Macromolecules

Kinetic Studies of the Alternating Copolymerization of Cyclic Acid Anhydrides and Epoxides, and the Terpolymerization of Cyclic Acid Anhydrides, Epoxides, and CO₂ Catalyzed by (salen)Cr^{III}CI

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Supporting Information

ABSTRACT: Copolymerization of a series of cyclic acid anhydrides with several epoxides using (salen)CrCl/onium salt catalysts has afforded polyesters with high molecular weights and narrow molecular weight distributions. The (salen)CrCl catalyst in the presence of the onium salts with formula PPNX (X = Cl⁻, N₃⁻) for the copolymerization of the anhydrides, maleic (MA), succinic (SA), phthalic (PA), cyclohexene (CHE), and cyclohexane (CHA) with the epoxides, cyclohexene oxide (CHO), propylene oxide (PO), and styrene oxide (SO) resulted in completely alternating enchainment of



monomers to provide pure polyesters. Temperature dependent studies of the ring-opening copolymerization of phthalic anhydride and cyclohexene oxide monomers in toluene solution have yielded activation parameters of $\Delta H^{\ddagger} = 67.5$ kJ mol⁻¹ and $\Delta S^{\ddagger} = -95.3$ J mol⁻¹, where the rate limiting step was ring-opening of the epoxide by the enchained anhydride. For the cyclic acid anhydride (CHA), the relative order of reactivity with epoxides decreased PO > CHO \geq SO, and for the epoxide (CHO) the relative rate of copolymerization was CHA > PA > CHE. The (salen)CrCl/PPNN₃ catalyst system was also shown to effectively terpolymerize CHO/phthalic anhydride/CO₂ to afford diblock copolymers, thereby producing in a one pot synthesis poly(ester-*co*-carbonate). T_g values of the synthesized polyesters displayed a temperature range over 130 °C, from +95 °C to -39 °C.

INTRODUCTION

It has become increasingly more apparent that there is a need to develop the synthesis of new polymeric materials which incorporate renewable resources.¹ In this regard, the synthesis of polyesters by way of ring-opening polymerization of cyclic anhydrides and epoxides offers the possibility of providing a wide variety of polyesters, including some from replenishable reserves. For example, copolymers from succinic anhydride and ethylene oxide or limonene oxide constitute polymeric materials from such sources (Scheme 1).^{2,3} Furthermore,

Scheme 1



many of these aliphatic polyesters exhibit a wide range of mechanical and thermal properties in addition to being biodegradable.

Several early publications have reported upon catalytic systems utilizing a range of metal initiators which are able to accomplish these copolymerization reactions.⁴ However, these processes generally display low catalytic activities and provide copolymers of relatively low molecular weights.^{5–8} More recently, Coates and co-workers have employed (BDI)ZnOAc

(BDI = β -diiminate) complexes as active catalysts for the ringopening polymerization of epoxides and cyclic anhydrides.⁹ In this manner, these researchers were able to synthesize new aliphatic polyesters in a highly alternating copolymerization of epoxides and cyclic anhydrides which afforded high molecular weight copolymers with narrow molecular weight distributions.

Because (salen)CrCl complexes in the presence of onium salts, like (BDI)ZnOAc complexes, have been very effective at coupling CO₂ and epoxides, it is anticipated that these complexes will be productive catalysts for the copolymerization of epoxides and cyclic anhydrides.^{10–13} Indeed, while this work was in progress, DiCiccio and Coates presented results on the ring-opening polymerization of maleic anhydrides with epoxides catalyzed by (salen)CoO₂CC₆F₅ or (salen)CrCl.¹⁴ Additional reports containing extensive MALDI–ToF–MS studies of the ring-opening co- and terpolymerization of cyclohexene oxide and a series of cyclic acid anhydrides and CO₂ catalyzed by chromium(III) porphyrinate and salen complexes have been published by Duchateau and coworkers.¹⁵ Herein, we report kinetic studies of the copolymerization of a variety of epoxides and cyclic anhydrides catalyzed by this single-site chromium(III) catalyst. In addition *in situ* infrared monitoring of the terpolymerization of phthalic

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Scheme 2



anhydride, cyclohexene oxide, and CO_2 to provide a diblock copolymer of polyester and polycarbonate, i.e., poly(ester-*co*-carbonate) is examined.

EXPERIMENTAL SECTION

Reagents and Methods. Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under an atmosphere of argon or in an argon filled glovebox. Propylene oxide, cyclohexene oxide, and styrene oxide were purchased from VWR and either distilled from CaH₂ or used as received. Phthalic anhydride, succinic anhydride, cyclohexane anhydride, cyclohexene anhydride, and maleic anhydride were purchased from VWR and used as received. Oxetane (Alfa Aesar) was freshly distilled from CaH₂ and stored in the freezer of the glovebox. (Salen)Cr^{III}Cl was purchased from Strem. PPNCl was purchased from Aldrich and recrystallized from diethyl ether and acetonitrile. PPNN₃ was synthesized by mixing molar equivalents of NaN₃, followed by recrystallization from diethyl ether and acetonitrile. n-Bu₄NCl was purchased from VWR and recrystallized before use. n-Bu₄NX, where X = Br^{-} , N_{3}^{-} , or I^{-} was synthesized from *n*- $Bu_{4}NCl$ and the appropriate salt, followed by recrystallization.

Measurements. All ¹H and ¹³C NMR spectra were performed in CDCl₂. ¹H NMR spectra were recorded at 295 K using an Inova Varian spectrometer at 500 MHz, and ¹³C NMR spectra were recorded at 295 K at 125 MHz. Chemical shifts are given in ppm relative to TMS and coupling constants (J) in hertz. High-pressure reaction kinetic measurements were performed using an ASI ReactIR 1000 reaction analyses system with stainless steel Parr autoclave modified with a permanently mounted ATR crystal (SiComp) at the bottom of the reactor (purchased from Mettler Toledo). In situ infrared experiments were performed using a ReactIR ic10 with a SiComp ATR crystal. $T_{\rm g}$ values were measured using a Mettler Toledo polymer DSC equipped with a liquid nitrogen cooling system and 50 mL/min purge of nitrogen gas. Samples (~10 mg) were weighed into 40 μ L aluminum pans and subjected to two heating cycles, first cycle was at 10 °C/min from -100 to +200 °C, second was at 5 °C/min over the same range of temperatures. Molecular weight determination was performed using a Viscotek GPC instrument with a low angle light scattering (LALS), right angle light scattering (RALS), and refractive index (RI) detectors with THF as eluent.

Representative ReactIR Monitored Copolymerization. A jacketed reaction vessel was charged with 64 mg (1 equiv) of (salen)Cr^{III}Cl, 57 mg PPNN₃ (1 equiv), and 3 g of phthalic anhydride (200 equiv) followed by purging with argon. Then 23 mL of toluene was added to the flask, at which point the flask was heated to 80 °C and allowed to equilibrate for 15 min. Once it became apparent that all the phthalic anhydride had dissolved, 2 mL of cyclohexene oxide (200 equiv) was injected into the flask, at which point the FTIR monitoring was started. Reactions were allowed to proceed until 100% conversion was achieved.

Representative Copolymerization. A vial was charged with a stirring bar, 2 g of phthalic anhydride (533 equiv), 16 mg of (salen)Cr^{III}Cl (1 equiv), and 7.5 mg of *n*-Bu₄NCl (1 equiv). The vial was purged for several minute with argon, then 10 mL of toluene and 1 mL of cyclohexene oxide (400 equiv) were injected into the vial. The vial was inserted into an oil bath heated to 80 °C and allowed to react



overnight. Excess anhydride and catalyst were removed by dissolution in 1.0 M HCl in methanol.

RESULTS AND DISCUSSION

The various epoxide and cyclic anhydride monomers examined in these studies are listed in Scheme 2. Initially we investigated the copolymerization of phthalic anhydride (PA) and cyclohexene oxide (CHO) employing the (salen)CrCl catalyst (Figure 1) in the presence of several onium salts to optimize



Figure 1. *N*,*N*'-Bis(3,5-di-*tert*-butylsalicylidine)-1,2-cyclohexane diaminochromium(III) chloride.

the catalytic activity. As illustrated in the infrared traces of polymer formation in Figure 2, the chromium(III) catalyst alone was ineffective and the onium salt alone was less effective than a combination of the two species. This is to be contrasted with the previous literature report where (salen)CrCl did not require a cocatalyst for the copolymerization of maleic anhydride and propylene oxide.¹⁴ On the other hand, in the Duchateau studies a DMAP (4-*N*,*N*-dimethylamino-pyridine) cocatalyst was necessary in the presence of (Salophen)CrCl to impart catalytic activity.¹⁵ In both instances employed in this study the polyesters afforded exhibited narrow molecular weight distributions, with PDIs ranging from 1.07 to 1.13. Utilizing the two monomers (PA and CHO) in the accompaniment of (salen)CrCl and various anions derived from PPN⁺ and *n*-Bu₄N⁺ salts we endeavored to determine the optimal anionic initiator.

The rates of copolymerization initiated by the anions of several PPN⁺ (bis(triphenylphosphine)iminium) salts in the presence of (salen)CrCl did not vary significantly with the anion or its concentration. For example, the second-order rate constants employing one equivalent of Cl⁻, N₃⁻, and DNP⁻ (dinitrophenoxide) spanned the range $1.44-1.76 \times 10^{-2} \text{ M}^{-1}$ s^{-1} at 80 °C and were not altered upon carrying out the process using two equivalents of onium salts. The use of n-Bu₄NX (X = Br or I) salts resulted in a modest decrease in the reaction rate. The lack of copolymerization rate on [onium salt] in the presence of the (salen)CrCl catalyst indicates that the process proceeds solely via a coordination insertion mechanism in these instances. Further confirmation of this mechanistic pathway is seen in the terpolymerization of PA/CHO/CO₂, where the coupling of CHO and CO₂ only occurs with the aid of the (salen)CrCl complex (vide infra).



Figure 2. Growth of polyester peak at 1738 cm⁻¹ as monitored by *in situ* ATR-FTIR spectroscopy for various combinations of catalyst and cocatalyst: (green line) [Cr]:[Cl]:[PA]:[CHO] = 1:1:200:200, (red line) [Cr]:[Cl]:[PA]:[CHO] = 1:0:200:200, and (blue line) [Cr]:[Cl]:[PA]: [CHO] = 0:1:200:200. Cr = (salen)CrCl, Cl = PPNCl, PA = phthalic anhydride, and CHO = cyclohexene oxide. Inset shows the linear plot of $\ln(A_{\infty}/A_{\infty} - A_t)$ vs time, where A_{∞} and A_t are the absorbances of the band at 1738 cm⁻¹ at t_{∞} = infinity and t = time, respectively.



Figure 3. ¹H NMR spectrum of PA/CHO. PA phenyl appears at 7.65 ppm. Encircled region represents where ether linkages should appear, hence copolymer is >99% completely alternating.

Since the common PPN⁺ salts of chloride and azide provide similar rates of initiation of polymerization, we have chosen to use the azide anion in our comprehensive studies because of its strong ν_{N_3} absorption band in the infrared. For these investigations we have synthesized a series of polyesters employing the combination of anhydride and epoxide monomers listed in Scheme 2. The appropriate monomers were dissolved in toluene and heated at 80 °C in the presence of (salen)CrCl and 1 equiv of PPNN₃. The resultant polyesters were characterized by infrared spectroscopy, ¹H NMR spectroscopy, differential scanning calorimetry (DSC), and selected samples were subjected to molecular weight analysis by gel permeation chromatography. Infrared analysis of the purified polyester confirmed the location of the $\nu_{\rm CO}$ stretching frequency at 1738 cm⁻¹ for all of the polyesters described herein. The $\nu_{\rm C=O}$ vibration is significantly different from that of the cyclic anhydrides, located at approximately 1770 cm⁻¹, which allows for the monitoring of polyester formation *via in situ* ATR-FTIR analysis. The ¹H NMR spectra of the polyesters displayed chemical shifts in the 4–6 ppm range indicative of hydrogens bound to the carbons α to the ester group, both from the anhydride and epoxide units (Figure 3). ¹H NMR

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Scheme 3



Figure 4. Copolymerization of equimolar quantities of cyclohexene oxide and phthalic anhydride in the presence of 4.05 mM (salen)CrCl and one equivalent of PPNN₃ in 2.5 mL of toluene at 80 °C. (A) Absorbance of the growth of the 1738 cm⁻¹ band of the polyester vs time. (B) Plot of $\ln(A_{\infty}/[A_{\infty} - A_t])$ vs time.

spectra of all other polyester synthesized in this report may be found in the Supporting Information. Furthermore, analysis of the ¹H NMR spectra revealed that the copolymerization of epoxide and anhydride takes place in an almost exclusive (>99%) alternating fashion.

Kinetic Studies. The suggested reaction pathways for the formation of alternating copolymers from epoxides and anhydrides are summarized in Scheme 3. As indicated, the rate of epoxide and CO_2 coupling to provide polycarbonates is slow relative to polyester formation (*vide infra*). This latter observation provides a one-step production of diblock copolymers of polyesters and polycarbonates as previously demonstrated by Coates and co-workers employing β -diiminate

zinc catalysts,⁹ and Duchateau and co-workers employing (salophen)CrCl/DMAP as catalyst.¹⁵ The rate of the alkoxide anion reacting with an anhydride monomer (k_2) is generally much faster than a carboxylate anion ring-opening an epoxide (k_3) , hence the latter process is rate-determining. At constant initiator concentration, the copolymerization is first-order with respect to the epoxide monomer (Figure 4) and to the initiator at equimolar ratios of monomers. An increase in the cyclic anhydride concentration by 50% lead to only a slight change in reaction rate.¹⁶ In the absence of the (salen)CrCl catalyst, a slower copolymerization pathway similar to that described in Scheme 3 presumably takes place initiated by ring-opening of the epoxide by the free anion from the onium salt followed by

successive alternating ring-opening of anhydride and epoxide. Such a reaction scheme is included in the Supporting Information.

The copolymerization reactions of equimolar quantities of phthalic anhydride and cyclohexene oxide at a constant catalyst concentration were monitored by *in situ* infrared spectroscopy over a temperature range of 40 $^{\circ}$ C. Table 1 lists the rate constants obtained from the linear plots in Figure 5 as a

Table 1. Temperature Dependent Rate Constants for the Copolymerization of PA and $CHO.^{a}$

temperature (°C)	$k_3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	$M_{\rm n} \ ({\rm PDI})^b$
70.0	4.42	13 000 (1.12)
80.0	7.06	-
90.0	17.8	18 000 (1.13)
100.0	29.6	17 000 (1.12)

^{*a*}Reaction conditions: (salen)CrCl/PPNN₃/PA/CHO = 1:1:200:200, where the [(salen)CrCl] = 4.05×10^{-3} M in toluene solution. ^{*b*}Determined by GPC in tetrahydrofuran using monodisperse polystyrene standards.



Figure 5. First-order plots for the copolymerization of PA and CHO as a function of temperature.

function of temperature, with an Eyring plot of these data shown in Figure 6. The ΔH^{\ddagger} and ΔS^{\ddagger} values derived from Figure 6 for the copolymerization of PA and CHO were determined to be 67.5 and -95.3 J/mol, respectively, with ΔG^{\ddagger} being 101 kJ/mol at 80 °C.

Consistent with earlier studies, the terpolymerization of cyclohexene oxide, phthalic anhydride, and CO₂ catalyzed by (salen)CrCl and PPNN₃ afforded a one-pot synthesis of a diblock copolymer of polyester and polycarbonate (Figure 7).¹⁵ As noted in Scheme 3 this observation requires that the route governed by k_2 and k_3 to be much faster that the pathway proceeding via CO₂ insertion and subsequent polycarbonate formation. This has been interpreted as resulting from a slower rate of CO₂ insertion vs cyclic anhydride insertion into the metal alkoxide intermediate.¹⁷ Alternatively, since CO₂ insertion into metal-alkoxides is highly reversible and generally thought to be nonrate-limiting, this behavior may be the result of a much slower ring-opening step of the metal–carbonate intermediate with the epoxide monomer, a process driven by k_4 in Scheme 4. Differential scanning calorimetry analysis of the



Figure 6. Eyring plot of the PA and CHO copolymerization reaction, with $R^2 = 0.980$.

resulting polymer revealed it to be a well-defined copolymer with two distinct $T_{\rm g}$ values (48 °C for PA/CHO and 115 °C PCHC).

The reaction rates for the copolymerization of cyclohexene oxide with various cyclic anhydrides observed under similar reaction conditions provided relative reactivities of CHA > PA > CHE. Additionally, employing the CHA monomer while varying the epoxide under identical reaction conditions afforded a reactivity trend of PO > CHO \geq SO (Figure 8). The percent conversions were determined by integration of monomer ¹H NMR peaks vs polymer peaks. A representative series of ¹H NMR spectra for the CHA/PO copolymerization process is included in the Supporting Information. However, the fourmembered cyclic ether, oxetane, was essentially unreactive under these reaction conditions.

Thermal Properties of Copolymers. The glass transition temperatures of the various polyesters synthesized from the monomers listed in Scheme 2 utilizing a (salen)CrCl/PPNN₃ catalyst system in toluene at 80 °C were determined by differential scanning calorimetry (DSC) analysis. These data, along with the corresponding molecular weight data for selected copolymers obtained from GPC measurements, are summarized in Table 2. As anticipated, the steric bulk of the pendant groups and rigidity of the monomeric structure have a direct effect on the $T_{\rm g}$ of the resultant polyester. That is, in general the $T_{\rm g}$ values increased with epoxides in the order CHO > SO > PO, and increased with cyclic anhydrides in the order $CHE > PA \ge CHA > MA > SA$. Specifically, the glass transition temperature found for the polyesters formed from propylene oxide and CHE, PA, MA, and SA were +36, +41, -23, and -39 °C, respectively. Similarly, the copolymer provided by the alternative coupling of SA with CHO or SO displayed corresponding T_g values of 34 and 4.4 °C.

The range of T_g values achievable from the alternating ringopening copolymerization of the studied epoxides and cyclic anhydrides is over 130 °C, with a high T_g of +95 °C for the copolymer from CHE and CHO and a low T_g of -39 °C for that produced from SA and PO. Furthermore, it has been shown that only a small percentage of cross-linking can drastically increase the T_g of resultant polyesters. In this regard, we have observed two vastly different T_g parameters (-23 and +28 °C) for maleic anhydride/propylene oxide copolymer samples obtained from very similar synthetic procedures. We speculate here that this is due to a spontaneous photodimerization reaction. Consistent with the suggestions is the



Figure 7. In situ FTIR analysis of block copolymerization process. Reaction conditions used were (salen)CrCl/PPNCl/PA/CHO = 1:1:200:600 under 500 psi CO₂, 80 °C with 19 mL toluene (solvent, volume totaling 25 mL). Deconvolution was performed by ReactIR ic10 software. Green line = polyester growth (1738 cm⁻¹), red line = anhydride consumption (1770 cm⁻¹), and blue line = polycarbonate growth (1750 cm⁻¹). The three-dimensional surface of the reaction is shown in the inset on the right.





Figure 8. Comparison of epoxides: polymer growth vs time. Reactions were performed in sealed NMR tubes using 2.0 mL of toluene- d_8 as solvent. Then 200 equiv of the appropriate epoxide was added to tube, which was then dissolved in a stock solution of 1.8 mL of toluene- d_8 , 300 mg of CHA (200 equiv), 6.3 mg of (salen)CrCl (1 equiv), and 5.7 mg of PPNN₃ (1 equiv). The tubes were then heated to 80 °C and allowed to react until 100% conversion was achieved.

observation that copolymers from MA and epoxides have the broadest polydispersity indices (~ 2.3) of all polyester

Table 2. GPC and DSC Data for Selected Polyesters

oolyester (cyclic anhydride/ epoxide)	$(\times 10^{-3})$	M_{w} (×10 ⁻³)	PDI	$(^{\circ}C)^{c}$
CHE/CHO	10	14	1.34	95
CHA/CHO	9.2	9.7	1.06	85
CHE/SO	5.7	6.5	1.14	53
MA/CHO	8.5	20	2.3	53
PA/SO	19	24	1.27	46
PA/CHO ^a	18	20	1.13	48
PA/CHO ^b	14	15	1.07	-

^aSample was synthesized using both PPNN₃ and (salen)CrCl. ^bSample was synthesized using only PPNCl as initiator. ^c $T_{\rm g}$ values represent the midpoint temperature during the second heating cycle.

synthesized in this report. That is, the other polyester synthesized displayed narrow polydispersity indices (<1.30) with M_w values of about 10 000 or greater.

CONCLUSIONS

Herein, we have reported kinetic studies of the alternating ringopening copolymerization of various epoxides with cyclic acid anhydrides to afford polyesters of high molecular weights and narrow molecular weight distributions using a (salen)CrCl catalyst in the presence of onium salts. The activation parameters for the process involving phthalic anhydride/ cyclohexene oxide monomers in toluene solution were determined to be $\Delta H^{\ddagger} = 67.5$ kJ mol⁻¹ and $\Delta S^{\ddagger} = -95.3$ J mol⁻¹, where the rate-determining step was ring-opening of the epoxide by the enchained anhydride. For a given cyclic anhydride, cyclohexane anhydride, the relative rate of coupling with epoxide decreased in the order PO > CHO \geq SO, whereas, for cyclohexene oxide the relative reactivity order with anhydrides was CHA > PA > CHE. This catalytic system was also shown to terpolymerize epoxide/cyclic anhydride/CO₂ to afford diblock copolymers with very little tapering, thereby providing a one-step synthesis of poly(ester-co-carbonate). In the polyester product resulting from the ring-opening polymerization of maleic anhydride and propylene oxide two vastly different $T_{\rm g}$ s were observed at -23 and +28 °C. We have proposed the higher $T_{\rm g}$ value to be the result of some degree of cross-linking by photoinduced dimerization. Further efforts are being directed at providing a more definitive assessment of this possibility.

ASSOCIATED CONTENT

S Supporting Information

Reaction scheme for cyclic anhydride/epoxide copolymerization initiated by onium salts alone, ¹H NMR spectra of all polyesters, and ¹H NMR monitoring of the copolymerization of cyclohexane anhydride and propylene oxide. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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