Supplementary Information for manuscript Entitled with

Tuning Phase Transition Temperature of Thermal-responsive OEGylated Poly-$_L$-glutamate via Random Copolymerization with $_L$-Alanine

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Characterization

^{1}H NMR spectra were recorded on a Bruker AV400 FT-NMR spectrometer (400 MHz). Gel permeation chromatography/Multi-angle light scattering (GPC/MALS) was performed at 50 °C using an SSI pump connected to the Wyatt Optilab DSP and Wyatt DAWN EOS light scattering (LS) detectors with 0.02 M LiBr in DMF as the eluent at flow rate of 1.0 mL/min. The refractive index increment (d*n*/d*c*) was measured using a Wyatt's rEX DRI detector and an Astra software d*n*/d*c* template. The d*n*/d*c* values of poly-$_L$-EG_2Glu in DMF containing 0.02 mol/L LiBr salt at wavelength of 658 nm are 0.0582 mL g^{-1}. All infrared spectroscopy measurements were performed using a Nicolet Avatar 330 FTIR spectrometer. The solid samples was milled with KBr at mass ratio of 1:100 and pressed into disk before IR measurements. FTIR spectra were analyzed using Multiple Peak Fit method in Origin 8.0 to calculate the composition of secondary structure. The clouding points (CPs) were determined by monitoring the transmittance of a 500 nm light beam through a quartz sample cell at concentration of 1 mg/mL on a Shimadzu UV is spectrometer and defined as the temperature corresponding to 50% transmittance of aqueous solution during the heating process. Circular dichroism spectra were recorded on a JASCO J-815 CD Spectrometer. Sample solutions of 0.2 mg/mL were placed into quartz cells with a path length of 1.0 mm. The content of secondary structure was calculated by the Provencher &Glockner method using the reference database SP175. The transmission electron microscopy (TEM) characterizations were performed on a JEM-2100 microscope. The TEM samples were prepared by cast sample solution on a carbon-coated copper grid and stained with 2.0% uranyl acetate

aqueous solution. Atomic force microscopy (AFM) was performed in tapping mode using a Multimode 8 scanning probe microscope (NanoScope V controller, Veeco, Santa Barbara, CA) in ambient atmosphere. Height signal images were recorded with 512×512 data points. All samples were tapped on freshly cleaved mica surfaces at room temperature. Rheological measurements were performed on an Anton Paar Modular Compact Rheometer (MCR 502) with 25 mm diameter parallel plate geometry and 0.1 mm gap distance. The rheometer was equilibrated at 20 °C prior to sample loading. Low-viscosity mineral oil was used to insulate the sides of the plate in order to suppress evaporation. Strain (γ) sweep experiments were performed to determine the linear viscoelastic regime (ω=1.0 rad/s, 20 °C). Frequency (ω) sweep experiments were performed with strain being 0.8 %. Dynamic sweep experiments were performed that the storage modulus (G′) and loss modulus (G″) were determined as a function of time and temperature variation from 20 to 50 °C with a heating rate of 0.5 °C/min (ω=2.0 rad/s, γ = 0.8%).

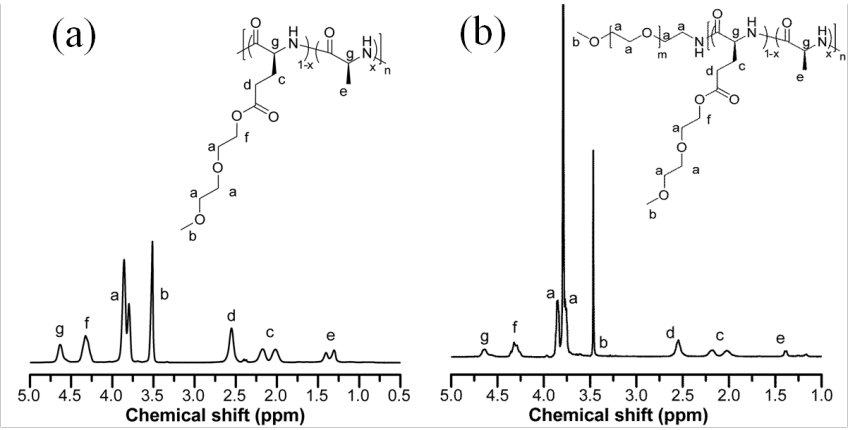

Fig. S1 ^{1}H NMR spectra of Poly-(EG_2Glu-co-Ala) (a) and mPEG-*b*-Poly-(EG_2Glu-co-Ala) (b) in $CDCl_3$/CF_3COOD *v*/*v* 1/1.

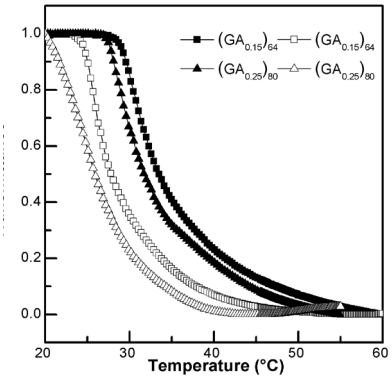

Fig. S2 Plots of transmittance of sample P3 and P8 as a function of temperature for anqueous solutions (1.0 mg/ mL). Filled symbol: heating; Open symbol: cooling.

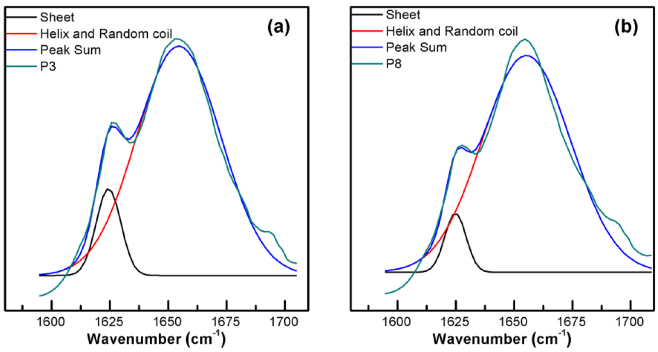

Fig. S3 FTIR spectra of (a) **P3** and (b) **P8** after the Multiple Peak Fit using Gauss peak function.

Table S1 Molecular parameters of Poly-(EG_2Glu-co-Leu).

Sample	Structure[a]	Leu(mol%)[a]	Mn(kDa)[b]	PDI[b]
P18	$(GL_{0.10})_{94}$	10	20.7	1.15
P19	$(GL_{0.14})_{96}$	14	20.0	1.12
P20	$(GL_{0.20})_{91}$	20	19.5	1.10
P21	$(GL_{0.24})_{95}$	24	19.0	1.17

[a] Determined from ^{1}H NMR spectra; G: EG_2Glu segments, L: Leu segments. [b] Determined from GPC analysis.

Table S2 Molecular parameters of mPEG-*b*-Poly-(EG_2Glu-co-Ala).

Sample	mPEG-NH_2[a]	Feed ratio[b]		DP[c]		PDI[d]	CGC(wt%)[e]
		EG_2Glu	Ala	EG_2Glu	Ala		
P11	44	30	5	30	6	1.10	5.0
P12	44	40	5	38	6	1.11	6.0
P13	44	45	11	44	8	1.15	8.5
P14	113	30	10	28	11	1.08	4.5
P15	113	30	6	31	6	1.11	5.5
P16	113	40	8	37	6	1.09	7.5
P17	113	40	13	40	11	1.15	7.0

[a] DP of mPEG-NH_2. [b] Feed ratio of NCA monomer to mPEG-NH_2 initiator. [c] Determined from ^{1}H NMR spectra. [d] obtained from GPC/MALS. [e] critical gelation concentration determined by the inverted tube method.

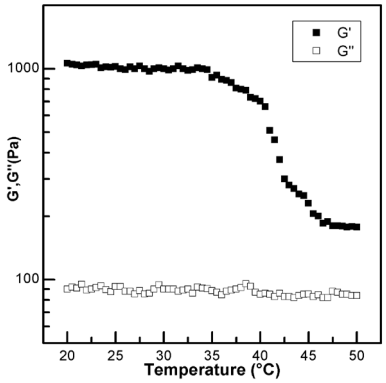

Fig. S4 G′ (■) and G″ (□) of sample P14 hydrogel as function of temperature at 5.0 wt %.

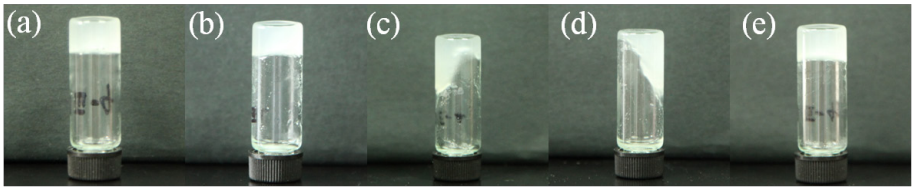

Fig. S5 Photographs of sample P14 at 5.0 wt% (a) room temperature (25°C); (b) 40°C; (c) 43°C; (d) 46°C and (e) recover at room temperature (25°C) after mechanical vortex.