

# **Polymerization of L-lactide catalyzed by initiators**

## **(Polimeryzacja L-laktydu katalizowana inicjatorami)**

by

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### **SUMMARY**

The title of my dissertation is „*Polymerization of L-lactide catalyzed by initiators*” („*Polimeryzacja L-laktydu katalizowana inicjatorami*”). My goal was to find organic compounds that bear the initiator and catalyst functions in a single molecule and allow to polymerize L-lactide (LA) in the controlled manner. Those compounds, called INICAT, are an object of the patent allowed CBMiM in 2014. The commonly used initiating – catalytic systems are composed of two separate molecules - a catalyst (a strong base) and an initiator (an alcohol or primary/secondary amine).

Every INICAT molecule composes of a fragment from strong organic base, acting as a catalyst, and a hydroxyl group, that acts as an initiator. The whole INICAT molecule binds itself with a growing polymer chain by a covalent bond and becomes its end-group. Such an

approach allows to reduce catalyst's toxicity. It also simplifies purification because after polymerization there is only polymer and unreacted monomer present in the polymerization vessel. What is more, the hydrophilic end group bound with hydrophobic chain could potentially allow to obtain short amphiphilic oligomers.

During screening experiments I have chosen two INICATs. The first one is the 6-(2-hydroxyethyl)-aminopurine (HEA) which allows to polymerize L-lactide in bulk in 120 °C with a control of  $M_n$  between 2 000 and 40 000. Second chosen INICAT is 3-[(4,5-dihydro-1H-imidazol-2-yl)amino]-propanol (HPG) that can polymerize L-lactide in the range of temperatures from 25 °C to 120 °C. The polymerization of L-lactide with HPG can be conducted both in solvent and in bulk obtaining poly(lactides) (PLAs) with  $M_n$  up to 13 000.

During my studies I have focused on both the determination of the structure of obtained polymers and the determination of the dependence of polymerization rate on conditions.

What is more a new method of online kinetic studies has been elaborated based on standard  $^1\text{H}$  NMR experiments and DOSY (Diffusion Ordered Spectroscopy). It allows to determine all fundamental kinetic parameters ( $M_n$ ,  $M_w$ ,  $D$ , monomer conversion) during one measurement in a sealed NMR tube.

The major tool I have used during structural studies was MALDI-ToF ms (MTms) spectroscopy. In both cases (HEA-PLA and HPG-PLA) there were only PLAs with INICAT end-groups visible on the spectra. To confirm MTms results, using another less invasive method, HPG-PLA and HEA-PLA samples were analyzed by DOSY NMR that allows to determine diffusion coefficients of all atoms in the macromolecule. In both cases the values of diffusion coefficients of the atoms of former INICATs were close to the values of the diffusion coefficient of the PLA main chain and order of magnitude lower than those, determined for low molecular weight compounds.

In more detailed structural studies I have applied  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^1\text{H}$ - $^{13}\text{C}$ / $^1\text{H}$ - $^{15}\text{N}$  NMR experiments. I have established that in case of HPG there are two PLA arms growing from a single INICAT molecule and only one PLA arm grows from a single HEA molecule. I have also determined that PLA arms growth starts on  $-\text{OH}$  groups and  $>\text{NH}$  groups that are not a part of aromatic system.

Kinetic results (online measurements by FTIR) show that after an acceleration period (HEA) or deceleration period (HPG) in both cases there are constant numbers of active species. This shows, that, at least during the studied period, both polymerization could be considered living.

Determined dependences of  $M_n$  on conversion for both HPG and HEA initiated/catalyzed polymerizations plots are linear. This indicates controlled nature of those processes (the number of growing chains is constant - there are no transfer reactions).