SUPPLEMENTARY INFORMATION

for:

Impact of Stereochemistry on Rheology and Nanostructure of PLA-PEO-PLA Triblocks: Stiff Gels at Intermediate L/D-lactide Ratios

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EXPERIMENTAL

Measurements: ^{1}H NMR spectra were recorded at room temperature with a Bruker spectrometer operating at 400, 500 and 700 MHz by using $CDCl_3$ as solvent with the solvent peak used as reference (δ 7.27 ppm). GPC data for all polymers were obtained at 40 °C with THF (HPLC grade, J.T. Baker) as the eluent at a flow rate of 1.0 mL/min. The apparatus consisted of a K-501 pump (Knauer), a K-3800 Basic Autosampler (Marathon), two PLgel 5 μm Mixed-D columns (300 × 7.5 mm, rated for polymers between 200 and 400 000 g/mol, Polymer Laboratories), and a PL-ELS 1000 Evaporative Light Scattering Detector (Polymer Laboratories). A PL Datastream unit (Polymer Laboratories) was used to acquire data, which were analyzed based on a calibration curve constructed from narrow polydispersity polystyrene standards in the molecular weight range of 580−400 000 g/mol (EasiCal PS-2, Polymer Laboratories)

MATERIALS

Polyethylene oxide (10k), D/L-lactide (a racemic mixture of D-lactide and L-lactide) and L-lactide, were obtained from Alfa Aesar. D/L-lactide and L-lactide were also obtained from Acros Organics and Sigma Aldrich. Ethyl acetate, toluene and dichloromethane (DCM) were obtained from BDH Chemicals. Tetrahydrofuran, 99.9% Extra Dry, stabilized (THF), Dichloromethane, 99.9% Extra Dry (DCM) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was obtained from Acros Organics. THF, benzene and methylene chloride were also obtained from EMD Millipore Corporation. 1,5,7-Triazabicyclo[4,4,0]dec-5-ene (TBD) was obtained from Santa Cruz Biotechnology Incorporated. Polyethylene oxide (PEO 10k, Alfa Aesar) was freeze-dried or vacuum dried at 40 °C for two days before stored in the glove box prior to polymerizations. D/L-Lactide and L-lactide from Acros Organics and Sigma Aldrich were both recrystallized inform either ethyl acetate or toluene and stored in the glove box. All other reagens were used without further purification.

Representative procedure for the DBU-catalyzed polymerization of lactide with Polyethylene oxide (10k). ***(S$_2$ 95/5)***

D/L-lactide (*rac*-LA, 0.62 g, 0.043 mmol) and L-lactide (L-LA, 0.62 g, 0.043 mmol) were weighed into separate vials in the glovebox, sealed with sure-seal caps and removed from the glove box. Dichloromethane (DCM, 6.0 mL) was added to each vial via a nitrogen purged syringe and swirled and sonicated to ensure complete dissolution. PEO 10 k (1.2 g, 0.12 mmol) in a round-bottom flask equipped with a magnetic stir bar was sealed with a rubber septum and removed from the glove box. D/L -lactide and L-lactide solutions were transferred to the round bottom flasks containing PEO, using the same syringes for the initial DCM transfer that were kept in the vials containing the lactide solutions. Subsequently, DBU was removed from the

glove box as a solution in DCM (0.04 g in 4.0 mL DCM from stock solution, 0.26 mmol, 5.5 mol%) via a capped syringe with needle and added to the stirring solution of lactide and PEO. The reaction was allowed to proceed for 4 hrs at room temperature. After 4 hrs was concentrated by a rotary evaporator. The crude polymer was then precipitated by addition into hexanes (~70 mL). The supernatant was subsequently decanted off, and the solid polymer was dried in a vacuum oven at 40 °C for 3 days. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.17 (m, –OOC–CH(CH3)–), 4.32 (m, –OOC–CH(CH3)–OH), 4.21 (m, COO–CH2– CH2–OPEO), 3.56 (m, –CH2–CH2–O–), 1.57 (d, –OOC–CH(CH3)–). Conversion by ^{1}H NMR = 96.8%. Yield = 83.5%

Table S1. Data for the polymerization of lactide with PEO as the macroinitiator in CH_2Cl_2.

Series	L-lactide (g)	L-lactide (mmol)	D,L-lactide (g)	D,L-lactide (mmol)	PEO 10Kg (g)	PEO 10Kg (mmol)	CH_2Cl_2 Added to LA (mL)	DBU Catalyst loading %	Conv.[a] %	total RU_{PLA} (Obs)[b]	total mass yield %	PDI[c]	M_n [d] (Kg/mol)
S_1 50/50			0.26	1.8	0.5	0.05	5	5.5	100*	74	94.7	1.27	15.3
S_2 50/50			0.62	4.3	1.2	0.12	12	6.5	95.5	88	95.3	1.21	16.3
S_1 75/25	0.13	0.9	0.13	0.9	0.5	0.05	5	5	100*	72	94.2	1.06	15.3
S_2 75/25	0.31	2.2	0.31	2.2	1.2	0.12	12	5.5	99.1	75	78.1	1.16	15.4
S_2 80/20	0.37	2.6	0.25	0.17	1.2	0.12	12	5.5	95.8	82	84.3	1.21	15.9
S_1 85/15	0.181	1.26	0.078	0.54	0.5	0.05	5	5	100*	72	88	1.06	15.2
S_2 85/15	0.44	3.0	0.18	1.3	1.2	0.12	12	5.5	99.2	77	94.2	1.1	15.5
S_1 90/10	0.207	0.144	0.052	0.36	0.5	0.05	5	5	100*	77	94.1	1.09	15.5
S_2 90/10	0.498	3.5	0.124	0.86	1.2	0.12	12	6	95.6	81	94.3	1.22	15.8
S_1 95/5	0.233	1.62	0.026	0.18	0.5	0.05	5	5	100*	74	93.2	1.07	15.3
S_2 95/5	0.56	3.9	0.062	0.043	1.2	0.12	12	6	96.8	81	83.5	1.17	16.1
S_1 100/0	0.26	1.8			0.5	0.05	5	5	100*	70	88.2	1.25	15
S_1 100/0	0.62	4.3					12	6.5	97.4	82	98.5	1.26	15.9

[a] Conversion estimated by 400 MHz ^{1}H NMR by comparison of polymer methine protons to residual monomer methine protons. For samples marked *, conversion was estimated using lower resolution 300 MHz NMR spectra. [b] Average number of PLA repeating units was estimated by comparing the integrated area of PLA protons to the integrated area of PEO methylene protons assuming a PEO M_n of 10 kg/mol. [c]PDI determined by PS calibrated GPC. [d]M_n (kg/mol) estimated by comparing the relative integrals of the methine protons of PLA and the methylene protons of PEO.

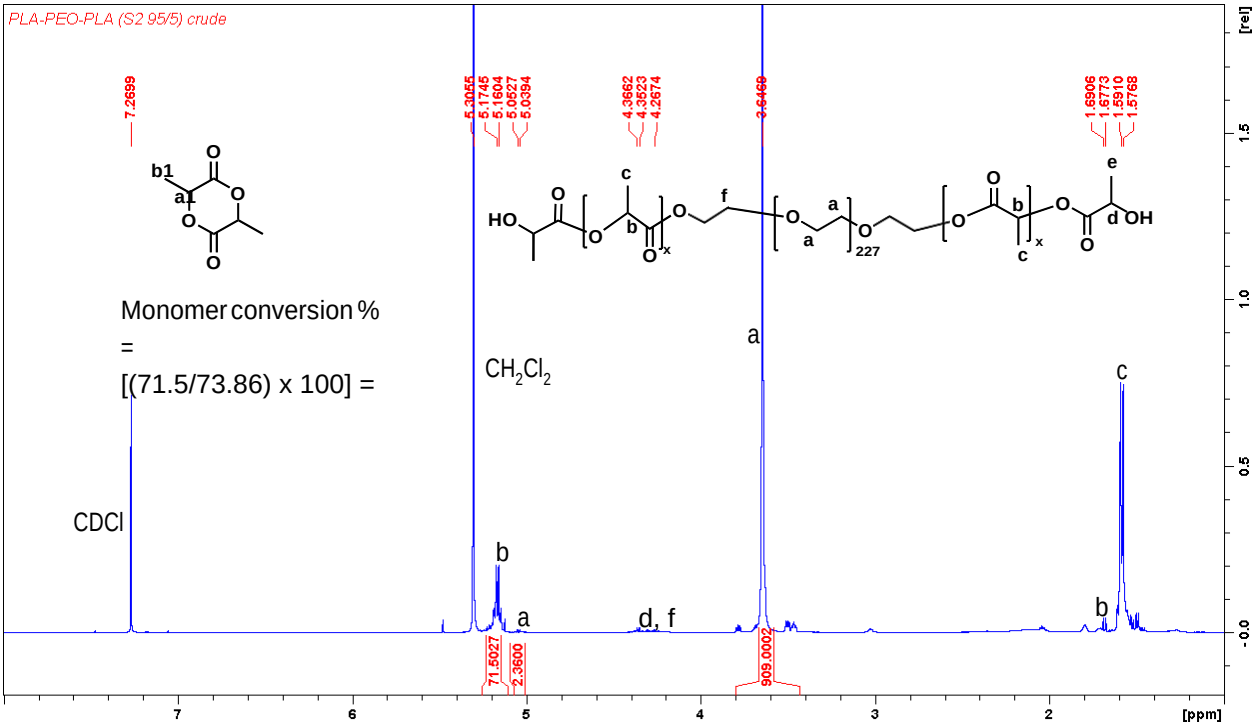


Figure S1. Representative ^{1}H NMR spectra of crude PLA-PEO-PLA triblock copolymers.

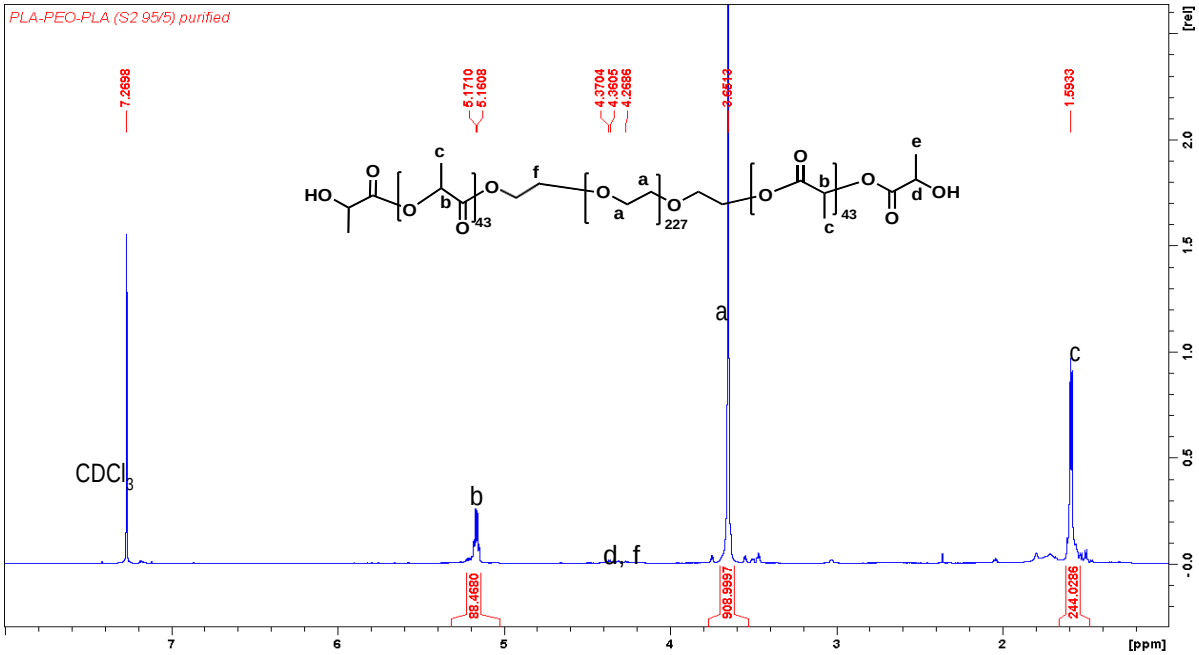


Figure S2. Representative ^{1}H NMR spectra of purified PLA-PEO-PLA triblock copolymers.

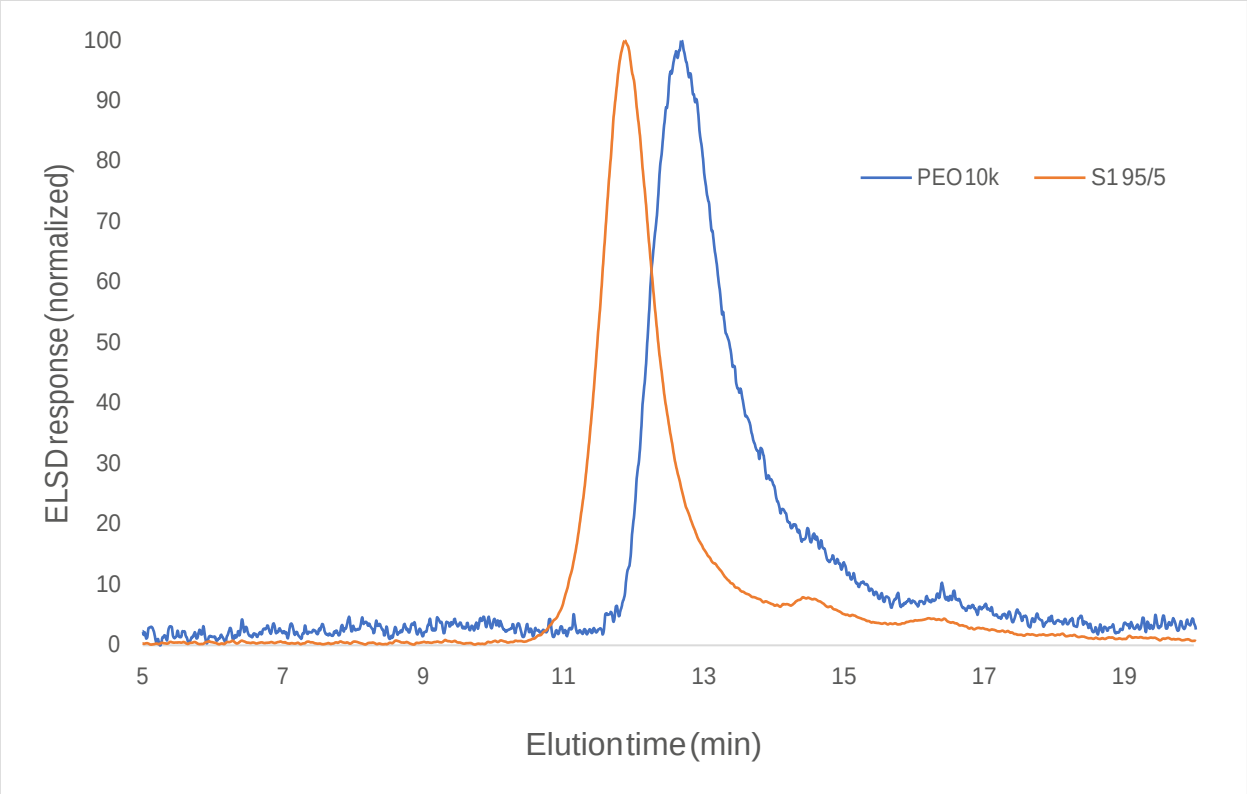
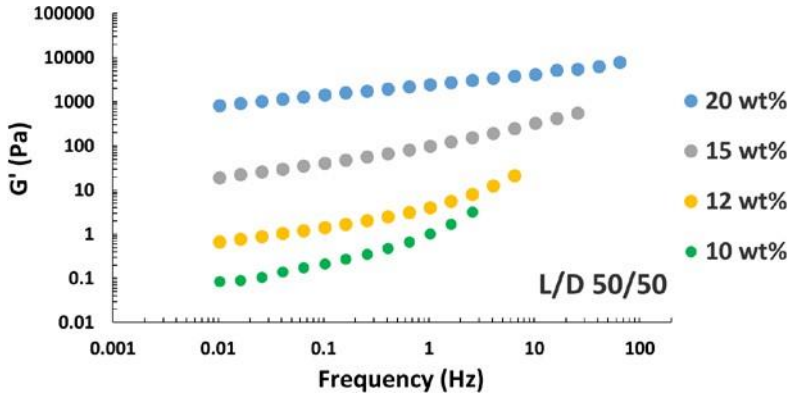
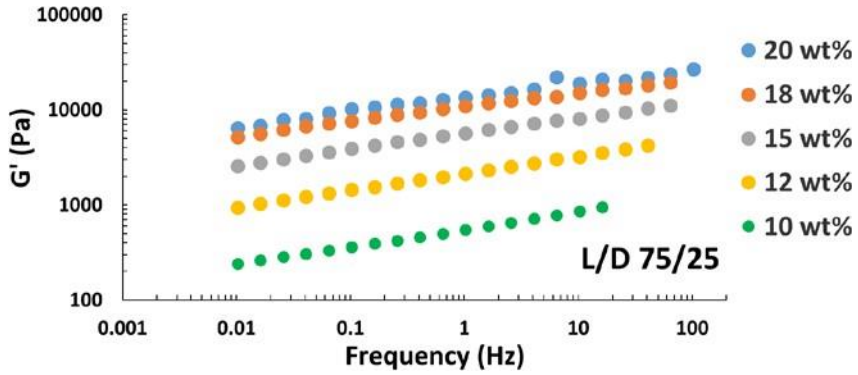


Figure S3. GPC chromatograms of PEO 10k and PLA-PEO-PLA (S_1 95/5) triblock copolymer.

(a)



(b)



(c)

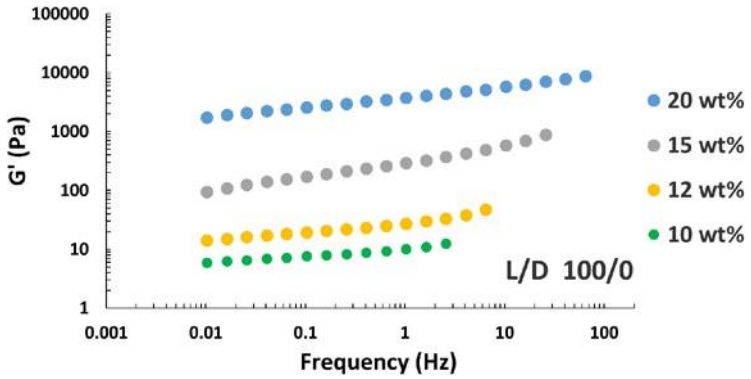
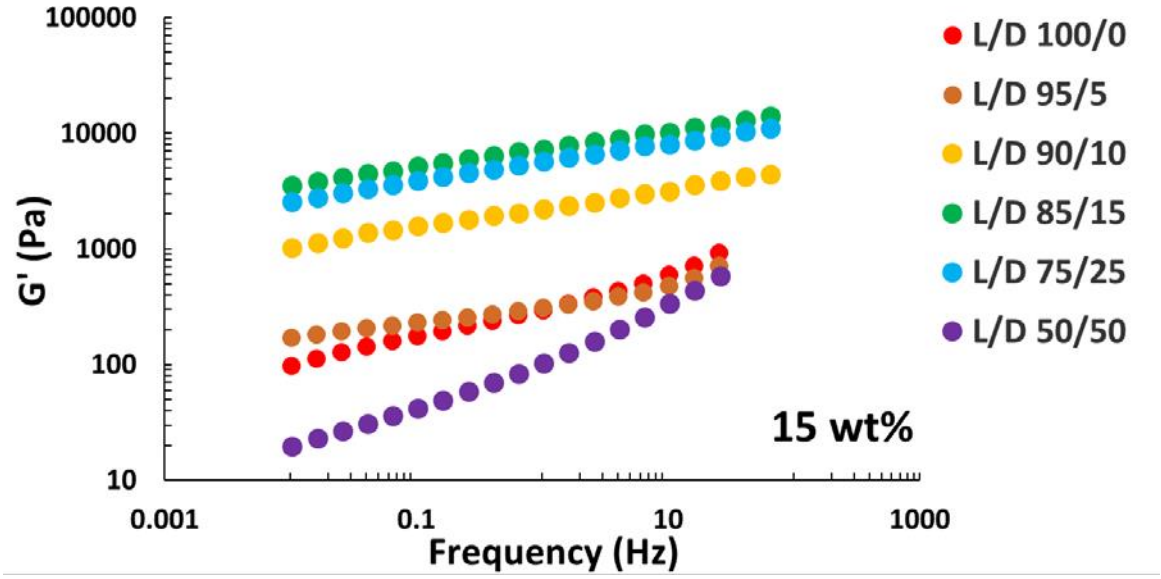


Figure S4. Moduli dependence on frequency of PLA-PEO-PLA triblock copolymer gels with L/D ratio (a) S1 50/50, (b) S1 75/25, and (c) S1 100/0.

(a)



(b)

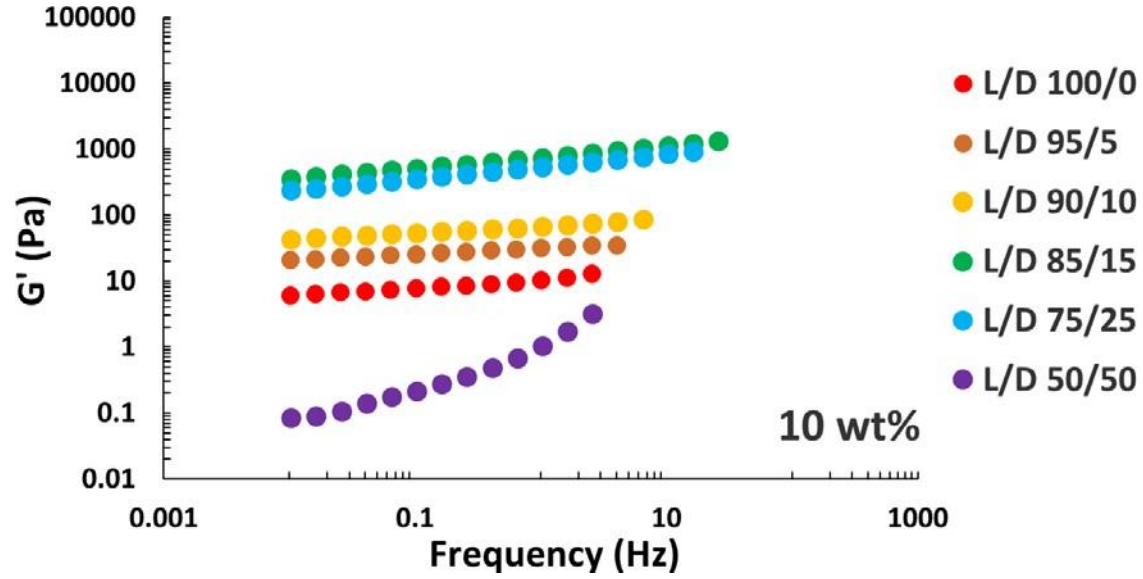
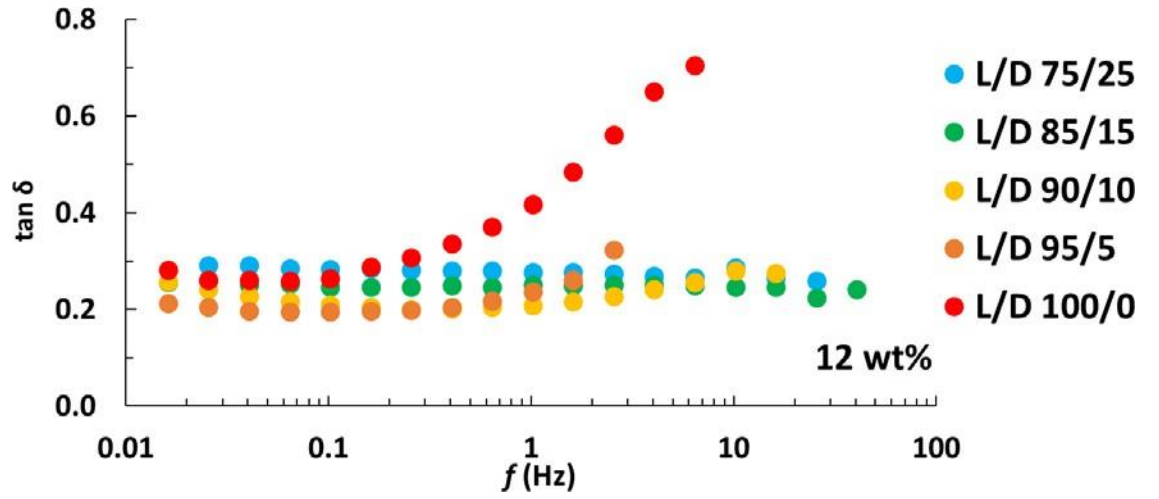


Figure S5. Moduli dependence on frequency of PLA-PEO-PLA triblock copolymer gels with varying L/D ratios at (a) 15 wt% and (b) 10 wt% copolymer.

(a)



(b)

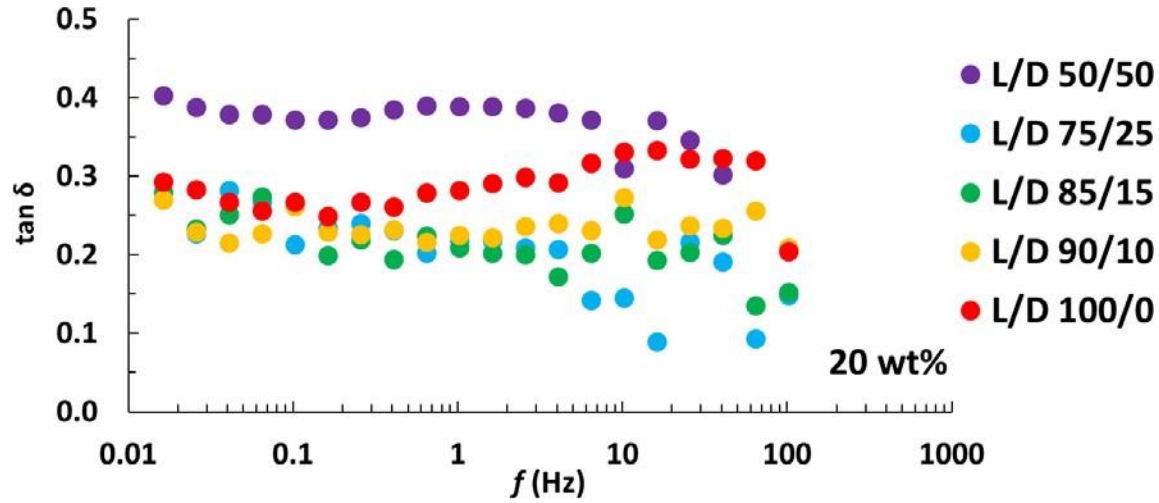


Figure S6. Damping factors of gels with varying L/D ratio at (a) 12 wt% and (b) 20 wt% copolymer.

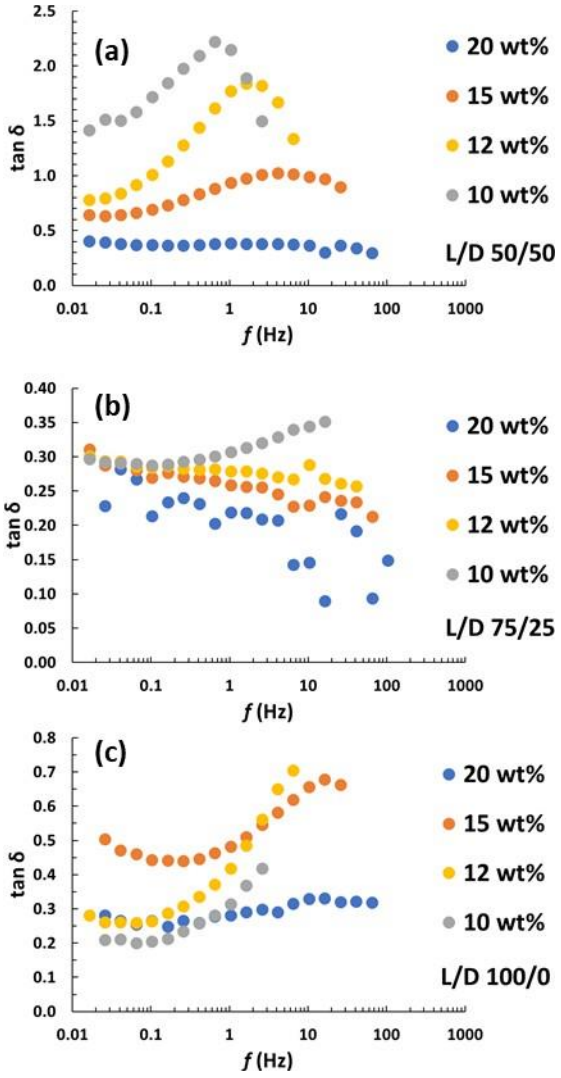


Figure S7. Damping factors of (a) S1 50/50, (b) S1 75/25, and (c) S1 100/0 gels at varying concentrations.