

Supplementary Materials

Stepwise Thermo-responsive Amino Acid-derived Triblock Vinyl Polymers: ATRP Synthesis of Polymers, Aggregation and Gelation Properties *via* Flower-like Micelle Formation

Nobuyuki Higashi^{1,*}, Sho Matsubara¹, Shin-nosuke Nishimura¹ and Tomoyuki Koga^{1,*}

Table S1. Characterization of poly(NAAMe₅₃-*b*-NAGMe₂₄₀-*b*-NAAMe₅₃) by means of SEC analysis and ¹H NMR spectroscopy.

run	Polymn. time (min)	M_n^a	PDI ^b	$2m/n^a$
1	15	40100	1.25	240/18
2	30	51100	1.35	240/53
3	360	57100	1.71	240/72

^a¹H NMR, ^bSEC analysis

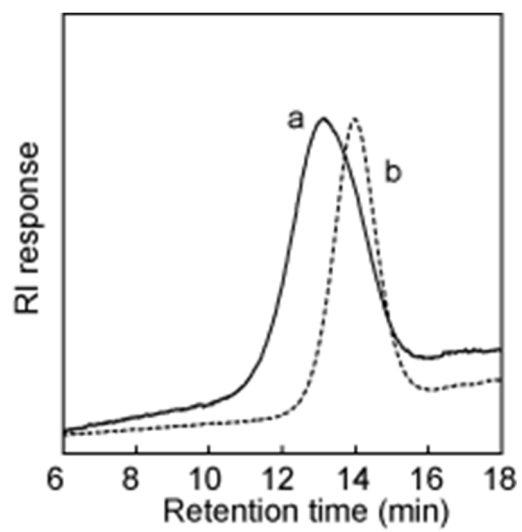


Figure S1. SEC traces of poly(NAAMe₅₃-*b*-NAGMe₂₄₀-*b*-NAAMe₅₃) (a) and poly(NAGMe₂₄₀) (macro-initiator) (b) recorded at 40 °C in DMF.

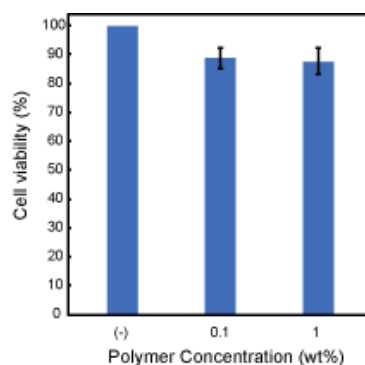


Figure S2. Viability of mouse fibroblast cells (NIH/3T3) cultured for 24 h in the presence of triblock copolymer poly(NAAMe₅₃-*b*-NAGMe₂₄₀-*b*-NAAMe₅₃) using the MTT assay. The 100% viability corresponds to the cells cultivated in the absence of the block copolymer. The experiment was performed in triplicates, in which six samples were measured per a trial.

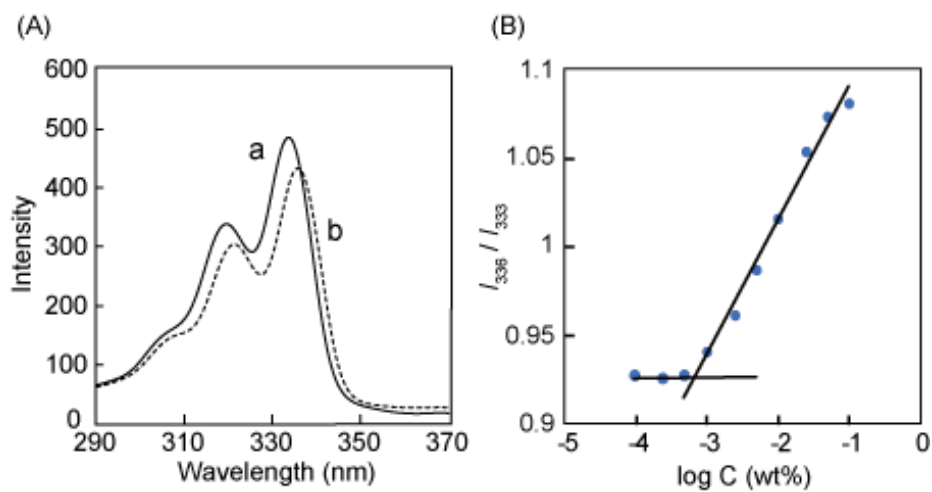


Figure S3. (A) Fluorescence excitation spectra of pyrene in poly(NAAMe₅₃-*b*-NAGMe₂₄₀-*b*-NAAMe₅₃) aqueous solutions at 1.0 × 10⁻⁴ wt% (a) and at 0.1 wt % (b), 35 °C. (B) Intensity ratio (I_{336}/I_{333}) obtained from the fluorescence excitation spectra of pyrene as a function of triblock copolymer concentration at 35 °C.

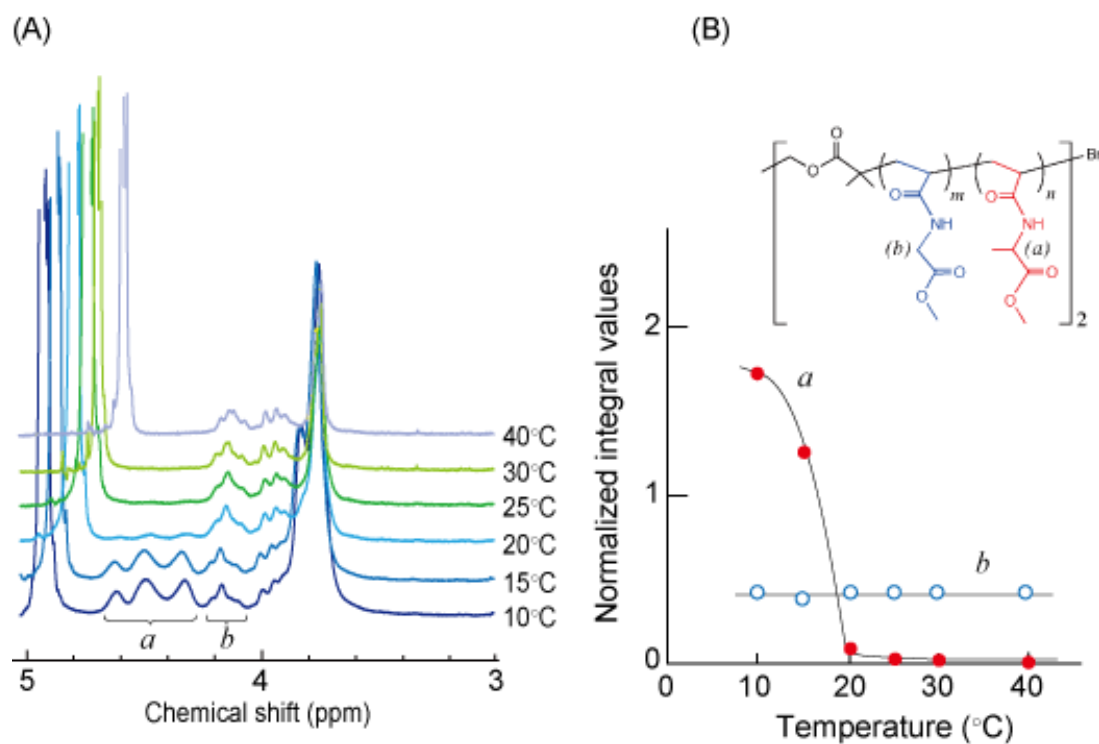


Figure S4. (A) ^1H NMR spectra of poly(NAAMe₅₃-*b*-NAGMe₂₄₀-*b*-NAAMe₅₃) in D₂O at different temperatures as indicated. Peaks of (a) and (b) in the spectra are assigned to the protons in the molecular structure as drawn in the inset. (B) Temperature dependences of the normalized peak intensities for such protons with PSS as an internal standard.

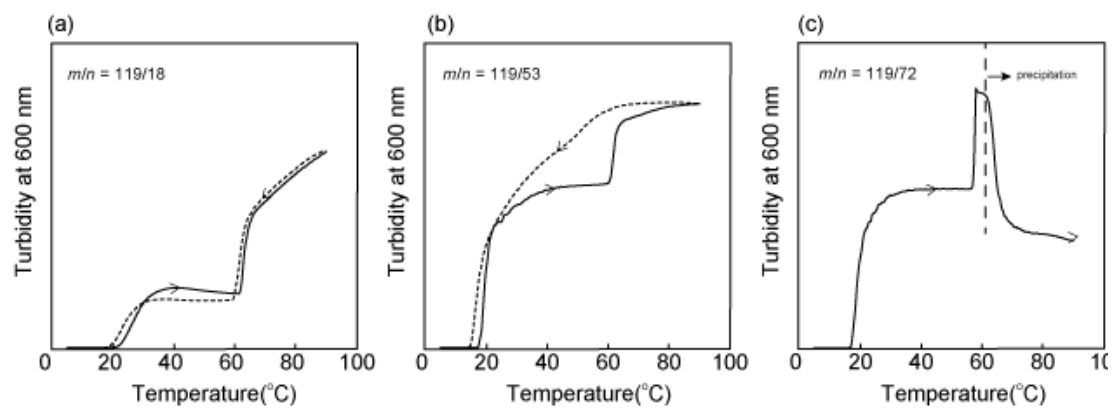


Figure S5. Comparison of the turbidity curves of triblock copolymers poly(NAAMe_n - b - NAGMe_{240} - b - NAAMe_n) (a: $n=18$; b: $n=53$; c: $n=72$) in water (0.25 wt %).

