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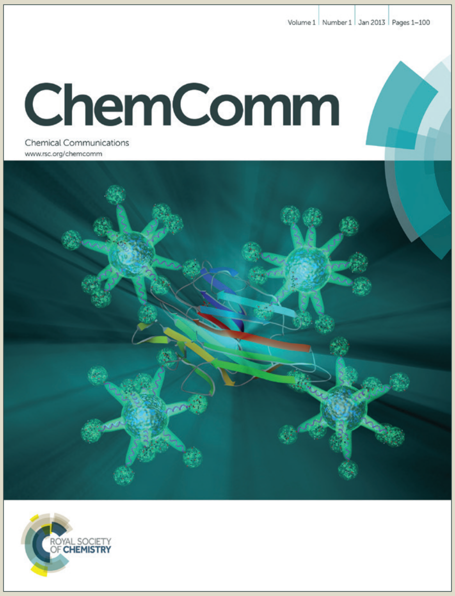

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Journal Name RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Dinuclear Zinc Catalysts with Unprecedented Activities for the Copolymerization of Cyclohexene Oxide and CO_2

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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A variety of new dinuclear zinc catalysts was developed and tested for the copolymerization of cyclohexene oxide and carbon dioxide. Electron-withdrawing groups thereby led to unprecedented activities with turnover frequencies up to 155000 h^{-1}. These are by far the highest polymerization rates ever reported for the copolymerization of cyclohexene oxide and CO_2.

Energy and environmental concerns of products that are widely dependent on the constant supply of crude oil resources have intensified the research on polymeric materials based on renewable resources.[1] One alternative source is CO_2 as an abundant, non-toxic and valuable carbon feedstock for a series of chemical products.[2] Already in 1969 Inoue *et al.* reported the copolymerization of carbon dioxide and propylene oxide to poly(propylene carbonate).[3] Polycarbonates exhibit promising properties as they are biodegradable, highly transparent, UV stable and have a high Young's modulus.[4] Over the last decades a variety of well-defined catalysts systems have been presented for this reaction type.[1,5] However, the development of an economic production process is still hampered by the availability of catalysts that are efficient enough to allow a continuous polymerization process. For commodity applications the catalyst must be active, non-toxic and colorless to remain in the resulting polymer product, which is one of the major prerequisite for such a continuous production. Under these aspects, zinc(II) as catalytically active species has tremendous advantages over other transition metals. It is an economic and ecofriendly metal providing ions that do not lead to colored polymer products. Several zinc-based catalyst systems for the copolymerization of epoxides and CO_2 are already well-known in literature.[4b,5b,6] Though, most of the reported structures are adversely affected by poor solubility and low polymerization activities.[6a,6c-e,7] Great progress was made by Darensbourg *et al*. with monomeric zinc phenoxides[6b,8] and by Coates *et al.* with the synthesis of *β*-diketiminato (BDI) zinc complexes[9]. Kinetic investigations revealed a necessary interaction between two zinc centers for the copolymerization of cyclohexene oxide and CO_2, whereas the epoxide ring opening emerged to be the rate determining step.[6a] Lee *et al*. followed with the synthesis of dinuclear anilido-aldimin zinc catalysts with turnover frequencies (TOF) up to 2860 h^{-1}.[6d,7c] Previous catalyst research in our group with zinc(II)glutarates for the copolymerization of propylene oxide and CO_2 also indicated an interaction between two zinc centers.[10] Continuing our research, we recently succeeded in synthesizing a highly active dinuclear zinc catalyst (Figure 1).[5d]

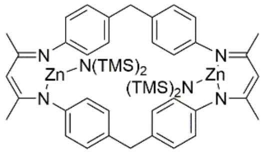

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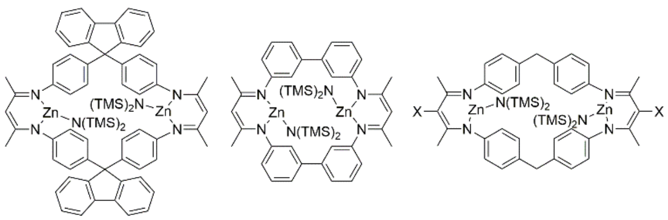
Figure 1. Highly active dinuclear zinc catalyst for cyclohexene oxide/CO_2 copolymerization

This homogeneous system turned out to be the first dinuclear zinc catalyst for the copolymerization of epoxides and CO_2 which exhibits a shift of the rate determining step from epoxide ring-opening to carbon dioxide insertion depending on the applied CO_2 pressure.[5d] This unique behavior is attributed to the flexible bridging units between both metal centers which leads to an acceleration of the epoxide ring-opening step. Therefore, the copolymerization reaction can be accelerated by simply increasing the CO_2 concentration in the reaction system. This zinc system showed the highest polymerization rate ever observed for the copolymerization of CHO and CO_2 (TOF up to 9130 h^{-1}).

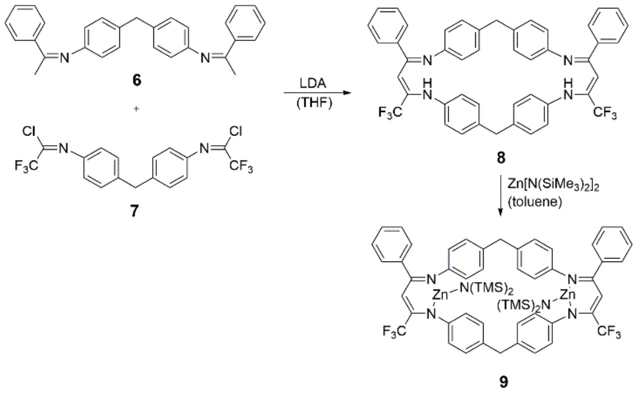
In favor of gaining further insights of the copolymerization reaction, we now focused on complexes with varying steric and electronic properties based on our lead structure. Concerning steric demand, we synthesized complex **2** bearing sterically demanding fluorenyl groups that replace the methylene bridge between the two *β*-diketiminato zinc units (Figure 2). Copolymerization experiments of cyclohexene oxide and carbon dioxide with catalyst **2** revealed drastically reduced activities with a turnover frequency of 830 h^{-1} at 30 bar CO_2 pressure. Reduction of the CO_2 pressure led to a decreased TOF value of 530 h^{-1} (at 10 bar CO_2) (table 1, entry 1). This behavior is in line with previous results for complex **1** as these results indicate a pressure dependent rate law. In our previous publication we reported the necessity of the flexible methylene bridge.[5d] Further copolymerization experiments with complex **3** which contains no bridging units resulted in even more reduced activities.[5d] Our results clearly demonstrate the necessity of an adequate accessibility of the catalytic centers combined with the mentioned flexibility. In doing so additional activation barriers from catalyst rigidity during copolymerization can be avoided and as a result high activities in CHO/CO_2 copolymerization are yielded.



2 **3** **4: X = Cl** **5: X = CN**

Figure 2. Dinuclear zinc complexes **2**, **3**, **4** and **5**

For changing the electronic properties, chloride, cyano and fluoride groups were introduced into the BDI backbone (complex **4**, **5** and **9**). These alterations were assumed to increase the Lewis acidity at the metal centers. Thus, the epoxides are stronger pre-coordinated to the metal centers which facilitates the ring opening by the relatively weak nucleophilic carbonato chain end. Consequently, higher activities for the copolymerization reaction were expected. Complex **5** turned out to be insoluble in all common solvents. As cyano groups are known to be efficient ligands for zinc, we attribute this behavior to the formation of coordination polymers which is obvious as both zinc centers have a free coordination site. Correct elemental analysis support this assumption. Besides, such behavior is literature known for mononuclear zinc complexes having cyano substituents.[11] Due to this heterogeneous nature we excluded complex **5** from further copolymerization experiments. As shown in scheme 2, the successful synthesis of ligand 8 required the development of an altered synthetic pathway.



Scheme 1. Synthesis route for complex **9**

Ligand 6 is formed *via* condensation reaction of acetophenone and 4,4-diaminophenylmethane. After deprotonation it is converted with pre-ligand **7** to form the desired ligand **8** which is purified by double recrystallization, first out of acetone followed by acetonitrile. Complexation leads finally to catalyst **9** with the electron withdrawing trifluoromethyl groups in the backbone (Scheme 2).

In 2009 Williams *et al*. presented a rigid dinuclear zinc complex having a macrocyclic ancillary ligand framework which catalyzes the copolymerization of cyclohexene oxide and CO_2 even at one atmosphere of CO_2 (TOF of 25 h^{-1}).[6c] Therefore, using the same CO_2 pressure we started with the investigation of catalyst **1** and 9 in the CHO/CO_2 copolymerization. Comparing the activity of catalyst **1**, that produces poly(cyclohexene carbonate) with a turnover frequency of 410 h^{-1} (calculated by the number of moles of consumed epoxide divided by the moles of catalyst), the activity using complex **9** is more than twice as high (940 h^{-1}) (Table S1). Concerning activity this exceeds by far the hitherto existing systems. The reduced carbonate content in the polymer chain can be explained by the reported rate law which depends on the applied CO_2 pressure. At low pressures the carbon dioxide insertion is the rate determining step and therefore the carbonate content is decreased to 85% **(1)** and 47% **(9)**, respectively. The more pronounced decrease with complex **9** can be explained by a stronger tendency towards consecutive ring opening as applying complex **9** in the homopolymerization of CHO resulted also in higher activities (Table S2). For all copolymerization experiments it has to be mentioned that due to very high reaction rates and therefore rapidly increasing viscosities all TOF values were determined *via* separate experiments. Thereby, the formation of the C=O vibration of poly(cyclohexene carbonate) was followed by *in situ* IR spectroscopy. The polymerization was immediately stopped by prompt CO_2 release and addition of methanol as soon as the increment of the absorption rate began to decrease. The elapsed reaction time was subsequently used to calculate the turnover frequencies of the isolated polymer (Figure 3). This affects especially the TOF values determined with the highly active catalysts **1**, **4** and **9**.

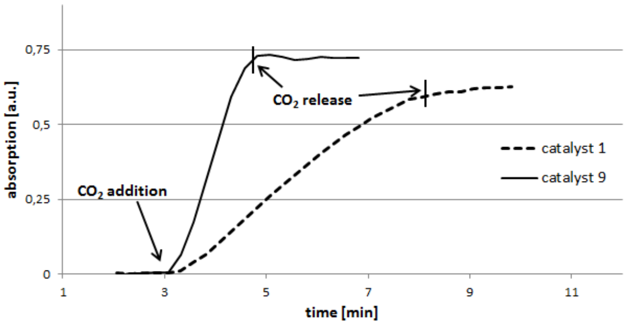


Figure 3. Following the C=O vibration of PCHC by in situ IR spectroscopy of CHO/CO_2 copolymerizations with catalyst **1** and **9** (table 1, entry 4 and 7)

Copolymerization experiments with complex **1** already resulted in TOF values up to 23300 h^{-1} (entry 4). The amount of carbonate linkages accounts for over 91% for all polymers obtained by catalyst **1**, **2** and **4**. Catalyst **4** not only leads to 94% carbonate linkages, it also polymerizes cyclohexene oxide and carbon dioxide with even higher activities at comparable conditions (entry 5). However, due to the following reasons, the focus of this study is on the catalytic behavior of the trifluoromethyl containing structure. Complex **9** revealed unprecedented activities for the copolymerization of cyclohexene oxide and CO_2.

Table 1. Copolymerization of cyclohexene oxide and CO_2 with catalyst **1**, **2**, **4** and **9**[a]

entry	Cat.	CO_2 [bar]	TON[b]	TOF[c] [h^{-1}]	%PCHC[d]	%Conversion	Mn[e] [g/mol]	PDI [M_w/M_n]
1[f]	2	10	560	530	97	14	32000	1.8
2[f]	2	30	890	830	99	22	114000	1.3
3	1	10	1800	14800	91	45	132000	1.6
4	1	30	3000	23300	95	74	228000	1.5
5	4	10	1850	16100	94	46	193000	1.5
6	9	10	2800	41000	70	70	103000	1.7
7	9	30	3500	80300	67	87	128000	1.8
8	9	40	3700	85500	83	90	207000	1.8
9[g]	9	30	3700	95500	90	75	350000	1.6
10[h]	9	10	4720	29600	81	59	278000	1.6
11[h]	9	30	6740	155000	88	85	280000	1.7

[a] Copolymerizations were conducted in a preheated reactor with online ATR-IR measurements for 20 minutes with 5 mL of cyclohexene oxide and 5 mL of toluene at 100 °C (unless otherwise mentioned). [b] The turnover number (TON) is calculated by the number of moles of consumed epoxide divided by the moles of catalyst. [c] The turn-over frequency (TOF = TON/time] is calculated by determining the initial linear reaction time by in situ spectroscopy [d] Assigned by the relative integrals of the signals at δ=4.65 ppm (polycarbonate), δ=4-4.08 ppm (cyclic carbonate) and δ=3.5-3.6 ppm (polyether) [e] Determined by gel-permeation chromatography (GPC), calibrated with polystyrene standards in tetrahydrofuran [f] reaction time of 60 min [g] 7.5 mL toluene [h] Catalyst/epoxide of 1/8000.

With the primary chosen reaction conditions (catalyst/epoxide of 1/4000 in a toluene/cyclohexene oxide mixture (1/1 v/v) at 100 °C and 30 bar CO_2 pressure) the reaction rate was already drastically limited by diffusion hindrance after 1.5 min. The initial linear increase of the polycarbonate formation is considerably shortened. TOF values are therefore increased to 85500 h^{-1} (entry 8). Besides, copolymerization experiments with 10, 30 and 40 bar CO_2 pressure again indicate a rate law depending on the applied pressure. Activity is almost doubled by increasing the CO_2 pressure from 10 to 30 bar whereupon even higher CO_2 pressure did not result in further improvement (table 1, entry 6, 7 and 8). In spite of different electronic properties of complex **9** compared to the lead-structure **1**, a switch of the rate determining step at similar conditions is indicated on the basis of these results. As expected higher CO_2 pressures entailed higher carbonate contents, even though the polycarbonate content is reduced to 67-90% which is due to diffusion problems of carbon dioxide. Apparently, the solving process of carbon dioxide into the reaction mixture is despite vigorous stirring too slow for consecutive insertion of epoxide and carbon dioxide. This is supported by an immediate decrease of the CO_2 vibration in the IR autoclave as soon as polymer formation begins (figure 4). Copolymerization with higher dilution led to even higher reaction rates due to less viscosity (entry 9). Generally, it can be concluded that high polymer selectivities ($\geq$99%) are observed and the content of carbonate linkages is adjustable between 67% and 99% by applying the appropriate catalytic system. In order to get even higher activities we doubled the [epoxide]/[cat] ratio. In doing so the turnover number is almost in the same way duplicated (entry 10 und 11). Some deactivation by residual water in the reaction mixture out of toluene and epoxide and diffusion limitation are probably the reasons for not giving the desired doubled TON at highly diluted conditions. The resulting turnover frequency of 155000 h^{-1} is by far the highest polymerization rate ever reported for copolymerization of epoxide and carbon dioxide (entry 11). By introducing electron-withdrawing groups into the ligand framework we successfully managed to decrease the activation barrier of the ring opening even more which was before asserted to be necessary to achieve higher activities.[5d] Although poly(cyclohexene carbonate) is currently of little commercial interest, this catalytic improvement depicts an impressive research development in CO_2/epoxide copolymerization. Similar activities with other epoxides could make an application in an industrial process feasible.

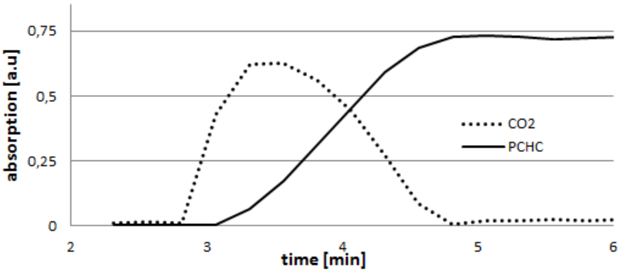


Figure 4. . Following the C=O vibration of CO_2 and PCHC by in situ IR spectroscopy of CHO/CO_2 copolymerization with catalyst **9** (entry 8)

Often polycarbonate formation shows a bimodal profile due to an initiation by residual water.[12] In contrast, the molecular weights produced by our catalysts show that high molecular weight polymers with a monomodal distribution are produced. Therefore, it can be assumed that the trimethylsilylamido-groups represent the only initiating species. By increasing the toluene/epoxide ratio the average molecular weight can even be increased up to 350000 g/mol (entry 9). Consideration of the molecular weight distributions revealed slightly broadened values between 1.3 and 1.8. We primarily attribute this behavior to the fast polymerization rates. As a consequence copolymerization proceeded very unbalanced in the reaction medium as copolymerization directly begins at the liquid-gas-interface after adding CO_2. In combination with an inefficient initiation process, these conditions finally ended in broadened molecular weight distributions.

Conclusions

In conclusion we were able to synthesize new dinuclear zinc complexes for the copolymerization of cyclohexene oxide and carbon dioxide. Sterically demanding bridging units again confirmed our hypothesis that for our catalytic system flexible methylene bridges between both BDI zinc moieties are essential for high activities. Further catalyst modifications in terms of different electronic properties of the ligands resulted in extraordinary activities for the poly(cyclohexene carbonate) formation with turnover frequencies up to 155000 h^{-1}, high carbonate content in the polymer chains and high molecular weights up to 350000 h^{-1}. These results represent an imposing progress in epoxide/CO_2 copolymerization. Currently, we are investigating our dinuclear zinc catalysts also for the copolymerization of CO_2 with other common epoxides (e.g. propylene oxide) and bio-based epoxides (e.g. limonene oxide).

Notes and references

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[b] BASF SE, 67056 Ludwigshafen, Germany..

† The financial support of the BASF SE is gratefully acknowledged. Thanks to Dr. Sergei Vagin for discussion and proofreading of the manuscript.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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