

## Supporting Information

**Table S1** Characterization of the homopolymers and copolymers of different compositions and initiators synthesized at 165 °C in a sequential bulk.

Sample	Reaction time		<sup>1</sup> H-NMR conversion		Feeding composition		<sup>1</sup> H-NMR composition	
	LA	VL	LA	VL	LA	VL	LA	VL
	(min)		(%)		mole ratio		mole ratio	
<sup>a</sup> Cy-PLA	30	-	100	-	1	0	1	0
<sup>a</sup> Cy-L7V3	30	60	97	57	0.7	0.3	0.9	0.1
<sup>a</sup> Cy-L5V5	30	60	98	96	0.5	0.5	0.6	0.4
<sup>a</sup> Cy-L3V7	30	60	96	96	0.3	0.7	0.3	0.7
<sup>a</sup> Cy-PVL	-	60	-	100	0	1	0	1
<sup>b</sup> Li-PLA	30	-	-	-	1	0	1	0
<sup>b</sup> Li-L5V5	30	60	98	98	0.5	0.5	0.6	0.4
<sup>b</sup> Li-PVL	-	60	-	100	0	1	0	1



Figure S1. Optical transmittance of all the obtained PLLA homopolymers and LnVm copolymers synthesized from Table S1.

➤ The number-average sequence lengths ( $l_i$ ) of LA and VL units

$$l_{LA} = \frac{2(LA)}{(LA-VL)}; \quad l_{VL} = \frac{2(VL)}{(LA-VL)}; \quad (LA - VL) = 2 \left( \frac{(A_{2.37} + A_{4.08})}{2} - A_{5.12} + \frac{(A_{2.27} + A_{2.37} + A_{4.01} + A_{4.08})}{2} \right)$$

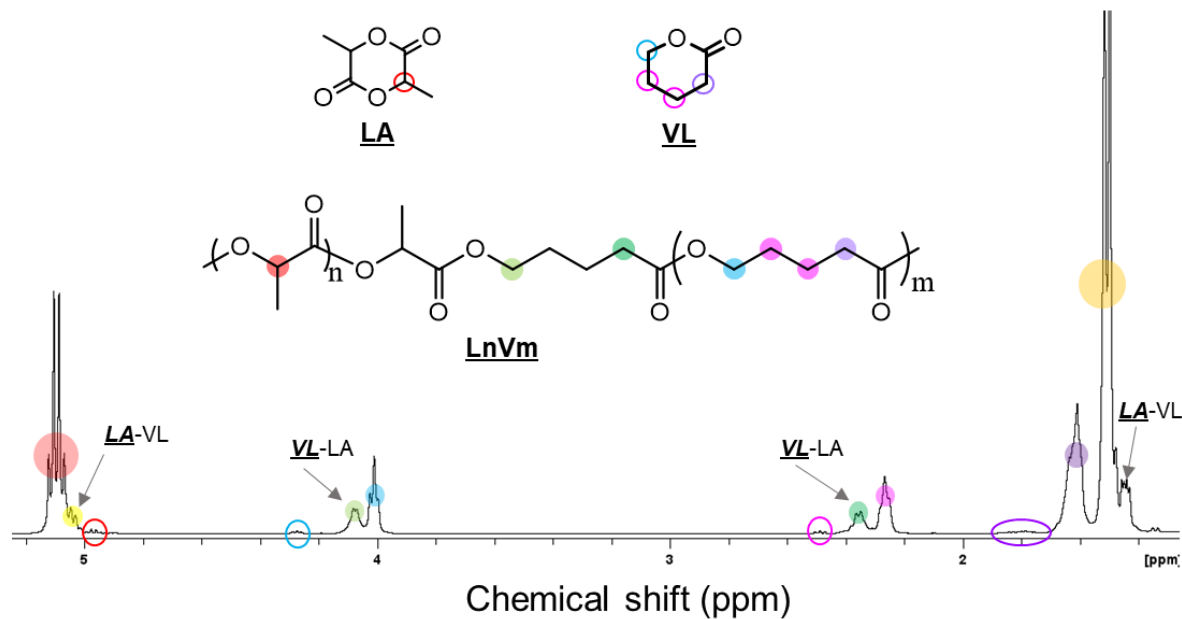


Figure S2. The representative of  $^1\text{H}$  NMR spectra of  $\text{LnVm}$  copolymers for calculating the number-average sequence lengths of LA and VL.

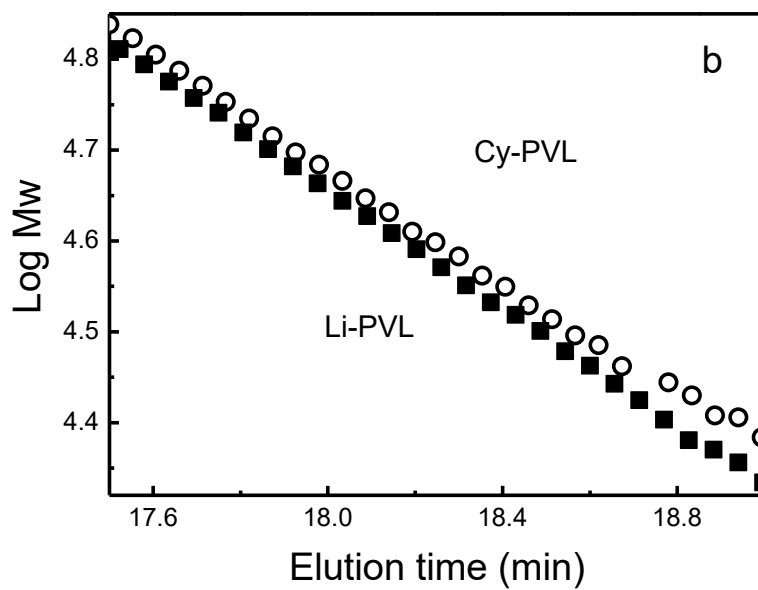
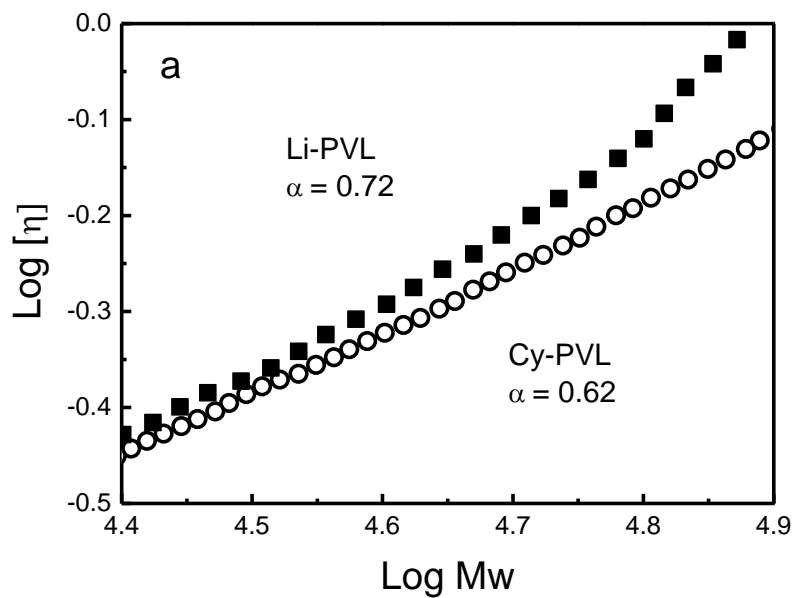


Figure S3. The double logarithmic plot of intrinsic viscosity against molecular weight (a) and the plot of logarithm molecular weight against elution time (b) of PVL homopolymers; where ■ = initiated by BnOH and ○ = initiated by salicylic acid.

DSC testing

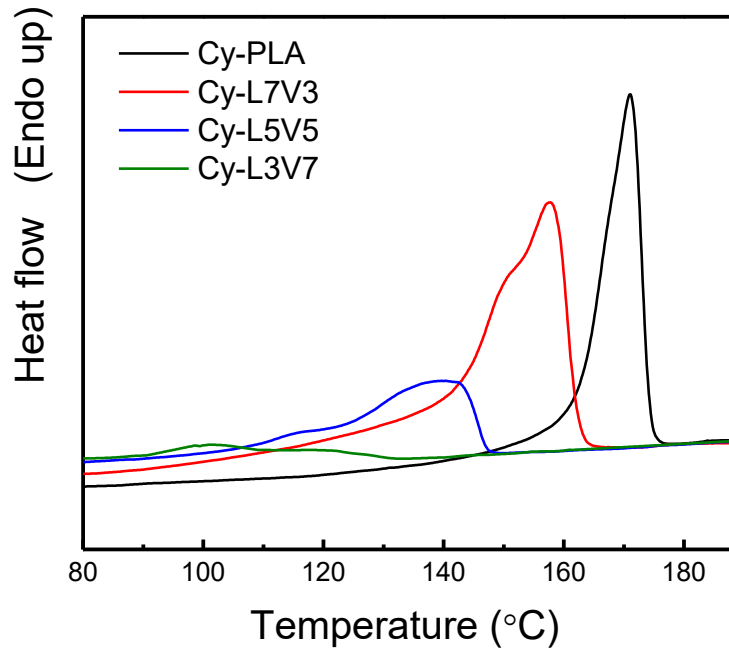


Figure S4. First heating calorimetric thermograms for the composting degraded samples; Cy-PLA, Cy-L7V3, Cy-L5V5, and Cy-L3V7 at the different incubation times in composting conditions at 58 °C.

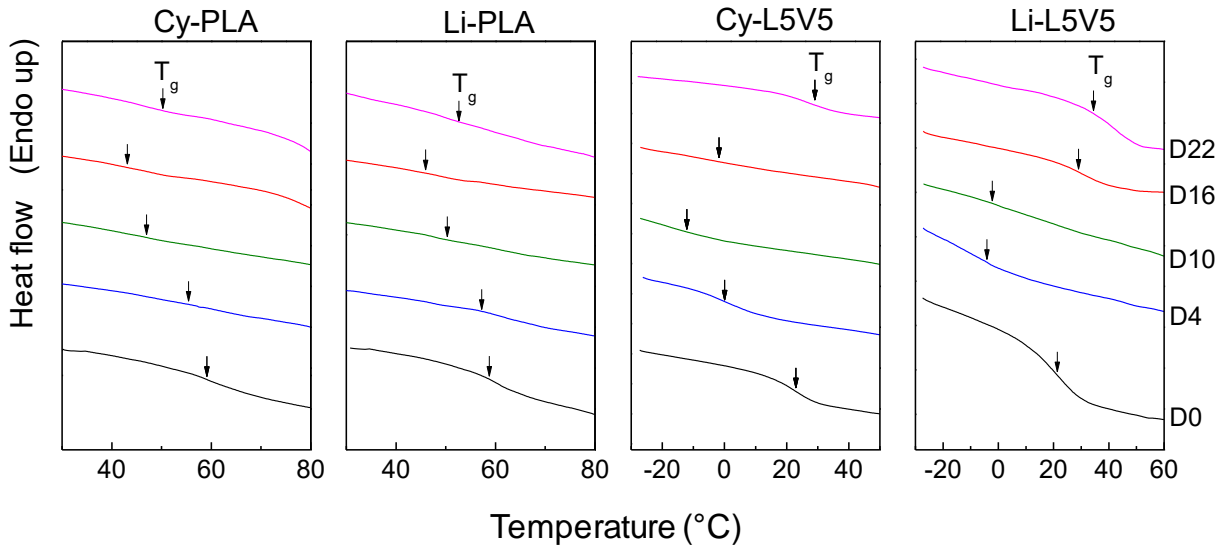


Figure S5. Cooling calorimetric thermograms for the composting degraded samples; Cy-PLA (a), Li-PLA (b), Cy-L5V5 (c), and Li-L5V5 (d) after different incubation times.

**Table S2** GPC traces for the composting degraded samples; PLA homopolymers and L5V5 copolymers at the different incubation times.

<b>Sample</b>	<b>Time</b> (Day)	<b>M<sub>w</sub></b> (g/mol)	<b>M<sub>n</sub></b> (g/mol)	<b>M<sub>w</sub>/ M<sub>n</sub></b>
<b>Cy-PLA</b>	0	161,558	65,054	2.48
	4	58,281	21,501	2.71
	10	16,514	6,671	2.48
	16	3,183	2,556	1.25
	22	2,705	2,259	1.20
<b>Li-PLA</b>	0	157,779	60,006	2.63
	4	72,464	28,512	2.54
	10	20,228	9,253	2.19
	16	4,899	3,641	1.35
	22	3,832	3,080	1.24
<b>Cy-L5V5</b>	0	62,260	28,315	2.20
	4	12,109	5,872	2.06
	10	3,718	1,681	2.21
	16	1,953	1,483	1.32
	22	-	-	-
<b>Li-L5V5</b>	0	68,379	31,854	2.15
	4	13,400	6,078	2.20
	10	4,495	2,326	1.93
	16	3,011	1,641	1.83
	22	1,363	1,168	1.17

**Table S3** Summary of the DSC scan data for the samples collected at various incubation times

	Time (Day)	1 <sup>st</sup> heating			1 <sup>st</sup> cooling		$X_c$ (%)
		$T_{cc}$	$T_m$	$\Delta H_m$	$T_g$	$T_c$	
		(°C)	(°C)	(J/g)	(°C)	(°C)	
Cy-PLA	0	-	173.5	44.2	59.1	119.4	41.7
	4	-	170.9	59.8	55.5	107.1	56.4
	10	-	162.4	85.6	47.1	118.9	80.8
	16	-	155.6	90.8	43.2	105.6	85.7
	22	-	153.6	91.9	50.5	105.5	86.7
Li-PLA	0	-	175.3	45.2	58.5	102.4	42.6
	4	-	173.4	56.6	57.2	111.1	53.4
	10	-	166.6	70.2	50.3	119.6	66.2
	16	-	160.5	77.1	45.6	118.5	72.7
	22	-	162.8	78.4	52.7	114.7	74.0
Cy- L5V5	0	84.5	138.6	21.3	22.9	-	29.4
	4	-	139.6	26.9	-0.7	92.9	37.1
	10	-	136.7	38.9	-13.2	92.7	53.7
	16	-	123.7	51.1	-1.76	72.4	70.6
	22	-	107.5,117.7	53.9	28.8	-	74.4
Li- L5V5	0	-	150.6	24.6	21.2	85.2	34.0
	4	-	151.7	39.9	-4.3	99.9	55.1
	10	-	139.3	42.8	-2.3	89.4	59.1
	16	-	133.1	52.5	30.5	-	72.5
	22	-	127.8	56.6	34.1	-	78.2