

Alternating Copolymerization of Carbon Dioxide and Cyclohexene Oxide and Their Terpolymerization with Lactide Catalyzed by Zinc Complexes of N,N Ligands

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Dedicated to Prof. Dr. Gregor Fels on the occasion of his 60th birthday.



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Abstract: For the alternating copolymerization of CO₂ and cyclohexene oxide, a variety of zinc acetate complexes with new aminoimidoacrylate ligands has been synthesized and tested as catalysts. All complexes catalyzed the reaction and structure-activity investigations revealed that the highest activities and selectivities were reached when the ligand's aromatic rings were 2,6-substituted by alkyl groups of different size (isopropyl *versus* methyl) and when the ligand backbone embodied an electron-withdrawing

cyano group. Furthermore, these complexes catalyzed the terpolymerization of CO₂, cyclohexene oxide and lactide to give poly(cyclohexyl carbonate-*co*-lactide) and the composition of the polymer was adjustable by the monomer feed.

Keywords: carbon dioxide fixation; copolymerization; green chemistry; homogeneous catalysis; ligand design; terpolymerization

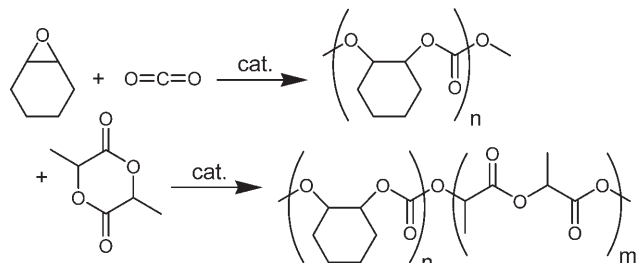
Introduction

The production of aliphatic polycarbonates by copolymerization of epoxides and carbon dioxide is attracting much attention because it combines several beneficial features. One major advantage is the incorporation of CO₂ as a C₁ building block. CO₂ is a very attractive synthon because it is abundant, independent from resources like fossil fuels, inexpensive and neither flammable nor toxic.^[1] A second advantage of this reaction is the perfect atom economy. Additionally, no solvent is needed. Last but not least, the produced aliphatic polycarbonates represent a new class of materials with interesting properties. For example, their biodegradability should allow their application in biomedicine. On the other hand, the reactivity of CO₂ is low and for most reactions catalysts are necessary to overcome the problem.^[2,3]

The CO₂/epoxide copolymerization was discovered by Inoue over thirty years ago.^[4] In the beginning mainly heterogeneous catalysts were used.^[5] Over the last decade the use of homogeneous catalysts has lead

to a drastic increase in catalytic activities.^[6–8] For the copolymerization of CO₂ and propylene oxide, salen complexes, especially of chromium^[9,10] and cobalt^[11–13] have come into focus. Yet, the highest activities for the alternating copolymerization of CO₂ and cyclohexene oxide so far have been reached by Coates' β -diketiminato (BDI) zinc complexes (see below).^[14,15] In general, the BDI ligand is of increasing importance for the field of homogeneous catalysis, because it exhibits a strong binding to the metal, a tunable steric demand and a diversity of binding modes.^[16] Metal complexes thereof have been used for several catalytic applications such as the oligomerization and polymerization of olefins,^[17–19] the polymerization of methyl methacrylate,^[20] or the polymerization of lactide^[21,22]. For the CO₂/epoxide copolymerization, tetradentate derivatives of this ligand have been developed to bind rare earth metals^[23] as well as to form a rigid bimetallic zinc acetate complex.^[24] As a new alternative to the classic β -diketimines, new aminoimidoacrylate (AIA) ligands and their zinc acetate complexes, which showed high activities in the CO₂/cyclo-

hexene oxide copolymerization, have been reported by our group.^[25] In this paper we present new derivatives of this group of ligands, their catalytic behavior, some insight into the CO₂/epoxide copolymerization and first results in the terpolymerization of CO₂, cyclohexene oxide and lactide (Scheme 1).



Scheme 1. Copolymerization of CO₂ and cyclohexene oxide and terpolymerization of CO₂ cyclohexene oxide, and lactide.

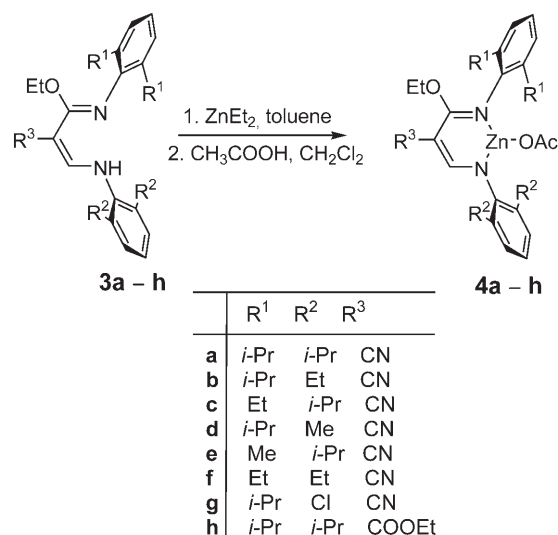
Results and Discussion

Synthesis of Catalysts

A variety of new AIA ligands has been synthesized. All ligands bearing a cyano group (**3a–g**) have been prepared by a four-step procedure as described earlier.^[25] For the ligand including an ester group (**3h**), a synthetic route with only two steps was developed (Scheme 2). Starting from ethoxymethylenemalonate, two ethoxy groups are substituted by 2,6-diisopropylaniline. Afterwards, the resulting amide (**2h**) is *O*-alkylated by triethyloxonium tetrafluoroborate to give the AIA ligand (**3h**).

From each ligand a zinc acetate complex was prepared and tested as copolymerization catalyst. The acetate serves as an initiating group. Mechanistic studies suggest that its resemblance to CO₂ affords the insertion of cyclohexene oxide into the metal-acetate bond as the first step of the copolymerization.^[26] Since the distance to the active metal center grows with each insertion of cyclohexene oxide and CO₂, the influence of the initiating group on the rate of

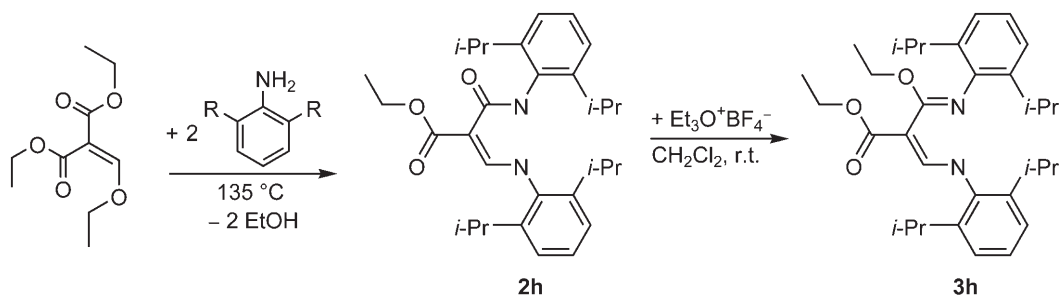
conversion is rather low. Consequently, zinc complexes with the same ligand, but different initiating groups like alkoxides^[14] or sulfates,^[27] show comparable activities. To sustain comparability, acetate was chosen as the only initiating group for this study. Preparation of the corresponding zinc complexes is well established and reliable.^[14,25] Reaction of the ligands **3** with diethylzinc gives a zinc-ethyl complex as an reactive intermediate.^[28] This is then carefully treated with an equimolar amount of acetic acid to give the zinc acetate complexes **4** (Scheme 3).



Scheme 3. Synthesis of the (AIA)Zn(OAc) complexes **4a–h**.

Solid-State Structures

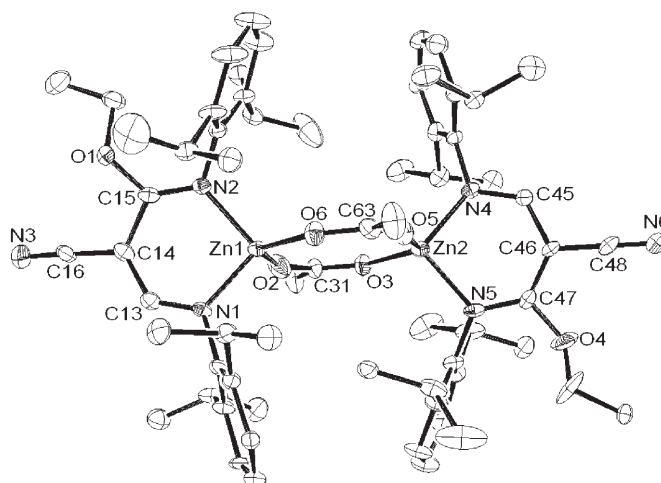
Selected bond lengths and angles are summarized in Table 1 and crystallographic data are summarized in Table 2. All complexes that could be crystallized had a dimeric motif in their solid-state structure. For **4a** and **4c** a dimer with two acetates bridging the two tetrahedral zinc centers was found (Figure 1 and Figure 2). In **4c**, the bulkier aromatic rings with isopropyl groups attached in the 2 and 6 positions, are orientated *anti* to each other so that each isopropyl-



Scheme 2. Synthesis of ligand **3h**.

Table 1. Selected distances (Å) and angles (deg).

	4a	4c	5d	6e
Zn–Zn	4.161	3.963	3.302	3.466
Zn–N1	1.989(7)	1.977(3)	1.998(4)	1.994(3)
Zn–N2	1.999(7)	1.987(3)	2.003(4)	1.976(3)
Zn–O2	1.937(8)	1.929(3)	1.974(4)	2.070(5)
Zn–O6	1.918(7)	1.922(3)	1.901(4)	1.957(7)
N1–C	1.266(11)	1.303(5)	1.309(6)	1.295(5)
C=C	1.368(13)	1.417(5)	1.405(7)	1.416(5)
C–C	1.495(12)	1.423(5)	1.429(7)	1.417(6)
C=N2	1.271(11)	1.310(5)	1.306(6)	1.294(5)
C–CN	1.452(13)	1.430(6)	1.443(7)	1.416(5)
C≡N	1.141(13)	1.145(5)	1.138(7)	1.149(5)
N–Zn–N	95.5(3)	97.41(13)	94.89(18)	97.67(13)
O–Zn–O	120.1(3)	122.18(14)	104.54(15)	95.0(2)
O–Zn–N	113.1(4)	111.30(13)	106.17(16)	109.55(13)

**Figure 1.** Thermal ellipsoid plot (25% probability level) of complex **4a**.

substituted aromatic ring faces a less bulky ethyl-substituted ring. Thus, steric repulsion is reduced and the Zn–Zn distance for **4c** (3.963 Å, see Table 1) is short-

er than that for **4a** (4.161 Å). Another remarkable difference between the two structures can be found on

Table 2. Crystal data and structure refinement details.

	4a	4c	6e	5d
Empirical formula	C ₆₄ H ₈₆ N ₆ O ₆ Zn ₂	C ₃₀ H ₃₉ N ₃ O ₃ Zn	C ₃₈ H ₅₁ N ₃ O _{13.5} Zn _{4.5}	C ₅₄ H ₆₈ N ₆ O ₅ Zn ₂ ·CH ₂ Cl ₂
CCDC-Nr.	266169	296832	296831	296833
fw [g mol ^{−1}]	1166.13	555.01	1130.88	2839.3(9)
Temperature [K]	200(2)	200(2)	200(2)	200(2)
Wavelength λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	<i>Pn</i> (No. 7)	<i>P21/n</i> (No. 14)	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)
<i>a</i> [Å]	13.575(1)	13.0495(11)	12.4028(9)	12.923(2)
<i>b</i> [Å]	16.181(2)	15.7780(13)	13.1442(9)	14.237(3)
<i>c</i> [Å]	15.323(1) Å	14.9811(13)	15.6593(11)	17.576(3)
α [deg]	90	90	73.3390(10)	108.979(3)
β [deg]	114.132(1)	110.5450(10)	82.8170(10)	110.490(2)
γ [deg]	90	90	80.4290(10)	90.184(3)
<i>V</i> [Å ³]	3071.4(5)	2888.3(4)	2403.9	2839.3(9)
<i>Z</i>	2	4	2	2
ρ _{calcd.} [g cm ^{−3}]	1.261	1.276	1.562	1.283
μ [mm ^{−1}]	0.835	0.844	2.387	0.988
<i>F</i> (000)	1240	1176	1154	1152
Crystal size [mm ³]	0.4 × 0.5 × 0.5	0.3 × 0.05 × 0.05	0.3 × 0.2 × 0.3	0.3 × 0.08 × 0.08
θ range [deg]	1.69 to 28.32°	1.79 to 28.32	1.63 to 28.50	1.32 to 28.55
Index ranges	−18 ≤ <i>h</i> ≤ 18 −21 ≤ <i>k</i> ≤ 20 −20 ≤ <i>l</i> ≤ 20	−16 ≤ <i>h</i> ≤ 17 −21 ≤ <i>k</i> ≤ 20 −19 ≤ <i>l</i> ≤ 19	−16 ≤ <i>h</i> ≤ 16 −17 ≤ <i>k</i> ≤ 17 −20 ≤ <i>l</i> ≤ 20	−16 ≤ <i>h</i> ≤ 16 −19 ≤ <i>k</i> ≤ 18 −23 ≤ <i>l</i> ≤ 23
Reflections collected	24807	34636	29328	36088
Reflections observed	10358	3184	7904	5404
Independent reflections	13749 [<i>R</i> (int) = 0.0405]	7116 [<i>R</i> (int) = 0.1177]	11639 [<i>R</i> (int) = 0.0348]	13809 [<i>R</i> (int) = 0.1592]
Data/restraints/param.	13749/4/759	7116/0/352	11639/0/596	13809/0/667
Goodness-of-fit on <i>F</i> ²	1.013	0.911	1.082	0.902
Final <i>R</i> indices	<i>R</i> 1 = 0.0565	<i>R</i> 1 = 0.0523	<i>R</i> 1 = 0.0448	<i>R</i> 1 = 0.0694
[<i>I</i> > 2σ(<i>I</i>)] ^[a]	<i>wR</i> 2 = 0.1303	<i>wR</i> 2 = 0.1244	<i>wR</i> 2 = 0.1225	<i>wR</i> 2 = 0.1496
<i>R</i> indices (all data) ^[a]	<i>R</i> 1 = 0.0811 <i>wR</i> 2 = 0.1486	<i>R</i> 1 = 0.1661 <i>wR</i> 2 = 0.1626	<i>R</i> 1 = 0.1661 <i>wR</i> 2 = 0.1626	<i>R</i> 1 = 0.1969 <i>wR</i> 2 = 0.1851

^[a] *R*1 = [Σ||*F*_o| − |*F*_c||]/Σ|*F*_o|, *wR*2 = [[Σ*w*(|*F*_o² − *F*_c²)²]/[Σ*w*(*F*_o²)]^{1/2}, *w* = 1/[(σ(*F*_o)² + (*aP*)²]. The value of *aP* was obtained from structure refinement.

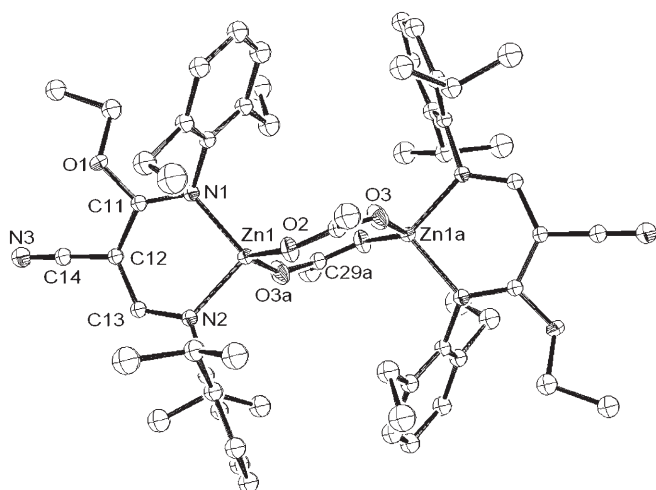


Figure 2. Thermal ellipsoid plot (25% probability level) of complex **4c**.

the ligand backbone. In **4a**, the original C–C single and double bonds of the amino-imidoacrylate backbone still have bond lengths corresponding to such a single and double bond, respectively (C13–C14: 1.368 Å, C14–C15: 1.495 Å). Contrary to this, the ligand backbone of **4c** (Figure 2) shows the features of a conjugated π -electron system. The former single and double bonds have nearly the same bond length (C13–C12: 1.417 Å, C12–C11: 1.423 Å) and so do the two C–N bonds (C13–N1: 1.303 Å, C15–N2: 1.310 Å).

The other two solid state structures originated from crystals which were accidentally exposed to traces of air and water. Although obtained by chance, the structures reveal how this class of zinc complex catalysts can be easily poisoned by traces of air and water. The structure of $[(3d)Zn(\mu, \eta^2\text{-OAc})(\mu, \eta^2\text{-OH})Zn(3d)]$ (**5d**) (Figure 3) stems from an attempt to crystallize **4d**. It resembles the structures of the zinc acetate complexes, but one acetate is replaced by a hydroxy group. As for **4a** and **4c**, the structure is dimeric and the less bulky methyl-substituted aromatic rings stand *anti* to each other. In this case, the two zinc centers are bridged by one acetate and one hydroxy group. Like **4c**, the ligand backbone shows bond lengths corresponding to a conjugated system (Table 1). The two zinc centers and the bridging ligands form a six-membered ring, compared to an eight-membered ring in **4a** and **4c**. Hence, the zinc–zinc distance (3.302 Å) is distinctly reduced. This unsolicited formation of a complex with a six-membered ring supports other findings with β -diketiminato zinc complexes that suggest a greater thermodynamic stability of such six-membered ring complexes compared to acetate-bridged eight-membered rings or alkoxy-bridged four-membered rings.^[26] Consequently, such a switch from an eight-membered ring to a six-membered ring is

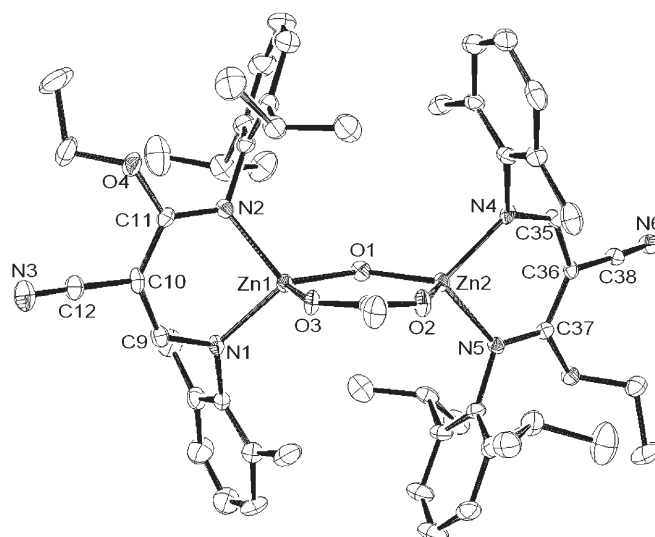


Figure 3. Thermal ellipsoid plot (25% probability level) of $[(3d)Zn(\mu, \eta^2\text{-OAc})(\mu, \eta^2\text{-OH})Zn(3d)]$ (**5d**).

likely to be the driving force in an initial insertion of cyclohexene oxide into the acetate-bridge of a catalyst. Unfortunately, attempts to react a zinc acetate complex with cyclohexene oxide yielded no crystals suitable for X-ray analysis, but a similar structure was obtained by Moore et al.^[26]

The structure of $[(\mu, \eta^2\text{-OAc})_5(\mu, \eta^4\text{-O})Zn_4(\mu, \eta^3\text{-3e})Zn(\mu, \eta^2\text{-OAc})(\mu, \eta^2\text{-OH})]_\infty$ (**6e**) is more complex (Figure 4). It has two different parts that are linked to

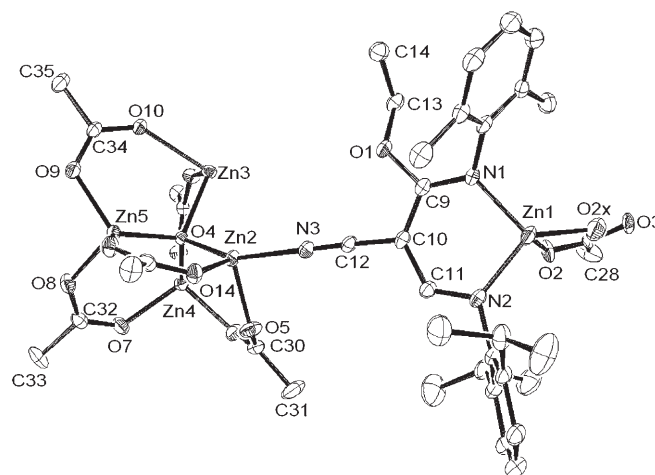


Figure 4. Thermal ellipsoid plot (25% probability level) of $[(\mu, \eta^2\text{-OAc})_5(\mu, \eta^4\text{-O})Zn_4(\mu, \eta^3\text{-3e})Zn(\mu, \eta^2\text{-OAc})(\mu, \eta^2\text{-OH})]_\infty$ (**6e**). Selected distances (Å) and angles (deg) not shown in Table 1: Zn(2)–N(3) 2.041(3), Zn(2)–O(4) 1.952(2), Zn(2)–O(14) 1.993(3), Zn(2)–O(5) 2.019(5), Zn(3)–O(4) 1.974(2), Zn(4)–O(4) 1.914(2), O(4)–Zn(2)–O(14) 108.27(10), O(4)–Zn(2)–N(3) 148.99(12), O(14)–Zn(2)–N(3) 97.11(13), Zn(5)–O(4)–Zn(2) 111.31(11), Zn(4)–O(4)–Zn(3) 111.89(11).

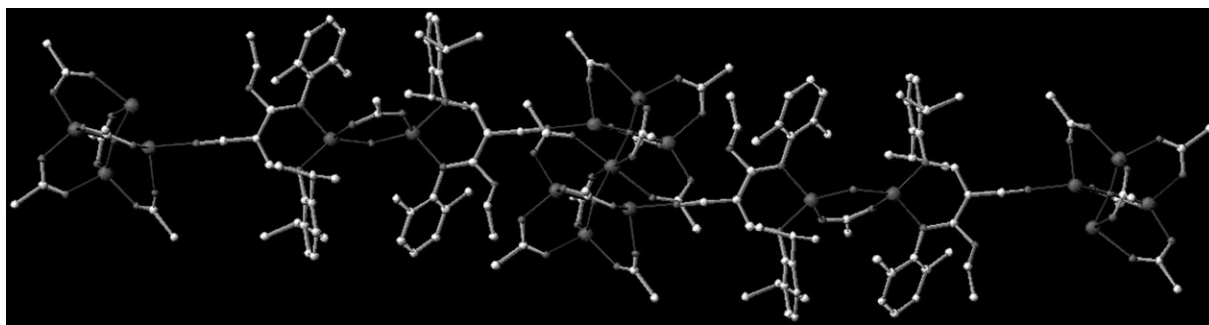


Figure 5. Plot of the band-like structure of $[(\mu, \eta^2\text{-OAc})_5(\mu, \eta^4\text{-O})\text{Zn}_4(\mu, \eta^3\text{-3e})\text{Zn}(\mu, \eta^2\text{-OAc})(\mu, \eta^2\text{-OH})]_\infty$ (**6e**).

form an endless band (Figure 5). On the one hand it incorporates one part, that is isostructural to **5d**. Two zinc centers are bridged by an acetate and a hydroxy group to give a six-membered ring. Again, the ligand backbone shows similar lengths for all C–C bonds as expected for a conjugated system and the aromatic rings with the bulkier isopropyl substituents stand apart from each other. But, on the other hand, the structure incorporates an unexpected second part. This second part consists of seven zinc atoms where the central zinc is located on an inversion center, so that the overall structure of this part can be described as two tetrahedral Zn_4 units, which are edge-bridged *via* one zinc atom. Each Zn_4 tetrahedron is placed around one central oxygen atom (O4), to which all four zinc atoms are connected. The three Zn atoms which are not located on the inversion center exhibit a distorted tetrahedral environment. Two of them take part in three acetate bridges whereas the third is only involved in two acetate bridges and completes its coordination sphere by a bond to the CN part of the ligand. Interestingly, some nickel complexes of similar ligands had only this cyano-metal coordination and did not form the expected *N,N*-chelate.^[29] The central zinc atom of the Zn_7 unit shows an distorted octahedral environment as it is coordinated to the two central O atoms of the tetrahedron plus to four oxygen atoms forming acetate bridges to the four Zn atoms which are not bound to the N atom of the ligands. Since the whole second part is linked to two ligands *via* the cyano group and the two respective zinc atoms, the whole structure forms a polymeric band. A similar structural $\text{Zn}_7\text{O}_2(\text{OOCR})_{10}$ motif has been observed several times before,^[30,31] which shows that the formation of such a unit is very likely in the presence of zinc, acetate and water. Overall, the existence of this structure shows how easily and how effectively catalyst poisoning can occur. One such structural unit binds seven zinc atoms, which could be potential active catalytic centers otherwise.

Copolymerization Experiments

Generally, all tested catalysts were able to catalyze the alternating copolymerization of CO_2 and cyclohexene oxide. ^{13}C NMR assignments^[32] of the resulting poly(cyclohexyl carbonate) (PCHC) revealed a random distribution of isotactic and syndiotactic carbonate, thus all polymers were atactic. With 114°C , the glass transition temperature (T_g) matched the known literature values.^[33] Some of the most active systems (**4d**, **4e**) were also tested in the alternating copolymerization of CO_2 and propylene oxide, but in this case only traces of polycarbonates were found. Up to now, only some special β -diketimine-based zinc complexes showed significant activities in this reaction.^[34] The copolymerization of CO_2 and cyclohexene oxide was carried out with catalyst loadings of 0.1 % under a CO_2 pressure of 4 MPa without using any further solvents. Optimization experiments proved a temperature window between 80°C and 100°C to be ideal.^[35] At higher temperatures, more and more cyclic carbonate is formed in an unwanted, thermodynamically-favored side reaction.^[36] In our experiments at and below 100°C the formation of cyclic cyclohexyl carbonate did not exceed 10%. At lower temperatures the catalytic activity decreases. Another undesired side reaction is the formation of polyether through the homopolymerization of the epoxide, since the reactivity of the epoxide is much higher than that of CO_2 . To suppress polyether formation, an ideal copolymerization catalyst should not catalyze the homopolymerization at all. Most of the presented catalysts showed good selectivities and at 90°C , polyether formation did not exceed 12–14 % (Table 3). An exceptional high polyether formation was observed for the symmetrically substituted catalysts, which were 2,6-isopropyl (**4a**, **4h**) or 2,6-ethyl (**4f**) substituted on both aromatic rings. Additionally, these catalysts were the least active. Exchanging the cyano group on the backbone for an ethyl acetate reduced the activity markedly (**4h**). On the other side, the catalysts with the biggest difference in the substitution pattern, that is, with 2,6-isopropyl substitution on one ring and 2,6-

Table 3. Performance of catalysts in the CO₂/cyclohexene oxide copolymerization.

Catalyst ^[a]	<i>t</i> [h]	<i>T</i> [°C]	<i>p</i> (CO ₂) [MPa]	TON ^[b]	TOF ^[b] [h ⁻¹]	<i>g</i> _{poly} <i>g</i> _M ⁻¹ [h ⁻¹]	Carbonate linkages ^[c] [%]	<i>M</i> _n ^[d] [kg mol ⁻¹]	<i>M</i> _w / <i>M</i> _n
4a	2	100	4	270	135	293	58	12.6	1.72
4b	2	100	4	327	164	356	72	20.0	1.26
4c	2	90	4	315	158	343	86	17.5	1.16
4d	2	90	4	367	183	399	88	24.5	1.15
4e	2	100	4	396	198	430	75	15.8	1.21
4f	2	90	4	85	43	185	74	5.5	1.20
4g	2	90	4.8	249	125	271	83	11.3	1.17
4h	2	90	4	144	72	157	48	8.4	1.81
4e	1	90	4	210	210	456	88	10.0	1.16
(BDI)Zn^[e]	2	90	4	751	375	816	98	25.0	1.14

^[a] A [CHO]:[Zn] ratio of 1000:1 was 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.

^[e] Synthesized as reported in the literature^[14].

methyl on the other (**4d**, **4e**), were the most active and selective. Catalyst **4e** reached high activities reaching turnover frequencies (TOF) beyond 200 h⁻¹ which come close to the performance of β-diketiminato zinc complexes (Table 3). The unsymmetrical catalysts bearing isopropyl and ethyl substituents (**4b**, **4c**) were only slightly less active. The two aromatic rings have distinguishable, slightly different chemical surroundings, but the activity remains nearly the same, whether the bulkier ring is on the bulkier imidoester side of the backbone (**4b**, **4d**) or *vice versa* (**4c**, **4e**). To see if the introduction of an electron-withdrawing substituent on the aromatic ring could increase activity, a 2,6-chloro-substituted ring was introduced in **4g**. However, the catalyst was less active than the unsymmetrical alkyl-substituted catalysts. Although the introduction of electron-withdrawing groups on the ligand backbone normally increases activities,^[37] the rather small effect of the chloro group might be due to the fact that it sits outside on the aromatic ring, while the conjugated electron system of the ligand backbone is in direct contact to the active metal center. Overall, catalyst **4e** turned out to be the most active. Generally, the more active catalysts produced polycarbonates with high molecular weights around 20,000 g mol⁻¹ and with narrow polydispersities *M*_w/*M*_n around 1.2. The narrow polydispersities indicate a living polymerization. This was corroborated by a kinetic study that showed the linear relation between monomer (CHO) conversion and chain length of the resulting polymer.^[35] Under the assumption that one polymer chain is growing on one active metal center (like it should do in a living polymerization), the length of the polymer can be calculated for each stage of monomer conversion, if the monomer to catalyst ratio is known. Interestingly, such calculations only fitted the experimental findings when the growth of

two polymer chains on one active metal center was assumed.^[35] This stands contrary to aforementioned findings (like the solid-state structures)^[26] that rather support a bimetallic mechanism and thus, further studies are necessary to clarify this remaining question.

Terpolymerization Experiments

A first experiment with solely racemic dilactide showed that complex **4e** is an active catalyst for the polymerization of lactide to produce polylactide (PLA). Then, terpolymerization experiments with CO₂, cyclohexene oxide and dilactide were carried out with catalysts **4d** and **4e**. Most reaction conditions were maintained as in the copolymerization experiments (*p*, *T*) and only the catalyst loading (0.25%) and the reaction time (16 h) were raised. Both complexes catalyzed the reaction, but the resulting poly(cyclohexyl carbonate-co-lactide) (PCLA) embodied a large fraction of lactide (Table 4). To reach a higher incorporation of polycarbonate, a three-fold excess of the CHO monomer was fed into the reactor. Since the reaction conditions were not optimized, the turnover frequency for the reaction was only moderate, but high molecular weight polymers with narrow polydispersities were produced. In general, reactions with racemic lactide led to higher activities and a higher polycarbonate content compared to reactions with *S*-lactide. Terpolymerization with *S*-lactide yielded semicrystalline copolymers with larger PLA fractions. The semicrystalline copolymers all had a melting point around 167 °C. As for the above copolymerization, catalyst **4e**, which has a less bulky aromatic ring (2,6-methyl-substituted) on the bulkier imidoester side of its backbone, was the most active catalyst

Table 4. Performance of catalysts in the CO₂/cyclohexene oxide/lactide terpolymerization.^[a]

Catalyst	Lactide	CHO:lactide	TOF ^[b] [h ⁻¹]	\bar{g}_{poly} \bar{g}_{M}^{-1}	Carbonate [%] ^[c]	Lactide [%] ^[c]	M_n ^[d] [kg mol ⁻¹]	M_w/M_n	T_g (T_m) [°C] ^[e]
4e	<i>rac</i>	0	22	387	0	100	28.5	1.74	
4e	<i>rac</i>	1.5	26	460	10	90	21.8	1.21	57
4e	<i>rac</i>	3	23	448	41	49	15.8	1.21	68
4e	<i>S</i>	3	20	371	19	71	29.5	1.12	68 (168)
4d	<i>rac</i>	3	22	424	27	65	11.3	1.96	63
4d	<i>S</i>	3	22	395	5	95	28.4	1.09	59 (169)
(BDI)Zn	<i>rac</i>	1	43	797	15	85	32.3	1.22	58
(BDI)Zn	<i>rac</i>	2	50	1145	73	27	41.6	1.11	74
(BDI)Zn	<i>rac</i>	3	57	1280	80	20	41.6	1.11	73
(BDI)Zn	<i>S</i>	2	29	524	12	88	27.5	1.13	62 (168)

^[a] All terpolymerization experiments were carried out for 16 h, at 90 °C, 4 MPa and 0.1 mol % catalyst loading.

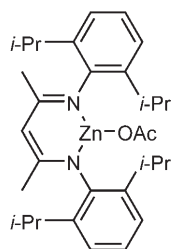
^[b] Mole of CHO consumed per mole of zinc per hour.

^[c] Determined by ¹H NMR, the difference from 100 % being the ether content.

^[d] Determined by GPC in THF.

^[e] Determined by differential scanning calorimetry (DSC).

and delivered the highest amounts of polycarbonate incorporation. Although a heterogeneously catalyzed terpolymerization with CO₂, propylene oxide and ϵ -caprolactone has been carried out before,^[38] to our knowledge, a terpolymerization of CO₂, cyclohexene oxide and lactide had not been done before. Previously, polycarbonate-*co*-polylactide polymers had only been made by ring opening polymerization of cyclic carbonates and lactide, which bears the drawback of a tedious cyclic carbonate monomer preparation.^[39,40] For comparison of catalytic activities some experiments with a literature-known BDI zinc complex (Scheme 4) were carried out under the same conditions.

**Scheme 4.** Catalyst (BDI)Zn(OAc)

It is known that such complexes selectively catalyze the polymerization of lactide.^[22,41] We found that it also catalyzed the terpolymerization. As before, an excess of CHO monomer had to be used to incorporate higher amounts of polycarbonate in the polymer. But overall, the BDI zinc catalyst showed higher activities and higher polycarbonate incorporations. This tendency to incorporate less lactide and more carbonate might have the same source as the fact that it

does not catalyze the homopolymerization of CHO, which is also a ring opening polymerization. The glass transition temperatures of the PCLA copolymers lay between the ones for pure PLA (*ca.* 50 °C, dependent on chain length) and pure PCHC (115 °C) and increase with growing PCHC content, which indicates a statistical distribution of lactide and polycarbonate in the polymer. Overall we have shown that new PCLA copolymers can be prepared with a broad bandwidth of compositions. This should result in a broad bandwidth of degradation times and makes this copolymer an interesting biomaterial, for example, for biomedical applications.

Conclusions

A broad variety AIA zinc acetate complexes was synthesized and several structure-activity relationships for the catalyzed alternating copolymerization of CO₂ and CHO were found. The least active and selective catalysts were those with the same substitution pattern on both sides. The highest catalytic activities were reached by catalysts with ligands that presented two sides with different steric demands, especially on the aromatic rings. The most active catalyst **4e** exhibited high activities (TOF > 200 h⁻¹) and selectivities. To the best of our knowledge, it was shown for the first time that a terpolymerization of CO₂, cyclohexene oxide and lactide is catalyzed to give poly(cyclohexyl carbonate-*co*-lactide). The reaction was catalyzed by literature-known BDI zinc acetate complexes as well as by the presented AIA zinc acetate catalyst system and it was possible to control the composition of the terpolymers by variation of the monomer feed. Thereby an interesting material with a variable biodegradability was prepared for the first time.

Experimental Section

General Considerations

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. NMR spectra were recorded on a Bruker spectrometer 250 MHz (^1H) and 62.9 MHz (^{13}C) at 293 K. Mass spectra were obtained using electron ionization (EI), electron spray ionization (ESI) or field ionization (FI). FI and EI spectra were recorded with Micromass GCT and Finnigan MAT GCQ spectrometers, ESI spectra were recorded with a Hewlett-Packard 1100 MSD spectrometer. Glass transition temperatures and melting points were determined by using differential scanning calorimetry (DSC) with a Mettler Toledo 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 Å and 100 Å) were run with tetrahydrofuran at 35 °C at 1 mL min $^{-1}$ and were calibrated by polystyrene standards.

Analytical data for all new compounds are given in the Supporting Information.

Materials

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-Cyano-*N*-(2,6-diisopropylphenyl)acetamide (1a)

Cyanoacetic acid (12.76 g, 0.15 mol) was added to a stirred suspension of phosphorus pentachloride (31.27 g, 0.15 mol) in dichloromethane (450 mL) at ambient temperature. The reaction mixture was heated at reflux for 30 min. After cooling, 2,6-diisopropylaniline (17.73 g, 0.10 mol) was added in 10 min and the reaction mixture was heated for 2 h under reflux. It was then cooled in an ice/water bath, and water (200 mL) was added. After stirring for 30 min, the reaction mixture was neutralized by addition of a sodium carbonate solution. The water phase was extracted twice with dichloromethane; the organic phases were then collected and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the obtained white solid was recrystallized from toluene and dried in vacuum; yield: 23.3 g (0.095 mol, 95 %).

2-Cyano-*N*-(2,6-diethylphenyl)acetamide (1b)

Cyanoacetic acid (12.76 g, 0.15 mol) was added to a stirred suspension of phosphorus pentachloride (31.27 g, 0.15 mol) in dichloromethane (450 mL) at ambient temperature. The reaction mixture was heated at reflux for 30 min. After cooling, 2,6-diethylaniline (22.39 g, 0.15 mol) was added in 10 min and the reaction mixture was heated for 2 h under reflux. It was then cooled in an ice/water bath, and water (200 mL) was added. After stirring for 30 min, the reaction mixture was neutralized by addition of a sodium carbonate solution. The water phase was extracted twice with dichloromethane; the organic phases were then collected and dried

over Na_2SO_4 . The solvent was removed under reduced pressure and the obtained white solid was recrystallized from toluene/ethyl acetate (3/1) and dried in vacuum; yield: 20.4 g (0.094 mol, 63 %).

2-Cyano-*N*-(2,6-dimethylphenyl)acetamide (1c)

Cyanoacetic acid (12.76 g, 0.15 mol) was added to a stirred suspension of phosphorus pentachloride (31.27 g, 0.15 mol) in dichloromethane (450 mL) at ambient temperature. The reaction mixture was heated at reflux for 30 min. After cooling, 2,6-dimethylaniline (18.18 g, 0.15 mol) was added in 10 min and the reaction mixture was heated for 2 h under reflux. It was then cooled in an ice/water bath, and water (200 mL) was added. After stirring for 30 min, the reaction mixture was neutralized by addition of a sodium carbonate solution. The water phase was extracted twice with dichloromethane; the organic phases were then collected and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the obtained white solid was recrystallized from toluene/ethyl acetate (5/2) and dried in vacuum; yield: 21.91 g (0.116 mol, 78 %).

Ethyl 2-Cyano-*N*-(2,6-diisopropylphenyl)ethanimidoate (2a)

A mixture of 2-cyano-*N*-(2,6-diisopropylphenyl)acetamide (1a) (14.70 g, 60 mmol) and a 1.0 M solution of triethyloxonium tetrafluoroborate in dichloromethane (66 mL, 66 mmol) was stirred for 5 d at ambient temperature. The solvent was removed in vacuum and the residue was washed twice with absolute diethyl ether. Then the residue was taken up in 60 mL of absolute diethyl ether and cooled to 0 °C. Triethylamine (9.2 mL, 66 mmol) was slowly added, and the mixture was stirred at room temperature for 2 h. The organic phase was separated and the residue was washed three times with absolute diethyl ether. The diethyl ether solutions were collected, dried over Na_2SO_4 , and the solvent was removed under reduced pressure. Distillation of the residue (13.7 g) gave the pure product; yield: 7.52 g (28 mmol, 46 %).

Ethyl 2-Cyano-*N*-(2,6-diethylphenyl)ethanimidoate (2b)

A mixture of 2-cyano-*N*-(2,6-diethylphenyl)acetamide (1b) (7.75 g, 35.8 mmol), dichloromethane (100 mL) and a 1.0 M solution of triethyloxonium tetrafluoroborate in dichloromethane (50 mL, 50 mmol) was stirred for 5 d at ambient temperature. The solvent was removed in vacuum and the residue was washed twice with absolute diethyl ether. Then the residue was taken up in 60 mL of absolute diethyl ether and cooled to 0 °C. Triethylamine (6.9 mL, 50 mmol) was slowly added, and the mixture was stirred at room temperature for 2 h. The organic phase was separated and the residue was washed three times with absolute diethyl ether. The diethyl ether solutions were collected, dried over Na_2SO_4 , and the solvent was removed under reduced pressure. Distillation of the residue gave the pure product; yield: 2.6 g (10.6 mmol, 30 %).

Ethyl 2-Cyano-*N*-(2,6-dimethylphenyl)ethanimidoate (2c)

A mixture of 2-cyano-*N*-(2,6-dimethylphenyl)acetamide (**1a**) (10.00 g, 53 mmol) and a 1.0 M solution of triethyloxonium tetrafluoroborate in dichloromethane (60 mL, 60 mmol) was stirred for 5 d at ambient temperature. The solvent was removed in vacuum and the residue was washed twice with absolute diethyl ether. Then the residue was taken up in 60 mL of absolute diethyl ether and cooled to 0 °C. Triethylamine (8.4 mL, 60 mmol) was slowly added, and the mixture was stirred at room temperature for 2 h. The organic phase was separated and the residue was washed three times with absolute diethyl ether. The diethyl ether solutions were collected, dried over Na₂SO₄, and the solvent was removed under reduced pressure. Extraction with hexane (4 × 15 mL) gave the pure product; yield: 2.2 g (10.2 mmol, 19 %).

Ethyl 2-Cyano-3-[(2,6-diisopropylphenyl)amino]-*N*-(2,6-diisopropylphenyl)prop-2-enimidoate (3a)

A mixture of ethyl 2-cyano-*N*-(2,6-diisopropylphenyl)ethanimidoate (**2a**) (1.18 g, 4.2 mmol), triethyl orthoformate (0.61 g, 4.2 mmol), and acetic anhydride (1.47 g, 8.4 mmol) was refluxed for 5 h. The solvent was removed under reduced pressure. The resulting thick oil was dissolved in methanol (5 mL), 2,6-diisopropylaniline (0.93 g, 4.7 mmol) was added and the solution was refluxed for 30 min. The reaction mixture was then stored overnight at 5 °C and the product crystallized. Recrystallization from methanol furnished colorless crystals of the product; yield: 0.77 g (1.68 mmol, 42 %).

Ethyl 2-Cyano-3-[(2,6-diethylphenyl)amino]-*N*-(2,6-diisopropylphenyl)prop-2-enimidoate (3b)

A mixture of ethyl 2-cyano-*N*-(2,6-diisopropylphenyl)ethanimidoate (**2a**) (1.5 g, 5.5 mmol), triethyl orthoformate (0.82 g, 5.5 mmol), and acetic anhydride (1.17 g, 11.5 mmol) was refluxed for 5 h. The solvent was removed under reduced pressure. The resulting thick oil was dissolved in methanol (7 mL), 2,6-diethylaniline (0.82 g, 5.5 mmol) was added and the solution was refluxed for 30 min. The reaction mixture was then stored overnight at 5 °C and the product crystallized. Recrystallization from methanol furnished colorless crystals of the product; yield: 0.74 g (1.7 mmol, 31 %).

Ethyl 2-Cyano-3-[(2,6-diisopropylphenyl)amino]-*N*-(2,6-diethylphenyl)prop-2-enimidoate (3c)

A mixture of ethyl 2-cyano-*N*-(2,6-diethylphenyl)ethanimidoate (**2b**) (2 g, 8.15 mmol), triethyl orthoformate (1.2 g, 8.15 mmol), and acetic anhydride (1.68 g, 16.6 mmol) was refluxed for 5 h. The solvent was removed under reduced pressure. The resulting thick oil was dissolved in methanol (7 mL), 2,6-diisopropylaniline (0.93 g, 5.88 mmol) was added and the solution was refluxed for 30 min. The reaction mixture was then stored overnight at 5 °C and the product crystallized. Recrystallization from methanol furnished colorless crystals of the product; yield: 0.98 g (2.26 mmol, 28 %).

Ethyl 2-Cyano-3-[(2,6-dimethylphenyl)amino]-*N*-(2,6-diisopropylphenyl)prop-2-enimidoate (3d)

A mixture of ethyl 2-cyano-*N*-(2,6-diisopropylphenyl)ethanimidoate (**2a**) (1.36 g, 5 mmol), triethyl orthoformate (0.74 g, 5 mmol), and acetic anhydride (1.13 g, 11 mmol) was refluxed for 5 h. The solvent was removed under reduced pressure. The resulting thick oil was dissolved in methanol (6 mL), 2,6-dimethylaniline (0.61 g, 5 mmol) was added and the solution was refluxed for 30 min. The reaction mixture was then stored overnight at 5 °C and the product crystallized. Recrystallization from methanol furnished colorless crystals of the product; yield: 0.60 g (1.49 mmol, 30 %).

Ethyl 2-Cyano-3-[(2,6-diisopropylphenyl)amino]-*N*-(2,6-dimethylphenyl)prop-2-enimidoate (3e)

A mixture of ethyl 2-cyano-*N*-(2,6-methylphenyl)ethanimidoate (**2c**) (3.93 g, 18 mmol), triethyl orthoformate (2.66 g, 18 mmol), and acetic anhydride (4.08 g, 40 mmol) was refluxed for 5 h. The solvent was removed under reduced pressure. The resulting thick oil was dissolved in methanol (15 mL), 2,6-diisopropylaniline (3.05 g, 17 mmol) was added and the solution was refluxed for 30 min. The reaction mixture was then stored overnight at 5 °C and the product crystallized. Recrystallization from methanol furnished colorless crystals of the product; yield: 2.09 g (5.2 mmol, 30 %).

Ethyl 2-Cyano-3-[(2,6-diethylphenyl)amino]-*N*-(2,6-diethylphenyl)prop-2-enimidoate (3f)

A mixture of ethyl 2-cyano-*N*-(2,6-diethylphenyl)ethanimidoate (**2b**) (2.5 g, 10.2 mmol), triethyl orthoformate (1.51 g, 10.2 mmol), and acetic anhydride (2.25 g, 16.6 mmol) was refluxed for 5 h. The solvent was removed under reduced pressure. The resulting thick oil was dissolved in methanol (5 mL), 2,6-diethylaniline (1.49 g, 10 mmol) was added and the solution was refluxed for 30 min. The reaction mixture was then stored overnight at 5 °C and the product crystallized. Recrystallization from methanol furnished colorless crystals of the product; yield: 1.13 g (2.82 mmol, 28 %).

Ethyl 2-Cyano-3-[(2,6-dichlorophenyl)amino]-*N*-(2,6-dimethylphenyl)prop-2-enimidoate (3g)

A mixture of ethyl-2-cyano-*N*-(2,6-methylphenyl)ethanimidoate (**2a**) (1.56 g, 3.3 mmol), triethyl orthoformate (0.49 g, 3.3 mmol), and acetic anhydride (0.71 g, 7 mmol) was refluxed for 5 h. The solvent was removed under reduced pressure. The resulting thick oil was dissolved in methanol (2 mL), 2,6-dichloroaniline (0.54 g, 3.3 mmol) was added and the solution was refluxed for 30 min. The reaction mixture was then stored overnight at 5 °C and the product crystallized. Recrystallization from methanol furnished colorless crystals of the product; yield: 0.60 g (1.3 mmol, 41 %).

Ethyl 3-[(2,6-Diisopropylphenyl)amino]-2-[(2,6-diisopropylphenyl)amino]acrylate (2h)

A mixture of diethyl ethoxymethylenemalonate (5.01 g, 23 mmol) and 2,6-diisopropylaniline (9.04 g, 46 mmol) was heated at 135 °C for 38 h; the produced ethanol was distilled out of the reaction mixture. The mixture was cooled and

20 mL of cold hexane were added under vigorously stirring. The solution was stored overnight at -30°C and a white precipitate was collected and filtered; yield: 7.43 g (16 mmol, 68 %).

Ethyl 2-{Ethoxy[(2,6-diisopropylphenyl)imino]methyl}-3-[(2,6-diisopropylphenyl)amino]-acrylate (3h)

A mixture of ethyl 3-[(2,6-diisopropylphenyl)amino]-2-[[2,6-diisopropyl-phenyl]amino]carbonyl]acrylate (**2g**) (4.00 g, 8 mmol) and a 1.0M solution of triethylxonium tetrafluoroborate in dichloromethane (12.45 g, 9 mmol) was stirred for 9 d at ambient temperature. The solvent was removed in vacuum and the residue was washed twice with absolute diethyl ether. Then the residue was taken up in 30 mL of absolute diethyl ether and cooled to 0°C . Triethylamine (1.3 mL, 9 mmol) was slowly added and the mixture was stirred at room temperature for 2 h. The organic phase was separated and the residue was washed three times with absolute diethyl ether. The diethyl ether solutions were collected, dried over Na_2SO_4 , and the solvent was removed under reduced pressure. An oil was obtained which crystallized slowly. This solid was filtered; yield: 2.57 g (5 mmol, 60 %).

[(3)Zn(OAc)]₂ (**4**)

Zinc acetate complexes of the ligand were prepared *via* the corresponding zinc-ethyl complex by the following procedure adapted from the literature.^[14] Ligands **3** were dissolved in toluene and an equimolar amount of a diethylzinc solution (1.1M in toluene) was added. The solution was heated to 75°C for 18 h and afterwards, the solvent was removed under reduced pressure. The resulting complex (**3**)Zn(Et) was used without further purification. It was dissolved in dichloromethane and after cooling to 0°C an equimolar amount of acetic acid was added dropwise. Within 18 h the solution was warmed gradually to room temperature. After removal of the solvent the complexes [(**3**)Zn(OAc)]₂ (**4**) were purified by crystallization from dichloromethane. X-Ray quality crystals were obtained by covering a dichloromethane solution with pentane.

General Procedure for Copolymerization Reactions

An autoclave (Parr) was heated to 95°C under vacuum for 16 h and cooled under vacuum. Catalyst **4e** (42 mg, 0.080 mmol) and cyclohexene oxide (7.81 g, 80 mmol) were brought into the autoclave, which was then heated to the reaction temperature and pressurized with CO_2 to the appropriate pressure (4MPa). 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 under vacuum to constant weight.

General Procedure for Terpolymerization Reactions

An autoclave (Parr) was heated to 95°C under vacuum for 16 h and cooled under vacuum. Catalyst **4d** (42 mg, 0.080 mmol), dilactide (1.44 g, 9.97 mmol) and cyclohexene oxide (5.87 g, 58.9 mmol) were brought into the autoclave,

which was then heated to the reaction temperature and pressurized with CO_2 to the appropriate pressure (4MPa). After 16 h the reactor was cooled, vented and a small sample taken for analysis. The resulting polycarbonate-co-poly lactide was dissolved in CH_2Cl_2 (5 mL), precipitated from MeOH (20 mL), collected and dried under vacuum to constant weight.

Crystal Structure Determination

The X-ray analyses were performed on a Siemens SMART CCD 1000 diffractometer using graphite-monochromated Mo-K_{α} radiation with an irradiation time of 10 s to 20 s per frame and collecting a full sphere of data using an ω -scan technique with a $\Delta\omega$ in the range from 0.3 to 0.45° . Lorentz and polarization as well as an experimental absorption correction was performed.^[42]

The structures were resolved by direct methods (SHELXS^[43]) and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97^[44]). The hydrogen atoms were localized by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically.^[44]

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 266169 and 296831–296833. Copies of this information may be obtained free of charge from: The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>.

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