Supporting Information

Highly Isoselective Ring-opening Polymerization of *rac-O*-Carboxyanhydrides Using a Zinc Alkoxide Initiator

Yaqin Cui, Jinxing Jiang, Xiaobo *Pan and Jincai Wu**

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Lanzhou University, Lanzhou 730000, People's Republic of China.

Materials and Methods

All operations of air and moisture sensitive materials were performed under a dry argon atmosphere in a glovebox or using standard Schlenk techniques. Toluene and THF were dried by refluxing with sodium and benzophenone. CH_2Cl_2 was distilled from P_2O_5; the ligand 1, 3, 5 - trimesityldipyrromethene (**TMPH**) was prepared by the method of the literature.[1] Diethylzinc(1.0M solution in toluene, MkSeal) were purchased from Shanghai Macklin Biochemical Co.,Ltd., *O*-Carboxyanhydrides were prepared according to literature procedures.[2] PheOCA and Try(Bn)OCA were sublimated at 90 °C and 105 °C vacuum, respectively. $CDCl_3$ was purchased from J &K Scientific, Ltd., in Beijing and deuteron solvents were dried over activated molecular sieves.

NMR spectra were recorded on Varian Mercury Plus 300 MHz, JNM-ECS 400 MHz spectrometers and Varian INOVA 600 MHz. ^1H NMR chemical shifts are reported in ppm versus residual protons in deuteron-solvents as follows: δ 7.26 ppm for chloroform-*d*. ^{13}C NMR chemical shifts are reported in ppm versus residual ^{13}C in the solvent: δ 77.00 ppm for chloroform-*d*. The molecular weights (M_n and M_w) and the molecular mass distributions ($Đ$) of the polymer samples were measured by gel permeation chromatography (GPC) at 40 °C using THF as a solvent, an eluent flow rate of 1 mL/min, and narrow polystyrene standards as reference samples. The measurements were performed via using a Shodex GPC KF-800 system that was equipped with a Shodex RI-201H detector using Shodex-KF-803 Styragel columns (400 - 70000 kg/mol). Each reported value was corrected using a factor of 0.58 for poly(LacOCA) according to the literature,[3] poly(PheOCA) and poly(Try(Bn)OCA) were not corrected. The MALDI-TOF mass spectroscopic data were obtained via using HCCA as the matrix and CH_3COONa as cationization agent in a Bruker auto flex speed MALDI-TOF mass spectrometer. The NMR molar masses of polyOCAs samples were determined from the relative integration of the signals for the main-chain methine units and chain ends.

The synthesis of the zinc alkoxide initiator (*rac*-TMP-Zn) supported by 1, 3, 5-trimesityldipyrromethene (TMPH): In an argon atmosphere, the dry ligand **TMPH** (0.5 mmol) was put into a 100-mL Schlenk flask, then 50 mL THF was added into the flask; subsequently, diethyl zinc (0.5 mL, 0.5 mmol) was added into the solution dropwise at an ice bath, the reaction mixture was refluxed for 12 h. After cooling the system to room temperature, the flask was brought into the glovebox, 0.5 mmol of *rac*-methyl lactate was added; the mixture continued to be refluxed for 3 h, and allowed to stand overnight at room temperature; then there were a lot of orange solid precipitation. Finally, the orange solid was filtrated and washed with a little THF, solvent was removed under vacuum to afford orange crystalline powder (0.22 g, yield 65%). ^{1}H NMR (400 MHz, chloroform-*d*, 25 °C):δ 6.94 (s, 2H, m-$C_6H_2(CH_3)_3$), 6.76 (br, 4H, m-$C_6\mathit{H}_2(CH_3)_3$), 6.57 (d, *J* = 4 Hz, 2H, pyrrole C-*H*), 6.20 (d, *J* = 4 Hz, 2H, pyrrole C-*H*), 3.59(s, 3H, $OC\mathit{H}_3$), 3.38(q, *J* = 6.8 Hz, 1H, $C\mathit{H}CH_3$), 2.38(s, 3H, m-$C_6H_2(C\mathit{H}_3)_3$), 2.22(s, 6H, m-$C_6H_2(C\mathit{H}_3)_3$), 2.19(s, 6H, m-$C_6H_2(C\mathit{H}_3)_3$), 2.09(br, 12H, m-$C_6H_2(C\mathit{H}_3)_3$), 0.52(d, *J* = 6.8 Hz, 3H, $CHC\mathit{H}_3$).^{13}C NMR (100MHz, chloroform-*d*, 25 °C): δ 191.00, 160.67, 145.45, 139.87, 137.41, 136.98, 136.63, 135.37, 133.04, 131.69, 127.46, 126.75, 117.83, 68.93, 53.35, 22.09, 21.14, 20.97, 20.25, 19.80.

General procedure for polymerization of *rac*-LacOCA

A typical polymerization procedure is illustrated by the synthesis of poly(α-Hydroxy acids) ([*rac*-LacOCA]$_0$ / [***rac*-TMP-Zn**]$_0$ = 100 : 1; Table S1, Entry 2). In the glove-box, ***rac*-TMP-Zn** (0.0067 g, 0.01 mmol) was dissolved in 5 mL THF in a 50 mL Schlenk flask, and put 5 mL THF solution of *rac*-LacOCA (0.1160 g, 1.0 mmol) in an addition tube, the reaction units were taken out of the glove box. Then, both of the solutions were cooled to 0 °C for 10 min, the solution of *rac*-LacOCA was added into the Schlenk flask, started timing. The reaction mixture was rapidly stirred at 0 °C for 8 s, and was immediately quenched by a few drops of water, stopped timing. After removing solvent under vacuum, a solid was obtained by recrystallization from a CH_2Cl_2/hexane mixed solvent and dried under vacuum.

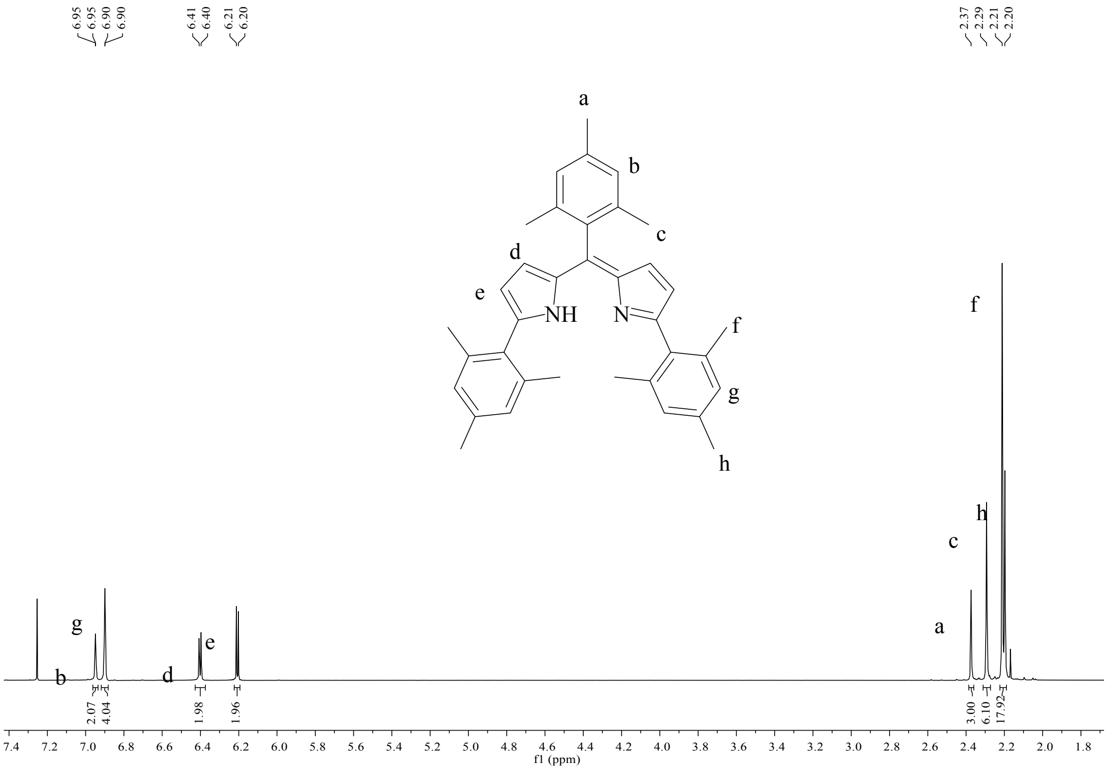


Fig. S1 ^{1}H NMR of **TMPH** (300 MHz, $CDCl_3$, 25 °C).

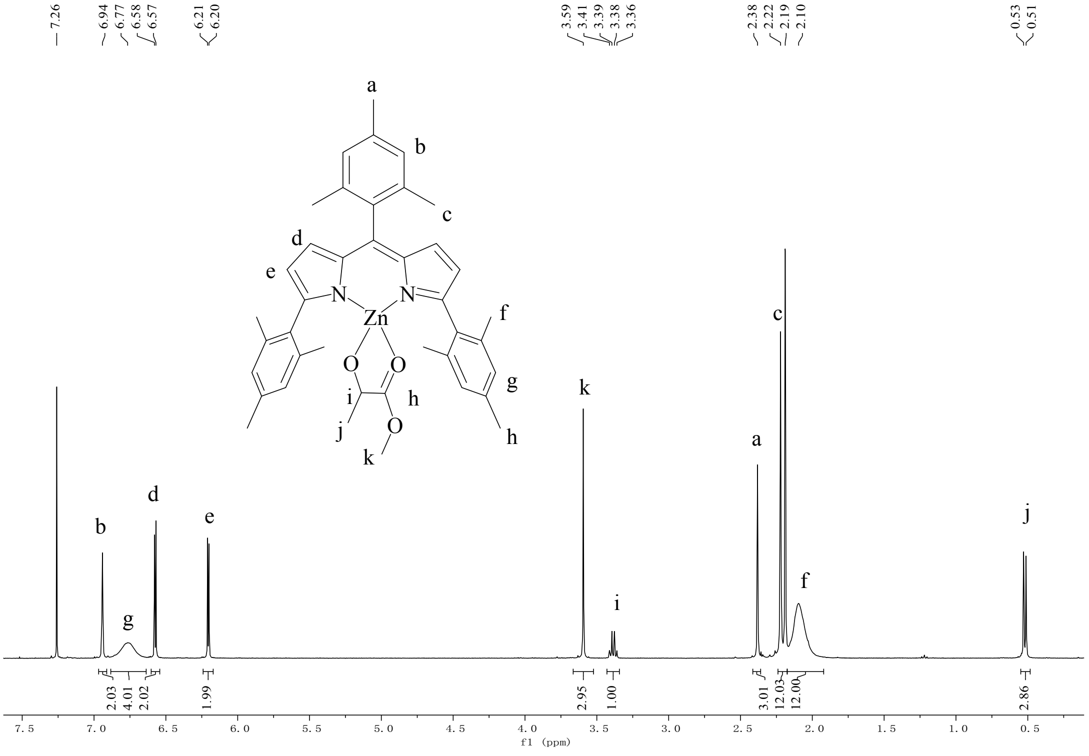


Fig. S2 ^{1}H NMR of **TMP-Zn** (400 MHz, $CDCl_3$, 25 °C).

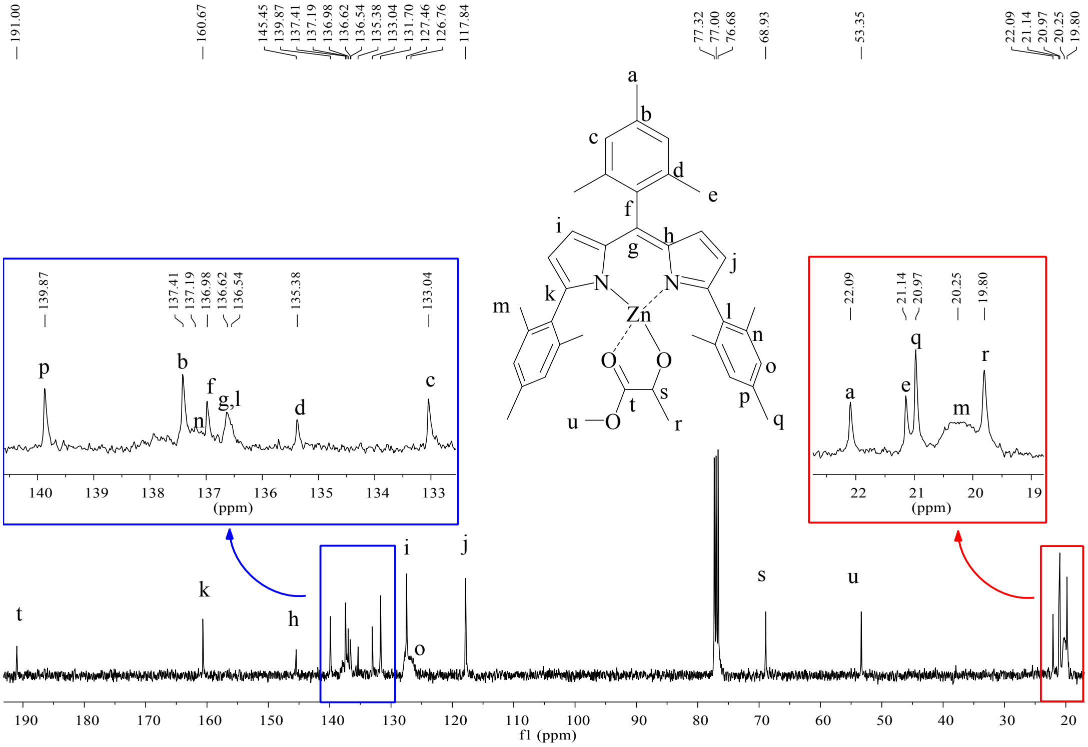


Fig. S3 ^{13}C NMR of **TMP-Zn** (100 MHz, CDCl$_3$, 25 ^{o}C).

Table S1 Isoselective ROP of OCAs initiated by **TMP-Zn**. [a]

Entry	OCAs	$[OCA]_0$/ $[\mathbf{TMP\text{-}Zn}]_0$	Time	*Conv.* *(%)* [b]	$M_{n,\ obsd}$ [c] *(g / mol)*	$M_{n,\ calc}$ [d] *(g / mol)*	$M_{n,\ NMR.}$ [e] *(g / mol)*	$Đ$ [c]	P_m [f]
1	*rac*-LacOCA	20:1	8±2 s	99	1300	1500	1500	1.14	0.92
2	*rac*-Lac*OCA*	100:1	8±2 s	99	7300	7300	7200	1.18	0.92
3	*rac*-Lac*OCA*	150:1	8±2 s	98	11200	10700	10700	1.24	0.92
4	*rac*-LacOCA	200:1	8±2 s	96	12300	13900	13900	1.32	0.92
5	*rac*-PheOCA	20:1	1.5 min	96	2100	2900	2700	1.06	0.84
6	*rac*-PheOCA	40:1	3.5 min	90	5000	5400	6200	1.14	0.83
7	*rac*-PheOCA	80:1	10 min	88	10500	10500	10000	1.21	0.84
8	*rac*-PheOCA	100:1	18 min	77	13000	11500	12200	1.43	0.84
9	*rac*-PheOCA	200:1	40 min	48	15300	14300	14000	1.24	0.83

[a] Conditions: Reactions were carried out under a dry nitrogen atmosphere, $[OCA]_0$ / $[\mathbf{TMP\text{-}Zn}]_0$ = 100: 1, 0.01 mmol of initiator, 10 mL of THF, at 0 °C to the annotated. [b] Determined by ^1H NMR spectra. [c] Experimental M_n and $Đ$ determined by GPC in THF against polystyrene standards, and corrected using the factor 0.58 for poly(LacOCA), and the M_ns of poly(PheOCA) were not corrected.[3] [d] Determined from the relative integration of the signals for the main-chain methine units and chain ends. [e] Calculated from the equation: (molar mass of OCA –molar mass of CO_2) × $[OCA]_0/[Cat.]_0$ ×Conv. % + the molar mass of the initiators. [f] Determined by analyses of all of the tetrad signals in the methine region of the ^1H NMR spectra for LacOCA, and determined by analyses of all of the triad signals in the methene region of the ^{13}C NMR spectra for PheOCA. [g] In 10 mL toluene. [h] In 10 mL dichloromethane. [i] At -70 °C.

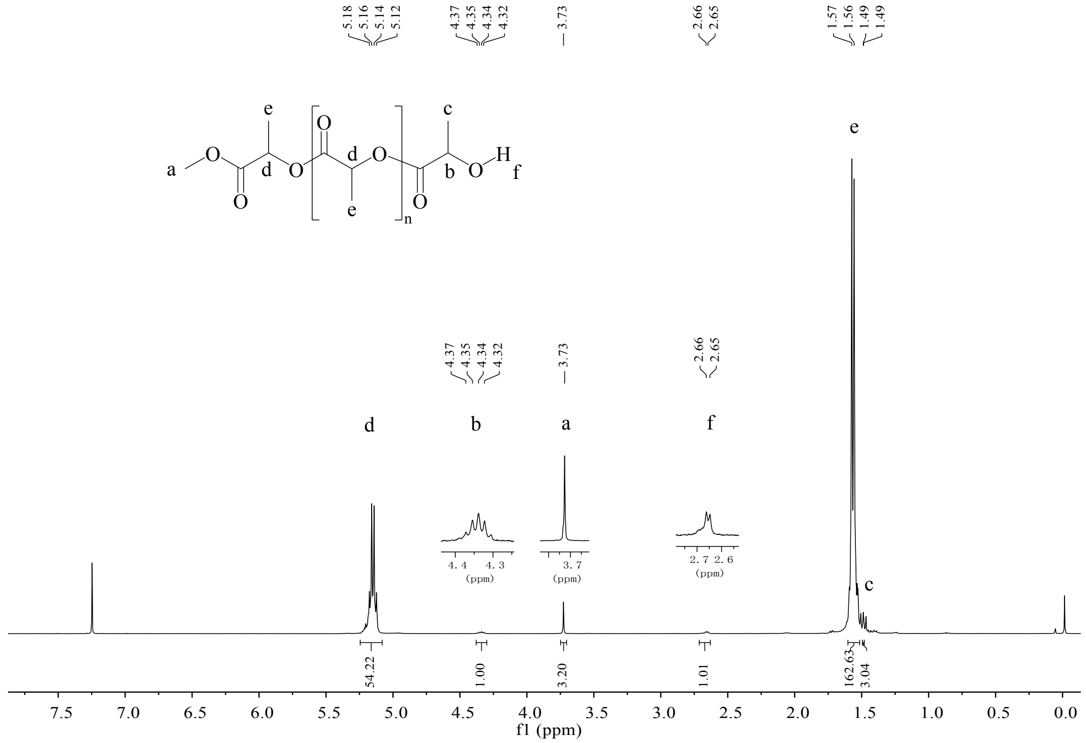


Fig. S4 ^1H NMR of the poly(*rac*-LacOCA) using ***rac*-TMP-Zn** as an initiator (400 MHz, $CDCl_3$, 25 °C) (Table 1, Entry 7).

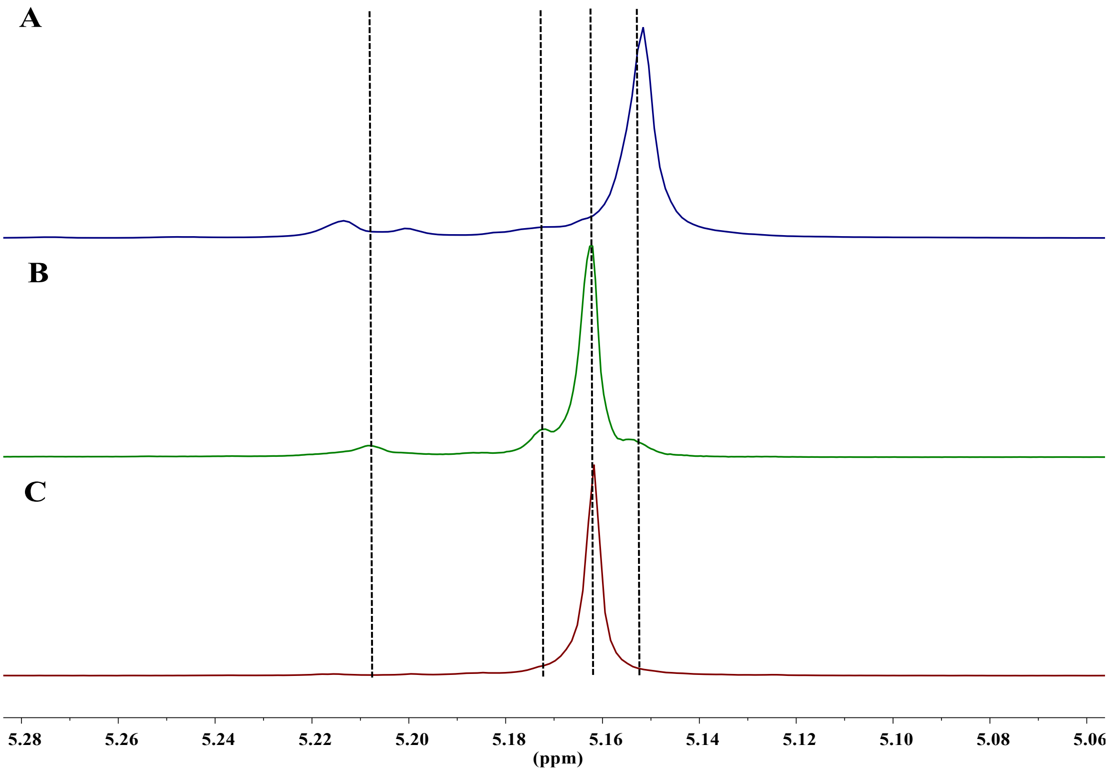
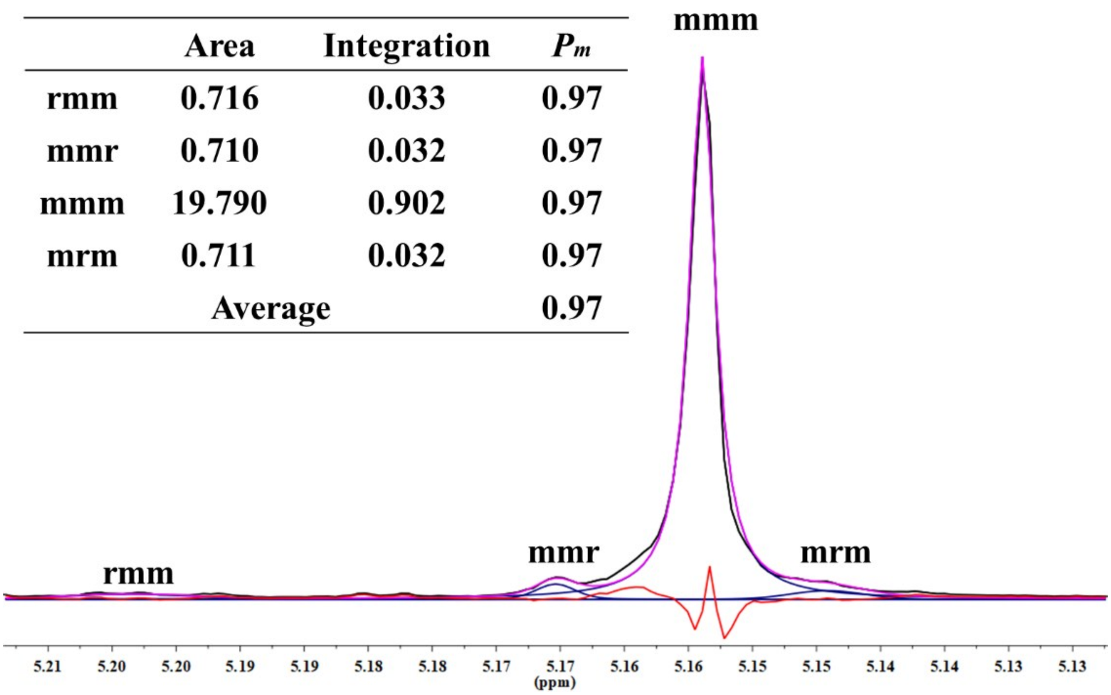
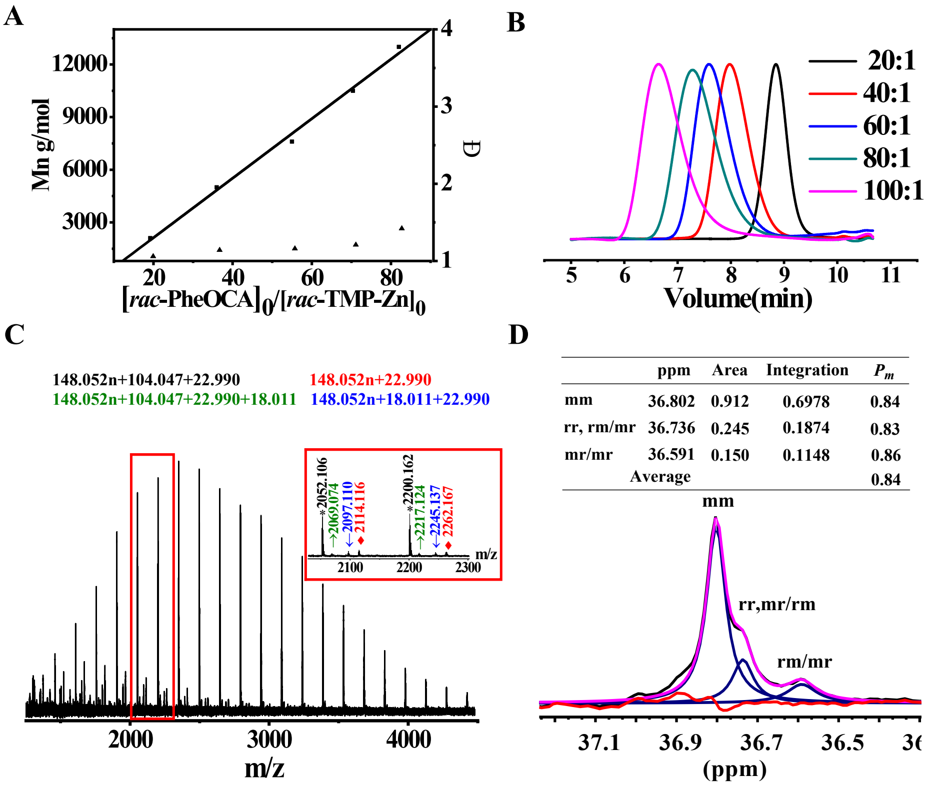


Fig. S5 The homonuclear decoupled ^{1}H NMR spectra of polymer obtained using different catalysts/initiators: (A) the syndiotactic poly(*rac*-LacOCA) obtained using Hf alkoxide as an initiator [2]; (B) poly(*rac*-LacOCA) using ***rac*-TMP-Zn** as an initiator; (C) poly(*L*-LacOCA) using ***L*-TMP-Zn** as an initiator.



	Area	Integration	P_m
rmm	**0.716**	**0.033**	**0.97**
mmr	**0.710**	**0.032**	**0.97**
mmm	**19.790**	**0.902**	**0.97**
mrm	**0.711**	**0.032**	**0.97**
	Average		**0.97**

Fig. S6 Deconvolution of the homonuclear decoupled ^{1}H NMR spectrum of the polymer with a P_m value of 0.97 (Table 1, Entry 8), the assignments of tetrads and the calculation method of P_m were conducted according to the literature[2].



	ppm	Area	Integration	P_m
mm	36.802	0.912	0.6978	0.84
rr, rm/mr	36.736	0.245	0.1874	0.83
mr/mr	36.591	0.150	0.1148	0.86
Average				0.84

Fig. S7 (A)Plots of M_n and $Đ$ of poly(*rac*-PheOCA) versus [*rac*-PheOCA]$_0$ / [***rac*-TMP-Zn**]$_0$ ratio; (B) GPC traces of the poly(*rac*-PheOCA) prepared by ***rac*-TMP-Zn**; (C) The MALDI-TOF spectrum of the polymer (Table S1, Entry 5); (D) The methene region of the ^{13}CNMR spectrum of poly(PheOCA) with a low deviation (red line) P_m = 0.84 (Table 1, Entry 11), the calculation method of P_m is consistent with the literature[2].

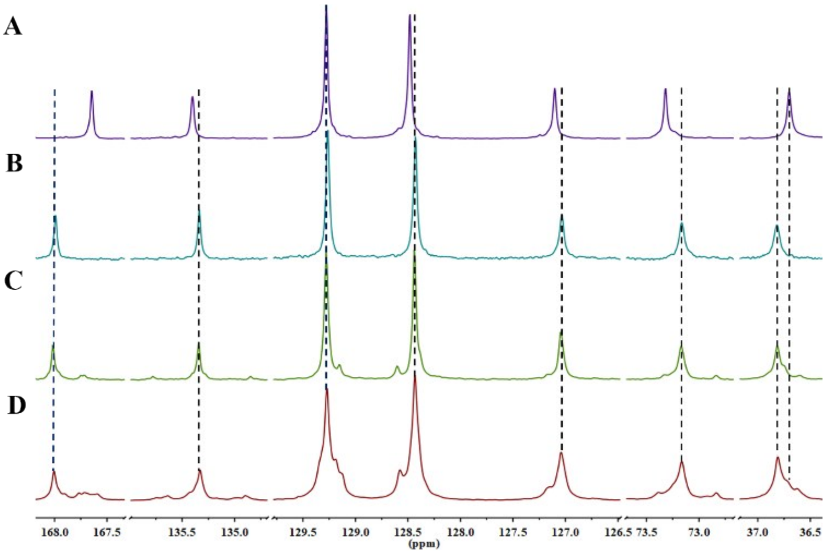


Fig. S8 Details of the regions of the ^{13}CNMR spectra of Poly(PheOCA) obtained using different catalysts/initiators: (A) the syndiotactic poly(*rac*-PheOCA) obtained using Hf alkoxide as an initiator[2]; (B) poly(*L*-PheOCA) using ***L*-TMP-Zn** as an initiator; (C) poly(*rac*-PheOCA) using ***rac*-TMP-Zn** as an initiator; (D) poly(PheOCA) (*L*-/*D*- =5: 1) using DMAP/*rac*-methyl lactate as catalysts.

	Area	Integration	Pm
mm	1.498	0.9316	0.97
rr, rm/mr	0.056	0.0348	0.96
mr/rm	0.054	0.0336	0.96
Average		0.96	

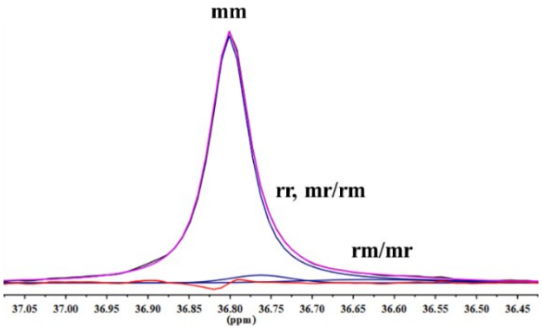
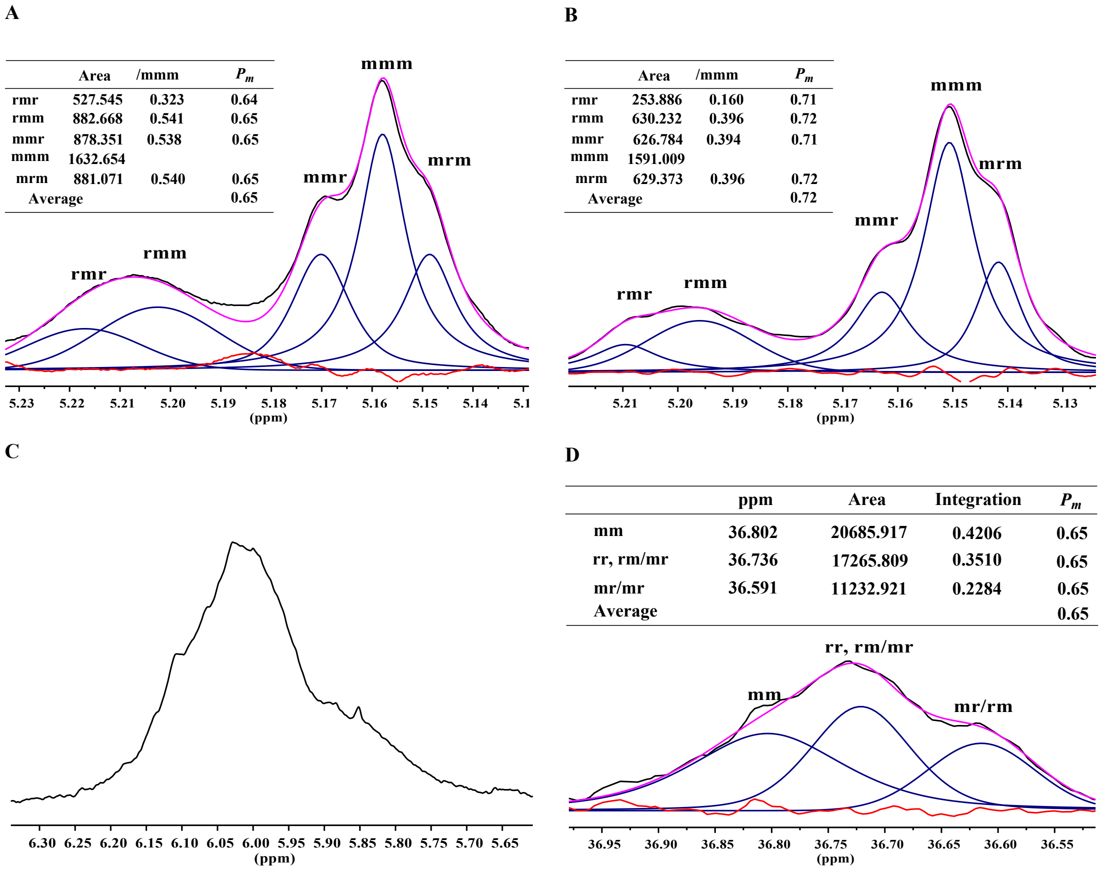


Fig. S9 Deconvolution of the ^{13}CNMR spectrum for the methene region of the resulting poly(PheOCA) with a high P_m value of 0.96 (Table 1, Entry 12), the assignments of triads and the calculation method of P_m were conducted according to the literature[2].



A

	Area	/mmm	P_m
rmr	527.545	0.323	0.64
rmm	882.668	0.541	0.65
mmr	878.351	0.538	0.65
mmm	1632.654		
mrm	881.071	0.540	0.65
Average			0.65

B

	Area	/mmm	P_m
rmr	253.886	0.160	0.71
rmm	630.232	0.396	0.72
mmr	626.784	0.394	0.71
mmm	1591.009		
mrm	629.373	0.396	0.72
Average			0.72

D

	ppm	Area	Integration	P_m
mm	36.802	20685.917	0.4206	0.65
rr, rm/mr	36.736	17265.809	0.3510	0.65
mr/mr	36.591	11232.921	0.2284	0.65
Average				0.65

Fig. S10 Tacticities of the polymers from *rac*-OCAs initiated by **BDI-Zn[4]**, the calculation method of P_m is consistent with the literature[2]: (A) Deconvolution of the homonuclear decoupled ^{1}H NMR spectrum of polymer with a low deviation (red line) $P_m = 0.65$, at room temperature; (B) Deconvolution of the homonuclear decoupled ^{1}H NMR spectrum of polymer with a low deviation (red line) $P_m = 0.72$, at 0 ^{o}C; (C) The *α*-methine in ^{1}H NMR spectrum of poly(*rac*-ManOCA); (D) The methene region of the ^{13}C NMR spectrum of Poly(PheOCA) with a low deviation (red line) $P_m = 0.65$, at 0 ^{o}C.

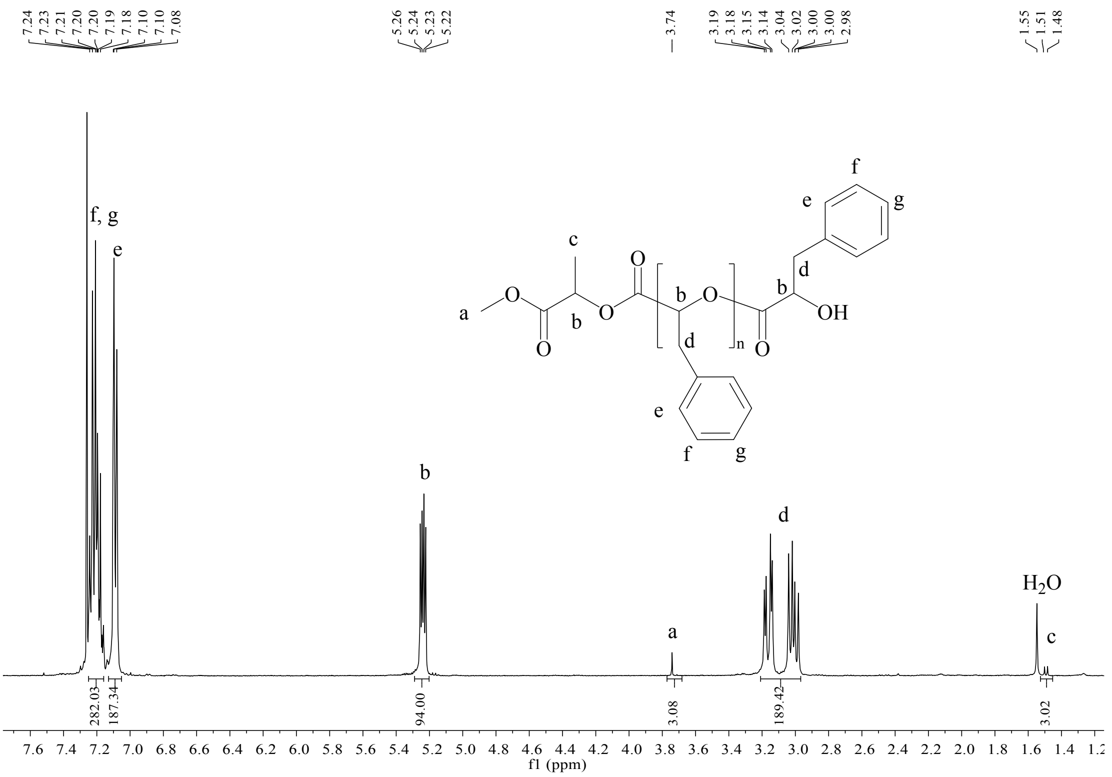


Fig. S11 ^{1}H NMR of the poly(*rac*-PheOCA) using ***rac*-TMP-Zn** as an initiator (400 MHz, $CDCl_3$, 25 °C) (Table 1, Entry 12).

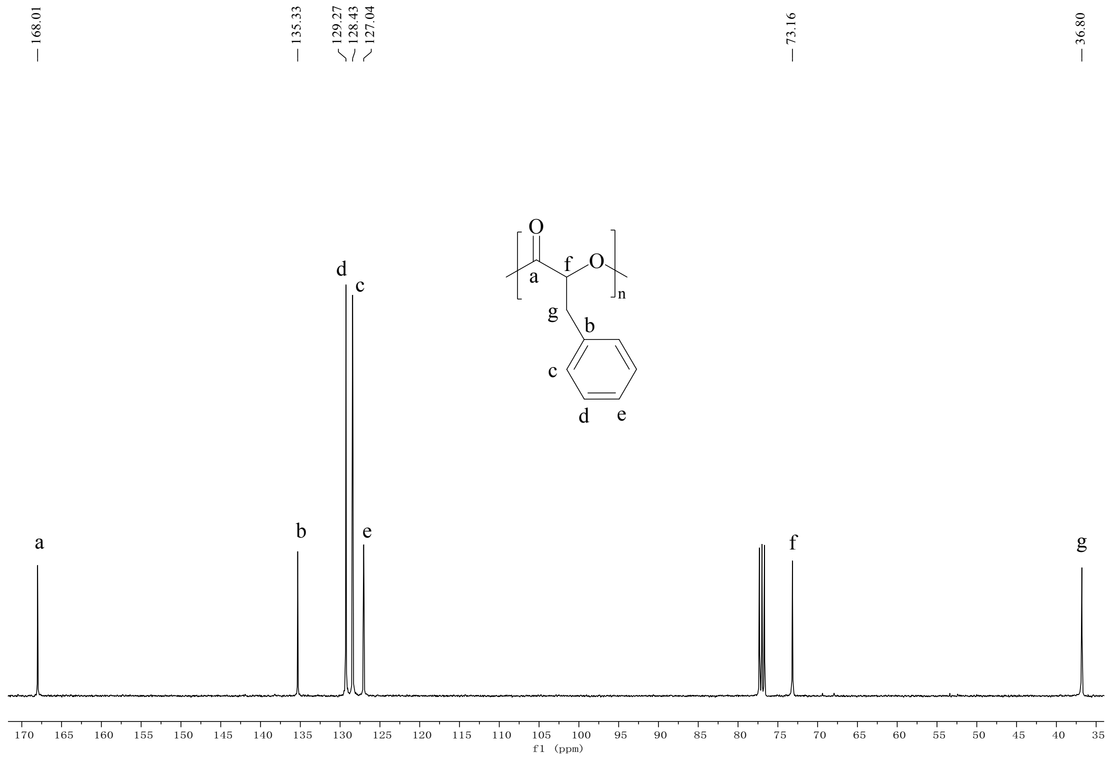


Fig. S12 ^{13}C NMR of the poly(*rac*-PheOCA) using ***rac*-TMP-Zn** as an initiator (400 MHz, $CDCl_3$, 25 °C) (Table 1, Entry 12).

Kinetics of the ROP of PheOCAs

As shown in the flowing Fig. S13, when the enantiopure ***L*-TMP-Zn** was utilized as an initiator, the ROP rates for *D*-PheOCA and *L*-PheOCAs are similar, which indicates the stereoselective mechanism is a chain end control mechanism and not an enantiomorphic site control mechanism. However, the rate of the ROP of *rac*-PheOCA is lower than that of the ROP of *D*- or *L*-PheOCA especially at the beginning stage, which may result from the mismatch between *L*-PheOCA and *D*-PheOCA (P_m = 0.84, Table S1, Entry 7), which is unfavourable for kinetic reasons.[5] It is emphasized the kinetic data we fitted with a first order on the monomer concentration in Fig. S13 show the intercepts of the three lines are not zero. As discussed in this manuscript, in the process of the ROP reaction, a side reaction of the ring-opening of OCA via a nucleophilic attack on the carbonate-like carbonyl group may occur and the resulting carboxylate complex is less active for the ROP of OCAs. Thus we can find the rate of ROP is quicker at the beginning stage and decreases when the conversion increases. Despite of that, we can obviously find the rates of the ROP of *D*-PheOCA and *L*-PheOCAs are similar and the rate of the ROP of *rac*-PheOCA is lower than that of the ROP of *D* or *L*-PheOCA (P_m = 0.84). All of these data can confirm the chain end control isoselective mechanism.

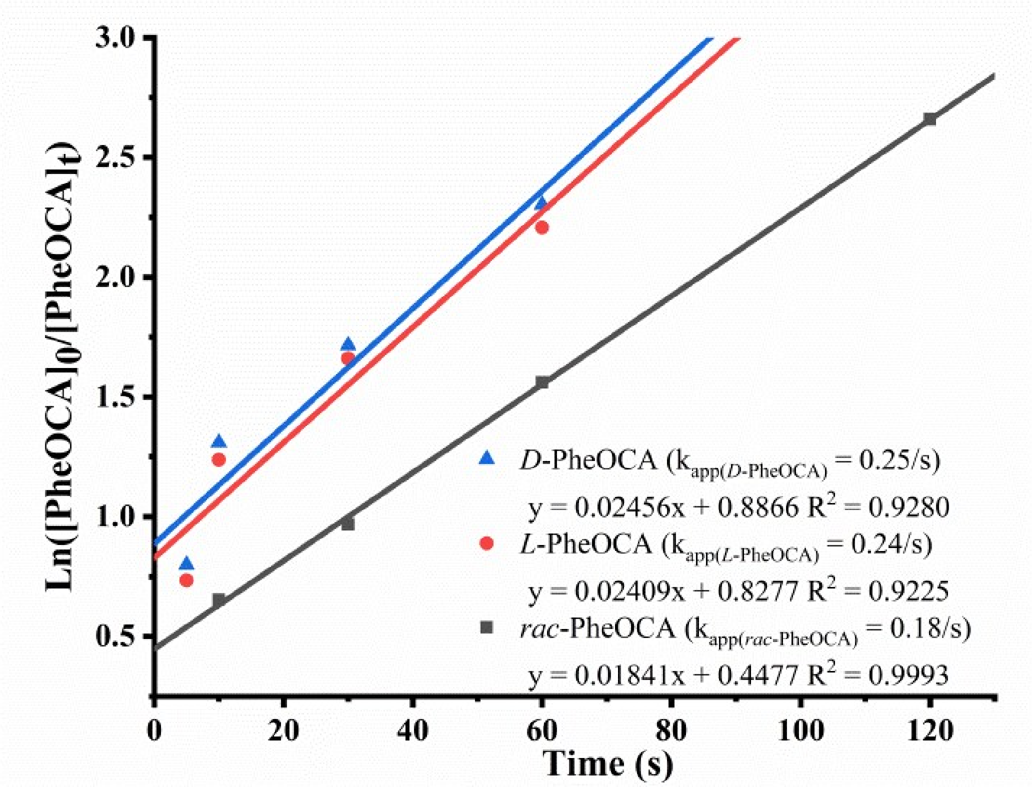


Fig.S13 Kinetic plots for the ROP of PheOCAs (*L*-PheOCA, *D*-PheOCA, and *rac*-PheOCA) initiated by ***L*-TMP-Zn**. [PheOCA] = 0.1 M, $[\text{PheOCA}]_0$ / $[\textbf{\textit{L}-TMP-Zn}]_0$ = 80 at 0 ^{o}C in THF.

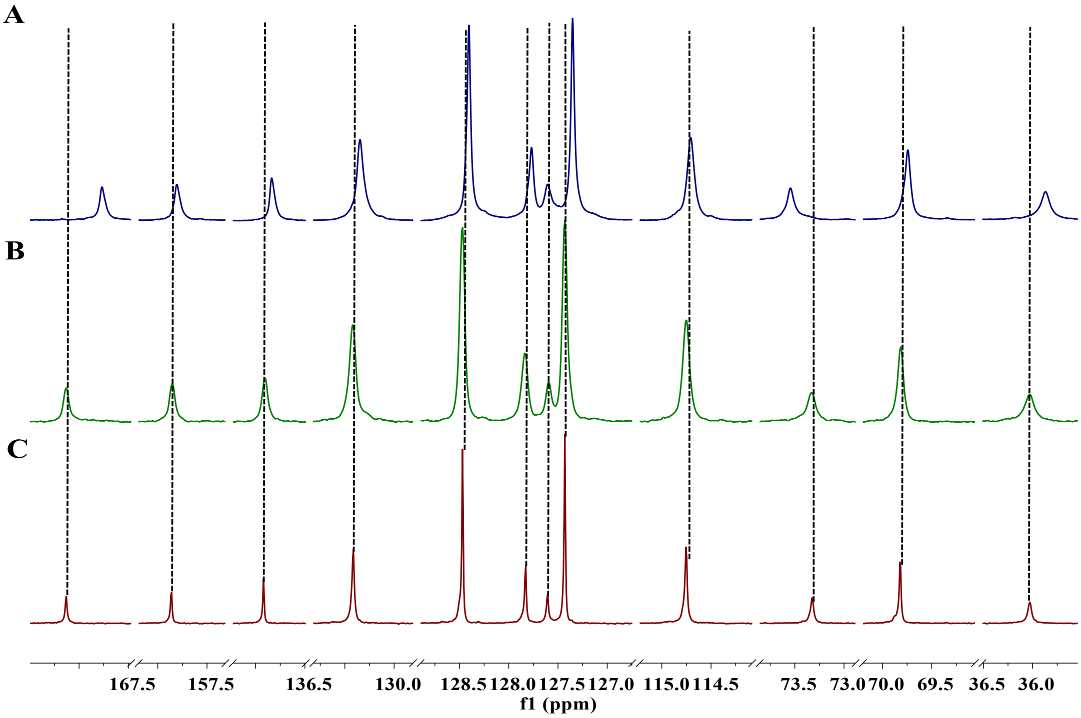


Fig. S14 Details of the regions of the ^{13}CNMR spectra of poly(Try(Bn)OCA) obtained using different catalysts/initiators: (A) the syndiotactic poly(*rac*-Try(Bn)OCA) obtained using Hf alkoxide as an initiator [2]; (B) poly(*L*-Try(Bn)OCA) using ***L*-TMP-Zn** as an initiator; (C) poly(*rac*-Try(Bn)OCA) using ***rac*-TMP-Zn** as an initiator.

	ppm	Area	Integration	P_m
mm	36.05	50429.1115	0.9444	0.97
rm, mr	35.99	2626.6644	0.0492	0.95
rr	35.96	343.4521	0.0064	0.92
Average				0.95

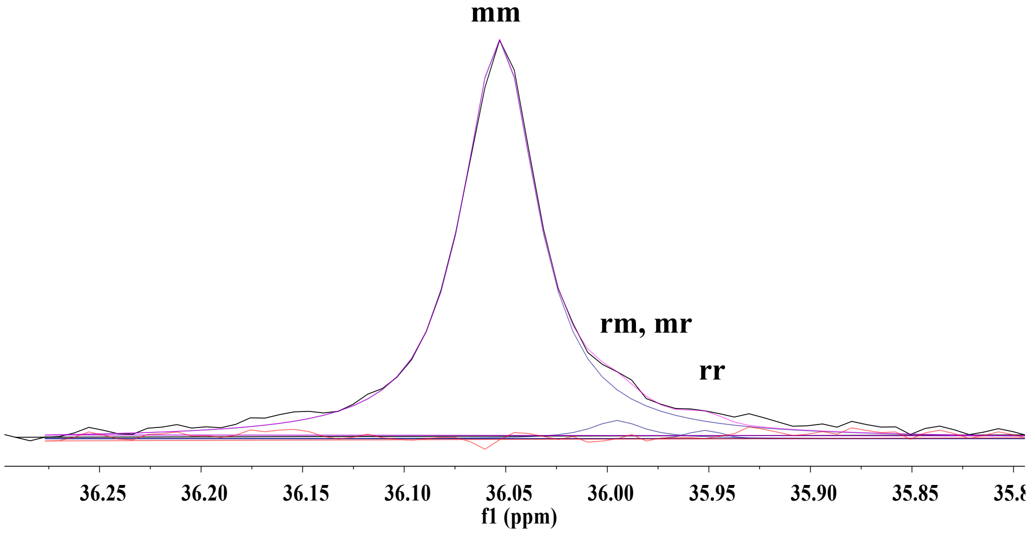


Fig. S15 Deconvolution of the ^{13}CNMR spectrum for the methene region of the resulting poly(*rac*-Try(Bn)OCA) with a high P_m value of 0.95 (Table 1, Entry 14), the assignments of triads and the calculation method of P_m were conducted according to the literature[2].

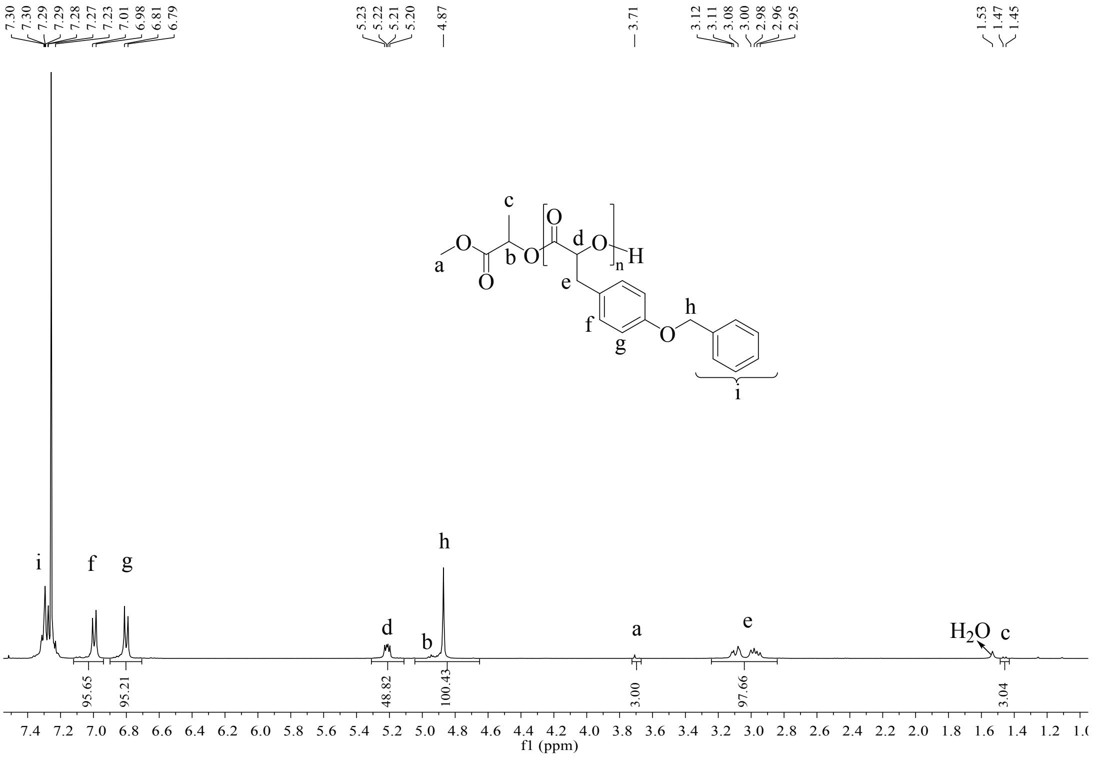


Fig. S16 ^{1}H NMR of the poly(*rac*-Try(Bn)OCA) using ***rac*-TMP-Zn** as an initiator (400 MHz, $CDCl_3$, 25 °C) (Table 1, Entry 14).

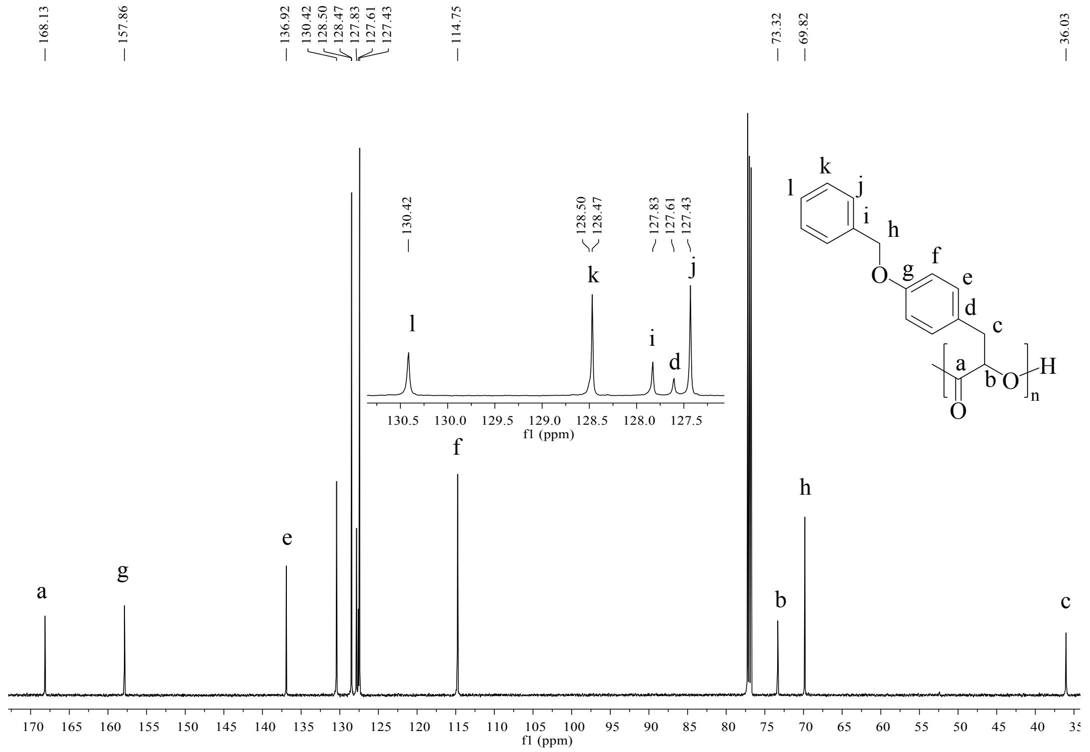


Fig. S17 ^{1}H NMR of the poly(*rac*-Try(Bn)OCA) using ***rac*-TMP-Zn** as an initiator (150 MHz, $CDCl_3$, 25 °C) (Table 1, Entry 14).

Reference

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