Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Copolymerization of *L*-Lactide and ε-Caprolactone Catalyzed by Mono- and Dinuclear Salen Aluminum Complexes Bearing Bulky 6,6'-Dimethylbiphenyl-Bridge: Random and Tapered Copolymer

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1. NMR spectra and thermal properties of the copolymers

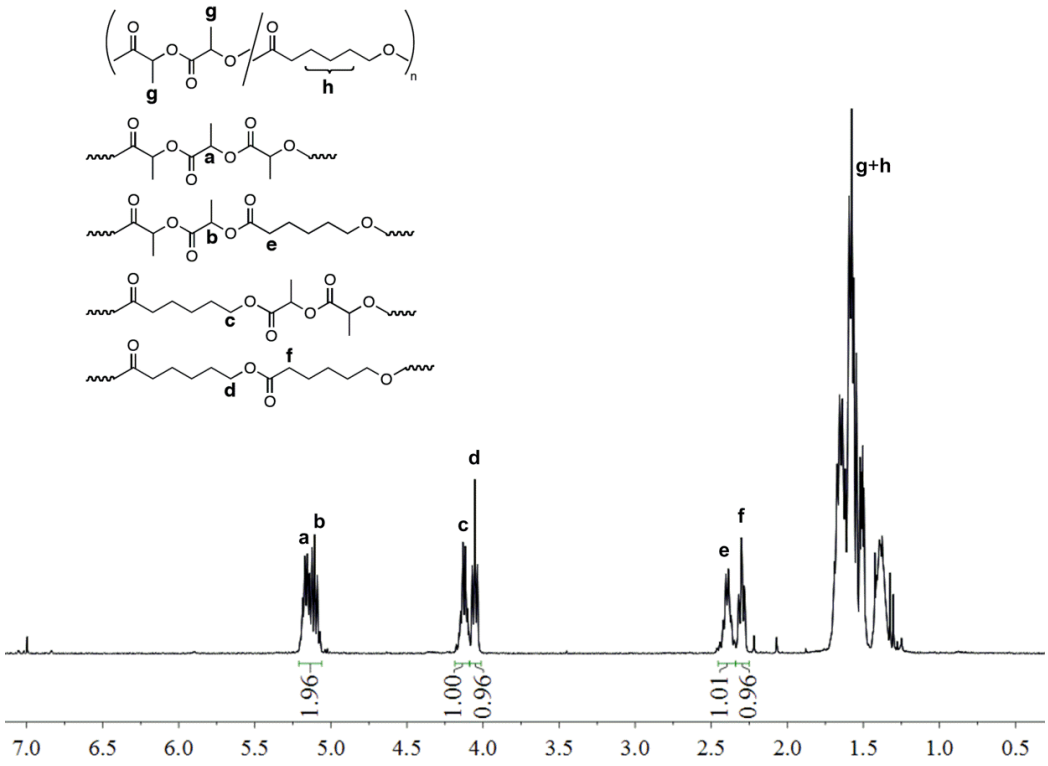

Figure S1. The ^{1}H NMR spectrum of poly(*L*-LA-*ran*-*ε*-CL) produced by complex **3**. ($CDCl_3$, 400 MHz)

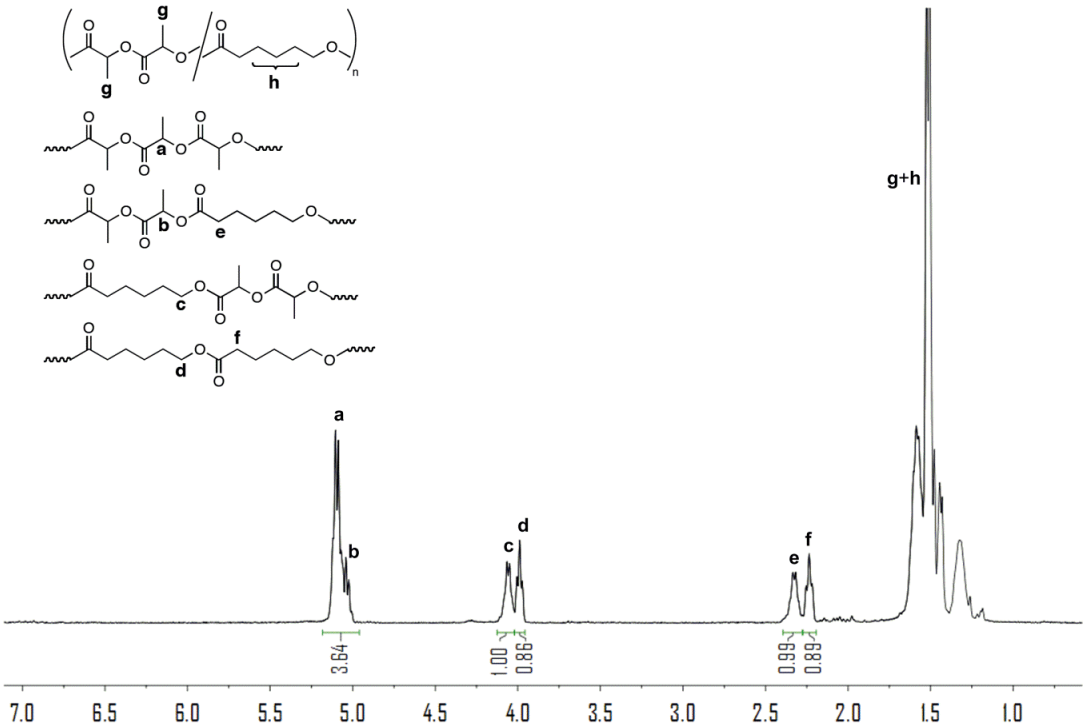

Figure S2. The ^{1}H NMR spectrum of poly(*L*-LA-*tap*-*ε*-CL) produced by complex **6**. ($CDCl_3$, 400 MHz)

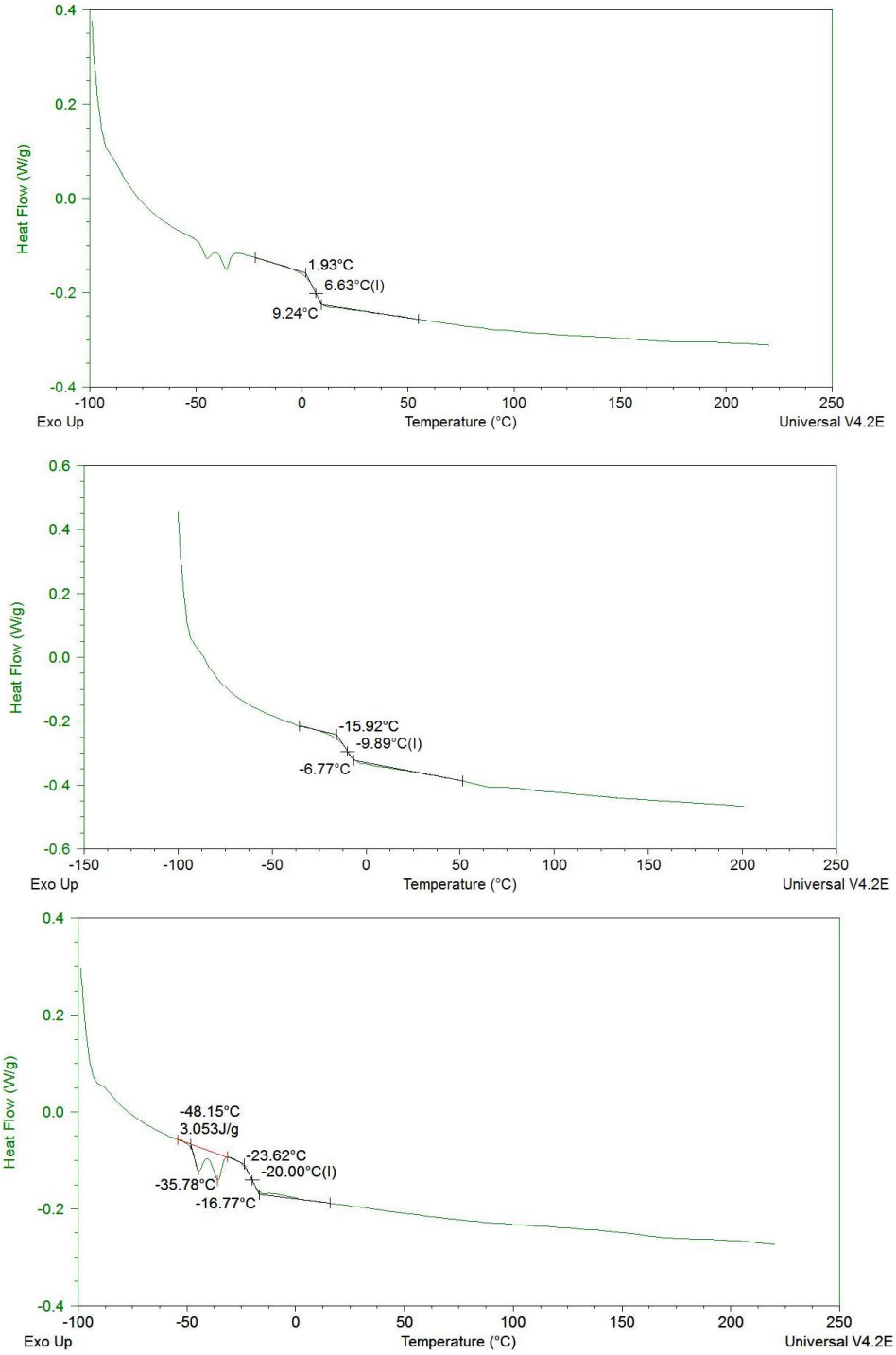

Figure S3. The DSC curves of poly(*L*-LA-*ran*-*ε*-CL) produced by complex **3**. (top: LA/CL = 6 : 4; middle: LA/CL = 5 : 5; bottom: LA/CL = 4 : 6)

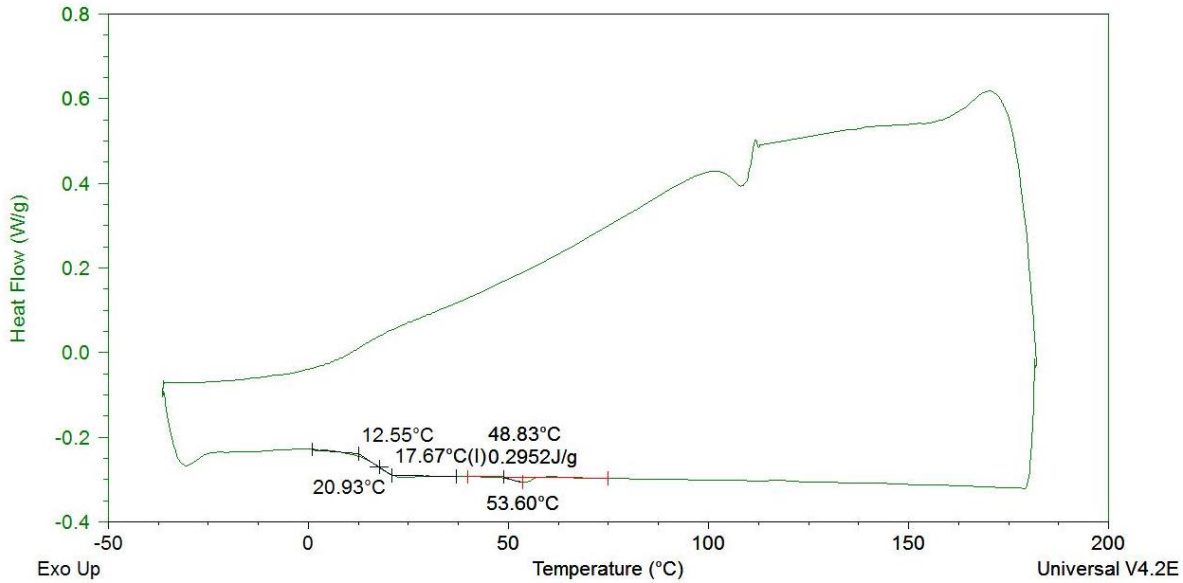

Figure S4. The DSC curves of poly(*L*-LA-*tap*-*ε*-CL) produced by complex **6**.

2. Determination of reactivity ratios: the reactivity ratios were calculated using the nonlinear least squares (NLLS) method, carrying out the copolymerizations at low conversion with different ratios of the two monomers.

Table S1. Copolymerization entries at low monomer conversions[a]

$f_{[LA]}$[b]	$f_{[CL]}$[b]	Conv.[c] LA	Conv.[c] CL	F_{LA}[d]	F_{CL}[d]	x	y	α	F	G	$F/\alpha+F$	$G/\alpha+F$
0.190	0.810	3.08	2.48	0.226	0.774	0.235	0.292	0.222	0.188	-0.569	0.460	-1.387
0.400	0.600	14.32	11.65	0.450	0.550	0.667	0.818	0.222	0.543	-0.148	0.710	-0.194
0.505	0.495	8.93	8.11	0.534	0.466	1.020	1.146	0.222	0.926	0.131	0.807	0.114
0.600	0.400	7.08	7.05	0.603	0.397	1.500	1.519	0.222	1.481	0.512	0.870	0.301
0.708	0.292	4.35	3.54	0.747	0.253	2.424	2.953	0.222	1.991	1.603	0.900	0.725
0.832	0.168	3.90	3.01	0.865	0.135	4.952	6.407	0.222	3.828	4.179	0.945	1.030

[a] T = 110 °C, in 0.4 mL toluene; [b] ([*L*-LA]+[ε-CL])/[Cat.] = 200, [Cat.] = 25mM; [c] mononer conversion as determined by ^{1}H NMR spectroscopy; [d] LA and CL composition in the copolymer.

$$r_{LA} = k_{LALA} / k_{LACL} \qquad r_{CL}=k_{CLCL}/k_{CLLA} \longrightarrow \frac{d[LA]}{d[CL]} = \frac{[LA]}{[CL]} \frac{r_{LA}[LA]+[CL]}{r_{CL}[CL]+[LA]}$$

$$r_{CL} = \frac{[LA]}{[CL]} \{\frac{d[LA]}{d[CL]}(1+\frac{r_{LA}[LA]}{[CL]}-1)\}$$

define: $y = F_{LA} / F_{CL}$ x=[LA]/[CL]

the above formula can be simplified to : $y = x\frac{r_{LA}+1}{r_{CL}+x}$

conversion: $x-\frac{x}{y} = r_{LA}\frac{x^2}{y} - r_{CL}$

define: $G=x-\frac{x}{y}$, $F=\frac{x^2}{y}$, $\alpha=(F_{min}/F_{max})^{1/2}$

simplified: $\frac{G}{\alpha+F} = (r_{LA}+\frac{r_{CL}}{\alpha})\frac{F}{\alpha+F} - \frac{r_{CL}}{\alpha}$

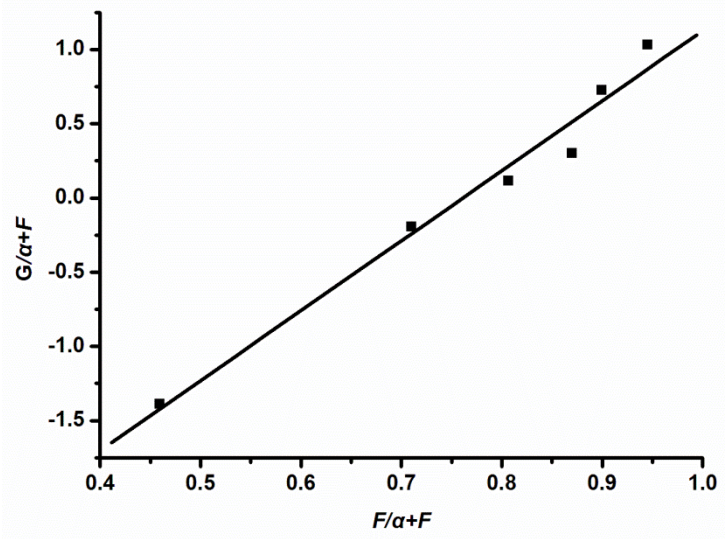

Figure S5. linear relationship of F/α+F and G/α+F (slope is 4.71, intercept of vertical is 3.59, R = 0.988)