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Copper acetate catalyzed bulk ring opening polymerization of lactides

Ravikumar R. Gowda, Debashis Chakraborty*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, Tamil Nadu, India

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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.

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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* Corresponding author. Tel.: +91 44 22574223; fax: +91 44 22574202.
E-mail address: dchakraborty@iitm.ac.in (D. Chakraborty).

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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	$[LA]_o/[Cu]_o/[H_2O]_o$	$[LA]_o/[H_2O]_o$	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 $MW_{LA}([LA]_o/[H_2O]_o) + MW_{water}$ 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	$[LA]_o/[Cu]_o/[i\text{-PrOH}]_o$	$[LA]_o/[i\text{-PrOH}]_o$	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 $MW_{LA}([LA]_o/[i\text{-PrOH}]_o) + MW_{i\text{-PrOH}}$ 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

^1H 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