Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information for

On the LCST Transition of PNIPAM-*b*-PVCL in Water: Cooperative Aggregation of Two Distinct Thermally Responsive Segments

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Polymer Synthesis

Synthesis of PNIPAM macro-CTA: NIPAM (3.39 g, 30 mmol), CTA (0.0678 g, 0.3 mmol), AIBN (0.0096 g, 0.06 mmol) and 10 g methanol were added to a dry ampule. The mixture was degassed by three cycles of freeze–evacuate–thaw and then placed in a thermostated oil bath previously maintained at 60 ^{o}C. After 24 h, the reaction was stopped by sudden cooling in liquid nitrogen and exposure to air. The polymer was isolated by precipitation into a large excess of diethyl ether and collected by vacuum filtration, then vacuum-dried for 24 h.

Synthesis of $PNIPAM_{75}$-*b*-$PVCL_{96}$ was described as follows: PNIPAM macro-CTA (0.56 g, 0.066 mmol), VCL (0.7 g, 10 mmol), AIBN (0.0016 g, 0.01 mmol) were dissolved in 3.8 g methanol. The solution was degassed by three freeze–evacuate–thaw cycles before immersion into a preheated oil bath maintained at 60 ^{o}C. The polymerization was conducted for 24 h and then quenched by rapid cooling in liquid nitrogen and exposure to air. After three times' precipitation by diethyl ether, the product was finally vacuum-dried for 24 h.

Bulk homopolymerization of $PVCL_{62}$: typically, a mixture of VCL (1.39 g, 10 mmol), CTA 0.0236 g, 0.1 mmol) and AIBN (0.0032 g, 0.02 mmol) was added to a dry tube and degassed by three cycles of freeze-vacuum-thaw. Then, the tube was immersed in thermostatic oil bath at 60 ^{o}C. After 24 h, the solution was cooled in liquid N_2 and diluted with THF, followed by dropping into a large amount of diethyl ether and collected by vacuum filtration; purification was carried out by repeating dissolution in THF and precipitation from ether, and finally dried under vacuum for 24 h.

Table S1. Molecular characterizations of the polymer samples.

sample[a]	M_n (SEC) [kg/mol][b]	M_n (NMR) [kg/mol][c]	PDI[d]	NIPAM [mol %][e]
$PNIPAM_{75}$	4.5	8.5	1.39	100
$PNIPAM_{75}$-b-$PVCL_{42}$	5.7	14.3	1.57	64
$PNIPAM_{75}$-b-$PVCL_{96}$	7.5	20.1	1.68	44
$PVCL_{62}$	2.1	8.6	1.96	0

[a]Number average degree of polymerization P_n of each component as obtained from M_n (^{1}H NMR). [b]Apparent number average molecular weight determined by GPC in DMF using PEG standards. [c]Determined by ^{1}H NMR end group analysis taking the mass of the RAFT agent into account. [d]Apparent dispersities determined by GPC in DMF. [e]Molar NIPAM ratio determined by ^{1}H NMR.

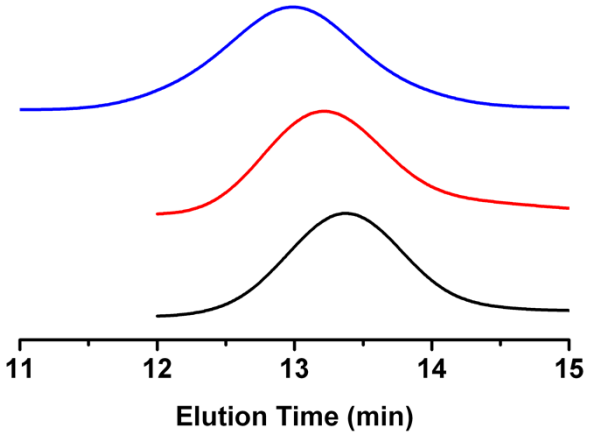

Figure S1. GPC traces of $PNIPAM_{75}$ (black), $PNIPAM_{75}$-*b*-$PVCL_{42}$ (red), $PNIPAM_{75}$-*b*-$PVCL_{96}$ (blue).

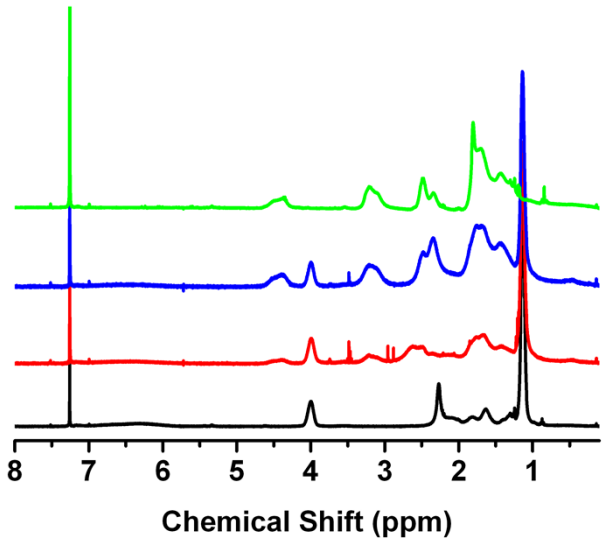

Figure S2. ^{1}H NMR spectra of $PNIPAM_{75}$ (black), $PNIPAM_{75}$-*b*-$PVCL_{42}$ (red), $PNIPAM_{75}$-*b*-$PVCL_{96}$ (blue) and $PVCL_{62}$ (green).