

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

Paramjit Kaur

Department of Chemistry, Bebe Nanaki University College,
Mithra, Kapurthala, Punjab 144620, India

Abstract

Poly(lactide), PLA was synthesized with Zinc Stearate as an initiator and Triphenylphosphine as co-initiator by ring opening polymerization. Monomer to initiator ratio is having very significant role in polymerization reactions and its value ranging from hundreds to two thousands. The polymerization in case of Zinc Stearate under different environment was carried out at 130°C for 76 hr. The maximum molecular weight of the poly(lactide) obtained was $M_n = 15398$. The polymerization in case of Zinc Stearate/Triphenylphosphine under different environment was carried out at 130°C for 155 hr. The maximum molecular weight of the poly(lactide) obtained was $M_n = 7776$. Very interesting results are obtained because molecular weight of the poly(lactide) obtained under vacuum atmosphere is more than under inert atmosphere. Various characterization techniques like FTIR, GPC were done for the confirmation of poly(lactide) obtained.

Keywords: Ring opening polymerization, poly(lactide), lactide, zinc stearate, triphenylphosphine

1. Introduction

Poly(lactide), PLA is one of the highest potential due to its availability on the market and its low price among all the biodegradable polyesters (Lunt, 1998, Sinclair, 1996 and Vert *et al.*, 1995). PLA can undergo cationic, anionic and co-ordination insertion polymerization mechanisms. However, high molecular weight polyesters have only been obtained by using anionic or coordination-insertion ring-opening polymerization.

PLA films show better ultraviolet light barrier properties than polyethylene, but were slightly worse than polystyrene (PS) and polyethylene terephthalate (PET). PLA films show better mechanical properties than PS, and comparable to those of PET. PLA has lower melting

and glass transition temperature than PET and PS. Solubility parameter predictions indicate that PLA will interact with nitrogen compounds, anhydrides, and some alcohols, and it will not interact with aromatic hydrocarbons, ketones, esters, and water. PLA, totally degraded in aerobic or anaerobic environments in two months to five years, and early chain fragmentation can be obtained at higher humidity and temperature in composting facilities as soon as fifteen days (Auras *et al.*, 2005).

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).

Copolymers with various compositions were synthesized by bulk ring-opening polymerization of glycolide and ϵ -caprolactone, using stannous (II) octoate or zirconium (IV) acetylacetonate as initiator. Reaction time and temperature were varied to induce different chain microstructures. Stannous (II) octoate leads to less transesterification than zirconium (IV) acetylacetonate, and lower temperatures lead to less transesterification than higher ones (Kasperczyk *et al.*, 2005).

Schwach *et al.* (1998) reported that the polymerization was moisture sensitive and that only a fraction of zinc used was active. Small quantities of a side-product was detected and identified as zinc lactate. This compound appeared to be an efficient initiator of the ring-opening polymerization in the bulk. Initiation by zinc lactate yielded high molecular weight polymers with a high degree of conversion and high polymerization rates.

The effective initiators for anionic polymerization of lactones are alkali metals, alkali

metal oxides, alkali metal naphthalenide complexes with crown ethers, etc. The reaction is initiated by nucleophilic attack of negatively charged initiator on the carbon of the carbonyl group or on the alkyl-oxygen, resulting in formation of linear polyester (Albertsson and Varma, 2003).

The temperature of bulk polymerization is generally in the range of 100-150 °C, whereas in solution polymerization, low temperatures have been used (0-25 °C) to minimize side reactions (inter and intra molecular transesterification). Racemic lactide was polymerized with various initiators containing Zn and Al. Three groups of initiators can be distinguished in view of their influence on transesterification: ZnCl₂ having the strongest transesterification activity, ZnEt₂ and ZnEt₂/Al(OiPr)₃ having medium activity and Al(acac)₃ with no transesterification activity at all (Kasperczyk *et al.*, 1990).

2 Materials

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

2.1 Synthesis of Polylactide, PLA using Zinc stearate with/ without Triphenylphosphine

2.1.1 Synthesis of PLA with Zinc stearate

Zinc stearate (as an initiator) was used for the synthesis of PLA under two different environments: inert atmosphere and vacuum. An anionic ring-opening polymerization mechanism has been proposed.

2.1.1.1 Polymerization under Inert Atmosphere

Synthesis of PLA was carried out with zinc stearate (as an initiator) over different monomer to initiator ratios (693, 1040 and 2594) under nitrogen atmosphere at 130 (± 1) °C. The monomer and initiator were vigorously mixed in a four-necked round bottom flask equipped with a teflon stirrer. The reactants were maintained at a constant temperature of 130 (± 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 65 hr. The products obtained were dissolved in chloroform and precipitated in methanol. These were dried in a

vacuum dessicator for 24 to 30 hr. Mostly unimodal peaks are shown in Size Exclusion Chromatography (SEC) chromatograms but some SEC chromatograms also show bimodality.

2.1.1.2 Polymerization under Vacuum

Zinc stearate (initiator) was used for the synthesis of polylactide under vacuum. Polymerization was carried out over different monomer to initiator ratios (520 to 2299) at 130 (± 1) °C. 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 (± 1) °C. The monomer to initiator (M₀/I₀) 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 76 hr. The products obtained were dissolved in chloroform, precipitated in methanol and were dried in a vacuum dessicator for 24 to 30 hr. Mostly single or unimodal peaks are shown in SEC chromatograms but some SEC chromatograms show bimodality also.

2.1.2 Synthesis of PLA with Zinc stearate/Triphenylphosphine

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

2.1.2.1 Polymerization under Inert Atmosphere

Synthesis of PLA was carried out with Zinc stearate (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 (± 1) °C. Same procedure was followed as written in section 2.1.1.1. The maximum polymerization time was 38 hr.

2.1.2.2 Polymerization under Vacuum

Zinc stearate as an initiator and triphenylphosphine as co-initiator in equimolar proportion were used for the synthesis of polylactide under vacuum only at 130 (± 1) °C. Same procedure was followed as written in section 2.1.1.2. The monomer to initiator ratio (M₀/I₀ ratio) 2572 was used during polymerization. The maximum polymerization time was 55 hr.

3. Results and Discussion

3.1 Synthesis of Polylactide, PLA using Zinc stearate with/without Triphenylphosphine

3.1.1 Synthesis of PLA with Zinc stearate

Table 1 lists the values of M_n , M_w and PD of PLA synthesized with Zinc stearate at different M_o/I_o ratios and reaction time under inert atmosphere and vacuum.

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

M_o/I_o ratio	Polym. time (hr)	M_n	M_w	PD	
Under Nitrogen Atmosphere					
693	34	6071	8278	1.36	
1040	19.66	5379	6869	1.27	
	25.92	6183	7910	1.28	
	29.42	6763	8883	1.31	
	39.16	6356	8316	1.31	
2594	30.58	3848	5178	1.34	
	32.58	4055	5337	1.31	
	41.42	4299	6102	1.41	
	46.42	4718	7105	1.50	
65	12679	19124	1.14		
	4464	5596	1.25		
Under Vacuum					
520	48.5	13330	14648	1.09	
		3361	4597	1.36	
	52	3294	6358	1.93	
	55	14638	16034	1.09	
		3539	4818	1.36	
	59	8887	11464	1.29	
2600		3031	1.16		
76	13090	15663	1.19		
	3616	4314	1.19		
2299	7	15398	25154	1.65	
	11	9400	19066	2.02	
	15	7551	14438	1.91	
	18	8285	15664	1.89	
	34.5	14389	27534	1.91	

The maximum number average molecular weight ($M_n = 12679$) of polylactide with narrow polydispersity (PD = 1.14) was obtained with monomer to initiator ratio (M_o/I_o ratio) 2594. The maximum number average molecular weight ($M_n = 15398$) of polylactide with narrow polydispersity (PD = 1.65) was obtained with monomer to initiator ratio (M_o/I_o ratio) 2299.

3.1.2 Synthesis of PLA with Zinc Stearate with Triphenylphosphine

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

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

M_o/I_o ratio	Polym. Time (hr)	M_n	M_w	PD
Under Inert Atmosphere				
508	14.25	5570	7768	1.39
	18	3718	8060	2.16
	20	6665	9336	1.40
	23	5979	9073	1.51
	30.50	6945	12154	1.75
2568	59.08	4706	7235	1.53
	60.08	4778	7350	1.53
	61.08	4697	7303	1.55
	63.08	4799	8148	1.69
	66.08	4316	9491	2.19
Under Vacuum				
518	42.5	4699	5064	1.08
	45.5	4901	5412	1.10
	48.5	1484	3628	2.44
	52.5	2046	3956	1.93
	66	1233	3428	2.78
2602	78.25	6447	9629	1.49
	123	5138	8698	1.69
	148.58	6870	12419	1.80
	154.08	7776	13297	1.70
	155.25	5455	8411	1.54

The maximum number average molecular weight ($M_n = 6945$) of polylactide with polydispersity (PD = 1.75) was obtained with monomer to initiator ratio M_o/I_o ratio = 508. The maximum number average molecular weight ($M_n = 7776$) of polylactide with polydispersity (PD = 1.70) was obtained with monomer to initiator ratio (M_o/I_o ratio = 2602).

4. Conclusion

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. In some cases broad polydispersity may be due to the thermal depolymerization as the polymerization time increases. It also has been observed that with the increase of monomer to initiator (M_o/I_o) ratio hundreds to two thousands, molecular weight goes on increasing but after that it decreased gradually with decreasing amount of initiator and prolonging polymerization time. It is possible that a higher

initiator concentration will result in more growing chains, thus giving a lower molecular weight product while a lower initiator concentration will produce less initiation sites, thus leading to lower monomer conversion and higher molecular weight of polylactide. The average molecular weight decreases at very high monomer to initiator ratio. This may be due to the reason that with such less number of growing polymer chains, presence of even a trace amount of chain terminating agent can limit the molecular weight.

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