Melt Polycondensation of L-Lactic Acid: The role of Polycondensation Strategy

Ebru Tektemur[1], Emine Bayraktar[2]*, Mehmet Saçak[3]

[1]Department of Chemical Engineering, Faculty of Engineering, Ankara University, Ankara, Turkey
[2]Ankara University, Faculty of Engineering, Department of Chemical Engineering, 06100, Ankara, Turkey
[3]Ankara University, Faculty of Science, Department of Chemistry, 06100, Ankara, Turkey

Abstract— *PLA is getting more important in terms of green chemistry and concern for the environment. The starting material for this polymer, lactic acid, can be made by a fermentation process using 100% annually renewable resources. Poly (L-lactic acid) (PLLA) was produced via melt polycondensation method in this study. Effects of catalyst type (Sb_2O_3, $SnCl_2$ and TSA binary system, $Sn(Oct)_2$) on the production of PLLA was investigated. The binary system of using $SnCl_2$ with the amount of 0.3 (wt %) based on oligolactic acid (OLLA) with an equimolar ratio to p-toluene sulfonic acid (TSA) was found the most efficient catalyst in enhancing polymers molecular weight. In order to investigate polycondensation strategy, different polymerization pressure and progressive pressure drop program was examined. It was found that the higher molecular weights were obtained with progressive pressure dropping relative to applying low pressure on polycondensation . Molecular weight of PLLA was obtained as 64000 Da at 2 h at 30 mm Hg, 3 h at 20 mmHg and 3 h at 10 mmHg. Also ultrasound was applied to OLLA and catalyst mixture before polycondensation. It reached to 77600 Da by applying ultrasound at 3 min at the same reaction conditions.*

Keywords— Polycondensation; polyesters; biopolymers; Poly (L-lactic acid).

I. INTRODUCTION

Plastics are indispensable materials in our modern world, as biodegradable polymers derived from renewable resources, getting more important. Poly (L-lactic acid) (PLLA) is one of the most studied biopolymers among the aliphatic polyesters. PLA possesses better mechanical properties, they have easier process ability and are non-toxic degradation products. This environmentally friendly polymer could be replaced by other petroleum based polymers [1-3]. Molecular weight determines the application fields of the polymer. An optically pure poly (L-lactide) is crystalline and brittle with a melting temperature at a range of 175-185°C. The conventional lactide process consists of multiple steps. The complicated purification process and high purification costs of lactides limits the method of usage by ring opening polymerization (ROP) [4]. Direct polycondensation of lactic acid is also a one-step process. However, direct polycondensation of lactic acid causes difficulty in diverting the dehydrative equilibrium to the direction of esterification. Long reaction periods at high temperatures cause racemization of polymer. Crystallinity influences the physical properties of PLA. It is possible to reduce brittleness of PLA and thus poly (L-lactide) can be used in many applications as an engineering plastic with a broad range of applications [5-7] and it can be used for production of transparent films and glues. As mentioned above the racemization degrees of polymer affect usage areas. These problems can be solved with a two-step method called melt polycondensation where racemization can be hindered with the usage of appropriate catalyst system and optimized polymerization temperature and pressure leads production of polymer with a sufficient molecular weight. Generally Sn(II) based catalysts are used for melt polycondensation of lactic acid. In recent years, several metal alkoxides or proton acids like TSA and boric acid (BA) have been used to enhance the catalytic activity of Sn(II) [8-11]. Moon et al. [9] used the proton acid (TSA) to activate the Sn(II) catalyst. They produced PLA with 43000 Da molecular weight with $SnCl_2.H_2O$ (0.4 wt % relative to OLLA) and TSA (1 mol %) binary catalyst system under 10 mmHg at 180°C in 5 h and reported that molecular weight was increased and racemization of PLA prevented. In the next study by Moon et al. [10], metal alkoxides were used as co-catalyst and molecular weight of PLLA reached 40000 Da (Mn) with the usage of $SnCl_2.2H_2O\text{-}Ge(OEt)_4$ catalyst system in 15 h. Chen et al. [12] obtained the high molecular weight of PLA (130000 Da) with melt polycondensation of lactic acid in the reaction time up to 40 h. Marques et al. [13] also reported that molecular weight of PLA reached 52000 using $SnCl_2$/p-TSA catalyst system with melt polycondensation at 11 h of polymerization time. Lei et al. [14] obtained PLA with 50000 Da molecular weight using $SnCl_2$/ε-caprolacton catalyst system at 16 h. They reported that after 16 h degradation of PLA occurred.

II. EXPERIMENTAL

Melt polycondensation of L-lactic acid involves two steps; firstly preparing a low molecular weight pre-polymer (oligomer) as oligomerization step was followed by polycondensation with the addition of catalyst [9]. The experimental system consists of a 250-mL two necked flask which was connected to a hot plate and a reflux condenser. Between the condenser and vacuum pump a cold trap was replaced. LA solution (90 wt %) was firstly heated to 150°C for 2 h at atmospheric pressure which was stirred by the magnetic stirrer. For further dehydration, vacuum pressure was applied stepwise, first 100 mmHg for 2 hours, then 30 mmHg for an hour. A viscous liquid of OLLA formed with nearly 2000 Da molecular weight which becomes solid in a few minutes. In the polymerization step 20 g of OLLA was used with desired amount of catalyst under vacuum pressure at 180°C. Vacuum pressure was applicated as 5, 10, 20, 30 mmHg or as a progressive pressure dropping. To investigate the effect of ultrasound, 20 g of OLLA and 0.3 % $SnCl_2$ plus 1 mol % TSA were added in the two necked flask and ultrasound was applied as desired time. The resulting polycondensate was cooled down and dissolved in chloroform and precipitated in methanol [8-10]. Polymer was obtained in a form of white solid kept at 35°C for 12 h in the desiccators before analyses. Molecular weight was determined by Gel Permeation Chromatography.

III. RESULTS AND DISCUSSION

Since lactic acid includes both a hydroxyl and a carboxyl group, the dehydrative condensation of lactic acid is driven by self-catalysis. While esterification reaction proceeds, high temperature and high vacuum conditions were applied by means of appropriate catalyst system for activating the dehydrative reaction and deactivating the formation of lactide.

For the selection of catalyst type, $SnCl_2$, Sb_2O_3 and $Sn(Oct)_2$ were used as polymerization catalyst after the oligomerization process (Fig 1). The starting OLLA has a molecular weight of 2000 Da. The experiments were carried out at 180°C and 10 mmHg vacuum pressure for 5 hours. The catalyst amount investigated with 0.05, 0.1, 0.3 and 0.5 wt % to OLLA amount. Molecular weight of the polymer was only 2800 Da with 0.05 wt % $SnCl_2$ as catalyst, while it reached 25000 Da with the addition of 0.1 wt % and 22700 Da with the addition of 0.5 % wt. Using 0.3 wt % provided a small increase on the molecular weight as 25800 Da. When $Sn(Oct)_2$ was used as polymerization catalyst, 0.05, 0.1, 0.3, 0.45 and 0.75 wt % amounts were examined at the same temperature and pressure and polymers with 5000, 17000, 28700, 36600 and 42800 Da molecular weight were obtained, respectively. With the use of Sb_2O_3 lower molecular weights were observed. 0.05, 0.1, 0.3, 0.5 and 0.75 wt % catalysts amounts were examined. 9800, 16900 Da molecular weights were observed with 0.05 and 0.1 wt % catalyst amounts. Using the catalyst with a 0.3 wt % amount provided a little increase and molecular weight reached at 18000 Da. When the amount of Sb_2O_3 increased to 0.5 wt % and 0.75 wt %, polymer molecular weight increased at 26900 Da and 27000 Da, respectively. Further increase on the catalyst amount caused a decrease on the molecular weight.

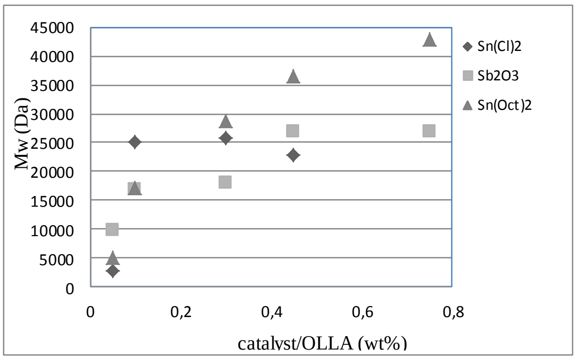

Fig.1: Effects of catalyst type and amount to the M_w of PLLA (at 180°C and 10 mmHg for 5 hours)

Generally Sn(II)-based catalysts activated with proton acids are used for melt polycondensation of lactic acid. The effects of proton acids on the melt polycondensation of L-lactic acid which were catalyzed by $SnCl_2$ are given in Table 1. The experiments were performed with 20 gr OLLA and 0.3 wt % $SnCl_2$ and desired amount of proton acids as a catalyst system at 180°C for 5h under 10 mmHg. BA and TSA were examined since they are thermally stable and less volatile proton acids [9]. When the polymerization was carried out without the use of any proton acid, M_w of the resulting PLLA was 25800 Da. BA almost could not provide a noteworthy increase on the molecular weight. $SnCl_2$-TSA system (with 1:1 catalyst/proton acid proportion) is a good catalyst for obtaining high molecular weights of PLLA than the single use of $SnCl_2$. Under these conditions, the molecular weight of the polymer reached 46600 Da. Similar results was obtained in the literature [9]. While they obtained 22000 Da poly (lactic acid) (PLA) with 0.4 wt % $SnCl_2$, it reached 43000 Da using 0.4 wt % $SnCl_2$ plus 1 mol % TSA.

Table.1: Effect of the proton acids on the melt polycondensation of OLLA

Catalyst type [1]	Molar ratio of proton acid/$SnCl_2$	Mw (Da)
$SnCl_2$	0	25800
$SnCl_2$+BA	1.5	26700
$SnCl_2$+TS	1	46600
$SnCl_2$+TS	1.5	48700

[1] *At 0.3 wt % $SnCl_2$ relative to OLLA*

Maques et al. [13] also obtained 32500 Da PLA with melt polycondensation at 7.6 mmHg vacuum pressure for 11 h without any co-catalyst and it was 52000 Da with using co-catalyst TSA. For the following experiments $SnCl_2$-TSA catalyst system was used with 0.3 wt % $SnCl_2$ and with 1:1 molar ratio of OLLA to TSA.

The spectra of the polymers synthesized with different catalyst, are nearly same with the PLLA standard (Fig 2). The structure of PLLA was characterized with IR. The characteristic absorption peaks of ester could be seen as (C=O) bonds at 1757 cm^{-1}, (C-O-C) bonds at 1188, 1130, 1092 cm^{-1} and saturated -CH- bonds at 2995, 1454 cm^{-1}. Absorption peak of hydroxyl group was at 3500 cm^{-1} and it almost disappeared due to reduction of hydroxyl groups when the polymer was synthesized. In order to determine the effect of polymerization pressure to the molecular weight of PLLA, different polymerization pressures were experimented (Fig 3). For these experiments, 0.3 wt % $SnCl_2$ was used relative to oligomer and TSA was added equal molar ratio to $SnCl_2$. When the pressure decreased from 10 atm to 5 atm, molecular weight of PLLA was increased from 46600 Da to 56000 Da. Also, it was reached 55000 Da with the progressive pressure drop program. 55000 Da of molecular weight was obtained without decreasing to this low vacuum pressure (5 atm). Therefore the pressure drop program was investigated (Table 2).

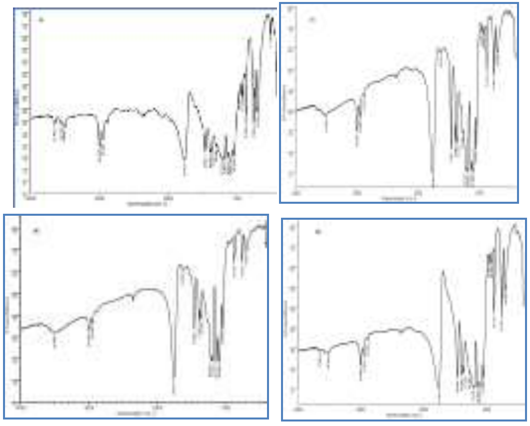

Fig.2: FTIR spectra of PLLA produced with different catalyst system; (a) PLLA standard, (b) $SnCl_2$-TSA, (c) Sb_2O_3, (d) $Sn(Oct)_2$

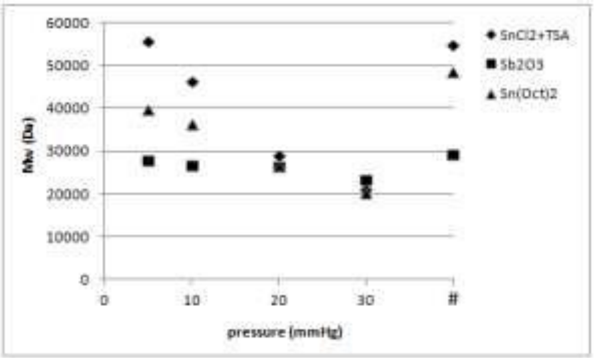

Fig.3: Effects of polymerization pressure to the M_w of PLLA (at 180°C, #: for 2 hours at 30 mm Hg, 2 hours at 20 mmHg and 1 hour at 10 mmHg)

The higher molecular weights were obtained at 1st and 5th cycle. The low vacuum pressure and time for this process are the most effective parameters. Molecular weight is 62353 Da applying 10 mmHg vacuum pressure for 3 h and 20 mmHg for 3 h (1st cycle). When the time was increased to 4 h for 20 mmHg and 4 h for 10 mmHg (total time was 8 h (2nd cycle)), molecular weight decreased. Besides 10 mmHg vacuum pressure for 3 h was applied, Mw decreased with increasing total time up to 8 h (7th cycle). This may be attributed to the thermal degradation. The maximum molecular weight was obtained as 64000 Da for 2 h at 30 mm Hg, 3 h at 20 mmHg and 3 h at 10 mmHg. Maques et al. [13] obtained 52000 Da PLA with $SnCl_2$/TSA catalyst systems for 11 h at 7.6 mmHg vacuum. In the present study, high molecular weight of PLA was obtained at total 8 h and less vacuum pressure. In the study by Lei et al. [14], 25000 Mw was obtained with 1 wt % $SnCl_2.2H_2O$+ 1% ε-caprolacton +0.1 % phosphoric acid at 10 h 112.5 mmHg vacuum. When the reaction was carried out for 16 h, Mw reached 50000 Da.

As a result, pressure drop program in our study gives the better result.

Table.2: Effects of duration to the progressive polymerization pressure dropping[1]

#	Pressure dropping programme (mmHg)	Duration (h)	Mw (Da)
1	20 : 10	3 : 3	62353
2	20 : 10	4 : 4	56214
3	30 : 20 : 10	2 : 2 : 1	55000
4	30 : 20 : 10	3 : 3 : 1	57000
5	30 : 20 : 10	2 : 3 : 3	64000
6	50 : 40 : 30 : 20 : 10	1 : 1 : 1 : 1 : 2	34000
7	50 : 40 : 30 : 20 : 10	1 : 1 : 2 : 2 : 3	52151

[1] *Catalyst type: $SnCl_2$ (wt% 0.3 relative to OLLA) + TSA (with 1:1 molar ratio),at 180˚C*

In order to increase the mass transfer at the beginning of the experiments, ultrasound was applied to reaction mixture included OLLA and $SnCl_2$/TSA catalyst system. The reaction condition was applied as 2 h at 30 mm Hg, 3 h at 20 mmHg and 3 h at 10 mmHg. When the applying time of ultrasound was 3 min, molecular weight was increased from 57000 Da to 77600 Da (Fig 4). The mechanism of the ultrasound effects in liquids is the phenomenon of acoustic cavitation. The ultrasound effects of chemical reactions or processes include increase in reaction speed and improvement of phase transfer of catalyst. Ultrasound is also known to cause cavitation effects. When cavitation bubbles collapse, a shock wave occurs that can provide rather efficient mixing. This enables the enhancement of the mass transfer rate [15]. The molecular weight decreases with increase in the applying time of ultrasound (Fig 4). Temperature increases with ultrasound, therefore thermal degradation can be take place with time.

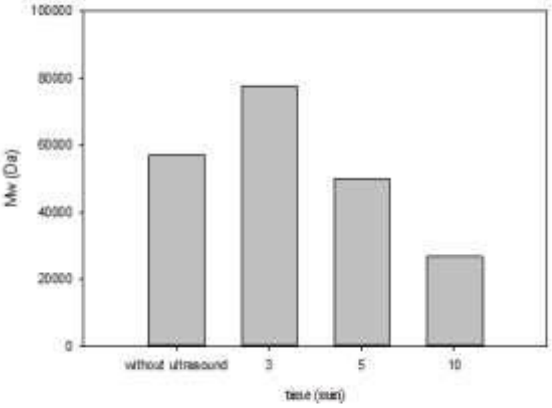

Fig.4: Changes in molecular weight with ultrasound application (catalyst by $SnCl_2$ (wt% 0.3 relative to OLLA) + TSA (with 1:1 molar ratio), at 180°C for total 7 hours (with 3 hours 20 mmHg, 3 hours 10 mmHg and 1 hours 10 mmHg application))

IV. CONCLUSION

The melt polycondensation of PLLA was carried out with $SnCl_2$-TSA catalyst system. The pressure drop program was applied. The maximum molecular weight was obtained as 64000 Da for 2 h at 30 mm Hg, for 3 h at 20 mmHg and for 3 h at 10 mmHg. High polymer weight was obtained at less vacuum pressure and relatively short reaction time. Molecular weight reached 77600 Da by means of applying ultrasound at the beginning of the polymerization.

This process might give way to new production processes of PLLA.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the funding of this work by the Scientific and Technical Research Council of Turkey, TUBITAK (Project no: 108M330).

REFERENCES

[1] K.. Fukushima and Y. .Kimura, “Stereocomplexed polylactides (Neo-PLA) as high-performance bio-based polymers: their formation, properties, and application.” Polym Int 2006, 55, pp.626-642.

[2] A. Gupta and V. Kumar, “New emerging trends in synthetic biodegradable polymers- Polylactide: A critique.” Euro Polym J, 2007.43, pp.4053-4074.

[3] S. Vouyiouka, P. Theodoulou, A. Symeonidou, C.D. Papaspyrides, R. Pfaendner, “Solid state polymerization of poly(lactic acid): Some fundamental parameters.” Polym Degrad Stabil, 2013. 12, pp.2473-2481.

[4] K.W. Kim and S.I. Woo, “Synthesis of high-molecular-weight poly(L-lactic acid) by direct polycondensation.” Macromol Chem Phys, 2002, 203, pp.2245-2250.

[5] H. Kricheldorf, “Syntheses and application of polylactides.” Chemosphere, 2001, 43, pp.49-54.

[6] T. .Maharana, B. Mohanty, Y.S. Negi, “Melt-solid polycondensation of lactic acid and its biodegradability.” Prog Polym Sci, 2009,.34, pp.99-124.

[7] A.M. El-Hadi, “Develpment of novel biopolymer blends based on poly(L-lactic acid), poly((R)-3-hydroxybutyrate), and plasticizer.” Polym Eng Sci , 2014, 45, pp.1395-1402.

[8] M. Lee, H. Tan, M. Chandrasekaran, C. Ooi, “Synthesis and characterisation of PLLA by melt polycondensastion using binary catalyst systems.” SIMTech Technical Reports, 2005, 6, **pp.**40-44.

[9] S. Moon, C. Lee, I. .Taniguchi, M. Miyamoto, Y. Kimura, “Melt polycondensation of L-lactic acid with Sn(II) catalysts activated by various proton acids: A direct manufacturing route to high molecular weight

poly(L-lactic acid).” J Polym Sci Part A: Polym Chem, 2000, 38, pp.1673-1679.

[10] S. Moon, C. Lee, I. Taniguchi, M. Miyamoto, Y. Kimura, “Polymer, Melt/solid polycondensation of L-lactic acid: an alternative route to poly(L-lactic acid) with high molecular weight.” Polymer, 2001, 42, pp.5059-5062.

[11] H.A. Essawy, F.M. Helaly, M.A. Shabana, “Synthesis of poly(lactide) blends by melt/solid polycondensation.” J Elastom Plast, 2007, 39, pp.303-316.

[12] G. Chen, H. Kim, E. Kim, J. Yoon, “Synthesis of high-molecular-weight poly(L-lactic acid) through the direct condensation polymerization of L-lactic acid in bulk state.” Euro Polym J, 2006, 42, pp.468-472.

[13] D.S. Marques M.H., Gil, C.M.S.G. Baptista, “Improving lactic acid melt polycondensation: The role of co-catalyst.” J Appl Polym Sci, 2013, 128, pp.2145-2151.

[14] Z, Lei, S. Wang, Y. Bai, “Synthesis of high-molecular-weight poly(lactic acid) from aqueous lactic acid cocatalyzed by ε-caprolactam and tin(II) chloride dihydrate.” J Appl Polym Sci, 2007, 105, pp.3597-3601.

[15] R. Songür, B. Lurçi, E. Bayraktar, Ü. Mehmetoğlu, A.S. Demir, “Enantioselective Production of Benzoin from Benzoin Acetate via Kinetic Resolution and Deracemization using *Rhizopus oryzae*.” Artif Cells Blood Substit Biotechnol, 2011, 39, pp.162-168.