Polymerization of Lactides and Lactones. III. Ring-Opening Polymerization of DL-Lactide by the (η^3-C$_3$H$_5$)$_2$Sm(μ_2-Cl)$_2$(μ_3-Cl)$_2$Mg(tmed)(μ_2-Cl)Mg(tmed) Complex

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ABSTRACT: Ring-opening polymerization of DL-lactide (LA) has been initiated with the (η^3-C$_3$H$_5$)$_2$Sm(μ_2-Cl)$_2$(μ_3-Cl)$_2$Mg(tmed)(η_2-Cl)Mg(tmed) complex both in bulk and solution. The effects of reaction conditions, such as reaction time, reaction temperature, and monomer/initiator molar ratio on the polymerization has been discussed. The results showed that (η^3-C$_3$H$_5$)$_2$Sm(μ_2-Cl)$_2$(μ_3-Cl)$_2$Mg(tmed)(μ_2-Cl)Mg(tmed) was more effective for the polymerization of LA, and high molecular weight of polylactide was obtained by this initiator. The solvent affected the polymerization significantly. The polymerization mechanism was in agreement with the coordination mechanism. The polymer was characterized by FTIR, ^{1}H-NMR, and DSC. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2857–2862, 1999

Key words: DL-lactide; ring-opening polymerization; (η^3-C$_3$H$_5$)$_2$Sm(μ_2-Cl)$_2$(μ_3-Cl)$_2$-Mg(tmed)(μ_2-Cl)Mg(tmed) initiator

INTRODUCTION

Ring-opening polymerization of lactides and lactones provides a convenient route to biodegradable polyesters that are of interest for a variety of practical applications.[1–3] Usually, the polymerization of lactides and lactones are carried out in the presence of tin salts, such as Sn(2-ethyl-hexanoate),[4–6] which is effective for lactide polymerization in bulk at higher temperatures. In other systems, many non-tin catalysts have been reported, such as Al(i-Bu)$_3$-H$_3$PO$_4$-H$_2$O, BuMgCl, Bu$_2$Mg and Mg(OEt)$_2$.[7–9] These catalysts showed several advantages, and high molecular weight polylactides have been synthesized in this way.

Recently, rare earth metal compounds have been used for the ring-opening polymerization of lactides and lactones. Shen[10] and Steve and McLain et al.[11,12] investigated the polymerization of lactide and lactones with lathanide alkoxides. Shen et al.[13] also reported rare earth halides showed high activities for the polymerization of lactones in the presence of epoxide. Yasuda,[14] Evans,[15] and Feijen[16] reported the living ring-opening polymerization of lactones with orgnolanthanide complexes, which were extremely active for these monomers. In recent years, we have focused on the investigation of ring-opening polymerization of lactones and lactides with rare earth compounds, and some new catalysts have been patented[17,18] and published.[19] In this article, we wish to report on the polymerization of lactide initiated by rare earth allyl complexes.

EXPERIMENTAL

Materials

DL-Lactide with an m.p. of 125–127°C was synthesized according to literature procedures.[26] Crude

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Table I Polymerization of LA with $(\eta^3-C_3H_5)_2Sm(\mu_2-Cl)_2(\mu_3-Cl)_2Mg(tmed)(\mu_2-Cl)Mg(tmed)$

No.	M/I[a]	Solvent	Mo./Solvent (w/v%)	Time (h)	Temp. (°C)	Yield (%)	M_η ($\times 10^4$)
1	350	THF	20	12	60	78	7.6
2	350	THF	26	12	60	84	6.8
3	350	THF	30	12	60	91	7.2
4	350	THF	20	12	40	64	6.3
5	350	THF	20	12	20	58	5.1
6	350	THF	20	12	0	oligomer	
7	135	CH$_2$Cl$_2$	30	12	40	oligomer	
8	135	CHCl$_3$	30	12	60	oligomer	
9	135	Dioxane	30	12	60	87	5.9
10	135	Toluene	30	12	60	oligomer	
11	135	Benzene	30	12	60	oligomer	
12[b]	250			8	150	89	7.1
13[b]	500			8	150	85	7.6
14[b]	500			12	150	84	6.9

[a] Initial monomer/initiator mol ratio.
[b] LA polymerization conducted in bulk.

products were thrice recrystallized from ethyl acetate. The monomer was dried for 24 h at 25°C under reduced pressure (5 mmHg) before polymerization. Toluene, benzene, tetrahydrofuran (THF), 1,4-dioxane, and ethyl ether (Et$_2$O) were dried and distilled from sodium immediately before use. CHCl$_3$ and CH$_2$Cl$_2$ were dried and distilled from di-phosphorus pentoxide immediately before use. Anhydrous rare earth halide was prepared by reacting rare earth oxide with HCl and then anhydrated by thionyl chloride.[27]

Tetramethylethylenediamine (tmed) was dried by refeux over KOH, distilled, and stored over 4-A molecular sieves. Allyl chloride was distilled and stored over 4-A molecular sieves.

Preparation of Initiator

Allyl-magnesium chloride was prepared by reacting magnesium with allyl chloride in Et$_2$O solution with stirring at 0°C. After the reaction was completed, Et$_2$O was distilled under reduced presure, and THF was added to the reaction mixture. The allyl-magnesium chloride solution of THF was filtered and sealed for use.

$(\eta^3-C_3H_5)_2Sm(\mu_2-Cl)_2(\mu_3-Cl)_2Mg(tmed)(\mu_2-Cl)Mg(tmed)$ was prepared according to literature procedures.[28] Five grams of SmCl$_3$ was added to 100 mL THF, the mixture was stirred 8 h at room temperature, and 25 mmol of allyl-magnesium chloride in THF solution was added dropwise with stirring at 0°C. The mixture was

stirred for an additional 12 h at room temperature and then filtered. The filtrate was concentrated under vacuum, and 5 mL of tmed was added dropwise to form a precipitate. The complex was filtered, washed with cold THF, and recrystallized from a THF/hexane solution three times to give a violet crystalline powder with the yield of 28%.

Anal. calcd. C 31.30, H 6.13, C l25.66, N 8.11, Sm 21.77, Mg 7.04; found: C 31.47, H 6.42, C l25.01, N 8.20, Sm 21.73, Mg 7.28%. IR (CH$_2$=CH—CH$_2$—) 1545 (s), (=CH—H) 3064 (w), (tmed) 3008 (m), 2965 (m), 2875 (m), 2846 (m), 2805 (m), 1026 (S). The results are in agreement with the literature.[28]

Polymerization Procedure

In Bulk

Monomer was added into a dried 20-mL glass reactor, which was flamed and nitrogen purged several times. The initiator was injected by means of a syringe in the form of a THF solution. The reaction was carried out at constant temperature during a suitable period of time as described in Table I. The polymerization was terminated by cooling in water. The reaction product was then dissolved in CHCl$_3$, and precipitated with an excess of diethyl ether. The purified product was dried under vacuum at 40°C for 48 h.

In Solution

Monomer was added into a dried 100-mL glass reactor. The reaction system was heated and nitrogen purged several times. Solvent was added and the initiator was injected by means of a syringe in the form of a THF solution. The reaction was carried out at constant temperature during a suitable period of time, as described in Table I. The reaction product was then dissolved in CHCl$_3$, and precipitated with an excess of diethyl ether. The purified product was dried under vacuum at 40°C for 48 h.

Measurements

^{1}H-NMR and ^{13}C-NMR spectra of polymer were recorded in CDCl$_3$ with a Bruker AC-P 300 MHz apparatus at 25°C. IR spectra were recorded on a NICOLET MX-1 IR apparatus. Intrinsic viscosity of poly(DL-Lactide) was measured with an Ubbelohde viscometer in THF at 37°C, and the viscosity average molecular weight ($M\eta$) was calculated from the following equation[29]:$[\eta] = 1.04 \times 10^{-4} M\eta^{0.75}$.

RESULTS AND DISCUSSION

$(\eta^3\text{-}C_3H_5)_2Sm(\mu_2\text{-Cl})_2(\mu_3\text{-Cl})_2Mg(tmed)(\mu_2\text{-Cl})Mg$-(tmed) is violet and crystalline, and it is important to recrystallize it from the THF/hexane solution before use. When this initiator at any ratio of the monomer/initiator (M/I) was added into the monomer, the color of the initiator soon disappeared. As the polymerization system was free from water or atmosphere, the disappearance of the color might indicate the beginning of the polymerization. The results obtained from the polymerization of DL-lactide (LA) with $(\eta^3\text{-}C_3H_5)_2Sm(\mu_2\text{-Cl})_2(\mu_3\text{-Cl})_2Mg(tmed)(\mu_2\text{-Cl})Mg(t\text{-}med)$ in tetrahydrofuran (THF) are recorded in Table I. From Table I, it is shown that this catalyst is effective for the polymerization of LA. The polymerization can be carried out either in bulk or in a THF solution. The reaction rate in bulk is higher than that in solution. In view of the high melting point of lactide (126–128°C), it is well known that most polymerizations of lactide with Sn salts and other initiators are conducted in bulk at high temperature, and a temperature of 127°C was the lowest possible reaction temperature. Furthermore, such initiators were rather inactive at a lower temperature (<100°C) or in

solution. It is interesting that the present initiator is effective for the polymerization of LA in a low temperature in the solution. We can see from Table I that high molecular weight PLA can be obtained in a THF or 1,4-dioxane solution at milder temperatures (40–60°C).

As summarized in Table I, the concentration of the monomer in the solvent affects the yield and molecular weight of PLA. A higher concentration of the monomer is beneficial for the polymerization of LA. This is in agreement with the reaction rate of bulk polymerization being higher than that of the solution polymerization. It is seen from Figure 1 that the reaction time affects the polymerization in both yield and molecular weight. When the reaction times reached 12 h, the molecular weight of PLA arrived at its maximum ($M\eta = 7.6 \times 10^4$). With longer reaction times, such as 24 h, the molecular weight of PLA showed a slight decrease. This suggests that the active samarium complex is also catalyzing the decomposition of the polymer. In other systems,[20] intramolecular transesterification has been discussed as a route to decrease molecular weight. To investigate the influence of the monomer/initiator (M/I) molar ratio on both the yield and molecular weight of PLA, some polymerizations were conducted at a temperature of 60°C in THF solution, and the M/I varied between 95 and 500°C (Fig. 2). The results indicated that, with the increase of the M/I molar ratio, the yield of PLA showed a slight decrease, but the molecular weight increased. When the M/I was 350, the molecular weight of PLA is the highest, due to the fact that the higher concentration of the initiator increased the number of active species. The reaction temperature also shows certain effects on the polymerization of LA (Table I). When the polymerization of LA is carried out at 20°C, both the yield and molecular weight of PLA are lower than those at 60°C. Moreover, only oligomer of PLA are obtained when the polymerization is conducted at 0°C.

It can be seen from Table I that the solvent has a desirable influence on the solution polymerization. To investigate the influence of solvents on the polymerization of LA, different solvents, such as THF, 1,4-dioxane, CH$_2$Cl$_2$, benzene, and toluene, have been used for the ring-opening polymerization of LA. High-yield and molecular weight PLA could be obtained in the THF or 1,4-dioxane solutions. However, with other solutions, only an oligomer of PLA was obtained. This is due to the good solubility of $(\eta^3\text{-}C_3H_5)_2Sm(\mu_2\text{-Cl})_2(\mu_3\text{-}Cl)_2Mg(tmed)(\mu_2\text{-Cl})Mg(tmed)$ in THF and 1,4-di-
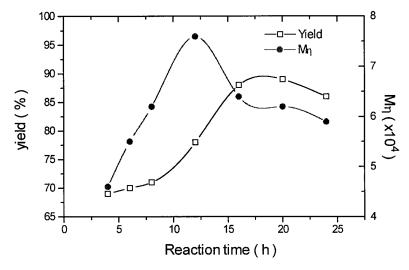
Figure 1 Effect of reaction time on the polymerization of LA reaction conditions: monomer/initiator molar ratio = 350, concentration of monomer = 20%, reaction temperature = 60°C.

oxane. It is reported[21–23] that, with other initiated systems of LA polymerization, such as $Al(O^iPr)_3$, the polymerization is usually carried out in toluene solution. Even in other rare earth-based initiator systems,[14–16] such as $(C_5Me_5)_2Sm(THF)x$, $SmMe(C_5Me_5)_2(THF)$, and $[SmH(C_5Me_5)_2]_2$, the polymerization is also carried out in toluene solution.

The IR spectrum of PLA prepared by the present initiator shows an absorption at 3500 cm^{-1}, which is characteristic of the hydroxyl functions, while the absorption at 935 cm^{-1} of the

lactide monomer has completely disappeared. To compare the basic structure and property of PLA synthesized by the present initiator, a sample of PLA with $M\eta = 7 \times 10^4$ was prepared by $SnCl_2$ as an initiator; this initiator is discussed in the references. The other sample is selected from Table I (No. 1). The samples were analyzed by ^{1}H-NMR, ^{13}C-NMR, and DSC, respectively. The results are recorded in Table II. There are no differences in the ^{1}H-NMR and ^{13}C-NMR spectrum between these two samples. The ^{1}H-NMR spectra of PLA show that the peaks at 1.54 and 5.17 ppm are
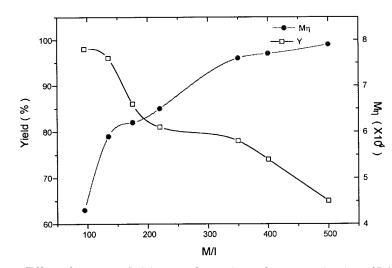

Figure 2 Effect of monomer/initiator molar ratio on the poymerization of LA reaction conditions: concentration of monomer = 20%, reaction temperature = 60°C; reaction time = 12 h.

Table II   Analysis Result of Samples 1 and 2

		^{1}H-NMR (ppm)		^{13}C-NMR (ppm)			DSC (°C)
		H_a	H_b	C_a	C_b	C_c	
Sample 1	ⓐ CH$_3$ O ∥ ┤O—CH—C├$_n$ ⓑ ⓒ	1.57	5.17	17.15	68.82	169.81	57
Sample 2	ⓐ CH$_3$ O ∥ ┤O—CH—C├$_n$ ⓑ ⓒ	1.57	5.17	17.15	68.82	169.81	58

1: Prepared by SnCl$_2$ as initiator; reaction temperature 150°C; reaction time 12 h; monomer/initiator = 500; in bulk. 2: Selected from Table I (No. 1).

assigned to methyl and methylene protons of PLA chains, respectively. The ^{13}C-NMR spectrum of the PLA indicates that the peaks at 17.15, 68.82, and 169.81 ppm are assigned to C_a, C_b, and C_c, respectively (see Table II). Table II also shows that the T_g of PLA with SnCl$_2$ is slightly lower than that of PLA with the present initiator; this suggests that the molecular weight distribution of PLA with SnCl$_2$ is slightly wider than that of PLA with the present initiator.

The polymerization of lactones, such as ε-caprolactone, δ-valerolactone, -βpropiolactone initiated by rare earth alkyl complexes are well documented in the literature[14−16]. Due to the presence of an Ln—C bond or an Ln—H bond, such as (C$_5$Me$_5$)$_2$Sm(THF)x, SmMe(C$_5$Me$_5$)$_2$(THF), and [SmH(C$_5$Me$_5$)$_2$]$_2$, complexes are more reactive and efficient for the polymerization of lactones. The mechanism for the polymerization of lactones has been demonstrated by coordination insertion. In general, a high molecular weight of PLA can be prepared by coordination catalysts,[24] while anionic catalysts lead to a living ring-chain equilibrium and produce cylic oligomers.[25] To investigate the possible polymerization mechanism of LA with the present initiator, the polymerization of LA with other allyl compounds such as allyl-magnesium chloride were conducted, and the reaction conditions were controlled to be identical with the polymerization of LA with the present initiator. Part of the results is summarized in Table III. The experiment shows that allyl-magnesium chloride is an effective initiator for the polymerization of LA. The detailed results are

published in another article.[30] Although the allyl-magnesium chloride is effective for the polymerization of LA, there are obvious differences in the polymerization of LA between allyl-magnesium chloride and (η^3-C$_3$H$_5$)$_2$Sm(μ_2-Cl)$_2$(μ_3-Cl)$_2$Mg-(tmed)(μ_2-Cl)Mg(tmed). Only in bulk polymerization of LA does allyl-magnesium chloride have high efficiency, but the yield and molecular weight of PLA is lower than that of PLA with (η^3-C$_3$H$_5$)$_2$Sm(μ_2-Cl)$_2$(μ_3-Cl)$_2$Mg(tmed)(μ_2-Cl)Mg(tmed). In solution, even after the reaction time reaches 30 h, only some oligomers of PLA can be obtained by allyl-magnesium chloride. It is shown that the catalyst efficiency of (η^3-C$_3$H$_5$)$_2$Sm(μ_2-Cl)$_2$(μ_3-Cl)$_2$Mg(tmed)(μ_2-Cl)Mg(tmed) is higher than that of allyl-magnesium chloride. It shows that the polymerization mechanism of LA with the present initiator is different with anionic allyl-magnesium chloride. It is possible that the polymerization of LA with (η^3-C$_3$H$_5$)$_2$Sm(μ_2-Cl)$_2$(μ_3-Cl)$_2$Mg-(tmed)(μ_2-Cl)Mg(tmed) runs by a coordination catalysis mechanism.

CONCLUSION

(η^3-C$_3$H$_5$)$_2$Sm(μ_2-Cl)$_2$(μ_3-Cl)$_2$Mg(tmed)(μ_2-Cl)Mg-(tmed) is more effective for the polymerization of LA, and the high molecular weight of polylactide was obtained by this initiator. The solvent affected the polymerization significantly. It is shown that the catalyst efficiency of (η^3-C$_3$H$_5$)$_2$Sm(μ_2-Cl)$_2$(μ_3-Cl)$_2$Mg(tmed)(μ_2-Cl)Mg-

Table III   Polymerization of LA with Ally-magnesium Chloride

No.	M/I	Solvent	Mo./Solvent (w/v%)	Time (h)	Temp. (°C)	Yield (%)	M_η ($\times 10^4$)
1[a]	130			12	150	89	4.52
2[a]	150			12	150	84	5.2
3[a]	180			12	150	78	4.2
4[a]	200			12	150	oligomer	
5[a]	350			12	150	oligomer	
6[b]	135	THF	20	12	60	oligomer	
7[b]	350	THF	20	12	60	oligomer	
8[b]	135	THF	20	30	60	oligomer	
9[b]	135	CHCl$_3$	20	12	60	oligomer	
10[b]	135	Dioxane	20	12	60	oligomer	
11[b]	135	Toluene	20	12	60	oligomer	
12[b]	135	Benzene	20	12	60	oligomer	

[a] LA polymerization conducted in bulk.
[b] LA polymerization conducted in solution.

(tmed) is higher than that of allyl-magnesium chloride. It shows that the polymerization mechanism of LA with the present initiator is different than with the anionic allyl-magnesium chloride. It is possible that the polymerization of LA with $(\eta^3\text{-C}_3\text{H}_5)_2\text{Sm}(\mu_2\text{-Cl})_2(\mu_3\text{-Cl})_2\text{Mg(tmed)}(\mu_2\text{-Cl})\text{-Mg(tmed)}$ runs by a coordination catalysis mechanism.

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