

SUPPORTING INFORMATION

A trinuclear Salen-Al complex for copolymerization of epoxides and anhydride: mechanistic insight into cocatalyst-free system

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Experimental

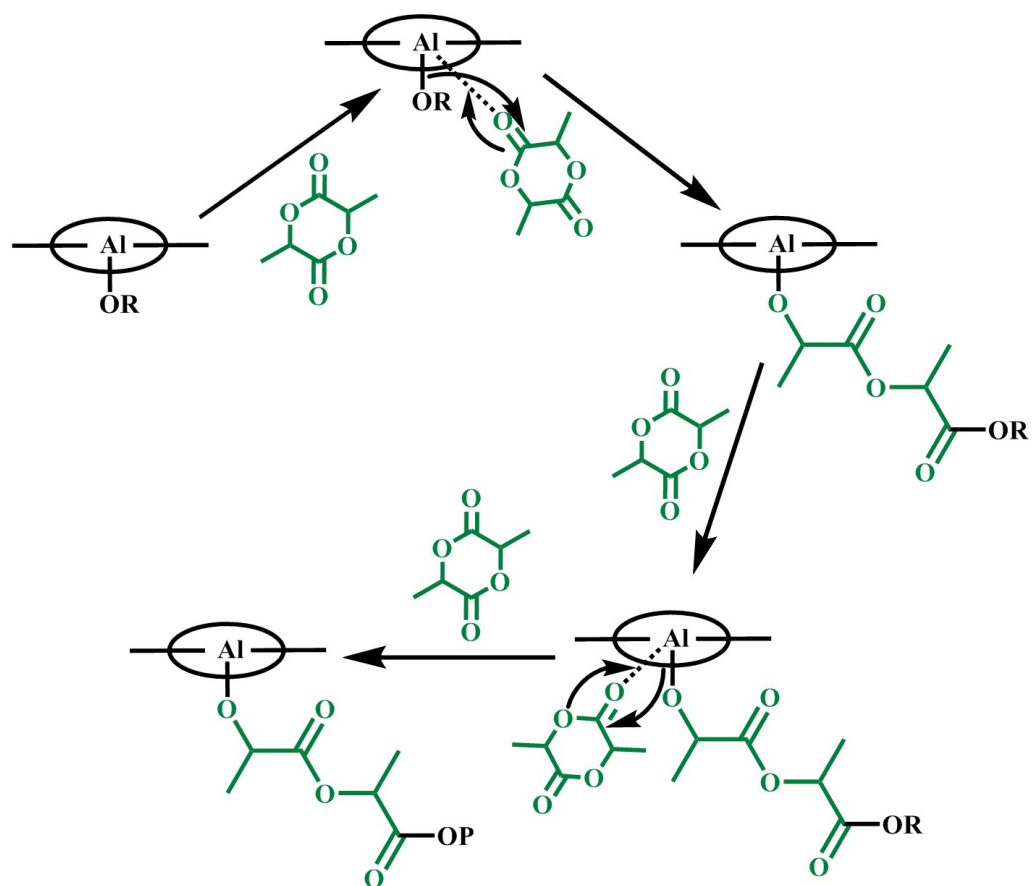
The synthesis of Salen Al complex was prepared following the method in our previous research¹. All manipulations involving air/water-sensitive operation were carried out in a glovebox under an argon atmosphere or standard Schlenk techniques. Propylene oxide (PO), Epichlorohydrin (POCl) and o-Phthalic anhydride (PA) were purchased from J&K chemical Company, PO, POCl, ethyl acetate (EA), and ϵ -caprolactone (CL) were purified by distillation after stirring and refluxing with CaH₂ under argon atmosphere. Lactide (LA) was purified by recrystallization from EA and dried under vacuum before use. PA was dissolved in chloroform and filtered, the filtrate was evaporated and the remaining solid was purified by recrystallization of EA. All copolymerization involving PO was carried out in the 25 mL steel autoclaves. The autoclaves were heated to 120 °C and dried for 24 hours before use, and then the autoclaves were placed in a glove box filled with argon and cooled to ambient temperature. In a typical copolymerization procedure, complexes, epoxides and cyclic anhydrides in suitable ratio were added into a reaction vessel with a magnetic bar and heated to the suitable temperature. After the designed time, the reaction vessel was cooled to room temperature and a small amount of crude product was taken out and dissolved in CDCl₃, the conversion of monomer was measured by ¹H NMR. The results of ¹H NMR were recorded on Bruker 300 or 400 MHz spectrometer and chemical shifts calibrated using 0.03% v/v TMS as internal standard. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) and the measurements were conducted on a Waters 515 system which equilibrated at 30 °C using CH₂Cl₂ as solvent. The values of molecular weights were calibrated by polystyrene (PS) standards.

Kinetic study details

To better understand the influence of intramolecular interactions on activity of the complex **1**, the kinetic behaviors of complex **1** with or without the cocatalyst were studied. As shown in **Figure S1**, under the identical [PA]/[Al], the k_p value of the bicomponent catalytic system (composed of complex **1** and PPnCl) was $7 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$. The k_p value was $2 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$ when using complex **1** alone. This result indicated that complex **1** maintained high activity in the copolymerization without cocatalyst. As shown in **Scheme 1**, PPnCl can change the electrophilicity of the Al by forming complex, thus improving the catalytic activity of Salen Al complexes, with the presence of PPnCl the copolymerization activity was higher than that in the absence of cocatalyst, which indicates that the change of electrophilicity of the Al by PPnCl was stronger than that of intramolecular interaction of complex **1**. In the presence of PPnCl, the copolymerization was carried out according to the mechanism shown in **Scheme 1** by using complex **1** as catalyst. Therefore, under this condition, Cl and alkoxy groups played the same initiating role in copolymerization, and this multi initiation process also caused the molecular weight distribution of the copolymer to broaden. The MALDI-TOF result of the copolymer also illustrated the existence of two initiator groups (**Figure S2**).

The data of PA conversion versus copolymerization time were showed in **Figure S3**, the conversions increased linearly with polymerization time. As the concentration of PA increased, the rate of the copolymerization decreased obviously. First-order kinetics in PA was observed by using complex **1**. To determine the order in catalyst, the k_{app} was investigated versus the concentration of complex **1**. As shown in **Figure S4**, k_{app} increased linearly with the concentration of complex **1**, this result manifested that the order in complex **1** was first-order too. The linear relationship between PA conversion and M_n was observed (**Figure S5**), and all copolymers exhibited narrow molecular weight distribution. Investigation of the influence of temperature on activity was proceeded. As shown in **Figure S6**, with the improvement of temperature, the activity of complex **1** increased obviously. The k_p value at 100°C was about 6×10^{-3}

$^3 \text{ L mol}^{-1} \text{ min}^{-1}$, which was 7.5 times higher than that at 60°C ($0.8 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$).



Scheme S1 The mechanism of polymerization of lactide using the Salen-Al complex as catalyst.

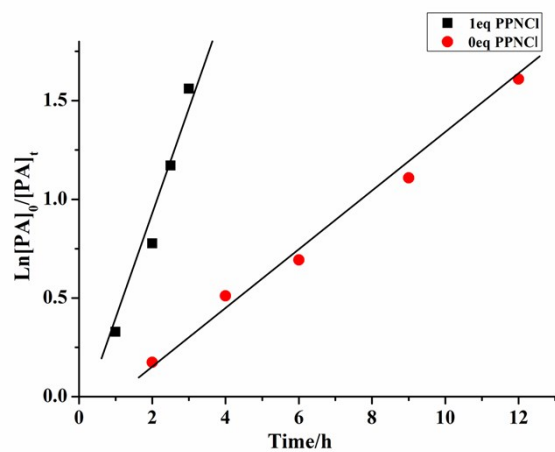


Figure S1. Kinetic plots of the PA conversion with or without cocatalyst using complex **1**, $[\mathbf{1}]:[i\text{-PrOH}]:[\text{PA}]:[\text{PO}]=1:3:300:3000$, $80\text{ }^\circ\text{C}$.

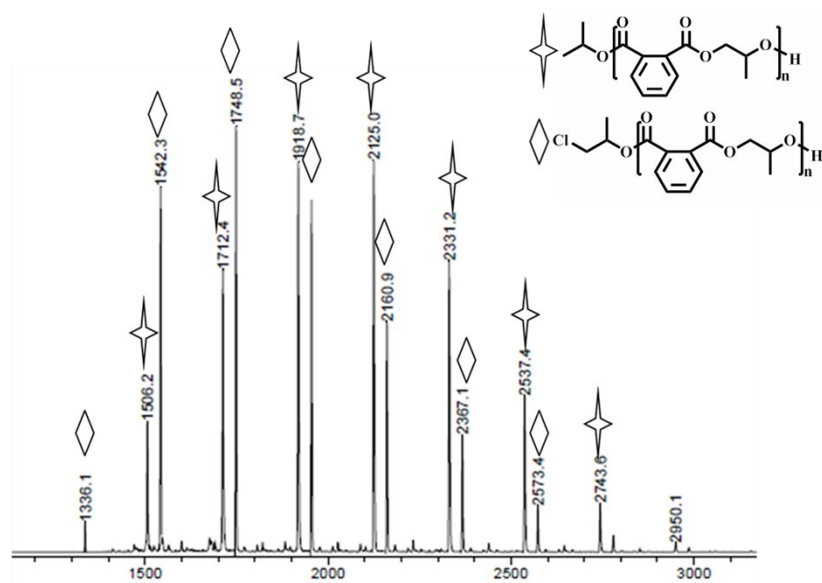


Figure S2 MALDI-TOF mass spectrum of copolymer (obtained from copolymerization using complex **1** with PPNCI).

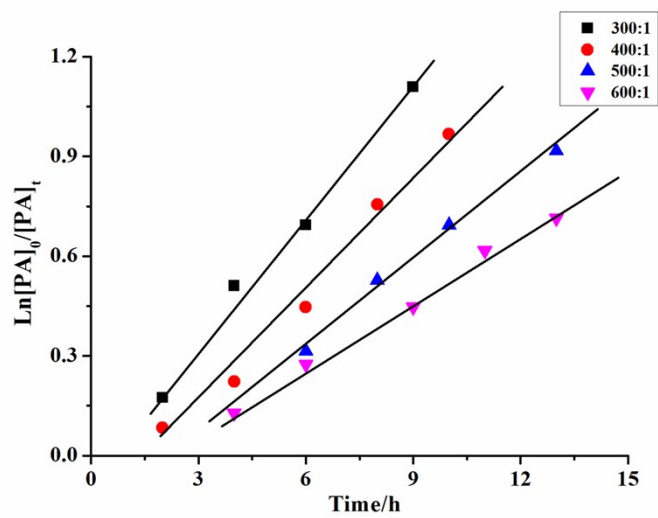


Figure S3. Kinetic plots of the PA conversion with different concentration using complex **1** without the presence of cocatalyst. $[\mathbf{1}]:[i\text{-PrOH}]:[\text{PO}]=1:3:3000$, $80\text{ }^\circ\text{C}$.

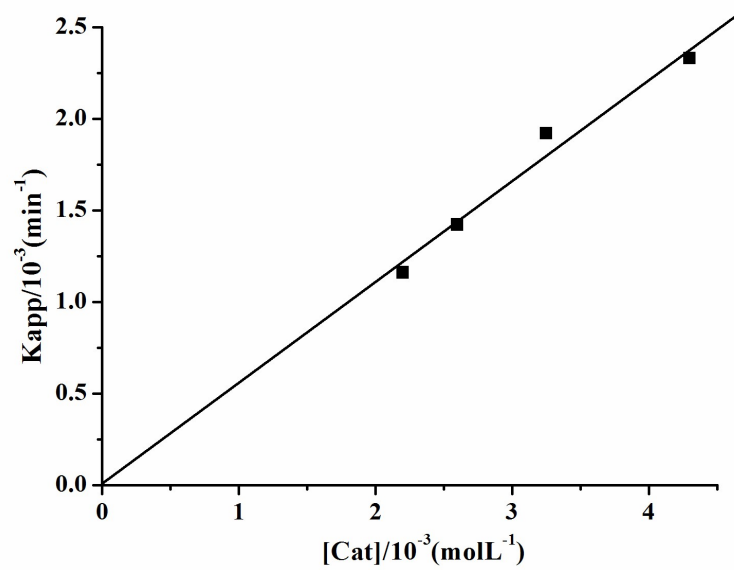


Figure S4 k_{app} vs the concentration of complex **1** for the copolymerization.

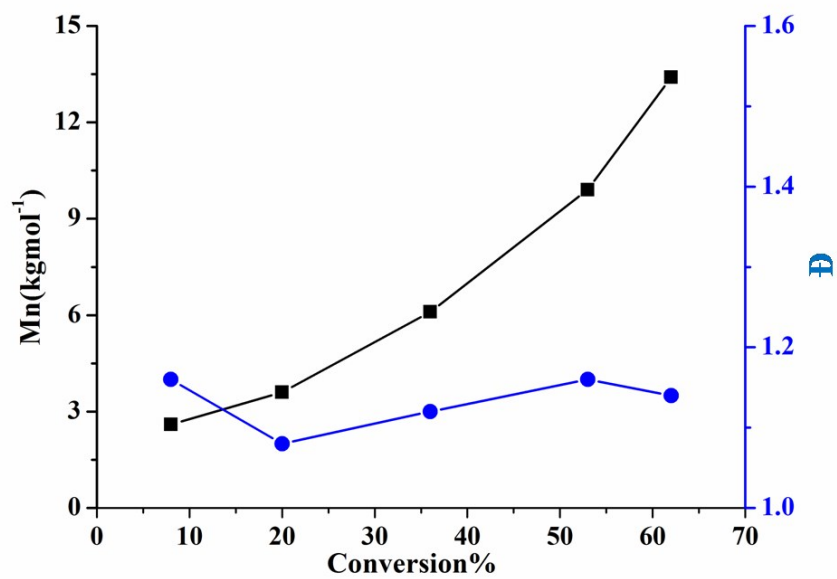


Figure S5 Plot of copolymer Mn and Đ as a function of PA conversion using complex **1** without the presence of cocatalyst, [1]:[i-PrOH]:[PA]:[PO]=1:3:300:3000, 80 °C.

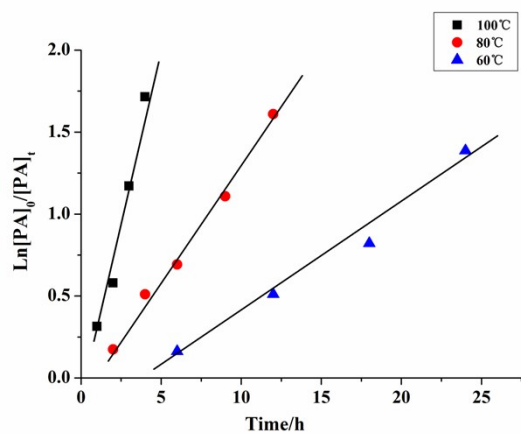


Figure S6 Kinetic plots of the PA conversion with different temperature using complex **1** without the presence of cocatalyst. $[\mathbf{1}]:[i\text{-PrOH}]:[\text{PA}]:[\text{PO}]=1:3:300:3000$, 80 °C.

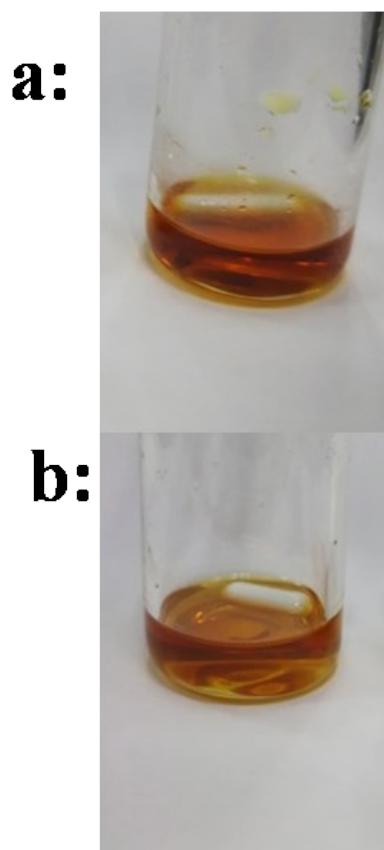


Figure S7 Photographs of copolymerization solutions after 24h. [1]:[i-PrOH]:[PA]:[POCl]=1:3:300:3000, 100 °C a: **a**: [1]:[PPNCl]=1:1 24 h, **b**: 1 equivalent PPNCl was added after copolymerization for 24 hours with catalyst free.

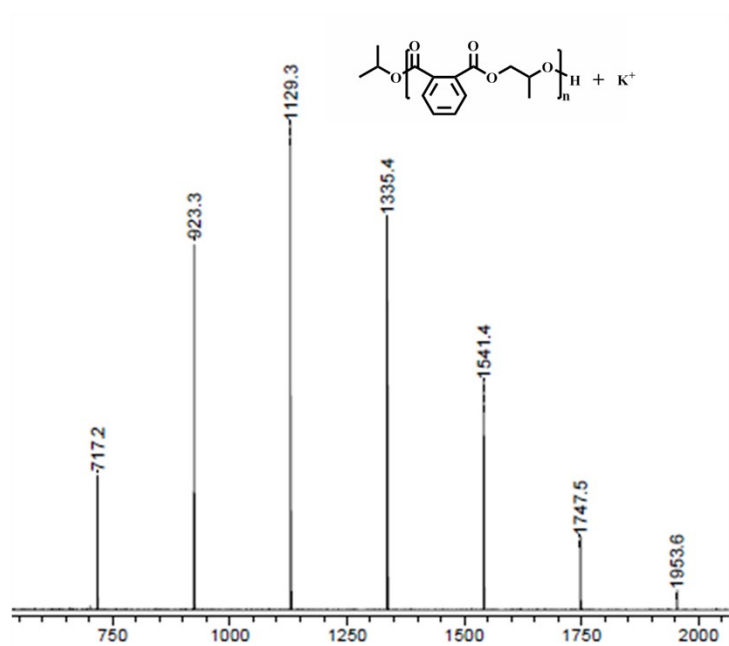


Figure S8 MALDI-TOF mass spectrum of copolymer (obtained from copolymerization using complex **1** without cocatalyst).

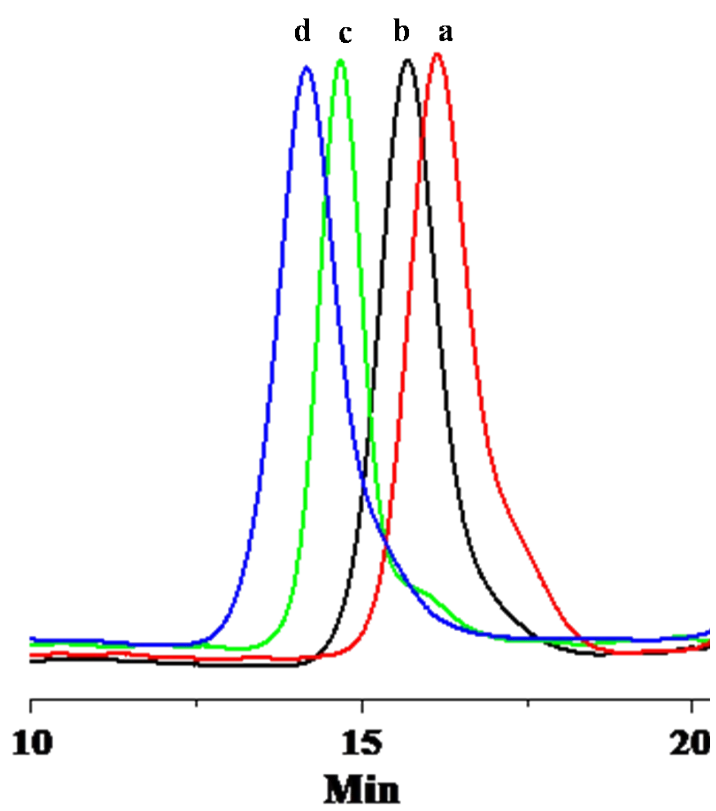


Figure S9. GPC analysis of copolymer obtained from **Table S1**, **a**: entry 3, **b**: entry 4, **c**: entry 5, **d**: entry 6.

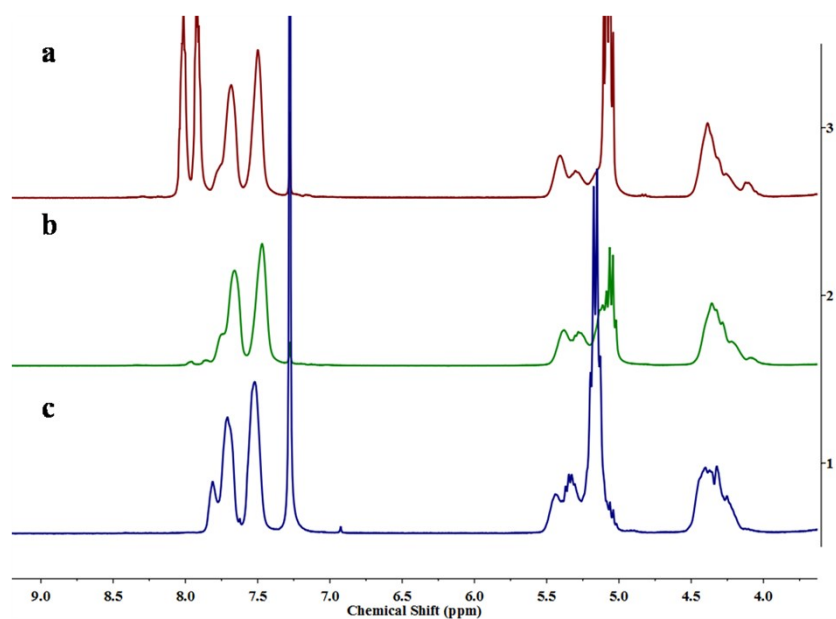


Figure S10 ^1H NMR (300MHz, CDCl_3) spectrum of crude product obtained from copolymerization in different time using complex **1**, $[\mathbf{1}]:[\text{initiator}]:[\text{PA}]:[\text{LLA}]:[\text{PO}]=1:3:300:300:3000$, 80°C , **a**:16 h, **b**:24 h, **c**:48 h.

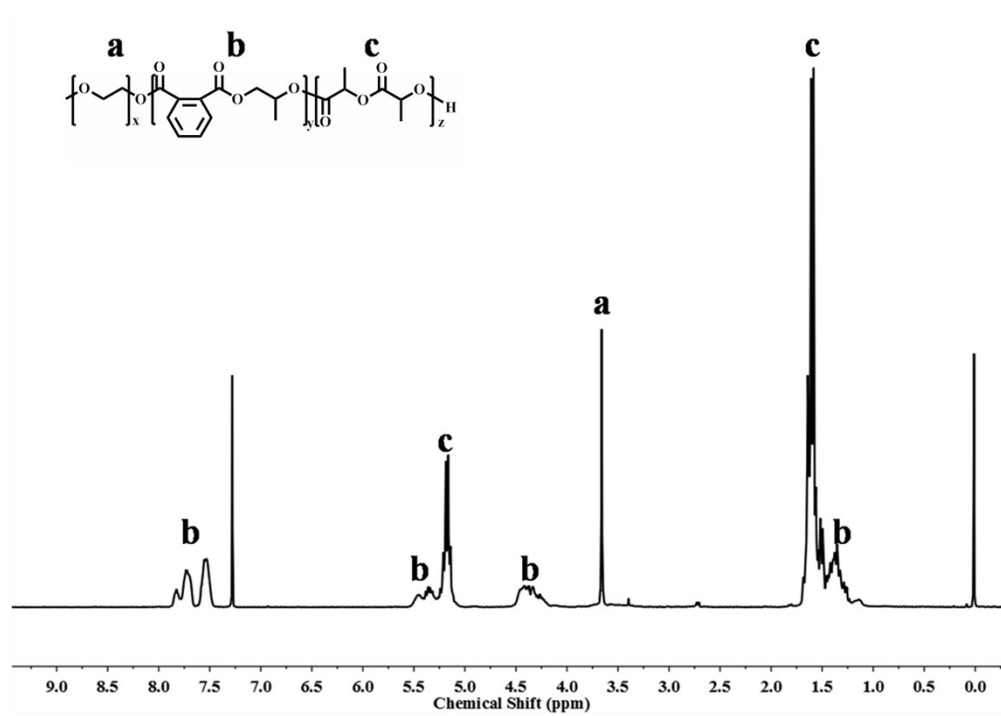


Figure S11 Assigned ¹H NMR (300MHz, CDCl₃) spectrum of LLA, PA and PO copolymer initiated by MPEG(2K).

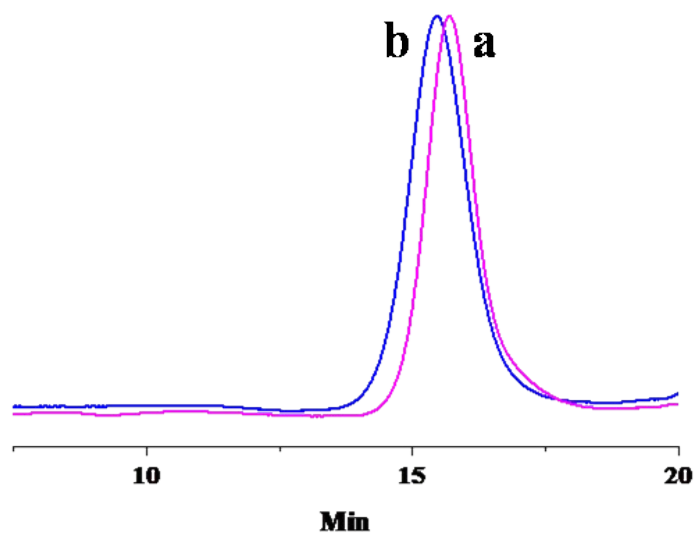


Figure S12. GPC analysis of copolymer obtained from **Table S1**, **a**: entry 4, **b**: entry8.

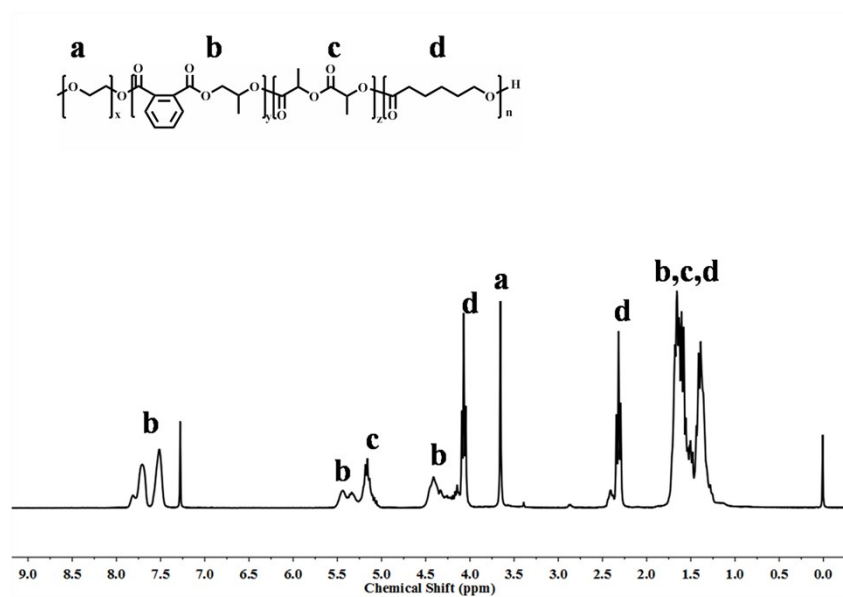


Figure S13 Assigned ¹H NMR (300MHz, CDCl₃) spectrum of LLA, CL, PA and PO copolymer initiated by MPEG(2K).

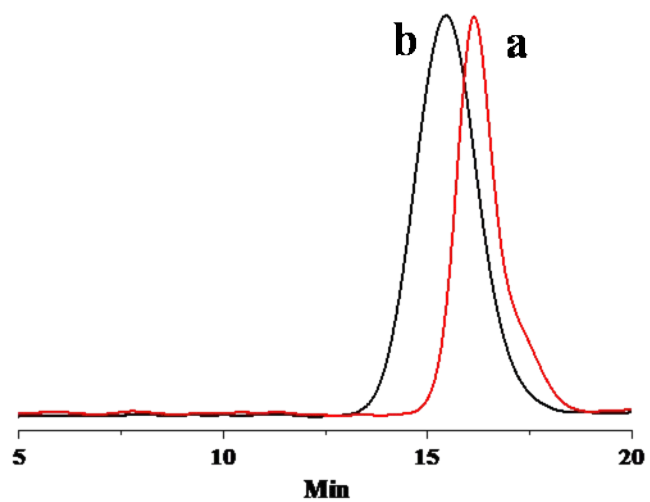


Figure S14. GPC analysis of copolymer obtained from **Table S1**, **a**: entry 8; **b**: entry 9.

Table S1. The ternary copolymerization catalyzed by complex **1**^a.

Entry	[Cat]:[initiator]:[PA]:[LLA]:[PO] _b	Temp/ ^o C	Time/h	Conv(LA)/% ^c	Mn/(kgmol ⁻¹) ^d	Đ ^d
1 ^e	1:3:300:300:3000	70	20	30	7.6	1.10
2 ^e	1:3:300:300:3000	70	48	90	9.4	1.11
3 ^e	1:3:300:300:3000	80	20	92	10.1	1.11
4 ^e	1:3:300:600:6000	80	24	90	13.7	1.10
5 ^e	1:3:600:3000:15000	80	36	95	24.3	1.07
6 ^e	1:3:2000:6000:15000	80	72	97	32.7	1.16
7 ^f	1:3:300:300:5000	80	20	98	10.1	1.16
8 ^f	1:3:300:600:6000	70	42	94	16.1	1.11
9 ^{f,g}	1:3:300:300:6000	80	54	98	16.3	1.18

^aThe designed amount of catalyst was dissolved in 2 mL PO and carefully added into 25 mL autoclave using complex **1** and the autoclave was heated up to suitable temperature. ^b Molar ratio. ^c The results determined by ¹H NMR analysis of the conversion of LLA in the crude reaction mixture and the conversion of PA higher than 99% in all polymerization. ^d Determined by GPC using CH₂Cl₂ as solution, calibrated with polystyrene standard. ^e The copolymerization used 2-propanol as initiator. ^f The copolymerization used MPEG(2K) as initiator. ^g The CL added after 20 h of copolymerization of entry **3** in **Table S1**.

Reference

1. X. Pang, R. Duan, X. Li, C. Hu, X. Wang and X. Chen, *Macromolecules*, 2018, **51**, 906-913.