稀土席夫碱配合物催化己内酯可控开环聚合

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摘要: 通过稀土氯化物与席夫碱钠盐的交换反应制备了一系列以 3,5-二叔丁基水杨醛缩苯胺为配体的稀土席夫碱配合物. 对其中的钕席夫碱配合物进行了 X 射线单晶衍射分析, 发现其单晶结构为五角双锥构型, 所得席夫碱稀土配合物可以单组分催化 ϵ -己内酯开环聚合. 深入研究了钕席夫碱配合物催化己内酯的开环聚合机理, 考察了不同聚合条件对单体转化率、产物分子量及分子量分布的影响. 结果表明, 该聚合反应速率为一级, 聚合反应具有较好的可控性. 聚合物端基分析表明, 聚合反应以配位-插入机理进行.

关键词: 己内酯; 开环聚合; 稀土催化剂; 席夫碱; 晶体结构

中图分类号: O643

文献标识码: A

Controlled Ring-Opening Polymerization of ϵ -Caprolactone Catalyzed by a Rare Earth Schiff-Base ComplexNI Xufeng[#], ZHU Weiwei, SHEN Zhiquan^{*}

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Abstract: Lanthanide Schiff-base complexes with the formula $[3,5-tBu_2-2-(O)C_6H_2CH=NC_6H_5]_3Ln(THF)$ ($Ln = Sc, Y, La, Nd, \text{ and } Gd$) were synthesized by the metathesis reaction of anhydrous $LnCl_3$ with a Schiff-base sodium salt in good yields (> 80%). The complex containing a neodymium center was characterized by X-ray diffraction and the structure around the neodymium atom could be described as a pentagonal bipyramid. The ring-opening polymerization (ROP) of ϵ -caprolactone (CL) was successfully carried out using the lanthanide Schiff-base complexes as catalysts, and the neodymium complex leads to a controlled ROP of CL. The influence of the reaction conditions on the monomer conversion, molecular weight, and molecular weight distribution of the resultant polymers was investigated. The polymerization rate was first-order with respect to the monomer concentration. End-group analyses of the oligomer of CL showed that the polymerization underwent a coordination-insertion mechanism.

Key words: ϵ -caprolactone; ring-opening polymerization; rare-earth catalyst; Schiff-base; crystal structure

Aliphatic polyester poly(ϵ -caprolactone) (PCL) is biodegradable and biocompatible [1] and is attracting interest because of its numerous applications in the biomedical field. An efficient way to synthesize PCL is by the metal complex catalyzed ring-opening polymerization (ROP) of ϵ -caprolactone (CL). Therefore, the development of simple, convenient, and efficient metal complexes as catalysts for the ROP of ϵ -caprolactone is important practically and theoretically. Catalysts for CL polymerization are tradition-

ally based on Sn, Al, Zns and lanthanide compounds [2–7]. Rare earth complexes are very attractive catalysts because of their low toxicity, low cost, and high reactivity [8–11].

Schiff-base ligands are considered to be privileged ligands and they are some of the most widely used non-cyclopentadienyl compounds in the coordination chemistry of transition and lanthanide metals [12]. They have also played an important role in progressing coordination chemistry over the past two decades [13]. Because

Received date: 26 March 2010.

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Foundation item: Supported by the National Natural Science Foundation of China (20774078), the Special Funds for National Basic Research Program of China (973 Program, G2005CB623802), and the Scientific Research Foundation for Returned Scholars, Ministry of Education of China.

English edition available online at ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

Schiff-base ligands have a hard donor atom framework and tunable steric and electronic effects, many metal Schiff-base complexes show high catalytic activity in various reactions [14–17]. Furthermore, the phenoxy-imine (FI) complexes of nickel (II) and the bis(phenoxyimine) group 4 metal complexes have been used as excellent catalysts for the polymerization of olefins [18–21]. Few rare earth Schiff base complex catalysts have been reported for the ring-opening polymerization of cyclic esters as well as the related lactides [22–24]. In these catalytic reactions, Schiff-base ligands are stable and act as ancillary ligands to stabilize the Ln-active bond.

Our group has developed some rare earth complexes as catalysts for the ROP of cyclic esters and they have worked very well [25–31]. We synthesized rare earth complexes bearing three Schiff-base ligands ($[3,5\text{-}t\text{Bu}_2\text{-2-(O)C}_6\text{H}_2\text{CH=NC}_6\text{H}_5]_3\text{Ln(THF)}$) by a facile reaction between anhydrous rare earth chlorides and a Schiff-base sodium salt. They were thus employed as single component catalysts for the controlled ROP of CL.

1 Experimental

1.1 General

All experiments were performed under argon with the rigorous exclusion of air and moisture using standard Schlenk techniques. Toluene, *n*-hexane, and tetrahydrofuran (THF) were refluxed over sodium/benzophenone and distilled just before use. ϵ -Caprolactone was purchased from Acros, dried over CaH_2 for 4 d and stored over 4A molecular sieves under argon after distillation under reduced pressure. Anhydrous rare earth chloride was prepared from Ln_2O_3 and HCl in accordance with a standard procedure [32]. Other reagents were used as received.

Elemental analysis was performed on a Flash EA1112 instrument and the rare earth metal content was measured using the EDTA-titration method. ^1H NMR spectra were obtained on a Bruker Avance DMX500 spectrometer in CDCl_3 at 25 °C with TMS as an internal reference. The molecular weight (M_n) and molecular weight distributions (MWD) of the formed polymers were measured by gel per-

meation chromatography (GPC) at 40 °C using THF as eluent at a flow rate of 1.0 ml/min against standard polystyrenes on a Waters 1515 apparatus with three PL Mixed-C columns. FT-IR spectra of the samples were measured as KBr pellets using a Bruker Vector 22 FT-IR spectrometer. X-ray diffraction (XRD) was performed as described below: suitable single crystals of a complex were sealed in thin-walled glass capillaries, and data collection was performed at 20 °C on a Bruker SMART diffractometer with graphite-monochromated $\text{Mo } K_\alpha$ radiation ($\lambda = 0.071\,073\text{ nm}$). The SMART program package was used to determine the unit-cell parameters. An absorption correction was applied using SADABS. The crystal structures of the neodymium containing complex was solved by a direct method using the SHELXS-97 program and expanded by the Fourier technique. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.95 Å) with assigned appropriate isotropic thermal parameters.

1.2 Synthesis of *N*-phenyl-3,5-di-*tert*-butyl-salicylaldehyde

3,5-Di-*tert*-butyl-salicylaldehyde (16.5 g, 0.07 mol) was dissolved in 30 ml ethanol, phenylamine (6.5 ml, 0.07 mol) was added dropwise into the solution. Then, the mixture was heated and refluxed for 3 h. Orange crystals formed after the reaction solution cooled to room temperature. The fine crystalline product was then filtered and recrystallized in ethanol (10.7 g, 49.4%). Anal. Calc. for $\text{C}_{21}\text{H}_{27}\text{NO}$: C, 81.51; H, 8.79; N, 4.53. Found: C, 81.81; H, 8.84; N, 4.59. ^1H NMR: $\delta = 1.33\text{--}1.48$ (m, 18H, $-\text{CH}_3$), 7.22–7.45 (m, 7H, phenyl-H), 8.63 (s, 1H, CH=N), 13.69 (s, 1H, $-\text{OH}$).

1.3 Synthesis of $[3,5\text{-}t\text{Bu}_2\text{-2-(O)C}_6\text{H}_2\text{CH=NC}_6\text{H}_5]_3\text{Nd}$ (THF) complex (1)

As shown in Scheme 1, NdCl_3 (0.54 g, 2.15 mmol) was suspended in 20 ml THF and stirred overnight at room temperature. A THF solution (20 ml) of *N*-phenyl-3,5-di-*tert*-butyl-salicylaldehyde (2.17 g, 7.0 mmol) was added dropwise to a THF (10 ml) suspension of NaH (0.20 g, 8.30

Scheme 1. Synthesis and structure of rare earth Schiff-base complexes.

mmol) at room temperature and further stirred for 4 h. After filtration, the yellow solution was added to the $\text{NdCl}_3\cdot\text{THF}$ suspension. The mixture was stirred at 80 °C in an oil bath for 4 d and then the formed precipitate was separated from the reaction mixture by centrifugation. The solvent was vaporized under reduced pressure and the residue was dissolved in *n*-hexane. $[\text{3,5-}i\text{Bu}_2\text{-2-(O)C}_6\text{H}_2\text{CH=NC}_6\text{H}_5\text{]}_3\text{-Nd(THF)}$ was isolated as yellow crystals at room temperature after a few days (1.67 g, 53.8%). Anal. Calc. for $\text{C}_{67}\text{H}_{86}\text{N}_3\text{NdO}_4$: C, 70.49; H, 7.59; N, 3.68; Nd, 12.63. Found: C, 70.64; H, 7.72; N, 3.74; Nd, 12.78%. IR (KBr, cm^{-1}): 2 957 (s), 2 903 (s), 2 867 (s), 1 608 (s), 1 585 (s), 1 546 (s), 1 532 (s), 1 484 (s), 1 459 (s), 1 430 (s), 1 413 (s), 1 384 (s), 1 359(s), 1 320 (s), 1 273 (s), 1 256 (s), 1 190 (s), 1 164 (s), 1 026 (s), 985 (w), 920 (w), 874 (m), 835 (s), 788 (m), 764 (m), 742 (s), 699 (w), 638 (w), 519 (s).

The other rare earth Schiff-base complexes were synthesized by the same method described above.

1.4 Polymerization of CL

All polymerizations were carried out in 20 ml ampoules using the Schlenk technique under argon. The catalyst was dissolved in toluene at a concentration of 2.0 mol/L. As a typical example, 0.55 ml (5.0 mmol) CL and the desired amount of solvent and catalyst solution were injected into a flame-dried ampoule sequentially at a specific temperature and polymerized over a predefined time. The polymerization was terminated by adding ethanol containing 5% HCl and the solution was poured into excess ethanol to precipitate the product, filtered and dried in vacuum at room temperature for 24 h to constant weight.

1.5 Oligomer for the end-group analysis

The oligomerization of CL was carried out with the Nd containing complex **1** in toluene at 30 °C with $[\text{CL}]/[\text{Nd}] = 20$ and a monomer concentration $[\text{CL}] = 2.0$ mol/L. The reaction was terminated with isopropanol containing 5% HCl after 5 min. The oligomer was precipitated from ethanol and purified by redissolving in THF, followed by precipitation in ethanol. After filtration, the product was dried in vacuum for 24 h.

2 Results and Discussion

2.1 Synthesis and characterization of the lanthanide Schiff-base complexes

The lanthanide Schiff-base complexes were synthesized by a salt metathesis reaction between LnCl_3 and Schiff-base sodium salts in a non-aqueous solution. Anhydrous LnCl_3 reacted with three equivalents of the sodium salts of the Schiff-bases formed in situ by the reaction of *N*-phenyl-3,5-di-*tert*-butyl-salicylaldehyde with NaH in THF, giving complexes in isolated yields of up to 80%. All these complexes have good solubility in THF, toluene, and even in hexane.

Among the above-mentioned complexes, only the neodymium complex (complex **1**) provided a suitable single crystal for X-ray structural determination. Complex **1** was also characterized by elemental analysis and FT-IR. In the IR spectrum of complex **1**, stretching vibration bands due to imine groups at $1\,608\text{ cm}^{-1}$ were observed. The paramagnetic property of complex **1** did not allow a resolvable NMR spectrum to be obtained. A definitive solid-state structure of

Fig. 1. ORTEP view of complex **1** with atom labels and showing 25% probability displacement ellipsoids.

Table 1 Crystallographic data and selected bond lengths and angles for the Nd containing complex **1**

Parameter	Value	Parameter	Value
Empirical formula	C ₆₇ H ₈₆ N ₃ NdO ₄	R(Nd1–O2)/nm	0.2215(5)
Formula weight (g/mol)	1141.63	R(Nd1–O3)/nm	0.2226(5)
Temperature (°C)	23(1)	R(Nd1–O4)/nm	0.2547(2)
Wavelength (nm)	0.071073	R(Nd1–N1)/nm	0.2691(6)
Crystal system	triclinic	R(Nd1–N2)/nm	0.2697(6)
Space group	P-1 (2)	R(Nd1–N3)/nm	0.2699(6)
<i>a</i> /nm	1.14235(6)	∠O2–Nd1–O3/(°)	166.57(17)
<i>b</i> /nm	1.63503(8)	∠O2–Nd1–O1/(°)	93.15(18)
<i>c</i> /nm	1.71564(9)	∠O3–Nd1–O1/(°)	90.10(18)
<i>α</i> /(°)	79.5588(16)	∠O2–Nd1–O4/(°)	90.94(14)
<i>β</i> /(°)	85.2927(13)	∠O3–Nd1–O4/(°)	94.06(13)
<i>γ</i> /(°)	79.9808(16)	∠O1–Nd1–O4/(°)	144.08(15)
<i>V</i> /nm ³	3.0991(3)	∠O2–Nd1–N1/(°)	89.55(18)
<i>Z</i>	2	∠O3–Nd1–N1/(°)	103.79(18)
<i>D</i> _{calc} /(g/cm ³)	1.22333	∠O1–Nd1–N1/(°)	69.80(16)
<i>μ</i> /mm ^{−1}	0.885	∠O4–Nd1–N1/(°)	74.56(15)
<i>F</i> (000)	1202	∠O2–Nd1–N3/(°)	97.48(18)
Crystal size (mm)	0.19×0.18×0.08	∠O3–Nd1–N3/(°)	69.98(17)
2 θ range (°)	51.0	∠O1–Nd1–N3/(°)	83.01(17)
Reflections collected	25672	∠O4–Nd1–N3/(°)	131.73(15)
Independent reflections	11384	∠N1–Nd1–N3/(°)	152.28(17)
Reflections with <i>I</i> ≥ 2.0 σ (<i>I</i>)	5690	∠O2–Nd1–N2/(°)	68.62(17)
Parameters refine	695	∠O3–Nd1–N2/(°)	101.63(18)
Goodness-of-fit on <i>F</i> ²	1.053	∠O1–Nd1–N2/(°)	144.54(18)
<i>R</i>	0.0768	∠O4–Nd1–N2/(°)	69.04(16)
<i>WR</i>	0.1435	∠N1–Nd1–N2/(°)	136.58(17)
R(Nd1–O1)/nm	0.2268(4)	∠N3–Nd1–N2/(°)	70.27(17)

complex **1** was provided by a single crystal X-ray determination. The ORTEP diagram of complex **1** is shown in Fig. 1, and the corresponding crystallographic data are given in Table 1. The selected bond lengths and angles are also listed in Table 1. The neodymium ion in complex **1** is ligated by three salicyladiminato ligands and a THF molecule. The geometry around the seven-coordinate neodymium metal center can be best described as a distorted pentagonal bipyramidal geometry (Fig. 2) with two oxygen atoms (O2, O3) from the Schiff-base ligands occupying the axial positions while two oxygen atoms (O4, O1) and three nitrogen atoms (N1, N2, and N3) form a plane. The average

Nd–N(Schiff-base) distance in complex **1** is 0.269 6 nm and the average Nd–O(Ar) bond length is 0.223 6 nm.

2.2 Polymerization of CL as catalyzed by the lanthanide Schiff-base complexes

The polymerization of CL was initially performed with various rare earth Schiff-base complexes (Ln(Salen)₃) (Ln = Sc, Y, La, Nd, and Gd) as shown in Table 2. We found that the yttrium complex had the highest catalytic activity for the ROP of CL under certain conditions and the scandium complex showed almost no catalytic activity for the ROP of CL.

Fig. 2. Conformation of the neodymium complex.

Table 2 ROP of CL catalyzed by $\text{Ln}(\text{Salen})_3$

Element	$n(\text{CL})/n(\text{Ln})$	$T/^\circ\text{C}$	t/min	Conversion (%)	M_n^a	MWD
Y	100	50	30	100	19200	1.31
Y	200	50	30	74.5	33400	1.30
Nd	50	50	30	100	15800	1.34
Nd	100	50	30	100	18300	1.42
Nd	200	50	30	51.5	26100	1.38
La	50	50	30	100	9600	1.14
La	100	50	30	55.8	11400	1.18
Gd	50	50	30	90.0	17700	1.47
Gd	100	50	30	43.3	18900	1.51
Sc	50	50	60	—	—	—
Sc	100	50	60	—	—	—
Nd	100	30	60	88.2	10400	1.52
Nd	200	30	60	41.7	13800	1.66
Nd	100	10	60	—	—	—

General polymerization conditions: $[\text{CL}] = 2.0 \text{ mol/L}$ in toluene.

^aMeasured by GPC against standard PSt samples.

The catalytic activity sequence for the different rare earth elements is $\text{Y} > \text{Nd} > \text{La} > \text{Gd} > \text{Sc}$. The ROP of CL was also carried out with the neodymium complex as a catalyst at 10 and 30 °C. A higher reaction temperature favors ROP of CL. Only a small amount of PCL was isolated at 10 °C.

We also found that the neodymium complex acts as an active single-component catalyst for the ROP of CL and gives a polymer with a high molecular weight and a reasonably narrow MWD. The polymerization process of the CL catalyzed by the neodymium complex was investigated in detail and the results are shown in Figs. 3–5.

When the CL/Nd molar ratio increases, the molecular weight of PCL increases linearly while the MWD broadens slightly from 1.33 to 1.52, as shown in Fig. 3. The kinetics of the polymerization reaction at 50 °C in toluene with a CL/Nd molar ratio of 200 was determined. The conversion increases as the polymerization time increases and a first-order kinetics plot of the polymerization is shown in

Fig. 3. Relationship between the M_n of PCL and the concentration of complex **1**. Polymerization conditions: $[\text{CL}] = 2.0 \text{ mol/L}$ in toluene, 50 °C.

Fig. 4. Figure 5 indicates that the number-average molecular weight M_n of PCL increases proportionally to the monomer conversion while the MWD of the polymer remains ≤ 1.50 . All these results indicate that the polymerization of CL catalyzed by the neodymium containing complex **1** is controllable.

To study the polymerization mechanism, a sample of low molecular weight PCL quenched with isopropanol was prepared and subjected to ^1H NMR analysis as shown in Fig. 6.

Fig. 4. Plot of $\ln([M]_0/[M])$ versus reaction time for the polymerization of CL. Polymerization conditions: CL/Nd molar ratio = 200, and the rest is the same as in Fig. 3.

Fig. 5. Plots of M_n versus monomer conversion. Polymerization conditions are the same as in Fig. 4.

Fig. 6. ^1H NMR spectrum of the PCL sample terminated by isopropanol.

Scheme 2. Initiation and termination reaction modes in the ROP of CL.

One end of the PCL chain is the esterified isopropyl group $-\text{COOCH}(\text{CH}_3)_2$ according to the signals at $\delta = 4.98$ (multiplet, H^f) for the CH group and $\delta = 1.23$ (doublet, H^g) for the CH_3 groups. Furthermore, the other end of the chain is $-\text{CH}_2\text{OH}$ according to the methylene proton signal at $\delta = 3.63$ (triplet, H^e). These signals prove that the ring of CL opened by acyl-oxygen bond cleavage (Scheme 2a). On the contrary, no isopropyl ether end group signal is detected in the ^1H NMR spectrum, indicating that the ring of CL does not open by a break of the alkyl-oxygen bond (Scheme 2b). This type of ring opening is similar to that previously reported [33].

3 Conclusions

Lanthanide Schiff-base complexes $[3,5\text{-}t\text{Bu}_2\text{-2-(O)C}_6\text{H}_2\text{CH=NC}_6\text{H}_5]_3\text{Ln(THF)}$ were prepared by the reaction of anhydrous LnCl_3 with the sodium salts of Schiff-bases in THF with a 3:1 molar ratio and in good yield. The neodymium containing complex was structurally characterized and was used as a single-component catalyst for the controlled ring-opening polymerization of ϵ -caprolactone giving PCL with a high molecular weight and a narrow molecular weight distribution.

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