Synthesis of indenyllanthanide amides: the effective initiators for polymerization of methyl methacrylate

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Diisopropylamido bisindenyl lanthanides $(C_9H_7)_2LnN(i\text{-}Pr)_2$ (Ln = Gd (1), Y (2), Er (3)) were successfully synthesized in satisfied yield by the reaction of $Ln(N(i\text{-}Pr)_2)_3(THF)$ with indene in 1:2 molar ratio in toluene. All of the complexes exhibit very high catalytic activity in the polymerization of methyl methacrylate. The resulting polymers have narrow molecular weight distributions and high syndiotacticity.

Keywords Synthesis, indenyllanthanide amides, MMA, polymerization

Introduction

Recently, the use of lanthanoids as single-component catalyst in polymer synthesis has attracted much attention. The application of lanthanocene hydride, alkyl compounds and lanthanoid alkoxide compounds in polymer synthesis has been extensively studied and reported.[1-8] On the contrary, the utilization of organolanthanoid amides as homogeneous catalysts for the polymerization of polar vinyl monomers remains relatively less explored.[9] Like lanthanocene hydride and alkyl compounds, in fact, lanthanocene amides also exhibit high reactivity towards the hydroamination/cyclization of aminoalkenes[10] and in the polymerization of methyl methacrylate (MMA).[9] More recently, it was found that bis(methylcyclopentadienyl)diisopropylamido lanthanoids and bis(methylcyclopentadienyl) piperidino lanthanoids are very effective initiators for MMA polymerization.[11,12] In order to further investigate the effect of auxiliary ligands around central metals on catalytic activity, indenyl was chosen as π-ligand in stead of usually used cyclopentadienyl.

Although triindenyllanthanide complexes were reported 30 years ago,[13] the indenyl ligand has found limited application in the organometallic chemistry of lanthanides.[14] The only example of the unsubstituted indenyl complex containing nitrogen to lanthanide σ bonds is $(C_9H_7)Ln(OEP)$.[15] The application of indenyllanthanide amides in polymer synthesis still remains intact. Herein, we report the synthesis of the bisindenyl diisopropylamido lanthanides and their application in catalytic polymerization of MMA.

Results and discussion

Synthesis of $(C_9H_7)_2LnN(i\text{-}Pr)_2$ (Ln = Gd (**1**), Y (**2**), Er (**3**))

Organolanthanoid amides were usually prepared by the ionic metathesis of alkali metal amides with lanthanocene chlorides.[16,17] However, the indenyllanthanide chlorides used as the important precursors are difficult to synthesize and are poorly characterized till now. For unsubstituted indenyllanthanide chlorides, only $[(C_9H_7)_2PrCl(THF)]_2$[18] and $(C_9H_7)GdCl_2(THF)_2$[19] are reported in the literatures. It was considered that lanthanide tris(diisopropylamides) may act as versatile starting material for the further transformation.[20] Our effects were given to synthesize bisindenyllanthanide

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amides by the reaction of $LnN(i\text{-}Pr)_3(THF)$ with 2 equivalents of indene. When $LnCl_3$ (Ln = Gd (**1**), Y (**2**), Er (**3**)) reacted with 2.5 equivalents of $LiN(i\text{-}Pr)_2$ in THF, followed by the treatment with two equivalents of indene in toluene, the neutral amido complexes were obtained in good yields as shown in the following equations:

$$LnCl_3 + 2.5LiN(i\text{-}Pr)_2 \xrightarrow{THF} Ln[N(i\text{-}Pr)_2]_3(THF) + LiCl \quad (1)$$

$$Ln[N(i\text{-}Pr)_2]_3(THF) + 2C_9H_8 \xrightarrow{toluene} (C_9H_7)_2LnN(i\text{-}Pr)_2 \quad (2)$$
(Ln = Gd (**1**), Y (**2**), Er (**3**))

As for Gd, the molar ratio of $LnCl_3$ and $LiN(i\text{-}Pr)_2$ should be kept in 1 : 2.8, otherwise, undesired $[Gd[N(i\text{-}Pr)_2]_2Cl(THF)]_2$ will be isolated.

Complexes **1**—**3** were fully characterized by elemental analyses, IR and ^1H NMR (for **2**). In the proton NMR spectrum of complex **2**, 6.99—7.58 are assigned to the protons of the six-membered ring of indene, 6.09—6.34 and 3.25—3.44 are for the protons of the five-membered ring, and at 2.98—3.17 and 1.24 for the protons of $N(i\text{-}Pr)_2$. The ^1H NMR of **2** showed no characteristic signals of the protons of THF (3.57 and 1.40).[21] IR spectra also showed typical absorption bands of indenyl rings (about 717, 767, 865, 1392, 3067 cm^{-1}) and diisopropylamido group (about 694, 1165, 1373, 2974 cm^{-1}), but no characteristic absorption bands of THF (about 1065 cm^{-1} and 910 cm^{-1}). These results indicated that the title complex is an unsolvated bisindenyllanthanide amide as shown in Eq. (2). These compounds are all extremely sensitive to air and moisture. They are highly soluble in THF, moderately soluble in aromatic solvents, and insoluble in aliphatic hydrocarbons.

Characterization of MMA *polymerization with indenyllanthanide amide initiators*

Complexes **1**—**3** all exhibit high catalytic activity for MMA polymerization. It can be seen from Table 1 that the polymerization using $(C_9H_7)_2GdN(i\text{-}Pr)_2$ as catalyst gives the conversion as high as 97.1% at 0℃ for 2 hours in the catalytic amount of 0.2 mol%. However, different catalytic activities among lanthanoid analogues have been observed. Table 1 shows the influence of the central metal on polymerization activity. The increasing order of activities for these compounds is in agreement with the order of seven-coordinated ionic radii, Er^{3+} (9.45 nm) < Y^{3+} (9.60 nm) < Gd^{3+} (10.0 nm).[22] This may be due to the larger ionic radius which makes the metal coordination sphere more open, so that it is easier for MMA to insert into Ln—N bonds.

Table 1 Polymerization of MMA with $(C_9H_7)_2LnN(i\text{-}Pr)_2$ (Ln = Gd (**1**), Y (**2**), Er (**3**))

Catalyst	Conversion (%)	$10^{-3}Mn$	Mw/Mn
1	97.1	154	1.26
2	93.9	116	1.23
3	91.1	163	1.20

Reaction conditions: catalyst amount = 0.2 mol%; solvent, toluene; temperature, 0℃; solvent/$[MMA]_0$ = 10 vol/vol; reaction time, 2 h.

Table 2 summarizes the results of MMA polymerization using yttrium catalyst $(C_9H_7)_2YN(i\text{-}Pr)_2$ at various catalyst amounts and at different temperatures. From Table 2, it can be found that the present polymerization can be carried out at a quite wide range of reaction temperature (from −78℃ to 40℃). However, the conversion decreases from 93.9% (Entry 4) to 63.3% (Entry 1) with the increasing of temperature when the catalytic amount is 0.2 mol%, and the molecular weight distribution (Mw/Mn) of polymers obtained becomes broad with the increasing of temperature (Entry 1—4). All of these results may be caused by thermally-activated side reactions.

In addition, the stereoregularity of the polymer depends greatly on polymerization temperature. Syndiotacticity of PMMA was determined with reference to the method reported.[23] Table 2 indicates that the syndiotacticity of the polymer increases from 72.8% to 91.8% when the reaction temperature decreases from 40℃ to −78℃. This is in line with the general trend observed in polymerization of MMA.

Table 2 Polymerization of MMA with $(C_9H_7)_2YN(i\text{-}Pr)_2$[a]

Entries	Catalyst amount (mol%)	Temperature (℃)	Conversion (%)	$10^{-3}Mn$	Mw/Mn	Tacticity (%)	
						rr	rm
1	0.2	40	63.3	236	1.71	78.1	21.9
2	0.2	25	86.2	224	1.36	/	/
3	0.2	0	93.9	116	1.23	82.6	17.4
4	0.2	-78	100	307	1.10	91.8	8.2
5	0.1	0	84.7	323	1.22		
6	0.07	0	64.6	331	1.36		
7	0.05	0	27.8	709	1.54		
8[b]	0.2	0	100	431	1.79		
9[b]	0.2	40	97.1	410	1.72	72.8	27.2
10[b]	0.2	-78	100	268	2.10	87.7	12.3

[a] Reaction conditions: solvent, toluene; solvent/$[MMA]_0$ = 10 vol/vol; reaction time, 2 h.

[b] Catalyst, $(MeC_5H_4)_2YbN(i\text{-}Pr)_2(THF)$; solvent, toluene; solvent/$[MMA]_0$ = 10 vol/vol; reaction time, 2 h.

It is noteworthy that the PMMA obtained with $(C_9H_7)_2YN(i\text{-}Pr)_2$ has much narrower molecular weight distribution (MWD) and better syndiotacticity when compared with the results reported on the polymerization of MMA using lanthanocene amide $(MeC_5H_4)_2YbN(i\text{-}Pr)_2(THF)$ (Entry 8—10).[11] For example, the MWD in Entry 4 is extremely narrow, only 1.10, and syndiotacticity is as high as 91.8%, while 2.10 and 87.7% respectively for the $(MeC_5H_4)_2YbN(i\text{-}Pr)_2(THF)$ (Entry 10). The difference between two catalytic systems might be that indenyl has more steric encumbrance than cyclopentadienyl has, which results in the side reactions that are inhibited more effectively.

This result enlightens us that we can further modify the coordination environment around the central metal to achieve the living polymerization with indenyllanthanide amides. In accordance with the coordination anionic mechanism proposed by Yasuda[1b] and above results, a similar process for the present polymerization can be proposed.

In the initiation step, the diisopropylamido attacks the CH_2 group of MMA and generates a transient $Ln\text{-}OC(OCH_3)=(CH_2)N(i\text{-}Pr)_2$ species. Then the incoming MMA molecule may participate in a 1,4-addition to afford the eight-membered ring intermediate. In the propagation step, another MMA molecule may attack the growing end, and the coordinated ester group would be liberated. The polymerization should proceed by repeating these reactions.

According to this mechanism, the end of the polymer chain must have $-N(i\text{-}Pr)_2$ group. This was confirmed by the end group analysis of methyl methacrylate oligomer. Fig. 1 shows typical ^1H NMR spectrum of methyl methacrylate oligomer obtained from the oligomerization of MMA at the room temperature in 1:3 feed ratio of initiator to monomer. The existence of the signals at 2.73 and 1.27 was assigned to the protons of $-N(i\text{-}Pr)_2$ which indicates that $-N(i\text{-}Pr)_2$ group incomes into the end of the polymer undoubtedly.

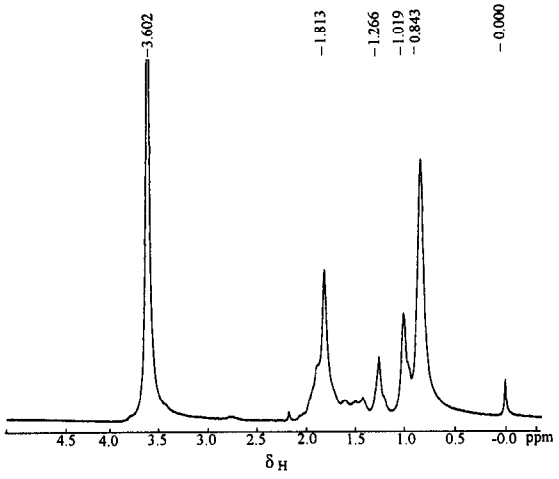

Fig. 1 ^1H NMR spectrum of oliger MMA.

Experimental

All manipulations were carried out under argon atmosphere using standard Schlenk techniques. THF, toluene, and diethyl ether were dried and free of oxygen by being refluxed over sodium or sodium benzophenone ketyl and distilled under argon atmosphere prior to use. MMA was distilled over fresh sieves 3A under argon at-

mosphere. Anhydrous $LnCl_3$ was made according to the published method.[24] $LiN(i\text{-}Pr)_2$ was obtained by the reaction of $HN(i\text{-}Pr)_2$ with n-BuLi in a solution of THF and hexane.[20]

Metal analysis was carried out by complexometric titration. Carbon, hydrogen and nitrogen analyses were carried out by direct combustion. The IR spectra were recorded on a Magna-500 spectrometer. ^1H NMR spectra were obtained on a Unity Inova-400 apparatus in C_6D_6. The number-average molecular weights (Mn) and the molecular weight distribution (Mw/Mn) were determined by GPC (gel permeation chromatography) using a Shimadzu GPC apparatus equipped with two Ultrastyragel linear columns in THF at 25℃.

Preparation of $(C_9H_7)_2GdN(i\text{-}Pr)_2$, **1**

To a slurry of $GdCl_3$ (2.15 g, 8.18 mmol) in THF (20 mL), 15 mL of solution of $LiN(i\text{-}Pr)_2$ (22.9 mmol) in THF was added at 0℃. The mixture was stirred at 0℃ for 1 hour, then warmed to room temperature and stirring was continued for 24 hours. THF was completely removed and the oily residue was extracted with toluene (30 mL). Then indene (1.49 mL) was added to toluene extracts by syringe. The mixture was stirred for another 48 hours. When the solution was concentrated and cooled to −20℃, pale yellow crystals were formed. Yield: 0.97 g (20.5%). ν_{max}(KBr, pellet, cm^{-1}): 3445(s), 3071(s), 2971(s), 1639(m), 1524(s), 1457(m), 1393(s), 1018(m), 866(m), 767(s), 717(m), 694(m), 550(m). Anal. $C_{24}H_{28}GdN$. Calcd: C, 59.11; H, 5.75; N, 2.87; Gd, 32.27. Found: C, 58.46; H, 5.42; N, 2.31; Gd, 32.14.

Preparation of $(C_9H_7)_2YN(i\text{-}Pr)_2$, **2**

The synthesis of compound **2** was carried out as the same as compound **1**, but using YCl_3 (1.68 g, 8.63 mmol) instead of $GdCl_3$. Colorless crystals were isolated. Yield 1.07 g (29.3%). ν_{max}(KBr, pellet, cm^{-1}): 3445(s), 3067(s), 2974(w), 2885(s), 1612(m), 1523(s), 1458(m), 1392(s), 1018(m), 865(m), 767(s), 717(m), 694(m), 551(m). δ_H (C_6D_6, 20℃): 6.99—7.58(m, 8H, C_9H_7); 6.09—6.34 (m, 2H, C_9H_7); 3.25—3.44(m, 4H, C_9H_7); 2.98—3.17(m, 2H, $N(i\text{-}Pr)_2$); 1.24(d, 12H, J = 6.40 Hz, $N(i\text{-}Pr)_2$). Anal. $C_{24}H_{28}YN$. Calcd: C, 68.75; H, 6.68; N, 3.34; Y, 21.22. Found: C, 68.05; H, 6.43; N, 3.02; Y, 21.56.

Preparation of $(C_9H_7)_2ErN(i\text{-}Pr)_2$, **3**

The synthesis of compound **3** was carried out as the same as compound **1**, but using $ErCl_3$ (2.41 g, 9.71 mmol) in place of $GdCl_3$. Colorless crystals were isolated. Yield 1.12 g (23.2%). IR (KBr, pellet, cm^{-1}): 3445(s), 3070(s), 2974(w), 2889(s), 1629(m), 1523(s), 1458(m), 1393(s), 1015(m), 863(s), 766(s), 718(m), 692(m), 552(m). Anal. $C_{24}H_{28}ErN$. Calcd.: C, 57.92; H, 5.63; N, 2.81; Er, 33.64. Found: C, 57.11; H, 5.37; N, 2.46; Er, 33.87.

Typical experiment for polymerization of MMA

All polymerization reactions were performed under dry argon. A typical example is given as follows. To a toluene solution (9 mL) of MMA (1 mL, 9.35 mmol) was added at once the toluene solution (1 mL) of $(C_9H_7)_2YN(i\text{-}Pr)_2$ (7.84 mg, 0.019 mmol) with vigorous magnetic stirring at the desired temperature. After the polymerization was held for 2 hours, the viscous solution was poured into ethanol containing 2% HCl (60 mL) to induce the precipitation of the polymer. The resulting polymer was washed for three times with ethanol and dried in vacuum at 50℃.

Oligomerization of MMA

To a toluene solution (20 mL) of $(C_9H_7)_2ErN(i\text{-}Pr)_2$ (0.5 g, 1 mmol) was added at once the toluene solution (2 mL) of MMA (3 mmol) with vigorous magnetic stirring at the desired temperature. After the solution had been stirred for 2 hours, water containing 0.2% HCl (60 mL) was added to terminate the reaction. After the water layer was removed, the solvent was completely removed in vacuum, and the remaining solid was extracted with toluene. When the toluene was removed for the second time, the residue was purified by reprecipitation from acetone to petroleum for several times.

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