

Zinc acetate as a catalyst for the bulk ring opening polymerization of cyclic esters and lactide

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ABSTRACT

$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ is found to be an effective bulk polymerization catalyst for the ring-opening polymerization of *rac*-lactide, L-lactide, ϵ -caprolactone and δ -valerolactone. The propensity of polymerizations can be enhanced by performing them in the presence of appropriate amounts of different alcohols. The major initiation pathway in the polymerization is found to proceed via the activated monomer mechanism and depending on the nature of the alcohol used, polymers with different end groups can be synthesized. These polymerization system constitutes an economical process, employing readily available inorganics such as $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ as catalyst and do not necessitate solvents. The overall system is green and eco friendly.

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1. Introduction

The conventional polyolefin synthesis has already manifested its culmination as a consequence of depleting petrochemical feedstock and the non-degradable fate of these commodity polymers. Increased environmental awareness and depleting fossil-fuel resources have made it mandatory to search for new catalytic processes leading to the synthesis of bio-degradable polymers [1,2]. The increasing need to search alternative polymeric materials to those based on non-renewable petroleum resources, along with the desire to produce environmentally benign biodegradable plastics has provided active impetus towards the polymerization of cyclic esters and lactide [3–7]. Aliphatic polyesters have been implicated for biomedical applications such as delivery medium for the controlled release of drugs and biodegradable surgical sutures [8,9]. Polylactones and lactides have potential utility for such applications as a result of their permeability, biocompatibility and biodegradability [10–12]. One of the convenient strategies in synthesizing these polymers is the ring-opening polymerization of the corresponding cyclic lactone monomers, functionally related compounds and lactide [13–15]. Lactide is the cyclic dimer of lactic acid and is produced from annually renewable food resources like corn and sugar-beet through bio-mass fermentation [16,17]. The polymerization of lactide yields poly(lactide) which has emerged recently as a bulk commodity material since it is

an environmentally friendly recyclable thermoplastic and is completely bio-degradable [10,12,18–21]. Such polymers are found to possess a bio-compatible nature with living tissue and bioassimilable. As a result, they have found useful applications biomedical and pharmaceutical applications, for example, in resorbable surgical sutures [22–25], drug delivery vehicles [24,25], and artificial tissue matrices [26,27]. Although a multitude of initiators are known for such polymerizations [28–32], the major hurdle regarding the commercialization of such processes is the difficulty in removing catalyst residues and the cytotoxicity associated with such residues, which limit the utility of these polymers in biomedical applications. An attractive process is envisioned to be engineered upon new catalysts that have environmentally benign metals that are constituents in the mammalian anatomy so that the residues are potentially harmless [33].

Among the various mechanistic modes of polymerization, the coordination-insertion ring-opening polymerization is the most popular because of its capability in producing polymers with narrow molecular weight distribution [3,29,34–43]. A large variety of metal complexes containing alkyl [44–48], alkoxide [34–43], carboxylates [49–51] and oxides [52] have been reported to possess good activity. Other metal alkoxides or aryloxides containing main-group as well a transition metals including lanthanides have been reported [3,29]. The medicinal value of such polymers has prompted active research into the synthesis of new catalysts containing biocompatible metals. These include examples from zinc [53–69], magnesium [70], calcium [71] and iron [72].

We have reported recently the use of simple iron and ruthenium chloride catalysts in the synthesis of polylactones [73].

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Here the polymerizations were found to proceed by the activated monomer mechanism [74,75]. We have been able to activate cyclic ester monomers and lactide by simple Lewis acids. Considerable control in the polymerization behavior was noticed in this method. Our contentions were again verified with different catalyst libraries of metal aryloxides of group 4 metals [76]. The key feature that is understood in these research is elaborate ligands on the metal catalyst is not a mandatory feature to facilitate such a process. What is really needed is a suitable initiating group that facilitates the cleavage of the acyl-oxygen bond of the monomer.

Although a multitude of zinc containing initiators have been reported in the recent past [53–69], what is most surprising is no detailed investigations have been reported with zinc acetate which is readily available and is stable under ambient conditions in the presence of oxygen and moisture. However, detailed studies with zinc octoate have been reported recently. Here the polymerization proceeds with coordination-insertion mechanism [77]. Our recent endeavor of having a thorough understanding of the activated monomer mechanism [73,76] initiated these investigations.

2. Experimental

2.1. Materials

L-Lactide (L-LA), *rac*-Lactide (*rac*-LA), ϵ -caprolactone (CL) and δ -valerolactone (VL) were purchased from Aldrich. L-LA and *rac*-LA were sublimed fresh prior to use. The other monomers were dried over CaH₂ overnight and distilled fresh before the commencement of the respective polymerizations. Benzyl alcohol (BnOH) and isopropanol (*i*-PrOH) used in these studies were purchased from Ranchem India and were used after drying using appropriate procedures. Zn(OAc)₂·2H₂O was purchased from Aldrich and used as received.

2.2. Instrumentation and characterization

¹H NMR spectra in CDCl₃ were recorded on a Bruker 400 MHz instrument. MALDI-TOF measurements were performed on a Bruker Daltonics instrument in dihydroxy benzoic acid matrix. Molecular weights and the polydispersity indices of the polymers were determined by GPC instrument with Waters 510 pump and Waters 410 Differential Refractometer as the detector. Three columns namely WATERS STRYGEL-HR5, STRYGEL-HR4 and STRYGEL-HR3 each of dimensions (7.8 mm × 300 mm) were connected in series. Measurements were done in THF at 27 °C. Number average molecular weights (M_n) and polydispersity (M_w/M_n) (MWD) of polymers were measured relative to polystyrene standards. For LA and CL, molecular weights (M_n) were corrected according to Mark-Houwink corrections [78].

2.3. Typical procedure for bulk polymerization

The procedures given are for polymerizations between the respective monomers and Zn(OAc)₂·2H₂O in 200:1 stoichiometric ratio.

For L-LA or *rac*-LA, polymerization, 17.34 μ mol of Zn(OAc)₂·2H₂O and 0.50 g L-LA or *rac*-LA were taken in a sealed tube. The contents were rapidly stirred at 145 °C. Once the monomer melted completely, rise in viscosity of the polymerization reaction was observed, finally the stirring ceased. The completion of reaction was confirmed by ¹H NMR spectroscopy and GC. The contents were dissolved into minimum quantity of CH₂Cl₂ and poured into cold methanol. The polymer precipitated immediately and was isolated by filtration. The filtered product was dried in vacuum until a constant weight was attained.

For, CL polymerization, 23.66 μ mol of Zn(OAc)₂·2H₂O was used for 0.50 mL of monomer. The polymerization was performed at 100 °C in a sealed tube. Rise in viscosity of the polymerization reaction was observed and finally the stirring ceased. The progress of the polymerization was followed by monitoring the disappearance of the monomer using TLC technique [73,76]. The contents were dissolved into minimum quantity of CH₂Cl₂ and poured into cold methanol. The polymer precipitated immediately and was isolated by filtration. The filtered product was dried in vacuum until a constant weight was attained. Similarly for, VL polymerization, 26.97 μ mol of Zn(OAc)₂·2H₂O was used for 0.50 mL of monomer. The polymerization was performed at 100 °C and same procedure for work up was followed.

2.4. Typical procedure for bulk polymerization in the presence of BnOH

The procedures given are for polymerizations between the respective monomers and Zn(OAc)₂·2H₂O and BnOH in 200:1:5 stoichiometric ratio.

For L-LA or *rac*-LA, polymerization, 17.34 μ mol of Zn(OAc)₂·2H₂O and 0.50 g L-LA or *rac*-LA along with 87.7 μ mol of BnOH were taken in a sealed tube. The contents were rapidly stirred at 145 °C. Once the monomer melted completely, rise in viscosity of the polymerization reaction was observed, finally the stirring ceased. The completion of reaction was confirmed by ¹H NMR spectroscopy and GC. The contents were dissolved into minimum quantity of CH₂Cl₂ and poured into cold methanol. The polymer precipitated immediately and was isolated by filtration. The filtered product was dried in vacuum until a constant weight was attained.

For, CL polymerization, 23.66 μ mol of Zn(OAc)₂·2H₂O was used for 0.50 mL of monomer along with 118.3 μ mol of BnOH. The polymerization was performed at 100 °C in a sealed tube. Rise in viscosity of the polymerization reaction was observed and finally the stirring ceased. The progress of the polymerization was followed by monitoring the disappearance of the monomer using TLC technique [73,76]. The contents were dissolved into minimum quantity of CH₂Cl₂ and poured into cold methanol. The polymer precipitated immediately and was isolated by filtration. The filtered product was dried in vacuum until a constant weight was attained. Similarly for, VL polymerization, 26.97 μ mol of Zn(OAc)₂·2H₂O was used for 0.50 mL of monomer along with 134.85 μ mol of BnOH. The polymerization was performed at 100 °C and same procedure for work up was followed.

3. Results and discussion

3.1. Polymerization activity and characteristics

A thorough inspection of the literature reveals that although a multitude of different zinc containing systems have been used for lactide and cyclic ester polymerization [53–69], there have been no detailed investigations carried out with simple and commercially available compounds. We surmised that Zn(OAc)₂·2H₂O should be potent towards such polymerizations. There have been a report which prove the viability of metal acetates as suitable catalyst [79]. We envisaged from experience [73,76] that the coordinated H₂O molecule in the catalyst must act as a viable initiator, facilitating the cleavage of the acyl-oxygen bond in these monomers, hence affecting such polymerizations in an effective manner. The use of water as an initiator is known, although claimed to be ineffective towards the enhancement of rate of polymerization and molecular weights of the resulting polymers for catalyst bearing ligating ini-

Table 1
Results of *rac*-LA, L-LA, CL, and VL polymerization with Zn(OAc)₂·2H₂O.

Entry	Monomer	T (°C)	[M] ₀ /[Zn] ₀ ratio	Time ^a (h)	Yield (%)	M _n ^b /M _{th} ^c (kg/mol)	M _w /M _n (MWD)
1	<i>rac</i> -LA	145	200	24	98	55.59/28.84	1.47
2	<i>rac</i> -LA	145	400	28	98	99.83/57.67	1.38
3	<i>rac</i> -LA	145	800	35	99	159.33/115.33	1.21
4	<i>rac</i> -LA	145	1000	41	97	185.36/144.15	1.12
5	L-LA	145	200	14	96	51.05/28.84	1.43
6	L-LA	145	400	19	98	98.43/57.67	1.37
7	L-LA	145	800	25	98	157.77/115.33	1.24
8	L-LA	145	1000	30	99	182.54/144.15	1.15
9	CL	100	200	17	97	30.03/22.84	1.45
10	CL	100	400	21	96	43.98/45.67	1.38
11	CL	100	800	28	98	66.63/91.33	1.23
12	CL	100	1000	36	98	79.66/114.15	1.18
13	VL	100	200	13	99	43.04/20.04	1.41
14	VL	100	400	15	97	71.73/40.06	1.32
15	VL	100	800	19	96	122.91/80.11	1.26
16	VL	100	1000	23	96	150.06/100.13	1.16

^a Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed.^b Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n in the case of LA and CL polymerizations.^c Calculated from MW_{Monomer}·([M]₀/[Zn]₀) + MW_{Water} at 100% conversion.**Table 2**
Results of *rac*-LA, L-LA, CL, and VL polymerization with Zn(OAc)₂·2H₂O in the presence of BnOH in 200:1:5 ratio.

Entry	Monomer	T (°C)	Time ^a (h)	Yield (%)	M _n ^b /M _{th} ^c (kg/mol)	M _w /M _n (MWD)
1	<i>rac</i> -LA	145	18	98	63.57/5.87	1.23
2	L-LA	145	8	97	64.87/5.87	1.20
3	CL	100	12	98	34.27/4.67	1.21
4	VL	100	6	99	53.04/4.11	1.21

^a Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed.^b Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n in the case of LA and CL polymerizations.^c Calculated from MW_{Monomer}·([M]₀/[BnOH]₀) + MW_{BnOH} at 100% conversion.**Table 3**
Results of *rac*-LA, L-LA, CL, and VL polymerization with Zn(OAc)₂·2H₂O in the presence of *i*-PrOH in 200:1:5 ratio.

Entry	Monomer	T (°C)	Time ^a (h)	Yield (%)	M _n ^b /M _{th} ^c (kg/mol)	M _w /M _n (MWD)
1	<i>rac</i> -LA	145	20	97	60.23/5.82	1.20
2	L-LA	145	10	97	60.11/5.82	1.18
3	CL	100	12	99	32.29/4.62	1.19
4	VL	100	9	99	51.84/4.06	1.18

^a Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed.^b Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n in the case of LA and CL polymerizations.^c Calculated from MW_{Monomer}·([M]₀/[*i*-PrOH]₀) + MW_{*i*-PrOH} at 100% conversion.**Table 4**
Results of *rac*-LA, L-LA, CL, and VL polymerization with Zn(OAc)₂·2H₂O in the presence of BnOH in different ratio.

Entry	Monomer	T (°C)	[M] ₀ /[Zn] ₀ /[BnOH] ₀ ratio	[M] ₀ /[BnOH] ₀ ratio	Time ^a (h)	Yield (%)	M _n ^b /M _{th} ^c (kg/mol)	M _w /M _n (MWD)
1	<i>rac</i> -LA	145	200:1:50	4	12	98	11.95/0.68	1.19
2	<i>rac</i> -LA	145	200:1:10	20	15	98	35.09/2.99	1.22
3	<i>rac</i> -LA	145	200:1:7	30	16	99	50.02/4.22	1.21
4	<i>rac</i> -LA	145	200:1:5	40	18	97	63.57/5.87	1.28
5	L-LA	145	200:1:50	4	5	96	10.79/0.68	1.16
6	L-LA	145	200:1:10	20	6	98	34.75/2.99	1.29
7	L-LA	145	200:1:7	30	7	98	51.73/4.22	1.29
8	L-LA	145	200:1:5	40	8	99	64.87/5.87	1.25
9	CL	100	200:1:50	4	7	97	8.06/0.56	1.18
10	CL	100	200:1:10	20	8	96	20.19/2.39	1.22
11	CL	100	200:1:7	30	10	98	27.05/3.36	1.24
12	CL	100	200:1:5	40	12	98	34.27/4.67	1.25
13	VL	100	200:1:50	4	2	99	8.95/0.50	1.16
14	VL	100	200:1:10	20	3	97	28.78/2.11	1.25
15	VL	100	200:1:7	30	5	96	40.17/2.96	1.20
16	VL	100	200:1:5	40	6	97	53.04/4.11	1.21

^a Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed.^b Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n in the case of LA and CL polymerizations.^c Calculated from MW_{Monomer}·([M]₀/[BnOH]₀) + MW_{BnOH} at 100% conversion.

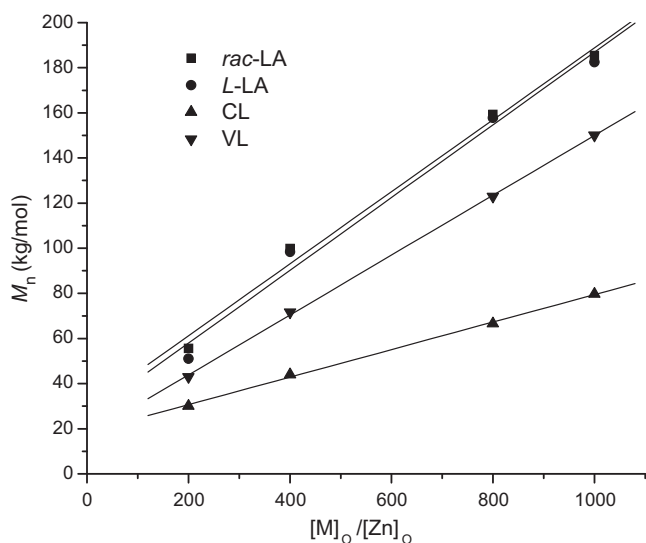


Fig. 1. Plot of M_n (vs polystyrene standards) vs $[M]_o/[Zn]_o$ for L-LA, *rac*-LA, CL and VL polymerization with $Zn(OAc)_2 \cdot 2H_2O$.

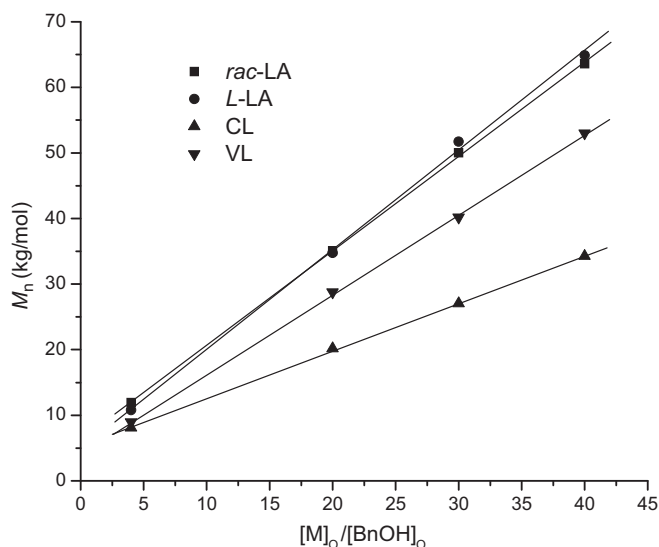


Fig. 2. Plot of M_n vs feed ratio of *rac*-LA, L-LA, CL, and VL to BnOH.

tiating groups [80]. Our results with hydrated iron and ruthenium chloride catalysts proved the reverse [73].

Various polymerizations were performed using L-LA, *rac*-LA, CL and VL independently with commercially available $Zn(OAc)_2 \cdot 2H_2O$ under different conditions of stoichiometry, temperature and in the presence of several alcohol initiators as indicated in Tables 1–3, respectively. These trials were performed under bulk conditions. Polymerization of L-LA and *rac*-LA, at room temperature in toluene, CL and VL under bulk condition yielded only low molecular weight oligomers after stirring for prolonged time periods.

Results from Table 1 reveals that there is a steady increase in the molecular weight (M_n) along with the increase in $[M]_o/[Zn]_o$ ratio at complete conversion. This is accompanied by a better control in these polymerizations as reflected by the MWDs. The variations of M_n with $[M]_o/[Zn]_o$ ratio are depicted in Fig. 1. The plots are linear indicating that there is a continual rise in M_n with an increase in $[M]_o/[Zn]_o$ ratio.

In the presence of an alcohol (Tables 2 and 3), for a given ($[M]_o/[Zn]_o$) ratio, reasonable degree of control was reflected in terms of lower MWDs and enhanced molecular weights (M_n) of the resulting polymers. In such cases the polymerization was found to proceed to completion faster, as reflected by the time. We have deliberately performed investigations with a primary alcohol (BnOH) and a secondary alcohol (*i*-PrOH). In both the cases the observations have been found similar and the reactivity of BnOH was found to be higher. This is because a primary alcohol is more nucleophilic in character, facilitating the acyl-oxygen bond cleavage. In the presence of different alcohols (Tables 2 and 3), the observed molecular weights (M_n) of the polymers were found to be higher in magnitude than those calculated. The theoretical molecular weights calculated are shown in Tables 1–4 and water taken into account as an initiator where no alcohol is used. Hence, it is reasonable to conclude that the rates of initiation and propagation are much more rapid than that of chain transfer. As a consequence, a better control over M_n is observed.

The dependence of molecular weight (M_n) upon varying the feed ratio of different monomers to BnOH as an initiator was examined with $Zn(OAc)_2 \cdot 2H_2O$ (Table 4 and Fig. 2). The molecular weight (M_n) increased almost linearly with increasing feed ratio of the respective monomers to BnOH.

In order to determine the tacticity of polylactide produced, we have performed homonuclear decoupling 1H NMR experiments for

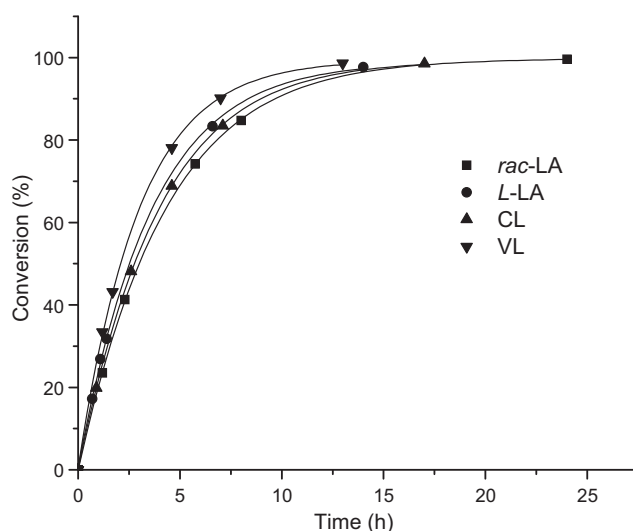


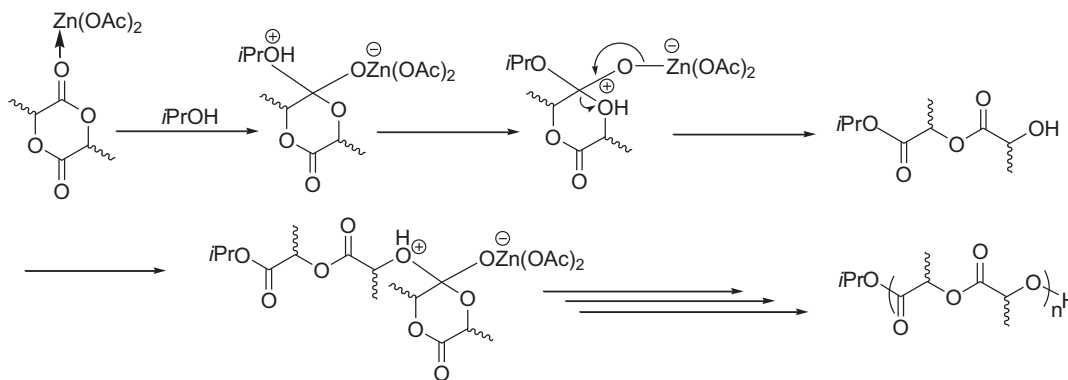
Fig. 3. *rac*-LA, L-LA, CL, and VL conversion vs time plot with $Zn(OAc)_2 \cdot 2H_2O$: $[M]_o/[Zn]_o = 200$.

polymer of *rac*-LA and L-LA. Homonuclear decoupling 1H NMR studies reveal that the polymerization of *rac*-LA using $Zn(OAc)_2 \cdot 2H_2O$ yields completely atactic polymer while with L-LA leads to isotactic polymer (see Supplementary data).

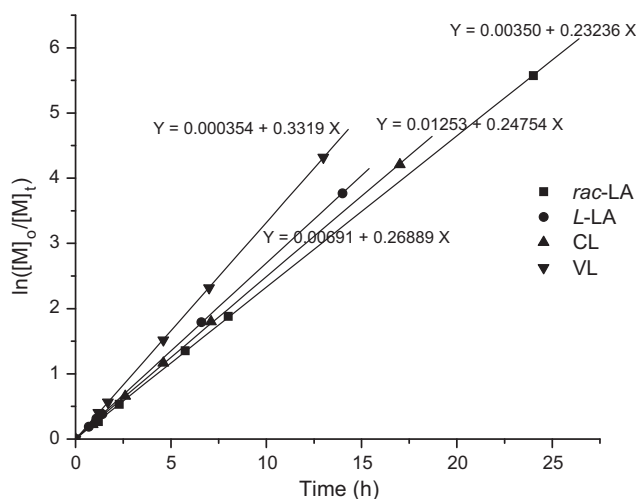
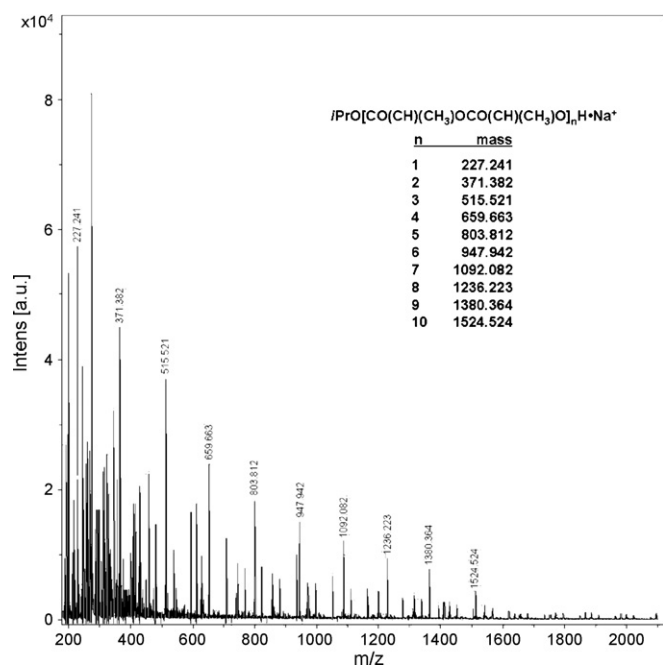
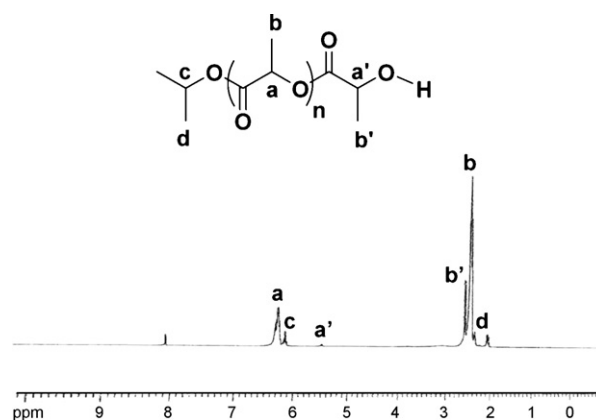
3.2. Kinetics of polymerization

Kinetic studies for the polymerization of *rac*-LA, L-LA, CL, and VL with $Zn(OAc)_2 \cdot 2H_2O$ in ratio $[M]_o/[Cat]_o = 200$ were performed (see Supplementary data). The results are shown in Fig. 3.

The plots suggest that at first there is a first-order dependence of rate of polymerization on monomer concentration. There is complete absence of induction period. The $\ln[M]_o/[M]_t$ vs time plots (Fig. 4) exhibit linear variation. From the slope of the plots, the values of the apparent rate constant (k_{app}) for *rac*-LA, L-LA, CL, and VL polymerizations initiated by $Zn(OAc)_2 \cdot 2H_2O$ were found to be $0.2323 h^{-1}$, $0.2688 h^{-1}$, $0.2475 h^{-1}$ and $0.3319 h^{-1}$, respectively. The k_{app} for L-LA and CL suggests that $Zn(OAc)_2 \cdot 2H_2O$ is less reactive than the literature precedents [62–64].



Scheme 1. Reaction pathway for LA polymerization.

Fig. 4. Semilogarithmic plots of *rac*-LA, L-LA, CL, and VL conversion in time initiated by Zn(OAc)₂·2H₂O: [M]₀/[Zn]₀ = 200.Fig. 5. MALDI-TOF spectrum of the crude product obtained from a reaction between *rac*-LA, Zn(OAc)₂·2H₂O and *i*-PrOH in 10:1:2 ratio at 145 °C.Fig. 6. ¹H NMR spectrum of the crude product obtained from a reaction between *rac*-LA, Zn(OAc)₂·2H₂O and *i*-PrOH in 10:1:2 ratio at 145 °C.

3.3. Mechanism of polymerization

For an understanding into the polymerization characteristics and final composition of the product, it was decided to investigate the polymerization of *rac*-LA more closely. Low molecular oligomers were synthesized by stirring *rac*-LA with Zn(OAc)₂·2H₂O and *i*-PrOH in 10:1:2 ratio at 145 °C. The polymerization was quenched with cold methanol and the residue recovered was subjected to MALDI-TOF and ¹H NMR spectroscopy. The major product of the composition is indicated in Figs. 5 and 6, respectively. This is an implication that *i*-PrOH has an active role as the initiator and the polymerization proceeds through the activated monomer mechanism [73–76]. No acetate peaks are seen in the ¹H NMR. The implication is that the coordination–insertion mechanism is absent. Based on MALDI-TOF and ¹H NMR spectroscopy evidences, our system prefers to proceed by the activated monomer mechanism as shown in Scheme 1. As per this mechanism, only one molecule of alcohol (or water in the absence of alcohol) is enough for this polymerization.

4. Conclusion

In summary, we have demonstrated that Zn(OAc)₂·2H₂O is a potent catalyst towards the ring-opening polymerization of cyclic esters and lactide. The propensity of polymerization was found to increase in the presence of alcoholic initiators resulting in the formation of telechelic polymers. The entire system contributes to an economical process employing readily available Zn(OAc)₂·2H₂O as catalyst and may be considered green, eco friendly and environmentally benign since zinc is a natural mammalian constituent and

these polymers being biodegradable. The achievement of obtaining good molecular weights without having to resort to elaborate ligands is a noted feature for our system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.10.013.

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