Supporting Information for

Synthesis and Aggregation Behavior of the Nonlinear Multi-Responsive Multi-Hydrophilic Block Copolymers

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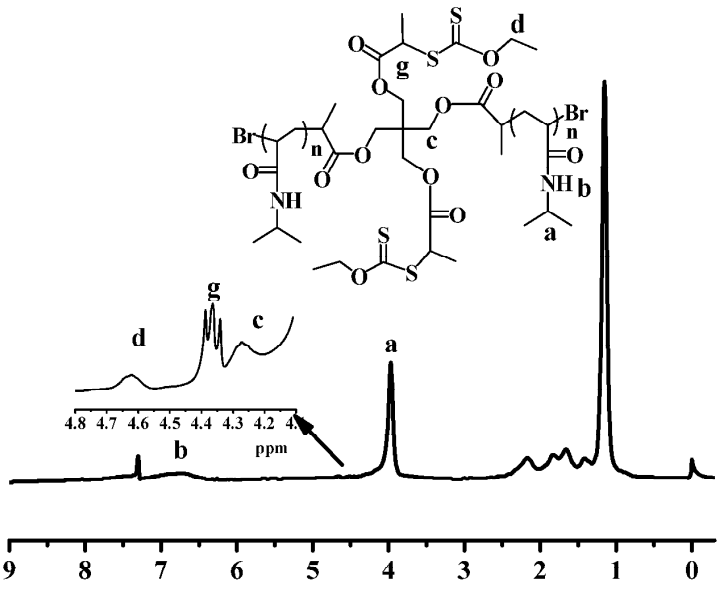

Figure S1. The ^{1}H NMR spectrum of two-armed $(PNIPAAM)_2$ in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard.

As shown in Figure S1, the characteristic signals at 4.58-4.70 ppm were corresponded to methylene protons of $CH_3C\boldsymbol{H_2}OCS_2$- of initiator ($Xanthate_2$-$Br_2$). The peak at δ = 4.00-7.20 ppm was ascribed to the one protons of -N***H***$CH(CH_3)_2$ in NIPAAM units, and the peak at δ = 3.80-4.20 ppm should be assigned to the methyne proton of -C***H***$(CH_3)_2$ of NIPAAM unit. The actual degree of polymerization (DP = 94) and molecular weight of $(PNIPAAM)_2$ was calculated from the ratio of the signal integration of **d** and **a** (Figure S1).

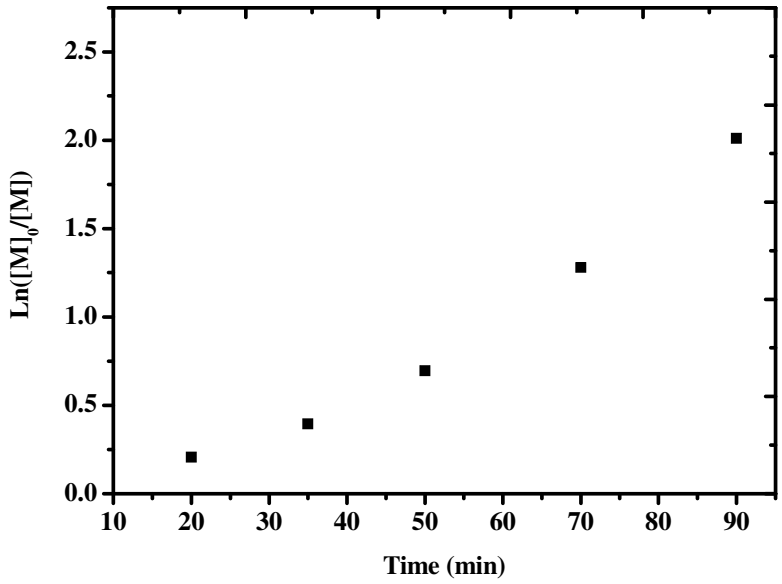

Figure S2. Relationship between $Ln([M]_0/[M])$ and reaction time for the SET-LRP of NIPAAM in the presence of $Xanthate_2$-Br_2. Polymerization conditions: $[NIPAAM]_0$: $[Xanthate_2\text{-}Br_2]_0$: $[Cu(0)]_0$: $[PMDETA]_0$ = 200 : 1 : 3 : 3, $[NIPAAM]_0/[acetone]_0$ = 1/1 (v/v), t = 25 °C.

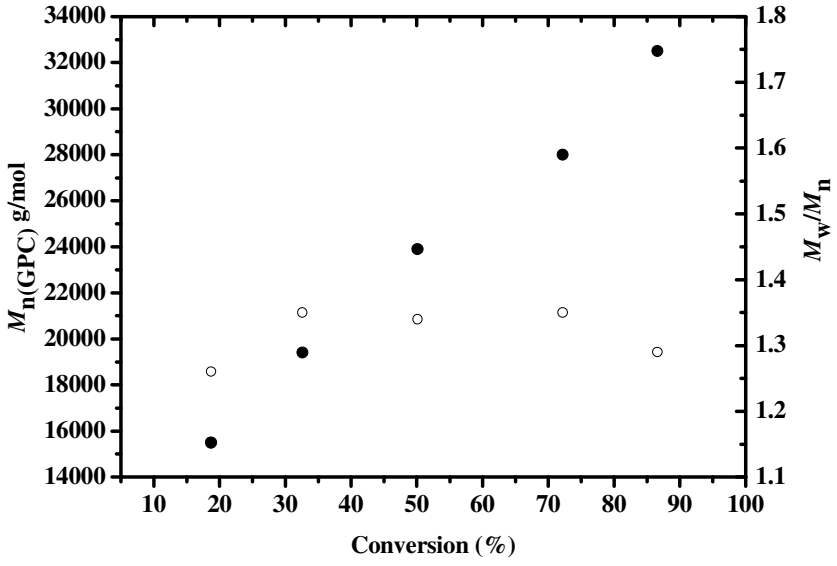

Figure S3. The dependence of the molecular weights and molecular weight distributions on the monomer conversions for the SET-LRP of NIPAAM. Polymerization conditions are the same as in Figure S2.

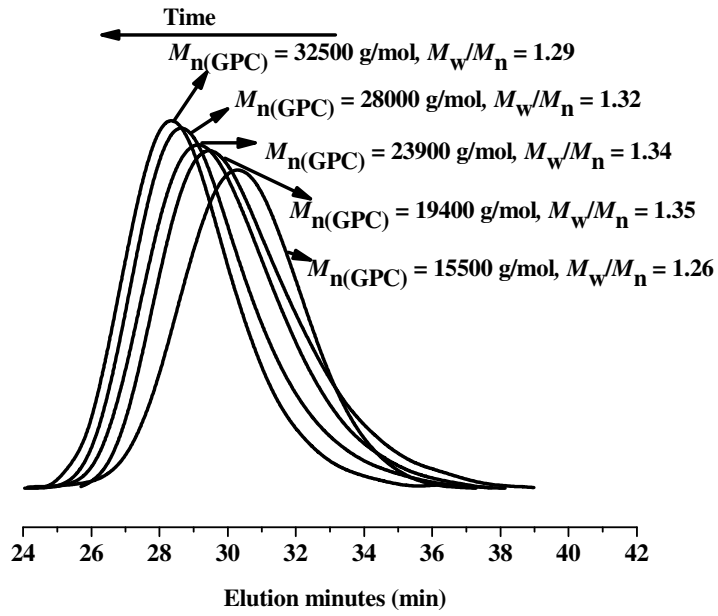

Figure S4. GPC traces of two-armed $(PNIPAAM)_2$ obtained from the SET-LRP of NIPAAM using $Xanthate_2$-Br_2 as initiator in acetone.

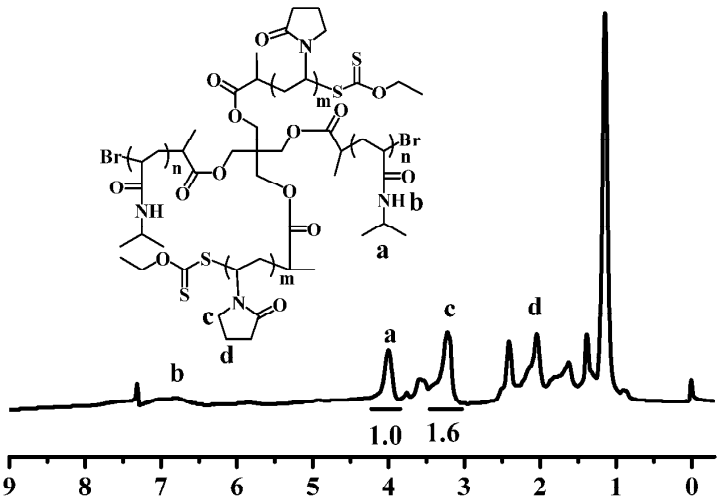

Figure S5. The ^1H NMR spectrum of nonlinear DHBCs $(PNIPAAM)_2(PNVP)_2$ ($M_{n(GPC)}$ = 29100 g/mol) in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard.

The characteristic peaks corresponding to PNIPAAM (δ = 3.7-3.9 ppm (**a**), δ = 6.0-7.0 ppm (**b**)), and PNVP (δ = 3.0-3.5 ppm (**c**), and δ = 1.9-2.2 ppm (**d**)) are both clearly observed in Figure S5. The number-average molecular weight of nonlinear DHBCs $(PNIPAAM)_2(PNVP)_2$ was calculated by comparison of the relative integration ratios ((**a**) and (**c**)) of these characteristic peaks.

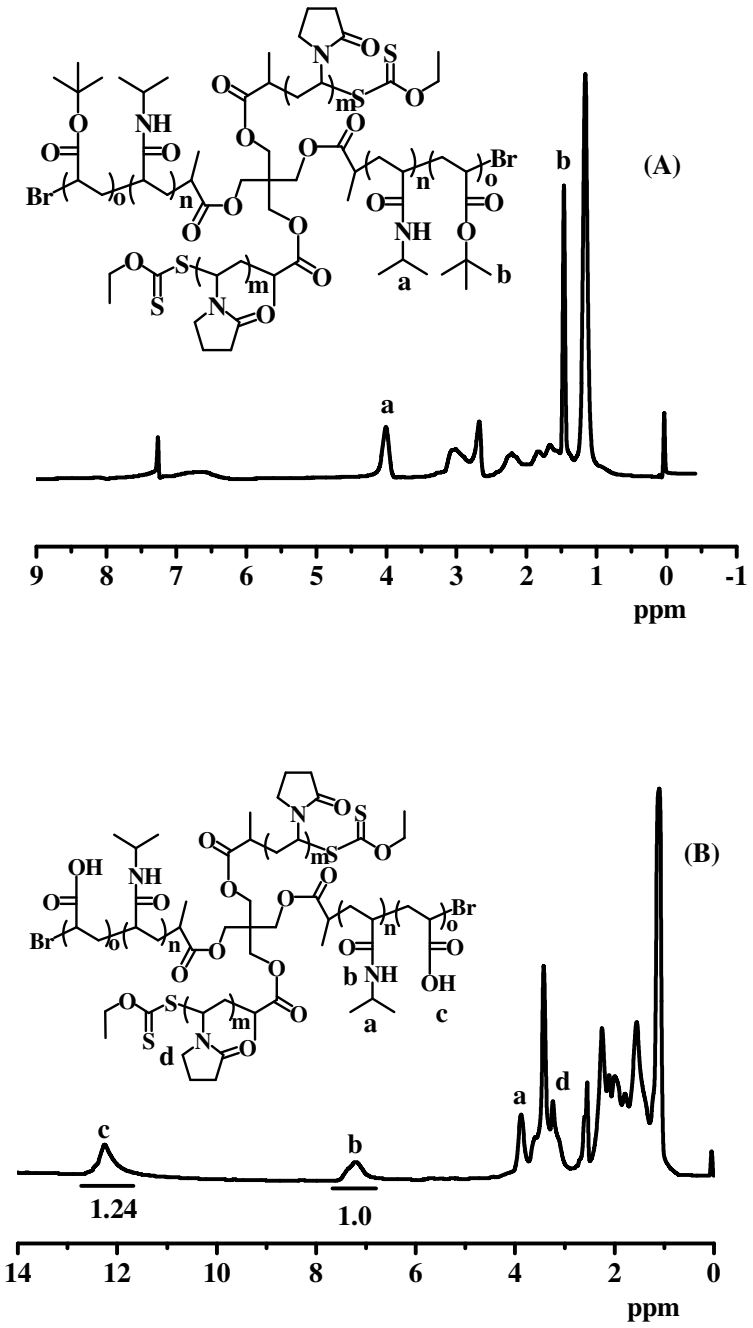

Figure S6. The ^{1}H NMR spectra of double hydrophilic miktoarm star terpolymers (A) (PNIPAAM-*b*-P*t*BA)$_2$(PNVP)$_2$ in $CDCl_3$ and (B) (PNIPAAM-*b*-PAA)$_2$(PNVP)$_2$ in DMSO-d_6 with tetramethylsilane (TMS) as the internal standard.

As shown in Figure S6(A), a sharp peak at 1.44 ppm was clearly observed due to the protons of the *t*-butyl group in the polymer chains. The number-average molecular

weight of double hydrophilic miktoarm star terpolymer (PNIPAAM-*b*-P*t*BA)$_2$(PNVP)$_2$ was calculated by comparison of the relative integration ratios of (**a**) and (**b**) in Figure S6(A). The characteristic signals at 11.6-12.8 (ppm) (Figure S6(B), **c**) assigned to active protons from carboxyl group was also observed, the relative integration ratios (Figure S6(B), (**c**) and (**b**)) was also close to the theoretical value (N_{tBA}/N_{NIPAAM} = 58/47), which demonstrated that the degree of the hydrolysis was complete.

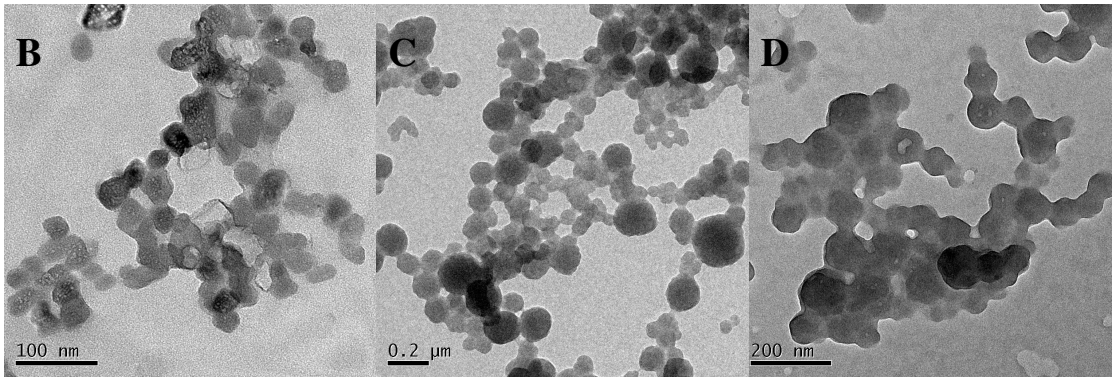

Figure S7. TEM images of the nonlinear MHBCs (PNIPAAM$_{47}$)$_2$(PNVP$_{38}$-*b*-PAA$_{45}$) formed on copper netting by casting the micelle solution. (B: 45 ^{o}C, pH = 10; C: 45 ^{o}C, pH = 6; D: 25 ^{o}C, pH = 6). The copolymer concentration is 0.1 mg mL^{-1}.

As presented in Figure S7, we observed typical sphere-shaped morphology of micelles and the sized are slightly smaller than that from DLS, which is typical as the samples collapse in dry state. At different conditions, the same trend compared to DLS is observed. The results indicated that the size and the sphere-shaped morphology can be well controlled by adjusting the solution condition.

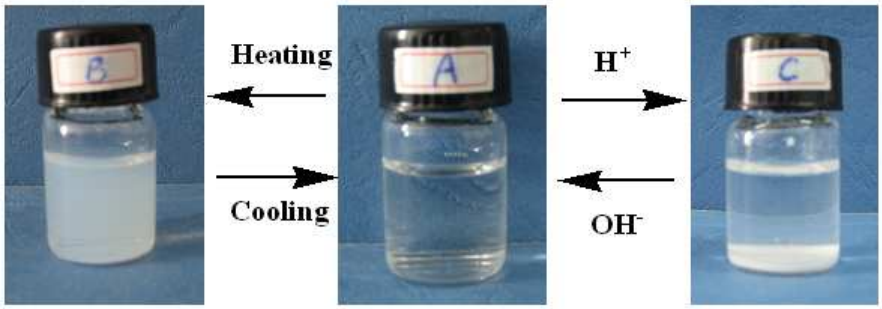

Figure S8. Photos of the original micellar solution (A: 25 ^{o}C, pH = 10; B: 45 ^{o}C, pH = 10; C: 25 ^{o}C, pH = 6). The copolymer ((PNIPAAM$_{47}$-*b*-PAA$_{58}$)$_2$(PNVP$_{38}$)$_2$) concentration is 0.1 mg/mL.