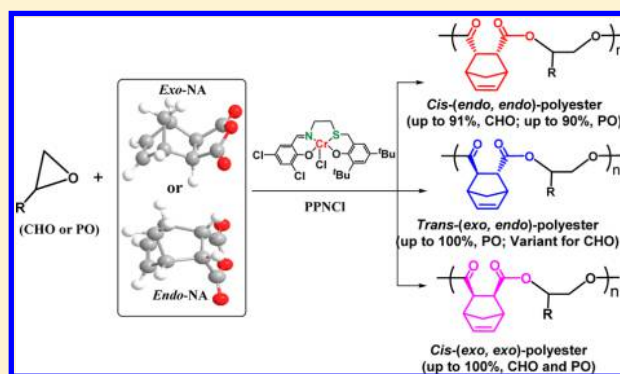


Highly *Cis/Trans*-Stereoselective (ONSO)CrCl-Catalyzed Ring-Opening Copolymerization of Norbornene Anhydrides and EpoxidesBing Han,[†] Li Zhang,[†] Min Yang,[†] Binyuan Liu,^{*,†} Xiaofang Dong,[†] and Patrick Theato^{*,‡}[†]Department of Polymer Science and Engineering, Hebei University of Technology, No. 8 Guangrong Road, Hongqiao District, Tianjin 300130, China[‡]Institute for Technical and Macromolecular, University of Hamburg, Bundesstrasse 45, D-20146 Hamburg, Germany

Supporting Information

ABSTRACT: A (ONSO)CrCl complex-based binary catalyst for efficient ring-opening copolymerization (ROCOP) of epoxide and norbornene anhydride (NA) in a stereoselective manner to afford polymers with variable stereoisomerism is reported. The role of (ONSO)CrCl complex on the *cis/trans* selectivity of resulting polyester as well as enhancement of the reaction rate has been revealed. The formation of chelates between the *endo*-diester unit of the polyester chain and the metal center plays a determinate role in the stereoselectivity of the *cis*-(*endo*, *endo*)-polyester in solution copolymerization of *endo*-NA with epoxides in the presence of metal complex. Additionally, the stereostructure of resulting polyester is also dependent on the polymerization method, NA type, and the bulkiness of the substituent of the formed ester units in the polyester chain. Accordingly, a proposed mechanistic pathway for the stereostructure formation of polyesters is provided.



INTRODUCTION

Aliphatic polyesters have found widespread use as drug delivery vesicles, bone screws, scaffold, and suture wires due to their good biodegradability and biocompatibility.¹ It has been found that stereochemical control of polyesters has a significant effect on their physical and chemical properties.² For instance, *cis*-poly(propylene fumarate) displays a lower glass transition temperature (T_g) compared to the *trans*-isomer.^{2a} The biodegradability of poly(ethylene fumarate) with a *trans* (*E*)-configuration was found to be superior to that of the *cis* (*Z*)-configured poly(ethylene maleate).^{2b} Further, fumarate exhibits a greater reactivity in copolymerization of styrene or other vinyl monomers than the isomeric maleic diester.^{2d} It is therefore of remarkable interest to control the stereochemistry of aliphatic polyesters to achieve desirable bulk properties.

Generally, aliphatic polyesters can be synthesized by three strategies, including step-growth polymerization of diols with diacids (or an acid derivative), ring-opening polymerization (ROP) of cyclic esters, and ring-opening copolymerization (ROCOP) of epoxides with cyclic anhydride.^{1a,3} Among them, substantial attention has been paid in recent years to the ROCOP method owing to the lower energy consumption compared to step-growth polycondensation method.^{3,4} Further, monomers for ROCOP are readily accessible, relatively cheap, and produced on a large scale compared to cyclic ester monomers that are utilized for the ROP strategy, representing an economic and environmental friendly approach.³ The first highly active catalyst for the alternating ROCOP reaction was reported by Coates and

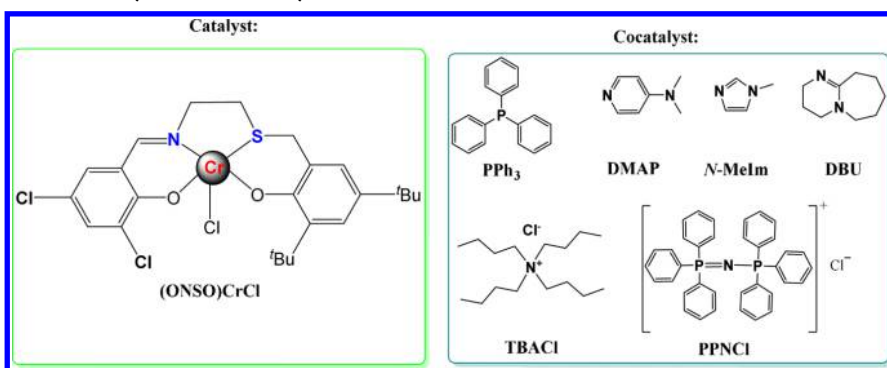
co-workers.^{2a} By utilizing a zinc β -diketiminato complex, they were able to copolymerize vinyl cyclohexene oxide and diglycolic anhydride, resulting in perfectly alternating polyesters with high number-average molecular weight. Subsequently, a range of structurally well-defined metal complexes featuring various ligands based on salen,^{4c,d,5} salalen,⁶ salan,^{4e,h} porphyrinato,⁷ corrole,⁸ etc., have been developed.⁹ All comprising hard oxygen and nitrogen donors have been developed to promote ROCOP of epoxides with cyclic anhydride. In 2015, we exploited a chromium based catalyst supported by a tetradentate (OSSO)-type bis(phenolato) ligand, in which a soft sulfur atom in place of nitrogen atom of a salen ligand as donor chelated with metal center.¹⁰ Interestingly, numerous metal complexes can catalyze the copolymerization of epoxides with carbon dioxide or epoxides with cyclic anhydrides, and they abide by a similar coordination–insertion mechanism.^{3,11} Further, additional efforts have been dedicated to elucidating the effect of chemical structure of monomers on the copolymerization and resulting polyester properties.^{10,12} Nevertheless, only a few studies have focused on the stereochemical structure of resulting polyesters obtained by the ROCOP approach. Indeed, to the best of our knowledge, we have only found four recent examples in the literature.^{4b,5b,13,14}

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Scheme 1. Structures of the Catalyst and Cocatalysts



Coates and co-workers found that unsaturated polyesters obtained from propylene oxide (PO) and maleic anhydride (MA) could undergo a rearrangement from the *cis*-maleate form to the *trans*-fumarate analogues in the presence of diethylamine.^{4b} We reported a facile strategy for the synthesis of highly stereoregular polyesters with *cis*-(*exo*, *exo*) or *trans*-(*exo*, *endo*) repeating units by alternating ROCOP of cyclohexene oxide (CHO) and norbornene anhydride (NA) stereoisomers using organocatalysts, with the resulting polyesters possess a high glass transition temperature (T_g) that make them suitable for a further functionalization via thiol-ene click chemistry.¹³ Noteworthy, usually the *endo*-type NA, the dominant adduct from the addition of cyclopentadiene with MA, displayed a much slower reaction rate in the copolymerization. In the same year, Cheng and co-workers¹² found that (salph)CrCl[salph = *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminobenzene] in conjunction with DMAP efficiently copolymerize *endo*-NA with epoxides with perfect alternation; however, they did not discuss the influences of the metal complex and reaction variables such as NA geometric structure and polymerization method on the stereochemistry of the resulting polyester. More recently, Coates and co-workers revealed that the Lewis acidity of metal center and loading of PPNCI strongly affect the *cis/trans*-selectivity of the resulting polyester.^{5b,14} Nevertheless, the role of metal complex in the *cis/trans*-selectivity and precise factors that govern the stereochemistry of a ROCOP reaction remain poorly understood.

Herein, we report the ROCOP of epoxides and NA catalyzed by a chromium complex supported by tetradentate dianionic thioimine diphenolate (ONSO) ligands ((ONSO)CrCl) assisted by a Lewis base or onium salt. This kind of complex has been successfully applied in the ROCOP of CHO and carbon dioxide with moderate activity and selectivity for the polycarbonate.¹⁵ The focus in this context is devoted to determining the influence of metal complex and monomer type on the copolymerization behavior under various conditions, especially on the *cis/trans* preference within the resulting polyesters. Of importance, the substantial role of metal complex on the stereochemical control of the ROCOP of NA and epoxides is highlighted.

EXPERIMENTAL SECTION

Reagents and Methods. All manipulations involving air- and/or water-sensitive compounds were carried out with the standard Schlenk and vacuum line techniques under an argon atmosphere. CHO and PO were refluxed over CaH₂ for 24 h and vacuum-distilled prior to use. Triphenylphosphine (PPh₃), 4-(dimethylamino)pyridine (DMAP), and tetrabutylammonium chloride (TBACl) were recrystallized from ethanol. *N*-Methylimidazole (*N*-MeIm) and 1,8-diazabicyclo[5.4.0]-

undec-7-ene (DBU) were stirred over CaH₂ overnight distilled under reduced pressure before use. Bis(triphenylphosphine)iminium chloride (PPNCI) was dissolved in acetone and precipitated into an excess amount of ether, and then the precipitate was dried under vacuum prior to use. Toluene and THF were refluxed and distilled over Na-benzophenone under nitrogen before use. The (ONSO) chromium complex was synthesized as previously described.¹⁵ *endo*-Norbornene anhydride (*endo*-NA) was recrystallized from acetone. *exo*-Norbornene anhydride (*exo*-NA) was prepared by thermal isomerization according to the literature.¹⁶

Measurements. All NMR spectra were recorded in CDCl₃ using a Bruker 400 spectrometer. Chemical shifts are given in ppm relative to TMS. The molecular weights of polymers were 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 the eluents at a flow rate of 1.0 mL/min.

Copolymerization of CHO and NA. In a typical copolymerization of CHO and NA isomer, the (ONSO)CrCl complex, cocatalyst (Lewis base or quaternary onium salts), NA, and a Teflon-coated stirring bar were added into predried 20 mL Schlenk flask fitted with a three-way stopcock under an argon atmosphere and stirred for 10 min. Then the solvent and CHO were added via a syringe at room temperature under argon. The polymerizations proceeded in oil bath at elevated temperatures. After a defined reaction time, methanol was added to the reaction mixture to induce precipitation of the polymer. After filtration, precipitate was immersed in excessive methanol for 4 h with stirring and filtrated. This process was repeated three times. The resulting polymer was dried under vacuum at 70 °C overnight.

Copolymerization of PO and NA. The copolymerization of PO and NA was performed in an autoclave at 5.0 MPa argon at 110 °C. After a defined reaction time, the mixture was cooled to room temperature and argon was slowly released, then methanol was added, and the precipitate was collected by filtration. The precipitate was redissolved in chloroform, reprecipitated in methanol for three times, and dried at 60 °C under vacuum.

Representative Polyester Reductive Degradation Procedure. 1.10 g of LiAlH₄ (29 mmol, 10 equiv) and dried THF (20.0 mL) were charged into a two-necked 100 mL flask equipped with a reflux condenser and a dropping funnel. 0.75 g (2.9 mmol, 1 equiv) of the polyester dissolved in 20 mL of THF was added dropwise into the flask at room temperature under argon. After the addition, the mixture was stirred at 60 °C for 24 h. The reaction was quenched by adding 0.6 mL of water, followed by 0.6 mL of 2 M NaOH. Afterward, the reaction system was cooled to 0 °C and then filtered. The filtrate was dried with anhydrous MgSO₄, and the mixture was filtered through sintered glass funnel and evaporated to dryness to yield 0.69 g (88%) of a colorless oil.

Isomerization of *cis*-(*exo*, *exo*)-Poly(NA-*alt*-CHO). *cis*-(*exo*, *exo*)-Poly(NA-*alt*-CHO) (1.0 g) and 2.0 mL of dried toluene were charged into a flask under an argon atmosphere and stirred to give a viscous homogeneous solution. A methanol solution of NaOCH₃ (1 mol/L, 0.2 mL) was added into the flask and stirred at 100 °C for 50 min. The mixture was cooled to room temperature, and 10 mL of methanol was

Table 1. Summary Copolymerization of CHO with NA^a

entry	NA	cat.	cocat.	time (min)	conv ^b (%)	TOF ^c (h ⁻¹)	$M_{n,th}$ ^d	M_n^e (g/mol)	PDI ^e
1	<i>endo</i> -NA	(ONSO)CrCl	TBACl	40	62	232.5	40610	5700	1.28
2	<i>endo</i> -NA	(ONSO)CrCl	PPh ₃	40	—	—	—	—	—
3	<i>endo</i> -NA	(ONSO)CrCl	PPNCl	40	96	360.0	62880	9300	1.31
4	<i>endo</i> -NA	(ONSO)CrCl	<i>N</i> -MeIm	40	57	213.8	37335	5300	1.27
5	<i>endo</i> -NA	(ONSO)CrCl	DMAP	40	77	288.8	50435	6400	1.26
6	<i>endo</i> -NA	(ONSO)CrCl	DBU	40	95	356.3	62225	8200	1.31
7	<i>exo</i> -NA	(ONSO)CrCl	PPNCl	15	97	970.0	63535	11900	1.28
8*	<i>endo</i> -NA	(ONSO)CrCl	PPNCl	60	31	77.5	20305	—	—
9	<i>endo</i> -NA	—	PPNCl	40	—	—	—	—	—
10	<i>endo</i> -NA	(ONSO)CrCl	—	40	13	48.8	8515	—	—

^aReaction conditions: [NA]/[CHO]/Cr/cocatalyst = 250/250/1/1; NA = 1.64 g (10 mmol), (ONSO)CrCl = cocatalyst = 40 μmol, 110 °C, apart from entry 8 in 2.0 mL of toluene, other copolymerizations were performed in neat CHO. ^b% NA conversion = $(m_{\text{isolated polyester}} \times M_{\text{NA}}) / [(M_{\text{NA}} + M_{\text{CHO}}) \times m_{\text{NA}}] \times 100$. ^cTurnover frequency as moles of NA consumed per mole of catalyst per hour. ^d $W_{\text{NA}}/W_{\text{complex}} \times (M_{\text{NA}} + M_{\text{CHO}}) \times \% \text{ NA conv.}$ ^eDetermined by GPC. “—”: not detected.

added. Precipitate was filtered and washed with methanol three times. At last, the solid product was dried at 60 °C under vacuum for 24 h, yielding 0.9 g (90%) of a white solid.

RESULTS AND DISCUSSION

Previous studies revealed that the catalytic activity and resulting polyester microstructure in the copolymerization of epoxides with anhydride are drastically dependent on the cocatalyst type.^{4a,c,d,6b,9} Thus, PPh₃, DMAP, *N*-MeIm, and DBU, TBACl, and PPNCl, which are the commonly used candidates as cocatalysts in (ONNO)MX and other homogeneous catalytic systems, were selected as a cocatalyst to estimate their efficiency for the copolymerization of CHO with *endo*-NA at a molar ratio of [CHO]/[*endo*-NA]/[(ONSO)CrCl]/[cocatalyst] = 250/250/1/1 in excess CHO at 110 °C. As listed in Table 1, entries 1–6, the conversion of *endo*-NA varied with the cocatalyst, in which the % conversion of *endo*-NA was found to be above 95% in 40 min when PPNCl and DBU were employed as cocatalysts, while TBACl, *N*-MeIm, and DMAP as cocatalysts showed a moderate catalytic activity, whereas PPh₃ as cocatalyst yielded practically no product. To figure out the roles of catalyst complex and cocatalyst, controlled experiments have been carried out separately with (ONSO)CrCl or PPNCl as the initiator for the copolymerization of CHO and NA with [CHO]/[(ONSO)CrCl] = 250 or [CHO]/[PPNCl] = 250 at the identified conditions. It was found that only small polyester was produced when PPNCl was used alone as the initiator for the copolymerization of CHO and *endo*-NA within 40 min. Although (ONSO)CrCl can catalyze the copolymerization at same conditions, the % conversion of NA was only 13%, far lower than the conversion obtained in the presence of PPNCl. In our previous studies on the role of PPNX (X = Cl or N₃) in (ONSO)CrY (Y = Cl or N₃) complex-based binary catalytic systems for CHO/CO₂ copolymerization, we found that the anion X⁻ can coordinate with the central metal to form a six-coordinated chromium active species and thus benefiting for the insertion of epoxides and carbon dioxide in initiating and propagating step, improving the catalytic activity for the synthesis of polycarbonates.¹⁵ This speculation could also account for the enhancement of catalytic efficiency in the case of *endo*-NA/CHO copolymerization under (ONSO)CrCl/PPNCl binary catalyst because both routes follow the similar coordination–insertion mechanism. As indicated from data of entries 3 and 8 in Table 1, the copolymerization rate in toluene (solution polymerization) is slower than that in neat CHO (bulk polymerization), where %

conversion of *endo*-NA was only 31% in toluene solution polymerization within 60 min (entry 8, Table 1), less than that of 96% conversion of *endo*-NA within 40 min in bulk copolymerization.

The copolymerization rate also remarkably depends on the employed NA isomer. As illustrated in curves 1 and 2 in Figure 1,

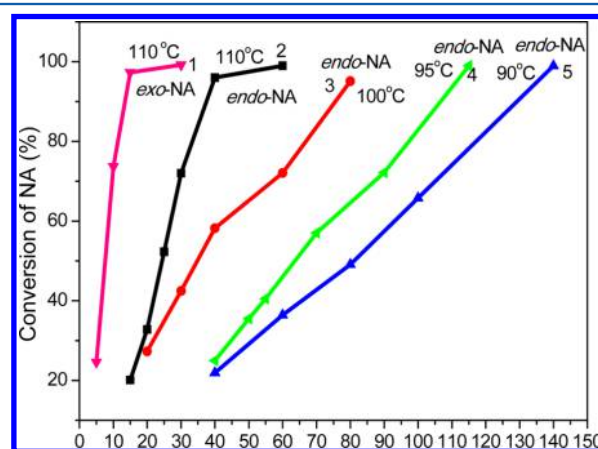


Figure 1. Dependence of NA conversions at different temperature and time.

the *exo*-NA isomer showed a higher copolymerization rate than the *endo*-isomer. Even so, the *endo*-NA conversion could reach 96% within 40 min at [NA]/[(ONSO)CrCl]/[PPNCl] ratio of 250/1/1 in neat CHO, the result clearly demonstrated that (ONSO)CrCl/PPNCl is a very efficient catalyst system for the copolymerization of CHO and NA. Curves 2–5 in Figure 1 display the dependence of copolymerization rates on temperature and time. Of course, the reaction rate is strongly influenced by the reaction temperature; i.e., rates were increasing with increasing reaction temperature; i.e., rates were increasing with increasing reaction temperature. From the early conversion times of curves 2–5, the corresponding propagation rate constants k could be calculated (Figure S1a) and subsequently assess the activation energy of 109.2 kJ/mol for the CHO/*endo*-NA copolymerization via an Arrhenius plot (Figure S1b).

The obtained molecular weights (M_n) of the polyesters were found to be lower than the theoretical M_n calculated on the basis of the monomer conversion (see Table 1). Further, GPC curves showed a bimodal distribution (Figure S2). We speculated that the discrepancy of M_n values is most likely arising from the presence of protic impurity traces, such as diacid resulting from

hydrolyzed anhydride and trace water in system that can act as chain transfer agents. Indeed, this phenomenon has been demonstrated to be common for numerous metal complex-catalyzed the ROCOP of anhydride and epoxide-^{4a,b,d,5-7} Although GPC curves show a bimodal distribution, the chain length increased linearly with NA conversion (Figure 2), as revealed in the copolymerization at molar ratio of [*endo*-

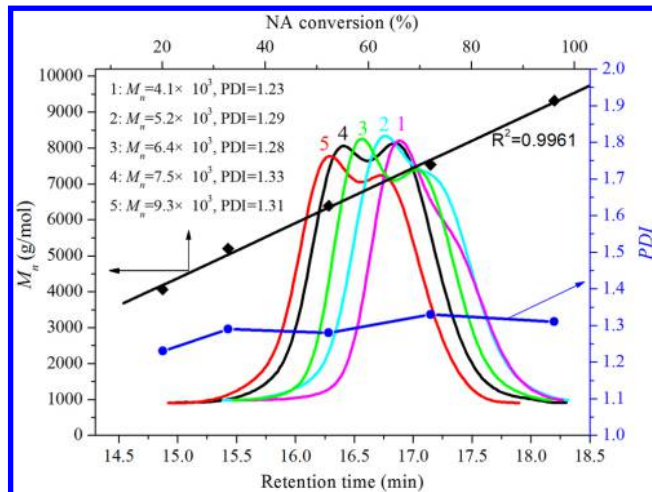


Figure 2. Development of M_n and PDI versus *endo*-NA conversion.

NA]/[(ONSO)CrCl]/[PPNCl] = 250/1/1 in neat CHO at 110 °C, with a dispersity (M_w/M_n) of 1.23–1.33, indicating that the copolymerization proceeds in a controlled manner.

Figure 3A presents the ^1H NMR spectra of polyesters prepared at 250:250 feed ratio of CHO to *exo*-NA in toluene using a (ONSO)CrCl/PPNCl binary catalyst system. The resonances

for olefinic protons are found at 6.18 ppm. Signals of the 2, 3-position methine protons and methine protons signals at the 1, 4-position of NB ring appeared at 2.60 and 3.02 ppm, respectively. The existence of only one peak at $\delta = 6.18$ ppm indicated that two ester groups at the C2 and C3 positions are placed on the same side as the methylene bridge (C7) of the NA ring. These NMR data further revealed that the obtained polyester consist of *cis*-2, 3-(*exo*, *exo*) ester units; i.e., *cis* polyester was obtained. Remarkably, except for the existence of resonance for *trans*-(*exo*, *endo*) olefinic protons at 6.25 and 6.02 ppm, signal characteristics of *cis*-(*exo*, *exo*) olefinic protons are appeared at around 6.18 ppm for the polyesters obtained from copolymerization in neat CHO (Figure 3B). Integration of these signals revealed that only 63% of the diester units in polymer chain are *trans*-form. This result obviously differs from the polyesters prepared from the bulk copolymerization using PPNCl as sole initiator, where polyester chain possesses full *trans*-configuration structure.¹³ Likewise, the stereochemistry of polyesters obtained from the ROCOP of CHO and *endo*-NA either in toluene or in excess CHO is distinct from that of polyesters obtained using PPNCl as the sole initiator (Figure 3E). As shown in Figures 3C and 3D, the olefinic protons of the NA ring and the protons H¹, H², H³, H⁴ showed broad signals in the region of 6.02–6.30 and 3.00–3.60 ppm, respectively, indicating that the obtained polyesters are a mixture of conformations, whereas the polyesters obtained using PPNCl as the sole initiator are exclusively *trans* isomers. The results suggested that the (ONSO)CrCl complex plays a special role in regulating the stereochemical structure of the resulting polyester. In addition, the absence of signals assigned to the repeating oxy(1, 2-cyclohexene) unit ($\delta = 3.65$ ppm) in all ^1H NMR spectra (Figure 3) indicated that the resulting copolymers are consisting of an highly alternating structure, even when prepared with an excess of CHO. This analysis was further supported by ^1H - ^{13}C

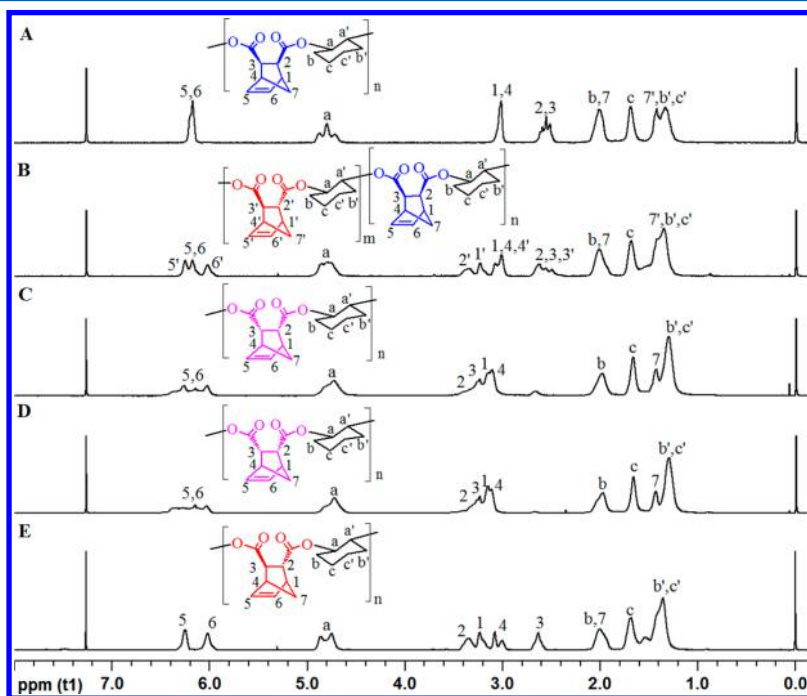
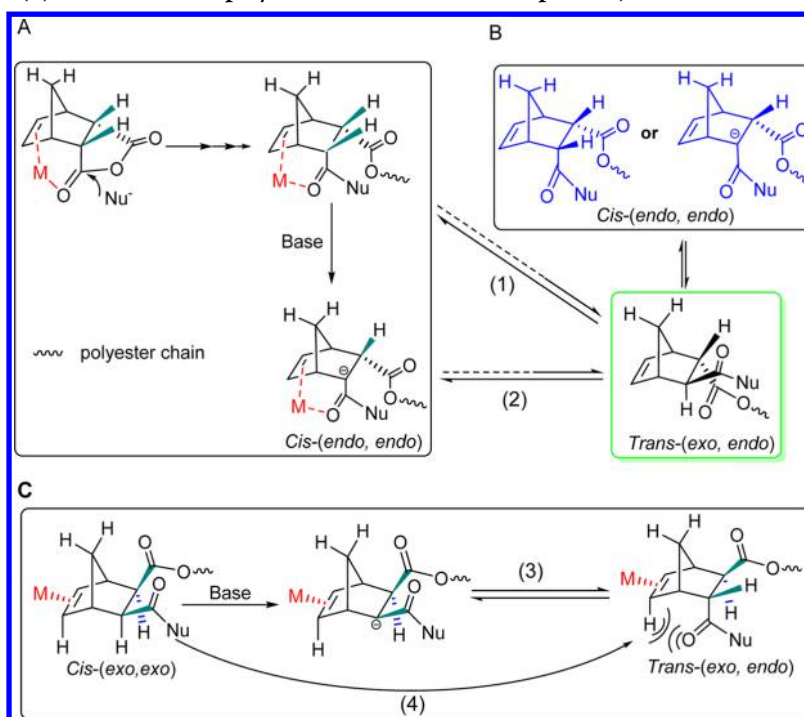


Figure 3. ^1H NMR spectra of poly(NA-*alt*-CHO) (condition: A: *cis*-(*exo*, *exo*) 100%, *exo*-NA, 180 min, 2.0 mL of toluene; B: *trans*-(*exo*, *endo*) 63%, *exo*-NA, 30 min, in excess CHO (2.0 mL); C: *cis*-(*endo*, *endo*) 91%, *endo*-NA, 180 min, 2.0 mL toluene; D: *cis*-(*endo*, *endo*) 91%, *endo*-NA, 40 min, in excess CHO (2.0 mL). 110 °C, NA/CHO/(ONSO)CrCl/PPNCl = 250:250:1:1; E: *trans*-(*exo*, *endo*) 100%, *exo*-NA/CHO/PPNCl = 50:100:1, 1.0 mL of toluene, 180 min, 110 °C (ref 13).

Scheme 2. Proposed Mechanism of *Cis–Trans* Isomerization of Polyester Chain ((1) and (4) for the Copolymerization at Equiv of Epoxide and NA; (2) and (3) for the Bulk Copolymerization in Excess of Epoxides)



HMQC spectrum of copolymer from *endo*-NA and CHO (entry 3 in Table 1), in which there is no the signals in the range 80–90 ppm (^{13}C NMR part) characteristics of polyether linkages (Figure S3).¹⁷

To gain further insights into the stereochemical information on the polyesters obtained either from *exo*-NA and CHO bulk copolymerization or *endo*-NA and CHO copolymerization, the respective polymers were subjected to a reduction with LiAlH_4 in THF. The chirality of the 1, 2-diols produced from the reduction of polyesters provide an insight into the main-chain chirality of the polyester.^{5b,14} The product that arose from reduction of polyesters obtained from *exo*-NA and CHO in neat CHO consisted of two kinds of 5-norbornene-2,3-dimethanol isomers, in which the percent of *cis*-2, 3-(*exo, exo*)-conformer and *trans*-(*exo, endo*)-isomer was 39% and 61%, respectively. This is very close to the isomer ratio that was estimated via integration of ^1H NMR spectra of polyesters, which led to an estimated 63% *trans*-isomer of the polyester. Poly(*endo*-NA-*alt*-CHO) was reduced to yield 5-norbornene-2,3-dimethanol with *cis*-2, 3-(*endo, endo*) conformation up to 91% (Figure S4). The case suggests that the parent poly(*endo*-NA-*alt*-CHO) predominantly consisted of *cis*-(*endo, endo*) conformational diester units, that is, *endo*-NA maintaining its *endo* conformational structure without occurrence of a rearrangement during the copolymerization process, which is in sharp contrast to our previous findings with using a PPNCI as catalyst,¹³ where the configuration of *endo*-NA underwent an isomerization from *endo* to *trans* in the copolymerization.

On the basis of the differently preferred stereochemistries of the resulting polyesters in the presence of (ONSO)CrCl complex, we proposed a *cis/trans*-selectivity mechanism for the metal complex-catalyzed the ROCOP of epoxide and NA as shown in Scheme 2. Three major contributions are presumably responsible for the *cis/trans*-preference of the diester unit in the polymer chain. First, the conformational energy of the *cis*-

configuration is higher than the *trans*-isomer due to the van der Waals repulsive force between the neighboring substituents,^{13,18} which results in the preferred formation of *trans*-form in the polymer. The second issue is the coordination ability of $\text{C}=\text{C}$ double bond and the formed ester substituent to the metallic active sites, which is significantly more effective at keeping the *endo*-configuration of ester substituent as depicted in Scheme 2A. This hypothesis of a chelation by coordination of the central metal to the carbonyl groups and the $\text{C}=\text{C}$ double bond along the *endo* face has also been found for norbornene derivatives by other authors.^{19–21} The last issue is that the alkoxide anion formed in the excess epoxide can serve as Lewis base to deprotonate the H^2 or H^3 atom at the norbornyl ring connected to carbonyl group of ester unit to generate the corresponding carbanions, where the lower activation barrier of carbanion allowed for a C–C bond rotation and consequent inversion of geometry changing from *endo* to *exo* to form the *trans* configuration by releasing the excess configurational energy. This case only occurs in the copolymerization with excess of epoxide. The absence of the coordination interaction between the metal active species and monomer or formed ester functionality could account for the *cis/trans*-selectivity of the resulting polyester using PPNCI as the sole initiator (Scheme 2B) for the ROCOP of *endo*-NA and epoxide. In this case, the energetically favorable *trans*-conformer should be the dominant product.

As for the not pure formation of *trans*-type product in the bulk ROCOP of *exo*-NA and CHO in the presence of (ONSO)CrCl complex, it could be explained by the unfavorable repulsive interaction originating from the steric repulsion between bulky cyclohexyl substituent and the vinylic hydrogen on the axial position, which hinder the transformation from *cis* to *trans* (Scheme 2C). Thus, the less steric hindrance of the substituent favors the *trans*-selectivity of the resulting polyester. To confirm this assumption, the copolymerization of PO with *exo*-NA isomer

Table 2. Copolymerization of Epoxides and NA Using (ONSO)CrCl/PPNCl Binary Catalyst^a

Entry	Epoxide	Exo-NA		Endo-NA	
		Bulk polymerization	Solution polymerization	Bulk polymerization	Solution polymerization
1*	CHO	 trans-(exo,endo)-polyester (100%)	 cis-(exo,exo)-polyester (100%)	 trans-(exo,endo)-polyester (100%)	 trans-(exo,endo)-polyester (100%)
2	CHO	 trans-(exo,endo)-polyester (63%)	 cis-(exo,exo)-polyester (100%)	 trans-(exo,endo)-polyester (9%)	 trans-(exo,endo)-polyester (9%)
		 cis-(exo,exo)-polyester (37%) 30 min, yield: 99%	180 min, yield: 95%	 cis-(endo,endo)-polyester (91%) 40 min, yield: 96%	 cis-(endo,endo)-polyester (91%) 240 min, yield: 92%
3	PO	 trans-(exo,endo)-polyester (100%) 300 min, yield: 93%	 cis-(exo,exo)-polyester (100%) 300 min, yield: 79%	 trans-(exo,endo)-polyester (100%) 300 min, yield: 92%	 cis-(endo,endo)-polyester (90%) 300 min, yield: 71%

^a110 °C, *cis/trans*-selectivity determined by ¹H NMR spectroscopy. Entry 1: see ref 13 using PPNCl as a sole initiator. Entries 2 and 3: bulk ROCOP in excess 2.0 mL of epoxide; solution ROCOP in 2.0 mL of toluene. [CHO]/[NA]/[(ONSO)CrCl]/ [PPNCl] = 250/250/1/1. [NA] = 1.64 g (10 mmol).

was performed in neat PO under same catalyst system. The ¹H NMR (Figure S5A) and ¹³C NMR (Figure S6A) spectra revealed that resulting polyester consisted of almost 100% *trans*-diester units in the polymer chain due to the less bulky isopropyl group compared to that of cyclohexyl group decreasing the repulsion force between the ester substituent at *exo* position and H atom at axial orientation (Scheme 2C, path 3).

Interestingly, contrary to the copolymerization of CHO with *endo*-NA in excess CHO to result in a polyester with dominant *cis*-(*endo, endo*) units (up to 91%), the bulk copolymerization of PO with *endo*-NA yielded exclusively a *trans*-form of the repeating ester units as evidenced by NMR in Figures S5B and S6B. This different *cis/trans*-selectivity for the copolymerization with PO compared to CHO can be likewise accounted for by the less hindrance of the isopropyl group, which leads to an easier rotation of the ester substituent tethered to the propagating carbanion resulting in the energetically favorable *trans*-configuration. However, the solution copolymerization at equiv of PO and *endo*-NA resulted in the *cis*-(*endo, endo*)-enriched (~90%) polyester. The reasons are of similar nature as for the copolymerization of *endo*-NA with CHO in toluene (Figure S5C); that is, the coordinating interaction plays the predominant role in determining the conformation of resulting polymer. According to path 4 in Scheme 2C, the copolymerization of *exo*-NA with CHO or PO leads to polyester with full *cis*-(*exo, exo*)

diester units in the polymer chain due to the absence of hypothesized interaction of issues 2 and 3 in Scheme 2 (Figures S5D and S6D). For clarity, the effects of NA type, epoxide used, and the polymerization method on the geometric structure of resulting polyesters are summarized in Table 2.

To address the different *cis/trans*-selectivity in the copolymerization in or without the presence of metal complex, the copolymerization was monitored by NMR spectroscopy. At the initial stage of the polymerization only one olefinic proton signal at around 6.18 ppm was observed, indicating that a polyester with an exclusive (*exo, exo*)-*cis*-type structure was formed in this case. With increasing reaction time, the signals at around 6.18 ppm assigned to *cis*-type vinylic protons gradually decreased. However, a simultaneous increase of the vinylic proton signals at 6.25 and 6.02 ppm attributed to the *trans*-type polyester (Figure 4) was observed, suggesting a occurrence of *cis*–*trans* transformation after complete NA consumption, which is similar to our previous findings of the copolymerization in the excess of CHO using PPNCl as initiator.¹³ The formed PPN alkoxide at the end of copolymerization in the excess CHO serves as a Lewis base to promote the *cis*–*trans* rearrangement by epimerization, similar to reports by the group of Coates and our group.^{13,14} This hypothesis is further evidenced by the following experiment. When the polyester with exclusive *cis*-(*exo, exo*)-diester units was heated to 100 °C in the presence of sodium methoxide, new

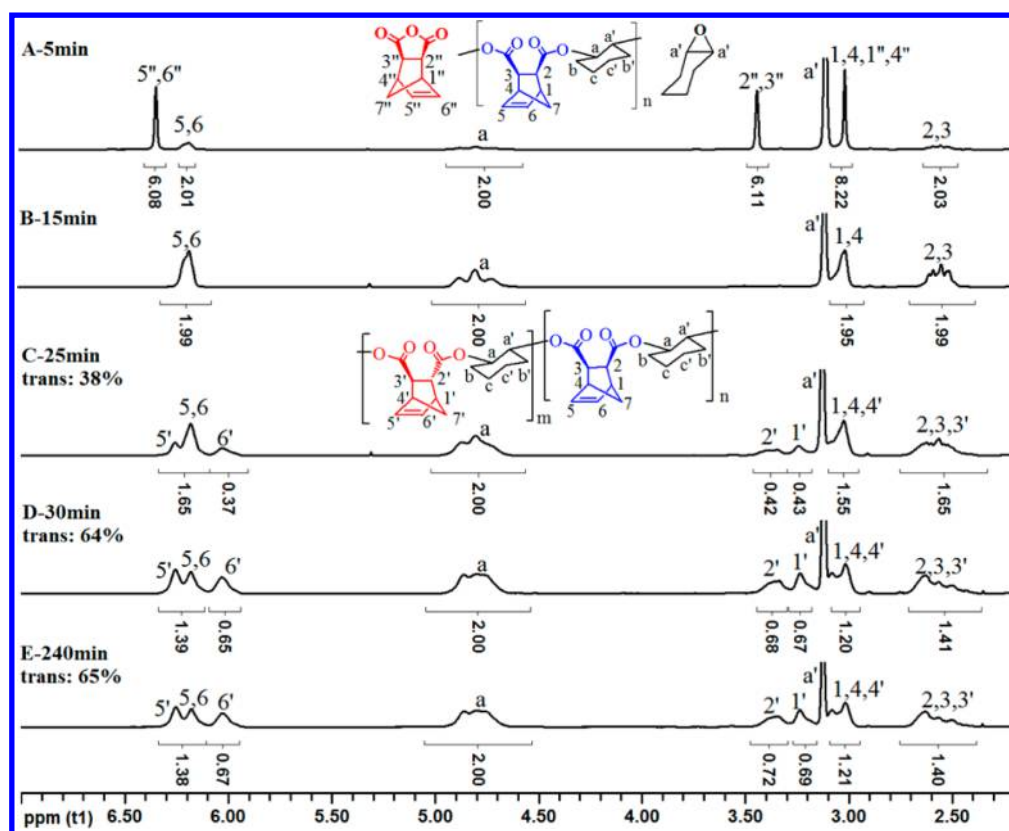


Figure 4. ^1H NMR spectra of the mixture under $[\text{exo-NA}]/[(\text{ONSO})\text{CrCl}]/[\text{PPNCl}] = 250/1/1$ molar ratio in excess of CHO at $110\text{ }^\circ\text{C}$ after (A) 5, (B) 15, (C) 25, (D) 30, and (E) 240 min.

olefinic protons signals at 6.25 and 6.02 ppm appeared owing to the *trans*-isomer configuration (Figure S7). The amount of *trans*-diester units reached up to 48% after heating for 50 min. Noteworthy, the rate of *cis*–*trans* isomerization in the presence of the (ONSO)CrCl complex is much slower than that when using PPNCl as the initiator due to the existing coordinative interaction between the ester functionality and the metal center. A fraction of *trans*-polyester of 65% was reached after a prolonged reaction time of 240 min in the presence of (ONSO)CrCl complex, whereas a complete *cis*–*trans* transformation was reached within 30 min for PPNCl as initiator after *exo*-NA consumption.

CONCLUSIONS

In summary, the ring-opening copolymerization of norbornene anhydride with epoxides using (ONSO)CrCl binary catalysts was studied. This catalyst system shows a high efficiency toward CHO during bulk copolymerization, with NA conversions more than 95% within 15 min for *exo*-NA, and within 40 min for relatively inert *endo*-NA at $[\text{NA}]/[(\text{ONSO})\text{CrCl}]/[\text{PPNCl}] = 250/1/1$. The polymerization method, substrate, and (ONSO)-CrCl have a dramatic effect on the stereochemistry of the resulting polyester. The coordination of the *endo* ester functionality and C=C double bond with metal sites is responsible for the observed *cis*-(*endo*, *endo*)-selectivity in solution copolymerization at equiv of *endo*-NA and epoxides.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b01099.

Plot of apparent activation energy, ^1H NMR spectra of polyesters after reduction and poly(NA-*alt*-PO), ^{13}C NMR spectra of poly(NA-*alt*-PO), GPC curves of poly(*endo*-NA-*alt*-CHO) at different cocatalysts, ^1H – ^{13}C HMQC spectrum of poly(*endo*-NA-*alt*-CHO) and ^1H NMR spectrum of polyester after isomerization (PDF)

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Notes

The authors declare no competing financial interest.

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