

Supporting Information for

Synthesis and Degradation study of Graft Copolymers of Poly (limonene carbonate)

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Table S1. Graft Copolymerization of ϵ -caprolactone onto PLimC backbone

Sample name	Feed ratio (PLimC: PCL) Molar ratio	Copolymer composition (PLimC: PCL) Molar ratio	Yield (%)	M_p (g mol ⁻¹)	\bar{D}^a	Grafting density (%)	$T_{5\%}^b$ (°C)
PLimC-g-PCL (1:0.5)	1:0.5	1:0.3	81	102353	1.29	100	226
PLimC-g-PCL (1:2)	1:2	1:1	72	141383	1.29	100	248
PLimC-g-PCL (1:10)	1:10	1:4.4	80	238225	1.28	100	277

^a Determined by THF-GPC; ^b Determined at a heating rate of 10 K min⁻¹ under N₂ atmosphere from TGA.

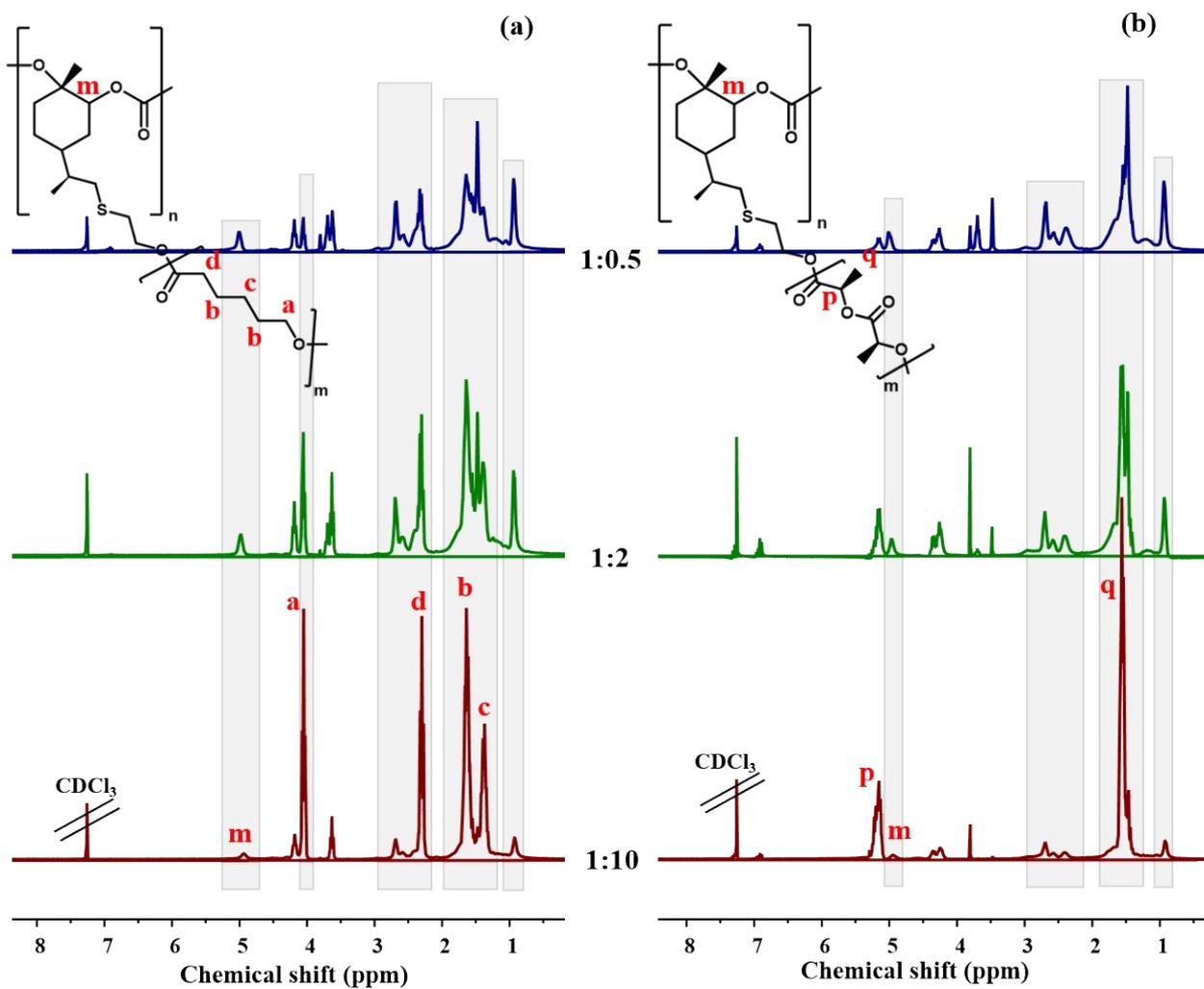


Figure S1. ^1H NMR of graft copolymers (a) PLimC-g-PCL and (b) PLimC-g-PDLLA with different feed ratios measured in CDCl_3 .

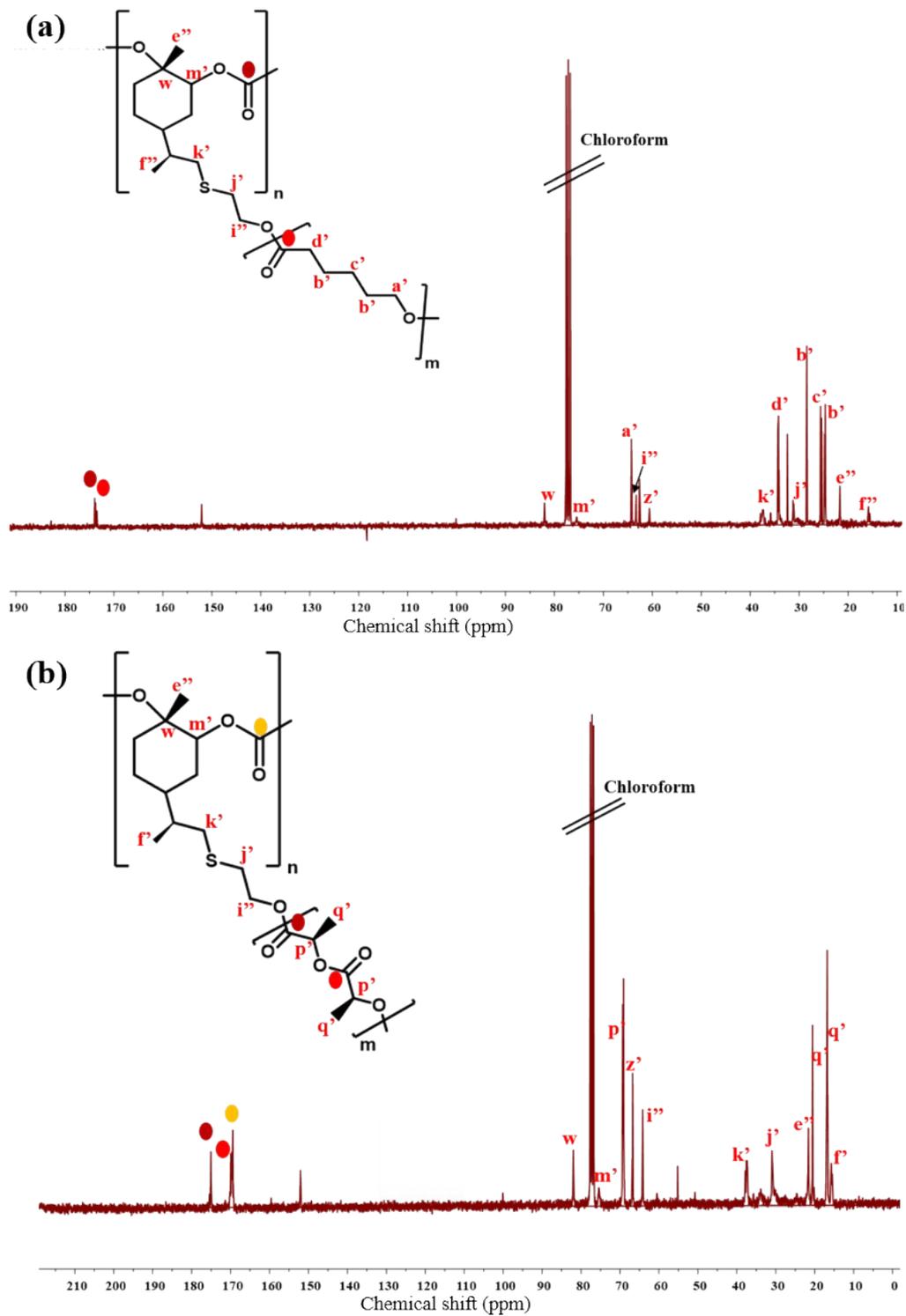


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR of graft copolymers (a) PLimC-g-PCL and (b) PLimC-g-PDLLA with different feed ratios measured in CDCl_3 .

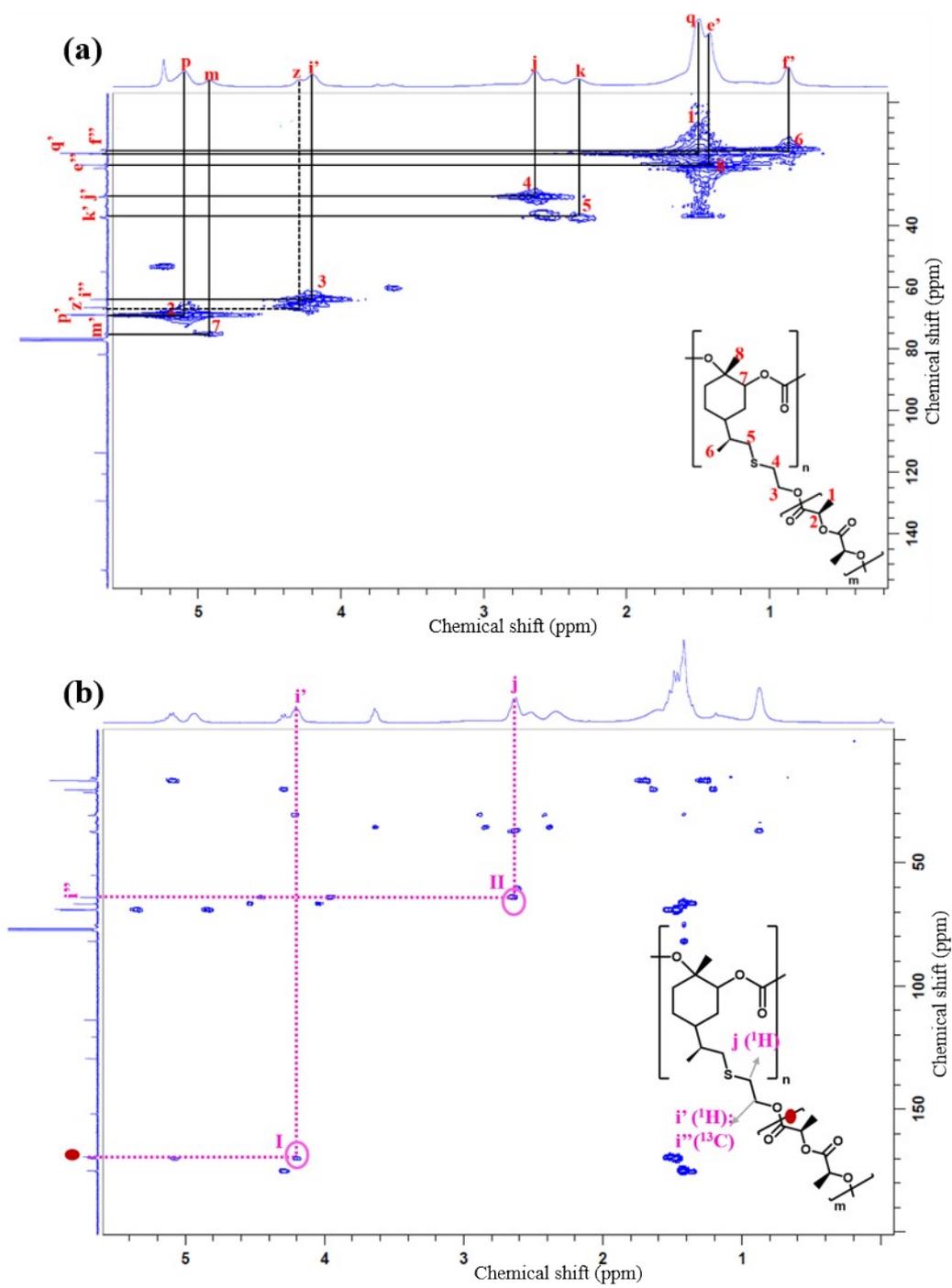


Figure S3. (a) HMQC NMR spectra and (b) HMBC NMR spectra of PLimC-g-PDLLA with feed ratio 1:2 measured in CDCl_3

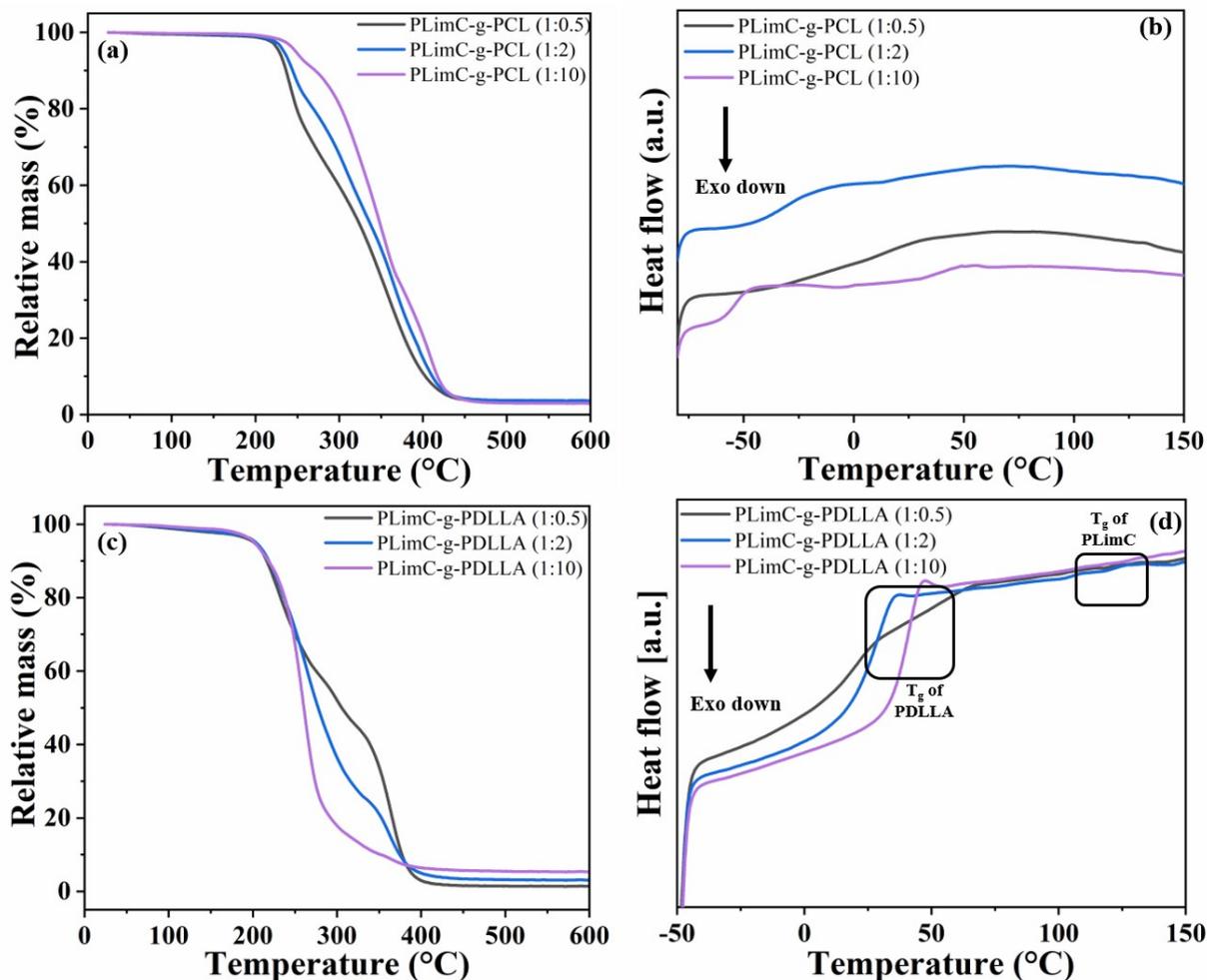


Figure S4. TGA thermograms of (a) PLimC-g-PCL and (c) PLimC-g-PDLLA with different feed ratios measured under nitrogen with 10 K min^{-1} . DSC thermograms (2^{nd} heating curve) of (b) PLimC-g-PCL and (d) PLimC-g-PDLLA with different feed ratios measured under nitrogen with 10 K min^{-1} .

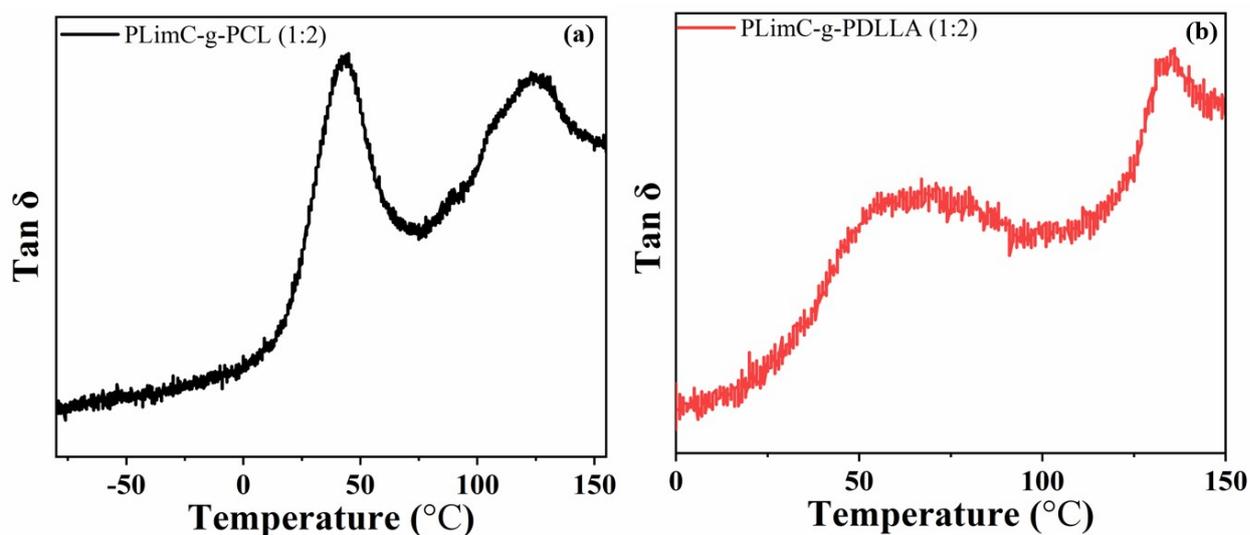


Figure S5. DMA curves measured for graft copolymers (a) PLimC-g-PCL (b) PLimC-g-PDLLA in the temperature range of -100 °C to 160 °C.

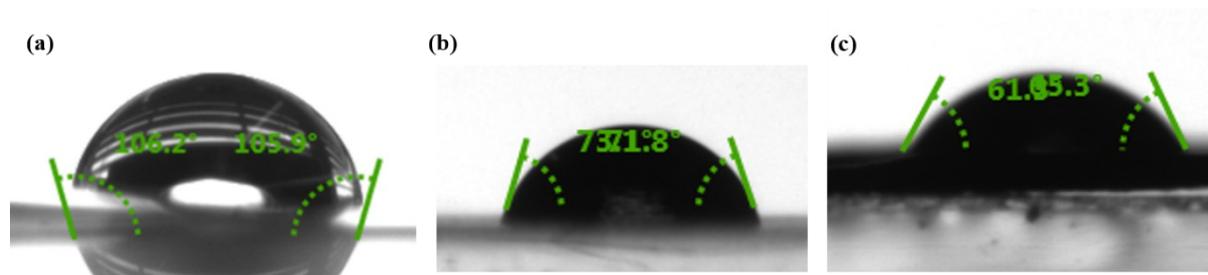


Figure S6. Contact angle measurement of (a) pure PLimC, (b) pure PDLLA and (c) pure PCL

Table S2. Mechanical properties of PLimC-g-PDLLA and PLimC-g-PCL

Sample name	Ultimate tensile ^a strength (MPa)	Elongation at break ^a (%)
Pure PLimC	38 ± 4	5 ± 2
Pure PCL	26 ± 1	403 ± 3
Pure PDLLA	68 ± 1	4 ± 1
PLimC-g-PDLLA (1:0.5)	12 ± 0.5	3 ± 2
PLimC-g-PDLLA (1:2)	17 ± 0.1	3 ± 1
PLimC-g-PDLLA (1:10)	9 ± 0.5	5 ± 2
PLimC-g-PCL (1:0.5)	15 ± 0.5	87 ± 11
PLimC-g-PCL (1:2)	16 ± 0.5	102 ± 9
PLimC-g-PCL (1:10)	15 ± 1	114 ± 12

^aMeasurement done at 10 mm. min⁻¹ test speed.

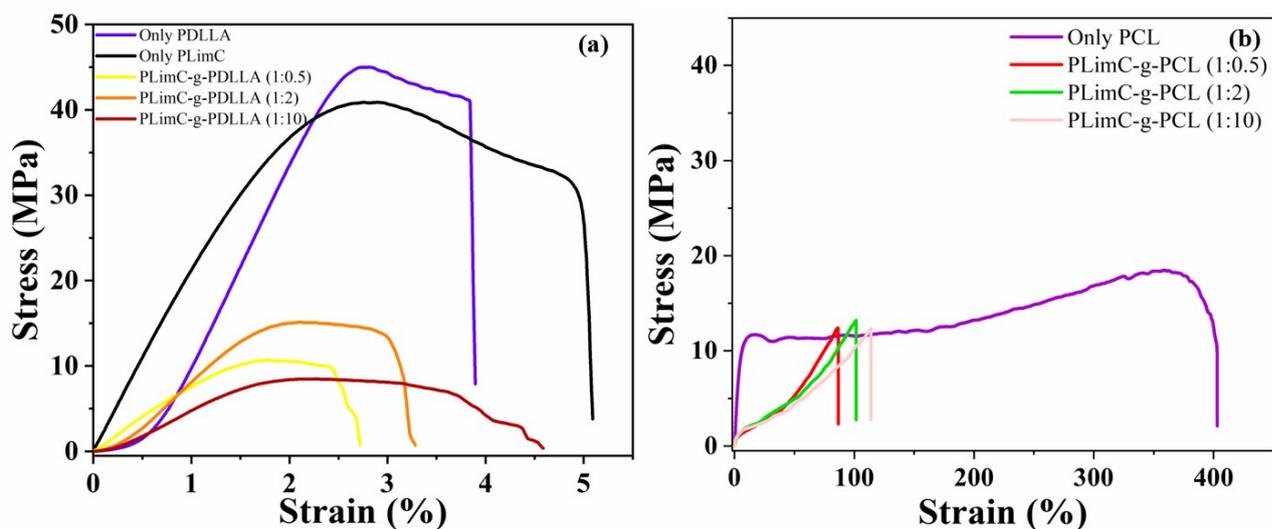


Figure S7. Stress-strain curves of PLimC-g-PDLLA and PLimC-g-PCL graft copolymers

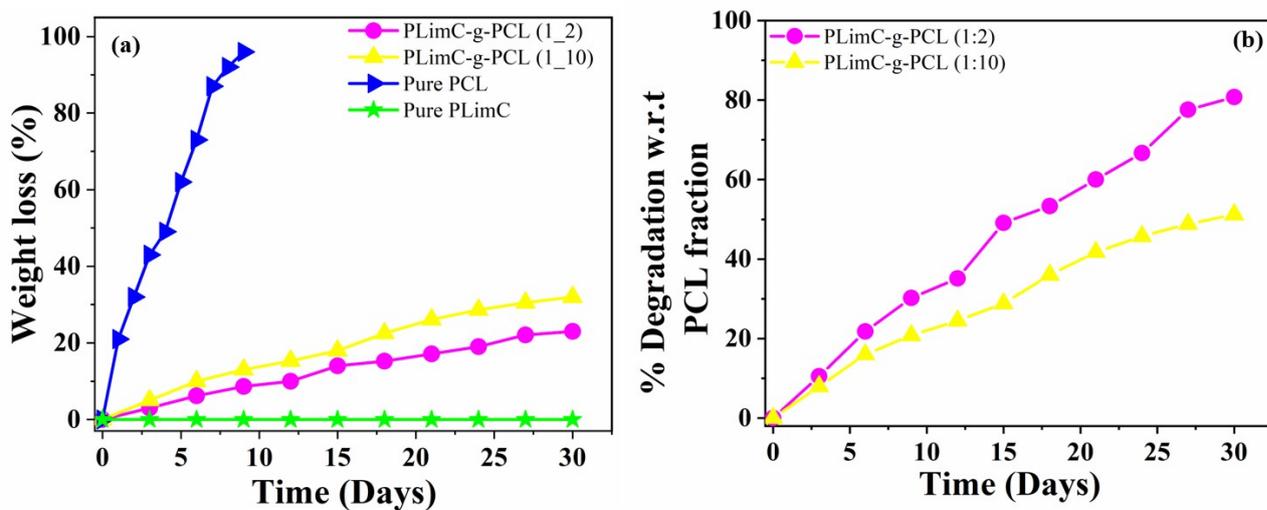


Figure S8. Enzymatic degradation of graft copolymers (a) PLimC-g-PCL films with Lipase (0.2 mg mL^{-1}) in phosphate-buffered solution (0.025M , $\text{pH} = 7.4$) and (b) percentage degradation with respect to PCL fraction in 30 days.

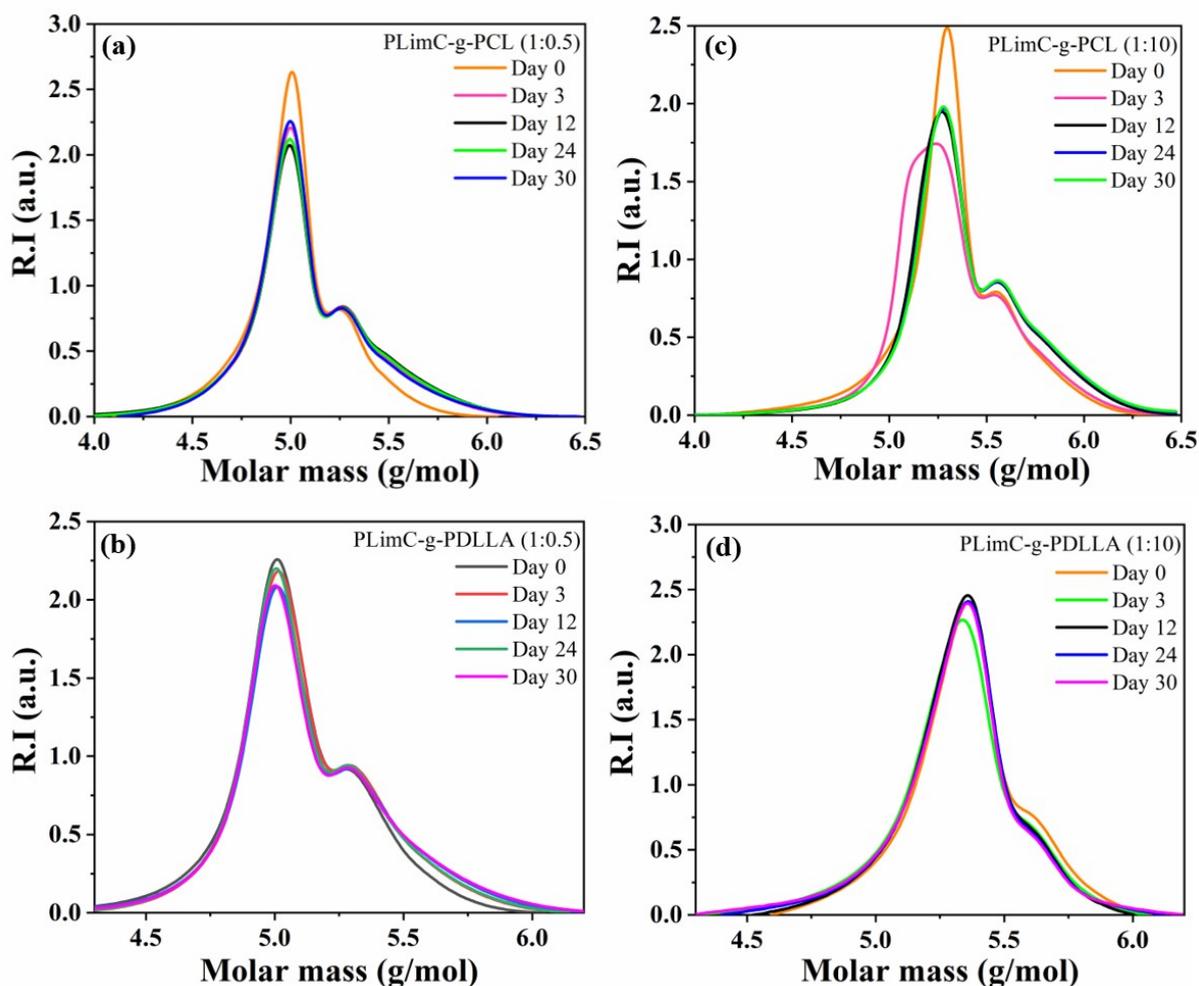


Figure S9. THF-GPC curves of graft copolymers (a) PLimC-g-PCL with 1:0.5 feed ratio (b) PLimC-g-PDLLA with 1:0.5 feed ratio (c) PLimC-g-PCL with 1:10 feed ratio and (d) PLimC-g-PDLLA with 1:10 feed ratio before and after enzymatic degradation.

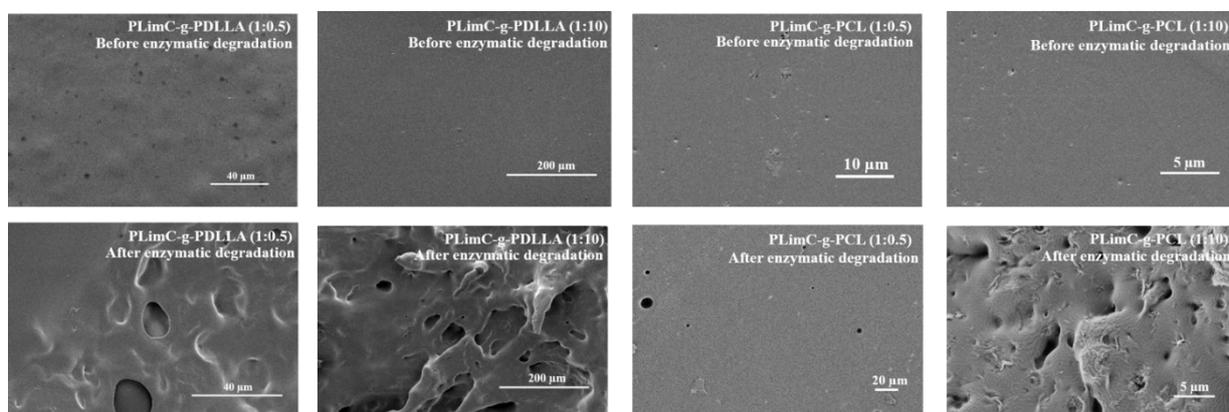


Figure S10. SEM images of PLimC-g-PDLLA and PLimC-g-PCL films before enzymatic degradation (1st row) and PLimC-g-PDLLA and PLimC-g-PCL films after enzymatic degradation (2nd row)

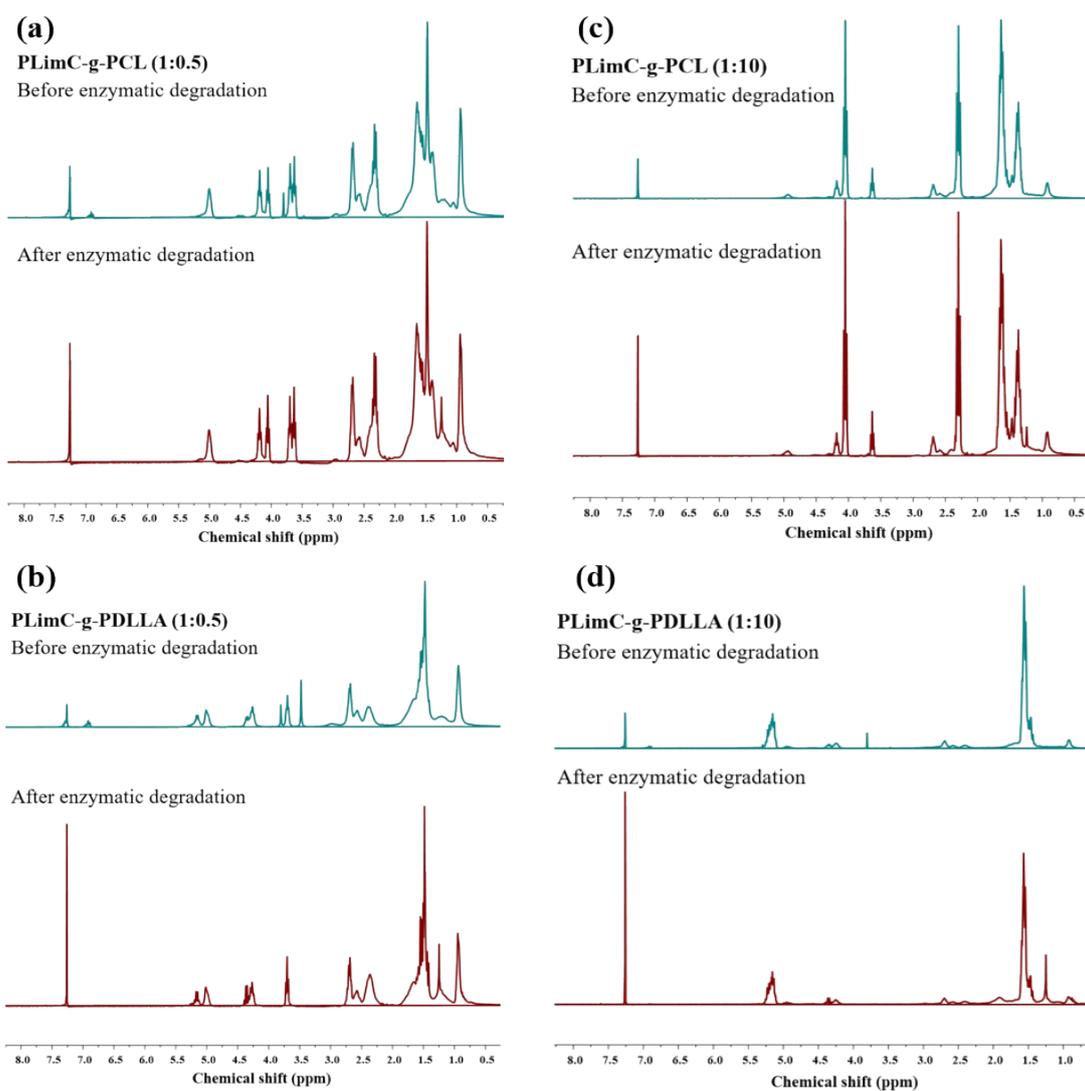


Figure S11. ^1H NMR of the graft copolymers before and after enzymatic degradation **(a)** PLimC-g-PCL with 1:0.5 feed ratio **(b)** PLimC-g-PDLLA with 1:0.5 feed ratio **(c)** PLimC-g-PCL with 1:10 feed ratio and **(d)** PLimC-g-PDLLA with 1:10 feed ratio.