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3-Amino-2-cyano-imidoacrylate ligands and their zinc complexes for the copolymerisation of CO_2 and epoxides: Living character and temperature optimisation

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Abstract

Zinc acetate complexes with 3-amino-2-cyano-imidoacrylate ligands exhibit high activities and selectivities in the copolymerisation of carbon dioxide and cyclohexene oxide to give aliphatic polycarbonates. In temperature optimisation experiments, temperatures around 90 °C were found to be ideal combining minimal formation of the cyclic carbonate side product with optimal catalytic activity. The living character of the polymerisation was shown by studying molecular weights of the polycarbonates at different levels of monomer conversion.

Keywords: Aminoidmidoacrylate ligands; Carbon dioxide fixation; Homogeneous catalysis; Living copolymerisation; Molecular weight distribution

1. Introduction

Carbon dioxide is a very attractive C_1 building block for green and synthetic chemistry, because it is abundant, nontoxic, not flammable and inexpensive [1]. The main obstacle preventing a wide and industrial use so far is its lack of activity, which has to be overcome by catalytic activation [2–4]. The alternating copolymerisation of epoxides and CO_2 is of great importance within this context, because it produces aliphatic polycarbonates, biodegradable polymers with interesting properties (Fig. 1) [5–7]. The reaction was first discovered by Inoue et al. [8] and in the beginning predominantly heterogeneous catalysts were used [9]. Zinc glutarate is the prevalent heterogeneous catalyst used to date combining facile preparation and fair activities [10,11]. In the past few years, new homogeneous catalysts with higher activities, like zinc phenoxides [12] or chromium salen complexes [13,14] were found to be good catalysts for the copolymerisation. Especially the highly active zinc β-diiminate [15–17] and cobalt salen complexes [18,19] made the epoxide/CO_2 reaction a promising candidate for commercial carbon dioxide utilisation. In addition to the enhanced activities, the use of homogeneous catalysts has allowed detailed mechanistic insights. While for the salen and porphyrin metal complexes the key reaction steps occur at a monometallic active single site [13,20], for zinc β-diiminate complexes implications for a bimetallic pathway have been found [21]. Several recent reviews document the rapid evolution in the field of epoxide/CO_2 copolymerisation [22–24]. Our group has developed zinc complexes with new aminoimidoacrylate (AIA) ligands **1**, which showed high catalytic activities in the alternating copolymerisation of cyclohexene oxide and carbon dioxide [25]. Herein we report the influence of the reaction temperature and some evidence for the living character of this catalytic copolymerisation.

2. Experimental

2.1. General

All reactions with air- or water-sensitive compounds were carried out under dry argon using standard Schlenk line techniques. NMR spectra were recorded on a Bruker spectrometer (250 MHz for ^1H, 62.9 MHz for ^{13}C) at 20 °C. The glass transition temperature of the polymer was measured by differential scanning calorimetry (DSC) with a Mettler Toledo

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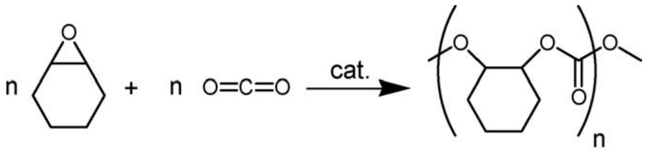

Fig. 1. Copolymerisation of CO_2 and cyclohexene oxide with zinc acetate complexes of amino-imidoacrylates (AIA).

DSC822e. IR spectra were recorded with a Perkin Elmer System 2000 FT-IR. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a Merck-Hitachi System (L-6200 intelligent pump, L-7490 RI-detector). A pre-column and two different GPC columns (PSS SDV 5 μ, 1000 and 100 Å) were run with tetrahydrofuran at 35 °C at 1 mL/min and were calibrated by polystyrene standards.

2.2. Chemicals

The AIA ligands have been synthesised in three steps from cyanoacetic acid (Fig. 2) [25]. Zinc acetate complexes of these ligands were made by a known literature procedure via the corresponding zinc ethyl complex [15,26].

2,6-Diisopropylaniline was distilled under vacuum and cyclohexene oxide was distilled from calcium hydride under vacuum. All other reagents were purchased commercially and used as received.

2.3. General procedure for copolymerisation reactions

An autoclave (Parr, 300 mL) was heated to 95 °C under vacuum for 16 h and cooled under vacuum. Catalyst **2b** [(AIA-1b)Zn(OAc)] (see Figs. 2 and 3, 50 mg, 0.095 mmol Zn) and cyclohexene oxide (9.29 g, 95 mmol) were brought into the autoclave, which was then heated to reaction temperature and pressurized with CO_2 to the appropriate pressure (4 MPa). After 2 h the reactor was cooled, vented and a small sample taken for analysis. The resulting polycarbonate was dissolved in CH_2Cl_2 (5 mL), precipitated from MeOH (20 mL), collected and dried in vacuo to constant weight.

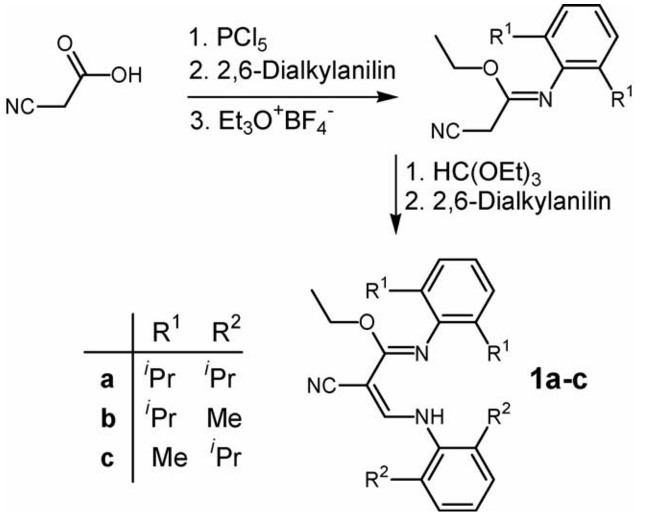

Fig. 2. Synthesis of the AIA (3-aminoimidoacrylate) ligands **1a–c**.

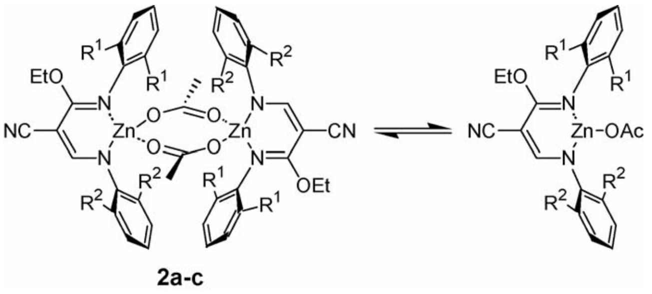

Fig. 3. Dimeric and monomeric structure of the catalyst.

2.4. Analytic assignments

The carbonate content of the polycarbonate was determined using ^1H NMR (C_6D_6) quantifying the polycarbonate (4.9 ppm) and polyether (3.6 ppm) methine protons. Syndiotactic and isotactic carbonate units were identified by ^{13}C NMR carbonate peaks at 154.63 ppm and 154.10–153.91 ppm, respectively, according to assignments made by Nozaki and co-workers [27]. The cyclic carbonates were quantified by their IR bands at 1822 cm^{-1} (*trans*) and 1804 cm^{-1} (*cis*) in comparison to the polycarbonate peak at 1749 cm^{-1} [28,29].

2.5. Calculations

Cyclohexene oxide (CHO) conversion was calculated as the amount of monomeric CHO converted into a perfectly alternating copolymer with CO_2 ($M_{\text{monomer unit}}$ = 142 g/mol). Turnover numbers and frequencies were calculated as CHO conversion per mole of zinc. For the calculation of theoretical molecular weight values of the copolymer in Fig. 5, the ideal molar mass of a monomeric unit (142 g/mol) was corrected according to the respective polyether content of the copolymer. Then the turnover was multiplied with the molar mass of the monomeric unit and divided by a factor of 2, because the growth of two polymer chains per metal center was assumed.

3. Results and discussion

3.1. Synthesis and activity of the catalysts

The majority of homogeneous single site catalysts contain sterically demanding spectator groups which shield the active metal center, where they remain during the whole course of the reaction and exert a directing influence on catalysis. For the use of such ligands in the copolymerisation of CO_2 and epoxides, a variety of new AIA ligands have been synthesised by an effective modular and flexible route starting from cyanoacetic acid (Fig. 2). First, an amide was formed by condensation with 2,6-dialkylaniline, which was then *O*-alkylated with triethyloxonium salt. The second half of the ligand was build up by a Claisen condensation with

Table 1
Catalytic activity of **2a–c** in the cyclohexene oxide/CO_2 copolymerisation

Catalyst[a]	*t* (h)	*T* (°C)	TON[b]	TOF[b] (h^{-1})	$g_{poly}g_{M^{-1}}$ (h^{-1})	Carbonate linkages (%)[c]	M_n[d] (kg/mol)	M_w/M_n
2a	2	100	270	135	293	58	12.6	1.72
2b	2	90	367	183	399	88	24.5	1.15
2c	2	100	396	198	430	75	15.8	1.21
2c	1	90	210	210	456	88	10.0	1.16

[a] A [CHO]:[Zn] ratio of 1000:1 and CO_2 pressures of 4 MPa in neat CHO were used throughout.
[b] Mole of CHO consumed per mole of zinc (per hour for TOF).
[c] Determined by ^1H NMR.
[d] Determined by GPC in THF.

Table 2
Temperature optimisation of the cyclohexene oxide/CO_2 copolymerization

Catalyst[a]	*T* (°C)	*p* (CO_2) (MPa)	Cyclic carbonate (%)[b]	TOF[c] (h^{-1})	$g_{poly}g_{M^{-1}}$ (h^{-1})	Carbonate linkages (%)[d]	M_n[e] (kg/mol)	M_w/M_n
2b	80	4	5	150	327	91	22.7	1.20
2b	90	4	7	183	399	88	24.4	1.15
2b	100	4	16	171	373	90	19.8	1.19

[a] A [CHO]:[Zn] ratio of 1000:1 was used throughout.
[b] Determined by IR.
[c] Mole of CHO converted to PCHC per mole of zinc and per hour.
[d] Determined by ^1H NMR.
[e] Determined by GPC in THF.

triethylorthoformate and consecutive substitution with another molecule of 2,6-dialkylaniline.

As an initiating group for the catalyst, acetate, which mimics the structure of an inserted carbonate, was used throughout all experiments. Therefore zinc acetate complexes of the ligands were prepared. Ligands were first treated with diethyl zinc to yield the zinc ethyl complex, which was then reacted with acetic acid to give the zinc acetate complexes. In the solid state, the catalysts have a dimeric structure [25]. If the two aromatic rings are differently substituted, they crystallise in such a way that the ring with the methyl group is facing the larger *iso*-propyl substituents (Fig. 3). The asymmetric architecture of the ligand allows us to distinguish between the two bulky aryl groups. By varying the *ortho*-alkyl groups on the two aromatic rings of the ligand, a significant increase in catalytic activity was observed. The catalytic performance of the different complexes is shown in Table 1. The best results were achieved employing complex **2c** with an *iso*-propyl and a methyl group on the aromatic ring. The resulting poly(cyclohexyl carbonates) (PCHCs) contained around 90% carbonate linkages and molecular weights up to 30 kg/mol were achieved with 0.1 mol% catalyst loading. The copolymers were atactic, as ^{13}C NMR analysis revealed a random distribution of isotactic and syndiotactic carbonate units. For a representative sample of poly(cyclohexyl carbonate) (Table 2, entry 3) a glass transition temperature of 114 °C was measured, closely matching the literature known value of 115 °C [7]. The catalytic activities were high and turnover frequencies above 200 h^{-1} were reached, which is slightly less than the activities reached by the zinc β-diiminate catalysts of Coates and co-workers [15], though the reaction conditions are not directly comparable.

3.2. Influence of the reaction temperature

At higher temperatures, the formation of cyclic carbonates becomes a competing side reaction of the polycarbonate formation (Fig. 4).

Formation of the cyclic carbonate is mostly the result of a degradation of the growing polymer chain by a so called backbiting mechanism: The alkoxide oxygen of a growing polymer chain, which is activated by the metal center, does not react with another carbon dioxide molecule. Instead, the close-by electrophilic carbonyl carbon of the polycarbonate is attacked and the cyclic carbonate is formed. Meanwhile the remaining nucleophilic oxygen is reacting with the active metal center to afford a shortened polymer chain. Interestingly, with propylene oxide, cyclic carbonate formation is a major drawback and low reaction temperatures are a prerequisite for polycarbonate formation [17]. On the other hand, with cyclohexene oxide, the copolymer is the major product, even at temperatures over 100 °C. Darensbourg et al. quantified the thermodynamic basis for this behaviour by comparing the energies of activation. According to these findings, formation of poly(propylene carbonate) is thermodynamically favoured over

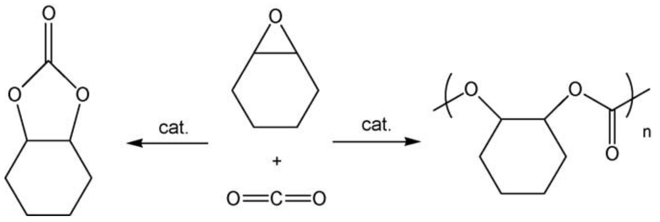

Fig. 4. Poly(cyclohexyl carbonate) (PCHC) vs. cyclic cyclohexene carbonate (CHC) formation.

cyclic propylene carbonate formation by only 33 kJ/mol, while the energy of activation for poly(cyclohexyl carbonate) (PCHC) is over 80 kJ/mol lower than the one for cyclic cyclohexene carbonate (CHC) [30]. Taking these general considerations into account, the optimal operating temperature for the (AIA)Zn(OAc) catalyst system was evaluated.

Experiments with catalyst **2b** and cyclohexene oxide at varying temperatures showed good results between 80 and 100 °C with an optimum at 90 °C (Table 2). At 80 °C almost no formation of CHC was observed, but the catalytic activity was only moderate. On the other hand, at 100 °C the catalytic activity was higher, but a significant amount of CHC (>15%) was formed, and thus, the PCHC yield was diminished. According to IR data, *cis*- and *trans*-CHC occurred in equal amounts. Consequently, the best results were obtained at 90 °C where the balance between high catalytic activity and only minor CHC formation (<10%) was the best. In conclusion, two temperature effects were observed: The catalytic activity (in terms of carbonate formation, regardless of its cyclic or polymeric nature) increases with temperature and so does the tendency to form the cyclic carbonate. This leads to a temperature window between 80 and 100 °C, where polycarbonates can be produced with high catalytic activities. Above this window, too much CHC is formed and below, catalytic activities are decreasing.

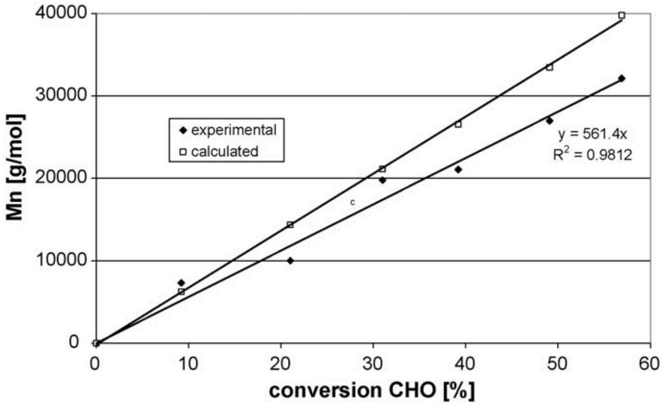

Fig. 5. Molecular weight of polycarbonates against monomer (CHO) conversion and calculated values assuming a growth of two polymer chains on one metal center.

3.3. Living character of the catalytic copolymerisation

In a "living" polymerisation, one polymer chain grows on each initiator molecule without chain transfer or other side reactions [31]. This results in a molecular weight distribution close to unity (or unity in an ideal case) and a linear relationship between molecular weight and monomer conversion (and initial monomer to catalyst ratio, respectively) [32]. Another beneficial feature of a living polymerisation is the ability to "recharge". If one batch of monomer is completely converted into the polymer, another batch of the same or another reactive monomer can be added and will also be converted. This allows the controlled design of block copolymers [33]. In the case of our zinc catalysts **2b** and **2c**, we found narrow molecular weight distributions with M_w/M_n values between 1.15 and 1.20, indicating a living polymerisation on a single site catalyst (see Tables 1 and 2). For a closer examination, we studied the reaction with 0.1 mol% of catalyst **2c** at 90 °C, 4 MPa and various reaction times. Monomer conversion to the polycarbonate did not exceed 60% even at long reaction times presumably because the reaction is carried out in neat CHO without any solvent. At higher conversions, the CHO/CO_2/polymer mixture gets more and more viscous. Finally so much CHO is used that PCHC is not dissolved any more and further reaction is hindered. Such a scenario would agree well with other investigations of phase behaviour [34]. An alternative explanation for the incomplete conversion, the lack of CO_2 in the vapour phase, can be ruled out, because the large CO_2 filled volume of the autoclave (300 mL) versus the small volume of cyclohexene oxide (<10 mL) provided a large excess of CO_2. The experimental data revealed a linear relationship between the molecular weight of the produced polycarbonates and conversion of the monomer, cyclohexene oxide (Fig. 5). The polydispersity in all experiments lay within 1.13 and 1.23. Thus, there must be growing similar polymer chains from each active catalytic center and the growth is controllable by the reaction time, which is a strong evidence towards the living character of the polymerisation.

Another open question regarding the mechanism of the copolymerisation was, whether the dimer or the monomer is the active catalytic species. Though the complex is a dimer in the solid state, MS data suggest a monomer/dimer equilibrium in solution (Fig. 3). ESI mass spectra in methanol showed molecular peaks for both species, the monomer and the dimmer [25].

As already mentioned above, in a controlled living polymerisation, where one polymer chain grows on one catalytically active metal center, the molecular weight at a defined grade of conversion is determined by the monomer to catalyst ratio. For another living system, aluminum initiators supported by tetradentate aminophenoxide ligands, Hormnirun et al. found that the molecular weights of the produced polylactides were in close agreement with calculated values [35]. In the case of our system, however, the assumption of one polymer chain growing on one metal center results in a calculated theoretical molecular weight of 142,000 g/mol at 100% conversion (with a molecular weight of 142 g/mol per monomer unit and a catalyst to monomer ratio of 1/1000). This is more than twice as high as the experimental value of 56,140 g/mol which is obtained by extrapolating our experimental results (Fig. 5) to complete conversion. Assuming, that a bimetallic active zinc complex produces one growing polymer chain, this results in an even higher calculated value which is four times higher than the experimental data. Instead, the number of growing chains seems to be higher than the number of zinc atoms and a good agreement between calculated and experimental values is found, if the growth of two polymer chains per zinc atom is assumed (Fig. 5). Additionally, the moderate divergence between experimental and calculated results fitted well in the other experimental data. The calculated ideal values were roughly 1.2 times higher than the experimental ones, which corresponds to deviations in similar experiments [35] and can well be explained by side reactions.

Especially the aforementioned cyclic carbonate formation can account for the deviation since it diminishes the molecular weight of the polymer chain (vide supra). The M_w/M_n values of 1.2 seem to point into the same direction. Ergo, the experimental data strongly support the assumption of two polymer chains growing on one active metal center. However, it is still questionable whether there is a simultaneous growth of multiple chains on one zinc atom or the occurrence of a chain transfer reaction that is much (two times) faster than chain propagation. This and other mechanistic details are an important part of our ongoing studies.

4. Conclusions

The alternating copolymerisation of CO_2 and epoxides represents one of the most promising ways for carbon dioxide utilisation as a chemical building block. New zinc acetate complexes of AIA ligands are highly active initiators for this reaction (TOF > 200) and produce atactic polycarbonates with over 90% carbonate content. The system has an optimum performance at temperatures around 90 °C, where a maximum of catalytic activity goes along with negligible formation of cyclic carbonates, which are formed at elevated temperatures. The copolymerisation is a living process, as analysis of molecular weights at different stages of monomer conversion revealed. Comparison with calculated data lead to the conclusion that one catalytically active metal center produces two polymer chains. Under this assumption, calculated data were well in line with the experimental ones. Overall, much about the nature of this important reaction was enlightened by a rather straightforward series of experiments. The knowledge gained is currently used to develop optimised catalytic systems and reaction conditions.

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