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# Binding of 4-(*N*,*N*-dimethylamino)pyridine to Salen- and Salan-Cr(III) Cations: A Mechanistic Understanding on the Difference in Their Catalytic Activity for $CO_2$/Epoxide Copolymerization

**Dun-Yan Rao, Bo Li, Rong Zhang,* Hui Wang, and Xiao-Bing Lu***

*State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China*

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The coordination chemistry of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) with Salen- or Salan- (where the tetradentate *N*,*N*′-disubstituted bisaminophenoxide is designated as Salan, a saturated version of the Schiff-base Salen ligand) chromium complexes was studied by electrospray ionization mass spectrometry (ESI-MS). The relative stabilities of mono DMAP adducts of these chromium complexes were characterized by collision-induced dissociation (CID) and further discussed with regard to the activity in catalyzing $CO_2$/epoxide copolymerization. $[SalenCr]^+$ cations preferably bind two DMAP molecules to form six-coordinated complex ions, while $[SalanCr]^+$ cations usually bind one molecule of DMAP to form five-coordinated complex ions, which were found to be relatively unstable. The remarkable difference in the coordination of DMAP to these two chromium complexes resulted in a significant difference in catalytic activity for the alternating copolymerization of $CO_2$ and propylene oxide. In the presence of 1 equiv of DMAP, the activity of the chromium-Salan complex **2a** was up to 86 $h^{-1}$ of TOF at ambient temperature, which was about 30 times that of the corresponding chromium-Salen complex **1a**. In sharp contrast to a long induction period up to 2 h with the use of **1a** in conjunction with DMAP as catalyst, no initiation time or a very short one was observed in the binary **2a**/DMAP catalyst systems. The initiator role of DMAP was confirmed by continuous determination of the propagating polymer species at various intervals using ESI-MS, which in combination with a kinetic study by means of infrared spectroscopy resulted in a mechanistic understanding on the difference in activity of the two catalyst systems for $CO_2$/epoxide copolymerization.

## Introduction

The coupling of $CO_2$ and epoxides producing either cyclic or polymeric carbonates is one of the most extensively studied reactions with respect to chemical fixation of $CO_2$.[1,2] This chemistry has its roots in Inoue's discovery, where it was shown that a heterogeneous catalyst derived from diethylzinc and water was active for this copolymerization reaction.[3] In recent decades, numerous catalyst systems have been developed for this transformation.[4−8] Prominent among these are binary or bifunctional catalyst systems based on metal-Salen complexes being the most efficient for the $CO_2$/epoxides coupling reactions even at mild conditions[6−8] and in some cases approach to the regio- and/or stereoselective polymerization.[7]

Obviously, an elucidation of mechanism should be beneficial to design highly efficient catalyst systems for $CO_2$/

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* To whom correspondence should be addressed. E-mail: rzhang@dlut.edu.cn (R.Z.), lxb-1999@163.com (X.-B.L.).

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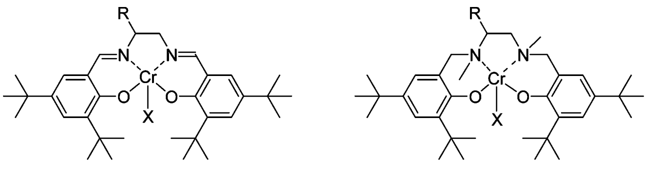
epoxides copolymerization.[9] Duchateau and co-workers have investigated some side reactions and chain transfer for zinc-catalyzed copolymerization of cyclohexene oxide and $CO_2$ by Matrix Assisted Laser Desorption Ionization-Time of Flight-Mass Spectrometry (MALDI-TOF-MS) analysis.[10] It is very important to identify active species during reactions to understand the possible pathways. However, the intermediates are usually unstable and fleeting, and thereby difficult to observe by conventional testing methods. Electrospray ionization (ESI) is a soft ionization method that can keep any weakly bound ligand intact in a complex ion. With this advantage, it has become more and more popular as an analytical tool in inorganic/organometallic chemistry.[11] ESI in combination with tandem mass spectrometry (MS/MS), has been employed to study mechanistic aspects of some reactions, such as the oxidation of unfunctionalized olefins with metal-Salen complexes.[12]

In 2004, Vairamani and co-workers reported the coordination behavior of the complex $[Cr^{III}(Salen)]PF_6$ with various amine ligands under ESI conditions.[13] In the recent report of Chen et al., the binding of aliphatic epoxides to Salen-M(III) cations (where M = Cr, Co, Ga, and Al) was studied in the gas phase by electrospray tandem mass spectroscopy, and the results were discussed in terms of the reactivity of these complexes in the ring-opening polymerizations of epoxides and copolymerizations with $CO_2$, respectively.[14,15]



**1a**: R = $CH_3$, X = $NO_3$
**1b**: R = H, X = $NO_3$
**1c**: R = $CH_3$, X = Cl
**1d**: R = H, X = Cl
**SalenCr(III)X**

**2a**: R = $CH_3$, X = $NO_3$
**2b**: R = H, X = $NO_3$
**2c**: R = $CH_3$, X = Cl
**2d**: R = H, X = Cl
**SalanCr(III)X**

**Figure 1.** Structures of Salen- and Salan- chromium complexes.

Recently, we noted with great interest an elegant kinetics studies on the copolymerization of $CO_2$ and epoxides catalyzed by binary SalenCrX ($X = Cl^-$, $N_3^-$)/Lewis base systems in which a copolymerization mechanism was proposed for which initiation occurred by a bimetallic process and propagation operated by monometallic enchainment of epoxides. These studies all have suggested that a Lewis base coordinates to the active metal center *trans* to the propagating metal−polymer chain, thereby labilizing the propagating alkoxide or carboxylate ligand and promoting the insertion of $CO_2$ into the metal-alkoxide bond. Interestingly, there exists a long induction period in the system of the chromium Salen complexes alone or consistent with an organic base.[6b,16] In sharp contrast to this result, our recent studies found no initiation time or very short ones were observed in the binary catalyst systems of the chromium complexes of tetradentate *N*,*N′*-disubstituted bisaminophenoxide (designated as Salan, a saturated version of the Schiff-base Salen ligand) in conjunction with 4-(*N*,*N*-dimethylamino)pyridine (DMAP). Notably, in the presence of 1 equiv of DMAP, the catalytic activity of chromium-Salan complexes is about 30 times that of the corresponding chromium-Salen complexes. The slight differences only in electrophilicity of the central metal ion and steric hindrance of the two similar catalyst systems resulting in a contrary tendency stimulates us to explore the real active species during this copolymerization reaction. Herein, we employed the ESI method in combination with MS/MS to study the binding of DMAP to SalenCr(III) or SalanCr(III) complexes (Figure 1), and further directly observe the propagating polymer species during the copolymerization of $CO_2$ with propylene oxide (PO). These investigations in combination with a kinetic study by means of infrared spectroscopy gave us an insight into the mechanistic understanding of the difference in catalytic activity of SalenCr(III) and SalanCr(III) complexes in the presence of DMAP.

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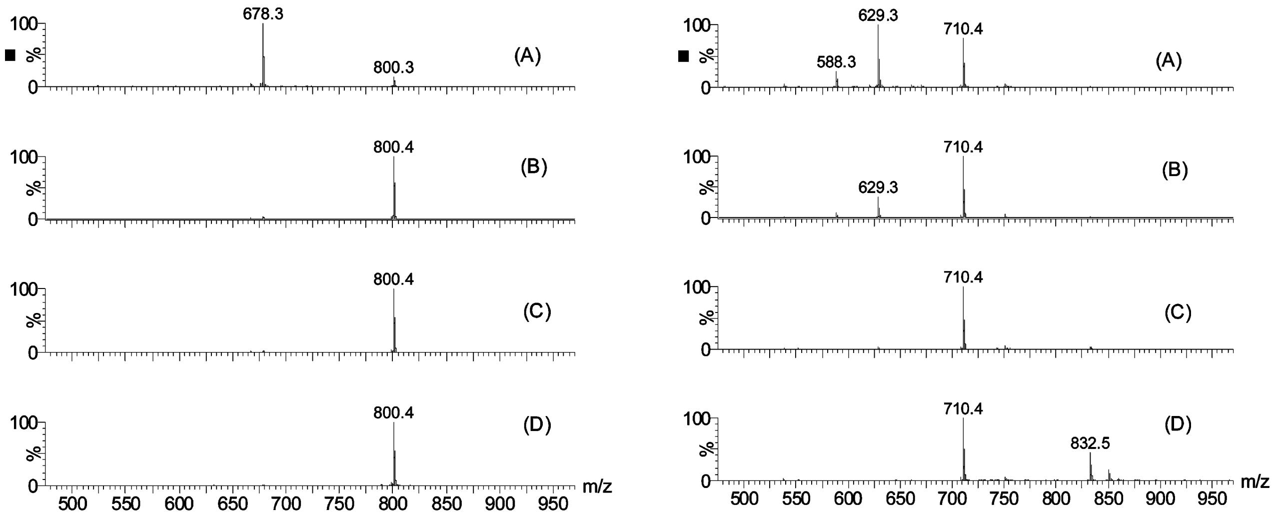

(1) **1a**/DMAP

(2) **2a**/DMAP

**Figure 2.** ESI mass spectra of the mixture resulting from the system of **1a**/DMAP and **2a**/DMAP with different molar ratios of (A) 1/0.5, (B) 1/1, (C) 1/2, and (D) 1/10.

## Results and Discussion

**Binding of DMAP to SalenCr(III) and SalanCr(III) Complexes.** First, we set out to investigate the binding of DMAP to these chromium complexes (Figure 1) in a solution that was prepared from **1a** or **2a** and DMAP dissolved in $CH_2Cl_2$. Direct analysis of the resulting solution containing the chromium complexes afforded a low-quality spectrum with poor ion intensity because $CH_2Cl_2$ is not an ideal solvent for the ESI process. As a result, the mixture solution was diluted with the equivalent volume of acetonitrile to improve ionization efficiency. The positive ion electrospray ionization mass spectrometry (ESI-MS) spectra of the **1a**/DMAP mixtures in different molar ratios are illustrated in Figure 2(1). When the molar ratio of **1a** to DMAP is 1:0.5, the spectrum mainly contains the species at *m/z* 678.3 and 800.3, corresponding to [**1a** − $NO_3^-$ + DMAP]$^+$ and [**1a** − $NO_3^-$ + 2DMAP]$^+$ cations, respectively. The solvated cations were not detected because of the strong affinity of DMAP toward the complex **1a**. With the increase of DMAP, the species at *m/z* 678.3 disappears completely, and only the species at *m/z* 800.3 was observed. The results indicate that **1a** preferably binds two molecules of DMAP to form **1a**·2DMAP adduct. As for the system of the chromium-Salan complex **2a** in conjunction with DMAP (Figure 2(2)), three species at *m/z* 588.3, 629.3, and 710.4 were observed in a molar ratio of 1:0.5 (**2a**/DMAP), assigned to [**2a** − $NO_3^-$]$^+$, [**2a** − $NO_3^-$ + $CH_3CN$]$^+$, and [**2a** − $NO_3^-$ + DMAP]$^+$ cations, respectively. With the increase of DMAP concentration, the relative abundance of the species at *m/z* 710.4 significantly increases, while the species at *m/z* 588.3 and 629.3 are negligible. This demonstrates a replacement for acetonitrile molecules coordinated in the central metal ion by DMAP with strong coordination ability. Interestingly, even in the presence of 10 equiv of DMAP, the species at *m/z* 710.4 is still the base peak in the mass spectrum, and a weak peak of the species at *m/z* 832.5 corresponding to [**2a** − $NO_3^-$ + 2DMAP]$^+$ was detected. It is worthy of note that the species at *m/z* 629.3 or 710.4 is dominant with various ratios of **2a** to DMAP, which means that the [**2a** − $NO_3^-$]$^+$ cation predominantly binds one molecule of acetonitrile or DMAP to form five-coordinated complex ions.

As anticipated, a change in diamine backbone from 1,2-diaminopropane to ethylene diamine, as well as axial X anion from $NO_3^-$ to more nucleophilic $Cl^-$, did not cause obvious changes in the coordination chemistry of DMAP with these Salen- or Salan-chromium complexes. For example, the Salen chromium complexes **1d** preferably bind two DMAP molecules; while the corresponding Salan chromium complexes **2d** predominantly bind one molecule of DMAP (see Supporting Information, Figure S2).

A competitive coordination experiment was also performed in the mixture solution of **1a**/**2a**/DMAP with a molar ratio of 1:1:2. The mass spectrum displays three species at *m/z* 678.2, 710.3, and 800.3, assigned to [**1a** − $NO_3^-$ + DMAP]$^+$, [**2a** − $NO_3^-$ + DMAP]$^+$, and [**1a** − $NO_3^-$ + 2DMAP]$^+$, respectively (Figure 3). The ion [**2a** − $NO_3^-$]$^+$ binds one molecule of DMAP, while the [**1a** − $NO_3^-$]$^+$ ion easily binds two DMAP molecules. The difference perhaps can be attributed to the steric hindrance resulting from the two-methyl groups in the diamine backbone of the complex **2a**. From the relative abundance of the species, it can be concluded that the [**2a** − $NO_3$]$^+$ ion has a very low affinity for DMAP. This is a clear indication of the weaker Lewis acidity of the chromium Salan complexes. Indeed, the presence of $sp^3$-hybridized amino donors and its *N*,*N*′-disubstituted groups in SalanCr(III) complexes are responsible for reducing the Lewis acidity of the central metal ion. We note with great interest that Rieger and co-workers have reported in the copolymerization of $CO_2$ and PO that the binary catalyst system of SalenCrCl and DMAP with a molar ratio of 1:0.5 is more beneficial to the formation of polycarbonates.[6c] As a result, we tentatively assume that in the binary catalyst system of the chromium complexes in conjunction with DMAP for the copolymerization reaction

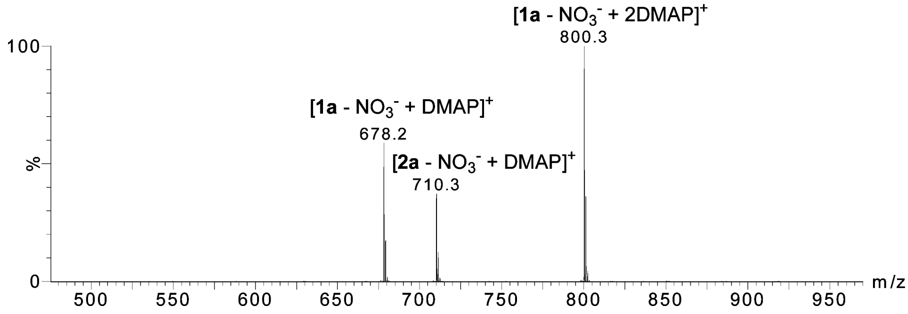

**Figure 3.** ESI mass spectrum of the mixture resulting from the system of **1a**/**2a**/DMAP = 1:1:2 (molar ratio).

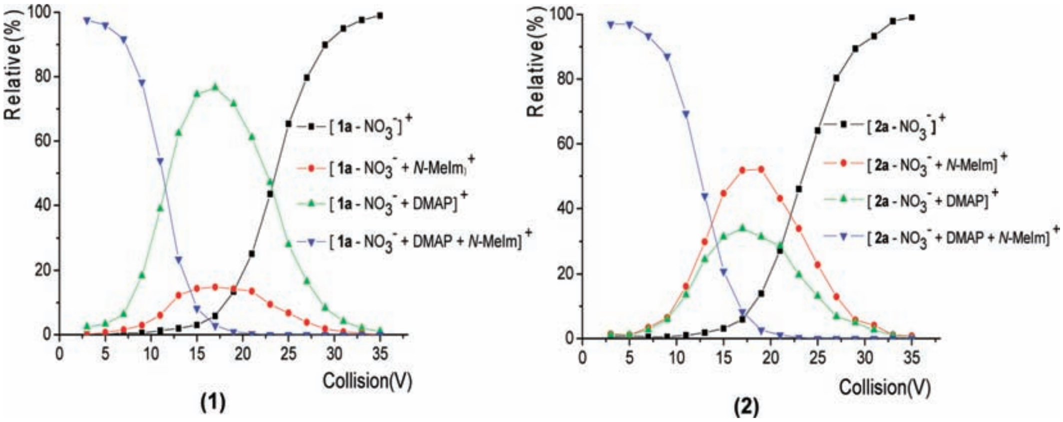

**Figure 4.** Plots of [**1a** $-$ $NO_3^-$ + DMAP + *N*-MeIm]$^+$ and [**2a** $-$ $NO_3^-$ + DMAP + *N*-MeIm]$^+$ versus collision voltage from CID experiments.

of $CO_2$ and epoxides, the species containing one DMAP molecule may be the active intermediate to initiate the reaction.

**Collision-Induced Dissociation of Mono-DMAP Adducts of SalenCr(III) and SalanCr(III) Cations.** The stability of the mono-DMAP adducts of SalenCr(III) and SalanCr(III) cations was first studied by collision-induced dissociation (CID) experiments on the basis of the interaction with the collision gas. Under a collision voltage of 17 V, about 60% of the ion [**1a** $-$ $NO_3^-$ + DMAP]$^+$ remained, while up to 50% of the ion [**2a** $-$ $NO_3^-$ + DMAP]$^+$ was decomposed. This indicates that SalanCr(III)-DMAP adducts exhibit relatively lower stability than the corresponding SalenCr(III)-DMAP adducts.

To further study the stability of the DMAP adducts of SalenCr(III) and SalanCr(III) cations, *N*-methylimidazole (*N*-MeIm) with strong coordination ability and relative small volume together with DMAP was added into the solution of the complex **1a** or **2a** to form a ion bound with two different bases, [Cr(III)$^+$ + DMAP + *N*-MeIm]. The ions [**1a** $-$ $NO_3^-$ + DMAP + *N*-MeIm]$^+$ and [**2a** $-$ $NO_3^-$ + DMAP + *N*-MeIm]$^+$ originating from the mixture solutions of DMAP, *N*-MeIm, and the complex **1a** or **2a** (2:2:1, molar ratio) were studied in CID experiments. The CID curves are shown in Figure 4. With the increase of collision voltage, the peak intensity of the ion [**1a** $-$ $NO_3^-$ + DMAP]$^+$ is significantly higher than that of the ion [**1a** $-$ $NO_3^-$ + *N*-MeIm]$^+$ (Figure 4(1)). This result demonstrates that *N*-MeIm was first lost from the ion [**1a** $-$ $NO_3^-$ + DMAP + *N*-MeIm]$^+$ during CID experiments. It can be reasonably assumed that [**1a** $-$ $NO_3^-$ + DMAP]$^+$ is more stable than [**1a** $-$ $NO_3^-$ + *N*-MeIm]$^+$, perhaps because of the relative high Lewis basicity of DMAP. On the contrary, in the CID experiment of [**2a** $-$ $NO_3^-$ + DMAP + *N*-MeIm]$^+$ (Figure 4(2)), the predominantly losing coordinated agent is DMAP rather than *N*-MeIm, probably resulting from the steric hindrance of the complex **2a**. Indeed, the sterically hindered structure of SalanCr(III) complexes should have a negative effect on the formation of [**2a** $-$ $NO_3^-$ + 2DMAP]$^+$.

**Direct Observation of the Propagating Polymer Species by Means of ESI-MS.** Recently, Darensbourg and co-authors have put forth a comprehensive mechanism description of the copolymerization of $CO_2$ and cyclohexene oxide utilizing binary catalyst systems consisting of SalenCrX and a heterocyclic nitrogen base such as DMAP, in which zwitterions were proposed to be formed from $CO_2$ and DMAP, and represented the active species for initiating the copolymerization reaction.[17] In previous papers, we have demonstrated that sterically hindered strong organic bases in the binary catalyst systems play an initiator role for polymer-chain growth in the copolymerization of $CO_2$ and PO by means of ESI-MS.[7d,18] The initiator role of DMAP in the binary Salen- or Salan-Cr(III)X/DMAP systems was also confirmed by this method. The ESI mass spectra of the binary **1a**/DMAP and **2a**/DMAP systems in positive ion mode are illustrated in Figure 5, from which we can observe the species of *m*/*z* 181.1 corresponding to [$^-OCH(CH_3)CH_2$-$DMAP^+$ + $H^+$] and *m*/*z* [181.1 + n(102)] corresponding to [$^-OCH(CH_3)CH_2$-$(CO_2$-*alt*-$PO)_n$-$DMAP^+$ + $H^+$], but with time the former species slightly decreases and the latter species moves to the high *m*/*z* region. The results clearly

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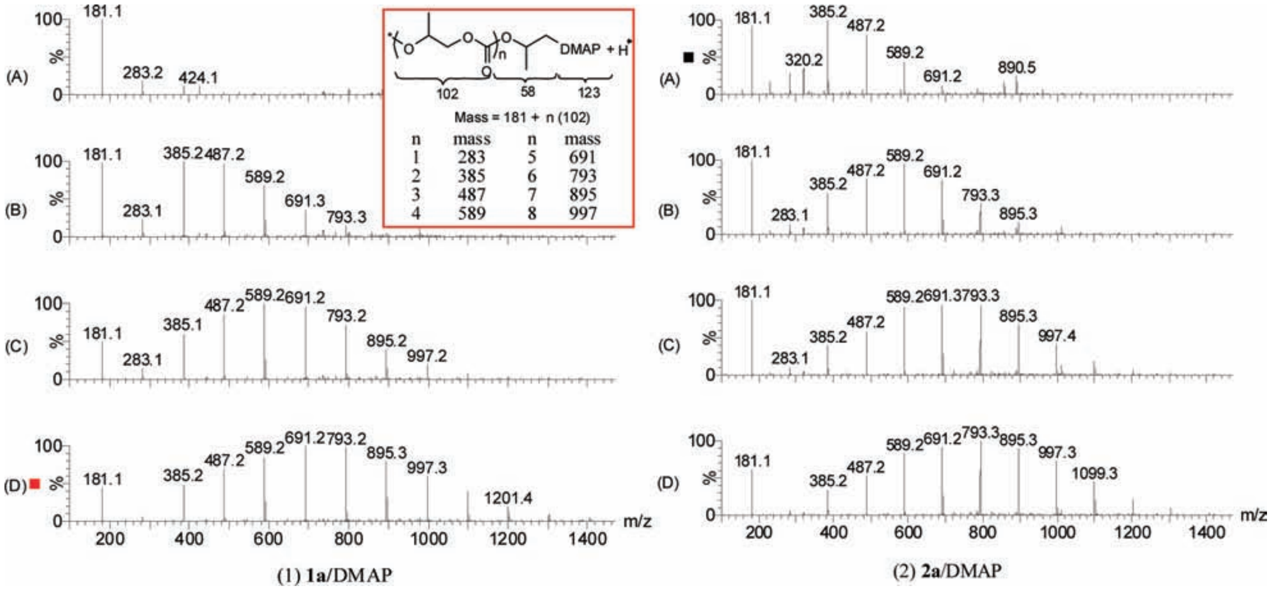

**Figure 5.** ESI mass spectra of the reaction mixture resulting from the system of **1a**/DMAP and **2a**/DMAP (1:1, molar ratio) for catalyzing $CO_2$/PO copolymerization at 25 °C and 0.6 MPa $CO_2$ pressure with various times (1) (A) 2 h, (B) 4 h, (C) 6 h, (D) 8 h; (2) (A) 10 min, (B) 20 min, (C) 35 min, (D) 50 min.

demonstrate that the formation of zwitterions with respect to DMAP is not a prerequisite for initiating the copolymerization reaction.

One of the most striking differences in the $CO_2$/PO copolymerization process is that as compared with the binary **1a**/DMAP system with an induction period up to 2 h, in the binary **2a**/DMAP system the initiation time is very short and the propagating polymer species with respect to DMAP were detected after the reaction proceeded with only 10 min. The control experiments further indicate that the complex **2a** in combination with DMAP predominantly exceeds the binary **1a**/DMAP system in catalytic activity at various conditions (see Supporting Information, Figure S3 and Table S1). In the presence of 1 equiv of DMAP as cocatalyst, the activity of the complex **2a** is up to 86 $h^{-1}$ of TOF at ambient temperature, which is about 30 times that of **1a** at the same conditions. Interestingly, with the increase of DMAP from 0.5 to 2 equiv, the activity of **1a** slightly decreases, while that of **2a** increases to a certain extent. The remarkable difference in activity of the two catalyst systems should be ascribed to the different coordination chemistry of DMAP with Salen- and Salan- chromium complexes. It is worthwhile noting here parenthetically that an obvious decrease in polymer selectivity and the resulting polycarbonate molecular weight was observed in both catalyst systems under high DMAP loading. A similar decrease in polymer selectivity in the presence of cocatalyst loading beyond 1 equiv was seen by the Rieger and Darensboug group for this reaction catalyzed by the binary systems of SalenCrX in conjunction with a heterocyclic nitrogen Lewis base.[6c,16]

**Mechanistic Understanding.** In efforts to further clarify the mechanistic aspects of the copolymerization process concerning these chromium complexes in the presence of DMAP as cocatalyst, we have performed infrared spectroscopic studies by monitoring the carbonate region. Typical data are illustrated in Figure 6, along with the time profile of the absorption at ~1750 $cm^{-1}$. As might be expected, the remarkable differences between the two catalyst systems lie in the induction period and copolymerization rate. A lengthening initiation time and a low reaction rate was observed in the binary **1a**/DMAP catalyst system, while very short induction period was found in the binary **2a**/DMAP catalyst system at 15 °C. The result is in agreement with the ESI-MS analysis described previously. The decrease in activity when DMAP loading changes from 0.5 to 2 equiv indicates that the mono DMAP-SalenCr(III) adduct is much more active than the corresponding six-coordinated chromium ion concerning the two DMAP molecules.

Indeed, apart from the initiator role of DMAP confirmed by ESI-MS method, the axial X anion of the chromium Salen or Salan complexes also initiates the copolymerization reaction. In previous paper, we have found that cyclohexyl $SalenCrNO_3$ alone could catalyze the coplymerization of $CO_2$ and PO to afford the corresponding polycarbonate.[18] As a result, we can reasonably assume that copolymer growth can be occurring at both sides of the Salan- or SalenCr(III) center, as is similar to that proposed by Inoue et al. using aluminum porphyrins combined with an ionic ammonium or phosphonium salt.[19] It is noteworthy that these two chromium(III) derivatives in the presence of a sixth ligand are quite different. Numerous SalenCr(III)X and adducts thereof have been structurally characterized as square-pyramidal or octahedral with the salen ligand being planar ($N_2O_2$).[2b] On the other hand, the presence of $sp^3$-hydridized amino donors and their *N*,*N′*-disubstituted groups in SalanCrX should lead to a distorted octahedral structure of SalanCrX•DMAP adduct, in which the coordinated DMAP probably lies in the *cis* position of the X anion rather than *trans* coordination mode

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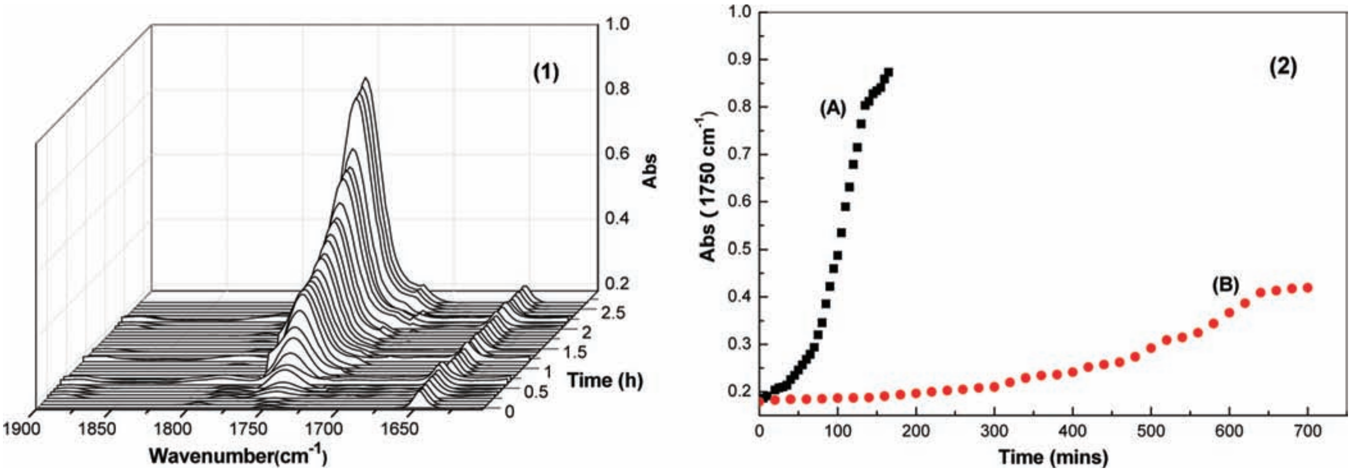
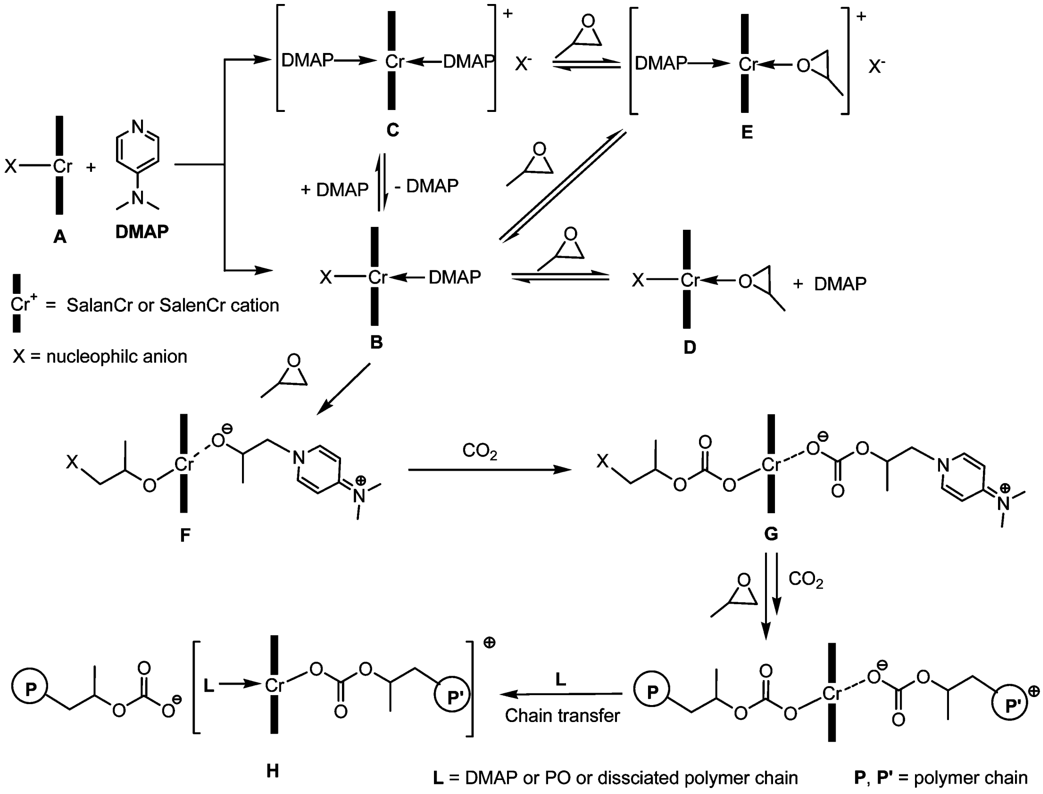


**Figure 6.** (1) Three-dimensional stack plot of the IR spectra collected at regular intervals during the reaction of $CO_2$ and PO catalyzed by binary **2a**/DMAP system. (2) Time profiles of the absorbance at 1750 cm$^{-1}$ (corresponding to polycarbonate) with the use of (A) **2a**/DMAP and (B) **1a**/DMAP as catalyst. Reaction conditions: 15 °C and 1.0 MPa $CO_2$ pressure with a molar ratio of chromium complex/DMAP/PO = 1/1/1000 (the samples were diluted with $CH_2Cl_2$ before FTIR analysis).

**Scheme 1.** Proposed Mechanism of $CO_2$/PO Copolymerization Catalyzed by Binary Salan- or Salen-Cr(III)X/DMAP Systems



usually present in the monoadduct of SalenCr(III)X.[20] However, whether initiation derived from DMAP and the axial anion occurs simultaneously, or whether the latter occurs first, is still a matter of debate. More recently, Darensbourg and co-workers proposed a unifying mechanism on the role of the cocatalyst in the copolymerization of $CO_2$ and cyclohexene oxide utilizing chromium Salen complexes as catalyst, where *N*-heterocyclic amines and phosphines provide inner salts or zwitterions, which behave in a manner similar to that of the anion as cocatalyst for this copolymerization reaction.[17] Notably, they first isolated single crystals of an oxetane•SalenCr(III) adduct, in which the oxetane is bound to the SalenCr(III) center without undergoing ring-opening at ambient temperature.[20]

On the basis of the above descriptions, we put forth a detailed mechanism of the copolymerization of $CO_2$ and PO catalyzed by Salan- or Salen-Cr(III)X/DMAP systems, as shown in Scheme 1. This mechanism suggests the preliminary equilibrium established between mono-DMAP adduct (**B**) and six-coordinated complex cation (**C**) with binding two DMAP molecules, which is affected by the competitive binding of epoxide to form (**D**) and (**E**). It should be

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[20] Darensbourg, D. J.; Moncada, A. I.; Choi, W.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2008**, *130*, 6523–6533.

emphasized that the structure of mono-DMAP adduct (**B**) in Scheme 1 represents not only *trans* coordination mode, but also *cis* mode of DMAP to the axial X anion. The striking difference in activity of SalanCr(III)X and SalenCr(III)X in the presence of DMAP cocatalyst should be ascribed to the differences in the nature of these chromium complexes, as well as coordination stability of DMAP to chromium ion. A prolonged initiation time for binary SalenCrX/DMAP catalyst systems predominantly originates from the difficult dissociation of DMAP from (**C**) to form mono-DMAP coordinated chromium complex (**B**) or (**E**), the real active species. Recently, Rieger and co-workers have reported a mechanistic understanding of the formation of polycarbonates from aliphatic epoxides and $CO_2$ copolymerization with chromium(III) and aluminum(III) metal-Salen complexes by a DFT theoretical calculation method, in which they proposed the propagating polymer chains easily dissociating from the metal center during the copolymerization.[21] High cocatalyst loading resulting in relative low molecular weight of the resulted polymer provides evidence of the chain transfer of the propagating polymer species. Although few study focused on the initiator role of DMAP during the copolymerization, they all suggested that mono DMAP-SalenCrX complex originated from the coordination of the Lewis base to the central metal ion *trans* to the axial X anion was real active species. Our mechanistic suggestion for the initiation process also is in agreement with this opinion.

As compared to the high activity of the binary SalanCr(III)X/DMAP catalyst system, the relative low copolymerization rate for the binary SalenCr(III)X/DMAP system should arise from the high Lewis acidity of the central metal ion, and thereby hinder the dissociation of the propagating polymer chains from the metal center, as well as the competitive binding of free DMAP against epoxides. As distinguished from the nature of SalenCrX, the presence of $sp^3$-hydridized amino donors and their *N*,*N*′-disubstituted groups in SalanCrX complexes not only effectively reduce the electrophilicity of the central metal ion,[22] but also benefit the formation of mono-DMAP coordinated chromium complex (**B**) rather than six-coordinated complex ions concerning two DMAP molecules (**C**). The mechanism also suggests that both DMAP and the nucleophilic X anion play an initiator role during the copolymerization process. The competitive binding of free DMAP and chain transfer caused by trace quantities of water significantly result in the decreases in not only of the catalyst activity but also of the polymer selectivity and its molecular weight.

## Conclusion

The positive ESI-MS spectra of SalenCr(III)X and SalanCr(III)X complexes in the presence of DMAP demonstrated that $[\text{SalenCr}]^+$ cations easily bound two DMAP molecules to form six-coordinated complex ions, while $[\text{SalanCr}]^+$ cations were found to predominantly bind one molecule of DMAP to form five-coordinated complex ions. The remarkable difference in coordination chemistry of DMAP with the two chromium complexes resulted in significant differences in the catalytic activity and induction period for the copolymerization of $CO_2$ and propylene oxide. In the presence of 1 equiv of DMAP, the activity of the chromium Salan complex **2a** was about 30 times that of the previously much-studied chromium-Salen complexes. Continuous determination of propagating polymer species at various times by the ESI-MS method confirmed the initiator role of DMAP in the $CO_2$/epoxides copolymerization, in which the species containing one DMAP molecule may be the real active intermediate to initiate the reaction.

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**Supporting Information Available:** General experimental information, synthesis of various Salan ligands and their chromium complexes, ESI-MS experimental, representative procedure for $CO_2$/epoxide copolymerization, as well as representative $^1H$ NMR and $^{13}C$ NMR spectra of these Salan ligands. This material is available free of charge via the Internet at http://pubs.acs.org.

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