Electronic Supplementary Information

Poly(lactic acid)/poly(ethylene glycol) stereocomplexed physical hydrogels showing thermally-induced gel-sol-gel multiple phase transitions

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Measurements

Gel Permeation Chromatography (GPC). Molecular weights were measured by GPC (Waters Co., Milford, MA, USA) at 30 ℃. The instrument was equipped with a Waters 2414 refractive index detector and three Waters Styragel columns (Styragel HR2, HR3 and HR4). THF was used as the mobile phase with a flow rate of 1.0 mL/min. Molecular weight was calibrated by using polystyrene as the standard.

Dynamic Light Scattering (DLS). Hydrodynamic diameter (D_h) of copolymers and copolymer mixture in dilute solution was measured by DLS (Zetasizer Nano ZS90, Malvern Co.). The micellar solutions (0.02 wt%) of PEG–PDLA and PLLA–PEG–PLLA were separately prepared by solvent exchange method.[1] The micellar solutions were filtered through a 0.45 μm membrane before the measurement at 20 ℃.

Reference

[1] Ma, C.; Pan, P.; Shan, G.; Bao, Y.; Fujita, M.; Maeda, M. Core–Shell Structure, Biodegradation, and Drug Release Behavior of Poly(lactic acid)/Poly(ethylene glycol) Block Copolymer Micelles Tuned by Macromolecular Stereostructure. *Langmuir* **2015,** *31*, 1527–1536.

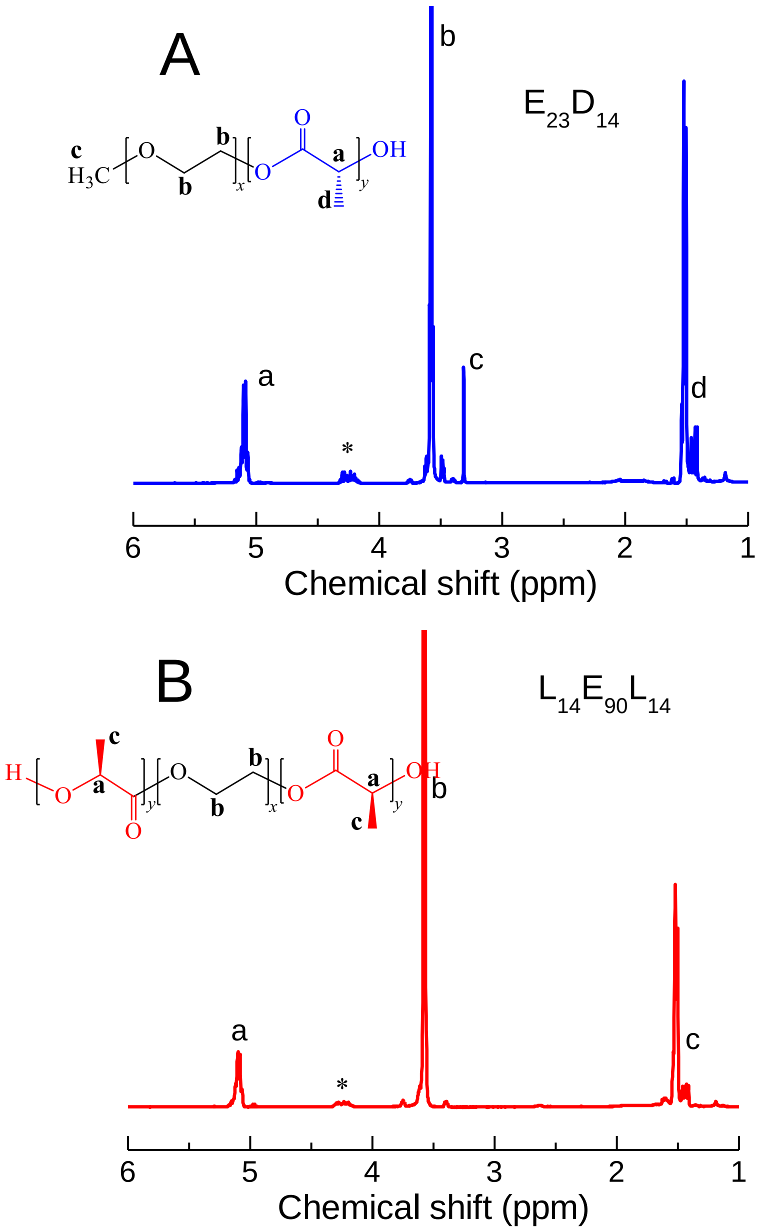

Fig. S1 Representative ^{1}H NMR spectra of PEG-PDLA diblock and PLLA-PEG-PLLA triblock copolymers: (A) PEG-PDLA; (B) PLLA-PEG-PLLA. The peak at 4.3 ppm (indicated by asterisk) is assigned to the terminal methine proton of PLLA/PDLA blocks and the terminal methylene protons of PEG block that is connected to PLA.

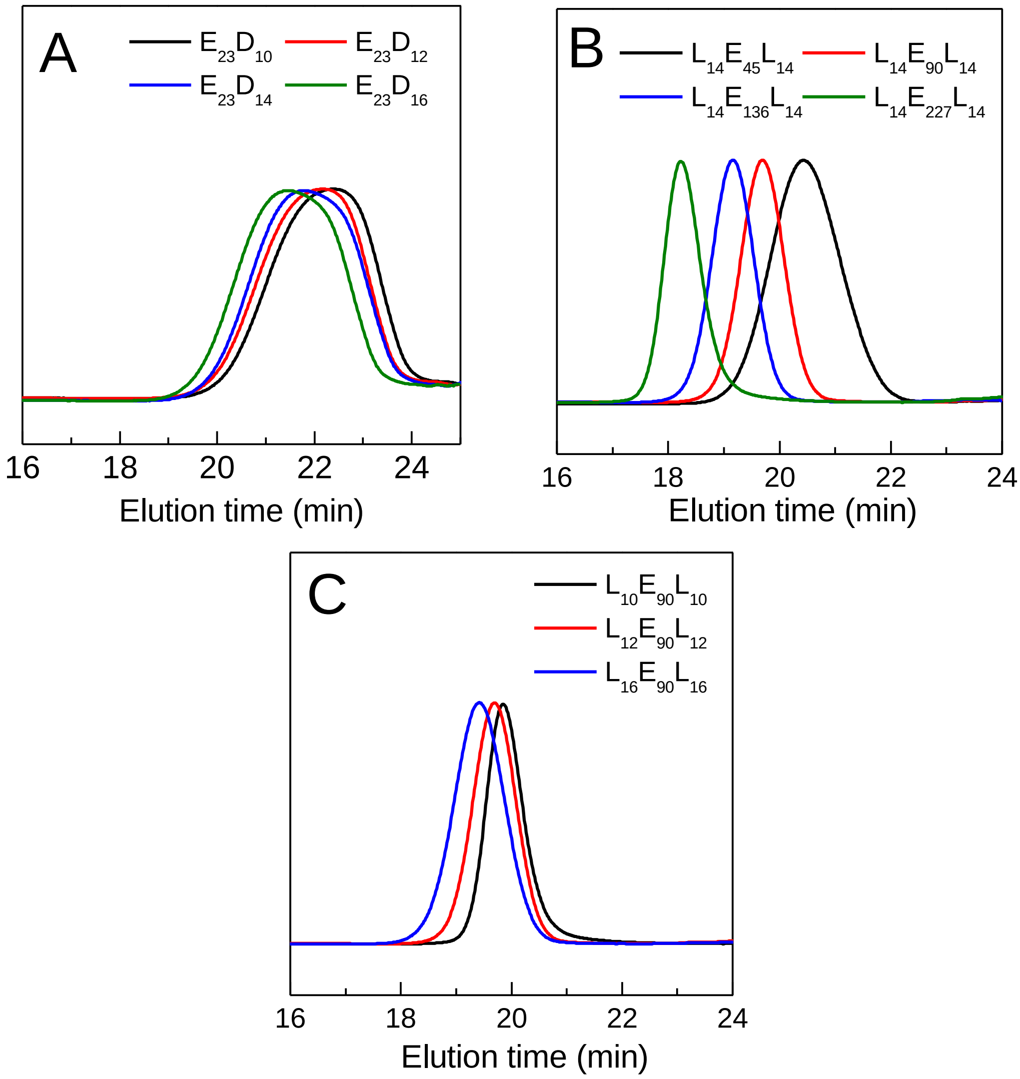

Fig. S2 GPC traces of PEG-PDLA diblock and PLLA-PEG-PLLA triblock copolymers: (A) PEG-PDLA diblock copolymers with different PDLA block lengths; (B) PLLA-PEG-PLLA triblock copolymer with different PEG block lengths; (C) PLLA-PEG-PLLA triblock copolymer with different PLLA block lengths.

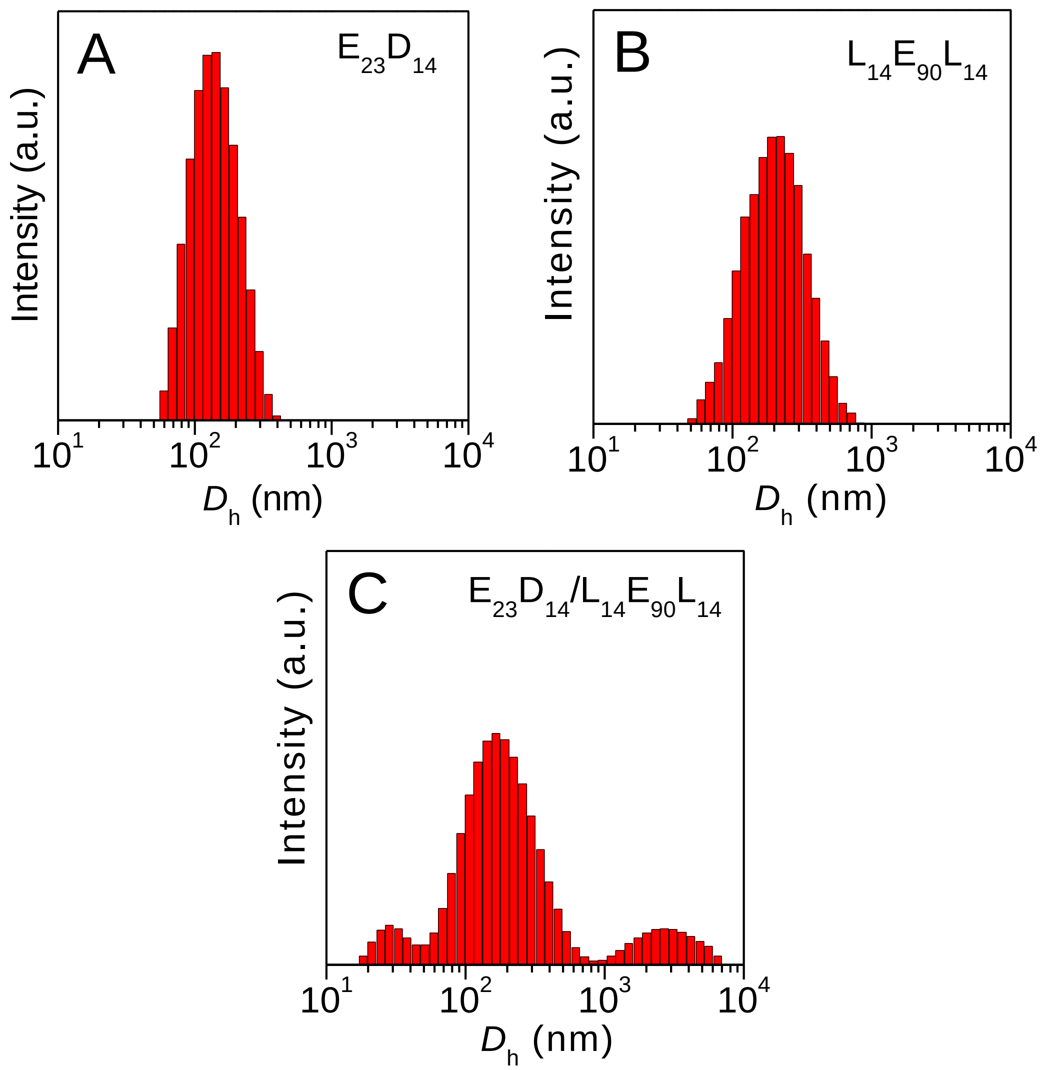

Fig. S3 Hydrodynamic diameter (D_h) and its distribution for PEG-PDLA, PLLA-PEG-PLLA, and PEG-PDLA/PLLA-PEG-PLLA enantiomeric mixture in water solution (0.02 wt%) at 20 ℃: (A) $E_{23}D_{14}$, (B) $L_{14}E_{90}L_{14}$, (C) $E_{23}D_{14}/L_{14}E_{90}L_{14}$ 5/5 mixture.

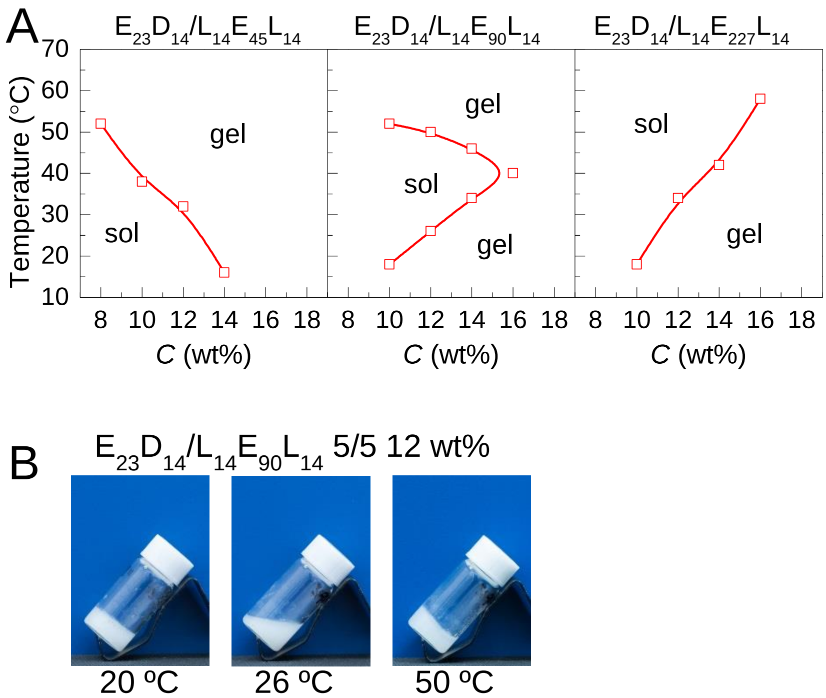

Fig. S4 (A) Phase diagrams of premixed PEG–PDLA/PLLA–PEG–PLLA 5/5 mixtures with the different concentrations in water. (B) Digital photographs of $E_{23}D_{14}/L_{14}E_{90}L_{14}$ 5/5 mixture (12 wt%) at different temperatures. In the premixing procedure, PEG-PDLA and PLLA-PEG-PLLA copolymers were mixed and dissolved in water together.