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Note

A new amidoimidomalonate zinc complex with a sedecameric solid state structure catalyzing the copolymerization of CO_2 and cyclohexene oxide

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Abstract

A new amidoimidomalonate ligand was synthesized in a short and effective way and the zinc acetate complex thereof was prepared. XRD investigation revealed an unprecedented solid state structure, where the sedecameric complex $[(lig)_2Zn_4(OAc)_4]_4$ builds the edges of a square cavity. Each edge is made up by a similar unit $[(lig)_2Zn_4(OAc)_4]$ with four zinc atoms. The complex is an active catalyst in the copolymerization of CO_2 and cyclohexene oxide and produces polyethercarbonates with broad molecular weight distributions.

Keywords: Carbon dioxide fixation; Copolymerization; Imidomalonates; Polycarbonates; Zinc complexes

1. Introduction

The fixation of carbon dioxide as a C_1 building block is still one of the most prominent goals in green and synthetic chemistry [1]. CO_2 is widely abundant, it exhibits no toxicity or flammability and it is inexpensive; thus it is a very attractive synthon. The only major drawback is its low reactivity, which can be overcome by catalytic activation [2–4]. One of the most important and promising routes towards the utilization of carbon dioxide is the copolymerization with oxiranes to produce aliphatic polycarbonates. Apart from the advantages of CO_2 utilization, this reaction combines several other features for high sustainability: A perfectly atom efficient route to polycarbonates that needs no other solvent and yields a biodegradable polymer. In the first years after the discovery of the reaction by Inoue [5], predominantly heterogeneous catalysts were developed, leading to rather low activities [6]. Only over the last decade, new homogeneous catalysts with higher activities, like zinc phenoxides [7] or chromium [8] and cobalt [9,10] salen complexes were discovered. The rapidly growing interest in the reaction has been thoroughly documented in several recent reviews [11–13]. The most active catalysts known to date are zinc complexes with β-diketiminate ligands [14–16]. In homogeneous catalysis, such β-diketiminate ligands play an important role as spectator ligands by means of their strong binding to the metal, their tunable steric demand and their diversity of binding modes [17]. With several metals, coordinately unsaturated complexes are formed, which can catalyze a number of important reactions like the oligomerization and polymerization of olefins [18–20], the polymerization of methyl methacrylate [21] or the polymerization of lactide [22,23]. Our group has reported a zinc complex with new aminoimidoacrylate ligands **1**, which showed high catalytic activities in the copolymerization of cyclohexene oxide and carbon dioxide (Scheme 1) [24]. Based on this active catalyst as a lead structure, we have developed a new ligand, the amidoimi-

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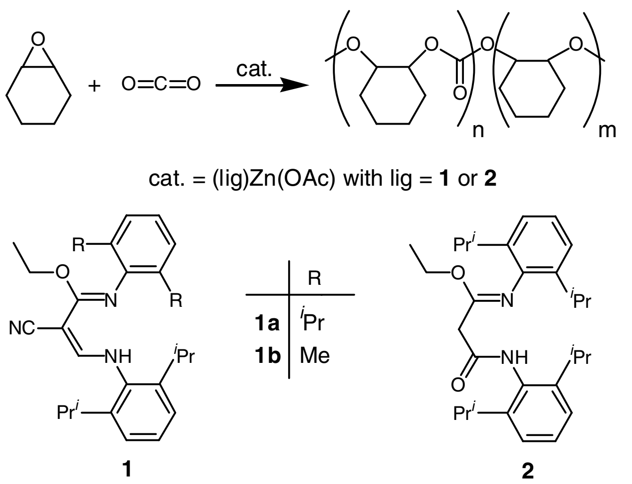


Scheme 1. Copolymerization of cyclohexene oxide and carbon dioxide catalyzed by zinc complexes with aminoimidoacrylate and amidoimidomalonate ligands.

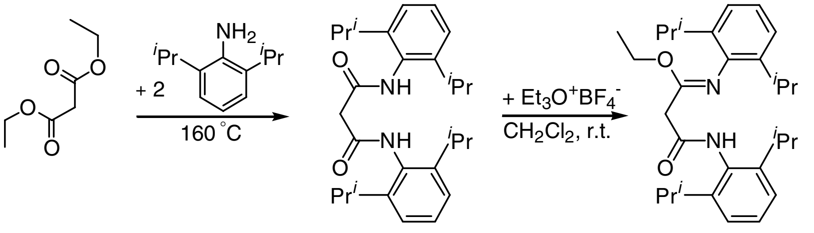
domalonate **2**. Herein we describe the ligand and complex synthesis, its catalytic activity and structure and compare it to the catalysts with the aminoimidoacrylate ligands.

2. Results and discussion

Since the synthesis of suitable aminoimidoacrylate ligands **1** needs three steps, alternative routes have been sought. The amidoimidomalonate ligand **2** has a similar structure, but can be synthesized in two steps (Scheme 2). In the first step, an amidomalonate is prepared by reaction of diethylmalonate with two equivalents of 2,6-diisopropylaniline. This reaction requires no solvent, the emerging ethanol can be distilled off easily and the yield is very good (90%). In the second step, one side of the symmetric malonamide is O-alkylated with the Meerwein salt triethyloxonium tetrafluoroborate to generate the imido group [25]. The desired amidoimidomalonate is obtained in 64% yield, corresponding to 58% overall yield for both steps.

A zinc acetate complex of the ligand was prepared analog to the zinc acetate complexes of aminoimidoacrylates **1** and β-diiminates [24,26]. Treating the ligand with diethyl zinc produces an ethylzinc complex as intermediate. Afterwards an equimolar amount of acetic acid is added to the ethylzinc complex to give the acetate complex. As expected, **1** acts as an N,N-chelating ligand. In the solid state, the resulting complex $[(\mathbf{1})Zn(OAc)]_2$ has a dimeric structure, where two tetrahedral zinc centers are bridged by two acetate ions [24]. For the amidoimidomalonate **2**, an N,N-chelated zinc complex was expected as well, because with nickel, such complexes were made and showed to be active as olefin oligomerization catalyst [27]. But, though in solution, the presence of monomeric and dimeric species is indicated by the mass spectra, the solid state structure contained much larger units. For the zinc acetate complex with **2**, an unprecedented solid state structure with the overall formula $[(\mathbf{2})_2Zn_4(OAc)_4]_4$ was found. One unit is a sedecamer, containing sixteen zinc atoms which build up the edges of a square cavity (Fig. 1). Each side of this square consists of identical $[(\mathbf{2})_2Zn_4(OAc)_4]$ units, which are linked by acetate bridges. All four edges of the square are occupied by the respective Zn3 atoms. The decisive feature in the crystallographic independent unit $[(\mathbf{2})_2Zn_4(OAc)_4]$ is, that the carbonyl oxygen acts as a μ-coordinated donor to two zinc atoms (Fig. 2). Overall, both ligands **2** are μ_3-η^4-coordinating. All four zinc atoms are N,O-connected to the ligands **2**. Two zinc atoms (Zn1 and Zn3) form an N,O-chelate with a single ligand and two zinc atoms (Zn2 and Zn4) bridge the two ligands **2**. With 98°, the bite angle of the N,O-chelates is slightly wider than the 96° for the N,N-chelates in $[(\mathbf{1})Zn(OAc)]_2$. All zinc atoms have a distorted tetrahedral coordination sphere. With their remaining two coordination sites, the zinc atoms are interconnected via acetate bridges. While the bridging zinc atoms (Zn2 and Zn4) are connected within the $[(\mathbf{2})_2Zn_4(OAc)_4]$ unit (to each other and Zn1 and Zn3, respectively), the N,O-chelated zinc atoms (Zn1 and Zn3) have a connecting acetate bridge to a neighboring unit. In both ligands **2**, the backbone has a conjugated π-electron system according to the mesomeric structures shown in Scheme 3. The C–C and C–N bonds are nearly of the same length and all bond lengths lie between the values for single and double bonds (Fig. 2).

Like the zinc acetate complexes of **1**, the described complex of **2** is an active catalyst for the copolymerization of carbon dioxide and cyclohexene oxide (Scheme 1). Nonetheless, due to the different catalyst structures, the copolymerization results are substantially different, even though the large complex structure **2** cannot be expected to remain intact during homogeneous catalysis in solution. While



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Scheme 2. Synthesis of the amidoimidomalonate ligand.

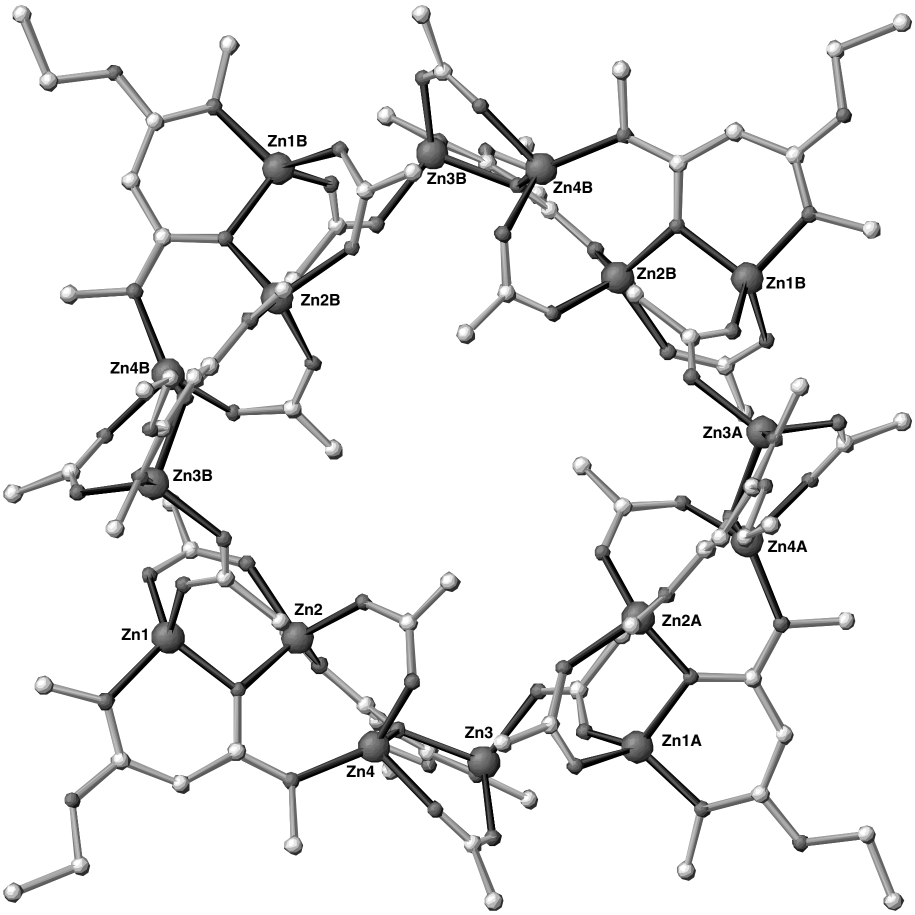


Fig. 1. Overall structure of $[(\mathbf{2})_2Zn_4(OAc)_4]_4$. Phenyl residues and H-atoms are omitted for reasons of clarity.

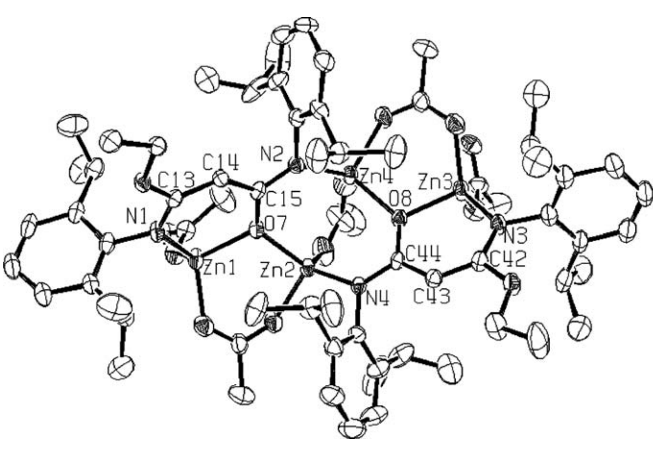
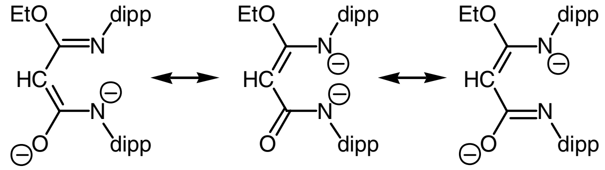


Fig. 2. View to the crystallographic independent unit of the elementary cell $[(\mathbf{2})_2Zn_4(OAc)_4]$ of $[(\mathbf{2})_2Zn_4(OAc)_4]_4$ drawn by ORTEP [28] with 25% thermal ellipsoids. Selected atom distances (Å) and angles (deg): Zn1–N1 = 1.929(6), Zn1–O7 = 2.013(5), N1–C13 = 1.322(9), N2–C15 = 1.322(9), O7–C15 = 1.332(8), C13–C14 = 1.409(10), C14–C15 = 1.406(9), Zn2–O7 = 1.999(4), Zn2–N4 = 1.949(6), Zn2–Zn4 = 2.9657(13), Zn4–O8 = 1.996(5), Zn4–N2 = 1.960(6), Zn3–O8 = 2.002(5), Zn3–N3 = 1.943(6), N3–C42 = 1.306(9), N4–C44 = 1.337(9), O8–C44 = 1.328(8), C42–C43 = 1.401(10), C43–C44 = 1.388(10); N1–Zn1–O7 = 98.2(2), N3–Zn3–O8 = 98.5(2).

$[(\mathbf{1})Zn(OAc)]_2$ acts like a selective single site catalyst and initiates a living polymerization, $[(\mathbf{2})_2Zn_4(OAc)_4]_4$ operates less selective (Table 1). First of all, the resulting polymer contains only about 40% carbonate linkages, so that it is rather a polyethercarbonate, which comprises both, polyether (*m*, see Scheme 1) and polycarbonate (*n*, Scheme 1) sequences. The polycarbonate and polyether portions were identified and quantified by their methine protons via ^1H NMR spectroscopy in deuterated benzene (Fig. 3). Cyclic polycarbonate, which can be a major side product, especially when propylene oxide is used as a monomer, was found only in small traces in these copolymerizations with cyclohexene oxide.



Scheme 3. Mesomeric structures of the deprotonated ligand **2**. (dipp = 2,6-diisopropylphenyl).

Secondly, the molecular weight distribution of the resulting polymer is very broad ($M_w/M_n > 10$) and resembles polydispersities that are produced by heterogeneous catalysts. This can be explained by the exceptional structure of the catalyst, though the active catalytic species, dissolved in cyclohexene oxide, certainly differs distinctly from the observed solid state structure. The catalyst contains at

Table 1
Performance of catalysts in the cyclohexene oxide/CO_2 copolymerization

catalyst[a]	t (h)	T (°C)	$p(CO_2)$ (MPa)	TON[b]	TOF[b] (h^{-1})	$g_{poly}g_M^{-1}$ (h^{-1})	Carbonate linkages (%)[c]	M_n[d] (kg mol^{-1})	M_w/M_n
[(**1a**)Zn(OAc)]$_2$	2	100	4	270	135	293	58	12.6	1.72
[(**1b**)Zn(OAc)]$_2$	2	100	4	396	198	430	75	15.8	1.21
[(**2**)$_2$Zn$_4$(OAc)$_4$]$_4$	2	100	4	108	51	235	40	4.9	19.99
[(**2**)$_2$Zn$_4$(OAc)$_4$]$_4$	2	90	4	46	23	101	34	3.0	13.75

[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.

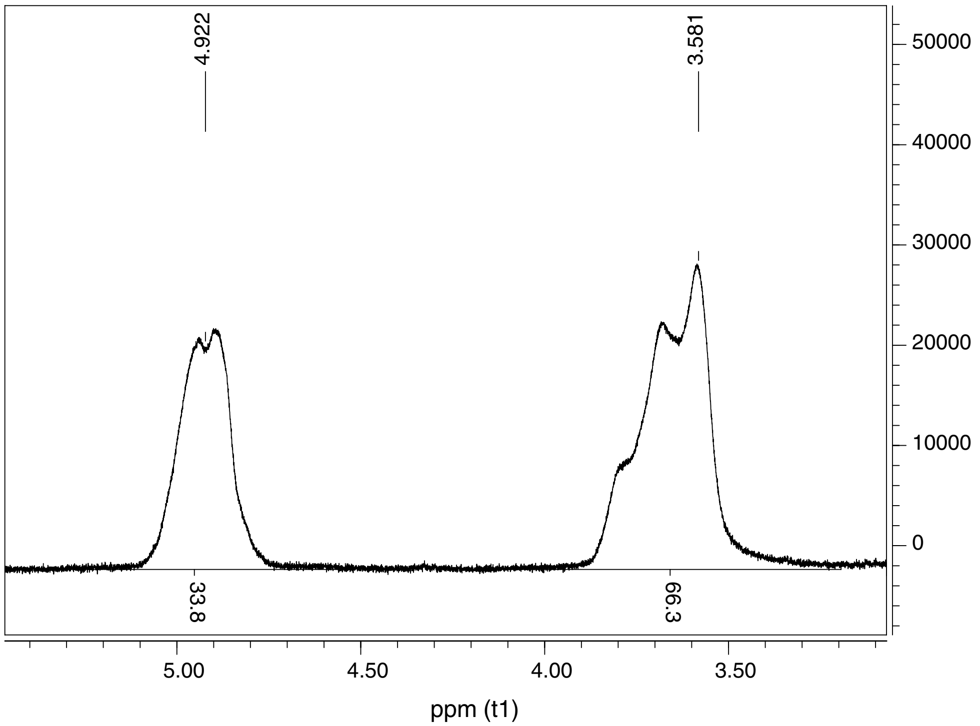


Fig. 3. ^1H NMR spectrum (methine region) of polyethercarbonate (last entry in Table 1) in deuterated benzene.

least two different zinc centers with completely different coordination spheres (Zn1 and Zn3 vs. Zn2 and Zn4, see above). Consequently, this different zinc centers exhibit different catalytic activities and hence polymer chains with different lengths are produced, leading to the observed broad polydispersities. The tendency of the catalyst to produce more polyether and less carbonate linkages, especially if compared to catalyst [(**1a**)Zn(OAc)]$_2$, can possibly be explained by the fact that the zinc atoms are N,O-coordinated. Such zinc centers exhibit a higher Lewis acidity and metal complexes with higher Lewis acidities, like aluminum triisopropoxide, are active catalyst for the ring opening polymerization of oxygen containing ring systems like epoxides or lactones [29]. Reactions of this type are normally initiated by the electrophilic metal center attacking the nucleophilic oxygen of the ring. Since CO_2 is much less reactive than the epoxide, a good catalyst for a perfectly alternating copolymerization should be a rather bad catalyst for epoxide homopolymerization. Overall, the catalytic activity of the presented system is good and much higher than for the known heterogeneous catalytic systems. The behaviour of [(**2**)$_2$Zn$_4$(OAc)$_4$]$_4$ seems to be comparable to aluminum triisopropoxide, which forms oligomeric solid state structures with different Al coordination spheres and exhibits similar catalytic activities and selectivities [29]. The produced polyethercarbonates are polymers with interesting material properties. For example, they exhibit a high solubility in supercritical CO_2 as was shown by Beckman et al. [30].

3. Conclusion

In conclusion, we prepared a new amidoimidomalonate ligand **2** and a zinc acetate complex thereof, which showed an exceptional sedecameric solid state structure and interesting catalytic activities in the copolymerization of carbon dioxide and cyclohexene oxide leading to polyethercarbonates with broad polydispersities.

4. Experimental

4.1. General considerations

NMR spectra were recorded on a Bruker spectrometer with 250 MHz (^1H) and 62.9 MHz (^{13}C) at 293 K. Mass spectra were obtained using electron ionisation (EI), electron spray ionisation (ESI) or field ionisation (FI). FI- and EI-spectra were recorded with Micromass GCT and Finnigan MAT GCQ spectrometers, ESI-spectra were recorded with a Helwett-Packard 1100 MSD spectrometer. Melting points were either determined by using capillaries and an apparatus of Büchi, or with 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 and 100 Å) were run with tetrahydrofuran at 35 °C at 1 mL/min and were calibrated by polystyrene standards.

4.2. Preparation of *N,N′-bis(2,6-diisopropylphenyl)-malonamide*

A mixture of diethyl malonate (10.10 g, 0.062 mol) and 2,6-diisopropylaniline (25.00 g, 0.127 mol) was heated at 160 °C for 10 h, while the produced ethanol was distilled out of the reaction mixture. The mixture was cooled to r.t. and the resulting powder was mixed with 200 ml of cold hexane and stirred for 1 h. The microcrystalline pale-pink powder was filtered and washed with hexane. Yield: 23.79 g (56 mmol, 90%). ^1H NMR ($CDCl_3$) δ 8.48 (s, 2H, NH), 7.20 (t, 1H, H_{Aryl}), 7.10 (d, 4H, H_{Aryl}), 3.62 (s, 2H, CH_2), 2.98 (m_7, 4H, CH), 1.11 (d, 24H, CH_3). ^{13}C NMR ($CDCl_3$) δ 167.1, 145.9, 130.7, 128.5, 123.5, 42.7, 28.9, 23.6. EI$^+$-HR-MS: m/z 422.2933 (calcd), found 422.2910 for $C_{27}H_{38}N_2O_2$, $\delta = 2.3$ mDa; m.p. 270.3–271.7 °C.

4.3. Preparation of *ethyl-N-(2,6-diisopropylphenyl)-3-[(2,6-diisopropylphenyl)amino]-3-oxopropanimidoate (**2**)*

A mixture of *N,N′*-bis(2,6-diisopropylphenyl)malonamide (10.00 g, 24 mmol) and a 1.0 M solution of triethyloxonium tetrafluoroborate in dichloromethane (74.08 g, 56 mmol) was stirred 20 d at ambient temperature. The solvent was evaporated in vacuum and the residue was washed with 160 ml of abs. diethylether and filtered. Then it was taken up in 60 ml of abs. diethylether, cooled to 0 °C and triethylamine (7.5 ml, 54 mmol) was slowly added. The mixture was stirred at r.t. for 2 h and then it was filtered. The ether phases were collected and the solvent was removed under reduced pressure; a white solid precipitated, which was recrystallized from toluene:hexane = 3:1. Yield: 6.97 g (15 mmol, 64%). ^1H NMR ($CDCl_3$) δ 7.59 (s, 1H, NH), 7.34–7.02 (m, 6H, H_{Aryl}), 4.50 (q, 2H, OCH_2), 3.25 (s, 2H, CH_2), 3.08 (m_7, 2H, CH), 2.87 (m_7, 2H, CH), 1.47 (t, 3H, CH_3), 1.21 (d, 12H, CH_3), 1.20 (d, 6H, CH_3), 1.16 (d, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ 165.4, 154.9, 146.2, 137.8, 131.0, 128.6, 123.8, 123.7, 123.6, 123.2, 62.6, 38.4, 28.8, 28.3, 23.4, 22.7, 14.5. EI$^+$-HR-MS: m/z 450.3246 (calcd.), found 450.3172 for $C_{29}H_{42}N_2O_2$, $\delta = 7.4$ mDa; m.p. 158.2–159.9 °C.

4.4. Preparation of *$[(\mathbf{2})_2Zn_4(OAc)_4]_4$*

The amidoimidomalonate **2** (2 g, 4.4 mmol) was dissolved in toluene (30 mL) and after cooling to 0 °C, a diethylzinc solution (7 mL of a 1.1 M solution in toluene, 7.7 mol) was added. The solution was stirred at 75 °C for 18 h, afterwards all volatiles were removed under vacuum. The intermediate ethylzinc complex was dissolved in dichloromethane (20 mL), cooled to 0 °C and acetic acid was added dropwise (264 mg, 4.4 mmol). The product crystallized, when the concentrated solution was layered with hexane. Yield: 1.37 g (2.3 mmol, 52%). ^1H NMR ($CDCl_3$) δ 7.21–6.82 (bm, 6H, H_{Aryl}), 3.49–3.03 (b, 6H, OCH_2, CH_2, CH), 2.93 (m_7, 2H, CH), 2.20 (bs, 3H, OC(O)CH_3), 1.41–0.81 (d, 27H, CH_3). ^{13}C NMR ($CDCl_3$) δ 165.7, 155.7, 147.8, 146.6, 138.3, 133.0, 129.6, 128.2, 124.5, 123.8, 123.5, 123.1, 122.5, 62.6, 28.7, 28.2, 27.9, 27.5, 24.5, 23.6, 23.3, 23.1, 22.6, 14.0. ESI$^+$-MS: m/z 573 ($[(\mathbf{2})Zn(OAc)]^+ + 1$), 1146 ($[(\mathbf{2})Zn(OAc)]_2^+ + 2$).

4.5. General copolymerization procedure

An autoclave (Parr) was heated to 95 °C under vacuum for 16 h. $[(\mathbf{2})_2Zn_4(OAc)_4]_4$ (43 mg, 0.075 mmol Zn) and cyclohexene oxide (7.34 g, 74.9 mmol) were brought into the autoclave, which was then heated to reaction temperature and pressurized with CO_2 (4 MPa). After 2 h the reactor was cooled, vented and a small sample was taken for analysis. The resulting polyethercarbonate was dissolved in dichloromethane (5 mL), precipitated from MeOH (20 mL), collected and dried under vacuum to constant weight. Characterization of the polymers was done by IR (polycarbonate CO band at 1749 cm^1), NMR and GPC. ^1H NMR (C_6D_6) δ 4.9 (bs, CH, polycarbonate), 3.6 (bs, CH, polyether), 2.2–1.1 (bm, CH_2, cyclohexyl).

4.6. Crystal structure determination

The intensity data for the compounds were collected by a Siemens Smart 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects, but not for absorption [31,32].

The structures were resolved by direct methods (SHELXS [33]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [34]). The hydrogen atoms were localized by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically [34] (For further details see Table 2).

Table 2
Crystallographic data

$[(\mathbf{2})_2\mathrm{Zn}_4(\mathrm{OAc})_4]_4$	
Empirical formula	$C_{264}H_{368}N_{16}O_{48}Zn_{16} \cdot 2.4CH_2Cl_2$
CCDC No.	283845
f_w ($g \cdot mol^{-1}$)	5783.48
Temperature (K)	200(2)
Wavelength λ (Å)	0.71073
Crystal system	Tetragonal
Space group	$P4_2/n$ (no. 86)
Unit cell dimensions	
a (Å)	29.3528(19)
b (Å)	29.3528(19)
c (Å)	20.7093(19)
α (°)	90
β (°)	90
γ (°)	90
V ($Å^3$)	17843(2)
Z	2
ρ_{calcd} ($g \cdot cm^{-3}$)	1.076
μ (mm^{-1})	1.145
$F(000)$	6058
Crystal size (mm^3)	$0.25 \times 0.1 \times 0.3$
θ Range for data collection (°)	1.70–28.28
Index ranges	$-39 \leqslant h \leqslant 38$, $-38 \leqslant k \leqslant 38$, $-26 \leqslant l \leqslant 27$
Reflections collected	160406
Reflections observed	9215
Independent reflections [R_{int}]	22031 [0.1262]
Data/restraints/parameters	22031/0/831
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0877$, $wR_2 = 0.2771$
R indices (all data)	$R_1 = 0.2070$, $wR_2 = 0.3607$

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 283845. 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 e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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