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Bulk solvent-free melt ring-opening polymerization of L-lactide catalyzed by Cu(II) and Cu(II)–Nd(III) complexes of the Salen-type Schiff-base ligand

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A monometallic (Cu^{2+}, 1) and a bimetallic (Cu^{2+}–Nd^{3+}, 2) Salen-type Schiff-base complexes with different reactive species, could efficiently catalyze the bulk solvent-free melt ring-opening polymerization (ROP) of L-lactide. Especially for the bimetallic complex 2, the involvement of rare earth ion was important and influential to the catalytic behaviors.

Supporting information may be found in the online version of this article.

Keywords: Salen-type Schiff base transition metal or mixed metal complex; bulk solvent-free melt ring-opening polymerization; L-lactide

Introduction

Polylactide (PLA) polymers, as one of the most important synthetic biodegradable, biocompatible polyesters for wide-ranging use in biomedical, pharmaceutical and agricultural applications,[1] can be prepared from the ring-opening polymerization (ROP) of lactide,[2] both in solution polymerization and in bulk solvent-free melt polymerization. In contrast to the solution polymerization,[3] commercially, the ROP of lactide is most commonly carried out with the bulk solvent-free melt polymerization,[4] which exhibits advantages over solution polymerization: (1) no solvent is required; (2) it is less vulnerable to impurity levels and unwanted side reactions; (3) it is often useful for the large-scale production of PLAs.[5] In the viewpoint of needed catalysts, two kinds of typically molecular catalysts have been reported: one is the metal complexes containing the characteristic initiators (alkoxide, amide or carboxylate), and the mechanism of the ROP of lactide is the same as that in solution polymerization, and generally recognized to proceed via the reaction pathway shown in Scheme 1, involving the attack of a characteristic group on the ketonic group of a coordinated lactide molecule;[6] the other is metal complexes lacking those normal initiators, while the excellent control of the polymerization could be well achieved from the molecular design of diverse catalysts and the selectivity of reaction conditions.[7] In spite of the limited knowledge on the possible polymerization mechanism, the coordination geometry and Lewis acidity of active species are probably responsible for metal-mediated ROP of lactide. Although these recent impressive developments have been achieved, there has been an intense search for new-generation catalysts with higher activity and lower toxicity.

Compared with the homogeneous or heterogeneous catalysis of Salen-type Schiff-base metal complexes in various chemical reactions,[8] efforts to use them for the ROP of lactide are relatively limited. Although many transition metal complexes[9] of Salen-type chiral or achiral Schiff-base ligands are well known to be efficient catalysts for the ROP of L-lactide, they are limited in solution polymerization, and to the best of our knowledge, few reports of their use for bulk solvent-free melt polymerization of L-lactide have been documented.[10] In particular, there has been no report on the low-toxicity d or d-f Salen-type Schiff-base complexes using as the catalysts for the bulk ROP of L-lactide. Herein, we report the synthesis, reactivity and the bulk solvent-free melt polymerization behavior of a monometallic (Cu^{2+}, **1**) and a bimetallic (Cu^{2+}—Nd^{3+}, **2**) catalysts capable of living ROP of L-lactide. The catalysis results showed that the two complexes (**1**–**2**) with different reactive species could efficiently catalyze the polymerization of L-lactide with moderate molecular weights and narrow molecular weight distributions, and the involvement of rare earth ions was important.

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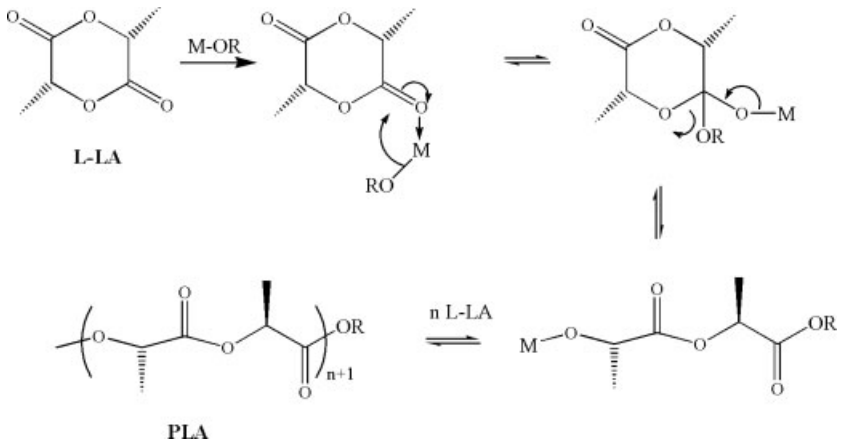
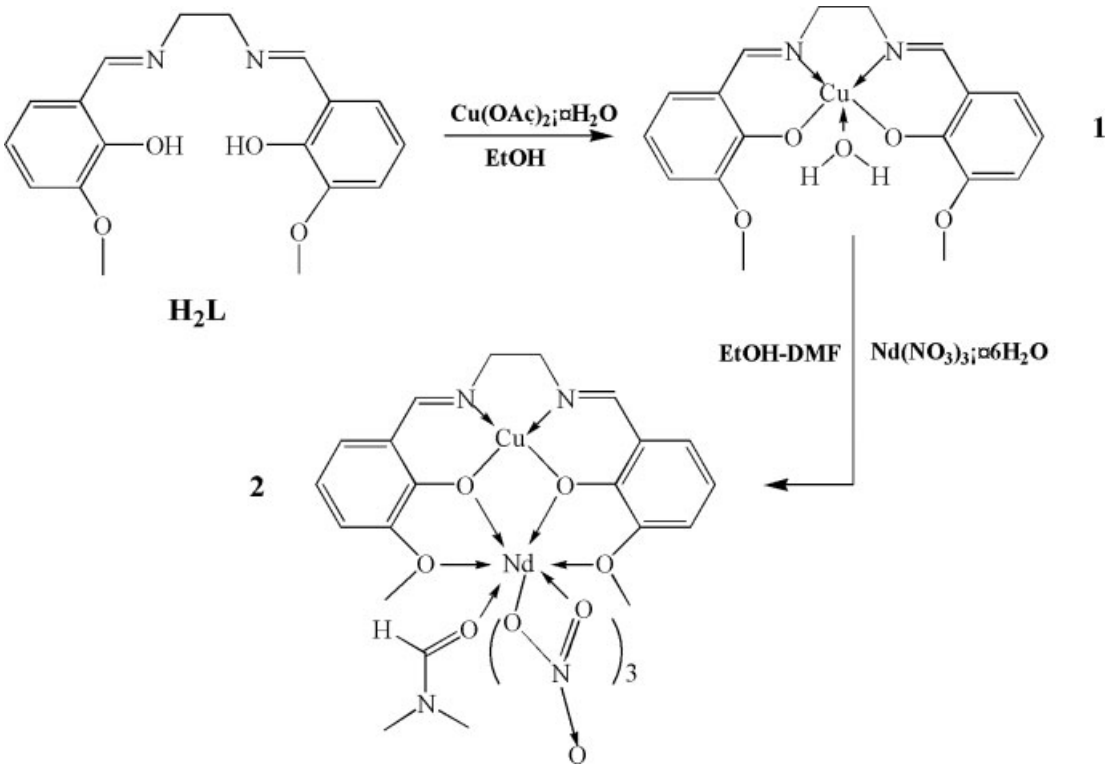


Scheme 1. Schematic representation of the typical ROP process of L-lactide initiated by the M–OR complex.



Scheme 2. Reaction scheme for the syntheses of complexes 1 and 2.

Results and Discussion

Synthesis and Characterization

As shown in Scheme 2, reaction of an equimolar **H_2L** and $Cu(OAc)_2{\cdot}H_2O$ in absolute EtOH afforded complex **1** in good yield. Further reaction of **1** with $Nd(NO_3)_3 \cdot 6H_2O$ in 1 : 1 molar ratio in EtOH–DMF resulted in the formation of complex **2** in the yield of *ca* 68%. The FT-IR spectra show the characteristic absorptions of the ν(C═N) vibration at 1646 cm^{-1} for **1** and 1629 cm^{-1} for **2**, which are slightly blue and red shifted by *ca* 14 and 3 cm^{-1} relative to those of the free Salen-type ligand **H_2L** (1632 cm^{-1} for **H_2L**) upon binding to metal ions.[11] For **2**, two strong absorption bands at 1470 and 1316 cm^{-1} can be attributed to $\nu(NO_3^-)$.[12] Thermogravimetric analysis (TGA) in the range 25–600 °C showed that the framework of **1** or **2** decomposed at temperature over 308 or 332 °C where an abrupt weight loss was observed, followed by a final weight loss in the 325 or 354–600 °C range. As for the solution behavior of complexes **1**–**2**, the ESI-MS spectra exhibit one peak at *m/z* 390.90 and 658.15, corresponding to the major species $[CuL]^+$ and $[CuLNd(NO_3)_2]^+$, respectively, indicating that the respective discrete monometallic or bimetallic molecule exists in dilute $CHCl_3$ solution. Further from the UV–vis absorption spectra of the ligand and the two complexes examined in $CHCl_3$ solution, as shown in Fig. 1, the free ligand **H_2L** exhibits absorption bands at 220, 263 and 424 nm, which could be assigned to the ligand-centered $\pi \rightarrow \pi^*$ transitions, while for the two complexes **1**–**2**, the lower energy bands are blue-shifted upon coordination to metal ions (233, 278 and 365 nm for **1**; 223, 275 and 351 nm for **2**).[13]

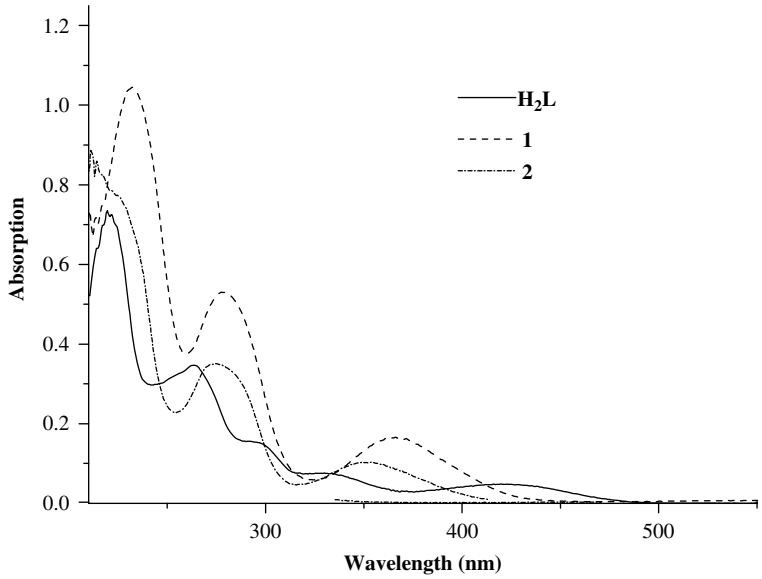


Figure 1. UV–vis absorption spectra of H_2L, 1 and 2 in $CHCl_3$ at 2×10^{-5} M at room temperature.

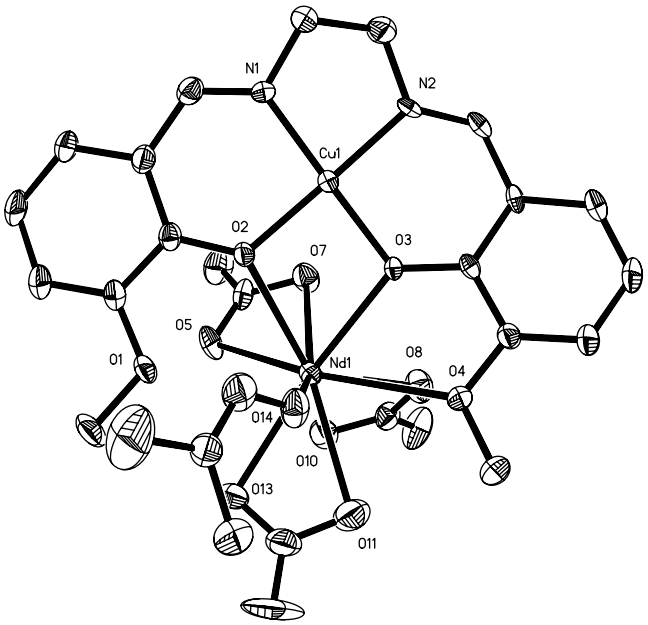


Figure 2. View of the X-ray structure of complex 2. Hydrogen atoms are omitted for clarity.

Structures

For complex **1**, the single crystal structure has been reported previously,[14] which shows a typical monometallic structure of [CuL(H_2O)], in which the five-coordinate Cu^{2+} ion has a near-square-pyramidal geometry (see Supporting Information, Fig. 1s). The X-ray crystal structure analysis of complex **2** unambiguously revealed the bimetallic Cu–Nd structure, as depicted in Fig. 2. The neutral [CuLNd(NO_3)$_3$(DMF)] (**2**) reveals that the relatively soft Cu^{2+} ion is located in the inner N_2O_2 core, and the relatively hard Nd^{3+} ion in the outer O_2O_2 cavity of the Schiff base $\mathbf{L}^{2-}$ ligand. The Cu^{2+} ion lies in a four-coordinate environment and adopts a slightly distorted square-planar geometry, with two sets of unequal Cu–N(imino) [1.902(5)–1.936(5) Å] and Cu–O (phenolic) [1.906(4)–1.925(5) Å] bond lengths and N–Cu–O bond angles [94.1(2)–95.0(2)° and 171.2(2)–175.7(2)°]. The Nd^{3+} ion is 10-coordinate and coordinated to three O atoms from the Schiff base $\mathbf{L}^{2-}$ ligand, one from the solvate DMF and six from three bidentate NO_3^- groups. Depending on the nature of the oxygen atoms, the Nd–O bond lengths vary from 2.396(6) to 2.956(5) Å, and the bond lengths from phenoxo oxygen atoms are shorter than those from oxygen atoms of NO_3^- anions. The coordination mode of the Schiff base $\mathbf{L}^{2-}$ ligand in **2** is asymmetrical, just endowing three oxygen atoms for the coordination of Nd^{3+} ion due to the occupation of the solvate DMF, which has been found in only one of our reported Zn–Nd chiral Salen-type Schiff base complexes,[15] while not comparable to those of magnetic Cu–Ln[16] or carboxylate-bridged luminescent Zn–Ln Salen-type Schiff-base complexes.[17]

ROP Studies of L-Lactide

The ROP of L-lactide using complexes **1–2** as catalysts in a stipulated molar ratio of [M]:[C] were carried out at 130 or 160 °C for the selected time under solvent-free melt conditions. Under these conditions (entries 3–14), the reaction mixture would form a monomer melt in which the polymerization would occur, and the results are summarized in Table 1. For complex **1**, at the polymerization temperature of 130 °C, the catalytic activities increased with the increase in reaction times, and well-controlled polymerization was observed from the narrow molecular weight distributions (PDI = 1.113–1.389). Although the higher M_n or M_w value of the products was achieved by polymerization for 24 h, the molecular weights decreased with the prolonging of polymerization time (36 h), which should be attributed to the thermal depolymerization as the polymerization time increases.[18] Similar to the polymerization with prolonged time, the result of ROP of L-lactide performed at temperatures ranging from 130 to 160 °C for 24 h showed that, with increasing temperature, the catalytic activity increased; however, the molecular weight (M_n) decreased and the molecular weight distribution broadened (PDI = 1.487). This may also be ascribed to the thermal depolymerization and the acceleration of transesterification as

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Table 1. Catalytic data in the bulk polymerization of L-lactide

Entry	Compound	Time (h)	T (°C)	[M] : [C] ratio[a]	Yield (g)	Activity (g mol^{-1} h^{-1})	M_n[b] (10^3)	M_w[c] (10^3)	PDI[d]
1	–	24	130		0	0	–	–	–
2	Ligand	24	130	1000 : 1	0	0	–	–	–
3	**1**	12	130	1000 : 1	1.51	18.13	13.413	15.201	1.133
4	**1**	24	130	1000 : 1	51.85	311.30	14.142	19.654	1.389
5	**1**	36	130	1000 : 1	58.03	152.22	14.880	18.247	1.226
6	**1**	24	160	1000 : 1	78.34	470.34	13.943	20.733	1.487
7	**1**	24	130	500 : 1	26.32	328.02	14.889	20.783	1.396
8	**1**	24	130	2000 : 1	41.12	246.88	16.809	23.414	1.393
9	**2**	12	130	1000 : 1	21.58	259.13	15.863	18.465	1.164
10	**2**	24	130	1000 : 1	35.18	211.21	21.785	26.099	1.198
11	**2**	36	130	1000 : 1	44.19	176.87	22.353	28.568	1.278
12	**2**	24	160	1000 : 1	53.80	323.01	22.344	27.489	1.225
13	**2**	24	130	500 : 1	37.60	225.74	20.059	24.277	1.318
14	**2**	24	130	2000 : 1	29.52	177.23	20.162	28.799	1.130

[a] [M] : [C] ratio is the molar ratio of L-lactide monomer and catalyst.
[b] M_n is the relative number-average molecular weight.
[c] M_w is the relative weight-average molecular weight.
[d] PDI = M_w/M_n.

the polymerization temperature increases.[19] When the [M] : [C] ratio was lower than 1000 : 1 at 130 °C for 24 h, little difference in the catalytic activities was observed. The molecular weights (M_n and M_w) of the polymerization products were also affected by the [M] : [C] ratio. The maximum molecular weight (M_n = 16 809 or M_w = 23 414) was achieved at an [M] : [C] ratio of 2000 : 1, which showed that the lower catalyst concentration could be helpful for the growth of the polymeric products, while a lower catalyst concentration produced fewer initiation sites, thus leading to the lower catalytic activity.[20] In the selected range (500–2000) of [M] : [C] ratios, the copper catalyst **1** could afford the PLAs with narrow molecular weight distributions (M_w/M_n = 1.389–1.396), while the blank experiment (entry 1) or the presence of free ligand (entry 2) showed that no polymeric products were obtained, both further demonstrating that the presence of single-site active species (Cu^{2+}) in **1** endows the controllable polymerization process.[21]

With the replacement of complex **1** with complex **2** as the catalyst, on the varied reaction conditions, more controllable polymerization of L-lactide was observed, which is also summarized in Table 1. It is significant to explore the correlation between the molecular structure of complex **2** and the catalytic behavior. In contrast to the near-square-pyramidal geometry of the five-coordinate Cu^{2+} ion in complex **1**, the further coordination of $Nd(NO_3)_3$ in complex **2** endowed the slight distortion of square-planar geometry and the increase of Lewis acidity of the four-coordinate Cu^{2+} ion. With short reaction time (12 h) at 130 °C, complex **2** showed higher catalytic activity than complex **1**, which indicates catalyst deactivation from the H_2O solvates in complex **1** as a first step. When the reaction time was prolonged or the catalyst concentration was decreased, an obvious decrease in catalytic activities was observed, which shows that the steric effect from the coordination of $Nd(NO_3)_3$ in complex **2** should prevent the further coordination of the active species for L-lactide monomers. In fact, due to the existence of nitrates around the Nd^{3+} ions in complex **2**, in agreement with its solution behavior, the second metal center (Nd^{3+}) was inactive to the ROP of L-lactide. However, for the obtained polymeric products by complex **2**, a significant increase in molecular weights (M_w or M_n) was observed, which suggests that the steric effect from the coordinated $Nd(NO_3)_3$ in complex **2** is suitable for the growth of polymer chains in further insertion for L-lactide monomers. A reasonable explanation for this is that the coordination of rare earth ions in complex **2** causes the Cu^{2+} ion to be more acidic, resulting in a stronger Cu–O=C (L-lactide) bond for the retarded insertion reaction of L-lactide monomers; therefore lower catalytic activities with higher molecular weight polymeric products are observed. For complex **2** the involvement of rare earth ions effectively passivated the catalytic behaviors on the ROP of L-lactide, which is shown by the controllable polymerization, even at 160 °C for 24 h or 130 °C for 36 h.

Thermogravimetric analysis (TGA) in the range 25–600 °C showed that these polymeric products (entries 4 and 9) decomposed at temperatures over 280 °C (281 °C for **1** and 300 °C for **2**), where an abrupt weight loss was observed, followed by a final weight loss in the 355–600 °C range. One of the identical FT-IR spectra shows the characteristic absorption bands of PLA with a very strong peak at 1758 cm^{-1} assigned to the –C=O stretching vibration and peaks at 1192–1245, 1090–1132 and 756 cm^{-1} attributed to the asymmetric –C–O–C- vibration, the symmetric –C–O–C- vibration and the –C=O bending vibration, respectively. One of the identical ^{1}H NMR spectra of the polymers (as shown in Supporting Information, Fig. 2s) showed a doublet at 1.59 ppm for the methyl (^{c}H) and a multiplet at 5.18 ppm for the methine (^{b}H) of main chain of PLA, indicating no inversion of the configuration of asymmetric carbon atoms of the monomer under the reaction conditions. The additional signals appearing at 1.50 (1.57), 4.37 and 3.60 ppm should be assigned to the methyl, the methine and the hydroxyl end group of PLA, respectively. One of the identical ^{13}C NMR spectra (as shown in Supporting Information, Fig. 3s) of the selected PLA showed peaks at 16.64, 69.00 and 169.62 ppm that should be assigned to methyl carbon, methane carbon and ester carbon, respectively, and the PLA was isotactic in nature.[22] Systems **1** and **2** are active for the bulk ROP

of L-lactide in the absence of normal initiators (alkoxide, amide or carboxylate), and the end groups of PLA are not from the catalysts, but from the replacement of methyl groups when terminating the polymerization with methanol containing 5% HCl. Thus, the initiation may occur through the metal–alkoxide bond of the catalysts, through the stable and selective acyl–oxygen bond cleavage of the monomer, and the ring-opening polymerization also proceeds via the typical 'coordination-insertion' mechanism.[23]

Conclusion

In conclusion, the monometallic Cu^{2+} complex **1** and the bimetallic Cu^{2+}–Nd^{3+} complex **2** were shown to efficiently catalyze the bulk solvent-free melt ROP of L-lactide with moderate molecular weights and narrow molecular weight distributions. The correlation of molecular structure vs catalytic activity showed that the different catalytic behaviors resulted from the different active species; in particular, the involvement of rare ions effectively passivated the catalytic behaviors on the ROP of L-lactide with bigger polymeric molecular weights (M_w or M_n) and better polymerization controllability. With these in mind, the design of more active and multiple activity species of catalysts is now underway.

Experimental Section

Materials and Methods

All chemicals of reagent grade were commercially available and used without further purification. Element analyses were performed on a Perkin-Elmer 240C element analyzer. Infrared spectra were recorded on a Bruker Equinox55 FT-IR spectrophotometer in the region 4000–400 cm^{-1} in KBr pellets. ESI-MS was performed on a Finnigan $LCQ^{DECA}XP$ HPLC-MS^n mass spectrometer with a mass to charge (*m*/*z*) range of 2000 using a standard electrospray ion source and toluene as solvent. ^1H NMR and ^{13}C NMR spectra were measured on a Varian Unity INOVA 400NB instrument using DMSO-δ_6 or $CDCl_3$ as solvent and TMS as internal standard at room temperature. Electronic absorption spectra in the UV–vis region were recorded with a Hewlett Packard 8453 UV–vis spectrophotometer. Thermogravimetric analyses were carried out on a Netzsch TG 209 Instrument under flowing nitrogen by heating the samples from 25 to 600 °C.

Preparations

*N,N′-Bis(3-methoxy-salicylidene)ethylene-1,2-diamine (**H_2L**)*

The Salen-type Schiff-base ligand **H_2L** was synthesized by the typical procedure[11] by condensation of *o*-vanillin (6.3 g, 40 mmol) and 1,2-diaminoethane (1.4 ml, 20 mmol) in absolute EtOH under reflux for about 10 h. After cooling to room temperature, the insoluble precipitate was filtered and was re-crystallized using absolute EtOH to give the yellow polycrystalline solid. Yield: 5.0 g, 76%. Calcd for $C_{18}H_{20}N_2O_4$: C 65.84, H 6.14, N 8.53%; found: C, 65.58, H, 6.06, N, 8.63%; IR (KBr, cm^{-1}): 3444b, 3001 w, 2930 w, 2840 w, 1632s, 1468s, 1410m, 1249s, 1080m, 958m, 736m, 695 w, 642 w, 564 w, 525 w. ^1H NMR (400 MHz, [D_6]-DMSO): δ 13.54 (s, 2H, -OH), 8.55 (s, 2H, -CH═N), 6.99 (m, 4H, -Ph), 6.77 (t, 2H, Ph), 3.91 (s, 4H, $-CH_2$), 3.74 (s, 6H, -MeO).

[CuL(H_2O)] ***(1)***

To a stirred solution of H_2L (0.165 g, 0.5 mmol) in absolute EtOH (5 ml), $Cu(OAc)_2 \cdot H_2O$ (0.100 g, 0.5 mmol) was added and heated under reflux for 5 h. The mixture was allowed to cool to room temperature and filtered. The resultant clear brown solution was left to stand at room temperature for several days to give a black crystalline product of **1** in 72% yield. Calcd for $C_{18}H_{20}N_2O_5Cu$: C, 53.26; H, 4.47; N, 6.90%; found: C, 53.38; H, 4.66; N, 6.88%. IR (KBr, cm^{-1}): 3291b, 2923 w, 2828 w, 1646s, 1603 w, 1444 vs, 1240m, 1215s, 728m, 697 w, 636 w, 582 w, 531 w, 463 w. ESI-MS (*m*/*z*): 390.90 $[M - H_2O + H]^+$.

[Cu(L)Nd(NO_3)$_3$(DMF] ***(2)***

To a solution of 1 (0.113 g, 0.3 mmol) in absolute EtOH (4 ml), a solution of $Nd(NO_3)_3 \cdot 6H_2O$ (0.132 g, 0.3 mmol) in absolute EtOH (5 ml) was added, and the mixture was refluxed for 3 h. Then 1 ml absolute DMF was added to give a clear green solution. Diethyl ether was allowed to diffuse slowly into this solution at room temperature and pale red single crystals of **2** were obtained in a few weeks. Yield: 0.162 g (68%). Calcd for $C_{21}H_{25}N_6O_{14}CuNd$: C, 31.80; H, 3.18; N, 10.59%; found: C, 31.72; H, 3.32; N, 10.56%. IR (KBr, cm^{-1}): 2987 w, 2846 w, 1629s, 1561 w, 1501s, 1470 vs, 1316s, 1279s, 1235s, 1167m, 1109 w, 1080m, 1027 w, 989 w, 956 w, 861 w, 811 w, 784 w, 740m, 685 w, 625 w, 582 w, 495 w. ESI-MS (*m*/*z*): 658.15 $[M - DMF - NO_3]^+$.

PLA

IR (KBr, cm^{-1}): 3442 w, 3000 w, 2950 w, 1758s, 1245m, 1192m, 1132m, 1090m, 756m, 693 w. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.18 (m, methine), 4.37 (d, methine), 3.60 (s, hydroxyl), 1.59 (s, methyl), 1.57 (s, methyl), 1.50 (s, methyl). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 169.62 (-C═O), 69.01 (-CH), 16.64 ($-CH_3$).

Crystallography

Single crystals of [Cu(L)(H_2O)] (**1**) and [Cu(L)Nd(NO_3)$_3$(DMF)] (**2**), of suitable dimensions, were mounted onto glass fibers for crystallographic analyses. The structure of **1** was similar to that previously reported in the literature.[15] For **2**, all the intensity data were collected at 293(2) K on a Bruker SMART CCD diffractometer (Mo-K_α radiation, $\lambda = 0.71073$ Å) in Φ and ω scan modes. Structure was solved by direct methods followed by difference Fourier syntheses, and refined by full-matrix least-squares techniques against F^2 using SHELXTL.[24] All the non-hydrogen atoms were refined with anisotropic thermal parameters. Absorption corrections were applied using SADABS.[25] All hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. Crystallographic data and refinement parameters for the complex **2** are presented in Table 2. Selected bond distances and bond angles for **1** and **2** are given in Table 3.

Polymerization Experiments

L-Lactide was prepared from L-lactic acid as previously reported.[26] The crude product was further purified by re-crystallization three times from dried ethyl acetate, then dried for 24 h in vacuum at 30 °C. Under nitrogen, 1.000 g (6.94 mmmol) of the freshly re-crystallized L-lactide monomer and the catalyst **1** or **2**, in a stipulated molar ratio ([M] : [C]), were charged in an ampoule inside a glove box. The ampoule was put under high vacuum

Table 2. Summary of crystallographic data and structure refinements for complex **2**

Compound	**2**
Empirical formula	$C_{21}H_{25}CuN_6O_{14}Nd$
Formula weight	793.25
Crystal system	Triclinic
Space group	*P2(1)/c*
a (Å)	8.197(3)
b (Å)	10.948(3)
c (Å)	16.466(5)
α (deg)	94.950(5)
β (deg)	99.492(5)
γ (deg)	104.829(4)
V (Å^3)	1396.1(7)
Z	2
ρ (g cm^{-3})	1.887
T (K)	273(2)
Crystal size (mm^3)	0.34 × 0.27 × 0.22
μ (mm^{-1})	2.680
F(000)	788
Data/restraints/parameters	4837/0/388
Quality-of-fit indicator	1.020
No. unique reflections	4837
No. observed reflections	6957
[$I > 2\sigma(I)$]	
R	0.0399
w R	0.1087

Table 3. Interatomic distances (Å) and bond angles (deg) with esds for **1** and **2**

1		2	
Cu(1)–N(1)	1.947(3)	Cu(1)–N(1)	1.902(5)
Cu(1)–N(2)	1.947(3)	Cu(1)–N(2)	1.936(5)
Cu(1)–O(2)	1.928(2)	Cu(1)–O(2)	1.925(5)
Cu(1)–O(3)	1.928(2)	Cu(1)–O(3)	1.906(4)
Cu(1)–O(5)	2.362(4)	Nd(1)–O(2)	2.531(5)
		Nd(1)–O(3)	2.439(4)
N(1)–Cu(1)–N(2)	82.3(2)	Nd(1)–O(4)	2.856(5)
N(1)–Cu(1)–O(2)	92.0(3)	Nd(1)–O(5)	2.544(6)
N(1)–Cu(1)–O(3)	167.5(3)	Nd(1)–O(7)	2.585(5)
N(1)–Cu(1)–O(5)	93.2(3)	Nd(1)–O(8)	2.547(5)
		Nd(1)–O(10)	2.667(6)
		Nd(1)–O(11)	2.605(7)
		Nd(1)–O(13)	2.578(6)
		Nd(1)–O(14)	2.396(6)
		N(1)–Cu(1)–N(2)	83.7(2)
		N(1)–Cu(1)–O(2)	93.1(2)
		N(1)–Cu(1)–O(3)	176.8(2)
		O(2)–Nd(1)–O(3)	63.46(15)
		O(4)–Nd(1)–O(14)	70.15(17)
		O(5)–Nd(1)–O(7)	49.26(19)
		O(8)–Nd(1)–O(10)	48.4(2)
		O(11)–Nd(1)–O(13)	48.9(2)

(about 12 Pa) for 1 h, after which the ampoule was sealed under vacuum. The polymerizations were performed in a thermostatically controlled oil bath at 130 or 160 °C for the selected time. Subsequently, the molten reactive polymer mixture was cooled by immersing the sealed ampoule in liquid nitrogen and terminated by introducing absolute MeOH with 5% (w/w) HCl to stop the polymerization. The resulting polylactide polymer was dissolve in absolute acetone and precipitate in water. The filtered precipitate was dried under vacuum to constant weight. Molecular weights (M_w and M_n) and molecular weight distributions (PDI = M_w/M_n) were determined by gel permeation chromatography (GPC) with polystyrene as standard.

Supporting Information

Supporting information can be found in the online version of this article. The view of X-ray structure of complex **1**, and the ^{1}H NMR and ^{13}C NMR spectra of the selected PLA are shown in Figs 1–3s. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center; CCDC reference number for **2** is 776510. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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