

Supporting information for

A new thermoresponsive polymer of poly(*N*-acryloylsarcosine methyl ester) with tunable LCST

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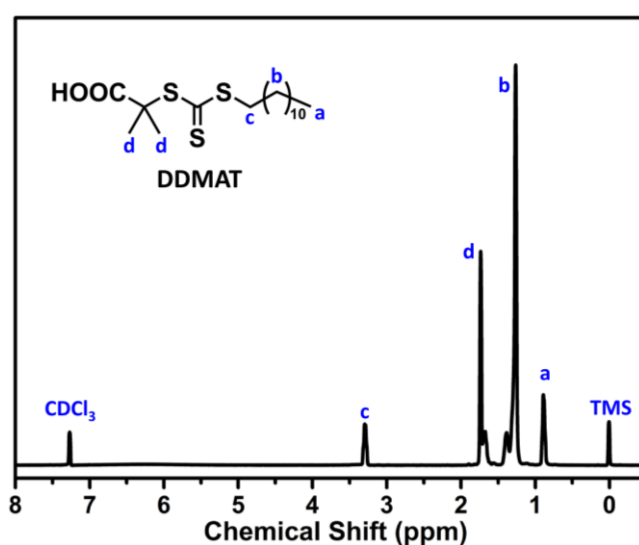


Figure S1. ¹H NMR spectra of DDMAT dissolved in CDCl₃.

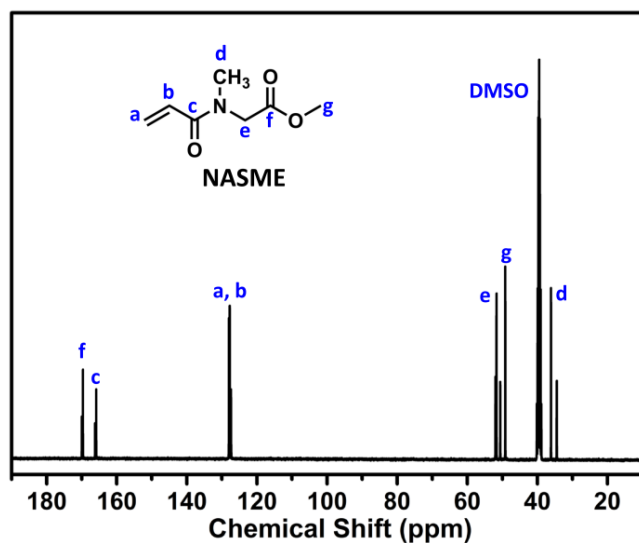


Figure S2. ¹³C NMR spectra of the NASME monomer dissolved in DMSO.

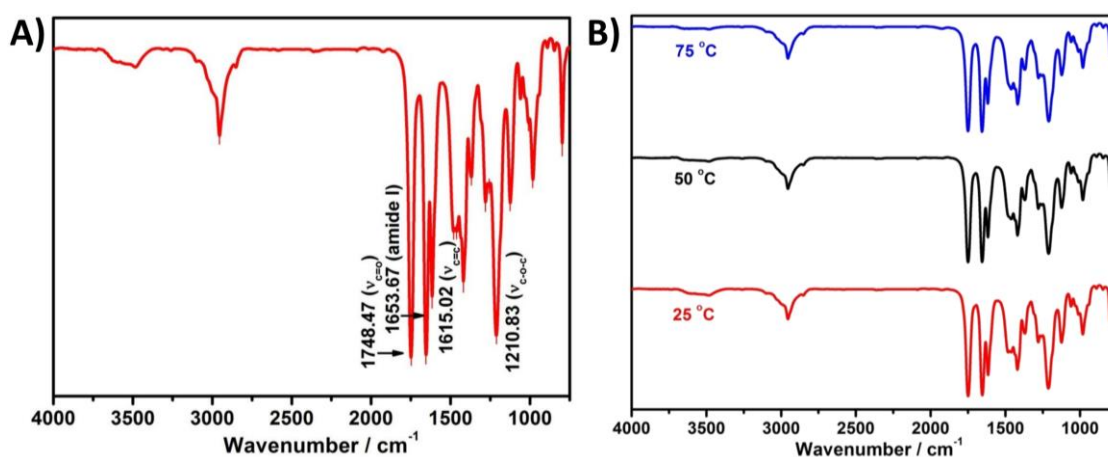


Figure S3. FTIR spectra of the NASME monomer at room temperature (A) and at various temperatures of 25 °C, 50 °C , and 75 °C (B).

$$k_c = \frac{k_I}{k_{II}} = \frac{\Delta \nu}{2\delta_{\nu\tau}} \quad \text{(Equation S1)}$$

$$\Delta G = 19.14T_c \left(10.62 + \log \frac{1+\Delta P}{1-\Delta P} + \log \frac{T_c}{k_c} \right) \quad \text{(Equation S2)}$$

Where k_c is the rate content, ΔG is the free energy of activation (the energy barrier) for exchange process; $\Delta \nu$ is the chemical shift difference (in Hz) of isomers, for NASME the value is given by 90 Hz; T_c is the coalescence temperature, for NASME the value is given by 343.15 K; ΔP is the relative concentration difference of isomers, for NASME the value is given by 0.36; $\delta_{\nu\tau}$ can be obtained according to the line-shape analysis showed in the literatures.^{1,2}

$$M_{n,th} = \frac{[\text{monomer}]_0 \times M_{\text{monomer}}}{[\text{RAFT}]_0} \times \text{Conversion} + M_{n, \text{RAFT}/\text{macro-RAFT}} \quad \text{(Equation S3)}$$

where $[\text{monomer}]_0$ and $[\text{RAFT}]_0$ represent the concentration of the fed monomer and the RAFT agent, the Conversion is determined by ¹H NMR analysis by comparing the integral areas of the monomer protons of C=C-H at $\delta = 5.60\text{-}5.80$ ppm with those of the 1,3,5-trioxane internal standard at $\delta = 5.10\text{-}5.20$ ppm, and M_{monomer} and $M_{n, \text{RAFT}/\text{macro-RAFT}}$ are the molar mass of the monomer and the RAFT/macro-RAFT agent, respectively.

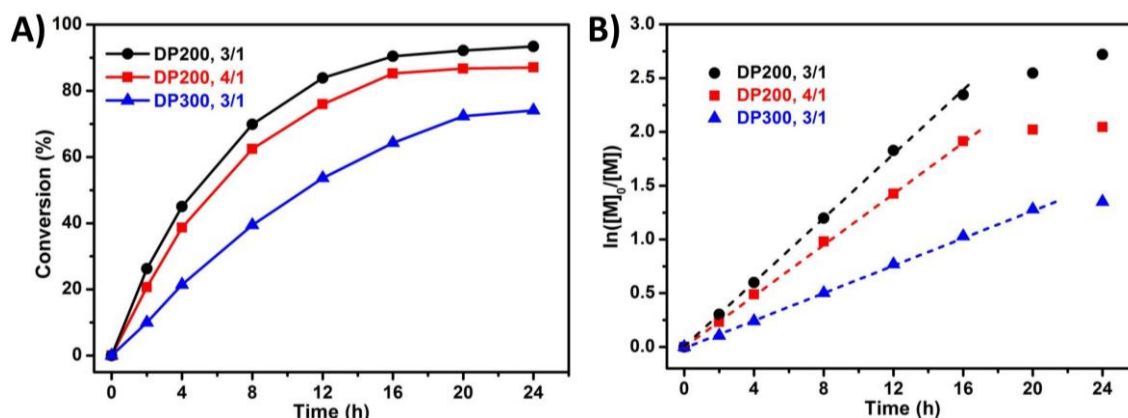


Figure S4. Three polymerization kinetics of solution RAFT polymerization of NAGME: the plots of time-dependent monomer conversion (A) and the $\ln([M]_0/[M])$ -time plots of the RAFT polymerization (B). Conditions: $[NASME]_0 = 4$ M, 1,4-dioxane, 70 °C. The lines are only meant to guide the eye. DP200,3/1, DP200,4/1 and DP300,3/1 represent the molar ratio of $[NASME]_0:[DDMAT]_0:[AIBN]_0 = 600:3:1, 800:4:1; 900:3:1$, respectively.

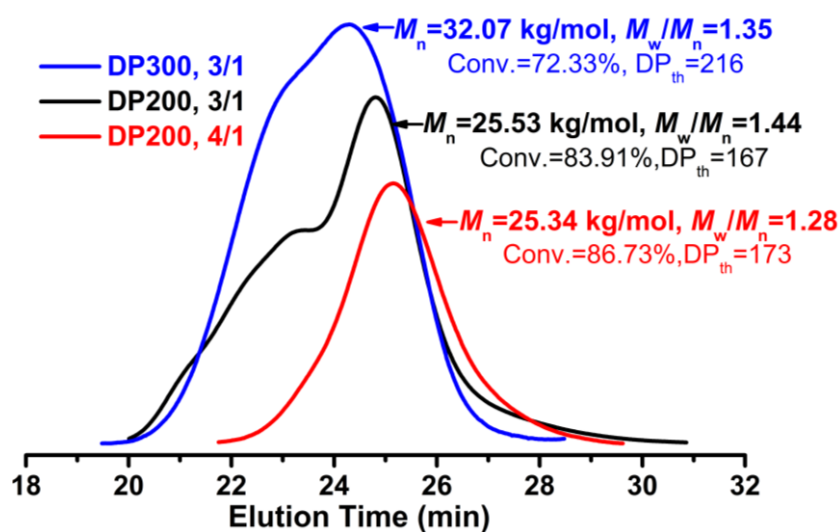


Figure S5. The GPC traces of PNASME at the maximum conversion under three different polymerization ratio. Note: the comments of the cures refer to Figure S3.

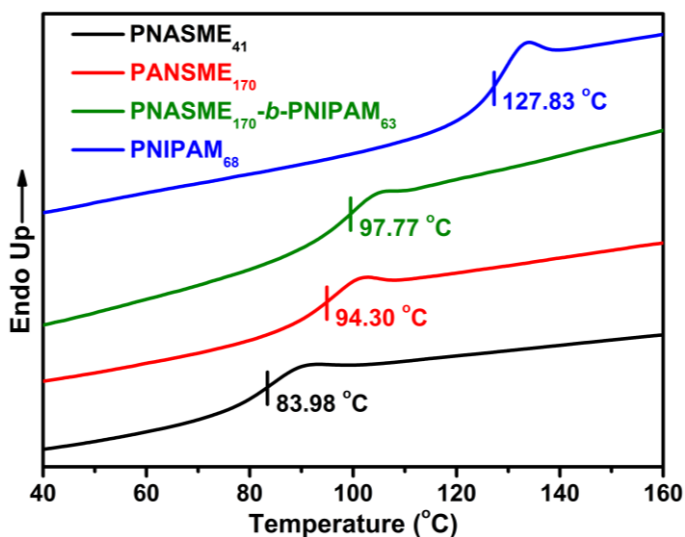


Figure S6. DSC thermograms of PNIPAM₆₈, PNASME₁₇₀-*b*-PNIPAM₆₃, PNASME₄₁, and PNASME₁₇₀, in which the subscripts represent the DP of the corresponding monomers. All the polymer samples were heated from 25 to 180 °C at a heating/cooling rate of 10 °C min⁻¹ for three cycles, and the second heating cure was used to determinate the glass transition temperature (T_g) at the middle of the step transition.

Table S1. Fitted values for c , B_{\max} and K_d from the CP tests of PNASME for anions.

Na ⁺ Counter anion	c (°C/mol)	B_{\max} (°C) ^a	K_d (M) ^a
SCN ⁻	-317.45	10.81	31.83
ClO ₄ ⁻	-159.97	3.56	20.02
I ⁻	-78.08	1.78	19.36
NO ₃ ⁻	-8.35	0.0094	0.46
Br ⁻	-7.96	0.0088	0.49
Cl ⁻	-7.88	0	0
F ⁻	-16.79	0	0
H ₂ PO ₄ ⁻	-26.86	0	0
S ₂ O ₃ ²⁻	-34.89	0	0
SO ₄ ²⁻	-51.65	0	0

^a The K_d values larger than 1 M⁻¹ represent binding weaker than those measured at the highest concentration of salt.

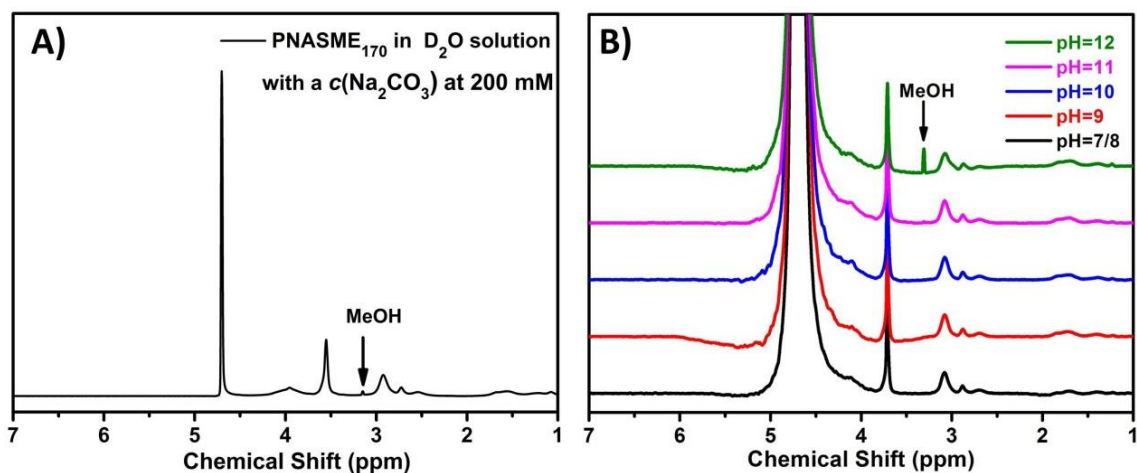


Figure S7. The ^1H NMR spectra of PNASME₁₇₀ in D₂O solution with a Na₂CO₃ concentration at 200 mM (A) and the ^1H NMR spectra of PNASME₁₇₀ in D₂O solution at different pH values adjusted with NaOH (B).

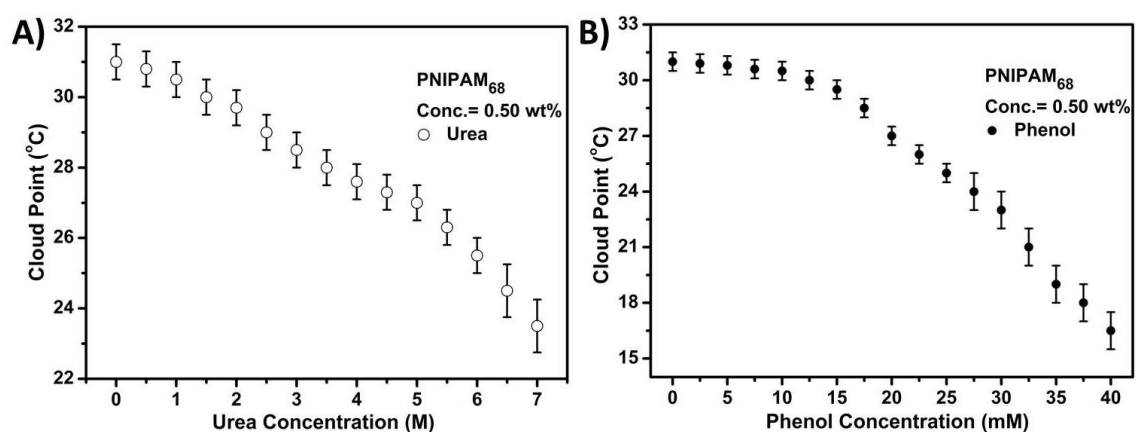


Figure S8. The CP PNIPAM₆₈ as a function of the concentration of urea (A) and phenol (B) with a polymer concentration of 0.50 wt%.

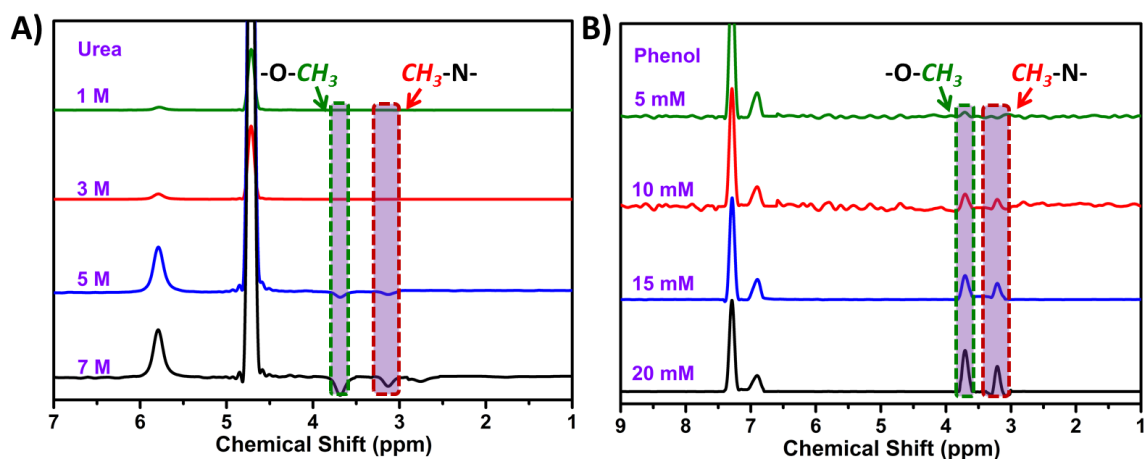


Figure S9. The pendants of PNASME₁₇₀ NOE correlated with urea (A) and phenol (B) at

different concentration. The negative column slices of urea are extracted from 5.77 ppm of urea protons, and the positive column slices of phenol are extracted from 7.28 ppm of phenyl protons. The peaks highlighted in gray indicate the cross-peaks of ester methyl (green dashed box) and amide methyl (red dashed box), respectively. The signals at 7.28 ppm and 6.90 ppm were assigned to the phenyl protons of phenol. Note: the urea-water cross peaks are barely detected at concentration lower than 3 M, because of the proton exchange between urea and D₂O.

References

- (1) Shanan-Atidi, H.; Bar-Eli, K. H. A convenient method for obtaining free energies of activation by the coalescence temperature of an unequal doublet. *J. Phys. Chem.* **1970**, *74*, 961-963.
- (2) Gutowsky, H. S.; Holm, C. H. Rate Processes and Nuclear Magnetic Resonance Spectra. II. Hindered Internal Rotation of Amides. *J. Chem. Phys.* **1956**, *25*, 1228-1234.