

Zinc-Based Catalyst for the Ring-Opening Polymerization of Cyclic Esters

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Received 4 June 2010; accepted 20 September 2010

DOI 10.1002/app.33956

Published online 21 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A zinc-based catalyst zinc bis[bis(trimethylsilyl)amide] was used for the polymerization of cyclic esters including L-lactide (L-LA) and 2-methyl-2-carboxylpropylene carbonate (MBC). The polymerization of L-lactide in THF could be carried out successfully under mild conditions in very short time by using the zinc catalyst and alcohols as the initiators. Kinetic study in solution polymerization proved the polymerization has high monomer conversion degree close to 100% and the molecular weight of the resulting polyester has linear increase with the increase of $[M]_0/[I]$ (molar ratio of monomer to initiator). Sequential polymerization of L-LA and MBC in THF also showed high MBC conversion of 94% with a narrow molecular weight maintained, indicating a living

nature of this polymerization. The zinc catalyst system has also been used for the L-LA bulk polymerization with a high monomer conversion. ^{13}C NMR indicated the polymer possesses high regioregularity and the minor regioirregular component was owing to the D-LA in the monomer inserted into the polymer mainchain during the transesterification. Interaction between monomer and zinc catalyst has been found to be a key factor to sustain a homogenous solution during the initiating procedure. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2378–2385, 2011

Key words: catalysts; polyesters; ring-opening polymerization

INTRODUCTION

Because of their fine mechanical properties, biocompatibility and biodegradability, polylactide (PLLA), poly(ϵ -caprolactone) (PCL) and other polyesters have been recognized as favorable biomedical materials and environmental friendly replacements of conventional oil-based materials. Polyesters are commonly obtained from the polymerization of cyclic esters via ring-opening polymerization process initiated by organometallic compounds.^{1–7} For the application of the polyesters in the area of pharmaceuticals and tissue engineering, several requirements must be satisfied, such as the low toxicity of the polyesters and the catalysts, high activity of initiator and high

performance of the polyesters, etc. Besides, initiators based on metals like zinc, calcium, magnesium and ferric are most favored, because these metals indicate high compatibility to the immune system and could be easily processed by the human metabolic scheme.^{8–22}

Many efforts have been focused in the design of new metal complex to improve the catalyst activity and the polymer configuration control.^{23–25} Among those organometallic initiators, metal alkoxides such as aluminum isopropoxide and tin butoxide, have already been used for the polymerization of L-LA and ϵ -CL with high efficacy.^{26,27} Recently, the *in situ* formed metal alkoxides initiating system, generated from alcohol and $\text{M}[\text{N}(\text{SiMe}_3)_2]_n$ has been developed.^{28–30} The amino groups linked to the metal atoms which are reactive to the alcohols could always be substituted during the initiation reaction. Polymerization and copolymerization of L-LA and ϵ -CL by this initiating system could be performed even under room temperature and conversion could be completed in a short time. It was found that, this *in situ* generated polymerization system possesses smooth and fast polymerization kinetics without induction period in comparison with the conventional metal alkoxides. However, explanation of the difference between the two initiating systems could hardly be found and seldom reports have referred to the racemization during the L-LA polymerization

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Contract grant sponsor: National Nature Science Foundation of China; contract grant numbers: 20774094, 50733003, 20874097.

Contract grant sponsor: Ministry of Science and Technology of the People's Republic of China; contract grant number: 2007AA03Z535.

Contract grant sponsor: Chinese Academy of Sciences; contract grant number: KGCX2-YW-802.

Contract grant sponsor: Jilin Provincial Science and Technology Department; contract grant numbers: 20082104, 20100588.

process initiated by these *in situ* generated system. It has been proved that the polymerization of L-LA is accompanied by transesterification, while intermolecular transesterification and intramolecular transesterification always vary at different monomer conversion and polymer properties in the matter of molecular weight distribution (M_w/M_n), and the content of cyclic macromolecules would vary correspondingly. Transesterification is also affected by different initiating systems, for example in the aluminum alkoxides systems the transesterification is mainly absent, and for other systems the transesterifications may be of various extent.^{31–44}

In this article we presented the ring-opening polymerization of cyclic esters by using zinc bis[bis(trimethylsilyl)amide], ($Zn[N(SiMe_3)_2]_2$), associated with an alcohol as the initiating system. L-LA, ϵ -CL and a cyclic carbonate were polymerized to get the homopolymers or copolymers under mild conditions. The polymerization kinetics, polymer properties, and the molecular structure influenced by racemization and transesterification reactions, were thoroughly investigated. A series of experiments were also designed to explain the mechanism of the initiating system as an *in situ* generated ternary structure.

EXPERIMENTAL

Materials

L-lactide (L-LA 98.6%, D-LA 0.143%, mesoLA 1.26%, determined by HPLC) was kindly donated by Haizheng Ltd, (China) and purified by recrystallization from dried benzyl ethyl for three times. ϵ -CL, benzyl ethyl and 2-propanol were purchased from Beijing Chemical Ltd, and dried over CaH_2 and distilled before use. 2-methyl-2-carboxyl-propylene carbonate and zinc bis[bis(trimethyl silyl)amide] were synthesized according to the reported method.^{45,46} Tetrahydrofuran (THF) and toluene were purchased from Beijing Chemical, Ltd (China), dried by refluxing and distillation over sodium before use. All glassware for the polymerization was flame dried and filled with argon before use. *n*-Butyl lithium was purchased from Aldrich.

Measurements

The content of LA isomers including L-LA, D-LA and mesoLA were measured by Shimadzu GC-14C gas chromatography equipped with a chiral capillary column using FID detection. Injector and detector temperature are both 250°C and nitrogen was used as mobile phase. NMR spectra were recorded on a Bruker AV 300M, Bruker AV 400M, and Bruker AV

600M in $CDCl_3$ at 25°C. Gel permeation chromatography (GPC) measurements were conducted with a Waters 410 GPC instrument with tetrahydrofuran (THF) as the eluent (flow rate = 1 mL/min, at 35°C). The molecular weights were calibrated against polystyrene (PS) standards ($[\eta] = 5.49 \times 10^{-2} M^{0.639}$). Differential scanning calorimetry (DSC) was carried out with a Perkin–Elmer DSC-Diamond apparatus calibrated with pure indium under nitrogen. The sample was heated from 50 to 200°C at a rate of 10°C/min, kept at 200°C for 1 min, and cooled to 50°C at a rate of 10°C/min, and then a second heating scan at a rate of 10°C/min was recorded. Matrix-Assisted Laser Desorption Ionization-Time of Flight Mass Spectrometry (MALDI-TOF MS) analyses was carried out with a commercial Reflex III MALDI-TOF mass spectrometer (Bruker Co., Germany) equipped with delayed extraction technology. Ions formed by a pulsed UV laser beam with 3 nm pulse (nitrogen laser, $\lambda = 337$ nm) were accelerated through 20 kV, and the detection voltage was set at 1.60 kV. The laser was adjusted by the experiments slightly above the threshold, and the mass spectra were obtained from the results of 35 laser shots in positive mode. The matrix, 2,5-dihydroxybenzoic acid (HABA), was dissolved in purified THF (0.1 mol/L), and the solution was mixed with the polymer solution in THF (5 mg/mL) in a 1 : 1 (v/v) ratio.

Polymerization of the cyclic esters

Polymerizations of L-LA or ϵ -CL at room temperature were carried out with THF as the solvent under argon atmosphere. Polymerizations of LA at higher temperature were performed in toluene. In a typical procedure, $Zn[N(SiMe_3)_2]_2$ was added under vigorous stirring to a mixture of L-LA and 2-propanol in THF. After the desired reaction time, polymerization was terminated by addition of acetic acid. A sample was taken for conversion determination using 1H NMR. PLLA was isolated by precipitation from excess methanol followed by filtration and drying at 40°C in vacuum. 1H NMR ($CDCl_3$): δ 0.05 (s, $HN(Si(CH_3)_3)_2$), 1.24 (t, $(CH_3)_2CHOC(O)-$), 1.56 (d, $-C(O)CH(CH_3)O-$), 2.66 (broad, $-C(O)CH(CH_3)OH$), 4.34 (q, $-C(O)CH(CH_3)OH$), 5.06 (m, $(CH_3)_2CHOC(O)-$), 5.16 (q, $-C(O)CH(CH_3)O-$). Copolymerizations of L-LA and MBC were performed in THF at room temperature with the same procedure as described above to afford block copolymer sample and random copolymer sample. Bulk polymerization of LA was performed in the glass ampoule immersed into the oil bath, while LA, catalyst and 2-propanol were added subsequently without any solvent.

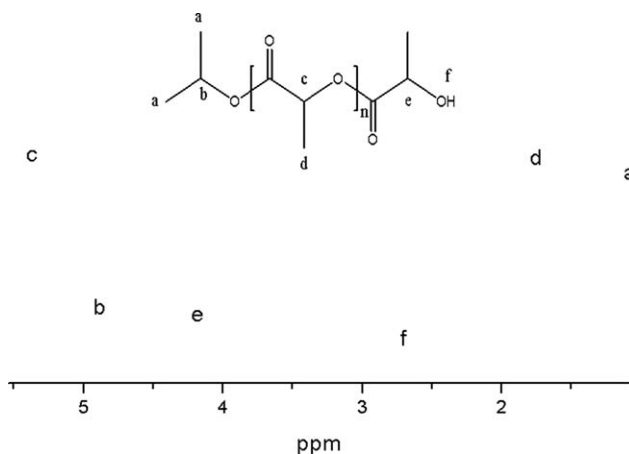


Figure 1 ^1H NMR profile of PLLA sample (Entry 1).

RESULTS AND DISCUSSION

The polymerization was first carried out without any alcohol or traces of water, resulted in the unreacted monomers left. While in the presence of $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ and 2-propanol, the polymerization of L-LA and ϵ -CL proceeded smoothly to afford the corresponding polyesters with narrow molecular weight distribution. For example, when $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ was mixed with 2-propanol and L-LA in a THF solution at a molar ratio of 115/2/1 ($[\text{L-LA}]_0/[\text{2-PrOH}]_0/[\text{Zn}]_0$) at room temperature, the monomer conversion reached to almost 100% within 40 min. PLLA isolated by precipitation from methanol had an M_n of 8.62×10^3 with M_w/M_n of 1.2 by GPC. The determined M_n was closed to the theoretical value (8.2×10^3) calculated from the monomer/alcohol molar ratio. The ^1H NMR spectrum as well as detailed peak assignments of the obtained PLLA is shown in Figure 1. The M_n calculated from NMR was 8.8×10^3 . The good agreement between the theoretical value of M_n with that determined by GPC or ^1H NMR indicated that the 2-propanol groups were incorporated into the catalyst system during the initiation process, and the polymerization proceeded exclusively by acyl-oxygen cleavage of the monomer. Similar results were observed for the ϵ -CL polymerization. The poly (ϵ -CL) chain also possessed an isopropoxyl group at one end and a

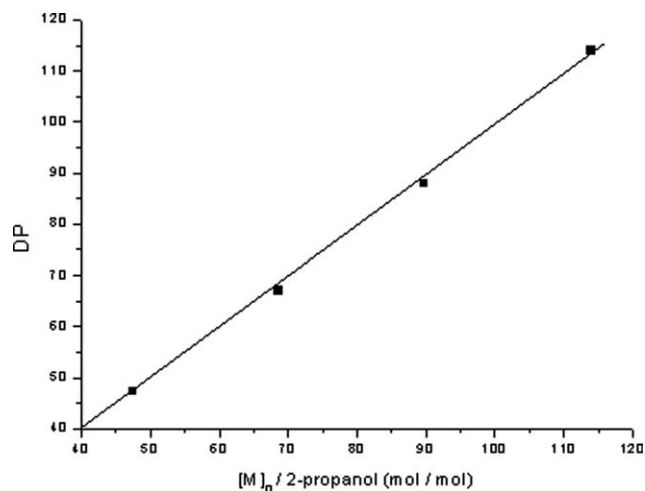


Figure 2 Dependence of degree of polymerization (DP) to monomer conversion on the initial monomer/2-PrOH molar ratio. DP was determined by ^1H NMR end group analysis.

hydroxyl group at the other end as revealed by the ^1H NMR analysis (data not shown).

It was reported that the combination of $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ and methanol in the homopolymerization of L-LA yielded polyesters having a much higher M_n than expected.⁴⁷ This was explained as the aggregation of *in situ* generated calcium methoxide and/or growing species.^{48,49} During our experiment, by changing the alcohol to methanol, the polymerization of L-LA could still proceed successfully. The molecular weight and M_w/M_n value of PLLA initiated by $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ /methanol were the same compare with the value of PLLA initiated by $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ /methanol (Table I). This phenomenon implied a different initiating mechanism.

The monomer conversions of PLLA were almost 100% within 40 min at room temperature under different L-LA/2-propanol ratios. And the polymerization degree (DP) of PLLA could increase proportionally with the increase of the initial monomer-to-alcohol ratio (Fig. 2). Moreover, the molecular weight of PLLA also followed a linear relationship in monomer conversion, with M_w/M_n maintaining

TABLE I
Results of Polymerization of L-LA and ϵ -CL

| Entry No. ^a | Monomer ^b | Initiator | Time (min) | Conversion (%) | $M_n (\times 10^{-3})$ | | |
|------------------------|----------------------|------------------------|------------|----------------|------------------------|-----|-----------|
| | | | | | GPC | NMR | M_w/M_n |
| 1 | L-LA | <i>i</i> Pr-OH | 40 | ~ 100 | 8.62 | 8.8 | 1.20 |
| 2 | L-LA | CH_3OH | 40 | ~ 100 | 8.59 | 8.8 | 1.21 |
| 3 | ϵ -CL | <i>i</i> Pr-OH | 10 | ~ 100 | 8.69 | 8.9 | 1.35 |
| 4 | L-LA | <i>i</i> Pr-OH | 2880 | ~ 100 | 7.84 | 7.8 | 1.82 |

^a All these polymerization were carried out at room temperature in THF.

^b $[\text{M}]_0 = 0.75\text{M}$, $[\text{M}]_0/[\text{OH}]/[\text{Zn}] = 2$.

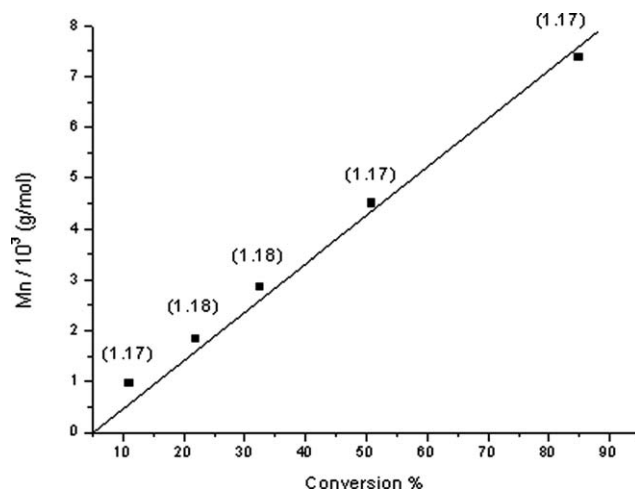


Figure 3 Relationship between molecular weight and M_w/M_n of PLLA with the monomer conversion ($[M]_0/[2\text{-PrOH}]_0/[Zn]_0 = 230/2/1$, room temperature, $[M]_0 = 0.75M$). M_w/M_n of each PLLA sample was noted in parentheses above each point.

around 1.17 (Fig. 3). The perfect control over molecular weight and low M_w/M_n value indicated that the polymerization of PLLA using Zn/alcohol catalyst system had a living nature.

To further investigate the living nature of this initiating system, the sequential copolymerization of L-LA and MBC was performed. In the first stage, $Zn[N(\text{SiMe}_3)_2]_2$ was added to a 10 mL THF solution of L-LA and 2-propanol mixture. After reacted for 30min, L-LA conversion reached to almost 100%. Then, MBC was added to the reaction mixture. The polymerization could achieve a 94% conversion of the MBC monomer after another 60 min, and the PLLA-PMBC block copolymer would still maintain a narrow polydispersity of 1.47. According to the ^1H NMR spectra in Figure 4, the two characteristic resonance peaks of Poly(MBC) at δ 7.30 and δ 4.27 indicated the existence of the MBC repeat units in the main chain of the PLLA-PMBC copolymer. We also synthesized the PLLA-PMBC random copolymer by mixing L-LA and MBC together at the beginning of the polymer-

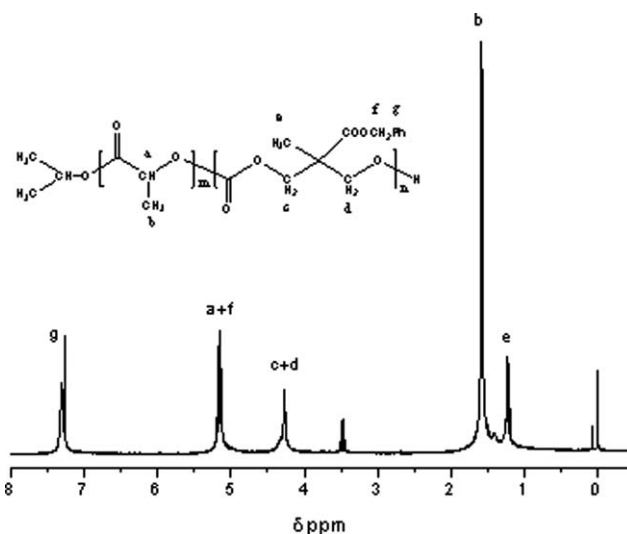


Figure 4 ^1H NMR spectrum of PLLA-PMBC block copolymer (sample Entry 5).

ization to confirm the sequence structure of the copolymer. However, although the polymerization of L-LA was completed within 1h, the conversion of MBC was very low (50%) in comparison to that of the PLLA-PMBC block copolymer. Interestingly, the homo polymerization of MBC under the same condition as described above was not smooth, either. Only 80% conversion of the MBC monomer could be obtained even after reacted for 10 h (Table II). We assumed that, when MBC monomer had more chance to interact with the catalyst, the coordination between MBC with the initial $Zn[N(\text{SiMe}_3)_2]_2/2\text{-propanol}$ system was strongly influenced by the bulky benzyl group in MBC, resulting in the interference on the activity of the initiating reaction. The sequence structure of copolymers could be easily judged by ^{13}C -NMR, because the resonance signal of methine carbons in the L-LA repeat units is quite sensitive to the sequence effects.⁵⁰ The ^{13}C NMR spectra of PLLA-PMBC block copolymer gave a single resonance signal of methine carbon at around δ 70

TABLE II
Copolymerization of L-LA with MBC in THF Using $Zn[N(\text{SiMe}_3)_2]_2/2\text{-Propanol}$ as the Catalyst at 25°C

| Entry No ^a | Mon. 1 ^b | Mon. 2 ^b | Conv. M1 (%) | Conv. | | t1 (h) | t2 (h) | $M_n (\times 10^{-3})^c$ | M_w/M_n^c |
|-----------------------|---------------------|---------------------|--------------|--------|--|--------|--------|--------------------------|-------------|
| | | | | M2 (%) | | | | | |
| 5 | L-LA | MBC | ~ 100 | 94 | | 0.5 | 1 | 11.0 | 1.47 |
| 6 | L-LA | MBC | ~ 100 | 50 | | 1 | – | 7.7 | 1.58 |
| 7 | – | MBC | – | 80 | | – | 10 | 6.3 | 1.71 |

^a Entry 5: PLLA-PMBC block copolymer; Entry 6: PLLA-PMBC random copolymer; Entry 7: MBC homopolymer.

^b $[M_1]_0 = 0.33M$, $[M_2]_0 = 0.4M$, $[M_1]_0/[M_2]_0/[OH]/[Zn] = 50/60/2/1$.

^c Calculated from GPC results.

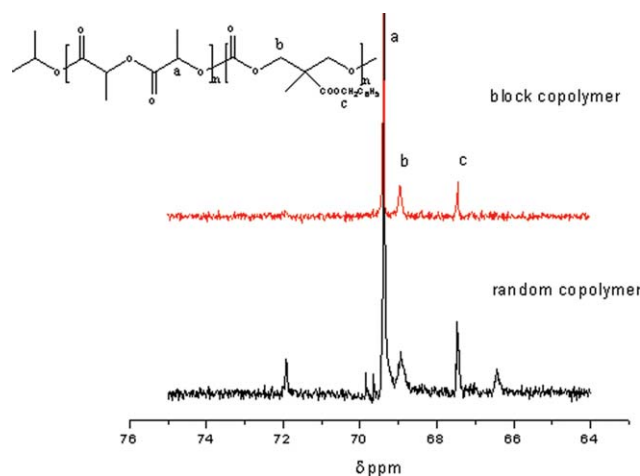


Figure 5 ^{13}C NMR spectrum of the methine carbon in PLLA-PMBC block copolymer, (sample Entry 5, upper) and PLLA-PMBC random copolymer, (sample Entry 6, lower). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicating the ideal block copolymer structure without random sequences. In contrast, the ^{13}C NMR spectra of the L-LA and MBC random copolymer demonstrated the various single peaks at δ 64 to δ 72 (Fig. 5).

Racemization would always occur during metal complex initiated lactide ring opening polymerization and introduce stereo defects into polymer chain, thus influence the crystallization behavior. Content of racemization would always shift with the change of polymerization conditions, and this is why the optically pure PLA is difficult to obtain even using optically pure LA monomer, especially in the case of industrial production. In our work, the solution polymerizations of L-LA at various temperatures ranging from 25 to 120°C were performed to investigate the temperature effect on the chain stereo regularity. High resolution ^{13}C NMR (600 MHz) spectrum of the all the PLLA samples polymerized at different temperatures displayed the resonance signals of the methine carbon with the dominant sequence of *iii*, accompany with the trace amount of *iss*, *isi*, *ssi*, and *sis* sequence (Fig. 6). The content of each sequence for the methine carbon was calculated from the ^{13}C NMR spectrum, and no significant change was identified by varying reaction temperatures, especially for the content of *iii* sequence (Table III). Bulk polymerizations of L-LA at different temperatures higher than 120°C for longer polymerization time were also carried out (Table IV), and the ^{13}C NMR spectrum of these PLLA samples showed the similar single resonance peak of methine carbon (Fig. 7). DSC profiles of PLLA sample (Entry 13) showed a high melting peak of 174°C during the second heat. Besides, a typical cold crystallization peak appeared indicating the high isotacticity (Fig. 8). These results indicated that the chain stereo regularity could

not be affected by polymerization temperature, solvent and polymerization time, implying that no racemization presented during the polymerization process in the zinc catalyst system, which was different from the report that the sequence distribution of PLLA samples would have the dramatic change under different temperatures leading to the decrease of the melting point.⁵¹

Another important issue during L-LA polymerization is the transesterification reaction which will also cause the dramatic change to the polymer chains. The MALDI-TOF Mass analysis is a helpful tool for detecting both the intermolecular and intramolecular transesterification reactions during polymerization. From Figure 9 of PLLA obtained under room temperature in 40 min, the first series of peaks at the m/z of 4839.3, 4911.3, 4982.5, and 5053.3 was noticed. There was a mass difference of 72 (half of the molecular weight of lactide) in m/z between every two neighboring peaks indicating that both even-membered and odd-membered oligomers were presented in the system. The presence of odd-membered oligomers cannot be explained by the pair-addition ring-opening polymerization process of DL-lactide, which only yields even-membered oligomers.⁵² It thus suggested that transesterification did take place during the polymerization, although the GPC result revealed a narrow polydispersity of the polymer with 100% monomer conversion in 40 min. While the polymerization process was extended to 48 h, the obtained polymer had the lower molecular weight and much broad polydispersity as shown in Figure 10, which implied that the transesterification reaction became dominant after the monomer converted completely. The MS spectrum of PLLA sample (Entry 4) also indicated a series of mass peak

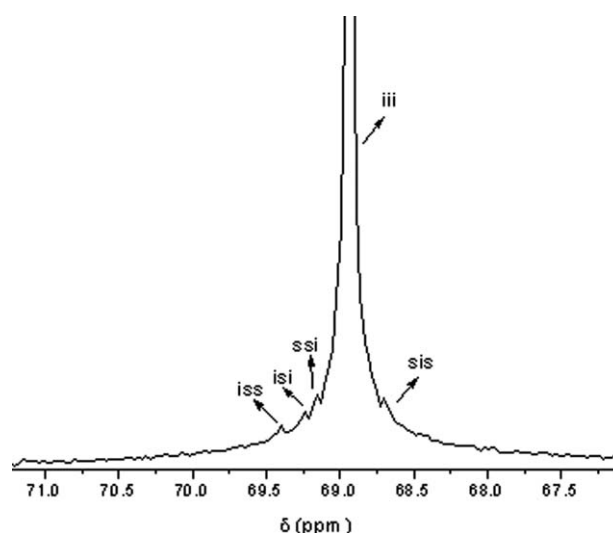


Figure 6 600 MHz ^{13}C NMR spectrum of the methine carbon in PLLA (sample Entry 9).

TABLE III
Solution Polymerization of L-LA at Different Temperatures

| Entry No. | Temp. (°C) | Time (min) | Solvent | Sequence content (%) | | | | | T_m (°C) |
|-----------|------------|------------|---------|----------------------|-------|-------|-------|-------|------------|
| | | | | [iss] | [isi] | [ssi] | [iii] | [sis] | |
| 1 | 25 | 40 | THF | 1.89 | 1.89 | 1.49 | 91.9 | 2.82 | 162 |
| 8 | 50 | 70 | Toluene | 1.39 | 0.98 | 1.26 | 93 | 3.37 | 170 |
| 9 | 70 | 70 | Toluene | 1.31 | 1.19 | 1.46 | 92.7 | 3.15 | 170 |
| 10 | 90 | 70 | Toluene | 1.46 | 1.33 | 1.17 | 92.7 | 3.33 | 173 |
| 11 | 120 | 70 | Toluene | 1.58 | 1.61 | 1.07 | 92.3 | 3.4 | 164 |

TABLE IV
Bulk Polymerization of L-LA at Different Temperatures

| Entry No. | Temp. (°C) | Time (h) | Conversion (%) | $M_n (\times 10^{-4})^b$ | M_w/M_n^b | T_m (°C) |
|-----------|------------|----------|----------------|--------------------------|-------------|------------|
| 12 | 120 | 24 | 82 | 6.6 | 1.67 | 161 |
| 13 | 130 | 48 | ~ 100 | 8.4 | 1.74 | 174 |
| 14 | 140 | 48 | ~ 100 | 8.7 | 1.73 | 170 |
| 15 | 160 | 50 | ~ 100 | 8.6 | 1.78 | 166 |

^a[M]₀/[OH]/[Zn]=1400/2/1.

^b Calculated from GPC results.

at m/z of 2184.3, 2256.6, 2328.8, 2400.5 corresponding to cyclic polymers with DP of 30, 31, 32, and 33, which could be due to the intramolecular transesterification via "back-biting" reaction.⁵² This is also considered as one of the most important route of polymer degradation during the polymerization process. While comparing with other catalyst systems as reported, this *in situ* generated zinc alkoxide initiating system can arise much faster polymer degradation rate in the polymerization solvent.⁵³

To detect the structure of this *in situ* formed initiating system, Zn[N(SiMe₃)₂]₂ was mixed with 2-propanol ([*i*Pr]/[Zn] = 2 : 1, mol/mol) in a benzene-D₆ (C₆D₆) solution without addition of any monomer. Unfortunately, the generated zinc alkoxide compound was a kind of flocculus and insoluble

in C₆D₆, which made it difficult to detect by means of ¹H-NMR. However, both trimethylsilyl and free isopropyl groups could be observed by checking the decanted upper solution using ¹H-NMR. The same phenomenon was also observed when THF or toluene was used as solvents. In this situation, further addition of L-LA monomer to the reaction mixture could only yield oligomer with DP of 3 to 4. In fact, in the case of the high molecular weight PLLA polymerization procedure, L-LA monomer was mixed with Zn[N(SiMe₃)₂]₂ in THF before the addition of 2-propanol at the beginning of the reaction. The whole system could afford a homogenous polymerization, and a smooth polymerization kinetic profile could be obtained with both fast initiation and propagation as Figure 11 revealed. This phenomenon implied

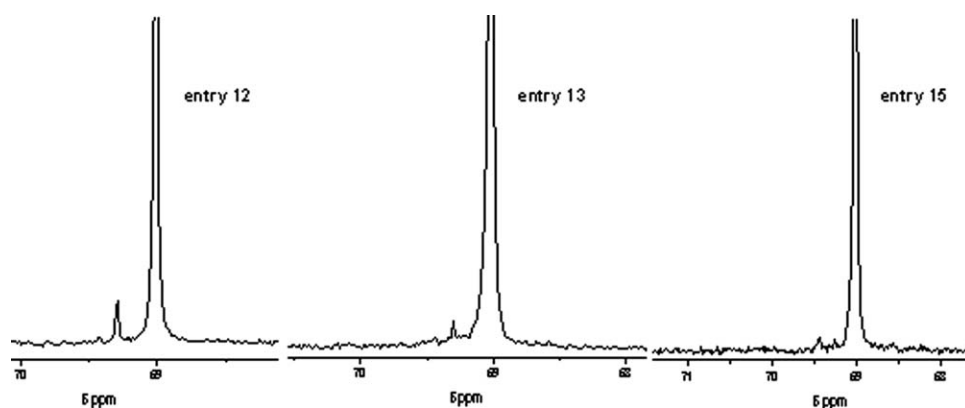


Figure 7 ¹³C NMR spectra of the methine carbon in PLLA samples.

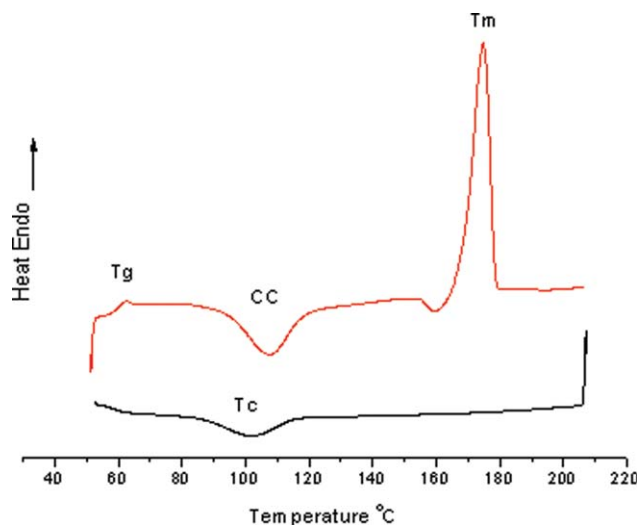


Figure 8 DSC profile of PLLA (sample Entry 13). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that, in this zinc initiating system, the existence of monomer in the initiating system was necessary to maintain the solubility of active species.

To study the interaction between the catalyst system and L-LA monomer, L-LA was mixed with $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ at the molar ratio of 1, 2, and 5. The three solutions showed the identical spectrum in ^1H NMR measurement. Both the methyl and methine groups in lactide molecules were in single average environment according to the ^1H NMR spectrum. The chemical resonance signals of methine and methyl groups were both shifted from 5.16 ppm and 1.63 ppm (original signals from L-LA monomer) to 4.09 ppm and 1.31 ppm, respectively. By addition of the same amount of 2-propanol ($[\text{OH}]/[\text{Zn}] = 2$,

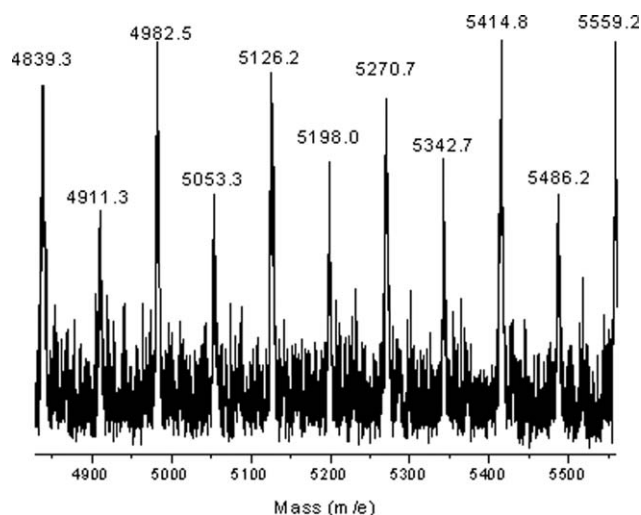


Figure 9 MALDI-TOF Mass spectra of PLLA (sample Entry 1) doped with Na^+ , reflector mode.

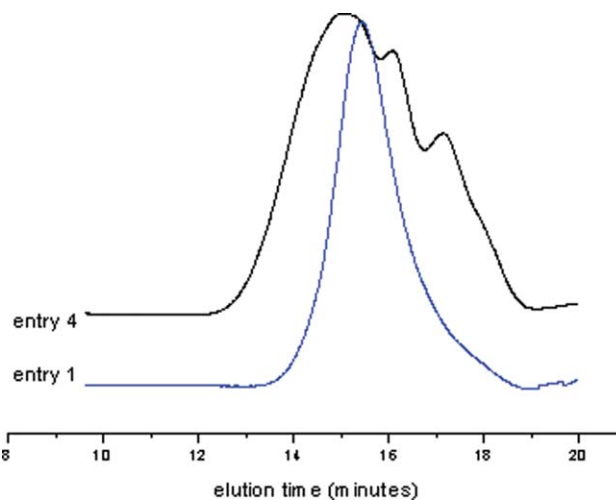


Figure 10 GPC profiles of PLLA samples obtained after different polymerization time (Entry 1: 40 min.; Entry 4: 48 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mol/mol) into the above three mixtures in THF, the one with $[\text{L-LA}]/[\text{Zn}]$ molar ratio of 5 could form a homogenous solution, while the ^1H NMR spectra indicated the ideal ring opening reaction of all the L-LA monomers. However, when the molar ratio of L-LA to $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ was 1 or 2, only gel-like deposit was obtained. These gel-like materials were insoluble in THF but soluble in the THF-L-LA solution, which implied that the living short chain species could still be formed under this situation. It is concluded that the interaction between L-LA with $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ catalyst is exist, which could effectively prevent the aggregation of zinc alkoxides and afford the fast ring-opening reactions which further lead to the fast and smooth polymerization.

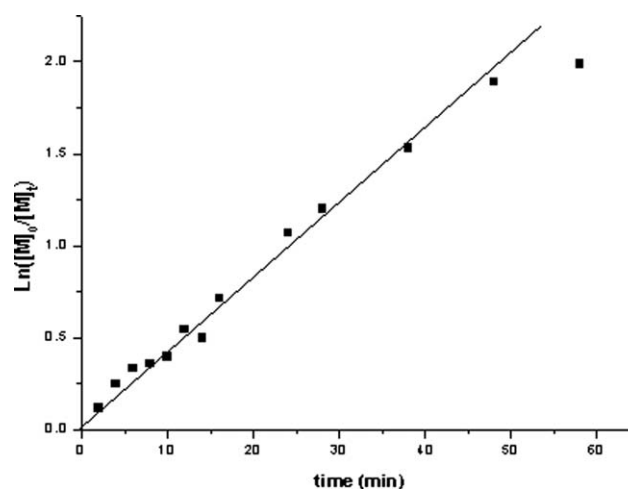


Figure 11 Kinetics profile of L-LA polymerization in THF at room temperature. ($[\text{M}]_0/[\text{OH}]/[\text{Zn}] = 57.5/2/1$, $[\text{M}]_0 = 0.37\text{M}$).

CONCLUSIONS

The zinc alkoxides generated *in situ* from $Zn[N(SiMe_3)_2]_2$ and alcohol was successfully applied in the polymerization of cyclic esters. The solution polymerization of L-LA was fast and smooth, and the polyesters were of expected molecular weight. The living PLLA species could initiate polymerization of cyclic carbonates affording an ideal block copolymer. Racemization of PLLA was not identified in both the solution and bulk polymerization at various temperatures for different time. Intermolecular transesterification did occur from the beginning of the polymerization, while M_w/M_n value of the polyester could still be maintained at a low level within the normal polymerization time. During the polymerization for a prolonged time, intramolecular transesterification became dominant and dramatically changed the molecular weight and M_w/M_n of the polymer. The interaction of L-LA was proved to be a dominant factor to maintain the solubility of the *in situ* formed zinc alkoxides system to afford a homogenous polymerization procedure without the effect of bulk of alcohol introduced.

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