Supporting Information

Strengthening the Shape Memory Behaviors of L-lactide based Copolymers via its Stereocomplexation Effect with Poly(D-Lactide)

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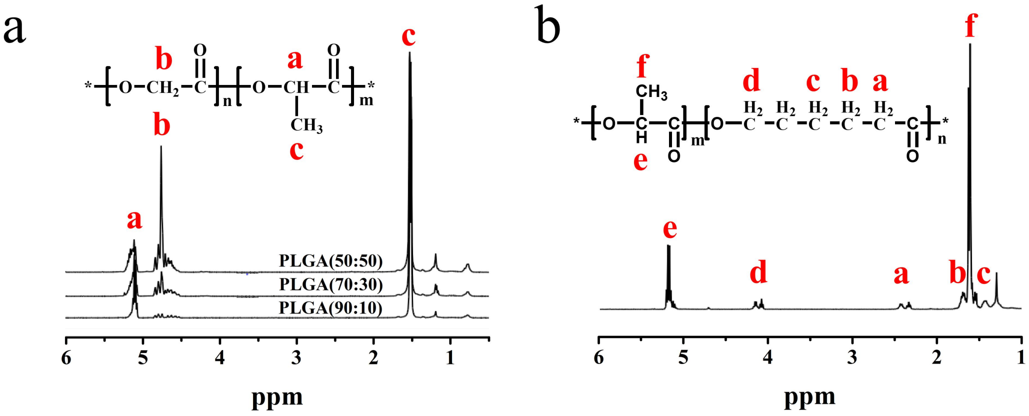


Figure S1. ^{1}H NMR spectra of various PLGA (a) and PLCL(75:25) (b) copolymers.

Figure S1(a) shows the ^{1}H NMR spectra of PLGA copolymers composed of L-lactide and glycolide at different molar ratios (50:50, 70:30, and 90:10). It is clear to observe that PLGA copolymers display three distinct proton signals in the spectra. Among them, the two peaks at 1.52 and 5.20 ppm are assigned to the methyl (CH_3) and methine (CH) group in the lactic unit, respectively. The peak at 4.85 ppm is attributed to the methylene (CH_2) protons in the glycolic unit, whose intensity increases alongside its content increasing in the PLGA copolymers. The practical compositions of resulting PLGA(50:50), PLGA(70:30) and PLGA(90:10) copolymers are estimated from the integral areas of corresponding groups from Figure S1(a) because the integral area is positively related to the proton numbers in methyl (CH_3), methylene (CH_2) or methine (CH) groups. The calculation results are shown in Table S1. Figure S1(b) shows the ^{1}H NMR spectrum of PLCL(75:25), in which, the peaks at 1.40 (peak c), 1.70 (peak b), 2.30 (peak a), and 4.00-4.20 ppm (peak d), are assigned to the characteristic peaks of methylene group in caprolactic unit. At the same time, the two peaks (1.52 and 5.20 ppm) attributed to lactic unit are also observed. Similarly, the practical composition of the resulting PLCL(75:25) copolymer is estimated from the integral areas from Figure S1(b) and is shown in Table S1.

Table S1. Molecular characteristics of various PLGA and PLCL copolymers.

Material	Yield (%)	Chemical composition LA/GA (CL) [a]	M_w [b] (x 10^4)	PDI [b]
PLGA(50:50)	> 85	52/48	9.9	1.60
PLGA(70:30)	> 85	71/29	10.8	1.57
PLGA(90:10)	> 85	89/11	10.2	1.64
PLCL(75:25)	> 85	77/23	22.1	2.17

[a] Estimated from the integral area of hydrogen signals shown in corresponding ^{1}H NMR spectrum. The molar ratio of LA to GA in PLGA copolymers were calculated from the ratios of the integrated areas of peak c and b presented in Figure S1(a), and the molar ratio of LA to CL in PLCL(75:25) was calculated from the ratio of the integrated areas of peak f and a presented in Figure S1(b).

[b] M_w and polydispersity index (PDI) were measured by GPC.

Table S2. Thermal-mechanical properties of PLGA(90:10) and PLGA(90:10)/PDLA (5K, 20K) blends.

Material	**HC-$X_{c,XRD}$ (%)[a]**	**SC-$X_{c,XRD}$ (%)[a]**	**T_g (℃)[b]**	**T_c (℃)[c]**	**T_m (℃)[d]**	**$\triangle H_m$ (J/g)[e]**	**σ (MPa)[f]**	**δ (%)[g]**	**E (GPa)[h]**	**E' (GPa)[i]**	**Tan δ[j]**
PLGA(90:10)	18.0	—	51.2	127.4	158.5	14.87	46.5 ± 2.5	6.7 ± 0.8	1.8 ± 0.05	0.9 ± 0.1	1.4
PLGA(90:10)/5%-5K	—	1.9	53.9	—	190	2.4	53.9 ± 1.1	5.1 ± 0.3	2.0 ± 0.08	1.0 ± 0.05	1.1
PLGA(90:10)/10%-5K	—	5.8	54.8	126.8	191.6	7.0	56.0 ± 1.5	4.8 ± 0.4	2.1 ± 0.04	1.1 ± 0.03	1
PLGA(90:10)/15%-5K	—	10.1	55.7	113.5	193.9	12.9	61.5 ± 1.4	4.5 ± 0.2	2.3 ± 0.05	1.2 ± 0.02	0.9
PLGA(90:10)/5%-20K	—	2.2	52.8	—	196.9	2.9	51.1 ± 1.8	5.8 ± 0.3	1.9 ± 0.04	1.0 ± 0.03	1.3
PLGA(90:10)/10%-20K	—	6.2	54.1	118.9	200.85	7.9	55.3 ± 0.9	5.4 ± 0.2	2.0 ± 0.03	1.0 ± 0.08	1.2
PLGA(90:10)/15%-20K	—	11.0	54.9	108.1	202.8	14.0	58.2 ± 1.2	5.0 ± 0.2	2.2 ± 0.07	1.1 ± 0.05	1.1

[a] Crystallinity, [b] Glass transition temperatures, [c] Crystallization temperatures, [d] Melting points, and [e] Melting enthalpy determined from the DSC runs. [f] Tensile Strength, [g] Stress at break, and [h] Young's modulus obtained from the stress-strain curve. [i] Storage modulus of the glassy state determined at 25 ℃. [j] Loss factor (Tan δ) taken from the peak maximum.

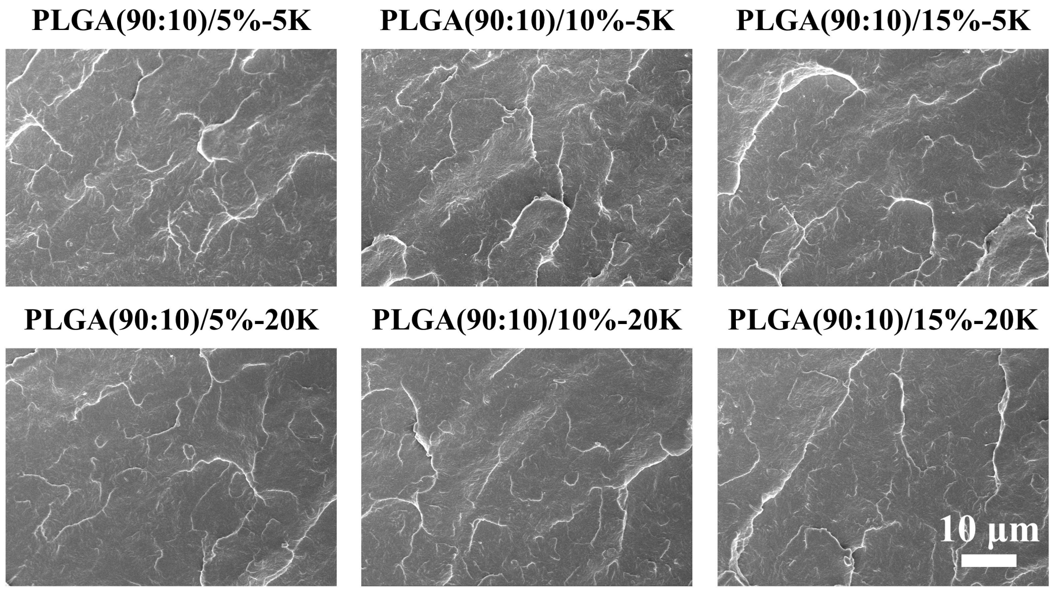


Figure S2. SEM images for the PLGA(90:10)/PDLA blends with by changing the molecular weights of PDLA (5K, 20K) and their blending ratios (5, 10, 15 wt.%).

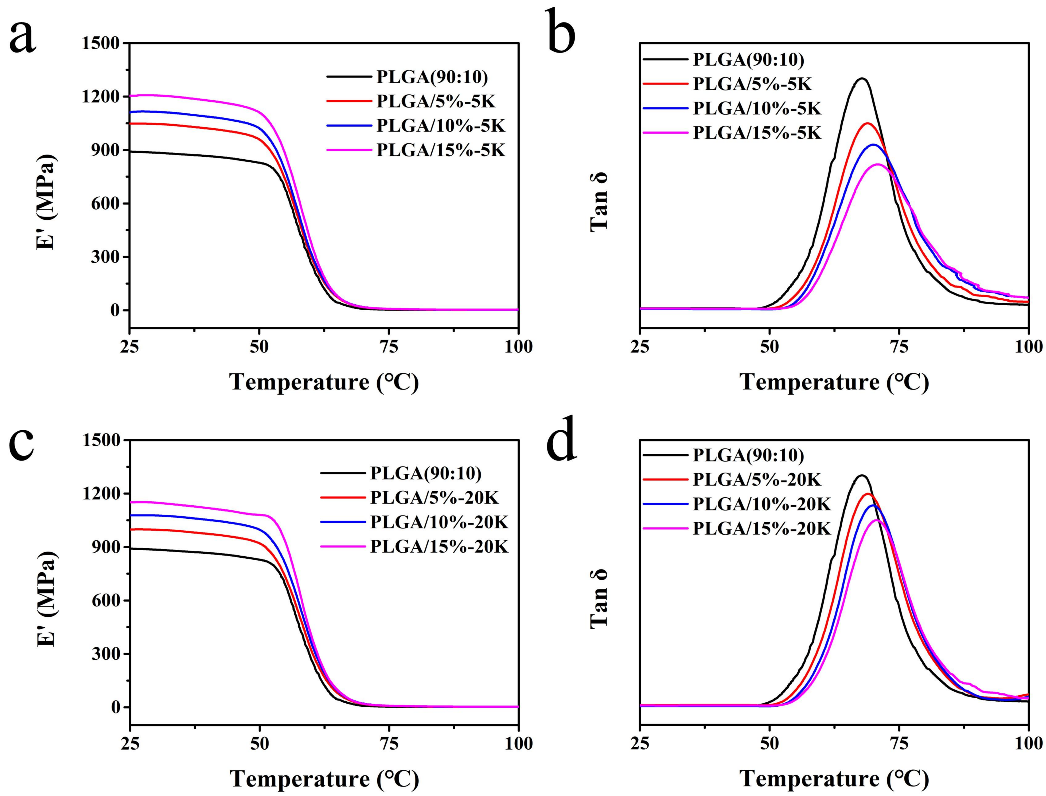
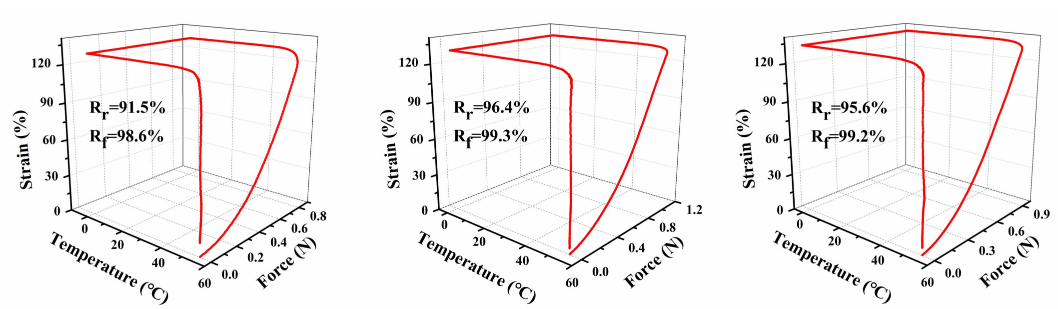


Figure S3. (a, c) Storage modulus, (b, d) loss factor of PLGA(90:10) and various PLGA(90:10)/PDLA blends containing different amounts of PDLA-5K or PDLA-20K.



PLGA(70:30) **PLGA(70:30)/10%-5K** **PLGA(70:30)/10%-20K**

Figure S4. Three-dimensional strain-stress-temperature diagrams for PLGA(70:30), PLGA(70:30)/10%-5K, and PLGA(70:30)/10%-20K.

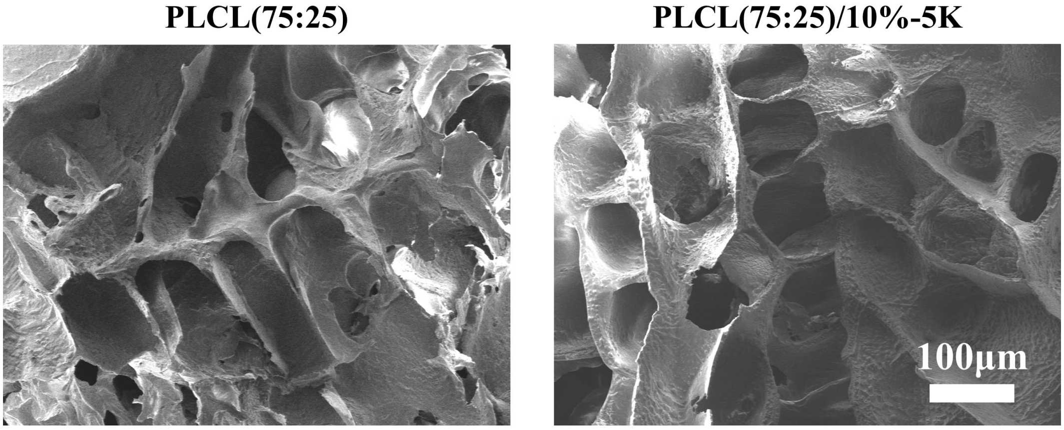


Figure S5. The porous structures of PLCL(75:25) and PLCL(75:25)/10%-5K blend scaffold.