Copper acetate catalyzed bulk ring opening polymerization of lactides

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ABSTRACT

Cu(OAc)$_2$ was assessed to be a good catalyst for the bulk ring opening polymerization of lactides. These polymerizations are highly controlled leading to the formation of polymer with expected number average molecular weights and narrow molecular weight distribution. This method may be used to synthesize polymers with different end terminal groups. The over all process is green, since these polymers being biodegradable and the system is independent of solvents.

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1. Introduction

In the recent years, there has been a gradual decline in research involving polymer synthesis in the area of commodity polymers. This is as a result of depleting petrochemical feedstock which provides a rich source of different monomers or intermediates leading to the manufacture of such materials. Another important reason for this decline is the non degradable fate of these commodity polymers. The increase in environmental awareness has provided an active impetus in research leading to the synthesis of biodegradable polymers [1,2]. The need of the present times is to search for alternative polymeric materials that have a potential for biodegradation [3–7]. This has provided new avenues focusing upon research related to the polymerization of lactide which is the cyclic dimer of lactic acid made from annually renewable food resources like corn and sugar-beet through a biofermentation process [8,9]. This material has great significance in modern polymer research due to permeability, biocompatibility, biodegradability [10–12] and widespread use in biomedical and pharmaceutical research [13,14] such as synthesis of resorbable surgical sutures [15–18], production of drug delivery vehicles [17,18] and fabrication of artificial tissue matrices [19,20]. The material resulting from the polymerization of lactide has recently emerged as an alternative bulk commodity polymer, being an ecofriendly recyclable thermoplastic that is completely biodegradable [10,12,21–24].

Ring opening polymerization of lactide has emerged as an easy and convenient method for poly(lactide) synthesis. A plethora of different types of initiators are available today for the ring opening polymerization of lactide. Out of the several methods that have emerged, metal containing initiators have become increasing popular and their use is industrially wide spread [25–29]. The limiting use in biomedical application is dependent on the extent to which the metal residues are removable upon quenching the polymerization. Since this parameter can never reach zero, a preferred and feasible industrial process would employ metals in which the residues are not cytotoxic. It is reasonable to use environmentally benign metals that are constituent of the mammalian anatomy, so that the metal residues remain potentially harmless [30].

The coordination–insertion mechanism [3,26,31–49] is the most preferred route to ring opening polymerization since it generally is able to produce high polymers with good number average molecular weights and narrow molecular weight distribution. Latest results from our group include thorough investigations of the cationic mechanism of ring opening polymerization. We have developed a method in which the cyclic ester or lactide monomers are activated by simple Lewis acids followed by ring opening step that is assisted by simple nucleophiles such as alcohols and water. Reasonable control was seen in such a method of polymerization. The summary of the results indicates that elaborate ligands on the metal initiator are not a mandatory feature to enable ring opening polymerization. The feature that is required is the presence of suitable initiating groups on the metal center that facilitates the cleavage of the acyl–oxygen bond present in the monomer [50–54]. The ligand controls the nuclearity of the metal initiator which has a profound influence on the chain growth step of the propagation

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Table 1
Results of *rac*-LA and *L*-LA with anhydrous Cu(OAc)$_2$ at 145 °C.

Entry	Monomer	[LA]$_o$/[Cu]$_o$	Time (h)[a]	Yield (%)	M_n[b]/M_{th}[c] (kg/mol)	M_w[b] (kg/mol)	M_w/M_n
1	*rac*-LA	200	28	96	28.99/28.84	30.15	1.04
2	*rac*-LA	400	33	96	57.92/57.67	61.98	1.07
3	*rac*-LA	800	37	97	108.51/115.33	117.20	1.08
4	*rac*-LA	1000	44	98	146.76/144.15	155.57	1.06
5	*L*-LA	200	24	96	28.87/28.84	31.18	1.08
6	*L*-LA	400	30	96	57.66/57.67	61.70	1.07
7	*L*-LA	800	36	97	116.10/115.33	120.75	1.04
8	*L*-LA	1000	42	98	147.83/144.15	156.70	1.06

[a] Time of polymerization measured by quenching the polymerization reaction when all LA was found consumed.
[b] Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark–Houwink corrections for M_n.
[c] Calculated from MW$_{LA}$([LA]$_o$/[Cu]$_o$) at 100% conversion.

Table 2
Results of *rac*-LA and *L*-LA polymerization with anhydrous Cu(OAc)$_2$ in the presence of water at 145 °C.

Entry	Monomer	[LA]$_o$/[Cu]$_o$/[H$_2$O]$_o$	[LA]$_o$/[H$_2$O]$_o$	Time (h)[a]	Yield (%)	M_n[b]/M_{th}[c] (kg/mol)	M_w[b] (kg/mol)	M_w/M_n
1	*rac*-LA	200:1:50	4	16	97	0.67/0.59	0.73	1.08
2	*rac*-LA	200:1:10	20	18	97	3.01/2.90	3.23	1.07
3	*rac*-LA	200:1:7	30	20	98	4.80/4.34	5.09	1.06
4	*rac*-LA	200:1:5	40	23	98	5.94/5.78	6.18	1.04
5	*L*-LA	200:1:50	4	9	97	0.69/0.59	0.72	1.04
6	*L*-LA	200:1:10	20	13	97	3.12/2.90	3.37	1.08
7	*L*-LA	200:1:7	30	16	97	4.60/4.34	4.88	1.06
8	*L*-LA	200:1:5	40	19	98	5.87/5.78	6.15	1.04

[a] Time of polymerization measured by quenching the polymerization reaction when all LA was found consumed.
[b] Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark–Houwink corrections for M_n.
[c] Calculated from MW$_{LA}$([LA]$_o$/[H$_2$O]$_o$) + MW$_{water}$ at 100% conversion.

Table 3
Results of *rac*-LA and *L*-LA polymerization with anhydrous Cu(OAc)$_2$ in the presence of *i*-PrOH at 145 °C.

Entry	Monomer	[LA]$_o$/[Cu]$_o$/[*i*-PrOH]$_o$	[LA]$_o$/[*i*-PrOH]$_o$	Time (h)[a]	Yield (%)	M_n[b]/M_{th}[c] (kg/mol)	M_w[b] (kg/mol)	M_w/M_n
1	*rac*-LA	200:1:50	4	15	97	0.78/0.64	0.83	1.06
2	*rac*-LA	200:1:10	20	17	97	3.57/2.94	3.86	1.08
3	*rac*-LA	200:1:7	30	19	99	4.84/4.38	5.14	1.06
4	*rac*-LA	200:1:5	40	22	96	6.76/5.82	7.31	1.08
5	*L*-LA	200:1:50	4	8	97	0.80/0.63	0.87	1.08
6	*L*-LA	200:1:10	20	12	97	3.40/2.94	3.64	1.07
7	*L*-LA	200:1:7	30	15	99	4.99/4.38	5.34	1.07
8	*L*-LA	200:1:5	40	18	98	6.18/5.82	6.68	1.08

[a] Time of polymerization measured by quenching the polymerization reaction when all LA was found consumed.
[b] Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark–Houwink corrections for M_n.
[c] Calculated from MW$_{LA}$([LA]$_o$/[*i*-PrOH]$_o$) + MW$_{i\text{-PrOH}}$ at 100% conversion.

cycle [55,56]. Our current focus includes the relationship between ligand stereochemistry and polymer tacticity.

It is known that copper complexes exhibit a plethora of useful properties that include high electron transfer ability, moderate Lewis acidity and stability associated with reactive intermediates. These properties make this elements a suitable candidate for indepth investigations. Copper is a biocompatible metal (>5 mg per kg body weight is toxic to human being and daily intake does not exceed 10 mg per day, higher levels of copper causes Wilson disease) assisting the existence of life and to the best of our knowledge there have been few reports on copper initiators containing ligand backbone. These include copper complexes derived from phenoxy-ketimine [57], salicylaldimine [58], and salen ligands [59]. These complexes are active towards polymerization of lactides and produce polymer with moderate number average molecular weights and narrow molecular weight distribution. Literature report for *L*-LA polymerization with 200:1 ratio using copper phenoxy-ketimine complex at 160 °C, M_w = 2.2 kg/mol and M_w/M_n = 1.09 reflects the formation of low molecular weight polymers [57]. There have been no systematic studies with simple salts like copper acetate. Polymerization with other benign metals such as bismuth [60] and zinc acetates [53] has been reported recently. The main aim of our studies is to ascertain the extent to which our simple initiator system i.e. copper acetate is successful in ring opening polymerization of lactides along with a thorough understanding of the polymerization pathway.

2. Experimental

2.1. Materials

rac-Lactide (*rac*-LA) and *L*-lactide (*L*-LA) were purchased from Aldrich and sublimed fresh prior to use and stored in a glove box. Isopropanol (*i*-PrOH) used in the study was purchased from Ranchem India, dried using appropriate procedure and distilled fresh prior to use. CDCl$_3$ used for NMR spectral measurements was purchased from Aldrich. THF (HPLC grade) for GPC measurements was purchased from Ranchem India. Cu(OAc)$_2$ (anhydrous) was purchased from Aldrich, stored in a glove box and used as received.

2.2. Instrumentation and characterization

^{1}H NMR was recorded with a Brüker Avance 400 MHz instrument. MALDI-TOF measurements were carried out using a Brüker Daltonics instrument in dihydroxy benzoic acid matrix. A GPC
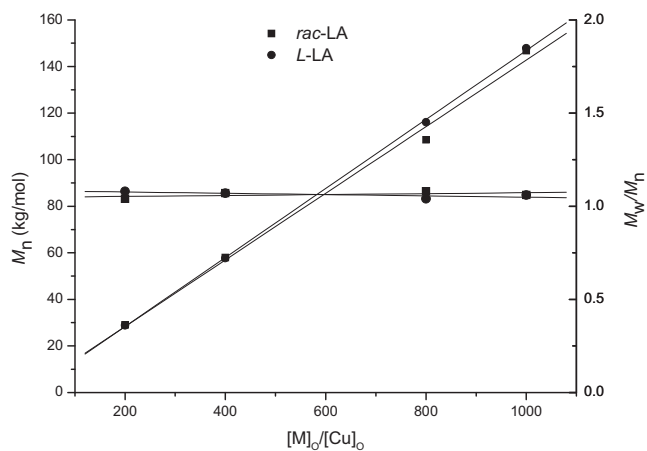
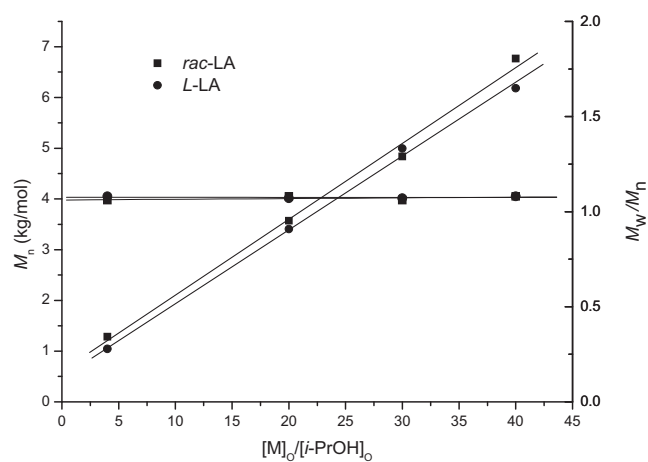**Fig. 1.** Plot of M_n and MWD's vs $[LA]_o/[Cu]_o$ ratio for *rac*-LA and *L*-LA.

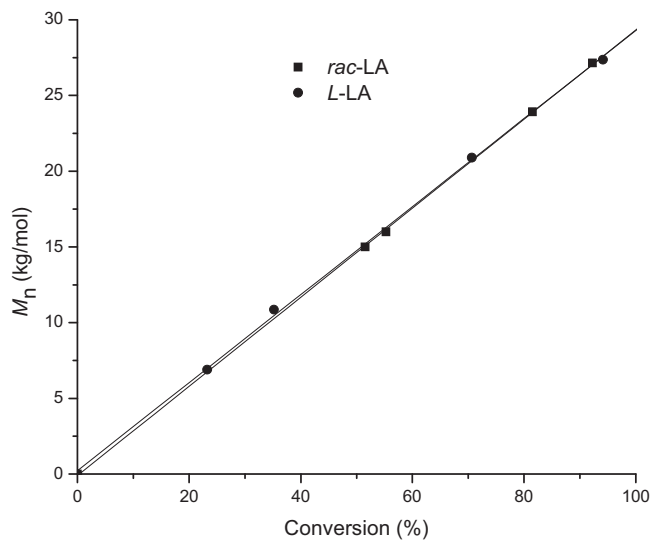**Fig. 4.** Plot of M_n and MWD vs feed ratio of *rac*-LA and *L*-LA to *i*-PrOH.

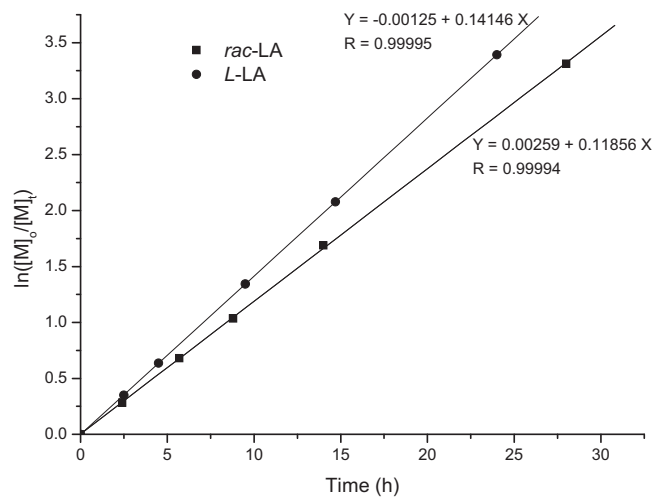**Fig. 2.** Plot of M_n vs conversion for *rac*-LA and *L*-LA.

Fig. 5. Semilogarithmic plots of *rac*-LA and *L*-LA conversion in time catalyzed by Cu(OAc)$_2$: $[LA]_o/[Cu]_o = 200$.
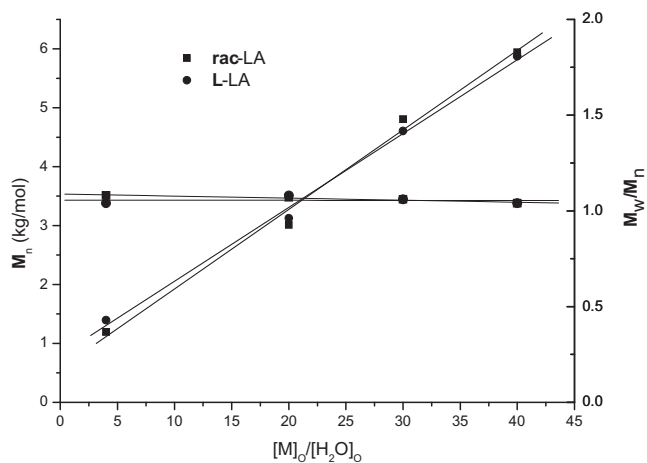

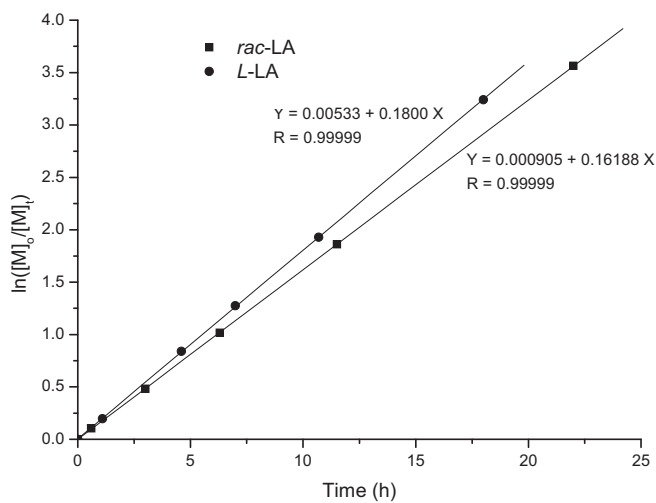**Fig. 3.** Plot of M_n and MWD vs feed ratio of *rac*-LA and *L*-LA to water.

Fig. 6. Semilogarithmic plots of *rac*-LA and *L*-LA conversion in time catalyzed by Cu(OAc)$_2$ in the presence of *i*-PrOH: $[LA]_o/[Cu]_o/[i$-PrOH$] = 200/1/5$.
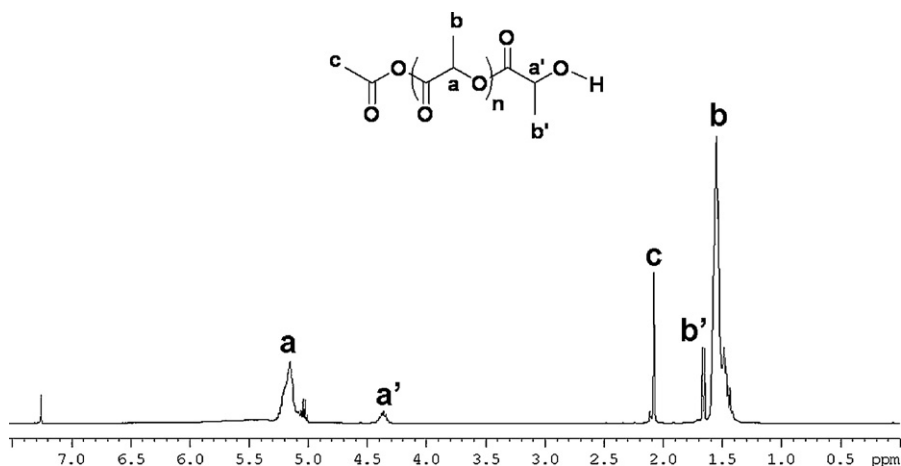
Fig. 7. ^{1}H NMR spectrum of the residue obtained from a reaction between *rac*-LA and anhydrous Cu(OAc)$_2$ in 10:1 ratio at 145 °C.

instrument with Waters 510 pump and Waters 410 differential refractometer as the detector was used to determine the molecular weight and molecular weight distribution of the resulting polymer samples. The columns namely WATERS STRYGEL-HR3, STRYGEL-HR4 and STRYGEL-HR5 each of dimensions (7.8 mm × 300 mm)

were connected in series. Measurement of number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) (MWD) of the resulting polymer samples were done in THF at 27 °C relative to polystyrene standards and were corrected according to Mark–Houwink corrections [61].
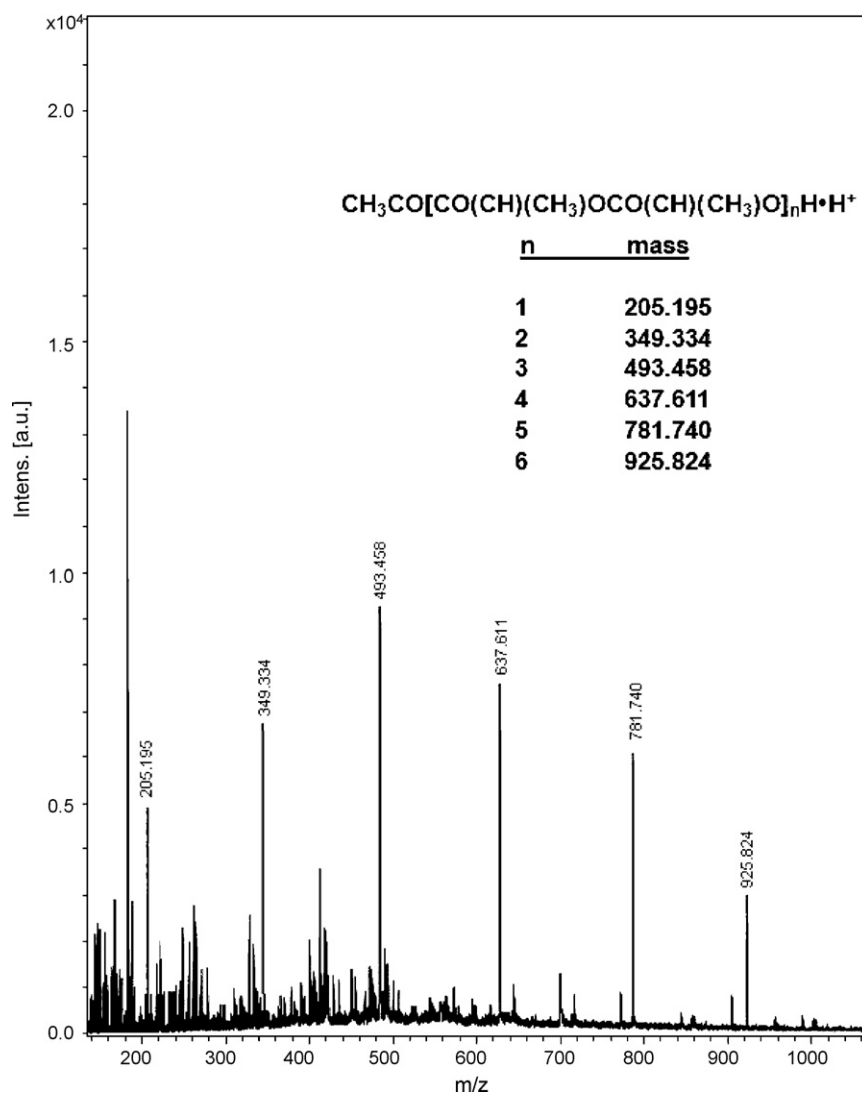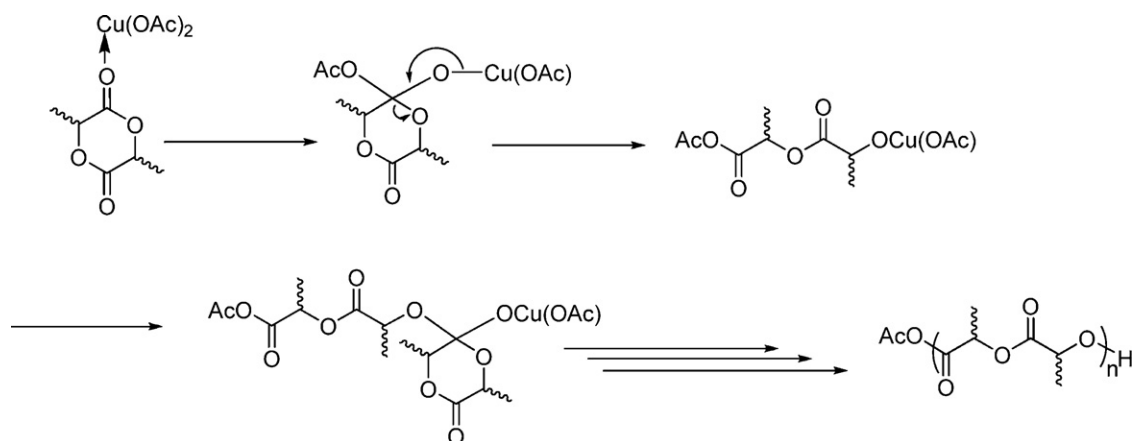

Fig. 8. MALDI-TOF spectrum of the residue obtained from a reaction between *rac*-LA and anhydrous Cu(OAc)$_2$ in 10:1 ratio at 145 °C.

Scheme 1. Coordination–insertion mechanism of lactide polymerization.

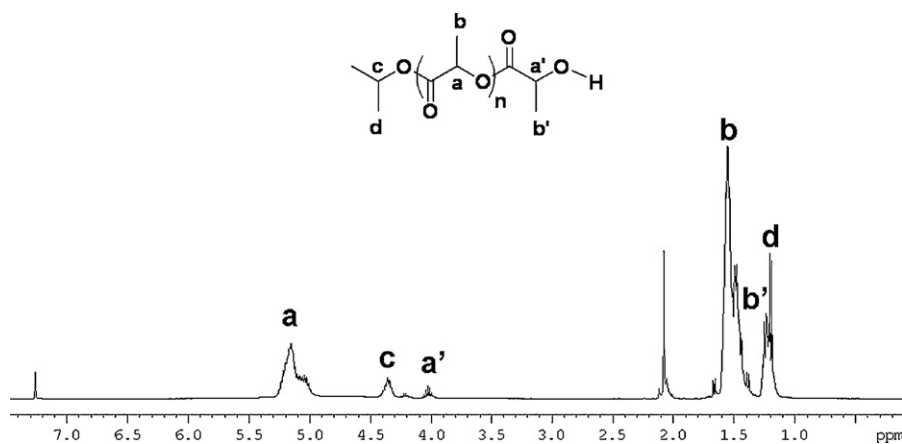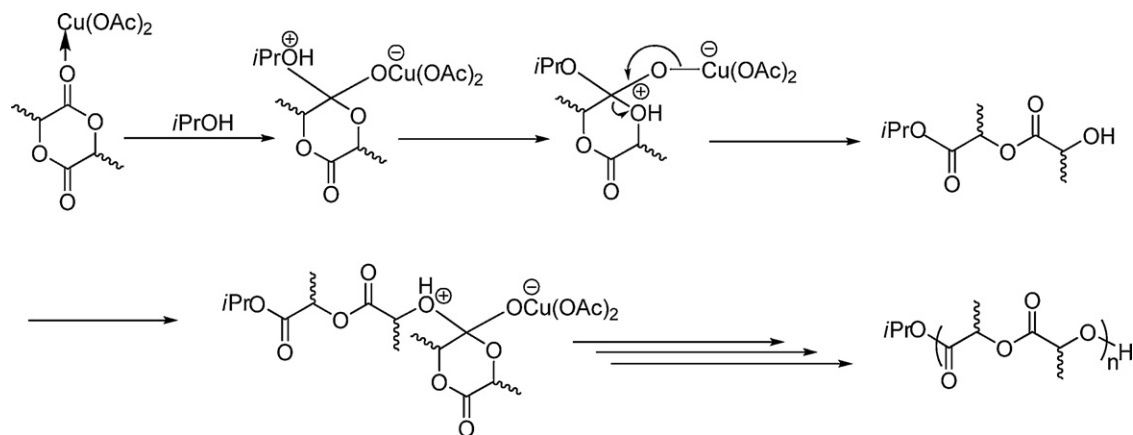**Fig. 9.** ^{1}H NMR spectrum of the residue obtained from a reaction between *rac*-LA and anhydrous Cu(OAc)$_2$ in the presence of *i*-PrOH in 10:1:2 ratio at 145 °C.

Scheme 2. Activated monomer mechanism of lactide polymerization.

2.3. Typical procedure for bulk polymerization of L-LA or rac-LA (200:1)/(200:1:5)

For *rac*-LA or *L*-LA polymerization, 17.34 μmol of copper acetate and 0.5 g (3.47 mmols) of *rac*-LA or *L*-LA or along with requisite amount of *i*-PrOH (87.7 μmol) were taken in a flask under a nitrogen atmosphere in a sealed tube. The contents were heated to 145 °C neat. The mixture was melted and rapidly stirred at the given temperature. A rise in viscosity was observed and finally the stirring ceased. The polymerizations were quenched by pouring the contents into cold methanol. The polymer was isolated by subsequent filtration and dried till a constant weight was attained.

3. Results and discussion

3.1. Studies on polymerization activity and characteristics

As mentioned earlier, metal acetates of environmentally benign metals [53,60] have been used catalytically for the polymerization of cyclic esters and lactide. A variety of bulk polymerization trials
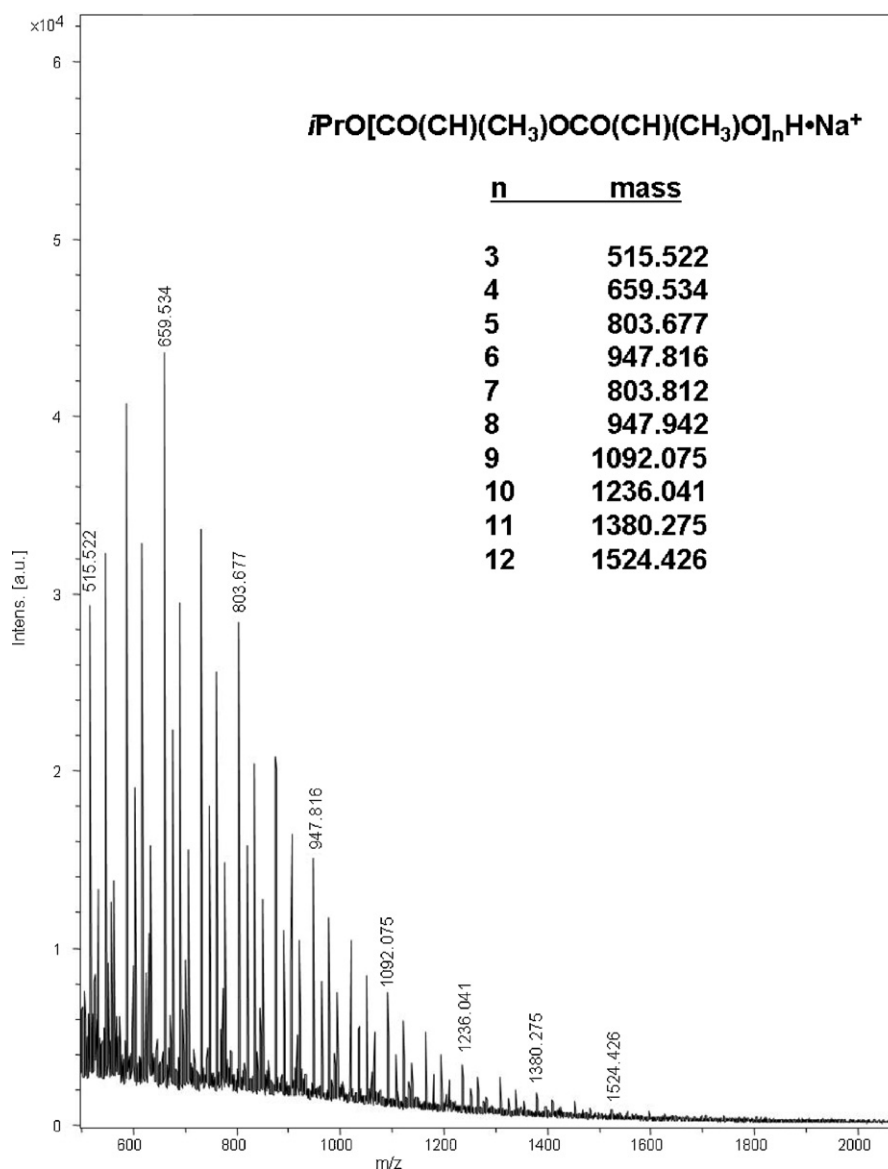
Fig. 10. MALDI-TOF spectrum of the residue obtained from a reaction between *rac*-LA and anhydrous Cu(OAc)$_2$ in the presence of *i*-PrOH in 10:1:2 ratio at 145 °C.

were performed with *rac*-LA and *L*-LA with anhydrous Cu(OAc)$_2$ under different stoichiometric ratios at 145 °C. The results are summarized in Table 1.

These results indicate that the bulk polymerization of lactide is highly controlled leading to the formation of polymer whose M_n is in close proximity to the theoretical molecular weight. Again the values of MWDs for various trials prove that this polymerization system possesses a great degree of control. The variations of M_n and MWDs with [LA]$_o$/[Cu]$_o$ for *rac*-LA and *L*-LA are depicted in Fig. 1. These plots are linear suggesting that there is a steady increase of M_n with the increase in [LA]$_o$/[Cu]$_o$. The MWDs remain almost invariant to changes in the [LA]$_o$/[Cu]$_o$ ratio. The plot of M_n vs conversion (Fig. 2) for [LA]$_o$/[Cu]$_o$ = 200 exhibits linear variations, authenticating a great degree of control in our system. Aliquots of the polymerization reaction were systematically quenched and subjected to ^{1}H NMR to determine the conversion.

With the initial results being impressive, we decided to study this polymerization system very closely. Previous results from our research group indicate that simple metal catalysts coordinated to suitable initiators (like alcohols and water) are able to facilitate the cleavage of the acyl–oxygen bond of the monomer [50–54].

Hence the polymerization continues in a very effective manner. We decided to study our polymerization system in the presence of water and *i*-PrOH as suitable initiators. The results are depicted in Tables 2 and 3 respectively.

Analysis of the results depicted in Tables 2 and 3 indicate that the polymerization is highly controlled and the observed M_n are in very close proximity to the calculated values. The MWDs recur in a narrow range. These conclusions indicate very clearly that the polymerization system leans towards a living character. To facilitate our conclusions, the polymerization conditions represented by entries 1 and 5 of Tables 1–3 were repeated and more monomer was added when the stirring ceased. We were pleased to observe continued polymerization and the polymer obtained from such studies were found to yield M_n and MWDs in close proximity to those indicated.

The dependence of M_n and MWD on the feed ratio of *rac*-LA and *L*-LA to water or *i*-PrOH as initiators was studied with Cu(OAc)$_2$. The results (Figs. 3 and 4) show that M_n increases almost linearly with the increase in feed ratio of the monomers and the dependence of MWDs is almost invariant.

Our polymerization results are much superior than those reported for copper complexes with elaborate ligands [57–59].

Literature report for the melt polymerization of *L*-LA with 200:1 ratio using three different copper phenoxy-ketimine complexes at 160 °C found to be, $M_w = 2.2$ kg/mol and $M_w/M_n = 1.09$, $M_w = 4.5$ kg/mol and $M_w/M_n = 1.43$ and $M_w = 6.5$ kg/mol and $M_w/M_n = 1.29$ [57], suggests our results are superior in terms of M_n and M_w/M_n (entry 5, Table 1). Low molecular weight oligomers are formed with silver acetate as catalyst under identical conditions for *rac*-LA and *L*-LA melt polymerization. To study the effect on the polymerization of lactides by changing the anion of the copper salt, we have used $CuBr_2$. For *rac*-LA, $M_n = 31.15$ kg/mol, $M_w/M_n = 1.08$ and $t = 48$ h; For *L*-LA, $M_n = 32.25$ kg/mol, $M_w/M_n = 1.06$ and $t = 46$ h. These results suggests that change over from acetate ion to bromide ion on the copper, polymerization activity became sluggish and M_n, M_w/M_n are found to be similar. Homonuclear decoupling ^{1}H NMR studies were taken up to ascertain the tacticity of these polymer samples. The studies reveal that the polymerization of *rac*-LA catalyzed by $Cu(OAc)_2$ yields completely atactic polymer while isotactic polymer is obtained from *L*-LA. DSC and ^{13}C NMR analysis confirms the isotacticity of PLLA.

3.2. Kinetics of polymerization

We have performed kinetic studies for the polymerization of *rac*-LA and *L*-LA using $Cu(OAc)_2$ as catalyst in the ratio $[LA]_o/[Cu]_o = 200$. In addition similar studies were done in the presence of an initiator like *i*-PrOH in the ratio $[LA]_o/[Cu]_o/[i\text{-}PrOH]_o = 200/1/5$. The results are depicted in Figs. 5 and 6 respectively.

These plots imply that the polymerization reaction obeys first order kinetics. There is complete absence of induction period. The $\ln[M]_o/[M]_t$ vs time plots are linear. The values of the apparent rate constant (k_{app}) may be calculated from the slope of these plots. The value of k_{app} for *rac*-LA and *L*-LA polymerization in the absence of initiator was found to be 0.11856 h^{-1} and 0.14146 h^{-1}. In the presence of *i*-PrOH, k_{app} for *rac*-LA and *L*-LA polymerization was 0.16188 h^{-1} and 0.1800 h^{-1} respectively. These results imply that these polymerizations are faster in the presence of *i*-PrOH.

3.3. Mechanism of polymerization

The various efforts made to study the ring opening polymerization of *L*-LA and *rac*-LA with anhydrous $Cu(OAc)_2$ suggest two limiting cases. Those are polymerization with anhydrous $Cu(OAc)_2$ alone and polymerization in the presence of initiators like water or *i*-PrOH. Accordingly low molecular oligomers were prepared by reacting *rac*-LA with anhydrous $Cu(OAc)_2$ in 10:1 stoichiometric ratio and reacting *rac*-LA with anhydrous $Cu(OAc)_2$ in the presence of *i*-PrOH 10:1:2 ratio. They were quenched in cold methanol and these low molecular weight oligomers were thoroughly characterized using ^{1}H NMR and MALDI-TOF. Analysis of the low molecular weight oligomers (Figs. 7 and 8) obtained by reacting *rac*-LA with anhydrous $Cu(OAc)_2$ shows the formation of polymer with acetate group as one of the end terminal groups.

On the basis of these data it is clear that under the conditions mentioned, the polymerization proceeds by the coordination–insertion mechanism as outlined in Scheme 1.

Again, analysis of the low molecular weight oligomers (Figs. 9 and 10) obtained by reacting *rac*-LA with anhydrous $Cu(OAc)_2$ in the presence of *i*-PrOH shows the formation of polymer with *i*-PrO as one of the end terminal groups. Similar results were observed in case of anhydrous $CuBr_2$. In order to ascertain the effect of *i*-PrOH, controlled experiments were carried out under identical conditions for *rac*-LA and *L*-LA in the absence of $Cu(OAc)_2$. For *rac*-LA, $M_n = 1.16$ kg/mol, $M_w/M_n = 1.07$ and $t = 30$ h; for *L*-LA, $M_n = 1.35$ kg/mol, $M_w/M_n = 1.08$ and $t = 25$ h. These results suggests that under the absence of $Cu(OAc)_2$, polymerization

activity became sluggish and low M_n compared to the presence of $Cu(OAc)_2$ (entries 4 and 8, Table 3). These implies that $Cu(OAc)_2$ is mandatory to activate the monomer.

It is apparent from these figures that the polymerization proceeds with the activated monomer mechanism as shown in Scheme 2. Peaks corresponding to the presence of polymer with acetate end terminal group are also seen. These observations imply that given a choice, the system has a natural tendency to proceed with both the activated monomer mechanism and coordination–insertion mechanism. In order to rule out the possibility of ligand exchange on the copper, 1:2 ratio reaction between $Cu(OAc)_2$ and *i*-PrOH at 145 °C performed over 24 h. After work up of the reaction mixture, ^{1}H NMR analysis confirms the absence of ligand exchange on the copper.

According to this mechanism, only one molecule of a suitable initiator is enough for such a mechanism of polymerization to exist. Again, it is important to disclose that the MALDI-TOF spectra (Figs. 8 and 10) show the presence of extensive transesterification. This may be interpreted to show that this polymerization system is not truly living [62].

4. Conclusion

In summary, $Cu(OAc)_2$ is a potent catalyst for the polymerization of *rac*-LA and *L*-LA. If given a choice, the polymerization has a spontaneous tendency to adopt the activated monomer mechanism. The overall system is green, since these polymers being biodegradable and the system is independent of solvents. The achievement of good control over the polymerization process without having to resort to elaborate ligands is a noted feature of this work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.08.024.

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