Electronic Supplementary Material (ESI) for Materials Advances.

[Supplementary Information]

Thermo-responsive injectable hydrogels from linear and star-shaped block copolymers composed of amino acid-derived vinyl polymer and poly(ethylene glycol) for biomedical applications

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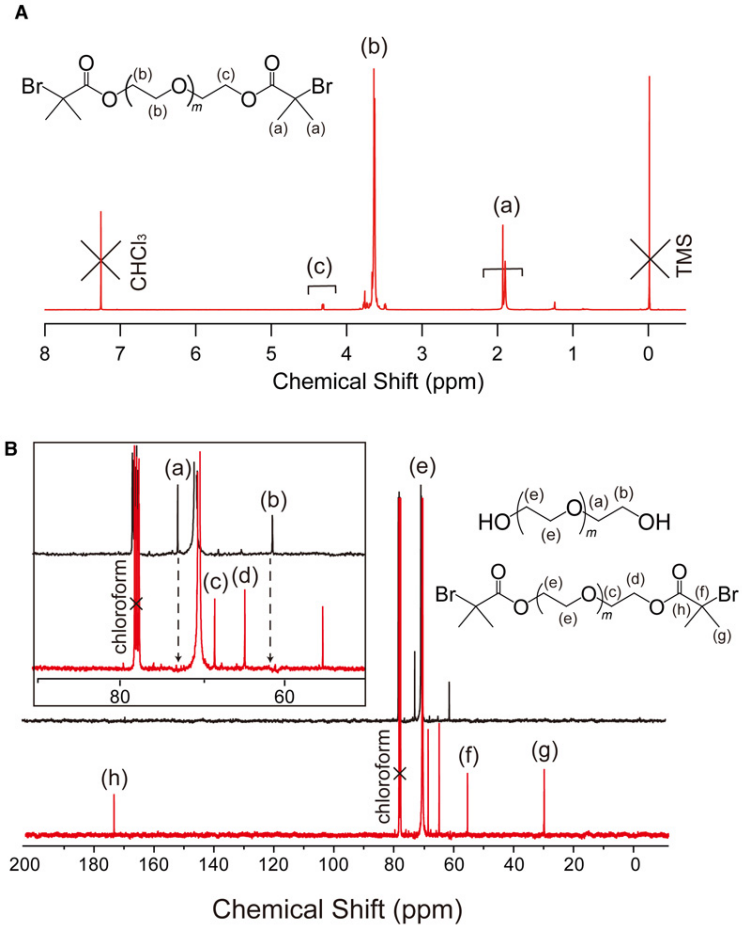

Figure S1. (A) ^{1}H-NMR spectrum of the macroinitiator, PEG-Br_2, and (B) ^{13}C-NMR spectra of the PEG-Br_2 (red line) and PEG (black line) in $CDCl_3$ at 25 °C (Internal standard: TMS). The inset in (B) shows the magnitude spectra.

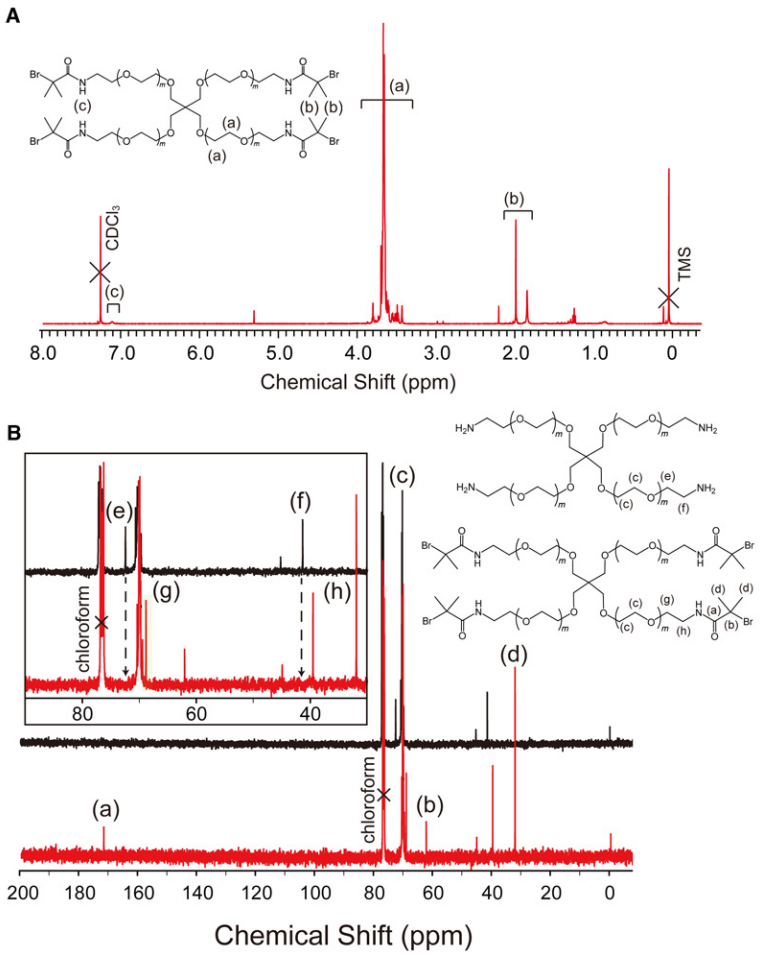

Figure S2. (A) ^{1}H-NMR spectrum of the macroinitiator, 4-arm PEG-Br_4, and (B) ^{13}C-NMR spectra of the 4-arm PEG-Br_4 (red line) and 4-arm PEG-NH_2 (black line) in $CDCl_3$ at 25 °C (Internal standard: TMS). The inset in (B) shows the magnitude spectra.

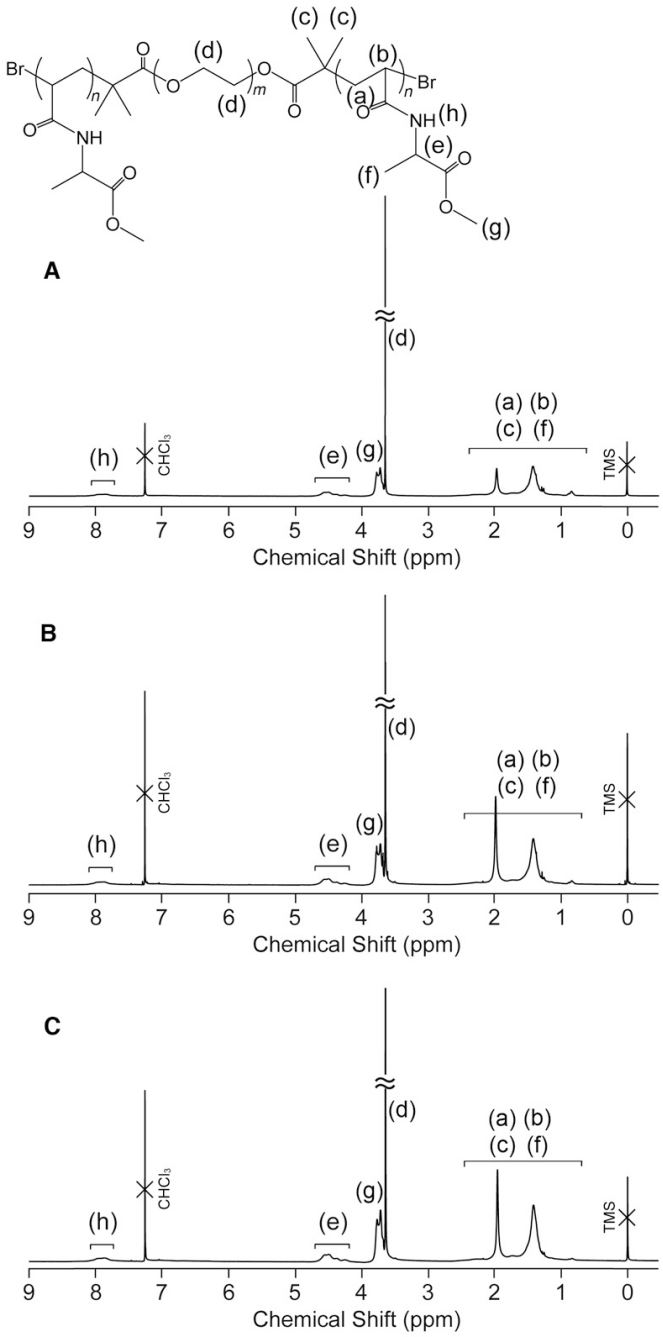

Figure S3. ^{1}H-NMR spectra of the linear-type PNAAMe/PEG block copolymers, $\mathbf{1_n}$; *n*=101 (A), 250 (B), and 321 (C) in $CDCl_3$ at 25 °C (Internal standard: TMS).

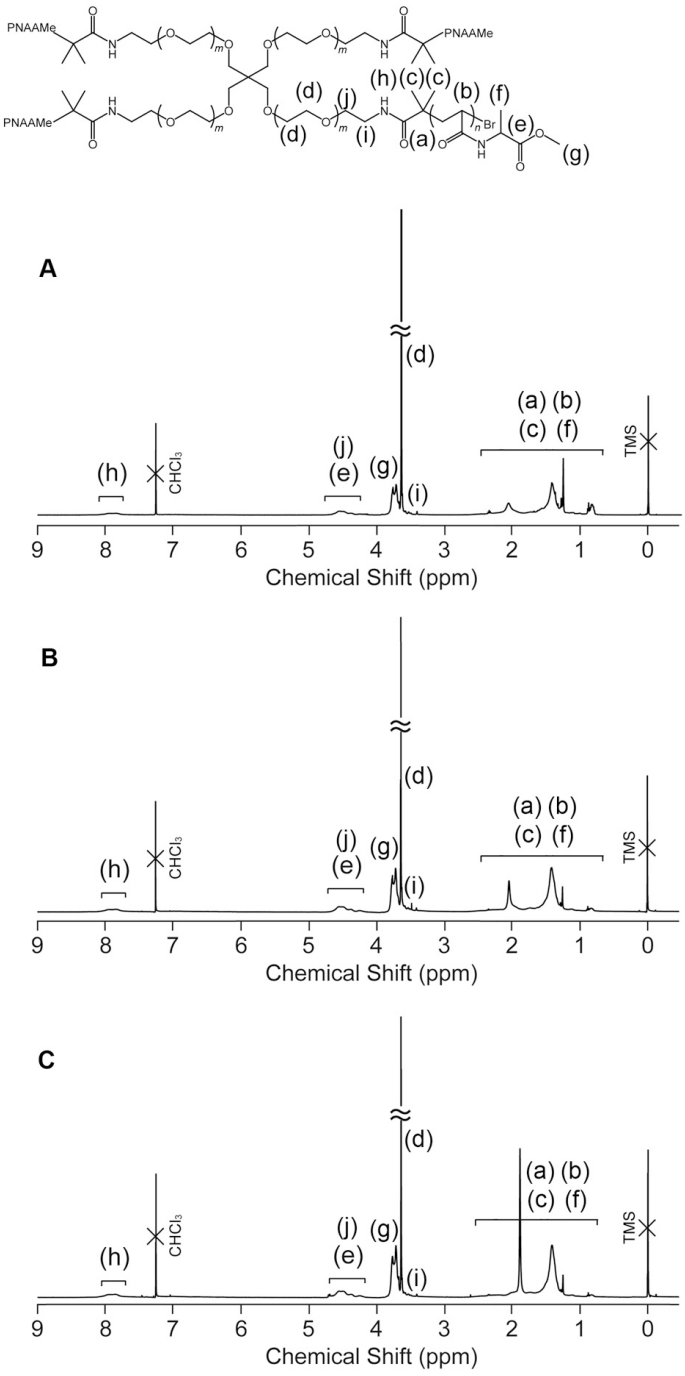

Figure S4. ^{1}H-NMR spectra of the star-shape PNAAMe/PEG block copolymers, $\mathbf{2_n}$; *n*=28 (A), 66 (B), and 118 (C) in $CDCl_3$ at 25 °C (Internal standard: TMS).

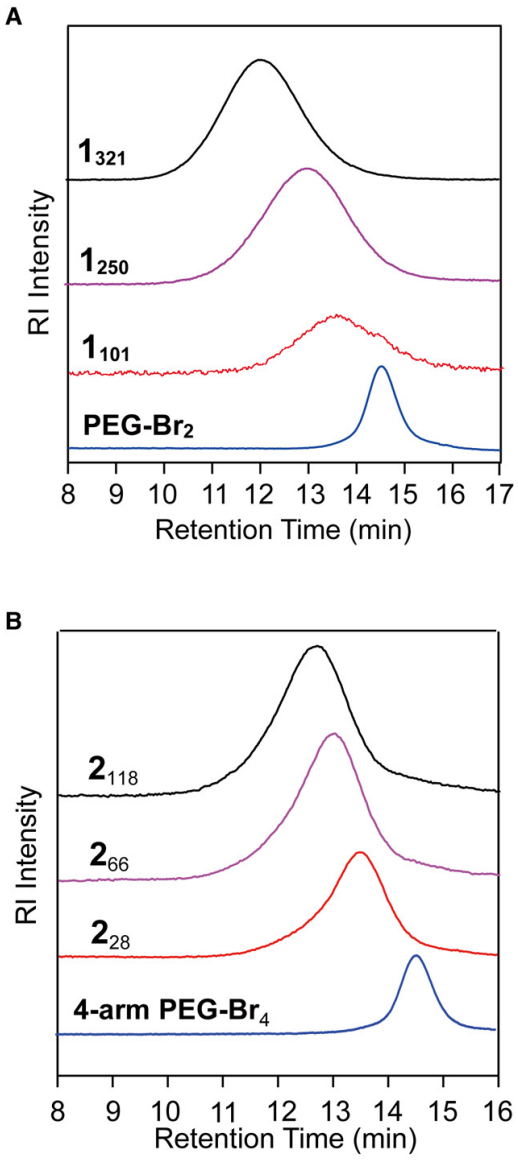

Figure S5. SEC charts (eluent: DMF (10 mM LiBr), 40 °C) of linear-type (**1**$_n$) (A) and star-type (**2**$_n$) (B) PNAAMe/PEG block copolymers. In these figures, SEC charts for corresponding macroinitiators were also included for comparison.

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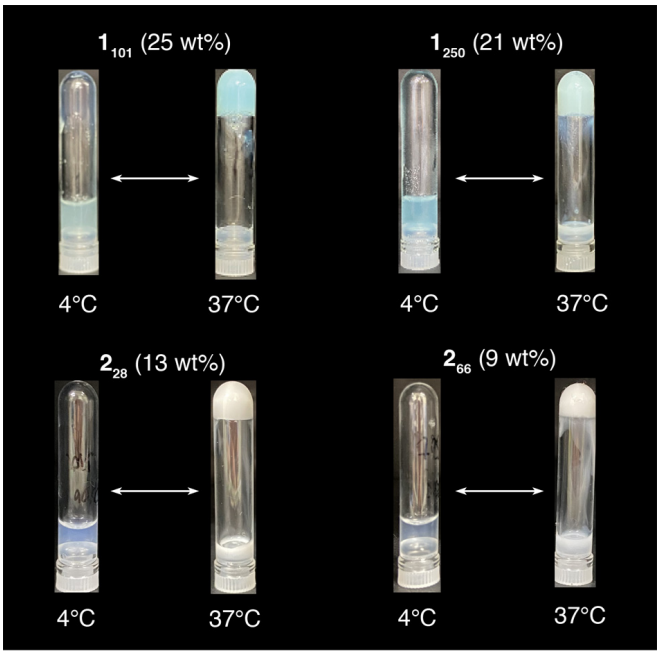

Figure S6. Photographs of thermo-reversible hydrogel formations of $\mathbf{1}_{101}$, $\mathbf{1}_{250}$, $\mathbf{2}_{28}$, and $\mathbf{2}_{66}$ at various concentrations indicated.

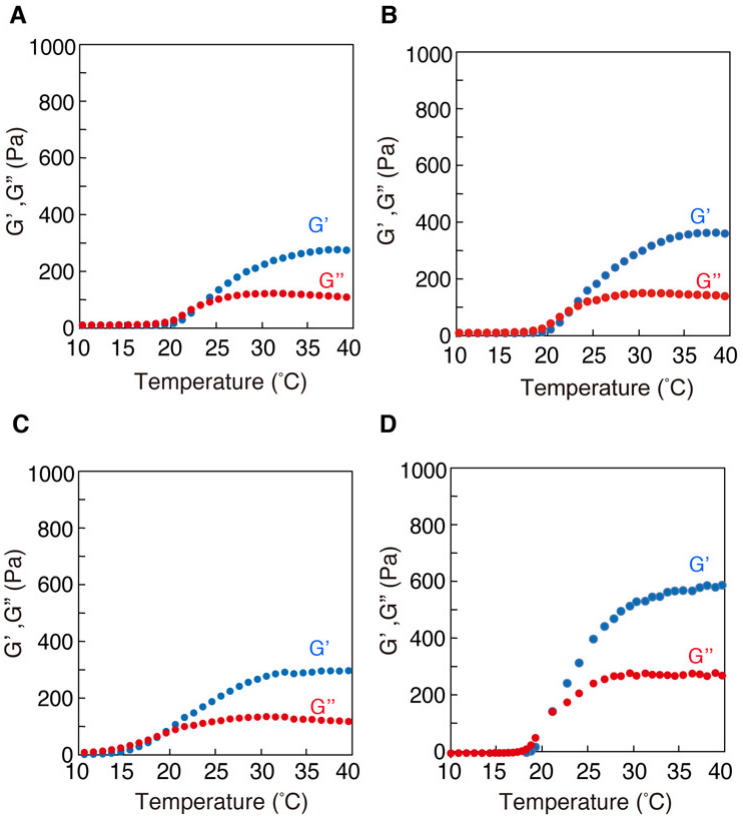

Figure S7. Temperature dependences of the storage (G') and loss (G") moduli for $\mathbf{1}_{101}$ (A), $\mathbf{1}_{250}$ (B), $\mathbf{2}_{28}$ (C), and $\mathbf{2}_{66}$ (D) from 10 °C to 40 °C at 6.3 rad/s and 1% strain. [polymer]=25 wt%.

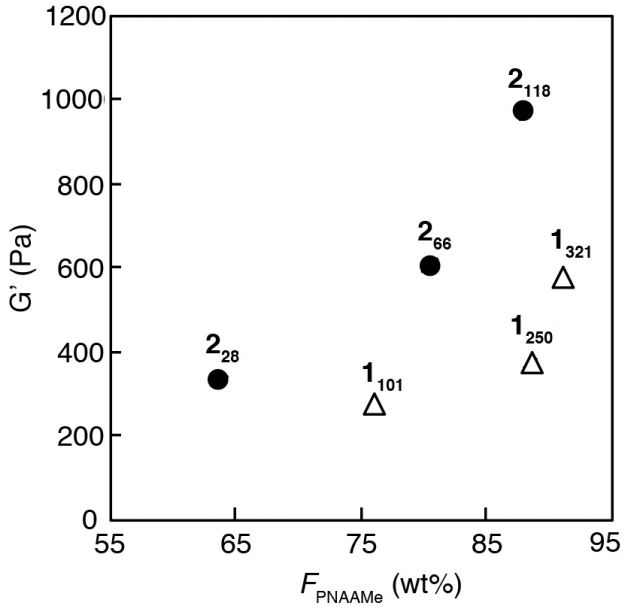

Figure S8. Plots of storage moduli (G') of $\mathbf{1_n}$ (open triangle) and $\mathbf{2_n}$-hydrogel (closed circle) (37°C, 6.3 rad/s, and strain 1%) as a function of F_{PNAAMe} values (PNAAMe length). [polymer]=25 wt%.

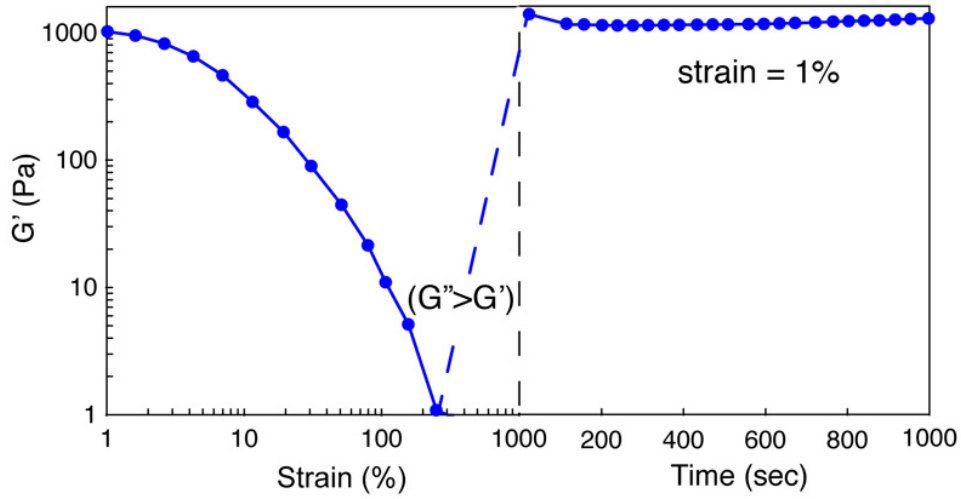

Figure S9. Recovery of stiffness (G') of $\mathbf{2}_{118}$-hydrogel (25 wt%) at 1% strain amplitude after large-amplitude oscillatory breakdown.

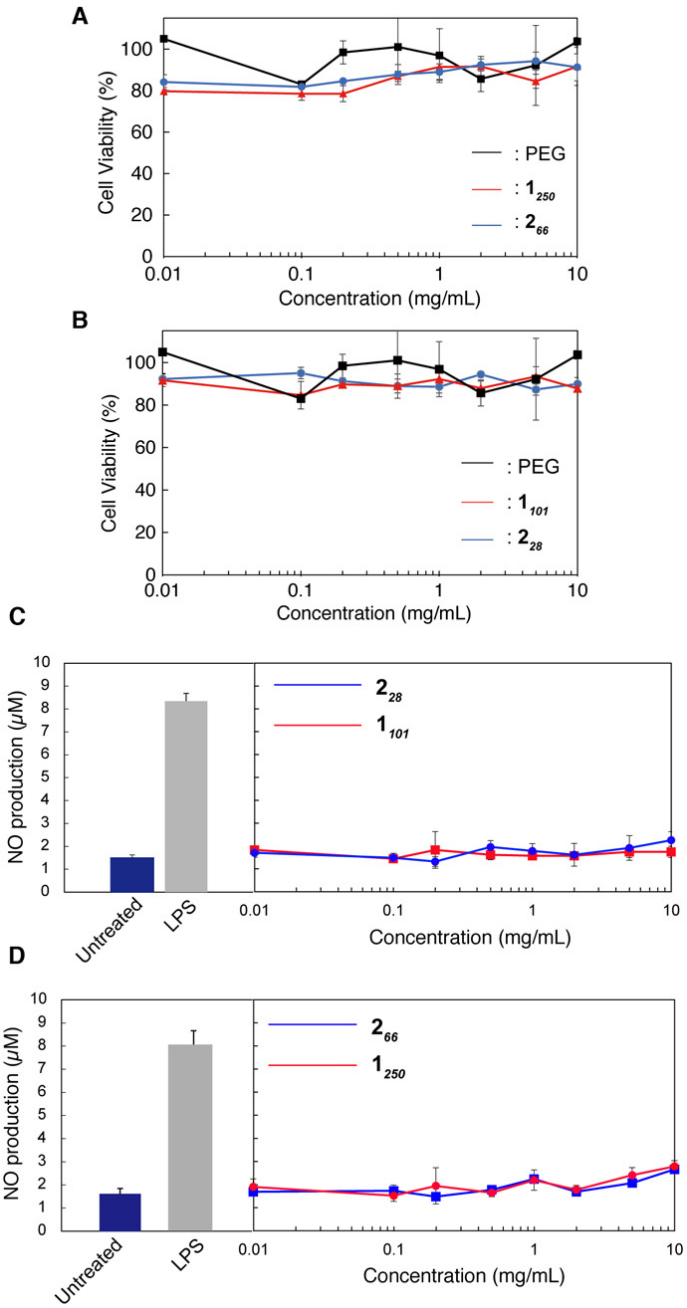

Figure S10. Biocompatibility tests for the PNAAMe/PEG block copolymers, $\mathbf{1}_{101}$, $\mathbf{1}_{250}$, $\mathbf{2}_{28}$, and $\mathbf{2}_{66}$. (A and B) Cell viability (RAW264.7) cultured for 24 h in the presence of the polymers (0.01–10 mg/mL) using the WST-8 assay. (C and D) NO production test of the polymers using RAW264.7 cultured for 24 h.