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# Zinc Complexes Supported by Maltolato Ligands: Synthesis, Structure, Solution Behavior, and Application in Ring-Opening Polymerization of Lactides

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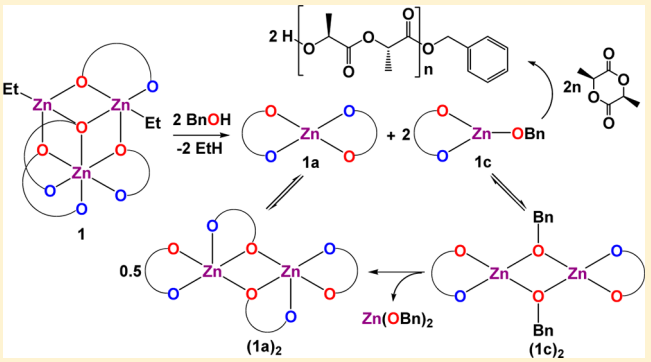
Supporting Information

**ABSTRACT:** A series of novel zinc alkoxides supported by chelating maltolato (MalO; MalOH = maltol) ligands were successfully synthesized and characterized. Reaction of MalOH with $ZnEt_2$ (3:4) gives a trinuclear cluster $[Zn_3(Et)_2(MalO)_4]$ (**1**), which spontaneously disproportionates in solution to mononuclear species $[Zn(MalO)_2]$ (**1a**) and $[Zn(Et)(MalO)]$ (**1b**); (**1a**) and (**1b**) form $[Zn(MalO)_2(py)]$ (**2**), $[Zn(Et)(MalO)(py)]$ (**3**), $[Zn(MalO)_2]_2$ ($(\mathbf{1a})_2$), $[Zn(MalO)(OBn)]_2$ ($(\mathbf{1c})_2$), and $[Zn_4(Et)_2(OEt)_2(MalO)_4]$ (**4**) on addition of pyridine, benzyl alcohol (BnOH), or dry $O_2$, respectively. Compounds **1**, **2**, $(\mathbf{1a})_2$, and **4** were characterized by elemental analysis, NMR, ESI-MS, and single-crystal X-ray structural analysis. Variable-temperature NMR experiments showed that $(\mathbf{1a})_2$ and $(\mathbf{1c})_2$ are in equilibrium with the monomeric form in solution. The addition of L-lactide (L-LA) to a combination of **1** and 2 equiv of BnOH in dichloromethane at room temperature in different molar ratios leads to rapid and efficient generation of poly(L-LA) with end-capped BnO groups. According to kinetic studies, propagation by $[Zn(OBn)(MalO)]$ (**1c**) is first-order with respect to both the monomer and **1c** concentrations; **1a** in ring-opening polymerization of L-LA shows no activity. These results suggest a single-site active species in the ring-opening polymerization of L-LA.




## INTRODUCTION

Polylactide (PLA) is a biodegradable, biocompatible, aliphatic polyester derived from renewable resources, such as corn, sugar beets, and agricultural waste.[1] PLA has found numerous specialty applications in the biomedical industry, such as biodegradable screws and sutures, scaffolds for tissue engineering, matrixes for controlled drug delivery systems,[2] and as environmentally friendly bulk packing biodegradable materials.[3] The concept of PLA synthesis is very well established. The ring-opening polymerization (ROP) of L-lactide (L-LA) for the preparation of PLA, the method used in this study, has been investigated extensively.[4] This process, in the presence of metal alkoxides (M−OR), is thought to occur via a coordination−insertion mechanism, whereby the metal center activates the carbonyl group of the incoming L-LA molecule toward attack by the alkoxide group. This is followed by insertion of an L-LA molecule into the M−OR bond with cleavage of the acyl oxygen bond of the monomer.[4] In industry, PLA is synthesized by ROP using tin(II) bis(2-ethylhexanate) as a catalyst. Although $Sn(Oct)_2$ has been accepted as a food additive by the U.S. Food and Drug Administration, the toxicity associated with most tin compounds is a considerable drawback in the case of biomedical applications.[4] There has, therefore, been much research devoted to finding well-defined complexes of high activity containing biologically benign metals.[4−8] In this context, magnesium,[4−6] calcium,[4,7] zinc,[4,5] and aluminum[4,8] are attractive metals of low toxicity. For example, β-diketiminate,[5,9] bisphenolate,[10] Schiff's bases,[11] phenoxyamine,[12] and tris(pyrazolyl)hydroborate[13] zinc complexes exhibit excellent activities for ROP of L-LA. Our group recently developed the aminophenolate zinc compound $[Zn(tbpca)_2]$ (tbpcaH = *N*-[methyl(2-hydroxy-3,5-di-*tert*-butylphenyl)]-*N*-methyl-*N*-cyclohexylamine), which showed high activity in L-LA polymerization.[14]

We turned our attention toward zinc compounds supported by MalO (MalOH = maltol) ligands, which are excellent for the production of polymers with low polydispersities and narrow molecular weight distributions.[4] Maltol is a very attractive ligand and is easily deprotonated to give an O,O′-bidentate chelating system for a number of biologically active metal ions, to form thermodynamically stable and neutral complexes.[15] For instance, metal−maltol complexes, such as $[Fe(MalO)_3]$,[16] $[Al(MalO)_3]$,[17] $[Ga(MalO)_3]$,[18] and $[VO(MalO)_2]$,[19] have found numerous medical applications as metallotherapeutic drugs and metal-based diagnostic agents.[15] We also chose maltol for its commercial availability and low cost, and because it is harmless to humans.[20]

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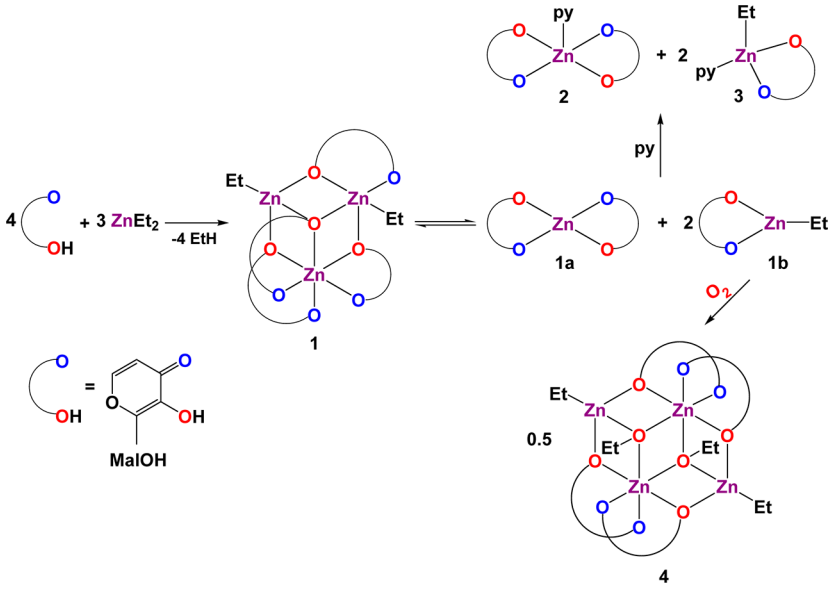
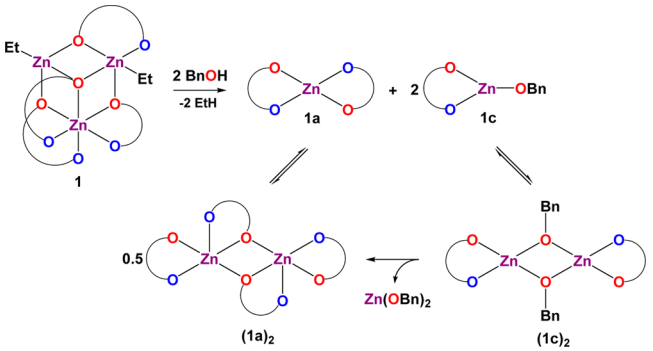
**Scheme 1. Synthesis of Zinc Complexes 1−4**




We describe here our results on the synthesis and characterization of a zinc−maltol polynuclear $[Zn_3(Et)_2(MalO)_4]$ cluster, which takes an active part in L-LA polymerization, and formation of compounds **2**−**4** (Scheme 1) and $(\mathbf{1a})_2$−$(\mathbf{1c})_2$ (Scheme 2) by reaction with pyridine, benzyl alcohol (BnOH), or dry oxygen.

**Scheme 2. Synthesis of Zinc Complexes $(\mathbf{1a})_2$ and $(\mathbf{1c})_2$**




## RESULTS AND DISCUSSION

**Synthesis and Characterization of Zinc Complexes 1−4.** As shown in Scheme 1, the zinc atom easily forms coordination compounds by reaction of the hydroxyl-group-containing MalOH with an active organometallic species, such as diethylzinc. Treatment of 4 equiv of MalOH with 3 equiv of $ZnEt_2$ in toluene at room temperature affords the cluster complex $[Zn_3(Et)_2(MalO)_4]$ (**1**, 75%). The compound was isolated as colorless crystals, which are readily soluble in hydrocarbons, chlorinated solvents, and THF. Its structure was confirmed by elemental analysis, X-ray crystallography, NMR spectroscopy, and ESI-MS. The molecular structure of **1** is shown in Figure 1, and selected bond distances and angles are given in the figure legend. Single-crystal X-ray diffraction (XRD) data showed that solid **1** is a trinuclear cluster containing an incomplete cubane $Zn_3O_4$ core with different coordination modes around the zinc atoms. The complex

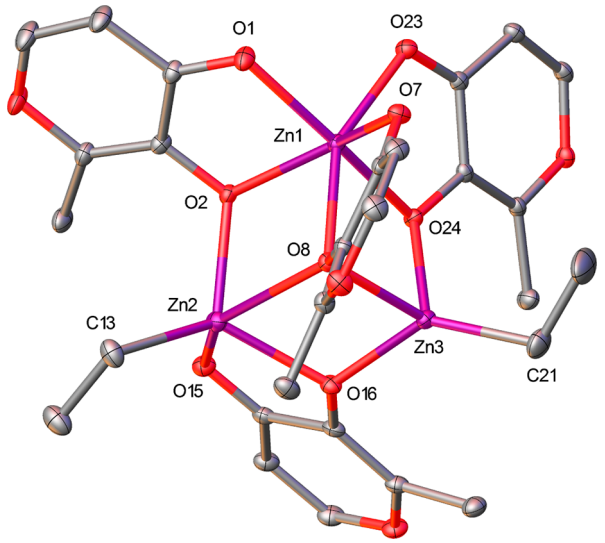



**Figure 1.** Molecular structure of $[Zn_3(Et)_2(MalO)_4]$·toluene (**1**). The displacement ellipsoids are drawn at the 30% probability level. Toluene molecule and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−O1 2.053(3), Zn1−O2 2.136(3), Zn1−O7 2.115(3), Zn1−O8 2.183(4), Zn1−O23 2.10(3), Zn1−O24 2.055(4), Zn2−O2 2.078(4), Zn2−O8 2.562(4), Zn2−O15 2.157(4), Zn2−O16 2.069(3), Zn2−C13 1.992(4), Zn3−O8 2.066(4), Zn3−O16 2.006(3), Zn3−O24 2.034(3), Zn3−C21 1.961(4), O1−Zn1−O8 111.6(4), O1−Zn1−O23 92.5(4), O1−Zn1−O24 161.8(4), O2−Zn1−O7 149.2(4), O8−Zn1−O23 151.8(4), O8−Zn1−O24 80.6(4), O23−Zn1−O24 80.1(4), O2−Zn2−O16 110.8(4), O2−Zn2−C13 116.2(4), O8−Zn2−O15 140.9(4), O16−Zn2−C13 131.4(4), O8−Zn3−O16 83.5(4), O8−Zn3−O24 83.9(4), O8−Zn3−C21 123.8(6), O16−Zn3−C21 137.5(6), O16−Zn3−O24 93.9(5), O24−Zn3−C21 118.6(7).

consists of one $[Zn(MalO)_2]$ and two $[Zn(Et)(MalO)]$ subunits. The metal ions are held together by three $\mu_2$-O(alkoxo) and one $\mu_3$-O(alkoxo) oxygen atom. The Zn1 ion forms a six-coordinated distorted octahedron with $O_6$ donor sets. The geometry around the Zn2 ion is a distorted trigonal bipyramid surrounded by $O_4Et$ groups, and the Zn3 ion geometry is a distorted tetrahedron with surrounding $O_3Et$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donor ligands. The $^1$H NMR spectrum of **1** in $C_6D_6$ shows one chemical equivalent of zinc-bonded ethyl groups and one environment for MalO ligands (Supporting Information, Figure S1), suggesting a dynamic process occurring in solution. We decided to investigate using a variable-temperature (VT) NMR study. Compound **1** shows VT $^1$H NMR (Supporting Information, Figure S5) behavior consistent with the dynamic monomer−trimer equilibrium shown in Scheme 1. Moreover, we conducted cryoscopic molecular weight determinations, which showed that compound **1** undergoes dissociation in *p*-xylene solution. It is worth to note that, when the reaction of MalOH with $ZnEt_2$ was carried out at a 1:1 molar ratio, the mixture of compounds **1** (isolated in crystalline form and identified by measuring the unit cell parameters), **1b**, and free $ZnEt_2$ was observed (Supporting Information, Figure S7). To trap the disproportionation products of **1**, pyridine was added, forming colorless crystals of complex $[Zn(MalO)_2(py)]$ (**2**, 26%). XRD analysis showed that **2** possesses a square-pyramidal geometry with four oxygen atoms of the chelating MalO ligands and one pyridine nitrogen atom occupying an apical position (Figure 2). The NMR data are fully consistent

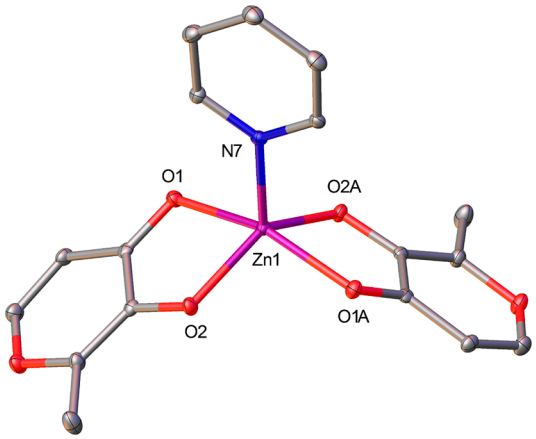


**Figure 2.** Molecular structure of $[Zn(MalO)_2(py)]$ (**2**). The displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−O1 2.140(2), Zn1−O2 1.980(2), Zn1−N7 2.034(3), O1−Zn1−O1A 160.3(3), O1−Zn1−O2 81.2(3), O1−Zn1−O2A 91.5(3), O2−Zn1−O2A 137.1(3), O1−Zn1−N7 100.1(2), O2−Zn1−N7 111.5(2).

with the anticipated formula (Supporting Information, Figures S8−S11). Complex $[Zn(Et)(MalO)(py)]$ (**3**, 47%) was isolated from the filtrate as a dark green solid by precipitation with hexane. Although we were not able to obtain single crystals, the $^1$H NMR spectra of **3** over a wide temperature range (Supporting Information, Figure S17) show a set of symmetric ligand resonances, indicating a simple structure, attributed to the tetrahedral geometry of $[Zn(Et)(MalO)(py)]$. ESI-MS studies support the proposed formula, giving a simple molecular ion at 268 *m*/*z*, corresponding to $[Zn(MalO)(py)]^+$ moieties (Supporting Information, Figure S18). To confirm the existence in solution of the tricoordinated intermediate $[Zn(Et)(MalO)]$ (**1b**), we carried out a reaction with dry $O_2$, as shown in Scheme 1. It is well known that oxygenation of three-coordinated alkylzinc species in solution affords alkylzinc alkoxide moieties.[21] A toluene solution of **1** was treated with an excess of dry $O_2$ at 0 °C, the reaction was stirred for 10 min, and then excess $O_2$ was removed. Work up gave colorless crystals of the tetranuclear compound $[Zn_4(Et)_2(OEt)_2(MalO)_4]$ (**4**, 39%). Single-crystal XRD measurements showed that **4** exists as a tetrameric cluster, which contains two environmentally different zinc centers, as shown in Figure 3. The zinc ions and bridging alkoxo groups

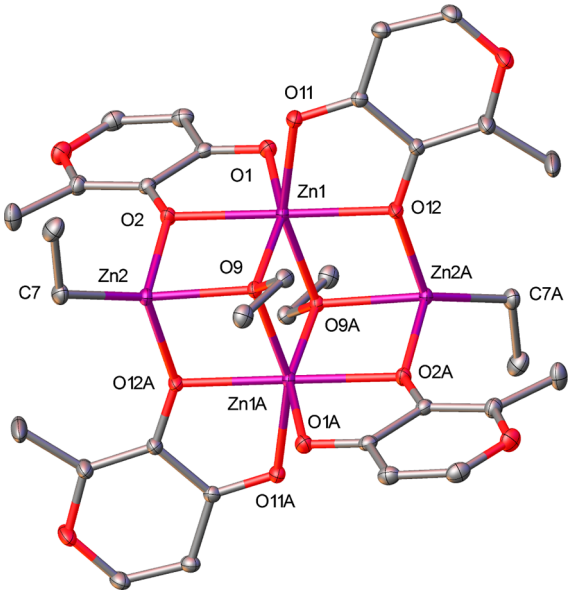


**Figure 3.** Molecular structure of $[Zn_4(Et)_2(OEt)_2(MalO)_4]$·toluene (**4**). The displacement ellipsoids are drawn at the 30% probability level. Toluene molecule and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−O1 2.087(4), Zn1−O2 2.124(4), Zn1−O9 2.084(4), Zn1−O9A 2.137(4), Zn1−O11 2.104(3), Zn1−O12 2.109(4), Zn2−O2 2.055(4), Zn2−O9 2.034(3), Zn2−O12A 2.048(4), Zn2−C7 1.983(4), O1−Zn1−O2 78.5(5), O1−Zn1−O9 156.4(4), O1−Zn1−O12 102.9(5), O2−Zn1−O9 78.9(4), O2−Zn1−O12 177.9(4), O2−Zn1−O12 177.9(4), O9−Zn1−O12 99.9(5), O9A−Zn1−O11 156.7(4), O2−Zn2−O9 81.7(5), O2−Zn2−O12A 98.1(5), O2−Zn2−C7 122.4(6), O9−Zn2−O12A 82.7(4), O9−Zn2−C7 134(5), O12A−Zn2−C7 125.1(5).

are arranged in a "double-open" face-sharing dicubane-like core with two missing vertices. The Zn1 adopts an octahedral coordination environment with $O_6$ donor sets. In contrast, Zn2 forms a distorted tetrahedral coordination geometry consisting of two $\mu_2$-O bridging MalO oxygen atoms, supported by one ethoxo and one ethyl group. The identity of **4** was additionally determined by NMR spectroscopic studies (Supporting Information, Figures S19−S22).

In the ROP of LA, it is very well established that the use of external alcohols in situ to activate alkylzinc species leads to the formation of active alkoxide complexes, with rapid and efficient chain transfer, to generate PLA end-capped with ester groups from the added alcohol.[22] To prepare zinc−alkoxide complexes useful for ROP catalysis,[23] alcoholysis of the ethylzinc complex **1** was investigated. The treatment of **1** with 2 equiv of BnOH in dichloromethane, followed by partial solvent removal, results in a crystalline material $[Zn(MalO)_2]_2$ ($(\mathbf{1a})_2$, 28%), which is weakly soluble in conventional solvents. Single-crystal X-ray analysis showed that $(\mathbf{1a})_2$ is a centrosymmetric dimeric complex, in which alkoxide groups bridge heavily distorted square-pyramidal zinc centers (Figure 4). The complex $[Zn(OBn)(MalO)]_2$ ($(\mathbf{1c})_2$, 59%) was isolated from the filtrate as a yellow solid by precipitation with hexane. Attempts to grow single crystals of $(\mathbf{1c})_2$ for XRD analysis were unsuccessful. The


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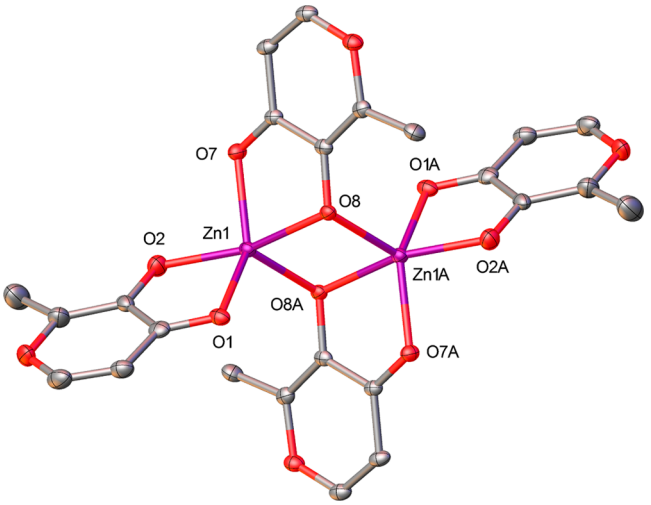
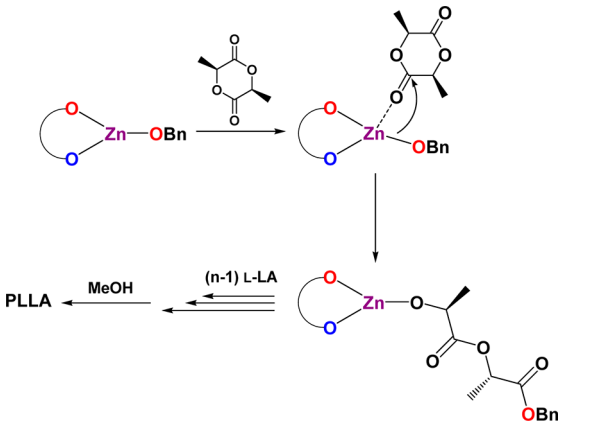



**Figure 4.** Molecular structure of $[Zn(MalO)_2]_2 \cdot 2CH_2Cl_2$ ($(\mathbf{1a})_2$). The displacement ellipsoids are drawn at the 30% probability level. Dichloromethane molecule and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−O1 2.037(3), Zn1−O2 2.006(3), Zn1−O7 2.014(3), Zn1−O8 2.168(3), Zn1−O8A 2.003(3), O1−Zn1−O2 83.4(2), O1−Zn1−O7 136.9(2), O1−Zn1−O8 93.6(2), O1−Zn1−O8A 105.7(2), O2−Zn1−O7 91(2), O2−Zn1−O8 162.5(2), O2−Zn1−O8A 113.1(2), O7−Zn1−O8A 115.6(2).

$^1$H NMR spectrum of $(\mathbf{1c})_2$ has no complexity and shows a dimeric species in which the two $[Zn(MalO)]^+$ units are bridged by two $\mu_2$-O oxygen atoms of benzyl alkoxides (Supporting Information, Figure S29). This is clearly shown by the aromatic and methylene resonances of the bridging BnO groups shifting upfield to 7.25 and 4.56 ppm, respectively, as compared with 7.68 and 5.27 ppm for the terminally coordinated BnO groups in the monomeric species **1c** (Supporting Information, S32). Further studies have shown that $(\mathbf{1c})_2$ tends to disproportionate into complex $(\mathbf{1a})_2$ and $Zn(OBn)_2$, as shown in Scheme 2. Such disproportionation of heteroleptic zinc alkoxides has previously been noted by Carpentier and co-workers, who proved that dimeric $[Zn(OiPr)(ON^{Ph,Bn})]_2$ is transformed into $Zn(OiPr)_2$ and $[Zn(ON^{Ph,Bn})_2]$ [$HON^{Ph,Bn}$ = (*E*)-4-(benzylimino)-1,1,1-trifluoro-2-(trifluoromethyl)-4-phenylbutan-2-ol].[24]

**Ring-Opening Polymerization of L-Lactide.** Because of the relative instability of the benzyl alkoxide $(\mathbf{1c})_2$ and the difficulty of isolating the pure compound in amounts large enough to carry out extensive catalysis studies, we investigated combinations of ethylzinc compound **1** with BnOH to generate $[Zn(MalO)_2]$ (**1a**) and $[Zn(MalO)(OBn)]$ (**1c**) in situ, as confirmed by VT $^1$H, $^{13}$C, COSY, and HMQC spectroscopic studies (Supporting Information, Figures S32−S36). Studies carried out using $(\mathbf{1a})_2$ in the ROP of L-LA in the presence of BnOH showed complete inactivity of this complex in the polymerization process. These results indicate that only **1c** acts as a single-site catalyst for the preparation of poly(L-LA) (PLLA). The polymerization of L-LA using **1c** as an initiator was systematically examined. Representative results obtained using this binary system are presented in Table 1. The standard procedure for the preparation of PLLA is outlined in Scheme 3.

**Scheme 3. Ring-Opening Polymerization of L-Lactide Initiated by in Situ Generated 1c**




The addition of L-LA to a combination of **1** and 2 equiv of BnOH in dichloromethane at room temperature in different molar ratios led to the rapid and efficient generation of PLLA with end-capped BnO groups. The monomer conversion and number-average molecular weight ($M_n$) values were determined using $^1$H NMR spectroscopy and calculated from the ratio of the aromatic peaks from the BnO group at ∼7.04 ppm to the methine peak from the polymer backbone (Figure 5; Supporting Information, Figures S37−S42). Furthermore, the $M_n$ and polydispersity index (PDI) values were determined by GPC (see Table 1). To identify the end groups using $^1$H NMR, the polymerization was conducted with a low ratio, L-LA/$Zn_{1c}$ = 10 ("oligomerization"), for 0.5 h at room temperature (Table 1, entry 1; Figure 5), and then quenched with methanol. The end groups of the obtained oligomer were analyzed and confirmed using $^1$H NMR and ESI-MS. From the $^1$H NMR spectrum, the number-average degree of polymerization of the L-LA units was determined by comparing the integrals of the signals corresponding to the benzyl ester groups with methine protons from the polymer backbone (labeled g and e, e″ in

**Table 1. Polymerization of L-Lactide Using in Situ Generated 1c at 25 °C in Dichloromethane**

| entry | [L-LA]/[$Zn_{1c}$] | *t* (h) | $M_w/M_n$ | $M_n$(GPC)[a] | $M_n$(calcd)[b] | $M_n$(NMR)[c] | *C* (%)[c] | $T_m$ (°C)[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | 10 | 0.5 | | | 1500 | 1600 | 99 | 136.8 |
| 2 | 25 | 1 | 1.26 | 3600 | 3600 | 3800 | 98 | 145.1 |
| 3 | 50 | 2.5 | 1.30 | 6200 | 7000 | 6700 | 96 | 150.8 |
| 4 | 100 | 6 | 1.12 | 14 800 | 14 400 | 14 800 | 99 | 159.0 |
| 5 | 200 | 12 | 1.16 | 23 700 | 27 200 | 28 700 | 94 | 169.4 |
| 6[e] | 50 | 2 | 2.15 | 9100 | 7300 | 9700 | 100 | 162.8 |

[a]Obtained from GPC analysis and calibrated by polystyrene standards. [b]Calculated from the molecular weight of L-LA × [L-LA]/[$Zn_{1c}$] × conversion yield plus $M_w$(BnOH). [c]Obtained from $^1$H NMR analysis. [d]Obtained from DSC analysis (Supporting Information, Figures S44−S49). [e]Obtained in bulk polymerization at 90 °C.


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**Figure 5.** $^1$H NMR spectrum of BnO−PLLA$_{10}$ oligomer in $C_6D_6$.

Figure 5). The calculated number-average degree of polymerization was 10. ESI-MS confirmed the proposed structure (Figure 6). Since the monoisotopic masses of the BnO moiety (107.05 Da) and of an L-LA unit (144.04 Da) are known, the molecular weight of the BnO−PLLA$_n$ polymer at any given value of $n$ can be calculated. For example, a sodium-cationized oligomer with $n$ = 10 has a monoisotopic mass of 1571.5 Da (Figure 6). Using the masses corresponding to the individual peaks and their respective intensities, the $M_n$ and weight-average molecular weight ($M_w$) of BnO−PLLA$_n$ can be calculated from the ESI-MS.[25] The calculated $M_n$ value corresponds to a number-average degree of L-LA units of 9. The results from $^1$H NMR spectroscopy and ESI-MS show the presence of one benzyl ester group per polymer chain and a degree of polymerization approximately that of the L-LA/Zn$_{1c}$ quotient. Furthermore, a plot of the PLLA $M_n$ obtained from $^1$H NMR analysis and polystyrene standards GPC as a function of [L-LA]/[Zn$_{1c}$] = 25−200 (Figure 7) demonstrates good polymerization control. The linear nature of this plot, in conjunction with the relatively narrow polydispersities ($M_w/M_n$ < 1.3), suggests that the polymerization is living and proceeds by a coordination−insertion mechanism.[26] Additionally, the agreement between the observed and theoretical values of $M_n$ along with the data obtained using ESI-MS for the BnO−PLLA$_{10}$ oligomer (Figures 5 and 6) is consistent with an initiation mechanism in which the MalO ligand remains bound to the zinc center while the BnO ligand initiates polymerization.

## CONCLUSION

This work demonstrates the application of the chelating MalOH ligand in L-LA polymerization. The advantages of the MalOH ligand are that it is readily available commercially, cheap, and harmless to humans. We have shown that the direct reaction of MalOH with $ZnEt_2$ (3:4) in toluene gave a trinuclear cluster [$Zn_3(Et)_2(MalO)_4$] (**1**), which spontaneously disproportionates in solution to the mononuclear species [$Zn(MalO)_2$] (**1a**) and [Zn(Et)(MalO)] (**1b**); these can be detected by monitoring the reaction mixture using VT $^1$H NMR spectroscopy. Furthermore, the disproportionation products of **1** were trapped by the addition of pyridine, BnOH, or dry $O_2$, resulting in the formation of [Zn(MalO)$_2$(py)] (**2**), [Zn(Et)(MalO)(py)] (**3**), [Zn(MalO)$_2$]$_2$ (**(1a)$_2$**), [Zn(MalO)(OBn)]$_2$ (**(1c)$_2$**), and [$Zn_4(Et)_2(OEt)_2(MalO)_4$] (**4**), respectively (Schemes 1 and 2). We also demonstrated that the heteroleptic complex **(1c)$_2$** is unstable in solution and easily disproportionates to the homoleptic **(1a)$_2$** and $Zn(OBn)_2$. The experimental results reported in this paper strongly suggest that the monometallic zinc complex **1c** mediates the insertion of the L-LA monomer and efficiently generates PLLA with end-capped BnO groups. The polymerization kinetic studies show a first-order dependence on both [L-LA] and [**1c**], leading us to propose a single-site active species. Finally, our observations represent an important advance in understanding the dynamic processes occurring in solution and should be considered in the design of new efficient zinc catalysts for the polymerization of heterocyclic monomers.

## EXPERIMENTAL SECTION

**Materials and Methods.** All the syntheses were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Reagents were purified by standard methods: toluene, hexane, $C_6D_6$, and $C_7D_8$ were distilled from Na; $CH_2Cl_2$ was distilled from $CaH_2$ and

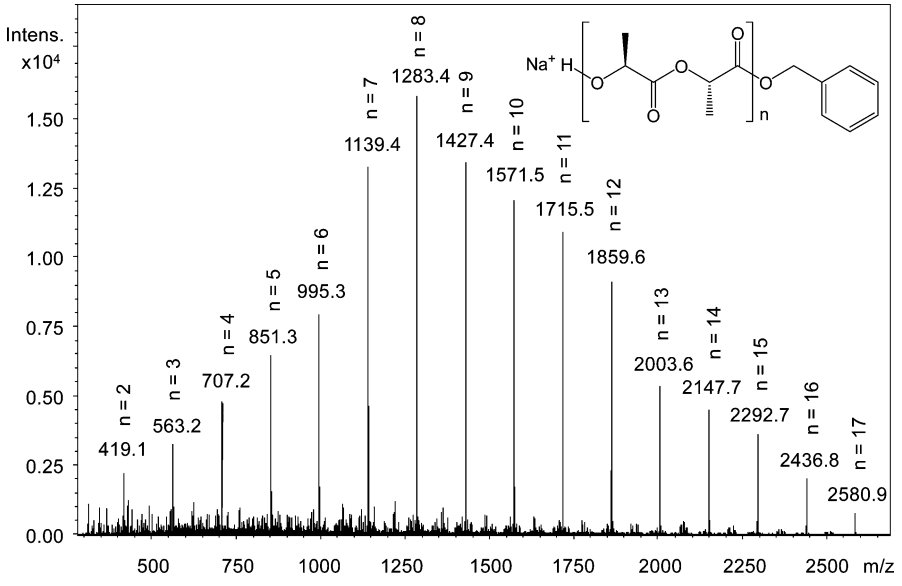


**Figure 6.** ESI-MS of BnO−PLLA$_{10}$ oligomer.


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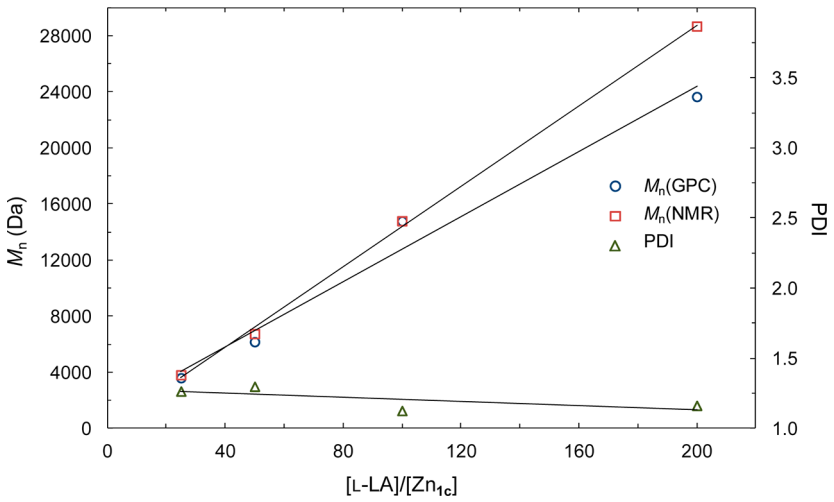


**Figure 7.** Plot of PLLA $M_n$ obtained from $^1$H NMR analysis and polystyrene standards GPC vs [L-LA]/[$Zn_{1c}$], with PDIs marked as open triangles.

then $P_2O_5$; BnOH was distilled from $P_2O_5$; L-LA was recrystallized from toluene and sublimed; and pyridine was predried and then distilled over solid KOH. MalOH, BnOH, L-LA, and $ZnEt_2$ were purchased from Aldrich (St Louis, MO). $^1$H, $^{13}$C, COSY, and HMQC NMR spectra were recorded at room temperature using Bruker Avance 300 and 500 MHz spectrometers. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents. ESI-MS data were collected on a Bruker micrOTOF-Q mass spectrometer. The thermal analysis of polymers was performed using a Universal V4.5A differential scanning calorimeter (TA Instruments, New Castle, DE) at a heating rate of 2 °C/min. Elemental analysis was determined on a PerkingElmer 2400 CHN Elemental Analyzer. The GPC measurements were performed on a Viscotek TDA 305 Triple detector array GPCmax. The GPC columns were eluted with dichloromethane at 35 °C at 1 mL/min and calibrated with polystyrene standards over a peak average molecular weight ($M_p$) range of 600−3 000 000 Da.

**Synthesis of [$Zn_3$(Et)$_2$(MalO)$_4$] (1).** $ZnEt_2$ (11.90 mL, 11.90 mmol) was added dropwise to a solution of MalOH (2 g, 15.86 mmol) in toluene (100 mL). The light green mixture was stirred at room temperature. After 1 h, the volume was reduced to 30 mL, and the light green precipitate was filtered off, washed with hexane (3 × 10 mL), and dried under vacuum. The light green solid was dissolved in hot toluene (100 mL) and recrystallized to yield colorless crystals. Yield: 2.25 g (75%). Anal. Calcd for $C_{28}H_{30}O_{12}Zn_3$: C, 44.56; H, 4.01. Found: C, 44.90; H, 4.20. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta$ 6.60 (4H, d, $J$ = 5.1 Hz, =CH−O), 6.02 (4H, d, $J$ = 5.1 Hz, =CH−C=O), 2.43 (s, 12H, $CH_3^{MalO}$), 1.50 (6H, t, $J$ = 7.9 Hz, $CH_3^{Et}$), 0.61 (4H, k, $J$ = 7.9, $CH_2$). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta$ 178.6 (4C, C=O), 152.9 (4C, =CH−O), 152.2−149.9 (8C, C−$CH_3$, C−O−Zn), 111.5 (4C, =CH−C=O), 15.5 (4C, $CH_3^{MalO}$), 13.3 (2C, $CH_3^{Et}$), 0.1 (2C, $CH_2$).

**Synthesis of [Zn(MalO)$_2$(py)] (2).** Pyridine (6 equiv, 0.64 mL, 7.95 mmol) was added dropwise to a solution of **1** (1 g, 1.33 mmol) in toluene (100 mL). The dark orange mixture was stirred at room temperature. After 4 h, the volume was reduced to 60 mL under vacuum. Single crystals for XRD analysis were obtained from the concentrated mother liquor at room temperature. The crystals were filtered off, washed with hexane (3 × 10 mL), and dried under vacuum. Yield: 0.41 g (26%). Anal. Calcd for $C_{17}H_{15}NO_6Zn$: C, 51.73; H, 3.83; N, 3.55. Found: C, 51.72; H, 3.73; N, 3.25. $^1$H NMR ($CD_2Cl_2$, 500 MHz): $\delta$ 8.57 (2H, m, py), 7.82 (1H, tt, $J$ = 7.7, 1.6 Hz, py), 7.74 (2H, d, $J$ = 5.1 Hz, =CH−C=O), 7.40 (2H, m, py), 6.50 (2H, d, $J$ = 5.1 Hz, =CH−O), 2.42 (6H, s, $CH_3$). $^{13}$C NMR ($CD_2Cl_2$, 125 MHz): $\delta$ 178.2 (2C, C=O), 152.7 (2C, =CH−O), 151.8−151.5 (4C, C−$CH_3$, C−O−Zn), 149.7 (2C, py), 138.7 (1C, py), 125.1 (2C, py), 110.9 (2C, =CH−C=O), 15 (2C, $CH_3$).

**Synthesis of [Zn(Et)(MalO)(py)] (3).** Hexane (50 mL) was added to the filtrate from **2** to give a dark green precipitate, which was filtered off, washed with hexane (3 × 5 mL), and dried under vacuum. Yield: 0.56 g (47%). Anal. Calcd for $C_{13}H_{15}NO_3Zn$: C, 52.28; H, 5.06; N, 4.69. Found: C, 52.33; H, 5.12; N, 4.63. $^1$H NMR ($C_6D_6$, 300 MHz): $\delta$ 8.48 (2H, m, py), 6.87 (1H, tt, $J$ = 7.7, 1.8 Hz, py), 6.74 (1H, d, $J$ = 5.1 Hz, =CH−C=O), 6.56 (2H, m, py), 6.15 (1H, d, $J$ = 5.1 Hz, =CH−O), 2.41 (3H, s, $CH_3^{MalO}$), 1.72 (3H, t, $J$ = 8.1 Hz, $CH_3^{Et}$), 0.84 (2H, k, $J$ = 8.1, $CH_2^{Et}$). $^{13}$C NMR ($C_6D_6$, 75 MHz): $\delta$ 179.3 (1C, C=O), 152.9−151.6 (2C, C−$CH_3$, C−O−Zn), 152.2 (1C, =CH−O), 149.4 (2C, py), 136.8 (1C, py), 124 (2C, py), 111 (2C, =CH−C=O), 15.1 (1C, $CH_3^{MalO}$), 13.7($CH_3^{Et}$), −1.71 (1C, $CH_2$).

**Synthesis of [$Zn_4$(Et)$_2$(OEt)$_2$(MalO)$_4$] (4).** A solution of **1** (1 g, 1.33 mmol) in toluene (100 mL) at 0 °C was exposed to an excess of dry $O_2$ for 10 min. After oxygenation, the excess $O_2$ was removed, and nitrogen was flowed through the system. The orange mixture was stirred for 1 h and allowed to warm to room temperature. After 3 h, the volume was reduced to 60 mL. Colorless crystals were obtained by slow evaporation from the toluene solution. Yield: 0.70 g (39%). Anal. Calcd for $C_{32}H_{40}O_{14}Zn_4$: C, 42.22; H, 4.43. Found: C, 42.30; H, 4.50. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta$ 6.65 (4H, m, =CH−O), 6.10 (4H, m, =CH−C=O), 4.48 (4H, m, $CH_2^{OEt}$), 2.42 (12H, s, $CH_3^{MalO}$), 1.56−1.36 (12H, m, $CH_3^{OEt}$, $CH_3^{Et}$), 0.80 (4H, m, $CH_2^{Et}$). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta$ 178.7 (4C, C=O), 152.2 (4C, C−$CH_3$), 151.8−150.8 (8C, =CH−O, C−O−Zn), 110.9 (4C, =CH−C=O), 62 (2C, $CH_2^{OEt}$), 21.8 (4C, $CH_3^{OEt}$, $CH_3^{Et}$), 15.2 (4C, $CH_3^{MalO}$), 6.9 (2C, $CH_2^{Et}$).

**Characterization of [Zn(MalO)$_2$] (1a) and [Zn(OBn)(MalO)] (1c).** BnOH (0.55 mL, 5.30 mmol) was added to a solution of **1** (2 g, 2.65 mmol) in dichloromethane (40 mL). After the yellow mixture had been stirred at room temperature for 1 h, the volume was reduced to 10 mL, and the yellow precipitate was filtered off, washed with hexane (3 × 10 mL), and dried under vacuum. Yield: 2.22 g (92%). Anal. Calcd for $C_{38}H_{34}O_{14}Zn_3$: C, 50.11; H, 3.76. Found: C, 50.60; H, 3.85. $^1$H NMR ($C_6D_6$, 300 MHz): $\delta$ 7.65 (4H, m, $m$-Ar$H^{BnO}$), 7.13−6.99 (6H, m, $o/p$-Ar$H^{BnO}$), 6.73 (4H, d, $J$ = 4.8, Hz, =CH−O), 6.08 (4H, d, $J$ = 4.8 Hz, =CH−C=O), 5.27 (4H, s, $CH_2$), 2.37 (12H, s, $CH_3$). $^{13}$C NMR ($C_6D_6$, 75 MHz): $\delta$ 178.6 (4C, C=O), 152.4 (4C, =CH−O), 151.1 (4C, C−$CH_3$), 145.8 (4C, Zn−O−C), 129.3−126.2 (10C, Ar$H^{BnO}$), 110.7 (4C, =CH−C=O), 68.3 (2C, $CH_2$), 15.3 (4C, $CH_3$).

**Synthesis of [Zn(MalO)$_2$]$_2$ ((1a)$_2$).** BnOH (0.28 mL, 2.66 mmol) was added to a solution of **1** (1 g, 1.33 mmol) in dichloromethane (50 mL). The reaction mixture was stirred for 2 h. The volume was reduced to 10 mL under vacuum to yield colorless crystals. The crystals were filtered off, washed with hexane (3 × 10 mL), and dried under vacuum. Yield: 0.29 g (28%). Anal. Calcd for $C_{24}H_{20}O_{12}Zn_2$: C, 45.67; H, 3.19. Found: C, 45.9; H, 3.21. $^1$H NMR ($CD_2Cl_2$, 300 MHz): $\delta$ 7.73 (4H, d, $J$ = 5.1 Hz, =CH−O), 6.49 (4H, d, $J$ = 5.1 Hz, =CH−C=O), 2.39 (s, 12H, $CH_3$). $^{13}$C NMR ($CD_2Cl_2$, 75 MHz): $\delta$


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178.1 (4C, C=O), 153.5 (4C, =CH−O), 153.3−150.4 (8C, C−$CH_3$, Zn−O−C), 111 (4C, =CH−C=O), 15.2 (4C, $CH_3$).

**Synthesis of $[Zn(OBn)(MalO)]_2$ ($(1c)_2$).** Hexane (50 mL) was added to the filtrate from $(1a)_2$. The orange precipitate was filtered off, washed with hexane (3 × 5 mL), and dried under vacuum. Yield: 0.55 g (59%). Anal. Calcd for $C_{26}H_{24}O_8Zn_2$: C, 52.46; H, 4.06. Found: C, 52.51; H, 4.11. $^1$H NMR ($C_6D_6$, 300 MHz): $\delta$ 7.25 (4H, m, *m* $ArH^{BnO}$), 7.12−7.06 (6H, m, *o*/*p*-$ArH^{BnO}$), 6.69 (2H, d, $J$ = 4.6 Hz, =CH−O), 6.07 (2H, d, $J$ = 4.6 Hz, =CH−C=O), 4.56 (4H, s, $CH_2$), 2.36 (6H, s, $CH_3$). $^1$H NMR ($C_7D_8$, 300 MHz): $\delta$ 7.27 (4H, m, *m*-$ArH^{BnO}$), 7.16−7.04 (6H, m, *o*/*p*-$ArH^{BnO}$), 6.73 (2H, d, $J$ = 4.9 Hz, =CH−O), 6.05 (2H, d, $J$ = 4.9 Hz, =CH−C=O), 4.49 (4H, s, $CH_2$), 2.38 (6H, s, $CH_3$). $^{13}$C NMR ($C_7D_8$, 75 MHz): $\delta$ 178.6 (2C, C=O), 152−151.1 (6C, =CH−O, C−$CH_3$, Zn−O−C), 127.1−127 (10C, $ArH^{BnO}$), 110.83 (2C, =CH−C=O), 65.7 (2C, $CH_2$), 15.2 (2C, $CH_3$).

**Polymerization Procedure.** A typical polymerization procedure is exemplified by the synthesis of PLLA at room temperature. BnOH (16 μL, 0.154 mmol) and 20, 50, 100, 200, and 400 equiv of monomer were added to solutions of **1** (0.058 g, 0.077 mmol) in dichloromethane (15 mL). The mixtures were stirred for 0.5−12 h. After removal of a small sample of the crude product for characterization using $^1$H NMR, the reaction was quenched by addition of methanol (2 mL), the solution was concentrated under vacuum, and the polymer was precipitated with excess methanol. The polymer was then dried under vacuum to a constant weight.

**Crystallography.** The XRD data were collected at 100 K using a KUMA KM4 CCD κ-geometry diffractometer (ω scan technique).[27] The experimental details and the crystal data are given in Table S1 (Supporting Information). The structures were solved by direct methods and refined by full-matrix least-squares on $F^2$ using the SHELXTL package.[28] Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were positioned geometrically and added to the structure factor calculations, but were not refined. The molecular graphics were created using OLEX2.[29]

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Figures giving selected NMR and ESI-MS spectra of compounds **1**−**4**; $^1$H NMR and DSC spectra of polymers obtained using in situ generated **1c**; kinetic study; and a CIF file giving crystallographic data for **1**, $(1a)_2$, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structural analyses reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre (CCDC), nos. 873545−873548. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk; home page: http://www.ccdc.cam.ac.uk).

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### Notes

The authors declare no competing financial interest.

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