Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Polyacrylamide "Revisited": UCST-type Reversible Thermoresponsive Properties in Aqueous Alcoholic Solution

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1. Synthesis

Table S1. Summary of the polymerization conditions for polyacrylamide synthesis.

Sample name	M:TTC	Monomer (g)	AIBN (mg)	TTC (mg)	DMSO (mL)	Yield (%)
PAM_{28}	50	0.31	4	35	3.5	57
PAM_{48}	100	0.61	4	35	5.1	53
PAM_{83}	150	0.92	4	35	7	60
PAM_{104}	200	1.23	4	35	9	54
PAM_{178}	250	1.54	4	35	12	60

Table S2. Summary of the characteristics of the synthesized polyacrylamides.

Sample name	M_n[a] (KDa)	DP[a]	M_n[b] (KDa)	M_w[b] (KDa)	Đ (M_w/M_n)	DP[b]	T_{CP} (°C) Water/EtOH (50% v/v)
PAM_{28}	2.1	30	2.0	4.5	2.2	28	8.8
PAM_{48}	4.2	61	3.4	8.8	2.5	48	12.3
PAM_{83}	4.9	69	5.9	17.0	2.8	83	16.6
PAM_{104}	7.7	108	7.4	22.9	3.0	104	20.7
PAM_{178}	9.7	136	12.6	39.1	3.1	178	23.2

[a] From NMR and [b] from GPC measurements in 0.1N $NaNO_3$ aqueous solution.

2. Characterization of polymers

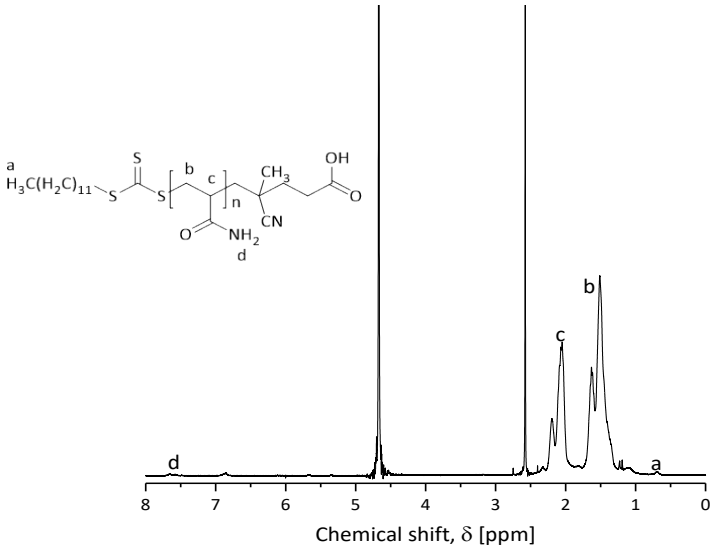

Fig. S1 ^{1}H-NMR spectrum of polyacrylamide measured in D_2O.

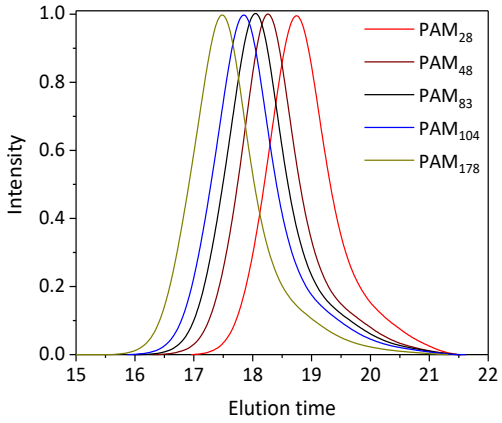

Fig. S2 GPC traces of polyacrylamide with various DP. Measurements were conducted using PSS-SUPREMA 10μ VS+30+3000 column and 0.1N aqueous $NaNO_3$ as an eluent with flow rate of 1.0 mL/min at 25 °C. The calibration standard was PEO in the molecular weight range of 600 to 2.0 $\times 10^6$ g.mol^{-1}.

3. DLS results

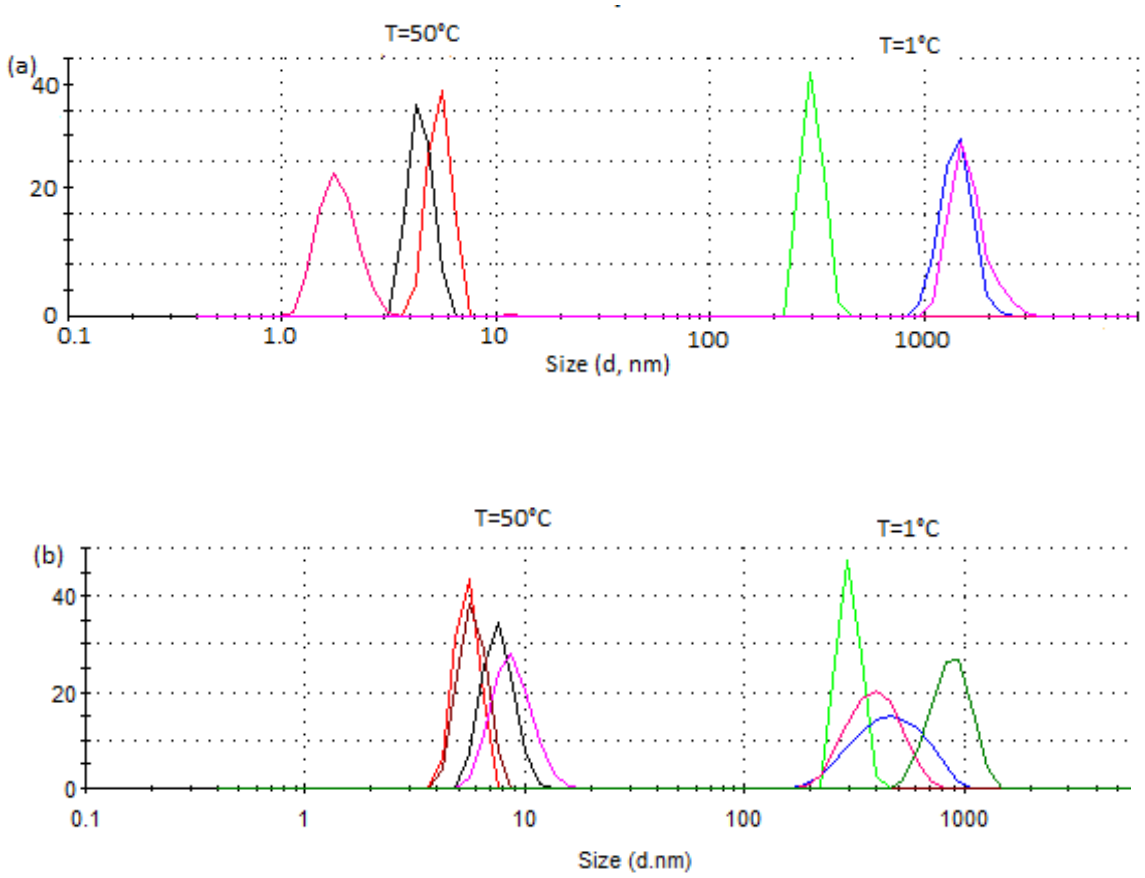

Fig. S3 Volume distribution of sizes of PAM_{104} in water/alcohol mixtures at fixed polymer concentration of 1 mg/mL below (T= 1°C) and above (T= 50°C) the phase transition temperature. (a) Comparison of different alcohols at fixed alcohol percentage of 45% (v/v) in water/alcohol mixtures. Black (50 °C) and green (1°C) lines for water/MeOH, red (50°C) and blue (1°C) lines for water/EtOH, purple (50°C) and pink (1°C) for water/iPrOH. (b) Comparison of different MeOH percentages in water. Wine (50 °C) and green (1°C) lines for 45% (v/v), red (50°C) and purple (1°C) for 50% (v/v), black (50°C) and blue (1°C) for 55% (v/v); pink (50°C) and olive (1°C) lines for 60% (v/v).

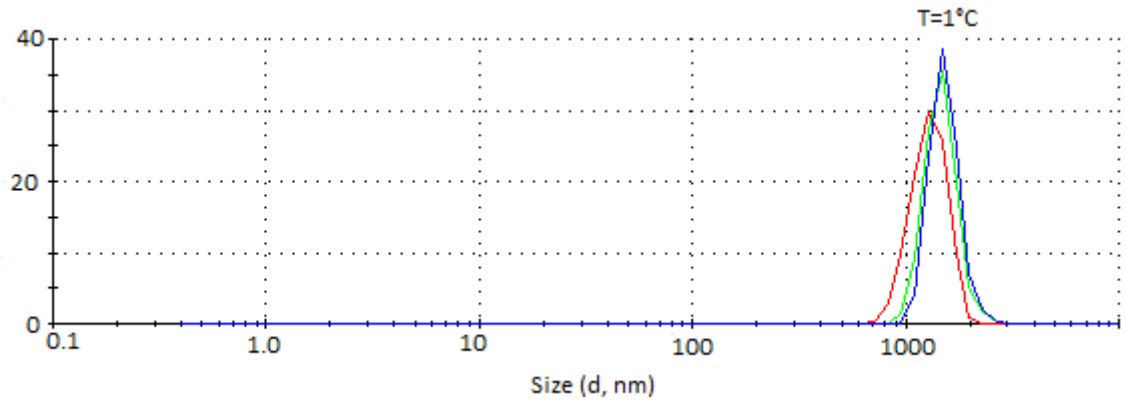

Fig. S4 Volume distribution of sizes of the PAM_{104} at different concentrations in water/EtOH mixture at fixed EtOH content of 50% (v/v) below the phase transition temperature (1 °C). Red line for 0.5 mg/mL, green line for 1 mg/mL and blue line for 2 mg/mL.

4. MD simulations

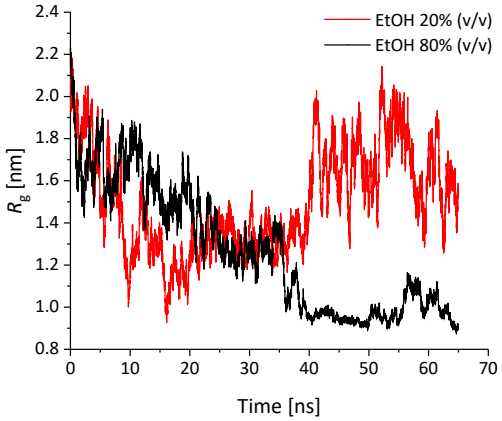

Fig. S5 Variation of *R*g as a function of time at constant temperature of 65°C with varying EtOH concentrations (20 % and 80%).