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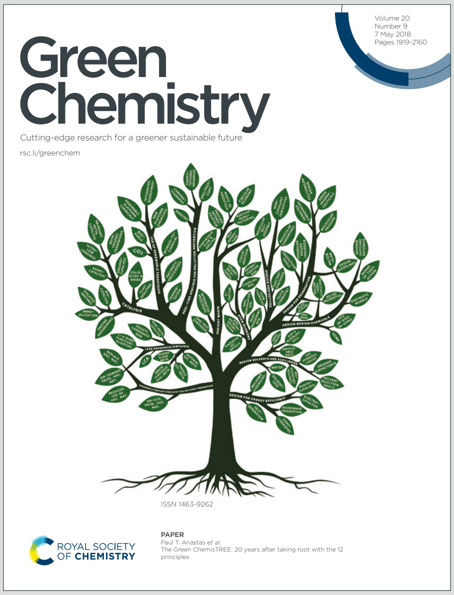

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ARTICLE

Bio-Based Polyesters by Ring-Opening Copolymerizations of Eugenyl Glycidy Ether and Cyclic Anhydrides Using Binuclear [OSSO]CrCl Complex

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A novel binuclear chromium complex of dianionic [OSSO]-type ligand has been synthesized and employed toward the ring-opening copolymerization of renewable eugenyl glycidyl ether (EGE) and cyclic anhydrides (CAs) (succinic anhydride (SA), phthalic anhydride (PA), maleic anhydride (MA), itaconic anhydride (IA), *endo*-norbornene anhydride (NA), and tetrahydrophthalic anhydride (THPA)), showing high activity in conjuction with bis(triphenylphosphine)iminium chloride (PPNCl). Most of the resultant polyesters show perfect alternating microstructures except polyesters derived from IA/EGE and MA/EGE copolymerimerization, where 14% and 11% of ether units are observed, respectively. Among the CAs tested, the renewable SA shows the highest reactivity with highly regioselective model, providing a facile way to preprare the fully biomass-based polyester bearing dominant head-to-tail structure. The results of ESI-MS indicate that the maximum coordination number of PPNCl to the dinuclear [OSSO]CrCl complex is only one molecule. The pendant ally groups onto the resultant polyesters backbone afford an additional versatility for further functionalizations.

Introduction

The ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides (CAs) is being considered to be one of promising methods to prepare polyesters.[1–3] Compared with traditional methods such as the ring-opening polymerization of cyclic esters and step-growth polymerization of diacids or diesters with diols, ROCOP demonstrates the advantages of atom-economy and convenient tuning of properties owing to the facile availability of structurally diverse monomers.[2, 3]

Bio-based polymers derived from biomass feedstocks have recently attracted considerable interest due to its sustainable feature and as one of promising alternatives to unrenewable fossil-fuel-based polymers.[4] In this context, polyesters based on the ROCOP of biomass epoxides and CAs have also been reported. For example, magnesium ethoxide was used as a catalyst for the ROCOP of SA, a derivative of succinic acid that can be produced by biological pathways from renewable resources, with ethylene oxide, yielding low molecular weight (MW) polyesters with high polydispersity index ($Đ$) at low catalytic activity.[5] Recently, a fully renewable polyester was synthesized via the ROCOP of sugar-based epoxide with CAs such as SA and glutaric anhydride using single aluminum alkoxide as a catalyst.[6] The resultant polyesters presented low MW with low $Đ$ and the reactivity of epoxide was sensitive to the length of methylene spacer between sugar and epoxide.[6] A noticeable breakthrough has been made by Coates and co-workers for the preparation of polyesters by the ROCOP of limonene oxide (LO) and diglycolic anhydride or MA using β-diiminate zinc catalysts.[7] The same group consecutively developed the functionalizable aliphatic polyesters with high glass transition temperature (T_g) based on the alternating ROCOP of renewable terpene-based CA with propylene oxide or cyclohexene oxide catalyzed by chromium and aluminum salen complexes.[8] An elegant tandem synthesis of CAs and subsequent ROCOP with epoxides was studied using a combination of (salcy)AlCl and PPNCl (PPN=bis(triphenylphosphoranylidene)iminium), where a proposed bis(alkoxide) species, $[(\text{salcy})\text{Al}(\text{OR})_2]^-$, was formed as the reactive catalyst.[9] The bio-based semi-aromatic polyesters were synthesized by the ROCOP of the renewable terpene-derived epoxides and PA catalyzed by metal *N*,*N*-bis(3,5-di-tert-butylsalicylidene)diimine complexes, $(^t\text{Bu–salophen})\text{MX}_n$ (M = Cr, Al, Co, Mn),[10] and by a binary catalyst composed of a Fe(III)-based aminotriphenolate complex in conjunction with PPNCl.[11] The resultant polyesters are potentially useful as coating and thermoset materials.[11] Meier and Williams[12] described the synthesis of unsaturated polyesters with T_g up to 128 °C by the ROCOP of PA with a 1,4-cyclohexadiene oxide, a derivative from self-metathesis of plant oil, by using di-zinc/magnesium complexes or Cr(III) or Co(III) salen complexes. Highly branched polyesters were also accessible by the ROCOP of methyl 9,10- epoxystearate with

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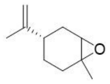
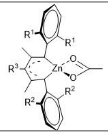
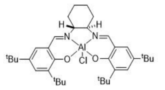
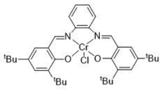
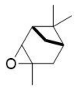
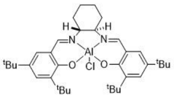
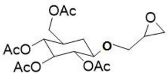
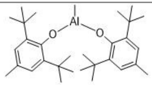
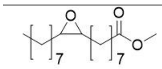
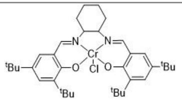
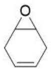
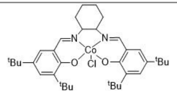
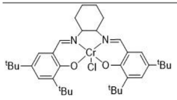
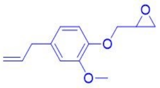
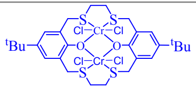
Table 1 Some typical examples of the ROCOP of bio-based epoxides with CAs using various types of catalyst

Epoxide monomer	Catalyst	CA [a]	Results [b]	Ref.
		MA	X = 55%, M_n = 12K; Đ =1.1	7
		CpA	Y = 100% M_n = 8.1K; Đ =1.3	9
		PA	X = 90% M_n = 7.2K; Đ =1.4	10
		GA	Y = 29% M_n = 8.4K; Đ =1.2	9
		SA	Y = 19% M_n = 1.4K; Đ =1.05	6
		PA	Y = 83% M_n = 7.6K; Đ =1.17	13
		PA	X = 48% M_n = 4.3K; Đ =1.23	12
			X = 91% M_n = 7.5K; Đ =1.17	
		SA, MA, IA, PA THPA, NA	*Vide infra*	This work

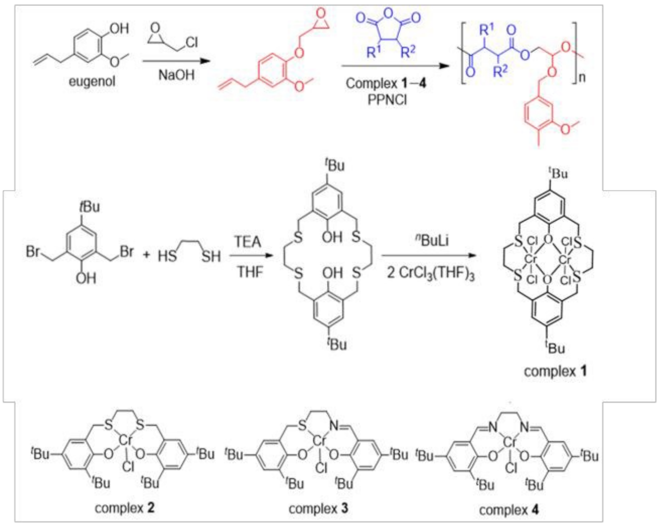
[a] Cyclic anhydride: MA=maleic anhydride; CpA = camphoric anhydride; PA = phthalic anhydride; GA = glutaric anhydride; SA = succinic anhydride; IA = itaconic anhydride; NA = norbornene anhydride; and THPA = tetrahydrophthalic anhydride; [b] X = conversion of epoxide monomer and Y = yield of polymer.

different CAs using a (salcy)Cr(III)Cl catalyst in combination with n-Bu$_4$NCl under neat conditions. The resulting polyesters were featured by a high renewable content and showed MWs of up to 10 kDa with low Đ.[13] Considering polymers originated from renewable resources are attractive for the production of environmental friendly and in many cases biodegradable consumer products, it is impossible to emphasize enough the importance of renewable epoxide monomers to expand the scope of biomass-based polyesters with desirable properties. For clarity, the results of the ROCOP of the biomass-based epoxides monomers and various types of CAs are summarized in Table 1.

We have explored the mononuclear chromium complexes with tetradentate-dianionic thiobis(phenolate)-[OSSO]-type ligands for the ROCOP of epoxides with CAs assisted by Lewis base or onium salts,[14] affording the corresponding alternating polyester with acceptable catalytic activity. Many reports showed that binuclear complexes could provide a circumstance facilitating cooperative binding, conformational control and activation, and thus led to enhanced catalytic performances over the monometallic analogues in the catalytic polymerization of olefins,[15] cyclic polyesters by lactide polymerization using the bis(imino)diphenylamido dizinc catalysts,[16] and copolymerization of epoxides with CO$_2$ using the bimetallic anilido-aldimine zinc complexes,[17(a)] the dizinc complexes having a macrocyclic ancillary ligands,[17(b),17(c)] a dizinc complex with mixtures of up to three different monomers,[17(d)] and binuclear cobalt(III) complexes.[17(e)]

As a means of expanding the scope of binuclear catalysis to the ROCOP of epoxide and CAs[17d,18] and developing a facile approach to synthesize allyl-functionalized bio-derived polyesters, the ROCOPs of eugenol glycidyl ether (EGE) prepared by reacting eugenol (4-allyl-2-methoxyphenol) with renewable epichlorohydrin[19] and various cyclic anhydrides were investigated by using a binuclear chromium complex **1** of dianionic [OSSO]-type ligand as depicted in Table 1 and Scheme 1. Note that eugenol is a phenol-based oily liquid extracted from certain essential oils especially from clove oil, nutmeg, cinnamon, basil and bay leaf. It could be potentially produced via pyrolysis of abundant lignin,[20] making it more affordable. Thus, eugenol has highly received attention as feedstock for development of polymeric materials such as thermoset resin[21] and antibacterial polyethylene by copolymerization with ethylene using a palladium aryl sulfonate catalyst.[22]

So far, no reports exist in literatures on the ROCOP of eugenol-derived epoxides with CAs. Particularly, the ROCOP of EGE and SA is to be discussed in detail in order to identify mechanistic pathways. The post-modification of resulting polyesters is also attempted using the allylic double bond on the EGE moiety. The results of this study make the scope of binuclear catalyzed ROCOP broad and provide us with an important information to develop a new class of bio-based functional polyester.



Scheme 1 Alternating ROCOP of EGE and CAs using binuclear (complex **1**) and mononuclear (complexes **2**–**4**) chromium complexes.

Results and discussion

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The macrocyclic [OSSO]-type ligand is prepared by the nucleophilic substitution between thiol group with C-Br bond (see Scheme S1). The binuclear [OSSO]CrCl complex was obtained by reacting 2 equivalents of $CrCl_3(THF)_3$ with the lithium salt of the corresponding pro-ligand in THF solution.[17] The product was recovered in 73% yield as dark green solid. The mass spectral data (ESI-MS, positive mode) of complex **1** show a peak with m/z of 803.15, which fits well with 802.93 of [complex **1**+ Na]$^+$ (see Fig.S1 in Supporting Information), indicative of achievement of binuclear [OSSO]CrCl complex. The stretching frequency of C–S bond in complex **1** showed a red shift compared to the parent ligand due to metal induced effect (Fig.S2). The binding energy of Cr in complex **1** determined by XPS is consistent with Cr(III) centres, where the $2P_{1/2}$ and $2P_{3/2}$ are 586.7 eV and 577.3eV, respectively (Fig.S3).[23a] Magnetic measurements of complex **1** are shown in Fig. S4, the χT value at 296 K of 3.53 cm^3 K mol^{-1} agrees with two isolated Cr(III) ions (3.75 cm^3 K mol^{-1}).[23b]

The binuclear complex **1** was initially investigated as a catalyst for the ROCOPs of EGE with various types of CA including maleic anhydride (MA), phthalic anhydride (PA), succinic anhydride (SA), itaconic anhydride (IA), tetrahydrophthalic anhydride (THPA), and *endo*-norbornene anhydride (NA) at molar ratio of [CA]/[EGE]/[Cr]/[PPNCl] = 250 : 250 : 1: 1 in toluene at 90 °C for 2 h. As summarized in Table 2, the rate of ROCOP is dramatically dependent on the type of CA. MA and IA present a relatively lower reactivity for the copolymerization with EGE (Entries 1 and 2, Table 2), and THPA, NA, and PA show medium reactivity. Note that SA gives the highest reactivity (87.1% yield) in the ROCOP with EGE. Since SA is derived from succinic acid that is one of the bio-derived building-block C_4 platform chemicals, the polyesters produced by the ROCOP of EGE and SA can be a good candidate of fully bio-based polymeric material. Mononuclear chromium complex **2** with [OSSO]-type ligand also displays a higher yield (60.8%) in the ROCOP of EGE and SA than that (36.0%) in the ROCOP of EGE and PA (see Table 3). Note that most of the previous reports showed that PA exhibits the highest reactivity in the ROCOP of CAs and epoxides (Table S1).[24] The similar results were obtained in the complex **1**-catalyzed ROCOPs of phenyl glycidyl ether and SA or PA, while the yield of the ROCOP of allyl glycidyl ether (AGE) and SA was almost half of that of the ROCOP of AGE and PA (Table 3). Chromium complexes with [OSNO]-(complex **3**) and [ONNO]-type (complex **4**) ligands also show higher reactivity toward PA rather than SA in the ROCOP with EGE. The ROCOP results collected in this study and from prior results (Table 3 and Table S1) clearly reveal that the efficiency to produce polyesters using the ROCOPs of CAs and epoxides is highly sensitive to various factors such as the types of ligand and metal, epoxide monomers, and CAs together with experimental parameters like [epoxide]/[CA]/[catalyst]/[PPNCl] ratio, temperature, time, amount of type of solvent.

Table 2 Effect of the type of CA on the ROCOP with EGE catalysed by complex **1**/PPNCl [a]

Entry	CA	Yield [b](%)	Ester Unit (%)	M_n [c] (g/mol)	*Đ* [c]
1	IA	24.1	86	4100	1.93
2	MA	39.2	89	4200	1.98
3	THPA	42.4	>99	3100	2.07
4	NA	51.7	>99	6600	1.94
5	PA	62.3	>99	8500	1.97
6	SA	87.1	>99	7600	1.91

[a] [CA]/[EGE]/ complex **1**[Cr]/[PPNCl]=250/250/1/1, Temperature: 90 °C, Time: 2 h, toluene: 1.0 mL, Complex **1**: 0.0117 g (0.03 mmol Cr), EGE:1.65 g (7.5 mmol); [b] According to the isolated mass of corresponding polyester; [c] Determined by gel permeation chromatography in THF.

The type of CA also played an important role in the selectivity for resulting polymers structure. As shown in ^1H NMR spectra (Figs.S5–S10) of polyesters in Table 2, the characteristic proton signal assigned to the ether linkages appears at δ=3.80–4.10 ppm ($H^{k'}$) for the polymers from Entries 1 and 2 in Table 3, showing incomplete alternating copolymerization. The integral areas corresponding to ether and ester linkages show that polymers produced by the ROCOP of EGE with IA and MA consist of ester linkages of 86% and 89%, respectively. It is worth noting that no conspicuous signals assignable to ether linkage are observed from the polyesters produced by the ROCOP of EGE with SA, NA and THPA, demonstrating perfect alternating ROCOPs. The highly

Table 3 Effect of complexes and epoxide monomers on the SA and PA reactive sequence in the copolymerization [a]

Entry	CA	Epoxide	Complex	Yield [b](%)	TOF [c](h^{-1})
1	SA	PGE	1	90.4	113
2	PA	PGE	1	79.1	99
3	SA	AGE	1	20.9	26
4	PA	AGE	1	36.6	46
5	SA	EGE	2	60.8	76
6	PA	EGE	2	36.0	45
7	SA	EGE	3	31.1	39
8	PA	EGE	3	56.5	71
9	SA	EGE	4	32.1	40
10	PA	EGE	4	92.3	115

[a] Entry 1-4 [CA]/[epoxide]/[Cr]/[PPNCl]= 250/250/1/1, Temperature: 90 °C, Time: 2 h, toluene: 1.0 mL, Complex **1**: 0.0117 g (0.03 mmol Cr); Entry 5-10 [CA]/[epoxide]/[Cr]/[PPNCl]= 250/250/1/1, Temperature: 90 °C, Time: 2 h, toluene: 1.0 mL, Complexs: 0.03 mmol Cr, epoxide: 7.5 mmol; [b] According to the isolated mass of corresponding polyester; [c] Turnover frequency (TOF) = mol of consumed epoxide/mol of catalyst per hour.

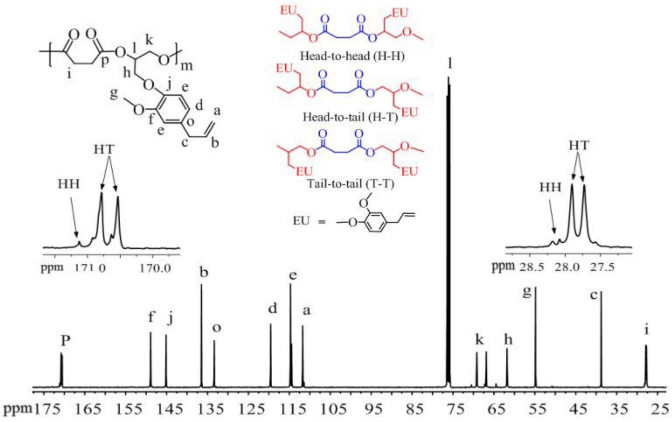

Fig. 1 ^{13}C NMR spectra showing the carbonyl and succinate methylene region of poly(SA-*alt*-EGE) in $CDCl_3$

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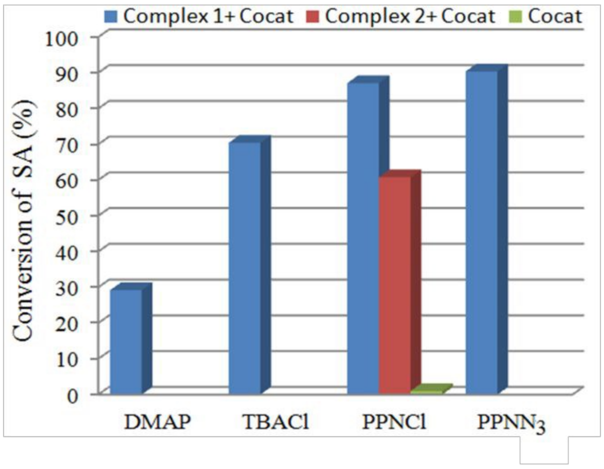

Fig. 2 The yield of SA/EGE copolymers under various cocatalysts in toluene. Conditions: toluene (1 mL) [SA]/[EGE]/[Cr]/[cocatalyst] = 250 : 250 : 1: 1 (molar ratio), 90 °C, 2 h.

alternating units were further supported by ^{13}C NMR spectrum of poly(SA-*alt*-EGE) (Fig. 1), where no characteristic resonance of the ether linkages in the range of 75–85 ppm is observed.[25] The carbonyl chemical shifts attributed to head-to-tail (HT) linkages of poly(SA-*alt*-EGE) chain are observed at 170.51 and 170.74 ppm, and representative signals of head-to-head (HH) linkages appeared at 171.25 ppm. In addition, chemical shifts owing to methylene signals of HT linkages are found at 27.68 ppm and 27.74 ppm; while two separated resonance peaks at 28.06 and 28.18 ppm represented methylene carbon signals of HH linkages, respectively. The content of HT connectivity is estimated to be about 96%, implying that a highly region-regular ROCOP of EGE and SA occurs at methylene C_β-O bond.

In order to collect further evidence on the ring-opening position of EGE, we have conducted a metal-assisted coordination ring-opening of EGE with benzoic acid in the presence of complex **1**(Cr)/PPNCl (molar ratio at 1:1) at 90 °C (see Supporting Information for detailed experimental procedures). The ring-opening of EGE can occur in two different positions of oxirane ring: i.e. one at methylene C_β–O bond to form a product consisting of secondary –OH (**I**) group and the other at methine carbon to form a product bearing primary –OH (**II**) groups.[26] The ratio of **I** to **II** is estimated to 94:6 from ^{1}H NMR spectrum (Fig. S11), demonstrating the ring-opening of EGE predominantly occurs at C_β-O bond rather than at methine carbon, being in line with the results that the ROCOP of SA and EGE occurs in a highly regio-selective manner at C_β-O bonds of EGE.

Complexes of Zn, Al, Co, Fe, Mg, and Cr with variety of ligands have proven to be active in the ROCOP.**[2]** Many catalyst systems require a suitable ionic or neutral nucleophilic co-catalyst, the most broadly used include 4-(N,N-dimethylamino)pyridine (DMAP), tetrabutylammonium chloride (TBACl) and bis(triphenylphosphoranylidene)-ammonium (PPN$^+$) salts, such as PPNCl and PPN-azide (PPNN_3). Our previous work**[14]** and reported results[2] revealed that the catalytic activity of the ROCOP of epoxides with CAs was drastically dependent on the amount and the type of cocatalyst. Thus, the effect of cocatalysts on the activity of the ROCOP of EGE and SA was investigated by using binuclear complex **1** and mononuclear complex **2**. DMAP, TBACl, and PPNX (X=Cl, N_3) were chosen for tests. The results of the ROCOPs performed at 90 °C for 2 h in toluene are illustrated in Fig. 2. Complex **1** shows the highest conversion of SA (90.4%) by combining with PPNN_3 and the lowest one with DMAP (29.2%), clearly demonstrating the choice of the type of cocatalyst is one of the significant parameters to achieve a high activity for a specific catalyst. PPNCl showed only a negligible activity in the same ROCOP, since the real catalytic species are most likely formed six-coordinate chromium centre by cocatalyst (Lewis base or onium salt) coordinating to central metal of complexes. This speculation is confirmed by the ESI- MS spectroscopy (Fig. S10). Furthermore, as demonstrated by Fig. 2, the catalytic performances of complex **1** is more effective than that of complex **2**. Based on these results, we may assume the existence of a synergistic effect in the binuclear catalyst system. Indeed, the bimetallic synergistic effects were frequently observed in the polymerization of epoxides and the copolymerization of epoxides with CO_2 under coordination polymerization catalysis.[17, 18a, 27, 28] In order to further demonstrate the catalytic performance of complex **1**, we have performed a series of ROCOPs of EGE and SA by varying the monomers dosage and reaction temperatures. As summarized in Table S2, as temperature increases, the yield monotonously increases (Entries 1-5, Table S2), whereas the monomer conversion declines with increasing the monomer due to the dilution effect (Entries 5-7, Table S2).

To figure out the formation of active species through a binding of cocatalyst to complex **1**, two series of ROCOP of EGE and SA were performed: i.e. one by fixing the amount of PPNCl with varying the amount of complex **1** and the other by fixing the amount of complex **1** with varying the amount of PPNCl. As illustrated in Fig. 3, as [Cr]/[PPNCl] ratio changes from 0.25/1.0, 0.50/1.0 to 1.0/1.0, the conversion of SA increases from 8.3% to 87.1% by about 10 times (line **A,** Fig. 3). At [Cr]/[PPNCl]=2, the conversion of SA reaches 100% within shorter reaction time of 1.5 h (line **B**, Fig. 3). At [Cr]/[PPNCl] of 2.5/1.0, the conversion of SA is slightly enhanced (line **C**, Fig. 3). It is note-

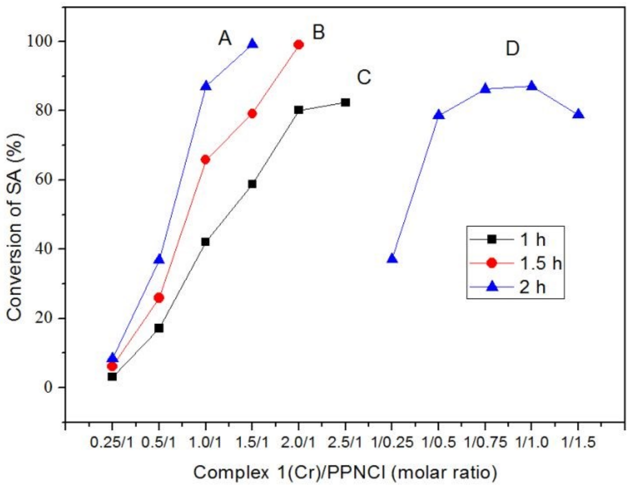

Fig. 3 Effects of molar ratio of complex **1** (Cr) to PPNCl on the copolymerization of SA and EGE. Solvent = toluene (l .0 mL), SA = 0.75 g (7.5 mmol), T = 90 °C.

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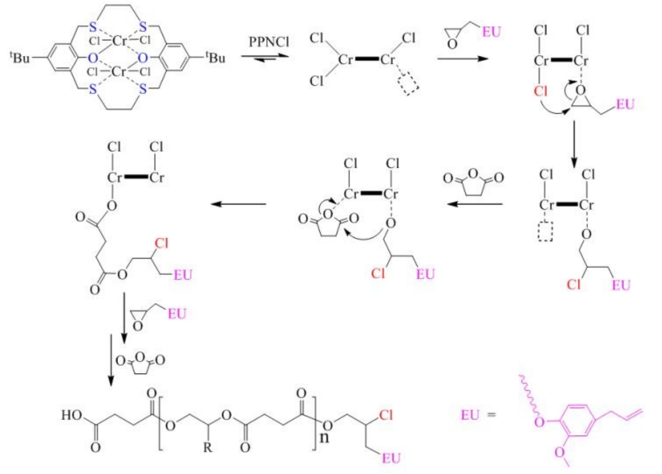
worthy that the highest catalytic activity occurs approximately at [Cr]/[PPNCl]=2.0, that is, at a point of one PPNCl coordinated to two Cr centers. Another series of ROCOPs performed by fixing the amount of complex **1** with varying the amount of PPNCl, the conversion SA is substantially increased at [Cr]/[PPNCl] ratio ranging from 1.0/0.25 to 1.0/0.5 (line **D** in Fig. 3). Whereas although the copolymerization reactivity is still slight enhanced with ranking [Cr]/[PPNCl] from 1.0/0.5 to 1.0/1.0, but the promotion is not apparent as from 1.0/0.25 to 1.0/0.5. Nevertheless, the conversion decreases when [Cr]/[PPNCl] becomes 1.0/1.5 as depicted by line **D.** These observations suggest that a maximum increase of the catalytic activity is also appeared at [Cr]/[PPNCl]=2.0.

Combining previous findings that the six-coordinated Cr centers were real active species in copolymerizations of epoxides with CO_2 or CAs using many different types of chromium complexes in the presence of cocatalysts,[29] with the results obtained in this work, proposed to operate through a bimetallic mechanism where a binuclear [OSSO]CrCl complex molecule binds one PPNCl to form six-coordinated complex ions, and the other metal centre activates the epoxide via its coordination. (Scheme 2) Thus, the catalytic activity increases with increasing [Cr]/[PPNCl] ratio from 0.25/1.0 to 2.0/1.0 at a fixed amount of PPNCl and with varying [Cr]/[PPNCl] ratio from 1.0/0.25 to 1.0/0.5 at a fixed amount of complex **1**. Approximately at Cr/PPNCl=2.0, both of the two series of polymerizations show the highest activities. since the amount of six-coordinated the metal active species reach to the highest concentration in this ratio. Further increase of the amounts of complex **1** or PPNCl does not show proportional effect on the formation of active species. The slow enhancement of copolymers' yield with increasing the amount of PPNCl leading to [Cr]/[PPNCl] in the range of 1.0/0.5-1.0/1.0 is reasonably originated from the copolymerization results using PPNCl alone showing lower efficiency at high loading.[30] The excessive PPNCl may competitively coordinate to metal active sites,[31] which impeded the approach and coordination of epoxide for the activation to participate the chain reaction. This could be responsible for the reduction of the copolymer yield at [Cr]/[PPNCl]=1.0/1.5 and even more.



Scheme 2 Proposed mechanistic pathways to form six-coordinated Cr active species and alternating addition of EGE and SA to form polyester.

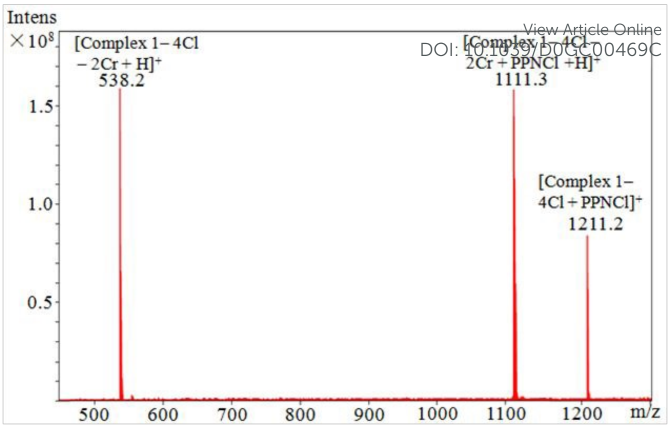


Fig. 4 ESI-MS spectrum of complex **1**/10-folded PPNCl.

Electrospray ionization (ESI) is a soft ionization method that can keep any weakly bound ligand intact in a complex ion,[32] so that it can be utilized to study the properties and reactions of metal complexes active sites and the role of metal complexes and cocatalysts.[33] Herein, we employed the ESI-MS to study the binding of PPNCl to complex **1**. The solution was prepared by mixing complexes **1** with 10-fold molar of PPNCl in CH_2Cl_2 and stirred for 30 min at 30 °C and stocked for 60 min before ESI-MS measurement (Fig. 4). ESI-MS spectrum of complex **1**/PPNCl mixture displays the singly charged species of [complex **1**+PPNCl-4Cl]$^+$ cation at 1211.2 in positive ion mode, suggesting that complex **1** highly preferred to the coordination of PPNCl to chromium ion with one molecule of PPNCl to form a complex **1**·PPNCl adduct. This observation and the again support formation of six-coordinated Cr active species (Scheme 2). However, the spectrum of the complex **2** in conjunction with PPNCl contains the two kinds of species at m/z 1153.3 and 1727.4, corresponding to [complex **2**+PPNCl-Cl]$^+$ and [complex **2**+2PPNCl-Cl]$^+$ cations, respectively, and intensity ascribed to the latter is far stronger than that of [complex **2**+PPNCl-Cl]$^+$ (Fig. S12). This means that the mononuclear complex **2** predominantly binds two molecules of PPNCl to generate complex **2**·2PPNCl adduct.

The number average molecular weight (M_n) values of the

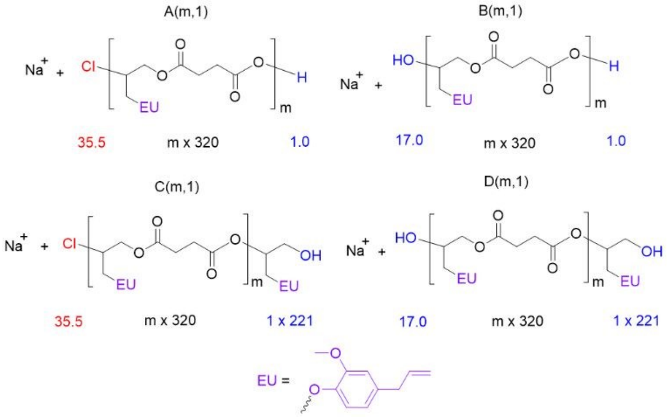


Fig. 5 Proposed structures of the end group in light of ESI-MS spectrum of poly(SA-*alt*-EGE).

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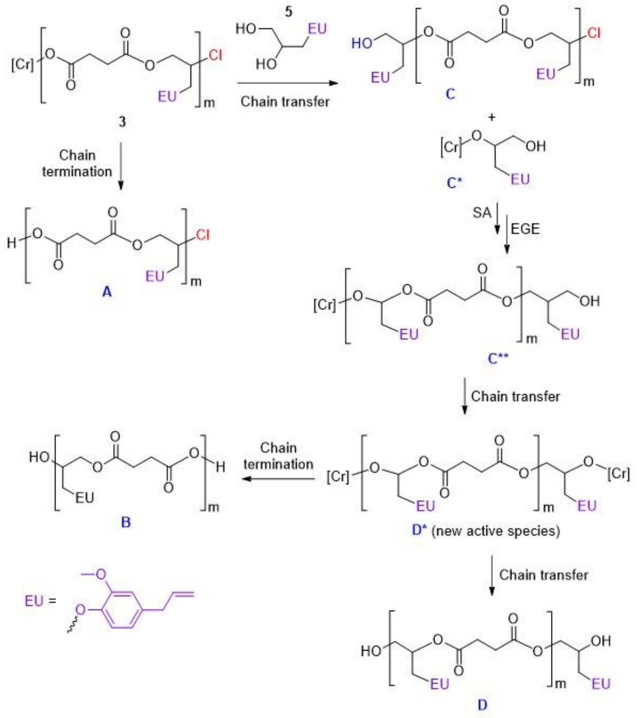
resultant polyesters are far lower than the theoretically expected M_n value. This phenomenon has been commonly found for the ROCOP of anhydride and epoxides catalyzed by different metal complexes-based catalyst systems.[14, 24b, 26] The discrepancy of M_n value has been attributed to several factors. First, as the copolymerizations are performed in neat monomer, conversions are not allowed to exceed 50%, after which a high viscosity makes stirring difficult.[34] Second, undesired chain transfer reactions can occur by the presence of active hydrogen compounds like the trace diacid and water that can directly act as chain transfer agents (CATs) or by diols derived from the hydrolysis of epoxides.[17b, 25, 34, 35]

The ESI-MS spectra allow an identification of the molecular structures of polymers including chemical nature of the end groups.[36] The ESI-MS spectra of crude SA/EGE copolymers exhibit an m/z interval of 320 between the consecutive peaks, corresponding to a [SA + EGE] repeating unit, confirming a perfectly alternating structure (Fig. S13). Furthermore, the resulting poly(SA-*alt*-EGE) possesses four kinds of polymer chains, i. e., distributions **A**, **B**, **C**, and **D** as shown in Fig. 6. Among them, distribution **A** is one of the main polymer chain ended with COOH group at one side and a Cl group on the other side, which is most likely originated from chain termination reaction of active species **3** by the presence of active hydrogen compounds (Scheme 3). A second independent distributions **B** corresponds to the polymer chains with $HO[C_{17}H_{21}O_6]_nH$ structure which indicates polymer chains terminated with COOH and OH. Minor distributions **C** has an OH end group of EGE at one side and a Cl group at the other side, possibly initiated from one chain transfer reaction with a diol of **5** arising from the hydrolysis of EGE.[37] Such transfer reaction yields new active species **C***(Scheme 3) that can continue to initiate the insertion polymerization of the anhydride and epoxies to form **C****. In turn, hydroxyl groups at the chain end undergo a chain transfer reaction with another polymer growth chain, producing new active sites **D***, which could lead to the formation of the minor distribution **D** having a hydroxyl group at both ends by chain transfer reaction with the active hydrogen compounds.[37] Interestingly, when 10 equiv. H_2O to catalyst was added (Fig. S14), the **D** series became the main distribution, and the relative content of **D** to **A** is 1:0.3 according to the intensity of ESI-MS of resultant polyester, and the content of **C** series is increased at the same time, indicating chain transfer reactions are significantly activated by adding excess amount of water.



Scheme 3 Proposed mechanism for chain growth, chain transfer and chain termination.

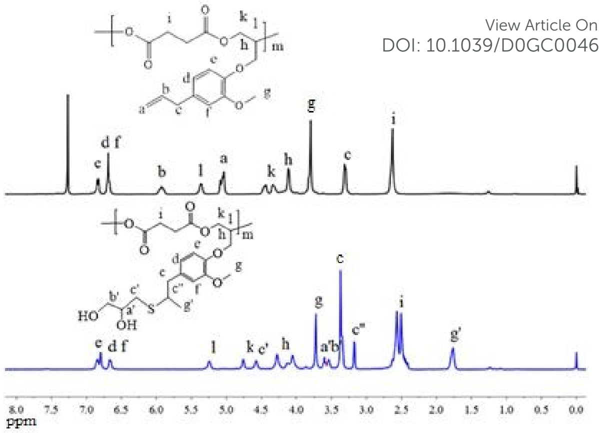


Fig. 6 ^1H NMR spectra of original poly(SA-*alt*-EGE) (A) and its post-modification product after *thiol-ene* reaction (B).

It is worthy of noting that the ally groups on the poly(SA-*alt*-EGE) scaffold afford a reactive platform for functionalization of the polymer. In order to demonstrate the versatility of the resultant polyesters, the thiol-ene reaction was performed between allylic double bonds in the side chain of poly(SA-*alt*-EGE) and 3-mercapto-1,2-propanediol using a UV-initiated free radical addition (see Supporting Information for detailed experi mental procedures). The disappearance proton signals of ally group at 5.26 ppm (H^a) and 5.78 ppm (H^b) and the appearance of a proton signal of 3-mercapto-1,2-propanediol moieties ($H^{a'}$, $H^{b'}$ and $H^{c'}$) after the reaction (Fig. 6B) verify that the *thiol-ene* click reaction was successfully occurred via Markovnikovs' addition in light of appearance of proton signal at 1.75 ppm. Further evidence arises from the observation of stretching vibration absorption peak at 3415 cm^{-1} of hhydroxyl group, and the peak at 3072 cm^{-1} attributed to $\upsilon_{=C\text{-}H}$ is vanished in the IR spectra (Fig. S15).

Experimental

Materials and methods

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All manipulations involving air- and/or water-sensitive compounds were carried out with the standard Schlenk and vacuum line techniques under argon atmosphere. All used cocatalysts including DMAP, PPNCl, and TBACl were purified by standard

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methods. Toluene and THF were refluxed and distilled over Na-benzophenone under nitrogen. PA was recrystallized from chloroform and dried under vacuum at 60 ℃ for 10 h. PA, THPA were recrystallized from chloroform, NA, SA, MA and IA were recrystallized from acetone, and all anhydrides dried under vacuum at 60 ℃ for 10 h. $PPNN_3$ was synthesized according to the report.[38] The [OSSO]-type ligands and chromium complexes[14, 7e] were synthesized as previously described (detailed procedure see Supporting Information). EGE was synthesized according to the literature.[39] Complexes **3**[40] and **4**[29a] were synthesized in light of reports.

All ^1H spectra were recorded on a Bruker-400 spectrometer at frequency of 400 MHz. Chemical shifts are given in ppm relative to TMS. Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer at a resolution of 4 cm^{-1} (16 scans collected). ESI-MS experiments were carried out using a Bruker Q-TOF mass spectrometer. Samples were inserted into the electrospray interface at a flow rate of 2 ml/min and the source temperature was kept at 200 °C. Mass spectra were acquired over the range of m/z 50-3000 in positive ion mode. The molecular weight of polymer was determined by using gel permeation chromatography (GPC) on a PL-GPC 220 instrument with a refractive index detector, calibrated with polystyrene standards. The columns used were MIXED-B 300 × 7.5 mm columns held at 40°C using THF as eluents at a flow rate of 1.0 mL/min.

General Procedure for the Copolymerization of epoxides and CAs

All polymerizations were carried out in a 15 mL tube fitted with a three-way stopcock under argon atmosphere free of moisture and oxygen. As a typical copolymerization of epoxides and CA, chromium complex, cocatalyst, CA and a Teflon-coated stirring bar were added into dried tube and stirred for 10min as solids. Then the corresponding epoxides and solvent were added by a syringe at room temperature under argon. The polymerizations were performed at certain temperature. The polymers were dissolved in $CHCl_3$/MeOH mixture and precipitated from methanol, this process was repeated 3-5 times to remove the catalyst completely. The resulting polymer was obtained by vacuum-drying.

Conclusions

A series of bio-based polyesters were successfully synthesized by the ROCOP of EGE with CAs using various Cr complexes including a novel binuclear [OSSO]CrCl complex as catalysts. The microstructure of resultant copolymers was dependent on the type CAs used. Specifically, the ROCOP of EGE with SA gave the highest catalytic activity to yield alternating polyesters with the dominant head-to-tail sequential structure. The binuclear [OSSO]CrCl complex **1** showed higher activity catalytic activity than its mononuclear Cr analogues, and prefers to bind one molecule of PPNCl to its Cr center to form six-coordinated Cr active sites. The complex chain transfer reactions were observed. The reactive ally groups in the resultant polyesters were successfully utilized for functionalization using a *thiol-ene* reaction via specific Markovnikovs' addition. The synthesis of poly(SA-*alt*-EGE) and its functionalization provide a new platform to design fully bio-based functional polyesters, since both EGE and SA can be obtained from biomass.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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