Electronic Supplementary Information for

Cyclodextrin-Tunable Reversible Self-Assembly of Thermoresponsive Y-shaped Polymer

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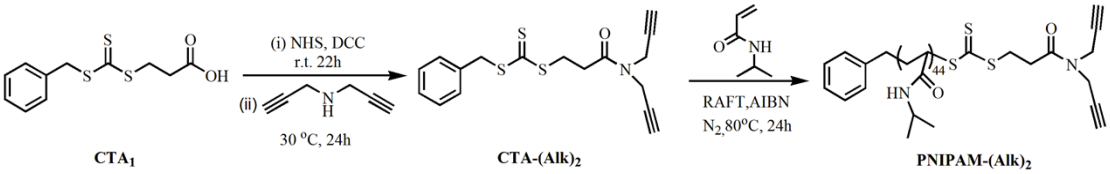
1. Synthesis and Characterization of PNIPAM-Alk$_2$



Scheme S1synthetic routesfor preparing PNIPAM-(Alk)$_2$

Synthesis of Dipropargyl end-functionalized RAFT agent (CTA-Alk$_2$). To obtain CTA-Alk$_2$, 3-(benzylthiocarbonothioylthio) propanoic acid (precursor RAFT agent CTA$_1$) was first synthesized according to the literature.[S1]CTA-Alk$_2$ RAFT agent was synthesized by the amidation reaction of Dipropargylamine and CTA$_1$. In an argon conditioned schlenk tube equipped with a magnetic stirrer, CTA$_1$ (2448 mg, 9mmol) was dissolved in chloroform (30ml). After cooling to 0°C, *N*-Hydroxysuccinimide (1035.81mg, 9mmol) and *N,N'*-Dicyclohexylcarbodiimide (1856.97 mg, 9 mmol) were successively added. After 1 h at 0°C and 22 h at room temperature, the reaction mixture was filtrated. After solvent removal, the product was twice dissolved in a minimum volume of ethyl acetate and filtrated. After drying under vacuum, a very viscous orange-red oil (CTA-NHS) was obtained. Then, CTA-NHS (3124.8mg, 7.62mmol) was dissolved in chloroform (40 ml). A solution of Dipropargyl (706.34 mg, 7.62 mmol) in 10 mL of chloroform was added in one portion to the solution of CTA$_2$. The reaction mixture was stirred at 30°C for 12 h. Then, it was washed three times with 100 mL of distilled water (to remove NHS) and dried over anhydrous magnesium sulfate. After solvent removal, two successive column chromatography (Silica gel 60, Merk)were performed (dichloromethane/ethyl acetate: 50/50 v/v then acetone; pure dichloromethane) to afford an orange-red oil (yield 84.3 %).FT-IR (KBr): 3217 cm^{-1} (ν, ≡C−H); 2106 cm^{-1} (ν, C≡C);1646 cm^{-1} (ν,−CON).^{1}H NMR ($CDCl_3$, δ, ppm): 7.14-7.32 (5H, Ph), 4.62 (2H, C***H$_2$***-Ph), 3.59 (2H, S-C***H$_2$***-CH$_2$), 2.75 (2H, S-CH$_2$-C***H$_2$***), 4.17 and 4.34 (4H, (CH≡C−C***H$_2$***)$_2$−N−)，2.25 (2H, (C***H***≡C−CH$_2$)$_2$−N−); ^{13}C NMR ($CDCl_3$, δ, ppm): 177.9 (−***C***ON−(CH$_2$)$_2$); 135.2-128.3 (***Ph***—); 76.75((***C***H≡C−CH$_2$)$_2$−N−); 72.60 ((CH≡***C***−CH$_2$)$_2$−N−); 38.75, 39.26 ((CH≡C−***C***H$_2$)$_2$−N−); 42.0 (—Ph—***C***H$_2$—); 33.4, 31.3 (S—***C***H$_2$—***C***H$_2$—).Electrospray ionization mass spectrometry ($CDCl_3$, m/z): calcdfor $C_{17}H_{17}ONS_3$:

370.0368; found for $[M-H]^+$: 370.0372.

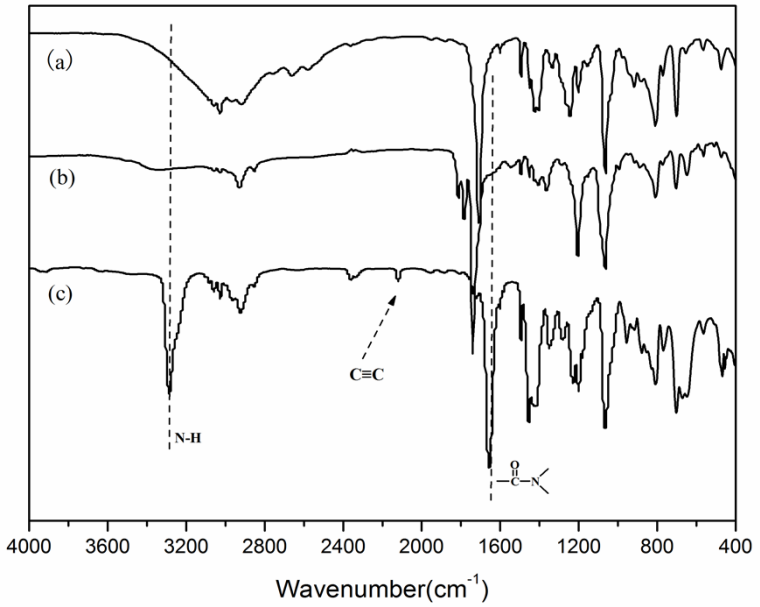


Figure S1 FTIR spectra of CTA-COOH(a), CTA-NHS(b),CTA-Alk_2(c).

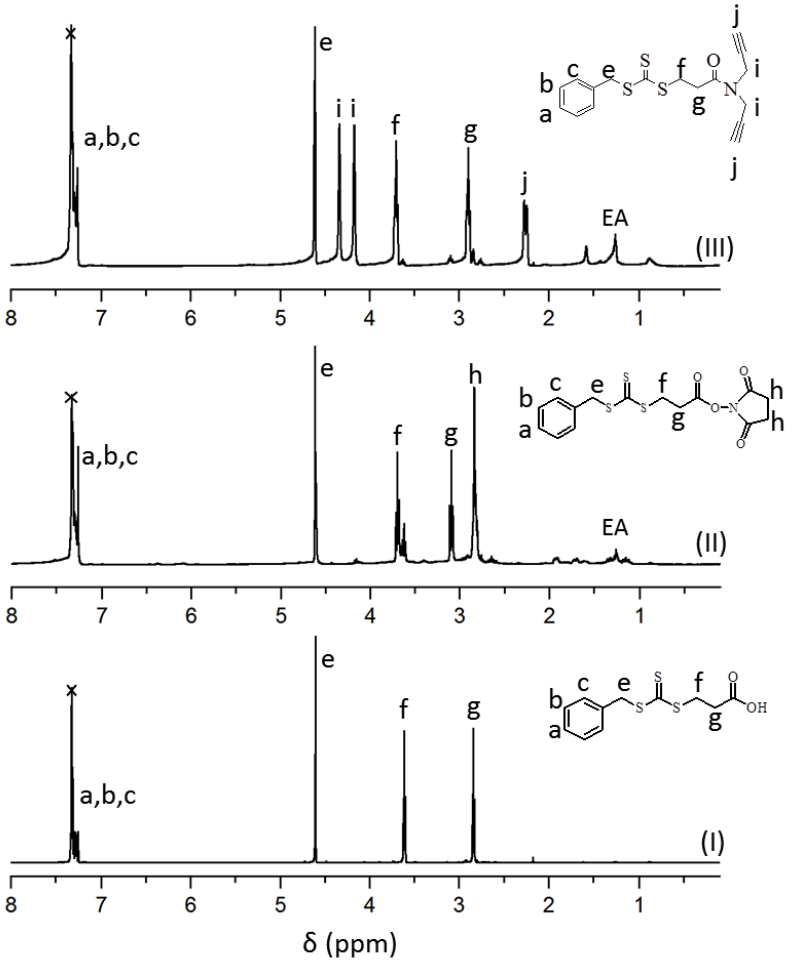


Figure S2 ^{1}H NMR spectra of CTA-COOH (I), CTA-NHS (II),CTA-Alk_2 (III) in $CDCl_3$.

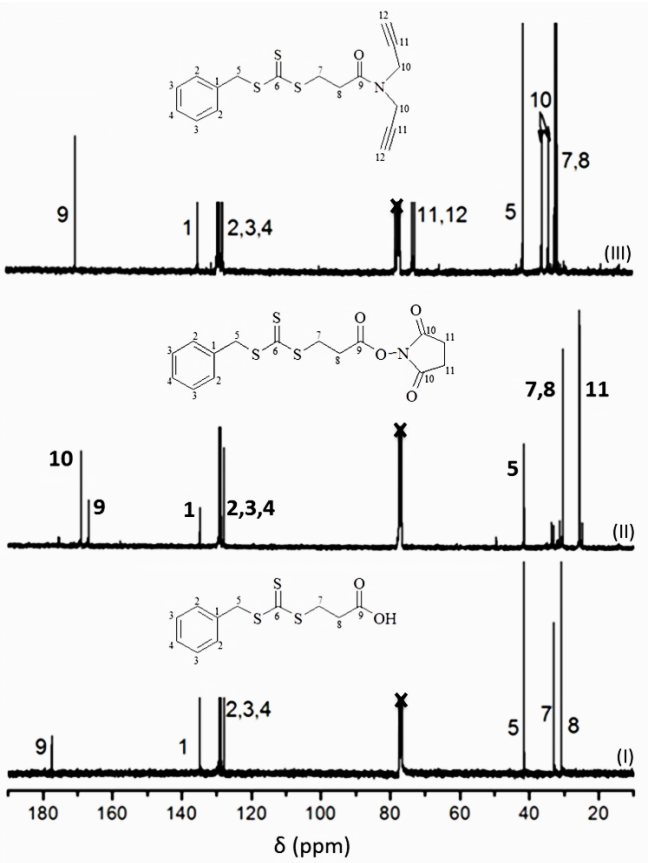


Figure S3^{13}C NMR spectra of CTA-COOH (a), CTA-NHS (b),CTA-Alk$_2$ (c) in $CDCl_3$.

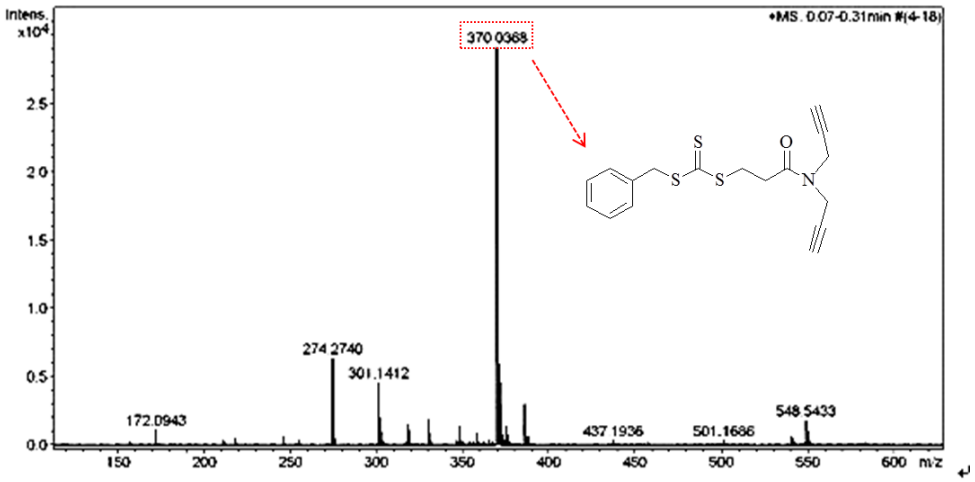
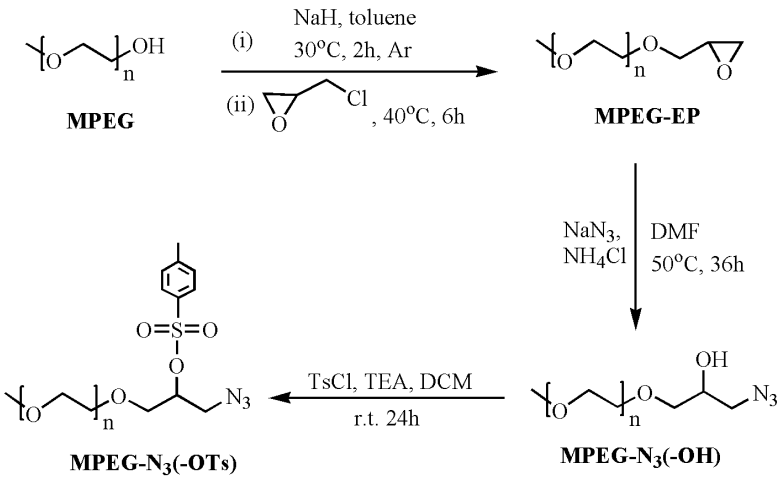


Figure S4 Electrospray ionization mass spectrum of CTA-Alk$_2$.
The $(M-H)^+$ peak was found at m/z = 370.0368, which is consistent with the calculated value m/z =370.0372.

Synthesis of Dipropargyl Terminated Poly (N-isopropylacrylamide) (PNIPAM-Alk$_2$). The dipropargylterminated poly (*N*-isopropylacrylamide) (PNIPAM-Alk$_2$) was synthesized by RAFT polymerization using the obtained CTA-Alk$_2$. The typical procedure was as follows: A Schlenk tube was added with NIPAM (509.22mg, 4.5mmol), AIBN (0.82mg, 0.005mmol), CTA(34.7mg, 0.1mmol) and 1, 4-dioxane (2

ml). The mixture was dissolved absolutely and subjected to three freeze-vacuum-thaw cycles. Then, the tube was immersed into an oil bath at 80 °C to perform polymerization. After 24 h, the mixture was precipitated into 300 ml diethyl ether. By repeating the precipitation and dried in a vacuum oven overnight, white product was obtained (yield 57.75 %).^{1}H NMR (DMSO-d_6, δ, ppm): 7.50-7.04 (—N***H***—CH$(CH_3)_2$—, ***Ph***—); 4.49 (2H, Ph-C$\boldsymbol{H_2}$—); 3.86 (—NH—C***H***$(CH_3)_2$); 1.97 (—C***H***(CO)—CH_2—); 1.45 (—CH(CO)—C$\boldsymbol{H_2}$—); 1.25-0.81 (—NH—CH (C$\boldsymbol{H_3}$)$_2$). ^{13}CNMR(DMSO-d_6, δ, ppm): 175.24 (—***C***O—NH—); 127.84(***Ph***—); 43.09 (—NH—***C***H$(CH_3)_2$);37.06 (—CH(CO)—***C***H_2—);23.69 (—NH—CH(***C***$H_3)_2$).FTIR (KBr): 3411 cm^{-1} (ν, ≡C—H); 3301 cm^{-1} (ν, N—H); 2124 cm^{-1} (ν, C≡C).

2. Synthesis and Characterization of MPEG–N_3(–OTs)



Scheme S2synthetic routesfor preparingMPEG-N_3(-OTs)

Synthesis of Epoxide Terminated MPEG, MPEG-EP. *M*PEG-EP was prepared according to literature[S2] procedures with a few modifications. MPEG-OH (5.0 g, 5 mmol) was dried under vacuum at 80 °C for 12 h and then dissolved with 20 mL fresh distilled toluene. NaH (600 mg, 15 mmol) was introduced under the protection of argon flow at room temperature. After H_2 evolution for about 10 min, the mixture was sealed under argon and stirred at 30 °C for 2 h. Epichlorohydrin (4162.5 mg, 45

mmol) was then added. The mixture was stirred at 40 °C for 6 h and then precipitated into an excess of cold diethyl ether. The collected precipitate was dissolved with CH_2Cl_2 (100 mL) and washed with distilled water (50 mL) three times. The organic phase was dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated by rotary evaporation and precipitated into cold diethyl ether. The product was wash with diethyl ether three times and dried under vacuum at 25 °C for 2 days. Yield: 76.3%. FT-IR (KBr): 2870 cm^{-1} (*v*, C─H); 1107 cm^{-1} (*v*, C─O─C). ^1H NMR ($CDCl_3$, *δ*, ppm): 3.65 (100H, ─OCH_2CH_2O─); 3.38 (3H, CH_3O─); 3.17 (1H, methine proton of epoxide ring); 2.80 and 2.62 (2H, methylene proton of epoxide ring).

*Synthesis of Azido and Hydroxyl Terminated MPEG, MPEG-N_3(-OH).*The synthesis of MPEG-N_3(-OH) was accomplished by the ring-opening of MPEG-EP with NaN_3.[S3] A typical procedure was as follows. MPEG-EP (3.96 g, 3.75 mmol), NaN_3 (731 mg, 11.25 mmol) and NH_4Cl (602 mg, 11.25 mmol) were first mixed with 15 mL DMF. The mixture was stirred at 50 °C for 36 h and then dialyzed (molecular weight cut off: 100) against distilled water for 5 days. MPEG-N_3(-OH) was obtained by freeze drying as white solid. Yield: 85.0%. FT-IR (KBr): 2870cm^{-1} (ν, C-H); 2098cm^{-1} (ν, N_3); 1111cm^{-1} (ν, C─O─C). ^1H NMR ($CDCl_3$,*δ*, ppm): 3.65 (100H, ─OCH_2CH_2O─); 3.38 (3H, CH_3O─); 2.86(1H, ─O*H*).

*Synthesis of Azido and tolylsulfonyl Terminated MPEG, MPEG-N_3(-OTs).*MPEG-N_3(-OH) (1758 mg, 1.6 mmol) anddriedtriethylamine(1616mg, 16mmol) were added to a 50mL round-bottomed flask and dissolved with 20mL fresh distilled DCM. Under the conditions of ice-water bath and magnetic stirring, Tosyl chloride (13954.6 mg, 16 mmol, dissolved in 10 mL DCM) was added dropwise to the flask. The mixture was then stirred at room temperature for 24 h and filtered. The filtrate was precipitated into an excess of cold diethyl ether. The precipitate was collected and dissolved with dried DCM. The dissolution-filtration-precipitation cycle was repeated for three times. After drying in a vacuum oven overnight at 30 °C, MPEG-N_3(-OTs) was

obtained. Yield: 65.3%.FT-IR (KBr): 2870 cm^{-1} (ν, C-H); 2102 cm^{-1} (ν, N_3); 1365 cm^{-1} (ν, S=O); 1107 cm^{-1} (ν, C—O—C). ^1H NMR ($CDCl_3$,δ, ppm): 7.82-7.37 (4H, Ph(***H***)—); 4.61 (1H, —C***H***CH_2N_3); 3.65 (100H, —OC***H₂***C***H₂***O—); 3.39 (3H, C***H₃***O—); 2.49 (3H, Ph-C***H₃***).1.68(4H, —***CH₂***CH***CH₂***N_3)

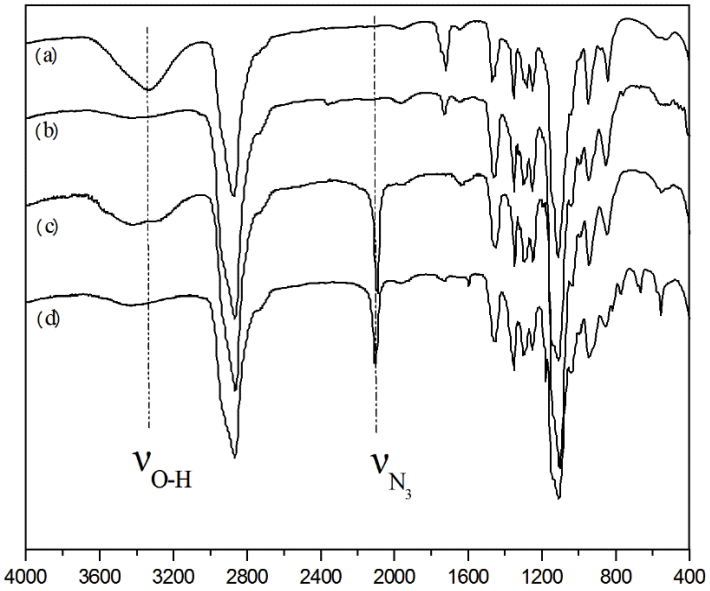


Figure S5 FT-IR spectra of MPEG-OH (a), MPEG-EPC (b), MPEG-N_3(-OH) (c), MPEG-N_3(-OTs) (d).

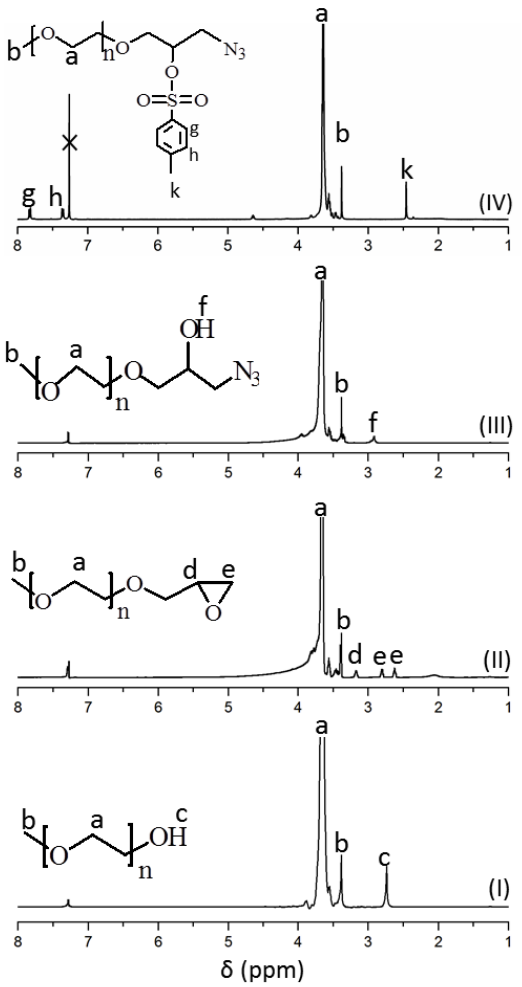


Figure S6 ^{1}H NMR spectra of MPEG-OH (I), MPEG-EPC (II), MPEG-N_3(-OH) (III), MPEG-N_3(-OTs) (IV) in $CDCl_3$.

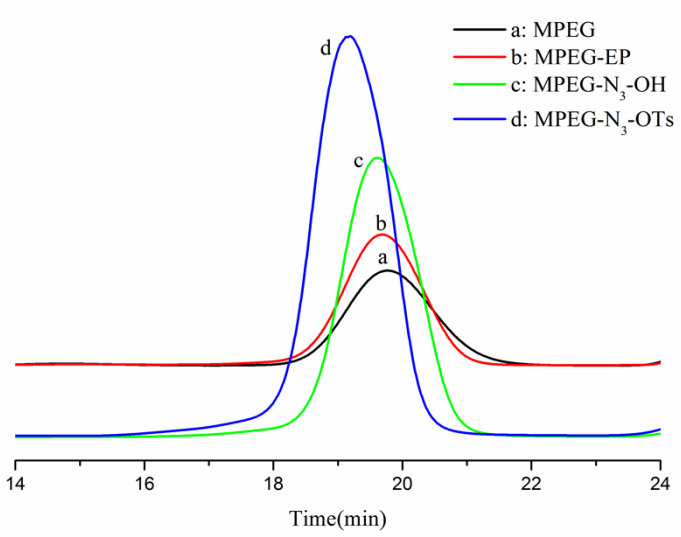


Figure S7 SEC/MALLS curves of MPEG-OH (I), MPEG-EPC (II), MPEG-N_3(-OH) (III), MPEG-N_3(-OTs) (IV) (in THF).

Table S1. Molecular weight and molecular weight distributions of MPEG-OH, MPEG-EPC, MPEG-N_3(-OH) and MPEG-N_3(-OTs)

Sample	M_n[a] (NMR)	M_w[b]	M_n[b]	M_w/M_n[b]
MPEG	1125	1350	1150	1.17
MPEG-EP	1221	1480	1330	1.12
MPEG-N_3-OH	1235	1540	1460	1.05
MPEG-N_3-OTs	1371	2030	1910	1.06

[a]Molecular weight determined by NMR;[b]Molecular weight and molecular weight distributions determined by SEC/MALLS.

3. Synthesis of Y-Shaped Polymer

Synthesis of Y-shaped precursor: PNIPAM-(2OTs-2MPEG). The Y-shaped precursor PNIPAM-(2OTs-2MPEG) was synthesized via click reaction. First, a mixture of PNIPAM-Alk_2 (300 mg, 0.0571 mmol), MPEG-N3(-OTs) (572.37 mg, 0.4568 mmol), PMDETA (80 mg, 0.46 mmol), and DMF (4 mL) was bubbled with $N_2$for 15 min. CuBr (66 mg, 0.46 mmol) was then introduced. Bubbled with N_2 for another 30 min, the reaction mixture was stirred at 80 °C for 48 h. It was terminated by exposing to air and diluting with THF. After passing through a column of neutral alumina for the removal of copper catalysts and evaporating most of the solvent. The residues were dialyzed (molecular weight cut off: 2000) against distilled water for 7 days. PNIPAM-(2OTs-2MPEG) was obtained by freeze drying (yield 36.24 %).^{1}H NMR (DMSO-d_6, δ, ppm): 7.50-7.04 (−N***H***−CH$(CH_3)_2$−, ***Ph***−); 4.49 (2H, Ph-C***H_2***−); 3.86 (−NH−C***H***$(CH_3)_2$); 3.6-3.4(−C***H_2***— of MPEG); 3.28(−C***H_3*** of MPEG); 1.97 (−C***H***(CO)−CH_2−); 1.45 (−CH(CO)−C***H_2***−); 1.25-0.81 (−NH−CH (C***H_3***)$_2$). ^{13}CNMR(DMSO-d_6, δ, ppm): 175.24 (−***C***O−NH−); 127.84 (***Ph***—); 69.28 (−***C***H_2— of MPEG);43.09 (−NH−***C***H$(CH_3)_2$);37.06 (−CH(CO)−***C***H_2−);23.69 (−NH−CH(***C***$H_3)_2$).FTIR (KBr): 3301 cm^{-1} (ν, N−H); 1365 cm^{-1} (ν, O=S).

Synthesis of Y-Shaped Polymer with β-CD Bonded at Branch Points: PNIPAM-(2CD-2MPEG). The branch points of the Y-shaped polymer were bonded with*β*-CD via the conjugation of *β*-CD carrying amino groups (EDA-*β*-CD) with the sulfonyl groups. Procedure was as follows: A Schlenk tube was added with PNIPAM-(2OTs-2MPEG) (226 mg, 0.03 mmol), EDA-*β*-CD (705 mg, 0.6 mmol) and dry DMF (5ml). Subsequently, the solution was subjected to three freeze-vacuum-thaw cycles and then conducted at 100°C for 48 h. After cooling to room temperature, the residues were dialyzed (molecular weight cut off: 2000) against distilled water for 5 days. PNIPAM-

(2CD-2MPEG) was obtained by freeze drying(yield 70.9 %).^{1}H NMR (DMSO-d_6, δ, ppm): 5.88 (2,3—O***H*** of β-CD), 4.97 (1—***H*** of β-CD), 4.69 (6—O***H*** of β-CD);7.50-7.04 (—N***H***—CH$(CH_3)_2$—,***Ph***—); 4.49 (2H, Ph-C$\boldsymbol{H_2}$—); 3.86 (—NH—C***H***$(CH_3)_2$); 3.6-3.4(—C$\boldsymbol{H_2}$— of MPEG); 3.28(—C$\boldsymbol{H_3}$ of MPEG); 1.97 (—C***H***(CO)—CH_2—); 1.45 (—CH(CO)—C$\boldsymbol{H_2}$—); 1.25-0.81 (—NH—CH (C$\boldsymbol{H_3}$)$_2$). ^{13}CNMR(DMSO-d_6, δ, ppm): 175.24 (—***C***O—NH—); 127.84 (***Ph***—); 72.16 (***2,3,5—C*** of β-CD) 69.28 (—***C***H_2— of MPEG);43.09 (—NH—***C***H$(CH_3)_2$);37.06 (—CH(CO)—***C***H_2—);23.69 (—NH—CH(***C***$H_3)_2$).FTIR (KBr): 3301 cm^{-1} (ν, N—H). 1113 cm^{-1} (ν, C—O—C)

Table S2. Molecular weight and molecular weight distributions ofPNIPAM-Alk$_2$, PNIPAM-(2OTs-2MPEG) and PNIPAM-(2CD-2MPEG)

Code	Sample	M_n[b]$_{NMR}$	M_w[a]	M_n[a]	M_w/M_n[a]	dn/dc(mL g^{-1})
1	PNIPAM-Alk$_2$	5236	9000	8000	1.13	0.067
2	PNIPAM-(2OTs-2MPEG)	7501	11400	10000	1.13	0.071
3	PNIPAM-(2CD-2MPEG)	9832	14300	12100	1.18	0.072

[a] Molecular weight and molecular weight distributions determined by SEC/MALLS, [b]Molecular weight determined by NMR

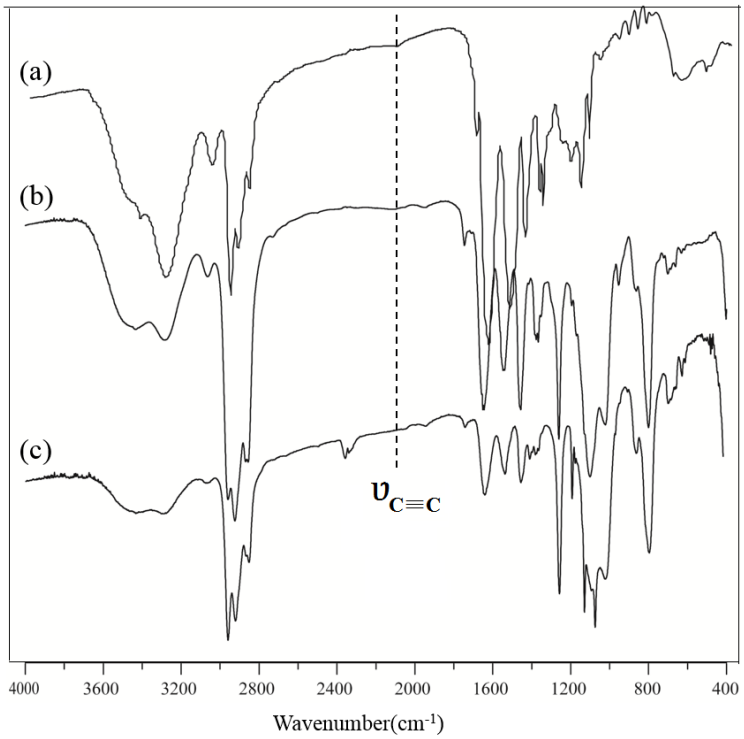


Figure S8 FTIR spectra of PNIPAM-Alk$_2$ (a), PNIPAM-(2OTs-2MPEG) (b) and PNIPAM-(2CD-2MPEG) (c).

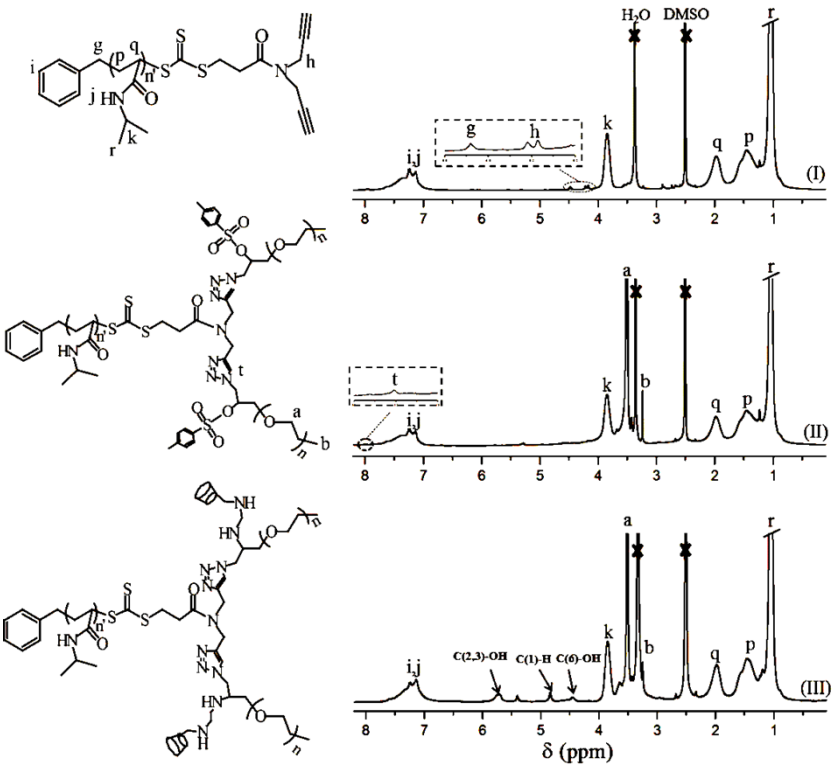


Figure S9 ^{1}H NMR spectra of PNIPAM-Alk$_2$ (I), PNIPAM-(2OTs-2MPEG) (II) and PNIPAM-(2CD-2MPEG) (III) in DMSO-d$_6$.

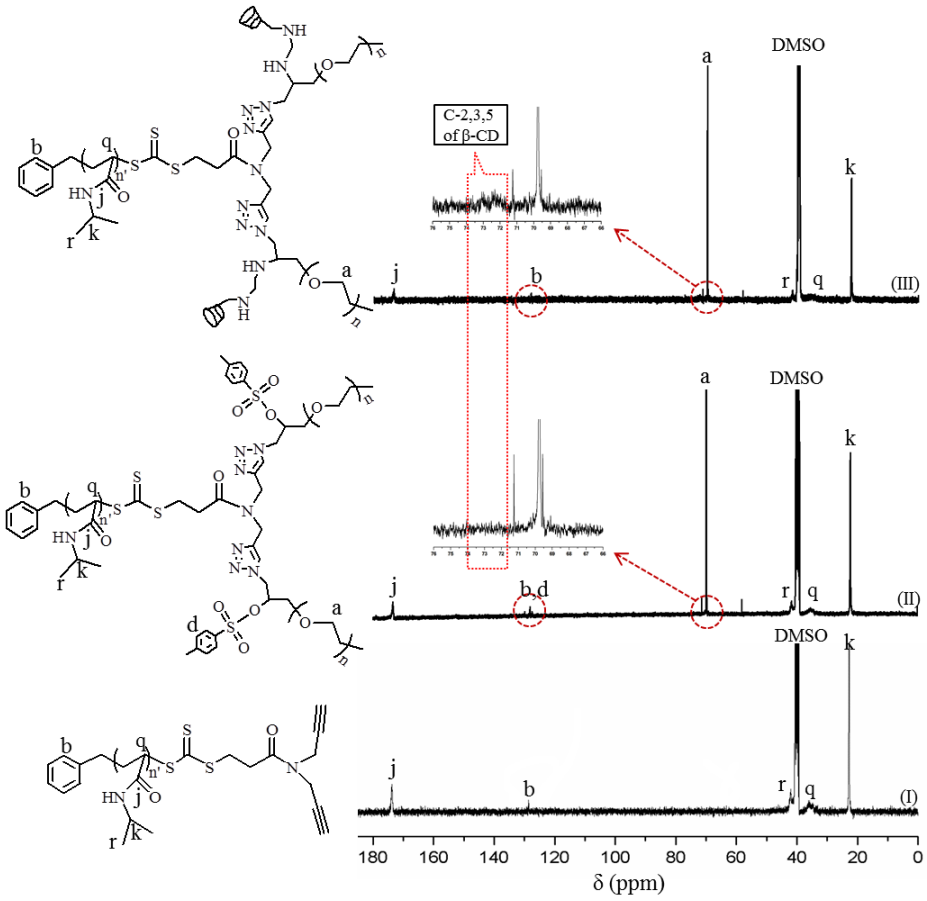


Figure S10 ^{13}C NMR spectra of PNIPAM-Alk$_2$ (I), PNIPAM-(2OTs-2MPEG) (II) and PNIPAM-(2CD-2MPEG) (III) in DMSO-d$_6$.

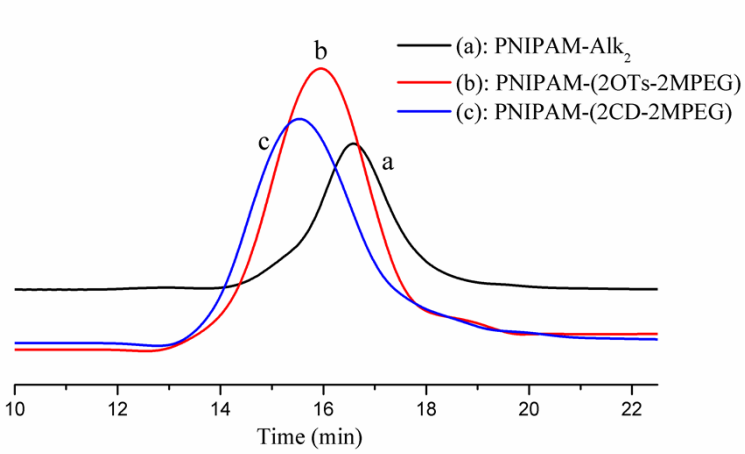


Figure S11 SEC/MALLS curves of PNIPAM-Alk_2(a), PNIPAM-(2OTs-2MPEG) (b) and PNIPAM-(2CD-2MPEG) (c) (in DMF).

4. Self-assembly of PNIPAM-(2OTs-2MPEG)

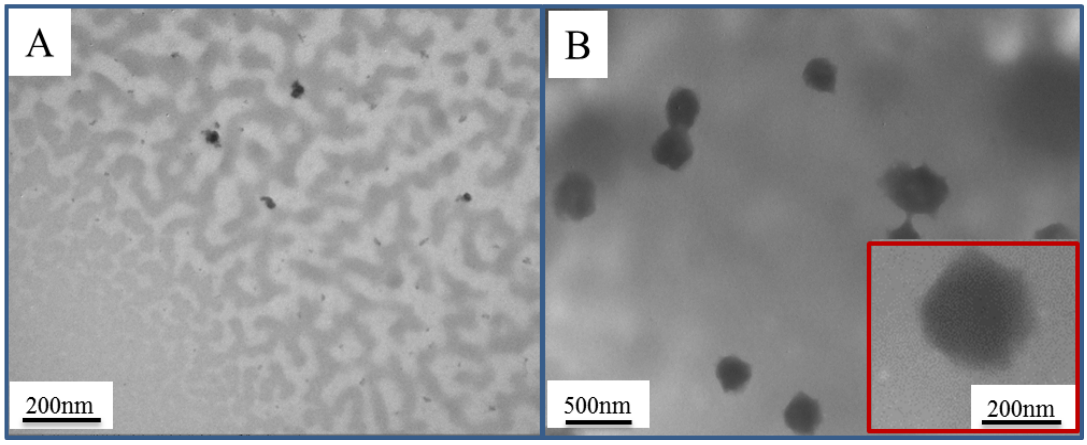


Figure S12 Typical TEM images of PNIPAM-(2OTs-2MPEG) aqueous solutions (1.0 mg/ml)at 20 °C (A)and 60 °C(B).

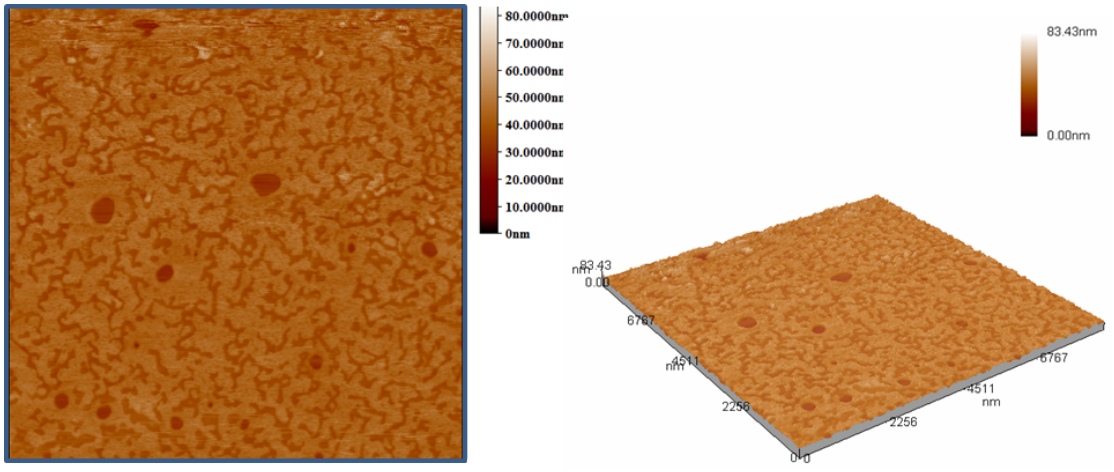


Figure S13 Typical AFM images of PNIPAM-(2OTs-2MPEG) at 1.0 mg/ml and 20 °C.

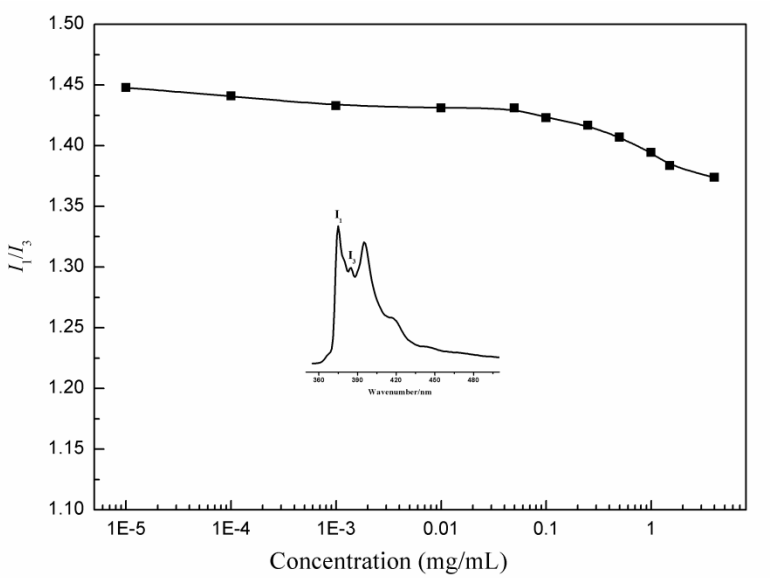


Figure S14 Relationship between the fluorescence intensity ratio (I_1/I_3) and PNIPAM-(2OTs-2MPEG) concentration in aqueous solution (Inset: fluorescence emission spectrum of pyrene).

5. LCST Determination of Polymer Aqueous Solutions

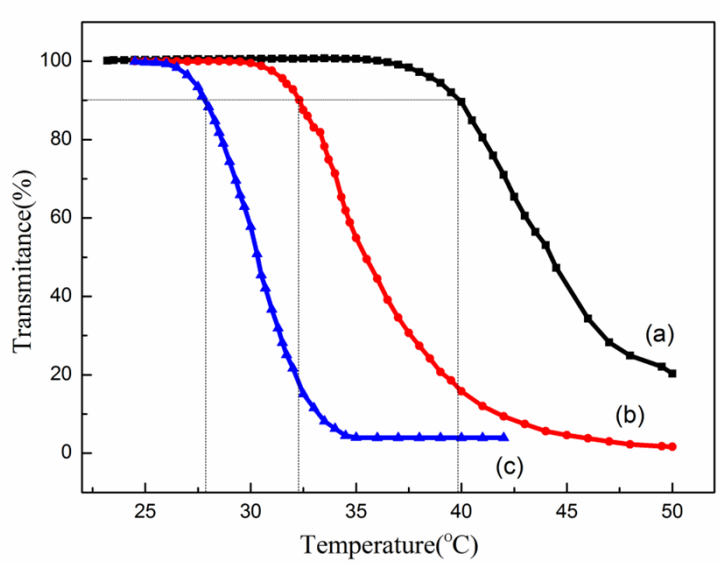


Figure S15 Variation in the transmittance at 550 nm of the homopolymer aqueous solution (PNIPAM-(2OTs-2MPEG) (a); PNIPAM-(2CD-2MPEG) (b); PNIPAM-Alk_2 (c)) with a concentration of 1 mg/mL as a function of temperature.

6. References

S1. J. Skey and R. K. O Reilly, *Chem Commun*, 2008, 4183.

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S3. N. V. Tsarevsky, S. A. Bencherif and K. Matyjaszewski, *Macromolecules*, 2007, **40**, 4439-4445.