Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

High-T_g PLA copolymers *via* base-catalyzed transesterification of PLA with 2,5,7-trioxabicyclo[2.2.2]octan-6-one

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1. Characterization of monomers

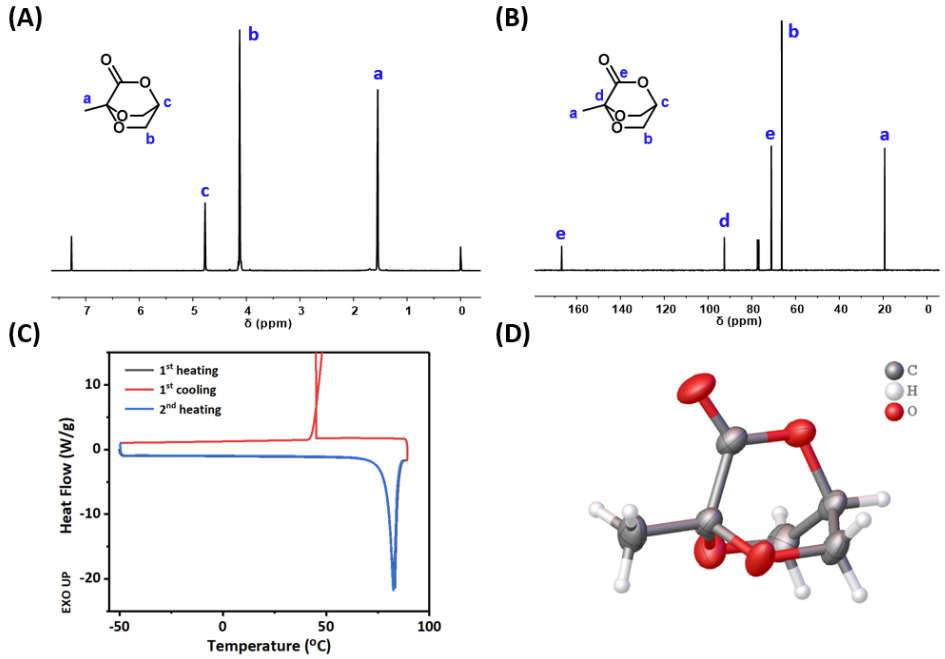

Fig. S1 Characterization of monomer **1Me-TOB**

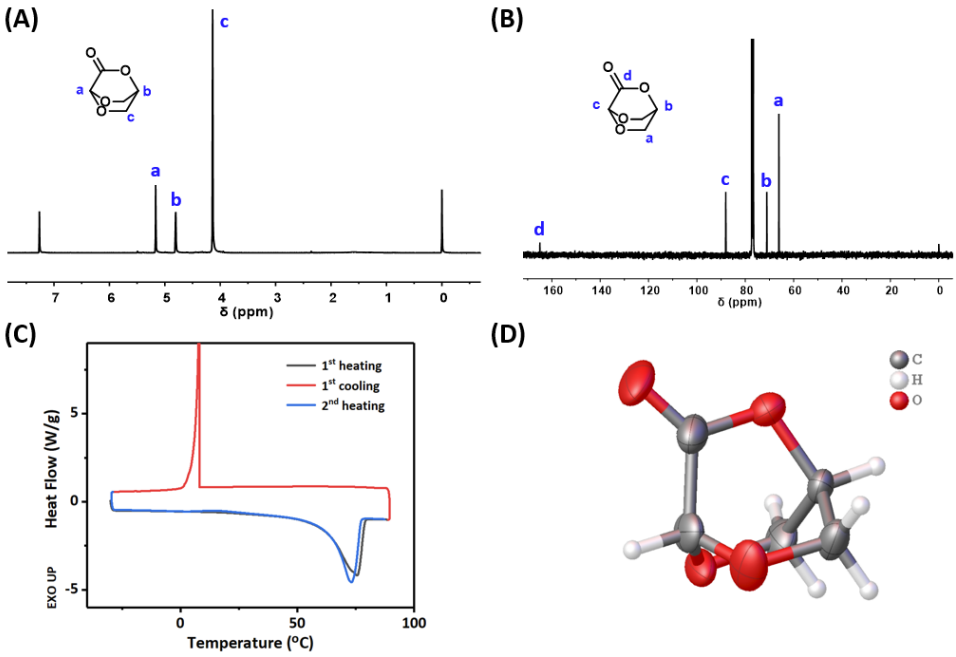

Fig. S2 Characterization of monomer **TOB**

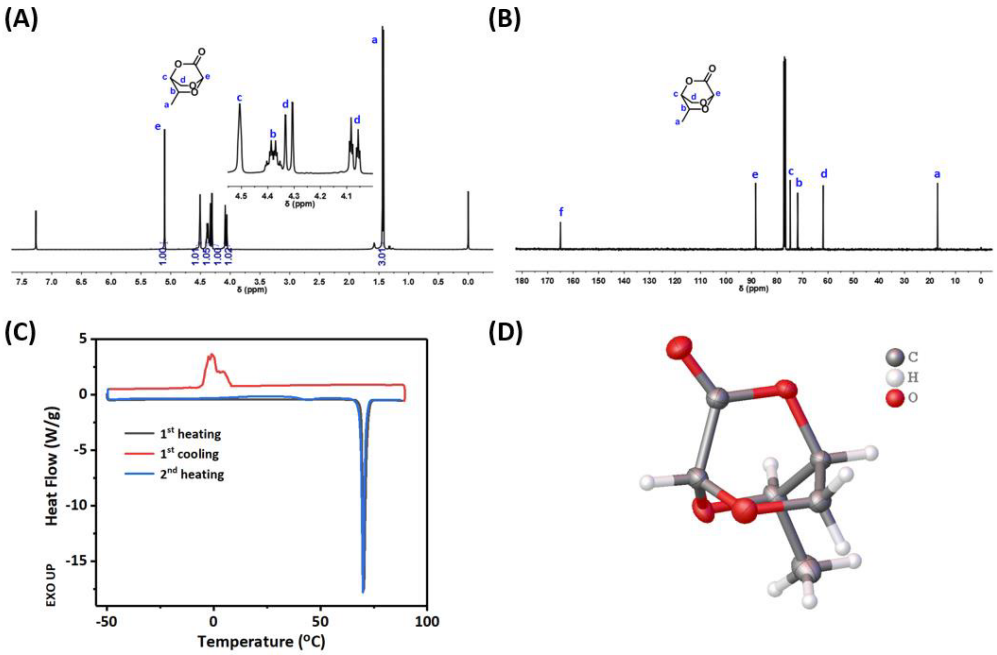

Fig. S3 Characterization of monomer **3Me-TOB**

Table S1 Crystal data and structure refinement for **1Me-TOB**

CCDC number	2216470
Empirical formula	$C_6H_8O_4$
Formula weight	144.12
Temperature/K	180.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	6.6336(3)
b/Å	10.5499(6)
c/Å	18.8351(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1318.15(14)
Z	8
ρ_{calc}g/cm^3	1.452
μ/mm^{-1}	0.124
F(000)	608
Radiation	Mo K\α
2Θ range for data collection/°	7.5040 to 56.7120
Index ranges	$-8 \leq h \leq 8$, $-13 \leq k \leq 13$, $-14 \leq l \leq 24$
Reflections collected	4711
Independent reflections	1503 [R_{int} = 0.0368, R_{sigma} = 0.0275]
Data/restraints/parameters	1503/0/92
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0597, wR_2 = 0.1181
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.1085

Table S2 Crystal data and structure refinement for **TOB**

CCDC number	2216468
Empirical formula	$C_5H_6O_4$
Formula weight	130.10
Temperature/K	179.99
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.5342(9)
b/Å	6.5619(4)
c/Å	9.7191(10)
α/°	90
β/°	115.851(12)
γ/°	90
Volume/Å^3	547.20(10)
Z	4
ρ_{calc}g/cm^3	1.579
μ/mm^{-1}	0.140
F(000)	272
Radiation	Mo K\α
2Θ range for data collection/°	4.994 to 60.124
Index ranges	$-13 \leq h \leq 11$, $-8 \leq k \leq 8$, $-13 \leq l \leq 13$
Reflections collected	3541
Independent reflections	1381 [R_{int} = 0.0407, R_{sigma} = 0.0337]
Data/restraints/parameters	1381/88/101
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ(I)]	R_1 = 0.0807, wR_2 = 0.1626
Final R indexes [all data]	R_1 = 0.0634, wR_2 = 0.1530

Table S3 Crystal data and structure refinement for **3Me-TOB**

CCDC number	2216471
Empirical formula	$C_6H_8O_4$
Formula weight	144.12
Temperature/K	100.00
Crystal system	orthorhombic
Space group	$P2_1\,2_1\,2_1$
a/Å	6.61470(10)
b/Å	8.8811(2)
c/Å	11.0758(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	650.66(2)
Z	4
ρ_{calc}g/cm^3	1.471
μ/mm^{-1}	1.082
F(000)	304
Radiation	Cu K\α
2Θ range for data collection/°	12.776 to 150.870
Index ranges	$-8 \le h \le 8$, $-10 \le k \le 11$, $-13 \le l \le 13$
Reflections collected	12322
Independent reflections	1315 [Rint = 0.0166, Rsigma = 0.0393]
Data/restraints/parameters	1315/0/92
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0271, wR_2 = 0.0613
Final R indexes [all data]	R_1 = 0.0254, wR_2 = 0.0606

2. Characterization of **PTOB**

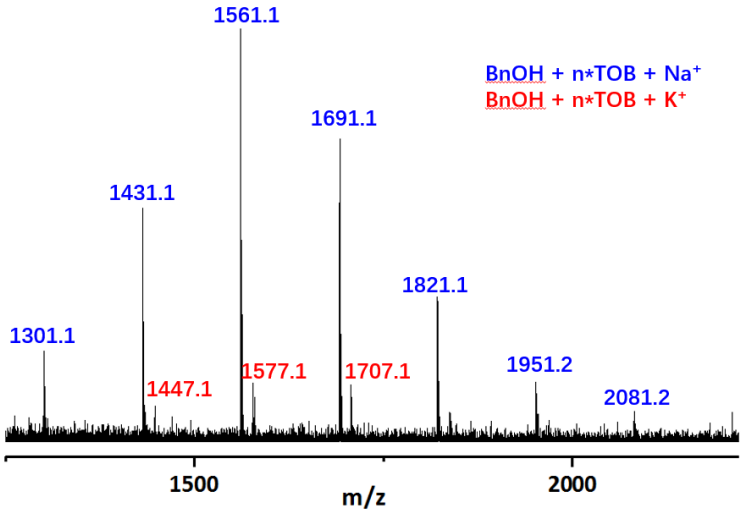

Fig. S4 MALDI-TOF mass spectrum of the BnOH-initiated linear **PTOB** (Table 1, entry 2)

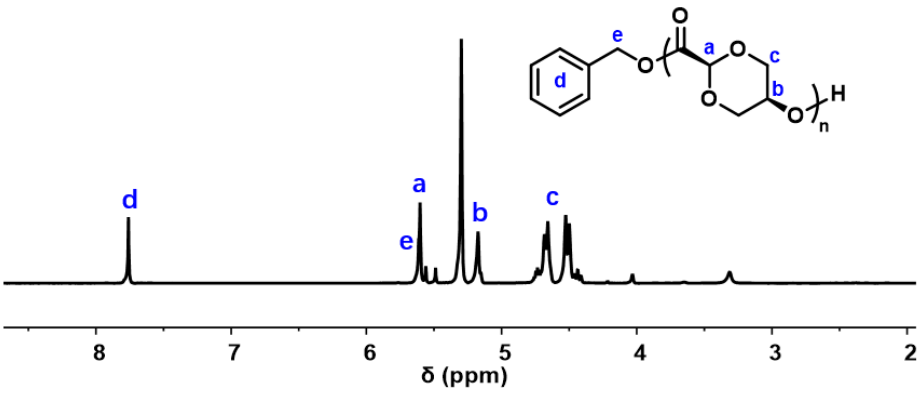

Fig. S5 ^{1}H NMR spectrum of P**TOB** (in d_2-HFIP) (Table 1, entry 2)

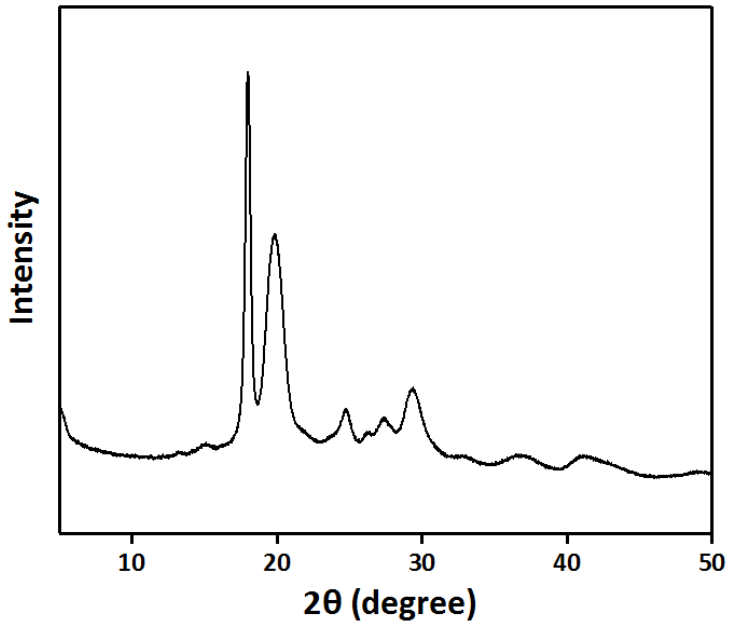

Fig. S6 Powder X-ray diffraction pattern of **PTOB**(Table 1, entry 2)

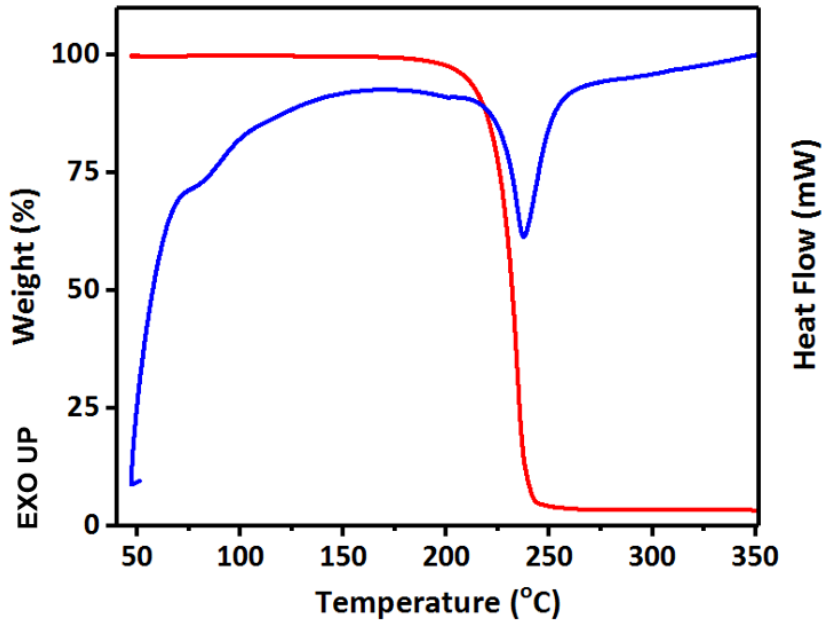

Fig. S7 TGA thermogram of **PTOB**. (20 °C/min, $T_{d,5\%}$ = 210 °C) (Table 1, entry 2)

3. Characterization of oligomers of **TOB**

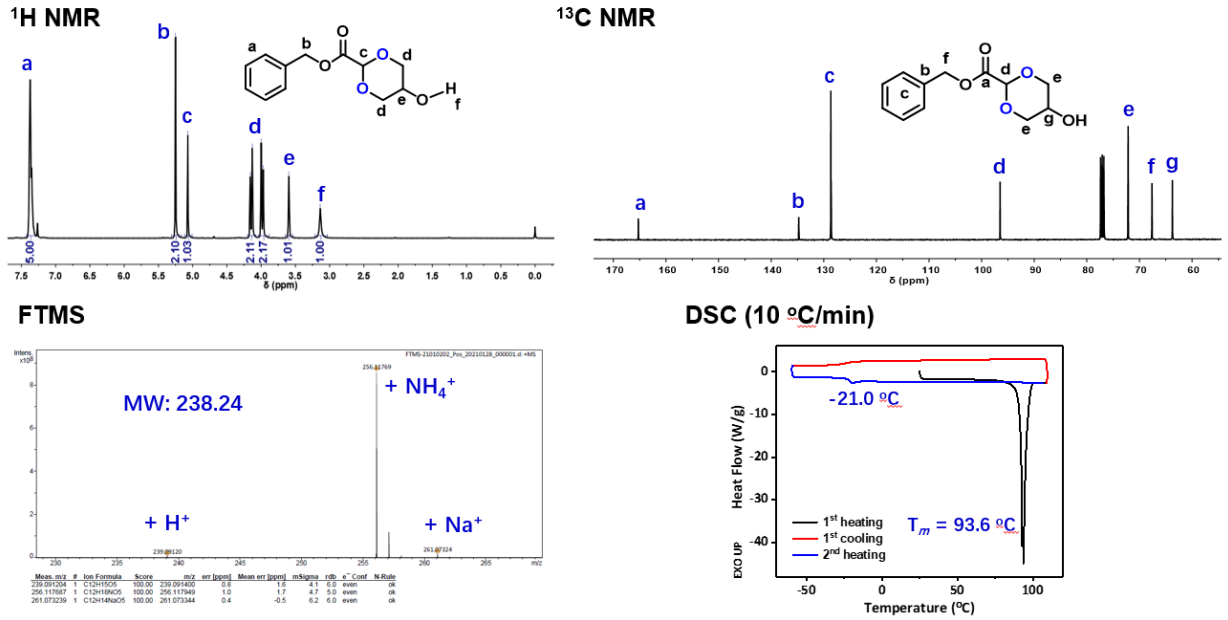

Fig. S8 Characterization data of compound **O1**

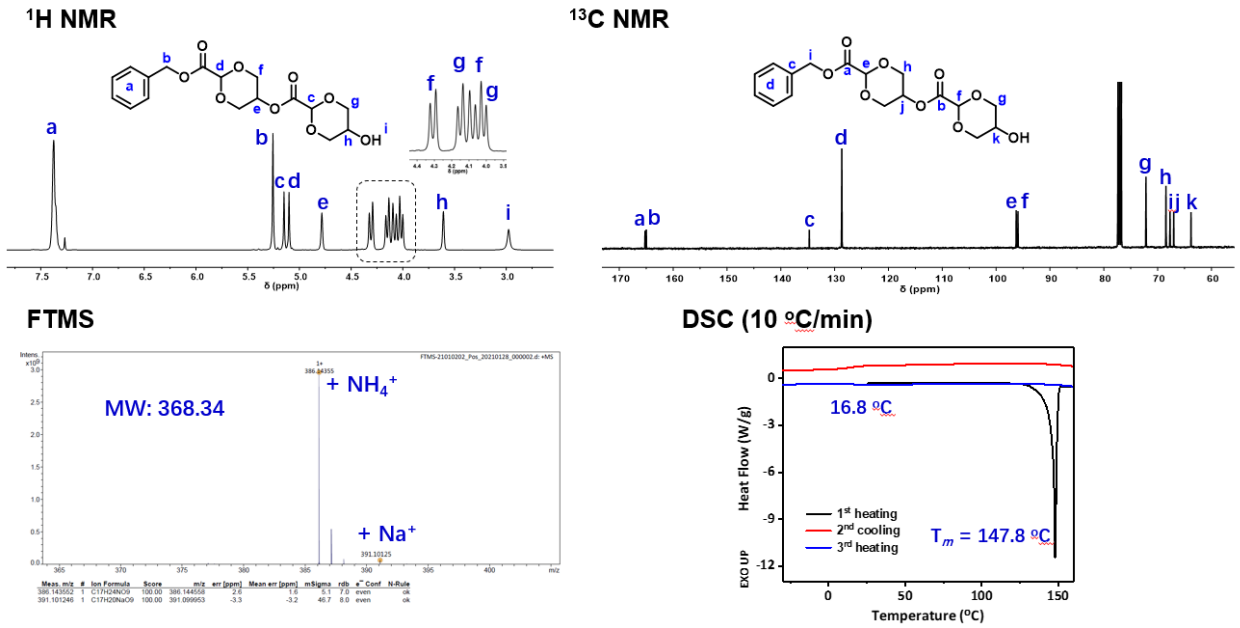

Fig. S9 Characterization data of compound **O2**

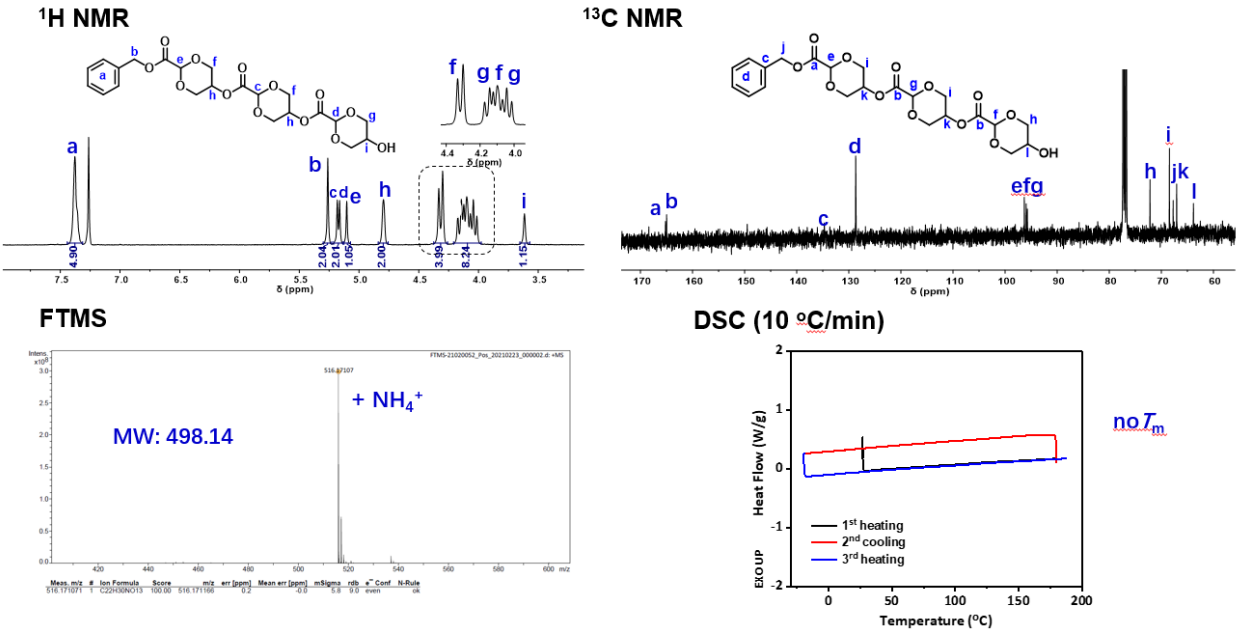

Fig. S10 Characterization data of compound **O3**

Table S4 Solubility, melting temperature of **TOB** oligomers

	O1	**O2**	**O3**
Solubility	Soluble in EtOAc & $CHCl_3$	Soluble in $CHCl_3$ & Insoluble in EtOAc	Insoluble in $CHCl_3$
T_m (°C)	93.6	147.8	> 190

Table S5 Crystal data and structure refinement for compound **O1**

CCDC number	2216477
Empirical formula	$C_{12}H_{14}O_5$
Formula weight	238.23
Temperature/K	169.99
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.1805(10)
b/Å	9.2464(10)
c/Å	11.1482(10)
α/°	90
β/°	105.801(10)
γ/°	90
Volume/Å^3	1108.945(19)
Z	4
ρ_{calc}g/cm^3	1.427
μ/mm^{-1}	0.941
F(000)	504
Crystal size/mm^3	0.23 × 0.21 × 0.05
Radiation	Cu K\α
2Θ range for data collection/°	8.218 to 150.402
Index ranges	$-13 \le h \le 13$, $-11 \le k \le 11$, $-13 \le l \le 13$
Reflections collected	14573
Independent reflections	2202 [R_{int} = 0.0160, R_{sigma} = 0.0089]
Data/restraints/parameters	1381/0/155
Goodness-of-fit on F^2	1.104
Final R indexes [I>=2σ(I)]	R_1 = 0.0336, wR_2 = 0.0867
Final R indexes [all data]	R_1 = 0.0341, wR_2 = 0.0869
Largest diff. peak/hole / e Å^{-3}	0.19/-0.27

Table S6 Crystal data and structure refinement for compound **O2**

CCDC number	2216478
Empirical formula	$C_{17}H_{20}O_9$
Formula weight	368.33
Temperature/K	170.01(10)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	11.74180(10)
b/Å	34.0977(4)
c/Å	8.47780(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3394.24(6)
Z	8
ρ_{calc}g/cm^3	1.442
μ/mm^{-1}	1.008
F(000)	1552.0
Crystal size/mm^3	0.31 × 0.25 × 0.03
Radiation	Cu K\a
2Θ range for data collection/°	5.184 to 151.064
Index ranges	$-13 \leq h \leq 14$, $-41 \leq k \leq 42$, $-13 \leq l \leq 10$
Reflections collected	19029
Independent reflections	5758 [R_{int} = 0.0198, R_{sigma} = 0.0195]
Data/restraints/parameters	5758/1/471
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ(I)]	R_1 = 0.0366, wR_2 = 0.1007
Final R indexes [all data]	R_1 = 0.0377, wR_2 = 0.1018
Largest diff. peak/hole / e Å^{-3}	0.77/-0.36

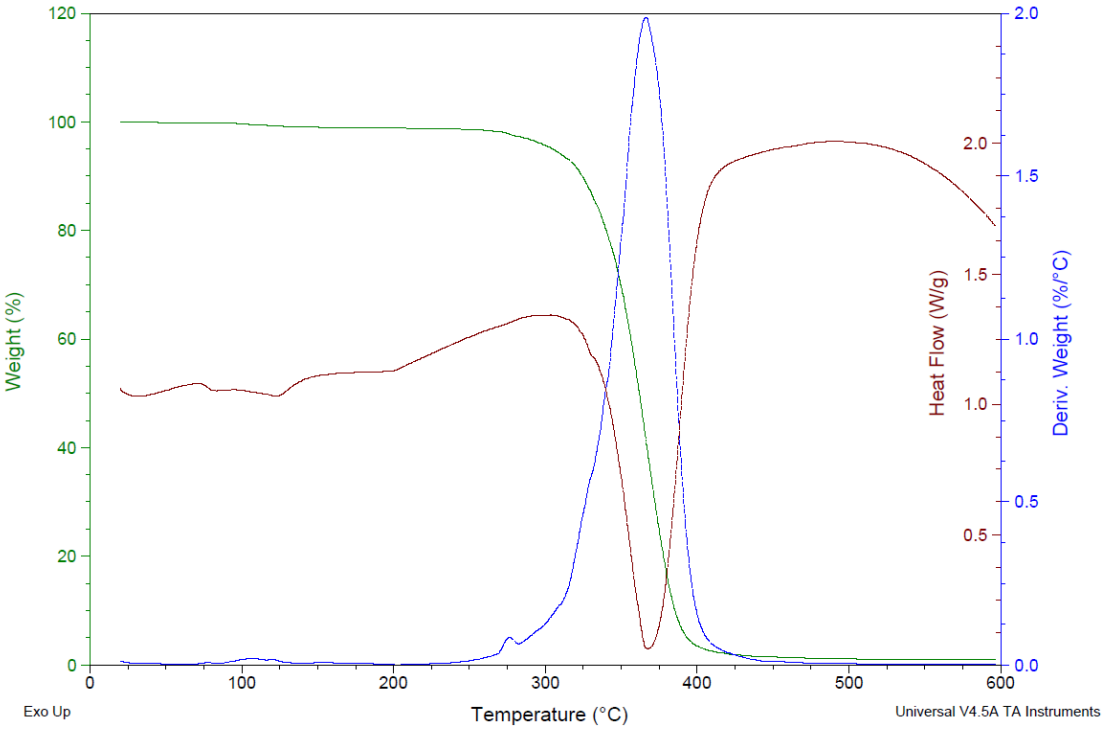

Fig. S11 TGA thermogram of PLA-*co*-**PTOB**. (20 °C/min, $T_{d,5\%}$ = 310 °C)

Table S7 Four typical copolymers for sequence analysis

Sample	Monomer	[LA]:[**TOB**]:[I]	**TOB** mol/%	T_g/°C
1[a]	*rac*-LA + **TOB**	50:150:1	49	99.1
2[a]	*rac*-LA + **TOB**	150:50:1	13	56.7
3[b]	*L*-LA + **TOB**	400:400:1	40	92.9
4[b]	*L*-LA + **TOB**	666:133:1	13	70.0

[a] BnOH as initiator, [M]=2 M, DCM, 30 °C, 6 h.;
[b] 1,4-benzenedimethanol as initiator, [M]=1 M, DCM, -20 °C, 12 h

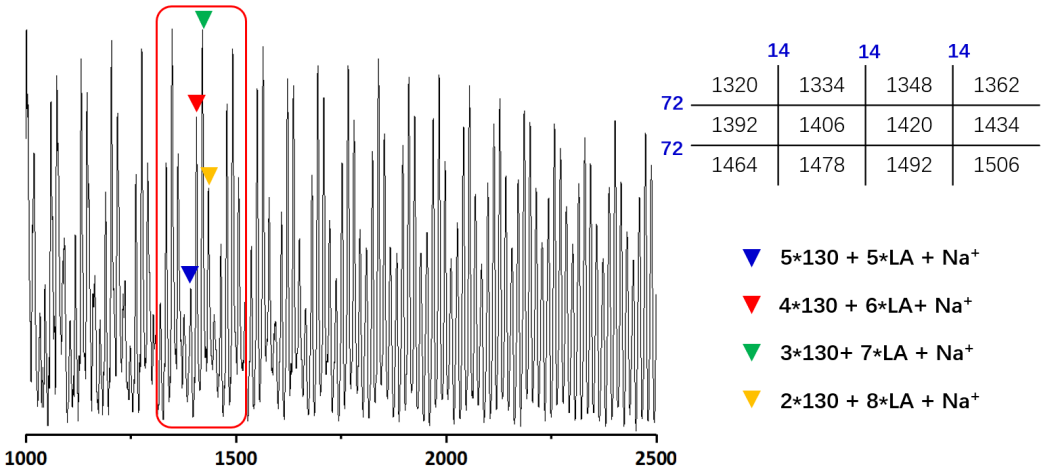

Fig. S12 MALDI-ToF mass spectra of PLA-*co*-**PTOB**. There are cyclic polymers due to transesterification and copolymers containing 1/2 LA units. The Δm/z of the three groups of peaks in the red square is 1/2 MW of LA. The four peaks of inverted triangulation, Δm/z = 14, are the difference of MW between **TOB** and LA.

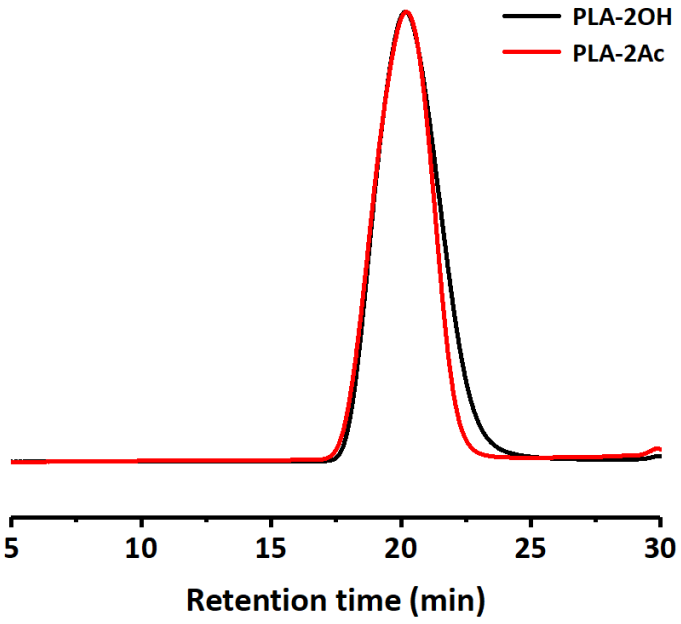

Fig. S13 GPC traces of PLA-2OH (M_n = 24.4 kDa, $Đ$ = 1.31) and PLA-2Ac (M_n = 28.1 kDa, $Đ$ = 1.26)

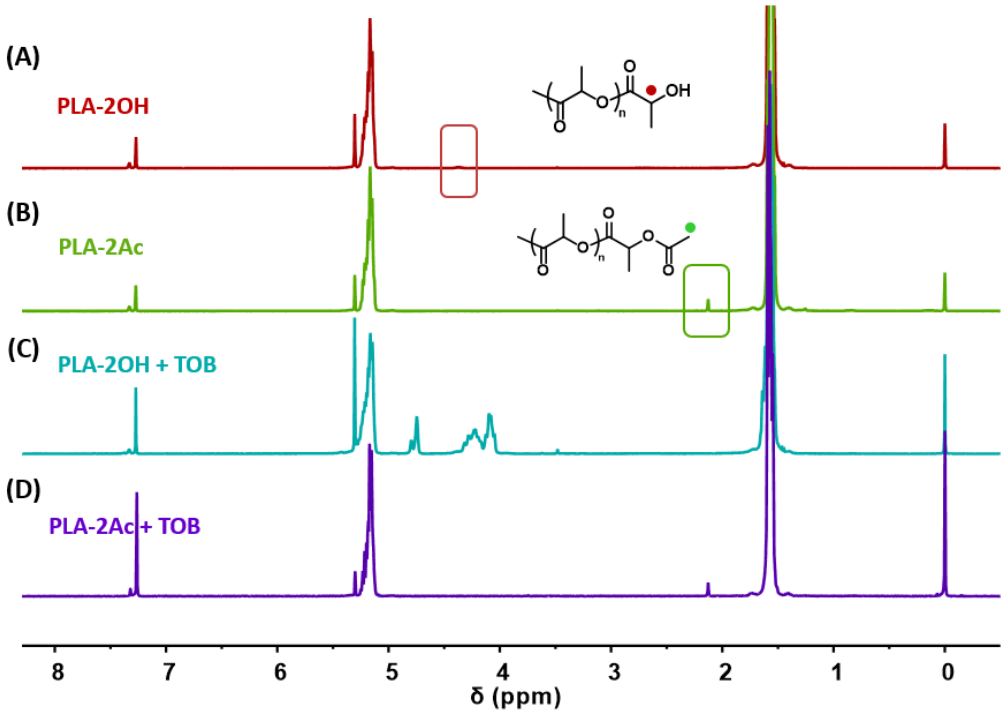

Fig. S14 ^{1}H NMR spectra of (A) α, ω-PLA diol sample (PLA-2OH); (B) acetyl-capped PLA sample (PLA-2Ac); (C) PLA-*co*-PTOB obtained by the TBD-catalyzed ring-opening transesterification polymerization of PLA-2OH with **TOB**; (D) recovered PLA-2Ac after being reacted with **TOB** in the presence of TBD.