

Mechanism-inspired Design of Heterodinuclear Catalysts for Copolymerization of Epoxide and Lactone

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Mechanism-inspired Design of Heterodinuclear Catalysts for Copolymerization of Epoxide and Lactone

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 Electronic Supplementary Information

Abstract Polyesters, as a class of high-performance and versatile polymer materials, often suffer from some drawbacks, such as hydrophobicity and brittleness due to their single structure nature. Thus, modifications have attracted much attention for enhancing their desirable properties, of which one efficient way is incorporating the aliphatic polyether segment into the main chain of the polyester. However, this approach is of much challenge because the obtained polyesters are problematic in either low alternating degree or low molecular weight. Herein, we describe an efficient strategy to incorporate polyether fragment into polyester by developing a novel Co-Al based heterodinuclear complex for mediating the copolymerization of propylene oxide (PO) with ϵ -caprolactone (CL). The tracking experiments reveal that PO and CL convert into the polymer chain throughout the polymerization process. Especially, the linear increase in the molecular weight with conversion of CL indicates the controllable nature of the copolymerization. The competition polymerization, offering the monomer reactivity ratios of $r_{CL} = 0.96$ and $r_{PO} = 1.04$, suggests that the tendency of self-propagation or incorporation of monomers is nearly identical. Interestingly, the obtained polymers with different ether contents exhibit tunable thermal properties with enhanced decomposition temperature for the polymer with higher ether content. The newly developed heterodinuclear complex for new polymerization provides an idea to synthesize new functional polymeric materials.

Keywords Heterodinuclear catalysis; Polyester-polyether copolymer; Lactone; Epoxide; Copolymerization

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INTRODUCTION

Introduction of ether functionality into polyester backbone is of much interest as a promising method for improving the desirable properties of polyesters.^[1–4] For example, incorporation of poly(ethylene glycol) segments into polylactides confers attractive features, such as high physical properties, good hydrophilicity,^[3] and excellent lithium ion conductivity.^[4] To this end, the synthesis of polyether-polyester copolymers has received considerable attention. For the most part, previous studies have focused on the preparation of di- and triblock copolymers,^[5–18] with only rare reports concerning the synthesis of copolymers with a statistical structure.^[19–22] In 1997, Gross and co-workers first reported the copolymerization of [L]-lactide and ethylene oxide to access a multiblock structure, though the resultant copolymers had a broad dispersity ($\bar{D}$).^[18] Recently, Zhao *et al.* made an elegant design to obtain statistical and random copolymers in the presence of organocatalyst *via* concurrent epoxide ring opening and transesterification

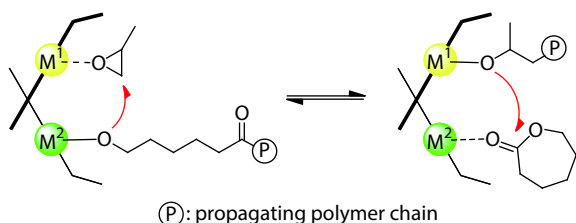
reactions, although it was becoming difficult to precisely control the molecular weights of copolymers in effect of transesterification.^[19,20] In addition, Lynd *et al.* realized the general statistical copolymerization of epoxides and lactones using an aluminum-based catalyst. However, a very low ether-ester content (alternating degree) was observed in the produced copolymers.^[21] Very recently, Waymouth and Coates developed a dual catalysis system in conjunction with an alcohol chain shuttling agent for the synthesis of polyether-polyester copolymers from propylene oxide (PO) and cyclic esters such as γ -butyrolactone, δ -valerolactone, and ϵ -caprolactone (CL). Although the alternating degree can be easily adjusted through variation of monomer and alcohol loadings, the presence of large amount of chain shuttling agent limits the molecular weight.^[22] As a consequence, the development of an efficient approach for precise synthesis of polyether-polyester copolymers is an important and challenging theme for research and development.

Matching the relative reactivity toward polymerization between multiple monomers plays a critical role in the synthesis of multifunctional materials. As heterocyclic compounds, epoxides and lactones have different ring strains for driving their ring-opening and various Lewis basicity for dictating their coordination equilibria with metal complexes.^[23]

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Thus, it is difficult to match the reactivity of epoxides and lactones by one metal active site to produce the corresponding copolymer. It is well documented that cobalt complexes are beneficial to the ring-opening of epoxides,^[24,25] while zinc or aluminum complexes are suitable for the activation of lactones.^[26–31] We therefore sought for a heterodinuclear catalysis strategy for the synthesis of polyether-polyester copolymers by the copolymerization of epoxide and lactone. Hypothesizing that a heterodinuclear metal complex is active for the ring-opening of both epoxide and lactone, polymer chain propagation between the two metal centers would produce polyether-polyester copolymers with a well-defined structure (Scheme 1). Herein, we report the design and synthesis of a heterodinuclear catalyst system based on Co-Zn or Co-Al complexes with a rigid bridging biphenyl linker, which is capable of mediating the copolymerization of PO and CL to yield polyether-polyester copolymers with a controlled molecular weight and narrow $\bar{D}$.



Scheme 1 Heterodinuclear catalysis strategy for the synthesis of polyether-polyester copolymers by the copolymerization of epoxide and lactone.

EXPERIMENTAL

Synthesis of Ligand

Synthesis of **LI-1**

Under nitrogen, 1,2-diaminocyclohexane (2.28 g, 20 mmol) and 3,5-bis(1,1-dimethylethyl)-2-hydroxy-benzaldehyde (4.68 g, 20 mmol) were dissolved in dry CH_2Cl_2 , the mixture with activated 5 Å molecular sieve was allowed to stir for 1 h at room temperature. Then 3,3'-diformyl-2,2'-dihydroxy-1,1'-biphenyl (6.28 g, 26 mmol) dissolved in CH_2Cl_2 was added. After stirring for 2 h, the reaction mixture was filtered through a dry sand core funnel, and the filter cake was washed with CH_2Cl_2 . Then all solvents were removed in vacuum. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20/1, V/V) to afford compound **LI-1** as a bright yellow solid (7 g, 63%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 14.14 (s, 1H), 13.60 (s, 1H), 11.30 (s, 1H), 10.03 (s, 1H), 8.33 (s, 1H), 8.25 (s, 1H), 7.61 (m, 2H), 7.37–7.31 (m, 2H), 7.19 (m, 1H), 7.08 (t, $J = 7.6$ Hz, 1H), 6.97 (d, $J = 2.4$ Hz, 1H), 6.86 (t, $J = 7.6$ Hz, 1H), 3.45–3.35 (m, 1H), 3.24 (m, 1H), 2.04–1.79 (m, 4H), 1.72 (d, $J = 11.5$ Hz, 2H), 1.57 (d, $J = 11.2$ Hz, 1H), 1.43 (s, 9H), 1.25 (s, 10H). HRMS (m/z) Calcd. for $[\text{C}_{35}\text{H}_{42}\text{N}_2\text{O}_4\text{H}]^+$: 555.3223, found: 555.3214.

Synthesis of **LI-2**

Under nitrogen, sodium *tert*-butoxide (4.61 g, 48 mmol) and 2-aminocyclohexanol hydrochloride (1.73 g, 15 mmol) were dispersed into 100 mL of dry THF followed by stirring for 30 min, and then 2-chloromethylpyridine hydrochloride (2.71 g,

16.5 mmol) and 100 mL of THF were added. After stirring for 24 h at 25 °C, the reaction mixture was diluted with ethyl acetate and then filtered through a dry funnel with celite 545 R, and all solvents were removed in vacuum. The residue was purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{MeOH} = 50/1$, V/V) to afford compound **LI-2** as a brown liquid (1.4 g, 45%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 8.57–8.53 (m, 1H), 7.70 (m, 1H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.22–7.15 (m, 1H), 4.79 (s, 1H), 4.61 (d, $J = 13.1$ Hz, 1H), 3.10 (m, 1H), 2.74 (m, 1H), 2.26 (s, 2H), 2.20–2.13 (m, 1H), 1.95–1.86 (m, 1H), 1.80–1.73 (m, 1H), 1.67 (m, 1H), 1.34–1.12 (m, 4H).

Synthesis of **LI-3**

Under nitrogen, **LI-1** (0.5 g, 0.9 mmol) and **LI-2** (0.2 g, 0.97 mmol) were dissolved into 30 mL of dry CH_2Cl_2 , and a drop of acetic acid was added as catalyst followed by stirring with activated 5 Å molecular sieve at room temperature for 2 h. The reaction mixture was filtered through a dry sand core funnel, and the filter cake was washed with CH_2Cl_2 . Then all solvents were removed in vacuum. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20/1, V/V) to afford ligand **LI-3** as a bright yellow solid (0.33 g, 50%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 13.97 (s, 1H), 13.85 (s, 1H), 13.67 (s, 1H), 8.44 (s, 1H), 8.43–8.39 (m, 1H), 8.35 (s, 1H), 8.23 (s, 1H), 7.50–7.29 (m, 5H), 7.29–7.14 (m, 7H), 7.06–6.83 (m, 5H), 4.69 (d, $J = 13.3$ Hz, 1H), 4.51 (d, $J = 13.3$ Hz, 1H), 3.37 (s, 2H), 3.22 (m, 2H), 2.23 (d, $J = 11.9$ Hz, 1H), 1.93 (d, $J = 21.3$ Hz, 3H), 1.84 (s, 1H), 1.70 (d, $J = 11.9$ Hz, 3H), 1.65–1.48 (m, 1H), 1.42 (s, 11H), 1.40–1.30 (m, 4H), 1.23 (s, 10H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ , ppm): 165.97, 165.13, 165.03, 159.13, 158.94, 158.87, 158.11, 148.90, 140.07, 136.71, 136.51, 134.37, 131.29, 131.06, 126.99, 126.23, 126.02, 125.79, 122.34, 121.93, 119.11, 119.07, 118.16, 118.08, 117.92, 81.25, 72.84, 72.81, 72.51, 72.19, 35.13, 34.22, 33.52, 33.26, 33.05, 31.62, 30.30, 29.61, 24.45, 24.39, 24.26, 24.08. HRMS (m/z) Calcd. for $[\text{C}_{47}\text{H}_{58}\text{N}_4\text{O}_4\text{H}]^+$: 743.4531, found: 743.4539.

Synthesis of Complexs 1 and 2

Synthesis of mono-Co(II) complex

In a glove box, ligand **LI-3** (600 mg, 0.81 mmol) was dissolved in *n*-hexane (10 mL), and then a solution of cobalt(II) acetate (144 mg, 0.81 mmol) in MeOH (3 mL) was added dropwise. As the solution was dropped, the mixture turned red. Continuously stirred for 15 min after dripping, all the solvents were then removed in vacuum. The resulting red powder was rinsed rigorously with *n*-hexane and further dried under vacuum at 50 °C (630 mg, 97%). HRMS (m/z) Calcd. for $[\text{C}_{47}\text{H}_{56}\text{CoN}_4\text{O}_4\text{H}]^+$: 800.3667, found: 800.3698.

Synthesis of mono-Co(III)- NO_3 complex

In a glove box, mono-Co(II) complex (630 mg, 0.80 mmol) and silver nitrate (134 mg, 0.80 mmol) were dissolved in dry CH_2Cl_2 (10 mL) and stirred in dark for 24 h. The reaction solvent was filtered to remove undissolved substances and dried under vacuum. The resulting black powder was rinsed rigorously with *n*-hexane and further dried under vacuum at 50 °C (650 mg, 94%). HRMS (m/z) Calcd. for $[\text{C}_{47}\text{H}_{56}\text{CoN}_4\text{O}_4]^+$: 799.3628, found: 799.3549.

Synthesis of complex 1

Under nitrogen, mono-Co(III)- NO_3 complex (200 mg, 0.23 mmol)

and zinc acetate (50 mg, 0.28 mmol) were dissolved in MeOH (5 mL) followed by stirring for 30 min at 30 °C. The reaction solvent was filtered to remove undissolved substances and MeOH was removed under vacuum. The resulting black brown powder was rinsed rigorously with *n*-hexane and further dried under vacuum at 50 °C (206 mg, 91%). ¹H-NMR (400 MHz, DMSO-*d*₆, δ, ppm): 8.53 (d, *J* = 5.3 Hz, 1H), 8.33 (s, 1H), 8.08 (t, *J* = 7.8 Hz, 1H), 8.03 (s, 1H), 7.86 (s, 1H), 7.66–7.53 (m, 4H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 2.5 Hz, 1H), 7.35–7.30 (m, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 4.98–4.84 (m, 2H), 3.05 (m, 2H), 2.50–2.49 (m, 2H), 2.00 (m, 4H), 1.84 (m, 4H), 1.73 (m, 4H), 1.59 (m, 4H), 1.43 (s, 9H), 1.36–1.31 (m, 3H), 1.26 (s, 9H). ¹³C-NMR (125 MHz, DMSO-*d*₆, δ, ppm): 177.01, 168.56, 164.56, 164.24, 163.08, 162.21, 156.06, 147.77, 142.05, 140.24, 136.55, 136.07, 135.29, 134.35, 133.90, 132.21, 128.95, 128.51, 123.94, 122.96, 119.50, 118.71, 117.70, 114.24, 113.01, 82.52, 69.61, 69.42, 66.25, 63.75, 56.00, 35.33, 33.48, 31.42, 30.29, 29.98, 29.46, 29.37, 24.24, 24.21, 23.68, 23.06, 18.54. HRMS (*m/z*) Calcd. for [C₄₉H₅₈CoN₄O₆Zn⁺]: 921.2980, found: 921.2978.

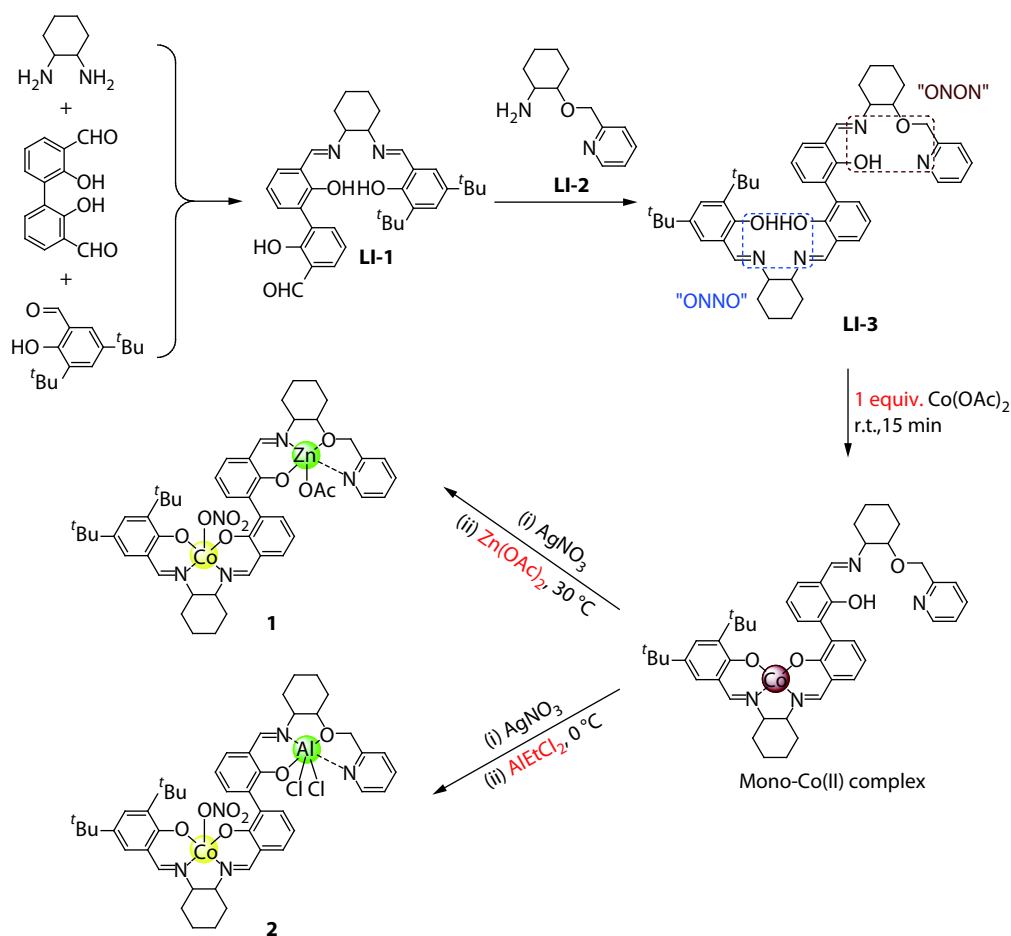
Synthesis of complex 2

In a glove box, mono-Co(III)-NO₃ complex (200 mg, 0.23 mmol) was dissolved in CH₂Cl₂ (2 mL) and then AlEtCl₂ (0.16 mL, 1.8 mol/L in toluene) was added dropwise at 0 °C. Continuously stirred for 2 h after dripping, the reaction mixture was filtered

through a dry sand core funnel, and the dark green filter cake was washed with toluene. The resulting dark green powder was further dried under vacuum at 50 °C (194 mg, 87%). ¹H-NMR (400 MHz, DMSO-*d*₆, δ, ppm): 8.69 (s, 1H), 8.44 (s, 2H), 8.38 (m, 1H), 8.27 (s, 1H), 7.64 (m, 1H), 7.54 (d, *J* = 8 Hz, 1H), 7.47 (m, 2H), 7.35 (m, 2H), 7.26 (s, 2H), 6.94 (m, 1H), 6.79 (m, 1H), 4.58 (m, 2H), 3.92 (m, 1H), 3.59 (m, 1H), 2.33 (m, 4H), 2.05–1.83 (m, 5H), 1.79–1.55 (m, 4H), 1.73–1.33 (m, 9H), 1.31–1.19 (m, 14H). ¹³C-NMR (125 MHz, DMSO-*d*₆, δ, ppm): 178.34, 164.54, 163.85, 163.23, 162.27, 161.91, 160.82, 159.01, 148.99, 141.55, 139.59, 137.78, 136.64, 134.92, 134.51, 131.32, 129.34, 128.65, 125.76, 121.04, 119.33, 119.11, 117.03, 115.00, 89.83, 72.72, 71.85, 63.82, 55.39, 35.33, 34.11, 31.81, 30.24, 29.64, 29.38, 29.12, 27.47, 27.36, 24.10, 23.93, 21.51. HRMS (*m/z*) Calcd. for [C₄₇H₅₅AlCl₂CoN₄O₄⁺]: 895.2748, found: 895.2788.

General Producer for the Copolymerization of PO and CL

In a glove box, catalyst (0.005 mmol), cocatalyst (0.005 mmol), and CL (2.5 mmol) were measured into a flame dried 10.0 mL vial equipped with a Teflon coated stir bar. PO (10 mmol) was added *via* syringe with care to wash all solids into the base of the vial. The vial was sealed with a Teflon lined cap and removed from the glove box. After an appropriate time at a certain reaction condition, a small aliquot of the mixture was analysed



Scheme 2 Synthetic route to the heterodinuclear complexes **1** and **2**.

by $^1\text{H-NMR}$ spectroscopy for conversion. The remainder mixture was then dissolved in CH_2Cl_2 and precipitated into an excess of MeOH. This process was repeated until no residual monomer was detected in the $^1\text{H-NMR}$ spectrum of the product. After several rounds of precipitation, the material was collected and dried under vacuum. Other polymerizations were carried out by the similar procedure as described above.

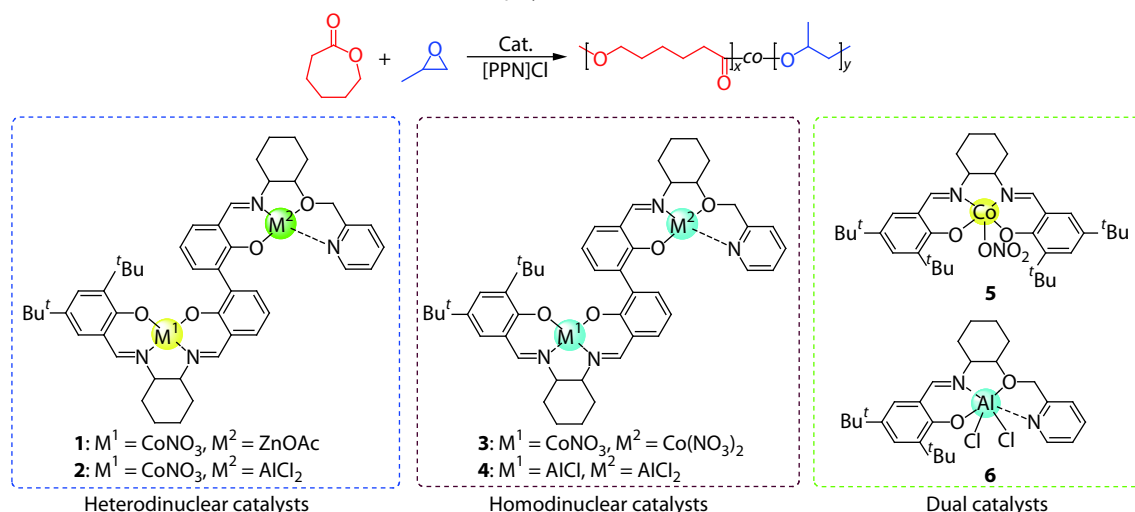
RESULTS AND DISCUSSION

To facilitate the synthesis of heterodinuclear complexes, an asymmetric ligand was designed and prepared by the route described in Scheme 2. In the metalation reaction, the mono-Co(II) complex was obtained since the “ONNO” moiety reacts with $\text{Co}(\text{OAc})_2$ more easily than the “ONON” moiety. Then the mono-Co(II) complex was oxidized by silver nitrate to form the Co(III) species, followed by further metalation reaction with $\text{Zn}(\text{OAc})_2$ or EtAlCl_2 to yield the corresponding heterodinuclear complexes **1** and **2**, respectively.

We initially performed the copolymerization of PO and CL using heterodinuclear Co(III)-Zn catalyst **1** in the presence of [PPN]Cl (PPN = bis(triphenylphosphine)iminium) as a cocatalyst. To our disappointment, almost no polymer formation

was observed when the copolymerization proceeded for 24 h at 25 °C (Table 1, entry 1). Then catalyst **2** was employed to mediate the copolymerization. It was found that the heterodinuclear Co(III)-Al complex in conjunction with [PPN]Cl exhibited a good activity for the transformation to afford the corresponding polyether-polyester copolymer with a number-average molecular weight (M_n) of 13.0 kg/mol and a narrow $\mathcal{D}$ of 1.27 (Table 1, entry 2). The $^1\text{H-NMR}$ spectrum of the isolated copolymer in CDCl_3 is shown in Fig. 1. A signal that was diagnostic for the presence of PO methine immediately adjacent to the ester unit was observed at 5.1 ppm. This assignment was consistent with the chemical shifts reported by Waymouth and Coates for the CL-PO copolymers.^[22] Additional signals consistent with methylene protons on PO in the PO-CL linkages were observed at 3.5 ppm. Furthermore, the copolymerization of PO and CL was studied in detail by changing the reaction conditions (Table 1, entries 3–9). A high ether content up to 51% was observed in the resultant copolymer with a M_n of 10.4 kg/mol and a narrow $\mathcal{D}$ of 1.21 at a PO:CL:2:[PPN]Cl feed ratio of 2000:500:1:1 under 50 °C. By way of contrast, homodinuclear Co(III) complex **3** and Al complex **4** were synthesized for mediating the copolymerization (Table 1, entries 10 and 11). At

Table 1 Copolymerization of PO and CL.^a



Entry	Cat.	PO:CL:Cat.: [PPN]Cl (molar ratio)	Temperature (°C)	Time (h)	Conv. CL ^b (%)	Ether content ^c (%)	M_n ^d (kDa)	$\mathcal{D}$ ^d
1	1	500:500:1:1	25	24	<1	<1	—	—
2	2	500:500:1:1	25	20	25	13	13.0	1.27
3	2	500:500:1:1	50	4	33	22	14.3	1.36
4	2	500:500:1:1	80	1	38	15	18.6	1.39
5	2	500:500:1:0	50	4	35	19	12.8	1.62
6	2	500:500:1:4	50	4	13	10	6.8	1.29
7	2	1000:500:1:1	50	4	24	36	11.6	1.25
8	2	2000:500:1:1	50	4	19	51	10.4	1.21
9	2	4000:500:1:1	50	4	8	32	4.0	1.30
10	3	2000:500:1:1	50	4	49	4	15.9	1.97
11	4	2000:500:1:1	50	0.2	45	4	16.0	1.90
12	5	2000:500:1:1	50	24	<1	<1	—	—
13	6	2000:500:1:1	50	0.1	50	<1	21.3	1.85
14 ^e	5/6	2000:500:1:1	50	1	31	3	12.3	1.96

^a Reactions were performed in neat PO (50 mmol). ^b Conversion of CL, determined by $^1\text{H-NMR}$ spectroscopy. ^c Final cumulative mole fraction composition of copolymer measured by $^1\text{H-NMR}$ spectrum. ^d Determined by gel permeation chromatography in THF, calibrated with polystyrene. ^e **5:6** = 1:1 (molar ratio).

the same reaction condition, only few ether units were presented in the resultant copolymers. Additionally, similar results were found in the situation of mononuclear Co(III) or Al complex as the catalyst as well as the dual Co(III)/Al cata-

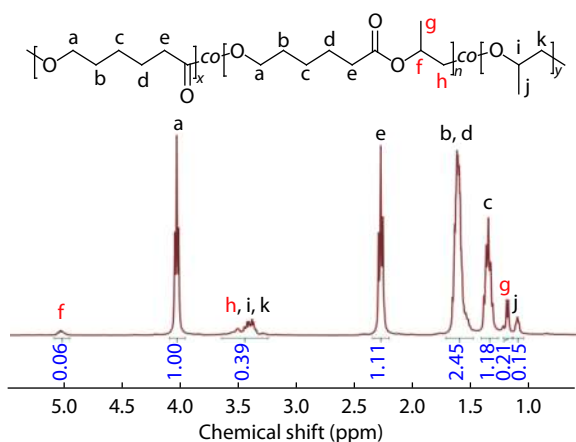


Fig. 1 ^1H -NMR spectrum of a representative sample of CL/PO copolymer in CDCl_3 (Table 1, entry 3).

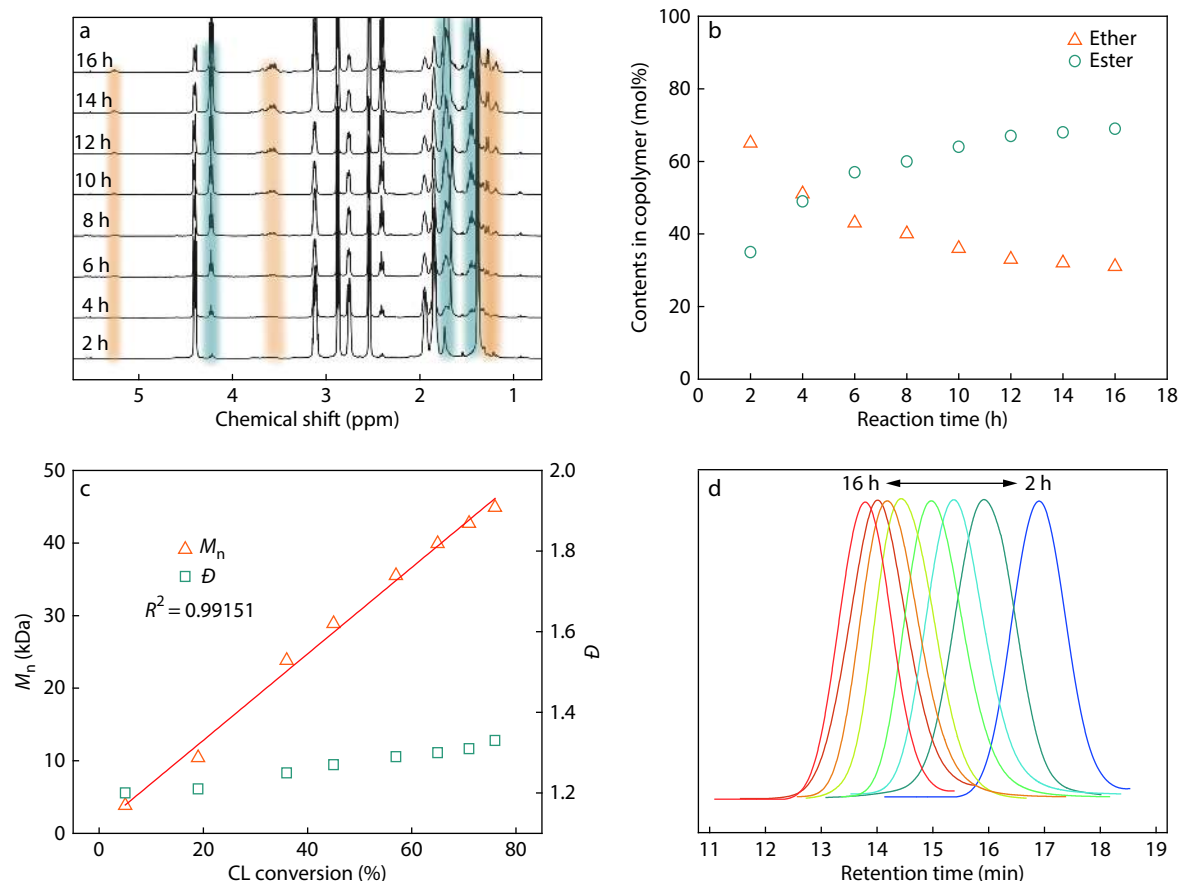


Fig. 2 (a) Stacked ^1H -NMR spectra (400 MHz, CDCl_3) of the copolymerization of CL and PO over 16 h. (b) Molar percent of the ester/ether in the copolymer. (c) Plots of the copolymer molecular weight and distribution versus the conversion of CL. (d) GPC traces of the CL/PO copolymers. Reactions were conducted in a neat PO with a PO:CL:2:[PPN]Cl ratio of 2000:500:1:1 (molar ratio) at 50°C . The corresponding relationship between reaction time and conversion rate is as follows. 2 h: Conv.(CL) = 5%; 4 h: Conv.(CL) = 19%; 6 h: Conv.(CL) = 36%; 8 h: Conv.(CL) = 45%; 10 h: Conv.(CL) = 57%; 12 h: Conv.(CL) = 65%; 14 h: Conv.(CL) = 71%; 16 h: Conv.(CL) = 76% (see Table S1 in ESI).

lyst system (Table 1, entries 12–14).

In order to better understand the copolymerization of CL/PO, ^1H -NMR and gel permeation chromatography (GPC) analyses were used to track the copolymerization process. (The experiment conditions and data are described in the electronic supplementary information, ESI, Table S1). The consumption of monomers and the formation of copolymers were measured with time by ^1H -NMR spectroscopy as shown in Fig. 2(a). In the stacked ^1H -NMR spectrum, the consumption of PO and CL could be observed by the decrease in methine (1H) of PO signal at 2.92 ppm, and methylene linked to oxygen signals at 4.20 ppm corresponding to 2H per CL. In addition, the signals at 5.05 ppm (CL-PO), 4.06 ppm (CL-CL), and 3.3–3.7 ppm (PO-PO, CL-PO) with increasing peak areas are characteristic signals of copolymers. Combined with the trend of content of ether and ester in copolymers (Fig. 2b), the ether content was higher than ester content in the early stage, and the consumption of PO was faster than that of CL. With the polymerization proceeding, the ether content gradually decreased as the consumption of PO gradually slowed down. This may be due to the reduction of Co(III) to Co(II) in the catalyst **2**. To verify this hypothesis, the heterodi-

nuclear Co(II)-Al complex was synthesized and the PO/CL copolymerization was performed (see Table S2 in ESI). It was found that the ester content in the polymer was always more than 95% during the polymerization reaction, suggesting the low activity of Co(II) species. In addition, analysis by GPC of the copolymer samples obtained at different time showed unimodal traces with a narrow $\bar{D}$. More importantly, the linear increase in M_n value of the resulting copolymers with CL conversion demonstrated that the copolymerization reaction showed a controlled characteristic (Figs. 2c and 2d).

Furthermore, a competition rate experiment was resorted to further identify the structure of the copolymer formed. Under control of conversion rate less than 10% and using various CL feed ratios (f_{CL}), CL molar fractions in copolymer (F_{CL}) were obtained by $^1\text{H-NMR}$ spectrum (see Table S3 in ESI). Calculated by Fineman-Ross equation and plotted to obtain monomer reactivity ratios of $r_{CL} = 0.96$ and $r_{PO} = 1.04$ (Fig. 3), r_{PO} and r_{CL} are both close to 1.0, indicating that the tendency of self-propagation or incorporation of monomers was basically the same. r_{PO} is slightly larger than r_{CL} , so the ether content was higher than the ester content in the early stage of the reaction. Along with the inactivation of Co(III) of the complex in the later stage, the ester content continued to rise, and finally a random copolymer was obtained.

To gain more insight into the copolymerization process, density-functional theory (DFT) calculation was employed. The methoxide anion (CH_3O^-) was substituted for the propagating polymer chain for the purpose of simplifying the

calculation. In this model, a CL or PO coordinated to one metal centre (Al or Co) inside the catalytic cleft and then ring-opened by the nucleophilic attack of a methoxide bound to the adjacent metal centre (Co or Al). The calculated Gibbs free energies of four transition states, where a CL or PO coordinated to different metal centre was ring-opened by the adjacent metal bound alkoxy anion, are displayed in Fig. 4. No significant differences in activation energies were observed for the four different transition states, which is consistent with the formation of polyether-polyester copolymers with a statistical structure.

The thermal properties of the resultant copolymers with different ether contents were determined by differential scanning calorimetry (DSC) in a nitrogen flow. The polyester with no ether incorporation shows a sharp melting endothermic peak at 63.2 °C in the second heating (Fig. 5Aa). For the case of the polyester with 20% ether content, the melting temperature shifts to 56.6 °C, accompanied by an extra small melting endothermic peak at 48.5 °C, which is the melting endothermic peak of the polyether (Fig. 5Ab). Further increase in the ether content to 50% to the polyester main chain results in two overlapped melting endothermic peaks with T_m of polyester and polyether fragments decreased to 43.1 and 36.6 °C, respectively (Fig. 5Ac). Though the increased content of ether in the polyester mainchain caused the decline in melting temperature, the decomposition temperature of the polyesters incorporated with polyether was enhanced (Fig. 5B).

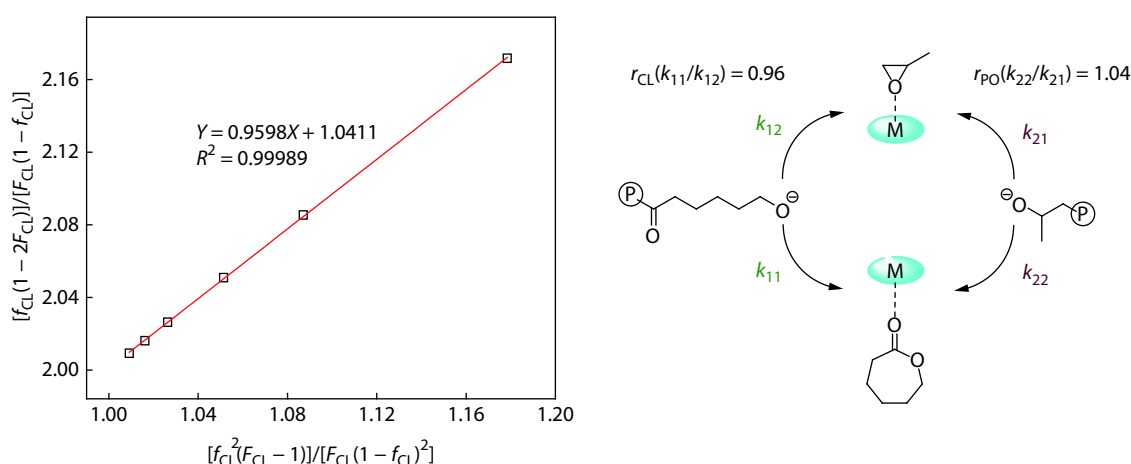


Fig. 3 Fineman-Ross plot and kinetic parameters for copolymerization of CL/PO by catalyst **2**/[PPN]Cl catalyst system.

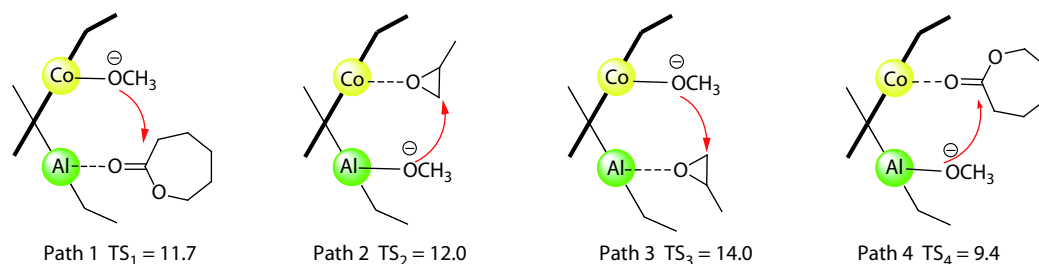


Fig. 4 Gibbs free energies of activation of the four transition states for the ring-opening of CL or PO by the methoxide anion enchainment to adjacent metal center. Energies are given in kcal/mol.

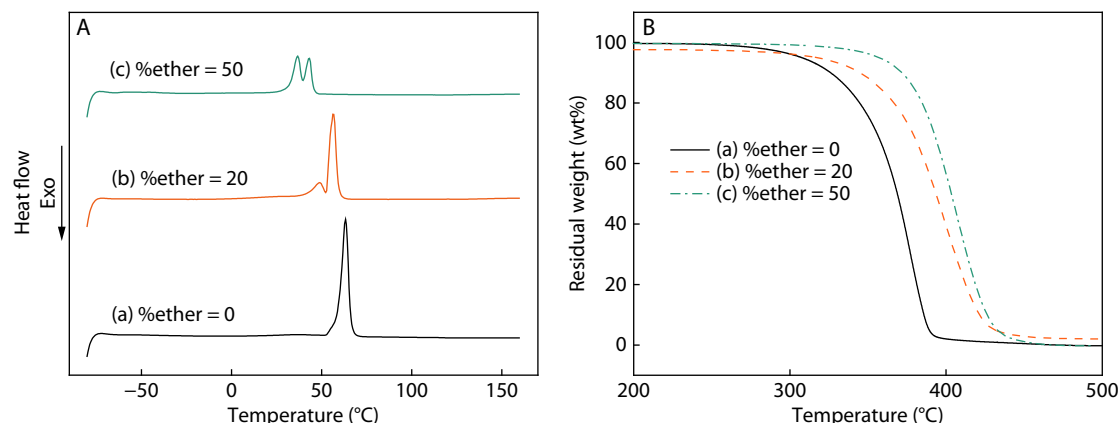


Fig. 5 (A) DSC profiles and (B) TGA curves of CL/PO copolymers of different ether contents: (a) 0, (b) 20%, (c) 50%.

CONCLUSIONS

We have demonstrated that the heterodinuclear catalysis strategy is efficient for the synthesis of polyether-polyester copolymers by copolymerizing lactone with epoxide. The Al-Co based heterodinuclear complex can mediate the copolymerization process smoothly in a controllable manner, therefore affording the corresponding copolymer with a narrow dispersity and tunable properties. More importantly, the strategy for synthesizing novel polymer by developing novel heterodinuclear complex for new polymerization provides an opportunity to expand the function of polymeric materials. The further research will focus on the completely alternating copolymerization of lactone and epoxide in progress in the same strategy.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2413-y>.

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