

Living Ring-Opening Polymerization of *O*-Carboxyanhydrides: the Search for Catalysts

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Abstract

Biodegradable poly(α -hydroxy acids) can be synthesized by means of ring-opening polymerization (ROP) of *O*-carboxyanhydrides (OCAs). Numerous catalysts have been developed to control the living polymerization of OCAs. Here we review the rationale for the use of OCA, the desirable features for and important attributes of catalysts for the ROP of OCAs, and specific examples that have been developed.

1. Introduction

Polymers, commonly called plastics, can be categorized as degradable and non-degradable. Non-degradable plastics, mostly from petrochemical resources, tend to have difficulty in recycling and ultimately pollute the environment.¹⁻² Substantial efforts have been devoted to develop degradable polymers.³ Poly(α -hydroxy acids), including polylactide and polyglycolide, and other polyesters are arguably the most successful examples.⁴⁻⁶ However, the mechanical and thermal properties of these materials still need to be improved to match non-degradable polymers.⁷⁻⁸

Besides efforts in processing with additives or developing new processing techniques,⁹⁻¹⁵ one major focus in polymer chemistry society is to generate new sets of monomers from natural resources to produce the new degradable polymers that potentially replace many commodity polymers in the market.¹⁶⁻¹⁹ Among these new monomers, 1,3-dioxane-2,4-diones, so-called *O*-carboxyanhydrides (OCAs), have emerged as an alternative class of highly active monomers for the synthesis of poly(α -hydroxy acids).²⁰⁻²² OCAs can be prepared from α -amino acid or α -hydroxy acids with a rich variety of side-chain functionalities (**Fig. 1**).^{20, 22} Note that the functionalization of corresponding lactide monomers often involves more synthetic steps with lower yield; and the polymerization of those functionalized lactide monomer can be difficult to achieve high molecular-weight (MW) polymers.^{17, 23}

OCAs are polymerized via the ring-opening polymerization (ROP). Such ROP process has been regarded thermodynamically more favorable than that of lactide due to the liberation of a carbon dioxide molecule during the polymerization process.²¹ However, challenges remain in exploring desirable catalysts for controlled ROP of OCAs, especially for potential industrial application. A number of review articles have discussed the development of polymerization of OCAs.^{20, 22, 24} It is not the intent of this review to attempt another similar comprehensive review of OCA polymerization, but rather to discuss the problems in ROP of OCAs. We shall outline some general consideration about living ROP of OCA, followed by the discussion of the recent literature from a catalyst-development perspective. On occasion, we refer to some polymerization reactions for purely illustrative purpose. Their mention is not an endorsement, nor is omission to be considered as a negative judgement.

2. Considerations in OCA polymerizations

2.1 Living and controlled polymerization of OCAs

Living polymerization—that is, all polymer chains grow at the same rate with no irreversible transfer or termination reactions—is central to current polymer chemistry.²⁵⁻²⁶ Generally, the rate of initiation (k_i) should be greater than the rate of propagation (k_p); the addition of monomer to polymer chain ends occurs irreversibly, without chain termination and side reactions; and the breadth of the MW distribution ($\mathcal{D}$) becomes extremely narrow ($\mathcal{D}$ approaches 1).²⁶ Living polymerizations can often be distinguished from kinetically-controlled (i.e. free radical) polymerizations by analyzing the evolution of the polymer's MW as a function

of time and/or monomer conversion: MW is directly proportional to monomer conversion in living polymerizations since all chain ends are growing at essentially the same rate.

Based on the consensus of the “living and controlled” polymerization, the generic properties of an ideal OCA polymerization catalytic system are summarized: (1) fast and complete initiation; (2) regioselective ring-opening of OCAs; (3) for practical reasons, converting monomer to growing polymer chains quantitatively and rapidly; (4) a linear relationship between the degree of polymerization (DP, typically measured as the number-average MW of the polymer, M_n) and monomer consumption; (5) $\bar{D} < 1.2$, which means the polymerization proceeding without an appreciable amount of (intramolecular or intermolecular) chain transfer or premature termination; (6) capable to control MW over a wide range (synthesis of high MW polymers). Last but not least, for future industrial application, the catalyst should show high stability towards moisture and air, and maintain cost-effectiveness.

2.2 Thermodynamics for OCA polymerization

At first glance, OCA bears multiple possible sites for nucleophilic attack (**Fig.1b**), similar to its analogue NCA (*N*-carboxyanhydrides) molecule. Nevertheless early studies by Smith and Tighe suggested that OCA is much stable and shows little tendency to polymerize compared with NCA.²⁷ the dimethyl-substituted OCA monomer (**10**) had a half-life over 1000 hours in 90 °C nitrobenzene solvent. However, these results remained relatively obscure over years; instead, the liberation of CO₂ from OCA monomers has been regarded as an considerable driving force for polymerization,²¹ in addition to the ring strain as in many other cyclic monomers for ROPs.²⁸⁻³⁰

One calculation showed that the ring-opening of of L-**1** is thermodynamically more favorable in terms of Gibbs free energy ($\Delta G_{298} = -14.0$ kcal/mol) than that of lactide (1.2 kcal/mol), catalyzed by 4-dimethylaminopyridine (DMAP) and methanol.^{21, 31} However, such calculation only considers the initiation step, and the results can be complicated when factors such as chain propagation and different catalysts are involved in. For instance, the ROP of L-**1** mediated by DMAP/*neo*-pentanol affords a controlled polymerization at room temperature ($M_n = 62.3$ kDa; $\bar{D} = 1.18$),²¹ superior to that of lactide by the same catalyst requiring few days in refluxing solvent.³² However, recent experimental studies on the yttrium complex-mediated ROPs of **1** showed that the Gibbs free energy of activation of L-**1** and L-lactide were essentially the same (16.5 *versus* 16.7 kcal/mol, respectively).³³ The obtained k_{app} (k_{app} , the apparent rate constant) values for both polymerizations were also in the same order of magnitude with less than 20% difference; though prolonged induction time for the ROP of L-lactide was observed.³³ In addition, in many cases,³⁴⁻³⁶ the fulfillment of thermodynamic requirements is a necessary – but not sufficient – prerequisite for a living polymerization to occur. The effects of catalysts can be seen pivotal to the success of ROPs; performing polymerization kinetic studies is essential in the mechanistic studies.

2.3 Molecular weight of the polyester

PLAs with M_n exceeding 100 kDa can be synthesized by $\text{Al}(\text{OiPr})_3$ or $\text{Sn}(\text{II})$ octanoate-based initiating systems.³⁷⁻³⁹ For example, the use of $\text{Sn}(\text{OBu})_2$ allows the polymer M_n over 900 kDa.⁴⁰ However, until recent, most polymers obtained from the ROP of OCAs have relative low MW (< 50 kDa). Research in PLA shows that the mechanical properties and crystallization behavior of PLA are very dependent on the MW and the polymer.⁴¹ For instance, the tensile modulus of PLA increases by a factor of 2 when MW is raised from 50 to 100 kDa;⁴² whereas tensile strengths increase from 15.5 to 150 MPa, when MW varies from 50 to 200 kDa.⁴³ Though PLAs used for biomedical applications often present a MW about 5–30 kDa,⁴⁴ PLA materials for orthopedic and other temporary implants used in bone surgery usually have MWs from 150 kDa to 300 kDa.⁴⁵ Those used to produce packaging materials necessitate high MW PLAs to exhibit the decent mechanical properties.^{41, 46} Therefore, it is critical for chemists to develop catalysts enable the synthesis of high-MW polyesters.

3. OCA monomer: synthesis and purification

In 1951 Davies first reported the synthesis of OCA by reacting α -hydroxyacid with phosgene, similar to the NCA synthesis.⁴⁷ To date, various OCAs have been synthesized. (**Fig. 1b**) In general, α -hydroxy acids are carbonylated using phosgene, diphosgene⁴⁸⁻⁴⁹ or triphosgene.⁵⁰⁻⁵¹ In case of the latter two carbonylation agents, activated charcoal is often used to promote the decomposition to phosgene and sometimes a tertiary amine (e.g., *N*-methylmorpholine) is added as an acid scavenger.⁵²⁻⁵³

In many cases, repetitive crystallization is enough to obtain pure OCA monomers.^{21, 54} However, methods are still needed for preparation of highly functional or low-melting-point OCAs that are difficult to recrystallize. A few reports suggested the use of flash chromatography for some OCA monomers purification.^{53, 55} Notably, NCAs can be purified by flash chromatography in the anhydrous environment;⁵⁶ the stability of OCAs in the column and the scope of such method have not been well studied. The reported rapid and facile microflow synthesis of NCAs is also worth experimenting for OCAs.⁵⁷

4. Organocatalyst for OCA polymerization

In early studies, the use of amines (e.g., pyridine and trimethylamine) and alkoxides (e.g., KOtBu , $\text{Ti}(\text{OBu})_4$) for ROP of OCAs failed to initiate controlled polymerizations, with M_n s less than 3 kDa.^{52, 58} Besides, acidic catalysts (e.g., triflic acid) do not work for the ROP of OCAs.²⁰ In 2006, Bourissou group started to apply the organocatalysts that had achieved success in the ROP of lactones to the OCA polymerization.²¹ Over the years, both DMAP and *N*-heterocyclic carbenes (NHCs) have been utilized for the ROP of OCAs (**1**, **2**, **6**, **8**) and obtained reasonable results.^{21, 51, 55, 59-61} However, most polymers catalyzed by organocatalysts exhibited MWs less than 30 kDa or low DPs (≤ 200).²⁰

4.1 The epimerization of α -proton

Early studies by Kricheldorf and Jonté showed that the ROP of **L-1** mediated by bases were accompanied by epimerization, as the optical rotations of the polymers decreased with the

increase of the catalyst basicity.⁵² The racemization of α -proton in the 5-aryl-OCA monomers (e.g., **3**) was also found in the alcoholysis mediated by a modified cinchona alkaloid, a aprotic nucleophile bearing tertiary amine and quinoline (**Fig. 2a**) at -70 °C.⁴⁸ The kinetic studies showed that the interconversion between *S*- and *R*-**3** was much faster than the enantioselective alcoholysis. When the aryl groups were replaced by alkyl groups, the reduced acidity of the α -proton renders unepimerizable by the cinchona alkaloid catalyst, which suggests the importance of the electronic property of the functional group on the 5-position of OCA monomer.⁴⁸

However, recent studies showed that the epimerization of α -proton still occurred to the DMAP-mediated ROP of OCAs bearing alkyl groups (e.g., **4** and **5**).⁶²⁻⁶³ The decreased epimerization of the α -proton occurred in poly(L-**4**) when DMAP ($pK_a = 9.7$) was replaced by less basic 4-methoxypyridine ($pK_a = 6.6$).⁶² Similarly, the improved isotacticity of the poly(D-**3**) was found by using pyridine derivatives with decreased basicity.⁶⁴

The use of acid/base crystalline adduct of mandelic acid and pyridine for the ROP of D-**3** could suppress the racemization and thereby (**Fig. 2b**), produced highly stereoregular isotactic polymers up to 48.0 kDa (over 80 hours with $\bar{D}$ of 1.17), which displayed enhanced thermal properties compared with the atactic poly(**3**).⁶⁴ Similarly, the adducts of 4-methoxypyridine with L-lactic acid and β -benzyl α -L-malate could also initiate ROP of L-**1** minimized epimerization of α -proton; however, those adduct failed to provide isotactic poly(L-**4**).⁶⁵ Note that at low [OCA]/[initiator] ratios, the epimerization still occurred in both polymers when using the acid-base adducts, suggesting that the pyridine adduct can still lead to the epimerization even with the decreased basicity.⁶⁵

4.2 Lewis pair catalyst for OCA polymerization

The use of a Lewis pair complex, that is a combination of Lewis acid with a base, has achieved recent success in controlled linear polymerization of acrylate, lactones and the synthesis of cyclic poly(lactide).⁶⁶ A very recent report showed that the use of the Lewis pair of $Zn(C_6F_5)_2$ with primary or secondary amines could initiate the polymerization of L-**2** and L-**3**.⁶⁷ The obtained polymers had M_n s up to 26.8 kDa with $\bar{D}$ s < 1.1. However, severe epimerization (isotacticity less than 80%) occurred in both polymers.⁶⁷ The use of bases in the Lewis pairs could be therefore detrimental to obtain stereo-regular polymers from OCAs. Note that the same Lewis pair afforded cyclic PLAs, presumably via the zwitterionic intermediate with $Zn(C_6F_5)_2$ and amine on each polymer chain terminus.⁶⁸ The discrepancy the two ROPs by the same Lewis pair indicated that the chain propagation of the chain propagation in the polymerization of OCAs was dominantly mediated by the Zn moiety without the influence of the amine. This also attributed to the relatively low MWs, similar to those polymerizations promoted only by Zn-alkoxides,^{63, 69} which is discussed section 5.

4.3 Other concerns in organocatalyst-mediated OCA polymerization

Computational studies by Bourissou *et al.* proposed that DMAP acts in a bifunctional nature by activating both the initiating alcohol and the carboxy oxygen O_5 in OCA.³¹ However,

another computational study hinted that the pyridine-catalyzed ROP of OCAs could occur in both O₁-C₅ (ester formation) and O₁-C₂ (carbonate formation), which probably leading to the epimerization (**Fig. 2c**). Besides these computation studies, no detailed mechanistic studies revealed the initiation and chain propagation for DMAP or pyridine-analogue mediated ROP. There also lacks the kinetic studies to reflect the reactivity order of DMAP and k_{app} during the chain propagation.

In addition, studies using most organocatalysts to promote the ROP of OCAs usually started from **1**, assuming that the success in **1** can be translated to other OCAs meaningfully. As observed in the ROP of lactones, when the methyl group of lactide is replaced with other groups, the polymerization conditions became harsh with incomplete monomer conversions and low DP_s.^{51, 70} The ROP of OCAs using organocatalysts is likewise. We found that at a high monomer to initiator ratio (500), the combination of DMAP / BnOH was not able to efficiently initiate the polymerization of L-**2** (conversion of **2** = 34% in 24 h), in contrast to the results of the ROP of L-**1** using the same catalysts.⁶⁹ Similarly, incomplete conversion of L-**2** (21% in 24 h) was found in the reaction catalyzed by NHC/BnOH.⁶⁹ As the motivation of OCA polymerization study is to synthesize polyesters with pendant functional groups, we suggest that researchers should start from the OCA monomers bearing functional groups (e.g. **2**) and validate the results in other monomers, instead of only reporting the results from **1**.

5. Metal catalyst for OCA polymerization

5.1 Development of metal catalysts

Compared with the organocatalysts, the development of organometallic catalysts in the OCA polymerization is surprisingly slow. Many organometallics that successfully mediated the ROP of lactide, lactones, and NCAs failed to translate to the polymerization of OCAs. Metal complexes that can promote ROPs of lactones or the copolymerization of epoxides and CO₂, including Sn(II), Al(III), Co(III), Nd(III) and Cr(III) complexes, did not mediate controlled ROP of L-**1** (**Fig. 3**).^{50, 71-72}

The Zn complexes with β -diiminate (BDI) ligands was the first metal catalyst system that can mediated controlled ROP of OCAs (**Fig. 3**).^{54, 63} Similar to the well-known ROP of lactide,⁷³ BDI-Zn complex requires an alcohol, even a very bulky one such as camptothecin or PEG,⁵⁴ to promote the polymerization, presumably through insertion-coordination mechanism.⁶³ Note monomeric BDI-Zn/alcohol complex performs more efficiently than dimeric complex, which also agree well with the reaction rate obtained in kinetic studies.⁶³ In addition, no epimerization was found in the ROP of OCAs (for **2**, **3**, **5**), indicating no nucleophilic attack towards α -proton occurred for BDI-Zn complexes.⁶³ As BDI-Zn-alkoxide can mediate the polymerization of either lactone or OCA, the sequential polymerization of lactone (including lactide) with OCAs can be smoothly achieved, regardless of monomer addition sequence.⁶³

Nevertheless, BDI-Zn/alcohol complex cannot efficiently produce polymers with a high DP (≥ 300).⁶⁹ This may be due to the inefficient chain propagation: the insertion of Zn-alkoxide

into L-2 was not followed by immediate decarboxylation, resulting in the inactive Zn-carbonate species at the chain end.⁶⁹ The mechanistic studies of using BDI-Zn to copolymerize epoxide and CO₂ indicate the equilibrium between Zn-alkoxide and Zn-carbonate.⁷⁴⁻⁷⁷ Note that very recent studies involving the use of Zr, Hf,⁷⁸ La and Y³³ complexes did not intend for the high-MW polyester synthesis (**Fig. 3**). For the reasons alluded above (section 2.3 on the polymer MW), it is therefore crucial to develop a highly efficient decarboxylation process for rapid chain propagation in the OCA polymerization.

We noticed that many metal catalysts for the lactone polymerization, such as BDI-Zn, are disqualified for decarboxylation as they have been also used for polycarbonate synthesis (e.g., Al, Fe, Cr, Co)^{16, 79-80} (so do many organocatalysts⁸¹). Aware of substantial studies in the metal catalyst-mediated NCA polymerization⁸²⁻⁸⁴ and the recent surge of interest in the photoredox catalysis,⁸⁵⁻⁸⁷ we developed a protocol for controlled photoredox ROP of enantiopure OCAs (**1**, **2**, **5**, **6**) to afford isotactic polyesters with high MWs (>140 kDa) and narrow *D*s (<1.1), without the epimerization at the α -methine hydrogen (**Fig. 4a**).⁶⁹ In such system, the combination of (bpy)Ni(0) complex (bpy, 2,2'-bipyridyl), a catalyst for NCA polymerization^{82, 84} but not reactive for controlled OCA polymerization *per se*,⁶⁹ and the photoredox catalyst **Ir-1**, are employed to efficiently promote the decarboxylation process under light irradiation, based on the decarboxylation mechanism reported by the MacMillan lab.⁸⁶⁻⁸⁷ Zn(HMDS)₂ was identified after screening a number of Zn complexes whereas the bulky BDI-Zn complexes does not provide high-MW polymers in the photoredox setting.⁶⁹ Kinetic studies indicated that the use of alcohol only involved in the initiation to form Zn-alkoxide for ring-opening reactions; and **Ir-1** only influenced Ni complex oxidative state but not affecting chain-end reactivity. Mechanistic studies suggested that a Ni(0) complex regioselectively inserted at the O₁-C₅ bond in the OCA monomer, followed by the Ir-mediated photoredox decarboxylation and transmetalation with a Zn complex to form a reactive Zn-alkoxide terminus for chain propagation.⁶⁹ Notably, the polymerization has to be performed at low temperature (-15–20 °C) to avoid undesired Ni-mediated decarbonylation that occurs at room temperature.⁸⁸⁻⁹⁰

5.2 Stereoselective ROP by metal catalysts

Organometallic catalysts are advantageous to prepare polyesters with various microstructures from lactides and β -lactones,⁹¹⁻⁹⁴ except a few recent reports about the utilization of organocatalysts.⁹⁵⁻⁹⁷ Nevertheless, the stereoselective synthesis of polyesters with pendant side-chain functional groups remains challenging. In 2017, Wu *et al.* identified a Hf-alkoxide complex with a C₃ symmetric amino-tris(phenolate) ligand for syndiospecific ROP of racemic OCAs (**1**, **2** and **7**, **Fig. 3**).⁷⁸ Most obtained polymers have MWs less than 20 kDa with a relative broad *D* (>1.1). The origin of such syndiospecificity (chirality influence of the metal), and the chain propagation mechanism, was not well understood (chain-end or enantiomorphic mechanism; see the discussion about the Ge complex with the same C₃ symmetric for lactide polymerization⁹⁸⁻⁹⁹). Such Hf complex was utilized to mediate alternative copolymerization of

the co-monomers with opposite chirality; however, all obtained copolymers had relative low MWs (< 10 kDa), and monomer conversions were even incomplete in many cases.⁷⁸

We have recently applied the photoredox Ni/Zn catalysts to stereoselective polymerization of OCAs.¹⁰⁰ (NNO-1)Zn complex with less bulky tridentate Schiff base ligand, compared with BDI, was identified to mediate stereoselective controlled polymerization of racemic OCAs (**1**, **2**, **5**, **6**) that afforded stereoblock polymers (**Fig. 4b**). The obtained stereoblock copolymers are highly isotactic with high MWs (>70 kDa) and narrow *D*s ($M_w/M_n < 1.1$) with a probability of *meso* dyad formation (P_m , i.e., isotactic enchainment) of 0.97. To elucidate the microstructures and polymerization mechanism, deuterated [D₂]-L-**2** was synthesized and used for kinetic studies together with D-**2** in the polymerization, as because the methine deuterium in [D₂]-L-**2** does not show up in the ¹H NMR spectrum; and the NMR results suggested the polymer chain end did not have a kinetic preference for a specific enantiomer in the (NNO-1)ZnEt-mediated photoredox ROP of *rac*-**2**. Different from the enantiomorphous site-control by using racemic chiral aluminum catalysts for stereoblock PLA synthesis, the (bpy)Ni/(NNO-1)Zn/Ir-**1** mediated stereoselective ROPs proceeds via the chain-end control; a stereoerror occurs during the chain propagation and the other enantiomer is incorporated and enchainment.¹⁰⁰ The computational study suggests the stereo hindrance in the NNO-1 ligand affected the isoselectivity of the Zn complex. Notably, the obtained stereoblock polymers exhibited melting temperatures close to the stereocomplex of two isotactic polymers.¹⁰⁰

Subsequent copolymerization studies expand the use of (NNO-1)Zn photoredox system for the gradient copolymer synthesis. We found that using monomers with opposite chirality and significant difference in the polymerization rates (i.e., k_{app}) results in the formation of gradient copolymers with M_n s close to the calculated MWs (over 40 kDa) and *D* values of <1.1. (**Fig. 4c**) The polymerization rates for OCA monomers in Ni/Zn systems have the following orders $k(\mathbf{2}) > k(\mathbf{1}) \approx k(\mathbf{6}) > k(\mathbf{5})$, and no obvious difference exists between the rates of the two enantiomers of a given monomer. On the other hand, copolymerizations of monomers with same chirality or similar polymerization rates can lead to the random copolymers.

6. Perspective

Despite the substantial number of catalysts that have been developed,²⁴ few have really hold promise for industrial production or commercialization. It remains difficult for organocatalysts to mediate stereoregular polymerization from OCAs as the racemization of α -proton persists when using most bases, even at low temperature⁴⁸ or with decreased basicity.⁶⁵ The detailed chain-propagation mechanism, including non-regioselective ring-opening of OCA,⁶² and the existence of active-monomer mechanism,^{31, 52} have not been well studied, compared with those results in the ROP of NCAs.¹⁰¹⁻¹⁰³ On the other hand, substantial progresses have been achieved in the use of metal complexes for the controlled OCA polymerization, which allows for the synthesis of high MW polymers and stereoselective polymerizations.^{69, 100} However, the use of low temperature and relatively exotic experimental conditions could prevent the direct translation of the photoredox Ni/Zn catalysts to industrial production. Our review is not able to

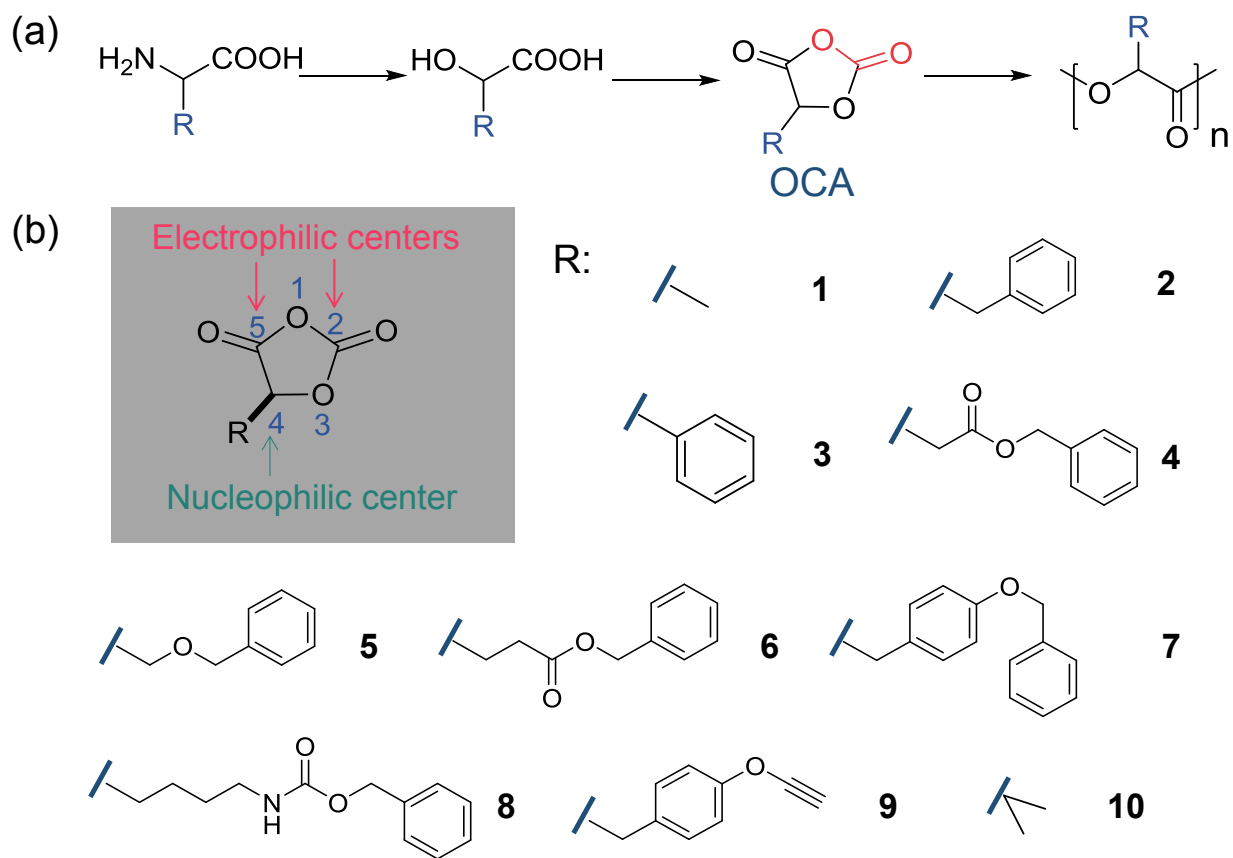
impart a perfect ability to predict what will work: the lessons learned in one context (e.g., polymerizations of lactide or NCAs) do not always translate into the ROP of OCAs, even when one might expect them to. Such instances reflect the fact that our understanding of the OCA polymerization mechanism remains incomplete.

Notably, as has been the case for decades, comparison of results from different catalytic systems remains difficult, with many inconclusive or incomprehensive studies. The standardized and systemic studies can be helpful for future chemistry development, together with the use of visualized experimental procedures.¹⁰⁴

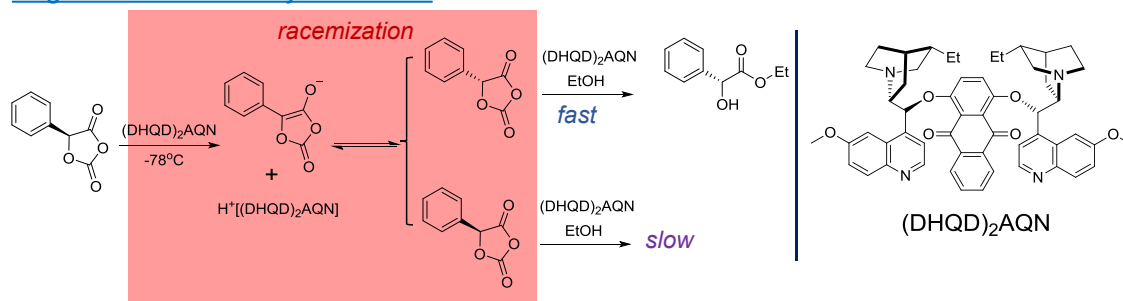
Additionally, as many new polymers have been synthesized from OCAs, it is important to characterize their physiochemical properties, including their degradation profiles, to identify their potential applications. It is also important to start design and perform studies on how to recycle the polymers for sustainable applications.^{1, 105-109} Irrespective of the industrial prospects for the polyesters, the rapidly developing OCA chemistry can be suggestive for other polymerizations, in such a way as it benefits from the great expansion of the polymer field.

Acknowledgement

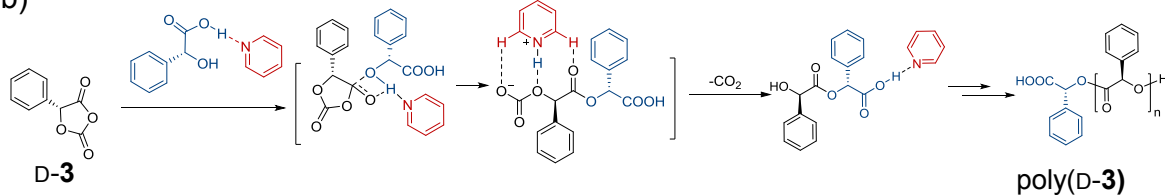
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(a) Regioselective alcoholysis of OCA



(b)



(c)

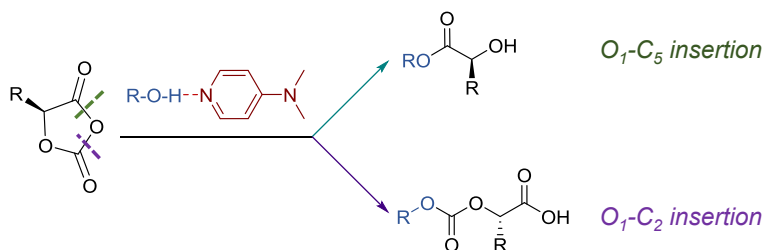


Figure 2. Epimerization of α -proton in the organocatalyst-mediated OCA polymerization.

(a) The reported racemization of aryl-OCA (**3**) at low temperature in the presence of amine. (b) The use of D-mandelic acid/pyridine crystalline adduct can suppress the epimerization and provide isotactic-dominant poly(D-3). (c) Another proposed mechanism of DMAP/alcohol induced epimerization by non-regioselective ring-opening of OCA.

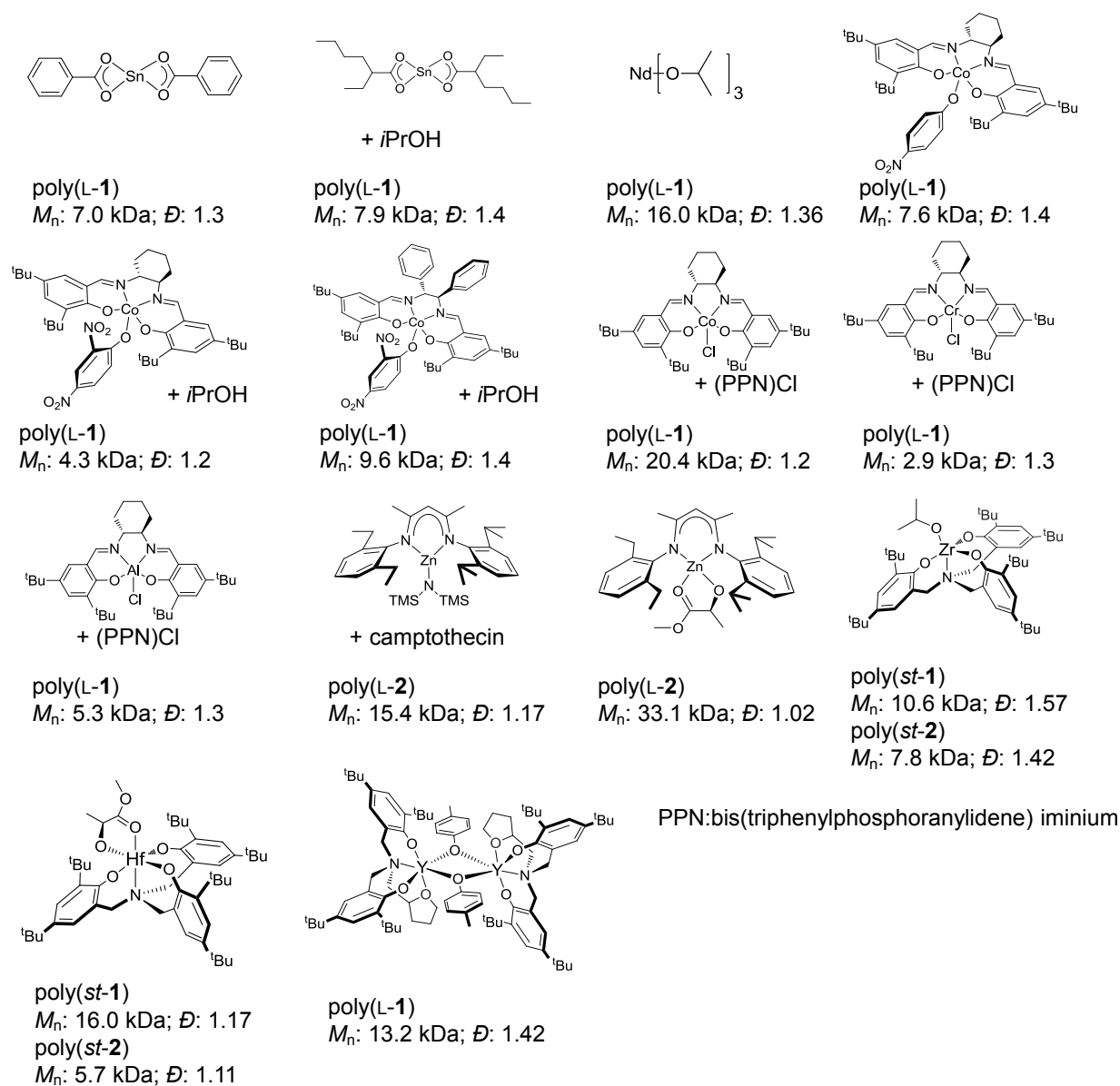
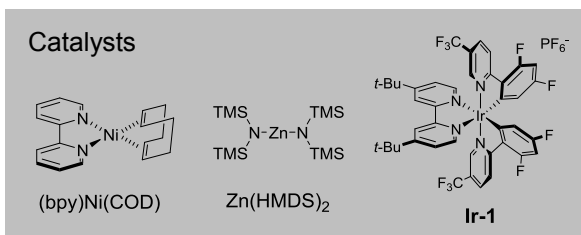
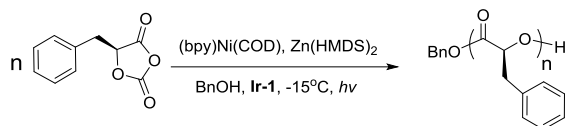
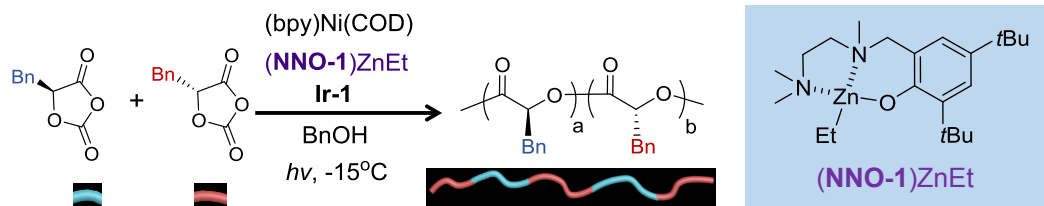


Figure 3. Representative results of various metal catalysts-mediated OCA polymerization. *st*, syndiotactic.

(a) *Photoredox ring-opening polymerization*



(b) *Photoredox stereoselective ring-opening polymerization*



(c) *Photoredox copolymerization to prepare gradient copolymer*

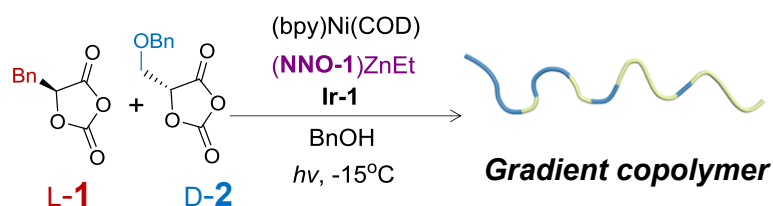


Figure 4. Photoredox polymerizations of OCAs. (a) The photoredox ROP of OCAs to prepare high MW isotactic polymers using (bpy)Ni/Zn(HMDS)₂/**Ir-1** catalysts. (b) Photoredox stereoselective copolymerization of racemic OCAs to prepare stereoblock polymers. (c) Photoredox copolymerization of two monomers with opposite chirality and significantly different reactivities to synthesize gradient copolymer.

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