Lanthanide(II) Amide Complexes: Efficient Initiators for the Living Polymerization of Methyl Methacrylate

Liying Zhou, Yingming Yao, Qi Shen

Key Laboratory of Organic Synthesis of Jiangsu Province, Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou, People's Republic of China 215123

ABSTRACT: Lanthanide(II) complexes supported by amido ligands, $[(C_6H_5)(Me_3Si)N]_2Ln(DME)_2$ [Ln = Sm (**1**) or Yb (**2**); DME = 1,2-dimethoxyethane] and $[(C_6H_3—^iPr_2-2,6)(Me_3Si)N]_2Ln(THF)_2$ [Ln = Sm (**3**) or Yb (**4**); THF = tetrahydrofuran], were found to initiate the polymerization of methyl methacrylate (MMA) as efficient single-component initiators (in toluene for **3** and **4** and in toluene with a small amount of THF for **1** and **2**) to produce syndiotactic polymers. The catalytic behavior was highly dependent on both the amido ligand and the polymerization temperature. Initiators **3** and **4** initiated MMA polymerization over a wide range of temperatures (20°C to −40°C), whereas the polymerization with **1** and **2** proceeded smoothly only at low temperatures (≤0°C). The kinetic behavior and some features of the polymerizations of MMA initiated by **3** and **4** were studied at −40°C. The polymerization rate was first-order with the monomer concentration. The molar masses of the polymers increased linearly with the increase in the polymer yields, whereas the molar mass distributions remained narrow and unchanged throughout the polymerization; this indicated that these systems had living character. A polymerization mechanism initiated by bimetallic bisenolate formed *in situ* was proposed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2403–2409, 2009

Key words: living polymerization; metal-organic catalysts/organometallic catalysts; monomers

INTRODUCTION

There is considerable interest in the design and synthesis of structurally well-defined organolanthanide complexes as single-component initiators in the controlled polymerization of methyl methacrylate (MMA) as the properties of poly(methyl methacrylate)s (PMMAs) are highly dependent on their stereoregularity, molar mass, and molar mass distribution. After pioneering work on the living syndiotactic polymerization of MMA with lanthanocene hydride or methyl complexes by Yasuda et al.,[1] a variety of trivalent lanthanide complexes were developed to serve as efficient initiators for the polymerization of MMA, including complexes containing Ln—C, Ln—N, and Ln—H σ bonds.[2–10] Divalent lanthanocene complexes were first reported by the Yasuda group as efficient initiators for the polymerization of MMA in a living fashion.[11] Then, several divalent complexes were found to be efficient initiators, and the catalytic behavior depended strongly on the central metal and the ancillary ligand around the metal.[2,12–21] However,

only a few divalent complexes were found to initiate controlled polymerizations of MMA, such as $(C_5Me_5)_2Ln(THF)_2$ (Ln = Sm or Yb; THF = tetrahydrofuran),[11] $(indenyl)_2Yb(THF)_2$,[11] $(C_5Me_5)_2YbAlH_3·NEt_3$,[14] and $bis[(2-pyridyl)_2CPh]Yb(THF)_2$.[15] Therefore, the demand for the development of novel tunable initiators for the controlled polymerization of MMA is increasing.

Amido ligands, alternatives to traditional cyclopentadienyl-based ligands, have advantages for initiator design as their electronic effects and steric properties can be tuned conveniently by the variation of the substituents on the nitrogen atom. A variety of lanthanide(II) amides have been synthesized and fully characterized[22–33]; however, their application as single-component initiators in polymerization reactions is still under development.[28–33] To explore lanthanide(II) amide as an efficient initiator for the controlled polymerization of MMA and to gain further insight into the relationship between the activity/controllability and the structure of lanthanide(II) amide, we synthesized four lanthanide(II) amides with different amido ligands as well as central metals, $[(C_6H_5)(Me_3Si)N]_2Ln(DME)_2$ [Ln = Sm (**1**) or Yb (**2**); DME = 1,2-dimethoxyethane] and $[(C_6H_3—^iPr_2-2,6)(Me_3Si)N]_2Ln(THF)_2$ [Ln = Sm (**3**) or Yb (**4**)], and tested their catalytic activity. All the complexes were found to be initiators, and their catalytic performance was highly dependent on both the amido ligand and

the polymerization temperature. The polymerization systems with **3** and **4** showed living character and produced syndiotactic polymers with high molar masses and narrow molar mass distributions [weight-average molecular weight (M_w)/number-average molecular weight (M_n) = 1.13 for Yb and 1.22 for Sm] at -40°C. Here we present the results.

EXPERIMENTAL

Materials

All the manipulations were performed under a pure argon atmosphere with rigorous exclusion of air and moisture with standard Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl before use. Deuterated benzene (C_6D_6) was purchased from Acros Organics (Belgium) and dried over sodium before use. MMA (Shanghai Chemical Reagent Company, Shanghai, China) (99%) was distilled over CaH_2 and stored over 4-Å molecular sieves at 0°C under an argon atmosphere. The amines $(C_6H_5)(Me_3Si)NH$ and $(C_6H_3-{}^iPr_2\text{-}2,6)(Me_3Si)NH^{34}$ and LnI_2^{35} were prepared according to literature procedures.

Initiator synthesis

Lanthanide(II) complex **1** was prepared by the metathesis reaction of SmI_2 with the sodium amide $(C_6H_5)(Me_3Si)NNa$ in a 1 : 2 molar ratio in a high yield according to the literature procedure.[33] Complexes **2** and **3** were synthesized in high yields by the reduction reaction of the corresponding trivalent chloride, $\{[(C_6H_5)(Me_3Si)N]_2YbCl(THF)\}_2$ or $[(C_6H_3-{}^iPr_2\text{-}2,6)(Me_3Si)N]_2SmCl_3Li_2(THF)_4$, with a sodium–potassium alloy according to the literature procedure.[33]

The analogue complex **4** was prepared with a procedure similar to that used for complex **1**. A Schlenk flask was charged with YbI_2 (67.0 mL, 4.02 mmol, $0.06M$ in THF) and a stirring bar, and then $(C_6H_3-{}^iPr_2\text{-}2,6)(Me_3Si)NNa$ (38.3 mL, 8.04 mmol, $0.21M$ in THF) was added with a syringe. The resulting solution was then stirred for 24 h, and the volatiles were removed *in vacuo*. The residue was extracted with toluene, and NaI was removed by centrifugation. After the extracts were concentrated and cooled to -30°C, the product was obtained as an orange-red powder. Recrystallization from toluene gave orange-red crystals. The yield was 2.45 g (75%). The decomposition point was 120°C.

ANAL. Calcd for $C_{38}H_{68}N_2O_2Si_2Yb$ (814.15): C, 56.06%; H, 8.42%; N, 3.44%; Yb, 21.25%. Found: C, 55.89%; H, 8.31%; N, 3.56%; Yb, 21.56%. IR (KBr pellet, cm^{-1}): 2962 (w), 2875 (w), 1645 (w), 1212 (s), 1154 (s), 744 (w), 721 (w), 667 (w), 639 (m), 555 (m), 504 (s), 429 (w). ^{1}H-NMR (400 MHz, C_6D_6, 25°C, ppm, δ): 6.90–7.35 (m, 6H, H—Ph), 3.12–3.40 [m,

12H, H—THF, —CH(CH$_3$)$_2$], 1.14–1.40 [br, 32H, H—THF, —CH(CH_3)$_2$], 0.15 [s, 18H, —Si(CH_3)$_3$].

Typical procedure for the polymerization of MMA

All polymerizations were carried out in a 50-mL Schlenk flask under a dry argon atmosphere with a similar procedure. A typical polymerization reaction (entry 13, Table I) was as follows. A 50-mL Schlenk flask equipped with a magnetic stirring bar was charged with a 1.00-mL solution of MMA in toluene (0.14 mL). To this solution was added a 1.86-mL solution of an initiator ($1.0 \times 10^{-2}M$ in toluene) with a rubber septum and syringe. The contents of the flask were then vigorously stirred for 1 h at 20°C. The polymerization was quenched by isopropyl alcohol with 5% HCl, precipitated from ethanol, and dried *in vacuo* at room temperature overnight. The polymer yield was determined gravimetrically.
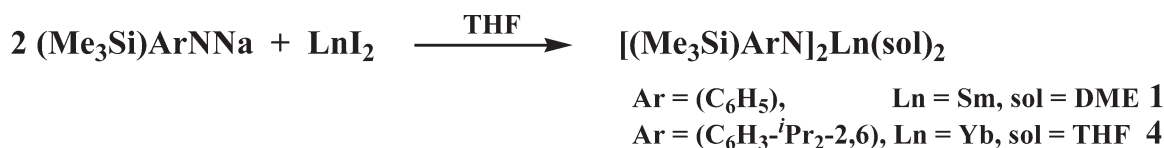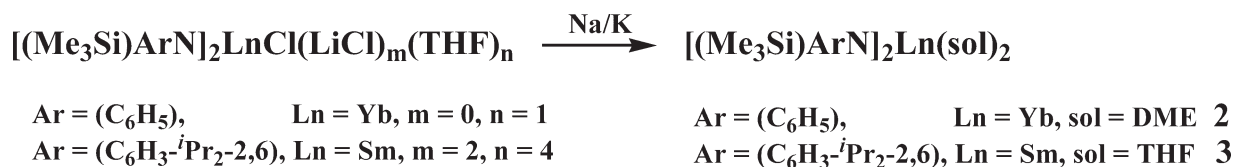
Measurements

Melting points were determined on a Yanaco MP-500 melting point apparatus (Japan) and were uncorrected. Metal analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA 1110 instrument (Italy). The IR spectra were recorded on a Magna IR 550 spectrometer (Thermo Nicolet Corporation, USA). Molar masses and molar mass distributions were determined against a polystyrene standard by size exclusion chromatography on a Waters 1515 apparatus (Waters Corporation, USA) with three HR columns (HR-1, HR-2, and HR-4); THF was used as an eluent at 30°C. ^{1}H-NMR spectra were measured on a Unity Inova 400 spectrometer (Varian, USA) in C_6D_6 or CDCl$_3$.

RESULTS AND DISCUSSION

Synthesis of the initiators

To address the influence of both the central metal and the amido ligand on the catalytic activity of lanthanide(II) amide complexes for the polymerization of MMA, four lanthanide(II) amides with different central metals and amido ligands, including bis(trismethylsilylphenyl) lanthanide(II) complexes **1** and **2** and bis(trimethylsilyl-2,6-diisopropylphenyl) lanthanide(II) complexes **3** and **4**, were synthesized by different approaches.

Complexes **2** and **3** were synthesized by the reduction reaction of the corresponding trivalent chloride with a sodium–potassium alloy, whereas complexes **1** and **4** were prepared by the metathesis reaction of LnI_2 with sodium amide in a 1 : 2 molar ratio:

$$[(Me_3Si)ArN]_2LnCl(LiCl)_m(THF)_n \xrightarrow{\text{Na/K}} [(Me_3Si)ArN]_2Ln(sol)_2$$

Ar = (C$_6$H$_5$),　　　Ln = Yb, m = 0, n = 1　　　　Ar = (C$_6$H$_5$),　　　Ln = Yb, sol = DME **2**
Ar = (C$_6$H$_3$-^{i}Pr$_2$-2,6), Ln = Sm, m = 2, n = 4　　Ar = (C$_6$H$_3$-^{i}Pr$_2$-2,6), Ln = Sm, sol = THF **3**

$$2\ (Me_3Si)ArNNa\ +\ LnI_2 \xrightarrow{\text{THF}} [(Me_3Si)ArN]_2Ln(sol)_2$$

Ar = (C$_6$H$_5$),　　　Ln = Sm, sol = DME **1**
Ar = (C$_6$H$_3$-^{i}Pr$_2$-2,6), Ln = Yb, sol = THF **4**

All the complexes were purified by recrystallization and used as fully characterized strong dark crystals for Sm complexes and orange-red crystals for Yb complexes according to the literature method.[33] All the complexes showed a monomeric solid structure in which the central metal coordinated to two nitrogen atoms of two amido ligands and four oxygen atoms of two DME molecules or two oxygen atoms of two THF molecules. These complexes were very sensitive to air and moisture. Complexes **3** and **4** were freely soluble in toluene, whereas complex **2** was sparingly soluble in toluene, and **1** was almost insoluble in toluene.

Polymerization of MMA with complexes 1–4

The catalytic activity of the four lanthanide(II) amides for the polymerization of MMA was tested.

TABLE I
Polymerization of MMA Initiated by Lanthanide(II) Amides

	Initiator	Temperature (°C)	[M]/[I]	Yield (%)[a]	M_n (×10^4)	M_w/M_n[b]	Tacticity (%)[c] mm	rm	rr
1	**1**	0	500	Trace					
2	**1**	−40	500	Trace					
3	**1**[d]	0	500	12.9					
4	**1**[d]	−40	500	47.3	18.2	1.76	8	26	66
5	**1**[d]	−78	500	90.3	22.4	1.39	16	16	68
6	**1**[e]	−40	500	45.2	20.5	1.85	17	21	62
7	**1**[f]	−40	500	0					
8	**2**	0	500	10.8					
9	**2**	−40	500	12.9					
10	**2**[d]	0	500	15.1	2.50	1.63			
11	**2**[d]	−40	500	45.2	21.1	1.54	22	27	51
12	**2**[d]	−78	500	86.0	21.3	1.52	18	21	61
13	**3**	20	500	36.6	4.35	1.83	18	13	69
14	**3**	0	500	96.8	7.21	1.67	9	14	77
15	**3**	−20	500	32.3	5.12	1.31	7	10	83
16	**3**	−40	500	6.5	2.22	1.22	6	9	85
17	**3**	−40	500 (3 h)	38.7	4.97	1.21			
18	**3**[e]	−40	500 (3 h)	10.8	4.91	1.60			
19	**3**[f]	−40	500 (3 h)	0					
20	**4**	20	500	81.7	12.7	1.44	17	13	70
21	**4**	0	500	100	13.6	1.36	19	10	71
22	**4**	−20	500	92.5	13.4	1.17	16	12	72
23	**4**	−40	500	21.5	3.32	1.13	9	16	75

Polymerization conditions (unless noted otherwise): 2 v/v sol/MMA, toluene, and 1 h.
[a] Yield = Weight of the polymer obtained/Weight of the monomer used.
[b] Measured by gel permeation chromatography calibrated with standard polystyrene samples.
[c] Determined from ^{1}H-NMR spectra (CDCl$_3$, 25°C).
[d] Polymerization condition: 2.5% THF/toluene.
[e] Polymerization condition: 1 : 1 toluene/THF.
[f] Polymerization condition: THF.

The results under various conditions are summarized in Table I.

As shown in Table I, complexes **3** and **4** with bulky amido ligands were efficient initiators for MMA polymerization in toluene over a wide range of temperatures (20 to −40°C) with a molar ratio of [M]/[I] = 500 ([M], molar concentration of monomer; [I], molar concentration of initiator), whereas complexes **1** and **2** with less bulky amido ligands initiated MMA polymerization at temperatures lower than 0°C in toluene with a small amount of THF due to their very poor solubility in toluene. The addition of a small amount of THF was only for dissolving the initiator. A greater amount of THF would have resulted in a decrease in the polymer yield, and no polymer was obtained when the polymerization was conducted in a THF solution (entries 7 and 19). The results indicate that this polymerization may proceed by a coordination/insertion mechanism, and the presence of THF was unfavorable for the polymerization because of the coordination of THF to the metal.

The polymerization temperature had a great effect on the polymerization of MMA for these systems. The relationship between the temperature and polymer yield differed, depending on the amido ligand of the initiators. For the systems with complexes **1** and **2**, the polymer yields increased as the polymerization temperature decreased from 0 to −78°C; the highest polymer yield was obtained at −78°C (entries 3–5 and 10–12). For the systems using bulky initiators **3** and **4**, the polymer yields increased first with the temperature decreasing from 20 to 0°C and then decreased when the temperature continuously decreased from 0 to −40°C; the highest yield was obtained around 0°C (entries 13–16 and 20–23). The differences in the relationship between the temperature and polymer yields caused by the different initiators may be attributed to the differences in the initiating and propagating rates and the terminating rates from back-biting and deactivation of the initiator due to the nucleophilic attack of the initiator against the carbonyl group of MMA in these initiator systems. As is well known, initiation and propagation reactions, which lead to the formation of polymers, and nucleophilic attack of the initiator against the carbonyl group of the monomer and back-biting, which result in deactivation of the initiator and termination of the polymer chain, coexist in the polymerization of MMA. These side reactions can be circumvented efficiently by the use of a bulky initiator with steric hindrance.[36] However, the utility of a bulky initiator will lead to decreased initiating and propagating rates because of the difficulty of coordinating the monomer to the initiator. Thus, the systems with the less bulky initiators (**1** and **2**) showed high activity at low temperatures (−40°C to −78°C)

as these side reactions were much slower in comparison with the initiation and propagation reactions (entries 4 and 11 and entries 5 and 12). In contrast, the polymerizations with **1** and **2** at temperatures higher than 0°C were sluggish because of the deactivation of the initiator by nucleophilic attack and the termination of polymer chains by back-biting. These side reactions could be circumvented efficiently by steric hindrance with bulky initiators **3** and **4**; therefore, the polymerizations with **3** and **4** could take place smoothly over a wide range of temperatures, even at room temperature. However, bulky initiators **3** and **4** became inefficient when the polymerizations proceeded at a temperature lower than 0°C (entries 15, 16, and 23) because less coordination space remained around the central metal in **3** and **4**; this made the coordination and insertion of the monomer more difficult in comparison with the less bulky initiators **1** and **2**. Table I shows that **4** was a more active initiator than **3** under the same conditions (entries 13–16 and 20–23). This may be because the ion radius of Yb^{II} is larger than that of Sm^{II}, and **4** is more soluble in toluene than **3**.

As expected, the molar mass distributions of the resulting polymers decreased with the polymerization temperature decreasing. On the basis of the low molar mass distributions of the polymers obtained with **3** ($M_w/M_n = 1.22$) and **4** ($M_w/M_n = 1.13$) at −40°C in toluene with the molar ratio of [M]/[I] = 500, controlled polymerization was expected in these cases. Thus, the kinetic behavior and some features of the polymerizations of MMA initiated by **3** and **4** at −40°C were investigated. The yield increased directly with the polymerization time for both systems, as shown in Figure 1. The catalytic activity of **4** was higher than that of **3**. Figure 2 shows pseudo-
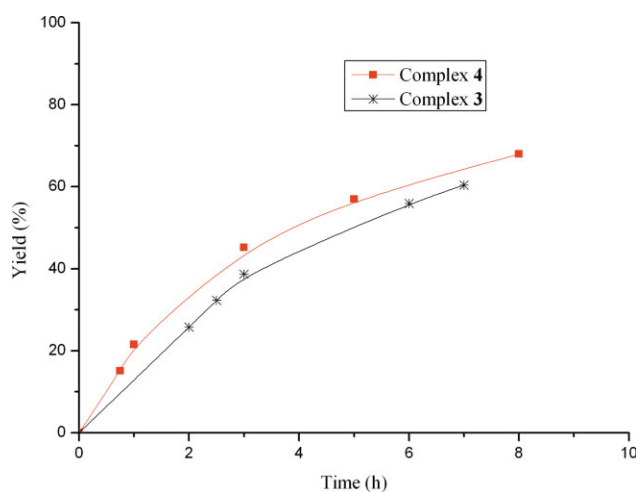

Figure 1 Plot of the reaction time versus the yield (conditions: [M]/[I] = 500 : 1, temperature = −40°C, sol/MMA = 2 v/v, toluene). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
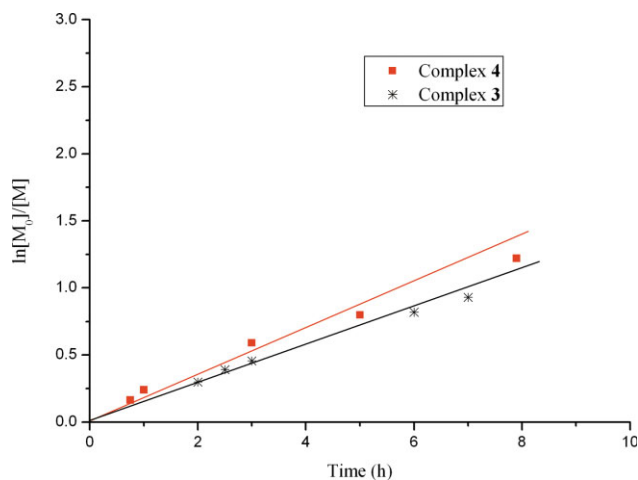
Figure 2 Plot of the reaction time versus ln $[M]_0/[M]$ (conditions: $[M]/[I] = 500 : 1$, temperature $= -40°C$, sol/MMA = 2 v/v, toluene). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3 Plot of the yield versus M_n and M_w/M_n (conditions: $[M]/[I] = 500 : 1$, temperature $= -40°C$, sol/MMA = 2 v/v, toluene). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

first-order kinetic plots of ln $[M]_0/[M]$ ($[M]_0$, original molar concentration of monomer) versus the polymerization time under the conditions presented in Figure 1, indicating that the concentration of the catalytic active species was kept constant throughout the polymerization. The relationships between the molar masses (M_n) and the molar mass distributions (M_w/M_n) of the resulting polymers with the polymer yields are shown in Figure 3. The molar masses of
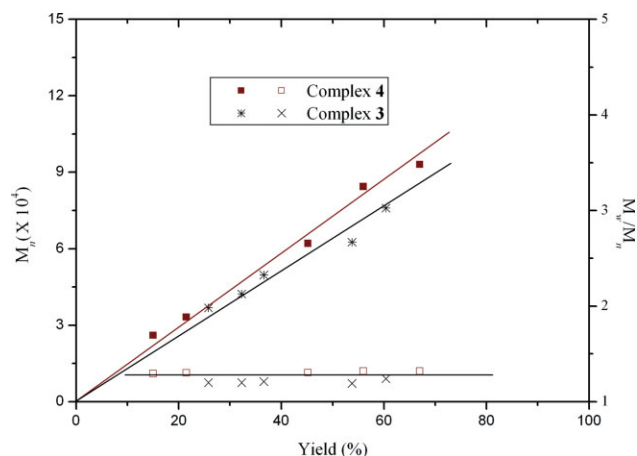
the polymers increased proportionally with the increase in the polymer yields, and the narrow molar mass distributions (1.13–1.25) were retained. The fact that the values of M_w/M_n obtained here deviated from 1.0 may be explained by partial chain termination caused by deactivation of the initiators by trace amounts of impurities introduced into the systems. All these results show that this polymerization of MMA initiated by **3** and **4** at $-40°C$ possesses
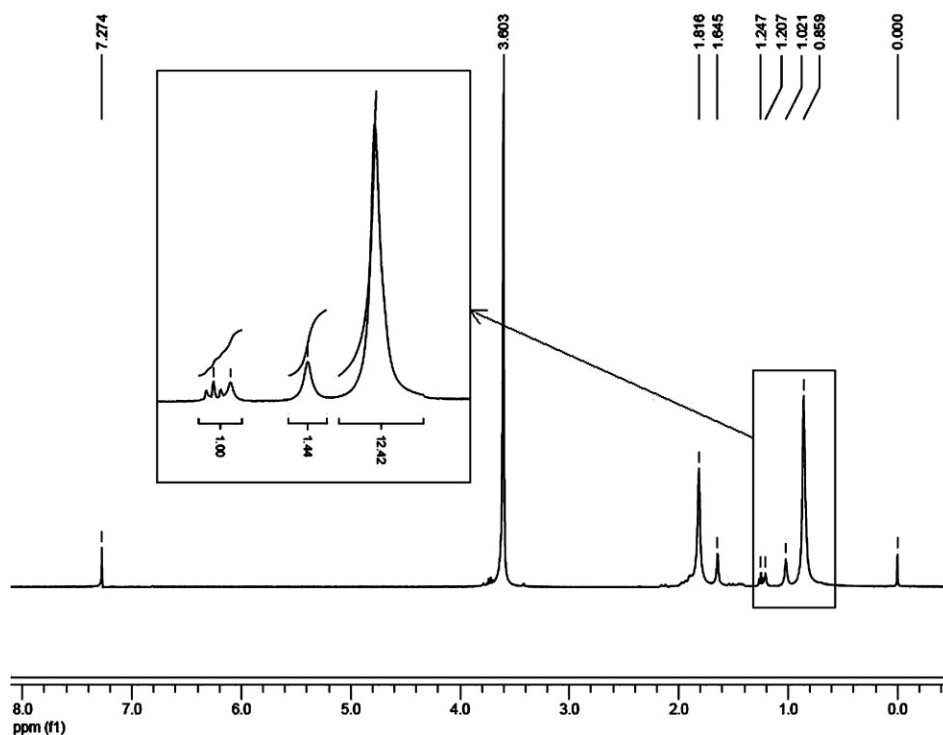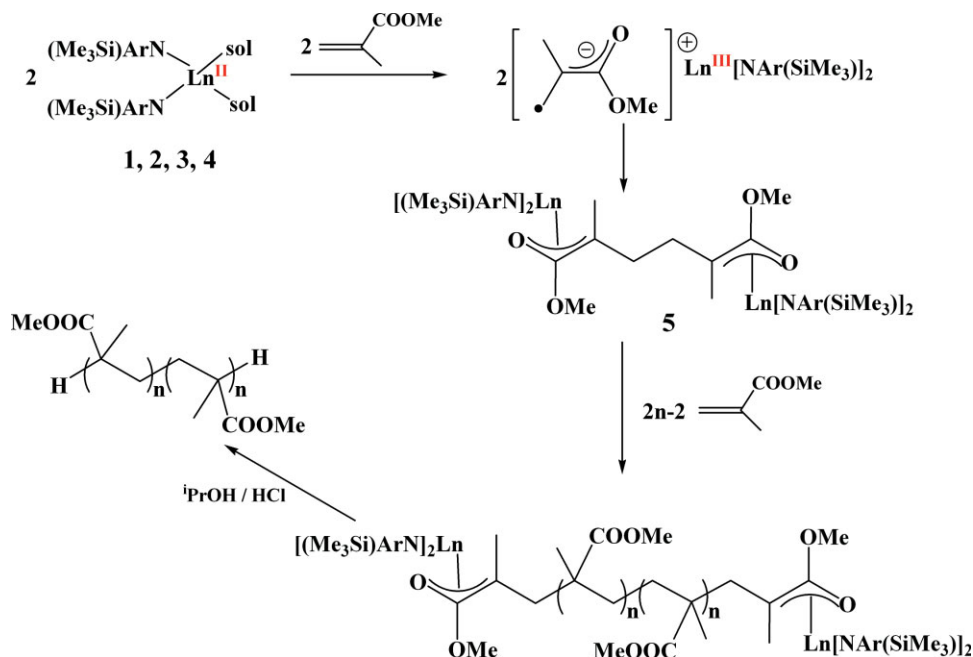

Figure 4 ^{1}H-NMR spectrum of PMMA (polymerization conditions: $[M]/[I] = 500 : 1$, temperature $= -20°C$, sol/MMA = 2 v/v, toluene, time = 1 h, initiator = complex **3**).

Scheme 1 Suggested polymerization mechanism for MMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

living character, which coincides with the living polymerization of MMA with divalent lanthanocenes as the initiators.[11]

A triad microstructural analysis of the polymers was carried out with ^{1}H-NMR spectra in CDCl$_3$ according to the literature.[37] These polymerization systems all yielded syndiotactic-rich PMMA. Figure 4 presents ^{1}H-NMR spectra showing a microstructural analysis of the resulting polymers initiated by complex **3** ([M]/[I] = 500 : 1, temperature = −20°C, sol/MMA = 2 v/v, toluene, and time = 1 h). As revealed in Table I, the microanalysis of the polymer showed that the amount of syndiotacticity increased with the polymerization temperature decreasing. For example, the syndiotactic content of the resulting polymers varied from 69 to 85% (for **3**) and from 70 to 75% (for **4**) when the polymerization temperature decreased from 20 to −40°C. A similar trend was also observed for less bulky initiators **1** and **2**. Moreover, the stereoregularity of the polymers with **1** and **2** as the initiators was lower than that of the polymers with **3** and **4** because of the more crowded coordination environment around the central metal caused by the bulky amido ligand in **3** and **4**, which resulted in control over the mode of the coordination/insertion reactions. The same behavior has also been found in systems with other lanthanide(II) initiators.[16,17,32]

The pioneering work by Novak's group on the polymerization mechanism with divalent lanthanocene complexes demonstrated that the polymerization is initiated by a trivalent bisinitiator formed by reduc-

tion dimerization of MMA mediated by a divalent complex.[38,39] According to the mechanism, the molar masses of the resulting polymers are twice the predicted values for monometallic polymerization. Size exclusion chromatography analyses in our case showed that the molar masses of the polymers obtained were almost twice the values calculated, depending on the molar ratio of the monomer to the initiator. These results support the supposition that this polymerization is initiated by a trivalent bisinitiator formed *in situ* by the reaction of a divalent amide complex with MMA molecules, and this is consistent with the results reported previously.[13,16,17,32,38,39] According to the mechanism proposed previously for systems with lanthanide(II) complexes[32,38,39] and on the basis of the results for the dependence of the solvent on the reactivity, the real active species and the coordination/insertion mechanism are proposed, as shown in Scheme 1. At first, the lanthanide(II) complex undergoes one-electron transfer to one molecule of MMA as a reducing agent, forming a trivalent radical anion. Subsequent dimerization of the radical anions gives the final actual bisinitiator, bimetallic bisenolate **5**. The continued coordination of MMA to each metal in **5** and the addition of activated MMA to each enolate of the active chain complete the polymerization.

CONCLUSIONS

Four lanthanide(II) amides with different amido ligands and central metals were found to initiate the

polymerization of MMA as efficient single-component initiators to produce syndiotactic polymers with high molar masses and narrow molar mass distributions. The syndiotactic content, molar mass, and molar mass distribution could be controlled by the choice of the precatalyst architecture and polymerization conditions. The polymerization kinetics of MMA initiated by **3** and **4** at −40°C indicated that these polymerization systems showed living character, that is, a pseudo-first-order kinetic plot of ln [M_0]/[M] versus the polymerization time, a linear relationship between the molar masses and yields, and narrow molar mass distributions. A possible polymerization mechanism of MMA initiated by lanthanide(II) amides was proposed.

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