

Ring Opening Polymerization of Polylactide using Dibutyltindimethoxide as an initiator and Triphenylphosphine as co-initiator

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Abstract: Dibutyltindimethoxide with Triphenylphosphine is found to be efficient initiators for ring opening polymerization of polylactide. The polymerization in case of dibutyltindimethoxide/ triphenylphosphine was carried out at 130°C for 40 hr. The monomer has been recrystallized 3 times with dry toluene to remove the meso compounds, which absorb moisture and affect polymerization reaction. Monomer to initiator ratio is having a very significant role in polymerization reactions and its value ranges from 500-5000. The monomer conversion calculated by FTIR analysis of reaction product indicates that polylactide has been formed. The average molecular weight has been calculated by using Gel permeation chromatography.

Index Terms: Ring opening polymerization, Polylactide, lactide, Dibutyltindimethoxide, triphenylphosphine

II. INTRODUCTION

PLA can be prepared by two different methods- by polycondensation of hydroxyl-carboxylic acids or, by ring-opening polymerization (ROP) of cyclic esters. The ROP can be performed either as a bulk polymerization, or in solution, emulsion or dispersion (Sosnowski *et al.*, 1996 and Gadzinowski *et al.*, 1996). An initiator is necessary to start the polymerization. Under rather mild conditions, high molecular weight aliphatic polyesters of low polydispersity can be prepared in short periods of time. The polycondensation technique is less expensive than ROP, but it is difficult to obtain high molecular weight polylactide to achieve specific end groups. Problems associated with condensation polymerization, such as the need for exact stoichiometry, high reaction temperatures and the removal of low molecular weight by products (e.g. water) are excluded in ROP (Brode *et al.*, 1972).

The mechanism of polymerization depends on the type of initiator. Three major reaction mechanisms are cationic, anionic, and coordination-insertion. However, high molecular weight polyesters have only been obtained by using anionic or coordination-insertion ring-opening polymerization.

Kricheldorf *et al.* (2000) observed the formation of octanoic acid when tin (II) 2-ethylhexanoate was heated above 100 °C. The acid, thus liberated, may bring about the esterification of alcohol (active hydrogen co-initiator) leading to the formation of water, which may react with Sn(Oct)₂ to form stannoxanes and tin hydroxides. Under such conditions, it would be difficult to control the molecular mass and side reactions because the presence of water or other hydroxyl compounds is likely to initiate polymerization. The relative reactivity of different metal alkoxide initiators for transesterification reaction depends on the metal and is lowest for aluminum alkoxides. The following order has been observed: $Bu_2Sn(OR)_2 > Bu_3SnOR > Ti(OR)_4 > Zn(OR)_2 > Al(OR)_3$

Stannous octoate has been the most widely used initiator because of high reaction rates, the solubility in the monomer melt and the ability to produce high molecular weight polylactide (Swift 1993, Schwach *et al.*, 1994, Cabaret *et al.*, 2004). The addition of an equimolar amount of Lewis base, particularly triphenylphosphine into 2-ethylhexanoic acid, significantly enhances the lactide polymerization rate in bulk. Triphenylphosphine has two beneficial effects: it increases the polymerization rate and delays the occurrence of the undesirable back biting reactions at monomer/initiator ratios greater or equal to 5000 (Degee *et al.*, 1999).

Bu₃SnOMe and Bu₂Sn(OMe)₂ are effective transesterification catalysts and cause 'back-biting' degradation even at 90 °C. In all series of polymerizations initiated with tin methoxides two tendencies are detectable: increasing randomization of the stereosequence with increasing reaction time and with higher reaction temperatures. In contrast, Sn(II) octoate does not cause transesterification at ≤ 120°C and even at

180°C randomization of the stereosequences is slow (Kricheldorf *et al.*, 1992). Initiators with higher nucleophilicity are required to initiate lactide and weaker bases such as zinc stearate, potassium phenoxide, and potassium benzoate initiate only at higher temperatures (120°C). Initiations at high temperature are in bulk but accompanied by racemization and other side reaction which are obstacle to propagation (Kricheldorf and Saunders, 1990, Kricheldorf and Boettcher, 1993, Kricheldorf and Serra, 1985 and Kleine and Kleine, 1959).

III. EXPERIMENTAL

3.1 Material

L-Lactide was purchased from Sigma Aldrich and was used as received. Dibutyltindimethoxide was purchased from Sigma Aldrich. Chloroform, acetone and methanol were purchased from Ranbaxy Ltd.

3.2 Synthesis of PLA with Dibutyltindimethoxide

Synthesis of PLA has successfully been carried out using Dibutyltindimethoxide as an initiator under two different environments: inert atmosphere and vacuum.

- (i) Under inert atmosphere, and
- (ii) Under vacuum

3.2.1 Polymerization Under Inert Atmosphere

Number of experiments were carried out over a wide range of monomer to initiator ratios (500 to 5000). The monomer and initiator were vigorously mixed in a four-necked round bottom flask equipped with a teflon stirrbar. The reactants were maintained at a constant temperature of 130 (\pm 1) °C by putting flask in an oil bath. One neck of the glass reactor was used for applying vacuum with a vacuum pump. Nitrogen gas was applied through drylite to the other side neck of glass reactor. Vacuum was applied at the start of reaction and dry nitrogen gas was allowed to pass through the reaction mixture throughout the course of the reaction. The third neck of the glass reactor was used to vent nitrogen gas. The maximum polymerization time was 40 hr. The products obtained were dissolved in chloroform and precipitated in methanol. These were dried in a vacuum dessicator for 24 to 30 hr.

3.2.2 Polymerization Under Vacuum

Dibutyltindimethoxide (initiator) was used for the synthesis of polylactide under vacuum. The recrystallized monomer and initiator were dispersed in diethylether and after proper dispersion, the solvent was evaporated using a rotaevaporator. The resultant mixture was equally distributed among five different reagent bottles, and vacuum was applied at the start of reaction. Reagent bottles were thermostated in an oil bath at 130 (\pm 1) °C. The monomer to initiator (M_0/I_0) ratio 2549 was used for polymerization because it has been observed from the previous polymerization (Table 1) that maximum molecular weight was produced at this range of monomer to initiator. The maximum polymerization time was 103 hr. The products obtained were dissolved in chloroform, precipitated in methanol and were dried in a vacuum dessicator for 24 to 30 hr.

3.3 Synthesis of PLA with Dibutyltindimethoxide/Triphenylphosphine

Triphenylphosphine as co-initiator with dibutyltindimethoxide as an initiator was used for the synthesis of PLA under two different environments: inert atmosphere and vacuum.

- (i) Under inert atmosphere, and
- (ii) Under vacuum

3.3.1 Polymerization under Inert Atmosphere

Synthesis of PLA was carried out with dibutyltindimethoxide (as an initiator) and triphenylphosphine (co-initiator) in equimolar proportion were used over a wide range of monomer to initiator ratios (518 to 5085) under nitrogen atmosphere at 130 (\pm 1) °C. The maximum polymerization time was 38 hr.

3.3.2 Polymerization Under Vacuum

Dibutyltindimethoxide as an initiator and triphenylphosphine as co-initiator in equimolar proportion were used for the synthesis of polylactide under vacuum only at 130 (\pm 1) °C. The monomer to initiator ratio (M_0/I_0 ratio) 2572 was used during polymerization. The maximum polymerization time was 55 hr.

IV. RESULTS AND DISCUSSION

4.1 Synthesis of Polylactide, PLA using Dibutyltindimethoxide with/without Triphenylphosphine

4.1.1 Synthesis of PLA with Dibutyltindimethoxide

Low molecular weight of PLA was obtained during polymerization. The reason might be due to the fact that Bu_3SnOMe and $Bu_2Sn(OMe)_2$ are effective transesterification catalysts and cause 'back-biting' degradation even at 90°C. In all series of polymerizations initiated with tin methoxides two tendencies are detectable: increasing randomization of the stereosequence with increasing reaction time and with higher reaction temperatures (Kricheldorf *et al.*, 1991).

Table 1 lists the values of M_n , M_w and PD of PLA synthesized with dibutyltindimethoxide at different M_0/I_0 ratios and reaction time under inert atmosphere and vacuum.

Table 1 Synthesis of PLA with dibutyltindimethoxide (initiator) at 130 (\pm 1) °C under inert atmosphere and vacuum

M_0/I_0 ratio	Polymerization time (hr)	M_n	M_w	PD
Under Inert Atmosphere				
1040	11.5	2921	3459	1.18
	16.75	3360	4300	1.28
	23.5	3759	4928	1.31
	28.75	4412	5838	1.32
	34.5	3504	4988	1.42
2555	10.92	3662	4300	1.17
	13.42	3637	4506	1.23
	16.42	3978	4962	1.24
	18.42	4229	5582	1.32
	39.66	4461	7896	1.77
Under Vacuum				
2573	16.5	3383, 210	3539, 416	1.04, 1.98
	32.5	290	1083	3.73
	58.33	393	1352	3.44
	80.33	415	1688	4.07
	102.33	2106	3166	1.50

The maximum molecular weight ($M_n = 4561$) was observed in monomer to initiator ratio (M_0/I_0 ratio) 2555. The reason for low molecular weight of polylactide obtained with dibutyltindimethoxide is only due to the occurrence of transesterification reaction. The maximum molecular weight ($M_n = 3383$) of polylactide with narrow value of polydispersity (PD = 1.04) was observed in monomer to initiator ratio (M_0/I_0 ratio) 2573.

4.1.2 Synthesis of PLA with Dibutyltindimethoxide with Triphenylphosphine

Table 2 lists the values of M_n , M_w and PD for PLA synthesized with dibutyltindimethoxide/triphenylphosphine at 130 (\pm 1) °C at different reaction time under inert atmosphere and vacuum.

Table 2 Synthesis of PLA with dibutyltindimethoxide/ triphenylphosphine at 130 (\pm 1) °C under inert atmosphere and vacuum

M_0/I_0 ratio	Polymerization time (hr)	M_n	M_w	PD
Under Inert Atmosphere				
518	8	2318	2826	1.21
	17.08	2662	3496	1.31
	18.75	2845	3777	1.32
	36.25	3326	5602	1.68
1061	10.25	2594	4649	1.79
	15.25	2240	2688	1.19
	20	2515	3081	1.22
	31.5	2913	3870	1.32
	37.25	3115	4186	1.34
1073	33	6828	9387	1.37
2564	7.33	5962	7788	1.30
	11	6222	8969	1.44
	28	6923	10825	1.56
5085	20	2455	2986	1.21
	26.33	3876	4718	1.21
	30.16	2843	3763	1.32
	33.75	2944	3993	1.35
	36.08	3098	4273	1.37
Under Vacuum				
2572	22.50	6722	10155	1.51
	32.50	9628	13271	1.37
	35.50	9701	15155	1.56
	38.50	10953	16967	1.54
	55	10256	18022	1.75

The maximum molecular weight ($M_n = 6923$) of polylactide with polydispersity value (PD = 1.56) was observed in monomer to initiator ratio (M_0/I_0 ratio) 2564. Table 2 shows that maximum molecular weight ($M_n = 10953$) of polylactide with polydispersity value (PD = 1.54) was observed. It has been seen that molecular weight of polylactide increased when polymerization was carried out under vacuum as compare to in an inert atmosphere. The polydispersity value also decreased in case of vacuum.

4.3 CHARACTERIZATION TECHNIQUES

The FTIR analysis showed that polylactide had been formed. The IR spectrum of PLLA shows that the strong band at 1758.0 cm^{-1} corresponds to C=O bond stretching and the bands at 2999.2 cm^{-1} and 2948.7 cm^{-1} are assigned to C-H stretching of $-\text{CH}_3$. The most characteristic absorption of ester C-O stretching at 1189.2 cm^{-1} is also observed. The peak at 3507.6 cm^{-1} is due to the stretching of hydroxyl group O-H. Figure 1 shows the FTIR of polylactide.

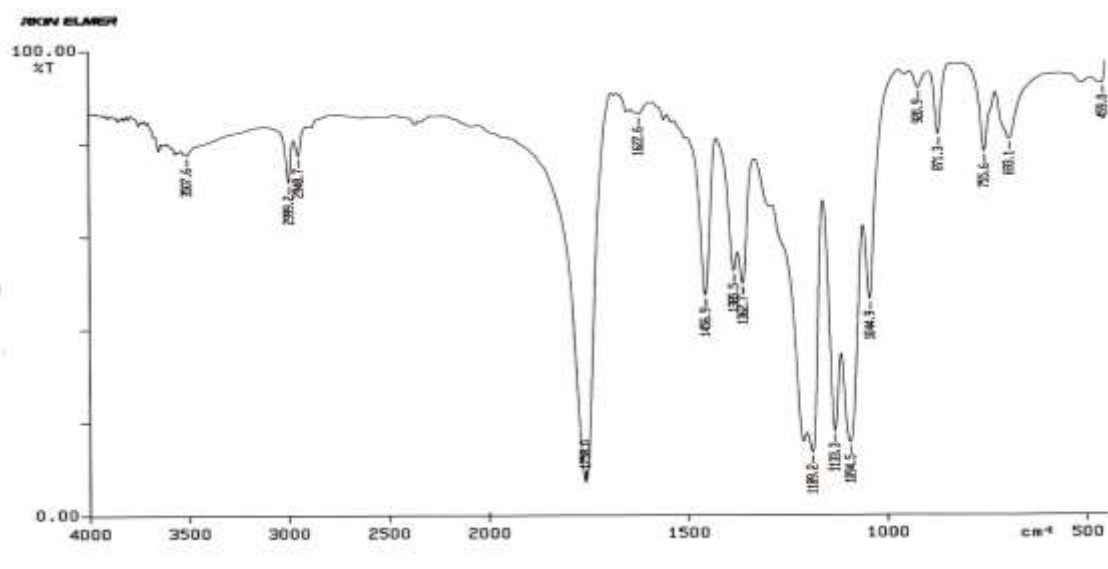


Figure 1 FTIR spectra of polylactide

The ^1H NMR spectra were recorded on Bruker Avance II Spectrometer operating at 400 MHz using CDCl_3 as solvent. Poly (L- lactic acid), PLLA product bears $-\text{OH}$ and $-\text{COOH}$ as its two end groups. The ^1H NMR spectrum of PLA is shown in Fig. 2. The resonance signal at ($\delta = 1.57$) and ($\delta = 5.13 - 5.20$) are assigned to PLLA. The resonance signal at ($\delta = 4.35$) corresponds to the methine linked to the end group $-\text{OH}$. Thus, the characterization explained above demonstrates the fine structure of PLLA formed in the ring-opening polymerization. The ^1H NMR showed the presence of pure PLLA (monomer used was L- lactide), and not its enantiomer or a racemic mixture of polylactide.

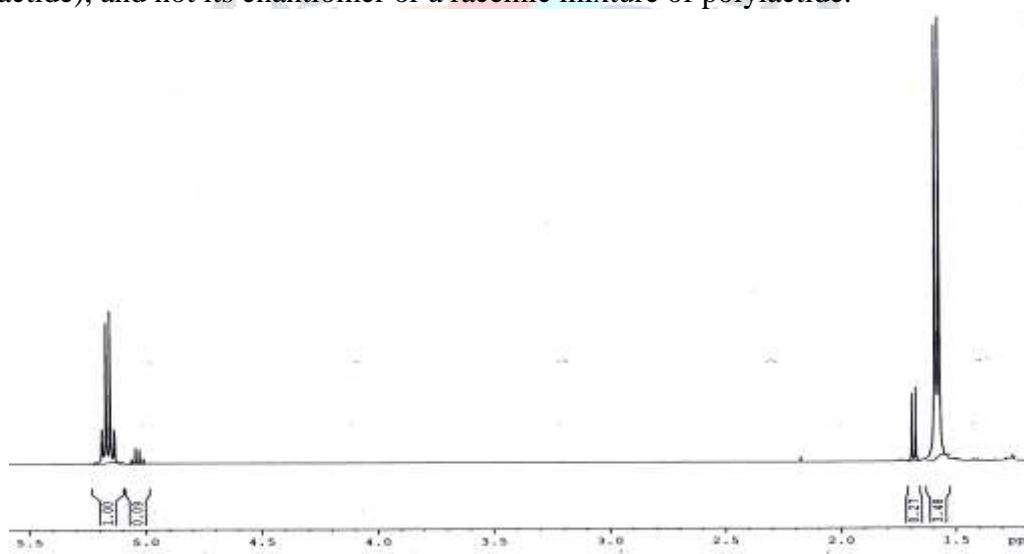


Figure 2 ^1H NMR spectra of PLLA

V. CONCLUSION

The PLA synthesised is of lower molecular weight than the theoretical value (related to ratio of monomer to initiator concentration). We suspect that the reason for low molecular weight is quick termination of growing polymer chain because of presence of water and other terminating agents in reaction vessel in general and in monomer in particular. On comparing, the molecular weight of polylactide was increased with vacuum than inert atmosphere as well as polydispersity has also been decreased in case of vacuum than inert atmosphere. We are synthesising PLA with other suitable initiators which increase the molecular weight and results will be reported soon.

VI. REFERENCES

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