MICROWAVE ASSISTED POLYMERIZATION OF LACTIDE AND *IN SITU* PREPARATION OF POLY (LACTIC ACID) - CLAY NANOCOMPOSITES

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By

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CERTIFICATE

This is to certify that the thesis entitled "**Microwave Assisted Polymerization of Lactide and *In Situ* Preparation of Poly (Lactic Acid) - Clay Nanocomposites**" being submitted by Ms. Pankil Singla in fulfillment of the requirements of the degree of **DOCTOR OF PHILOSOPHY**, in the School of Chemistry and Biochemistry, Thapar University, Patiala is a record of the candidate's own work carried out by her under our supervision and guidance. The matter embodied in this thesis has not been submitted in part or full to any other university or institution for the award of any degree.

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ABSTRACT

Poly(lactic acid), PLA is made from renewable agricultural products and is readily degradable. Since PLA can be synthesized from lactic acid, which is a product of fermented starch, and can be degraded into nontoxic end-products thus it is an environment friendly material.

This thesis embodies the subject matter resulting out of this study and is arranged in five chapters. A brief introduction, historical background and applications of PLA have been described first. A brief account of the advantages of using microwave for the synthesis of PLA has been included. The mode of heating (conventional and microwave heating) for the synthesis of PLA has been compared. The importance of lactic acid, the starting material, used in the synthesis of polylactide has also been discussed. The important method of synthesizing PLA is the ring-opening polymerization technique which is more useful than polycondensation for the production of high molar mass PLA. Polymerization kinetics of microwave-assisted synthesis of PLA has also been discussed.

Microwave heating has been used for the synthesis of PLA from l-lactide and the ring-opening polymerization method has been chosen for the present work. Relevant literature for the polycondensation method and ring-opening method used in microwave oven has been reviewed. *In-situ* preparation of PLA-clay nanocomposites under microwave irradiation has also been reviewed. Two types of microwave heating system: domestic microwave and monomode microwave have been used to synthesize PLA and its clay nanocomposites in the present work. Studies on the effects of different parameters: polymerization temperature, polymerization time, monomer to initiator ratio, nature of initiator, effect of clay etc. which affect the polymerization of l-lactide to give PLA and its clay nanocomposites have been studied and discussed. The *in-situ* ring-opening polymerization of l-lactide to synthesize PLA/Clay nanocomposites by the addition of different types of clays have been successfully carried out under microwave irradiation. In this part of the work, effects of clay loading have been studied and nanocomposite products have been examined with respect to their morphology and degree of nanoclay dispersion. The present study reports for the first time the degradation of the polymer in chloroform solvent when the solution is left overnight before SEC characterization, resulting in a lower molar mass PLA.

To carry out ring-opening polymerization using microwave irradiation for synthesizing PLA, three different experimental set-ups were used for the polymerization of lactide and to prepare its clay nanocomposites. The first set-up was used for the synthesis of PLA in a domestic microwave oven and a second set-up was used in a monomode microwave oven. The third set-up was used for the synthesis of PLA/Clay nanocomposites in the monomode microwave oven. Here, an ultrasonic probe was used for proper dispersion of clay in the solvent.

Synthesis of PLA was carried out using initiators like stannous octoate ($SnOct_2$), dibutyltin dimethoxide (DBTM) and one co-initiator, dimethyl aminopyridine (DMAP). The reason for selecting these initiators was that bulky groups attached to the metal atom would provide the steric hindrance around metal atom during ring-opening polymerization reaction. A new catalyst DBTM and co-initiator DMAP have been used for the first time in microwave assisted synthesis of PLA.

PLA has been successfully synthesized in domestic microwave oven with molar mass above 50,000. Different molar ratios of monomer and initiator have been used for the synthesis of PLA in monomode microwave. In monomode microwave the ring-opening polymerization time was reduced to few mins from several hours reported for conventional heating. Size exclusion chromatography (SEC) was used to determine the molar mass of synthesized PLA. The molar mass of PLA obtained using $SnOct_2$ was above one lakh. The initial increase in the molar mass with an increase in $[M_o]/[I_o]$ ratio, followed by a decrease at higher $[M_o]/[I_o]$ ratio can be explained as follows: as $[M_o]/[I_o]$ ratio increases, the relative number of initiator molecules decreases. So with an increase in $[M_o]/[I_o]$ ratio there is reduction in the number of chains onto which given monomer molecules can distribute themselves. Thus, the molar mass increases with an increase in $[M_o]/[I_o]$ ratio. In few cases, with further increase in $[M_o]/[I_o]$ ratio, the molar mass decreases. It is possible that at very low initiator concentration the effect of impurities on termination of a few growing chains may become the controlling factor with regard to molar mass. Additionally, it is known that during conventional polymerization of PLA at higher reaction times and at higher temperature, back-biting and transesterification reactions become significant leading to lowering of the average molar masses. In case of DBTM, PLA with low molar mass of a few thousands has been obtained as DBTM is known to be an effective transesterification catalyst and also known to cause ‘back-biting’ degradation.

DMAP is a better nucleophile and good esterification catalyst; hence it prevents the back-biting reaction. Hence use of DMAP as a co-initiator with $SnOct_2$ was expected to enhance the polymerization rate and much higher molar mass of PLA. In fact high molar mass PLA has been obtained only in case of $SnOct_2$ as the initiator and DMAP as the co-initiator.

Nano-dispersion of clay was achieved by using an ultrasonic probe. Ultrasonication provides tremendous amount of energy to the clay layers, so that they get separated to a larger extent. It is known that the addition of clay can efficiently improve the mechanical and barrier properties provided that they are well dispersed in the matrix and form an exfoliated structure. The present work showed that the incorporation of organically modified clay into PLA enhances thermal degradation temperature and hence markedly increases the thermal stability of the resulting PLA/Clay nanocomposites**.** The effect of clay loading was of much significance with respect to the polymerization yield. It showed negative effect on the polymerization yield. The formation of exfoliated structures was confirmed by X-ray diffraction studies and transmission electron microscopy.

The kinetics of PLA synthesis in a microwave reactor is very different from its conventional synthesis where it has been reported that the rate of reaction is first order with respect to both monomer concentration and initiator concentration. The results indicate that the microwave-assisted ROP is accelerated not only by the microwave-induced temperature conditions (thermal microwave effect) but also by the microwaves themselves, that is, the non-thermal microwave effect.

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Symbol	Description
ASTM	American Society for Testing of Materials
k_{app}	Apparent rate constant
^{13}C NMR	Carbon nuclear magnetic resonance spectroscopy
CEC	Cationic exchange capacity
$CHCl_3$	Chloroform
C_o	Concentration of monomer at time 0
C_t	Concentration of monomer at time t
ε’	Dielectric constant
ε”	Dielectric loss
DCM	Dichloromethane
DBTM	Dibutyltindimethoxide
DMAP	Dimethyl aminopyridine
Δ	Dissipation factor
Bu_2SnCl_2	Dibutyltindichloride
DCTB	1,3-dichloro-1,1,3,3-tetrabutyldistannoxane
DMF	Dimethylformamide
DSC	Differential scanning calorimetry
ELSD	Evaporative light scattering detector
FNPs	Ferrite nanoparticles
FDA	Food and drug administration
FTIR	Fourier transform infra-red
GPC	Gel permeation chromatography
T_g	Glass transition temperature
GHz	Giga hertz
^1H-^{13}C HSQC NMR	^1H-^{13}C Correlation Heteronuclear Single-Quantum Coherence (HSQC) Nuclear Magnetic Resonance
ISO	International Standards Organization
$[M]_o$	Initial monomer concentration

I	Initiator
$[I]_o$	Initial initiator concentration (mol/l)
k_o	Initiation rate constant (l/mol.min)
c_i	Injected concentration
LA	Lactide
tan δ	Loss tangent
T_m	Melting temperature
MPa	Mega pascal
MW	Microwave
MAROP	MW-assisted ring opening polymerization
M	Monomer
$[M_o]/[I_o]$	Monomer to initiator ratio
MPS	Methacryloxypropyltrimethoxysilane
MALDI-TOF MS	Matrix-assisted laser desorption/ionization time of flight mass spectrometry
MALDI MS	Matrix-assisted laser desorption/ionization mass spectrometry
MgO	Magnesium oxide
Cloisite® 15A	Montmorillonite modified with dimethyl dehydrogenated tallow quaternary ammonium cations
Cloisite® 30B	Montmorillonite modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium cations
NPCs	Nanomagnetic polymer composites
M_n	Number-average molar mass
OMMT	Organically modified montmorillonite
PHAs	Poly(hydroxyalkanoates)
PLA	Poly(lactic acid)
PLLA	Poly(l-lactic acid)
PDLA	Poly (d-lactic acid)
PDLLA	Poly(d,l-lactic acid)

PBS	Poly(butylene succinate)
PCL	Poly(caprolactone)
PTFE	Poly(tetrafluoroethylene)
PAN	Poly(acrylonitrile)
PEG	Poly(ethylene glycol)
k_p	Propagation rate constant (l/mol.min)
PD	Polydispersity
^{1}H NMR	Proton nuclear magnetic resonance spectroscopy
RID	Refractive index detector
d[P]/dt	Rate of formation of polymer
ROP	Ring-opening polymerization
SEM	Scanning electron microscopy
SiC	Silicon carbide
SEC	Size exclusion chromatography
Na^+-MMT	Sodium montmorillonite
$SnCl_2$	Stannous chloride
$Sn(Oct)_2$	Stannous octoate
THF	Tetrahydrofuran
PTFE	Teflon
TAS	*p*-toluenesulphonic
p-TsOH	*p*-Toluenesulfonic acid
k_t	Termination rate constant corresponding to termination by transfer to monomer (l/mol.min)
TiO_2	Titanium dioxide
TGA	Thermo-gravimetric ananlysis
TEM	Transmission electron microscopy
M_v	Viscosity average molar mass
WVTR	Water vapor transmission rate
M_w	Weight-average molar mass
WAXRD	Wide angle X-ray diffraction

XRD	X-ray diffraction
ZnS	Zinc sulphide

CHAPTER – 1

INTRODUCTION

CHAPTER-1 INTRODUCTION

1.1 Background

1.1.1 Biodegradable polymers

The technological advancements in the field of petrochemical-based polymers have brought many benefits to mankind. However, it is also becoming more and more evident that the ecosystem has been considerably disturbed and damaged as a result of the extensive use of non-degradable petro-plastics. The environmental impact of plastic wastes is causing global concerns as their disposal methods are limited. Incineration of the plastic wastes produces a large amount of carbon dioxide and other toxic gases, which contribute to global warming as well as and pose serious health risks. On the other hand, satisfactory landfill sites are also limited. Thus, there is an urgent need to develop renewable resource-based environmentally benign biodegradable plastic materials, especially for short-term packaging and other disposable applications that would not involve the use of toxic components in their manufacture and would facilitate composting with the naturally occurring biodegradable products.

Degradable plastics, as defined by the American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO), are those which can go through a significant change in the chemical structure under specific environmental conditions (Kolybaba *et al*., 2003). Biodegradable plastics get degraded with the help of naturally occurring microorganisms such as bacteria and fungi. The main attraction of these polymers is their biodegradation and mineralization to benign end-products after the use of the main product by consumers and their disposal into the bio-waste collection system for composting. This whole process will finally leave behind only CO_2 and H_2O as final products.

There are two broad types of biodegradable polymers natural and synthetic. Natural polymers include polysaccharides (starch, cellulose), proteins (gelatine, wool, silk), lipid fats (fats and oil), polyesters produced by plants or microorganisms [poly(hydroxyalkanoates) PHAs], polyesters derived from bio-derived monomers [poly(lactic acid) PLA], and several miscellaneous polymers like natural rubber and composites. The second group includes non-renewable petroleum based synthetic, and biodegradable plastics such as poly(butylene succinate) (PBS) and poly(caprolactone) (PCL). There are some biodegradable polymers which do not come into either category. These are poly anhydrides and poly vinyl alcohol. The most widely studied biodegradable polymers which are likely to be the most promising replacement for petrochemical based thermoplastic are polyesters. In recent years, the application of such biodegradable aliphatic polyesters has got a boost with their increasing use in everyday use materials and medical and health care devices.

1.2 Poly(Lactic Acid) (PLA)

One of the most promising and widely studied polyester is poly (lactic acid), PLA. PLA can be synthesized from lactic acid, which is a fermentation product of starch, and can be degraded into non-toxic end-products thus it is an environment friendly material.

Carothers *et al*. (1932) were the first to synthesize PLA successfully but high molecular weight polymer was not obtained until improved lactide purification techniques were developed by DuPont in 1954. After that PLA has attracted tremendous interest for application in different fields, such as packaging, daily consumable items and medical applications [Duncan and Kopecek (1984); Gilding and Reed (1979); Mainil Varlet *et al*. (1997); Vert *et al*. (1992)]. PLA is expected to have wide applications not only as degradable plastic, but also as a biomedical material, because of its degradability, biocompatibility, drug permeability, and good mechanical

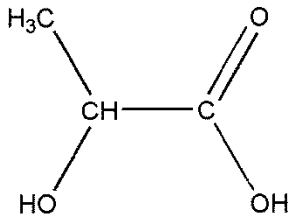
properties. Furthermore, lactic acid is easily obtained by a biotechnological process from inexpensive raw materials, such as starch, glucose, and oligosaccharides. Therefore, PLA is attracting increasing interest globally.

PLA is the product that has high potential due to its availability in the market and low price as compared to the others biodegradable polyesters [Vert *et al*. (1995); Sinclair (1996); Lunt (1998)]. Cargill-Dow has developed processes that use corn and other feedstock to produce different grades of PLA (NatureWorks®) [Steinbuchel and Doi (2002]. In 2002 NatureWorks® finished construction of a major lactic acid plant, capable of producing over 300 million pounds of lactic acid and PLA per year [Vink *et al*. (2003)]. Different companies such as Mitsui Chemicals (Japan), Galactic (Belgium), Treofan (Netherland) or Dainippon Ink Chemicals (Japan) produce PLAs on a relatively smaller scale.

1.2.1 Lactic Acid (Monomer)

Lactic acid is a carboxylic acid having the chemical formula $C_3H_6O_3$. It has a hydroxyl group adjacent to the carboxyl group. Lactic acid was first isolated in 1780 by a Swedish chemist, Carl Wilhelm Scheele from sour milk as impure brown syrup and gave it a name based on its origin: 'Mjolksyra'. The French scientist Fremy produced lactic acid by fermentation and this gave rise to industrial production in 1881 (http://www.lactic-acid.com/history.html). Lactic acid is soluble in water or ethanol and is hygroscopic. Pure and anhydrous racemic lactic acid is a white crystalline solid with a low melting point. Lactic acid is chiral and has two optical forms, L(+) and D(-). L(+)-lactic acid is the biological isomer as it is naturally present in the human body. The lactic acid dimerises to give lactide, which upon ring-opening polymerization yields PLA

(http://en.wikipedia.org/wiki/Lactic_acid). General structure of lactic acid is shown in **Figure 1.1**.



Lactic acid

Figure 1.1 Structure of lactic acid

1.2.2 Properties of PLA

Figure 1.2 shows the chemical structure of PLA. The properties of PLA, such as melting point, crystallinity, and mechanical strength are affected by the polymer structure and its molecular weight. PLA has the glass transition temperature (T_g) in the range of 50 to 80 ^oC while the melting temperature (T_m) ranges from 130 to 180 ^oC. The physical and mechanical properties of PLA are given in **Table 1.1**.

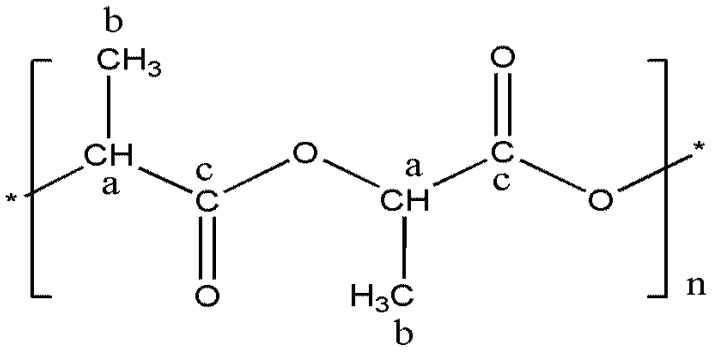


Figure 1.2 Chemical structure of PLA

Table 1.1 Physical and mechanical properties of poly (lactic acid), PLA [http://www.biodeg.net/biopolymer.html, accessed on 1st December, 2013)

S.No.	Properties	
1.	Density (g/l)	1.25
2.	Melting point, in °C (DSC)	152
3.	Glass transition, in °C (DSC)	58
4.	Crystallinity (in %)	0-1
5.	Modulus, in MPa (NFT 51-035)	2050
6.	Biodegradation* Mineralization in %	100
7.	Water permeability WVTR at 25 °C (g/m^2/day)	172
8.	Surface tension** (g) in mN/m. gd (Dispersive component) gp (Polar)	50

(*) At 60 days in controlled composting according to ASTM 5336.

(**) Determinations from contact angles measurements of probes liquid.

PLA exists in distinct forms due to the chiral nature of lactic acid. These are poly(l-lactide) (PLLA), poly (d-lactide) (PDLA) and poly(d,l-lactide) (PDLLA) as shown in **Figure 1.3**. Two units of l-lactic acid and d-lactic acid condense to form l-lactide and d-lactide, respectively. The l-lactide and d-lactide give PLLA and PDLA, respectively through ring-opening polymerization. However, racemic (50% d- and 50% l-Lactide) mixture gives poly (d,l-lactide), which is an amorphous polymer. In addition, PLA can be synthesized with varying fractions of l- and d-lactide also.

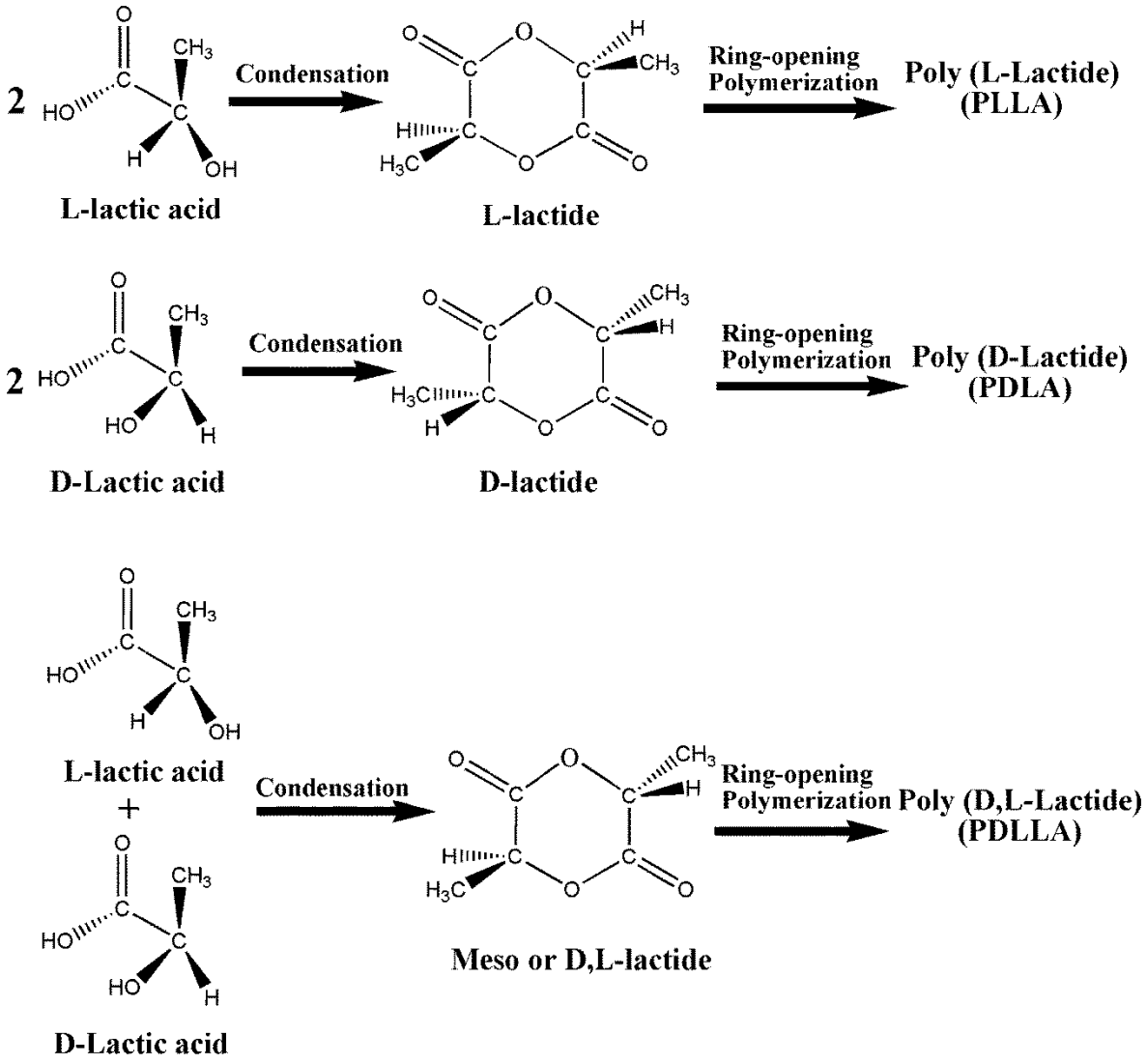


Figure 1.3 Different forms of PLA

1.2.3. Importance and Relevance of PLA and its Nanocomposites

1. The ring opening polymerization produces high molecular weight poly (lactic acid).

2. Applications of PLA-

(a) PLA is an environmentally friendly polymer that can be designed to biodegrade controllably; it is ideally suited for many applications in the environment, where recovery of the product is not practical, such as agricultural mulch films and bags.

(b) PLA is excellent for food contact and related packaging applications.

(c) PLA burns with low smoke generation, has good ultraviolet resistance, is easily dyed, and brings good wick-ability of moisture to applications.

3. PLA nanocomposites enhance the range of properties of polymer poly (lactic acid). It improves the mechanical, thermal and barrier properties.

4. It increases the strength and stiffness, permeation resistance, flame retardancy and heat deflection temperature. Because of the large surface area of the nanofiller, only small quantities need to be used and there is no need for new processing equipment to mix these fillers into the polymer.

5. The composite is recyclable.

1.2.4 Synthesis of PLA

PLA can be prepared using lactic acid via two synthetic routes, direct polycondensation and ring-opening polymerization (ROP) as shown in **Figure 1.4**. Direct polycondensation is a single-step method to produce PLA but the difficulty in removing water from the reaction medium results in a low molecular weight polymer having limited applications. The ROP method has attracted much more interest from industry and is widely used in commercial processes than the direct route because of the higher molecular weight product. PLA has been synthesised by conventional heating method (heating by conduction/ convection) since long using various catalysts. Both poly-condensation and ROP methods require long time for the polymerization

reactions to be completed using conventional heating. Hence there is need to reduce the reaction time through an alternate way of heating (e.g. microwave irradiation) for synthesizing PLA.

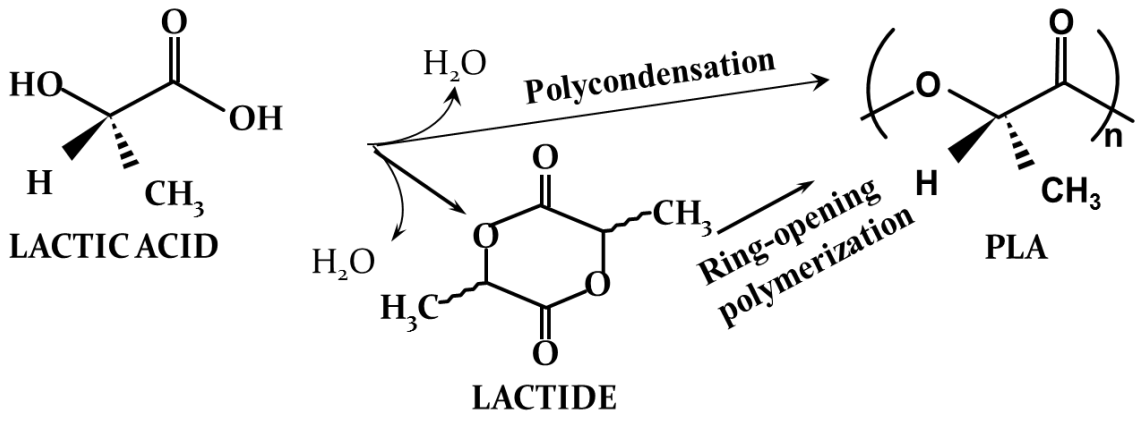


Figure 1.4 Synthesis routes of PLA (Source: http://www.nonwoven.co.uk/reports/Prague%202000.html)

1.2.4.1 Poly-condensation Method

Poly-condensation results in the formation of a polymer by the condensing molecules of a monomer with the release of water, or a similar simple substance. The major disadvantage of this synthesis route is that it does not produce high molecular weight PLA due to complication in removing impurities and water. Other drawbacks of this technique are the need for large reactor, evaporation, solvent recovery and increased racemization [Fisher *et al*. (1973)]. High molecular weight PLA can be synthesized by the process of polycondensation followed by solid state polycondensation. In this method, the residual monomer present in the polymer is substantially less because, during the solid-state polycondensation process, the monomer and catalyst are concentrated in the amorphous regions of the polymer and as a result almost 100% of the monomer is converted in to polymer [Maharana *et al*. (2009)].

1.2.4.2 Ring-Opening Polymerization (ROP)

The other method to synthesize PLA from lactic acid is the ring-opening polymerization (ROP) of lactide. This is a type of polymerization in which a cyclic monomer yields a monomeric unit that is either acyclic or contains fewer cycles than the monomer. In this type of polymerization two moles of lactic acid condenses to produce lactide which is a dimer and has ring type structure. Lactide ring opens to form PLA through ring-opening polymerization. This method produces high molecular weight PLA as it does not produce water as the side product. The mechanism of polymerization depends on the type of initiator. Three major reaction mechanisms proposed by earlier workers are cationic, anionic, and coordination-insertion. However, high molecular weight polyesters have only been obtained by using anionic or coordination-insertion ring-opening polymerization. As one type of chain polymerization, ROP consists of a sequence of initiation, propagation, and termination [Odian *et al*. (2004)]. ROP has been widely used and it plays an important role in academic research and industrial production.

1.3 Heating Methods

There are two ways of heating- conventional and microwave heating for synthesizing PLA. The conventional way of heating needs longer time to polymerize lactide. It takes several hours to days to complete the polymerization process. Hence there is a need to use a heating method which requires less time to complete the polymerization. The microwave technology gives answer to this question. Microwave technology is an environmentally benign process and microwave irradiation offers several advantages, such as instantaneous and rapid bulk heating, direct heating, high temperature homogeneity, selective heating (with material that can strongly absorb microwaves in a less polar reaction medium) and energy savings, over conventional heating (**Table 1.2)**. Over the last decade, microwave irradiation has developed into a highly

useful technique and provides an effective alternative and efficient energy source for chemical reactions and processes [Adam *et al*. (2003)].

Table 1.2 Differences between conventional and microwave heating [Dubey *et al*. (2008)]

Conventional Heating	**Microwave Heating**
Heating of reaction mixture proceeds from a surface usually inside surface of the reaction vessel.	Heating proceeds directly inside the reaction mixture.
The vessel should be in physical contact with a surface source that is at a higher temperature source (e.g. heating mantle, oil bath, steam bath etc.)	No need of physical contact of the reaction vessel with the higher temperature source, while the vessel is kept in microwave cavity for irradiation.
Thermal or electric heating of reaction mixture takes place.	Heating takes place through electromagnetic waves.
Heating mechanism involves- conduction and convection.	Heating mechanism involves dipolar polarization and ionic conduction.
Transfer of energy occurs from the wall of the vessel to the mixture and eventually to reacting species.	The core mixture is heated directly while surface (vessel wall) is the source of loss of heat.

The highest temperature (for an open vessel) that can be achieved is limited by the boiling point of the reaction mixture.	The temperature of mixture can be raised more than its boiling point i.e. superheating take place.
The entire compound in mixture is heated equally.	Specific component can be heated specifically.
Heating rate is less.	Heating rate is several folds high.

1.4 Microwaves

Microwaves are electromagnetic waves having a frequency ranging from 0.3 GHz to 300 GHz with corresponding wavelengths ranging from 1 m to 1 mm [Gabriel *et al*. (1998)]. Most commercial microwave ovens produce microwave with wavelength of 12.25 cm, which corresponds to a frequency of 2.45 GHz [Horikoshi *et al*. (2008); Gedye *et al*. (1988)].

1.4.1 Principle of Microwave Heating

The basic principle of the heating in microwave oven is the interaction of charged species of the reaction material with electromagnetic wavelength of a particular frequency. The phenomenon of heat production by electromagnetic irradiation is ether by collision or by conduction [Dubey *et al*. (2008)]. Microwave heating is a very efficient process due to the direct coupling of microwave with the molecules that are present in the reaction mixture, leading to a fast rise in temperature and hence faster reaction kinetics. The–microwave has an electric field and a magnetic field associated with it (**Figure 1.5**). The electric field will interact with any molecule that has a dipole or is ionic. Because it is a wave, at any given point in time, the electric field is

constantly oscillating, from positive to negative and back. These oscillations cause the molecules to rotate such that the appropriate pole gets aligned with the changing field. As the molecules move, they generate heat, or thermal energy, as a byproduct, leading to the rapid temperature rise commonly associated with microwave irradiation.

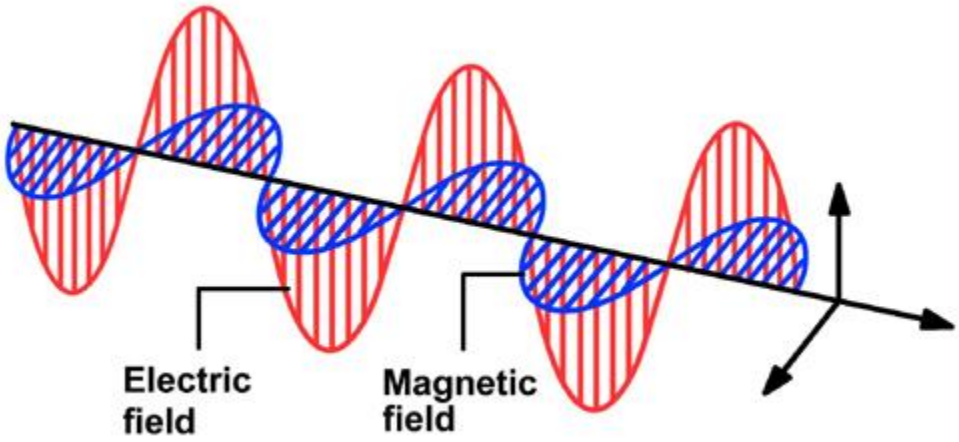


Figure 1.5 The two components of a microwave (http://www.chem.info/articles/2012/03/ comparing-microwave-conventional-heating-drying#.Uq8skvQW1XM accessed on Dec 20, 2013)

Microwave heating is directly dependent on dielectric properties of a substance, dielectric constant (ε') and dielectric loss (ε''). The ability of a material to convert electromagnetic energy into heat energy at a given frequency and temperature, is calculated using the relation

$$\varepsilon'' / \varepsilon' = \tan \delta \qquad (1.1)$$

where δ is the dissipation factor of the sample, ε'' measures the efficiency with which heat is generated from the electromagnetic radiation and ε' is a measure of the ability of a molecule to be polarized by an electric field. The high value of dissipation factor δ indicates large susceptibility to microwave energy.

1.4.2 Heating Mechanisms

The two fundamental mechanisms for transferring energy from microwaves to the substance are dipolar polarization and ionic conduction. Dipolar polarization is the interaction in which polar molecules try to align themselves with the rapidly changing electric field of the microwave as shown in **Figure 1.6**. The interaction of electric field component with the polar molecules is called the dipolar polarization mechanism. Strong agitation, provided by the reorientation of molecules, in phase with the electrical field excitation, causes an intense internal heating. The dipolar polarization phenomenon is responsible for the majority of microwave heating. It depends upon nature of the solvent and the compound polar, less polar or non-polar.

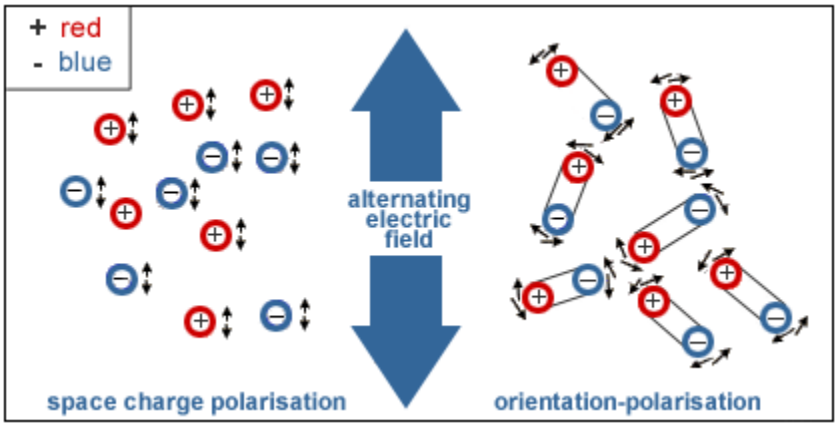


Figure 1.6 Dipolar polarization

The other mechanism is the ionic conduction. In ionic conduction the dissolved charged particles in a sample (ions) oscillate back and forth under the influence of the electric component of microwave irradiation (**Figure 1.7**). They collide with their neighbouring molecules or atoms and these collisions cause agitation or motion which result into heating. The ionic conduction mechanism has a much stronger effect than the dipolar rotation mechanism with regard to the heat-generating capacity. This is the reason why the media containing ions are heated more

efficiently by microwaves than just polar solvents [Kappe and Stadler (2006)]. The ionic conduction is needed for those solvents which have low polarity and absorb very less microwaves. For those solvents, polar additives such as ionic liquids or passive heating elements that consist of strongly microwave absorbing materials can be added to low microwave absorbing reaction mixtures in order to increase the absorbance level of the medium. The reaction vessels employed in microwave are made out of essentially microwave transparent materials such as glass or Teflon (tan $\delta < 0.01$), hence, only the reaction mixture heats up and not the reaction vessel [Kappe and Stadler (2006)].

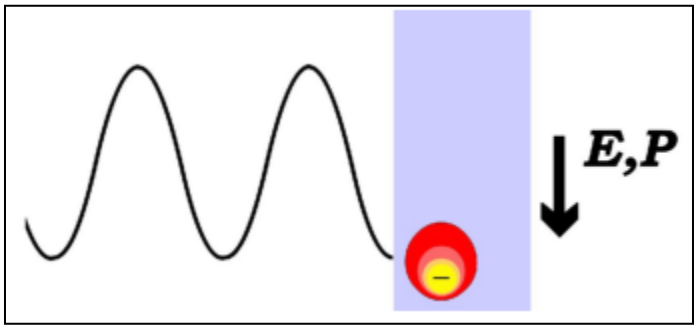


Figure 1.7 Ionic conduction

Microwave enhances the rate of reaction by as much as 1,000 fold. With the elevated energy generated by the transfer of microwave energy, reactions which require many hours or even days to complete, have been accomplished in minutes [Dubey *et al*. (2008)]. The reason for the rate enhancement of chemical processes under microwave irradiation is the purely thermal (kinetic) effect in majority of cases [Chemat *et al*. (2001)]. It means that high reaction temperature, achieved rapidly under microwave irradiation of polar materials, causes increase in the chemical reaction rate. There is some controversy as to whether the increase in reaction rate emerges only from the thermal effects or from non-thermal (microwave effects) as well [Wiesbrock *et al*.

(2004)]. The non-thermal (microwave effects) is classified as acceleration of chemical processes in a microwave field that cannot be rationalized in terms of either purely thermal/kinetic or specific thermal microwave effects. The role of non-thermal process can be answered simply by comparing the reaction rates for the situations where the same reaction is carried out under microwave irradiation and under conventional heating. In fact, no non-thermal effect has been found in the majority of reactions, and the acceleration of the reaction rate is only due to superheating [Hoz *et al*. (2005)]. It is clear, though, that the nonthermal effects do play a role in some reactions [Kappe and Stadler (2006)].

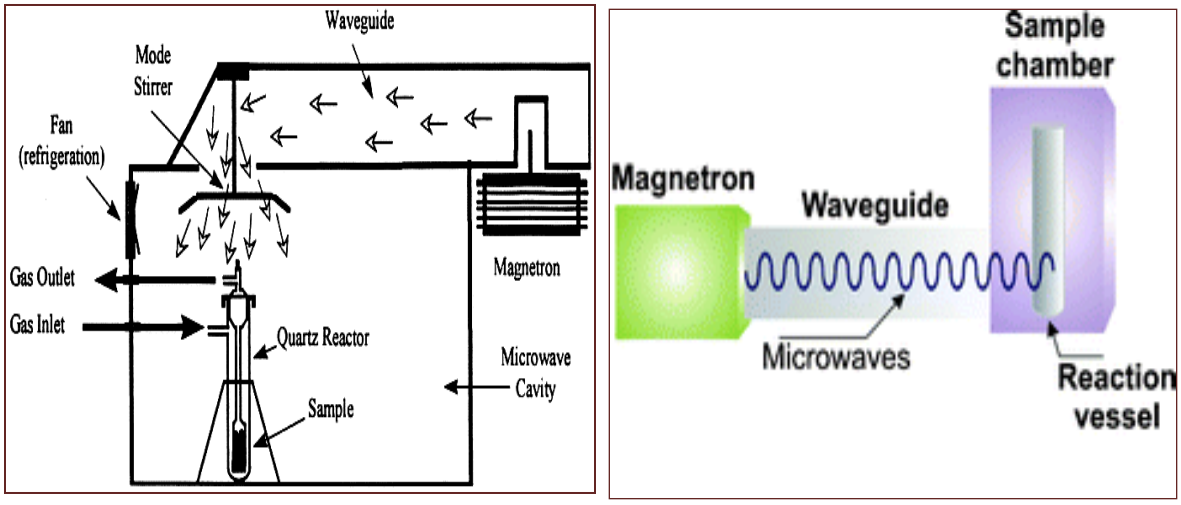
During recent years, microwaves have been extensively used for carrying out chemical reactions and have become a useful energy source for performing organic synthesis [Gedye *et al*. (1999)]. This is supported by a large number of publications [Kappe, (2003)] related to the application of microwaves as a consequence of the availability of dedicated and reliable microwave systems [Vanderhoff (1969); Mingos *et al*. (1997a, b); Nuchter *et al*. (2000, 2001)].

1.4.3 Microwave Ovens

The early experiments on MW-assisted synthesis were carried out in domestic MW ovens typically working with a pulsed irradiation, inaccurate temperature control, inhomogeneous MW field, and lack of safety precautions, which often prevented appropriate reaction control. Since the development of dedicated MW ovens for synthesis in the 1990s it has been possible to obtain more reliable results with high reproducibility. The currently available MW ovens can be divided into two categories: monomode and multimode. Their basic features are described below.

1.4.3.1 Multimode and Monomode Microwave Ovens

The multimode or domestic ovens are characterized by a non-homogeneous distribution of electric field due to several reflections off the metallic walls of the oven (**Figure 1.8a**). Modifications of domestic microwave ovens have also been suggested by various workers [Caddick *et al*. (1995)] such as introduction of condensers [Villemin *et al*. (1995)] by boring through the top of the oven or reaction flasks fitted with condensers [Plazl *et al*. (1994)] and charged with pre-cooled, microwave-inactive coolants, like xylene, carbon tetrachloride, etc. In addition to these, there are many dedicated large multimode versions with rotors claimed to have in-phase microwave irradiation achieved by special design of the equipment. The use of multimode ovens has some limitations like the distribution of electric field inside the cavity results from multiple reflections off the walls and reaction vessel and is consequently heterogeneous, the temperature cannot be accurately and simply measured and the power is not tunable. In the monomode microwave oven the dimensions of wave beam and excitations are specially calculated to allow only one mode of propagation (**Figure 1.8b**). They are able to obtain a homogeneous distribution of the electric field in the wave belt and hence in the heated reaction mixtures [Barlow and Marder (2003)]. Utilization of monomode microwave oven is energy efficient and leads to better yields in organic synthesis.



(a) (b)

Figure 1.8 (a) Multimode microwave oven (b) Monomode microwave oven

1.4.4 Advantages and Disadvantages of Microwaves

Microwave energy offers many compelling advantages in materials processing over conventional heat sources. These advantages include greater flexibility, greater speed, higher energy savings, improved product quality and properties, and synthesis of new materials that cannot be produced by other heating methods [Lidstrom (2001); Lew *et al*. (2002); Ley and Baxendale (2002)]. Studies of microwave assisted synthesis of polymeric materials led to a successful industrial application in the rubber industry. It is used to speed up the chemical reactions, to obtain high purity of products, give less side-products and improved yields. It simplified and improved the synthetic procedure, used for wider range of temperature and offers higher energy efficiency.

There are some disadvantages as heat source control is difficult and water evaporation in closed container is dangerous because it could burst. From the past 10 years there has been a great deal of interest in microwave processing of polymeric materials worldwide [Varma (1999); Zong *et al*. (2003)].

1.4.5 Applications of Microwave in Chemical Synthesis

Microwave-assisted chemical synthesis has been known since 1986. The first results of microwave irradiation in chemical synthesis were published in 1986 [Giguere *et al*. (1986); Gedye *et al*. (1986)]. The use of microwave for synthesis of inorganic solid is a very efficient and useful technique in material chemistry. The microwave has been used in preparation of ceramics and theoretical modeling of microwave interaction with ceramic materials have been studied by Ayappa *et al*. (1997); Kenkre *et al*. (1991); Lee *et al*. (1997); Rao *et al*. (1994). They reported that when Si and C (Charcoal) in their powder form are taken in silica crucible and ~~is~~ exposed to microwave for 4 to 10 min in a domestic microwave oven operating at 2.45 GHz, SiC is obtained [Ramesh *et al*. (1994)]. SiC is a large volume ceramic material and is extensively used for industrial application such as for grinding wheels and in the manufacture of abrasion tools. Microwave technology in nanoscience [Pileni *et al*. (1997); He *et al*. (1999)] is being applied in the fields of synthesis of single-site catalyst, antimicrobial nanocomposites, fire retardant materials, novel electro-optical devices, sensors, ultra-soft magnets and also in the area of drug delivery systems [Larhed and Hallberg (2001)]. The application of microwave irradiation in the field of analytical chemistry includes sample digestion and solvent extraction techniques [Camel (2000); Wang *et al*. (2007)]. Development of high pressure asher focused microwave, a novel approach to microwave digestion, is described by Matusiewics *et al*. (1999). The system uses focused MW operating at 2.45 GHz at 650 W power. Using this apparatus the methodology was developed for digestion of biological reference material such as bovine liver.

Application of MW in polymer synthesis has been known for the past ten years. Microwave-assisted polymer synthesis was used in radical polymerization~~s~~, step-growth polymerization~~s~~, ring-opening polymerization~~s~~, and polymer modification~~s~~. The MW-assisted radical cross-

linking of unsaturated polyester with styrene was reported first by Gourdenne *et al*. (1979). Extensive reviews on microwave-assisted polymer synthesis presented by Sinnwell and Ritter (2007); Zhang *et al*. (2007) focus on ring opening polymerization and Kempe *et al*. (2011). The synthesis of polyacrylamide (PAM) was studied under microwave irradiation [Li *et al*. (1992)]. The use of microwave in the synthesis of biodegradable polymers has attracted the attention of researchers during the last few years. The examples are polycaprolactone (PCL) [Kappe and Stadler (2006)], and polylactic acid (PLA). PCL has been synthesized by ROP of caprolactone with $Sn(Oct)_2$ as a catalyst, which has been approved by FDA as a food additive.

1.5 Polymer Clay Nanocomposites

Nanocomposites are defined as polymers bonded with nanoparticles to produce materials with enhanced properties. The reinforcing material has the dimensions in nanometric scale. Such composites are called nanocomposites. Conventional composites are prepared using inorganic or natural fillers to improve some of the properties of biodegradable polymers such as thermal stability, gas barrier properties, strength, melt viscosity, and biodegradation rate. Nano-reinforcements of biodegradable polymers have been carried out to design eco-friendly green nanocomposites for several applications. The main reasons for preparing nanocomposites is that due to the nano-scale dispersion, even with very low levels of nanofillers (5 wt.%) the process results in a product of high aspect ratio and high surface area.

1.5.1 Clay as Nanofiller

Different types of nano-reinforcement are used for the preparation of nanocomposites but most commonly used filler is a nanoclay material called montmorillonite (a layered smectite clay) due to its easy availability, low cost and more importantly its environment friendly nature.

Montmorillonite, and other layered silicate clays, are naturally hydrophilic. This makes them poorly suited to mixing and interacting with most polymer matrices which are mostly hydrophobic. The clay must be treated before it can be used to prepare a nanocomposite. Making a composite out of untreated clay would not result in a very effective use of material, because most of the clay would stuck inside and would be unable to interact with the matrix. To make the two compatible, the clay's polarity must be modified to be more "organic" to interact successfully with polymers. One way to modify clay is by exchanging organic ammonium cations for inorganic cations from the clay's surface (Sherman, 1999).

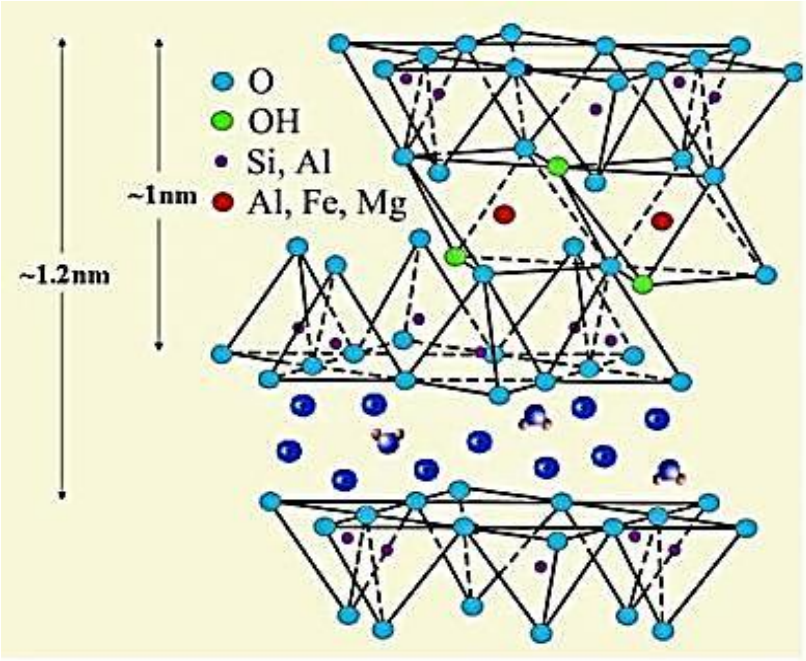


Figure 1.9 Structure of clay

1.5.1.1 Specific Advantages of Nano-clays in Medical Devices and Packaging

a) It controls permeation rates of therapeutic agents in the device

b) It controls the degradation behavior of devices and packaging [e.g tissue scaffolds, shedding of surface bio-films from tubing].

c) It offers better high-temperature performance and thus improved performance in sterilisation of packs/devices

d) It extends property range of medical polymers

There are three common methods used to enhance polymers with nanofillers to produce nanocomposites: melt compounding, *in situ* polymerization and the solvent method. Melt compounding of nanofillers into a polymer is done simultaneously when the polymer is being processed through an extruder, injection molder, or other processing machines. The polymer pellets and filler (clay) are pressed together using shear forces to help in the exfoliation (**Figure 1.10**) and dispersion (Chen, 2004). With *in situ* polymerization, the filler is added directly to the liquid monomer during the polymerization stage. Using the solution method, fillers are added to a polymer solution using solvents such as toluene, chloroform and acetonitrile to integrate the polymer and filler molecules (Chen, 2004). Since the use of solvents is not environment-friendly, melt processing and in-situ polymerization are the most widely used methods for nanocomposite production.

The microwave technology for the synthesis of clay nanocomposites is emerging as an environment friendly and cost effective technique.

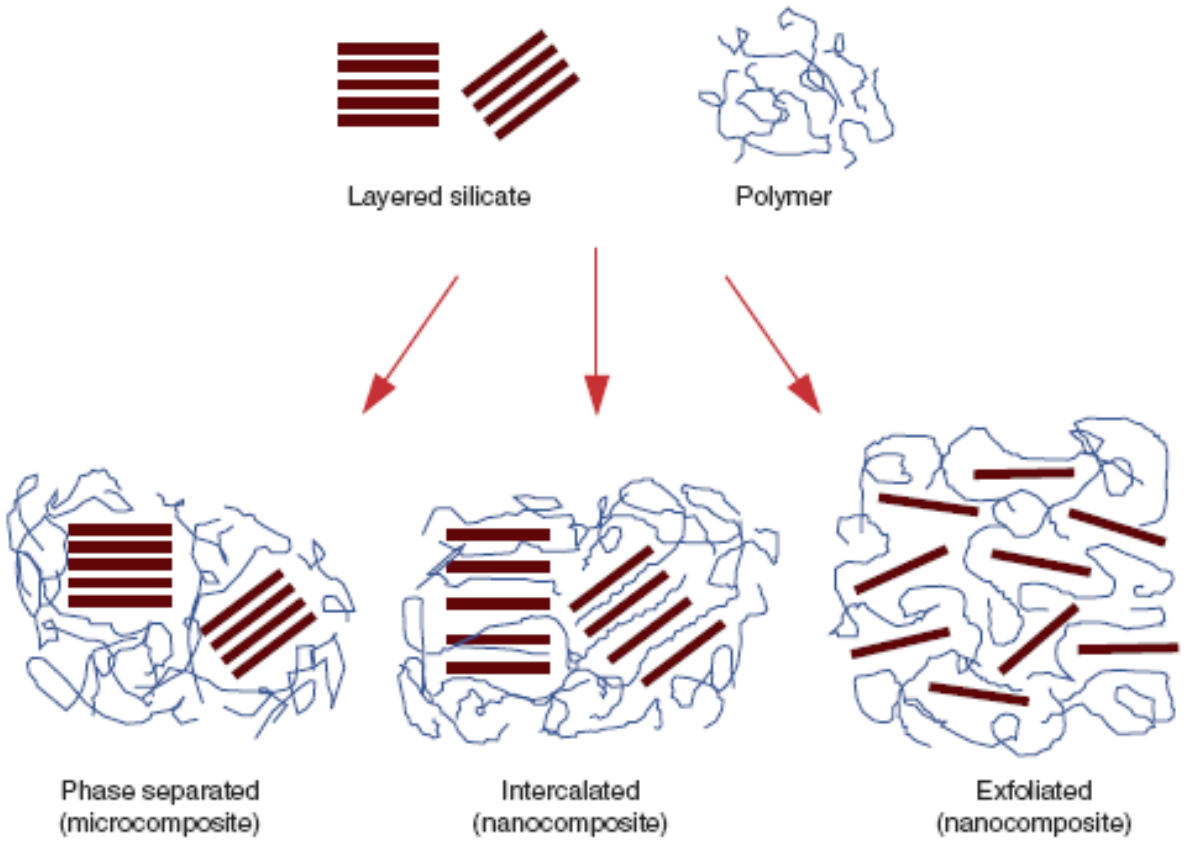


Figure 1.10 Interaction of polymer and layered silicates to form polymer nanocomposites

1.5.2 Use of Microwave Technology in Preparation of Polymer Nanocomposites

Microwave heating is widely employed in the sintering of ceramic materials, chemical analysis and synthesis of organic/inorganic materials, electro-catalysts, etc due to its several distinctive characteristics- rapidity, simplicity, uniformity and energy saving, in comparison to the conventional heating method [Rustum *et al*. (1999); Rao *et al*. (1999); Agazzia *et al*. (2000); Cheng *et al*. (2002); Tian *et al*. (2006)]**.** Very few reports on the microwave assisted synthesis of polymer nanocomposites are available in the open literature. The synthesis of the poly(tetrafluoroethylene) (PTFE) supported on carbon black (PTFE/C) nanocomposite powder had been done using microwave irradiation. The PTFE/C composite powder synthesized was

characterized by uniformly distributed and nano-sized PTFE/C powders without any mechanical milling treatment [Tian *et al.* (2006)]. The microwave assisted synthesis of nanomagnetic polymer composites (NPCs) based on poly(acrylonitrile) (PAN) was carried out by Agarwal *et al*. (2012). The process involves 2,2-azobisisobutyronitrile initiated in-situ polymerization of acrylonitrile in presence of Tween -20 stabilized ferrite nanoparticles (FNPs) under MW irradiation ranging from 25 to 100 Watt over 10 min. With MW power, the polymerization reaction has been progressed resulting in NPCs (Nanomagnetic polymer composites) with enhanced rheo-viscosity and yield over PAN. Cao *et al.* (2009, 2010) investigated the microwave assisted synthesis of PLA nanocomposites. These studies have been elaborated further in Chapter 2.

From the above it is clear that the PLA and PLA/Clay nanocomposites have several advantages over other biodegradable polymers making them suitable for agricultural, food and medical applications. In view of this in the proposed work it has been planned to synthesise PLA of high molecular weight using appropriate catalysts and microwave heating. The PLA-clay nano-composites will be prepared *in situ* dispersion of clay during polymerization of lactide.

CHAPTER – 2

LITERATURE REVIEW

CHAPTER-2 LITERATURE REVIEW

During the past few years use of microwave irradiation in polymer synthesis has become an established technique for enhancing the rate of reaction. A significant increase in the use of this technique for the synthesis of a number of polymers has been reported in the past 10 years, in particular, on the microwave assisted synthesis of PLA. This section presents a review of the available literature on the microwave assisted synthesis of PLA with special emphasis on polycondensation and ring-opening polymerization. Available results on the PLA kinetics and *in situ* preparation of PLA/Clay nanocomposites are also presented.

2.1 Poly (Lactic Acid)

Polylactic acids (PLA) are degradable polymers produced from raw materials obtained by fermenting biomass such as corn and sugarcane [Lunt (1998)]. These polymers have good transparency and are used as degradable polymeric materials for agricultural mulch-films (**Figure 2.1a**), greenhouse films, cases of home electrical appliances etc. Owing to their degradability, they are also used as functional food materials and medical materials such as sutures (**Figure 2.1b**), cell scaffold [Gupta et al. (2013)], artificial bones, and controlled drug release devices (**Figure 2.1c**) [Drumright *et al*. (2000); Anders *et al*. (2002)]. These are useful for tissue replacements, intraocular lenses, dental and breast implants, and artificial organs for temporary and permanent assist (e. g. artificial kidney, artificial heart and vascular graft) [Cheng *et al*. (2009)]. PLA has also been used as implant to correct facial lipoatrophy in human immunodeficiency virus 1-positive individuals receiving combination antiretroviral therapy [Cattelan *et al*. (2006)].

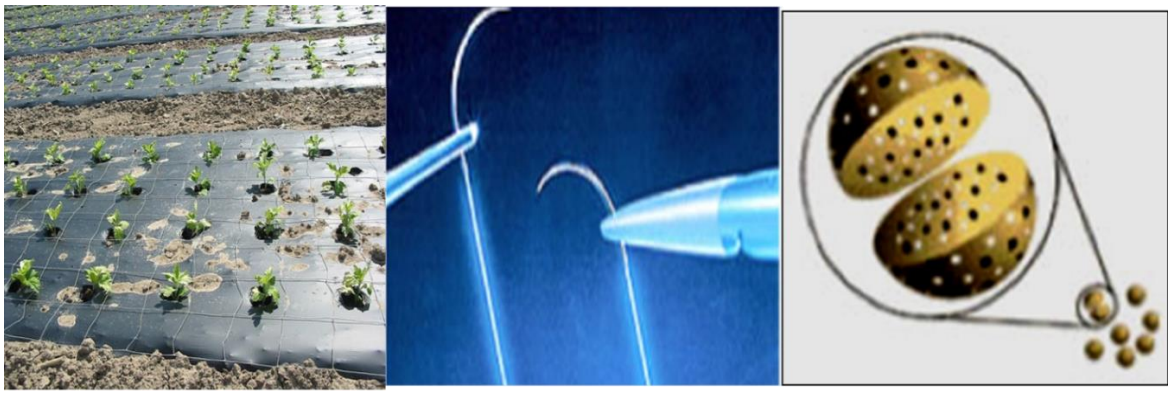


Figure 2.1 (a) Agricultural mulch-films, (b) Sutures, (c) Drug delivery system (http://www.pitt.edu/~tmeyer/Projects.html, accessed on 14-12-2013)

PLA are synthesized by condensation polymerization of lactic acid [Maharana *et al.* (2009)] and ring opening polymerization of lactide [Zhang *et al*. (2007)]. The life cycle of PLA is shown in **Figure 2.2**. Generally, commercial PLAs are blends of poly (L-lactic acid) (PLLA) and poly (D, L-lactic acid) (PDLA). The ratio of L and D enantiomers influences the properties of poly (lactic acid), such as melting temperature and crystallinity. Poly (lactic acid) can exhibit classical crystallization during both cooling and heating. This phenomenon probably depends on its molecular weight [Miyata *et al*. (1998); Di *et al*. (2005); Salmeron *et al*. (2005)].

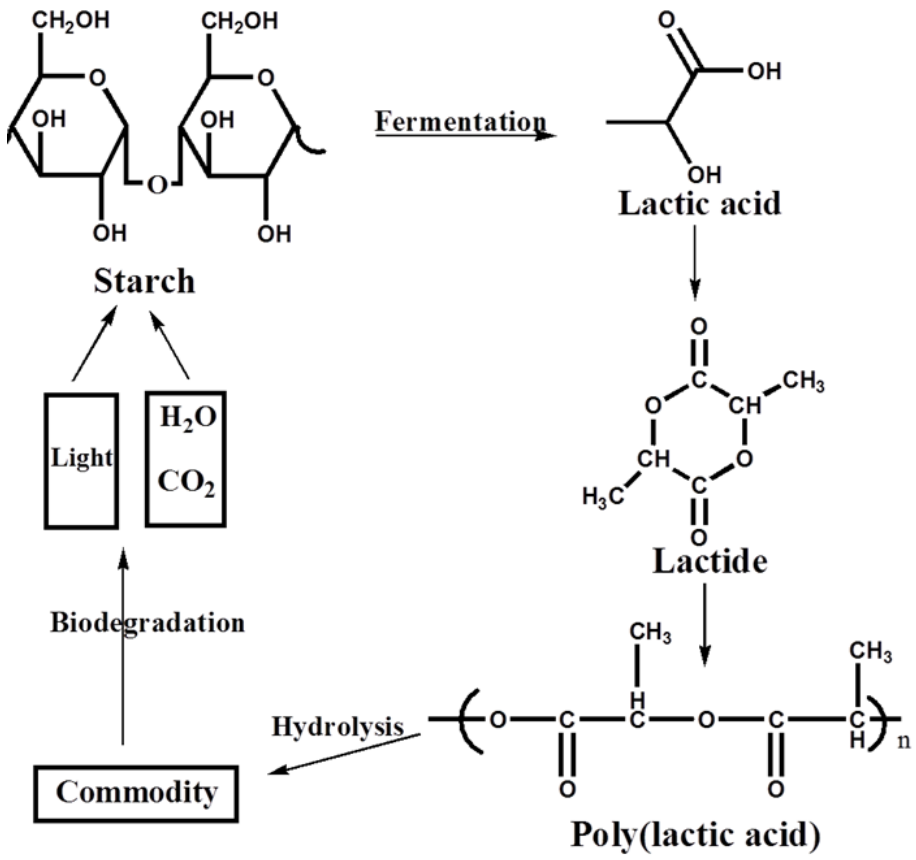


Figure 2.2 Life cycle of PLA

The most important and general way to prepare high molecular weight PLA is through ring-opening polymerization [Ajioka *et al*. (1995); Sung *et al*. (2000)]. During ring-opening synthesis of PLA, heating of reaction mixtures can be done in two ways: conventional and microwave heating. More recently, there has been growing interest in using microwave irradiation for carrying out polymerization reactions. The rate of polymerization is much faster in case of microwave heating compared to conventional heating [Jin *et al*. (1999); Wang *et al*. (2003); Mallakpour *et al*. (2004); Shu *et al*. (2006)]. The reaction generally requires tin compounds and sulfuric acid as catalysts and is carried out at a high temperature using conventional heating for long duration due to low reactivity of lactic acid. It is believed that the reaction proceeds faster

because microwaves efficiently heat the polar intermediates of the reaction [Barlow *et al*. (2003)].

Several reviews on PLA [Garlotta. (2001); Sodergard and Stolt. (2002); Mehta *et al*. (2005); Gupta and Kumar. (2007); Lim *et al*. (2008); Cheng *et al*. (2009); Jamshidian *et al*. (2010); Inkinen *et al*. (2011); Hirao *et al*. (2011)] have appeared in the open literature, including some good books [Henton *et al*. (2005); Auras *et al*. (2010); Sin *et al*. (2012)]. Mehta *et al*. (2005) presented a detailed review on PLA with a focus on its stereochemistry, synthesis via ring-opening polymerization, reaction kinetics and thermodynamics, synthesis of low molecular weight polymer, a continuous process for production of PLA from lactic acid, and blends.

2.1.1 Conventional Synthesis of PLA

Poly (lactic acid) can be prepared in two different ways: ring-opening polymerization of lactide or direct polycondensation of lactic acid. The ring-opening polymerization of lactide was first demonstrated by Carothers in 1932, but high molecular weight PLA was not obtained until improved lactide purification techniques were developed by Du Pont in 1954. Lactide can be prepared through a decompression method in which water is removed from the system, and then catalysts are added into the reactor. After reacting for several hours, lactide is obtained. During polymerization reaction the lactide ring opens up a polymerization proceeds. The catalyst used industrially is mostly stannous octoate. The choice of catalyst/initiator, co-initiator as a chain control agent, catalyst concentration, monomer-to-initiator ratio, and polymerization temperature and time significantly affect the polymer properties. Jedlinski *et al*. (1991) have shown that the use of primary alkoxides such as potassium methoxide can yield well-defined polymers with negligible racemization, termination, or transesterification. Many catalysts and initiators have been studied for conventional synthesis of PLA. Mehta *et al*. (2005); Platel *et al*. (2008);

Averous *et al*. (2013) have reported the work on biocompatible initiators for lactide polymerization. Lopez et al. (1980) and Vert *et al.* (1995) presented a comprehensive review on synthesis of PLA copolymers. A continuous process for the manufacture of PLA of controlled optical purity has been described by Gruber *et al*. (2001a, b).

2.1.2 Microwave-assisted Synthesis of PLA

Microwave (MW) heating provides the advantage of enormous saving in the reaction time and much higher yields compared to the conventional synthetic methods. The microwave-assisted polymer synthesis, however, is a rather new emerging field and only limited information is available in open literature. There are few reports on polycondensation and ring-opening polymerization methods for the synthesis of poly (l-lactic acid) using microwave. During the last five years there has been considerable work done on the ring-opening polymerization method for the synthesis of poly (lactic acid) using microwave irradiation.

2.1.2.1 Polycondensation Method

There have been many reports in the literature on direct polycondensation of L-lactic acid to poly(L-lactic acid) using conventional heating but a few on the microwave assisted synthesis [Keki *et al*. (2001); Jing *et al*. (2006); Nagahata *et al*. (2007)]. The use of microwave irradiation to synthesize PLA by direct polycondensation of lactic acid has been shown to accelerate the rate of polymerization significantly [Achmad *et al*. (2009); Zeng *et al*. (2009); Maharana *et al*. (2009); Konishi *et al*. (2010)]. The direct polycondensation of D,L-lactic acid was firstly carried out using a domestic microwave oven by Keki *et al*. (2001). The microwave apparatus used was a NILE-type domestic microwave oven operating at a power level of 800 W. They irradiated d, l-lactic acid in a beaker for 10, 20, and 30 min. The results of polycondensation by means of microwave were compared to those obtained through conventional heating of lactic acid at

100^{o}C, and it was found that the reaction proceeds with much higher rate using microwave irradiation. The oligomer mixtures formed were investigated by means of matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS). MALDI MS spectra of the reaction products obtained at constant microwave power after different reaction times are shown in **Figure 2.3**.

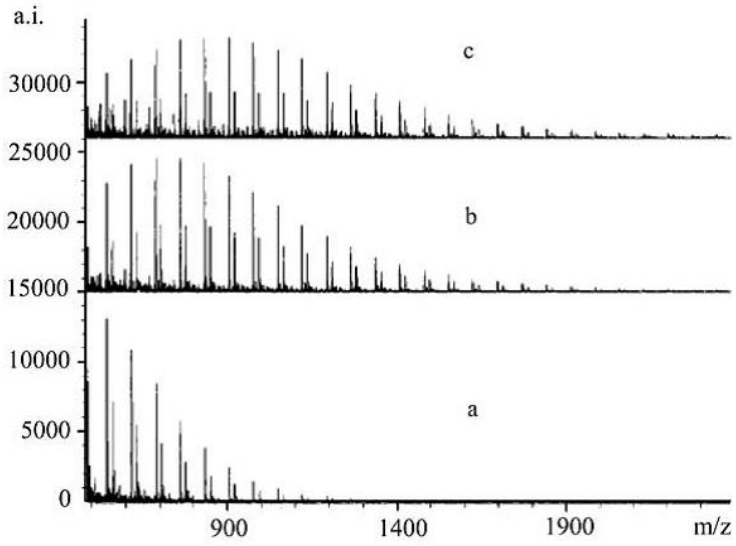


Figure 2.3 MALDI MS spectra of the products of the melt polycondensation of lactic acid performed under microwave irradiation for 10 min (a), 20 min (b), and 30 min (c) [Keki *et al*. (2001)].

This figure shows that the molecular mass of the oligomers obtained increases with increasing reaction time. After 20 min of irradiation, oligomers formed have nearly the same molecular mass as those produced through conventional heating at 100^{o}C for 24 h. The results showed that the synthesis of linear PLA could be achieved effectively through microwave irradiation and the reaction time is significantly reduced as compared to that for the conventional polycondensation at 100^{o}C.

Jing *et al*. (2006) synthesized PLA through melt polycondensation of L-lactic acid under microwave irradiation. By employing a co-catalyst *p*-toluenesulphonic acid (TAS) with catalyst $SnCl_2$, an increase in the molar mass of PLLA was obtained that depended on the catalyst concentration. As the catalyst concentration increased, the molar mass increased up to a certain value and then decreased due to competition between polymer decomposition and polycondensation. They also calculated the viscosity average molar mass. Increase in power level of MW increased the molar mass and the highest molar mass of 5.08×10^4 $g.mol^{-1}$ was obtained at 528 W in 40 minutes.

The first use of monomode microwave to synthesize PLA was made by Nagahata *et al*. (2007). They studied the microwave-assisted direct polycondensation of lactic acid to form poly (lactic acid) with various catalysts at suitable reaction conditions as listed in **Table 2.1**.

Table 2.1 Microwave-assisted polycondensation of LA with various catalysts [Nagahata *et al*. (2007)]

Catalyst	**Catalyst ratio, (mol. %)**	**Reaction temperature (^oC)**	**Polymer yield (%)**	**M_w**	**M_w / M_n**	**Appearance**
None	0	200	Trace	410	-	-
$SnCl_2$	0.2	200	53.5	1800	3.6	White
$Sn(Oct)_2$	0.2	200	55.0	2100	2.4	White
Sn, powder	0.2	200	Trace	230	-	-

Bu_2SnCl_2	0.2	200	Trace	570	-	-
DCTB	0.2	200	Trace	1200	-	-
p-TsOH	0.2	200	Trace	780	-	-
H_3PO_4	0.2	200	Trace	-	-	-
H_2SO_4	0.2	200	Trace	-	-	-
SiO_2/Al_2O_3	0.2	200	Trace	160	-	-
$HfCl_4(THF)_2$	0.2	200	Trace	850	-	-
Zeolite	0.2	200	Trace	-	-	-
Nafion-NR50	2 wt %	200	Trace	-	-	-
$Ti(O^iPr)_4$	0.2	200	Trace	430	-	-
$Ti(OMe)_4$	0.2	200	Trace	1500	-	-
$Al(CF_3SO_3)_3$	0.2	150	Trace	-	-	-
$In(CF_3SO_3)_3$	0.2	150	13.8	1000	3.2	White
$Sc(CF_3SO_3)_3$	0.2	150	34.0	1600	4.1	White

$Y(CF_3SO_3)_3$	0.2	150	Trace	-	-	-
$Sm(CF_3SO_3)_3$	0.2	150	Trace	-	-	-

The polymerization was carried out under a reduced pressure of nitrogen atmosphere with microwave heating by using a single-mode microwave synthesizer of frequency 2.45 GHz and maximum power of 300 W. The synthesised polymer was characterized by ^{1}H and ^{13}C NMR, matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) and gel permeation chromatography (GPC). The use of tin compounds like $SnCl_2$, $Sn(Oct)_2$, Bu_2SnCl_2, and 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane (DCTB) as catalysts accelerated the polymerization and gave colourless polymers with 3 to 5 times higher molar mass as compared to that in the absence of catalyst. The molar mass of PLA obtained was 1800 at 30 min and increased from 6400 to 15000 as the time increased from 60 to 300 min. The authors also used a binary catalyst system ($SnCl_2$/*p*-TsOH) under microwave irradiation. The average molar mass of the PLA obtained with a binary catalyst of $SnCl_2$/*p*-TsOH (0.2/0.2 mol %) was 4200 which was more than ten times as high as one obtained with $SnCl_2$ which was 400. The effect of pressure on polymerization yield and molar mass was also investigated. The graph between pressure and molecular weight showed the decreasing pattern of molecular weight with increase in pressure as depicted in **Figure 2.4**. The molecular weight initially increased and then decreased with increase in pressure. The colorless PLA with M_w of 16000 within 30 min under a reduced pressure of around 30 mm Hg was obtained and after that as the pressure increased the molecular weight decreased significantly.

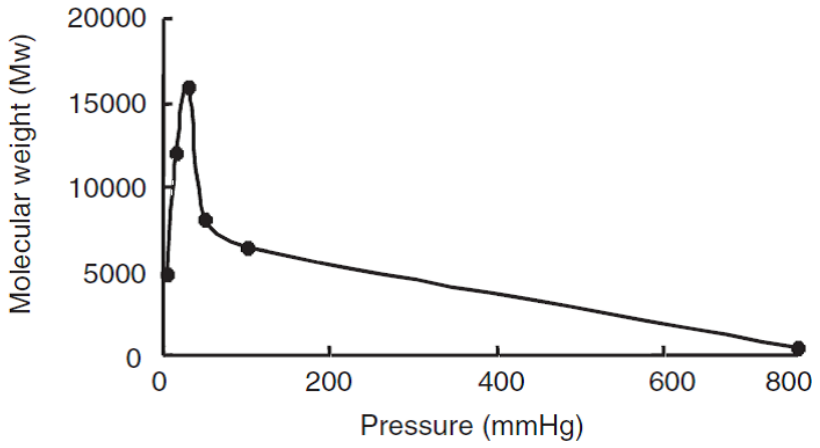


Figure 2.4 Effect of pressure on the microwave-assisted polycondensation of Lactide [Nagahata *et al*. (2007)].

Zhang *et al*. (2007) reported the condensation of D,L-lactic acid to form D,L-lactide under microwave irradiation and compared the results with those for conventional method. The synthesis of D,L-Lactide was done by using $SnCl_2$ as catalyst under continuous microwave irradiation in less than 1 hour. The yield obtained was 36% which was less than expected. The MW heating gave a polymer of higher molecular weight.

Hirao *et al*. (2009) reported non-catalytic polycondensation of L-lactic acid under microwave irradiation. The polycondensation reaction was initiated by an oligomer of weight-average molecular weight 1,380 $g.mol^{-1}$ under microwave irradiation. It was demonstrated that higher molecular weight PLLA could be obtained under microwave irradiation compared to the conventional heating.

2.1.2.2 Ring Opening Polymerization

The MW-assisted ring opening polymerization (MAROP) of D,L-lactide in the presence of stannous octoate ($Sn(Oct)_2$) was first studied by Liu *et al*. (2001, 2003) in a domestic MW oven. The weight-average molar mass (M_w) the product obtained ranged from 3.9×10^4 to 6.7×10^4

and the polydispersity index ranged from 1.3 to 1.7. The polymerization rate was much faster than that for the conventional thermal polymerization. They also observed degradation of the newly formed PLA in the reaction mixture by microwave irradiation. McCarthy *et al*. (2002 a, b) presented some preliminary results for MAROP of L-lactide. Various power levels were selected for irradiation and it was found that the polymerization proceeded much more rapidly at higher power levels and complete conversion of the monomer could be reached after about 1.5 min at 1300 W for 3.0 g lactide. Bodnar *et al*. (2003) successfully carried out melt polymerization of D,L-lactic acid under microwave radiation. The resultant polymer, poly (D,L-lactic acid), obtained was in the form of very viscous fluid and had a very low molecular mass (0.5–1 kDa). They observed the formation of linear polymeric chains at low temperatures (T <120 ^{o}C) and both cyclic and linear polymeric chains were formed at higher temperatures. Similar results have been reported by Zhang *et al*. (2004). They synthesized poly (D,L-lactide) (PDLA) (M_w of 4×10^5 g.mol^{-1}, yield over 90% in 10 min) by the ring opening polymerization of D,L-LA under 255 W microwave irradiation. The influence of catalyst concentration on polymerization was also reported (**Table 2.2**).

Table 1.2 Influence of catalyst concentration on MAROP of D, L-lactide [Zhang *et al*. (2004)]

Catalyst conc.	**$M_w \times 10^{-3}$ (g/mol)**	**M_w/M_n**	**Yield %**
0.5	9.7	2.5	90
0.1	18.5	2.1	94
0.05	12.8	2.4	91
0.025	13.8	2.0	69

Degradation of PDLA was also induced by microwaves at power levels over 340W as shown in **Figure 2.5**. The average M_w of PDLA was dependent upon the kinetics of polymerization of D, L-lactide and the degradation of the resulting polymer.

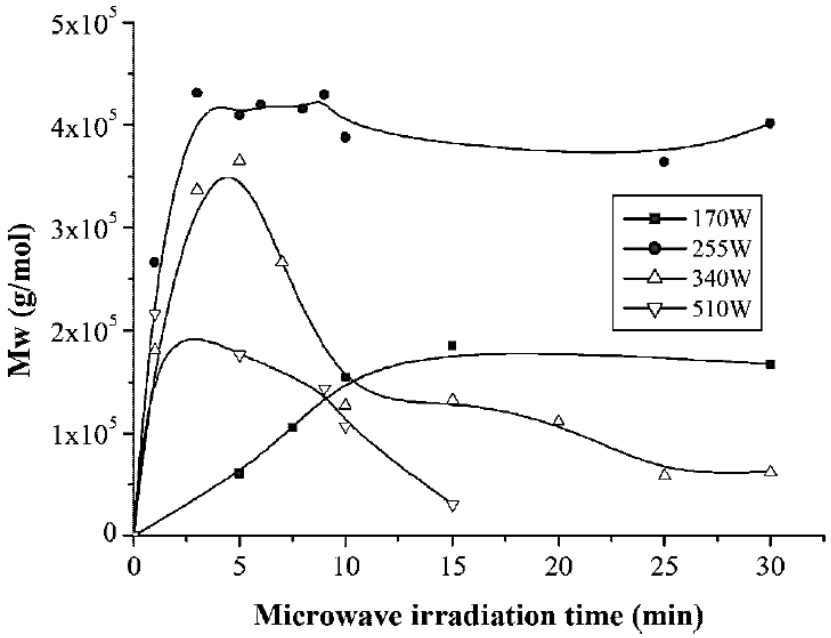


Figure 2.5 Profiles of molar mass versus microwave irradiation time [Zhang *et al*. (2004)].

Jing *et al*. (2006) investigated MAROP of D,L-Lactide under atmospheric conditions with carborandum as the heating assist material. The assist material was used for the conduction of heat to the reaction mixture to ensure uniform heating. Effects of heating medium, monomer purity, catalyst concentration, MW irradiation duration and vacuum level were investigated. It was observed that presence of SiC reduced the reaction time substantially, increased the molar mass of polymer and also its yield (M_w > 2.0 x10^5 g. mol-1, yield > 80%).

Gong *et al*. (2007a, b) polymerized L-Lactide in the presence and absence of $Sn(Oct)_2$ by using poly(ethylene glycol) and methoxy poly(ethylene glycol) as macro-initiators. The ROP was performed in a monomode MW reactor and yielded poly (l-lactide)-block-poly (ethylene glycol)-block-poly (l-lactide) tri-block and methoxy poly (ethylene glycol)-block-poly (l-lactide) di-

block copolymers, respectively. In both cases, 20 min of MW irradiation at 100 °C led to high conversions using different monomer/initiator ratios and the poly (ethylene glycol) of different molecular weights.

Pandey *et al*. (2009) studied the microwave-assisted polymerization of lactide both with and without the aid of stannous octoate catalyst. The molar mass of the synthesised polymer was determined by gel-permeation chromatography (GPC). The work clearly showed that polymerization of L-lactic acid by microwave heating was possible with or without the use of Sn octoate catalyst. Polymerization rates were higher, and a molar mass of 30×10^3 value was obtained within 2 h of heating compared to 24-48 h required during conventional heating. It was concluded that in the polymerization process, the two most important factors determining the yield and the final molecular weight are the reaction environment and the temperature. For ring-opening polymerization of PLA, very high vacuum and temperature of about 130 ± 1^oC were maintained. This study clearly shows that the high-molecular-weight PLA can be synthesized by microwave heating within a few hours compared to 1 or 2 days required using the conventional synthesis method.

Nikolic *et al*. (2010) synthesized PDLA using tin(II) 2-ethylhexanoate initiated ring-opening polymerization for 30 mins at 120 °C. The influence of monomer/initiator molar ratio on the product properties was studied. Different molar ratios of monomer and initiator, $[M_o]/[I_o]$, of 1,000, 5,000 and 10,000 were used. A higher monomer/initiator ratio resulted in polymers with higher molar masses and lower polydispersity as shown in **Figure 2.6.**

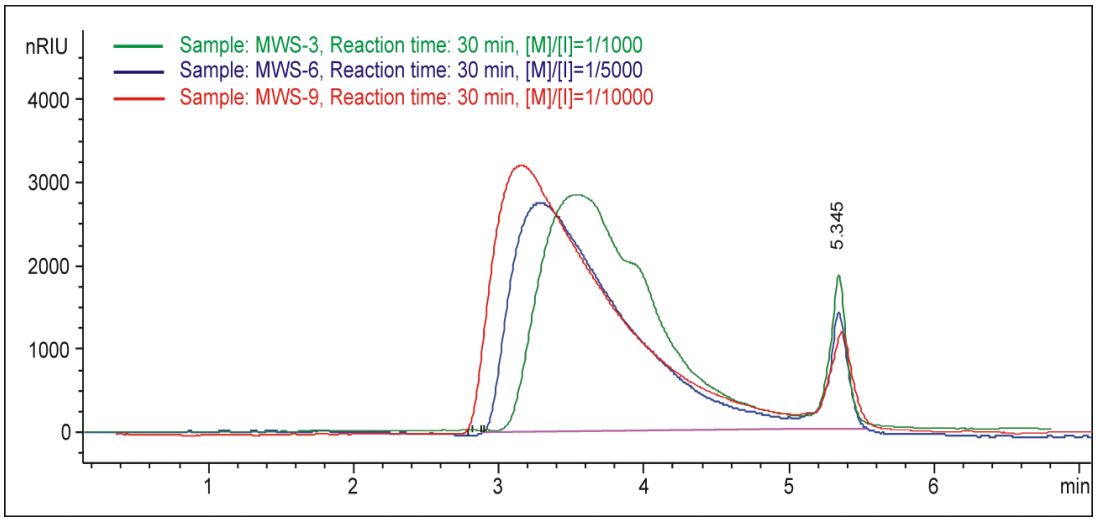


Figure 2.6 The signal at RID detector in function of elution volume for samples with different monomer to initiator $[M_o]/[I_o]$ ratio [Nikolic *et al*. (2010)]

At a reaction temperature of 100 °C, the prolonged microwave irradiation time showed a significant effect on the increasing polymer molar mass. The use of microwave makes the same bulk polymerization process with the same initiator much faster and energy efficient with a reaction time of about 30 minutes at 100 °C. Here, the poly (lactic acid) synthesis was done in a microwave reactor, using MW of frequency of 2.45 GHz with a maximum power of 150 W.

Frediani *et al*. (2010) used Ti metal complex [calix[4]arene-titanium (IV)] as a catalyst for the synthesis of PLA in a microwave reactor at various monomer to initiator ratios. The highest molar mass of 18,600 g/mol was obtained in 50 mins for the monomer to initiator ratio of 202. This is quite low compared to those obtained with other initiators under microwave irradiation. However, this work established the usefulness of metal complexes in polymer synthesis.

The studies reported in the open literature on microwave-assisted PLA polymerization variables and molecular weights available are summarized in **Table 2.3**. These are the few reports on the

synthesis of poly (lactic acid) under microwave irradiation reported so far. Thus, there is need to investigate the processing and synthesis of PLA in a microwave reactor.

Table 2.3 A summary of the reported studies on microwave-assisted PLA polymerization

S.No.	**Monomer**	**Catalyst**	**Microwave reactor type**	**Temp (^oC)**	**Power (W)**	**Time (mins)**	**Molar mass ($g.mol^{-1}$)**	**References**
Polycondensation								
1.	L-lactic acid	-	NILE-type domestic microwave	-	650	10-30	500-2,000	Keki *et al*. (2001)
2.	L-lactic acid	$SnCl_2$/ TAS	Gland domestic microwave	-	320, 528, 600	15-50	50,800	Jing *et al*. (2006)
3.	L-lactic acid	Various tin based and binary catalysts ($SnCl_2$/*p*-TsOH)	CEM model Discover	200	40	30-300	410-16,000	Nagahata *et al*. (2007)
4.	D,L-lactic acid	$SnCl_2$	Domestic microwave	-	70-90	10-40	1,500-6,400	Zhang *et al*.(2007)
5.	L-lactic acid	Non-catalytic	-	-	-	-	1,380	Hirao *et al*. (2009)
Ring opening polymerization								

6.	D,L-lactide	$Sn(Oct)_2$	Domestic microwave	-	-	-	39,000-67,000	Liu *et al*. (2001)
7.	L-lactide	$Sn(Oct)_2$	Panasonic The Genius 1300	-	390-1300	10	40,000	McCarthy *et al*. (2002a, b)
8.	L-lactide	$Sn(Oct)_2$	Domestic microwave	-	-	5-30	2,25,000	Liu *et al*. (2003)
9.	D,L-lactide	$Sn(Oct)_2$	Domestic microwave		170-510	5-30	97,400-4,00,000	Zhang *et al*.(2004)
10.	D,L-lactide	$Sn(Oct)_2$	Gland domestic microwave	180	450	25-45	1,00,000-2,00,000	Jing *et al*.(2006)
11.	L-lactide	$Sn(Oct)_2$/PEG & methoxy PEG (macroinitiators)	CEM Discover monomode microwave	100	-	3-30	17,840-49,180	Gong *et al*. (2007a, b)
12.	L-lactide	$Sn(Oct)_2$	Panasonic domestic microwave	130	130, 400	5-195	30,000	Pandey *et al*. (2009)
13.	D,L-lactide	$Sn(Oct)_2$	CEM Discover monomode microwave	100	150	10-30	78,461-3,09,940	Nikolic *et al*. (2010)

14.	L-lactide	calix[4]arene-titanium (IV)]	CEM Discover monomode microwave	130	200	20-80	8100-18,600	Frediani *et al*. (2010)

2.2 Kinetics of MAROP of Lactide

Polymerization of lactide proceeds through cationic, anionic and co-ordination insertion polymerization mechanisms. The mechanism involves the usual steps of initiation, propagation and termination. Anionic polymerization is initiated when the nucleophilic anion of the initiator attacks the carbonyl group of the lactide, which cleaves the carbonyl carbon and endocyclic oxygen bond. This oxygen becomes a new anion, which continues to propagate the chain [Gupta and Kumar, (2007)]. Due to highly active catalysts and high temperatures, racemization, back biting action and other side reactions may also take place. Cationic polymerizations are carried out when the exocyclic oxygen of one of the lactide carbonyls is either alkylated or protonated by the initiator, which causes the resulting O-CH bond to become positively charged. Nucleophilic attack then occurs by a second monomer to break this bond and create another electrophilic carbonium ion, and thus the reaction propagates as additional monomers continue this attack. The coordination-insertion mechanism is the most widely used scheme for explaining the synthesis of high molecular weight poly (lactic acid). Several types of metal catalysts such as magnesium, tin, titanium, zirconium, and zinc alkoxides, which contain free p- or d- orbitals, are used for this type of polymerization. Stannous octoate is currently the preferred catalyst in microwave assisted synthesis of PLA. Rate constants arrived at through modeling and simulation using conventional ring-opening polymerization route has been reported by Mehta *et al*. (2006). The progress of lactide polymerization has been simulated

using a computer program wherein the mechanism is assumed to be a ring-opening reaction comprising of initiation, propagation and termination. Mehta *et al*. (2006) presented the kinetic constants (**Table 2.4**) for various PLA polymerization catalysts, by matching the simulated results with the experimental data. They further continued their work with stannous octoate as initiator and with triphenylphosphine co-initiator under vacuum (**Table 2.5**) and under N_2 atmosphere (**Table 2.6**) [Kaur *et al*. (2011)]. It would be appropriate to mention here that these rate constants are for ROP of lactide using conventional heating.

Table 2.4 Summary of rate constants (k_o , k_p and k_t are the initiation, propagation and termination rate constants respectively) determined for various catalysts [Mehta *et al*. (2006)].

S.No.	**Polymer**	**Catalyst**	k_o **(l/mol.min)**	k_p **(l/mol.min)**	k_t **(l/mol.min)**
1.	PDLLA	Aluminum	0.002	0.5	0.00025
2.	PLLA	Iron isobutyrate	0.020	31.5	0.025
3.	PLLA	Iron Trifluoroacetate	Not Determined	9.5	0.006
4.	PDLLA	Zinc lactate	0.03	5.7	0.0050
5.	PDLLA, PLLA	Stannous octoate	0.003	0.9	10^{-6}

Table 2.5 Summary of rate constants determined with various initiators for the polymerization carried out under vacuum at 130 (± 1) °C [Kaur *et al*. (2011)].

S.No.	**Initiators**	**k_o (l/mol.min)**	**k_p (l/mol.min)**	**k_t (l/mol.min)**
1.	Stannous octoate	0.200	5	0.020
2.	Stannous octoate and Triphenylphosphine	0.200	5	0.020

Table 2.6 Summary of rate constants determined with various initiators for the polymerization carried out under nitrogen atmosphere at 130 (± 1) °C [Kaur *et al*. (2011)].

S.No.	**Initiators**	**k_o (l/mol.min)**	**k_p (l/mol.min)**	**k_t (l/mol.min)**
1.	Stannous octoate	0.003	15	0.060
2.	Stannous octoate and Triphenylphosphine	0.200	15	0.023

The kinetics of synthesis of PLA under microwave irradiation has been discussed by calculating molar masses and yield percentage with reaction time. The effect of microwave power level has been investigated with reaction time on the molar mass of PLA formed (**Figure 2.7**) [Zhang *et al*. (2004)].

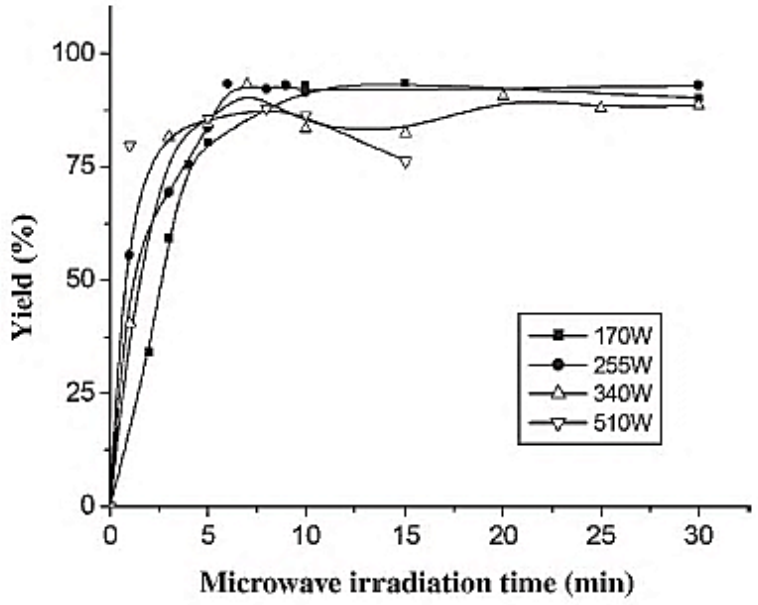


Figure 2.7 Influence of microwave power levels on yield of PDLLA [Zhang *et al*. (2004)]

The microwave power level has a significant influence on the equilibrium temperature. A higher level of microwave power induces a higher equilibrium temperature. The ROP of L-lactide proceeds quickly under microwave irradiation, with a simultaneous degradation of the resulting PLLA. The M_w of PLLA depends on the competition between the polymerization of L-LA and the degradation of the resulting polymer, which is greatly influenced by the microwave power level. PLLA with an M_w of 10^5 g mol^{-1} was obtained when the MAROP of L-LA was carried out at 170 W microwave irradiation for 10 min.

The ROP of LA is extremely sensitive to the presence of hydroxyl groups that act as chain transfer agents. The most likely sources of hydroxyl group are impurities in lactide and absorbed moisture. The effect of monomer purity on molar mass of D,L-lactic acid (**Figure 2.8**) was described by Jing *et al*. (2006).

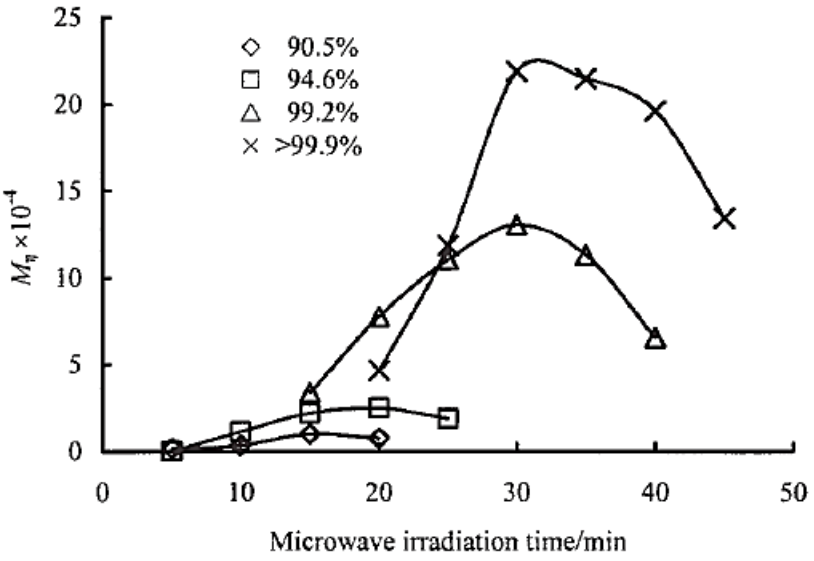


Figure 2.8 Changes of M_n of PDLLA with time under different lactide purity [Jing *et al*. (2006)]

Comparisons were made between the microwave-assisted and the conventionally heated polycondensation in terms of the reaction time and the M_n of the DLLA (**Fig.2.9**) [Yang *et al*. (2008)].

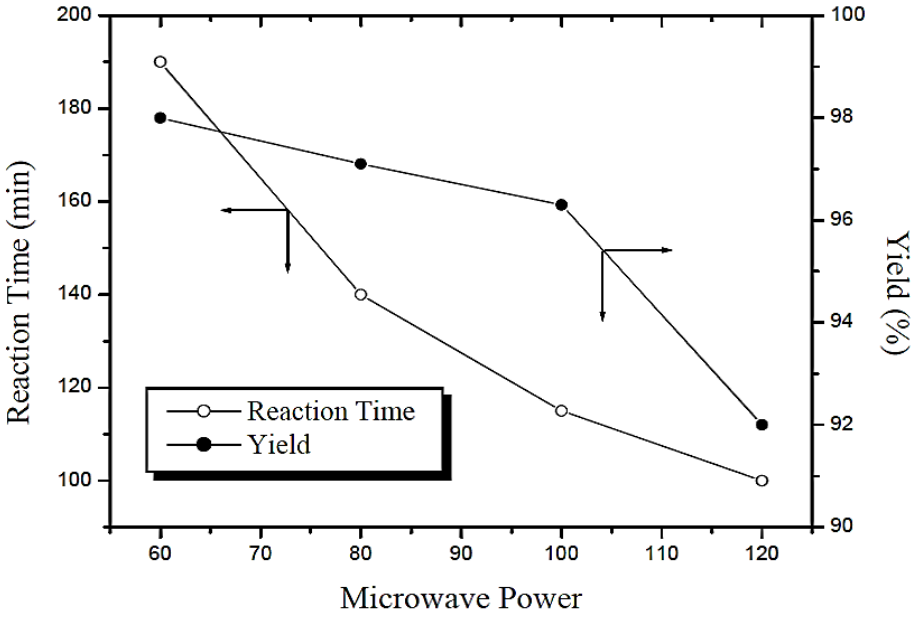


Figure 2.9 Effect of microwave irradiation power on polycondensation time and yield of PDLLA [Yang *et al*. (2008)]

2.2.1. Non-thermal Microwave Effect

During microwave irradiation of the reaction mixture there is a specific effect of microwave activation that cause an increase in the reaction rates for which bulk temperature of the reaction mixture is inadequate to explain. Such an effect has been accepted to be called the non-thermal microwave effect or the specific microwave effect. These effects don't require the transfer of microwave energy into thermal energy but it directly couples itself to energy modes within the molecule. The issue of specific microwave effects is still a controversial matter. Several theories have been postulated and also some predicted models have been published [Loupy *et al*. (2001); Nuehter *et al*. (2000); Hoz *et al*. (2005)].

Non-thermal effects have several origins and may arise also from interactions between the microwave field and the material, similar to thermal effects. In this way, microwave heating

strongly interferes with possible non-thermal effects and these cannot be easily separated in mechanistic studies.

2.3 PLA Nanocomposites

Polymer composites are manufactured commercially for many diverse applications such as sports items, aerospace components, automobiles, etc. In the last 20 years, there has been a strong emphasis on the development of polymeric nanocomposites, where at least one of the dimensions of the filler material is of the order of a nanometer. The final product does not have to be of nanoscale, but can be of micro- or macroscopic scale in size. The surge in the field of nanotechnology has been greatly facilitated through the advent of scanning/ tunneling electron microscopy and scanning probe microscopy in the early 1980s. With these powerful tools, scientists are able to see the surface structure with atomic resolution. Simultaneously, the rapid growth in computational techniques has made it easier to characterize and predict the properties at the nanoscale via modeling and simulation. Polymer nanocomposites are class of composites derived from ultrafine inorganic particles with sizes of the order of nanometers that are homogeneously dispersed in a polymer matrix. Due to the nanometer sizes of fillers, nanocomposites possess properties that are superior to those of conventional composites because of the maximization of interfacial adhesion. Nanoscale composites of polymers with clays or organoclays have been studied extensively by several workers [Yano *et al*. (1993); Usuki *et al*. (1995); Giannelis *et al*. (1996); Lagaly *et al*. (1999); Chang *et al*. (2002)]. There have been several attempts to improve properties of PLA by synthesizing PLA/silicate-layered nanocomposites. Ogata *et al*. (1997) first prepared micrometer-scale phase separation of the organoclays filler with the PLA matrix instead of without nanometer-range dispersion. The organically modified montmorillonite (OMMT) was used to reinforce PLLA in composites

produced by solution casting. Ray *et al*. (2002a, b, c, d; 2003) and Maiti *et al*. (2002) were able to produce intercalated nanocomposites with PLA by using organically modified clay and melt intercalation. They reported the effects of clay particle size and clay cationic exchange capacity (CEC) on the overall extent of intercalation.

2.3.1 *In situ* Preparation of PLA Nanocomposites through Conventional Heating

The *in situ* polymerization techniques involve the addition of nanofiller directly to the monomer during polymerization. It is an effective technique for preparing nano-composites with enhanced mechanical and thermal properties [Paul *et al*. (2003)]. The *in situ* ring-opening polymerization of lactide involves the formation and purification of lactide from the oligo-condensation of lactic acid, which also increases the cost of PLA production [Mehta *et al*. (2005); Garlotta *et al*. (2001)] and prevents its application in various commodities.

TiO_2/PLA nanocomposites with different contents of organically modified TiO_2 were prepared through *in situ* polymerization of L-lactide [Zhuang *et al*. (2009)]. The highly hydrophilic TiO_2 was treated with MPS (γ-methacryloxypropyltrimethoxysilane) to modify it to be hydrophobic enough to disperse in the PLA matrix. The size of the organically modified TiO_2 particles was investigated by X-ray diffraction (XRD) analysis. The TiO_2 dispersion on nanoscale in PLA was characterizaed by scanning electron microscopy (SEM). Differential scanning calorimetry (DSC), thermo-gravimetric ananlysis (TGA) and the tensile test indicated an increase in thermal stability and mechanical properties compared to those of pure PLA [Zhuang *et al*. (2009)]. Silicon dioxide [Wu *et al*. (2008)] was used as nanofiller for the *in situ* polymerization of lactide. An intercalated *in situ* polymerization of lactide in supercritical carbon dioxide was reported by Urbanczyk *et al*. (2009). The intercalative morphology of nanocomposites was achieved for 3

wt% of clay. It was observed that there is a decrease in polymerization rate with increase in the amount of clay which was attributed to steric hindrance.

Ye *et al*. (2012) synthesized PLA/ZnS nanocomposites through solvothermal method by cationic ring-opening *in situ* polymerization of lactide in the presence of stannous chloride as catalyst. Effects of the various factors on the molecular weight, morphology, and optical properties were investigated. Sedaghat *et al*. (2012) prepared PLA/organo-clay nanocomposites by *in-situ* polymerization technique. The effect of modifiers on the structure of poly (lactic acid) nanocomposite samples were studied by using DSC and wide angle X-ray diffraction (WAXRD). An exfoliated morphology of PLA/organo-modified montmorillonite nanocomposite was successfully obtained by *in situ* coordinative polymerization of L-lactide in bulk [Paul *et al*. (2003)]. Clay exfoliation was achieved by the grafting reaction of the growing PLA chains onto the hydroxy-functionalized ammonium cations used as clay-surface organo-modifiers. Exfoliation of clay platelets led to an improved thermal stability as compared to that of pure PLA. Li *et al*. (2010) synthesised PLA nanocomposites by *in situ* melt polycondensation of L-lactic acid with different loadings of surface-hydroxylated magnesium oxide (MgO) nanocrystals.

2.3.2 *In situ* Preparation of PLA/Clay Nanocomposites under Microwave Irradiation

There are only a few reports in the open literature on *in-situ* preparation of poly (lactic acid)/clay nanocomposites under microwave irradiation. Microwave technology was used for synthesis of polylactide (PLA)/organo-montmorillonite (OMMT) nanocomposites in bulk through the *in situ* ring-opening polymerization by Cao *et al*. (2009) and *in situ* melt polycondensation of D,L-lactide by Cao *et al*. (2010).

Cao *et al*. (2009) synthesized PLA/Clay nanocomposites through ring-opening polymerization of DLLA using stannous octoate as catalyst. The microwave oven (Sanyo MCL-2, with a frequency of 2.45 GHz) was used for microwave irradiation. The influence of the microwave power, irradiation time, catalyst dose and amount of OMMT on tensile strength was studied. The polymerization time used was 10 min under 90W of microwave irradiation. The mechanical and thermal properties of the PLA/OMMT nanocomposites were found to be significantly improved. The composite with the highest mechanical properties was obtained when the dosages of the OMMT and the catalyst were 1.0 and 0.6 wt % of the lactide, respectively as shown in **Figure 2.10**.

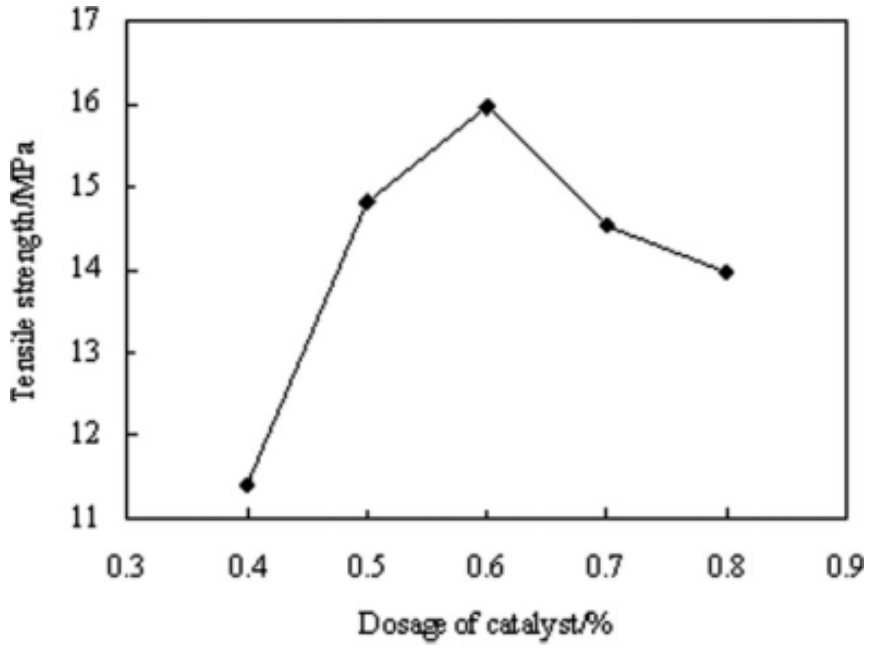


Figure 2.10 Effects of the dosage of catalyst on the tensile strength [Cao *et al*. (2009)]

The initial decomposition temperature of the PLA/OMMT (1.0 wt % OMMT) nanocomposite was enhanced by 11.5 ^{o}C compared to that of pure PLA (**Figure 2.11**) [Cao *et al*. (2009)]. The

PLA nanocomposite containing 1.0 wt % OMMT exhibited a more stable thermal resistance due to the good thermal insulation effect of the nanoscale OMMT.

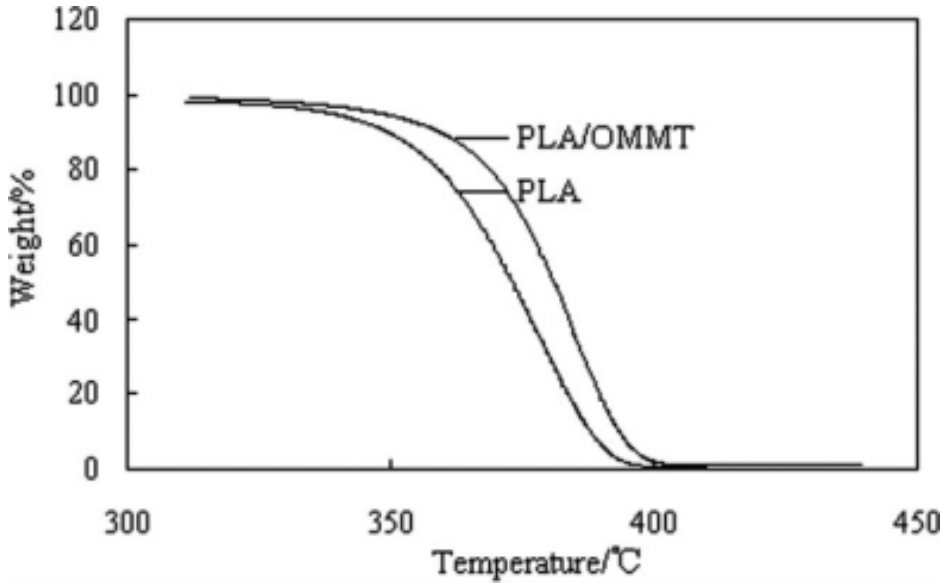


Figure 2.11 TGA of PLA and PLA/OMMT [Cao *et al*. (2009)]

The transmission electron microscopy (TEM) and XRD confirmed the formation of exfoliated and intercalated nanocomposites morphology. The TEM of synthesised PLA/Clay nanocomposites (**Figure 2.12**) showed the distribution of OMMT among the PLA matrix [Cao *et al*. (2009)].

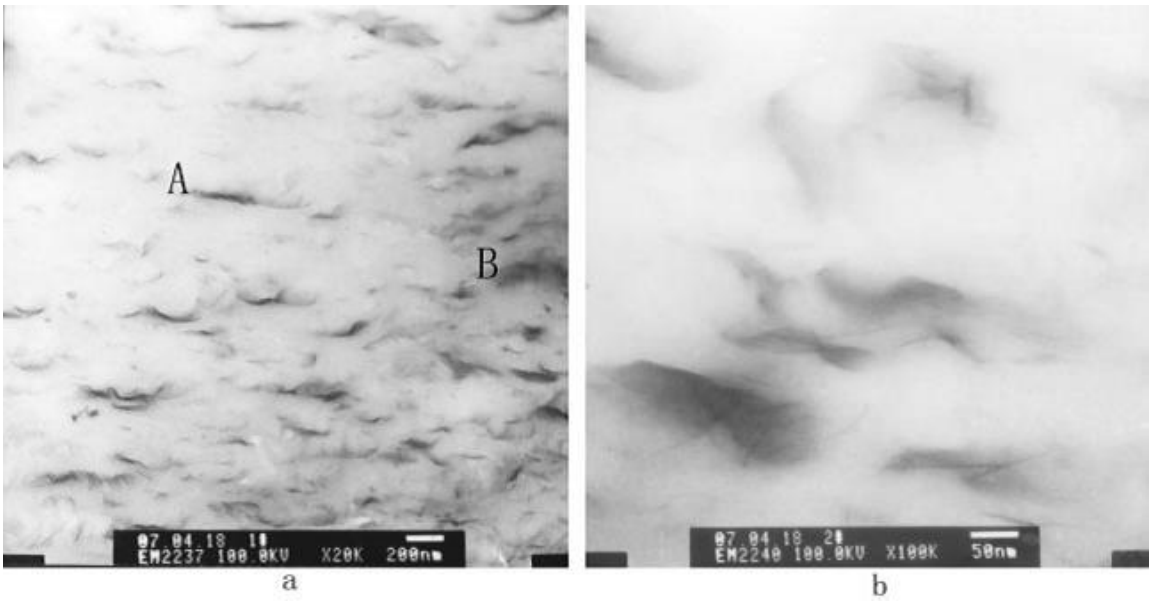


Figure 2.12 TEM images of the PLA/OMMT nanocomposite at (a) low magnification and (b) high magnification [Cao *et al*. (2009)]

The results showed that the exfoliated OMMT platelets (**Figure 2.12(a-B)**] coexisted with a limited amount of intercalated stacks [**Figure 2.12(a-A)**] and were extremely well dispersed. The ordered lamellar structure of the OMMT was destroyed as shown in **Figure 2.12(b)** and the interlayer d-spacing was enlarged.

In another study, the authors reported their results on the synthesis of poly (lactic acid)/Na-montmorillonite nanocomposite by microwave-assisted *in situ* melt polycondensation [Cao *et al*. (2010)]. The microwave oven (Sanyo MCL-2, with a frequency of 2.45 GHz) was used for the preparation of PLA/Na^+-MMT nanocomposites using $SnCl_2$/TSA as catalyst. The effects of the Na^+-MMT on the molecular weight, tensile strength and thermal loss were studied. The bonding between PLA and Na^+-MMT surface was analysed by FTIR **(Figure 2.13)** [Cao *et al*. (2010)].

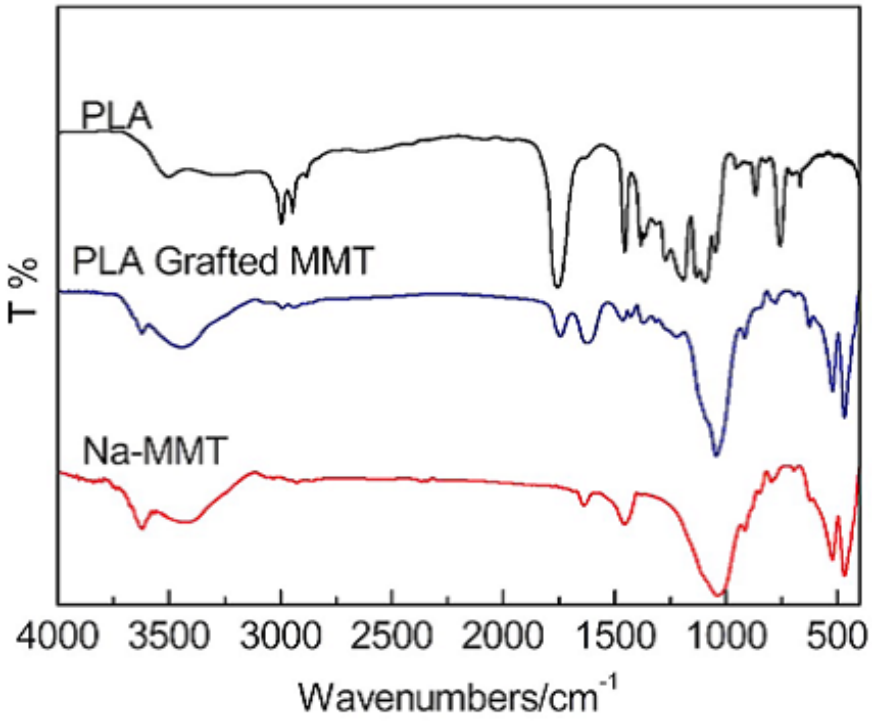


Figure 2.13 FTIR spectra of PLA, Na^+-MMT, and PLA grafted MMT [Cao *et al*. (2010)]

The dispersion morphology of Na^+-MMT was examined using XRD, TEM, and SEM techniques. The mechanical and thermal properties of the PLA/Na^+-MMT nanocomposites got enhanced with the addition of the Na^+-MMT. The TEM images showed effective dispersion of clay in the polymer matrix as shown in **Figure 2.14** [Cao *et al*. (2010)].

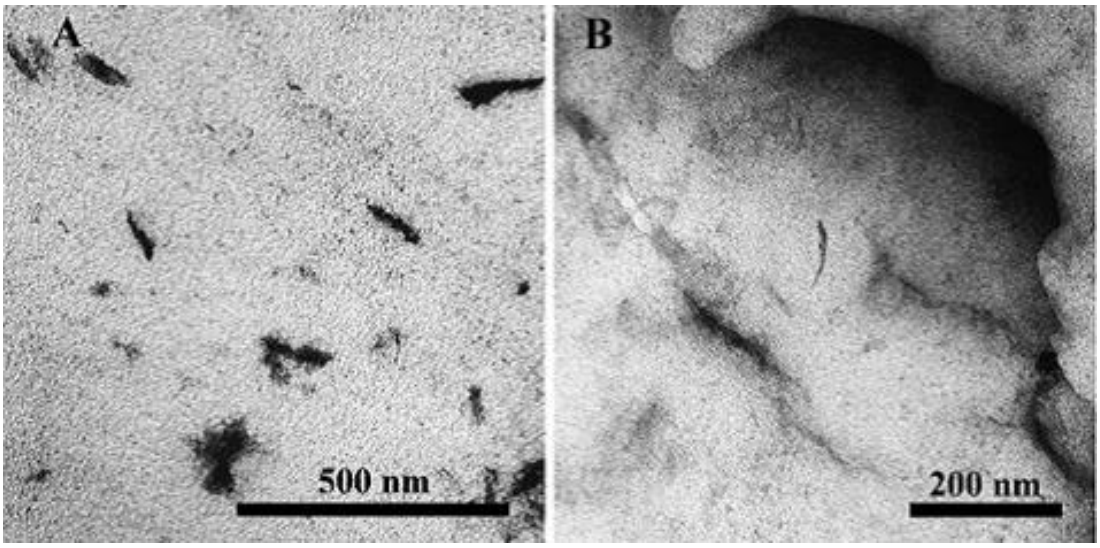


Figure 2.14 Typical TEM images of PLA/MMT nanocomposite at (A) low magnification and (B) high magnification [Cao *et al*. (2010)]

The *in situ* melt polycondensation was beneficial for the grafting of PLA on the surface of the MMT layers to improve the compatibility. On the other hand, the application of microwave irradiation could accelerate the whole process and help in the formation of exfoliated structure [Paul *et al*. (2003)].

From the foregoing discussion on the status of research on the synthesis of PLA it is seen that attempts have been made to obtain the polymer of large molar mass using appropriate initiator and operating conditions. The initiators used are stannous octoate, $SnCl_2$/ TAS, various tin based and binary catalysts ($SnCl_2$/p-TsOH), $Sn(Oct)_2$/PEG & methoxy PEG (macro-initiators) and calix[4]arene-titanium (IV)]. Effects of reaction time, temperature, and mode of heating (microwave /conventional thermal) have been studied. The same procedure [Mehta *et al*. (2006)] can be used to calculate the rate constants for polymerization under MW irradiation if non-thermal effect can be neglected in microwave assisted synthesis. However, no data are available in the literature to check the efficacy of such calculations. However, issues related to

the use of different initiators to synthesize PLA in microwave of higher molar mass with low polydispersity and calculation of kinetic rate constants remain yet to be resolved and need more work.

In case of PLA/Clay nanocomposites, prior work does not present comprehensive understanding of how microwave polymerization occurs in the presence of clay or if clay intercalation and exfoliation are promoted by microwave irradiation. A very little information is available in the open literature regarding its synthesis under microwave irradiation. In view of its capability to yield polymer nanocomposites of high strength having wider possible application, are also needed to be explored further.

In view of the above, the present work has been planned to carry out microwave assisted ring-opening polymerization of lactide for PLA synthesis and to study its reaction kinetics and to prepare PLA/Clay nanocomposite using organically modified montmorillonite clay in-situ and to characterize the nanocomposites of PLA.

The materials used in the study and method adopted are fully explained in the successive chapter.

CHAPTER - 3

MATERIALS AND METHODS

CHAPTER-3 MATERIALS AND METHODS

This chapter presents details of materials and experimental procedures adopted during the synthesis of PLA and its nanocomposites using clay. Quality and source of materials (monomer, initiators, co-initiator and solvents) used and the procedure adopted for recrystallization of L-lactide are given in Section 3.1. Details of experimental procedure and equipment are given in Section 3.2 and experimental conditions are described in section 3.3. Various characterization techniques used for polymer and its nanocomposites are discussed in Section 3.4.

3.1 Materials

Stannous octoate ($SnOct_2$), dibutyltin dimethoxide (DBTM) and dimethylaminopyridine (DMAP) were purchased from Sigma Aldrich, India and used as received. AR-grade chloroform, diethyl ether, hexane, and methanol were obtained from Merck Ltd., India. The following solvents were used in size exclusion chromatography (SEC): AR-grade tetrahydrofuran (THF) (POCH, Poland), distilled immediately before use and stabilized with 0.2 g L^{-1} of 2,6-di-tert-butyl-4-methyl phenol, HPLC grade chloroform (POCH, Poland) and HPLC grade dimethylformamide (DMF) (Scharlau, Spain). The latter two solvents were used as received.

3.1.1 Types of Clay

Three different clays - Cloisite® Na^+ (natural unmodified montmorillonite), Cloisite® 15A (montmorillonite modified with dimethyl dehydrogenated tallow quaternary ammonium cations), and Cloisite® 30B (montmorillonite modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium cations) were procured from Southern Clay Ltd, Mumbai, India and were used as such after drying.

3.1.2 L-Lactide ({3S, 6S}-3, 6-Dimethyl-1, 4-Dioxane-2, 5- Dione)

L-lactide was used as monomer in polymerization experiments and was purchased from Sigma Aldrich, India. The recrystallization of L-lactide was done three times with ethyl acetate (solvent) and final drying in vacuum desiccator for 24 h before use. The recrystallization was done to improve the purity and the yield of PLA. **Figure 3.1** shows the chemical structure of the L-lactide monomer.

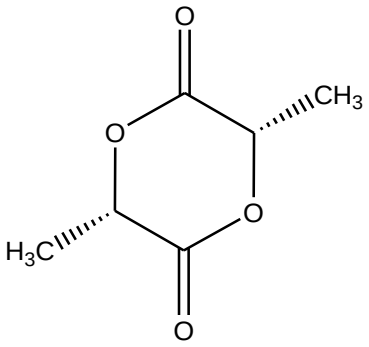
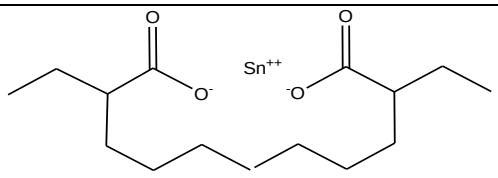


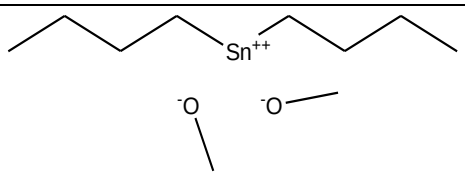
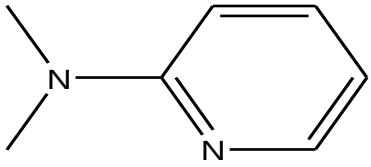
Figure 3.1 Chemical structure of l-lactide

3.1.3 Initiator (s) and Co-Initiator

Stannous octoate and dibutyl tin dimethoxide were used as initiators during polymerization reactions. Dimethylaminopyridine (DMAP) was used as co-initiator. **Table 3.1** shows the chemical structures of various initiators and the co-initiator.

Table 3.1 Chemical structures of initiator (s) and co-initiator used for the polymerization

S.No.	Name of initiator	Structure of initiator
1.	Stannous octoate	

2.	Dibutyl tin dimethoxide, DBTM	
3.	Dimethylaminopyridine, DMAP (Co-initiator)	

3.2 Experimental Set-up

Three different experimental set-ups were used for the polymerization of lactide and to prepare its clay nanocomposites. The first set-up was established for the synthesis of PLA in a domestic microwave oven and the second set-up was established for the synthesis of PLA in monomode microwave oven. The third set-up was used for the synthesis of PLA/clay nanocomposites in the monomode microwave oven. Here, an ultrasonic probe was used for proper dispersion of clay in the solvent.

3.2.1 PLA Synthesis in Domestic Microwave Oven

A microwave (MW) oven (LG MC-8048WR) with an operating frequency of 2.45 GHz was used for the irradiation of the reaction mixture. The reagent glass bottles of 30 ml capacity with appropriate modification were used as reaction vessels (**Figure 3.2**). L-lactide was weighed into a reagent bottle and vacuum degassed. A solution of the initiator $Sn(Oct)_2$ in diethyl ether solvent (1 ml of solvent) was then added using a micropipette. Initially the reaction mixture was subjected to three cycles of vacuum using vacuum pump to get rid of the solvent and the bottles

were then sealed under vacuum. The reaction mixture was divided into five reaction bottles for MW irradiation for different durations.

Figure 3.2 Reaction vial equipped with adapter for domestic microwave oven

3.2.2 PLA Synthesis in Monomode Microwave Oven

A Monomode microwave oven (Monowave 300, Anton Parr) (**Figure 3.3**) with an operating frequency of 2.45 GHz was used for irradiation of the reaction mixture. Glass vials of 10 ml capacity were used as reaction vessels. A solution of the initiator in hexane solvent was added into reaction vials using a micropipette. Hexane has a long carbon chain and easily evaporates by applying vacuum. Hence, hexane was used as the solvent in the monomode microwave unit in place of diethyl ether which was found to interfere with the polymerization and affects the polymerization yield, possibly due to presence of oxygen. L-lactide was weighed and then added into the reaction vials. Initially the reaction mixture was subjected to three cycles of 90 mm (Hg)

vacuum using vacuum pump to get rid of the solvent and the bottle was sealed with silicon septum under N_2 atmosphere. The reaction mixture was then irradiated with MW for different durations. The crude product was cooled, dissolved in chloroform and the product polymer was precipitated by pouring the solution into excess of methanol. The precipitate was recovered through vacuum filtration and further dried under vacuum. A schematic representation of the experimental procedure is shown in **Figure 3.4**.

Figure 3.3 Monomode microwave oven for polymerization of l-lactide

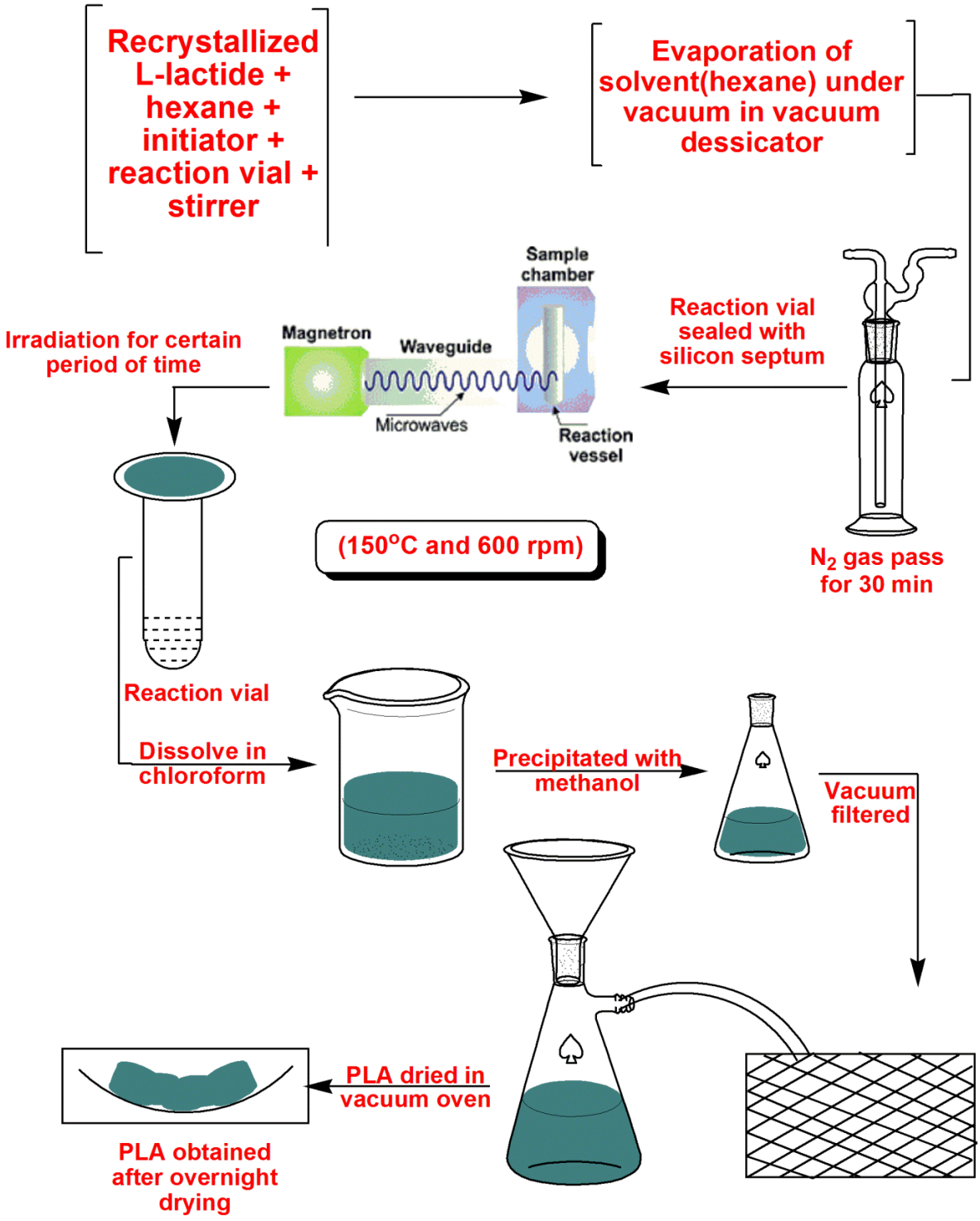


Figure 3.4 Schematic of synthesis of PLA

3.2.3 Synthesis of PLA/Clay Nanocomposites

Monomode microwave oven was also used for synthesizing *in situ* PLA/clay nanocomposites. Nano dispersion of clay is required to achieve the best possible combination of matrix-nanoparticle properties. This was achieved by using an ultrasonic probe (Qsonica Q700 Sonicator operating at the frequency of 20 kHz at 110V) **(Figure 3.5)**. Ultrasonication provides tremendous amount of energy to the clay layers, so that they get separated to a larger extent. The sonication was done for 10 mins to obtain a uniform dispersion of clay in hexane (solvent). After addition of the initiator and the monomer, the sonication was continued for an additional 10 mins. Then the solvent was evaporated and reaction mixture was fully dried under vacuum. Borosilicate vials of 10 ml capacity were used as reaction vessels. The vials containing reaction mixture were sealed under N_2 atmosphere with silicon septum and were then irradiated.

Figure 3.5 Ultrasonic probe

3.3 Polymerization of L-Lactide to Synthesis PLA

3.3.1 PLA Synthesis in Domestic Microwave Oven

Three different molar ratios of monomer and initiator 1040/1, 5069/1 and 2534/1 were used for the synthesis at two different MW power levels of 180 W and 360 W. The temperature was kept at 180^{o}C. A few experiments were carried out at 130^{o}C which has been reported in literature for conventional synthesis of PLA but a good yield could be obtained at 180^{o}C. This is in confirmatory with the literature where $SnOct_2$ as initiator has been studied in a domestic microwave oven. Compositions of reaction mixtures used for the synthesis in MW oven are given in **Table 3.2**.

In the MW oven, certain amount of heat transfer medium (silicon carbide, SiC) was placed into a beaker, and then the reaction bottles containing reactants were placed into the beaker for MW irradiation. Alternatively, direct heating of the reaction bottles was also done. The direct heating led to the formation of only oligomers and at higher reaction time the product degraded. In case of direct heating of the polymerization mixture, the possibility of heating at lower rate occurs as compared to that when a heat transfer medium is used. In this way, two heating modes could be compared, namely direct microwave irradiation and thermal conduction from the heat transfer medium to the glass bottles. The reaction mixture was irradiated at selected microwave power levels without stirring during the polymerization. However, as detailed in section 3.2.1., a solvent was used to uniformly disperse the initiator in monomer (lactide). The solvent was subsequently evaporated. The temperature was set at 180^{o}C. The crude product was cooled, dissolved in chloroform and precipitated by pouring into the excess of cold methanol. The precipitates were recovered through vacuum filtration and further dried under vacuum.

Table 3.2 Composition of reaction mixtures for the synthesis of PLA in domestic microwave oven: Molar concentration of monomer [M_o] and initiator [I_o] for various time intervals.

S.No.	$[M_o]/[I_o]$	Sample [a)]	MW Power (W)
1.	1040/1	PLA 1A, 1B, 1C, 1D,1E	180
2.	1040/1	PLA 2A, 2B, 2C	360
3.	5069/1	PLA 3A, 3B, 3C, 3D, 3E	180
4.	2534/1	PLA 4A, 4B, 4C, 4D,	180

[a)] A, B, C, D, E correspond to time period of 5, 10, 15, 20, 30 min respectively and 1, 2, 3 and 4 corresponds to different set of experiments for different $[M_o]/[I_o]$ ratios.

3.3.2 PLA Synthesis in Monomode Microwave Oven

Four different molar ratios of monomer and initiator 1040/1, 5069/1, 2534/1 and 10,069/1 were used for the synthesis at 150^{o}C. Some exploratory experiments were performed at 180^{o}C but experiments at 150^{o}C showed better yield and minimum degradation. Hence further experiments were carried out at 150^{o}C in monomode microwave. Compositions of reaction mixtures used for the synthesis in monomode MW oven are given in **Table 3.3**.

Table 3.3 Composition of reaction mixtures for the synthesis of PLA in Monomode microwave oven: Molar ratios of monomer [M_o] and initiator [I_o] for various time intervals.

S.No.	Name of Initiator	$[M_o]/[I_o]$	Sample [a)]
1	Stannous octoate	1040/1	PLA 1A, 1B, 1C, 1D,1E
		2534/1	PLA 2A, 2B, 2C, 2D, 2E
		5069/1	PLA 3A, 3B, 3C, 3D, 3E
		10069/1	PLA 4A, 4B, 4C, 4D, 4E
2	Dibutyl tin dimethoxide	1040/1	PLA 5A, 5B, 5C, 5D, 5E
		2534/1	PLA 6A, 6B, 6C, 6D, 6E
		5069/1	PLA 7A, 7B, 7C, 7D, 7E
		10069/1	PLA 8A, 8B, 8C, 8D, 8E
3	Stannous octoate/ Dimethylaminopyridine	1040/1	PLA 9A, 9B, 9C, 9D, 9E
		2534/1	PLA 10A, 10B, 10C, 10D, 10E
		5069/1	PLA 11A, 11B, 11C, 11D, 11E
		10069/1	PLA 12A, 12B, 12C, 12D, 12E

[a)] A, B, C, D, E corresponds to time period of 5, 10, 15, 20, 30 min, respectively and 1, 2, 3, 4,5,6, 7,8,9,10,11 and 12 corresponds to different set of experiments for different $[M_o]/[I_o]$ ratios.

In the MW oven, vigorous stirring of reaction mixture takes place and helps in proper dispersion of initiator in the L-lactide solution. This unit allows maintaining a very uniform temperature profile by automatically adjusting the power supplied without sequencing the value of actual absorbed energy.

3.4 Characterization Techniques

Several instrumental techniques are used to characterize polymer molecules and polymer nanocomposites. In this work, ^{1}H-NMR, ^{1}H-^{13}C HSQC NMR, FTIR, SEC, XRD, TGA, SEM and TEM techniques have been used.

3.4.1 Proton Nuclear Magnetic Resonance (^{1}H-NMR) Spectrometry

The ^{1}H-NMR technique was used for the characterization of polymer structure. NMR is a unique technique for the direct detection of hydrogen bonding interactions, chemical identification and conformational analysis of chemicals whether synthetic or natural. ^{1}H-NMR spectra were recorded using $CDCl_3$ solvent using Bruker Avance II Spectrometer, Germany operating at 400 MHz frequency.

3.4.2 ^{1}H-^{13}C Correlation Heteronuclear Single-Quantum Coherence (HSQC) Nuclear Magnetic Resonance (NMR) Spectrometer

The ^{1}H & ^{13}C NMR techniques were used for the characterization of polymer structure. The Heteronuclear Single Quantum Coherence (HSQC) was used to correlate the chemical shift of proton with the chemical shift of the directly bonded carbon. The spectra were recorded using $CDCl_3$ solvent and tetramethylsilane as an internal standard using a Bruker Avance II Spectrometer operating at 400 MHz frequency. For analysis of the aliphatic region, spectra were

recorded from 5.5 to 1.0 ppm in ^{1}H (acquisition time, 0.156 s; 1024 data points) and from 120 to 10 ppm in ^{13}C (acquisition time, 11.3 ms; 256 increments).

3.4.3 Fourier Transform Infrared (FTIR) Spectrometer

Fourier transform infrared (FTIR) spectrometer (Perkin Elmer, SPECTRUM 400) was used to confirm the formation of PLA and to study the compatibility of PLA and clay in PLA/Clay nanocomposites. The FTIR spectrometer is used primarily for qualitative and quantitative analyses of organic compounds, and also for determining the chemical structure of many inorganic compounds. Efforts were made to record the FTIR spectra of samples as soon as possible. The spectra were recorded from 450 to 4000 cm^{-1}. For all measurements, the sample was ground with KBr and made into a pellet for measurement in diffused reflectance mode at 4 scans and at 2.0 cm^{-1} resolutions.

3.4.4 Size Exclusion Chromatography (SEC)

The molar masses of products were determined by SEC using a common instrument that consisted of a pump from Watrex, Czech Republic (flow rate 1 $mL.min^{-1}$), an injection valve from Rheodyne, USA, a column system and a detector. The sample volume was 50 µL and ambient temperature was about 22 °C.

Three different column systems were employed for the PLA molar mass determination the synthesised in domestic microwave oven. JORDI GEL DVB 1000 Å + JORDI GEL DVB 100 Å columns from Jordi, USA were applied using DMF/THF 30/70 as eluent. THF mobile phase was utilized with AM GEL 10 µm linear column from American Polymer Standards, USA and chloroform with SHODEX GPC KF 806L column, Japan.

Polystyrene equivalent molar mass averages M_w (weight average molar mass) and M_n (Number average molar mass) of samples were calculated with the help of Clarity software from DataApex, Czech Republic, using polystyrene standards for calibration.

3.4.5 X-ray Diffraction (XRD) Analysis

X-ray diffraction studies were performed using Panalytical's XPERT-PRO with Cu Kα radiation. The generator was operated at 40 mA and 45 kV at room temperature. Samples were scanned in a continuous mode with counting time of 1.8 s at diffraction angles (2θ) ranging from 2 to 15°.

3.4.6 Thermogravimetric Analysis (TGA)

The thermal stability of polymeric materials was evaluated through thermo-gravimetric analysis (TGA). The weight loss due to the formation of volatile products after degradation at high temperature is monitored as a function of temperature. TGA was performed from room temperature to 650°C using a Diamond TG/DTA Thermo-gravimetric Analyzer from Perkin Elmer, USA at a heating rate of 10^oC/min under N_2 gas flow using a horizontal differential type balance.

3.4.7 Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) FEGSEM JEOL JSM-7600F FEG-(HRSEM) was used and operated at 3 kV to study the surface morphology of PLA/clay nanocomposites.

3.4.8 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) was performed with a Hitachi H-7500 apparatus using an acceleration voltage of 90-100 kV and fine powders of each sample absorbed onto carbon-coated 200-mesh copper grid.

The results obtained through above experiments and characterization studies are presented and discussed in the following chapter (Chapter 4).

CHAPTER – 4

RESULTS AND DISCUSSION

CHAPTER-4 RESULTS AND DISCUSSION

The ring-opening polymerization of l-lactide to synthesize PLA and its clay nanocomposites have been successfully performed using microwave ovens. To synthesize PLA, the microwave heating units used were domestic as well as monomode microwave ovens. Results obtained through polymerization experiments are presented in this chapter. Sections 4.1 and 4.2 incorporate the discussion of the results on the synthesis of PLA using domestic and monomode microwave ovens, respectively. Section 4.3 discusses the effect of clay on *in situ* ring-opening polymerization of l-lactide to synthesize PLA/Clay nanocomposites in monomode microwave oven.

Several initiators have been tried to polymerize l-lactide using microwave ovens. These initiators include $SnOct_2$, DBTM, DMAP, zinc stearate and salen based metal complexes. But out of these initiators only $SnOct_2$ and DBTM resulted into PLA polymer formation. Zinc stearate has been studied by several researchers for the ring-opening polymerization of l-lactide using conventional method of polymerization [Kaur *et al*. (2011)]. Although it does not result into PLA of much higher molar mass but it does result in PLA product formation. In the present work, use of zinc stearate as an initiator did not yield any polymer. Similarly, salen based metal complexes had also been reported to give high molar mass PLA through conventional route but again did not give any PLA product in the microwave oven, in the present study. The use of molecular sieves has also been reported for producing high molecular weight PLA by conventional heating method. But in the present study, use of molecular sieves resulted into a reduction in the polymer yield. In the present study, several quaternary ammonium ions and DMAP have been used as co-initiators in the ring-opening polymerization. Only DMAP has been found to work as a good co-initiator when used with $SnOct_2$ in microwave assisted

synthesis of PLA. Thus in the present work $SnOct_2$ and DBTM were used as the initiators and DMAP as the co-initiator for further investigations involving synthesis of PLA and clay nanocomposites using microwave oven for heating.

4.1 Ring-opening Polymerization of Lactide to Poly(Lactic Acid), PLA using Stannous Octoate as an Initiator in Domestic Microwave Oven

The microwave-assisted ring-opening polymerization (ROP) of l-lactide to poly (lactic acid), PLA was studied using stannous octoate, $Sn(Oct)_2$ as an initiator under vacuum. The synthesis was carried out using a domestic microwave oven as the heating device.

The preliminary set of experiments in domestic microwave oven were performed using the monomer to initiator ratio $[M_o]/[I_o]$ = 1000/1 to synthesise PLA. The borosilicate glass bottle with suitable modification **(Figure 3.2)** was used as the reaction vessel. The initiator and monomer were added to the reaction vessel, vacuum was created and contents were irradiated with microwaves. The temperature and the power level were kept at 180 ^oC and 180 W, respectively. But the molar mass of PLA synthesized was very low. The possible reasons for these are explained below. Microwaves use electromagnetic radiations to add energy to a material or product, but not all materials or products will absorb microwave energy and therefore not all will get heated up in a microwave oven. Some materials, like PTFE (Teflon), polypropylene, many types of glass, some high purity ceramics and quartz, do not heat well in a microwave. But materials like water, carbon, silicon carbide (SiC), iron oxide and many ceramics get heated quite well. Hence an appropriate heat transfer material has been used for absorbing the microwave and transfer the thermal energy to the reaction mixture so that it gets heated up. In the MW oven, certain amount of the heat transfer medium (silicon carbide, SiC) was placed into a beaker, and then the reaction bottles containing reactants were placed into it for

MW irradiation. Alternatively, direct heating of the reaction bottles was also done. In the latter case, direct heating led to the formation of only oligomers and at longer reaction time the product was degraded. In case of direct heating of the polymerization mixture, the possibility of heating at lower rate occurs as compared to that when a heat transfer medium is used. In this way, two heating modes could be compared, namely the direct microwave irradiation and the thermal conduction from the heat transfer medium to the glass oven. The crude product thus obtained was cooled, dissolved in chloroform and precipitated by pouring into the excess of cold methanol. The precipitate was recovered through vacuum filtration and dried under vacuum.

4.1.1 Characterization of PLA

PLA synthesized was characterized by using Size Exclusion Chromatography (SEC)**,** Nuclear Magnetic Resonance (NMR) Spectroscopy and Fourier Transform Infrared (FTIR) Spectroscopy.

4.1.1.1 Size Exclusion Chromatography (SEC)

The number and weight average molar masses of product PLAs have been determined by SEC. The molar mass averages and polydispersities (PD) of PLA obtained at 180 W and $[M_o]/[I_o]$ ratio 5069 were calculated from the SEC chromatograms shown in **Figure 4.1a, 4.1b and 4.1c**, and the average molar mass and the yield are tabulated in **Tables 4.1, 4.2** and **4.3**. The number average and weight average molar masses obtained with $[M_o]/[I_o]$ ratio 1041 are listed in **Table 4.1**. It is seen that for the $[M_o]/[I_o]$ ratio 1041, the molar mass of PLA increases with the polymerization time up to 15 min and thereafter the product degrades due to irradiation. As the $[M_o]/[I_o]$ ratio increases to 2534, the molar mass increases significantly up to 20 min as compared to $[M_o]/[I_o]$ ratio 1041. The values of molar masses for $[M_o]/[I_o]$ ratio 2534 are listed in **Table 4.2.** The measurements were done using Shodex column with two different detectors,

refractive index detector (RID) and evaporative light scattering detector (ELSD). The SEC analysis for $[M_o]/[I_o]$ ratio 5069 was done by using three different columns and the values of molar masses are listed in **Table 4.3.**

Table 4.1 Mean molar masses M_n, M_w and polydispersity of PLA as a function of the polymerization time for the monomer/initiator $[M_o]/[I_o]$ ratio=1041/1.

Power level (W)	**Irradiation time (mins)/ Sample code**	**$M_n \times 10^{-3}$ a)**	**$M_w \times 10^{-3}$ b)**	**PD**	**Yield %**
180	10 (1B)	4	4	1.10	65
	15 (1C)	7	17	2.45	81
	20 (1D)	6	10	1.62	88
	30 (1E)	significantly degraded			
360	5 (2A)	6	8	1.27	70
	10 (2B)	7	9	1.29	65
		3	3	1.03	
	15 (2C)	5	7	1.37	66
	20 (2D)	significantly degraded			

a), b) M_n and M_w are the number average and weight average molar masses determined by size exclusion chromatography using the set of JORDI columns.

Table 4.2 Mean molar masses M_n, M_w and polydispersity of PLA [synthesized at power level (180W)] as a function of the polymerization time for the monomer/initiator $[M_o]/[I_o]$ ratio of 2534/1 measured with ELSD and RID detectors.

Irradiation time (mins)/ Sample code	**RID**			**ELSD**			**Yield %**
	$M_n \times 10^{-3}$	**$M_w \times 10^{-3}$**	**PD**	**$M_n \times 10^{-3}$**	**$M_w \times 10^{-3}$ b)**	**PD**	
5 (4A)	17	25	1.46	15	20	1.36	54
10 (4B)	25	65	2.64	34	64	1.87	89

15 (4C)	32	65	2.03	37	66	1.76	94
20 (4D)	37	77	2.07	37	75	1.99	97

Table 4.3 Comparison of values of mean molar mass, M_n, M_w and PD of PLA (synthesized at power level 180W for $[M_o]/[I_o]$ ratio = 5069/1) determined using different SEC columns and different mobile phases

Irradiation time (min)/ Sample code	**SEC columns**									**Yield %**
	JORDI			**AM GEL**			**SHODEX**			
	$M_n \times 10^{-3}$	**$M_w \times 10^{-3}$**	**PD**	**$M_n \times 10^{-3}$**	**$M_w \times 10^{-3}$**	**PD**	**$M_n \times 10^{-3}$**	**$M_w \times 10^{-3}$**	**PD**	
10 (3B)	14	23	1.61	4	15	3.40	9	21	2.27	86
15 (3C)	22	35	1.64	6	21	3.65	18	29	1.55	80
20 (3D)	21	37	1.80	12	33	2.75	22	37	1.66	92
30 (3E)	9	21	2.24	10	23	2.24	13	24	1.82	81

These results are discussed in the following section. The sample 3C is bimodal as it contains more than one molar mass fraction. Other chromatograms exhibit symmetrical unimodal shape. Molar mass of PLA increases with increasing $[M_o]/[I_o]$ ratio at lower power input of 180 W. As the $[M_o]/[I_o]$ ratio increases, the number of initiator molecules decrease for a given number of monomer molecules. It results in reduction of the number of chains onto which a given number of monomer molecules can attach themselves. Hence, rise in the molar mass is observed as the $[M_o]/[I_o]$ ratio increases.

The molar mass obtained for $[M_o]/[I_o]$ ratio 2534 is much higher as compared to other two $[M_o]/[I_o]$ ratios as shown in (**Figure 4.2a)**. There are sufficient numbers of initiator molecules for a given number of monomer molecules, which results in reduction of number of chains.

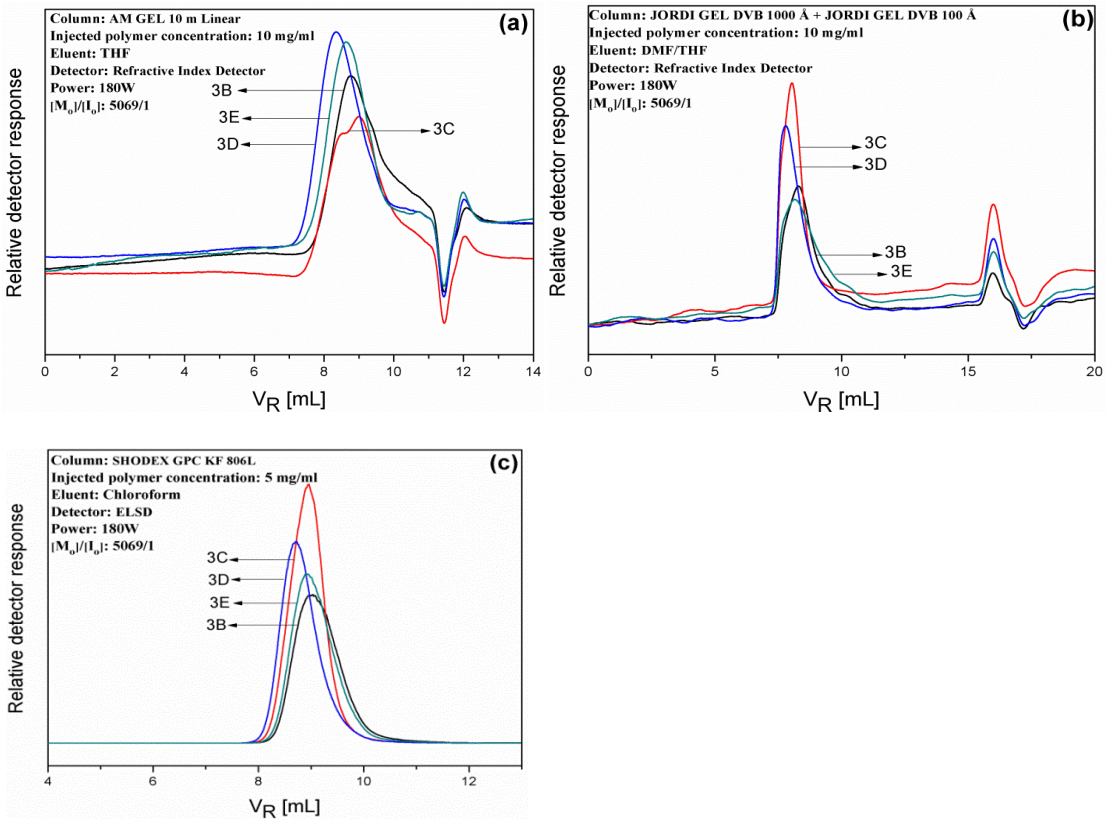


Figure 4.1 (a,b,c) SEC chromatograms of PLA synthesized using different detectors.

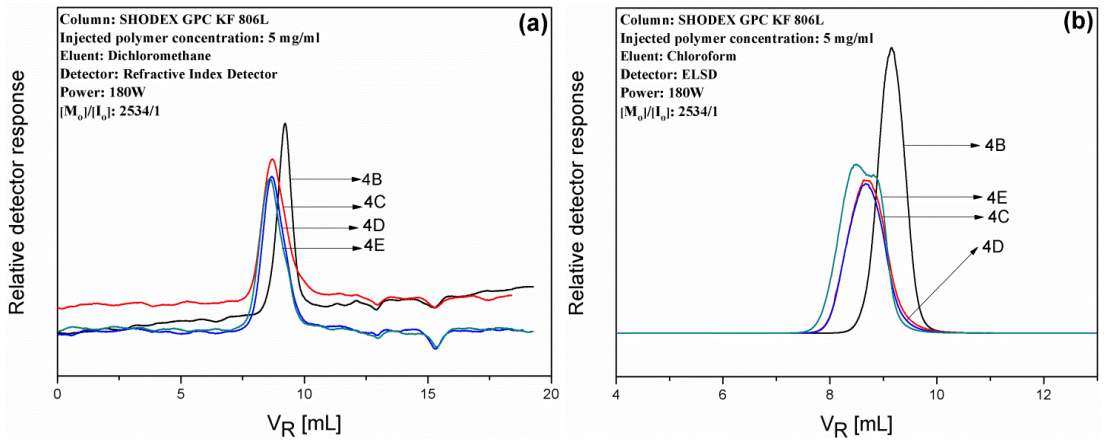


Figure 4.2(a,b) SEC chromatograms of PLA synthesized using different detectors.

The data collected has shown that for RID, chloroform is not a suitable eluent. To detect PLA, the injected concentration has to be quite high (in the range of 20-25 $mg.mL^{-1}$). At such a high

injected concentration, columns got overloaded, the peaks became distorted and their retention volumes were significantly shifted to higher values (**Figure 4.1a)**. Most samples were soluble in tetra hydro furan (THF) at ambient temperature though some of them had to be heated to about 50^{o}C to dissolve. Phase separation (turbidity) was not observed when temperature dropped back to ambient (about 23^{0}C). However, formation of polymer aggregates could not be excluded. In order to improve solubility of PLA and to suppress its possible adsorption on the active SEC column packing, 30% of dimethyl formamide (DMF) (RI =1.431) was added to THF. The RID detectability of the sample was reduced correspondingly. Higher content of dimethyl formamide (DMF) is undesirable because the column packing particles could shrink and the gel bed would be destroyed. The best results were obtained with chloroform as eluent and ELSD. Injected concentration could be reduced to 5 mg mL^{-1} and base-line was very good, not distorted with system peaks. The column AM Gel **(Figure. 4.1a)** does not result in good separation in the low molar mass range. This is why the peaks contain large tail, which is overlapped with the system peaks. The column system Jordi 1,000 plus Jordi 100 **(Figure. 4.1b)** well separates system peaks from the polymer peaks but the latter are partially excluded and the molar masses are slightly higher.

PLA is a challenge polymer for SEC characterization. First problem is the solubility of PLA. Therefore, the measurements have also been carried out in $CHCl_3$. There is no problem with the solubility in $CHCl_3$, but the refractive index of $CHCl_3$ is too high and similar to that of PLA. Therefore, high concentration had to be injected and this was problematic for obtaining reliable data, as well. High RI detector sensitivity had to be used and as a result, the base line was rather poor. The measurements with samples obtained with $[M_o]/[I_o]$ ratio 5069 **(Figure. 4.1c)** and those obtained with $[M_o]/[I_o]$ ratio 2534 **(Figure. 4.2a)** were performed with the Shodex column,

using $CHCl_3$ as eluent and evaporative light scattering detector. Samples obtained with $[M_o]/[I_o]$ ratio 2534 were also measured with RID **(Figure. 4.2b).** With RID the unimodality of samples was much improved. Presence of a fraction with low molar mass cannot be excluded with all samples except for sample 4A. It is visible in Sample 4D and a little with Sample 4C. On the contrary, there may be a higher molar mass fraction present in Sample 4A. With ELSD, the peaks were elegant. The qualitative agreement between RID and ELSD is clear, especially with Sample 4D. In Sample 4A, which exhibits very low M_w/M_n = PD value, it seems that the separation selectivity in $CHCl_3$ is a little lower than with dichloromethane (DCM). The difference in the molar mass values obtained in distinct eluents can be easily explained by the difference in the constants of Kuhn-Mark-Houwink-Sakurada equation [Wagner *et al*. (1985)]. The important conclusion is that the tendency of mean molar mass evolution remains the same.

It is interesting that for $[M_o]/[I_o]$ ratio 2534, the width of molar mass dispersion is quite high-and the yield of polymerization is also comparatively high. Thus the observation about $[M_o]/[I_o]$ ratio is more qualitative than quantitative.

4.1.1.2 Proton Nuclear Magnetic Resonance (^{1}H-NMR)

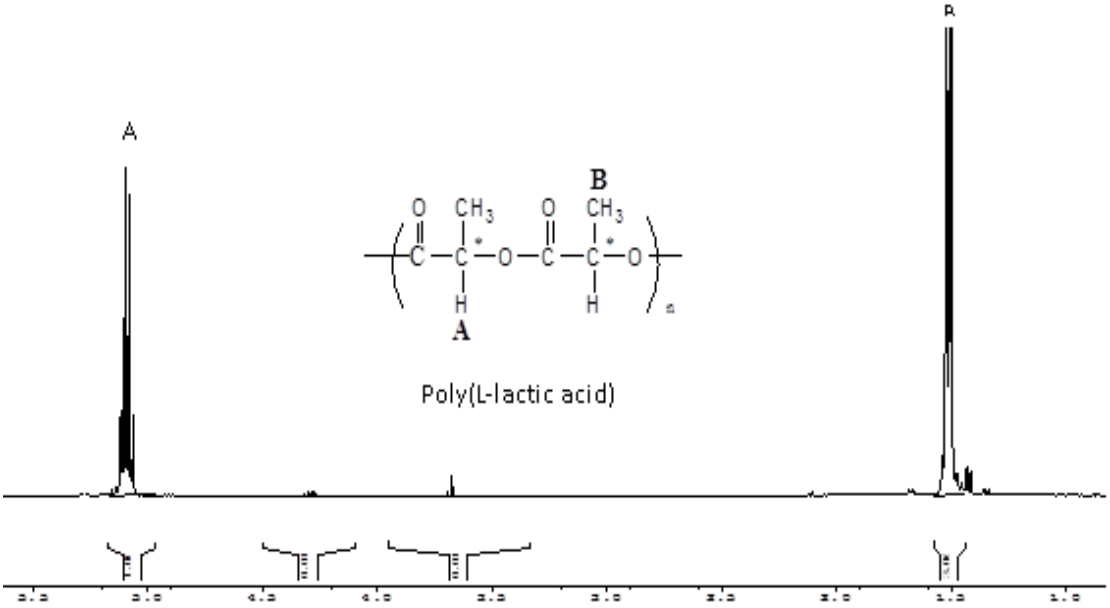


Figure 4.3 ^{1}HNMR spectra of PLLA

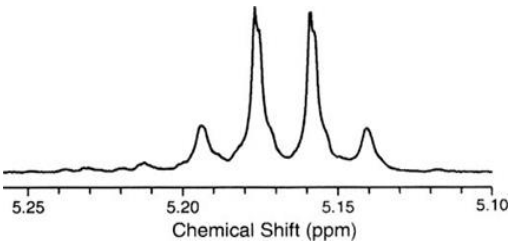


Figure 4.4 ^{1}HNMR spectra of PLLA

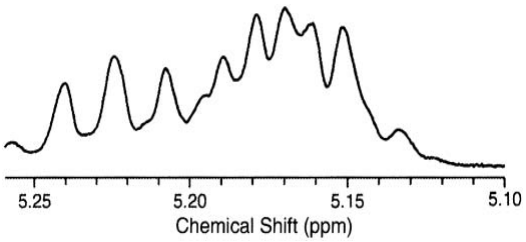


Figure 4.5 ^{1}HNMR spectra of PDLLA

The precipitates obtained were confirmed as poly (l-lactic acid), PLLA by means of ^{1}H NMR spectroscopy. PLLA has –OH and –COOH groups at its two ends. The ^{1}H-NMR spectrum of PLLA is shown in **Figure 4.3**. The resonance signal at 1.3-1.6 (d, 3H, CH_3) is assigned to methyl protons (-CH_3) and at 5.06–5.15(q, 1H, CH) to methine protons (-CH) of the repeat unit of PLLA. The resonance signal at (δ = 4.28) corresponds to the methine linked to the end group –OH. Thus, the characterization explained above demonstrates the formation of PLLA by the ring opening polymerization.

Lactide has two asymmetric carbons and is commercially available in the enantiomerically pure form, (l-lactide), or as the racemic mixture of (d,l-lactide).

In the present study, the monomer used is l-lactide. The formation of PLLA is confirmed by comparing the product spectra with the spectra of PLLA and PDLLA [Rober *et al*. (2008)]. The methine region for PDLLA displays several superimposed quartets. But the specimen spectra of PLLA show a well-defined methine region quartet without any superimposed quartets. **Figures 4.4** and **4.5** show the ^{1}H-NMR spectra of PLLA and PDLLA specimens, respectively. ^{1}H-NMR of product PLA confirmed the presence of pure PLLA and not its enantiomer or a racemic mixture of PLA.

4.1.1.3 Fourier Transform Infrared (FTIR) Spectroscopy

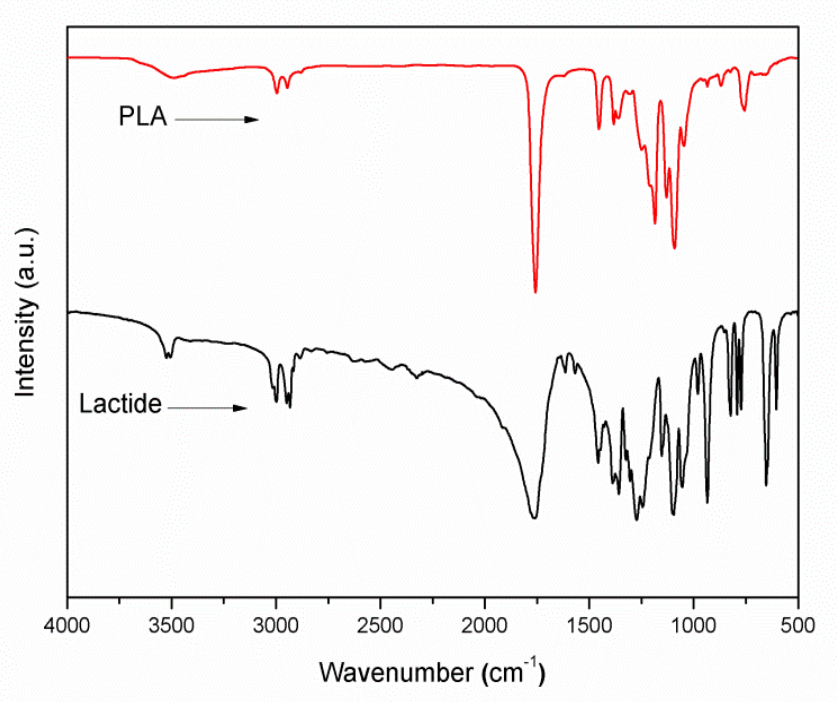


Figure 4.6 FTIR spectra of l-lactide and PLA

The chemical structure of PLA is also confirmed from the FTIR spectroscopy. **Figure 4.6** shows the FTIR spectra of the monomer l-lactide and PLA. The IR spectra of PLA and l-lactide show the band at 1757.33 cm^{-1} corresponds to C=O bond stretching. This band shows shifts of monomer to polymer and also shows a difference in the peak intensity which suggests the arrangement of molecules in the polymer chain. The bands at 2996.37 cm^{-1} and 2945.82 cm^{-1} correspond to symmetric and asymmetric valence vibrations of C-H from $-CH_3$, respectively. The most characteristic absorption of ester C-O stretching is at 1187.45 cm^{-1} which is present in monomer as a weak band at 1151.72 cm^{-1}. The absorption band in the region of 3500 cm^{-1}, a characteristic for the hydroxyl groups was very prominent in the spectrum of lactide. These peaks in the monomer resulted quite likely from the presence of O-H bending vibration due to traces of humidity, which was possibly present in it. The FTIR spectrum of PLA corresponds to the IR spectra reported in literature [Wu *et al*. (2005)].

4.2 Need for using Monomode Microwave Oven over Domestic Microwave Oven

The PLA synthesized in the domestic microwave oven has lower molar mass than that synthesized in monomode microwave ovens. Monomode microwave oven is used with less power emitted with a high return of energy, and thus, the utilization of monomode oven is energy efficient and leads to better yields in organic synthesis. In view of this, the ring-opening polymerization of l-lactide to synthesize PLA was carried out in monomode microwave oven which results in higher molar mass PLA than domestic microwave oven.

4.3 Ring-opening Polymerization of L-lactide to Poly(Lactic Acid), PLA using Monomode Microwave Oven

4.3.1 Temperature-Power Profile of Polymerization Reaction in Monomode Microwave

The polymerization reaction of l-lactide to poly (l-lactide) has been carried out by using stannous octoate and dibutyltin dimethoxide. **Figure 4.7** shows the profile of temperature, power and pressure of the reaction mixture as a function of the reaction time. Three stages occur in the course of reaction. The first stage includes attaining target temperature that has been set at 150 °C. During this stage, the temperature rises rapidly up to the target value and the reaction mixture is heated up. L-lactide, being polar, readily absorbs the microwaves. Second stage is the polymerization reaction, during which the power supply decreases significantly because polymerization is slightly exothermic as reported by Schlinder *et al*. (1979). In about 69 seconds the preset temperature is attained and power supply becomes zero. The temperature of the polymerizing batch remains nearly constant with the help of a heater and a compressor.

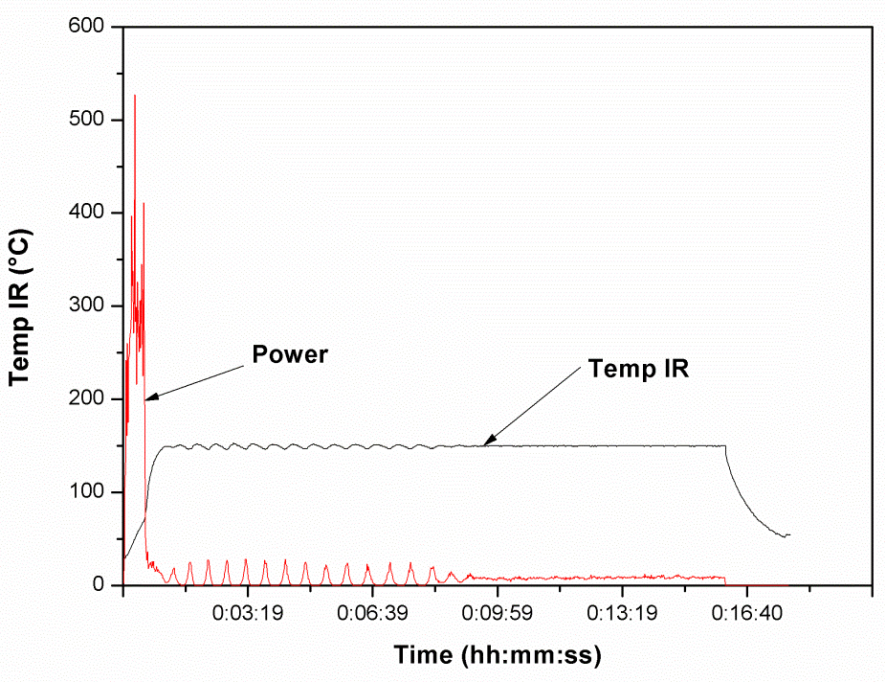


Figure 4.7 Temperature and power profile with reaction time (sample PLA 6C) for poly (l-lactic acid)

4.3.2 Characterization of PLA Samples Synthesized in Monomode Microwave Oven

PLA synthesized in monomode microwave oven was characterized by using Size Exclusion Chromatography (SEC), ^{1}H-^{13}C Correlation Heteronuclear Single-Quantum Coherence (HSQC) Nuclear Magnetic Resonance (NMR) Spectroscopy, and Fourier Transform Infrared (FTIR) Spectroscopy.

4.3.2.1 ^{1}H-^{13}C Correlation Heteronuclear Single-Quantum Coherence (HSQC) Nuclear Magnetic Resonance (NMR) Spectroscopy

The ^{1}H and ^{13}C NMR spectra of l-lactide are shown in **Figures 4.8** and **4.9**, respectively**.** The ^{1}H NMR exhibits a resonance signal at 1.61-1.63 (d, 3H, CH_3) and 5.13–5.18 (q, 1H, CH) which are assigned to methyl protons (-CH_3), and methine protons (-CH) of the l-lactide ring, respectively. The methyl protons exhibit a doublet due to methine protons and methine proton shows a quartet due methyl protons. This phenomenon is known as the spin-spin splitting effect. The ^{13}C NMR spectra of L-lactide (**Figure 4.9**) shows a resonance signal at 72.5 (C, CH), 15.53 (C, CH_3), 167.5 (C, C=O) and 76.9-77.5 (C, $CDCl_3$) which are assigned to methine carbon, methyl carbon (-CH_3), carbonyl carbon and carbon of deuterated chloroform, respectively. As seen in **Figure 4.10**, the signal at 1.61-1.63 in ^{1}H NMR corresponds to 15.53 signals in ^{13}C NMR spectra. It means that the methyl protons correspond to –CH_3 carbon and methine protons correspond to –CH carbon.

Similarly, **Figures 4.11** and **4.12**, respectively, show the ^{1}H and ^{13}C NMR spectra of PLLA. The ^{1}H NMR of PLLA shows a resonance signal at 1.57-1.60 (d, 3H, CH_3) and 5.13–5.19 (q, 1H, CH) which are slightly shifted toward lower value with comparison to L-lactide spectrum values. This is due to the polymerization of l-lactide to PLLA [poly (l-lactic acid)] during which the formation of polymer backbone takes place. The ^{13}C NMR spectra of PLLA exhibit resonance signals at 69.01 (C, CH), 16.64 (C, CH_3), 169.61 (C, C=O) and 76.7-77.3 (C, $CDCl_3$), which

show shift toward higher value due to polymerization. The correlation between protons and carbons can be found by HSQC technique. As seen in **Figure 4.13**, the methine protons correspond to carbon of –CH and methyl protons correspond to carbon of $–CH_3$.

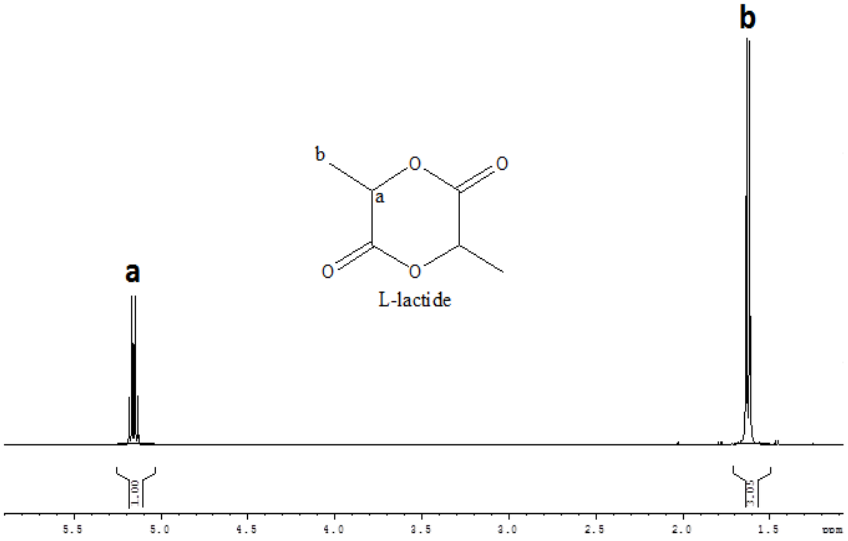


Figure 4.8 ^{1}H NMR spectra of l-lactide

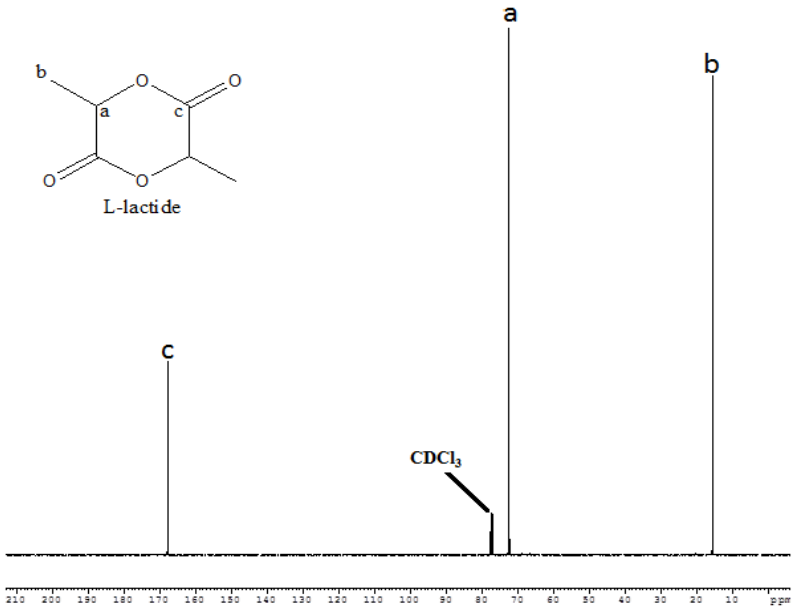


Figure 4.9 ^{13}C NMR spectra of l-lactide

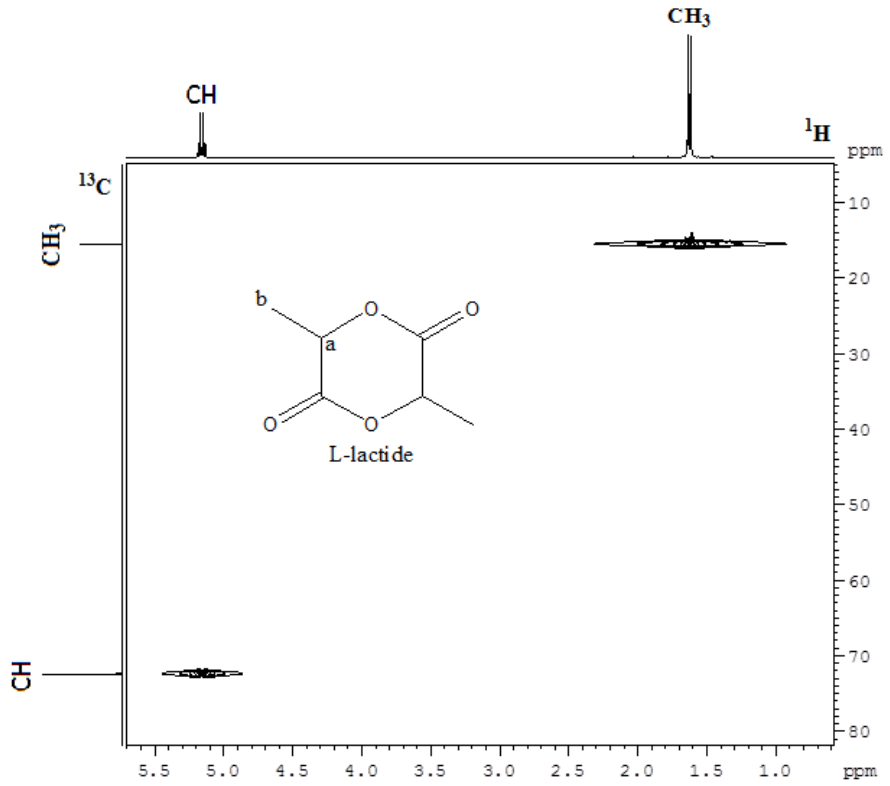


Figure 4.10 HSQC spectra of l-lactide

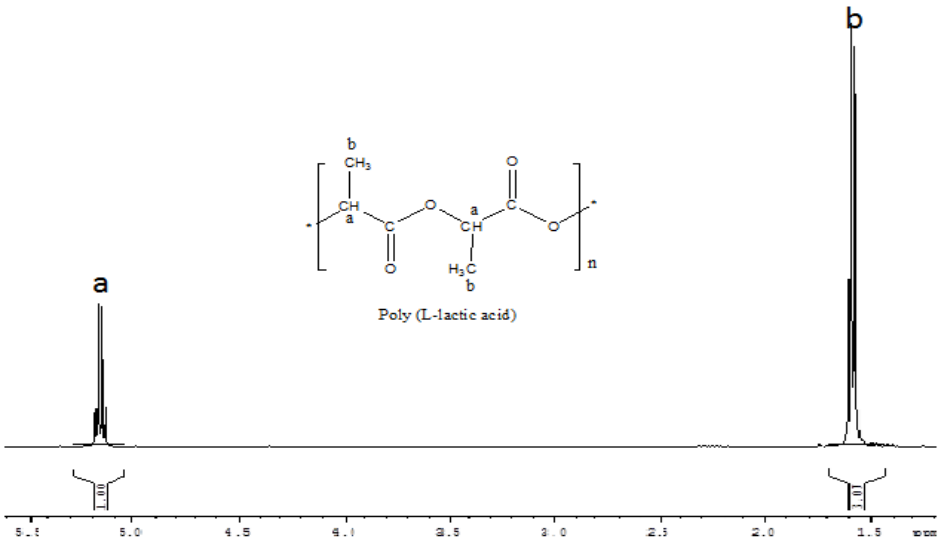


Figure 4.11 [1]H NMR spectra of PLLA

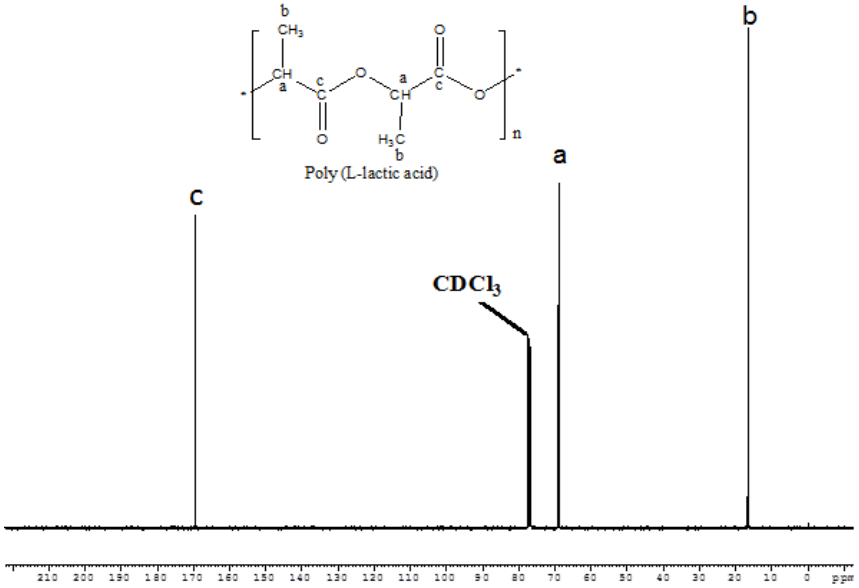


Figure 4.12 ^{13}C NMR spectra of PLLA

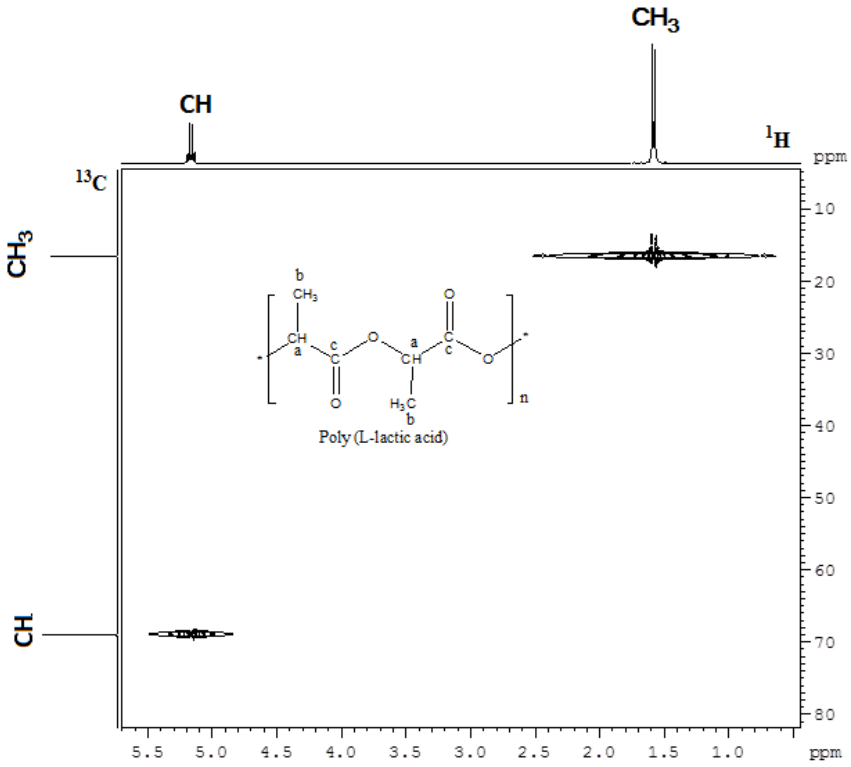


Figure 4.13 HSQC spectra of PLLA

5.3.2.2 Fourier Transform Infrared (FTIR) Spectroscopy

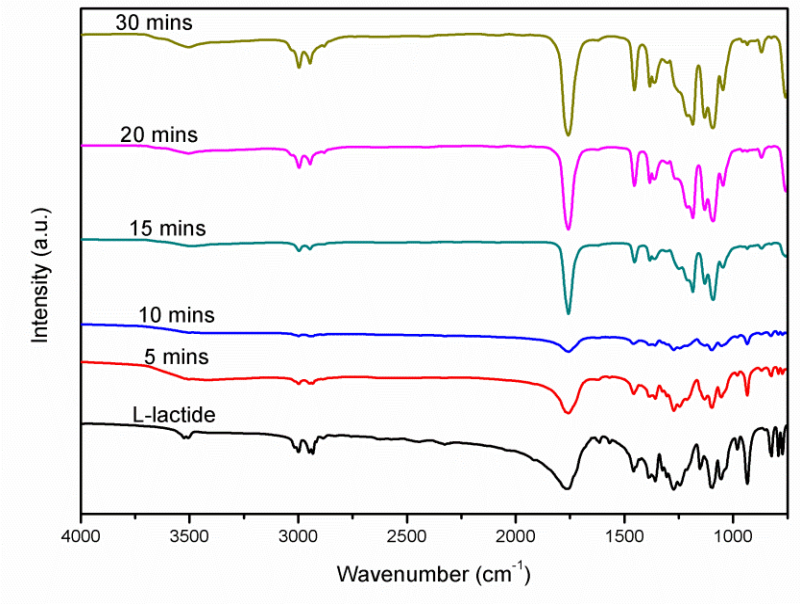


Figure 4.14 FTIR spectra of L-lactide and resulting PLA at various polymerization times

Both the progress of the polymerization process and the changes in chemical structure of the polymer formed were assessed from the FTIR spectra. A small amount of sample was taken out at different time intervals during polymerization. The difference in the structure of l-lactide and PLA is that the former has a ring structure and the latter has long linear chains consisting of C-C linkages as backbone (l-lactide on initiation opens up into a linear dimer which further polymerizes to give a PLA chain). The difference in their spectra is also due to ester linkage -C(=O)-O- which is different due to steric effects. With an increase in the chain length, a stretching band at 1760 cm^{-1} changes into a large sharp band as shown in **Figure 4.14.**

There is an absorption band in the region of 3500 cm^{-1}, which is characteristic for the hydroxyl groups and is very prominent in the spectrum of lactide. A band appeared at 1090 cm^{-1} during polymerization which did not correspond to the monomer. This band was due to the absorption of ester C-O-C stretching. The asymmetric bending C-H vibrations were observed around 1450

cm^{-1} in monomer and subsequently also at 1454 cm^{-1} in polymer. These peaks in the monomer quite likely resulted from the presence of O-H bending vibration due to traces of humidity, which was possibly present in the monomer. It is known that lactide monomer is always associated with some amount of water even after multiple recrystallizations and evacuations.

5.3.2.3 Size Exclusion Chromatography (SEC)

As indicated above, the poly(styrene)-equivalent molar masses of PLA samples were determined by size exclusion chromatography. **Tables 4.4** and **4.5** summarize the number average and weight average molar masses of polymer formed at different monomer to initiator ratio for stannous octoate and for dibutyltin dimethoxide, respectively. Molar mass of PLA increases with the polymerization time up to 10 to 15 minutes and in some cases up to 20 minutes and after that it starts decreasing (cf. **Figures 4.18** and **4.19** also). The highest molar mass M_w obtained is 1.02×10^5 $g.mol^{-1}$ for monomer/ initiator ratio 5,069 using $SnOct_2$.

Table 4.4 Mean molar masses M_n, M_w and polydispersity of PLA as a function of the polymerization time and monomer/initiator $[M_o]/[I_o]$ ratio for stannous octoate

$[M_o]/[I_o]$ ratio	Irradiation time (mins)	$M_n \times 10^{-3}$ a)	$M_w \times 10^{-3}$ b)	PD (Polydispersity)	Yield %
1041/1	5	11	15	1.36	65
	10	18	25	1.38	79
	15	14	22	1.57	81
	20	11	22	2.0	82
	30	11	23	2.09	78
2534/1	5	7	15	2.14	74
	10	12	25	2.08	78
	15	30	46	1.53	88
	20	8	18	2.25	74

	30	7	17	2.43	73
5069/1	5	30	36	1.2	28
	10	38	48	1.26	42
	15	57	90	1.57	76
	20	62	102	1.64	84
	30	28	62	2.21	75
10069/1	5	6	8	1.33	18
	10	26	33	1.27	61
	15	21	27	1.28	54
	20	17	21	1.23	28

[a), b)] M_n and M_w are the number average and weight average polystyrene equivalent molar masses determined by size exclusion chromatography, respectively.

Table 4.5 Mean molar masses M_n, M_w and polydispersity of PLA as a function of the polymerization time and monomer/initiator $[M_o]/[I_o]$ ratio for dibutyltin dimethoxide

$[M_o]/[I_o]$ ratio	**Irradiation time (mins)**	**$M_n \times 10^{-3}$ a)**	**$M_w \times 10^{-3}$ b)**	**PD (Polydispersity)**	**Yield %**
1041/1	5	19	32	1.68	85
	10	16	29	1.81	83
	15	16	27	1.68	86
	20	18	30	1.66	86
	30	15	26	1.73	87
2534/1	5	22	36	1.63	82
	10	24	40	1.66	85
	15	15	26	1.73	86
	20	7	12	1.71	81
5069/1	5,10,15,20,30	Very low yield (Non recoverable)			
10069/1	5,10,15,20,30	Very low yield (Non recoverable)			

[a), b)] M_n and M_w are the number average and weight average polystyrene equivalent molar masses determined by size exclusion chromatography, respectively.

The SEC chromatograms for PLA using $SnOct_2$ and DBTM initiators are shown in **Figures 4.15** and **4.16,** respectively. The SEC results show that polymers obtained with DBTM exhibit lower molar mass than those initiated with $SnOct_2$. The highest molar mass M_w of PLA obtained with DBTM was 4×10^4 $g.mol^{-1}$ while the highest molar mass obtained with $SnOct_2$ was over 10^5 $g.mol^{-1}$. This was probably due to the fact that DBTM is a transesterification catalyst and it may provoke back-biting degradation during polymerization. This is in accordance with several reports in the literature [Kubota *et al*. (1995); Kricheldorf *et al*. (2000); Wang *et al*. (2005); Kasperczyk *et al*. (2000); Dubois *et al*. (1991)]. Molar mass of PLA initiated with $SnOct_2$ increases with increasing $[M_o]/[I_o]$ ratio up to 5069/1 and then starts decreasing. At this optimum $[M_o]/[I_o]$ ratio for $SnOct_2$, the yield of polymer obtained with DBTM was very low. The present results indicate that from the viewpoint of preparation of high molar mass PLA, $SnOct_2$ is a better initiator than DBTM. As seen from chromatograms that the polydispersity of PLA prepared with DBTM seems to be a little lower than that initiated with $SnOct_2$, however, the difference hardly exceeds the experimental errors.

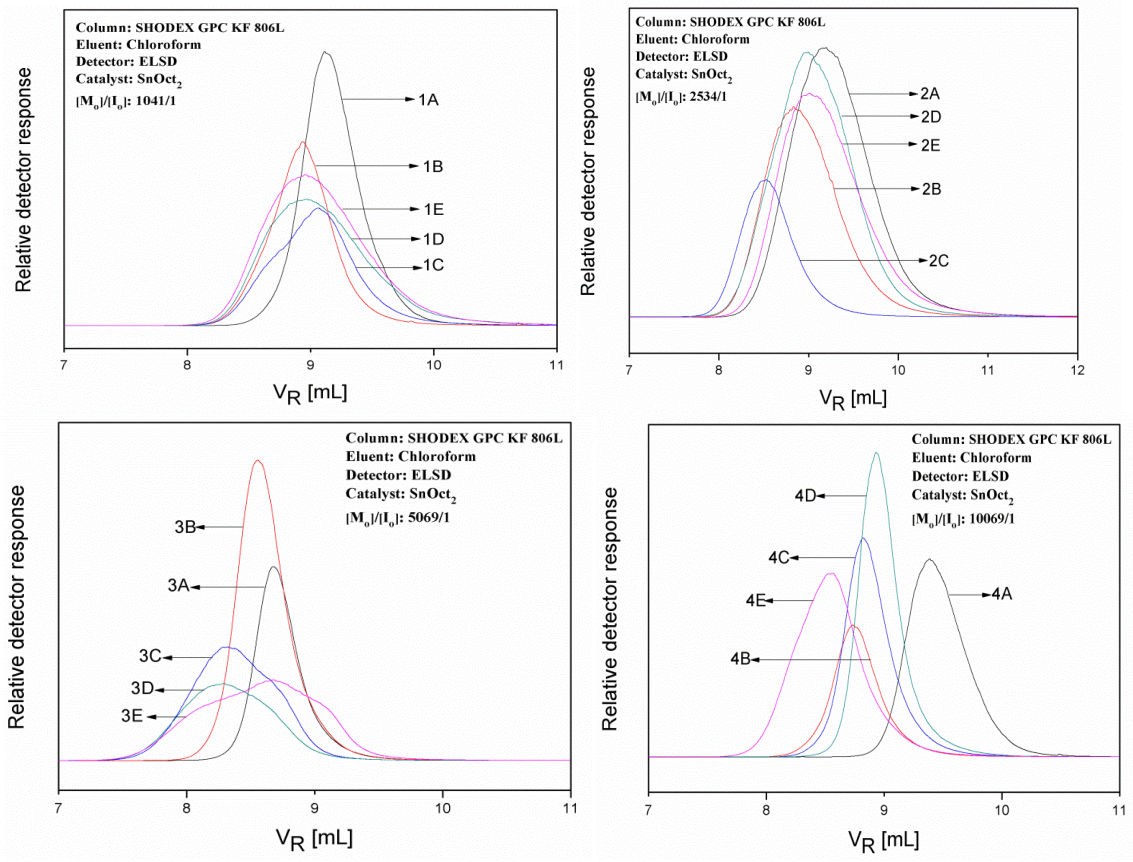


Figure 4.15 SEC chromatograms of synthesized PLA for $SnOct_2$ at different time durations and different $[M_o]/[I_o]$ ratios

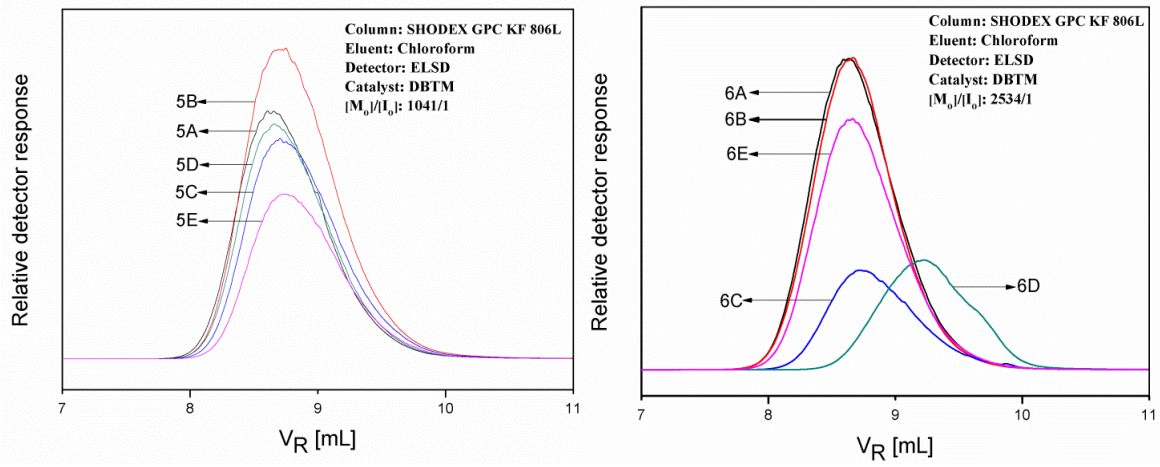


Figure 4.16 SEC chromatograms of synthesized PLA for DBTM at different time durations and for two different $[M_o]$ /$[I_o]$ ratios

Almost as a matter of chance, it was observed that significant degradation of PLA takes place in chloroform solvent. One of the PLA samples was injected into the SEC column about 18 hours after its dissolution in chloroform. Its degradation is clearly evident from **Figure 4.17**, where the chromatograms obtained with freshly prepared and stored solution of a PLA sample are overlaid. The injected concentration $c_i = 4$ mg.mL^{-1} was nearly constant. It is evident that one part of the polymer was degraded while another part remained unchanged. This does not correspond to the common principles of oxidative degradation of polymers. The possible reasons for such a behavior of PLA may be the presence of traces of phosgene and hydrochloric acid in the solvent. The background and course of this unusual behavior deserve further study.

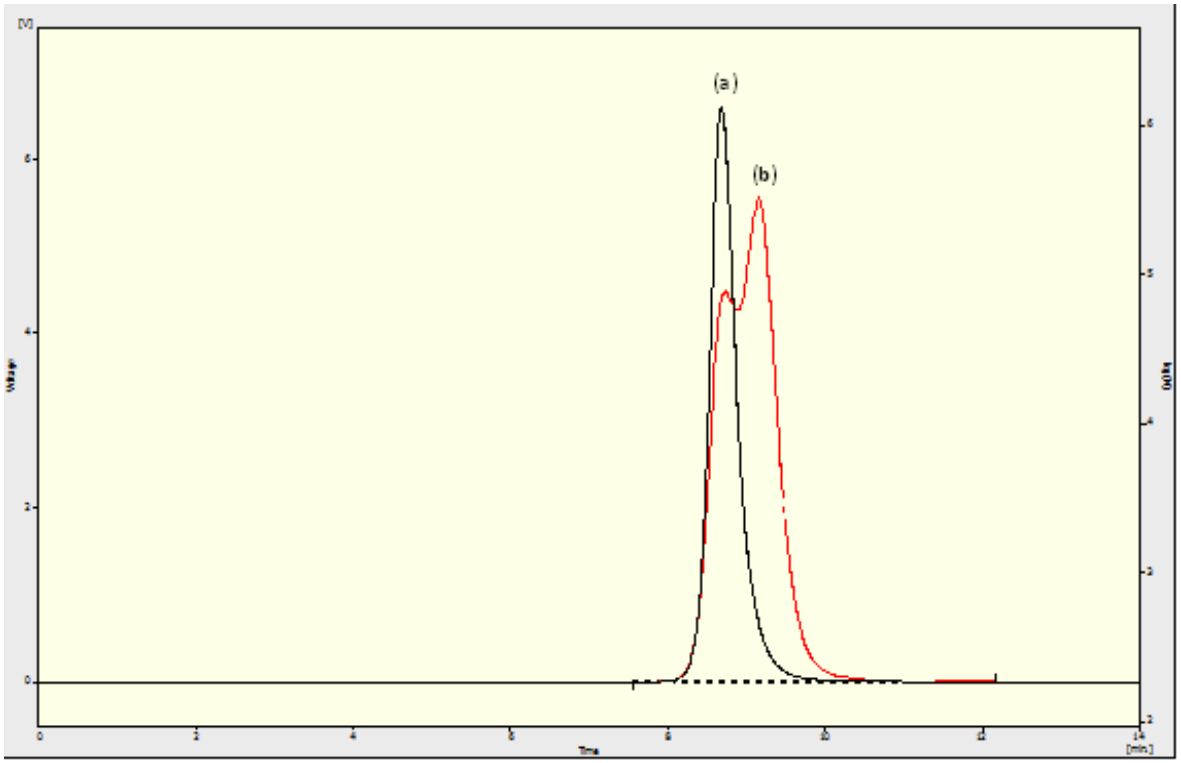


Figure 4.17 Chromatogram showing the SEC analysis for a) fresh sample b) sample stored in chloroform for 18 h

Variation in PLA molar mass with the polymerization time is manifested in **Figures 4.18** and **4.19** for both $SnOct_2$ and DBTM, as well as for different $[M_o]/[I_o]$ ratios. The molar mass increases rapidly up to 10-20 minutes but afterwards it starts decreasing. In all cases the same pattern of the molar mass evolution is seen. The molar mass decrease is accompanied with the coloring of polymerization batch. The presence of the maxima in PLA molar mass is likely to be due to back-biting reactions and thermal degradation of polymer chains with higher molar masses. This is consistent with the view in the literature about the backbiting and degradation of PLA synthesized through conventional method [Kubota *et al*. (1995); Kricheldorf *et al*. (2000); Wang *et al*. (2005); Kasperczyk *et al*. (2000); Dubois *et al*. (1991)].

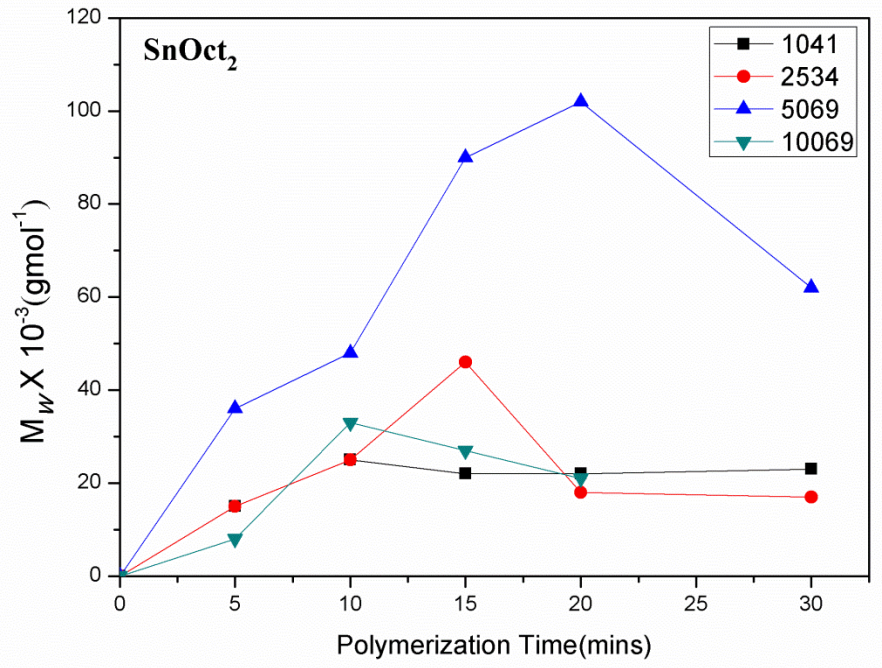


Figure 4.18 M_w (weight average molar mass) of PLA as a function of polymerization time for different monomer to initiator ratio ($[M_o]/[I_o]$) for $SnOct_2$

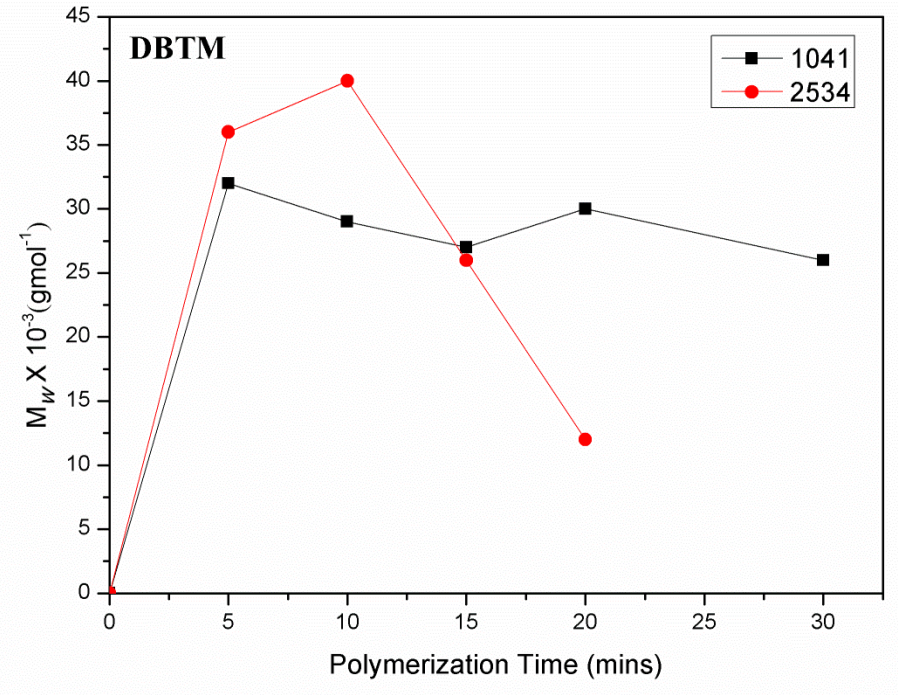


Figure 4.19 M_w (weight average molar mass) of PLA as a function of polymerization time for different monomer to initiator ratio ($[M_o]/[I_o]$) for DBTM

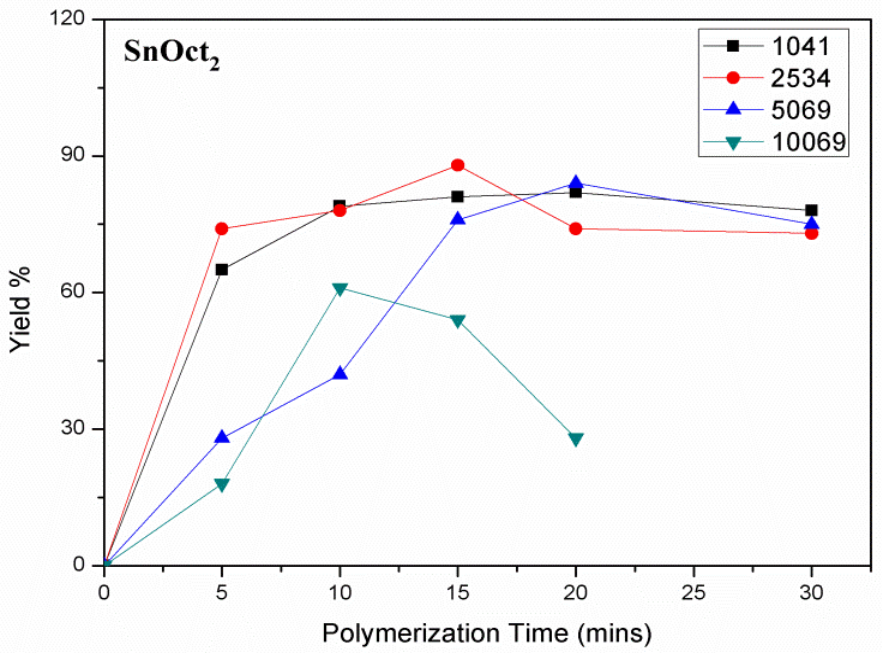


Figure 4.20 Yield of PLA obtained at various polymerization times for different monomer initiator ratio for $SnOct_2$

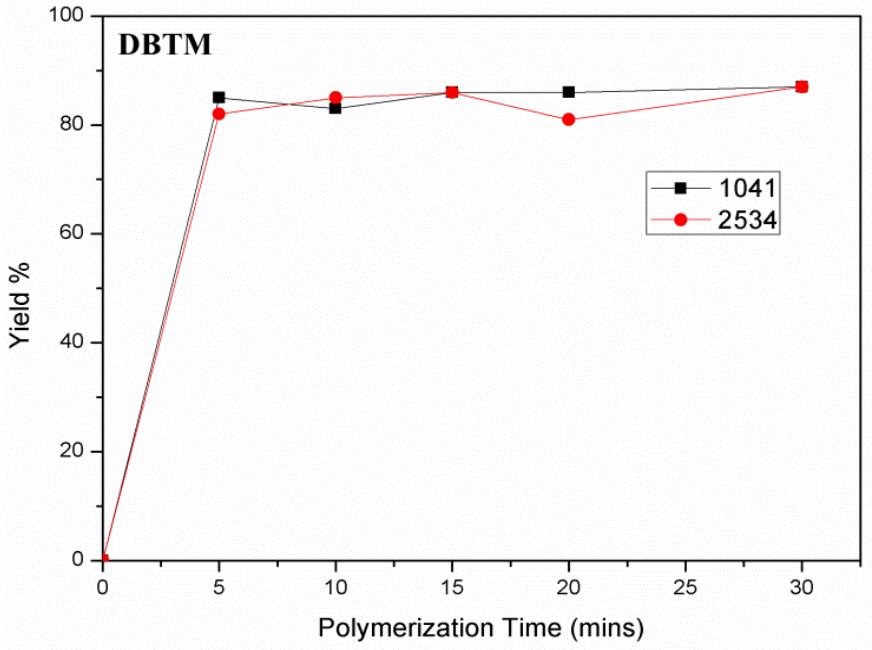


Figure 4.21 Yield of PLA obtained at various polymerization times for different monomer initiator ratio for DBTM

As shown in **Figures 4.20** and **4.21**, the maximum yield was obtained within the polymerization time of 10-15 mins for $SnOct_2$ catalysed reactions and in less than five minutes for DBTM catalysed reactions. From the thermodynamic considerations, the theoretical maximum yield of PLA polymerization is about 98% [Wagner *et al*. (1985)]. In the present study, the product was obtained by the bulk polymerization. There is an inherent drawback in this type of polymerization that at high conversion of the monomer, the reaction mixture becomes very viscous and this result in a lower yield compared to that from the theory. The yield of polymerization in the present study is in the range of 80-88%, with the only exception being the polymerization initiated with $SnOct_2$ at $[M_o]/[I_o] = 10069$ where the yield is only 60%. This may be due to lower number of propagating chains terminated by very small amount of impurities including water, residual lactic acid etc. as reported in the literature [Mehta *et al*. (2006)]. Peng

et al. (2006) reported $SnOct_2$ catalysed synthesis of PDLLA in a microwave with an M_v (viscosity average molar mass) of over 2×10^5 g.mol^{-1} and a yield of over 85% in 30 min. This compares well with present results wherein maximum M_w obtained is 1.02 x 10^5 g.mol^{-1} for $[M_o]/[I_o]$ = 5069 in 20 min. They have also reported an optimum catalyst concentration for obtaining high M_v. This agrees with our conclusion that for obtaining the highest M_w an optimum $[M_o]/[I_o]$ is needed. The present study has been carried out in a monomode microwave oven as compared to the use of domestic microwave in the earlier study of Peng *et al*. (2006). Also, in the present work, a new initiator DBTM has been used for ring-opening polymerization of lactide. The present study reports for the first time the degradation of the polymer in chloroform solvent when the solution is left overnight before SEC characterization, resulting in a lower molar mass PLA.

4.4 PLA/Clay Nanocomposites

PLA is of relatively low mechanical strength hence it is necessary to improve its mechanical properties by appropriate modification. The introduction of nanofillers in PLA matrix has allowed improvement in the range of properties and possible uses of PLA. To improve the dispersability of the nanoparticles in the matrix of polymers, *in situ* polymerization has been found to be an effective technique. Use of layered silicates, which consist of sheets arranged in a layered structure, such as montmorillonite (MMT), has been extensively studied. In addition to mechanical properties these layered silicates can potentially force gas and water molecules to follow a more tortuous path through the polymer matrix. The intercalation of polymer chains into the interlayer spacing of layered silicates (MMT) brings noticeable improvements in the mechanical, thermal, and barrier properties in contrast to pure polymers. The complete

delamination of the clay platelets (exfoliation) by polymer chains has the potential to enlarge the extension of its application.

The *in situ* ring-opening polymerization of l-lactide to synthesize PLA/Clay nanocomposites by the addition of different types of clay has been successfully carried out under microwave irradiation. In this part of the work effects of clay loading have been studied and nanocomposite products have been examined with respect to thermal and morphological properties.

4.4.1 Microwave Assisted *In Situ* Ring-Opening Polymerization of PLA/Clay Nanocomposites

4.4.1.1 Effect of Clay Loading

Tables 4.6 and **4.7** summarize percentage yield of PLA/Clay nanocomposites formed, using $SnOct_2$ and DBTM, respectively.

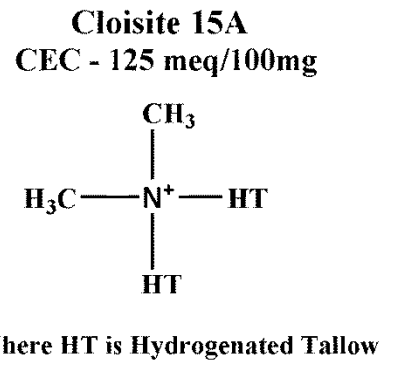
Use of Cloisite® Na^+ Clay as nanofiller, did not result into any polymer formation. The reason appears to be the presence of Na^+ ions and H_2O molecules within the interlayer spacing of unmodified clay. These H_2O molecules and Na^+ ions would cause instant termination of the growing polymer/oligomer chains. However, the formation of oligomers cannot be ruled out since the polymer recovery method involves dissolving the polymerization product in chloroform followed by polymer precipitation in methanol. The un-reacted monomer and oligomers would also dissolve in chloroform but they will not precipitate in methanol.

The experiments with Cloisite® 15A (d_{001} = 3.15 nm) clay clearly shows a decreasing yield with increasing weight percentage of clay. Though there is some scatter in the data, but from the trend, it is clear that in situ polymerization of lactide in presence of modified/unmodified clay which is added as nanofiller has a negative effect on the polymerization yield.

It is believed that ring-opening polymerization of l-lactide proceeds through coordination-insertion mechanism wherein the initiator attaches to one end of the monomer and coordinates the addition of one monomer molecule one at a time. If there are any terminating agents present e.g. water, polar solvents or any other moiety carrying a positive or negative charge, then the propagation reactions of the growing polymerization chain would be terminated. More the concentration of such species higher will be the termination effect leading to shorter polymer chains. In the extreme case no polymer chain will be formed at all.

In the case of organically modified clays, Cloisite® 15A (**Figure 4.22**) and Cloisite® 30B (**Figure 4.23**), the organic modifier also contains a positive charge which potentially can act as a polymer chain terminating agent. This is consistent with the results wherein at low concentration of clay weight percentage yields some polymerization yield and at higher clay weight percentage no polymer is formed at all.

The yield obtained with Cloisite® 30B (d_{001} = 1.85 nm), however, remains more or less unaffected even as the amount of Cloisite® 30B is increased from 0.1 to 5%. The remarkable difference between Cloisite® 15A (**Figure 4.22**) and Cloisite® 30B (**Figure 4.23**) on the in situ polymerization yield may be due to the presence of different organic modifiers in their respective structures. The structure of Cloisite® 30B contains two hydroxyl groups which can take part in termination of polymer chain and results in low polymerization yield at higher weight percentage of clay loading. But the polymerization yield obtained using Cloisite® 30B is higher than Cloisite® 15A due to the presence of less positive charge in its moiety as two hydroxyl groups are there in the structure of Cloisite® 30B which are not there in Cloisite® 15A.



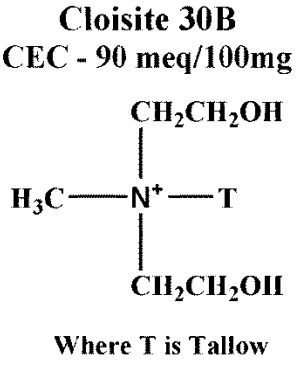


Figure 4.22 Structure of Cloisite® 15A clay

Figure 4.23 Structure of Cloisite® 30B clay

Table 4.6 PLA/Clay nanocomposites synthesized with monomer to initiator ratio of 2534:1 (Time: 15 mins, T: 150^{o}C, Initiator: $SnOct_2$)

S.No.	Type of clay	Clay %	Yield %
1.	Cloisite® 15A	0.5	72
2.		1.0	64
3.		2.0	7
4.		3.0	34
5.		5.0	4
6.	Cloisite® 30B	0	88
7.		0.1	68
8.		0.75	68
9.		0.5	81
10.		1.0	78
11.		2.0	58
12.		3.0	82
13.		5.0	79
14.	Cloisite® Na^+	0.1	83
15.		0.5	Non recoverable
16.		1	
17.		2	
18.		5	

Table 4.7 PLA/Clay nanocomposites synthesized with monomer to initiator ratio of 2534:1 (Time: 15 mins, T: 150^{o}C, Initiator: DBTM)

S.No.	Type of clay	Clay %	Yield %
1.	Cloisite® 30B	0	83
2.		0.1	Non recoverable
3.		0.5	
4.		0.75	47
5.		1.0	48
6.		2.0	Non recoverable
7.		3.0	
8.		5.0	
9.	Cloisite® Na+	0.1	Non recoverable
10.		0.5	
11.		1	
12.		2	
13.		5	

Using DBTM as the initiator, the presence of clay severely affects the yield of polymer. In case of Cloisite® 30B, the percentage yield of nanocomposites is significantly higher for $SnOct_2$ even at low clay loading but for DBTM it is very low and is mostly non-recoverable. This may be due to the size difference of both initiators. Even in conventional synthesis, it is known [Kaur *et al*. (2012)] that $SnOct_2$ is a much better initiator than DBTM in terms of nucleophilicity.

4.4.2 Characterization of PLA/Clay Nanocomposites

4.4.2.1 Thermo-gravimetric Analysis

The TGA curves for PLA/Clay nanocomposites synthesized are given in **Figure 4.24**. The heating occurred under N_2 gas flow. The samples undergo non-oxidative degradation. The incorporation of clay into the PLA polymer matrix is found to enhance the thermal stability of

polymer. It is evident from the TGA curves that there is shift of peaks towards the right in the PLA/Clay nanocomposites at around 263^{o}C and 280^{o}C compared to PLA which has a degradation temperature of about 250^{o}C. This may be due to the incorporation of nanometer-scale dispersed clay in the PLA matrix. The PLA/Clay nanocomposites synthesized by using DBTM as initiator(1% clay was used in the TGA study as higher clay content than this would have very poor polymerization yield) enhanced the degradation temperature from 250 to 280^{o}C and with $SnOct_2$ as an initiator with 2% clay enhanced the degradation temperature from 250 to 263^{o}C. The presence of clay significantly enhances the thermal degradation temperature of the polymer blend indicating that PLA/Clay nanocomposites are thermally more stable. This effect is more pronounced for the composite polymer prepared using DBTM compared to that for $SnOct_2$ probably because of higher interaction of clay with the former initiator than the latter. This also probably explains why in case of DBTM, the presence of clay severely affects the polymerization yield.

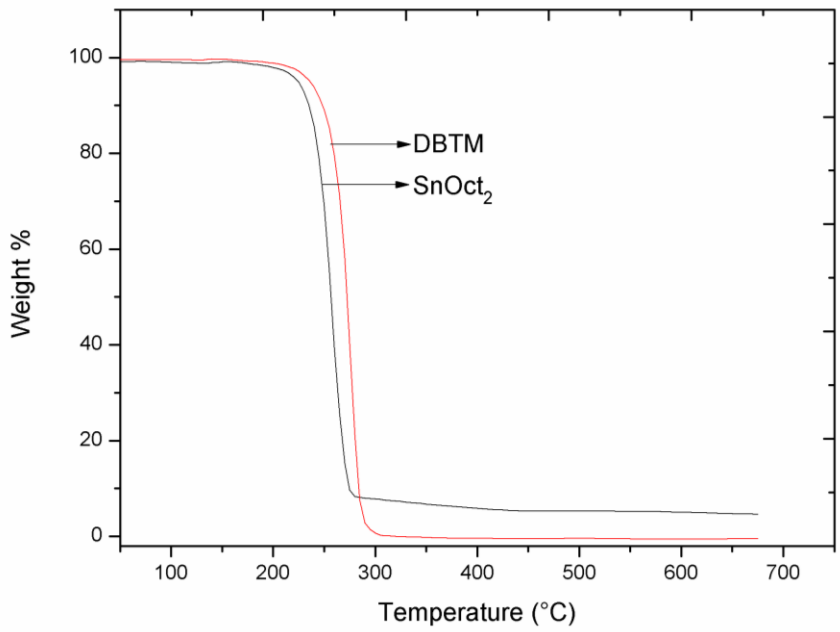


Figure 4.24 TGA of PLA/Clay nanocomposites synthesized by DBTM and $SnOct_2$.

4.4.2.2 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of neat Cloisite® Clay, PLA and PLA/Clay nanocomposites are shown in **Figure 4.25**. Cloisite® 30B reveals absorption bands at 3631 and 3394 cm^{-1} representing O-H stretching band for the silicate group and water, respectively, at 1638 cm^{-1} representing O-H bending, at 1048 cm^{-1} representing stretching vibration of Si-O-Si from silicate, and at 918 cm^{-1} due to Al-OH-Al deformation of aluminates [Bora *et al*. (2000)]. The bands located at 2925, 2853 and 1470 cm^{-1} are due to the organic modifications, which are assigned to C-H vibrations of methylene groups (asymmetric stretching, symmetric stretching and bending, respectively). The FTIR spectra of PLA/Clay nanocomposites show a characteristic peak of carboxyl group at 1759 cm^{-1} which can be observed in the spectrum of neat PLA also. The stretching band of the Si-O-Si is slightly shifted to 1044 cm^{-1} and the peak of the stretching band of (OH) is weakened. By comparing the spectra of Cloisite® 30B, PLA/Clay nanocomposites and PLA, one can conclude that there is an interaction between the clay and the polymer.

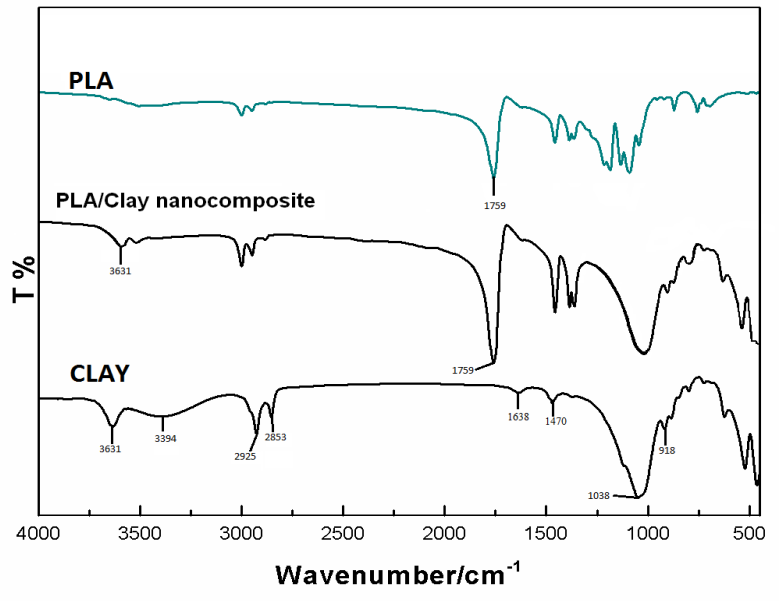


Figure 4.25 FTIR spectra of PLA, Cloisite® 30B, and PLA grafted clay.

4.4.2.2 X-ray Diffraction Studies

The interlayer spacing of the Cloisite® 30B and Cloisite® 15A are 1.85 and 3.15 nm, respectively. X-ray diffraction patterns of neat PLA synthesized using $SnOct_2$ as an initiator, neat organoclays, and with 0.1, 0.5, 0.75, 1, 2, 3, and 5 wt % clay in PLA nanocomposites are shown in **Figure 4.26** for Cloisite® 30B and **Figure 4.27** for Cloisite® 15A. The comparison of the diffractograms of the PLA/Clay nanocomposites with those of the neat organoclay revealed that there is a total absence of the diffraction peak at low 2θ angles. It is, therefore, clear that there is a formation of an exfoliated morphology. Even at such a low weight percentage of clay loading, if the clay is nano dispersed, the clay layers will be present in the entire sample at nanometer scale. In support of this argument, it is helpful to know that the 8 micron size clay particle can fill a large area of a football field if dispersed at a nano scale in exfoliated morphology [Koo *et al*. (2006)].

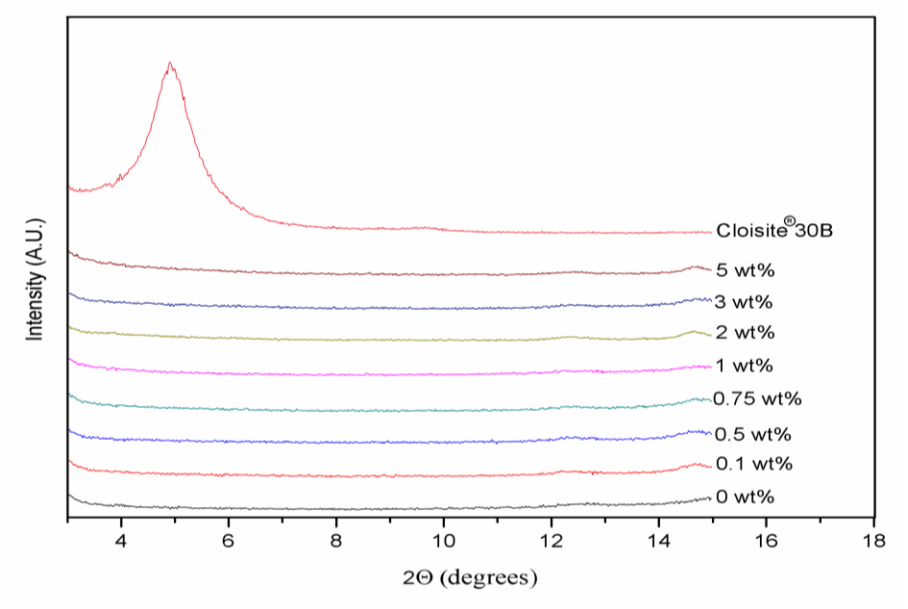


Figure 4.26 XRD patterns showing effect of clay wt% of Cloisite® 30B in PLA nanocomposites synthesized using $SnOct_2$ as an initiator (showing exfoliation)

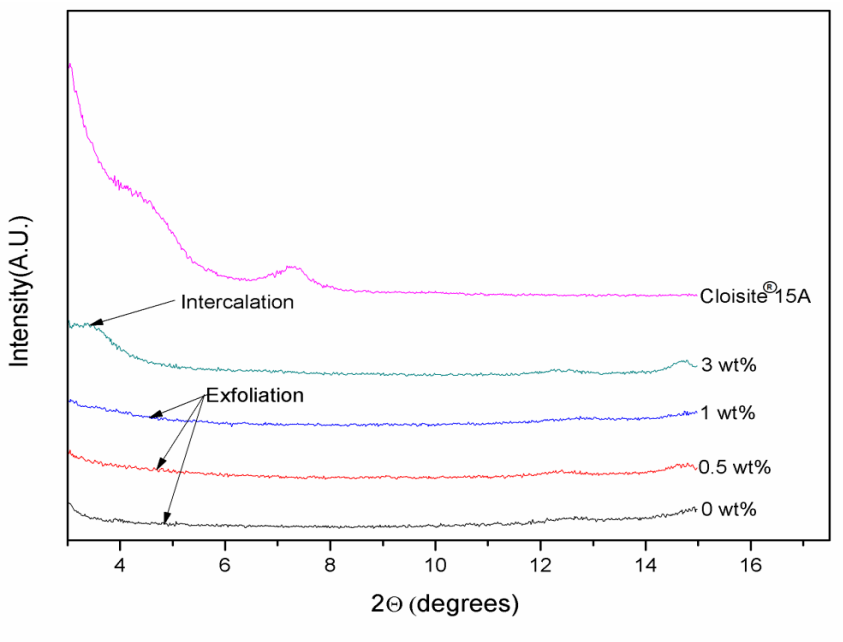


Figure 4.27 XRD patterns showing effect wt % of Cloisite® 15A in PLA nanocomposites synthesized using $SnOct_2$ initiator (showing intercalation in 3 wt% and exfoliation at lower wt %)

At higher clay loading of 3 wt%, the d_{001} peaks shift towards left (**Figure 4.27**). The intercalation of polymer in between clay layers will increase the interlayer spacing resulting in an increase in d_{001} value. Possibly in this case, at such a high clay loading, there are simply too many clay layers which cannot be completely exfoliated and dispersed in polymer matrix. It is known from both experimental and theoretical studies that at around 2 to 3 wt% clay, exfoliation is not observed [Paul *et al*. 2003].

X-ray diffraction patterns of neat PLA synthesized using DBTM as an initiator, neat organoclays, and 0.75 and 1 wt % clay in PLA nanocomposites are shown in **Figure 4.28**. The patterns show exfoliation due to disappearance of the characteristic peak.

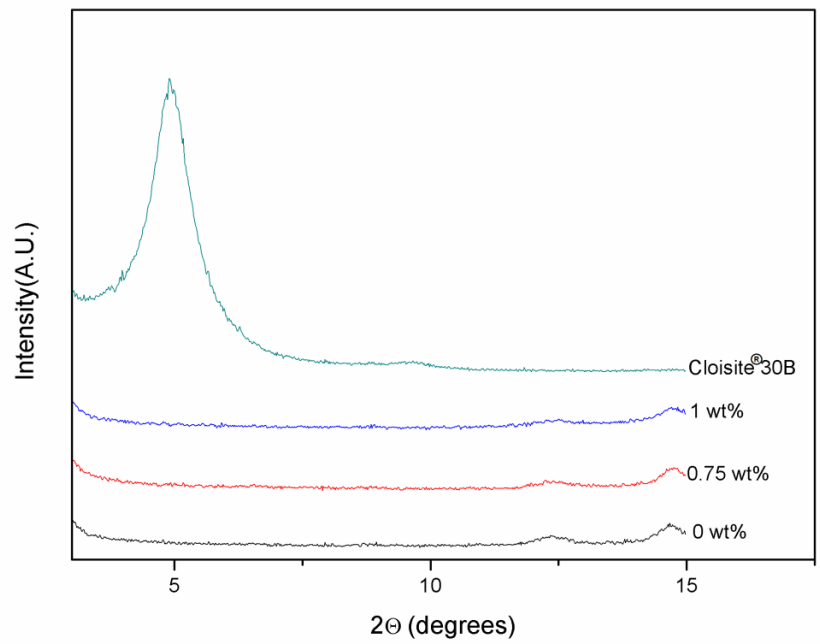
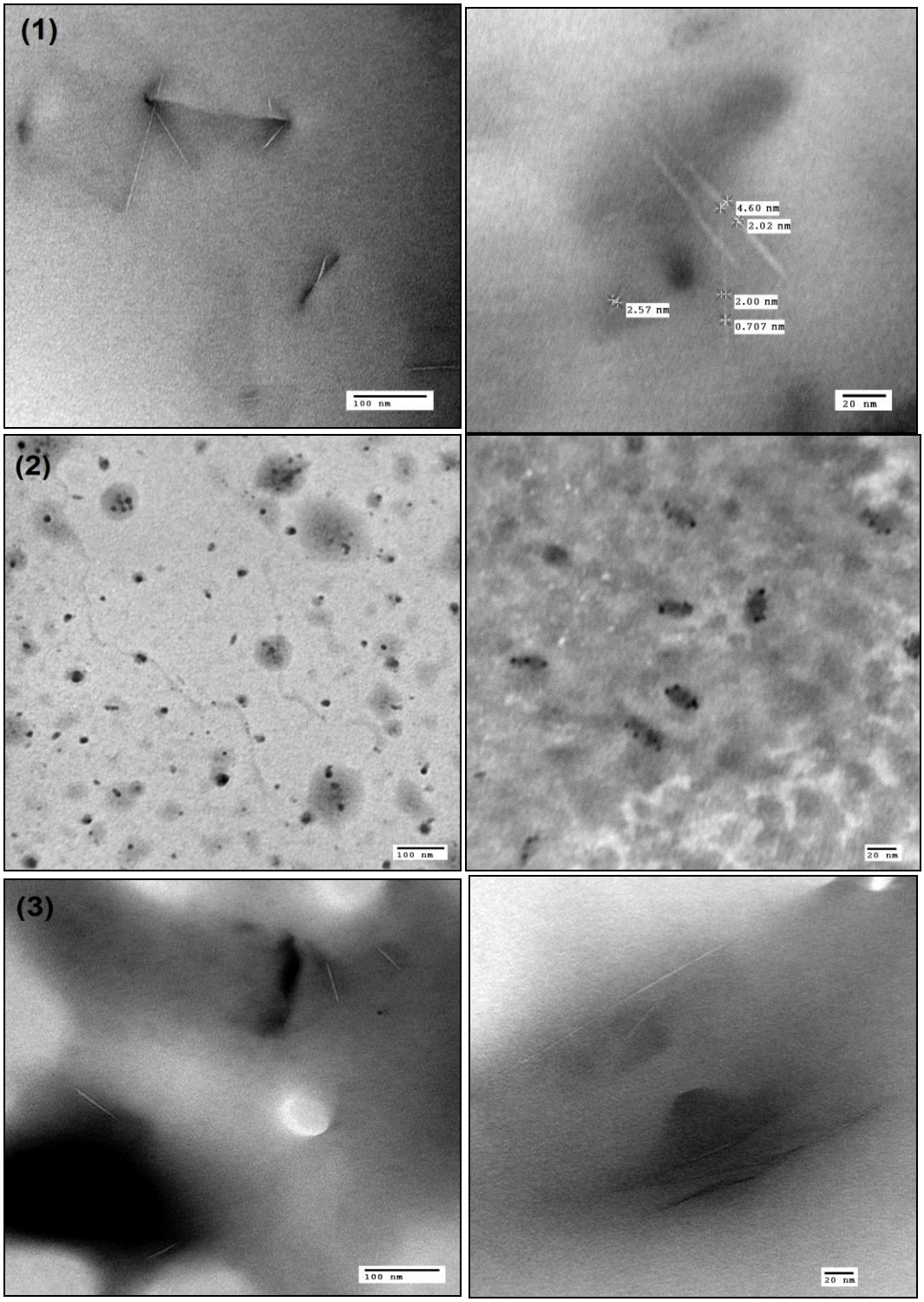


Figure 4.28 XRD patterns showing exfoliation of Cloisite® 30B (different wt %) in PLA nanocomposites synthesized using DBTM initiator

4.4.2.3 Transmission Electron Microscopy (TEM)

Through the comparison of the diffractograms of the PLA/Clay nanocomposites with those of neat clay, it is found that the total absence of a diffraction peak at low 2θ angles (complete disappearance of the d-spacing at 1.83 nm) suggests the formation of an exfoliated morphology. The TEM images of PLA/Clay nanocomposites are shown in **Figure 4.29**. These images clearly show that clay platelets are exfoliated and are randomly scattered in the PLA matrix. The ordered lamellar structure of the clay has been destroyed, and the interlayer d-spacing has increased. The clay platelets are known to have a size of about 100-150 nm in width and length and have 1-3 nm interlayer spacing [Scocchi *et al*. (2007)]. It is evident from the TEM images shown in **Figure 4.29(b)** that the clay platelets are dispersed at nano-scale as the thickness of the clay platelet is of the order of 1 nm.



(a) (b)

Figure 4.29 TEM images of the PLA/Clay nanocomposite (a) low magnification and (b) high magnification.

4.4.2.4 Scanning Electron Microscopy (SEM)

SEM is used to study the surface morphology of the polymer nanocomposites. The interaction of clay layers with polymer matrix was studied using SEM analysis. The SEM images of PLA/Clay nanocomposites are shown in **Figure 4.30** (for DBTM) and **Figure 4.31** (for $SnOct_2$). The images clearly indicate the formation PLA/Clay nanocomposites and completely covered clay platelets in PLA indicate good compatibility between the dispersed clay platelets and PLA matrix. On comparing the SEM micrographs for DBTM and $SnOct_2$, it can be seen that for DBTM there is higher compatibility with clay particles. It is further supported by the TGA analysis in which the thermal stability for DBTM is higher than for $SnOct_2$.

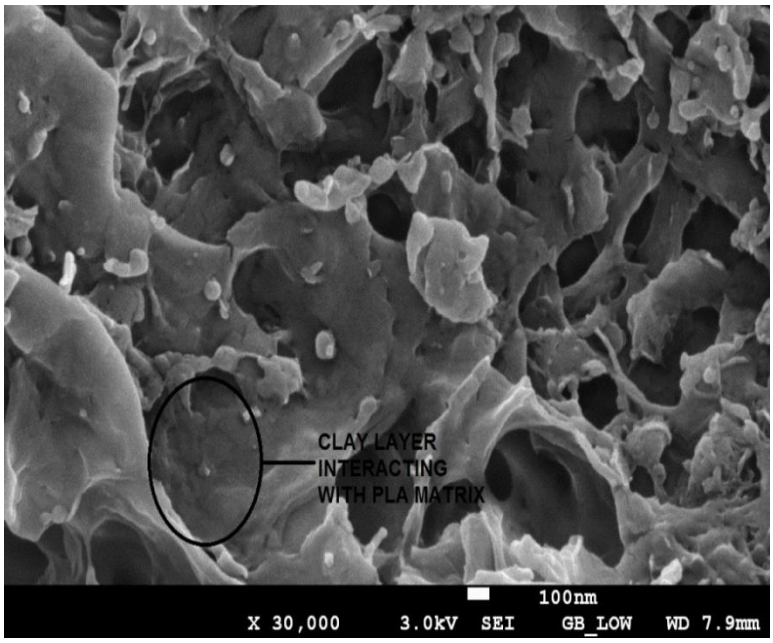


Figure 4.30 SEM image of PLA/Clay nanocomposite synthesized by DBTM as an initiator

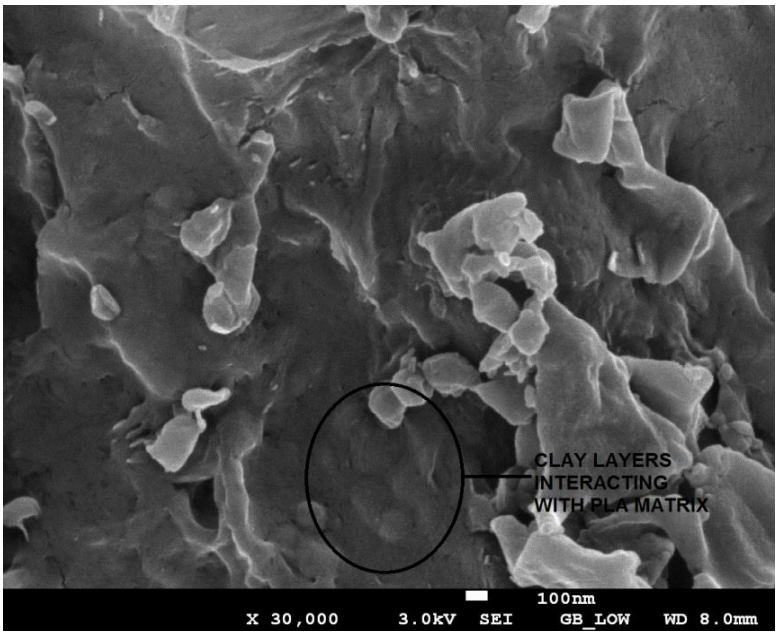


Figure 4.31 SEM micrograph of PLA/Clay nanocomposite synthesized by $SnOct_2$ as an initiator.

4.5. Monomode Microwave Assisted Ring-Opening Polymerization of L-lactide and *In Situ* Preparation of PLA/Clay Nanocomposites using Stannous Octoate as an Initiator and Dimethylaminopyridine as Co-Initiator

4.5.1. Synthesis of PLA

An effective ring-opening polymerization of l-lactide to poly (lactic acid), PLA was carried out under N_2 atmosphere and microwave irradiation using stannous octoate ($SnOct_2$) and dimethyl aminopyridine (DMAP) as a co-initiator. Four different molar ratios of monomer and initiator 1040/1, 5069/1, 2534/1 and 10,069/1 were used for the synthesis at the temperature of 150^{o}C. The polymer molar mass obtained was much higher than that obtained with $SnOct_2$ as an initiator alone. The molar mass for almost all molar ratios of monomer and initiator is above 50,000. The highest molar mass of PLA obtained was 1.2×10^5 g.mol-1 with an excellent dispersity of

1.46. The molar mass of PLA has been characterized using size exclusion chromatography, SEC. The structural analysis of PLA has been done by using ^{1}H NMR, ^{13}C NMR and FTIR.

4.5.1.1. Proton and ^{13}C Nuclear Magnetic Resonance (^{1}H & ^{13}C NMR) Spectroscopy

The polymer product obtained was confirmed to be poly (l-lactic acid), PLLA by means of ^{1}H NMR spectroscopy. The ^{1}H NMR and ^{13}C NMR spectra of PLLA are shown in **Figure 4.32 and Figure 4.33**. The spectra have been already explained in detail in Section 4.3.2.1.

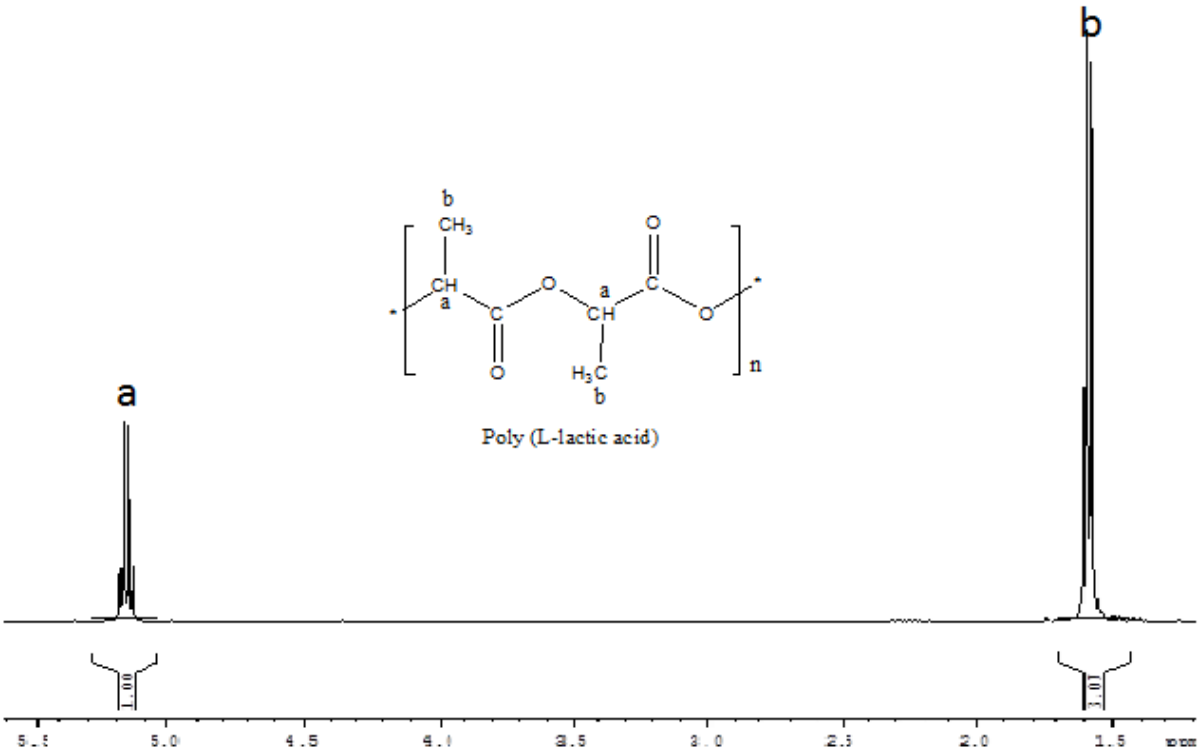


Figure 4.32 ^{1}H NMR spectrum of PLLA

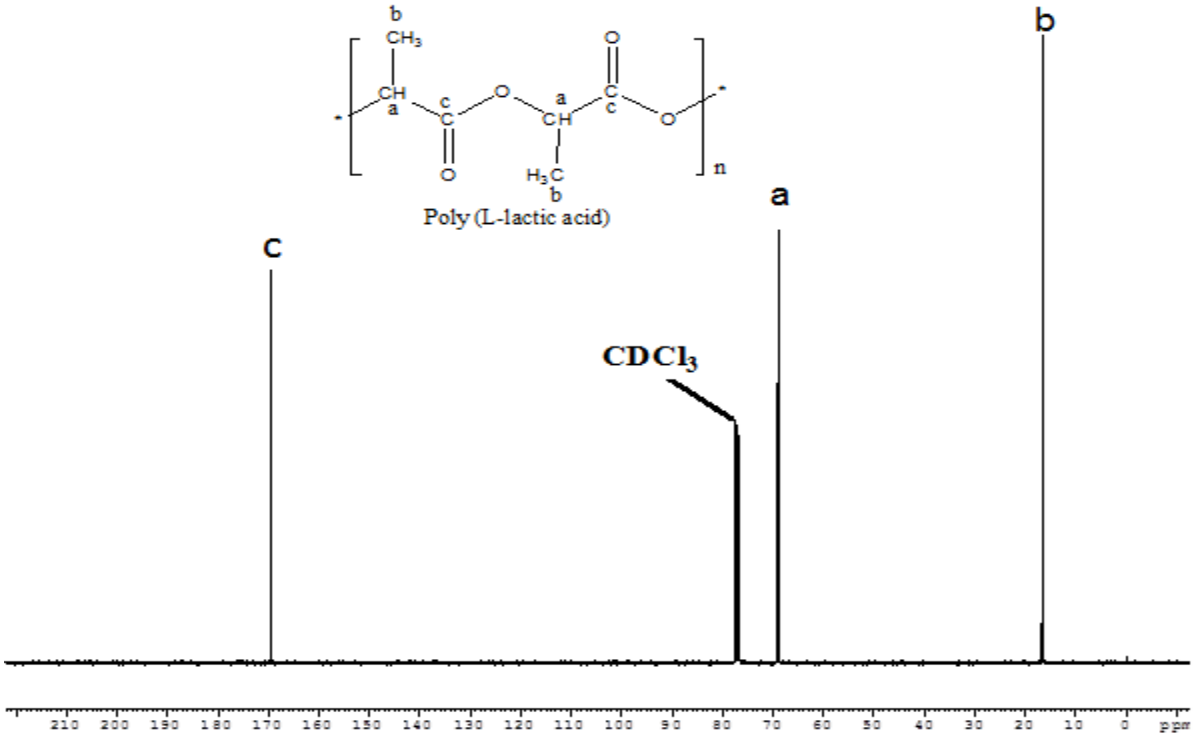


Figure 4.33 ^{13}C NMR spectrum of PLLA

4.5.1.2. Fourier Transform Infrared (FTIR) Spectroscopy

The further confirmation of formation of PLA was done by FTIR spectroscopy. The FTIR spectrum of PLA synthesized by using $SnOct_2$/DMAP is shown in **Figure 4.34**. The details of spectrum have been already explained in Section 4.1.1.3.

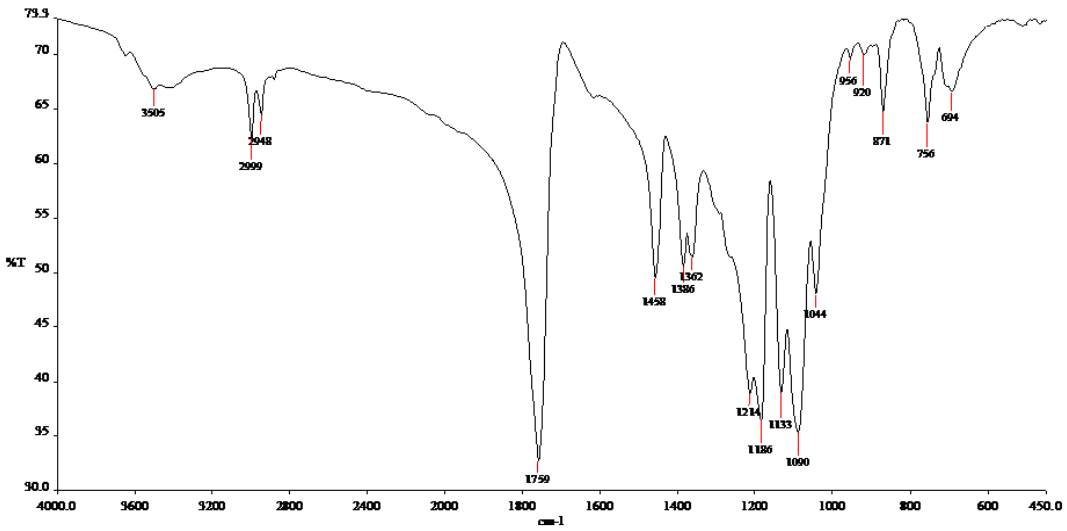


Figure 4.34 FTIR spectrum of PLA

4.5.1.3. Size Exclusion Chromatography

The poly(styrene)-equivalent molar masses of PLA samples were determined by the size exclusion chromatography, SEC. **Table 4.8** summarizes the number average and weight average molar masses and polydispersities of polymer formed at different monomer to initiator ratios for stannous octoate as the initiator and dimethyl aminopyridine as the co-initiator.

Table 4.8 Mean molar masses M_n, M_w and polydispersity of PLA as a function of the polymerization time and monomer/initiator $[M_o]/[I_o]$ ratio for Stannous octoate/DMAP (1:1)

Initiator	**Monomer to initiator ratio**	**Time (mins)**	**Yield %**	**Molecular weight**		**(PD) Polydispersity**
				$M_n \times 10^{-3}$*	**$M_w \times 10^{-3}$****	
Stannous octoate/	1041/1	3	30	28	37	1.32
		5	76	60	83	1.39
		10	25	28	39	1.39

Dimethyl aminopyridine		15	78	52	78	1.51
		20	78	50	77	1.55
		30	87	33	79	2.36
	2534/1	3	42	32	51	1.59
		5	70	54	81	1.50
		10	16	3	7	2.08
		15	58	53	81	1.53
		20	82	54	85	1.58
		30	55	25	45	1.81
	5069/1	5	8	3	5	1.47
		10	5	2	4	1.56
		15	15	9	12	1.29
		20	75	63	94	1.48
		30	74	69	102	1.46
	10069/1	10	15	12	15	1.23
		15	14	4	5	1.30
		20	20	20	28	1.42
		30	**78**	**82**	**120**	**1.46**

*, ** M_n and M_w are the number average and weight average polystyrene equivalent molar masses determined by size exclusion chromatography, respectively.

The SEC results show that polymers obtained with DMAP as the co-initiator used with $SnOct_2$ exhibit much higher molar mass than those reported in the literature for microwave assisted ring-opening polymerization of l-lactide [Liu *et al*. (2001); Zhang *et al*.(2004)]. DMAP as a co-initiator with $SnOct_2$ enhanced the molar mass to a greater extent compared to $SnOct_2$ alone. The highest molar mass M_w of PLA obtained with DMAP as co-initiator used with $SnOct_2$ was 1.2×10^5 $g.mol^{-1}$ with polydispersity of 1.46. This is probably due to the fact that DMAP is a nucleophilic

molecule and is known to be a good esterification catalyst as it helps to prevent back-biting reaction. Evolution of PLA molar mass with the polymerization time is manifested in **Figure 4.35** for $SnOct_2$/DMAP, as well as for different $[M_o]/[I_o]$ ratios.

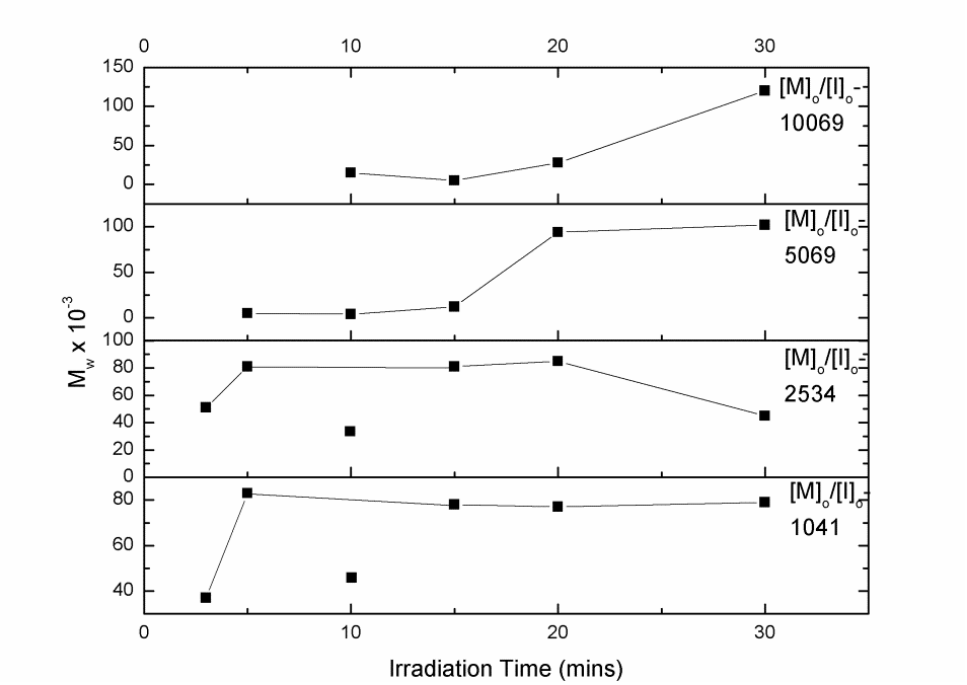


Figure 4.35 M_w (weight average molar mass) of PLA as a function of polymerization time for different monomer to initiator ratio ($[M_o]/[I_o]$) $SnOct_2$/DMAP

It has been observed that as $[M_o]/[I_o]$ ratio increases the molar mass also increases. This is due to the reason that as the $[M_o]/[I_o]$ ratio increases, the number of initiator molecules decrease for a given number of monomer molecules. It results in reduction of the number of chains onto which a given number of monomer molecules can attach themselves. Hence, rise in the molar mass is observed as the $[M_o]/[I_o]$ ratio increases. For $[M_o]/[I_o]$ ratio 1041 and 2534, the PLA formation started at 3 min but it was of very low molar mass and increased up to 5 mins and then decreased

till 10 mins and there after followed the same trend as discussed earlier. This drop in molar mass of PLA at 10 min might be due to some experimental error.

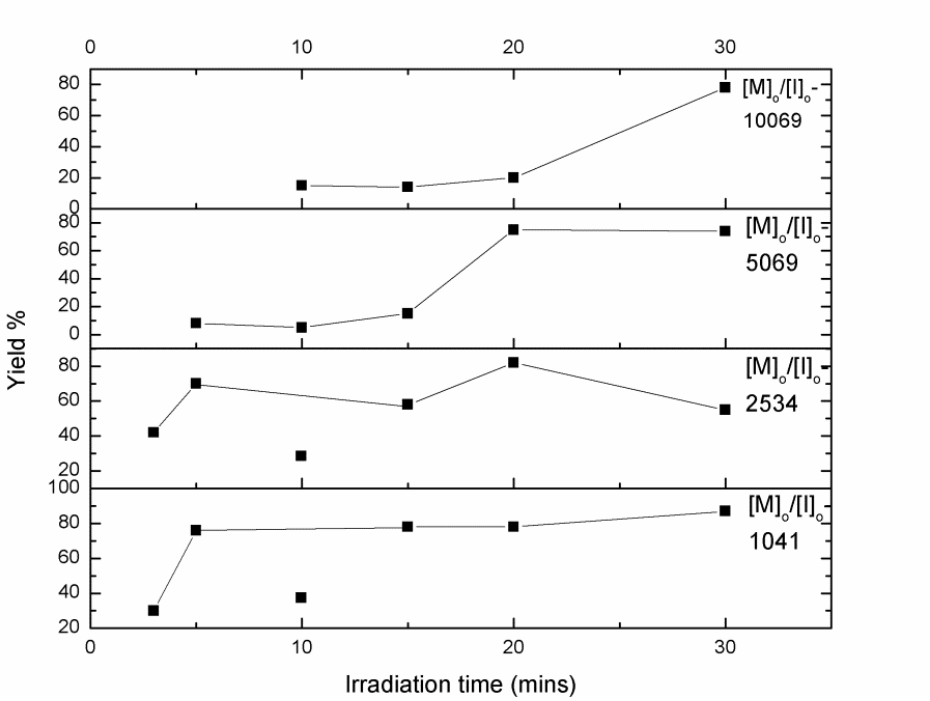


Figure 4.36 Yield obtained of PLA at various polymerization times for different monomer to initiator ratio ($[M_o]/[I_o]$) $SnOct_2$/DMAP

As shown in **Figure 4.36**, the percentage yield of PLA obtained followed the same pattern as the molar mass. As discussed earlier, the yield of polymerizations in the present study is in the range of 80-87% in most of the cases but in a few cases, very low yield was also obtained. This may be due to the lower number of propagating chains being terminated by very small amount of impurities including water, residual lactic acid etc. as reported in the literature [Mehta *et al.* (2006)]. For $[M_o]/[I_o]$ ratio 1041,5069 and 10069, the percentage yield went on increasing till 30 min which is slightly different from the ususal trend in which percentage yield decreased after 20 min. The presence of the maxima in the molar mass of PLA for $[M_o]/[I_o]$ ratio 2534 is likely to be due to two reasons: Firstly, thermal degradation of polymer chains due to longer exposure

to microwave radiation takes place as also indicated by the coloring of the polymerization solution and secondly, due to backbiting reactions starting at high temperature. Backbiting reaction refers to the formation of cyclic compounds through intra-molecular reactions between the carboxylic end group of the growing chain of PLA and the ester bond of the chain backbone. These reactions are equilibrium reactions which depend upon temperature. This is consistent with the view in the literature about the backbiting and thermal degradation of PLA synthesized through conventional method [Kubota *et al*. (1995); Kricheldorf *et al*. (2000); Wang *et al*. (2005); Kasperczyk *et al*. (2000); Dubois *et al*. (1991)]. But in the present work, by the use of DMAP as a co-initiator with $SnOct_2$, the yield went on increasing till 30 min of polymerization time and results in higher molar mass due to its property of better nucleophilicity and esterification capacity. It enhances the polymerization reaction in the forward direction, hence it results in higher yield at longer polymerization time. The SEC chromatograms for $SnOct_2$/DMAP initiated PLA are shown in **Figure 4.37**.

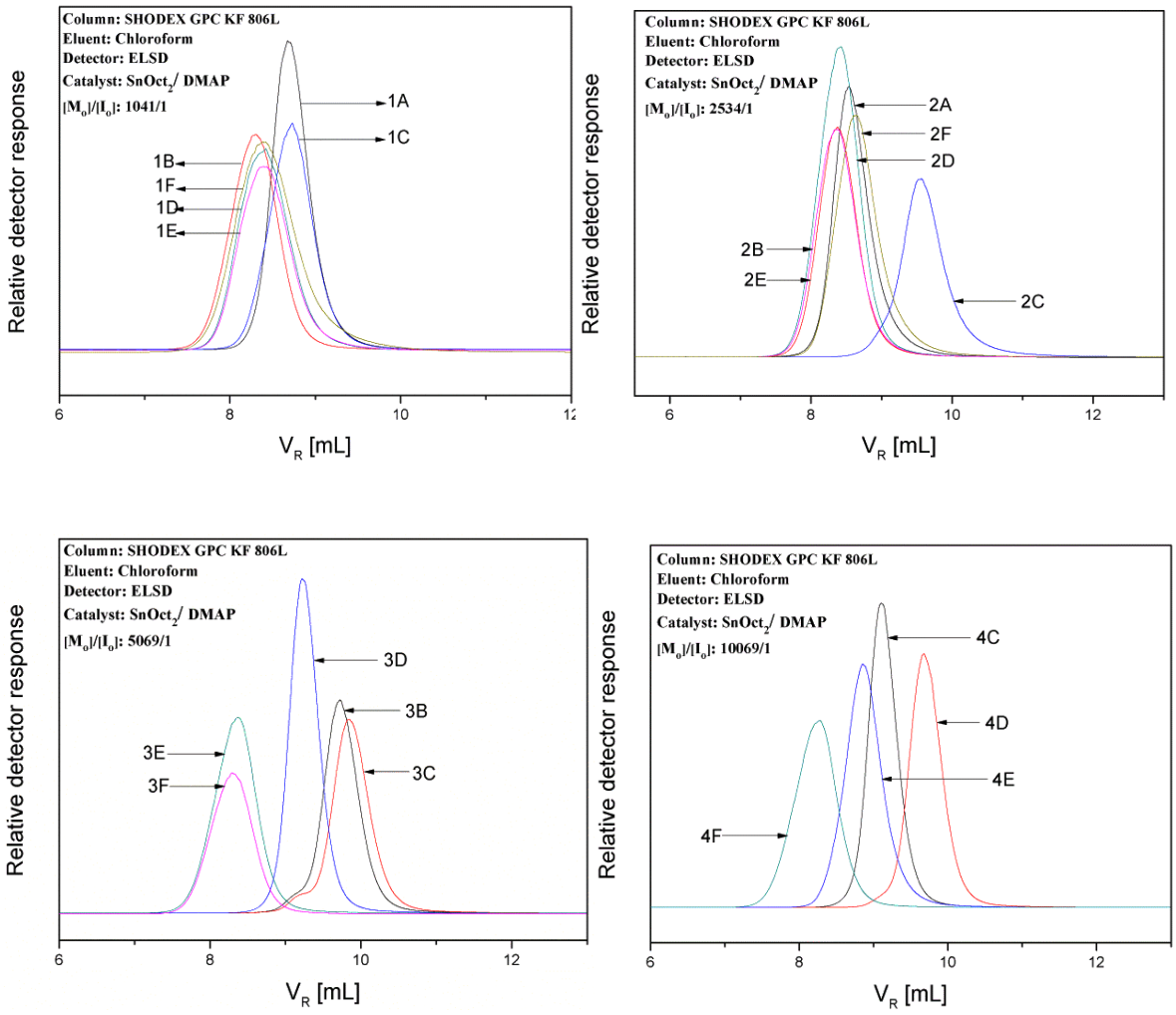


Figure 4.37 SEC chromatograms of synthesized PLA for $SnOct_2$/DMAP at different time durations for different $[M_o]/[I_o]$ ratios

The shift in curve to the left side indicates the higher molar mass polymer product. Our results indicate that from the viewpoint of preparation of high molar mass PLA, DMAP is a better co-initiator to be used with $SnOct_2$ initiator. As seen in chromatograms, polydispersity of PLA prepared is nearly one which is very encouraging for using DMAP as the co-initiator with $SnOct_2$.

4.5.2. PLA/Clay Nanocomposites

The *in situ* ring-opening polymerization of l-lactide to synthesize PLA/Clay nanocomposites by the addition of different types of clay using $SnOct_2$/DMAP as initiator/co-initiator has been successfully carried out under microwave irradiation. In this part of the work effects of clay loading have been studied and nanocomposite products have been examined with respect to their thermal and morphological properties.

4.5.2.1. Effect of Clay Loading

Table 4.9 summarizes percentage yield of PLA/Clay nanocomposites formed, using $SnOct_2$/DMAP.

Table 4.9 PLA/Clay nanocomposites synthesized with monomer to initiator ratio of 2534:1 (Time: 15 mins, T: 150^{o}C, Initiator/co-initiator: $SnOct_2$/DMAP, 1:1)

S.No.	Type of clay	% Clay	% Yield
1.	Cloisite® 15A	0.1	16
2.		0.5	64
3.		1	55
4.		2	Non recoverable
5.		3	
6.	Cloisite® 30B	0.1	Non recoverable
7.		0.5	63
8.		1	50
9.		2	Non recoverable
10.		3	
11.	Cloisite® Na^+	0.1	Non recoverable
12.		0.5	
13.		1	
14.		2	
15.		3	

When Cloisite® Na^+ Clay was used as nanofiller, it did not result into any polymer formation with $SnOct_2$/DMAP similar in the case of $SnOct_2$ only. The reason appears to be the presence of Na^+ ions and H_2O molecules within the interlayer spacing for unmodified clay as discussed in Section 4.4.1.1.

The experiments with Cloisite® 15A (d_{001} = 3.15 nm) clay resulted in very low yield at 0.1 % but increased at 0.5 %. The polymerization yield deceased at 1 % and then the product became non-recoverable on further increase in weight percentage of clay. Though there is some scatter in the data, but from the trend, it is clear that *in situ* polymerization of lactide in presence of modified/unmodified clay which is added as nanofiller has a negative effect on the polymerization yield. The pattern of yield obtained with Cloisite® 30B (d_{001} = 1.85 nm), however, remains the same as that obtained with Cloisite® 15A. The use of DMAP as co-initiator with $SnOct_2$ exhibits a remarkable effect on the polymerization yield. It has been seen that the degradation phenomenon occurs for higher weight percentage of clay at 15 mins of polymerization time which results into non-recoverable polymerization yield. The reason for non-recoverable yield at higher weight percentage of clay has been explained earlier in Section 4.4.1.1.

4.5.2.2 X-ray diffraction (XRD)

X-ray diffraction studies of PLA/Clay nanocomposites have been done to find out the interlayer space between the clay layers. X-ray diffraction patterns of neat PLA synthesized using $SnOct_2$/DMAP, neat organoclays, and 0.1, 0.5 and 1wt % of Cloisite® 15A and Cloisite® 30B in PLA nanocomposites are shown in **Figures 4.38** and **4.39,** respectively. From **Figure 4.38**, it has been seen that the Cloisite® 15A shows the characteristic peak at 2θ=7.2° (*d*-spacing = 3.15

nm). The PLA/Clay nanocomposite shows a total absence of the peak at low 2θ angles for all three wt % of clay loadings. This indicates that there is formation exfoliated morphology. Similarly **Figure 4.39**, showing the diffraction pattern of PLA/Clay nanocomposites using Cloisite® 30B, depicts the formation of exfoliated morphology. In case Cloisite® 30B, there is absence of diffraction peak at low 2θ angles for all wt % of clay loading. For low wt % of clay loading, an exfoliation has been observed. This may be due to the fact that at such a low wt % clay loading there are less number of clay layers, hence it is easy to disperse them in the solvent using ultrasonication. The second reason may be the presence of long polymer chain between the clay layers which produce stearic effect and help in the formation of exfoliated morphology. The further confirmation of exfoliation has been done by transmission electron microscopy (TEM).

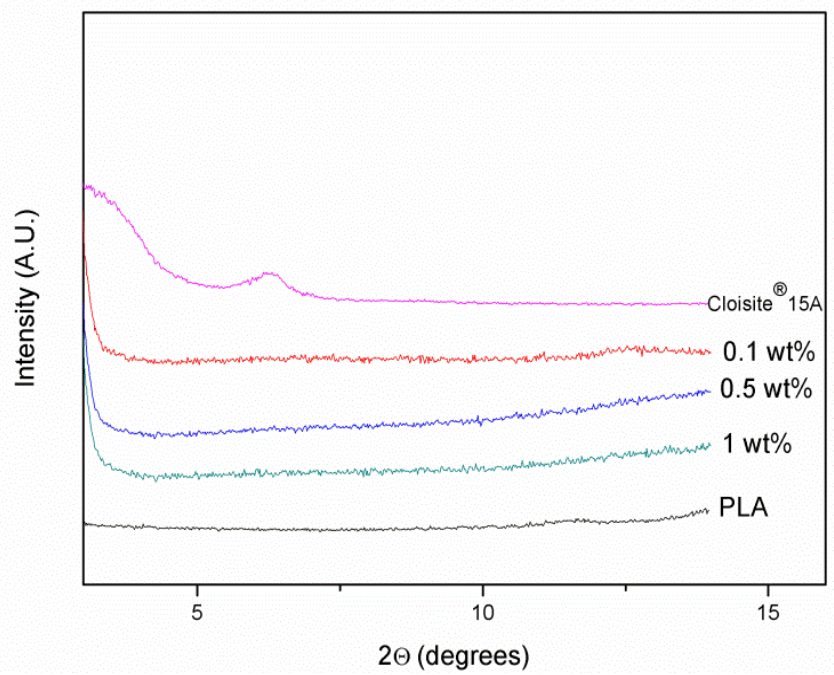


Figure 4.38 XRD patterns showing effect of wt % of Cloisite® 15A in PLA nanocomposites synthesized using $SnOct_2$/DMAP

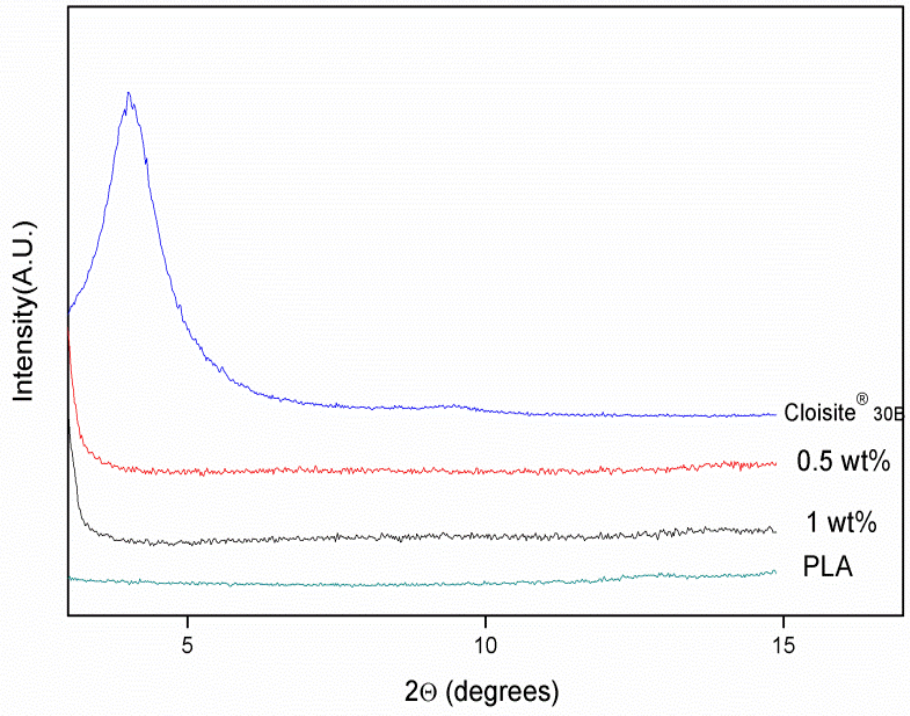
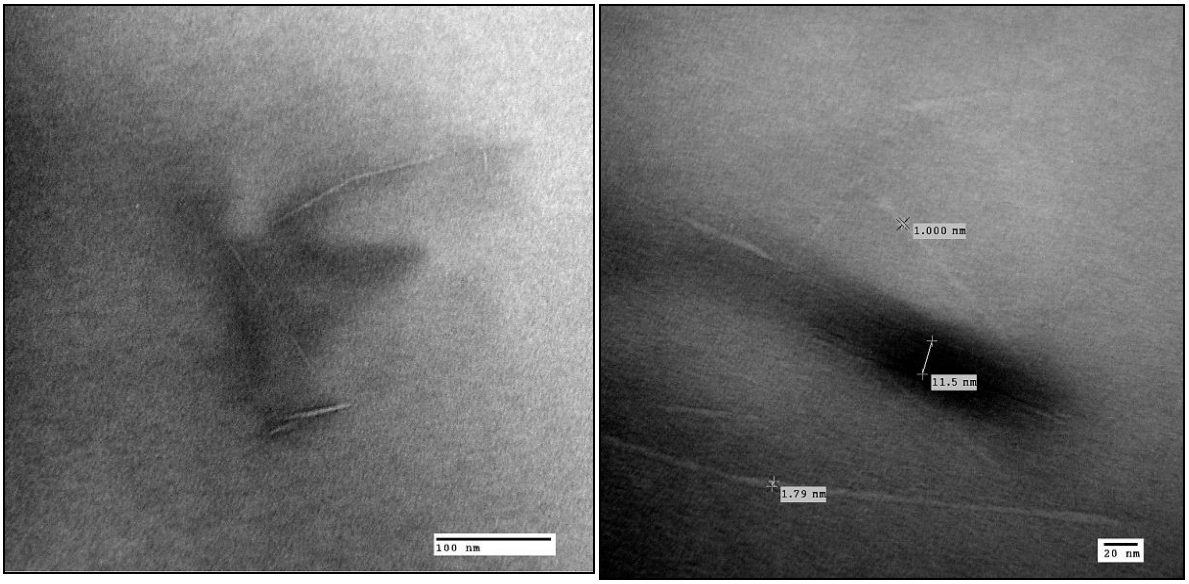


Figure 4.39 XRD patterns showing effect of wt % of Cloisite® 30B in PLA nanocomposites synthesized using $SnOct_2$/DMAP.

4.5.2.3 Transmission Electron Microscopy (TEM)

Through the comparison of the diffractograms of the PLA/Clay nanocomposites with those of neat clay, it is found that the total absence of a diffraction peak at low 2θ angles (complete disappearance of the d-spacing peak) suggests the formation of an exfoliated morphology. This has also been confirmed by TEM. The TEM images of PLA/Clay nanocomposite are shown in **Figure 4.40**.



(a) (b)

Figure 4.40 TEM image of the PLA/Clay nanocomposite showing exfoliation (a) low magnification (b) high magnification

Figure 4.40 shows the TEM images of PLA/Clay nanocomposite at two different magnifications in which white lines are clay platelets and bright area is the PLA matrix. TEM images clearly demonstrate that clay platelets are exfoliated, randomly scattered and nicely dispersed in the PLA matrix. It is evident from the TEM image shown in **Figure 4.40(b)** that the clay platelets are dispersed at nano-scale as the thickness of the clay platelet is of the order of 1 nm.

4.5.2.4. Thermo-gravimetric Analysis (TGA)

The TGA curves of PLA/Clay nanocomposites synthesized using Cloisite® 30B and Cloisite® 15A are shown in **Figure 4.41**. The heating occurs under N_2 gas flow. The samples undergo non-oxidative degradation. It has been observed that the thermal stability of PLA increases upon adding the clay as nanofiller. The neat PLA degraded at a temperature of 250^{o}C. When clay was incorporated into the PLA matrix then the degradation temperature shifted from 250 to 268^{o}C in

case of Cloisite® 15A (1%) and to 256°C in case of Cloisite® 30B (1%). The reason for an increase in thermal degradation temperature is as explained earlier in Section 4.4.2.1. In addition, the increase in thermal stability may also be due to the high thermal stability of clay which is used as nanofiller in PLA matrix.

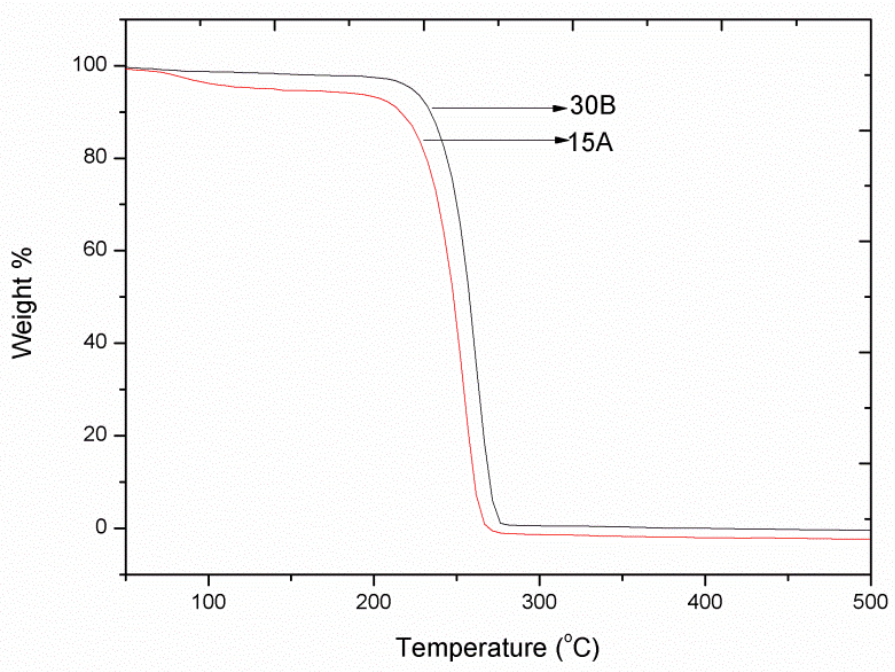


Figure 4.41 TGA curves of PLA/Clay nanocomposites synthesized by using Cloisite® 30B and Cloisite® 15A

4.6. Polymerization Kinetics Under Microwave Irradiation

The polymerization kinetics was studied by plotting graphs between molar mass and percentage yield versus polymerization time. There were several attempts made to find the order of the polymerization reaction and the apparent rate constant, k_{app}. However, the data did not fit even after assuming different orders of the reaction. These plots of $\ln(C_o/C_t)$ and irradiation time (t); $1/C_t^{\,2}$ and (t); and $1/C_t$ and (t) are shown in Appendix B.

The apparent rate constant k_{app} has been calculated using the following equation:

$$d[P]/dt = k_{app} [M] [I] \quad (4.1)$$

where [P] is polymer concentration, [M] is monomer concentration and [I] is an initiator concentration.

It is observed that there is no single order dependency of the rate of reaction on either monomer concentration or on initiator concentration. Therefore, the kinetics of PLA synthesis in a microwave reactor is very different from its conventional synthesis where it has been reported that the rate of reaction is first order with respect to both monomer concentration ([M]) and initiator concentration ([I]) [Dubois *et al*. (1991); Nijenhuis *et al*. (1992)]. The results suggest that the microwave-assisted ROP is accelerated not only by the microwave-induced temperature conditions (thermal microwave effect) but also by the microwaves themselves, that is, the non-thermal microwave effect or specific microwave effect. During microwave irradiation of the reaction mixture there is a specific effect of microwave activation that cause an increase in the reaction rates, which bulk temperature of the reaction mixture is inadequate to explain. Such an effect has been accepted to be called as non-thermal microwave effect or the specific microwave effect. These effects don't require the conversion of microwave energy into thermal energy but the microwave energy itself directly couples to the energy modes within the molecule. Both the kinetics and thermodynamics of ring-opening polymerization of l-lactide to PLA in microwave are distinct from conventional synthesis. It may be because of long polymeric chains, the coupling of energies is difficult. Hence it is difficult to find the kinetics of ring-opening polymerization of l-lactide to PLA using microwave irradiation in a simple way.

CHAPTER – 5

CONCLUSIONS AND RECOMMENDATIONS

CHAPTER-5 CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

5.1.1. PLA Synthesis

The ring-opening polymerization of l-lactide to synthesize PLA under microwave irradiation has been carried out. PLA has been successfully synthesized using domestic and monomode microwave oven. Effects of polymerization temperature, polymerization time, monomer to initiator ratio, and nature of initiator have been investigated. On the basis of present results the following significant conclusions may be drawn:

a) PLA has been successfully synthesized in domestic microwave oven with highest molar mass (M_w) in the range of 7.4×10^4 g.mol^{-1}. The different $[M_o]/[I_o]$ ratios were used for the investigation using stannous octoate as an initiator.

b) PLA has also been successfully synthesized in monomode microwave oven using stannous octoate and dibutyl tin dimethoxide initiators. PLA has been synthesized with a molar mass above one lac (100000) at laboratory scale in less than 30 mins using microwave irradiations as compared to conventional synthesis which takes many hours to several days for polymerization. The co-initiator dimethyl aminopyridine gave remarkable results when used with stannous octoate.

c) The effect of monomer to initiator ratio on the polymerization yield and polymer molar mass has been investigated. The maximum molar mass obtained has been observed for the monomer to initiator ratios of 5069 and 10069. The highest molar mass obtained was 1.02 ×

10^5g.mol^{-1} for $[M_o]/[I_o]$ = 5069 for $SnOct_2$ as compared to dibutyl tin dimethoxide indicating $SnOct_2$ to be a better initiator compared to DBTM, which is known to be an effective transesterification catalyst and also known to cause back-biting degradation. The molar mass of PLA over one lac was obtained with stannous octoate which is very useful for commercial purpose.

d) The molar mass of PLA increases up to 20 min of microwave irradiation time and decreases up to 30 mins as the back-biting and degradation phenomena took place at higher irradiation time. The molar mass of PLA increases with increasing $[M_o]/[I_o]$ ratio as the number of initiator molecules decrease for a given number of monomer molecules which results in reduction of the number of chains onto which a given number of monomer molecules can attach themselves.

e) An enhancement in molar mass has been observed when DMAP is used as the co-initiator with stannous octoate. At 30 min the increase in molar mass is exceptionally high as compared to that with only $SnOct_2$. The molar mass in almost all reactions is above 50,000 which are very encouraging. The highest molar mass obtained was 1.2×10^5 g.mol^{-1}.

f) It was also observed that a significant degradation of PLA takes place in chloroform when kept for long time for SEC analysis.

5.1.2. PLA/Clay Nanocomposites

The *in situ* ring-opening polymerization of l-lactide to synthesize PLA/Clay nanocomposites by adding different types of clay has been successfully carried out under microwave irradiation using stannous octoate, dibutyl tin dimethoxide and dimethyl aminopyridine as co-initiator with stannous octoate. In monomode microwave the *in situ* polymerization time was reduced to few mins from several hours for

conventional heating. Based on the present study for the synthesis PLA/Clay nanocomposites it is possible to draw following significant conclusions:

a) The effect of clay loading is of much significance with respect to the polymerization yield. The polymerization yield decreases on increasing the clay percentage. It has also been shown that no PLA is obtained when Cloisite® Na^+ clay is used during *in situ* polymerization in the microwave oven.

b) A remarkable difference between Cloisite® 15A and Cloisite® 30B has been observed on the *in situ* polymerization yield possibly due to the presence of different organic modifiers in their respective structures. The polymerization yield obtained for Cloisite® 30B was higher than that obtained with Cloisite® 15A.

c) Ultrasonication provides tremendous amount of energy to the clay layers, so that they get separated to a larger extent.

d) The presence of clay significantly enhances the thermal degradation temperature of the polymer blend indicating that PLA/Clay nanocomposites are thermally more stable. The excellent compatibility of clay with PLA matrix is confirmed by SEM.

e) X-ray diffraction studies showed that in case of $SnOct_2$, using Cloisite® 30B clay as a nanofiller, there is a total absence of the diffraction peak (d_{001}) at low 2θ angles of the X-ray diffractograms of the PLA/Clay nanocomposites as compared with those of neat organoclay. It is, therefore, clear that there is a formation of an exfoliated morphology. This has been further confirmed by TEM.

f) $SnOct_2$ is a better initiator for *in situ* PLA polymerization through microwave irradiation compared to DBTM as the yield is much better.

g) The application of microwave irradiation accelerates the polymerization process and helps in the formation of exfoliated structure. The results indicate that microwave assisted *in situ* polymerization

is likely to be an efficient, cost effective and environment friendly technique for preparation of PLA/Clay nanocomposites.

5.2. Recommendations for Future Work

a) A number of catalysts that have been used for the conventional synthesis of PLA are recommended for the microwave assisted synthesis of PLA. It would be interesting to evaluate their relative efficacy.

b) Various types of nanofillers other than clay can be used in the *in situ* synthesis of nanocomposites of PLA under microwave irradiation.

c) The microwave technology developed need to be scaled-up to pilot plant or industrial plant.

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APPENDIX A

The work presented in the thesis is fully documented and has resulted in following publications/presentations:

Publications/Communication in International journals

1. **P. Singla., R. Mehta., D. Berek., S.N. Upadhyay.**, "Microwave Assisted Synthesis of Poly(Lactic Acid) and its Characterization using Size Exclusion Chromatography", *Journal of Macromolecular Science, Pure and Applied Chemistry*, A49, 11, 2012.
2. **P. Singla., R. Mehta., D. Berek., S.N. Upadhyay.** "Ring Opening Polymerization of Lactide in a Monomode Microwave using Stannous Octoate and Dibutyltin Dimethoxide Catalysts", *Journal of Macromolecular Science,* Pure *and Applied Chemistry,* A51, 4, 2014 (Accepted).
3. **P. Singla., P. Kaur., R. Mehta., D. Berek., S.N. Upadhyay.** "Ring-Opening Polymerization of Lactide Using Microwave and Conventional Heating", *Procedia Chemistry (Elsevier)* 4, 179-185, 2012.
4. **P. Singla., R. Mehta., S.N. Upadhyay.**, "Clay Modification by the Use of Organic Cations", *Green and Sustainable Chemistry*, 2, 21-25, 2012.
5. **P. Singla., R. Mehta., S.N. Upadhyay.** "Microwave Assisted *In-situ* Ring-opening Polymerization of Polylactide/Clay Nanocomposites: Effect of Clay Loading", *Applied Clay Science*, (communicated April, 2013).
6. **R. Mehta, P. Singla, D. Berek, S.N. Upadhyay**. "Polylactic Acid And A Process For Preparation Thereof", *Patent application no. 236/DEL/2014*, 28th January 2014, New Delhi, India.

Chapters Contribution in Encyclopedia

1. **P. Singla., R. Mehta., S.N. Upadhyay.**, "Polylactic Acid (PLA): Microwave Assisted Synthesis", *Encyclopedia of Biomedical Polymer & Polymeric Biomaterials*, 2013 (Accepted).
2. **R. Mehta, P. Singla, V. Kumar, S.N. Upadhyay**, Synthesis of Poly(Lactic Acid): A Review" *Encyclopedia of Biomedical Polymers and Polymeric Biomaterials*, 2013 (Accepted).

Presentations at International/National Conferences

1. **Pankil Singla,** Rajeev Mehta, S.N. Upadhyay, "*Microwave vs Conventional Synthesis of Poly(lactic Acid)*", Second International Conference on Polymer Processing and Characterization (ICPPC – 2010), Kerala, January 15-17, 2010.
2. **Pankil Singla,** Rajeev Mehta, D. Berek, S.N. Upadhyay, "*Microwave Assisted Ring-Opening Polymerization of Lactide*", International Conference on Polymer Science and Engineering: Emerging Dimensions (PSE-2010), University Institute of Chemical Engineering and Technology, Punjab University, Chandigarh, November 26-27, 2010.
3. **Pankil Singla,** Rajeev Mehta, D. Berek, S.N. Upadhyay, "*Microwave Assisted Ring-Opening Polymerization of Lactide to Poly (Lactic Acid)*", International Conference POLYCHAR 19 - World Forum on Advanced Materials, March 20-24, 2011, Kathmandu, Nepal.

APPENDIX B

PLOTS FOR KINETIC STUDY OF SYNTHESIS OF PLA IN MICROWAVE

The graphs were plotted between $\ln(C_o/C_t)$ and irradiation time (t); $1/C_t^{\,2}$ and (t); and $1/C_t$ and (t) for four different $[M_o]/[I_o]$ ratios to find out the order of the polymerization kinetics. But the linear fit for $[M_o]/[I_o]$ ratio = 1041 satisfy all three types of order i.e. first order, second order and three order, as the R^2 value comes out to be greater than 0.9. Also, data of one $[M_o]/[I_o]$ ratio follows one type of order and at other $[M_o]/[I_o]$ ratio it follows a different type of order. Hence it is not possible to fit the experimental data to get the kinetic rate constants. Some of these plots have been shown in Figures A.1, A.2 and A.3 which shows first, second and third order linear fit for $[M_o]/[I_o]$ ratio = 1041 and Figures A.4 for $[M_o]/[I_o]$ ratio = 2534, Figure A.5 for $[M_o]/[I_o]$ ratio = 5069, Figure A.6 for $[M_o]/[I_o]$ ratio = 10069 which do not show a unique fit for any reaction order. Thus, the reaction kinetics in the microwave reactor does exhibit an interaction between the microwave radiations and exhibiting a non-thermal microwave effect or the specific microwave effect.

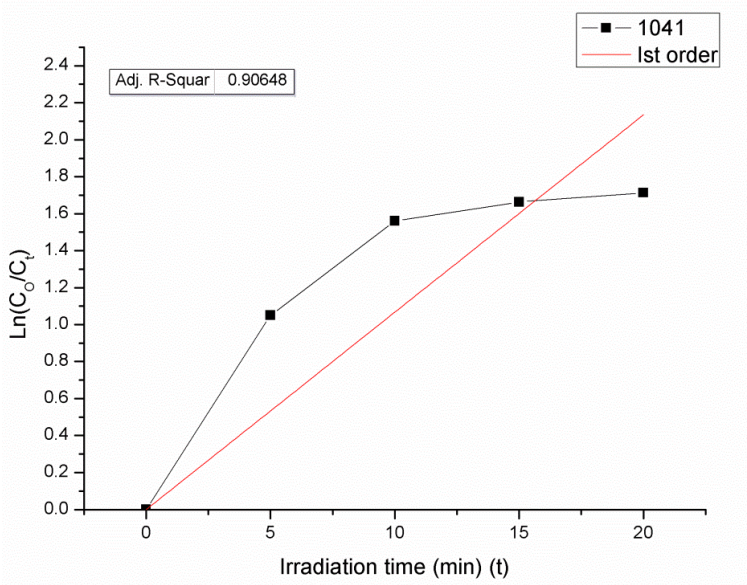

Figure A. 1 Graph plot of $\ln(C_o/C_t)$ Vs irradiation time (t) for $[M_o]/[I_o]$ ratio = 1041

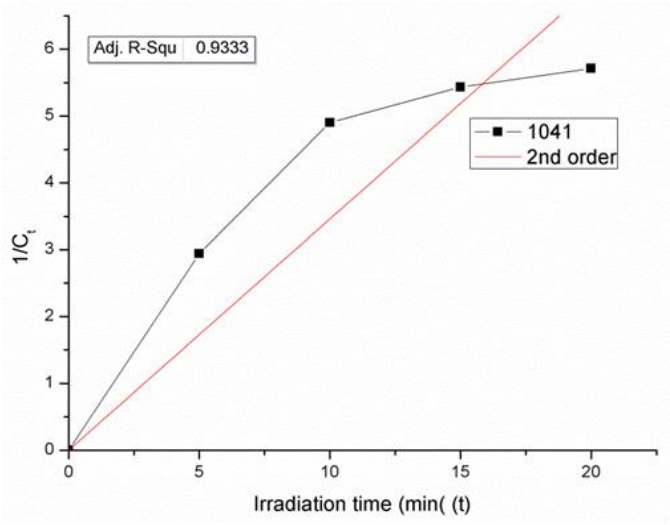

Figure A. 2 Graph plot of $1/C_t^{\,2}$ and (t) for $[M_o]/[I_o]$ ratio = 1041

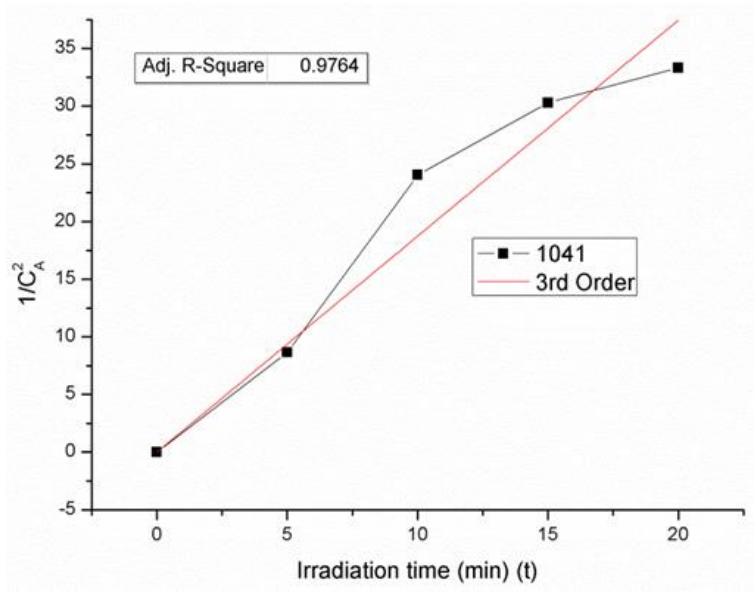

Figure A. 3 Graph plot of $1/C_t$ and (t) for $[M_o]/[I_o]$ ratio = 1041

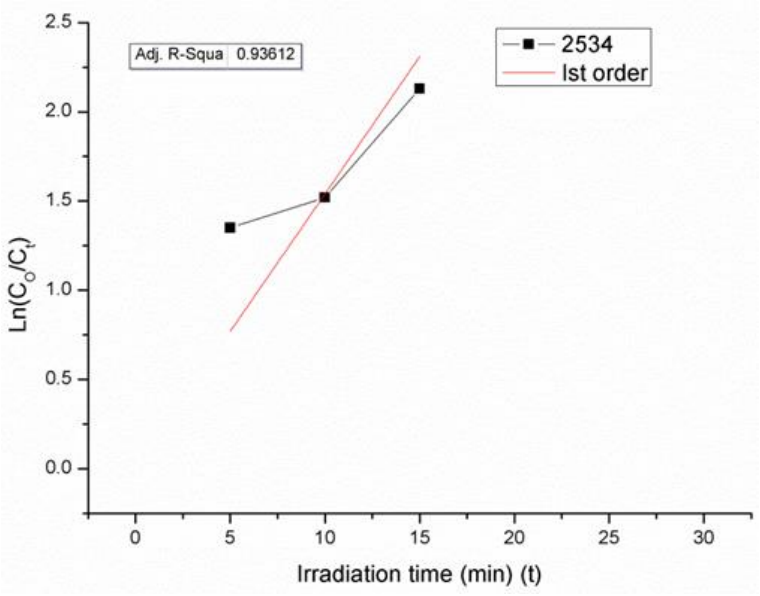

Figure A. 4 Graph plot of ln(C_o/C_t) Vs irradiation time (t) for [M_o]/[I_o] ratio = 2534

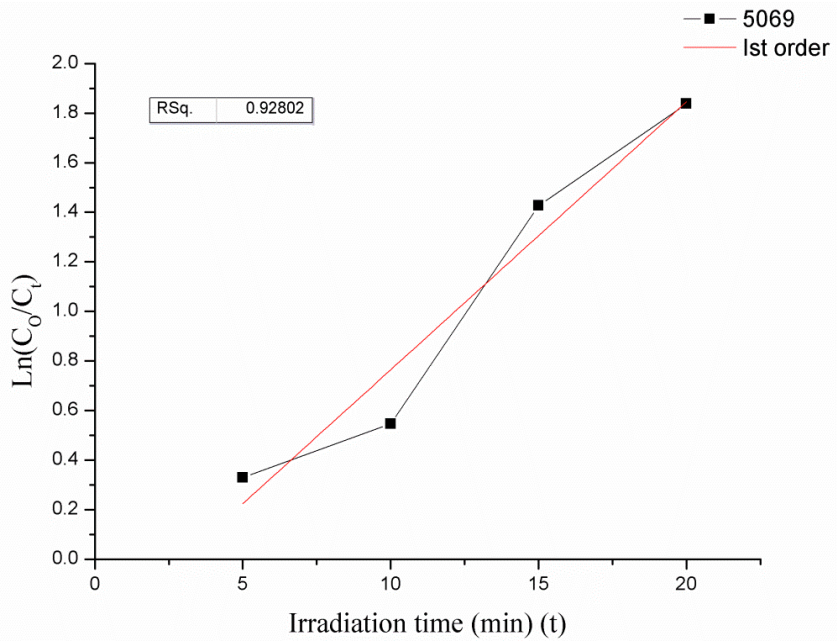

Figure A. 5 Graph plot of ln(C_o/C_t) Vs irradiation time (t) for [M_o]/[I_o] ratio = 5069

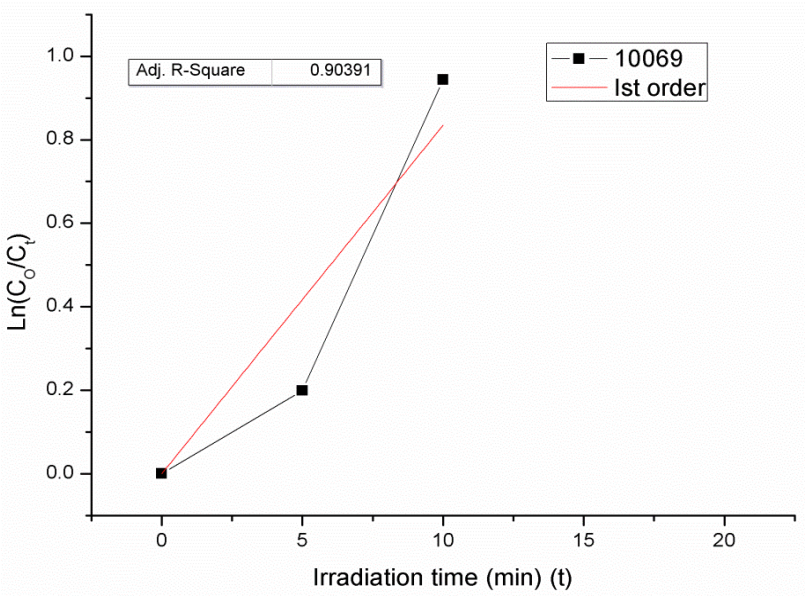

Figure A. 6 Graph plot of $\ln(C_o/C_t)$ Vs irradiation time (t) for $[M_o]/[I_o]$ ratio = 10069