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Kinetic and Mechanistic Investigation of Mononuclear and Flexibly Linked Dinuclear Complexes for Copolymerization of CO_2 and Epoxides

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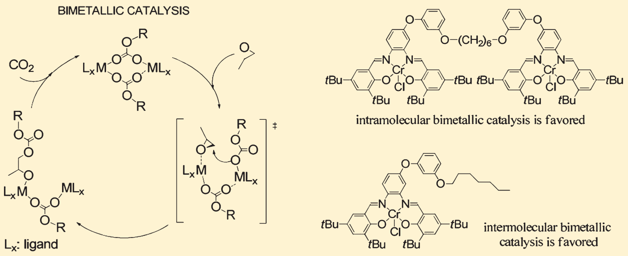
S *Supporting Information*

ABSTRACT: Mono- and dinuclear salphen-type complexes were developed and investigated in CO_2/epoxide copolymerization reactions. Kinetic investigations indicate that the reaction occurs predominately in a bimetallic fashion in the absence of cocatalysts for both mono- and dinuclear complexes. The dinuclear system, therefore, maintains its activity even under highly diluted conditions of [PO]/[M] = 20000 at which the mononuclear system loses its efficiency. The effect of the nature and amount of added cocatalyst on catalytic performance was investigated as well, indicating a binary propagation mechanism both in mononuclear and dinuclear systems in the presence of cocatalysts.



INTRODUCTION

Polymers belong to the chemical products that are widely dependent on the constant supply of crude oil sources. As those will perish in a foreseeable future, the interest in alternative and renewable sources is increasingly gathering the focus of global research activities.[1−4] The greenhouse gas CO_2 is released in many combustion processes and constantly generated, thereby potentially impacting our atmosphere.[5−8] Utilization of CO_2 as C_1-feedstock for copolymerization reactions, e.g., with epoxides would help to deliver high-value polymeric products by partly utilizing this renewable source.[9−12] Since the initial discovery by Inoue et al. in 1969,[13] innumerable works on different homogeneous and heterogeneous catalyst systems have been conducted. Nevertheless, the progress in improvement of catalysts for CO_2/epoxide copolymerizations was rather slow. The generally low catalytic activities and undesired side products like cyclic carbonate or high contents of ether linkages in the polymer were reported as the main drawbacks of many systems (Scheme 1).

Noticeably improved results in copolymerization were achieved only recently.[14−16] Even though the advances made in this field of chemistry to the present, the underlying mechanisms have been rather speculatively discussed and clear evidence for the occurring processes from a mechanistic point of view are still missing.

Most recent publications consider homogeneous systems to polymerize in a cooperative (bimetallic or binary) pathway. This behavior has extensively been summarized in several recent reviews.[17−19] The bimetallic reaction pathway involves two metal complexes and an interaction of two active sites (Scheme 2). The copolymerization proceeds by two iteratively alternating reactions: (i) CO_2 insertion into a metal−alkoxide bond; (ii) nucleophilic attack of a precoordinated epoxide by a carbonate.

In a previous theoretical study, we predicted chain growth to take place via the attack of the metal-bound alkyl carbonate on a metal-coordinated epoxide.[20]

Such a bimolecular process has also been observed by Jacobsen et al. for the asymmetric ring-opening of epoxides.[21−23] Also others have reported a bimetallic initiation, which to their believe is followed by a monometallic propagation step.[24−27] β-Diiminate (BDI) complexes have been shown to be most active in their dimeric state as well.[28−30] However, the hugest advance in terms of activity has been achieved with functionalized Co−salen-type complexes.[16,31−33] For this reason, the interest in new catalysts based on the related ligands is especially high. The corresponding dinuclear complexes have particularly attracted the attention, as these systems help to elucidate the underlying copolymerization mechanisms and improve catalyst efficiency and selectivity. A set of well-defined, rigid and semirigid dinuclear complexes has been designed and applied in CO_2/epoxide copolymerization reactions in the recent years.[34−42]

Other systems are based on the flexibly linked salen-type complexes developed by Jacobsen et al.,[21−23] which were further

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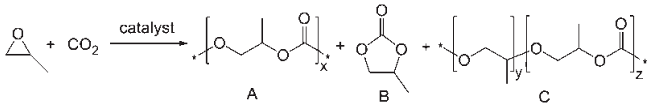
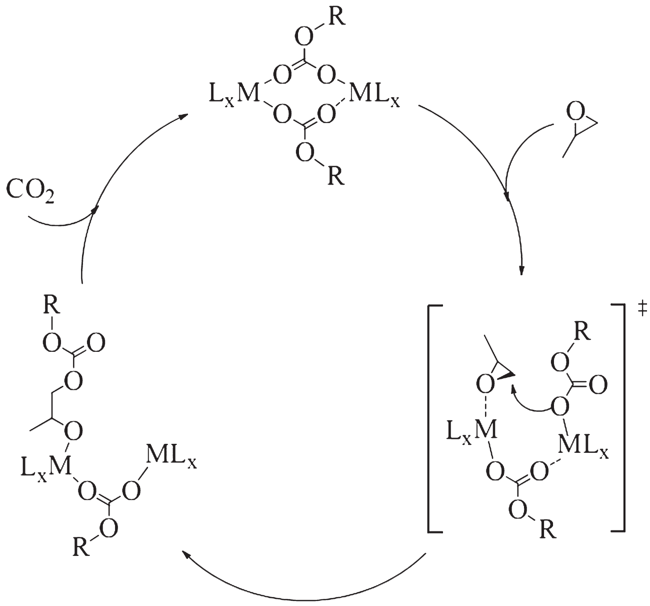
Scheme 1. Copolymerization of CO_2 and Propylene Oxide with Formation of the Polypropylene Carbonate PPC (A) and Undesired Side-Products Like Cyclic Carbonate cPC (B) and Alternating Copolymer with Excess of Ether Linkages (C)



Scheme 2. Bimetallic Catalytic Mechanism for CO_2/PO Copolymerization



investigated by Nozaki et al. in 2010.[43] We have recently reported a new synthetic strategy, which allows an easy modular design of flexibly linked dinuclear salphen-type species.[44]

In this work we report on an extended investigation of copolymerization reaction and kinetics using the mononuclear complex **1** as well as the flexibly linked dinuclear complex **2** (Figure 1).

The detailed kinetic investigations of the copolymerization with these two complexes give support for a catalysis in a bimetallic fashion. In case of the mononuclear system **1**, two metal complexes need to come spatially close for the propagation step to occur. This is evident from the concentration dependence of the activity of the mononuclear catalyst. The dinuclear system **2** introduces both metal sites in one ligand system and therefore maintains its activity even under highly diluted conditions of [PO]/[Cr-center] = 20000, at which **1** is completely inefficient.

The effect of the nature and amount of added cocatalyst on catalytic performance was also investigated, indicating a monometallic propagation mechanism both in mononuclear and dinuclear systems in the presence of cocatalysts. In general, the important role of bifunctional catalysis in the copolymerization of epoxides and CO_2 was demonstrated.

■ EXPERIMENTAL SECTION

Methods and Materials. All manipulations were carried out using a double manifold Schlenk vacuum line under an argon atmosphere or an argon-filled glovebox unless otherwise stated. Propylene oxide was freshly distilled from CaH_2 before use. CO_2 of purity grade 4.5 was purchased from Westfalen AG and was applied in all experiments without additional purification. Solvents were purified by an MBraun Manual Solvent Purification System packed with Alcoa F200 activated alumina desiccant. The complexes **1** and **2** were synthesized according to our previously reported procedure.[44]

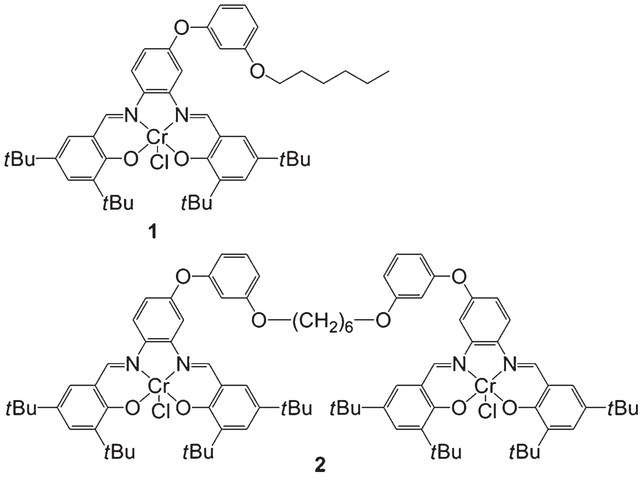


Figure 1. Mononuclear and dinuclear salphen-type complexes.

Kinetic Studies. Copolymerization experiments with *in situ* monitoring were performed using a React-IR/MultiMax four-autoclave system (Mettler-Toledo). Here, 50 mL steel autoclaves equipped with a diamond window, a mechanic stirring and a heating device were thoroughly washed and heated under vacuum to 130 °C for several hours prior to use. A corresponding amount of catalyst in 5 mL of CH_2Cl_2 in a vial equipped with an injection septum was mixed with 5 mL of PO and rapidly transferred into the reactor using a syringe. The reactor was pressurized to 35 bar of CO_2 for 2 min, sealed, and heated to 60 °C, while the pressure was rising to 40 bar. The course of copolymerization at various catalyst concentrations was followed *in situ* by monitoring the growth of the specific carbonyl-band of polypropylene carbonate (PPC) as well as of cyclic propylene carbonate (cPC) at 1753 and 1812 cm^{-1}, respectively. The relative polymerization reaction rates r_{obs}, were obtained directly from the change of the PPC signal intensity as slope of the signal dependency on time.

Copolymerization Procedure. All standard copolymerization experiments were performed in 100 mL steel autoclaves equipped with glass inlay, magnetic stirring, and oil bath heating. The autoclaves were heated to 130 °C and dried in an oven under vacuum prior to use.

The catalyst and cocatalyst in the desired ratio were transferred into an autoclave, followed by addition of the calculated amounts of PO. The reactor was closed, prepressurized with CO_2 and heated to 60 °C or to 80 °C, respectively. After reaching the set temperature, the pressure in the autoclave was adjusted to the desired value and heating was continued for 2 or 24 h. After cooling down the reaction vessel to 0 °C, CO_2 was slowly released. ^1H NMR measurement was done from the crude reaction mixture to determine the ratio of cPC and polymeric products. Protons adjacent to carbonate linkages in poly(propylene carbonate) show a signal at 4.8−5.1 ppm and the content of polyether linkages was verified by the signals at 3.4−3.8 ppm.

The viscous reaction mixture was diluted with CH_2Cl_2 and transferred to acidified (HCl) methanol. Immediately, polycarbonate precipitated. The mixture was then stirred for several hours and isolated polycarbonate was dried under vacuum at 60 °C. Polycarbonates were analyzed by GPC against polystyrene standards in THF or in $CHCl_3$.

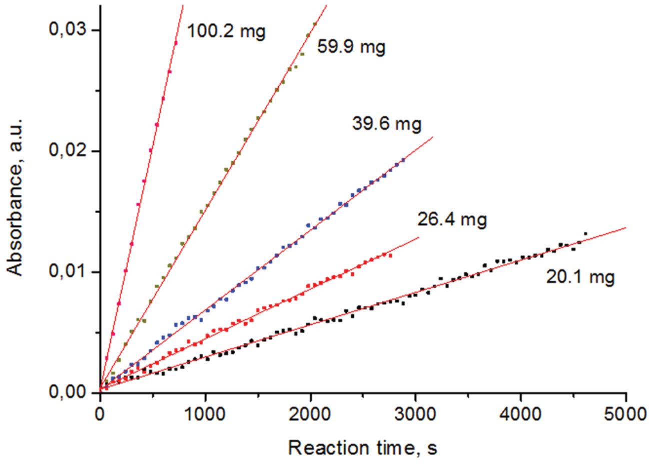


Figure 2. Determination of the copolymerization rate r_{obs} as a change of absorbance at 1753 cm^{-1} with time at different loadings of catalyst **1**.

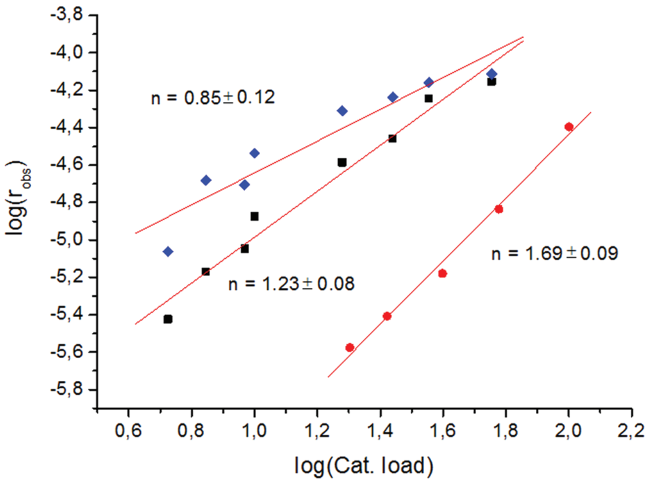


Figure 3. Determination of catalyst order in copolymerization reaction: catalyst **1** (red circles) and catalyst **2** at the heterogeneous stage (blue rhombs) and at the homogeneous stage (black squares).

RESULTS AND DISCUSSION

General Kinetic Considerations in CO_2/Epoxide Copolymerization. The catalyst reaction order can deliver additional information on the mechanism of the copolymerization. Over the initial reaction period, both epoxide and CO_2 concentrations can be considered as constant and the reaction rate can be formally expressed as follows:

$$r_{obs'} = k_{eff}[\text{catalyst}]^n \tag{1}$$

The logarithmic plot of r against catalyst concentration gives the catalyst reaction order as a slope *n*:

$$\ln(r_{obs'}) = n \ln([\text{catalyst}]) + \ln(k_{eff}) \tag{2}$$

For a mononuclear catalyst, which copolymerizes in a bimetallic fashion, a reaction order $n = 2$ can be expected. For a dinuclear catalyst, where the two interacting metal sites are incorporated into one ligand framework, a reaction order of 1 or higher is predicted. Formally, this value is dependent on a ratio of intramolecular and intermolecular reaction rate constants in case of a bimetallic mechanism.[45,46]

Kinetic Investigations with Mononuclear and Dinuclear Catalysts. Our recent experiments on CO_2/PO copolymerization using other catalytic systems have shown that addition of 50% v/v CH_2Cl_2 to the system insures its complete homogeneity. In this respect, here we have applied the same conditions using catalysts **1** and **2**. It was found that in case of monomeric catalyst the rate of formation of cyclic propylene carbonate relative to polymer formation becomes noticeable at prolonged reaction time. However, during the first hour nearly no cPC is formed. Subsequent growth of the cPC concentration is proportional to the reaction time in power of two (see Figure S1 in Supporting Information), whereas the polymer signal growth is decelerating with time. In this respect, the calculations of copolymerization rate for catalyst **1** were performed using the copolymer signal growth within the first hour of reaction after temperature stabilization as shown in Figure 2.

According to our estimation (from the calibration of the PPC signal in CH_2Cl_2), in the experiment with the highest catalyst concentration the calculation of reaction rate was performed over at least six insertions of CO_2 per catalyst molecule, and in all other experiments this value was higher. As shown in Figure 3, the logarithmic dependency of reaction rate on catalyst loading, which is proportional to catalyst concentration since all experiments were performed under equal conditions, gave the reaction order of 1.69 on catalyst **1**. The value is demonstrating a considerable contribution of the bimetallic processes in course of the reaction along with the monometallic rate-determining steps.

The situation is quite different in case of catalyst **2**. It was surprising to find out that it is insoluble in CH_2Cl_2 as well as in the mixture with PO under normal conditions. This is reflected, in general, in three stages of copolymerization reaction behavior as was found by the IR monitoring, namely initiation, heterogeneous reaction and homogeneous copolymerization (Figure 4). After pressurizing the mixture with CO_2 at high catalyst loadings, the copolymerization occurred immediately. Stopping the reaction after first 20 min showed that a considerable homogenization of the mixture occurred, although some polymer covered particles of catalyst could be filtered off. The longer reaction time of ca. 40 min resulted in optically homogeneous reaction mixture. At low catalyst loadings, the residual water in the copolymerization system starts to play a role, which is reflected in the initiation period. Addition of water to the system increases the initiation time, but shows no influence on the rates of copolymerization and cPC formation. For example, copolymerization using 10 mg of catalyst **2** in presence of additional 10 equiv of water has shown an initiation period of ca. 1 h. The same effect was found later for the copolymerization with catalyst **1**. Ring-opening of epoxide by water with the formation of propylene glycol takes place first, which most probably acts as a chain-transfer reagent in the subsequent copolymerization. Followed by initiation, the copolymerization starts rapidly, and in ca. 1 h (30−100 insertions of CO_2 per metal center) there is a noticeable damping in the reaction rate, after which the copolymerization rate remains nearly constant with only slow decay. The period of fast copolymerization is connected with the heterogeneous occurrence of the process. This is reflected first of all in a very poor linear fit of the logarithmic dependence of the reaction rate vs. catalyst loading during this period, as well as in an unusually low value of the slope for this linear fit (ca. 0.8, see Figure 3 and Figure S2 in the Supporting

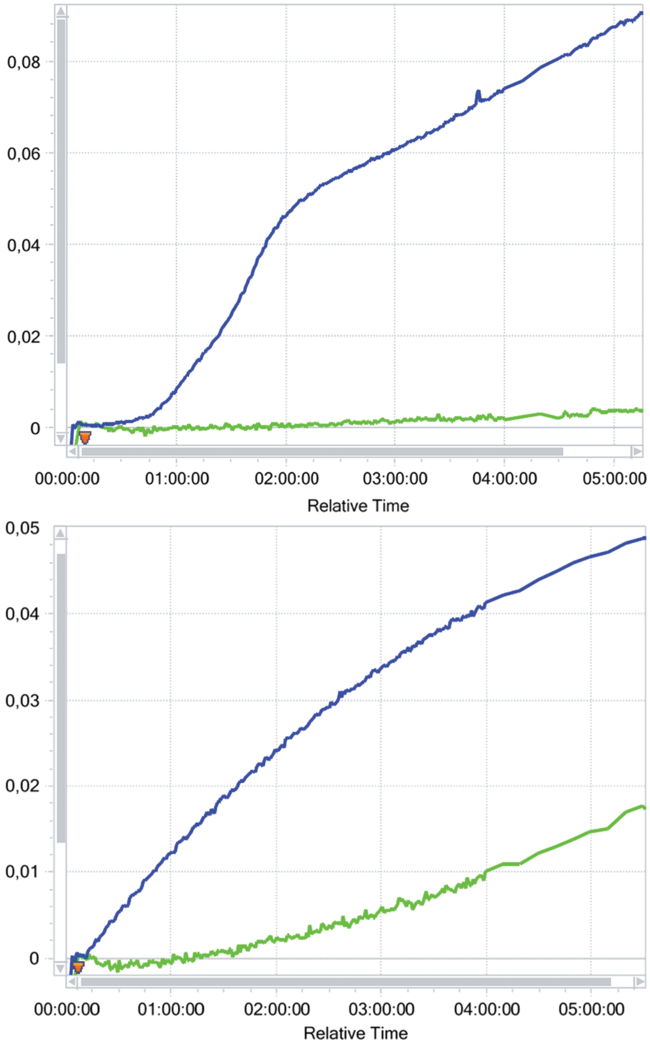


Figure 4. FT-IR-signal traces of PPC (blue) and cPC (green) during the PO/CO_2 copolymerization in PO/CH_2Cl_2 media. Top: 5.3 mg loading of catalyst **2** shows an initiation period due to the residual water, followed by the heterogeneous and homogeneous copolymerization stages. Bottom: 26.4 mg loading of catalyst **1**.

Information). Also, we did not observe such a period in case of mononuclear catalyst, which was completely soluble in CH_2Cl_2 (see Figure 4). The heterogeneous stage of reaction is followed by a homogeneous one, for which a better correlation of copolymerization rate vs. catalyst loading at comparable conversions has been observed (Figure 3, Figure S3, and Table S1 in Supporting Information).

A lower value (ca. 1.2) of the reaction order on catalyst **2** compared to catalyst **1** clearly indicates the occurrence of intramolecular catalysis in the dinuclear system accompanied by the intermolecular bimetallic catalysis. The occurrence of monometallic processes cannot be excluded as well. However, the higher activity of the dimeric catalyst **2** in comparison to mononuclear catalyst indicates the importance of dinuclearity for the catalytic system in this copolymerization reaction. This is also congruent with the higher activity of the dimeric complex during the heterogeneous stage of reaction compared to homogeneous, where a higher local concentration of chromium centers is maintained.

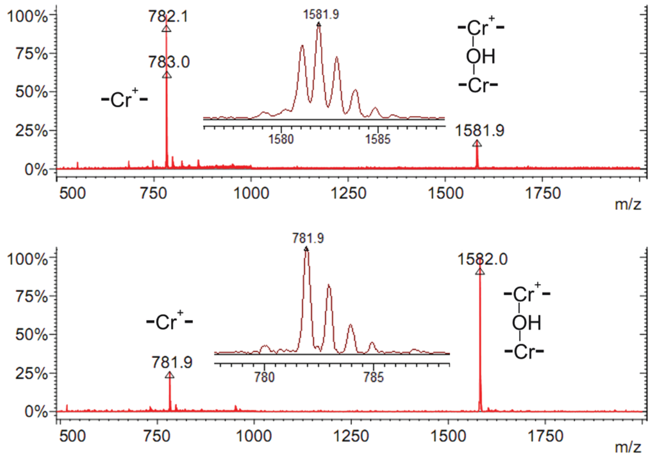


Figure 5. ESI−MS spectra of catalyst **1** as synthesized (top), and after treatment with KOH (bottom). Peak at 1582 m/z belongs to a μ-hydroxo bridged species.

The initial insolubility of the dimeric catalyst **2** can be explained by the formation of coordination polymer structures due to the μ-bridging via axial ligands such as Cl^-, OH^-, or water, which is a known phenomenon for chromium complexes. In case of monometallic salen or salphen complexes, this leads to μ-bridged dimers, which still remain soluble. Indeed, crystal structures of such complexes have been published,[47] and ESI-MS investigations on catalyst **1** as well as on other analogous complexes support an easy formation of μ-hydroxo dimers under ESI conditions (Figure 5 and Figure S4 in Supporting Information). Under CO_2 pressure in course of the copolymerization reaction, the dissolution of coordination polymer chains of **2** takes place.

Interestingly, the ratio of cPC to PPC formed in the reaction in presence of catalyst **2** is noticeably lower than in case of catalyst **1**. Analysis of experimental data reveals that for monomeric catalyst the absolute amount of the formed cPC for the same reaction time was higher for higher catalyst loadings, whereas the PPC/cPC ratio was not strongly affected for the short reaction time. Moreover, practically the same loadings of monomeric and dimeric catalysts produced nearly the same amounts of cPC for the same reaction period. Because of the substantially higher activity of the dimeric catalyst in the copolymerization reaction, this accounts for the high PPC/cPC ratio observed for the catalyst **2**. These findings fit relatively well into the backbiting scheme for cPC formation, as explained below.

Copolymerization Experiments without Online Monitoring of the Reaction. For control purposes, the effect of catalyst concentration and reaction time onto activity was also studied by routine copolymerization experiments without online monitoring in neat PO.

Mononuclear catalyst **1** at a 1:2000 ratio to PO has an average activity of 74 h^{-1} in CO_2/epoxide copolymerization at 60 °C and 40 bar pressure for 2 h (Table 1, entry 1). Extending the reaction period leads to a slight but systematic decrease of the average activity (Table 1, entries 1−5), which drops to 61 h^{-1} after a reaction time of 24 h.

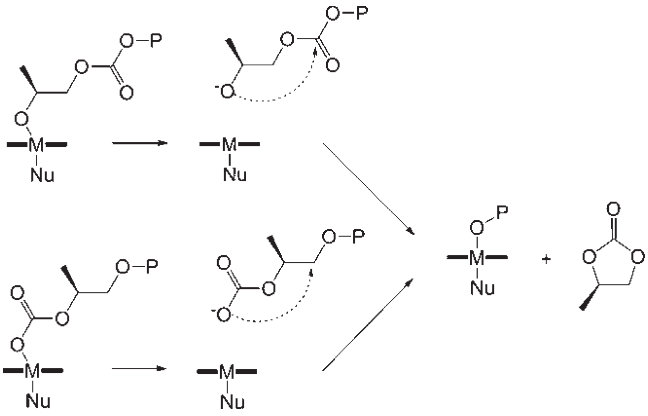
Diluting the system by a factor of 10 significantly reduces the catalytic efficiency of **1** (Table 1, entries 6 and 7). A polymerization attempt for 2 h did not yield any product. Prolonging the reaction time to 24 h gave a small quantity of PPC with a comparatively high amount (17%) of cPC as side-product.

Table 1. Effect of Catalyst Concentration and Reaction Time on the Copolymerization of PO and CO_2 with Mononuclear and Dinuclear Catalysts[a]

entry	catal	PO/Cr ratio	time (h)	T (°C)	p (bar)	TON[b]	TOF[c] (h^{-1})	PPC[d] (%)	cPC[d] (mol %)	M_n[e] (kg/mol)	M_w/M_n[e]
1	**1**	2000	2	60	40	148	74	73	<1	7	1.2
2	**1**	2000	4	60	40	284	71	74	<1	13	1.2
3	**1**	2000	8	60	40	547	68	69	<1	21	1.3
4	**1**	2000	16	60	40	1045	65	65	<1	24	1.5
5	**1**	2000	24	60	40	1473	61	51	3	32	2.0
6	**1**	20000	2	60	40	0	0	/	/	/	/
7	**1**	20000	24	60	40	176	7	75	17	4	2.0
8	**2**	2000	2	60	40	102	51	59	<1	8	1.5
9	**2**	2000	24	60	40	1177	49	41	<1	22	1.8
10	**2**	20000	2	60	40	182	91	43	<1	2	3.5
11	**2**	20000	24	60	40	1975	82	40	<1	15	2.2

[a] Polymerization conditions: propylene oxide 5 mL of neat propylene oxide. [b] Turnover number in mol of polymer per mol of Cr. [c] Turnover frequency in mol of polymer per mol of Cr per hour. [d] Estimated by ^1H NMR spectroscopy. PPC content is expressed in percents of carbonate linkages in the obtained polymer; cPC: cyclic carbonate content in molar percent of the consumed PO. [e] Determined by GPC, calibrated with polystyrene standard in THF.

Scheme 3. Release of Coordinated Polymer Chain and Backbiting Leading to the Formation of Cyclic Carbonate as Side-Product[20]



These observations are in trend with the results of kinetic studies in PO/CH_2Cl_2 with online FT-IR-monitoring and correlate well with the existence of the bimetallic mechanism. Indeed, besides the strong concentration dependence of the reaction rate, the effect of the catalyst concentration onto the ratio of formed products is very characteristic.

The formation of cyclic carbonate can be attributed to a backbiting reaction (Scheme 3). Here, the anionic chain end is released from the metal center in an equilibrium process, thus rendering it able to split off a cPC molecule via intramolecular nucleophilic attack.[20]

In case of a bimetallic polymerization mechanism, lower loadings of the mononuclear catalyst decrease the polymerization rate proportionally to the second order of the catalyst concentration, whereas the backbiting reaction rate remains directly proportional to the concentration of the dissociated polymer chain, which is reflected in a growth of cPC/PPC ratio. In addition, the dissociation equilibrium at the catalytic center is shifting toward dissociation products upon dilution, thus again promoting the backbiting reactions. For example, in equilibrium with small dissociation constants, the degree of dissociation increases approximately 3 times upon 10 time dilution.

As can be seen from Table 1, besides the decrease in activity of catalyst **1** with time, the PPO/PPC ratio in the resulting polymer becomes higher for longer reaction times. Simultaneously, very long polymerization time leads to the formation of detectable amount of cPC. These effects can be attributed to various factors such as the lowering of the CO_2 concentration in the reaction medium, which undergoes alteration of composition, viscosity and polarity upon formation of the polymer, thus rendering a PO insertion and backbiting more favorable. At 10 times lower catalyst concentration, the overall change of the reaction medium remains small and the composition of the polymer after 24 h reaction time is comparable to that of the polymer obtained after 2 h of copolymerization at high catalyst loading.

Accordingly, the composition of the polymer obtained with **2** in 24 h is close to the composition of the polymer produced in 2 h at low catalyst concentration (Table 1, entries 10 and 11), whereas at high catalyst loading the longer reaction times (higher conversions) clearly increase the PPO/PPC ratio.

Variation of CO_2 pressure in 2 h polymerization experiments with catalyst **2** has shown a marginal effect on the copolymer composition (see Table 2). In general, the obtained values indicate a quite poor selectivity of the studied catalysts toward the formation of alternating copolymer (see Scheme 1).[43]

However, in contrast to catalyst **1**, dilution of system **2** leads to an increase of its efficiency in terms of TOF (Table 1, entries 8 and 10, respectively 9 and 11), corroborating the necessity of joining two catalytic metal sites into one ligand framework and supporting once again the proposed bimetallic catalysis mechanism.

Molecular Weight Analysis of the Obtained Copolymers. The polymer molecular weights obtained with complex **1** in a 2000-fold excess of neat PO are rising with reaction time and reach M_n of 32 kg/mol after 24 h (Table 1, entry 5). The effect of reaction time onto M_n in polymerizations with catalyst **2** is similar (Table 1, entries 8 and 9 and then 10 and 11, respectively).

It is worth to note that polymers obtained with a dimeric catalyst feature a higher PPO/PPC ratio. The dimerization of

Table 2. Effect of CO_2 Pressure and Temperature on the Efficiency of Dinuclear Complex[a]

entry	catal	PO/Cr ratio	time (h)	T (°C)	p (bar)	TON[b]	TOF[c] (h^{-1})	PPC[d] (%)	cPC[d] (mol %)	M_n[e] (kg/mol)	M_w/M_n[e]
1	**2**	2000	2	60	20	73	37	56	<1	3	1.5
2	**2**	2000	2	60	40	102	51	59	<1	8	1.5
3	**2**	2000	2	80	20	80	40	50	<1	3	1.6
4	**2**	2000	2	80	40	121	60	56	<1	11	1.6

[a] Polymerization conditions: 5 mL of neat propylene oxide. [b] Turnover number in mol polymer per mol of Cr. [c] Turnover frequency in mol polymer per mol of Cr per hour. [d] Estimated by ^1H NMR spectroscopy. PPC content is expressed in percents of carbonate linkages in the obtained polymer; cPC: cyclic carbonate content. [e] Determined by GPC, calibrated with polystyrene standard in THF.

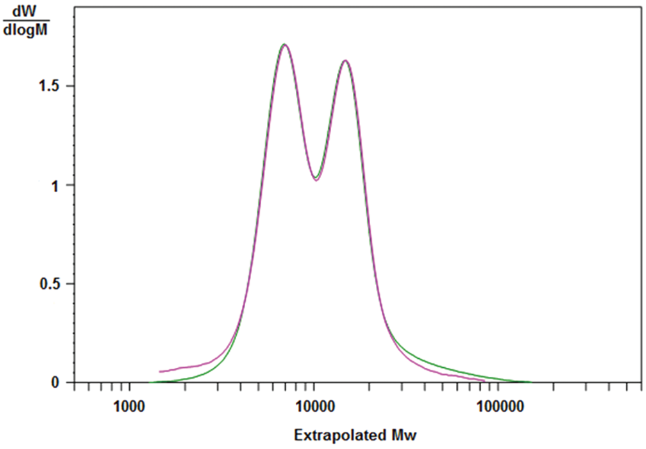
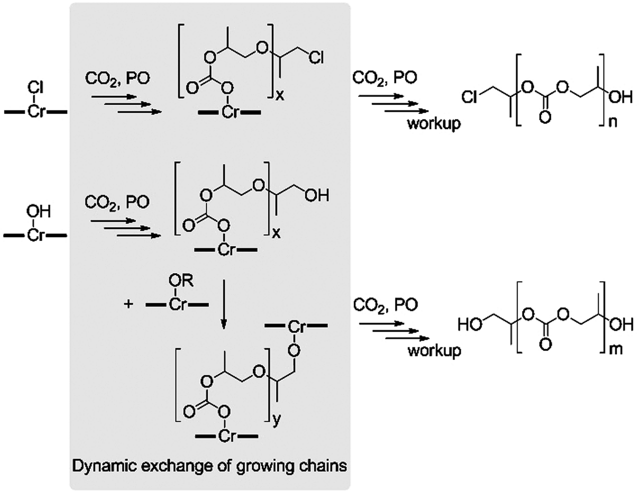


Figure 6. Molecular weight distribution of polycarbonate: crude (pink) and treated with CH_3COOH as described (green).

Scheme 4. Possible Generic Pathway for the Bimodal Copolymerization *via* Hydroxy Catalyst Species ($m \approx 2n$)[a]



[a] The sixth ligand is omitted for clarity. OR = OH or alkoxide of the growing polymer chain.

salphen catalyst renders the homopolymerization of PO more favorable in comparison to the alternated copolymerization with CO_2. This seems to be a consequence of the bimetallic catalytic mechanism of PO homopolymerization, reported recently for salen and salphen complexes.[43,48] A rise of the reaction temperature favors homopolymerization of PO as well (see Table 2). Optimal conditions allowing to minimize the PPO/PPC ratio in polymers and at the same time to maintain the reasonable activity of the dinuclear catalyst seem to be realized at a reaction temperature of 60 °C and a CO_2 pressure of 40 bar.

Interestingly, the polymers obtained both with catalyst **1** and **2** in neat PO show bimodality in their molecular mass distribution in GPC elugrams, which is pronounced in most cases. Such a bimodal distribution is often observed with similar catalysts in this reaction. The observed peak molecular mass of low-M_w fractions corresponds approximately to a half of that of the high-M_w fractions of the polymer batch. After a major part of catalyst was removed from the polymer by treatment with acetic acid in THF and precipitation with pentane, the GPC-characteristics of polymer remained absolutely identical with the untreated material (see Figure 6).

This fact excludes the possibility of bridging of two polymer chains via catalyst molecules under conditions of GPC analysis. It can rather be explained as a result of the residual water in the system in course of copolymerization, originating either from PO or, more probably, from the catalyst as aqua-chloro complex. During the initiation (the first ring-opening reaction of PO), it leads to the generation of two species, namely chloropropanol and propylene glycol. The latter supports the copolymerization by the chain growth at both chain ends, whereas the first one gives the polymer chain growing only at one chain end. Taking into account a relatively low copolymerization rate of PO and CO_2 in the studied systems, the dynamic nature of this process with all its complex network of axial ligand coordination and dissociation reactions averages the polymer growth rate at each chain end. Thus, a double molecular weight of one polymer fraction compared to the other can be obtained (Scheme 4).[49]

Analysis of the copolymers obtained during the IR-online-monitored experiments in PO/CH_2Cl_2 system also shows bimodality, but only at high catalyst loadings and with a low-molecular-weight fraction appearing only as a shoulder (see Figure S5 in Supporting Information). Low catalyst loadings as well as addition of water to the system lead to a narrow monomodal distribution of polymer molecular weight. Simultaneously, the number of generated polymer chains per catalyst molecule was noticeably higher than at high catalyst loadings. Therefore, it is expected that under such conditions, the major polymer fraction was initiated by water.

On the other hand, we were anticipating that the existence of catalysts as a mixture of chloro and hydroxo or μ-oxo species could also be a reason for the bimodal distribution. That is, the chloro species would be able to generate the polymer chains, which can grow only at one chain end, whereas the hydroxo and μ-oxo species could initiate the polymer chains capable of growing at both ends, as shown in Scheme 4. Indeed, according to EDX analysis, we could prepare the chloride-free complexes of

Table 3. Effect of Cocatalyst Nature and Cocatalyst Ratio on the Copolymerization of PO and CO_2[a]

entry	catal	cocat[b] (catal:cocat)	PO/Cr ratio	time (h)	T (°C)	p (bar)	TON[c]	TOF[d] (h^{-1})	PPC[e] (%)	cPC[e] (mol %)	M_n[f] (kg/mol)	M_w/M_n[f]
1	**2**	*N*-MeIm (1:0.5)	2000	2	60	40	3	2	86	<1	na	na
2	**2**	DMAP (1:0.5)	2000	2	60	40	16	8	75	<1	na	na
3	**2**	DMAP (1:5)	2000	2	60	40	8	4	79	<1	na	na
4	**2**	TBAB (1:0.5)	2000	2	60	40	91	46	85	6	7	2.2
5	**2**	(PPN)Cl (1:0.5)	2000	2	60	40	164	82	83	7	4	2.2
6	**2**	(PPN)Cl (1:0.5)	20.000	24	60	40	1321	55	90	10	15	1.8
7	**2**	(PPN)Cl (1:1)	20.000	24	60	40	1456	61	/	100	/	/
8	**1**	(PPN)Cl (1:0.5)	2000	2	60	40	170	85	92	27	6	1.7
9	**1**	(PPN)Cl (1:0.5)	20.000	24	60	40	1640	68	93	31	13	1.8
10	**1**	(PPN)Cl (1:1)	20.000	24	60	40	1604	67	/	100	/	/

[a] Polymerization conditions: 5 mL of neat propylene oxide. [b] Equivalent to Cr. [c] Turnover number in mol polymer per mol of Cr. [d] Turnover frequency in mol polymer per mol of Cr per hour. [e] Estimated by ^1H NMR spectroscopy. PPC content is expressed in percents of carbonate linkages in the obtained polymer; cPC: cyclic carbonate content. [f] Determined by GPC, calibrated with polystyrene standard compound in THF.

catalyst **1** and **2** by the treatment with KOH solution, which have shown practically the same activity in the copolymerization reaction in PO/CH_2Cl_2 medium as their chloro-precursors.

However, we believe that the most common reason for the bimodal distributions of polymer molecular weight is the residual water in the copolymerization system. This would also explain the sometimes incongruent molecular weights and weight distributions of polymers from different polymerization batches, which make the exact analysis of polymer growth kinetics difficult.

Influence of Cocatalyst Nature and Ratio on CO_2/Epoxide Copolymerization. It has widely been discussed in literature that addition of cocatalysts to salen-type catalysts can strongly influence their efficiency.[24,50−56]

However, the nature and the amount of cocatalyst added have to be carefully chosen. At first, ionic and neutral cocatalysts must be differentiated. Neutral cocatalysts such as DMAP (4-dimethylaminopyridine) and *N*-MeIm (*N*-methylimidazole) may weakly coordinate to the metal center.

Thus, they promote the dissociation of anionic ligand from the metal, which is required for the initiation of polymerization. Directly added ionic species such as Cl^- or Br^- with bulky counterions are good initiators and are able to open a precoordinated epoxide by nucleophilic attack.

However, ionic species are also able to strongly coordinate to the metal center, therefore concurring with the monomer addition or polymer coordination to the metal site. DFT-calculations in a preview report give a hint that the backbiting can even happen on coordinated carbonate chain ends.[20] When a polymer chain is released from the coordination sphere of the metal, backbiting can occur, followed by the cleavage of polymer to cPC. In this respect, the effects of the cocatalyst nature and of the cocatalyst/catalyst ratio onto polymerization results are pronounced. To verify these considerations, two different ionic and neutral cocatalysts were tested for copolymerization with the dinuclear catalyst.

The two neutral cocatalysts *N*-MeIm and DMAP render the dinuclear system almost inactive (Table 3, entries 1 and 2). Probably the neutral species competitively coordinate to the metal site and thereby inhibit monomer addition by simultaneously being incapable of ring-opening an epoxide and initiating copolymerization. Darensbourg et al. observed a similar, but less pronounced behavior for mononuclear complexes with phosphines as cocatalysts in amounts beyond 1 equiv.[57] As expected, addition of a multiple equivalent per catalyst did not improve the efficiency of the catalyst/cocatalyst system (Table 3, entry 3).

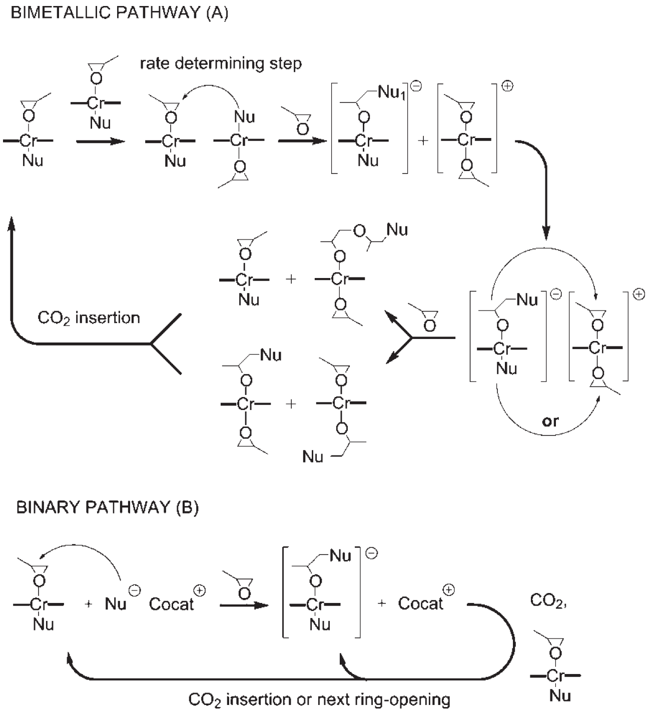
Comparison of the two ionic cocatalysts TBAB (tetrabutylammonium bromide) and (PPN)Cl (bis(triphenylphosphine)-iminium chloride) shows that the anionic halogenids alter the system selectivity (Table 3, entries 4−6), with (PPN)Cl being the most efficient cocatalyst. The amount of added cocatalyst is of outmost importance to the product formation. Addition of half an equivalent cocatalyst per Cr-center leads to formation of polypropylene carbonate with high carbonate content for both catalyst systems investigated (Table 3, entries 4−6 for complex **2**, entries 8 and 9 for complex **1**).

Addition of one equivalent ionic cocatalyst (PPN)Cl per Cr-center noticeably increases the TON and TOF values for low loadings of catalyst **1** (Table 3, entry 10). However, the activity at high loadings of catalyst **1** as well as of catalyst **2** at any concentration is not much affected. At a 1:1 ratio of catalyst to cocatalyst, cPC is formed as sole product (Table 3, entries 7 and 10). Apparently, the equilibrium between the coordinated and dissociated growing polymer chain end is effectively shifted to the uncoordinated species and the backbiting reaction is dominating under such conditions.

Addition of 0.5 equiv of (PPN)Cl per Cr center allows to improve the product selectivity without loss of catalyst activity. The selectivity toward copolymer under such conditions is higher for the dimeric catalyst system **2**, with an amount of formed cPC of about 10%. The cocatalytic effect of TBAB onto activity of **2** is not that obvious, therefore the system in combination with this additive was not investigated in detail. However, the PO/CO_2 ratio in copolymer is drastically improved upon addition of both TBAB and (PPN)Cl cocatalysts from almost 2.0 (Table 2) to 1.1−1.3 (Table 3).

Apparently, upon addition of cocatalysts, the copolymerization mechanism is optimized toward alternating insertion of PO and CO_2. The bimetallic pathway is exchanged against a binary reaction sequence, where one metal species as well as the PO monomer can interact with an added cocatalyst. In such systems the mononuclear catalyst can even be rendered active at higher dilutions. In other words, salphen-complexes employed solely in the reaction copolymerize via a bimetallic pathway. Upon addition of cocatalysts, the complexes are both able to copolymerize at high dilutions supposedly via a previously reported monometallic pathway or, alternatively, via a binary pathway.[58] A similar

Scheme 5. Bimetallic and Binary Pathways of Copolymerization[a]



[a] Nu = carbonato chain end; Cocat (+) = cation of the cocatalyst.

behavior has also been reported for the related dinuclear and mononuclear salen-structures.[43] This idea was subsequently transferred to new complex structures with anchored cocatalyst groups, which are the most active known to date.[16,31] Despite numerous reports on such effects, their mechanistic background is not completely understood.

Probably, in absence of the cocatalyst the nucleophilicity of the coordinated carbonato chain end is relatively low (neutral complex), thus rendering its nucleophilic attack to open the coordinated epoxide ring as a rate-determining step (Scheme 5A). The polymerization under such conditions proceeds via a complex sequence of reactions including ligand exchange. Addition of the anionic cocatalysts generates an excess of “more active” anionic chains, either coordinated at the chromium center to give an anionic complex, or even as free ionic species, which alters the overall kinetics (Scheme 5B).

CONCLUSIONS

We investigated the copolymerization of PO with CO$_2$ by using flexibly linked dinuclear and mononuclear salphen complexes. Kinetic studies indicate that the reaction occurs predominately *via* a bimetallic mechanism in the absence of cocatalysts for both mono- and dinuclear complexes. The dinuclear system maintains its activity even under highly diluted conditions of [PO]/[M] = 20.000 at which the mononuclear system loses its efficiency. However, the bimetallic and binary pathways need to be distinguished depending on the catalyst/cocatalyst system used. In the presence of cocatalysts, such as onium salts (e.g., (PPN)Cl, TBAB) the mechanism probably shifts to a binary mode (Scheme 5), in which a metal and the added cocatalyst take over the role of the bifunctional pathway. This enables the monomeric catalyst to retain activity also at high dilution.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Growth of the IR signals of polyproylene carbonate and cyclic propylene carbonate with time, calculated relative reaction rates, determination of reaction rates r_{obs} at different loadings of catalysis, formation of μ-hydroxo-bridged species, copolymerization with 30 mg of monomeric hydroxo-catalyst, comparison of polymer molecular weight distributions, dependence of relative reaction rate on loading. This information is available free of charge via Internet at http://pubs.acs.org/.

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