Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Polypeptoids with Tunable Cloud Point Temperatures Synthesized from *N*-Substituted Glycine *N*-Thiocarboxyanhydrides

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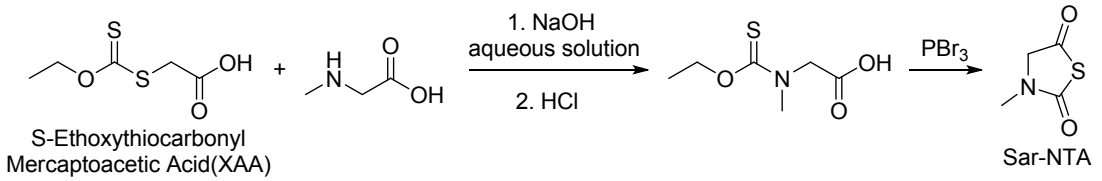
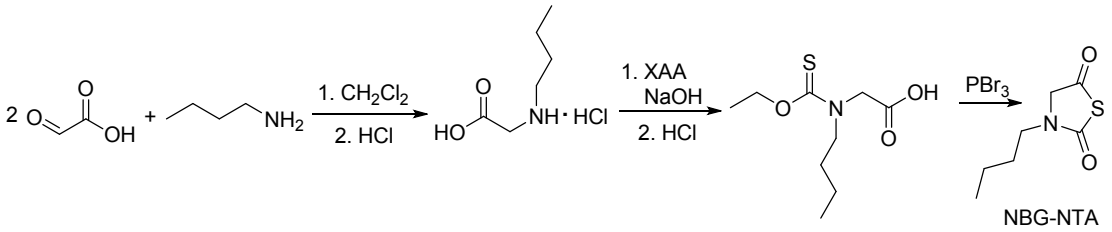


Scheme S1. Synthesis of sarcosine *N*-thiocarboxyanhydride (Sar-NTA).



Scheme S2. Synthesis of *N*-butylglycine *N*-thiocarboxyanhydride (NBG-NTA).

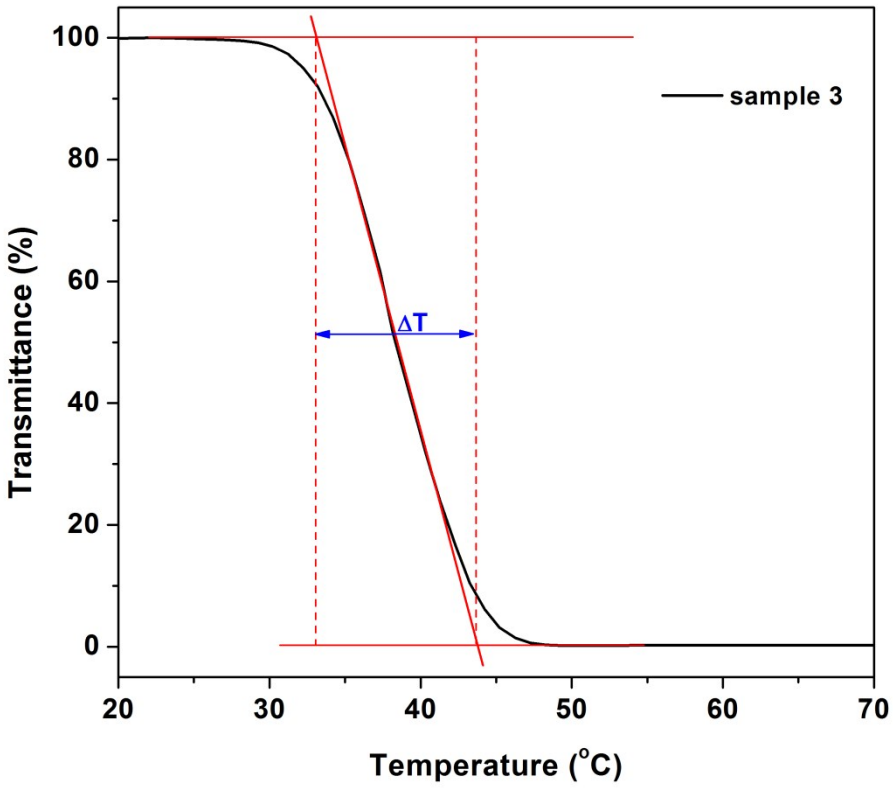


Figure S1. Illustration of onset determination of transition window (ΔT).

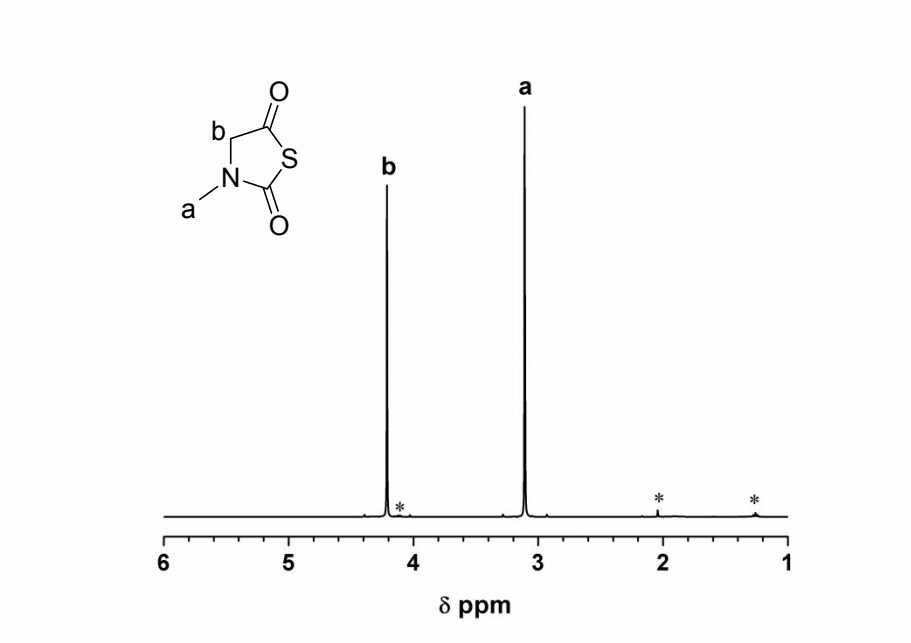


Figure S2. ^{1}H NMR spectrum of Sar-NTA in $CDCl_3$ (*: ethyl acetate).

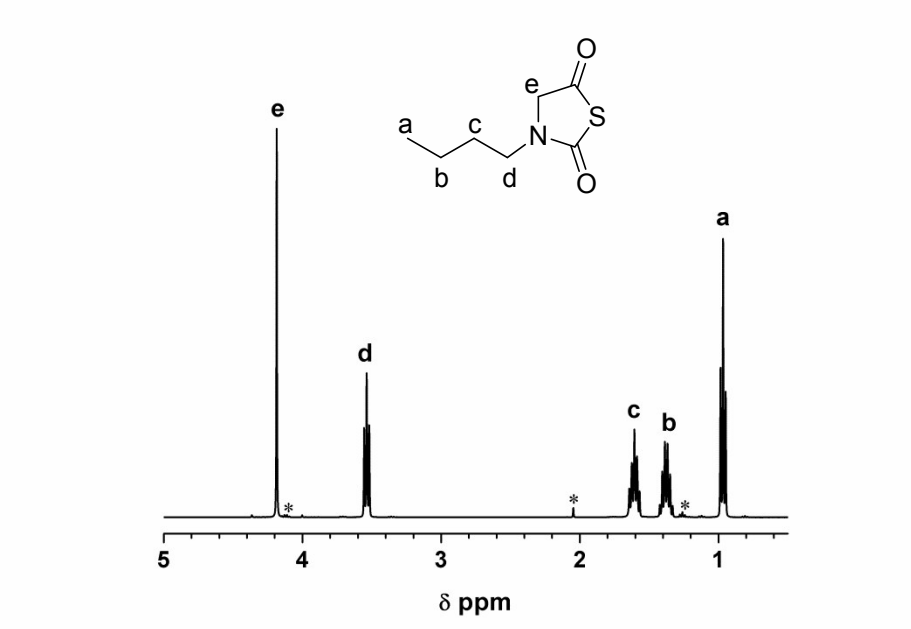


Figure S3. ^{1}H NMR spectrum of NBG-NTA in $CDCl_3$ (*: ethyl acetate).

Table S1. Copolymerization of Sar-NTA with NBG-NTA initiated by benzylamine[a]

Run	[Sar]/[NBG] /[benzylamine]	Conversion[b] (%)			Yield (%)	$M_{n\ theo}$[c] (kDa)	Copolypeptoid Composition[d]	$M_{n\ NMR}$[d] (kDa)
		Sar	NBG	total				
S1	117/79/1	75.8	55.8	67.2	60.2	11.4	P(Sar_{95}-*r*-NBG_{55})	13.1

[a] Polymerization conditions: [Sar]+[NBG] = 0.5 mol/L, 48 h in THF at 60 °C. [b] Determined by taking a small amount of reaction mixture and dissolving in DMSO-d_6 for ^{1}H NMR analysis. Monomer conversions were calculated from the relative integration of the proton resonance of monomers and copolymers. [c] Defined as Equation (S1). [d] Calculated by ^{1}H NMR analysis of isolated copolypeptoid products with DMSO-d_6 as the solvent.

$$M_{n,theo} = \frac{[Sar]}{[benzylamine]} \times Conversion_{sar} \times 71 + \frac{[NBG]}{[benzylamine]} \times Conversion_{NBG} \times 113 + 107 \qquad (S1)$$

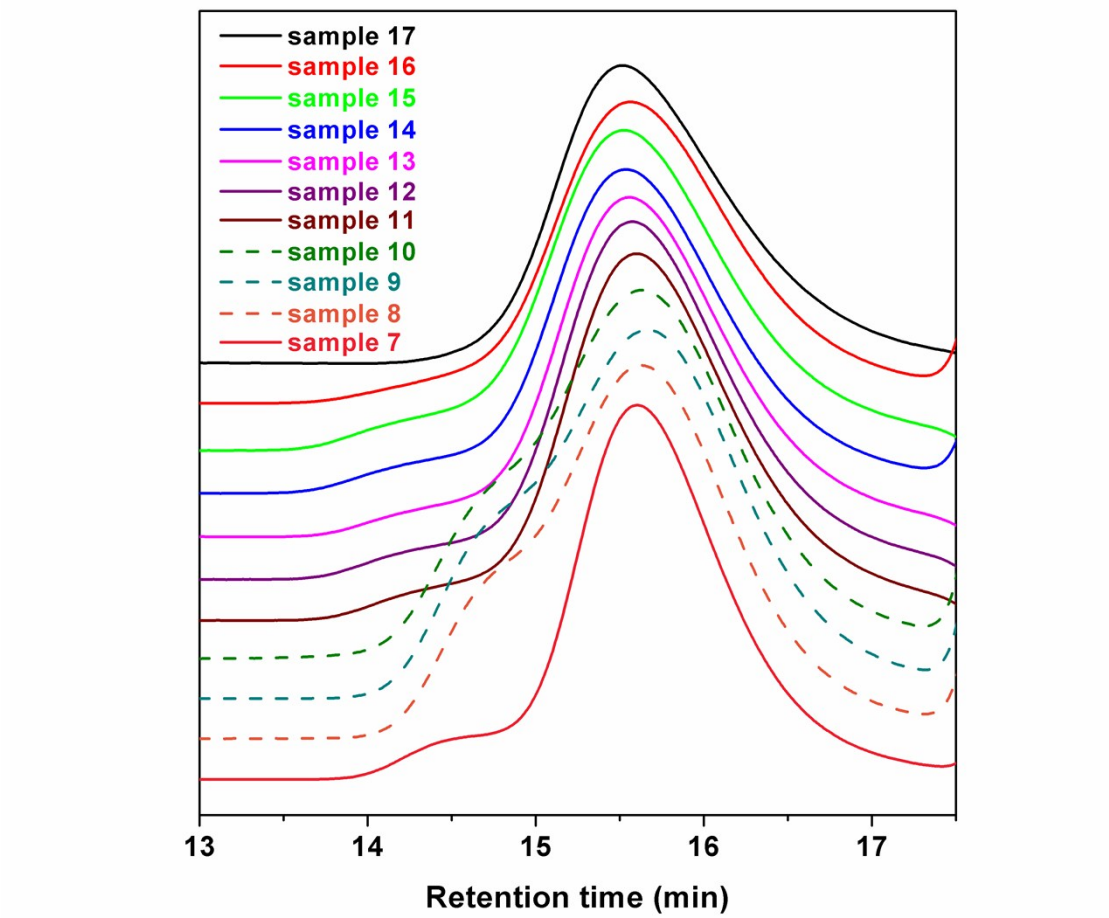


Figure S4. SEC traces of samples **7**–**17** in Group **II**.

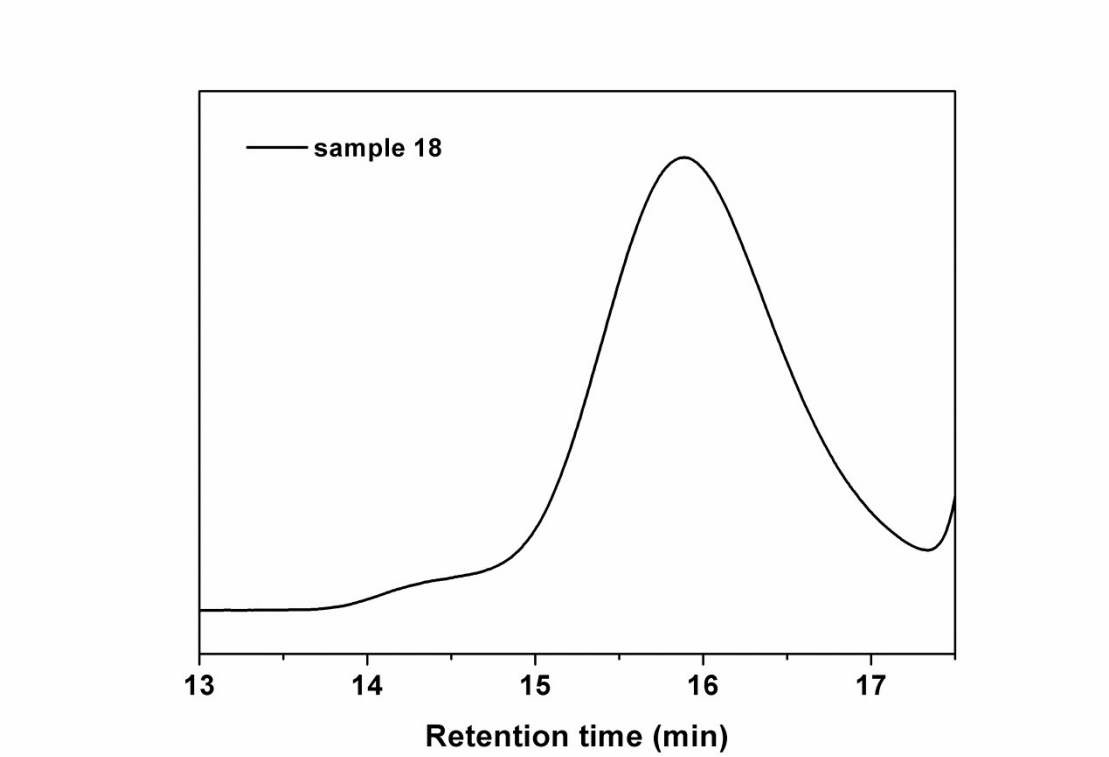


Figure S5. SEC trace of sample **18** in Group **III**.

Table S2. Copolymerization of Sar-NTA with NBG-NTA for reactivity ratios measurement[a]

Run	$[Sar]_0/[NBG]_0$	Conversion (%)[b]	Sar mol% in copolymers[c]	Copolymer composition (f)[d]
S2	4.608	17.4	88.6	7.802
S3	1.816	18.3	74.7	2.956
S4	0.983	17.1	64.0	1.781
S5	0.541	16.0	45.1	0.822

[a] Copolymerization were carried out in THF at 60 °C for 4 h with feed molar ratios of monomers ([Sar]+[NBG]) to initiator around 200, [Sar]+[NBG] = 0.5 mol/L; [b] Determined by taking a small amount of reaction mixture and dissolving in DMSO-d_6 for ^{1}H NMR analysis. Monomer conversions were calculated from the relative integration of the proton resonance of monomers and copolymers. [c] Calculated by ^{1}H NMR analysis of isolated copolypeptoid products with DMSO-d_6 as the solvent. [d] Defined as Equation (S3).

$$F = \frac{[Sar]_0}{[NBG]_0} \qquad (S2)$$

$$f = \frac{Sar\ mol\%}{100 - Sar\ mol\%} \quad (Sar\ mol\%\ in\ copolymer\ composition) \qquad (S3)$$

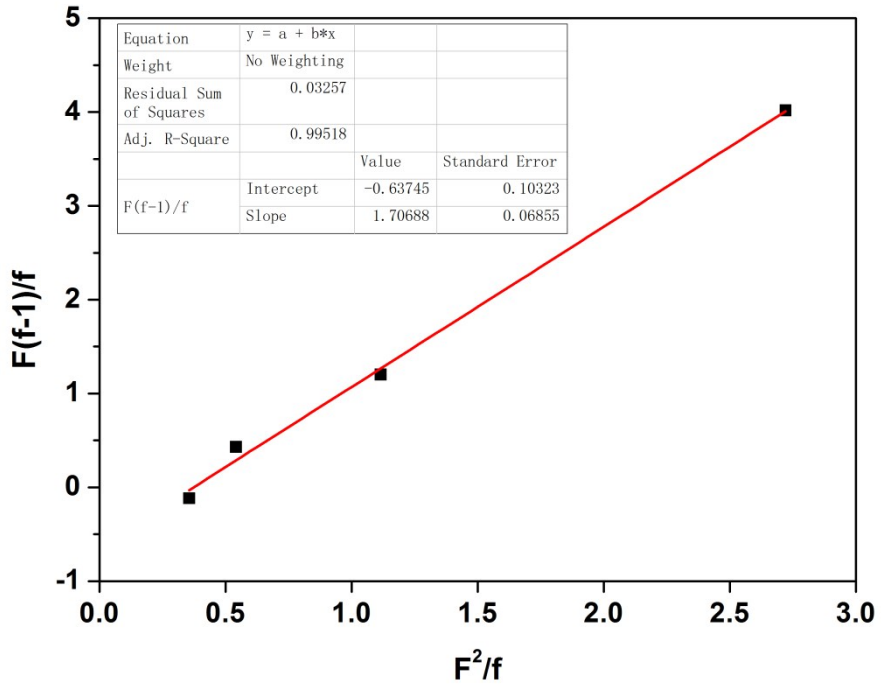


Figure S6. Plots of F(f-1)/f *versus* (F^2/f) for the benzylamine-initiated copolymerization of Sar-NTA with NBG-NTA and the linearly fitted line whose slope is r_1 [1.70(7), Sar-NTA] and intercept is r_2 [0.63(7), NBG-NTA] by the Fineman-Ross method.

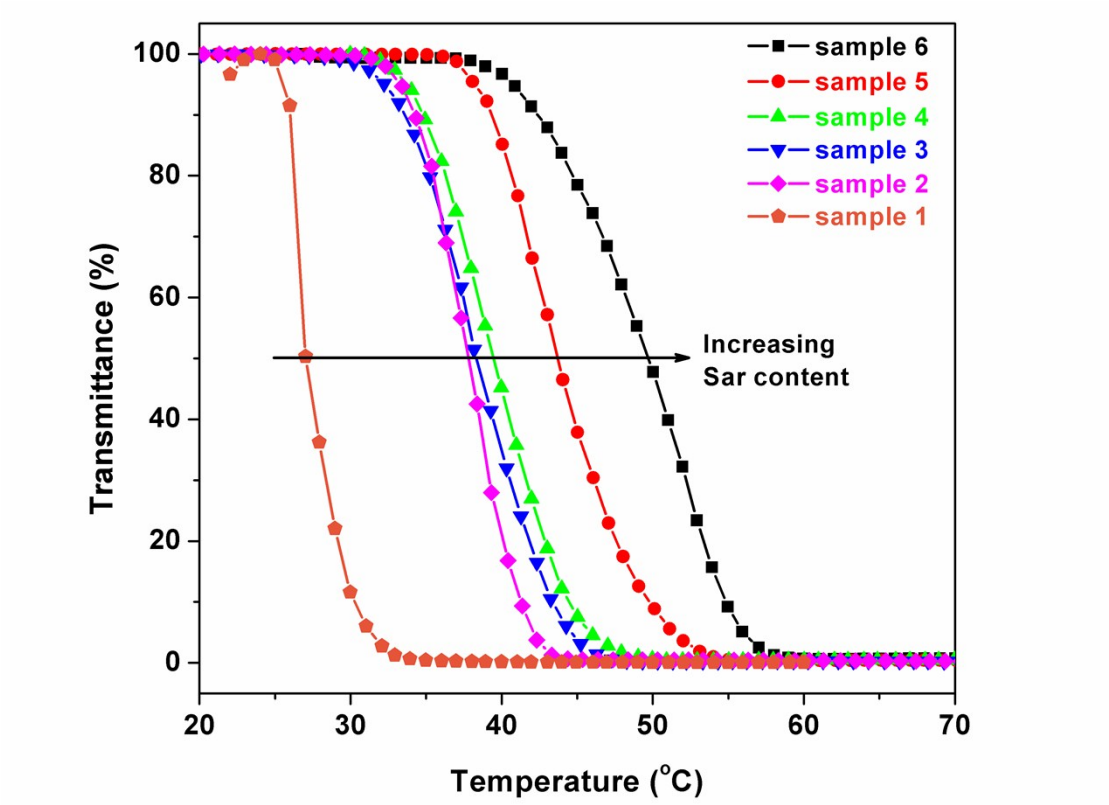


Figure S7. Plots of transmittance at λ = 450 nm *versus* temperature for samples of Group **I** (**1**–**6**) with a concentration of 3.0 mg/mL during heating procedure.

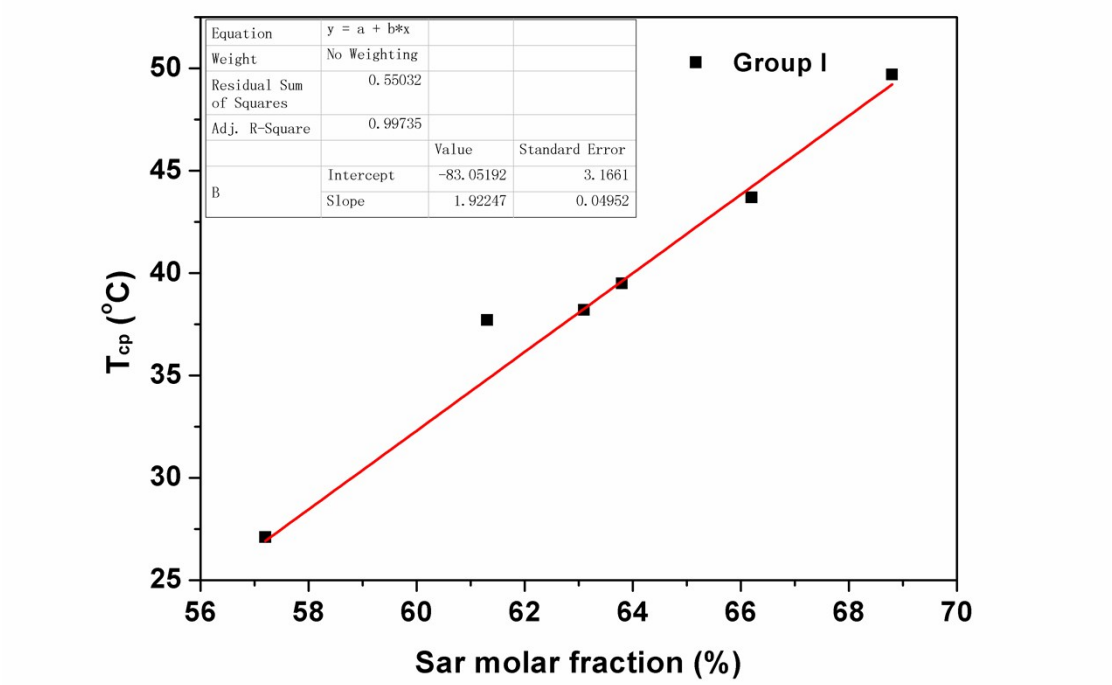


Figure S8. Plots of T_{cp} *versus* the molar fraction of Sar segment for samples of Group **I** (**1**–**6**) and the corresponding linearly fit curve.

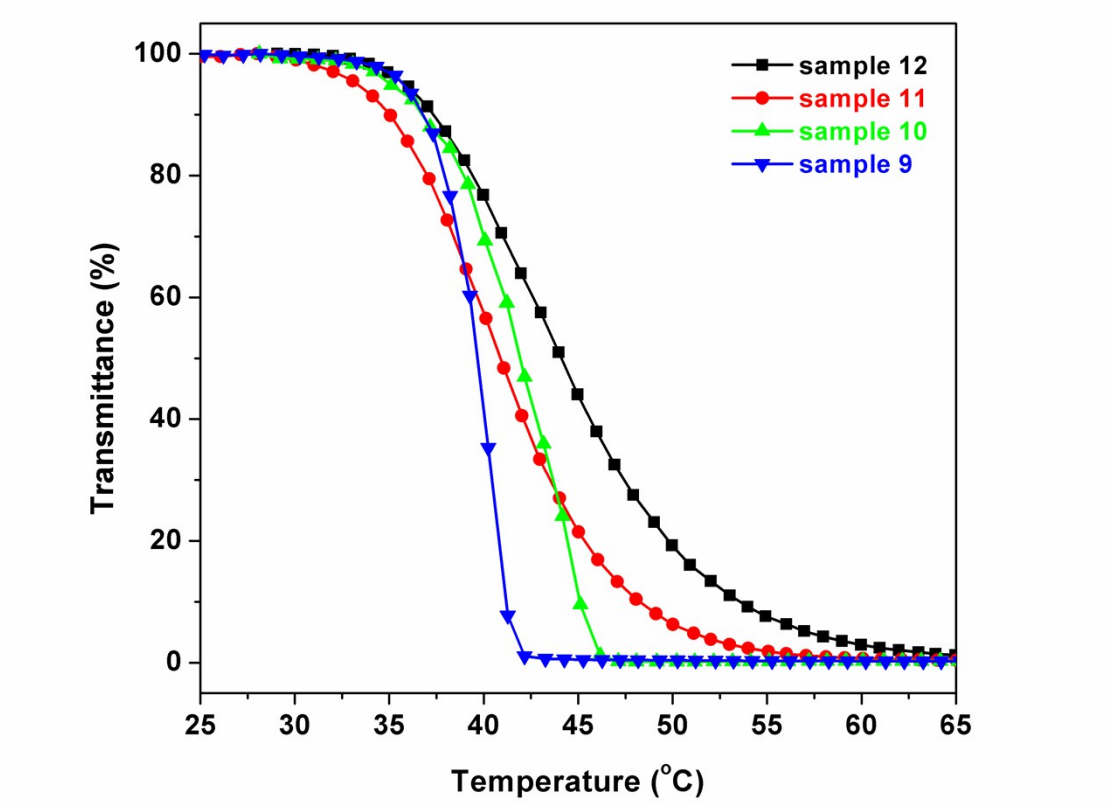


Figure S9. Plots of transmittance at λ = 450 nm *versus* temperature for samples of **9**–**12** (Group **II**) with a concentration of 3.0 mg/mL during heating procedure.

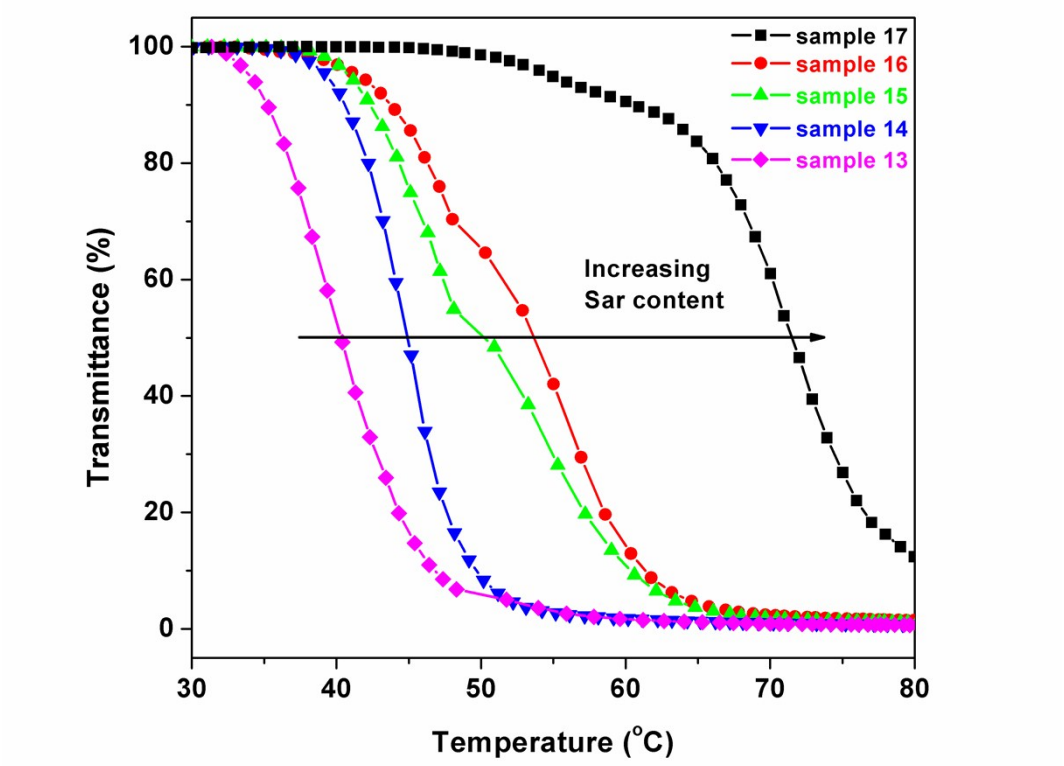


Figure S10. Plots of transmittance at λ = 450 nm *versus* temperature for samples of **13**–**17** (Group **II**) with a concentration of 3.0 mg/mL during heating procedure.

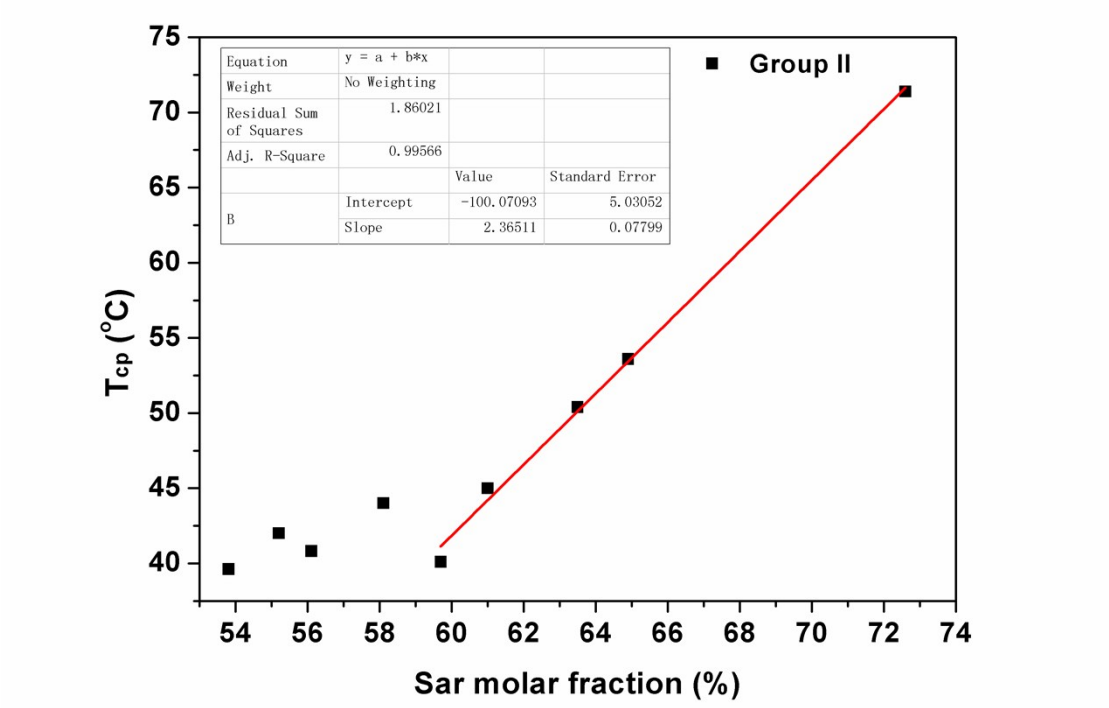


Figure S11. Plots of T_{cp} *versus* the molar fraction of Sar segment for samples of Group **II** (**9**–**17**) and the corresponding linearly fit curve of samples **13**–**17**.

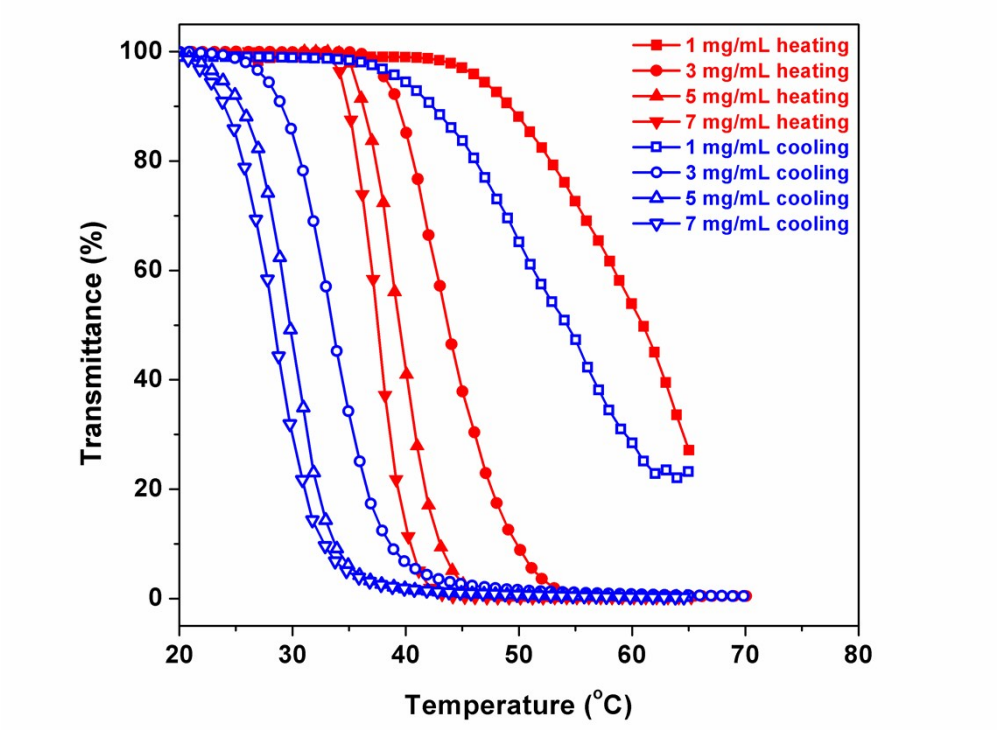


Figure S12. Plots of transmittance at λ = 450 nm *versus* temperature for the sample **5** with different concentrations (heating and cooling cycles are symbolized by the filled and unfilled symbols, respectively).

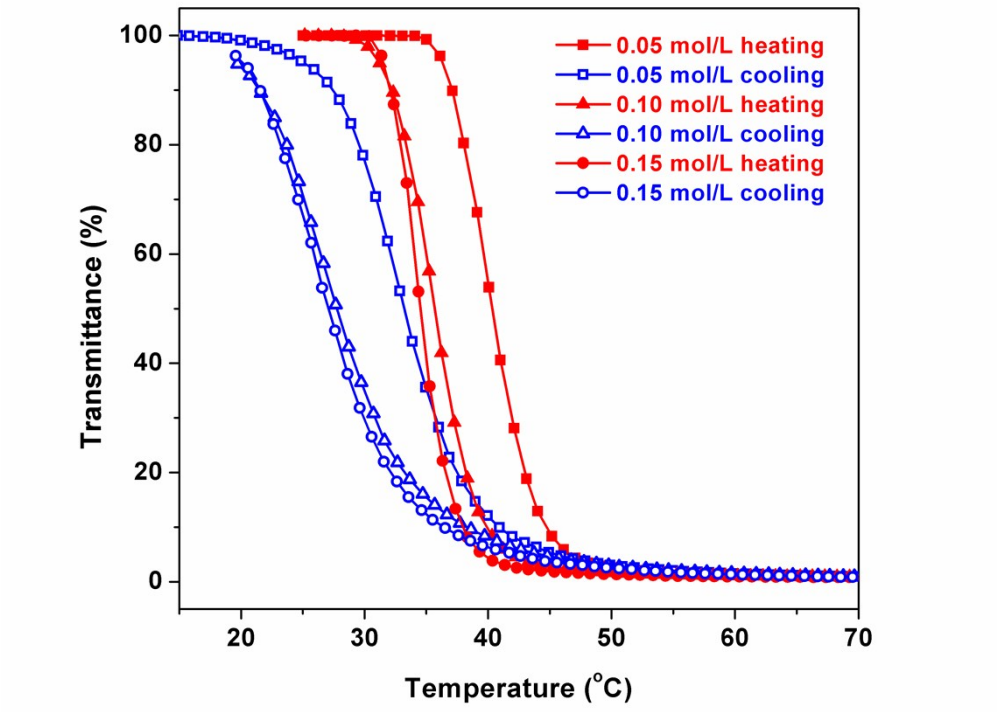


Figure S13. Plots of transmittance at λ = 450 nm *versus* temperature for the sample **6** of 3.0 mg/mL aqueous solution with the addition of Na_2SO_4 at various concentrations (heating and cooling cycles are symbolized by the filled and unfilled symbols, respectively).

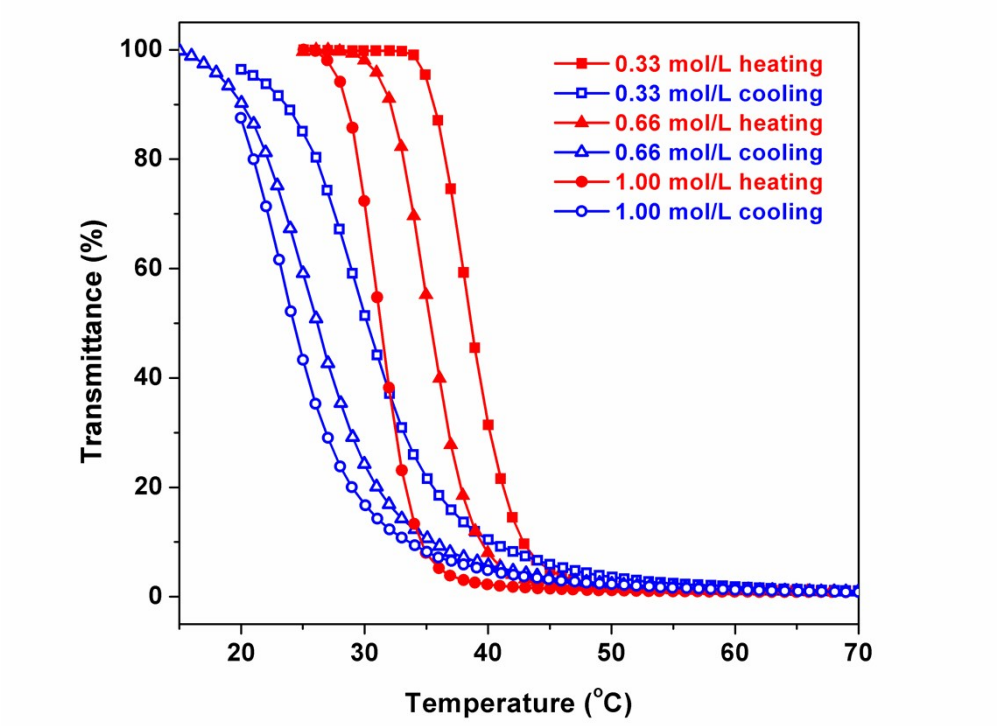


Figure S14. Plots of transmittance at λ = 450 nm *versus* temperature for the sample **6** of 3.0 mg/mL aqueous solution with the addition of NaCl at various concentrations (heating and cooling cycles are symbolized by the filled and unfilled symbols, respectively).

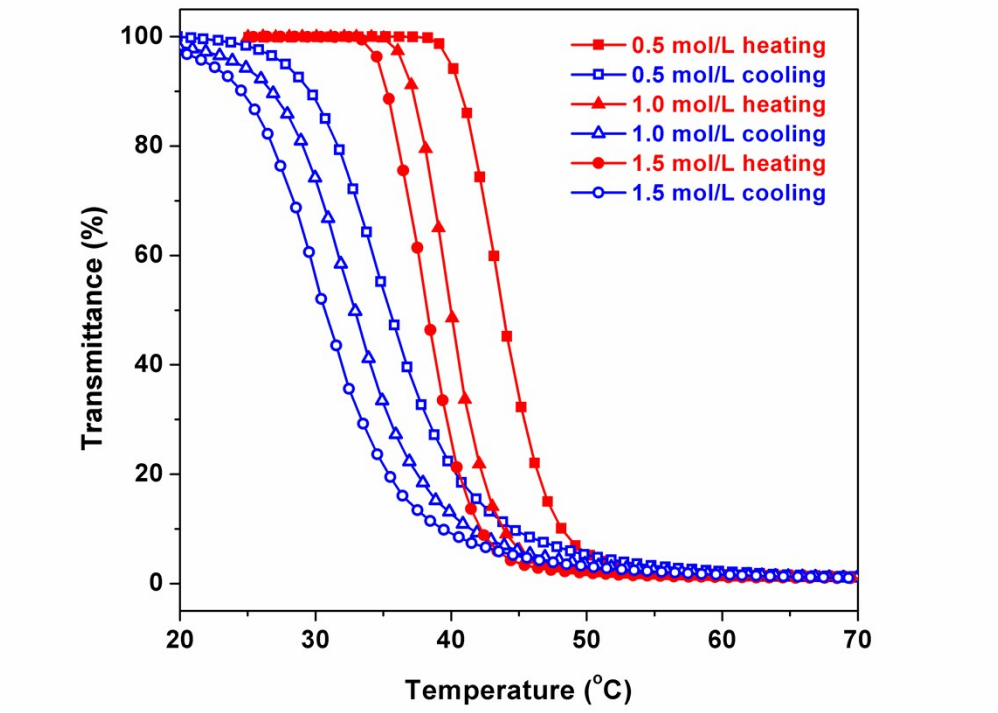


Figure S15. Plots of transmittance at λ = 450 nm *versus* temperature for the sample **6** of 3.0 mg/mL aqueous solution with the addition of NaBr at various concentrations (heating and cooling cycles are symbolized by the filled and unfilled symbols, respectively).

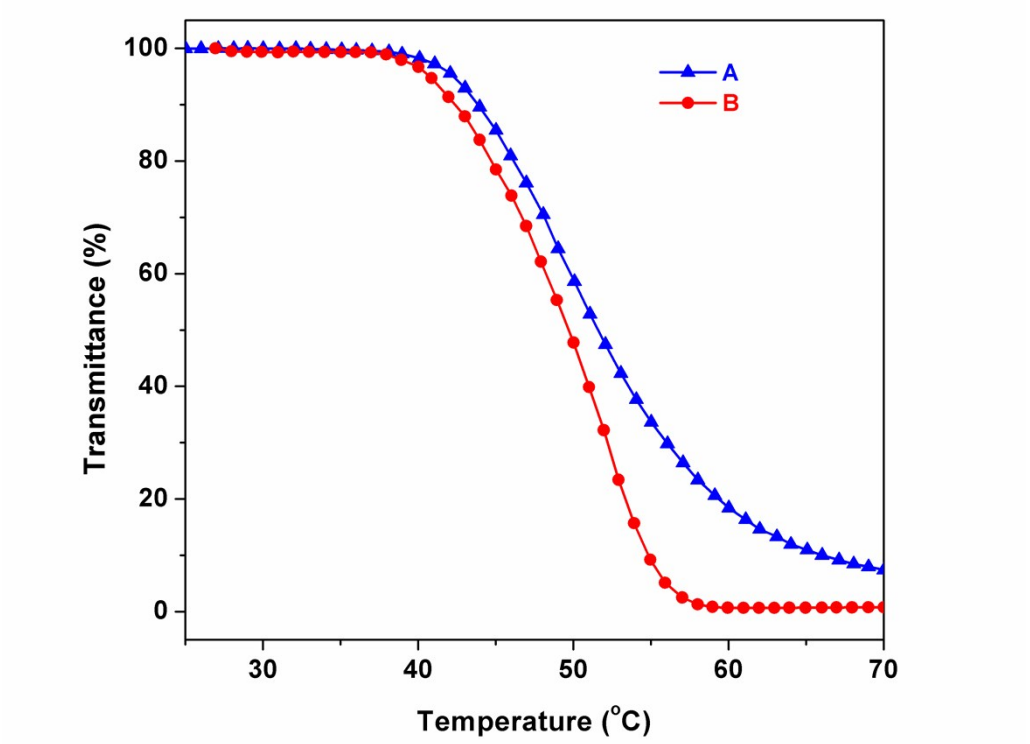


Figure S16. Plots of transmittance at λ = 450 nm *versus* temperature for (A) 0.83 mg/mL aqueous solution of sample **6** with the addition of 0.18 mol/L Na_2Cl and (B) 3.0 mg/mL aqueous solution of sample **6**.

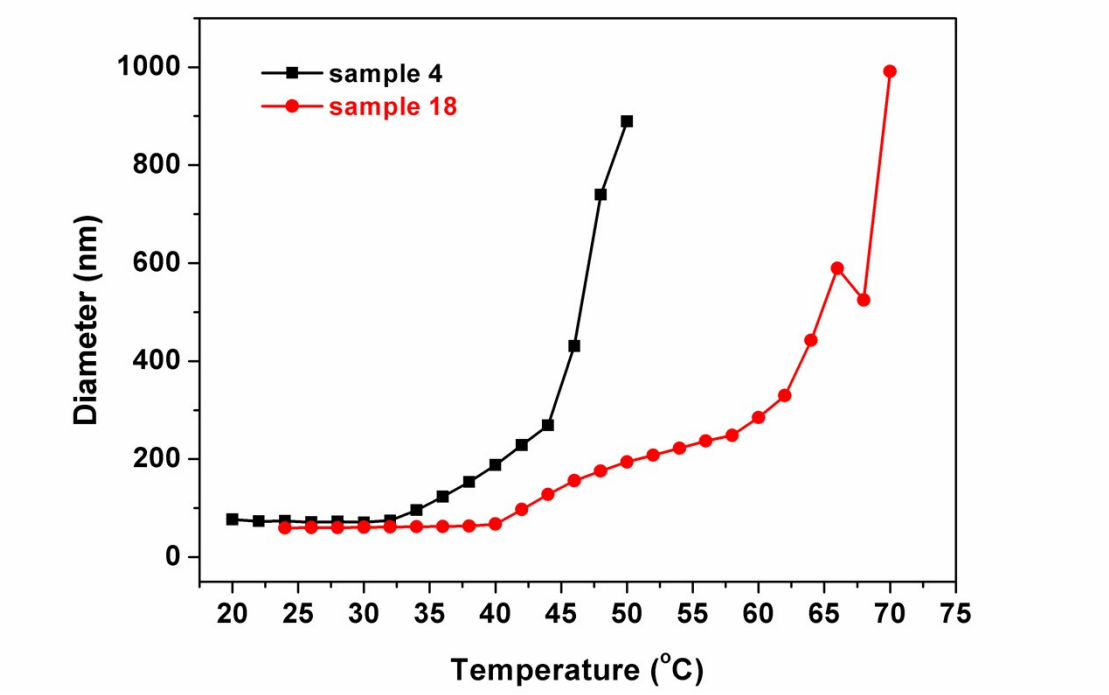


Figure S17. Aggregations diameter *versus* temperature for the aqueous solutions of sample **4** and sample **18** at a concentration of 3.0 mg/mL.