

molar hydrogen/ feedstock ratio. The dynamics of flow changes in the reactor is carried out from 4.0 l/h to 12.0–14.0 l/h for the entire cycle with the temperature increase in the reactor.

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## Comparison of HPLC, GPC and MS-TOF techniques for determination of the average molecular mass of PLA oligomer

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Poly-lactic acid (PLA) is a biodegradable aliphatic polyester produced industrially both on large and small scale. It is used for a wide variety of applications, ranging from biomedical applications to raw material for food packaging, bottles and consumables in general.

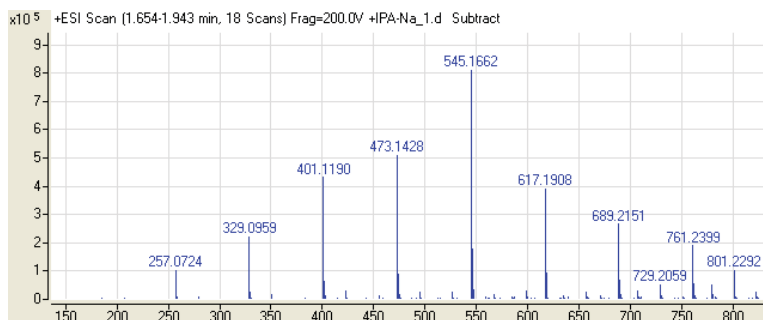
The most popular industrial production process is actually a multistep process. Firstly, lactic acid (LA) is polymerized to low molecular weight polymer (LMW PLA, < 10 kDa) by bulk Melt Polycondensation and then depolymerized and converted to the lactide, cyclic dimer of LA, in a catalytic step usually carried out at high temperature and low pressure. Finally, purified and dried lactide undergoes the Ring-Opening Polymerization for obtaining high molecular weight polymer (HMW PLA, > 100 kDa). The first step has to be carefully performed in order to optimize the extent of polymerization and minimize the multiple side reactions like discoloration, cyclization, transesterification and racemization which affect the purity of the final cyclic dimer produced from the PLA oligomers itself [1, 2].

The purpose of this study is to compare the various characterization techniques for monitoring the molecular weight of PLA oligomers.

PLA oligomer was obtained from lactic acid (PUREAC, Spain) in presence of ZnO as a catalyst and at constant temperature 160 °C.

Average molecular mass of obtained oligomer was determined by Gel Permeation Chromatography (GPC), High Performance Liquid Chromatography (HPLC) and High Resolution Mass-Spectrometry with Time-of-Flight detection (MS-TOF). GPC analysis was carried out on a PLgel 5 µm MIXED-C column (300 mm × 7.5 mm) using a series apparatus Agilent 1200

equipped with RI detector. MS-TOF analysis was performed on Time-of-Flight detector Agilent 6320, sample ionization was performed with sodium acetate solution. Reversed phase HPLC analysis was done using an YL9100 HPLC system with UV/Vis detector, the analytical column was a Tracer Excel 120 ODSA (250 mm  $\times$  4.6 mm, 5  $\mu$ m), chromatographic separation and calculation were carried out in accordance with article [3]. MS-TOF mass-spectra of LMW PLA is shown in Figure 1.



**Fig. 1.** Mass-spectra of PLA oligomer ionized with  $\text{Na}^+$ , positive mode

Among the various analytical techniques for molecular weight of polymers GPC is the most popular since the complete molecular weight distribution is provided. However, for LMW PLA the calibration with expensive PLA standards is required. The universal calibration based on polystyrene standards can be applied, but the selection of reliable values of the Mark-Houwink constants is an issue, due to the largely different values that leading to the significant error in calculations. HPLC represents an alternative analytical technique for investigating the entire chain length distribution of LMW PLA. This provided the basis for the development of a new separation method which was more accurate, easy and efficient. The developed HPLC technique is validated by comparison to MS-TOF method. Results are shown in Table 1.

**Table 1.** Comparison of values of average molecular mass of LMW PLA

Parameter	GPC	HPLC	MS-TOF
Mn	1190	443	512
Mw	2110	498	557
D	1.8	1.1	1.1

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## Spectroscopic Methods Applied to the Characterization of Phenol Oxidation Intermediates

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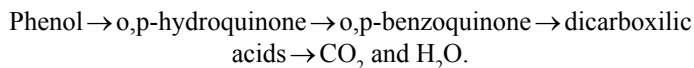
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Phenols and substituted phenols are important raw materials for wide variety of organic compounds, dyes, pharmaceuticals, plasticizers, antioxidants, etc. Phenols are present effluent from the chemical process industries which are either manufacturing or using them.

Combined oxidation of phenolic wastes offers an alternative treatment method to destroy phenolics totally. It consist, in essence, of the electrochemical generation of high-reactivity intermediates, and on either a cathode or an anode (or, possibly, on both the cathode and the anode simultaneously) and their subsequent chemical decay of phenol in an electrolytic solution. In this work oxidizing agent is generated in aqueous sulfuric acidic solutions under direct current. It has been identified that the maximum rate of phenol cleavage achieved with the sulfuric acid concentration of 30%. The assumed scheme of phenol cleavage by electrogenerated oxidizing system is a typical oxidation process of phenol in the liquid phase [1].



We carried out the identification of intermediates and final products by means of UV spectrophotometry, gas chromatography with mass selective detector and high performance liquid chromatography.

For UV spectrophotometry a samples were prepared by following procedure: 0.1 ml of a solution from electrolyzer diluted to 1 ml with distilled water and then record the spectrum using quartz cell.

A sample preparation for gas chromatography with mass selective detec-