Homoleptic Lanthanide Amidinate Complexes: A Single-Component Initiator for Ring-Opening Polymerization of Trimethylene Carbonate and Copolymerization with ε-Caprolactone

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ABSTRACT: The ring-opening polymerization of trimethylene carbonate (TMC) using homoleptic lanthanide amidinate complexes [CyNC(R)NCy]$_3$Ln as single component initiators has been fully investigated for the first time. The substituents on amidinate ligands and center metals show great effect on the catalytic activities of these complexes, that is, Me > Ph, and La > Nd > Sm > Yb. Among them, [CyNC(Me)NCy]$_3$La shows the highest catalytic activity. Some features of the TMC polymerization initiated by [CyNC(Me)NCy]$_3$La were studied in detail. A mechanism that the polymerization occurs via acyl-oxygen bond cleavage rather than alkyl-oxygen bond cleavage was proposed. The copolymerization of TMC with ε-caprolactone initiated by [CyNC(Me)NCy]$_3$La was also tested. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 22–28, 2006

Key words: amidinate complexes; initiators; polymerization; copolymerization; polycarbonates; trimethylene carbonate; ε-caprolactone

INTRODUCTION

Both aliphatic polycarbonates and copolymers of cyclocarbonates and lactones are of great potential for applications in various areas, such as agriculture and medicine, because of their good biodegradability, biocompatibility, and low toxicity. Ring-opening polymerization of six-member ring carbonates is the convenient route for synthesis of these biodegradable polymers and copolymers. Up to date, many kinds of catalysts were explored and among them lanthanide catalysts have attracted much more attention, as most of them have well-defined structures and act as single-component catalysts. For example, structurally defined complexes of (C$_5$Me$_5$)$_2$SmMe(THF) (tetrahydrofuran (THF)),[1–3] homoleptic lanthanide(III) aryloxides,[4–7] Y$_5$(μ-O)(O^{i}Pr)$_{13}$,[8] and (C$_5$Me$_5$)$_2$Sm(THF)$_2$[1] have been reported to be efficient single-component catalysts for ring-opening polymerization of cyclocarbonates. Recently, we have reported that samarocene thiolate, homoleptic samarium thiolate,[9] as well as homoleptic lanthanide guanidinate[10,11] are all highly active catalysts.

The bidentate amidinate anions, [RC(NR')$_2$]$^-$, which are easy to modify their electronic properties and steric bulky by variation of the R and R' substituents, have attracted attention in organolanthanide chemistry. Moreover, homoleptic lanthanide amidinates were found to act as highly active single-component catalyst for ring-opening polymerization of ε-caprolactone (ε-CL).[12–14] To further develop the application of these complexes, we are interested in understanding their potential application as a single-component catalyst in polymerization of trimethylene carbonate (TMC). In this article, several homoleptic lanthanide amidinates were synthesized, and the solid-state structure of samarium complex, [CyNC-(Me)NCy]$_3$Sm, was determined by X-ray diffraction. The catalytic activity of these complexes for TMC polymerization and the copolymerization of TMC with ε-CL were examined for the first time. The effect of the substituents on ligands and central metals, and some features and mechanism of the TMC polymerization were studied in detail.

EXPERIMENTAL

General procedures

All manipulations were performed under pure argon, with rigorous exclusion of air and moisture, using

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standard Schlenk techniques.[15] Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. The IR spectra were recorded on a Magna-IR 550 spectrometer. ^{1}H-NMR spectra were measured on a Unity Inova-400 spectrometer. Molecular weight and molecular weight distributions were determined against a polystyrene standard by gel permeation chromatography (GPC) on a water 1515 apparatus with three HR columns (HR-1, HR-2, and HR-4). THF was used as an eluent at 30°C.

Materials

All solvents were analytical grade and were distilled from Na/benzophenone ketyl prior to use. N,N'-Dicyclohexylcarbodiimide was purchased from Aldrich and used as received without further purification. ε-CL was purchased from Acros, dried over CaH_2, and distilled under argon atmosphere at reduced pressure. Anhydrous $LnCl_3$ [16] and TMC[17] were prepared according to literature procedures.

Initiator synthesis

The complexes of $[CyNC(Me)NCy]_3La$ (**1**), $[CyNC(Me)NCy]_3Sm$ (**2**), $[CyNC(Me)NCy]_3Yb$ (**3**), $[CyNC(Ph)NCy]_3La \cdot 2THF$ (**4**), $[CyNC(Ph)NCy]_3Sm \cdot 1.5THF$(**5**), and $[CyNC(Ph)NCy]_3Nd \cdot 2THF$(**6**) were synthesized in good yield by metathesis reactions of anhydrous $LnCl_3$ with freshly prepared amidinate lithium in 3 : 1M ratio according to literature procedures.[12,14,18] Because complexes of **2** and **4** were not reported yet, the detailed procedure for **2** and the full characterization for both **2** and **4** were given.

Preparation of 2

A glass ampoule was charged with N,N'-dicyclohexylcarbodiimide (2.73 g, 13.2 mmol), THF (30 mL), and a stir bar. The solution was cooled to 0°C, and MeLi (11.2 mL, 13.2 mmol, 1.18M in Et_2O) was added dropwise. The solution was slowly warmed to room temperature and stirred for 1 h. Then it was added slowly to a pale-gray slurry of $SmCl_3$ (1.13 g, 4.4 mmol) in THF. The color of the solution immediately changed to yellow. The resulting solution was stirred for another 24 h, and evaporated to dryness in vacuum. The residue was extracted with toluene, and LiCl was removed by centrifugation. After being concentrated and cooled to -30°C, the product was obtained as pale-yellow crystals.

Yield: 2.92 g (82%). Anal. Calcd. For $C_{42}H_{76}N_6Sm$: C, 61.96; H, 9.34; N, 10.33. Found: C, 61.90; H, 9.49; N, 10.69. IR (KBr pellet, cm^{-1}): 3427 (s), 2927 (s), 2853 (s), 1642 (s), 1517 (s), 1449 (s), 1110 (m), 962 (m), 890 (s), 795 (m), 657 (s).

Preparation of 4

The analogue complex **4** was prepared as colorless crystals from N,N'-dicyclohexlcarbodiimide (2.85 g, 13.8 mmol), PhLi (12.3 mL, 13.8 mmol, 1.12M in Et_2O), and $LaCl_3$ (1.14 g, 4.6 mmol) in THF (60 mL), by using the procedures described earlier.

Yield: 3.7 g (71%). Anal. Calcd. for $C_{65}H_{97}N_6LaO_2$: C, 68.90; H, 8.57; N, 7.42. Found: C, 68.26; H, 8.56; N, 7.38. IR (KBr pellet, cm^{-1}): 3446 (s) 2932 (s), 2858 (s), 2665 (w), 1635 (s), 1578 (m), 1493 (s), 1450 (s), 1365 (m), 1246 (m), 1072 (m), 1030 (m), 979 (m), 895 (m), 775 (m), 698 (s).

Polymerization of TMC

All polymerizations were carried out in a 50-mL Schlenk flask under dry argon atmosphere with a similar procedure. A typical polymerization reaction is given later: a 50-mL Schlenk flask equipped with a magnetic stir bar was charged with a solution of TMC (0.46 g, 4.53 mmol) in toluene (4.08 mL). A toluene solution of complex **1** (0.45 mL, 1.0×10^{-2} mol/L, 4.0×10^{-3} mmol) was added to this solution using a rubber septum and syringe. The reaction solution was vigorously stirred for 30 min at 40°C. The polymerization was quenched by adding 1 mL of 5% HCl/MeOH. The polymer (PTMC) was precipitated from methanol and dried in vacuum at room temperature overnight. The polymer yield was determined gravimetrically.

Copolymerization of TMC and ε-CL

All copolymerizations were carried out in a 50-mL Schlenk flask under dry argon atmosphere. A typical copolymerization reaction is given as follows: TMC (0.26 g, 2. 52 mmol), ε-CL (0.28 mL, 2.52 mmol), and toluene (4 mL) were added into a dry flask at 40°C in turn. Then the toluene solution of complex **1** (1.01 mL, 1.0×10^{-2} mol/L, 1.01×10^{-3} mmol) was introduced by a syringe into the reaction solution. After 30 min, the copolymerization was quenched by adding 1 mL of 5% HCl/MeOH. The copolymer was precipitated from methanol and dried in vacuum. The polymer yield was determined gravimetrically.

Oligomers for end group analysis

The oligomerization of TMC was carried out with complex **2** in toluene at 40°C under the condition of [TMC]/[initiator] mole ratio of 10. The reaction was terminated by adding 1 mL of 5% HCl/iPrOH after 2 h. The oligomer was precipitated from methanol. The product was dissolved in THF, followed by precipitation in methanol. After filtration, the white product was dried in vacuum.

TABLE I
Crystallographic Data for Complex [CyNC(Me)NCy]$_3$Sm (2)

Formula	C$_{42}$H$_{75}$N$_6$Sm
Formula weight	814.43
Temperature (K)	193($\pm$2)
Wavelength (Å)	0.71073
Size (mm^3)	0.26 × 0.22 × 0.19
Crystal system	Triclinic
Space group	P-1
a (Å)	11.547($\pm$2)
b (Å)	12.903($\pm$2)
c (Å)	16.466($\pm$2)
α (degrees)	103.033($\pm$3)
β (degrees)	90.659($\pm$2)
γ (degrees)	115.887($\pm$4)
V (Å^3)	2133.2($\pm$6)
Z	2
D$_{calc}$ (g cm^{-3})	1.268
Abs. coeff. (mm^{-1})	1.411
F(000)	862
θ range (degrees)	3.03–25.34
Reflections collected	41858
Data/restraints/parameters	7751/0/446
R [I > 2σ(I)]	0.0394
R$_w$	0.0826
Goodness-of-fit on F^2	1.095

Structure solution and refinement for 2

A suitable single crystal of complex **2** was sealed in a thin-walled glass capillary, and the intensity data were collected on a Rigaku Mercury CCD equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The structure was solved by direct methods, expanded using Fourier techniques and refined on F^2 by full-matrix least-squares method. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were geometrically fixed using the riding model. All the calculations were carried out with a Siemens SHELXTL PLUS program. Details of the intensity data collection and crystal data are summarized in Table I.

RESULTS AND DISCUSSION

Synthesis and structural characterization

All homoleptic lanthanide amidinate complexes were synthesized in good yield by metathesis reactions of anhydrous LnCl$_3$ with freshly prepared lithium amidinate in 3 : 1M ratio, according to literature procedures.[12,14,18] The new complexes [CyNC-(Me)NCy]$_3$Sm (**2**) and [CyNC(Ph)NCy]$_3$La·2THF (**4**) were fully characterized by elemental analysis and IR. The molecular structure of **2** was further determined by X-ray diffraction. As shown in Figure 1, complex **2** is a monomer in solid state. The samarium ion is ligated by three bidentate amidinate moieties, and the geometry around the central metal is described as a

trigonal planar, with each chelating bidentate amidinate ligand to occupy one coordination vertex. According to previous reports, complexes **1**, **2**, and **3** are isomorphous, and the coordination number of central metal is six. The C—N bond lengths within the chelating NCN unit in complex **2** are nearly equal and the average value is 1.331 Å, which reflect the delocalization of the π bond in the N—C—N unit. The averaged Sm—N bond length and the averaged N—Sm—N bond angles in each SmN$_2$C moieties are 2.429($\pm$3) Å and 55.18($\pm$11)° respectively, which are similar to those found in [Ph$_2$NC(NCy)$_2$]$_3$Sm·2C$_7$H$_8$ [2.442($\pm$6) Å, 54.9($\pm$2) degree],[10] [CyNC(Ph)NCy]$_3$Sm [2.424($\pm$3)–2.431($\pm$3) Å, 55.69($\pm$10) degree][18] and [(SiMe$_3$)$_2$-NC(NCy)$_2$]$_2$SmCH(SiMe$_3$)$_2$ [2.417($\pm$4)Å, 55.33($\pm$13)°].[19]

The ring-opening polymerization of TMC with [CyNC(R)NCy]$_3$Ln

The results of ring-opening polymerization of TMC initiated by homoleptic lanthanide amidinate complexes [RC(NCy)$_2$]$_3$Ln are shown in Table II. It can be seen that all of the homoleptic lanthanide amidinate complexes synthesized here show extremely high catalytic activity. The conversions are all greater than 84% at 40°C for 30 min in the case of [M]/[I] = 500 (mole ratio), with relatively broad molecular weight
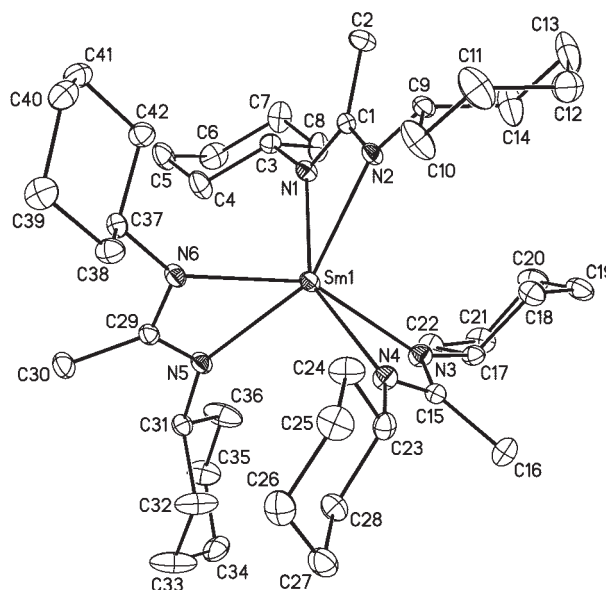

Figure 1 Molecular structure of [CyNC(Me)NCy]$_3$Sm (**2**). (The hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and bond angles (degrees) are as follows: Sm(1)—N(1) 2.430($\pm$3); Sm(1)—N(2) 2.432($\pm$3); Sm(1)—N(3) 2.426($\pm$3); Sm(1)—N(4) 2.425($\pm$3); Sm(1)—N(5) 2.427($\pm$3); Sm(1)—N(6) 2.434($\pm$3); N(1)—C(1) 1.337($\pm$5); N(2)—C(1) 1.327($\pm$5); N(3)—C(15) 1.324($\pm$5); N(4)—C(15) 1.336($\pm$5); N(5)—C(29) 1.332($\pm$5); N(6)—C(29) 1.328($\pm$5); N(1)—Sm(1)—N(2) 55.17($\pm$10); N(4)—Sm(1)—N(3) N(5)—Sm(1)—N(6) 55.16($\pm$10).

TABLE II
Polymerization of TMC Initiated by Homoleptic Lanthanide Amidinate Complexes [CyNC(R)NCy]$_3$Ln[a]

Entry	Initiator	[M]/[I][b]	Temperature (°C)	Time (min)	Yield (%)	M_n (10^4)	M_w/M_n[c]
1	**1**	500	40	30	100	0.85	1.85
2	**1**	1000	40	30	87.1	0.69	1.97
3	**1**	1200	40	30	75.1	0.62	2.17
4	**2**	500	40	30	90.1	0.70	2.05
5	**2**	1000	40	30	86.8	0.64	1.94
6	**3**	500	40	30	89.1	0.89	1.69
7	**3**	1000	40	30	13.9	–	–
8	**4**	500	40	30	92.7	0.79	1.88
9	**4**	1200	40	30	74.1	0.68	2.01
10	**5**	500	40	30	83.8	0.74	2.27
11	**5**	1200	40	30	60.1	0.55	2.06
12	**6**	500	40	30	90.8	0.78	2.06
13	**6**	1200	40	30	62.9	0.46	2.11

[a] Conditions: [TMC] = 1 mol/L, toluene.
[b] [M]/[I] = [Monomer]/[Initiator].
[c] Measured by GPC calibrated with standard polystyrene samples.

distributions (M_w/M_n = 1.69–2.27; M_w is the weight-average molecular weight and M_n is the number-average molecular weight). Lanthanum complex [CyNC(Me)NCy]$_3$La exhibited the highest activity for the TMC polymerization, giving the conversion as high as 87% even if the amount of [M]/[I] increased to 1000 under the condition used (entry 2, Table II). The activity is comparable with those of [RNC(NR'$_2$)-NR]$_3$Ln[11] and La(OAr)$_3$ (Ar = 2,6-di-*tert*-butyl-4-methyl phenolate).[5] The substituents on the carbon atom of amidinate ligand bring certain influence on the catalytic activity. For example, for Sm(III)-based initiators, the catalytic activity of [CyNC(Ph)NCy]$_3$Sm **5** was lower than that of [CyNC(Me)NCy]$_3$Sm **2**. The polymerization of TMC with **5** gives 83.8% conversion while 90.1% is gained with **2** under the same conditions (entries 10 and 4). The similar difference in the activity is also observed between the analogous complexes of [CyNC(Me)NCy]$_3$La **1** and [CyNC(Ph)-NCy]$_3$La **4** (entries 1 and 8). This might be because the electronic effect is different between the two ligands, which results in different nucleophilicity of the bidentate [RC(NCy)$_2$]$^-$ anion. Therefore, the active order of R on amidinate ligand is Me > Ph, which is consistent with the literature reports.[12] The central metal has a great influence on the catalytic activity. The active order is La > Sm > Yb (according to the polymer yield, entries 2, 5, and 7) and La > Nd > Sm (according to the polymer yield, entries 8, 12, and 10), which agrees with the order of the six-coordinate ionic radii, La > Nd > Sm > Yb. This suggests that the activities in catalytic TMC polymerization are highly dependent on the metal ionic radius, with best activities being obtained for larger-sized metals. This similar behavior has already been observed in the MMA polymerization system.[20]

Polymerization mechanism aspects

Figure 2 shows a relationship between the conversion and the reaction time for the ring-opening polymerization of TMC initiated by **1**. It can be seen that the polymerization of TMC proceeded very fast at 40°C even at low concentration of initiator ([TMC]/[**1**] = 1000). For example, the polymer yield arrives at 75.6% in 10 min. We know that the ring-opening polymerization of cyclocarbonate can proceed by either acyl-oxygen bond cleavage or alkyl-oxygen bond cleavage, as illustrated in Scheme 1. To clarify the reaction mechanism, an oligomer of TMC, terminated by 2-propanol, has been prepared from the oligomerization of TMC with a [TMC]/[**2**] molar ratio of 10. The ^{1}H-NMR spectrum shows the signals at ~5.0 ppm and
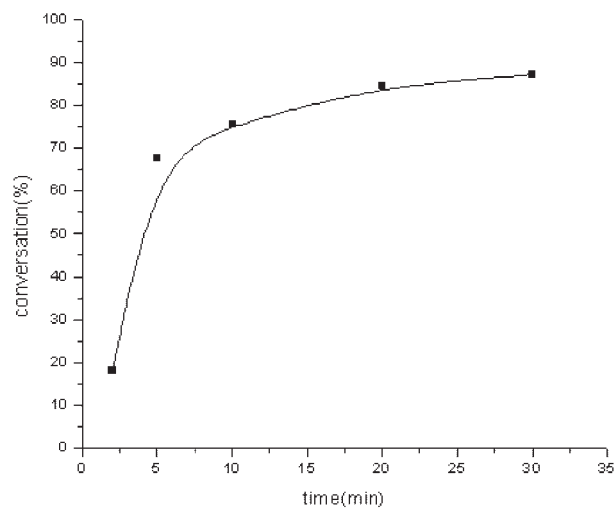
Figure 2 Plot of reaction time versus conversation ([TMC]/[1] = 1000, [TMC] = 1 mol/L, toluene, temperature = 40°C).
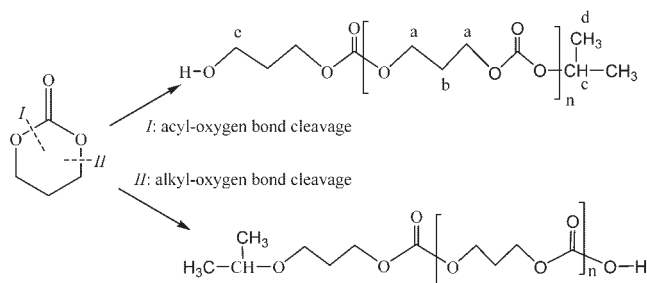
Scheme 1 Ring-opening modes of TMC.

1.3–1.4 ppm assigned to isopropyl group of one end of PTMC chain (H[c] and H[d] in Scheme 1), the signals at 3.7–3.8 ppm to methylene protons of the other ending group CH$_2$OH (H[e] in Scheme 1) and no signal of an isopropyl ether group. Therefore, it could be concluded that the ring-opening polymerization of TMC occurs via a coordination mechanism by acyl-oxygen bond cleavage (mode I in Scheme 1). The postulated coordination mechanism for the ring-opening polymerization of TMC initiated by homoleptic lanthanide amidinate complexes [CyNC(R)NCy]$_3$Ln was described in Scheme 2.

The copolymerization of TMC/ε-CL with 1

The copolymerization is a direct access to adjust the properties of the polymer required for the different

applications by changing the composition of the copolymer. Therefore, we investigate the catalytic activity of the homoleptic lanthanide amidinate complex **1** for the copolymerization of TMC with ε-CL. The experimental results are listed in Table III. The data show that complex **1** is also an efficient initiator for the copolymerization of TMC and ε-CL at 40°C. The copolymerization gives the copolymer in quantitative yield, with relatively broad molecular weight distributions in the case of ([TMC] + [ε-CL])/[I] = 500 (mole ratio). The GPC profiles of the copolymer showed to be unimodal, which
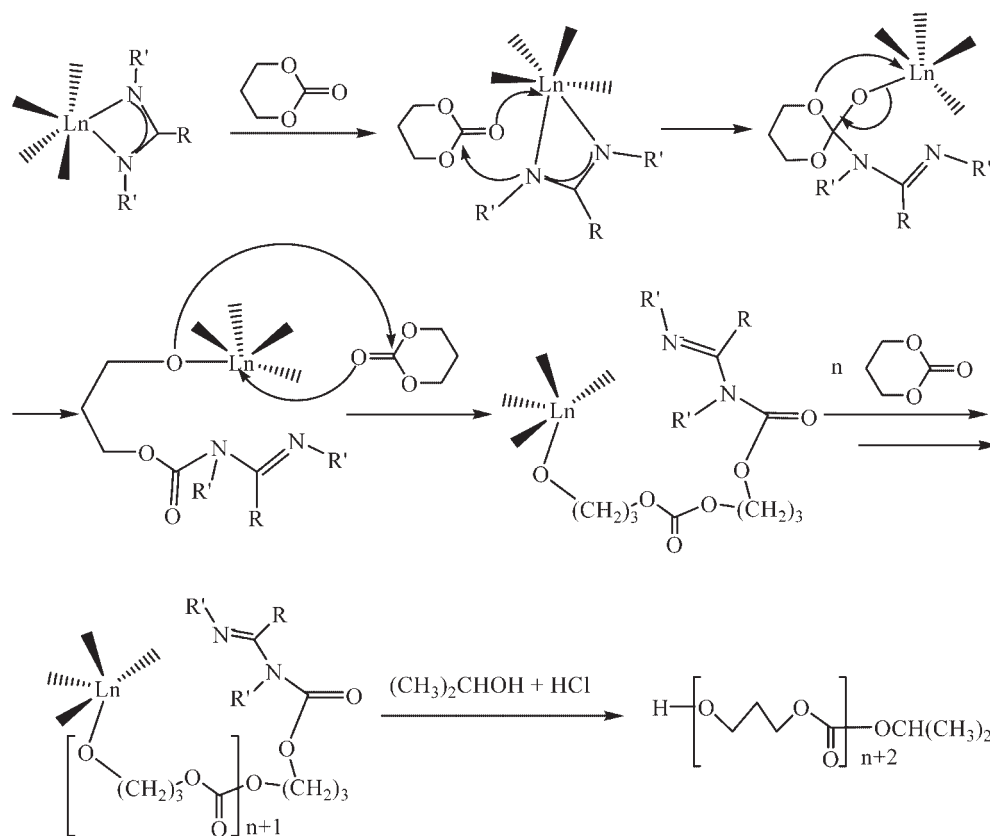
Scheme 2 Postulated mechanism for the ring-opening polymerization of TMC.
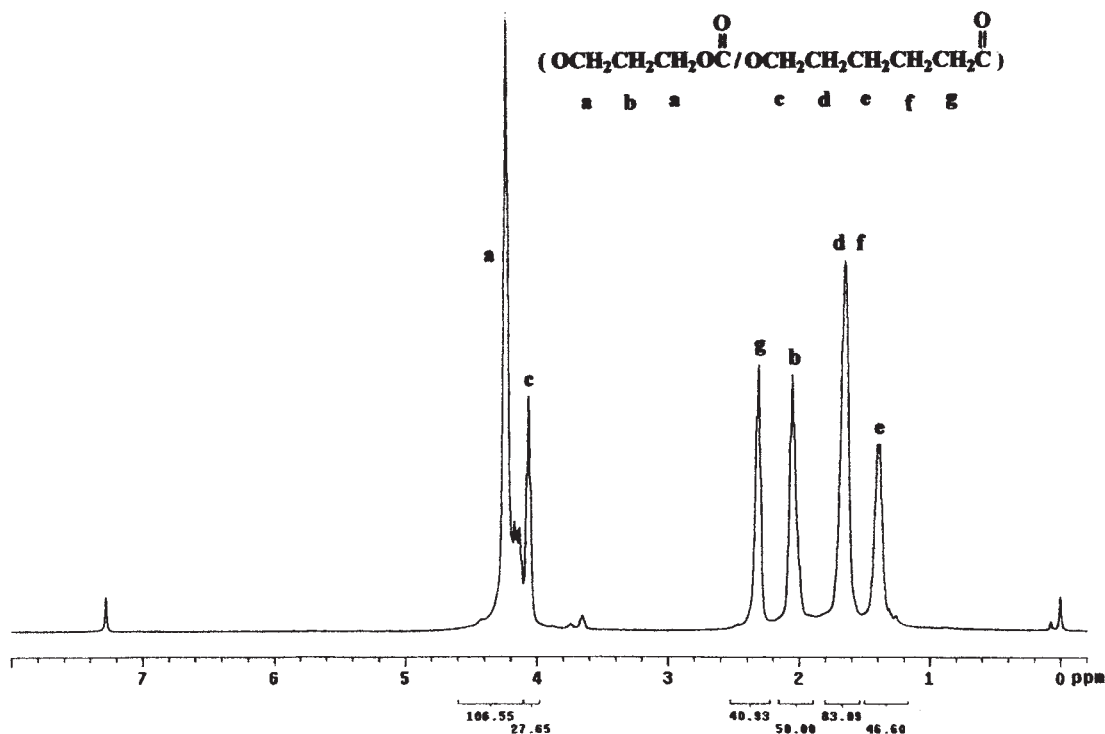
Figure 3 ¹H-NMR spectrum of a typical poly(TMC-*co*-ε-CL).

CONCLUSIONS

A series of homoleptic lanthanide amidinate complexes [CyNC(R)NCy]₃Ln are found to be a novel kind of single component initiator for the ring-opening polymerization of TMC and the copolymerization of TMC with ε-CL. The substituent R on the amidinate ligand [CyNC(Me)NCy]⁻ and the center metal have great effect on the catalytic activity. The active order is Me > Ph and La > Nd > Sm > Yb (according to the polymer yield). The mechanism study on the ring-opening polymerization of TMC initiated by **2** shows that the polymerization mostly occurs via a coordination mechanism through the acyl-oxygen bond cleavage. The lanthanide amidinate complex **1** is also an efficient initiator for the copolymerization of TMC with ε-CL at 40°C. The obtained product was characterized to be a random copolymer.

means that only one active center exists in the growing chain and the resulting copolymer is a random one. The mole ratio of TMC units and ε-CL units in the copolymer can be determined according to the two characteristic resonance in their ¹H-NMR spectra at ~2.05 ppm (TMC unit) and at ~2.3 ppm (ε-CL unit), respectively (Fig. 3). The copolymerization of TMC and ε-CL are shown in Table IV in the case of ([TMC] + [ε-CL])/[I] = 1000 (mole ratio). It is obvious that the polymerization of TMC is somewhat faster than ε-CL. However, the mole composition of the copolymer could be in agreement with the ratio of monomers charged when the content of TMC in the comonomer is lower than 50%.

TABLE IV
The Mole Composition of the Resulting Copolymer[a]

Entry	$n_{TMC} \sim n_{\varepsilon\text{-CL}}$	Yield (%)	PTMC≈PCL[b]
1	80~20	73.0	91~9
2	60~40	66.4	85~15
3	50~50	89.0	55~45
4	40~60	55.7	45~55
5	20~80	69.0	21~79

[a] Conditions: $[M_{TMC}]+[M_{\varepsilon\text{-CL}}]$ = 1 mol/L; ([M_{TMC}] + [M_{\varepsilon\text{-CL}}])/[I] = 1000; toluene, 30 min, 40°C, initiated by complex **1**.
[b] Calculated by comparing the area of the PTMC signal (at 2.05 ppm) and the PCL one (at 2.3 ppm).

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