

## THE INFLUENCE OF REACTION TIME ON THE PROPERTIES OF MICROWAVE SYNTHESIZED POLY(LACTIDE)

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**Abstract:** The consequence of drastic reduction in fossil fuel reserves has forced the scientific community to find and develop new ways to exploit renewable resources and optimize the process of polymer materials production. The aim is to obtain applicable polymer whose complete life cycle is set in ecological framework. Poly(lactide) (PLA) meets these requirements as biodegradable polyester whose monomer is derived from the plant feedstock containing carbohydrates. PLA could be prepared using the different synthesis routes, but from the point of energy saving, as well as environmental protection, the microwave synthesis of PLA is the best solution. In this work, poly(L-lactide) were synthesized in microwave reactor. Reaction time was varied, while the other parameters of the synthesis were constant. The structures of obtained polymers were confirmed by Fourier – transform infrared spectroscopy (FT-IR). For determination of molar masses of poly(L-lactide) samples, the gel permeation chromatography (GPC) was applied. Thermal properties were investigated by differential scanning calorimetry (DSC).

**Keywords:** poly(lactide), microwave synthesis, molar mass, thermal properties.

### 1. INTRODUCTION

Industrial revolution in 18<sup>th</sup> century has imposed the need for the increased use of fossil fuels as energy resources and raw materials for polymer synthesis. Drastic reduction of fossil fuels reserves followed by large production costs as well as environmental pollution have forced the scientific community to investigate the use of alternative energy resources and development of biobased polymer materials. Within the framework of concept of energy saving and development of sustainable product, the methods for obtaining, modifying and applying of biopolymers have been investigated. Complete life cycle of such materials, starting from their preparation to the application of final product and its disposal, corresponds to ecological and environmental demands. Biopolymers are biodegradable polymers extracted from the biomass or synthesized from the monomers obtained from the renewable resources. High availability and biodegradability make

biopolymers more suitable for obtaining and disposing in comparison with conventional plastic.

By developing of adequate method for modification of their functional properties, biopolymers could become appropriate replacement for polymers derived from fossil fuels. Poly(lactide) (PLA) as biodegradable polyester whose monomer is derived from the plant feedstock containing carbohydrates, meets requirements imposed by concept of sustainable management. The two main monomers used for synthesis of PLA are lactic acid (2-hydroxypropanoic acid) and the cyclic diester lactide. For preparation of lactic acid, two industrial routes are used: bacterial fermentation of carbohydrates and chemical synthesis from acetaldehyde, but fermentation is the most common procedure for lactic acid obtaining because of implementation the concept of energy and resources saving [1,2]. Waste products of the food industry and agriculture, rich in carbohydrates, can be used for the preparation of lactic acid by fermentation, which not

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only decreases the cost of polymer manufacture, but also solves the problem of waste disposal. PLA also possess the property of biocompatibility that makes it one of most commonly applied bioplastic; subject to hydrolysis, it gives a lactic acid that can be metabolized in human body as well as in natural environment. Two enantiomers of lactic acid (L and D) can give three forms of cyclic di-ester: L-lactide, D-lactide and D,L-lactide. Depending on the ratio of enantiomers, it is possible to obtain PLA polymers with different properties [3]. Direct polycondensation of lactic acid gives only the low molecular weight polymer – poly (lactic acid). Every step of the polyesterification generates one equivalent of water as by-product, which is undesirable because water can act as a chain transfer agent leading to the low molecular weight polymer [4]. The higher conversions could be achieved by removing water from the system during the synthesis or by applying the two-step process. The first step encompasses the condensation of lactic acid units into PLA oligomers, those are being combined in second step using the coupling agent. Removing of water during the synthesis as well as using a coupling agent to obtain higher molecular weights makes this process longer, more complicated and more expensive. For the preparation of high molecular weight polymer, ring opening polymerization (ROP) of cyclic lactide is used [5] (Figure 1). This process can be carried out via cationic, anionic and non-ionic insertion mechanism [3]. ROP process demands high purity of the monomer, specific catalyst and solvent and depending on methods, high temperature, high pressure or vacuum. Cationic polymerization is efficiently initiated by trifluoromethanesulfonic acid (as a catalyst) in organic solvent such as dichloromethane [6]. The reaction takes place for at least four hours. Various metallic alkoxides are employed as initiators for anionic mechanism of ROP polymerization [7]. Tin (II) 2-ethylhexanoate  $\text{SnOct}_2$  is one of the commonly used catalyst for the synthesis of poly(lactide). Two mechanisms are suggested for synthesis of PLA initiated by this catalyst. The first proposed mechanism is an activated monomer mechanism in which the monomer coordinates with  $\text{SnOct}_2$  [8]. In the second proposed mechanism  $\text{SnOct}_2$  reacts with compounds containing OH groups giving an initiator such as tin (II) alkoxide or hydroxide. Chain growth is achieved via inserting of monomer [9]. Therefore, different mechanisms are proposed for polymerization of lactide in solution. These traditional methods of synthesis require large consumption of energy, time and reagents. Polymerization in organic solvent takes place from 4 to 50 hours, depending on applied mechanism,

temperature, catalyst and solvent. The applied temperature ranges from 40 to even 280 °C. Long polymerization time and high temperature require significant quantities of energy.

Difficulties that occur during the traditional methods of PLA synthesis can be overcome using a microwave heating [10]. This procedure simplifies and accelerates the reaction of polymerization of lactide reducing the reaction time to 5-30 minutes. Sensitivity of the reaction to impurities and moisture from the air is significantly reduced due to the fact that the reaction takes place very quickly, so there is no need for recrystallization of monomers or carrying out of reaction under the vacuum [3,11]. Homogenous heating of the whole reaction mixture and high transfer energy per unit of time result in faster polymerization rate [11–13]. Microwave synthesis allows obtaining a high molecular weight polymer in a short time in improved yield [11]. The group of authors compared the parameters of different method for synthesis of PLA as well as properties of obtained polymers. They have performed synthesis in vacuum sealed vessels, synthesis in high pressure reactor, in dichloromethane and in microwave reactor [3,11]. Synthesis in vacuum sealed vessels has taken 110-150 minutes, in high pressure reactor 4-8 hours, as well as in solution. Microwave synthesis has lasted just for 0.17–0.5 hours. The consequence is reduced energy consumption followed by improved yield. Poly(lactide) samples synthesized in microwave reactor have high molecular weights, higher than the ones synthesized by traditional methods [11,14]. The aim of this work is microwave-assisted synthesis of poly(L-lactide) polymers and investigation of the influence of synthesis duration on their molecular weights and thermal properties with emphasis on the aspects of energy and resources saving accomplished by using this type of synthesis.

## 2. EXPERIMENTAL PART

### 2.1. Materials

Monomer L-Lactide (3,6-dimethyl-1,4-dioxane-2,5-dione) and initiator tin(II)2-ethylhexanoate were purchased from Sigma-Aldrich Wiscosin. Chloroform and toluene were supplied from Merck Chemical Co.

### 2.2. Microwave synthesis of PLLA

L-lactide, pre-crystallized from methanol was placed in evaporating bowls together with tin(II)

2-ethylhexanoate whereby the monomer to initiator ratio was 2000 ( $[M]/[I]$ ). After addition of toluene, a mixture was homogenized and toluene was evaporated at 60 °C for 12h. The reaction system was then replaced into glass ampoule and closed under reduced pressure. Polymerization was carried out in microwave reactor, CEM Corporation,

Matthews, NC, USA at frequency of 2.45 GHz and power of 150 W. During the microwave synthesis reaction time was varied (5, 10, 20, 30 min), while the other parameters were constant. The temperature regulation was carried out by infrared mass measuring system and maintained at 100 °C.

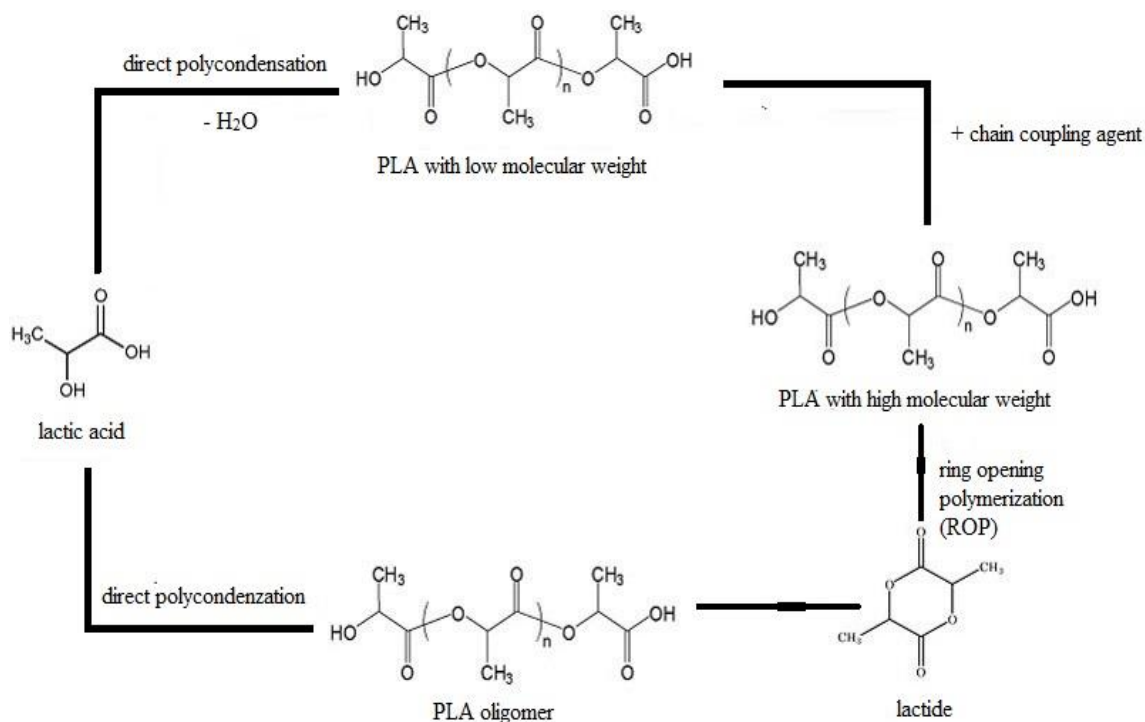


Figure 1. Synthesis of PLA by direct polycondensation and ROP method

### 2.3. Methods

The chemical structure of obtained samples were analyzed by Fourier transform infrared spectroscopy (FTIR spectrophotometer Bomem Hartmann & Braun MB-series). The chemical bond vibrations were recorded in the range of 4000–400  $\text{cm}^{-1}$ , using the KBr pellets for the sample preparation.

The molecular weight of obtained polymers was determined by gel permeation chromatography, GPC, using Agilent 1100 Series system with refractive index, RID 1200, and diode array, DAD, 1200 (recording at 212 nm) detectors. Used column ZORBAX PSM 300, 250  $\times$  6.2 mm, 5  $\mu\text{m}$ , covered molecular mass range  $3 \times 10^3 - 3 \times 10^5$  g/mol and operated at temperature 25 °C. Tetrahydrofuran was used as eluent (flow 1  $\text{cm}^3/\text{min}$ ). Sample injection volume was 10  $\mu\text{l}$ . Software Agilent ChemStation for LC and GPC was used for determination of average molar masses,  $M_n$ ,  $M_w$  and poly(L-lactide) polydispersity index Q. Poly(styrene) standards were used to make calibration curve (FLUKA).

Thermal properties of synthesized polymers were investigated using the differential scanning calorimeter (TA Instruments Q20) under nitrogen atmosphere in temperature regime from 20 to 200 °C, at heating rate of 10 °C/min. For monitoring the heat degradation of synthesized polymers, the instrument TGA Q50 TA Instruments was used. Platinum vessels were used for placement of the examined samples. The decomposition of the samples was monitored in nitrogen atmosphere with a flow rate of 20  $\text{cm}^3/\text{min}$  and heating rate 10 °C  $\text{min}^{-1}$ , in the temperature range from 20 to 650 °C. The sample weight was about 13 mg.

### 3. RESULTS AND DISCUSSION

Figure 2 shows the temperature and applied power dependence on time. The plot is divided into three parts. Monomer lactide, as a very polar compound, absorbs the microwaves very well, so the temperature of reaction mixture rises fast in the first 80 s.

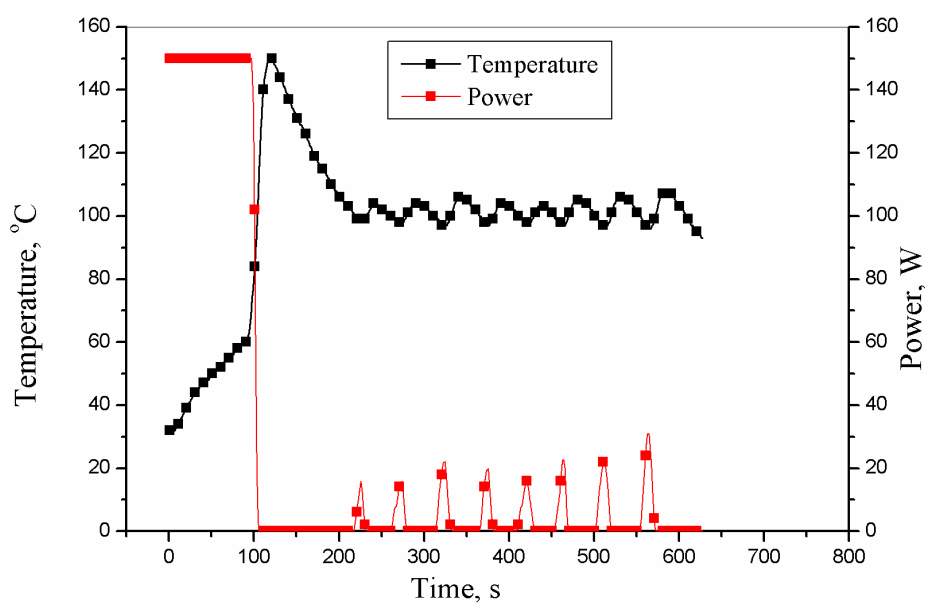


Figure 2. Temperature and microwave radiation power dependence on reaction time

Realised heat during the exothermic effect of ROP reaction resulted in temperature increasing in the second part. It can be observed that polymerization begins at 70 °C, when the absorption of microwaves decreased as a result of increasing of polymer content and reducing the content of monomer lactide. After achieving appointed temperature value (100 °C), a microwave radiation switched off and applied power of 150 W from the beginning of reaction becomes zero. In the sequel of polymerization, a power of 20 W is applied to maintain appointed temperature. In the third part, a very small absorption of microwaves is observed. That implies the presence of significant amount of linear polymer.

Chemical structure of synthesized polymers was confirmed by FTIR analyses (Figures 3 and 4). Broad peak at 3465  $\text{cm}^{-1}$  corresponds to the O-H stretching. Weak peak at 2995, indicates the presence of C-H stretching and peaks at 2879 and 2831  $\text{cm}^{-1}$  indicates the presence of C-CH<sub>3</sub> bond. CH<sub>2</sub> bending vibrations are confirmed by weak peak at 1453  $\text{cm}^{-1}$ . Sharp peak at 1757  $\text{cm}^{-1}$  implies the C=O stretching vibrations. In lactide FTIR spectrum (Figure 3), this peak appears at 1770  $\text{cm}^{-1}$ . In FTIR spectrum of lactide, C-O-C stretching vibrations are detected at 1267 and 1099  $\text{cm}^{-1}$ (Figure 3). The asymmetrical valence vibrations of C-O-C of the aliphatic chain were shifted at 1188  $\text{cm}^{-1}$  and symmetrical valence vibrations of C-O-C to 1090  $\text{cm}^{-1}$  (Figure 4).

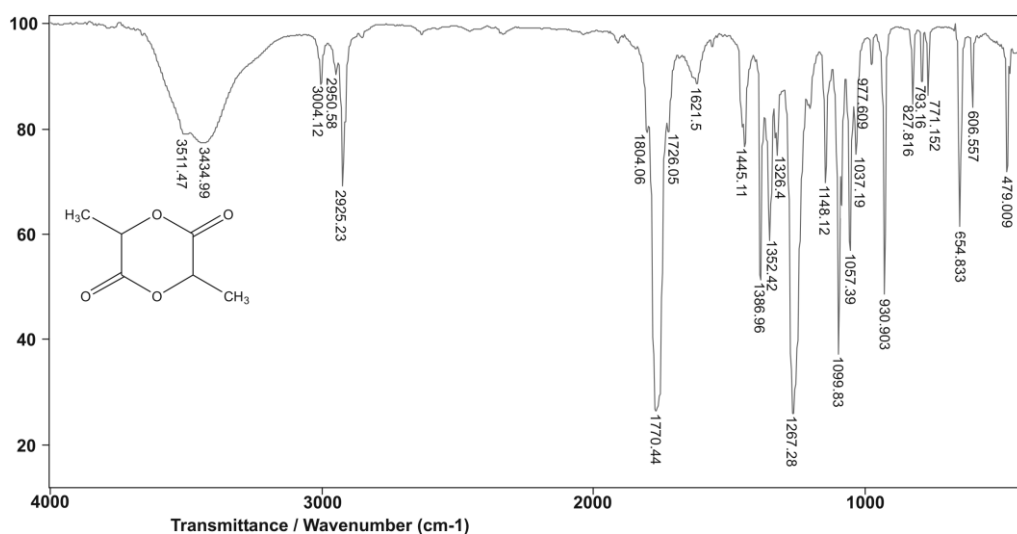


Figure 3. FTIR spectrum of monomer L-lactide

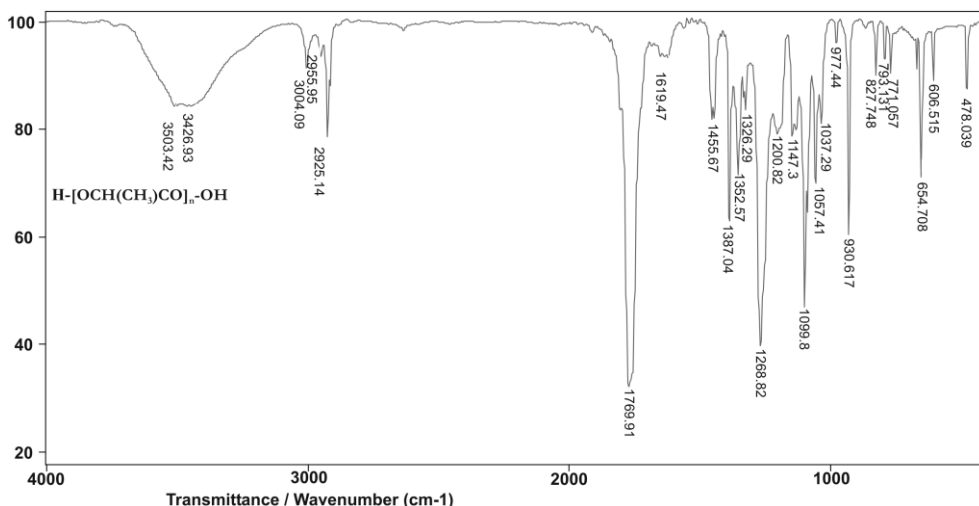


Figure 4. FTIR spectrum of poly(L-lactide)

The results of GPC analysis of average molar masses of synthesized polymers are shown in Table 1 and Figures 5 and 6. Average molar mass increase as a reaction time increases. In only 5 minutes, it is possible to obtain poly(lactide) with molar mass of around 50000 g mol<sup>-1</sup>. After 20 minutes of synthesis,

further increasing of reaction time had not significantly influence the molar masses values. Applied method also provided very narrow molar mass distribution, which is also important for application of obtained poly(lactide).

Table 1. Average molar masses for PLLA samples synthesized in microwave field obtained by GPC analysis

Sample	Reaction time (min)	Mn, x10 <sup>4</sup>	Mw, x10 <sup>4</sup>	Mw/Mn
PLLA 1	5	4.980	6.439	1.293
PLLA 2	10	5.341	6.110	1.144
PLLA 3	20	6.403	8.090	1.263
PLLA 4	30	6.662	8.495	1.275

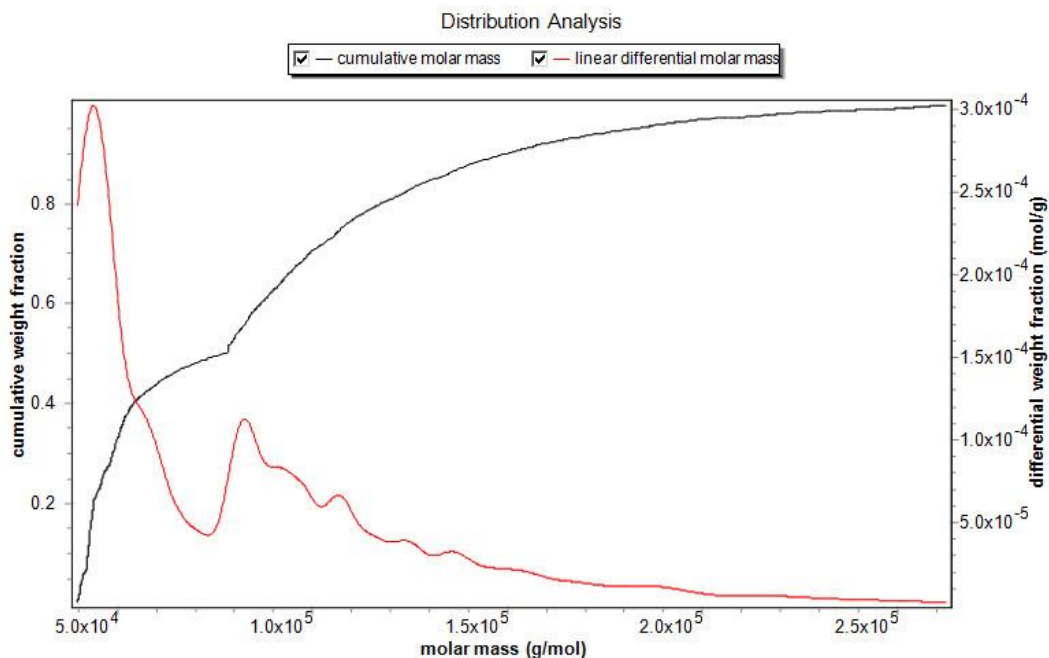


Figure 5. Cumulative and differential molar mass of PLLA 1 (synthesized in microwave in 5 minutes)

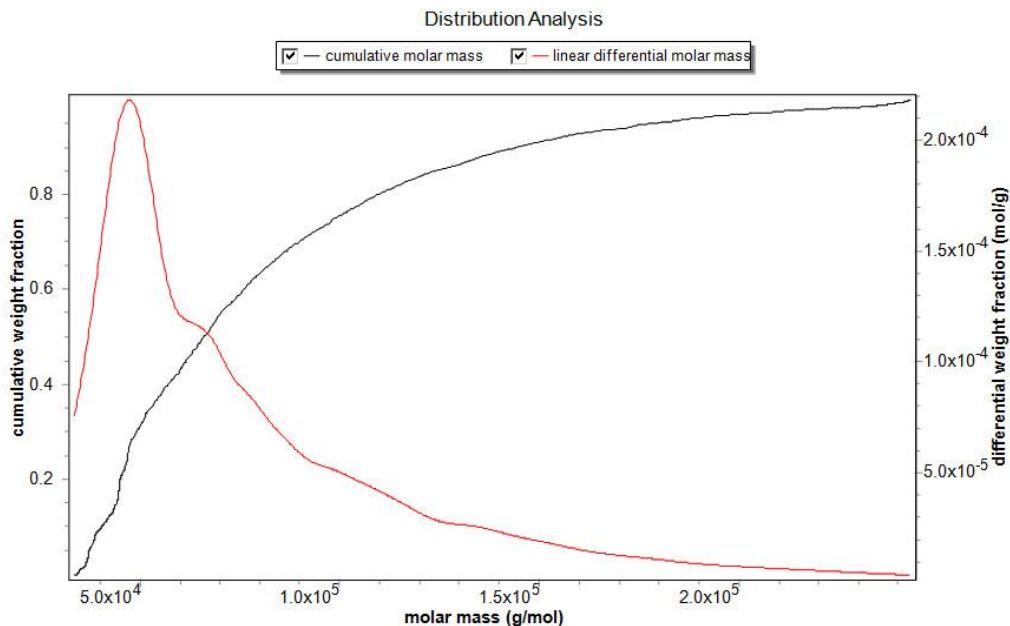


Figure 6. Cumulative and differential molar mass of PLLA 2 (synthesized in microwave in 10 minutes)

The comparative DSC curves of PLLA samples are given in the Figure 7. Significant changes in glass transition temperature are not observed for the samples synthesized for different time intervals. However, temperature of “cold” crystallization increases with increasing of reaction time, which is the consequence of higher molar mass of polymer achieved after longer reaction time. Sudden rise in enthalpy (from 18 to 31 J/g) is observed after increasing the synthesis duration time from 5 to 10 minutes. Other increasing in polymerization time, above 10 minutes, does not result in significant increasing of enthalpy. It can be explained by

achieving the maximal degree of conversion in the time interval of around 10 minutes. Regularity in change of melting temperature and enthalpy over time is not observed, indicating that increasing of PLLA molar mass is primary realized by increasing of amount of amorphous phase in polymer sample.

Thermal stability of PLLA samples was investigated by thermo-gravimetric analysis. Recorded thermo-gravimetric curves for all samples were put at the same plot (Figure 8). It can be observed that onset temperature rises with increasing of reaction time, so the PLLA 4 sample has the best thermal stability.

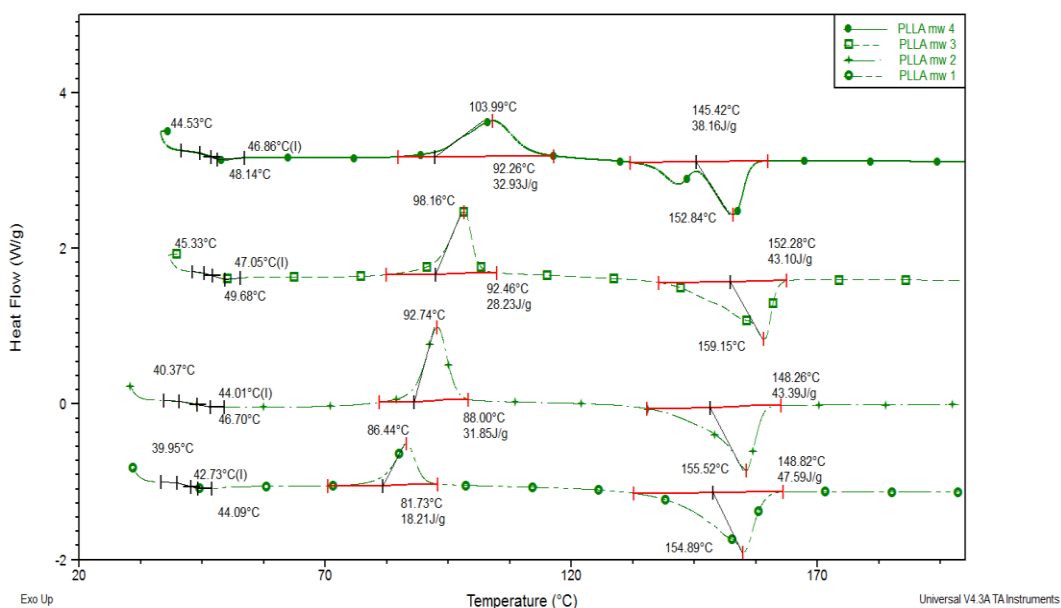


Figure 7. DSC curves for PLLA samples synthesized in microwave reactor during the different reaction time

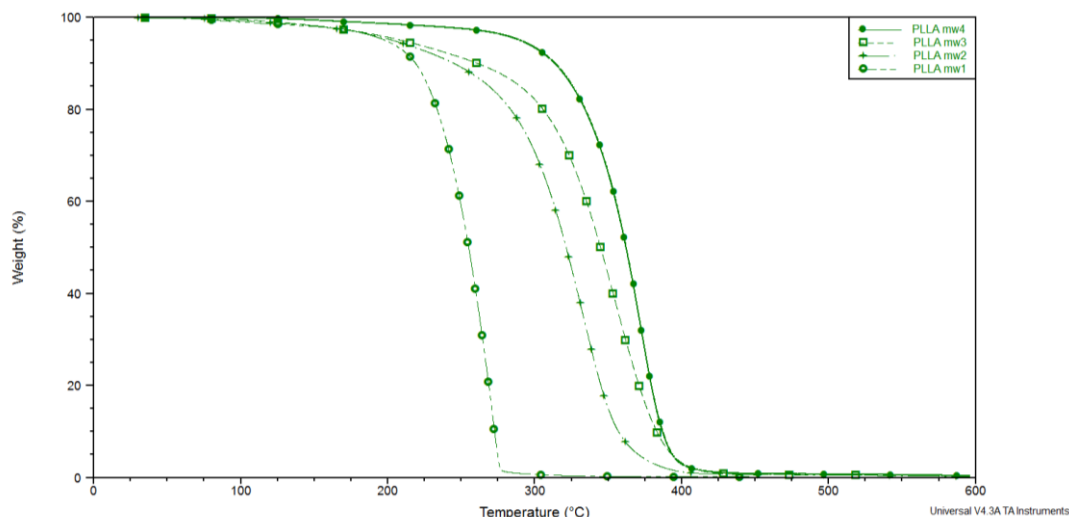


Figure 8. TG curves for PLLA samples synthesized in microwave reactor during the different reaction time

#### 4. CONCLUSION

The use of microwaves for poly(L-lactide) synthesis enables homogenous heating of reaction mixture, lower consumption of organic solvent and drastic reduction in polymerization duration, achieving, in the same time, high molecular weight polymers. Obtained results have showed that molar mass of PLLA increases with increasing of reaction time in the range from 5 to 30 minutes. That reflects to thermal properties of obtained polymers as increasing the temperature of “cold” crystallization and shifting the temperature of the beginning of decomposition to higher values.

#### 5. ACKNOWLEDGEMENTS

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#### УТИЦАЈ ВРЕМЕНА РЕАКЦИЈЕ ПОЛИМЕРИЗАЦИЈЕ НА СВОЈСТВА ПОЛИ(ЛАКТИДА) СИНТЕТИСАНОГ У МИКРОТАЛАСНОМ ПОЉУ

**Сажетак:** Дрaстично смањење резерви фосилних горива мотивисало је научну заједницу да пронађе и развије нове начине за експлоатацију обновљивих ресурса и оптимизацију процеса производње полимерних материјала. Циљ је добити одговарајући полимер чији је комплетан животни циклус постављен у еколошком оквиру. Поли(лактид) (ПЛА) испуњава ове захтеве као биоразградив полиестер чији мономер се добија из биљних сировина богатих угљеним хидратима. ПЛА се може добити користећи различите поступке синтезе, али са становишта уштеде енергије, као и заштите животне средине, микроталасна синтеза ПЛА је најбоље решење. У овом раду, поли(Л-лактид) је синтетисан у микроталасном реактору. Време реакције је варирао, док су остали параметри синтезе били константни. Молекулска структура добијених полимера анализирана је инфрацрвеном спектроскопијом са Фуријеовом трансформацијом (ФТ-ИЦ). За одређивање молских маса поли(Л-лактида), примењена је гел пропусна хроматографија (ГПЦ). Термичка својства су испитивана диференцијалном скенирајућом калориметријом (ДСЦ).

**Кључне речи:** поли(лактид), микроталасна синтеза, молска маса, топлотна својства.



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