SYNTHESIS OF POLYLACTIC ACID

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ABSTRACT

The goal of this project is to investigate the possibility of using alternative methods, like Ultrasonic Sonochemistry and Microwave Induced Polymerization to synthesize polylactic acid and discuss the possibility of applying mentioned techniques for industrial production.

Polylactic acid (PLA) is biodegradable, highly versatile, aliphatic polyester which can be produced from 100 % renewable resources, like corn and beets. PLA proved to be a promising alternative to petroleum-based polymers as its properties are on a par with currently widely used polymers like PET, PVC etc.

Current industrial production methods of PLA require high temperatures and high pressures in order to achieve the required final product. Alternative methods, like Sonochemistry and Microwave Induced reaction are growing in popularity and could be considered as faster and more energy-efficient methods to synthesize PLA.

Experimental set-up was created according to the information provided in the literature and attempt was made to successfully synthesize PLA with properties comparable to PLA produced by the industrial methods.

Analyses of the products were performed using Raman Spectroscopy and then analyzed using Principal Component Analysis (PCA), in order to understand progression of the reaction.

None of the produced PLA could be compared to industrial products as resulting polymer showed subpar properties. Analysis with PCA suggested that reaction was happening in the right direction. Experimental set-up should be adjusted further in order to achieve more successful results. However, none of these alternative methods alone seemed to be as a viable pick for industrial application.

PREFACE

This Master's Thesis is written by 10th semester student of Master programme in Chemical Engineering at Aalborg University, Esbjerg.

The thesis contains overview of the current biopolymer market, overview of possible polylactic acid production paths and attempt to apply alternative techniques, like Ultrasound and Microwaves to achieve high-quality polymer.

All plots and charts used for interpretation of spectroscopic data are provided in the report.

Full reference list is provided in the end of the report.

The author would like to thank Erik G. Søgaard and Sergey V. Kucheryavskiy for supervision and useful advices during the project work.

Contents

INTRODUCTION

Plastics are a wide family of materials derived from organic products, like cellulose, coal, natural gas, salt and crude oil. Plastic materials are considered as extremely resource efficient not only during their production phase, but also during their use phase, meaning that their service life is long and specifically designed polymers can outperform most alternative materials. For example, in insulation, plastic materials save more than 140 times amount of energy than it is needed for their production. They are also considered as top choice for protection of goods and food, as advanced packaging materials can prevent breakage of goods while transporting and great barrier properties of these materials can protect food for extended periods, resulting in less waste. [1]

Due to wide possibilities of adjusting polymers properties for specific needs, plastic materials are used for a wide range of applications in many different sectors, like packaging, building and construction, automotive and aeronautics, electrical and electronic equipment, agriculture, leisure and sports equipment, medical and health products, etc. [1]

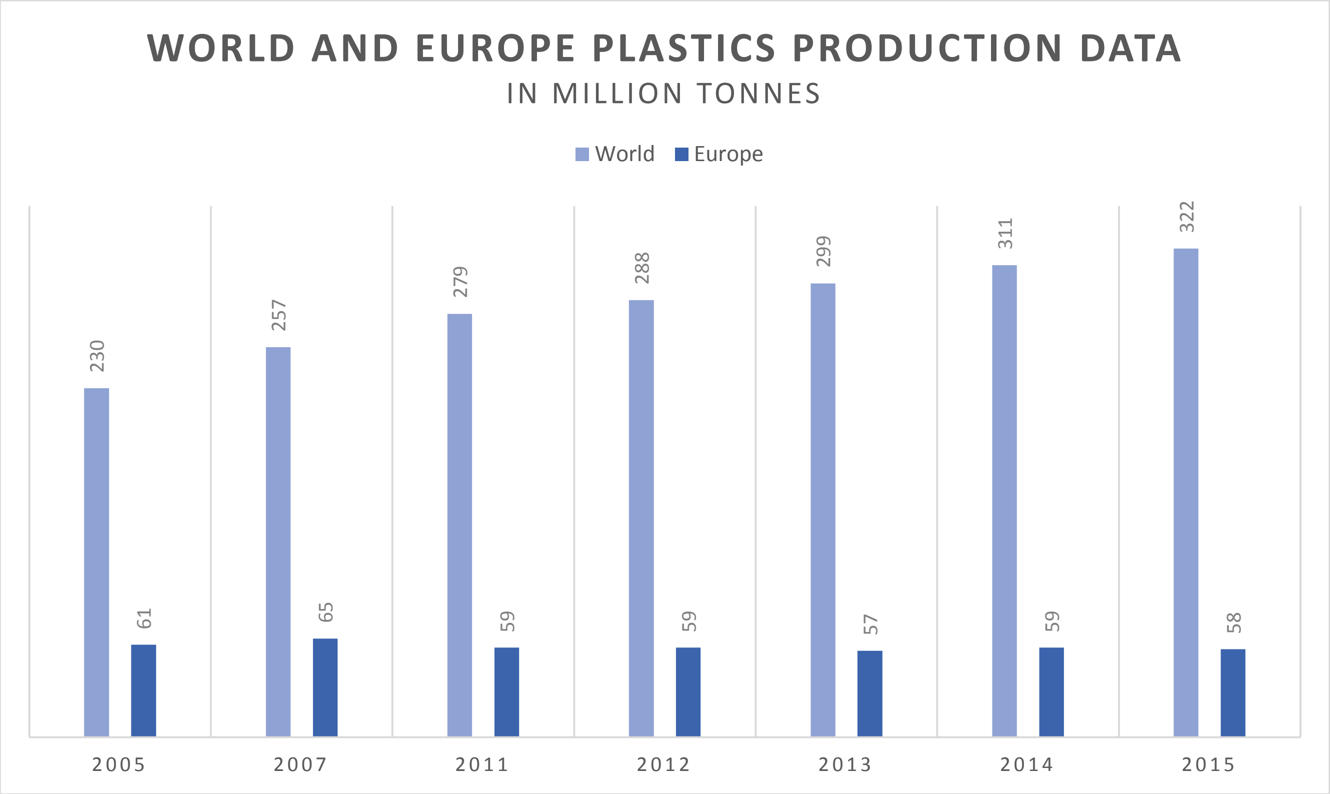


Figure 1. World and Europe (EU28+NO/CH) plastics production data. Does not include fibers of PET-, PA-, PP- and polyacryl-fibers. [1]

Plastics industry is constantly growing all over the world due to growing demand and increasing consumption of these materials in related industries, as it can be confirmed by the constantly growing amount of plastic materials produced worldwide, as seen in Figure 1. Furthermore, plastics industry is an important part of world's economy. Considering these numbers just for EU28 Member States (data includes plastics raw materials producers, plastics converters and plastics machinery manufacturers) [1]:

- The plastics industry gives direct employment to over 1.5 million people in Europe;
- Close to 60,000 companies operate in this industry;
- The European plastics industry had a turnover of more than 340 billion euros in 2015;
- The European plastics industry had a trade balance of over 16.5 billion euros in 2015;
- The European plastics industry contributed close to 27.5 billion euros to public finances and welfare in 2015;
- The European plastics industry ranks 7th in Europe in industrial value added contribution. At the same level as Pharmaceutical industry.

It is obvious, that it is an important and valuable economical sector, which will keep growing as advancements in polymer science will lead to wider possible applications and thus higher consumption of plastic materials.

Demand of plastics by polymer in Europe are provided in Figure 2. According to this data, almost all polymers produced are made from fossil fuels, like crude oil and natural gas. These polymers are also known as petrochemical-based polymers.

Currently petrochemical-based polymers have advantages over alternatives, which encourages their usage in most of the industries [2]. Mentioned advantages are:

- High-speed production
- Low production cost
- High mechanical performance
- Good barrier properties
- Good heat sealability

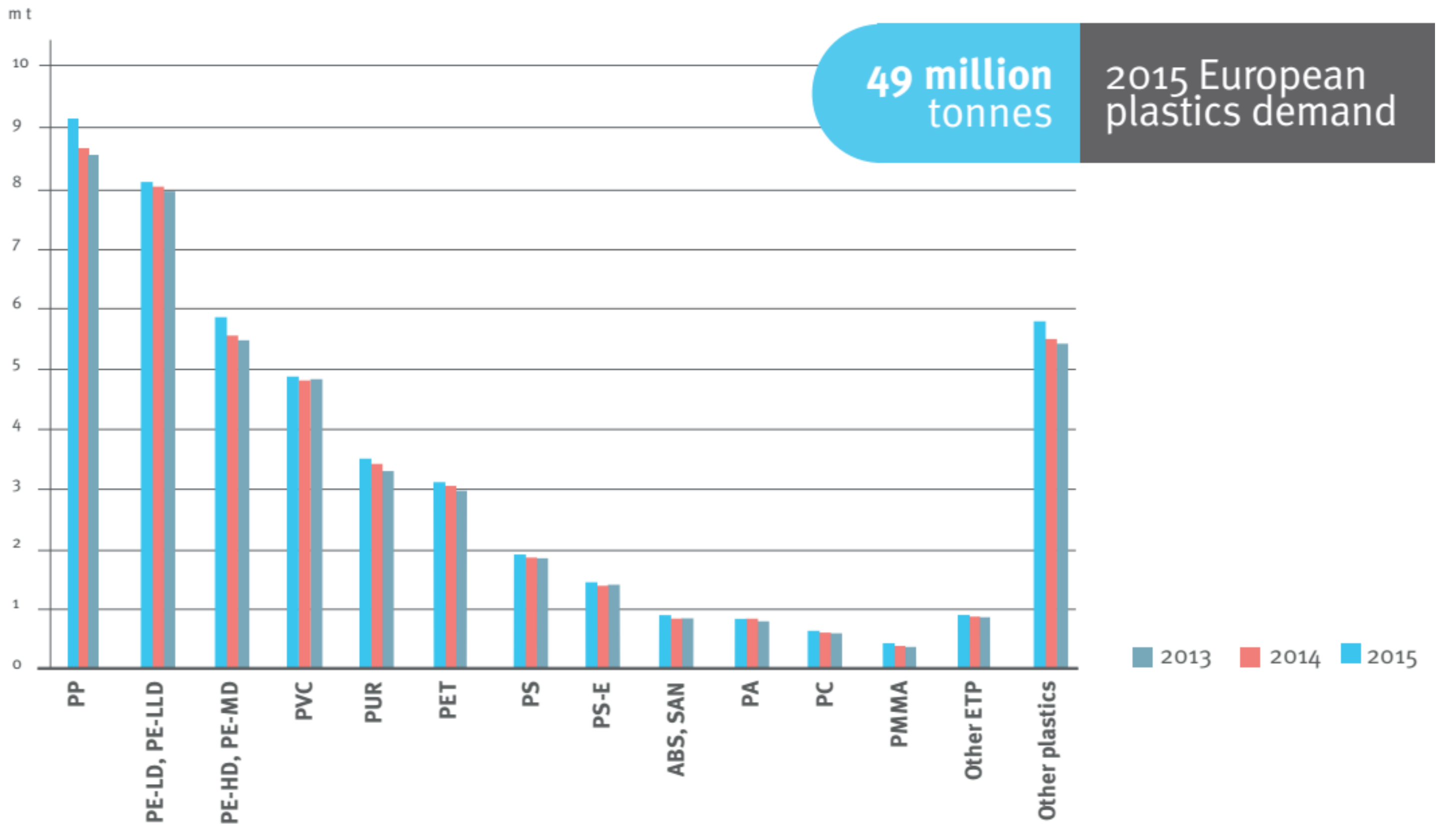


Figure 2. European plastics demand in recent years. [1]

However, there are several disadvantages to them, which are getting more and more important as consumption and necessity for polymers increase, while resources decrease causing growing prices of oil and natural gas [2]. It could be summed up to following disadvantages of petrochemical-based polymers:

- Diminishing oil and gas resources
- Growth of oil and gas prices in recent times
- Environmental concerns in regard to their degradation or incineration
- Uneconomical costs of recycling and cross-contaminations in the processes
- Possibility of toxic monomers or oligomers migrating to edible materials when used for packaging of food

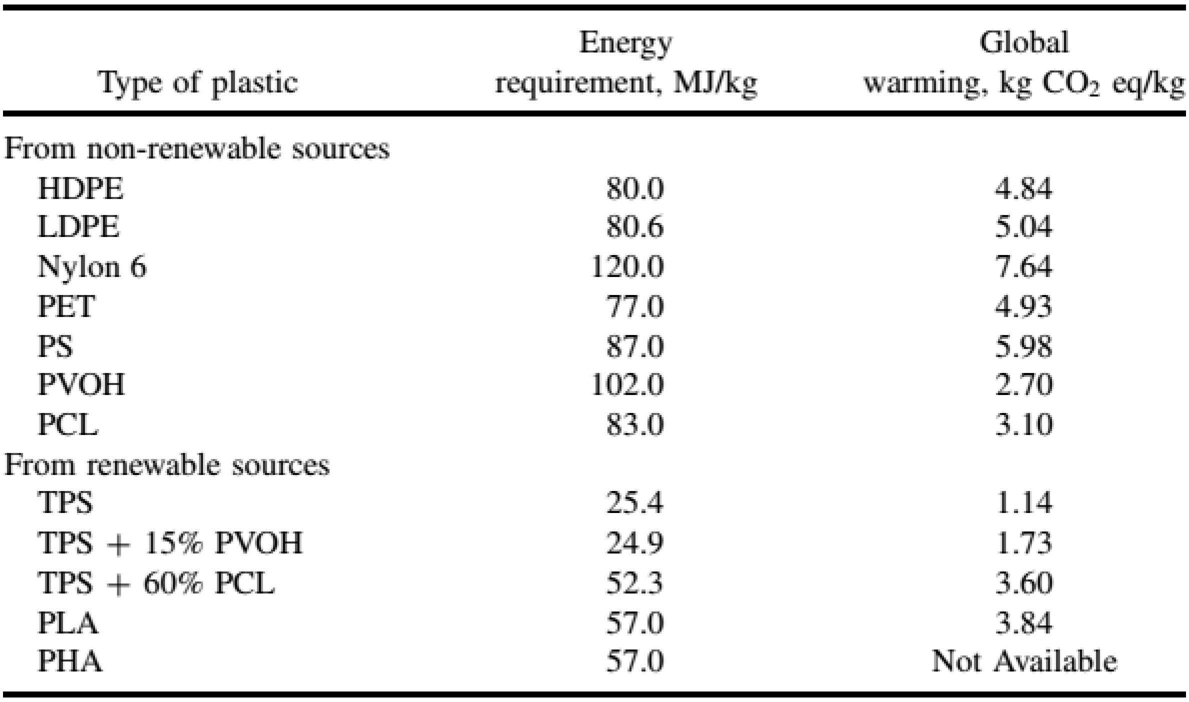
Technologies are being made to deal with mentioned issues, such as mechanical recycling (segregated plastics, mixed plastics), biological recycling (sewage, compost, soil) and energy recovery (incineration, pyrolysis). These 3 methods are alternative ways to deal with plastics waste management, each with its own advantages and disadvantages, although more advanced processes and technologies should be created to fully deal with the issues petrochemical-based polymers are creating. [2]

Currently another alternative to petrochemical-based polymers are rapidly growing in popularity and it offers a solution for a future of plastics industry while dealing with the disadvantages of polymers made from fossil fuel. That solution could be bioplastics which are described in greater detail in the following chapter.

BIOPLASTICS

In recent years, development of bioplastics, or biopolymers, became more popular not only due to motives of environmental but also strategic nature. In order to reduce the impact on environment, especially amount of CO_2 released, part of the products obtained from agriculture, like cellulose, starch, wood etc., are used as raw materials for polymer production. This way, part of the CO_2 which is released in the environment is balanced out by the amount of CO_2 consumed during the growth cycle of the plant. Data in Figure 3 confirms, that bioplastics has smaller impact on nature and consume less energy to produce. Additionally, constantly growing petroleum prices are becoming less problematic as it is replaced by the renewable raw materials obtained from agriculture. [3]

According to the statistics from 2011, worldwide production of bioplastics was around 1,000,000 tons/year, when compared to about 280 million tons/year of conventional petroleum-based plastics. It is expected, that amount of bioplastics produced will grow exponentially in the near future [3]. European Bioplastics annual market data suggests that the market will grow to approximately 7.8 million tonnes in 2019 from 1.7 million tonnes observed at 2014 [4].



Type of plastic	Energy requirement, MJ/kg	Global warming, kg CO_2 eq/kg
From non-renewable sources		
HDPE	80.0	4.84
LDPE	80.6	5.04
Nylon 6	120.0	7.64
PET	77.0	4.93
PS	87.0	5.98
PVOH	102.0	2.70
PCL	83.0	3.10
From renewable sources		
TPS	25.4	1.14
TPS + 15% PVOH	24.9	1.73
TPS + 60% PCL	52.3	3.60
PLA	57.0	3.84
PHA	57.0	Not Available

Figure 3. Amount of energy required from non-renewable sources and CO_2 emissions for different types of plastics currently on the market. [3]

One of the biggest advantages for biopolymers is their biodegradability in the natural environment. [5] Concept of biodegradability will be further explained in the following section.

Biodegradability

It is important to understand what biodegradable means and have universally accepted definition. Many groups and organizations have tried to clearly define terms like "degradation", "biodegradation" and "biodegradability", but there are several reasons suggested why it is difficult to establish an internationally acclaimed definition for these terms [5]:

- Clear definition of different environments in which the material is to be introduced and its impact on those environments
- Different opinions considering scientific approach or reference points used for determining biodegradability
- The divergence of opinion concerning the policy implications of various definitions
- Problems arising from language differences around the world

These issues led to creation of many different definitions, depending on the organisation, their background and their particular interests. However, defining the universal criteria for being able to call a material "biodegradable" was still the biggest issue as the term itself does not provide any information about the time needed for material to degrade neither the final degree of materials degradation [5].

In 1992, an international workshop concerning biodegradability was organised to bring together experts from around the world to finally achieve an agreement on definitions, standards and methodologies used for testing. Following key points were established in the meeting [6]:

- For all practical purposes of applying a definition, material manufactured to be biodegradable must relate to a specific disposal pathway such as composting, sewage treatment, denitrification, or anaerobic sludge treatment
- The rate of degradation of a material manufactured to be biodegradable has to be consistent with the disposal method and other components of the pathway into which it is introduced, such that accumulation is controlled.

- The ultimate end products of aerobic biodegradation of a material manufactured to be biodegradable are carbon dioxide, water and minerals and that the intermediate products include biomass and humic materials.
- Materials must biodegrade safely and not negatively impact on the disposal process or the use of the end product of the disposal

As a result, specified periods of time, specific disposal pathways, and standard test methodologies were incorporated into definitions. Furthermore, standardisation organisations like CEN, ISO and ASTM were therefore encouraged to swiftly come up with standard biodegradation tests so these could be determined. As society further demanded non-debatable criteria for polymers suitability for disposal in specific waste streams, definitions like ecotoxicity, effects on waste treatment processes, etc. appeared and are used to fully describe materials behaviour when it is exposed to environment or one of the waste treatment processes. This led to many standards and certification procedures which are necessary to describe “biodegradability” of materials [5].

Looking from a chemical point of view the biodegradation can be described by polymers capability to undergo complete mineralisation in the environment and the resulting products would depend on conditions in which process took place: oxidised form if it was aerobic degradation or reduced form if the degradation was anaerobic. If a simple example is considered where polymer $C_{POLYMER}$ is composed of only carbon, oxygen and hydrogen, it can be represented by following expressions for mentioned conditions:

Aerobic: $$C_{POLYMER} + O_2 \rightarrow CO_2 + H_2O + C_{RESIDUE} + C_{BIOMASS}$$

Anerobic: $$C_{POLYMER} \rightarrow CO_2 + CH_4 + H_2O + C_{RESIDUE} + C_{BIOMASS}$$

Complete biodegradation is achieved when no residue of the original substrate ($C_{POLYMER}$) remains and it is completely converted into gaseous products and salts or usually biomass as mineralisation is a very slow process under natural conditions. Therefore, complete biodegradation and not mineralisation is the measurable goal when removal from the environment is concerned [5].

Bioplastics classification

Bioplastics are biodegradable polymers, as explained before, they can undergo reactions in the nature to degrade into simpler compounds, which then can be further absorbed and used by the environmental processes. In general, biodegradable polymers can be classified into four categories depending on the raw materials source and the type of synthesis used to make them. [7]

The first category of biopolymers are polymers generated from biomass. This group includes agro-polymers made from agro-resources, mainly polysaccharides and proteins. Polysaccharides are mostly limited to derivatives of starch and cellulose, created for practical applications as plastics or as water-soluble polymers. Both of these materials are composed of D-glycopyranoside (derivative of D-glucose) repeating units, which usually produce products of very high molecular weight and consist of thousands of units [8].

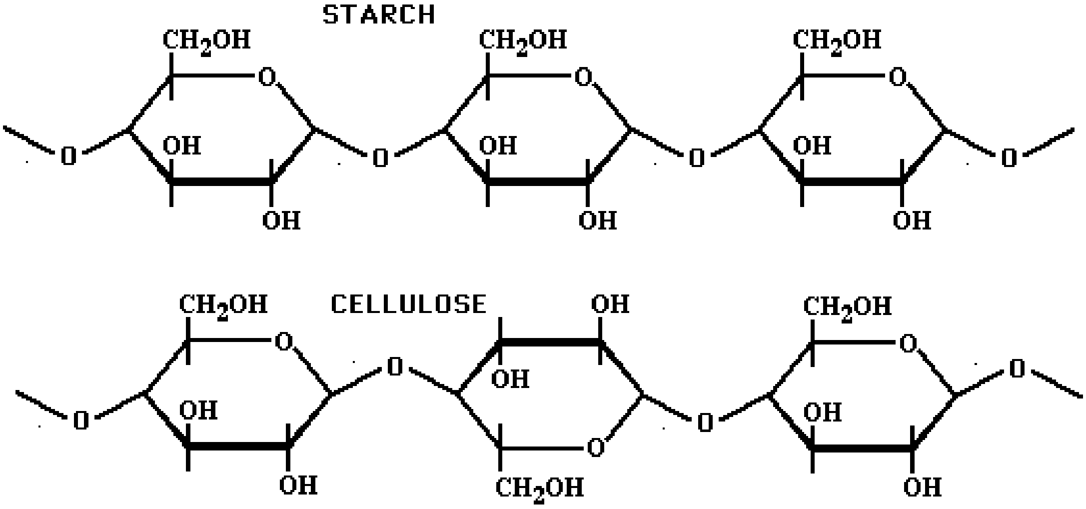


Figure 4. Basic structural differences between starch and cellulose molecules. [9]

Proteins, which belong to the same category, are mainly naturally occurring polymers and by comparison are not soluble or fusible without decomposition. Their structure consists of extended chain of amino acids joined through amide links, which can be easily degraded by enzymes, especially proteases. Proteins are widely used as fibers in many forms, like wool, silk, gelatin (collagen) etc., and found their use in many sectors. [10]

The second category is biodegradable polymers obtained by microbial production routes, for example – polyhydroxyalkanoates. They are naturally produced aliphatic polyesters via a microbial process in a sugar-based medium and are used by bacteria as carbon and energy storage materials. Aliphatic polyesters are most easily biodegraded synthetic polymers and were the first biodegradable polyesters utilized in plastics. [11]

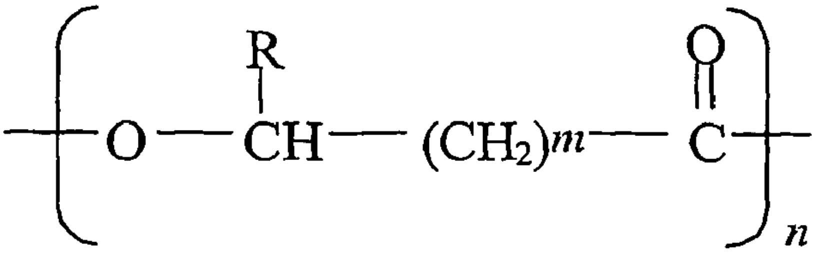


Figure 5. General structure of polyhydroxyalkanoates. [12]

The third category of biodegradable polymers consist of monomers from agro-resources, which then are synthesized into products like polyglycolic acid and polylactic acid. Both of these polymers found success in medical applications as biodegradable and non-toxic materials. Polylactic acid is especially interesting due to wide application possibilities and its biocompatibility [8]. For these reasons and it's growing popularity, it was chosen as compound of interest for this project and will be further discussed in following chapters.

The fourth and last category of biodegradable polymers is obtained from non-renewable resources, like fossil fuel. These polymers would still have most of the disadvantages of conventional polymers due to their raw material sources, although they are made to be biodegradable thus making them easier to deal with in a long run. Some examples of these polymers would be polycaprolactones, polyesteramides, poly(butylene succinate adipate) etc. [13]

Following chapters will deal with polylactic acid and methods of synthesizing it.

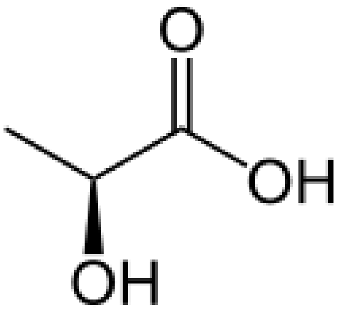
POLYLACTIC ACID

Poly-lactic acid (PLA) is highly versatile, biodegradable, aliphatic polyester which can be derived from 100 % renewable resources, like corn and sugar beets. PLA proved itself to be a promising alternative for petroleum-based polymers as its properties are on a par with currently widely used polymers like PET, PVC etc. However, the commercial viability of PLA is still limited by its high production costs compared to its petroleum-based counterparts. As the usage and limitation of fossil fuels become a bigger concern every day, industry is gradually leaning towards renewable sources to meet their needs thus PLA is considered as one of the best alternatives for current demands. [14, 15]

Lactic Acid

Lactic acid (LA) is the most widely occurring hydroxycarboxylic optical active acid. It was first discovered in 1780 by the Swedish chemist Scheele. LA is a naturally occurring organic acid that can be produced by fermentation or chemical synthesis. It can be found in many foods, especially dairy, as it is present there naturally or as a product of *in situ* microbial fermentation as in yoghurt, buttermilk, sourdough breads and many other foods which were fermented or had processing steps involving fermentation. Lactic acid is also a principal metabolic intermediate in most living organisms, ranging from anaerobic prokaryotes to mammals like humans. [16] Its skeletal formula and main chemical properties are provided in Table 1 below:

Table 1. Chemical properties of Lactic acid. [17]

 L-Lactic Acid	**Molecular formula**	$C_3H_6O_3$
	Molar mass	90.08 g/mol
	Density	1.209 g/mL
	Melting point	L: 53 °C D: 53 °C D/L: 16.8 °C
	Boiling point	122 °C at 15 mmHg

Lactic acid exists in two optically active forms, where the more common one is L-lactic acid, as a fermentation derived LA consists of 99.5 % of the L-isomer. It is known, that thermal, mechanical and biodegradation characteristics of lactic acid polymers are dependent on the concentration of stereoisomers within the initial mixture used for polymerization. Usage of high purity L- or D-isomer results in stereo regular isotactic polymers with superior properties compared to polymers produced from *meso* or lower isomeric purity lactic acid. [15]

Polymerization

Poly-lactic acid can be produced using different routes. In general, three methods are usually used to produce high molecular mass PLA of about 100 000 Daltons. First one is direct condensation polymerization, but it usually leads to low molecular weight polymers which then can be converted to higher molecular weight polymers by addition of chain coupling agents. Second method is azeotropic dehydrative condensation where organic solvents are introduced into reaction mixture to ease up removal of water thus producing higher molecular weight product. Third method is ring-opening polymerization (ROP), where PLA is produced by formation of lactide monomer first and by help of catalyst then converted into final product. It allows producing PLA with controlled molecular weight and by controlling ratio of initial D- and L-lactic acid isomers concentration, properties of final product can be adjusted for specific needs [18]. Schematic representation of mentioned methods is presented in Figure 6.

Currently only two of the mentioned methods are mainly used in industrial production – direct condensation polymerization and ROP. However new methods are appearing, such as polymerization induced by microwaves or melt/solid-state polymerization, which could lead to faster and cheaper production of PLA. The mentioned methods will be described in more detail in following chapters together with possible alternative routes for PLA synthesis – microwave irradiation and ultrasonic sonochemistry, which were chosen as the methods of interest for this project.

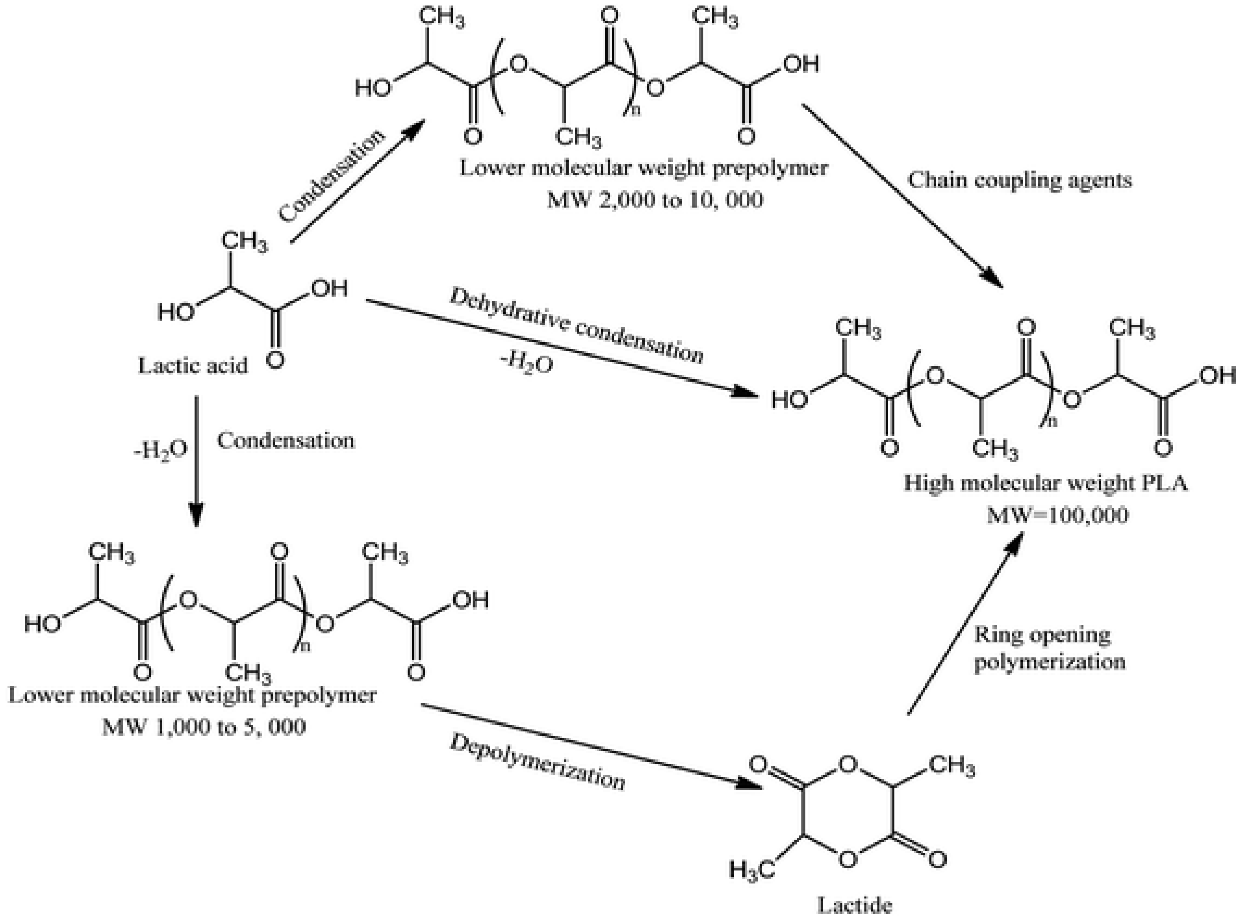
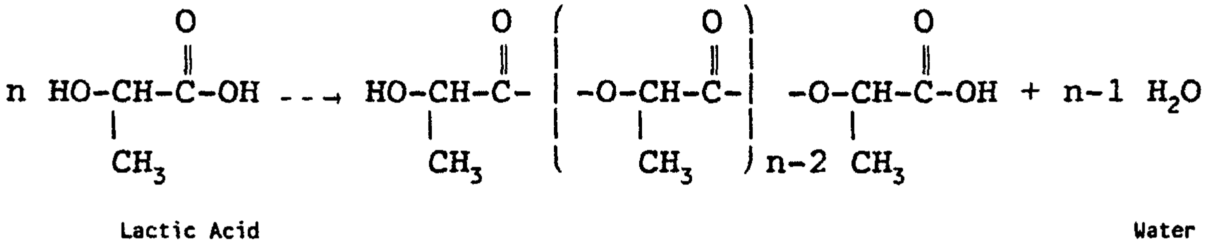


Figure 6. Schematic representation of PLA synthesis methods [19]

Direct condensation polymerization

Polycondensation of lactic acid is a relatively simple process to produce PLA. Lactic acid monomers with the presence of hydroxyl and carboxyl groups can undergo self-esterification, which leads to reversible step-growth polymerization and production of water as byproduct (schematic representation of the reaction is provided in Figure 7). High temperatures and vacuum are used to remove produced water from bulk solution to reduce reversibility of reaction, but usually it still results in low- to intermediate-molecular-weight polymers, mainly because of the presence of water and impurities. Other disadvantages of this route are the requirement of relatively large reactors and huge energy consumptions for necessary high temperature and vacuum leading to expensive final product. Furthermore, LA is known to undergo racemization at high temperatures thus the final product could be lower than expected quality. [20, 21]



$$n\ \mathrm{HO{-}\underset{\underset{CH_3}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}OH} \dashrightarrow \mathrm{HO{-}\underset{\underset{CH_3}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}} \left(\mathrm{{-}O{-}\underset{\underset{CH_3}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}} \right)_{n-2} \mathrm{{-}O{-}\underset{\underset{CH_3}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}OH} + n-1\ \mathrm{H_2O}$$

Figure 7. Schematic representation of LA polycondesation reaction. [22]

For a long period of time it was believed that a high molecular weight polymer could not be achieved via polycondesation due to LA owing to inherent difficulty in driving the dehydration equilibrium in the direction of esterification – which is necessary to obtain sufficiently high molecular weight PLA. [21]

A solution to this problem was proposed. By using either an organic solvent or a multifunctional branching agent it is possible to manipulate the equilibrium between LA, H_2O and PLA to obtain a high molar mass final product via direct polycondensation [21]. However, usage of multifunctional branching agent leads to star-shaped polymers, which exhibit lower melting temperatures, lower crystallization temperatures and lower degree of crystallinty than compared to linear polymers, thus making them possibly unsuitable for wider applications [23]. Usage of organic solvents (e.g. diphenyl ether) requires complex process control which results in expensive PLA; furthermore, it is difficult to remove solvent completely from the final product. To avoid these problems, a new process was developed for production of high molecular weight PLA at reduced cost, called melt polycondesation. [21]

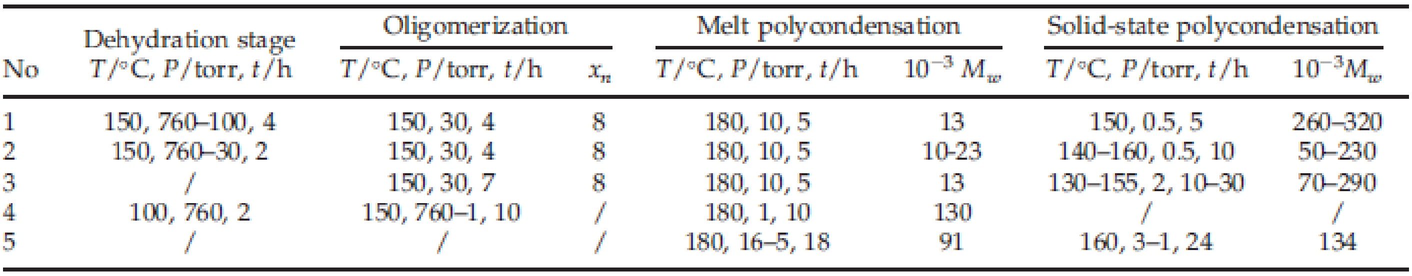
Melt Polycondesation

Melt polycondesation for synthesis of PLA was first reported by Kimura and coworkers [24-26]. During the melt polycondesation, aqueous L-Lactic Acid (LLA) solution is dehydrated and oligomerized to obtain LLA oligomers, which then are melt polycondensed to produce a PLA prepolymer. This prepolymer is then crystallized during the solid-state polycondesation (SSP) process and finally polycondensed at solid state below melting temperature to achieve high molecular weight PLA. [26]

According to works of Kimura and coworkers, performing this reaction in solid-state favors polymerization over the depolymerization or other side reactions; furthermore, during the process of crystallization of the resultant polymer, leftover monomer and catalyst can be separated and concentrated in the noncrystalline part allowing the polymer formation to reach 100%. This process led to PLA of molecular weight over 600,000 Da in relatively short time, making it comparable to the results of ring-opening polymerization. [25]

Melt/Solid-state polycondesation requires catalyst system to be effective, as the process described by the authors of [25] was performed using Sn(II) compounds which then were activated by proton acids acting as co-catalysts. Furthermore, the reported highest molecular weight was achieved only after 20 h of solid-state polycondesation at 150°C and under 0.5 Torr (~67 Pa) pressure. Also, it was reported that after 20 h, sharp decrease in the molecular weight and crystallinity were observed. [25]

Table 2. Some typical Conditions and Results for MP/SSP of PLA [26]



No	Dehydration stage	Oligomerization		Melt polycondensation		Solid-state polycondensation	
	T/°C, P/torr, t/h	T/°C, P/torr, t/h	x_n	T/°C, P/torr, t/h	$10^{-3} M_w$	T/°C, P/torr, t/h	$10^{-3} M_w$
1	150, 760–100, 4	150, 30, 4	8	180, 10, 5	13	150, 0.5, 5	260–320
2	150, 760–30, 2	150, 30, 4	8	180, 10, 5	10-23	140–160, 0.5, 10	50–230
3	/	150, 30, 7	8	180, 10, 5	13	130–155, 2, 10–30	70–290
4	100, 760, 2	150, 760–1, 10	/	180, 1, 10	130	/	/
5	/	/	/	180, 16–5, 18	91	160, 3–1, 24	134

Furthermore, it is obvious from Table 2, that different methods were tested out for this process and usually it results or can result in PLA polymer of molecular weight of over 100,000 Da, although it is required to sustain high temperature and drastically reduced pressure for extended periods of time. A lot of efforts were put into industrializing this process, but it was not successful due to relatively slow reaction rate thus leading to very long reaction times needed to achieve high molecular weight and, at least for now, deeming this process economically ineffective. [26]

Ring-Opening Polymerization

The most common way to obtain high molecular weight PLA is through ring-opening polymerization (ROP). The resulting polymer is formed from an intermediate of lactic acid polycondesation – lactide. Lactide is a cyclic dimer of lactic acid, which is formed by removal of water from the reaction mixture during oligomerization of lactic acid. As Lactic Acid is an optically active compound it is possible to obtain different lactides corresponding to the mixture of enantiomers present in the beginning of reaction. Three stereoforms of lactide are possible: L-lactide, D-Lactide or meso-lactide. [10] These forms can be seen in Figure 8.

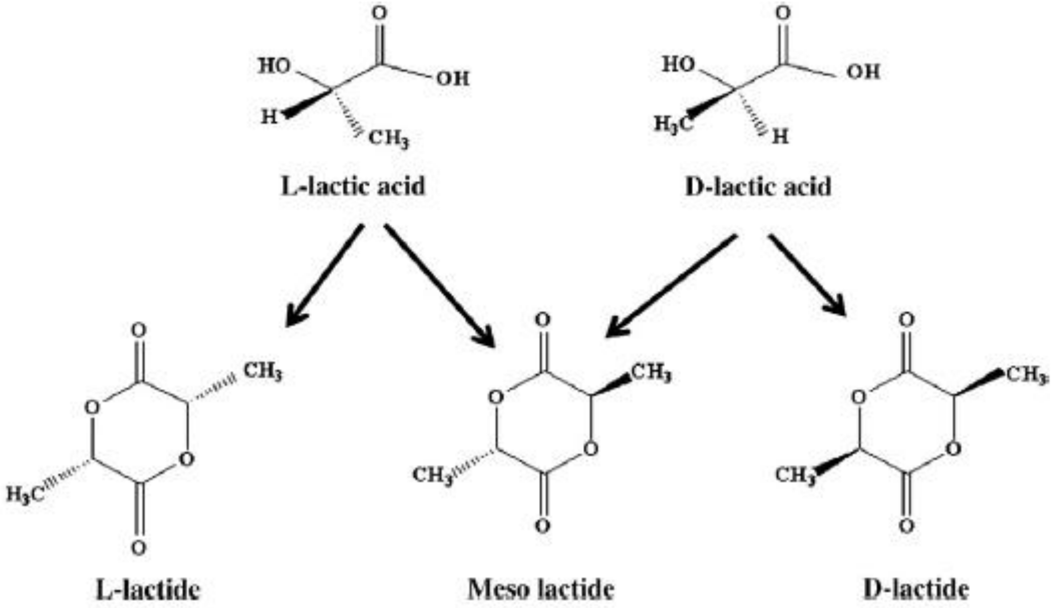


Figure 8. Different Stereoforms of Lactide [27]

Formed lactide is then put through ROP usually using metal alkoxides as catalysts resulting in high molecular weight polyester – PLA. Most commonly used catalyst is Stannous Octanoate (Tin(II) 2-ethylhexanoate), due to its efficiency and low toxicity, making it one of the best choices to use for production of biodegradable and environment-friendly polymers like PLA. [21]

Resulting PLA and its properties depend on the initial mixture of lactic acid enantiomers. Usage of racemic mixture will lead to meso-lactide thus resulting in the poly-DL-lactide and then to an amorphous final polymer. Many important properties as the degree of crystallinity can be controlled by the ratio of D and L enantiomers used in the initial mixture. Polymers with high L-isomer concentration produce crystalline products, while higher D-isomer levels (more than 15%) result in an amorphous final product. Differences between properties of the resulting polymers can be observed in Table 3, where physical properties of polymers produced by DURECT Corporation, Birmingham Polymers, AL, USA are compared. [21]

Table 3. Physical properties of PLA. [21]

Property	L-PLA	DL-PLA
Glass Transition Temperature (T_g}	60 – 65 °C	50 – 60 °C
Melting Point (T_m)	184 °C	Amorphous
Specific Gravity	1.24	1.25
Tensile Strength (MPa)	55.2 – 82.7	27.6 – 41.4
Elongation (%)	5 – 10	3 – 10
Modulus (MPa)	2758 – 4137	1379 – 2758
Inherent viscosity (dl/g)	0.90 – 1.2	0.55 – 0.75

Most of the commercial L-PLA products are semicrystalline polymers with a high melting point ca. 180 °C and having their glass transition temperature in the range of 55 – 60 °C, as it is desirable that PLA should have some crystalline content to benefit the quality of the finished product. [21]

Currently, the biggest producer of PLA, NatureWorks (NB, USA) produces PLA with L-Lactic acid content of 94% using specific solvent free process where combination of melt polycondensation and ROP is utilized. Furthermore, ROP currently dominates as the process of choice for industrial PLA producton due to low time consumption and a high molecular weight final product, making it probably the most used and viable method to produce PLA, although high temperatures and low pressure must be still used to achieve the final product. [21]

In this project, it was decided to attempt synthesizing polylactic acid via alternative methods, as mentioned before. The methods of choice were:

- Microwave irradiation;
- Ultrasonic sonochemistry.

These methods were chosen due to their growing application potential in the industry and energy efficiency. Both of these methods could reduce the need of high temperature and extremely low pressures for this reaction and could be a potentially cheaper solution for production of PLA.

For analyses, Raman spectroscopy was chosen. Raman provides characteristic spectra of sample thus allowing to observe process progression online quickly and accurately. Combined with statistical analysis it is expected to provide all necessary information about the process and the resulting polymer.

In order to successfully apply these methods, concepts behind these techniques need to be understood. An overview of theory behind these methods will be provided in following chapters.

METHODS

Sonochemistry

Sonochemistry is the discipline dealing with understanding of the specific effects of formation of acoustic cavitation in liquids due to ultrasound. To better understand the principles of processes happening in the bulk during the ultrasound initiated reactions, overview of the main concepts will be provided in this section of the work.

Ultrasound

Sound is a pressure wave. All sound waves are similar as all of them are longitudinal pressure waves which are passing through the medium, although they are categorized by their frequencies to different types of sound waves, as shown in Figure 9. The range of human hearing is in a region of around 20 Hz to 20 kHz. Sound waves below the range detectable by humans are considered Infrasound, while Ultrasound refers to the range above the 20 kHz range. Ultrasound can further be divided into two zones: Power ultrasound (20 kHz – 1 MHz) and Diagnostic ultrasound (>1MHz). Diagnostic ultrasound is mainly used for medical and industrial imaging purposes thus it will not be discussed further in this paper. Power ultrasound, or just ultrasound, can be used to enhance the rates of chemical reactions due to acoustic cavitation phenomenon taking place in the liquid [28]. It makes it an interesting option for this project as usage of ultrasound as the processing technique is currently growing in popularity and sound waves are generally considered as safe, non-toxic and environmentally friendly [29].

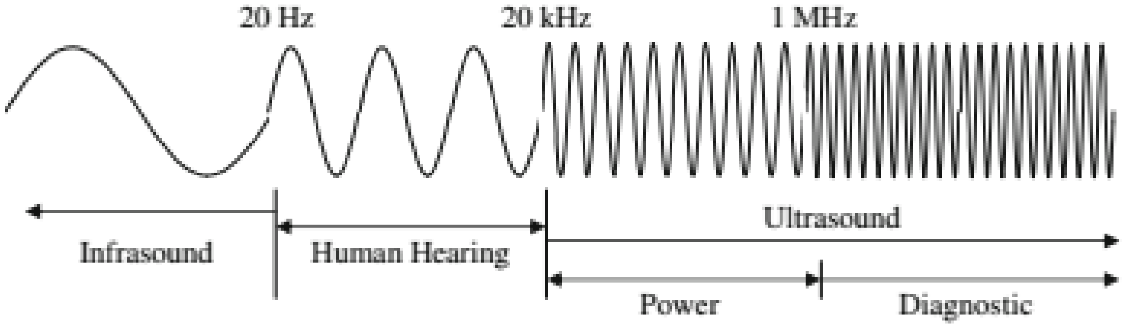


Figure 9. The spectrum of sound waves [29]

Effects of Ultrasound

As previously mentioned, ultrasound represents a high-frequency pressure wave and, as it passes through the medium, high and low pressure regions are created where the size of these variations are directly proportional to the amount of energy applied to the system. In gases, which are elastic and compressible, these pressure variations can be easily accommodated. Although liquids, which are incompressible and cannot respond easily to the pressure variations, can get “torn” apart forming microbubbles to relieve the stresses created by the ultrasound. This bubble formation process is known as *cavitation*. [29]

During cavitation, bubbles are formed and will begin to expand and collapse under the acoustic field thus expansion-collapse cycle can be sinusoidal, mimicking acoustic wave applied for the process. As the bubbles collapse, localized high pressure (>1000 atm) and high temperature (>5,000 K) zones are created, causing number of possible chemical changes to occur at the vapor phase inside the bubble and the surrounding liquid. Due to extreme temperatures inside the bubble, primary radicals are formed, for example, if the water vapor is present in the bubble, H and OH radicals will be formed, leading to multiple possible reactions as shown in Figure 10. Sonication of air-saturated solutions often lead to a decrease of pH, due to creation of NO_2 followed by formation of nitric acid in the solutions, all because of the presence of nitrogen and oxygen in the system. [29]

$$H_2O \longrightarrow H\bullet + OH\bullet$$

$$H\bullet + H\bullet \longrightarrow H_2$$

$$OH\bullet + OH\bullet \rightarrow H_2O_2$$

$$H\bullet + OH\bullet \longrightarrow H_2O$$

Figure 10. Possible reactions for radicals formed from the water vapor. [29]

The amount of heat generated inside the bubble depends upon the size which it can expand to. At 20 kHz cavitation bubbles grow to the largest size of 60-100 µm thus resulting in a relatively high amount of heat generated. It also means, that at 20 kHz there are more primary radicals generated per bubble compared to the amount generated at higher frequencies. However, it was proven, that dominant factor for radical yield is not the bubble temperature, but the amount of bubbles generated. As higher frequencies lead to more bubbles generated, it would result in higher yield of radicals compared to the yield obtained from fewer bigger bubbles created by lower frequencies. Representation of this can be seen in Figure 11, where OH radical yield was measured over time at 3 different frequencies. Because of this, sonochemical effects are strongest at the frequencies range between 200-500 kHz, while for frequencies >1MHz acoustic pressure becomes lower and cavitation is usually not observed. [29]

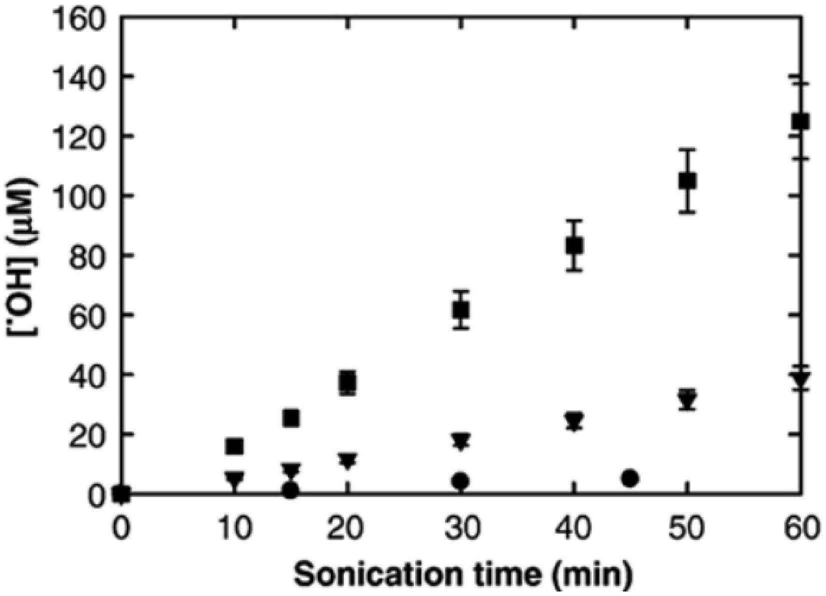


Figure 11. OH radical yield over the sonication time at frequencies of ●20 kHz, ■ 358 kHz, and ▼1062 kHz [29]

The physiochemical properties of the compounds subjected to sonochemical processes play a big role, as the nature of the solvent, solute or gas in the microbubbles can dramatically affect the results of the cavitational collapses. [30]

When solvents with high vapour pressure (VP), low viscosity (μ) and low surface tension (σ) are used, cavities form much more rapidly. Although, the intensity of cavitation is benefited by the solvents with exactly opposite characteristics, like low VP, high μ and σ, and high density (ρ). As mentioned before, in order to form a microbubble a liquid must be "torn" apart or the intermolecular forces in the liquid must be overcome. Due to this, solvents with high densities, surface tensions and viscosities have higher threshold to overcome in order to form bubbles, but once the cavitation begins, harsher conditions are obtained. [31]

Several properties of gases can affect the resulting sonochemical processes. Polytropic ratio (γ) or the heat capacity ratio (C_P/C_V) of the gas in the bubble affects the amount of heat released, thus the final temperature achieved by the adiabatic compression and the cause of the reaction. The maximum temperatures and pressures achieved within the collapsed cavitation bubbles, assuming adiabatic bubble collapse, can be predicted by Noltingk and Nepprias from approximate solutions of Rayleigh-Plesset equations. Noltingk and Nepprias equations are provided in Figure 12. [32]

$$T_{\max} = T_{\mathrm{o}}\left[\frac{P_{\mathrm{a}}(\gamma - 1)}{P_{\mathrm{v}}}\right]$$

$$P_{\max} = P_{\mathrm{v}}\left\{\frac{P_{\mathrm{a}}(\gamma - 1)}{P_{\mathrm{v}}}\right\}^{[\gamma/\gamma-1]}$$

Figure 12. Noltingk and Nepprias equations for prediction of max T and max P in cavitational microbubbles. [32]

Where T_0 – temperature of bulk solution, P_V – vapour pressure of the solution or pressure in the bubble at its maximum size, P_a – pressure in the bubble at the moment of transient collapse and γ – polytropic index of the cavity medium. [32]

As these equations dictate, higher temperatures and pressures can be achieved with monatomic gases that have higher γ than polyatomic gases with lower values of γ. Another important factor is the thermal conductivity of the gas. Although compression is considered as adiabatic in the sonochemical processes, but small amounts of heat are still being transferred to the bulk liquid. A gas that has low thermal conductivity reduces heat dissipation from the cavitation site after the collapse thus favouring higher collapse temperature compared to that of gas with high thermal conductivity. Additionally, gases with high thermal conductivity reduce the temperature which is achieved in a moment of microbubbles collapse. The solubility of the gases in the liquid is also an important factor, as more soluble gases tend to diffuse to cavitation bubble thus forming the nuclei for cavitation. The more soluble gases should result in the larger amount of cavitation nuclei and extensive bubble collapse as highly soluble gases would readily move back to the liquid phase. [32]

For the sonochemical reactions, lowering temperature increases the rate of reaction in contradiction to the most chemical reacting systems. This can be explained by the lowering of the solvent vapour pressure resulting in the increase of the cavitation intensity. At low vapour pressures, less of the vapour can diffuse into the microbubble and thus cushion the collapse, resulting in the more violent implosion. At the same time, as liquid temperature decreases, the amount of gas dissolved increases resulting in the decrease of the vapour pressure of the liquid. Volatile solvents lead to relatively high pressures inside the bubbles thus cushioning the collapse. For some cases, the increase of temperature could favour the reaction kinetics up to a point where further increase in the temperature would lead to the decrease in the reaction rate. [32]

The influence of ultrasonic energy on chemical reaction can involve any or all the following factors: production of heat, promotion of mixing or mass transfer inside the system, promotion of contact between materials, dispersion of contaminated layers of chemicals and production of free chemical radicals. The physical effects of ultrasound can enhance the reactivity of the catalyst in the system due to enlarged surface area or just accelerate the reaction by heightened mixing of the reagents. The chemical effects of ultrasound can enhance reaction rates by formation of highly reactive free radicals formed during cavitation process. The cavitation process can also give rise to microstreaming or formation of micro-jets within the liquid thus enhancing the mass and heat transfer in the bulk phase. [32]

In general, most studies of sonochemistry have adopted the “hot spot” concept to explain the reactions occurring due to ultrasound effects. It could be understood as formation of micro-reactors inside the bulk phase, as shown in Figure 13. Nuclei with extreme conditions are formed in the middle, interfacial area with radial gradient in temperature and local radical density surrounds every nucleus and is then followed by the bulk solution at ambient temperature. Reaction may occur inside the bubble between the formed radicals, at the interface and in the surrounding liquid due to the exchange of free radicals during the implosion or just because of heat transfer and agitation during the implosion of these “hot spots”. [32] It could be an interesting alternative technique for polymerization reactions as it could enhance monomers movement in the bulk and possibly ease up the removal of water during the polycondesation reactions.

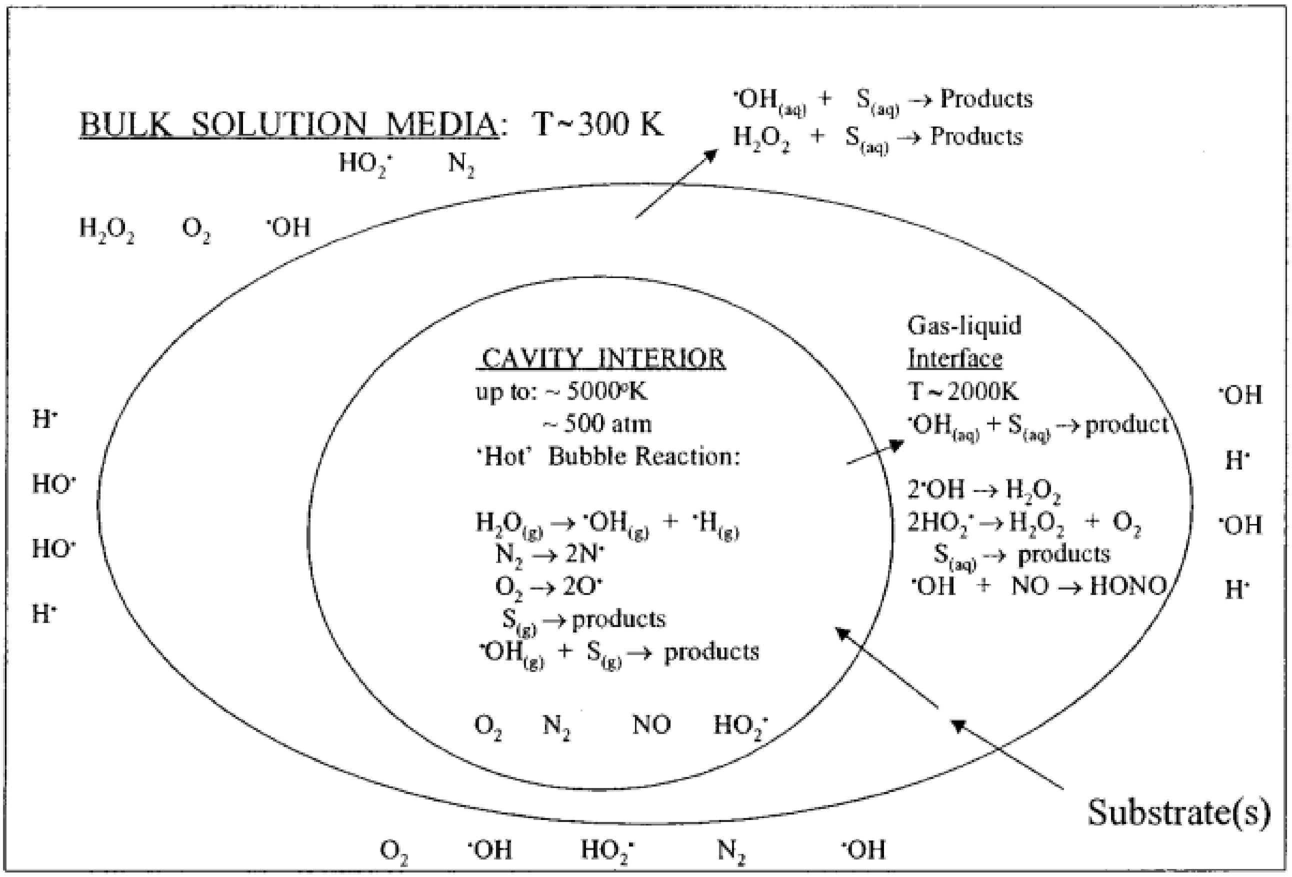


Figure 13. Three zones of cavitation microbubble. [32]

Microwave Irradiation

Microwave irradiation is a well-known method for drying and heating materials and is widely utilized in industry as well as in home kitchen for those purposes. Furthermore, microwave heating has been used by many researchers in chemical synthesis because of its high efficiency, speed and uniform heating. [33]

Nowadays the usage of microwave irradiation as an alternative source for heat is gaining more and more popularity in chemistry. Almost every modern organic and pharmaceutical chemical laboratory is equipped with some kind of microwave synthesizer due to greater reaction speeds attributed to it. These enhanced reaction rates are usually explained by the greater reaction temperatures that are achieved by faster and more thorough heating induced by microwaves and usage of closed and usually pressurized reaction vessels or reactors. The closed reaction vessels allowed replacing high-boiling solvents with, easier to deal with, low-boiling solvents, further simplifying isolation and purification of products. Furthermore, the direct heating of molecules under irradiation by microwaves leads to very fast and homogenous heating, resulting in diminished side reactions, higher yields and cleaner final products. [34]

To better understand the mechanics and principles behind microwave assisted reactions, overview of the history and principles behind this technique will be provided in following sections.

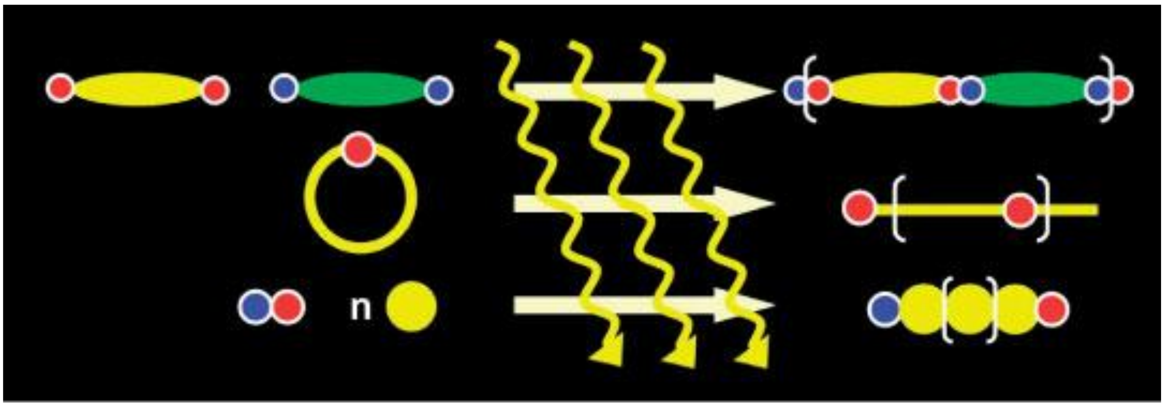


Figure 14. Simplified scheme of possible Microwave-assisted polymerization reactions [34]

History of Microwave-Assisted Synthesis

Nowadays fire is almost never used as a heat source in synthetic chemistry, but that was not the case until 1855 when Robert Bunsen invented the burner which is still known by his last name. The Bunsen burner was a new way to apply energy from the heat source in a focused manner. After that came isomantle, the hot oil bath, hot plate and other ways to apply heat to the chemical reaction. In recent years, microwave energy as a source for heating chemical reaction started growing in popularity and further investigations are performed by scientific community to better understand the processes involved.

Originally microwave energy was applied for heating of food products by Percy Spencer in the 1940s. Since the 1950s, microwaves found multiple application possibilities in chemical and related industries, in particular: food industry, drying and polymer industries. Other possible applications include analytical chemistry, biochemistry and even for specific medical treatments. Surprisingly microwave heating was used for organic synthesis only in the mid-1980s, by the groups of *Gedye et al.* (Figure 15) and *Giguere et al.* in 1986. At those times, reactions were performed in sealed Teflon or glass vessels using simple domestic microwave oven, without any temperature or pressure measurements, which often led to violent explosions due to rapid heating of closed-vessel organic solvents.

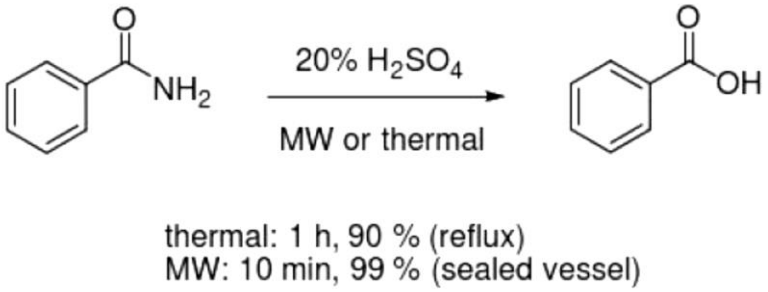


Figure 15. Hydrolysis of benzamide. First published example of microwave-assisted organic synthesis at 1986. [35]

Several groups started to experiment with solvent-free microwave synthesis (so-called dry media reactions) in the 1990s, which distinguished the possibility of explosions. In this method reagents were absorbed onto either a microwave-transparent (silica, clay, etc.) or strongly absorbing (graphite) inorganic media that additionally could be covered with catalyst or other reagents. In the early days this approach was very popular due to possibility of performing solvent-free reactions, which allowed using domestic microwave ovens safely and standard open-vessel technology. Although large number of interesting reactions using "dry media" approach have been performed and published in the literature, there were still issues with non-uniform heating, mixing and determination of precise reaction temperature, specifically when questioning the possibility to scale-up these reactions. [35]

Other option was to carry out reactions using standard organic solvents in open vessels. Under atmospheric pressure in an open vessel, the boiling point of the solvent usually limits the achievable reaction temperature. To reach higher reaction rates and temperatures, high-boiling microwave suitable solvents were used in an open-vessel microwave reaction, which led to more problems regarding product recovery and solvent recycling possibilities. [35]

Recent availability of modern microwave reactors, which provided online monitoring of temperature and pressure in sealed off vessels with standard solvents, succeeded in bringing back popularity to this method. This can be seen in Figure 4, where it is obvious that since 2001 popularity in microwave-assisted organic synthesis is on the rise. According to the authors of [35], out of the approximately 1000 original publications in 2010, that 90% of the time sealed-vessels processing (autoclave technology) in dedicated microwave instruments were used. Furthermore, the practice of using domestic microwave ovens in the experiments is currently banned by most of the respected scientific journals today.

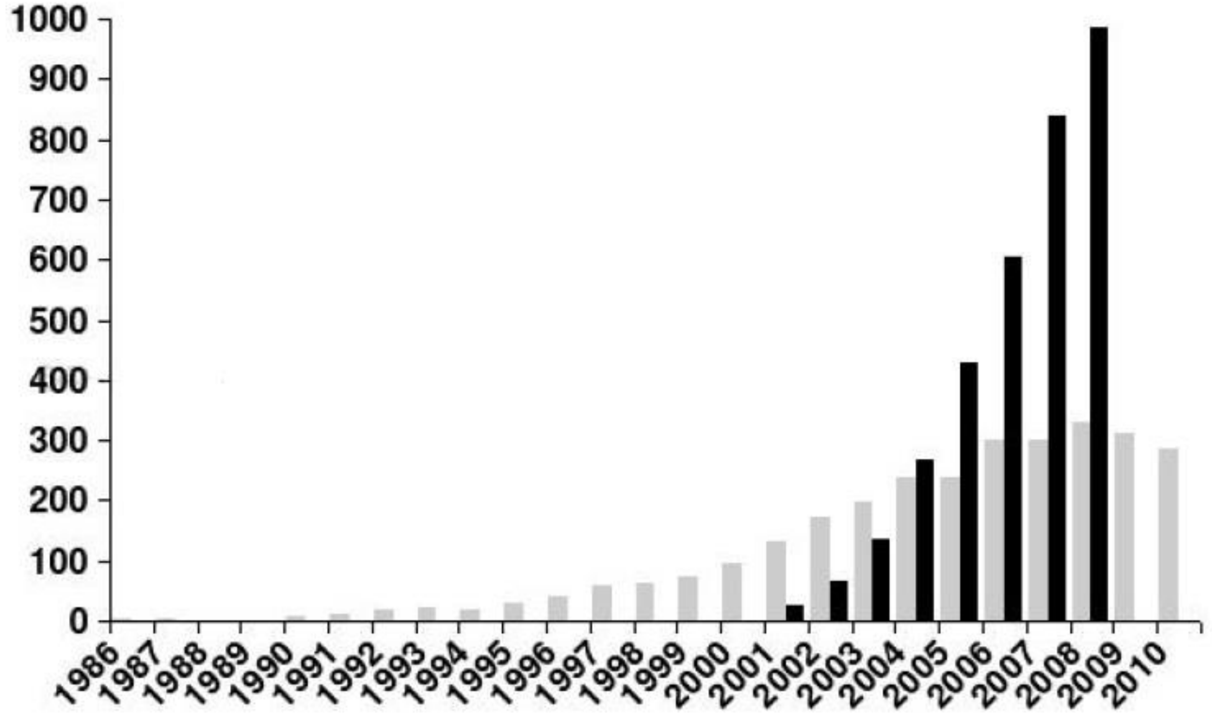


Figure 16. Publications on microwave-assisted organic synthesis. Grey graphs: numbers of articles in seven selected synthetic organic chemistry journals (Journal of Organic Chemistry, Organic Letters, Tetrahedron, Tetrahedron Letters, Synthetic Communications, Synthesis, and Synlett). Black graphs: the number of publications in dedicated reactors with adequate process control. [35]

The initially slow rise in the interest in the microwave technology in the late 1980s and 1990s has been attributed to its lack of controllability and reproducibility. Adding that general knowledge of microwave heating was not yet understood as well as it is now, coupled with the risks of flammable organic solvents, lack of dedicated microwave reactors possible of controlling temperature and pressure were all major concerns, repulsing scientists from this technique. [35]

Rate accelerations and sometimes different products distribution compared to oil bath experiments observed in the early days led to speculations on the existence of “specific” and “non-thermal” effects, only linked to microwaves. These theories were dismissed and currently majority of scientific community agrees that observed rate enhancement is a purely thermal/kinetic effect, achieved by high reaction temperatures that can be rapidly reached by irradiating polar materials in a microwave field, although the unique nature of the microwave dielectric heating mechanism and effects caused by it still need to be considered. Microwave synthesis as a synthesis method has matured and moved on from just being a laboratory curiosity to a well-established tool in both academia and industry. [35]

Microwave Radiation

A microwave is an electromagnetic wave with a frequency between 300 MHz and 3 THz and therefore it lies between infrared and radio wave frequencies. It is used for various purposes like communication, remote sensing, spectroscopy, power transmittance and heating. The frequency which is used for microwave heating reactors, including "domestic" kitchen microwaves, is 2.45 GHz (corresponds to wavelength of 12.25 cm), there can be other frequencies used for microwave heating in specific industries, but chemical syntheses are usually performed at 2.45 GHz frequency. Frequency range for microwave heating is limited so it would not interfere with any of the communication systems and wireless networks. [36]

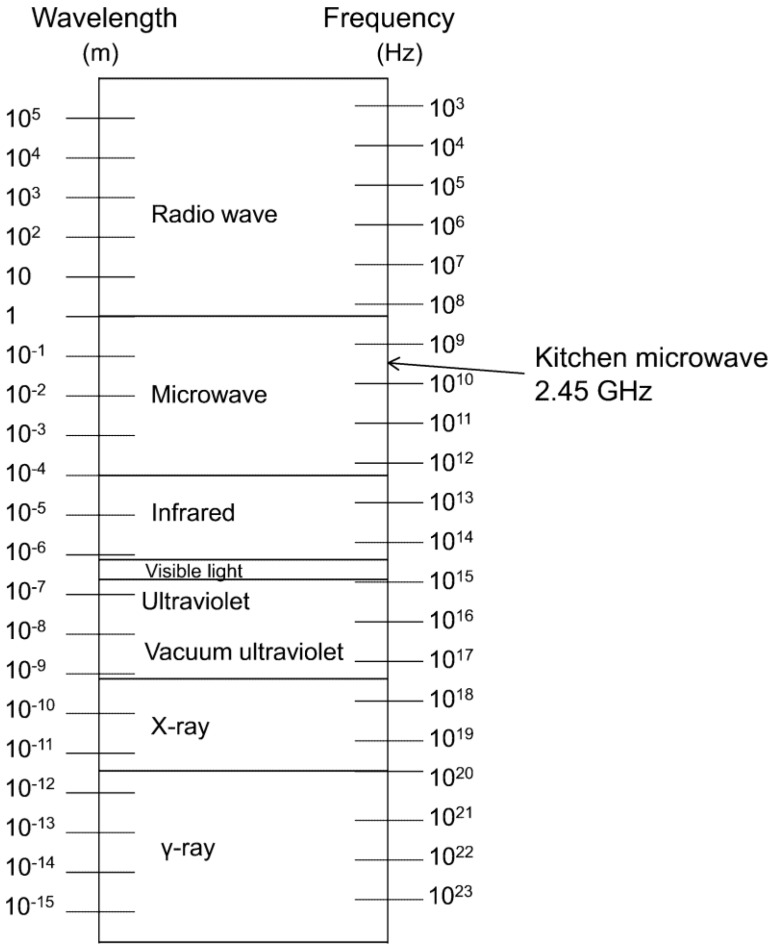
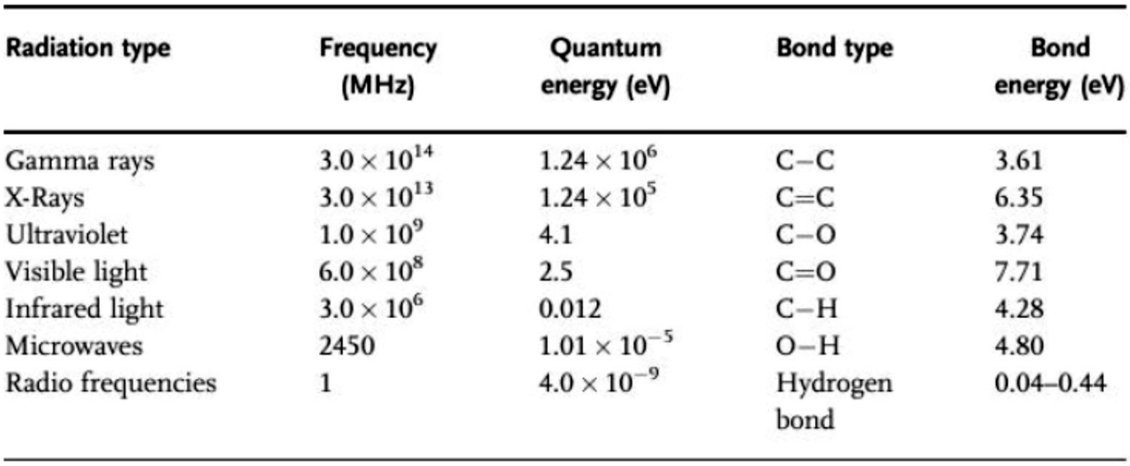


Figure 17. Wavelength and frequency of the Electromagnetic Field [36]

Energy which is carried by microwave photon at a most commonly used 2.45 GHz frequency is equal to about 10^{-5} eV, which is too low to cleave any molecular bonds. According to the data in Table 1, it is clear that microwaves itself cannot induce chemical reaction by pure absorption as the energy carried by the microwave photon is too low, opposed to the energy amounts of Visible and Ultraviolet radiation. [35]

Table 4. . Comparison of Radiation types and Bond energies [35]



Radiation type	Frequency (MHz)	Quantum energy (eV)	Bond type	Bond energy (eV)
Gamma rays	3.0×10^{14}	1.24×10^{6}	C–C	3.61
X-Rays	3.0×10^{13}	1.24×10^{5}	C=C	6.35
Ultraviolet	1.0×10^{9}	4.1	C–O	3.74
Visible light	6.0×10^{8}	2.5	C=O	7.71
Infrared light	3.0×10^{6}	0.012	C–H	4.28
Microwaves	2450	1.01×10^{-5}	O–H	4.80
Radio frequencies	1	4.0×10^{-9}	Hydrogen bond	0.04–0.44

To better understand how microwave radiation works, it is necessary to apprehend the effects of microwaves on the molecules and how it interacts with each other.

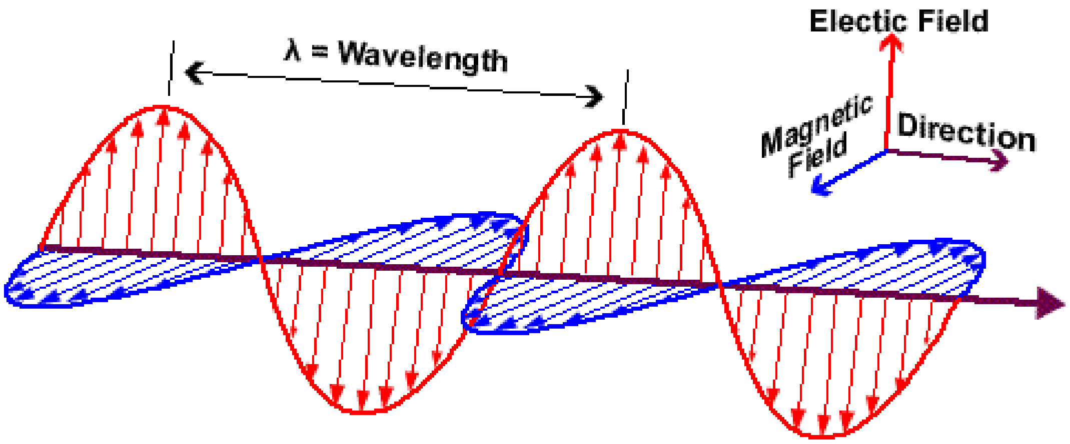


Figure 18. Diagram of Electromagnetic wave [37]

Microwave Dielectric Heating

Microwave chemistry is based on the efficient heating of materials by “microwave dielectric heating” effects, which depends on the specific material ability to absorb microwave energy and converting it into heat. As concluded before, microwaves are electromagnetic waves, which are composed of electric and magnetic field components (Figure 18), where electric component is of greater importance for wave-material interactions. Heating by the electric component of an electromagnetic field is caused by two main mechanisms: dipolar polarization and ionic conduction.

The dipolar polarization mechanism is the electric field components interaction with the materials matrix. It is necessary for a substance to possess a dipole moment to be capable to generate heat when irradiated by microwaves. As the sample is exposed to microwaves, the dipoles of the material align with the applied alternating electric field and start to oscillate to match the frequency of the electric field thus losing energy in the form of heat from dielectric loss and molecular friction (Figure 6a). Ability of the matrix to align itself with the frequency of the applied electric field is directly linked to the amount of the heat generated in the process. [35]

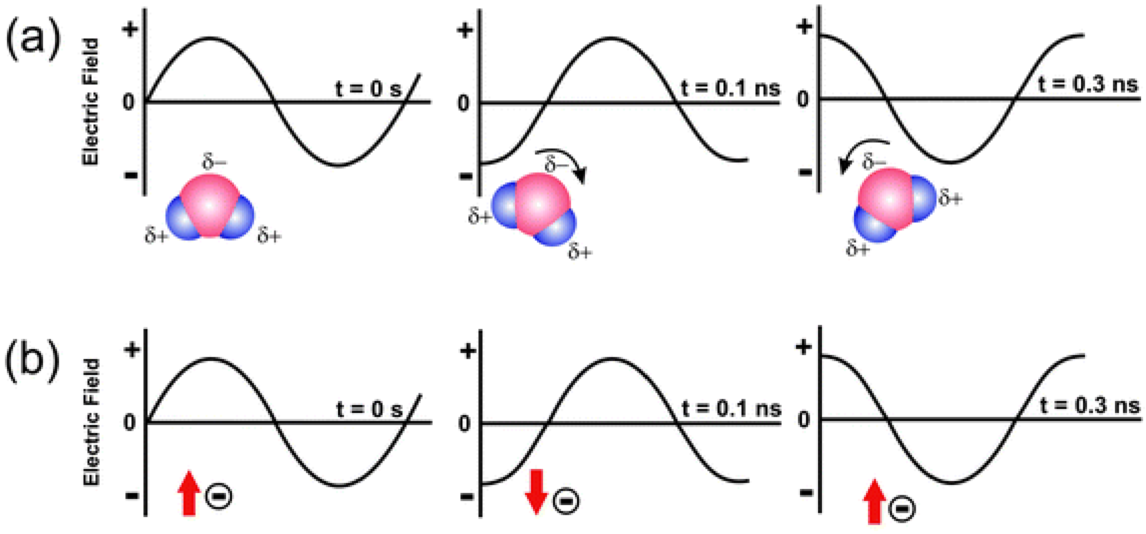


Figure 19. Graphic representation of (a) Dipolar polymerization and (b) Ionic conduction mechanisms. [38]

No heating will occur if the dipole does not have enough time to realign or if it realigns too quickly with the applied electric field, respectively if the irradiation frequency is too high or too low. Thus the dedicated frequency of 2.45 GHz, used for microwave heating, lies between these two extremes giving the molecular dipole time to align itself in the field but not follow the oscillating electric field precisely. Therefore, the dipole is not capable of aligning itself to electric field generating a phase difference between the two, thus causing energy to be lost in the process due to molecular friction and collisions which leads to dielectric heating. To summarize, electric field energy is transferred to the medium, where it is converted into kinetic or thermal energy and finally into heat. It should be noted that the energy transfer is not a property of specific molecule but a result of a collective phenomenon involving the bulk and the heat is produced by frictional forces between the microwave irradiated polar molecules. Due to this, some limitations exist for microwave heating. Gases cannot be heated under microwaves, because distance between the rotating molecules is just too big, where, for example, ice is also nearly microwave transparent, because water molecules are bound by the crystal lattice and the dipoles cannot move as freely as in the liquid state. [35]

The ionic conduction mechanism is the second major heating mechanism caused by microwave irradiation. During this phenomenon, dissolved charged particles in a sample (usually ions) start to oscillate under the influence of the microwaves (Figure 19b), thus leading to the multiple collisions between neighboring particles in the sample. Colliding particles create agitation or motion in the sample, leading to heating of the bulk. For example, if two equal amounts of water are taken, one of distilled water and another one of the water from the tap, and both samples are put under the same fixated power of microwave irradiation, the tap water sample will heat more rapidly due to its ionic content. The ionic conductivity mechanism has much stronger heating effect than that of the dipolar rotation mechanism, naturally with regard to the samples heat-generating capacity. [35]

Dielectric properties

The behavior of a specific material and the heating characteristics of it under microwave irradiation depend on the dielectric properties of the material. The loss tangent, tan δ, determines the ability of specific material to convert electromagnetic energy into heat at a specified frequency and temperature. The loss factor can be expressed as:

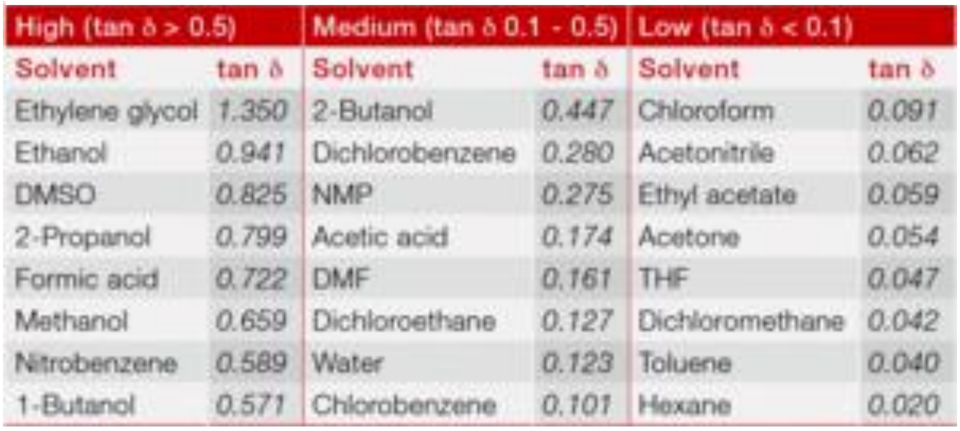
$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Where ε'' is the dielectric loss, describing the efficiency of electromagnetic radiation being converted to heat, and ε' is the dielectric constant, which describes the polarizability of molecules in the electric field. To get efficient absorption of microwaves leading to rapid heating, a reaction medium must have a high tan δ value. Materials with high dielectric constants do not necessarily have high tan δ values, for example, by comparing water (ε' = 80.4 at 25°C) and ethanol (ε' = 24.3 at 25°C) primary assumption could be made that water would heat up faster, but when the loss tangents of both materials are compared (water = 0.123, ethanol = 0.941) it is obvious that ethanol will heat up much more rapidly than water under the microwave irradiation due to higher loss tangent value. Generally, solvents can be classified in three categories according to their loss tangent values:

- High microwave-absorbing – tan δ values > 0.5
- Medium microwave-absorbing – tan δ values $0.1 - 0.5$
- Low microwave-absorbing – tan δ values < 0.1

Commonly used solvents without a permanent dipole moment, like benzene, carbon tetrachloride and so on, are pretty much microwave transparent. Still, it must be concluded, that if a solvent has a low tan δ value, it does not mean that it is unsuitable for reaction with microwave heating due to presumption that either the substrate or part of the reagents or catalysts are likely to be polar, thus making the whole reaction bulk to be capable of producing sufficient heat from the microwaves. Furthermore, specific additives can be added into the reaction mixture (like polar solvents or ionic liquids) to increase the absorbance level of the medium. A list of some common solvents with their loss tangent values are provided in the table 5. [35]

Table 5. Loss tangent values for commonly used solvents *[39]*



High (tan δ > 0.5)		Medium (tan δ 0.1 - 0.5)		Low (tan δ < 0.1)	
Solvent	tan δ	Solvent	tan δ	Solvent	tan δ
Ethylene glycol	1.350	2-Butanol	0.447	Chloroform	0.091
Ethanol	0.941	Dichlorobenzene	0.280	Acetonitrile	0.062
DMSO	0.825	NMP	0.275	Ethyl acetate	0.059
2-Propanol	0.799	Acetic acid	0.174	Acetone	0.054
Formic acid	0.722	DMF	0.161	THF	0.047
Methanol	0.659	Dichloroethane	0.127	Dichloromethane	0.042
Nitrobenzene	0.589	Water	0.123	Toluene	0.040
1-Butanol	0.571	Chlorobenzene	0.101	Hexane	0.020

As mentioned before, loss tangent values are frequency and temperature dependent. Figure 20 shows the dependence of dielectric properties of water on the frequency and temperature. It can be observed, that loss factor ε'' at 25°C reaches its maximum at around 18 GHz meaning that at that frequency the heating would be most rapid. Nevertheless, as the higher loss factor would mean more intense heating, at the same time that heating would occur only in the outer layers of material due to loss in the penetration depth. The penetration depth is inversely proportional to tan δ thus meaning that materials with high tan δ values also have low values of penetration depth and microwave irradiation could be absorbed within the exterior of the material. By using 2.45 GHz frequency for heating, deeper penetration depth is achieved thus leading to more thorough heating of whole material. [35]

These aspects are especially important when considering large scale experiments or industrial application of the process. If, for example, water is used as the solvent (at 25°C and 2.45 GHz tan δ = 0.123) its penetration depth is only on the order of few centimeters, thus in large scale experiments it could mean that the inner part of the reaction mixture would be heated only by conventional heat convection and conduction mechanisms. [35]

Figure 20 also illustrates that increase in temperature would mean decrease in the dielectric properties for water as it is true for most other organic solvents. In other words, higher temperatures would mean lower absorption of microwave radiation thus slower heating. In perspective it would be much easier to reach 100°C for water at 2.45 GHz than raise the temperature further to 200°C in the sealed vessel as the water becomes more and more microwave transparent as its temperature increases, although some materials can behave differently and become better microwave absorbers as the temperature increases. That is true for some inorganic and polymeric materials and can lead to thermal runaway [41]. Another situation which is worth mentioning would be ionic liquids, which are heated by the ionic conduction mechanism rather than by dipolar polarization thus increase in temperature for ionic liquid can lead to a dramatic increase in the dielectric loss ε'' and should be taken into account. [35]

In summary, the microwave irradiation interaction with matter can be characterized by three different processes: absorption, transmission and reflection. It should be taken into account when planning a reaction by microwave irradiation, same as the dielectric properties of the materials used. Highly dielectric materials provide a strong absorption of microwaves thus leading to a rapid heating of the medium, while materials with lower dielectric properties have weak absorption and high depth penetration values for process and can be used as construction materials for reactors or just as additives to increase the depth of penetration for reaction medium. All these aspects should be taken into account when considering reactions by microwave irradiation. [35]

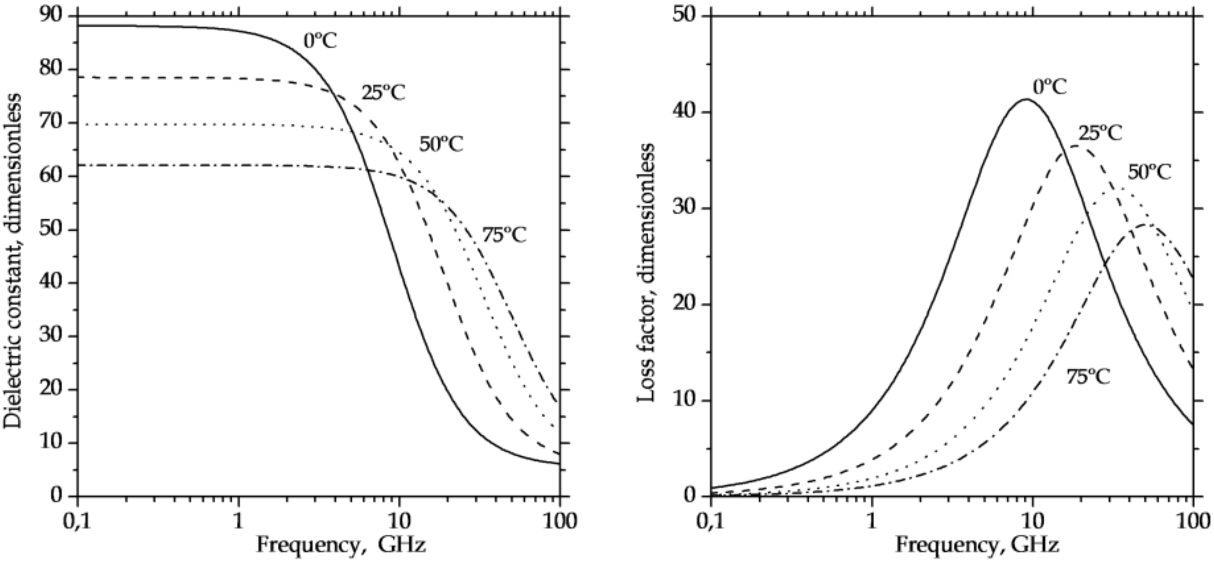


Figure 20. Dielectric properties of water dependence on frequency and temperature. *[40]*

Microwave Heating against Thermal Heating

Conventional thermal heating by external heat source, like an oil bath, is a traditional method to perform organic synthesis, but it is comparatively slow and inefficient due to convection currents and thermal conductivity of different materials that must be penetrated. In general, it leads to overheated reaction vessel while the reaction mixture's temperature will stay lower. When it is necessary to perform reaction under reflux conditions, it usually leads to keeping the temperature of heating source at around 10 – 30 °C higher than the boiling point just to ensure an efficient reflux of reaction mixture. This can lead to temperature gradient within the mixture which can result in decomposition of product, substrate or reagent. [35]

By comparison, irradiation by microwaves produces efficient internal heating by direct interactions with the molecules present in reaction mixture. Therefore, microwave irradiation raises the temperature of the whole volume at the same time, while conventional heating would first lead to heating of only the reaction mixture which is in contact with reaction vessel wall. It is illustrated in Figure 21.

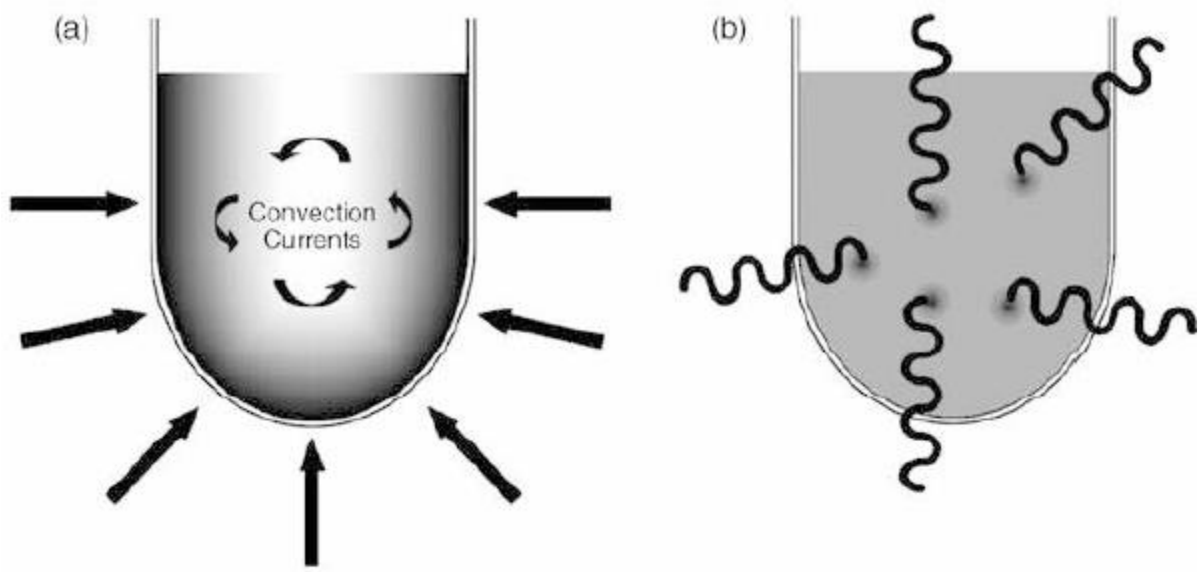


Figure 21. Comparison of Conventional Thermal Heating (a) and Microwave Heating (b) [35]

Reaction vessels used in modern microwave reactors are usually made out of nearly microwave transparent materials like quartz, Teflon or borosilicate glass. Radiation passes through the walls of these vessels and could result in an inverted temperature gradient, compared to the one of conventional heating. Although in modern reactors with well-designed microwave cavities the increase of the temperature will be uniform throughout the sample. Furthermore, some other specific microwave effects could be observed in reaction due to principles of this process, but in most cases it could be attributed to thermal/kinetic effects induced by rapidly raising temperature of polar ingredients/mixtures by microwave irradiation in closed-vessel conditions. [35]

In conclusion, it is very difficult to compare convectional thermal heating and microwave dielectric heating as they are totally different processes, but as the microwave irradiation could be a faster and easier way to achieve required products it was chosen as the process of interest for this project.

Raman Spectroscopy

Raman spectroscopy was chosen as the analytical method for this project. As Raman spectroscopy is part of the vibrational spectroscopy, the concepts behind this method should be understood.

Vibrational Spectroscopy

The nature of the spectra in molecular spectroscopy is the absorption, emission or scattering of a photon when there is presence of changes in the energy of the molecule. These changes can correspond to electronic transitions and/or changes in vibrational and rotational states of molecules. Every molecule absorbs characteristic frequencies that specifies their structure thus resulting in complex spectra. From these spectra, it is possible to obtain information about the molecule, like bond length, angle and strength of the bond. These particular changes can be observed in the region of IR electromagnetic radiation, where Raman spectroscopy is used. [42]

It was observed experimentally that intensity (I) depends on the length of the sample (L) and the molar concentration (C) of the absorbing component. Out of these observations following equation was derived which is known as Beer-Lambert law:

$$I = I_0 10^{-\varepsilon CL}$$

Where I_0 is the original intensity of the radiation and ε is the extinction (molar absorption) coefficient that depends on the frequency of radiation and reaches greatest value where absorption is most intense. The dimensions of this coefficient are 1/(concentration*length), meaning that it corresponds to the property that longer and more concentrated samples will absorb more of the specific radiation passing through the sample. [42]

Terms of transmittance (T) and absorbance (A) are more commonly used to describe the spectral characteristics of samples and they are expressed as:

$$T = \frac{I}{I_0}$$

$$A = \log \frac{I_0}{I}$$

These two properties are related to each other and can be written as:

$$A = -\log T$$

In accordance to this, Beer-Lambert law then can be expressed as:

$$A = \varepsilon C L$$

Where the right side of the equation, εCL, was known as the optical density of the sample. [42]

Different spectroscopic techniques result in different spectra, which then need to be interpreted in order to understand the meaning of it. In vibrational spectroscopy the appearance of spectrum depends on the possible vibrational modes of the molecule. Simple diatomic molecules have only one mode of vibration – bond stretching. Although, more complex polyatomic molecules have several vibrational modes as all the bonds in the molecule can change their length, due to stretching, and their angle, due to rocking, thus resulting in the complex vibrational spectra. [42]

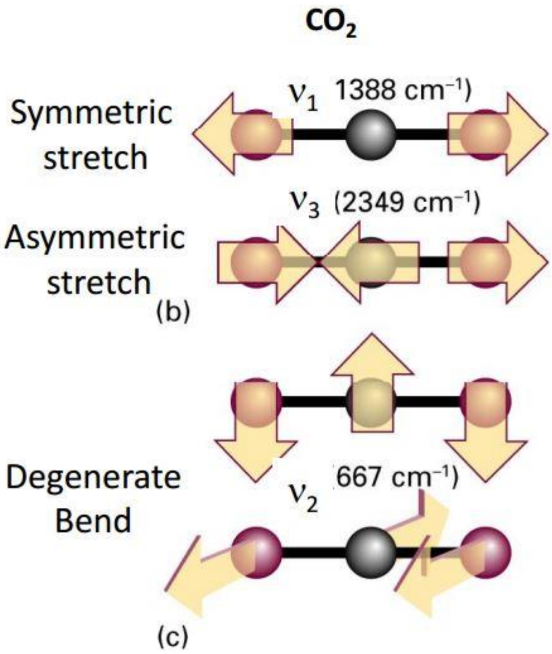


Figure 22. Possible vibrational modes of CO2 molecule. [43]

In order to calculate the all possible vibrational modes in the molecule a simple formula can be used,

$$3N - 6 = X$$

where N is the number of atoms in the specific molecule and X is independent modes of vibration for the molecule. For linear molecules, 6 should be exchanged for 5 in this equation.

In order to see these changes in Raman spectra, the change in molecules polarizability should occur. In other words, there must be changes of the electron distribution in the molecule from the illumination source. [42]

Principles of Raman spectrum

Raman spectrum shows photons which get inelastically scattered during the light-sample interaction. This phenomenon is called the Raman effect and was discovered in 1922 by Sir Chandrasekhara Raman.

In Raman spectroscopy photons of single wavelength are focused onto a sample, in current times it is performed by a laser as a strong monochromatic light source. As mentioned before, photons can get absorbed, transmitted or scattered, and the later ones are the ones of interest in Raman spectroscopy. As photons interact with the molecules they are most commonly scattered elastically and have the same wavelength as the incident light. This process is called Rayleigh scattering. Although, very small amount of photons scatter inelastically, meaning that the wavelength at which they are scattered is shifted either lower or higher. This means that photon lost or gained energy and it is known as Stokes Raman shift or anti-Stokes Raman shift respectively and is illustrated in Figure 23. The specific change in energy is directly related to the functional group, structure of the molecule to which this group is attached, types of atoms in the molecule and the surrounding environment. Not all molecules and/or functional groups exhibit Raman scattering, as different factors like the polarization state of the molecule must be considered. [44]

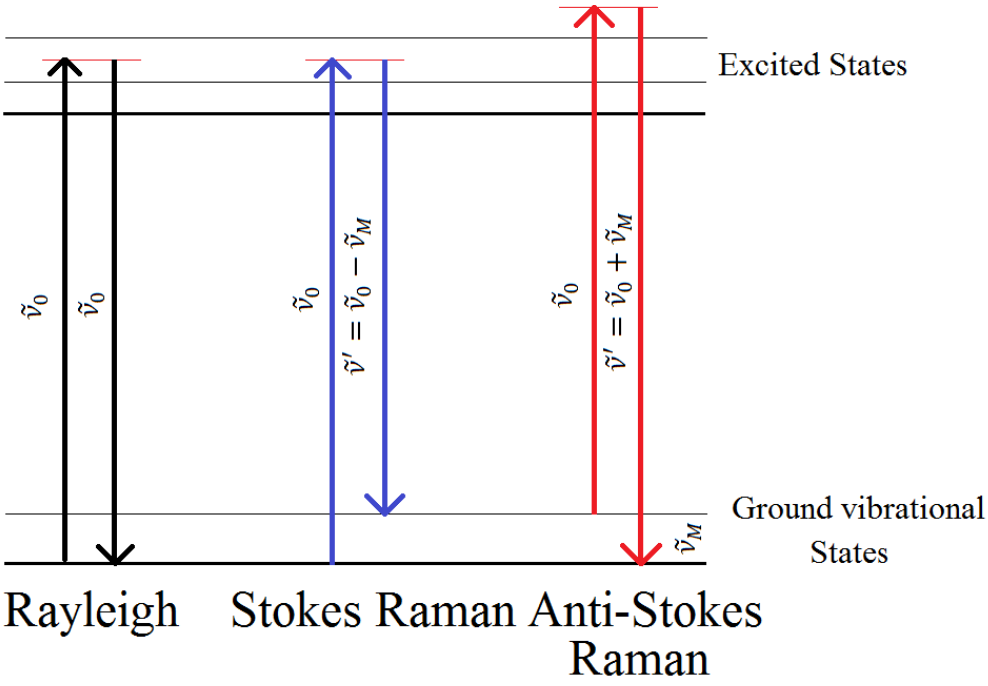


Figure 23. Representation of an energy transfer during Rayleigh, Stokes Raman and anti-Stokes Raman scattering. [45]

Raman spectroscopy provides a characteristic spectrum which allows to specify the structure of the sample and identify the compound due to the fingerprint region in the spectrum, which for organic molecules is in the wavenumber range of 1500-500 cm^{-1}. However, to be able to compare and identify changes that occur between samples data needs to be preprocessed and normalized. Methods used for that will be described in following section.

Preprocessing

In order to obtain comparable results and to extract all the information from the data, it needs to be correctly preprocessed. Choosing correct methods makes a huge difference as it allows accurate interpretation of the data without making false presumptions. To deal with the spectral data it is important to clear noisy parts and normalize it in order to be able to compare the results. For this project It was chosen to use baseline correction by asymmetric least squares (ALS) as baseline problems are common problem when dealing with Raman spectroscopy, and mean centering (MC) to normalize the data for comparison and before subjecting to principal component analysis (PCA).

Asymmetric least squares for baseline correction

Raman spectroscopy usually suffers from baseline problems due to fluorescence effects. If it is not dealt with, fluorescence can create an uneven baseline for the Raman spectra that can hide some of the features of the spectra and will provide false information during the PCA, as the slope of the spectra will be considered as relative information.

Asymmetric Least Squares will be used to deal with the baseline issues. ALS incorporates smoothening and weighting of the data points in order to compensate for the slope of the baseline. Adjustment of two parameters, smoothening and penalty, allows to estimate the correction of the baseline for every spectrum which then is subtracted from the raw data. Primary assumption of the correction parameters will need to be made and they will be applied to all of the samples in order to normalize the baseline and keep the data comparable. This method works well for analytical techniques that result in narrow, characteristic peaks in the spectra, like Raman and IR spectroscopies, chromatography etc [46].

As this method performs particularly well with Raman spectroscopy data, it was chosen to be used in this project.

Mean Centering

This method is relatively straightforward approach to treat the data before subjecting it to PCA. It involves subtracting column mean from the variables, and can be written as:

$$x_{MC;ij} = x_{ij} - \overline{x_j}$$

Where x_{ij} are variables in column j, and $\overline{x_j}$ is the mean value of the column. This allows to translate the collection of data to the origin of the multivariate space where analysis will be performed. It should help revealing more important information during the PCA. [47]

Principal Component Analysis

Principal component analysis is the most basic method to multivariate data analysis. It works by decomposing the original data matrix into "structure" or important information, and "noise" part that is considered unnecessary. New axis is being drawn in the direction of maximum variance, that are called Principal Component (PC). Every additional PC is drawn in the direction which allows capturing the most of data variance and every PC is orthogonal. Data points are then projected to the PCs and are being represented by vectors, known as scores. Any data variance that is not captured by these projections is considered as unnecessary or just noise, which is not important for following analysis. [48]

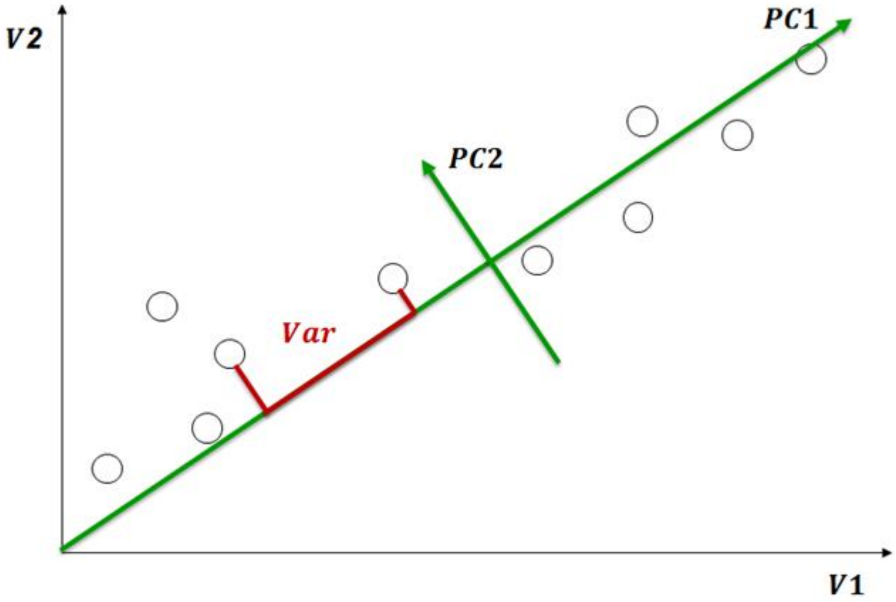


Figure 24. Example of PCs drawn for achieved data. [49]

After applying the PCA, the original data X is expressed in the variable space through the following equation:

$$X = TP^T + E$$

Where, X – original data, T – data projections on variable space, or scores, P^T – unit vectors showing the direction of PCs, or transposed loadings. The variance of the original data which is explained by the PC model is called the explained variance and is described as TP^T. The variance from the original data which is considered as unnecessary for the model is called the residual variance, or noise, and is expressed as E. [48]

The advantage of PCA is that it allows to analyse complex multivariate data just by looking at several plots. The cumulative variance plot (Figure 25) shows how much data is captured by the specified number of PCs by the model and allows to check how many PCs are needed to achieve required coverage of the data.

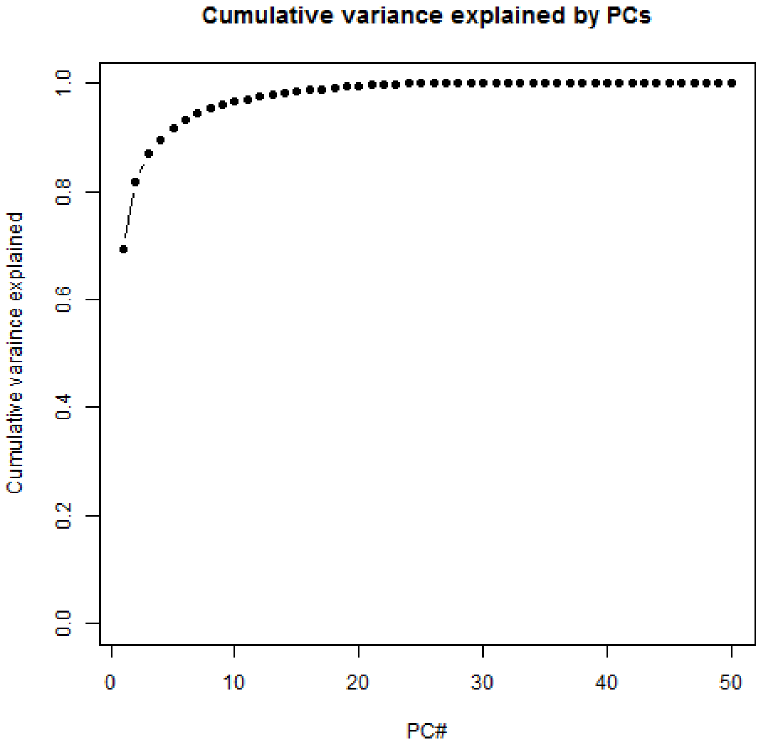


Figure 25. Cumulative variance plot [50]

The scores plot (Figure 26) corresponds to the projections of the samples on the PC space. It is used to find the relations between the data points and potential groupings or trends that data follows.

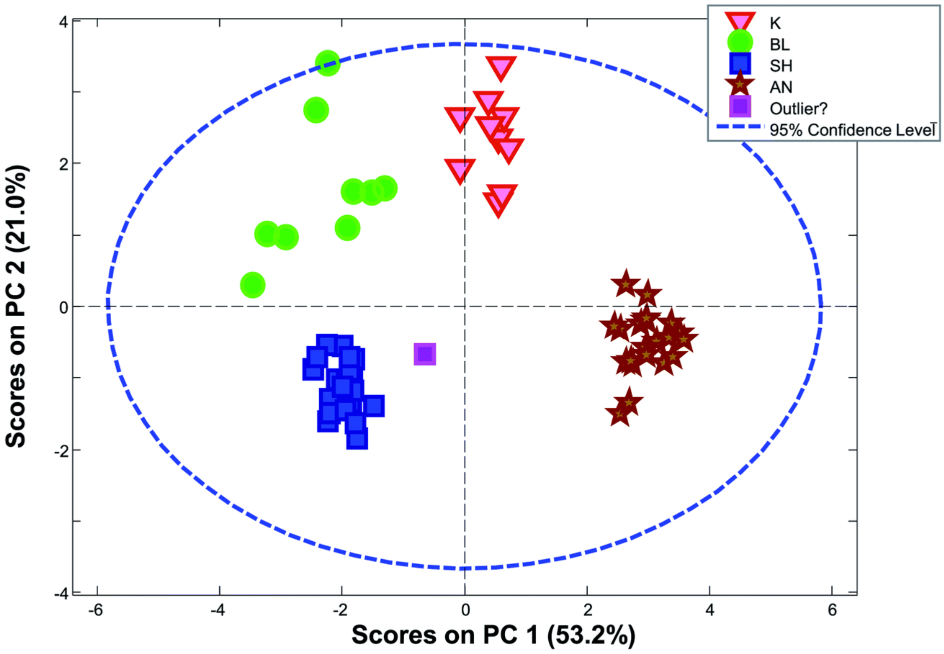


Figure 26. The scores plot [51]

The residuals plot (Figure 27) is made by projecting T^2, the explained variance that shows how far from the origin of coordinates the projection is, against Q, the residual variance showing how far the original point is from the projection. This plot allows to see how well the data is covered by the model and detect outliers (large Q values) and extreme samples (large T^2 values).

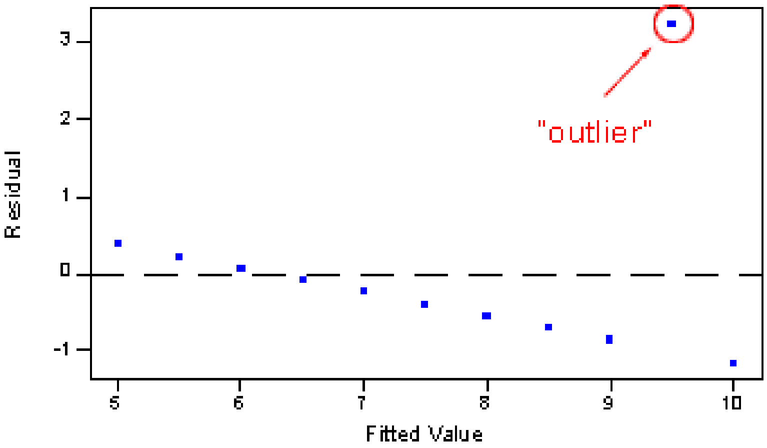


Figure 27. The Residuals plot [52]

The loadings plot (Figure 28) shows contribution of each variable to each PC and also relationship between the variables. This plot is useful for detecting variables that are considered as the most important for the model.

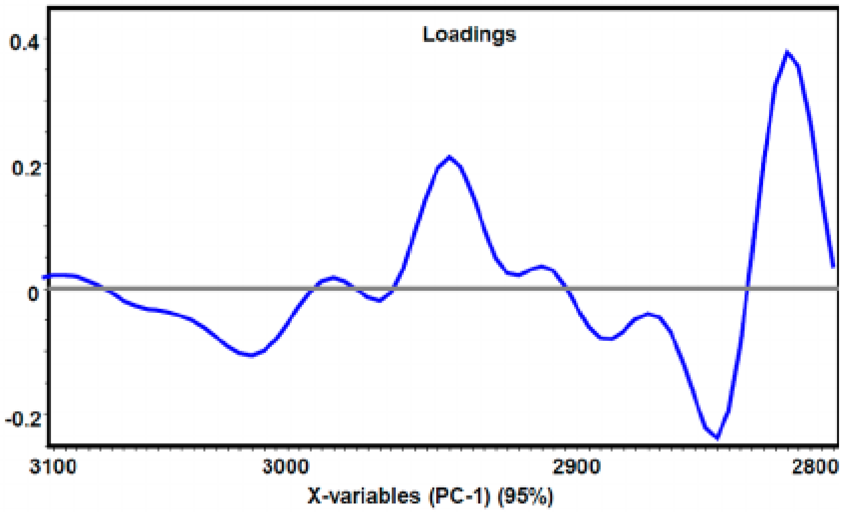


Figure 28. The Loadings plot [53]

PCA often allows to uncover the hidden factors and correlation in multivariate data by the usage of newly created variables PCs. It is capable of capturing the bigger and usually more important part of the variance thus revealing the important information. [48]

By using PCA in this project, it is expected to see the variation in the spectra during the reactions and possibly uncover the "important peaks" that could accurately describe progression of the reaction.

Synthesis of Polylactic Acid in Literature

As it was already mentioned in the section of this project covering PLA, there are several ways to obtain PLA through different methods. In order to create an experimental set-up that could suit this project, several sources will be investigated, which should provide assistance on deciding the initial conditions for experimental setup. In this section, only key elements leading to specific experimental decisions will be provided. For full overview of the experiments performed by mentioned authors please refer to Appendix 1.

An extensive study on the influence of catalyst concentration, polymerization time and temperature on the yield, molecular weight and optical rotation during polycondesation and ROP was performed by the authors of [54].

Catalyst influence for the conversion and resulting molecular weight was investigated for reactions performed at 130 °C for 72 h. The resulting graph is provided in Figure 29. Authors made a conclusion that best results were obtained when 0.05 wt% of stannous octoate was used, as that particular concentration of catalyst led to highest molecular weight and conversion rate. It was assessed that higher concentrations of catalyst result in smaller molecular weight, which is typical for addition polymerization reactions. [54]

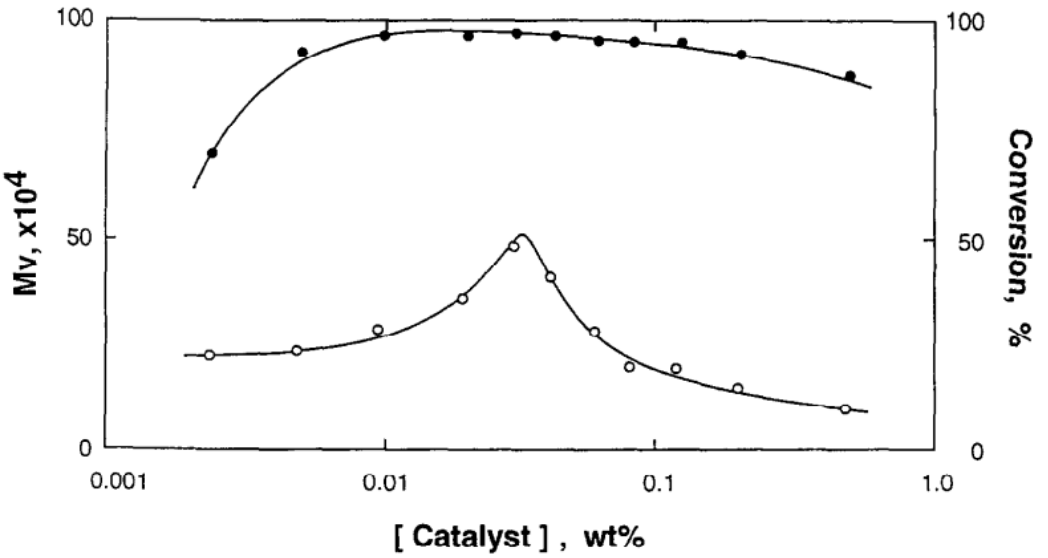


Figure 29. Influence of catalyst concentration for molecular weight and conversion of PLA. ● – Conversion, ○ – Molecular weight. [54]

After observation by the authors of [54] and reviewing other works, it was decided to use 0.1 weight % of catalyst in this project's experimental part. Although, the 0.05 % should result in higher molecular weight, but as the molecular weight will not be measured in this work, it was exchanged for increased initial catalyst concentration to achieve higher reaction rate in the experiments. Furthermore, it was obvious that the choice of Stannous Octoate was correct, as most of the authors tend to use it with successful results.

In order to choose optimal conditions for the microwave induced reaction, works by authors of [55, 56, 57] showed that optimal output of the microwave should be in the region of 150 – 250 W. It was proven by [55, 57] that higher power outputs lead to destruction of polymer chains even after 5 min of reaction. Furthermore, conversion of >90 % can be achieved after 15 min at relatively low 170 W output [57]. Thus it was decided to run the microwave experiment for only 20 min as further irradiation could lead to destruction of polymer.

Initial conditions for preparation of lactic acid for following experiments was chosen to be 180 °C under vacuum. As the results of authors of [18, 58, 54] suggest, these conditions should allow full removal of water from the lactic acid and would result in slight oligomerization, which would be preferable before starting following experiments with ultrasound and microwaves, as it should increase the probability of successfully achieving high conversion rate of the polymer.

Conditions and equipment used in the experiments will be provided in greater detail in the following section of this project.

EXPERIMENTS AND RESULTS

Experimental Set-up

Considering observations and results of authors mentioned before, experimental set-up was created. L-Lactic acid was put through partial polycondensation under vacuum and high temperature, thus leading to a mixture of dehydrated lactic acid and oligomerization products. This mixture, considered as prepolymer, was used as a primary reagent for following experiments, using ultrasound and microwaves. Visual representation of experimental plan can be seen in figure 30.

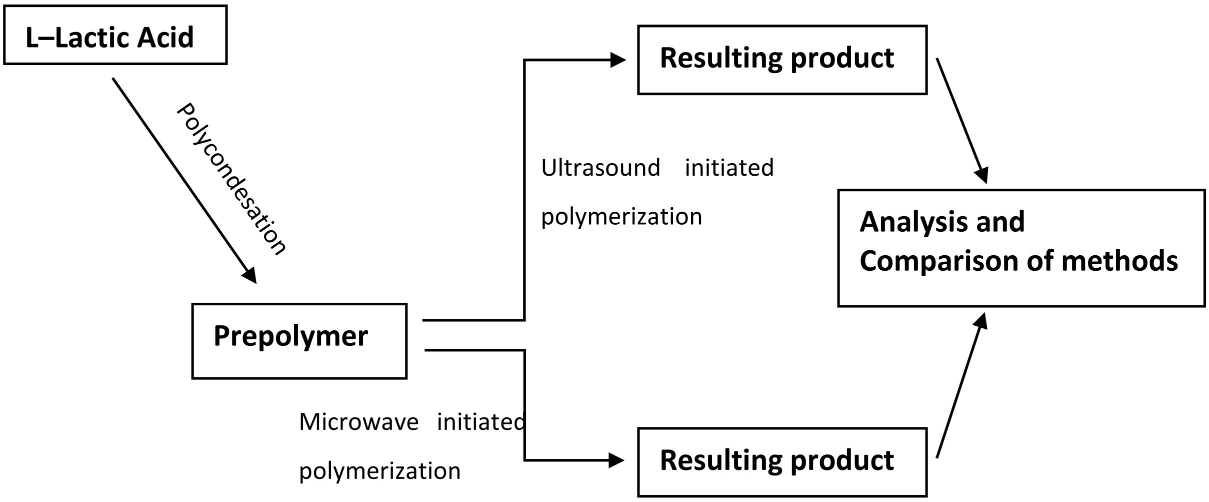


Figure 30. Graphic representation of Experimental plan.

Polycondesation

200 mL of L-lactic acid ($C_3H_6O_3$, 80%, Sigma-Aldrich Co. LLC, USA) was added to a round bottom flask, equipped with a thermometer, then connected to a water-cooled condenser and a 50 mL round bottom flask which was used as a collector for distillate. Oil bath, used for temperature control, was put on a heating plate with magnetic stirring RH basic 2 (IKA Works GmbH & Co. KG, Germany) and vacuum was applied by using water pump Büchi B-169 (Büchi Labortechnik AG, Switzerland). Oil bath temperature was measured by an immersed thermometer. Experimental set-up can be seen pictured in a Figure 31. Resulting product and distillate were analyzed by Raman spectroscopy, using Kaiser RamanRXN1 Analyzer (Kaiser Optical Systems, Inc. Ann Arbor, MI, USA).

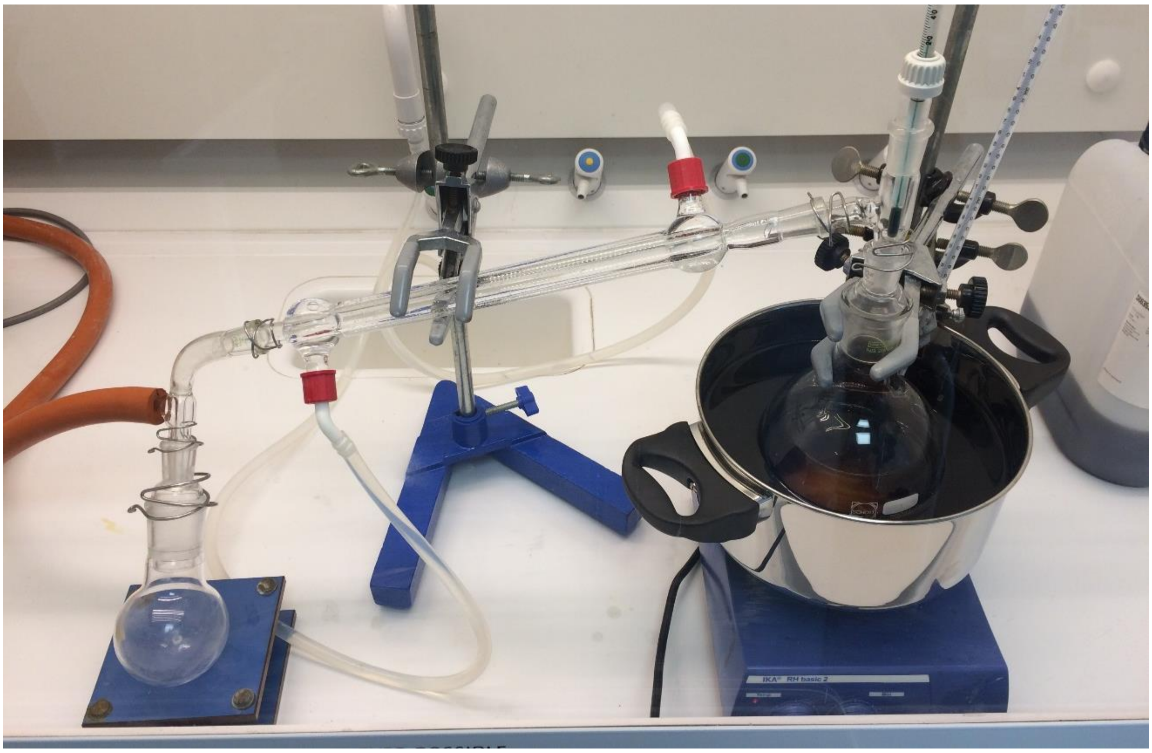


Figure 31. Experimental set-up for polycondeation reaction.

Ultrasound initiated polymerization

The initial experiment of using ultrasound for polymerization was performed in an open beaker (150 mL) with a 60 mL of prepolymer, obtained after polycondensation. Ultrasonic processor Vibra-Cell VCX-750 (Sonics & Materials Inc., USA) was used for the reaction. Ultrasound probe was immersed in the beaker equipped with nitrogen gas inlet and thermocouple. Experiment ran for 4 hours with only prepolymer present, then 10 mL sample was taken, in the remaining 50 mL of prepolymer 0.1 % molar mass of initiator, stannous octoate, was added and reaction ran for 4 more hours. Both samples, before initiator and resulting product, were analyzed with Raman spectroscopy to check the progress of polymerization. Experimental set-up for this reaction can be seen in Figure 32.

Following experiment was run with 50 mL of prepolymer mixed with 0.1 % of stannous octoate for 4 hours without nitrogen inlet and temperature of the reaction was measured in one hour intervals. Raman spectra was taken every 5 min to check on the progression of the reaction until the end of the process.

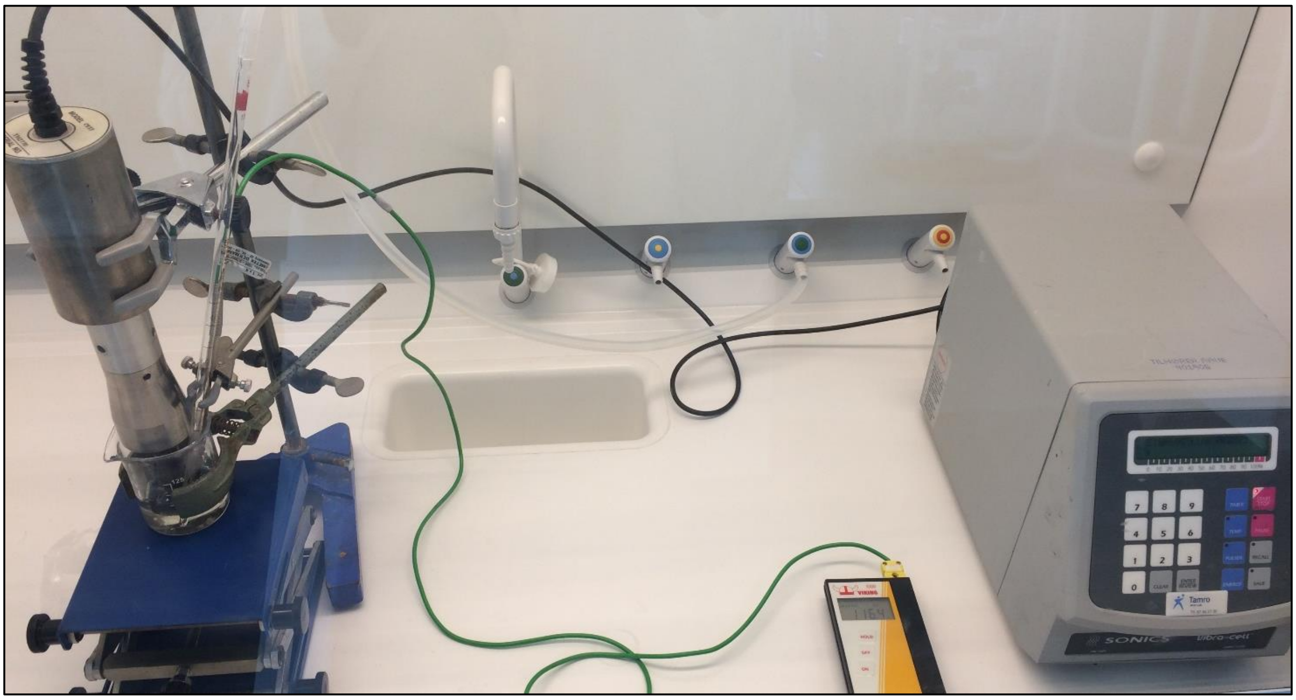


Figure 32. Experimental set-up for Ultrasound initiated polymerization

Microwave initiated polymerization

Microwave reaction was performed in the domestic microwave oven with adjustable power output at 231 W. Closable vials were filled with 5 mL of prepolymer mixed with stannous octoate if applicable. Three concentrations of initiator were tested – 0 %, 0.1 % and 1 % with samples taken at 5 min, 10 min and 20 min mark. Vials were opened just before subjecting them to microwaves to prevent possible pressure build-up and possible explosion. Three vials were put at once inside the empty beaker and removed by one at according times. After the removal of the sample from the oven, the temperature was measured with a thermocouple, vials closed and afterwards subjected to the analysis by Raman. All experiments at every concentration were repeated three times.

Results

Polycondensation

Polycondesation reaction was performed in two days, to achieve expected qualities of the prepolymer. Initially, 160 °C were chosen as the temperature, which was expected to be high enough to remove excess water and initiate oligomerization. Distillation began when oil bath's temperature reached 105 °C and the temperature of the bath was slowly increased to 160 °C. After around 2 hours at 160 °C, distillation drastically slowed down and the reaction was stopped. Reaction vessel was closed from the atmosphere and left overnight. Collected distillate was kept for analysis.

Following day, resulting product was visually inspected and it was observed that viscosity has not increased as much as it was expected, if the water would be totally removed. It was decided to proceed the distillation with a temperature increased to 180 °C, as it should allow further removal of water. The same set-up was used for the reaction. Temperature was gradually increased to 180 °C and after about 2 hours at 180 °C distillation was stopped and the resulting product was left in the closed flask to cool. Distillate was collected and kept for analysis. Resulting prepolymer is pictured in Figure 33.

Resulting product was again visually inspected and obvious increase in viscosity was observed. Due to definite increase in viscosity (solidification), pictured in Figure 4, assumption was made that water was removed from the lactic acid and resulting product was purified lactic acid with the presence of low molecular weight oligomers. Small amount of product was dissolved in dichloromethane and subjected to analysis by Raman spectroscopy together with the distillates from both days.

Following productions of prepolymer, were performed at 180 °C with almost the same set-up and vacuum as used in the initial experiment. For one of the experiments, electronic monometer was connected between reaction vessel and distillation thermometer in order to measure the vacuum achieved by the pump. It was measured that pressure for the reactions was 150 mbar (approximately 112 mmHg). Reaction was kept at the 180 °C for 2 hours or until the distillation would stop being visible. Product flask, as before, was closed and left to cool in a room temperature overnight.

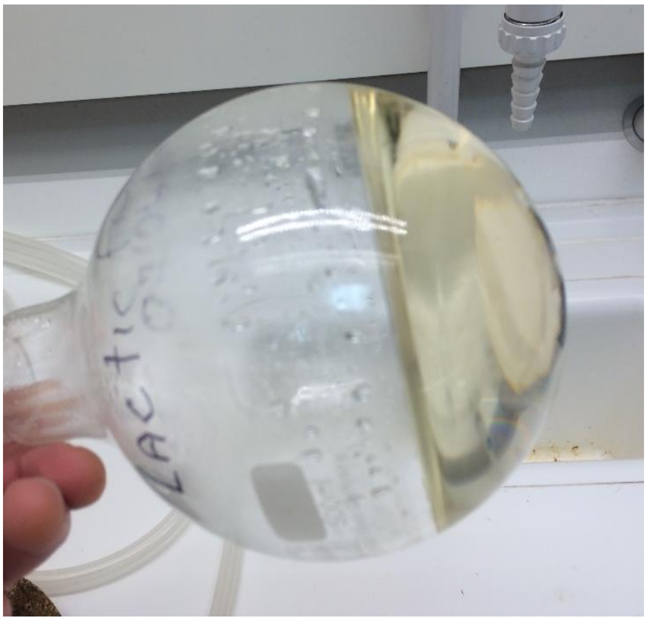


Figure 33. Solidification, observed after 2nd distillation

Prepolymer analysis

Prepolymer, resulting after polycondesation reaction, and collected distillates were subjected to Raman spectroscopy. Distillates were analyzed as received, while small amount of prepolymer was dissolved in dichloromethane before analysis. Resulting spectras are shown in Figure 34.

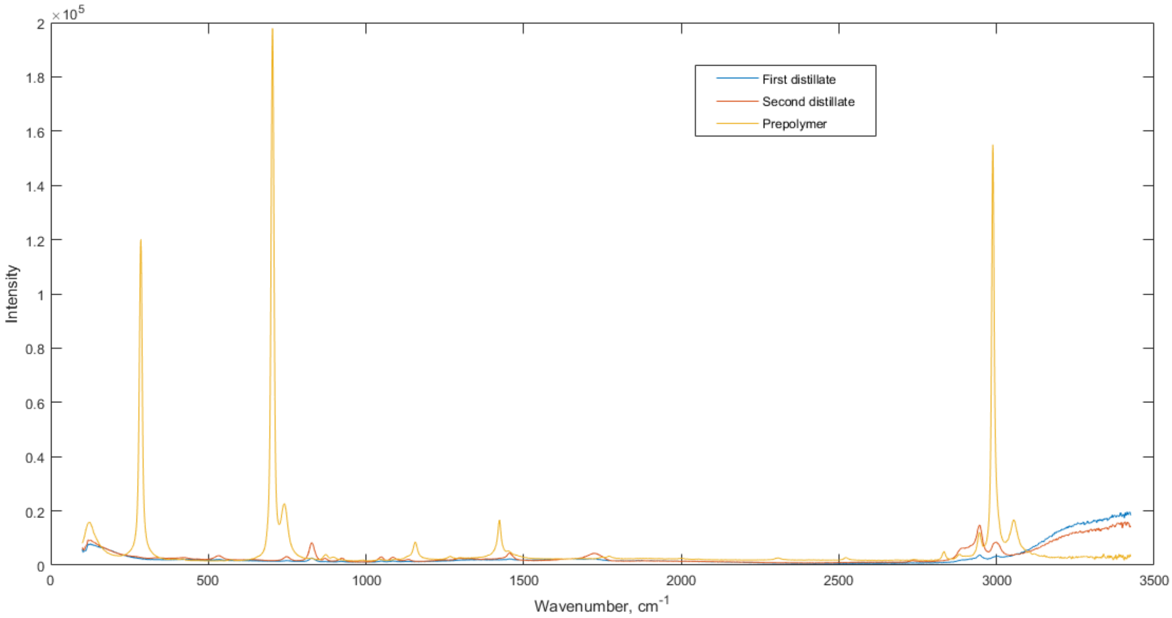
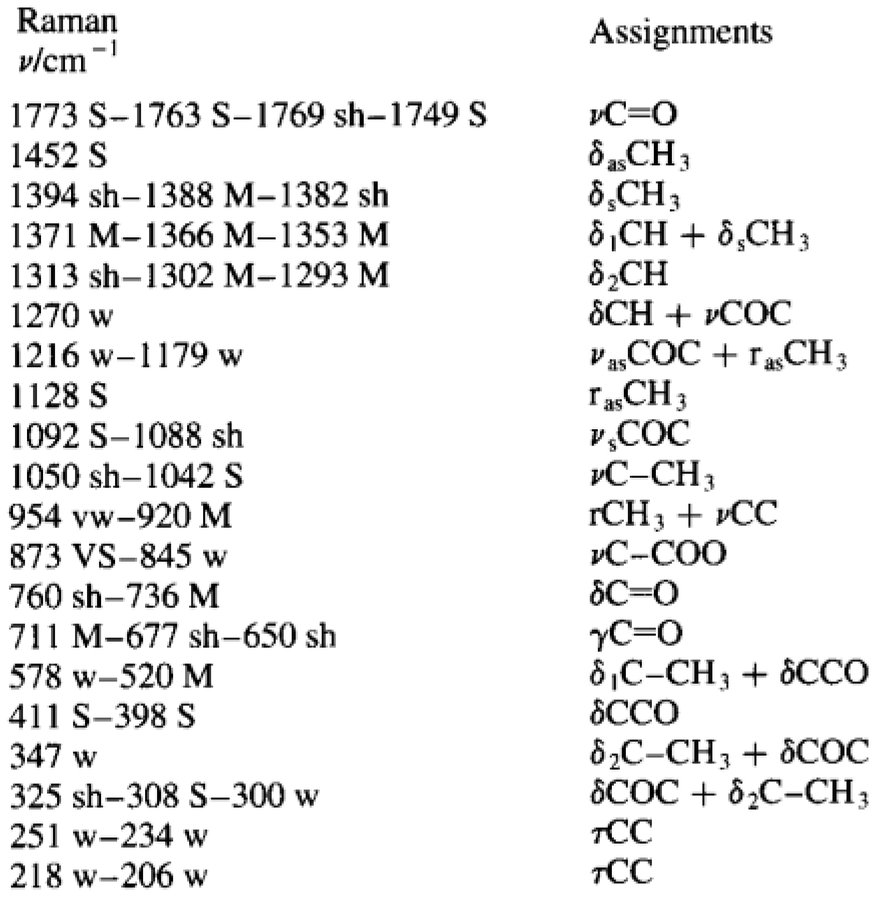


Figure 34. Raman spectras of distillates and prepolymer, resulting after polycondesation reaction

As it can be seen from the spectra provided, slight traces of lactic acid and possibly smaller oligomers were distilled during the 2nd distillation and prepolymer achieved was considered as purified lactic acid and subjected to following experiments. Second batch of prepolymer was not subjected to Raman analysis as the resulting product had similar properties thus was considered to be identical to the product of first batch.

The peaks assignment to corresponding vibrational modes at the fingerprint area of PLA with estimated molecular weight of 100,000 (100 – 1850 cm^{-1}) are provided in figure 35. [57]



Raman ν/cm^{-1}	Assignments
1773 S–1763 S–1769 sh–1749 S	$\nu\mathrm{C{=}O}$
1452 S	$\delta_{as}\mathrm{CH_3}$
1394 sh–1388 M–1382 sh	$\delta_{s}\mathrm{CH_3}$
1371 M–1366 M–1353 M	$\delta_{1}\mathrm{CH} + \delta_{s}\mathrm{CH_3}$
1313 sh–1302 M–1293 M	$\delta_{2}\mathrm{CH}$
1270 w	$\delta\mathrm{CH} + \nu\mathrm{COC}$
1216 w–1179 w	$\nu_{as}\mathrm{COC} + r_{as}\mathrm{CH_3}$
1128 S	$r_{as}\mathrm{CH_3}$
1092 S–1088 sh	$\nu_{s}\mathrm{COC}$
1050 sh–1042 S	$\nu\mathrm{C{-}CH_3}$
954 vw–920 M	$r\mathrm{CH_3} + \nu\mathrm{CC}$
873 VS–845 w	$\nu\mathrm{C{-}COO}$
760 sh–736 M	$\delta\mathrm{C{=}O}$
711 M–677 sh–650 sh	$\gamma\mathrm{C{=}O}$
578 w–520 M	$\delta_{1}\mathrm{C{-}CH_3} + \delta\mathrm{CCO}$
411 S–398 S	$\delta\mathrm{CCO}$
347 w	$\delta_{2}\mathrm{C{-}CH_3} + \delta\mathrm{COC}$
325 sh–308 S–300 w	$\delta\mathrm{COC} + \delta_{2}\mathrm{C{-}CH_3}$
251 w–234 w	$\tau\mathrm{CC}$
218 w–206 w	$\tau\mathrm{CC}$

Figure 35. Raman wavenumber corresponding to the structural assignments of PLA [57]

Spectra from following experiments will be identified according to the provided list of peaks and compared to the spectra provided by the authors of [57].

Ultrasound initiated polymerization

During the initial experiments with ultrasonic sonochemistry, slight increment of temperature was observed during the period of the reaction. Data is provided in the Figure 36.

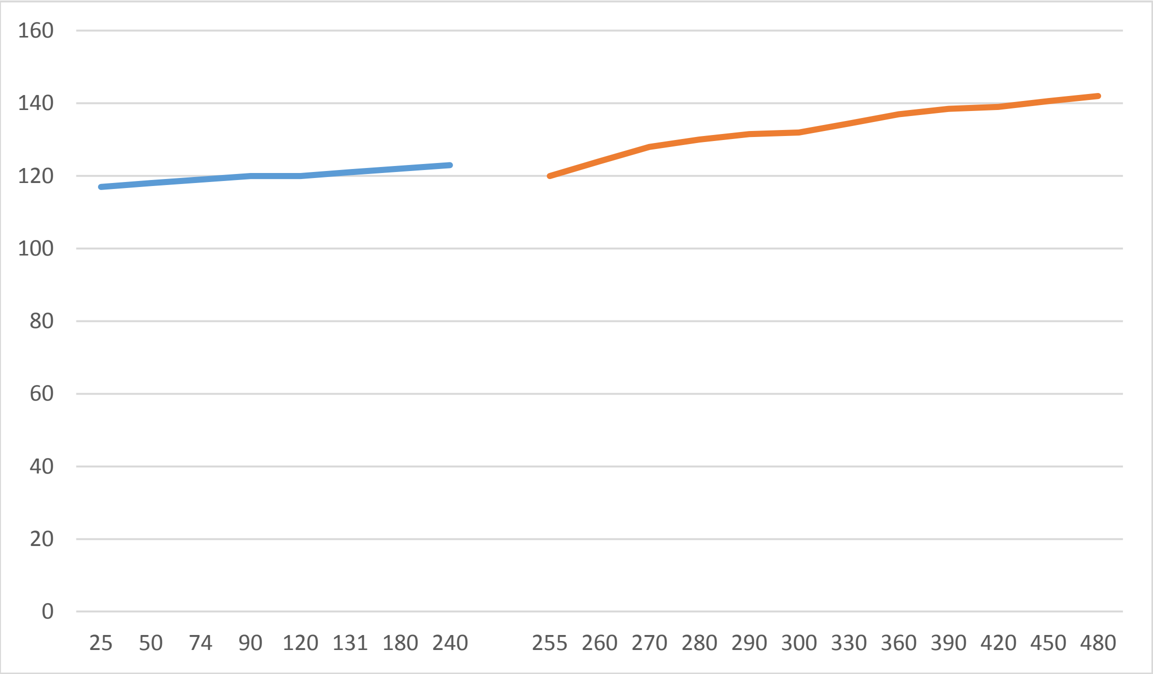


Figure 36. Reactions mixture temperature in C over time, min. Blue line corresponds to first 4 hours of reaction, Orange line corresponds to following 4 hours with addition of 0.1 % catalyst.

This temperature increase during the period of the reaction was considered due to increasing viscosity of the reaction mixture, as the theory of sonochemistry would suggest. As it can be observed, addition of catalyst to the reaction accelerated the increase in the temperature thus also confirming the idea, that polymerization was progressing and viscosity was increasing due to rising amount of polymer in the bulk phase.

Samples were taken after 4 and 8 hours and subjected to Raman. Resulting spectra baseline was treated using ALS (Smoothness = 100000, Penalty = 0.0001) and provided in the following Figure 37.

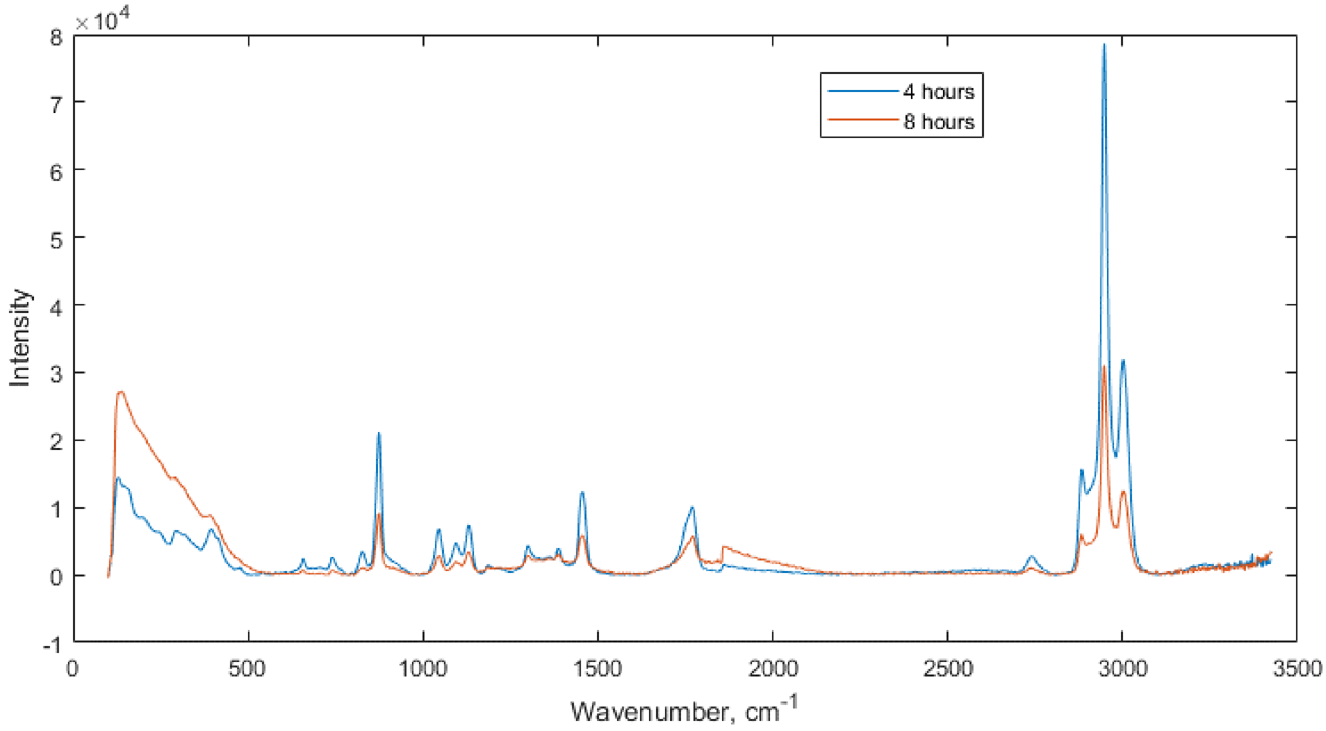


Figure 37. Raman spectra of Ultrasound experiment after 4 hours and after 8 hours

As it can be seen from the spectra, fluorescence for the sample taken after 8 hours made the peaks less intense, although comparison can still be made. In order to check if there are obvious differences between the two samples the fingerprint region of Raman spectra should be investigated more thorough. It is provided in the Figure 38.

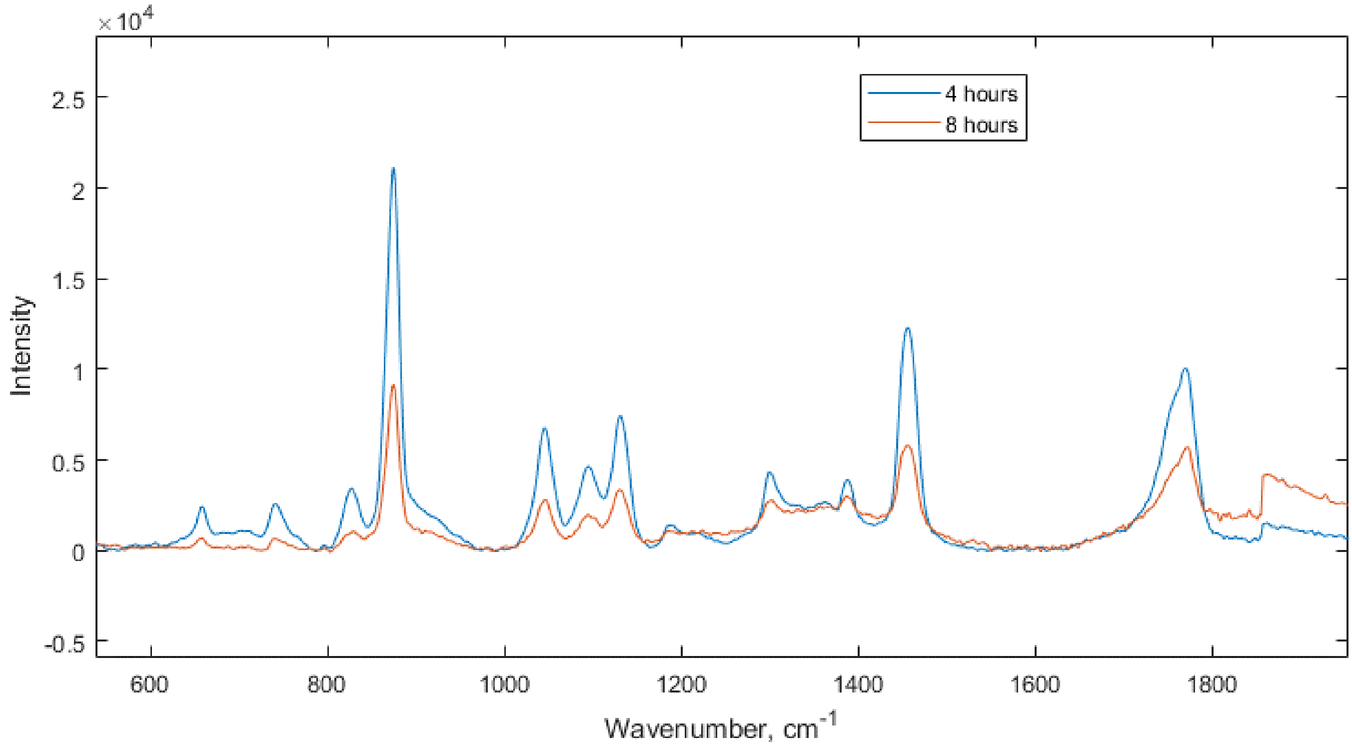


Figure 38. Fingerprint region for the initial Ultrasound experiment.

It can be seen, that although intensity for the spectra are different, same peaks are observed for both samples. By comparing them to the same observed peaks (Figure 39) from the authors of [57] it can be expected that in both cases polymerization has occurred and PLA was produced. However, due to different resolution of spectra it is hard to confirm if the assumption is correct, but it could be assumed that after 8 hours, and by comparison to peaks in Figure 39, the PLA corresponds more to the spectrum of amorphous polymer, while after 4 hours, more distinct peaks in the 1350 cm^{-1} region, would suggest semi-crystalline structure of resulting polymer. This could be potentially explained by the extreme conditions produced by ultrasonic sonochemistry and possibility should be considered, that after prolonged reaction destruction of polymer structure occurs, resulting in more amorphous product.

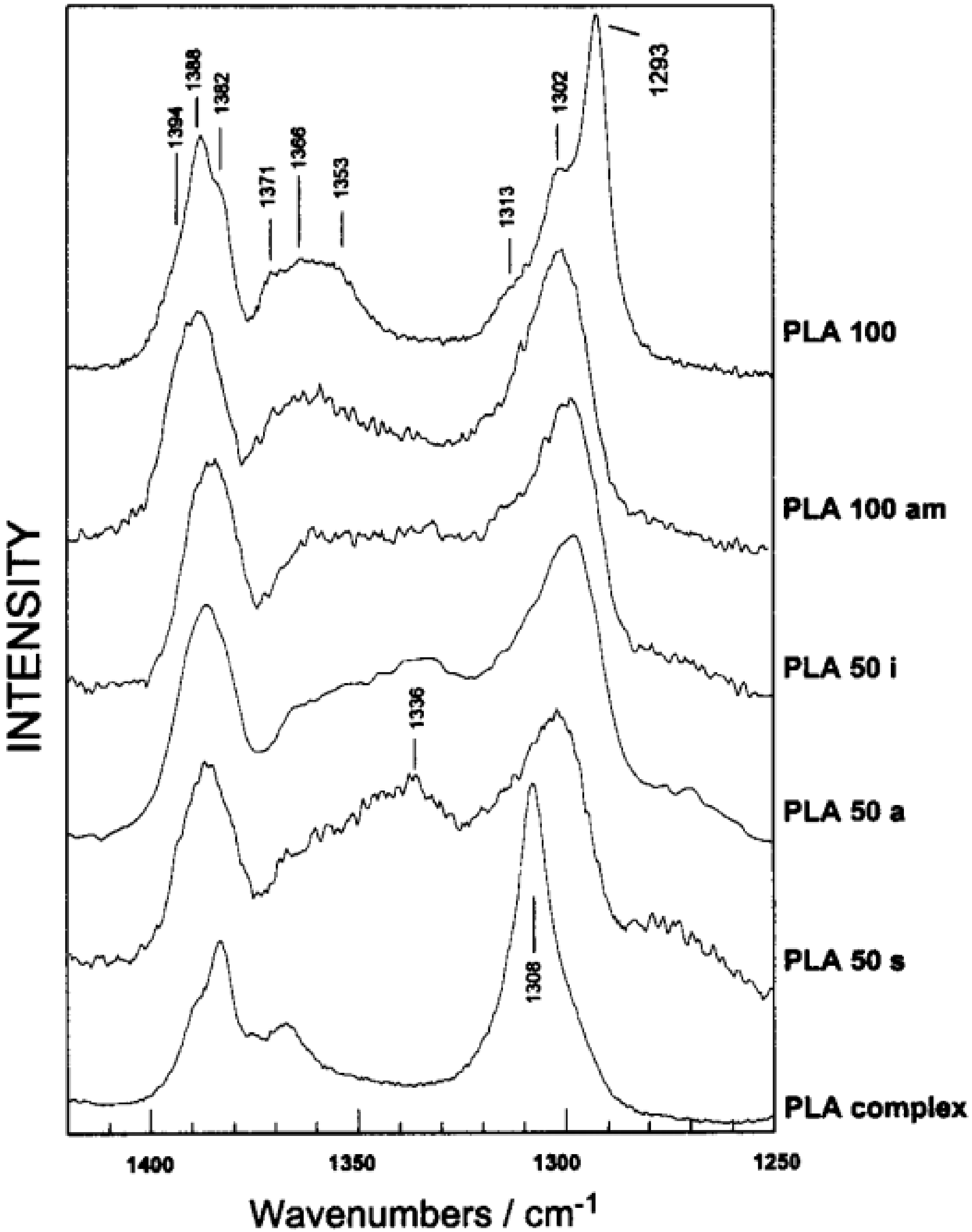


Figure 39. Raman spectra (1250–1420 cm^{-1} region) of poly(L-lactic acid)s: PLA100 (semi-crystalline), PLA100am (amorphous), PLA 50i (isotactic), PLA50a (atactic), PLA50s (syndiotactic) and PLAcomplex (stereocomplex) [57]

Raw Raman spectra for the second experiment with ultrasound is provided in the Figure 40 for samples at 0, 60, 120, 180 and 240 min.

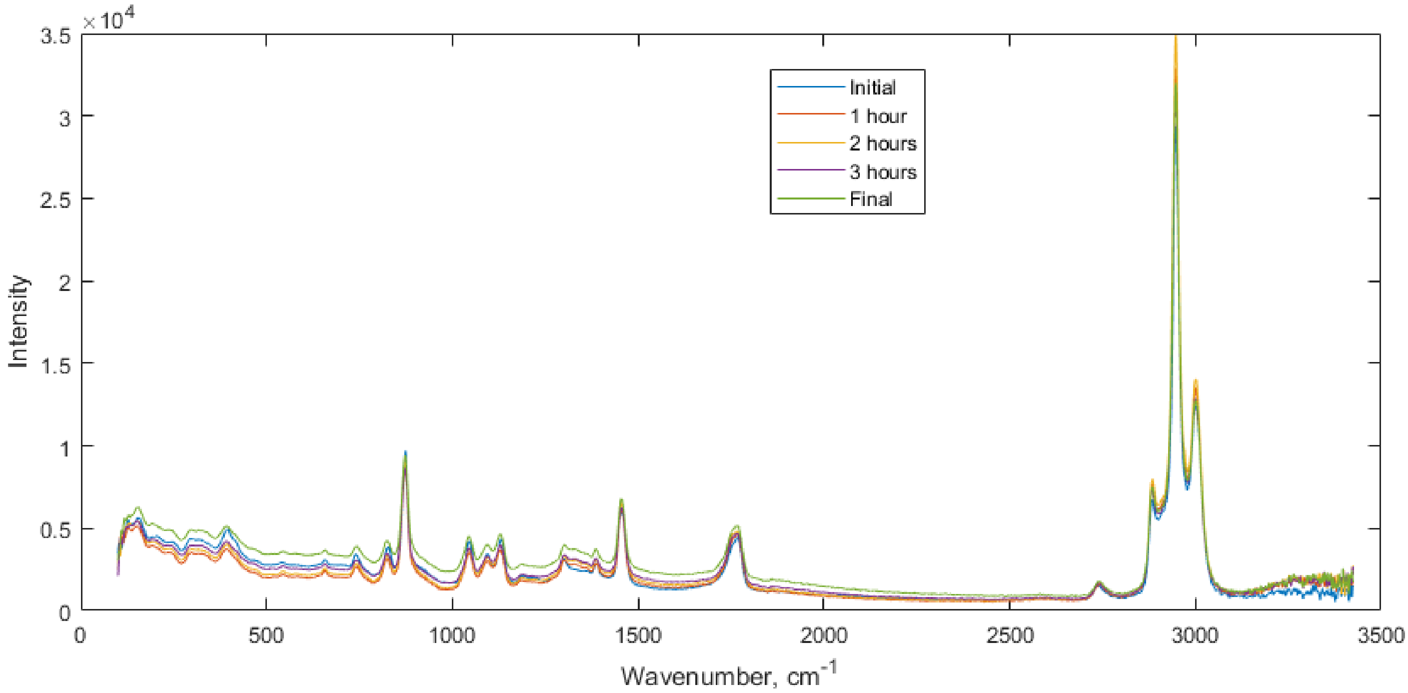


Figure 40. Raw Raman spectra from second experiment with Ultrasound.

From the provided raw spectra it looks like that reaction did not progress as expected over the 4 hours. Furthermore, temperature measurements were taken at every hour and it stayed constant at 103 °C during the whole experiment, which could suggest that none of the properties of the mixture changed. ALS with the same parameters as before was applied to the spectra and results are provided in the Figure 41.

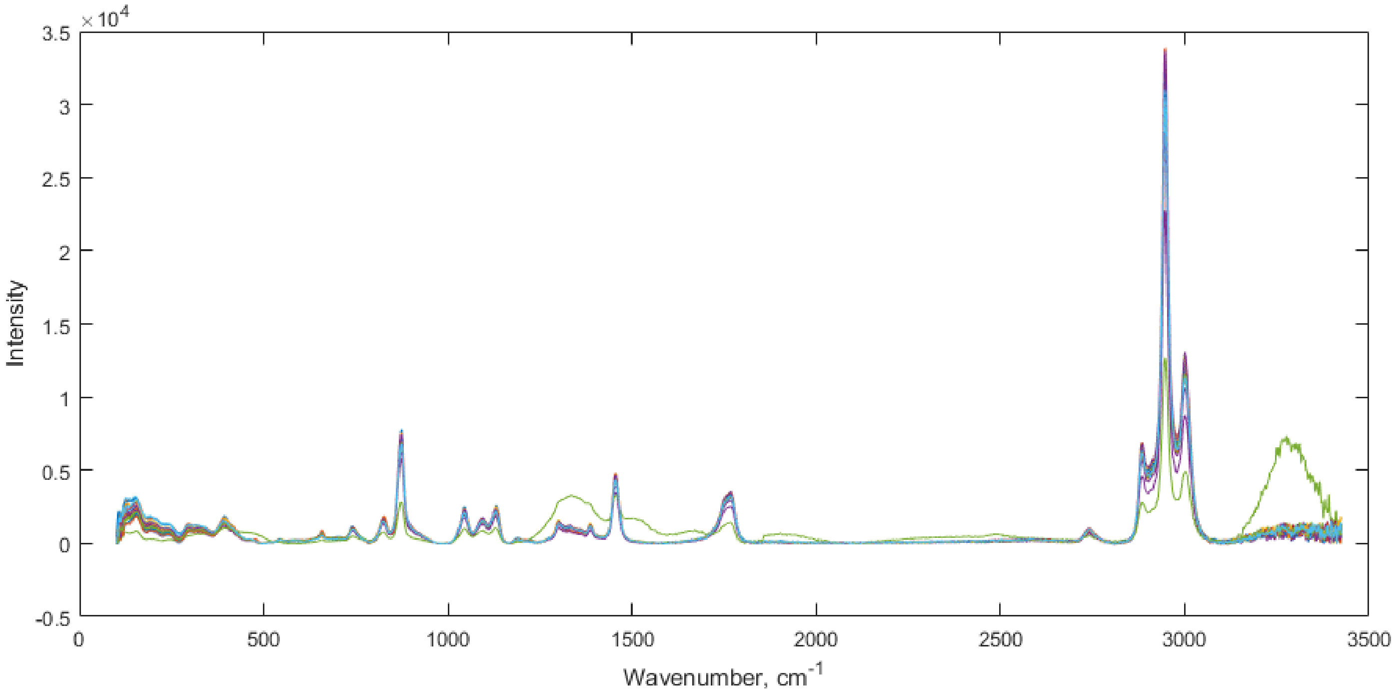


Figure 41. Full raw spectra of the second ultrasound experiment after ALS baseline correction

From the full raw spectra after baseline correction few things can be observed. There is one outlier, corresponding to spectrum taken at 25 min mark, which was observed during the experiment, when laser caught the side of ultrasonic probe, thus it will be removed from further analysis. Furthermore, after putting all 47 spectra on one plot, no distinct differences can be seen. Figure 42 shows the fingerprint region for the same data, with the outlier removed.

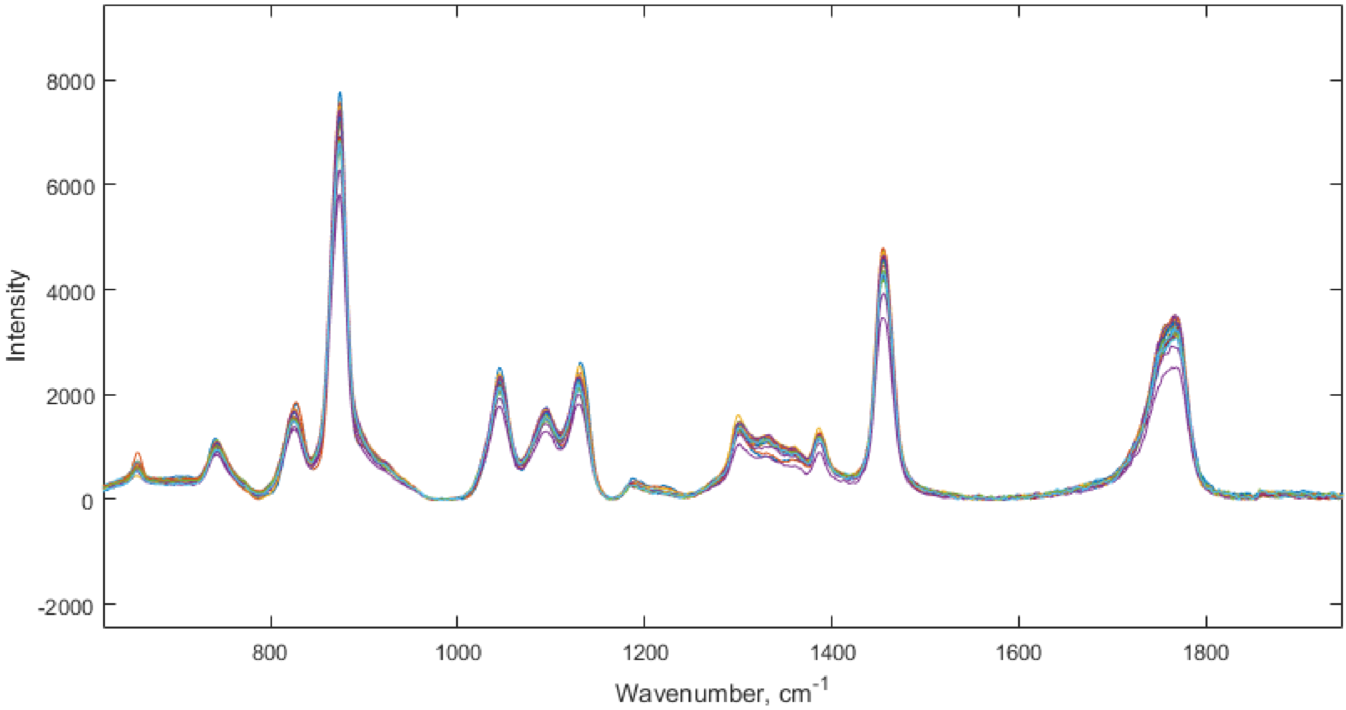


Figure 42. Fingerprint region for the full data with the outlier removed for the second ultrasound experiment.

By taking the closer look at the fingerprint region, slight variation of peak size can be observed. In order to analyze the data mean centering will be applied to the data and PCA will be performed.

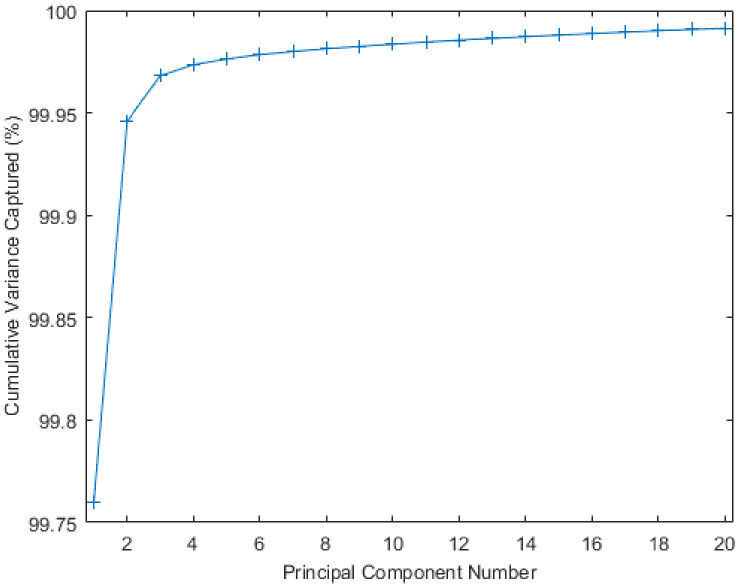


Figure 43. Cumulative variance plot for ALS+MC treated data.

As it can be seen from cumulative variance plot, 2 PCs cover 99.95 % of the variance in the data. Although, by checking the score plots for PC 2 and PC 3 (Figure 44) interesting trend was observed. It seems that PC 1 covers the spectra itself, while PC 2 and PC 3 reveals some hidden information which shows a trend, following the path of the reaction.

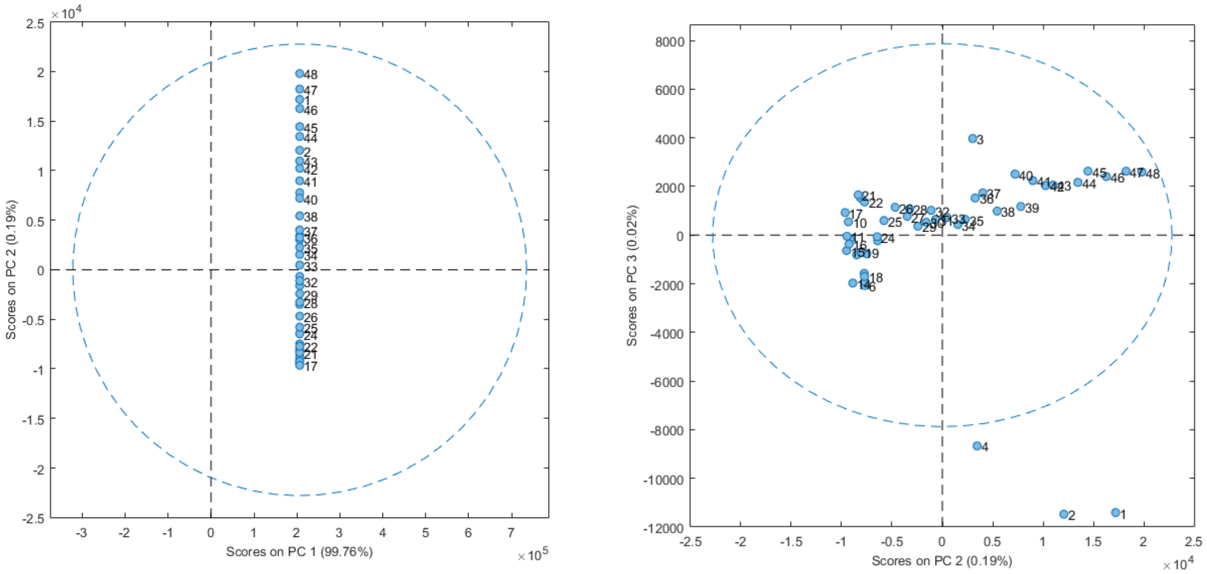


Figure 44. Scores plot for PC 1 vs PC 2 and PC 2 vs PC 3

From the plot of PC 1 vs PC 2 it is clear that second PC follows the progress of the reaction over time. From the plot of PC 2 vs PC 3 it can be seen that the same reaction's progression over time is covered by third component also. Furthermore, it reveals that first fours spectra acts like outliers. Considering that reaction vessel was properly stabilized only after "incident" with 5th sample, it can be assumed that first 5 samples (0 – 25 min) should be removed to make a better model. Resulting scores plots are shown in Figure 45 and 46.

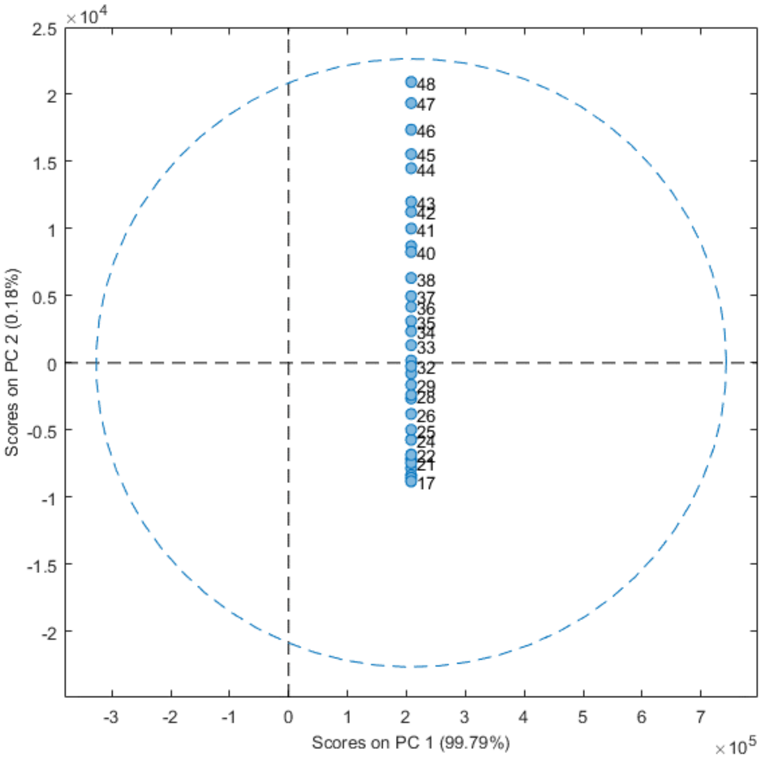


Figure 46. PC 1 vs PC 2, after removal of first 5 samples

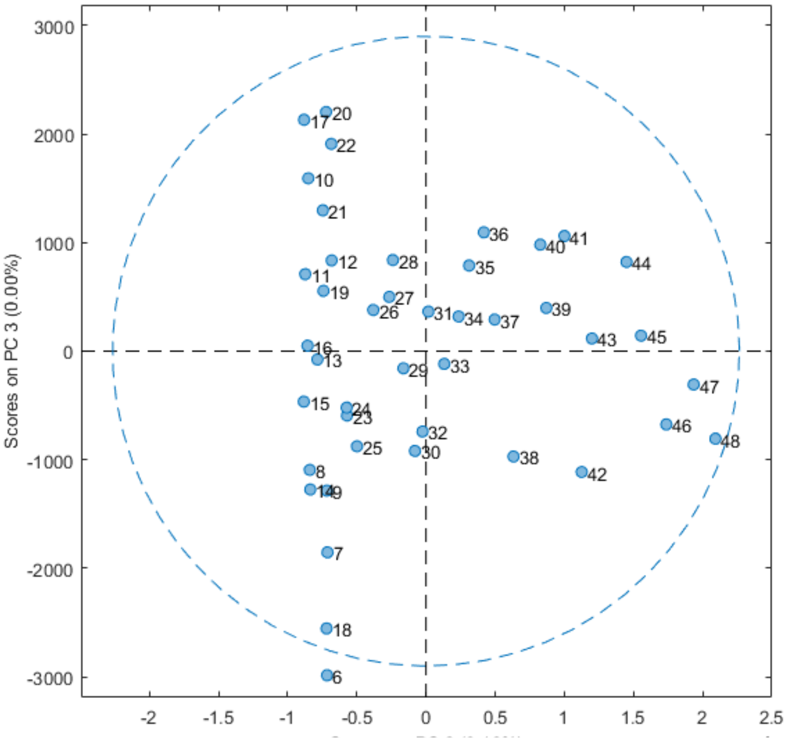


Figure 45. PC 2 vs PC 3, after removal of first 5 samples

After observing the scores plots with first 5 samples removed, it can be concluded that PC 2 still captures the progression of reaction, while PC 3 no longer shows visible trend. It was decided to keep the data without the first 5 samples and use only 2 PCs, covering 99.97 % of cumulative variance.

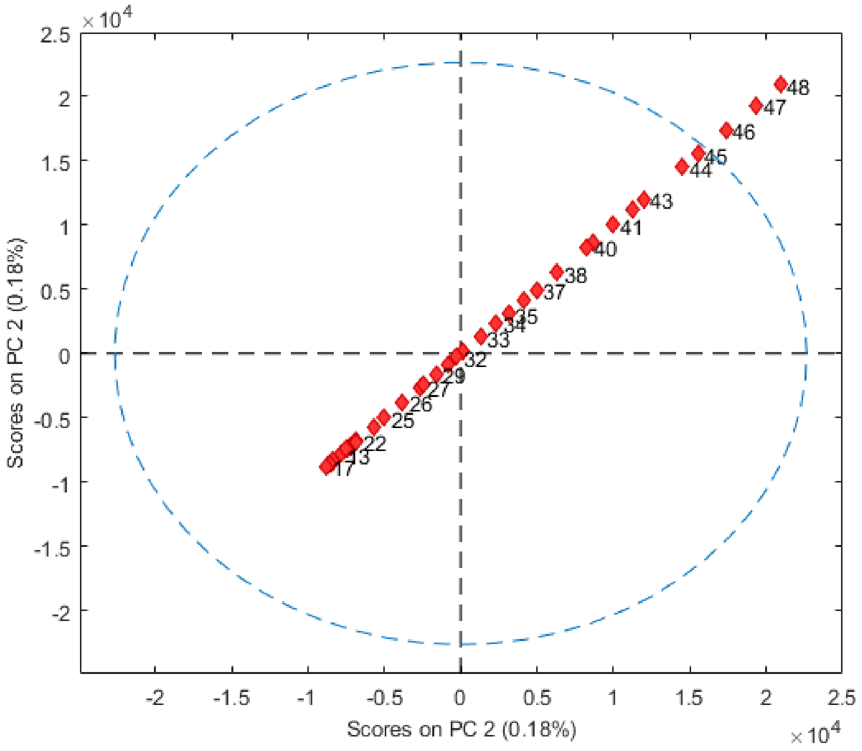


Figure 47. PC 2 scores plot

As the model was rebuilt for 2 components, it is clear that even by covering only 0.18 % of variation, PC 2 captured the important part of spectra, which was changing according to the progressing reaction. By looking at the loadings plot for PC 2 (Figure 48), it can be seen, that two regions were responsible for capturing the trend: fingerprint region (around 1500 – 500 cm^{-1}) and peaks corresponding to aliphatic chain vibrational modes at around 3000 cm^{-1}. As the fingerprint region, responsible for carbon-oxygen vibrational modes was increasing, and peaks responsible for CH_2 and CH_3 peaks were decreasing, it could be assumed that the polymerization reaction slowly progressed and conversion was increasing over the time of the experiment.

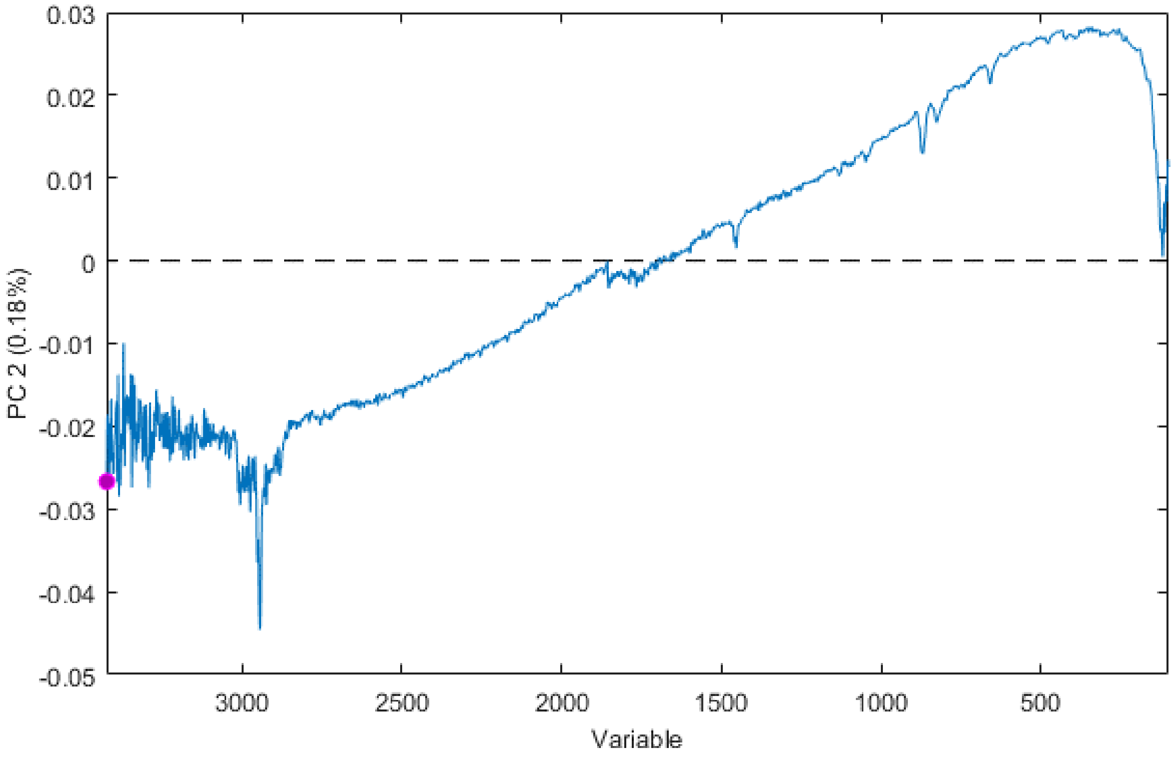


Figure 48. Loadings plot for PC 2 for ultrasound experiment.

Microwave induced polymerization

Average temperatures, obtained for 3 different concentrations of catalyst at 231 W power output and at specified times of 5, 10 and 20 minutes are provided in the following figure 49.

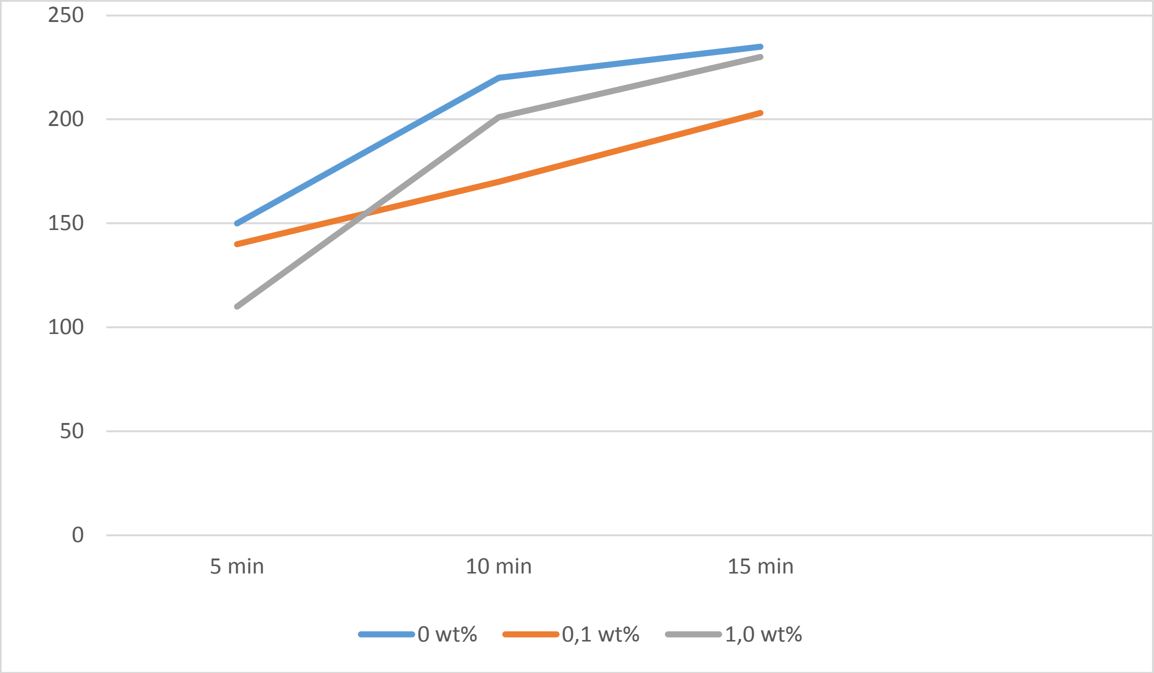


Figure 49. Temperature over time during the microwave irradiation reaction.

It can be observed from the chart, that on average, temperature after 5 min of irradiation was around 130 °C, after 10 min – 195 °C, and after 20 min – 215 °C. It does not correspond well with the theory thus it is possible, that domestic microwave oven used for this experiment was not as efficient as expected originally. However, considering the temperature data provided and observations during the experiment, it could be assumed, that maximum temperature was achieved at around 13-15 min mark, as at that point boiling started at all samples.

All resulting samples were subjected to Raman spectroscopy, except one sample of 0.1 % catalyst concentration and 20 min, due to crack in the vial, which led to loss of the sample. All spectra were subjected to ALS baseline correction and are shown in Figure 50.

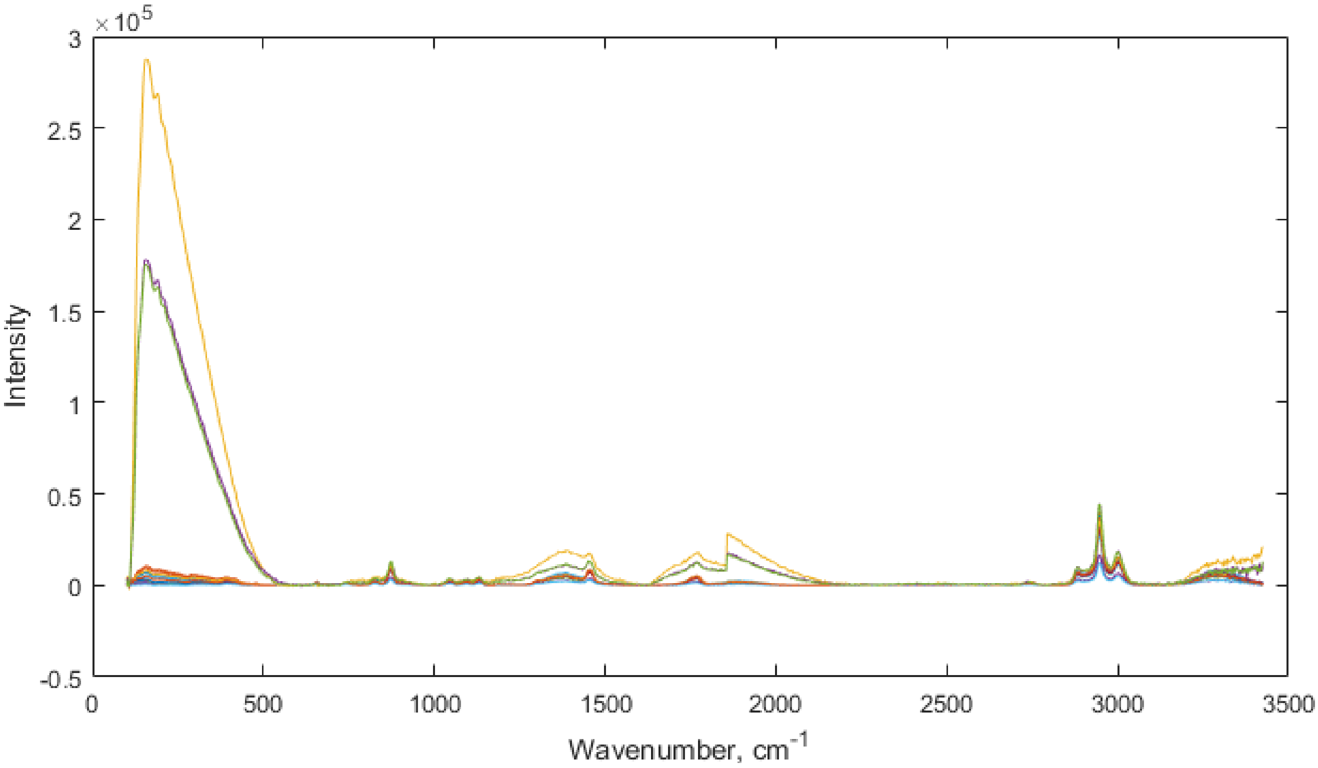


Figure 50. Spectra for microwave experiment after ALS baseline correction.

Obvious extreme samples correspond to all 3 samples with 1 % catalyst concentration after 20 minutes. Additionally, it was the only 3 samples which changed the color to dark yellow/brown and the resulting Raman spectra are obviously polluted by the fluorescence effect thus will not be included in further analysis. Adjusted fingerprint region of the spectra is shown in Figure 51.

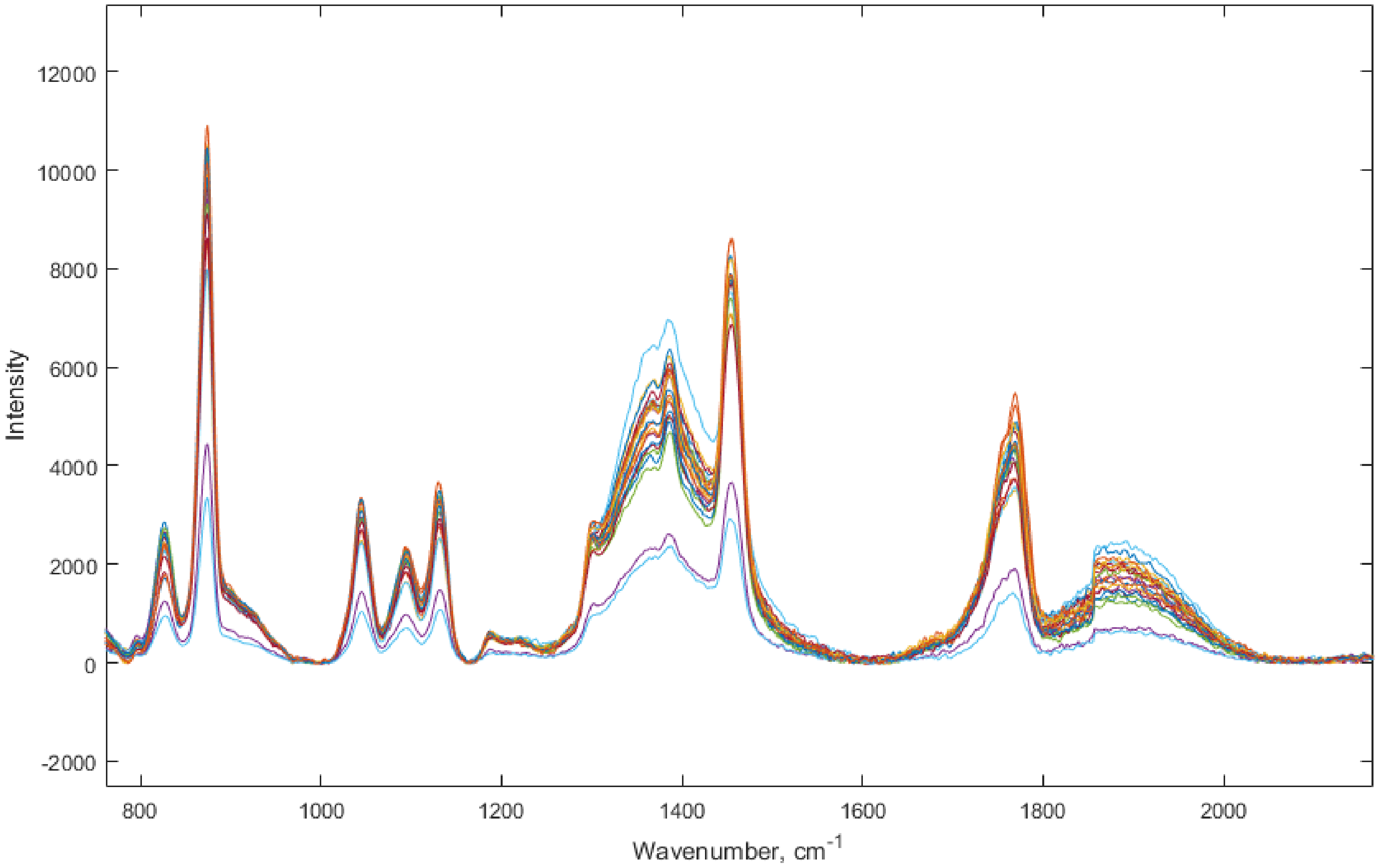


Figure 51. Fingerprint region of Raman spectra for microwave experiment without extreme samples.

It can be seen from the Figure 51 that obvious differentiation between the samples exist. Sets of samples corresponding to different concentration are submitted to PCA to check if any trends can be observed in the resulting products.

First 9 samples, corresponding to reaction without catalyst, were mean centered and subjected for PCA. Model was build using 2 PCs (Cumulative Variance = 99.36 %) and resulting score plot is shown in Figure 52.

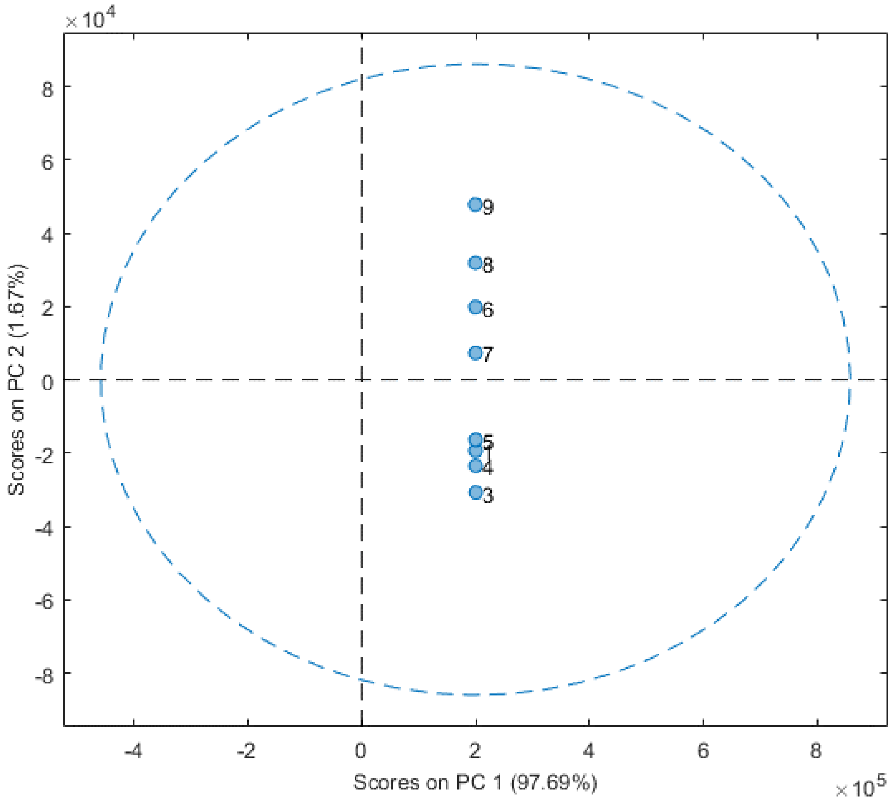


Figure 52. Score plot for MW induced reaction without catalyst.

From the score plot it can be seen, that PC 2 covers the reaction progression the same way as it was for ultrasound experiment. Samples 7, 8 and 9 correspond to 20 min samples, while sample 6 is 10 min sample. Loadings plot suggests, that PC 2 covers the variation of characteristic peaks thus it is expected that results correspond to reaction which progressed over time.

Second set of 8 samples were also mean centered and PCA was performed. Resulting Score plot can be seen in Figure 53.

Although the trend was visible, according to Q vs T^2 plot (Figure 54), it was noticed that sample number 13 could be considered as outlier and was removed from the model. Resulting new score plot is provided in Figure 55.

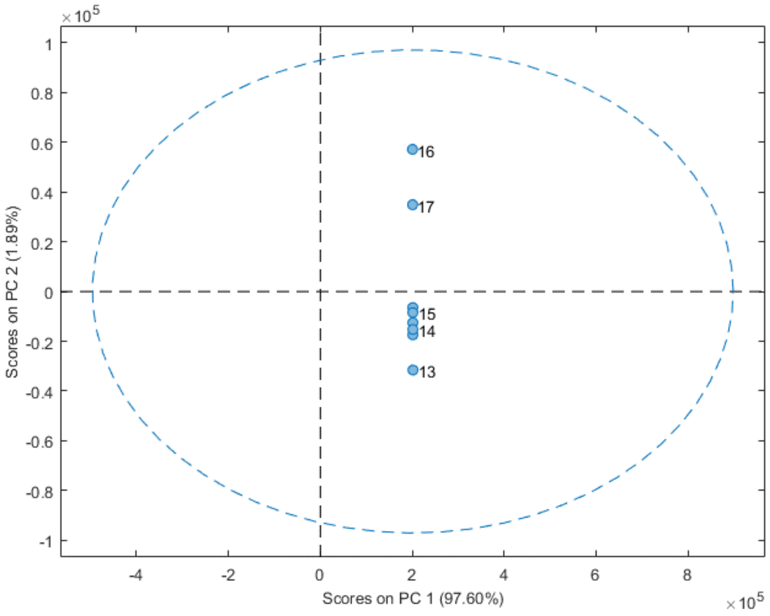


Figure 53. Scores plot for samples with 0.1 % catalyst concentration.

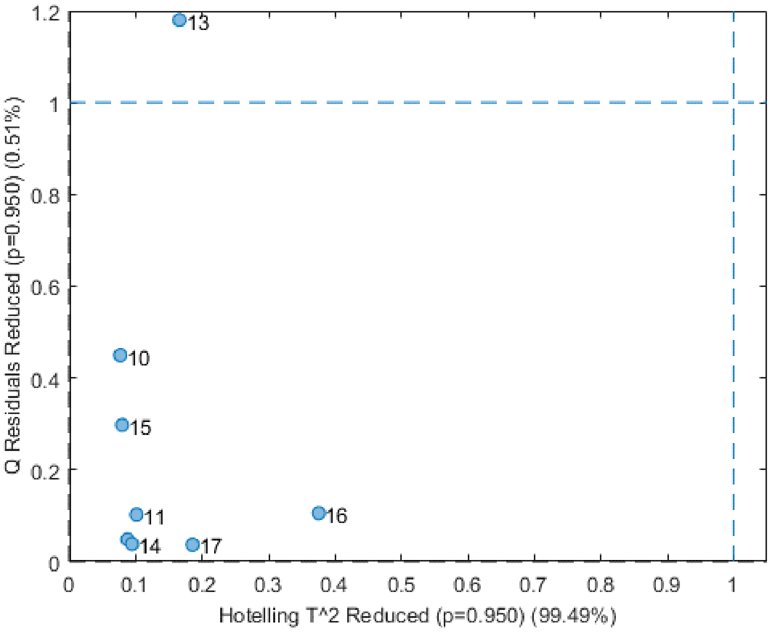


Figure 54. Q vs T^2 plot for second set of samples

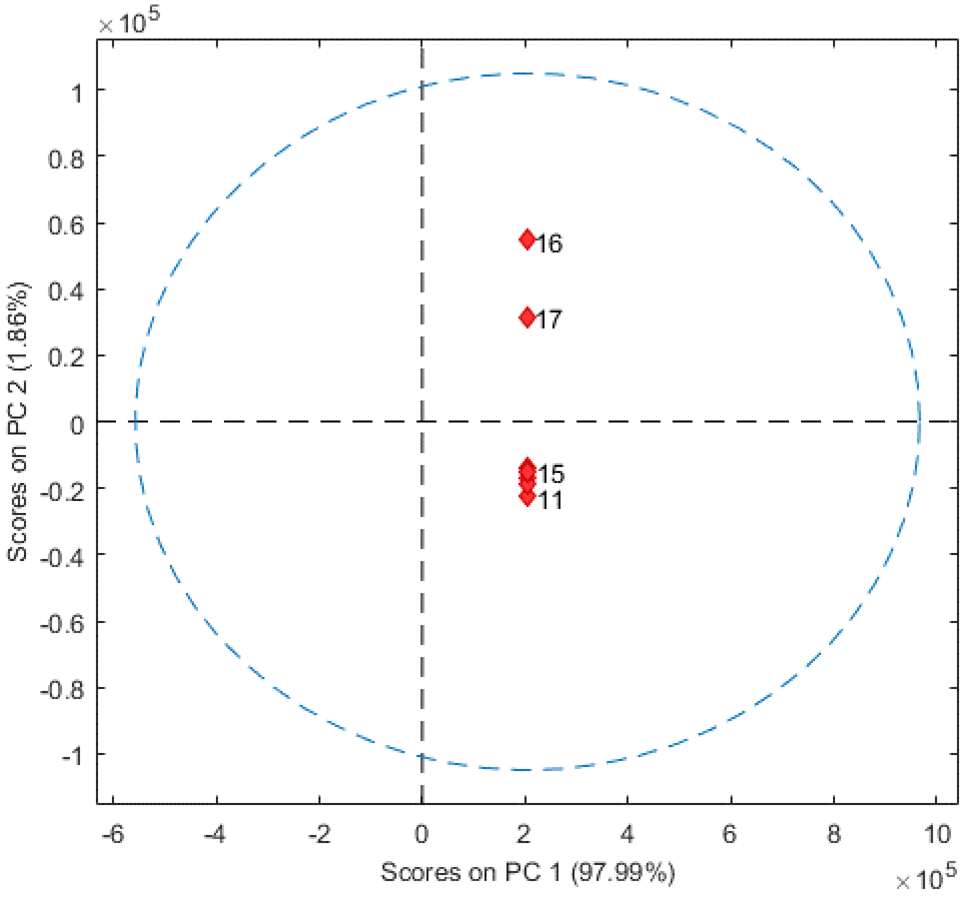


Figure 55. Updated scores plot for 2nd set of samples

It can be seen that new scores plot does show any new trends and both samples after 20 min (16 and 17) are considered more progressed by the model.

Same procedure was performed for the remaining 6 samples with catalyst concentration of 1 %. Resulting scores plot can be seen in Figure 56.

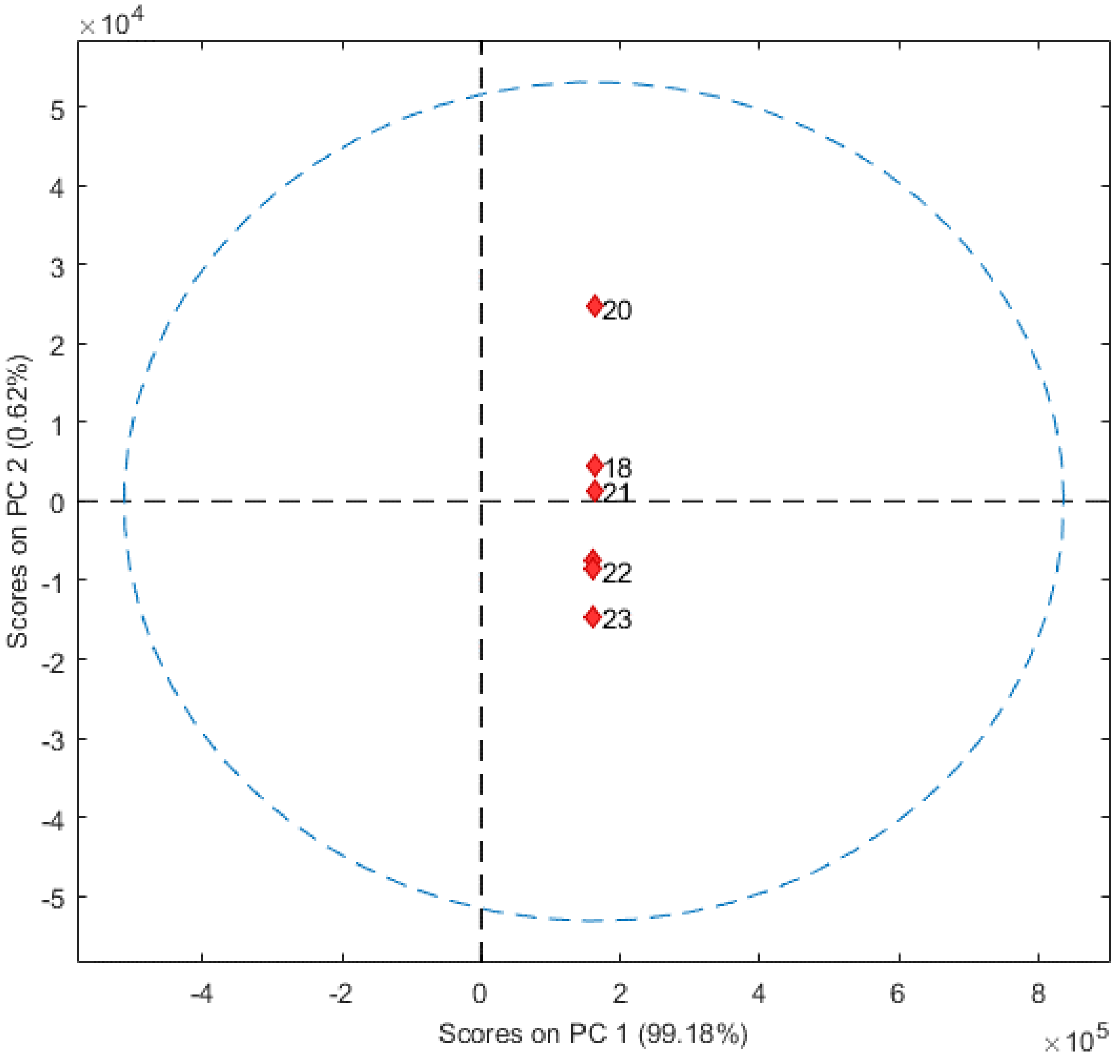


Figure 56. Scores plot for samples with 1% concentration of catalyst.

As the samples of 20 min were removed from the reaction due to unusable spectra, no specific trends were observed for this set of samples. Although all of the samples follow the same trend that only the products of 20 min microwave irradiation differentiate from other samples with a few exceptions.

Discussion

Ultrasonic Sonochemistry

After initial experiments that ran for 8 hours, promising results were observed in the increasing temperature during the reaction. However, crystallization of the polymer could not be achieved when followed the literature and measured melting temperature of the resulting product, which was only slightly higher than the melting point of pure lactic acid (82 °C compared to 53 °C of pure LA) suggests that either conversion of the reaction was small and/or polymerization achieved was of very low degree, resulting in the mixture of short oligomers and pure lactic acid still present in the product. This could be explained by the extreme localized conditions achieved by this method, resulting in polymerization reaction competing with the destruction of the polymer chains.

As the PCA of the second experiment revealed, reaction progresses, but it is not fast and results are less than satisfactory to be considered for application in industry. It could be considered as the complementary technique to other synthesis method, although the conditions should be chosen carefully, as cavitation could lead to competitive destruction reaction. It should be mentioned that it was chosen not to use N_2 inlet for second experiment, which could be the reason why the reaction was happening slower. As the nitrogen could ease up the removal of water from the resulting polycondesation reaction, although for both experiments the resulting product was subpar and could not be considered as a polymer of any value.

Microwave induced polymerization

Microwaves were described in the literature as very successful and fast option to create high molecular weight PLA. Although, when the same reaction was done in the domestic microwave oven, the results were similar to those of the reaction initiated by the ultrasound. Melting points of the resulting products was similar to those of produced by ultrasound (ranging from 60 to 90 °C). One of the biggest possible issues was incapability of achieving vacuumed, closed off vessels for the reaction, which could be the reason of results obtained. Almost all authors use closed off systems for PLA production as the water in the environment interacts with the polycondesation reaction and pushes the equilibrium towards the hydrolysis of the produced polymer.

By analyzing the samples with PCA it was observed that reaction still occurs and progresses in 20 minutes. It still shows that microwaves are potentially fast and efficient way to synthesize smaller amounts of polymer thus it could be considered as great option for laboratory experiments or small scale needs. However, as the microwave radiation has a very short permeation into the sample, it is difficult to design an industrial process which could be effective enough to produce economically sufficient amounts of PLA. As the technology is advancing and new reactors are created, microwave irradiation could become a great alternative for standard heating, as faster and less energy consuming method to obtain PLA.

CONCLUSIONS

Ultrasonic Sonochemistry

Experiment was performed and increasing temperature during the experiment, suggested increasing viscosity and progressing polymerization. However, properties of final product were unsatisfactory.

Second experiment without nitrogen inlet, but with constant monitoring by Raman spectroscopy did not show any increase in temperature and reaction was considered unsuccessful. PCA analysis of the data suggested that reaction occurred to some extent, although it was not sufficient to achieve wanted final polymer.

Microwave induced polymerization

Experiment was performed using domestic microwave oven with power output of 231 W and using three sets of samples with different catalyst concentrations (without catalyst, 0.1 % and 1%). Resulting properties of the polymers were not sufficient for the experiment to be considered as successful.

PCA analysis of the data showed that even running the experiment in open vessel conditions, after 20 min reaction to some extent progressed forward. However, the problematic nature of microwave radiation could be problematic for any bigger applications and probably will not be considered as industrial alternative in the near future.

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APPENDIX 1. Synthesis of Poly(Lactic Acid) in Literature

As mentioned in the previous section, there are several ways to obtain PLA through different methods. In order to create a technique that could suit this project, several sources will be investigated, which should provide assistance on deciding the initial conditions for experimental setup.

Authors of [18] chose to use ROP path for the reaction as the reaction through lactide formation allows to produce a polymer with controlled molecular weight. The process was separated into three distinctive stages: polycondensation, obtainment of lactide and ROP. 85% pure reagent grade Lactic Acid combined with Stannous octoate as the catalyst was chosen for the experiment. First step, polycondensation, was performed at 160 °C for 2 hours to remove the water from the LA to form oligomers of PLA. Reaction was performed at atmospheric pressure using inert N_2 atmosphere and the system setup can be seen in a Figure 57.

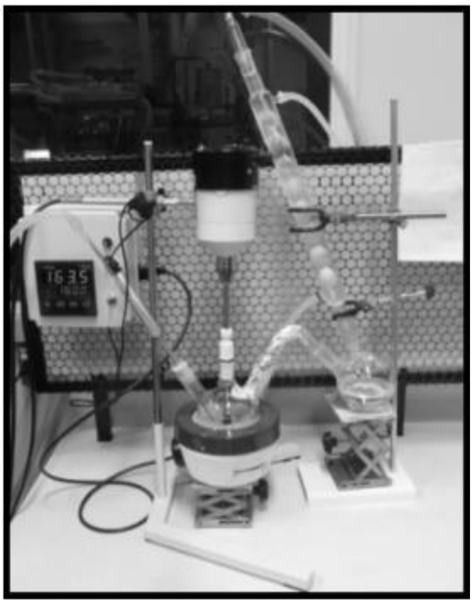


Figure 57. Experimental setup for polymerization [18]

After the removal of water, second reaction step was taken, where system was heated to a temperature of 220 °C and the pressure reduced to 200 mmHg to distill produced lactide and collect it in the condensate flask. The condenser was kept at around 90 °C to prevent solidification of the product for 4 hours, while the reaction was running. Distilled lactide was recovered in condensing flask, washed with cold water, separated by filtration and dried overnight at a temperature of 40 °C. In the third step, produced lactide was mixed with the catalyst (1 wt%) at a temperature of 140 °C for 2 hours to form PLA. For analysis of functional groups of PLA and LA, Fourier Transform Infrared spectroscopy (FTIR) was used [18].

The observation was made, that when reaction was performed without nitrogen, water removal became slower [18], thus implying that the flow of nitrogen helps with the removal of water vapors that are formed in the reactor. FTIR analyses of the authors, proved that during the reaction time intensity of the bands, corresponding to the end groups, decreased while other ones increased, proving the progress of polymerization reaction. Characteristic bands of lactide were obtained by FTIR from the sample of the second step, thus confirming the formation of lactide. Following analyses by FTIR proved that PLA was produced by the experiment and that the process is a viable way to produce PLA [18].

An extensive study on the influence of catalyst concentration, polymerization time and temperature on the yield, molecular weight and optical rotation during polycondesation and ROP was performed by the authors of [54]. In their work, polycondensation was performed without catalyst, simply by distilling out the water from the 90 wt% solution of lactic acid. Reaction was performed in a four-necked round-bottom flask, fitted with a Teflon stirrer, a water-cooling condenser, a thermometer and capillary inlet for nitrogen gas to ease up the removal of water. At first, temperature was gradually increased from 120 °C to 180 °C under atmospheric pressure. When the water stopped distilling, the pressure was gradually reduced from 760 mmHg to around 100 mmHg leading to a further removal of water and the formation of viscous lactic acid oligomers, which made stirring practically impossible. After this, the temperature was set at 180 °C, the pressure was reduced to 25 mmHg and the reaction was performed under these conditions for 25 h. [54]

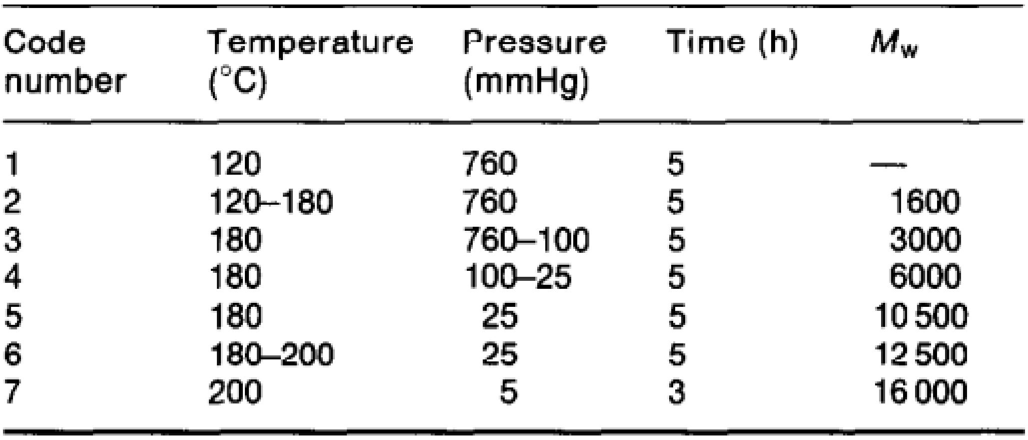
Lactide for the ROP was synthesized through the depolymerization of the corresponding oligomers catalyzed by inorganic metal salts. 0.1 wt% of antimony trioxide was added to the oligomer and the reaction was performed under reduced pressure of 2 mmHg. The formation of gaseous lactide monomer was observed when the temperature was gradually raised from 150 °C to 180 °C. Temperature for the depolymerization was kept between 180 °C and 220 °C. Produced lactide was recrystallized from ethyl acetate at least four times, dried lactide had a melting point of 97.5 °C and the yield was about 75 %. [54]

ROP was conducted in bulk using Stannous octoate as a catalyst. The catalyst was dissolved in ethyl ether and mixed with the dried lactide in the ampules, which were sealed after evacuation to 10^{-3} mmHg. Sealed ampules were kept in a silicone oil bath at the temperature of 120 °C to 220 °C while shaken vigorously until the catalyst got completely mixed with the molten monomer. After different reaction times, the ampules were put to room temperature to stop the polymerization. Reaction products were dissolved using dichloromethane and precipitated with methanol. The monomer conversion was determined with gravitational method and a thermal method, using thermobalance. [54]

Several analytical methods were used to measure the molecular weight of the products. Gel permeation chromatography (GPC) was performed to measure the oligomers of lactic acid using four columns (Microstyrogel® of 10^6, 10^5, 10^4 and 10^3 Å normal pore size), where monodispersed polystyrenes were used for calibration and tetrahydrofuran as the mobile phase. [54] Intrinsic viscosities were measured in chloroform at 25 °C, while specific optical rotation was measured in a 0.82 g/dl concentration of dioxane solution at 25 °C and at a wavelength of 578 nm. [54]

Polycondesation results are provided in Table 6. It was noticed by the authors that reduced pressure and increase in a temperature leads to a formation of longer polymer chains. However, when the reaction temperature exceeded 220 °C, generation of monomeric lactides were observed due to depolymerization reaction because of high temperature. In the end, polycondesates with molecular weight higher than 20000 were not obtained from this reaction. [54]

Table 6. Conditions and molecular weights of polycondesation of L-Lactic acid [54]



Code number	Temperature (°C)	Pressure (mmHg)	Time (h)	M_w
1	120	760	5	—
2	120–180	760	5	1600
3	180	760–100	5	3000
4	180	100–25	5	6000
5	180	25	5	10 500
6	180–200	25	5	12 500
7	200	5	3	16 000

Catalyst influence for the conversion and resulting molecular weight was investigated for reactions performed at 130 °C for 72 h. The resulting graph is provided in Figure 58. Authors made a conclusion that best results were obtained when 0.05 wt% of stannous octoate was used, as that particular concentration of catalyst led to highest molecular weight and conversion rate. For this reason, further experiments were performed with the catalyst concentration of 0.05 wt% to achieve best results. It was also assessed that higher concentrations of catalyst result in smaller molecular weight, which is typical for addition polymerization reactions. [54]

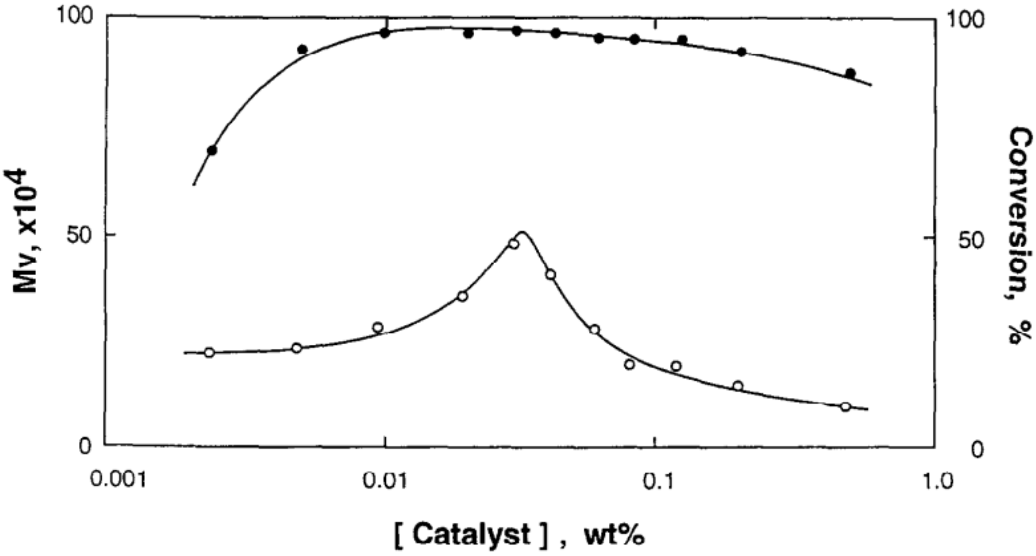


Figure 58. Influence of catalyst concentration for molecular weight and conversion of PLA. ● – Conversion, ○ – Molecular weight. [54]

The results of their temperature influence test are provided in Figure 59. Authors concluded that the lower rate of polymerization leads to higher molecular weight and conversion. It was assumed that, as it was for polycondensation, higher temperatures lead to faster reaction, but it also accelerates depolymerization thus resulting in the smaller molecular weight. Interestingly it was pointed out that optical rotation of poly-L-lactide obtained by ROP remained the same even at 200 °C and regardless of the polymerization time. [54]

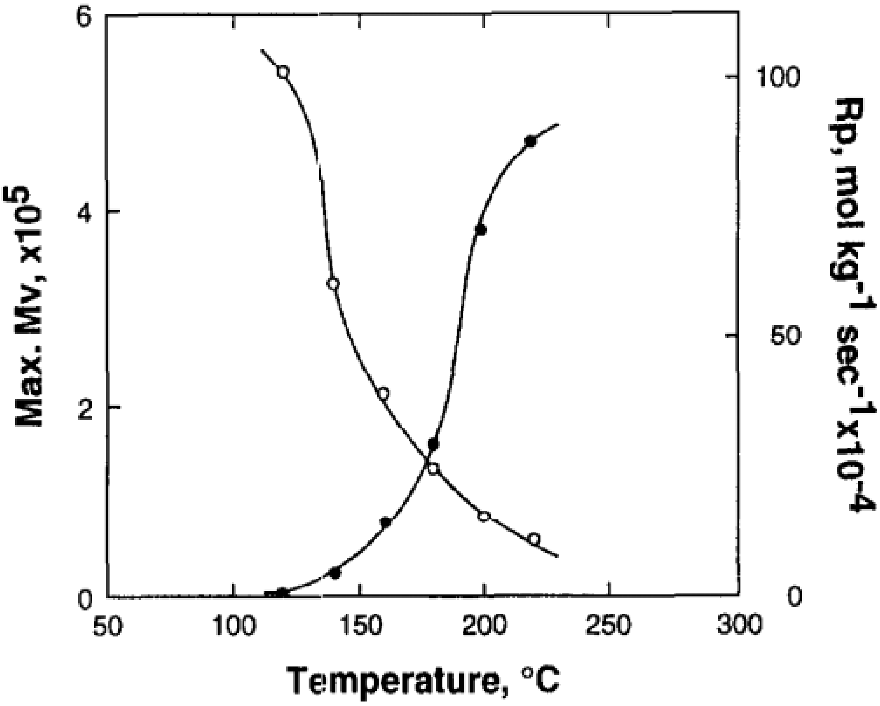


Figure 59. Effect of temperature on a maximum molecular weight and rate of polymerization for PLLA. ● – Rate of polymerization, ○ – Molecular weight. [54]

Authors of [59] questioned how the stannous octoate and PLA polymerization are affected by the presence of alcohols and carboxylic acids. Commercially available L-lactide was used with stannous octoate as the catalyst. Reactions were performed in 2 mL glass ampoules that were sealed under high vacuum. For these experiments 1-hexadecanol was chosen as the alcohol and stearic acid and/or DL-lactic acid were added as the carboxylic acid, while the monomer to catalyst ratio was kept at 5000 for all reactions. Reactions were stopped by simply taking out ampoules from the oven at desired times. Molecular weight was determined by using viscosity average molecular weight using Mark-Houwink equation, PLLA yield - by precipitating PLLA methylene chloride solution into ethanol. [59]

Results of the analyses from [59] are provided in Figure 60. They concluded that both hydroxyl and carboxylic acid substances influenced the polymerization reaction. It was observed, that while the presence of alcohol increased the production rate of PLLA, carboxylic acid decreased it, although in both cases resulting molecular weight was smaller compared to reactions without the additives. The assumption was made that the real initiator was stannous alkoxide, the product of a reaction between stannous octoate and alcohol. To support this, alcohol increased the rate of the reaction, while carboxylic acid in high concentrations caused induction period that could be explained by deactivation of the initiator. [59] As it was shown previously in work done by authors of [54], higher concentration of catalyst leads to lower molecular weight, and that confirms the assumption of stannous alkoxide being the real initiator by the authors of [59]. Authors also added that in cases when there is no alcohol or acid added, the stannous octoate would react with the impurities in the bulk phase, including lactic acid and water, to form the stannous alkoxide. Furthermore, it was mentioned that water is already present in the catalyst due to its hygroscopicity and production method. [59]

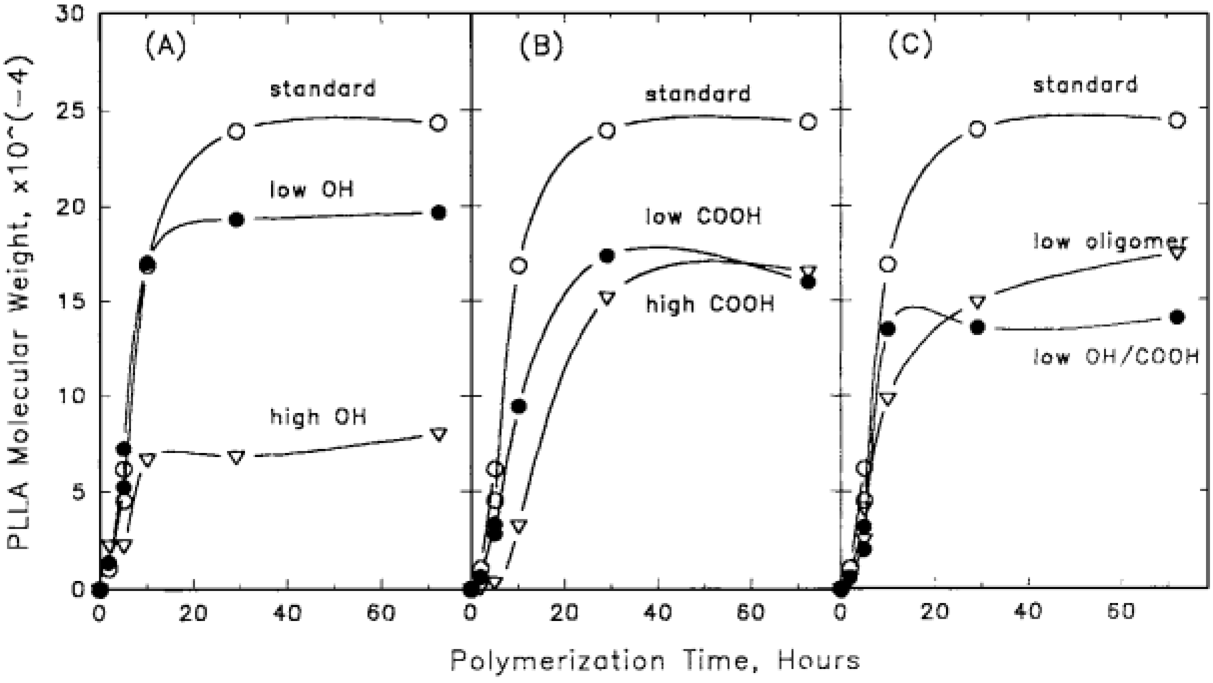


Figure 60. The effects of alcohol and carboxylic acid presence for the molecular weight of PLLA. [59]

Study of two steps direct polycondensation of poly(D-lactic acid) (PDLA) was performed by authors of [58]. Reaction was performed by combining melt polymerization and solid state polymerization as the second step. The reaction started with a D-Lactic Acid (DLA) combined with 0.5 wt% of 2-Naphtalenesulfonic acid without metal catalyst at room temperature and under atmospheric pressure. The temperature was gradually increased to 160 °C, while pressure was reduced to 30 torr and left for 4 h. Degree of polymerization for the oligomers was 4-7 and the oligomers were annealed at their crystallization temperature for 2 h. The formed pre-polymer was ground to a fine powder and then subjected for a solid state polymerization at the temperature under its melting temperature with reduced pressure of 10 torr. [58]

Differential scanning calorimetry was used to analyze the thermal properties of the oligomers and PDLA obtained from the reaction (Figure 61). Some of the samples were washed with acetone to remove oligomers and impurities before performing thermal properties analyzes. It was noticed that melting temperature (T_m) started increasing as the solid state polymerization progressed, from 155.98 °C to 177.56 °C after 30 h of reaction. However, T_m started decreasing for the samples of reaction over 30 h, which was assumed to be caused due to thermal chain scissions. [58]

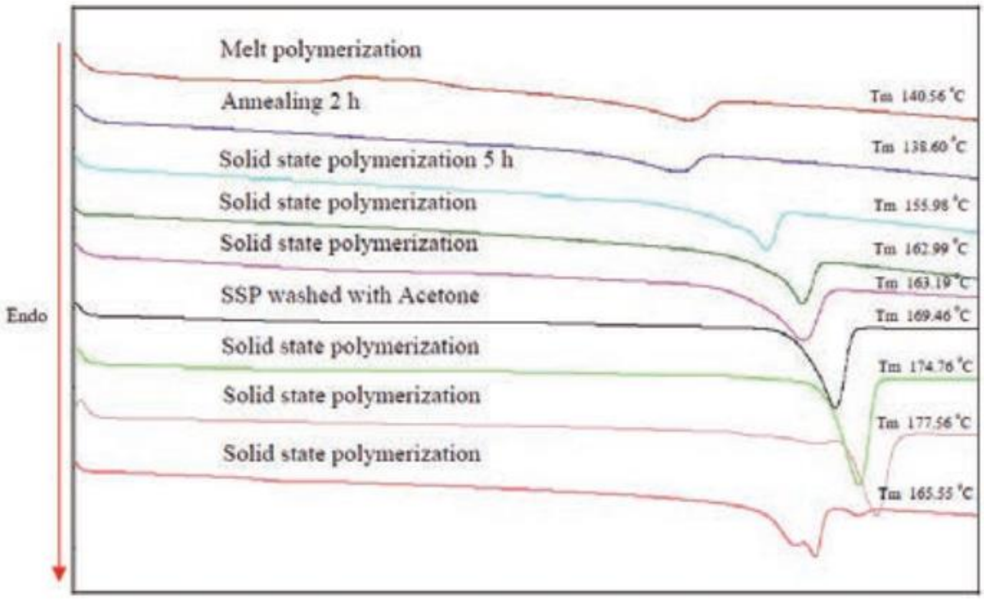


Figure 61. DSC analysis of pre-polymers and PDLA over the course of reaction. [58]

Gel Permeation Chromatography was used for the samples by the authors to deduce their molecular weight and the data was represented graphically as it can be seen in Figure 62. As the authors deducted, it is obvious that molecular weight increased in respect to reaction time and the molecular weight distribution (Mw/Mn) showed the same tendency over the increased reaction time. [58]

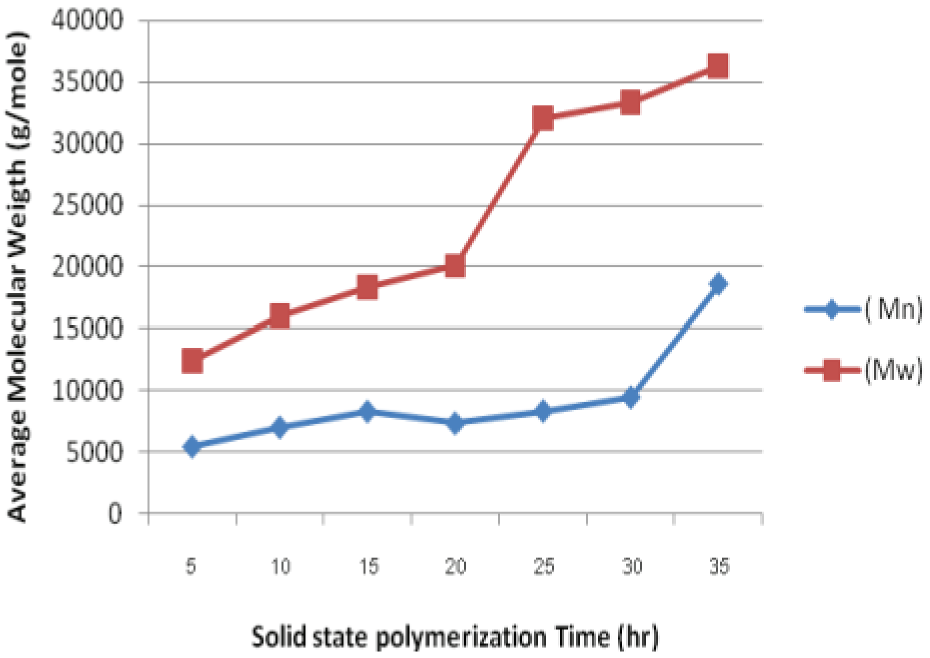


Figure 62. Polymer molecular weight relationship to time for the solid state polymerization. [58]

Authors of [60] performed a ROP using ε-caprolactone (CL) with stannous octoate as the catalyst with microwave irradiation. 2.45 GHz microwave oven was used with a maximum output power of 850 W, while the temperature was measured by insertion of thermocouple into ampoules. Experiment was conducted by mixing CL with 0.1 % of stannous octoate in a silanized ampoule that was sealed under vacuum after three dry nitrogen exhaust cycles. Ampoules were placed in a microwave oven for predetermined time, while taking temperature measurements every minute. Reaction was stopped by immersing ampoules into ice water, product was precipitated in methanol after being dissolved in methylene chloride and then filtrated and dried under vacuum. Identification of product was performed by ^{1}H-NMR by comparing it to known sample provided by producers of PCL, while weight-average molar mass (M_W) and polydispersity index (M_W/M_N) were obtained by gel permeation chromatography (Chloroform as eluent and calibrated by standard polystyrene). [60]

Four levels of microwave power were used (170, 340, 510 and 680 W) with CL in different sample sizes of 1, 5, 10, 15 and 20 g, which were named accordingly as CL1, CL5, CL10, CL15 and CL20. Observation was made that initial amounts of CL influenced heating drastically, after irradiation for 5 min at 170 W power, CL15 temperature was 289 °C, while CL1 was 72 °C, CL5 – 143 °C, CL10 – 219 °C and CL20 – 286 °C. In the interval from 5 to 10 min temperature differences varied only by 5 – 16 °C and after 15 min the temperatures stabilized for each sample due to achievement of thermal equilibrium. However, CL20 exploded at 6 min mark and was excluded from further investigations. Similar tendencies of temperature increase were observed at different power levels, although a linear relationship was observed between power levels and temperature for first 5 min, as higher power meant higher initial temperature. [60]

Similar tendencies were observed when stannous octoate was added to the reaction mixture, although equilibrium temperatures were slightly lower and in some cases initial temperature jumped higher before it self-regulated to equilibrium. The samples were renamed from CL1 to MCL1 accordingly to the initial amount of CL in them (CL5 to MCL5 etc.). [60]

Promising results were posted by the authors of [15] as they managed to achieve PCL with M_W of 52,400 g/mol after 3 min at 680 W with a yield of 90 % by ROP under microwave irradiation. They deducted that ROP was nearly completed after 5 min with M_W of 123,000 g/mol and yield of 95 %. Observation was made that after prolonged reaction time of 15 and 60 min M_w of MCL10 decreased to 65,800 g/mol (92 %) and 33,000 g/mol (86 %) respectively, while MCL1 reached M_W of 124,000 g/mol only after 30 min. Authors concluded that higher level of microwave power and a larger amount of CL induced higher temperature thus making the reaction rate faster. Accordingly, conclusion was made that PCL of high M_W can be synthesized by ROP under microwave irradiation in several minutes at 300 °C or by prolonged reaction of tens of minutes at around 200 °C. Comparison of results for MCL1 and MCL10 are provided in a Figure 63. [60]

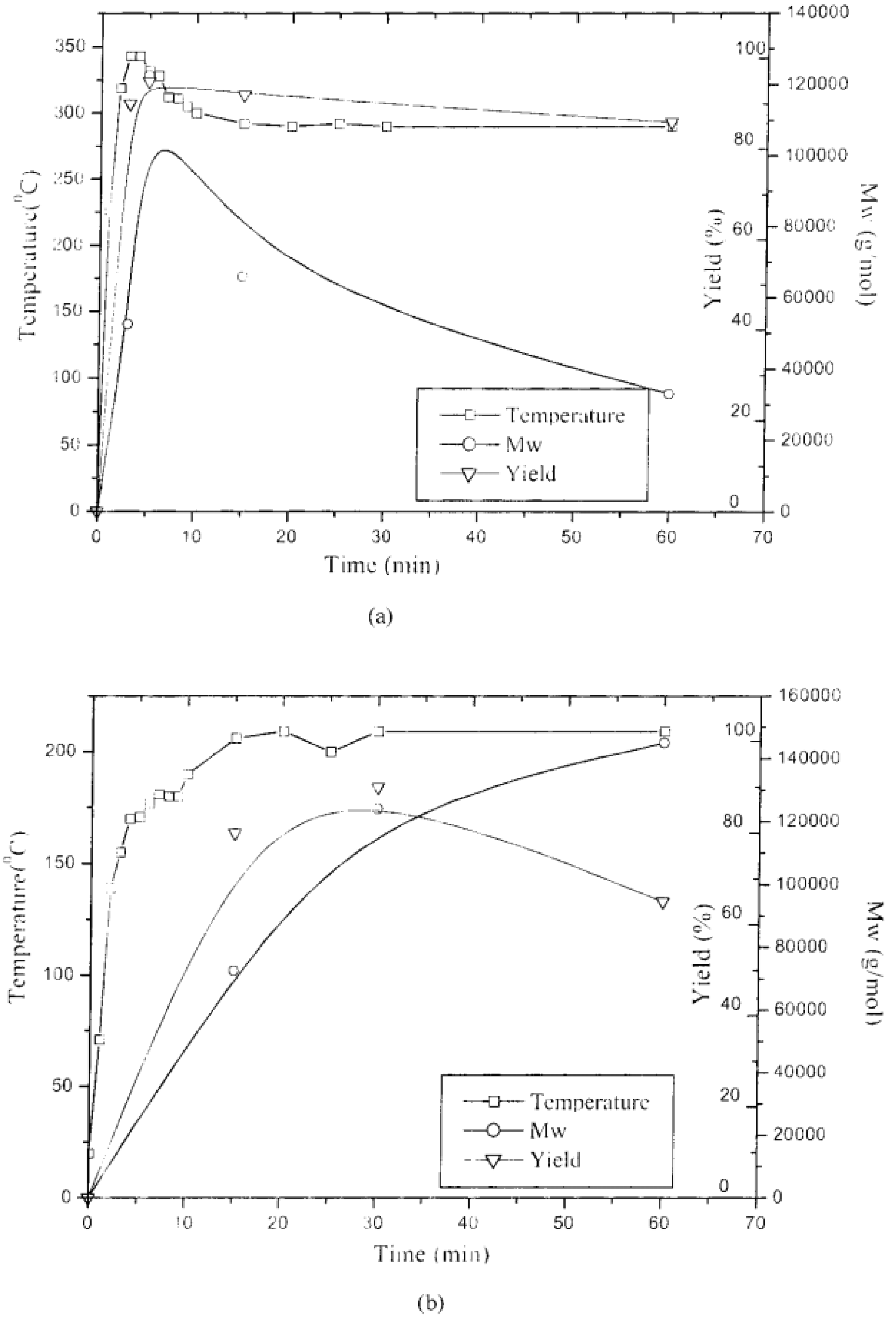


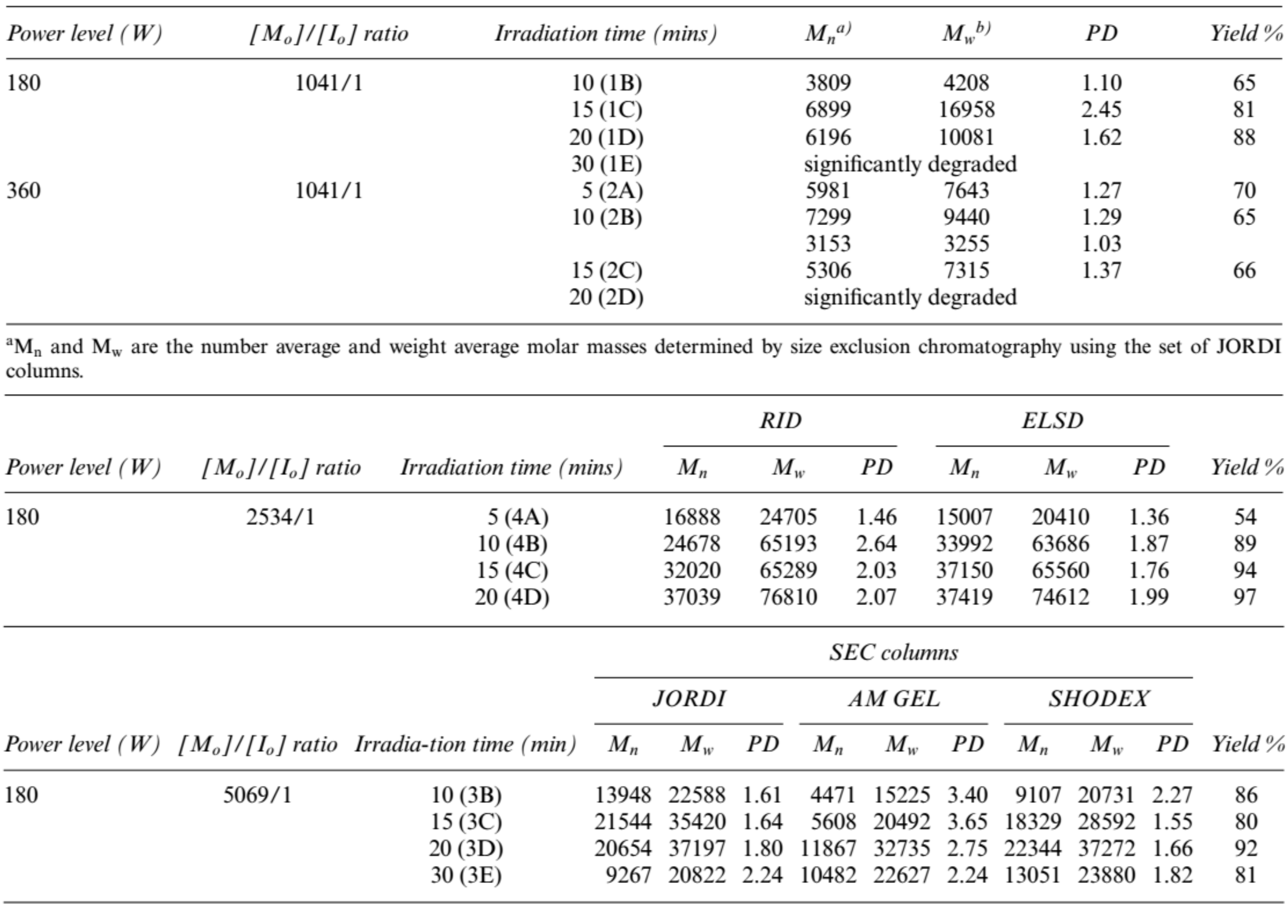
Figure 63. Plots of temperature, yield and M_W versus the time of ROP at 680 W: (a) MCL10; (b) MCL1. [60]

Microwave assisted ROP of L-lactide to PLA by using stannous octoate as catalyst was performed by authors of [56]. The reaction was performed at different power levels (180 and 360 W) and different monomer to catalyst ratio (1040/1, 2534/1 and 5069/1). The products were characterized by using FTIR and ^{1}H-NMR spectroscopy, while the molar mass of PLA was determined by the size exclusion chromatography (SEC). [56]

Reaction was performed in a microwave oven with working frequency of 2.45 GHz, while the reagent bottles of 30 mL were used as reaction vessels. L-lactide was mixed with a solution of the stannous octoate in diethyl ether solvent, then three cycles of vacuum were used to remove the solvent and the vessel was closed under the vacuum. After the reaction, product was cooled and dissolved in chloroform and precipitated in methanol. [56]

Authors of [56] discovered that prolonged exposure time to microwaves decreased the molar mass of PLA. For the ratio of monomer to catalyst $[M_0]/[I_0]$ of 1040, the molar mass of PLA was increasing for time up to 15 min and significantly degraded after 30 min of reaction. For the $[M_0]/[I_0]$ ratio of 2534, molar mass increased up to 20 min of microwave irradiation until it started degrading. For the $[M_0]/[I_0]$ ratio of 5069, the molar mass also increased for up to 20 min until the degradation began, but it was observed that it was slower than for $[M_0]/[I_0]$ ratio 2534. Resulting molecular weights for the experiment are provided in table 7. [56]

Table 7. Resulting molar masses and yields of the reactions with different monomer to catalyst ratios under microwave irradiation. Different SEC columns and detectors are marked, where used. [56]



Power level (W)	*$[M_o]/[I_o]$ ratio*	*Irradiation time (mins)*	*M_n*[a)]	*M_w*[b)]	*PD*	*Yield %*
180	1041/1	10 (1B)	3809	4208	1.10	65
		15 (1C)	6899	16958	2.45	81
		20 (1D)	6196	10081	1.62	88
		30 (1E)	significantly degraded			
360	1041/1	5 (2A)	5981	7643	1.27	70
		10 (2B)	7299	9440	1.29	65
			3153	3255	1.03	
		15 (2C)	5306	7315	1.37	66
		20 (2D)	significantly degraded			

[a]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.

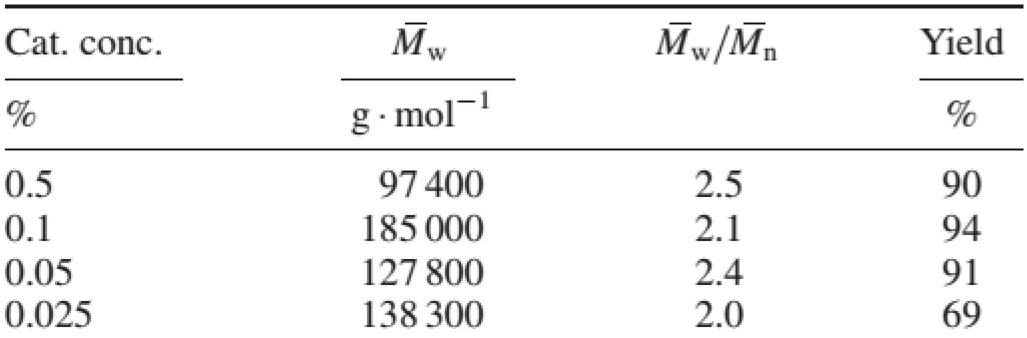
			RID			*ELSD*			
Power level (W)	*$[M_o]/[I_o]$ ratio*	*Irradiation time (mins)*	*M_n*	*M_w*	*PD*	*M_n*	*M_w*	*PD*	*Yield %*
180	2534/1	5 (4A)	16888	24705	1.46	15007	20410	1.36	54
		10 (4B)	24678	65193	2.64	33992	63686	1.87	89
		15 (4C)	32020	65289	2.03	37150	65560	1.76	94
		20 (4D)	37039	76810	2.07	37419	74612	1.99	97

			SEC columns									
			JORDI			*AM GEL*			*SHODEX*			
Power level (W)	*$[M_o]/[I_o]$ ratio*	*Irradia-tion time (min)*	*M_n*	*M_w*	*PD*	*M_n*	*M_w*	*PD*	*M_n*	*M_w*	*PD*	*Yield %*
180	5069/1	10 (3B)	13948	22588	1.61	4471	15225	3.40	9107	20731	2.27	86
		15 (3C)	21544	35420	1.64	5608	20492	3.65	18329	28592	1.55	80
		20 (3D)	20654	37197	1.80	11867	32735	2.75	22344	37272	1.66	92
		30 (3E)	9267	20822	2.24	10482	22627	2.24	13051	23880	1.82	81

It was concluded by authors of [56] that PLA of high molar mass of 7.6 × 10^4 g/mol with a yield >95 % can be synthesized under microwave irradiation through ROP in only 20 min. Final polymer is influenced by the microwave power level, monomer to catalyst ratio and simultaneous degradation of macromolecules, thus careful optimization of experimental conditions was proposed to achieve PLA with desired properties. Conclusion was also made, that size exclusion chromatography is a difficult method to use for the assessment of molar mass for PLA, due to limited polymer solubility in common SEC eluent, tetrahydrofuran. Solution was offered, chloroform as the mobile phase combined with evaporative light scattering detector (ELSD). [56]

Authors of [57] performed a microwave induced ROP of D,L-lactide using stannous octoate as the catalyst. D,L-Lactide for the reaction was prepared according to the literature, used by the authors, and recrystallized five time from ethyl acetate prior use. Stannous octoate was distilled and dissolved in dried toluene. Analyses were performed by ^{1}H-NMR, using tetramethylsilane dissolved in toluene as an internal standard, and GPC, where chloroform was used as eluent and calibration performed with polystyrene standards. Microwave oven (2.45 GHz working frequency) was used as a reactor. D,L-lactide was put into ampoules, degassed under vacuum and injected with a catalyst solution, then treated by three cycles of vacuum-argon to remove the solvent and sealed under vacuum. Different microwave power levels were used, formed product was dissolved in dichloromethane, precipitated in methanol and dried under vacuum. [57]

Table 8. Catalyst concentration influence on microwave induced ROP of D,L-Lactide (170 W for 15 min) [57]



Cat. conc.	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Yield
%	$g \cdot mol^{-1}$		%
0.5	97 400	2.5	90
0.1	185 000	2.1	94
0.05	127 800	2.4	91
0.025	138 300	2.0	69

It was concluded by ^{1}H-NMR spectroscopy, that the resulting compound is poly(D,L – lactic acid) (PDLLA), furthermore several interesting observations were made by the authors of [57]. It was noticed, that initial catalyst concentration influences the resulting polymer, as it is shown in Table 8. According to the results, 0.1 % molar ratio of catalyst gave the best results, as the increase in the concentration led to smaller polymer chains and increased polydispersity index, while polymers obtained by smaller concentrations of catalyst were also comparatively smaller, thus it was decided that further experiments would be performed with 0.1 % of stannous octoate. [57]

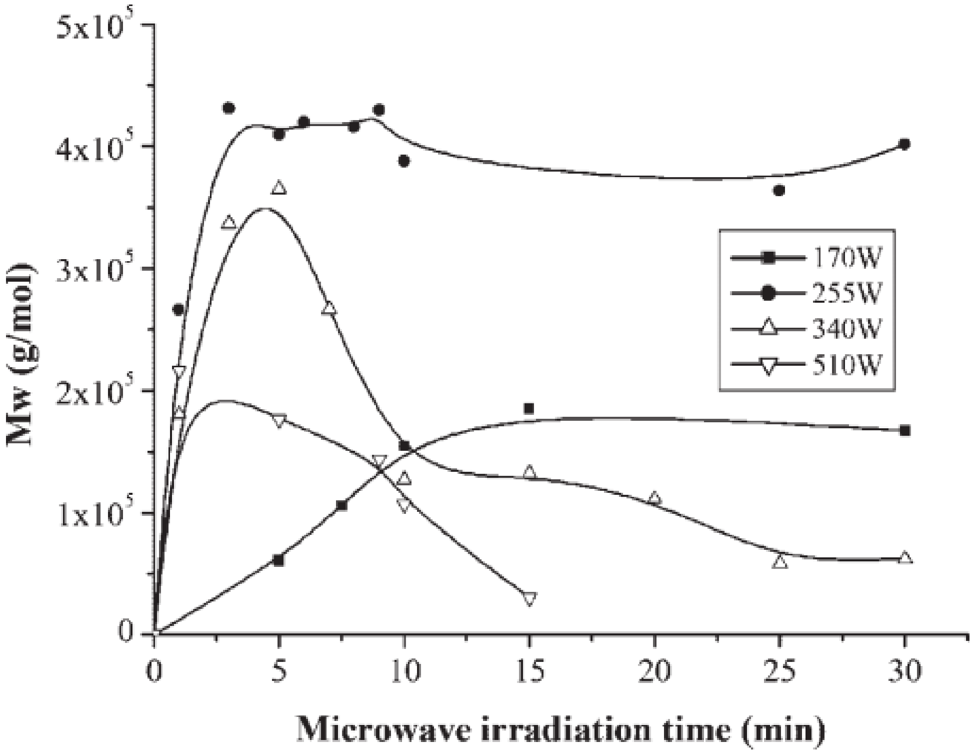


Figure 64. Different microwave power levels influence on molar mass over time. [57]

Investigation of four microwave power levels were performed (170, 255, 340 and 510 W) with measurements of the yield and resulting masses of polymers. Two tendencies of reaction profile were observed according to the power level used, type 1 (170 and 255 W) showed that the molar mass increased to nearly constant value over irradiation time, while type 2 (340 and 510 W) started showing decrease in molar mass after extended reaction time. To compare, PDLLA at 170 W showed increase in molar mass within 15 min of reaction (5 min – 61,100 g/mol; 10 min – 154,300 g/mol; 15 min – 185,000 g/mol) and after that showed no increase in molar mass. After 3 min at 255 W, the molar mass of PDLLA was 431,000 g/mol and stabilized at around 400,000 g/mol for remaining reaction time of 30 min. For type 2 reactions, at 340 W, molar mass reached maximum value at 5 min (365,200 g/mol) and started decreasing after 7, 10 and 30 min with the results of 266,900, 127,200 and 62,400 g/mol, respectively. For reaction at 510 W, decrease was observed after 1 min. Results were also presented graphically and can be seen in Figure 64. [57]

Conclusion was made by authors of [57], that the results for type 2 reactions (340 and 510 W) were influenced by a degradation reaction. After analyzing the yields for different experiments, they obtained that the yield of PDLLA at 170 W was 34, 59, 75, 80 and 94 % for 2, 3, 4, 5 and 15 min, respectively, while at 255 W it was 56, 69 and 84 % for 1, 3 and 5 min, and by the time of 6 min it reached 93 %. After increase of power to 340 W, highest molar mass obtained was 365,200 g/mol at 5 min mark, which was surprisingly smaller than 431,000 g/mol at 3 min for reaction at 255 W. It was noticed that for any period of time, even at 1 min mark, the molar mass at 255 W was higher than that at 340 W, thus confirming that the rate of degradation reaction was increased together with an increase in power. This was also confirmed by an observation that the yield was growing for the reaction at 340 W, although the molar mass was decreasing due to scissions in the polymer chains caused by increase in rate of degradation. For reaction at 510 W, degradation was assumed

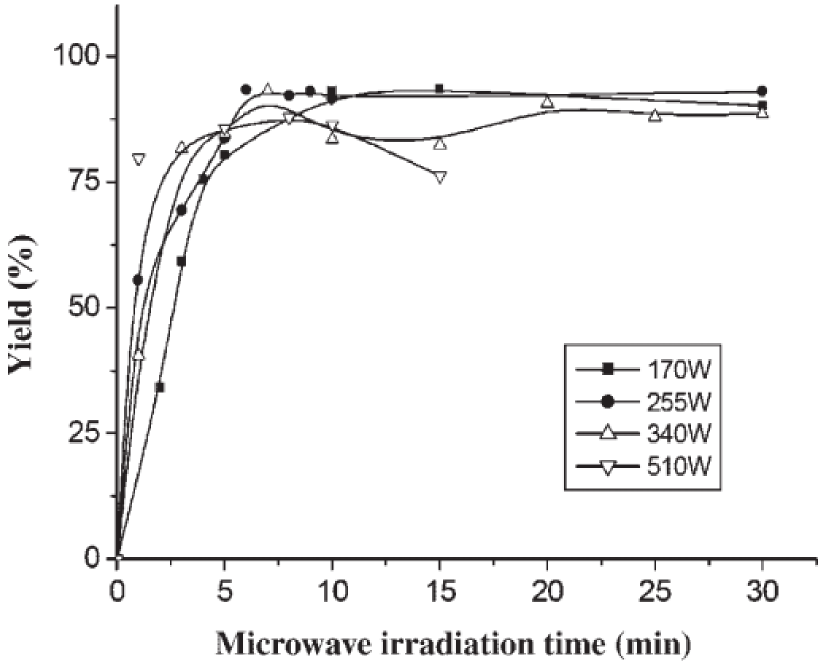


Figure 65. Influence of microwave pover on yield for ROP of PDLLA (1.8 g D,L-lactide + 0.1 % Stannous octoate). [57]

to be predominant thus resulting in fast decrease in molar mass from the beginning. The graphical representation of yield over time for the mentioned experiments are provided in Figure 65. [57]