

Ring-opening copolymerization of CHO (cyclohexene oxide) and MA (maleic anhydride) catalyzed by the Co(III)–Salalen complex

Xingmei Zhang, Yaoju Liu, Yan Chen, Zhao Zhang, Daidi Fan, Xingqiang Lü *

School of Chemical Engineering, Shaanxi Key Laboratory of Degradable Medical Material, Northwest University, Xi'an 710069, Shaanxi, China

ARTICLE INFO

Article history:

Received 17 June 2014

Received in revised form 20 August 2014

Accepted 22 August 2014

Available online 23 August 2014

Keywords:

Co(III)–Salalen complex

Copolymerization of CHO and MA

Polyester and poly(ester-co-ether)

ABSTRACT

A new complex $[\text{Co}(\text{L})(\text{OAc})]$ (**1**), obtained from the coordination and subsequent oxidation reactions with $\text{Co}(\text{OAc})_2$ and the asymmetrical Salalen ligand **H₂L** (**H₂L**: (E)-2-((2–3,5-di-*tert*-butyl-2-hydroxybenzylideneamino)phenylamino)methyl)-4,6-di-*tert*-butylphenol), is shown to be an effective catalyst for ring-opening copolymerization of CHO (cyclohexene oxide) and MA (maleic anhydride) in the presence of one of the three co-catalysts (DMAP (4-(dimethylamino) pyridine), TPP (triphenylphosphine) and *n*-Bu₄NBr). **1**/DMAP gives relatively higher CHO monomer conversions than that of **1**/TPP or **1**/*n*-Bu₄NBr, and especially on the condition of lower temperature (50–80 °C), shorter reaction time (75 min) or lower catalyst feeding molar ratio (CHO:MA:**1**:DMAP = 500:500:1:1), all the solution polymerizations afford perfectly alternating polyester. © 2014 Elsevier B.V. All rights reserved.

Polyesters based on maleic anhydride (MA), as an important class of biodegradable and biocompatible polymers, are currently of particular interest because of their potential applications in drug delivery [1] and biological materials [2]. Moreover, the unsaturated alkene groups provided by MA endow the availability of new polymers with enhanced properties through further post-polymerization modifications [3]. The common method for MA-based polyester synthesis is the step-growth polymerization from diol and diester [4], where it usually requires high energy input and long reaction time, and the inevitably additional side reactions often afford low-molecular-weight polymers. In contrast, an alternative mild chain-growth copolymerization of epoxide and MA could circumvent many of the disadvantages of step-growth route.

The catalytic coupling of propylene oxide (PPO) and MA with AlR_3 [5] or $\text{Mg}(\text{OEt})_2$ [6] catalysts was early reported. However, the difficulty of obtaining high monomer conversions and high polymer molecular weights and the undesirable PPO homo-polymerization impede its popularity for quite some time. Until 2007, the achievement by Coates [7] on a zinc 2-cyano- β -diketiminato complex as the catalyst for the solution copolymerization of LO (*trans*-(R)-limonene oxide) and MA, giving 55% LO conversion and up to 12,000 g/mol alternating polyester, renewed the attention to the scientific area. Recently, a series of porphyrinato- and Salen-based M(III) complexes [8,9] were successfully used to catalyze ring-opening bulk or solution copolymerization of MA with a broad range of epoxides, where one of nucleophilic co-catalysts is usually needed to obtain high monomer conversions. Nevertheless, in most cases, poly(ester-co-ether)s are obtained, and the effectiveness of copolymerization is at the cost of high ether contents. Especially for

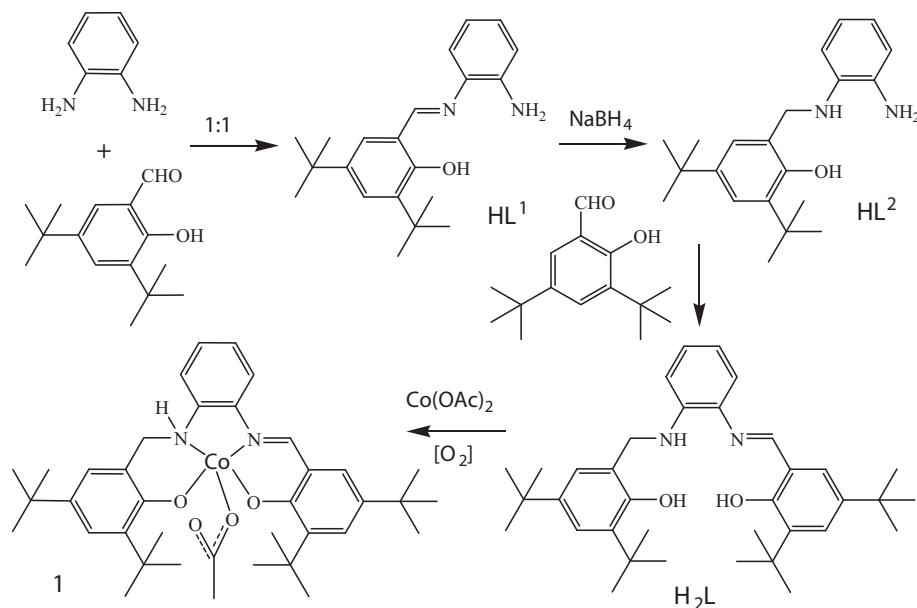
the M(III) (Al(III), Cr(III), Mn(III) or Co(III)) catalyst systems [10] based on symmetrical Salen-type Schiff-base ligands, although the effect of active metal centers, ligand-diamine backbones, co-catalysts, axial anions or polymerization procedures on the copolymerization behaviors has been explored in detail, the pursuit of low ether content poly(ester-co-ether)s or perfectly alternating polyesters remains a challenge. In consideration of distinctive advantage of transition metal catalysts based on asymmetrical Salalen-type ligands relative to those from symmetrical Salen-type ligands on the stereo-regular olefin polymerization [11] or exoxide and CO₂ copolymerization [12], herein, a new $[\text{Co}(\text{L})(\text{OAc})]$ (**1**) complex based on the selected Salalen-type ligand **H₂L** is used to catalyze the ring-opening solution copolymerization of CHO (cyclohexene oxide) and MA, and the goal to the formation of perfectly alternating polyesters is expected.

As shown in Scheme 1, the Salalen-type Schiff-base ligand **H₂L** was obtained from the condensation reaction of 3,5-di-*tert*-butylsalicylaldehyde with the precursor **HL²**, which was reduced from the mono-imine Schiff-base ligand **HL¹** product by reacting 1,2-diaminobenzene with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde. Further through the coordination reaction of the ligand **H₂L** and anhydrous $\text{Co}(\text{OAc})_2$ under the dry N₂ atmosphere and the subsequent oxidation reaction in the presence of dry air at room temperature, the product of Co(III) complex $[\text{Co}(\text{L})(\text{OAc})]$ (**1**) was obtained.

The precursors **HL¹** and **HL²**, the Salalen-type ligand **H₂L** and its complex **1** were well characterized by EA, FT-IR and ¹H NMR analyses, and X-ray quality crystals were obtained for $[\text{Co}(\text{L})(\text{OAc})]_2 \cdot \text{H}_2\text{O}$ ($[(\text{1})_2 \cdot \text{H}_2\text{O}]$). The selected crystallographic data for $[(\text{1})_2 \cdot \text{H}_2\text{O}]$ are given in Tables 1–2S. Complex $[(\text{1})_2 \cdot \text{H}_2\text{O}]$ crystallizes in the monoclinic space group of C2/c, in which two neutral $[\text{Co}(\text{L})(\text{OAc})]$ molecules lie about an inversion axial. As shown in Fig. 1, each central Co³⁺ ion (Co1 or Co1a) is six-coordinated and adopts a slightly distorted

* Corresponding author.

E-mail address: lvxq@nwnu.edu.cn (L. Xingqiang).



Scheme 1. Synthesis scheme for HL^1 , HL^2 , H_2L and complex **1**.

octahedral geometry, where two N atoms (N1 and N2) and two O atoms (O1 and O2) from the Salalen-type Schiff-base ligand H_2L form an equatorial plane, and two other O atoms (O3 from the coordinated OAc^- anion and O5 from the coordinated H_2O) occupy the two axial positions of the coordination polyhedron. The solvate H_2O molecule is bridged to the two mononuclear units and exhibits the homo-binuclear host framework. It is worth noting that the stable octahedral geometry of Co(III) ion in complex $[(\mathbf{1})_2 \cdot \text{H}_2\text{O}]$ is also shown in the analogue $[\text{Co}(\text{Salen}(\text{OMe})(\text{MeOH}))]$ [13] while incomparable to the tetrahedron of the Co(II) ion in ferromagnetic $[\text{Co}(\text{Salen})]$ complex [14]. As to the room temperature ^1H NMR spectrum in $\text{DMSO}-d_6$ of *anti*-ferromagnetic complex **1**, besides the distinctive disappearance of the two phenolic proton signals and the slight spread ($\delta = 8.75$ –

1.32 ppm) of one set of proton resonances of $(\text{L})^{2-}$ ligand in relative to those ($\delta = 8.69$ –1.34 ppm) of the free Salalen-type ligand H_2L , the proton signals ($\delta = 1.06$ ppm) of coordinated OAc^- anion are also observed. Especially, the ESI-MS spectrum (Fig. 1S) of complex **1** exhibits the strong mass peaks at m/z 599.30477 and 659.32590, assigned to the major species $[\text{M}-(\text{OAc})]^+$ and $[\text{M} + \text{H}]^+$, respectively. Both indicate that the mononuclear $[\text{Co}(\text{L})(\text{OAc})]$ unit is retained in the dilute solution.

The copolymerization behaviors of CHO and MA employing complex **1** as the catalyst in the presence of one of three common nucleophilic co-catalysts (DMAP, TPP or $n\text{-Bu}_4\text{NBr}$) are examined, and the results are summarized in Table 1. In comparison, a series of blank experiments (entries 1–6 in Table 1) with catalyst **1** and/or DMAP as the initiator for the homopolymerization of CHO or MA have been carried out. The catalytic results show that no polymeric products are produced from each of homopolymerizations of low activity MA monomer. However, although the homopolymerization of CHO is conducted in the presence of **1** and/or DMAP, the low molecular weights ($M_n = 562$ –1304 g/mol) and the large PDIs ($\text{PDI} = M_w/M_n$) of 2.46–3.15 of polyethers are shown due to the high polymerization temperature of 110 °C. Simultaneously, the solution copolymerization with catalyst **1** alone (entry 7 in Table 1) shows that almost no polymer is observed, while DMAP alone (entry 8 in Table 1) gives the poly(ester-co-ether) with up to 57% ether content as the literature [15]. Nonetheless, the combination of catalyst **1** and one of the three co-catalysts (DMAP, TPP and $n\text{-Bu}_4\text{NBr}$) at the stipulated molar ratio (250:250:1:1) of CHO:MO:catalyst:co-catalyst under the same reaction condition endows the effective copolymerization (entries 9–11 in Table 1), where both higher CHO conversions (53–86%) and larger copolymer molecular weights ($M_n = 7900$ –11,200 g/mol) from DMAP or TPP than those (38% of CHO conversion and 5700 g/mol of M_n) from $n\text{-Bu}_4\text{NBr}$ are observed. The relatively lower activity of **1**/TPP or **1**/ $n\text{-Bu}_4\text{NBr}$ than that of **1**/DMAP should be due to the low nucleophilicity from the large cone angle of three steric phenyl groups in TPP [16] or the positive bulky cation charge distribution in $n\text{-Bu}_4\text{NBr}$ [12,17], respectively. Further through the detailed ^1H NMR analysis on the obtained copolymers, although they are the typical poly(ester-co-ether)s (as shown in Fig. 2S), the low ether contents (4–7%) are observed, respectively. In contrast, the control of either lower reaction temperature (50–80 °C, entries 12–13 in Table 1) or shorter reaction time (75 min, entry 14 in Table 1) endows the formation

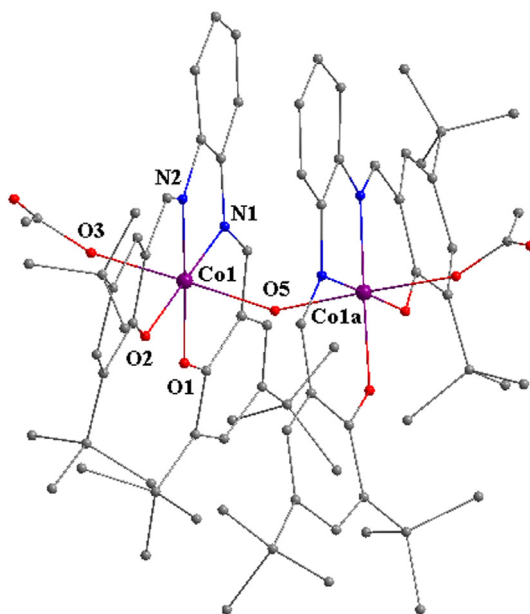


Fig. 1. View of X-ray structure of $[(\mathbf{1})_2 \cdot \text{H}_2\text{O}]$; hydrogen atoms are omitted for clarity.

Table 1
Ring-opening solution copolymerizations of CHO and MA catalyzed by complex **1**.

Entry	Cat sys.	Molar ratio	Time Min	T °C	Conv. ^a %	Ether ^a %	M _n ^b g/mol	PDI ^b
		CHO:MA:Cat:Co-cat						
1	DMAP	0:250:0:1	150	110	–	–	–	–
2	1	0:250:1:0	150	110	–	–	–	–
3	DMAP	250:0:0:1	150	110	6	100	1012	2.46
4	1	250:0:1:0	150	110	3	100	562	2.78
5	1 /DMAP	0:250:1:1	150	110	–	–	–	–
6	1 /DMAP	250:0:1:1	150	110	9	100	1304	3.15
7	DMAP	250:250:0:1	150	110	4	57	984	2.23
8	1	250:250:1:0	150	110	–	–	–	–
9	1 /DMAP	250:250:1:1	150	110	86	6	11,200	1.33
10	1 /TPP	250:250:1:1	150	110	53	7	7900	1.30
11	1 /n-Bu ₄ NBr	250:250:1:1	150	110	38	4	5700	1.26
12	1 /DMAP	250:250:1:1	150	50	21	<1	4700	1.14
13	1 /DMAP	250:250:1:1	150	80	55	<1	6200	1.21
14	1 /DMAP	250:250:1:1	75	110	49	<1	6900	1.25
15	1 /DMAP	250:250:1:1	300	110	>99	13	9600	1.82
16	1 /DMAP	250:250:1:3	150	110	>99	48	7200	1.74
17	1 /DMAP	250:250:3:1	150	110	90	29	13,000	1.45
18	1 /DMAP	125:125:1:1	150	110	92	54	9600	1.40
19	1 /DMAP	500:500:1:1	150	110	67	<1	8300	1.16

^a Determined by ¹H NMR.

^b Determined by GPC.

of perfectly alternating polyesters (as shown in Fig. 3S) at the cost of relatively lower CHO monomer conversions (21–55%) and relatively lower molecular weights (M_n = 4700–6900 g/mol). It is worth noting that for copolymerization of CHO and MA, especially in the presence of co-catalyst DMAP or TPP, asymmetric Co–Salalen **1** exhibits the slightly higher catalytic activity (53–86% CHO conversion) than that (45% CHO conversion) from the symmetrical Cr–Salen complex with n-Bu₄NCl as the co-catalyst [15], but **1**/n-Bu₄NBr is the poorer one due to the active species difference between Co(III) and Cr(III) ions. Especially after 300 min (entry 15 in Table 1), the copolymerization has been completely finished. Much to our dismay, the typical poly(ester-co-ether) with lower copolymer molecular weight (M_n = 9600 g/mol) and higher ether content (13%) became, which should be attributed to the chain transfer effect of DMAP for long reaction time besides positive monomer conversion [18]. The higher the feeding ratio of DMAP is (entry 16 in Table 1), the lower the copolymer molecular weight is observed. Similar to the effects of temperature and time, the CHO monomer conversions are almost linear relative to the catalyst concentrations (entries 17–19 in Table 1), while low catalyst concentration (entry 19 in Table 1) is also helpful for the formation of perfectly alternating polyester.

In conclusion, the asymmetrical Co–Salalen complex **1** is shown to be an effective catalyst for CHO–MA ring-opening solution co-polymerization in the presence of co-catalyst (DMAP, TPP or n-Bu₄NBr), where the polymerization condition control of lower temperature (50–80 °C), short reaction time (75 min) or lower catalyst feeding molar ratio (CHO:MA:**1**:DMAP = 500:500:1:1) is in favor of the formation of perfectly alternating polyesters despite lower CHO monomer conversions. Further studies that focused on increasing the efficiency and expanding the monomer scopes with the asymmetrical Salalen metal catalysts are currently in progress.

Acknowledgments

This work is funded by the National Natural Science Foundation (21173160, 91222201 and 21173165), the Program for New Century Excellent Talents in University from the Ministry of Education of China (NCET-10-0936), the research fund for the Doctoral Program of Higher Education of China (20116101110003), the Science, Technology and Innovation Project (2012KTCQ01-37) and the Education Committee Foundation of Shaanxi Province (11JK0588) in P.R. of China.

Appendix A. Supplementary Data

The synthesis and characterization of **HL**¹, **HL**², **H₂L** and complex [Co(L)(OAc)] (**1**), and the detailed copolymerization of CHO and MA are found in the Supporting information. Crystallographic data for [(**1**)₂·H₂O] in Tables 1–2S, the ESI-MS spectrum of complex **1** in dilute DMSO and the representative ¹H NMR spectra of poly(ester-co-ether) and polyester from the ring-opening solution copolymerization of CHO and MA are shown in Figs. 1–3S, respectively. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.inoche.2014.08.018>.

References

- [1] M. Dadsetan, Z. Liu, M. Pumberger, C.V. Giraldo, T. Ruesink, L. Lu, M.J. Yaszemski, A stimuli-responsive hydrogel for doxorubicin delivery, *Biomaterials* 31 (2010) 8051–8062.
- [2] J.W. Lee, K.S. Kang, S.H. Lee, J.Y. Kim, B.K. Lee, D.W. Cho, Bone regeneration using a microstereolithography-produced customized poly(propylene fumarate)/diethyl fumarate photopolymer 3D scaffold incorporating BMP-2-loaded PLGA microsphere, *Biomaterials* 32 (2011) 744–752.
- [3] J.L.T. Mathieu, B. Emilie, H. Pierre, M.T. Christophe, Synthesis of biodegradable polymers from renewable resources, *Polym. Chem.* 3 (2012) 836–851.
- [4] J. Luston, F. Vass, Anionic copolymerization of cyclic ethers with cyclic anhydride, *Adv. Polym. Sci.* 56 (1984) 91–133.
- [5] H.L. Haieh, Terpolymerization of cyclic ethers with cyclic anhydride, *J. Macromol. Sci. Chem.* A7 (7) (1973) 1525–1535.
- [6] S. Takenouchi, A. Takasu, Y. Inai, T. Hirabayashi, Effects of geometrical difference of unsaturated aliphatic polyester on their biodegradability II, isomerization of poly(maleic anhydride-co-propylene oxide) in the presence of morpholine, *Polym. J.* 34 (2002) 36–42.
- [7] R.C. Jeske, A.M. DiCiccio, G.W. Coates, Alternating copolymerization of epoxides and cyclic anhydride: an improved route to aliphatic polyesters, *J. Am. Chem. Soc.* 129 (2007) 11330–11331.
- [8] A.M. DiCiccio, G.W. Coates, Ring-opening copolymerization of maleic anhydride with epoxides: a chain-growth approach to unsaturated polyesters, *J. Am. Chem. Soc.* 133 (2011) 10724–10727.
- [9] E.H. Nejad, A. Paoniasari, C.E. Koning, R. Duchateau, Semi-aromatic polyesters by alternating ring-opening copolymerization of styrene oxide and anhydrides, *Polym. Chem.* 3 (2012) 1308–1313.
- [10] E.H. Nejad, C.G.W. van Melis, T.J. Vermeer, C.E. Koning, R. Duchateau, Alternating ring-opening polymerization of cyclohexene oxide and anhydride: effect of catalyst, cocatalyst, and anhydride structure, *Macromolecules* 45 (2012) 1770–1776.
- [11] H. Makito, H. Terao, A. Iwashita, T. Fujita, F1 catalysts for olefin polymerization – a comprehensive treatment, *Chem. Rev.* 111 (2011) 2263–2449.
- [12] K. Nakano, M. Nakamura, K. Nozaki, Alternating copolymerization of cyclohexene oxide with carbon dioxide catalyzed by (salalen)CrCl complexes, *Macromolecules* 42 (2009) 6972–6980.
- [13] H. Ajiro, K.L. Peretti, E.B. Lobkovsky, G.W. Coates, On the mechanism of isospecific epoxide polymerization by salen cobalt(III) complexes: evidence for solid-state catalysis, *Dalton Trans.* (2009) 8828–8830.

- [14] K.L. Peretti, H. Ajiro, C.T. Cohen, E.B. Lobkovsky, G.W. Coates, A highly active, isospecific cobalt catalyst for propylene oxide polymerization, *J. Am. Chem. Soc.* 127 (2005) 11566–11567.
- [15] D.J. Darensbourg, R.R. Poland, C. Escobedo, Kinetic studies of the alternating copolymerization of cyclic acid anhydride and epoxides, and the terpolymerization of cyclic acid anhydride, epoxides and CO₂ catalyzed by (salen)Cr^{III}Cl, *Macromolecules* 45 (2012) 2242–2248.
- [16] A. Decortes, M.M. Belmonte, J. Bent-Buchholz, A.W. Kleij, Efficient carbonate synthesis under mild conditions through cycloaddition of carbon dioxide to oxiranes using a Zn(salohen) catalyst, *Chem. Commun.* 46 (2010) 4580–4582.
- [17] X.B. Lu, L. Shi, Y.M. Wang, R. Zhang, Y.J. Zhang, X.J. Peng, Z.C. Zhang, B. Li, Design of highly active binary catalyst systems for CO₂/epoxide copolymerization: polymer selectivity, enantioselectivity, and stereochemistry control, *J. Am. Chem. Soc.* 128 (2006) 1664–1674.
- [18] J. Wu, D.F. Liu, L.Y. Wu, X.M. Zhang, L.Q. Zhu, D.D. Fan, X.Q. Lü, Q. Shi, Electronic and steric effects of substituents in series of Zn²⁺ asymmetrical bis-Schiff-base ligands complexes on catalytic ring-opening copolymerization of CHO and MA, *J. Organomet. Chem.* 749 (2014) 302–311.