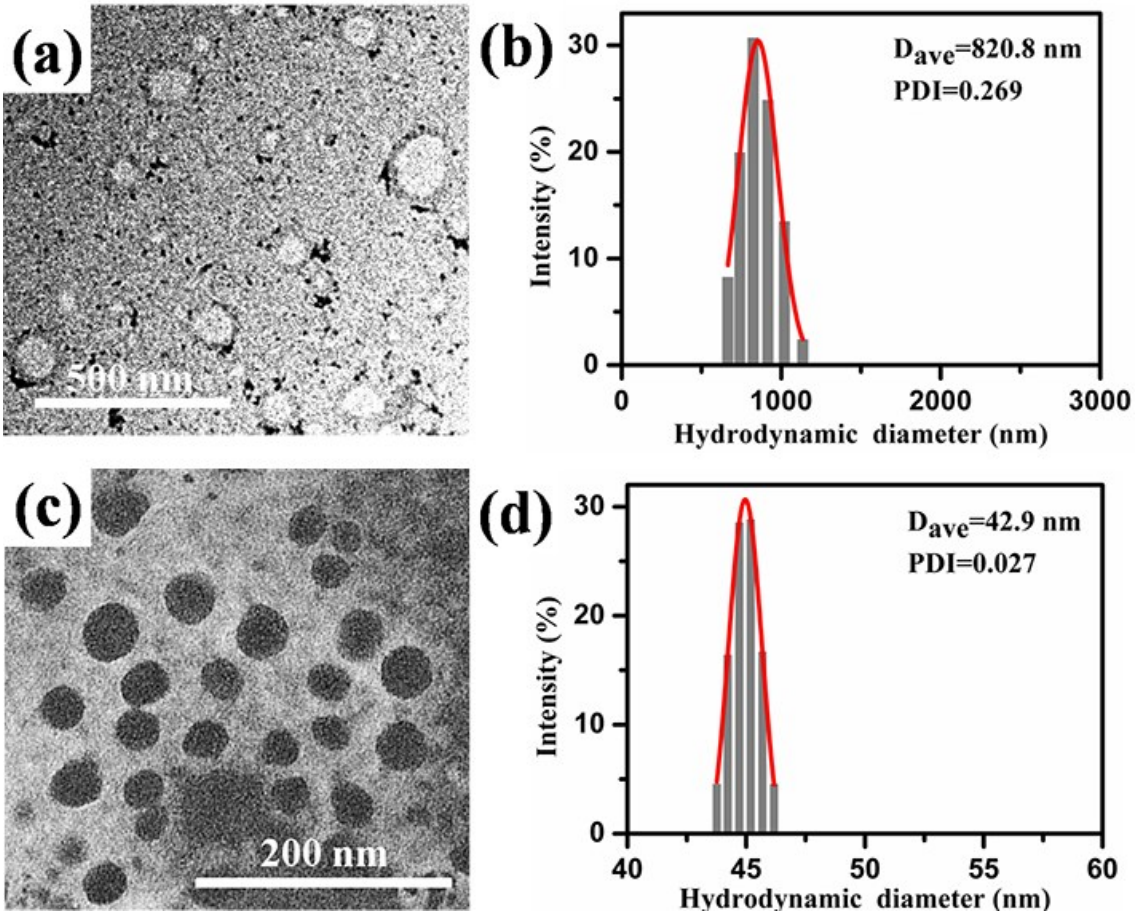

Figure S16. TEM images and size distributions of P(NIPAAm)$_{92}$-*b*-P(OEGMA300)$_{17}$ aqueous solution (1 mg/ml) at 39 ^{o}C ((a), (b)) and 43 ^{o}C ((c), (d)).

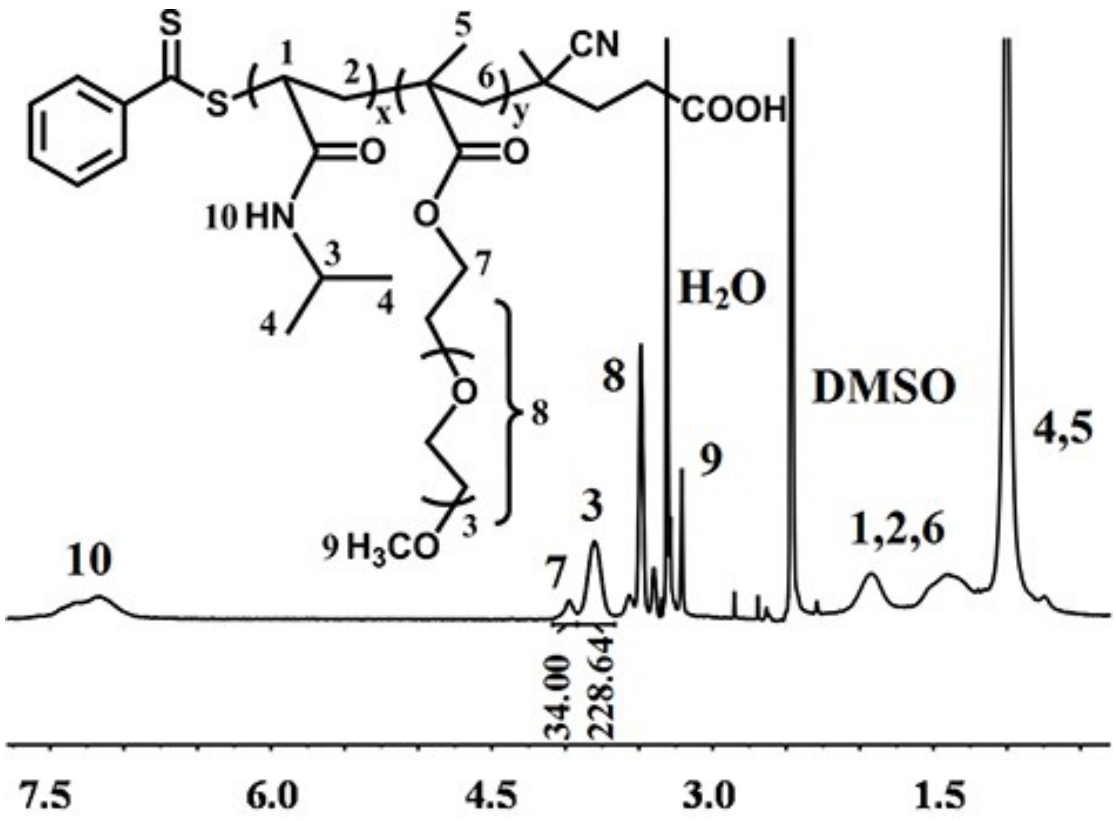

Figure S17. ^{1}H NMR spectrum of P(NIPAAm)$_{229}$-*b*-P(OEGMA300)$_{17}$ in d_6-DMSO.

The DP (n) of PNIPAAm was determined by comparing integral intensity of peak 3 and peak 7 in the ^{1}H NMR spectrum of the polymer (Figure S17) as follows,

$$\frac{DP(PNIPAAm)}{2 \times DP(P(OEGMA300))} = \frac{integral\ of\ signal\ 3}{integral\ of\ signal\ 7}$$

$$\Rightarrow \quad DP(PNIPAAm) = \frac{integral\ of\ signal\ 3}{integral\ of\ signal\ 7} \times 2 \times DP(P(OEGMA300))$$

The DP of PNIPAAm was calculated to be 229.

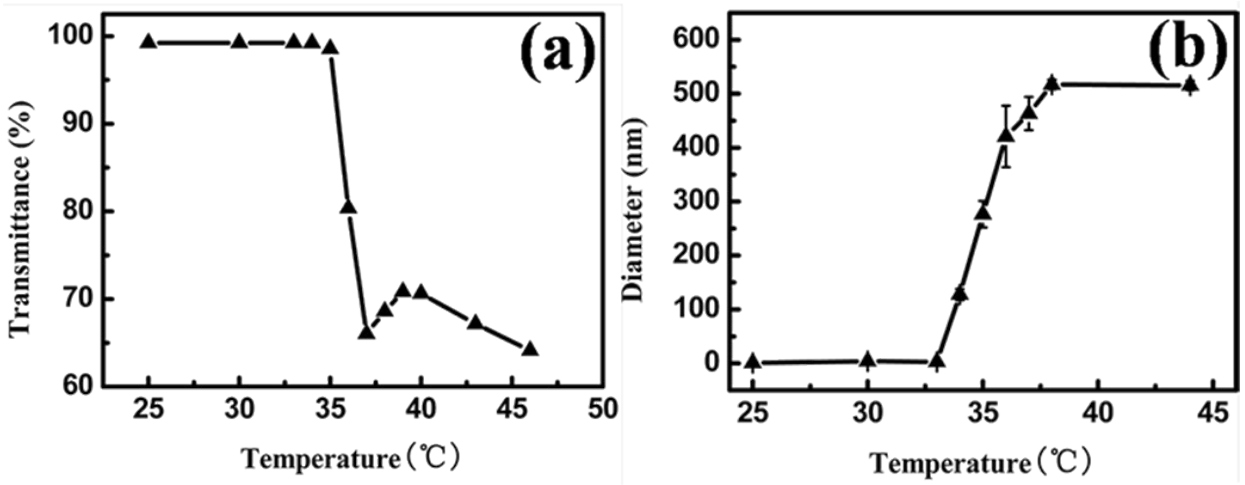

Figure S18. Temperature-dependent optical transmittance at 500 nm (a) and average size (b) of $P(NIPAAm)_{229}$-*b*-$P(OEGMA300)_{17}$ ([polymer] =1 mg/ml).

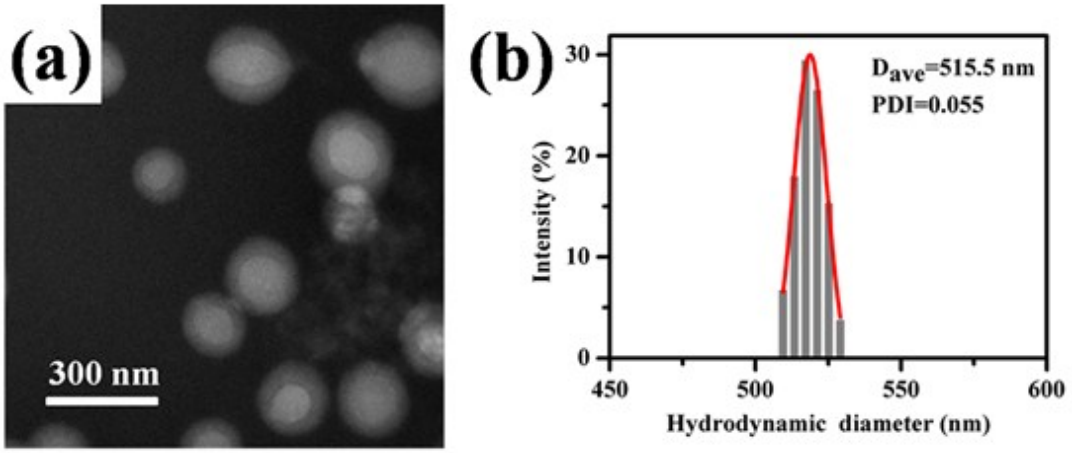

Figure S19. TEM image (a) and size distribution (b) of $P(NIPAAm)_{229}$-*b*-$P(OEGMA300)_{17}$ aqueous solution (1 mg/ml) at 44 °C.