

## **PREPARATION OF POLYLACTIDE FROM SYNTHESIZED LACTIC ACID AND EFFECT OF REACTION PARAMETERS ON CONVERSION**

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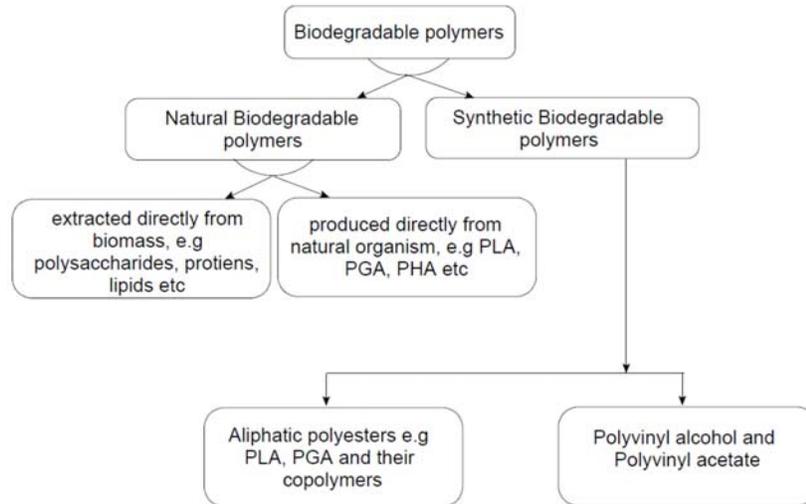
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### Abstract

Lactic acid (LA) is widely used in the food, chemical and pharmaceutical industries. Recently there has been an increase in demand for lactic acid as a raw material for the production of biodegradable polymers. LA can be manufactured either by synthetic routes or by a fermentation process. The methods for recovery of lactic acid are solvent extraction, adsorption on an ion-exchange resin, reactive distillation and electro dialysis. In this study, the lactic acid recovery was carried out by reactive distillation using cation exchange resin as a catalyst. Reactive distillation involved, two reactions mainly esterification and hydrolysis. The effect of operating variables such as catalyst loading, temperature of reaction, reaction time and reactant mole ratio on the yield of methyl lactate was studied. Further, poly (d,l-lactic acid) was synthesized by microwave radiation and azeotropic polycondensation technique using stannous octoate as a catalyst. The effects of catalyst concentration, microwave irradiation power, reaction time and reaction temperature on molecular weight of polymer were discussed. The obtained products were characterized with differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and Fourier transform infrared spectroscopy (FTIR).

### 1. Introduction

For past several decades, wide range of polymers such as PE, PP, PVC, PS, UF, MF etc. are available for packaging, agriculture, adhesives, coatings and medical application. A polymer is a large molecule composed of many repeating smaller structural units called monomers that are connected by covalent chemical bonds. Polymers are classified into two types, natural and synthetic. With their excellent properties and wide applications, synthetic polymers have become integral part of our daily life but possess disposal and environmental issues due to their resistance to microbial degradation. To overcome these problems biodegradable and renewably derived polymers are used for last several years. Biodegradable polymers are classified according to their origin into two groups: natural polymers which are obtained from natural resources and synthetic polymers which are produced from oil as shown in (Figure 1).



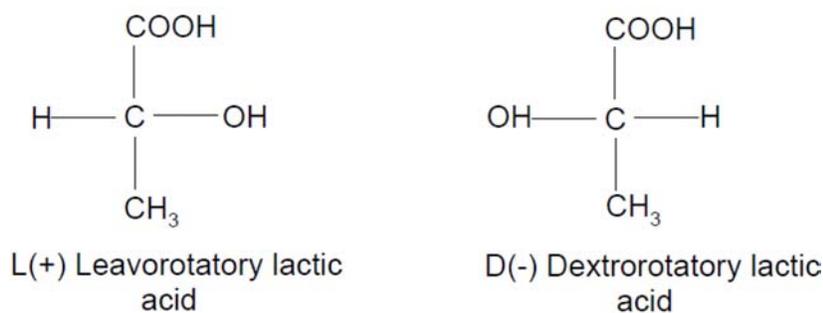
**Figure 1.** Classification of biodegradable polymers.

Natural biodegradable polymers include polysaccharides (starch, cellulose etc.), proteins (gelatine, wool, silk, etc.), lipid fats (fats and oil), polyesters produced by plants or microorganisms (polyhydroxyalkanoates PHAs), polyesters derived from bioderived monomers (polylactic acid), and several miscellaneous polymers like natural rubbers and composites. The other types are non-renewable, synthetic, biodegradable plastics which are petroleum based such as polybutylene succinate (PBS) and polycaprolactone (PCL). Other polymers which are biodegradable but do not fit neatly into either category are polyanhydrides and polyvinyl alcohol (Nampoothiri et al. [1], Carole et al. [2]).

## 2. Lactic Acid

Lactic acid was discovered by C. W. Scheele in 1781. It is widely used in food, chemical and pharmaceutical industries. Recently, there has been an increase in demand for LA as a raw material for the production of biodegradable polymers. Lactic acid is a non-volatile, odorless organic acid and has mild acidic test. Lactic acid is classified as GRAS (generally recognized as safe) for use as a general-purpose food additive by FDA in

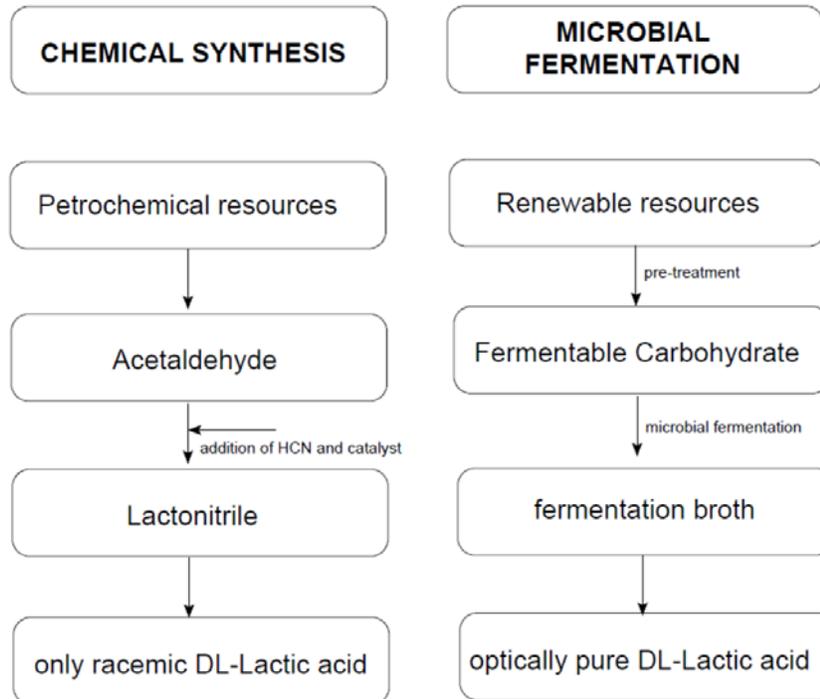
the USA and other regulatory agencies (Datta et al. [3]). Lactic acid,  $\text{CH}_3\text{CHOHCOOH}$ , is a naturally occurring organic acid. A world's crude oil resources diminish and the price of petroleum product continue to increase; the production of chemical by biological processes is becoming more competitive. High purity and heat stable lactic acid, which was mainly available from synthetic manufacture, is now being produced by fermentation. About 85% of the estimated 50,000ton year of lactic acid produced worldwide is used in food industry. These markets are projected to grow at 2-4%/year (Evanagelista et al. [4]). Lactic acid (2-hydroxypropanoic acid) is the simplest 2-hydroxycarboxylic acid (or  $\alpha$ -hydroxy acid) with a chiral carbon atom and exists in two enantiomeric forms as shown in (Figure 2) (Joung et al. [5]).



**Figure 2.** Two enantiomers forms of lactic acid.

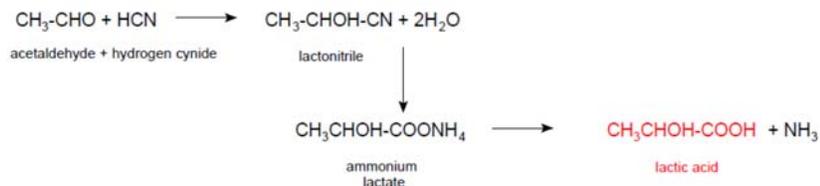
### 2.1. Production of lactic acid

Lactic acid can be produced by either microbial fermentation or chemical synthesis (Figure 3). In the early 1960s, a method to synthesize lactic acid chemically was developed due to the need for heat-stable lactic acid in the baking industry (VickRoy et al. [6]).



**Figure 3.** Manufacturing methods of lactic acid.

There are two optical isomers of lactic acid: L (+) -lactic acid and D (–) -lactic acid but D (–) -lactic acid is at times harmful to human metabolism and can result in acidosis and decalcification (Datta et al. [3]). Although racemic D, L-lactic acid is always produced by chemical synthesis from petrochemical resources, an optically pure L (+) - or D (–) -lactic acid can be obtained by microbial fermentation of renewable resources (Hofvendahl et al. [7]). In chemical industry, about 90% of lactic acid is manufactured by fermentation route. In chemical synthesis, acetaldehyde is treated with hydrogen cyanide in the presence of catalyst to yield lactonitrile. Lactonitrile on hydrolysis with sulphuric acid gives lactic acid along with ammonium salts as byproduct. This is the conventional way for the production of lactic acid. Reactions scheme for production of lactic acid is as follows (Vaidya et al. [8]).



**Figure 4.** Manufacturing methods of lactic acid.

Drawbacks of chemical synthesis of lactic acid include generation of racemic mixture of lactic acid, dependence on hydrocarbon source and employing corrosive & hazardous chemical like hydrogen cyanide. Biological method of synthesis consists of fermentation of carbohydrates by specific micro-organisms (bacteria such as lactobacillus & fungi). A large number of carbohydrate materials (such as starch and cellulosic materials, whey, and molasses) have been used, tested or proposed for the manufacture of lactic acid by fermentation. The feed stocks material for the synthesis of lactic acid can be selected based on the following desirable qualities such as low cost, low levels of contaminants, fast fermentation rate, high lactic acid yield, little or no by-product formation, ability to be fermented with little or no pre-treatment, availability, high productivity, use of low cost nitrogen resources (Young et al. [9]).

## 2.2. Poly (lactic acid)

Poly (lactic acid), PLA is a bio-degradable, thermoplastic polymer and can be made from renewable resources such as sugarcane and corn. It is highly versatile aliphatic polyesters commonly made from  $\alpha$ -hydroxy acid. It is one of the most promising biodegradable polymers (biopolymers) and has been the subject of abundant study over the last two decades.

It is relatively cheap and has some remarkable properties, which make it suitable for different applications. There are several methods which can be employed for the polymerization of lactic acid. The main methods include the condensation of lactic acid, azeotropic dehydrative polycondensation, solid state polymerization, and ring opening

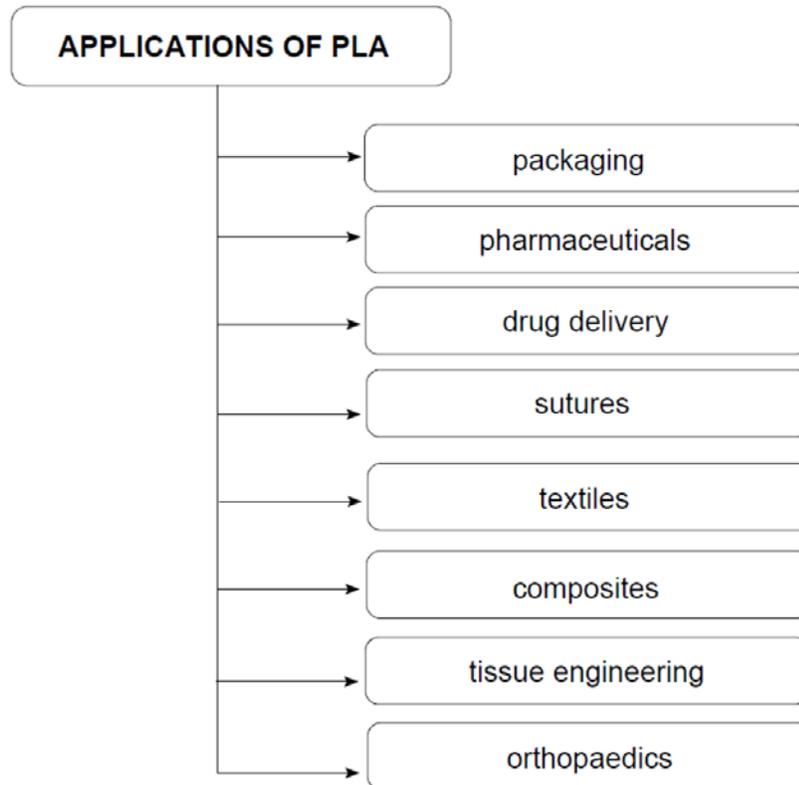
polymerization of lactide. Commercially available high molecular weight polylactic acid (PLA) is mainly produced via ring-opening polymerization of lactide (Abderramane et al. [10]). PLA has numerous advantages over other polymers such as: (1) it is produced from renewable resources, (2) permits considerable energy savings, (3) can be recycled back to lactic acid which is a non-toxic and naturally occurring metabolite through hydrolysis or alcoholysis, (4) helps in capturing carbon dioxide, (5) improvement of farm economics, (6) decline of landfill volumes (Auras et al. [11], Dorgan et al. [12]).

### **2.3. Properties of poly (lactic acid)**

Polylactic acid is generally known for its good processability, biocompatibility, and biodegradability. However, due to the chirality present in the carbon atom, L, D, and DL isomers of the polymer are possible. Physical and mechanical properties are greatly affected by the isomeric composition, as well as degradation rates. The L isomeric form of PLA is often used when a high degree of crystallinity is required in the polymer. Poly(l-lactic acid), however, can be made to be highly crystalline polymer and shows a melting range of about 170°C to 183°C. In addition, the density of poly (l-lactic acid) is slightly higher than for racemic PLA, at about 1.25-1.29g/cm<sup>3</sup> compared to about 1.24g/cm<sup>3</sup> for amorphous forms of PLA (Gupta et al. [13]). PLA possesses the tensile strength and stiffness similar to polyethylene terephthalate and processing characteristics of polystyrene, but it suffers low impact resistance. The poor toughness limits its use in the applications that need plastic deformation at higher stress level (Rasal et al. [14]).

### **2.4. Applications of PLA**

PLA is a biodegradable thermoplastic because, of its good mechanical property, biodegradability, and non-toxicity degradation products, it is being used for number of application from biomedical to conventional thermoplastics (Figure 5).



**Figure 5.** Applications of polylactic acid.

PLA and its copolymers have been used for applications like drug delivery system, protein encapsulation and development of microspheres and hydrogels etc. articles. PLA has practical medical applications as dissolvable sutures, as matrices for drug delivery, and bone fracture internal fixation devices in surgery. Other applications include its role as agricultural plant growth promoter, in textiles, and non-woven applications such as fiberfill, crop covers, geotextiles, wipes, diapers, binder fibers, etc. (Rajeev et al. [15]). PLA also finds applications in agricultural films, degradable rubbish bags; thermoformed trays for fruits and vegetables, disposable plates and cups, toys, cutlery, fibre composites, PLA layered silicate nanocomposites (Plackett et al. [16]).

## 2.5. Purification and separation of lactic acid

Lactic acid is the simplest hydroxyl carboxylic acid with an asymmetric carbon atom. It can be produced from biomass, coal, petroleum, or natural gas liquids. Polymers and copolymers of lactic acid are known to be environmentally compatible because of their degradability into harmless products, which makes them desirable as substitutes of petrochemical polymers. Lactic acid (LA) is widely used in the food, chemical and pharmaceutical industries. Recently, there has been an increase in demand for LA as a raw material for the production of biodegradable polymers. Lactic acid can also be used in prosthetic devices, pesticide formulation, plastic production, etc. (Lipinsky et al. [17]) for their production, highly purified monomeric lactic acid is needed. LA can be manufactured either by synthetic routes or by a fermentation process. Fermentative production of LA is more attractive because of the availability of cheap raw material and the selective production of an optically active form of LA. In chemical industry, about 90% of lactic acid is manufactured by fermentation route. The obtained fermented broth contains not only lactic acid but also unfermented carbohydrates, biological fermenting agents (micro-organisms), and other impurities like side reaction products, water etc.

Recovery of lactic acid is difficult due to its chemical structure. Lactic acid has a strong affinity to water, tends to oligomerise at high temperature, presence of low volatile impurity and the presence of other organic acids (Sanz et al. [18]). Therefore, lactic acid separation and purification is an important technical problem. Several methods have been reported in literature for the purification and separation of lactic acid from fermentation broth including, Reactive distillation, solvent extraction, adsorption on an ion-exchange resin, and electro dialysis. Each process is associated with some advantages and disadvantages.

## 2.6. Reactive distillation

Purification of lactic acid by distillation becomes difficult due to its low volatility, solubility in water, and its polymerizing tendency at higher temperature. To overcome these limitations, the lactic acid is esterified by reacting it with alcohol, yielding corresponding lactate ester. The lactate ester is purified by distillation, and then hydrolyzed to obtain pure lactic acid. Reactive distillation offers some advantages over conventional processes where reaction and purification are carried out separately. Some of them are the reduction of capital and operating costs, high selectivity, reduced energy uses, and reduction or elimination of solvents. The esterification process is highly equilibrium controlled reaction hence low reaction rate. The process requires more time due to number of distillation and reaction steps. Rate of equilibrium reactions can be increased by the continuous removal of one of the products from the reaction mixture. In order to enhance the rate of reaction (esterification of lactic acid and hydrolysis of lactic esters), different types of ion exchange resin has been used by various researchers. The summary of this work is given as follows: (Seo et al. [19]) investigated the recovery of lactic acid by two batch reactive distillation using cation exchange resin as catalyst. A strongly acidic cation exchange resin, DOWEX-50W in the  $H^+$  form, this ion exchange resin was in gel form and consisted of sulfonated styrene with 8% divinyl benzene. For lactic acid recovery, two reactions, esterification and hydrolysis, were involved. They studied the effect of catalyst loading, reactant mole ratio, feed lactic acid concentration, type of alcohol and partial condenser temperature on lactic acid recovery. It was found that lactic acid yield increased as the catalyst loading in the esterification part increased. The methanol seems to be more effective than other alcohols. It has been stated that the maximum yield was about 90%. (Joung et al. [5]) proposed model for purification of lactic acid with batch distillation and simultaneous reaction. They used two Oldershaw columns for this purpose. Methanol is used for the esterification of reaction. A strongly acidic cation resin

DOWEX 50W in the  $H^+$  used as solid catalyst. The operation was batch type to allow proper sufficient residence time for the reaction. About 6 hours were required to get high purity lactic acid. The recovery yield of lactic acid was 84% after 6 hours. The column increased the fractionation of boil ups from reboilers. (Rakesh Kumar et al. [20]) studied various aspects of esterification of lactic acid followed by hydrolysis with the help of experiments and simulation. The experiment mainly consists of a two-phase CSTR, which is used for esterification of lactic acid coming from the evaporator. The vapour stream consisting methyl lactate coming from CSTR is then fed to continuous reactive distillation column to separate out lactic acid. The generated methanol is recycled back to esterification process. The experimental results were verified with simulation results. And optimum conditions also found out using simulation. The cation exchange resin Amberlyst-15 and Amberlyst CSP2 were used as catalyst during the experiments. Higher conversion was obtained in case of lower reflux ratio during hydrolysis reaction. (Rakesh Kumar et al. [21]) in his another research article proposed a reactive distillation strategy to perform esterification and distillation in single system. The effects of parameters like feed concentration, mole ratio, catalyst loading, boil up rate etc. were analyzed. The catalyst used was Amberlyst 15 which is strongly cationic ion exchange resin. The above system is useful in case of highly concentrated lactic acid solution. It reduces the equipment cost. But in case of dilute feed, the water also needs to be vapourized with the methyl lactate. This increases heating cost. Kim et al. [22] studied the dynamic behaviour of the reactive distillation system. The rate of reaction was increased by controlling the boilup rate and residence time of each species during the operation with the change of methanol recycle stream condition and feeding mode. Acidic cation resin DOWEX 50W in the  $H^+$  used as solid catalyst. It is found that the flow rate of methanol recycle stream is controlled by temperature of partial condenser and effect of residence time of the light boilers. Temperature slightly above boiling point of methanol was considered to be optimum. Zhang et al. [23]

proposed the integrated process of lactic acid separation by using dividing wall column for reactive distillation. The dividing wall column provides much more thermodynamic efficiency with respect to the conventional one. The optimization of process is done to reduce the cost of energy. Effect of feed mole ratio and feed methanol composition has been analyzed on production of lactic acid. It has been stated in the paper that given system may decrease the equipment cost as well as energy cost compared to the conventional distillation operation. Zhao et al. [24] studied the recovery of lactic acid from fermentation broth produced from kitchen garbage by esterification method. In esterification procedure, the cation-exchange resin modified by  $\text{FeCl}_3$  was used as a catalyst to replace a traditional sulfuric acid catalyst, and the esterification yield of  $\text{NH}_4\text{LA}$  in the fermentation broth of kitchen garbage at 6-th hour was 96%. Pure LA was hydrolyzed from the obtained butyl lactate in presence of a cation-exchange resin in the  $\text{H}^+$  form as a catalyst. From these literature reports, it was observed that IER can be used for purification of lactic acid, but with extra additional cost of regeneration. Basava Rao et al. [25] studied the recovery of lactic acid by batch reactive distillation using *n*-butanol as reactive entrainer. They studied the effect of initial concentration, mole ratio, and catalyst weight on removal of water from aqueous lactic acid solution. A strongly acidic cation resin amberlite in the  $\text{H}^+$  used as solid catalyst. It is observed that the yield of recovered lactic acid increased with increasing catalyst loading. In the esterification reaction, it is observed that the feed concentration of the lactic acid and the reactant mole ratio decreased, the recovery yield of lactic acid increased. The maximum yield of recovered lactic acid is 95%. Patricia et al. [26] investigated the kinetic study for the esterification of lactic acid with ethanol and the hydrolysis of the corresponding ester, ethyl lactate. Amberlyst 15 is used as a catalyst for this study. The effect of the reaction temperature, catalyst loading and initial reactant molar ratio on conversion (%) was studied in a stirred batch reactor. The reaction rate

has been found to increase with temperature and catalyst loading. The activation energy was reduced from 62.50 to 52.29 kJ mol<sup>-1</sup> in the presence of Amberlyst 15 for the esterification reaction. Amrit et al. [27] studied the kinetic behaviour of esterification of lactic acid with isopropanol over an acidic cation exchange resin, Amberlyst 15, was studied under isothermal condition. The experiments were carried out in a stirred batch reactor in the temperature range of 323.15 to 353.15K. They studied the effect of various parameters such as temperature, molar ratio and catalyst loading on conversion. It was found that the reaction rate increased with the increasing reaction temperature, weight of the catalyst, and molar ratio. Yang et al. [28] studied the esterification of lactic acid with ethanol in the presence of five different cation exchange resins as a catalyst. The experiments were carried out in a batch reactor in the temperature range of 333 to 361K. They studied effect of catalyst type, catalyst loading, and temperature on reaction kinetics. The order of catalytic activity was found to be: D002 < D001 < Amberlyst-15 < NKC < 002.

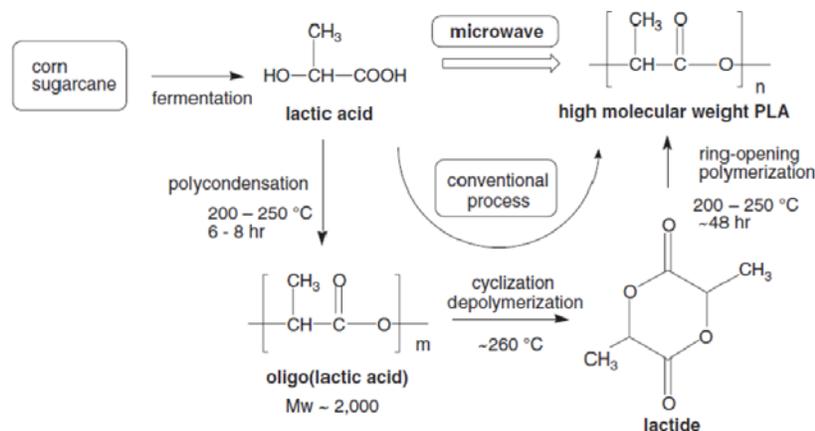
### **2.7. Polymerization of lactic acid**

There are several methods which can be employed for the polymerization of lactic acid. The main methods include the condensation of lactic acid and ring opening polymerization of lactide as shown in Figure 6. The poly-condensation route it is difficult to prepare PLA with high molecular weight. The most important and general way to prepare high molecular weight PLA is through ROP. However, both methods need long time and should be run under high vacuum level or in an inert gas environment to complete the polymerization (Andreopoulos et al. [29]).

### **2.8. Polycondensation of lactic acid**

The structure of lactic acid, since it contains both an alcohol and a carboxylic acid group allows it to undergo condensation polymerization. Synthesis of high molecular weight of polylactic acid (PLA) by a direct

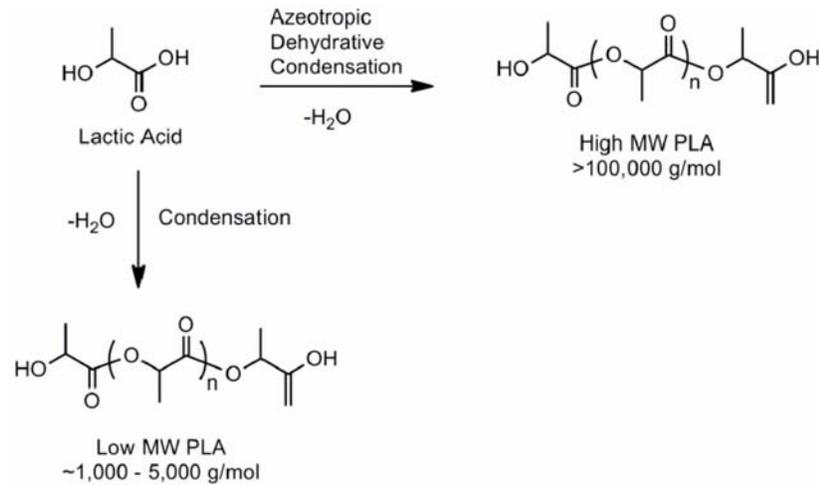
dehydration condensation reaction is not feasible due to the equilibrium reaction not favoring a high molecular weight polymer. PLA prepared from polycondensation has low molecular weight and poor mechanical properties and therefore is not suitable for many applications. The commercial interest for solving this problem has increased because of the need of cost-effective approaches in the manufacturing of lactic acid based polymers with a high molecular weight. Solvent-assisted polycondensation is one way to overcome this problem (Ajoka et al. [30]) and melt polycondensation followed by solid-state polycondensation is another one (Moon et al. [31]). In polycondensation reaction, removal of water become more difficult due to the increased viscosity of reaction mixture. By means of applying vacuum, the water removal can be enhanced. However, during the polycondensation of lactic acid, other side reactions also occur, such as transesterification, resulting in the formation of ring structures (lactide) of different sizes (Kéki et al. [32]).



**Figure 6.** Condensation of lactic acid and ring opening polymerization of lactide.

The lactide formation becomes substantial at high reaction temperatures ( $> 200^\circ\text{C}$ ). To suppress the lactide formation, the polycondensation reaction should thus be carried out at temperatures

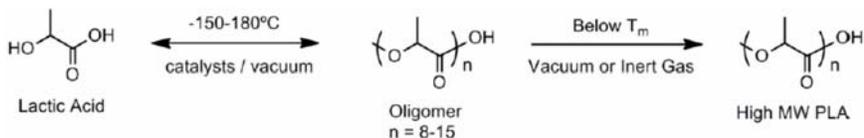
below 200°C. Conducting the polycondensation at low temperatures again has a negative effect on the removal of water due to the relatively high viscosity of the reaction mixture in addition to a lowered reaction rate (Duda [33]). The mechanism for the condensation of lactic acid is shown in Figure 7.



**Figure 7.** Mechanism for condensation of lactic acid.

### 2.9. Solid state polymerization

Solid state polymerization can also be employed for the synthesis of PLA. This process involves heating a semi-crystalline solid prepolymer of low molecular weight to a temperature above its glass transition temperature ( $T_g$ ) but below its melting temperature ( $T_m$ ). This allows for mobility of the chain ends, and the polymerization occurs mostly in the amorphous regions of the polymer. This method causes much slower rates of polymerization than other polymerization methods, but allows for very high molecular weight polymer to be synthesized. Also, because the reaction proceeds at a lower temperature than other methods, side reactions are less likely to occur. The reaction scheme for the solid state polymerization method is shown in Figure 8.



**Figure 8.** Reaction scheme for the solid state polymerization method.

A metal catalyst can catalyze the solid state polycondensation in the amorphous phase as well as the melt polycondensation. These catalysts can be different metals or metal salts, from metals such as Sn, Ti, and Zn. The removal of water can be further enhanced by carrying out the reaction under vacuum conditions in an inert atmosphere. Wang et al. [34] synthesized high molecular weight poly(lactic acid) (PLA) by direct melt/solid polycondensation of lactic acid using various catalyst. This is two step reactions, first-step melt polycondensation reaction carried out at  $150^\circ\text{C}$  for 4 hrs, then  $160^\circ\text{C}$  for another 4 hrs using predetermined amount of catalyst and followed solid polycondensation by using *p*-toulenesulfonic acid monohydrate (TSA) as the catalyst in the second step. They studied the effect of various catalysts and reaction temperature on the molecular weight and crystallinity of resulting polymer. It was found that  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O/TSA}$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O/succinic anhydride}$ , and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O/maleic anhydride}$  binary catalysts should be effective binary catalysts to obtain high molecular weight PLA of more than  $1.2 \times 10^5$ . They used conventional melt spinning method to spin PLA fibers, which displayed tensile strength of  $(382.76 \pm 1.41)\text{MPa}$  and tensile modulus of  $(4.36 \pm 0.07)\text{GPa}$ . Kazuki et al. [35] synthesized stereo-block poly(lactic acid) by solid-state polycondensation of the melt-blend of the medium-molecular-weight PLLA and PDLA, which were both obtained by melt polycondensation of L- and D-lactic acids with 0.1-0.3wt.-% of the catalyst ( $\text{SnCl}_2/\text{TSA}$ ), respectively. In the first step, melt-polycondensation of L- and D-lactic acids is conducted to synthesize poly (L-lactic acid) and poly (D-lactic acid) with a medium-molecular-weight, respectively. In the next step, these poly(L-lactic acid) and poly(D-lactic acid) is melt blended in 1:1 ratio to allow formation of their

stereo complex. In the last step, this melt-blend is subjected to solid-state polycondensation at temperature where the dehydrative condensation is allowed to promote chain extension in the amorphous phase with the stereo complex crystals preserved and obtained high molecular weight stereo-block poly(lactic acid). The highest Mw of the stereo-block PLA reached 1,00,000 when the solid-state polycondensation was conducted above 180°C.

### 3. Materials and Experimental Work

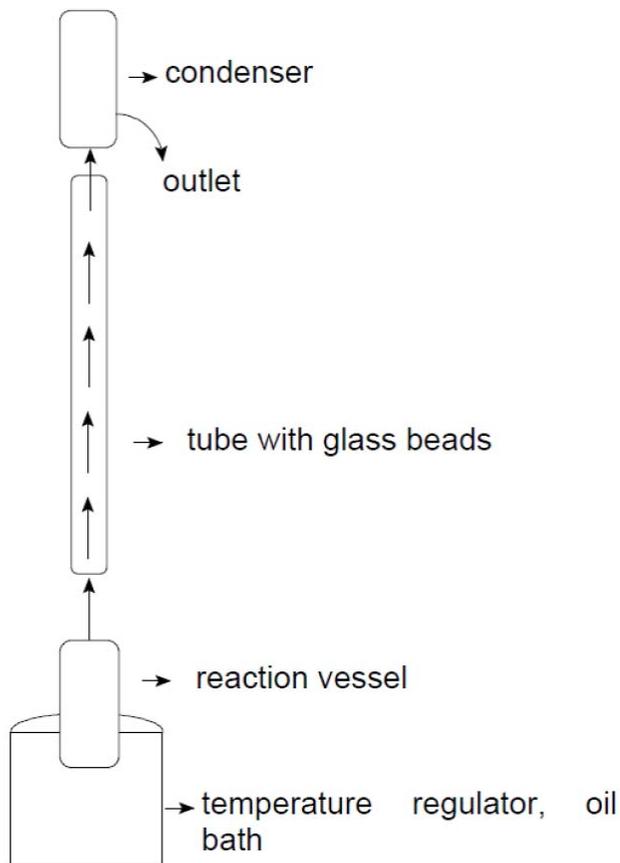
Methanol was purchased from Merck Speciality Pvt. Ltd., India. Lactic acid was synthesized by fermentation process in lab. A strong cation-exchange resin, Amberlyst 15 dry in the H<sup>+</sup> form, was purchased from Sigma Co. and used as a solid catalyst. This cation exchange resin was washed several times with distilled water before use to completely remove moisture and dried at 95°C to avoid desulphonization, which takes place over 120°C. The properties of ion exchange resins are as shown in Table 1.

**Table 1.** Properties of ion exchange resins

Properties	Amberlyst-15 dry	Amberlite IR-120	Indion-730	Tulsion T-42 MP
Matrix	Styrene divinyl benzene copolymer			
Cross-linking density	20%	8%	–	–
Particle size	600-850µm	620-830µm	0.3-1.2mm	0.3-102mm
Total exchange capacity	4.7meq/g	1.8meq/mL	1.7meq/mL	1.6meq/mL
Ionic form	H <sup>+</sup>	H <sup>+</sup>	H <sup>+</sup>	H <sup>+</sup>
limit	120°C max temp.	121°C max temp.	120°C max temp.	120°C max temp.

### 3.1. Apparatus

The distillation column used was a glass packed column of diameter 1 inch and height 60cm for the esterification and hydrolysis part. The capacity of reactor for esterification was 250ml and for hydrolysis 500ml. The reaction temperature was controlled by putting the flask in the constant temperature oil bath.



**Figure 9.** Distillation column.

### 3.2. Esterification of lactic acid

**Table 2.** Esterification of lactic acid

Esterification of lactic acid									
Batch no.	LA/MeOH ratio	Reaction temp. (°C)	Catalyst (wt %)	Reaction time (hrs)	Stirring speed (rpm)	Acid value (mg KOH/gm of sample)	Methyl lactate (gm)	Conversion (%)	
1	1:4	70		12	400	21.57	1.5	28.84	Without catalyst and column
2	1:4	70		13	400	16.77	1.67	32.11	
3	1:2	70		13	400	13.75	1.4	26.92	
4	1:3	70	2	7	–	38	1.62	31.15	Without stirring
5	1:7	70	0.7	7	800	25.39	1.68	32.30	With catalyst and column
6	1:5	70	0.8	7	400	12.36	1.8	34.61	
7	1:5	70	4	7	400	22.22	0.6	11.53	
8	1:4	70	2	8	400	18.06	1.72	33.07	Without column

**Table 2.** (Continued)

Batch no.	LA/MeOH ratio	Reaction temp. (°C)	Catalyst (wt %)	Reaction time (hrs)	Stirring speed (rpm)	Acid value (mg KOH/gm of sample)	Methyl lactate (gm)	Conversion (%)	
9	1:3	70	2	9	400	10.81	1.63	31.34	With catalyst and column
10	1:5	70	1.5	9	400	20	1.92	36.92	
11	<b>1:5</b>	<b>70</b>	<b>3</b>	<b>9</b>	<b>400</b>	<b>16.45</b>	<b>1.96</b>	<b>37.69</b>	
12	1:4	70	2	9	400	22.15	1.81	34.8	
13	1:5	70	2	9	400	19.8	1.93	37.11	
14	1:5	70	0.5	9	400	20.59	1.01	19.42	
15	1:5	70	2	9	400	15.59	1.41	27.11	
16	1:5	70	2	9	400	16.40	1.23	23.65	
17	1:5	70	3	9	400	2.99	2.65	50.9	Amberlyst-15
18	<b>1:5</b>	<b>70</b>	<b>3</b>	<b>9</b>	<b>400</b>	<b>2.52</b>	<b>2.89</b>	<b>55.57</b>	Amberlite IR-120
19	1:5	70	3	9	400	2.64	2.83	54.42	Indion-730
20	1:5	70	3	9	400	2.79	1.74	33.4	Tulsion T-42 MP

### 3.3. Procedure

In case of esterification reaction, initially water was removed from fermentation broth (150ml) at 100°C. After complete removal of water, a solution of lactic acid and catalyst was charged into the 250ml of three necked flask, equipped with magnetic stirrer, thermometer and packed column. The reaction mixture was heated at 50°C. Once the desired temperature has been reached methanol was added into the reaction mixture. The end of this addition was taken as zero reaction time for a run. The temperature of reaction mixture was increased up to 70 to 80°C. The reaction was continuously carried out for 9 hrs at 400rpm. The temperature of three necked flask was continuously monitored with the help of thermometer. As esterification of lactic acid with methanol proceed in reactor, water and methyl lactate which have midway volatilities are produced. The catalyst was removed from reaction mixture. After removal of catalyst NMP (solvent) was added into the reactor and methyl lactate, water and unreacted methanol were distilled out. Further, several washings of chloroform were given to methyl lactate in order to ensure complete removal of impurities and purified product was analysed for acid value. The reaction conditions and % conversion are depicted in Table 2.

### 3.4. Analysis of lactic acid synthesized

#### Acid value

The concentration of lactic acid in the esterification and hydrolysis reactors was determined by a titration method. Samples were titrated with the standard 0.1N sodium hydroxide (NaOH) solution using phenolphthalein as an indicator.

#### High performance liquid chromatography

The purity of L (+) -lactic acid was analyzed by high performance liquid chromatography (HPLC) with UV detector (diode array detector L-2455) at 214nm using C-8 (5 $\mu$ m) column (250  $\times$  4.6mm).

### 3.5. Hydrolysis of methyl lactate

#### Procedure

In the hydrolysis part, the distilled water and pretreated cation-exchange resins were first charged into the 250ml of three necked flask, equipped with magnetic stirrer, thermometer and packed column and reaction mixture were heated up to the desired reaction temperature (60°C); once desired temperature has been reached the second reactant, methyl lactate was added into the reactor. The end of the addition of methyl lactate was considered to be the starting time of the reaction. The temperature of reaction mixture was increased up to 90 to 95°C. The reaction was continuously carried out for 9 hrs at 400rpm. The temperature of reaction mixture was continuously monitored with the help of thermometer. The reaction conditions and % conversion are depicted in Table 3.

**Table 3.** Hydrolysis of methyl lactate

Hydrolysis of methyl lactate									
Batch	Methyl lactate/H <sub>2</sub> O (mole)	Reaction temp. (°C)	Catalyst type	Catalyst %	Reaction time (hrs)	Stirring speed (rpm)	Acid value	Lactic acid (gm)	Conversion %
21	1:5	90-95	Amberlite IR-120	3	9	400	49.09	3	8.33

### 3.6. Polymerization of lactic acid by azeotropic dehydration polycondensation technique

#### Procedure

Initially, 25gm of D, L-lactic acid and xylene solution was placed in the four necks round bottom flask, equipped with stirrer, thermometer, and condenser. D, L-lactic acid was azeotropically dehydrated with a nonpolar, organic solvent for 5h at 140°C without any catalyst in order to remove the free water. After the removal of water in the trap of the Dean-Stark condenser, the reaction vessel was cooled to 50°C, the required amount of catalyst was added into the flask and polymerization was carried out at 170°C. The reaction time was 14hrs in all cases. Nitrogen gas was continuously purged in to the reaction flask in order to safely perform polymerization at high temperature.

To determine the yield of PDLLA, the cooled crude product was dissolved in chloroform and precipitated in methanol, and the precipitate was dried at 70°C for 4 hrs. The yield was determined from the weight ratio of the precipitated polymer to the monomer. The reaction conditions and molecular weight are depicted in Table 4.

**Table 4.** Polymerization of lactic acid by azeotropic dehydration technique

Batch no.	Lactic acid	Stannous octotrate (mole %)	Reaction temp. (°C)	Reaction time (hrs)	solvent	Yield (%)	Mn	Mw	PDI
11	25	0.1	170	13	Xylene	53.6	26.348	57.601	<b>2.186</b>
12	25	0.15	170	13	Xylene	50.8	28.823	59.178	<b>2.053</b>
13	25	0.20	170	13	Xylene	47.2	24.799	53.853	<b>2.172</b>
14	25	0.15	180	13	Xylene	52.8	25.004	62.408	<b>2.496</b>
15	25	0.15	190	13	Xylene	49.6	12.930	26.656	<b>2.062</b>
16	25	0.15	170	15	Xylene	54.4	23.363	62.795	<b>2.688</b>

### 3.7. Analysis of PDLLA

The structure of PDLLA was determined by FTIR. The FTIR spectra were evaluated on Perkin Elmer 781 spectrophotometer. The FTIR spectrum of samples was evaluated by using 0.5% KBr pellets. The molecular weight (number-average molecular weight (Mn), weight-average molecular weight (Mw), and polydispersity index [Mw/Mn]) were calculated by gel permeation chromatography (GPC) instrument. THF was used as eluent at a flow rate of 1.0mL/min, and the molecular weights were calibrated with polystyrene standards. Differential scanning calorimetry (DSC) measurements were performed in a nitrogen atmosphere. The measurements were run from 0 to 200°C at a heating rate of 10°C/min and at a cooling rate of 10°C/min. The glass transition temperature and melting temperature of polymer were determined by using DSC.

## 4. Result and Discussions

### • Recovery of lactic acid from fermentation broth by reactive distillation

#### (1) Effect of presence of catalyst on conversion

Methyl lactate was prepared with and without catalyst. The reaction time and percentage conversion are given in Table 5. In the presence of catalyst, the reaction time has come down to 9 hrs with the acid value 18.06 compared to 12 hrs with the acid value 21.57 of the product. This suggests that amount of catalyst enhances the rate of reaction between lactic acid and methanol.

**Table 5.** Effect of presence of catalyst on conversion

LA/MeOH ratio (mole)	Catalyst (%)	Reaction time (hrs)	Conversion (%)
1:4	–	12	28.84
1:4	2	9	33.07

### (2) Effect of the reactant molar ratio on conversion

To investigate the effect of reactant mole ratio on the yield of methyl lactate, the initial molar ratio of LA:MeOH was varied from 1:3 to 1:5 while keeping the rest of the experimental condition similar. The results obtained are presented in Table 6, as the reactant mole ratio increased, the yield of lactic acid increased.

From this table, it can be observed that the conversion of 31.34% is obtained from 1:3 of LA/MeOH and increased up to a value of 37.69 for LA/MeOH = 1:5 at reaction time of 9 hrs. From the experimental result, it can be observed that reactant molar ratio 1:5 gives highest % conversion. According to Le-Chatelier's principle, in a chemical reaction excess amount of one reactant drives the reaction in forward direction. Therefore, high ratios of LA/MeOH are preferred to maximize the conversion. But, because of the presence of the large excess of one of the reactants, the recovery of the product will become more expensive. Therefore, it is desirable to use optimum initial reactant molar ratio.

**Table 6.** Effect of molar ratio on conversion

LA/MeOH ratio (mole)	Catalyst (%)	Reaction time (hrs)	Conversion (%)
1:3	2	9	31.34
1:4	2	9	34.8
1:5	2	9	36.92

### (3) Effect of catalyst loading on % conversion

The effect of catalyst loading in esterification part was investigated and the results obtained are presented in Table 7. The catalyst loading was varied from 0.5 to 3% (weight/volume) of reaction mixture at a temperature of 70°C and reactant mole ratio of 1:5. The conversion increased with catalyst loading up to 3%. With the increase in catalyst loading, the surface area and the total number of active acid sites for the reaction increase. Therefore, the production rate of methyl lactate was increased.

**Table 7.** Effect of catalyst loading on % conversion

LA/MeOH ratio (mole)	Catalyst (%)	Reaction time (hrs)	Conversion (%)
1:5	0.5	9	19.42
1:5	1.5	9	36.72
1:5	2	9	37.11
1:5	3	9	37.69

**(4) Effect of temperature on % conversion**

The effect of the temperature is very important since it is useful to calculate the activation energy of the reaction. Kinetic experiments were performed in a temperature range from 55 to 70°C for the esterification reaction. Typical results are shown in Table 8 and it can be seen that the reaction rate increases with increasing reaction temperature. The final conversion obtained at 55°C was around 23.65% while conversion obtained at 70°C was around 37.11%.

**Table 8.** Effect of temperature on % conversion

LA/MeOH ratio (mole)	Catalyst (%)	Reaction temp. (°C)	Conversion (%)
1:5	2	55	23.65
1:5	2	60	27.11
1:5	2	70	37.11

**(5) Effect of catalyst type on conversion**

Four acid ion-exchange resins, Amberlyst-15, Amberlite IR-120, Indion-730, and Tulsion T-42 MP were selected as catalysts for esterification reaction. Table 9 shows the comparison of the % conversion of methyl lactate obtained with catalyst in the esterification reactions of lactic acid with methanol. Experiments were carried out under identical conditions except for the type of catalyst. Tulsion T-42 MP showed the lowest acid activity and Amberlite IR-120 showed the highest, because of the differences in ion exchange capacity and degree of cross linking of catalyst.

**Table 9.** Effect of catalyst type on % conversion

Catalyst type	LA/MeOH ratio (mole)	Catalyst (%)	Reaction time (hrs)	Reaction temp. (°C)	Conversion (%)
Amberlyst-15	1:5	3	9	70	50.9
Amberlite IR-120	1:5	3	9	70	55.57
Indion-730	1:5	3	9	70	54.42
Tulsion T-42 MP	1:5	3	9	70	33.4

• **Polymerization of lactic acid by azeotropic polycondensation technique**

**(1) Effect of catalyst concentration on molecular weight of polymer**

Effect of catalyst concentration on molecular weight of polymer was first studied by using stannous octoate as a catalyst. Table 10 shows that the molecular weight of synthesized PDLA was about 28,800 when 0.15 mole% of catalyst was used at 170°C. However, when more than 0.15 mole% of catalyst was used, the rate of termination becomes higher than the rate of propagation which results in the formation of low molecular weight PDLA.

**Table 10.** Effect of catalyst concentration on molecular weight of polymer

Lactic acid	Stannous octoate (mole %)	Reaction temp. (°C)	Reaction time (hrs)	Mn	Mw	PDI
25	0.1	170	13	26,348	57,601	<b>2.186</b>
25	0.15	170	13	28,823	59,178	<b>2.053</b>
25	0.2	170	13	24,799	53,853	<b>2.172</b>

**(2) Effect of temperature on the molecular weight of PLA**

The changes in molecular weight of PDLA as a function of reaction temperature during the polycondensation reaction are shown in Table 11. High reaction temperature was useful to promote the removal of water

therefore all polymerization reactions were carried out at 170°C. Above 170°C, molecular weight of PDLLA was decreased sharply from 28,823 to 12,930 due to occurrence of depolymerisation.

**Table 11.** Effect of temperature on the molecular weight of PLA

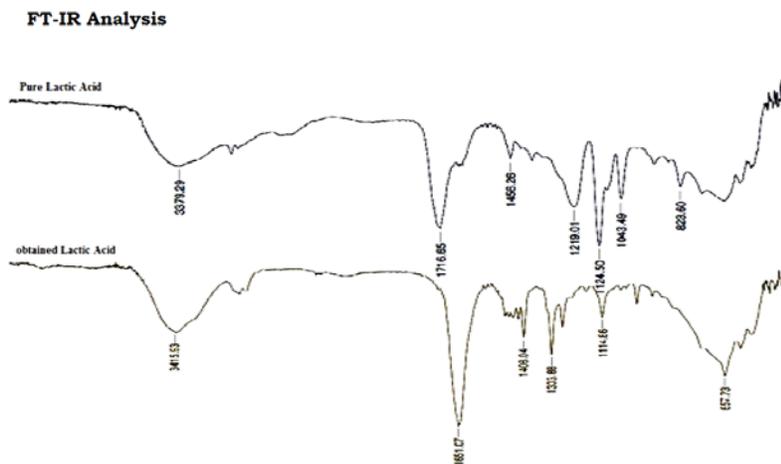
Lactic acid	Stannous octoate (mole %)	Reaction temp. (°C)	Reaction time (hrs)	Mn	Mw	PDI
25	0.15	170	13	28,823	59,178	<b>2.053</b>
25	0.15	180	13	25,004	62,408	<b>2.496</b>
25	0.15	190	13	12,930	26,656	<b>2.062</b>

### (3) Effect of reaction time on molecular weight

Based on the same dosage of stannous octoate and reaction temperature, the relationship between the different reaction times and PDLLA's molecular weights was also evaluated. Table 12 shows that the highest molecular weight was obtained when the reaction was carried out for 13 hours. The impact of the reaction time on polymerization is reflected into three stages. First, the longer the reaction time, the longer the polymer chain and the higher molecular weight can be obtained. Second, with the reaction carrying on, less monomer remains for further reaction which leads to slower polymerization while the competitive depolymerization is accelerated. Finally, the PDLLAs are also easily degraded at elevated temperatures. When the reaction time varied, the low molecular weight and wide molecular weight distribution of PDLLAs can be obtained. The results prove that the optimal reaction duration is 13 hours.

**Table 12.** Effect of temperature on the molecular weight of PLA

Lactic acid	Stannous octoate (mole %)	Reaction temp. (°C)	Reaction time (hrs)	Mn	Mw	PDI
25	0.15	170	13	28,823	59,178	<b>2.053</b>
25	0.15	170	15	23,363	62,795	<b>2.688</b>

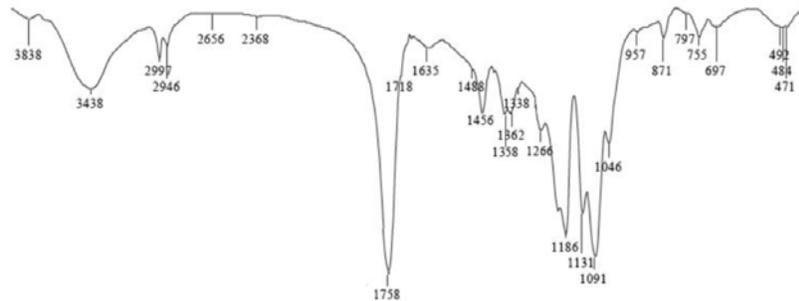


**Figure 10.** FT-IR spectrum of lactic acid.

FT-IR results of pure lactic acid and obtained lactic acid monomer are shown in Figure 10. In the lactic acid, the strong hydroxyl peak observed around  $3415\text{cm}^{-1}$  shows the terminal  $-\text{OH}$  groups. The peaks at  $1112.16\text{cm}^{-1}$  are observed due to  $\text{C}-\text{O}$  alcoholic stretching. A band corresponding to bending vibrations of  $\text{C}-\text{H}$  was found in  $1408.04\text{cm}^{-1}$  in the spectrum. The presence of the strong  $\text{C}=\text{O}$  absorption at about  $1651.07\text{cm}^{-1}$  indicate the carbonyl stretching. Hence, the functionality of L-lactic acid was proved, but due to some impurity the observed peaks were very broad than standard lactic acid peak.

Figure 11 shows FTIR spectrum of the PDLLA with a molecular weight of 28,800, which was prepared by azeotropic polycondensation of D, L-lactic acid at a temperature of  $170^\circ\text{C}$  and with a polymerization time of 13 hrs. The intense bands are observed at  $2997\text{cm}^{-1}$  and  $2946\text{cm}^{-1}$  due to  $\text{C}-\text{H}$  stretching of methyl and methylene groups. The intense bands at  $1756\text{cm}^{-1}$  due to the ester carbonyl group, other significant band are in the region  $1091\text{cm}^{-1}$  typical of the ester sequence  $-\text{CO}-\text{O}-$ . A band corresponding to bending vibrations of  $\text{C}-\text{H}$  was found in

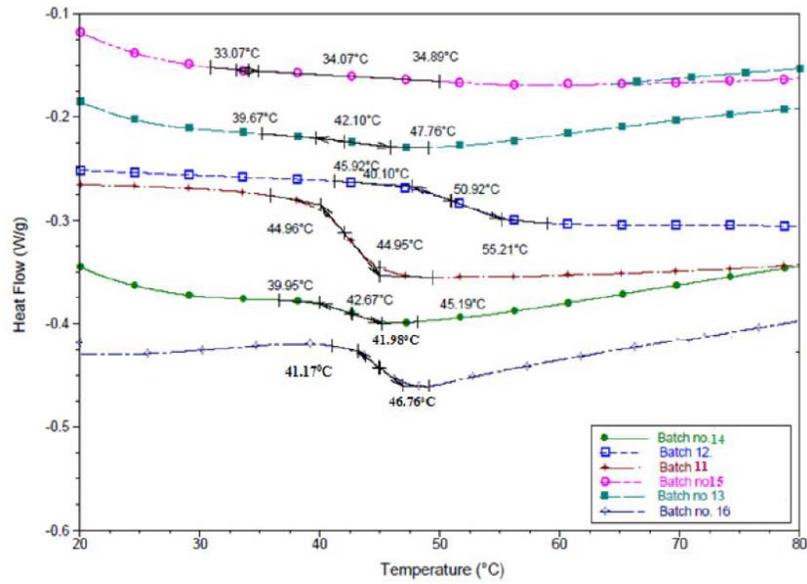
1456-1385 $\text{cm}^{-1}$  in the spectrum. The strong hydroxyl peak observed around 3438 $\text{cm}^{-1}$  shows the terminal  $-\text{OH}$  groups, may be used as an indication of the low molecular weight of the polymer.



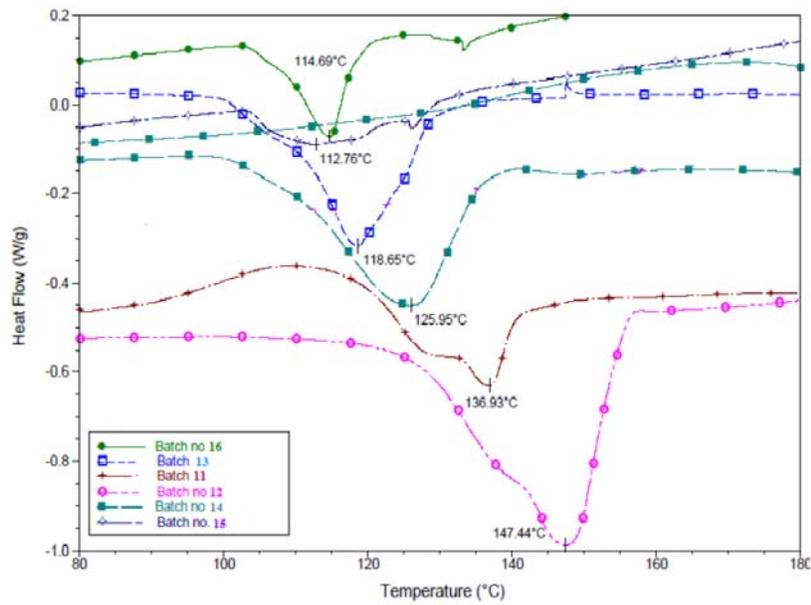
**Figure 11.** FT-IR spectrum of poly (D, L-lactic acid).

#### (4) Differential scanning calorimetry study of PDLA

Figures 12 (a), (b) show the DSC thermographs of PDLA produced by azeotropic polycondensation technique by using stannous octoate as a catalyst. The thermographs were recorded by a differential scanning calorimeter, at heating rate of 10°C/min, and in the temperature range from 0–200°C. The curve of PDLA exhibited two thermal transitions, i.e., glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ). The low molecular weight (i.e., 12,930g/mol) PDLA showed  $T_g$  and  $T_m$  peak located at 34.07°C and 112.76°C, respectively. The high molecular weight (i.e., 28,823g/mol) PDLA showed  $T_g$  and  $T_m$  peak located at 50.92°C and 147.44°C, respectively, indicating partly-crystalline structure formed. Figures 8(a), (b) show that glass transition temperature and melting point of PDLA was increased with increasing molecular weight of polymer.



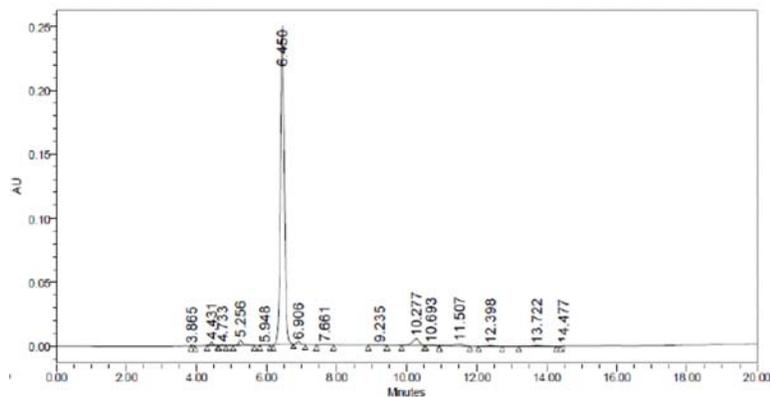
**Figure 12(a).** Glass transition temperature ( $T_g$ ) of PDLLA.



**Figure 12(b).** Melting temperature ( $T_m$ ) of PDLLA.

**(5) HPLC after separation and purification**

After separation and purification of lactic acid from fermentation broth, the sample was analysed to confirm the purity of separated lactic acid on HPLC as shown in Figure 13. It was observed that purity of lactic acid was achieved up to 95%, but trace amount of some impurity was observed as indicated by the graph at a different retention times.



**Figure 13.** HPLC after separation and purification.

RT	Area	% Area	Height
3.865	286	0.01	102
4.431	14231	0.67	2811
4.733	2665	0.13	535
5.256	34912	1.64	4329
6.450	1433425	90.93	248837
6.906	14707	0.69	2033
7.661	1884	0.09	195
9.235	3150	0.15	225
10.277	70143	3.30	5151
10.693	2372	0.11	211
11.507	31012	1.46	1778
12.398	5910	0.28	390
13.722	9879	0.46	431
14.477	187	0.01	- 31

## 5. Conclusion

The objective of present investigation was purification and separation of lactic acid from fermentation broth by reactive distillation technique and polymerized it via azeotropic dehydration technique. In esterification & hydrolysis reaction cation exchange resin was used as a catalyst. The effect of catalyst, catalyst loading and reactant mole ratio on the yield was studied in esterification reaction.

Polymerization reaction was carried out by using stannous octoate as catalyst under inert atmosphere. The effect of catalyst concentration, reaction time and reaction temperature on molecular weight of polymer was studied.

On the basis of the experimental data, the following conclusion can be drawn from these investigations:

- Catalyst enhances the conversion & reaction rate in esterification reaction.
- Amberlite IR-120 was found to be the best catalyst amongst Amberlyst-15, Indion-730, and Tulsion T-42 MP catalysts that are used for esterification reaction.
- The esterification reaction rate increased with increasing temperature, catalyst loading and molar ratio of reactant.
- PDLLA was synthesized with a molecular weight 28,800g/mol at laboratory scale using stannous octoate as a catalyst by azeotropic dehydration technique and structure of PDLLA was confirmed by FTIR spectroscopy.
- The maximum molecular weight of PDLLA is obtained when the catalyst concentration is 0.15 mole% and reaction time is 13 hrs.
- The DCS results indicate that the  $T_g$  &  $T_m$  of PLA increased with increasing molecular weight of PLA.

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