Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information for

Comparison of LCST-transitions of homopolymer mixture, diblock and statistical copolymers of NIPAM and VCL in water

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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-*b*-PVCL 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.

Synthesis of PVCL (bulk homopolymerization): 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	M_n (SEC) [kg/mol][a]	PDI[b]	NIPAM [mol %][c]
PNIPAM	12	1.58	100
Diblock Copolymer	12	1.72	0.55
Statistical Copolymer	9.1	1.45	0.58
PVCL	10	1.66	0

[a]Apparent number average molecular weight determined by GPC in DMF using PMMA standards.

[b]Apparent dispersities determined by GPC in DMF. [c]Molar NIPAM ratio determined by ^{1}H NMR.

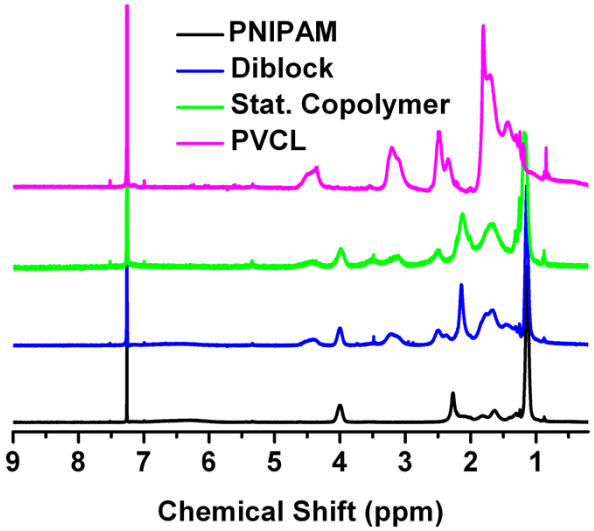

Figure S1. ^{1}H NMR spectra of PNIPAM (black), Diblock (blue), Statistical Copolymer (green) and PVCL (pink) in $CDCl_3$.

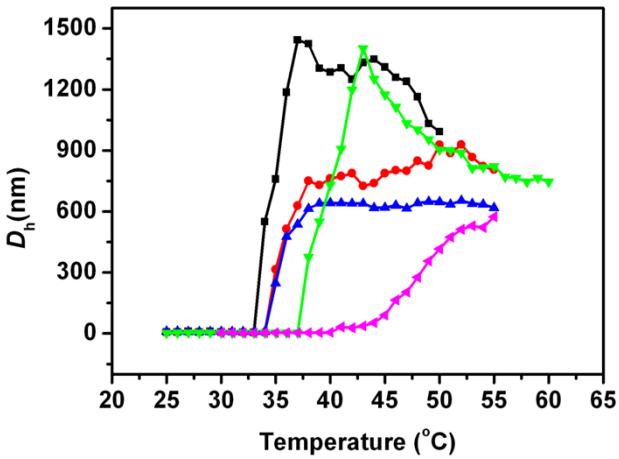

Figure S2. DLS curves of PNIPAM (black), Mixture (red), Diblock (blue), Statistical Copolymer (green) and PVCL (pink) in H_2O upon heating at the concentration of 0.2 mg/ml.

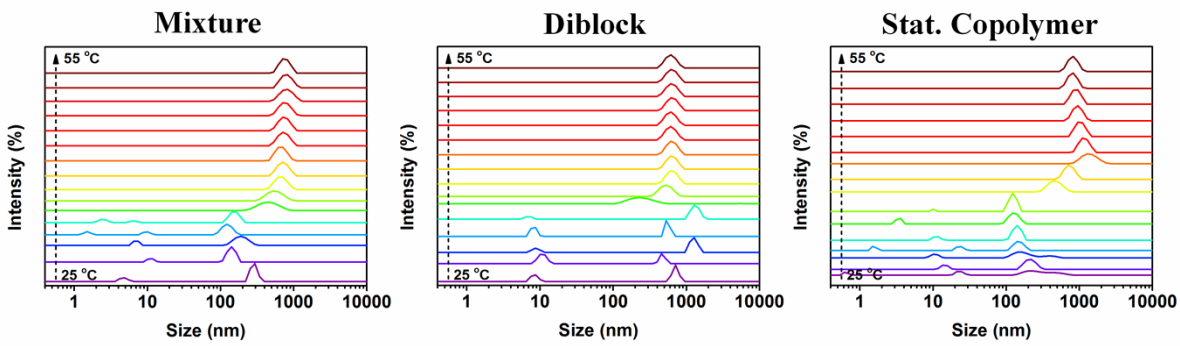

Figure S3. Hydrodynamic diameter (D_h) distribution of Mixture, Diblock and Statistical Copolymer during the heating process obtained from the DLS measurements.