

3-Amino-2-cyano-imidoacrylate ligands and their zinc complexes for the copolymerisation of CO₂ 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.

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1. Introduction

Carbon dioxide is a very attractive C₁ 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 CO₂ 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/CO₂ 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/CO₂ 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 ¹³C) 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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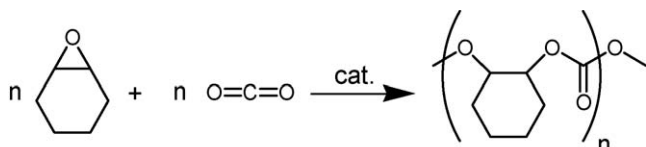


Fig. 1. Copolymerisation of CO₂ and cyclohexene oxide with zinc acetate complexes of amino-imidoacrylates (AIA).

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 CO₂ 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 CH₂Cl₂

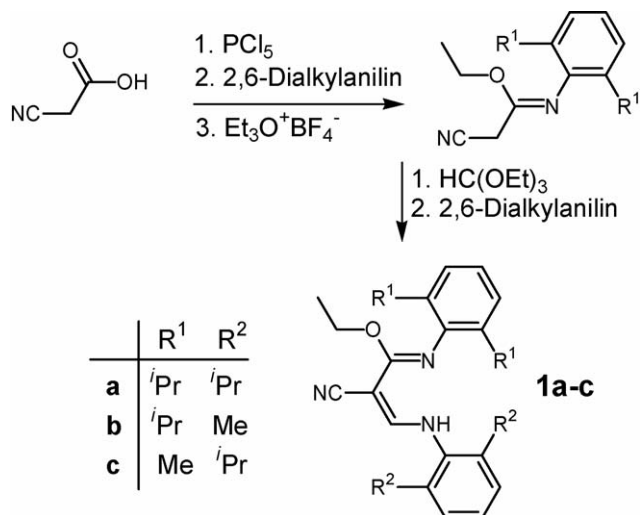


Fig. 2. Synthesis of the AIA (3-aminoimidoacrylate) ligands **1a–c**.

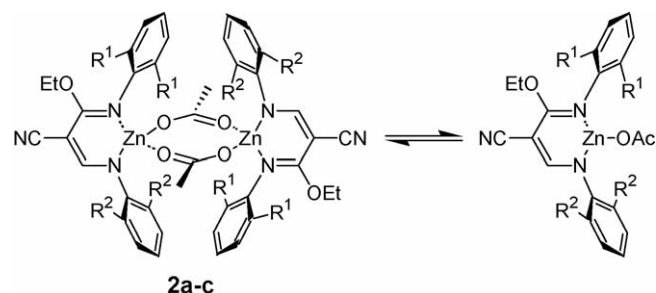


Fig. 3. Dimeric and monomeric structure of the catalyst.

(5 mL), precipitated from MeOH (20 mL), collected and dried in vacuo to constant weight.

2.4. Analytic assignments

The carbonate content of the polycarbonate was determined using ¹H NMR (C₆D₆) quantifying the polycarbonate (4.9 ppm) and polyether (3.6 ppm) methine protons. Syndiotactic and isotactic carbonate units were identified by ¹³C 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 CO₂ ($M_{\text{monomer unit}} = 142$ 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 CO₂ 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

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