Synthesis and investigation of potentially biodegradable, polylactic acid based polymers

Doktori (Ph. D.) értekezés tézisei

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I. Introduction and objectives

One of the essential problems of 21th century is the handling of non-biodegradable plastics. These plastics were synthetized in large quantities all over the world because these materials are very cheap and useful.

Nowadays, the main goal of polymer research is the preparation of new types of polymers, which meet environmental expectations, namely they are biodegradable and show biocompatible properties.

The polylactic acid (PLA) as a biodegradable and biocompatible material is one of the main interest of research.

At the Department of Applied Chemistry of the University of Debrecen, the synthesis of polylactic acid and urethane type polymers has been studied for years. This gave the idea, that we incorporate the polylactic acid into urethane compounds by adequate reactions to get new type polymers with good properties.

In this work, we also examined the monomers, i. e., the lactic acid (LA) and the reaction between the D,L-lactic acid and diphenylmethane diisocyanate (MDI). The starting reagent, PLA, is a hard material from the aspect of polymer-chemistry and it is a hard segment in the chain to be built. Therefore our goal was to soft this segment in order to get linear chain-polymers which are expected to show thermoplastic properties. At most, rare branching is allowed when products with thermoplastic properties are produced.

Polyethylene-glycols (PEG, M=400-6000 g/mole) and polypropylene-glycols (PPG, M=400-8000 g/mole) were used as softening reagents. MDI and toluilene diisocyanate (TDI) were applied as chain-linking agents to obtain urethane type copolymers. By using these raw materials, we can get foil type products. We tried to find the mildest and simplest reaction conditions for the synthesis of the planned polymers.

In my dissertation, besides the synthesis of the starting materials and their widespread investigation, the reaction between polylactic acid and diisocyanates, the properties of multiblock copolymers, reaction conditions and structure analysis are discussed. The investigation of the mechanical properties of polylactic acid based multiblock copolymers was also performed.

II. Applied methods and equipment

The macro- and half-micro methods of the modern preparative organic chemistry were applied in the synthetic work. The applied microwave apparatus was a domestic microwave oven.

Size Exclusion Chromatography (SEC) was used for determination of the average molecular weight of polymers and modern spectroscopic methods (one- and two dimensional NMR, IR and MALDI-TOF MS) and dinamic light scattering (DLS) were applied for the verification of the structure of the synthesized compounds.

For the determination of mechanical properties, tensile tests and hardness measurement were applied.

III. New scientific results

1. Polycondensation of LA (mainly D,L-lactic acid, some L-lactic acid and the mixture of these monomers) was performed at 100, 120, 150, 180, 200 and 220 ^{o}C without any catalysts. Enough time (24 hours) was allowed for the reactions to reach the equilibrium state.

At low temperature, i.e., up to 120 ^{o}C linear, and at higher temperature both linear and cyclic oligomers were formed. The number average molecular weight of the oligomers was 400-1500 g/mole by SEC which were favourable for the urethane-forming reactions. **[3, 7]**

2. The polycondensation of D,L-lactic acid upon microwave irradiation was studied. Since polycondensation of LA is accompained by the relase of water and both LA and its oligomers posses high polarity, it is reasonable to expect the influence of microwave irradiation on the reaction. The results of polycondensation initiated by microwave were compared to those obtained by conventional heating of lactic acid, and it was found that the reaction proceeds much faster upon microwave irradiation. The formed oligomer mixtures were investigated by MALDI-TOF MS method.

The molecular mass of polylactic acid formed under microwave irradiation was found to increase with the irradiation time, and formation of cyclic oligomers was also recognized after 20 min reaction time. It was shown that the synthesis of polylactic acid can be effectively achieved and the reaction time can be considerably shortened upon microwave irradiation. The molecular mass range of the obtained polylactic acid is 400-1000 g/mole by SEC and MALDI MS. **[5]**

3. Mainly linear-chain cooligomers are formed in the reaction between D,L-lactic acid (LA) and diphenylmethane diisocyanate (MDI) but there are many other parallel side reactions which were explored during our study. We followed the formation of cooligomers produced with the variation of reaction time, molar ratio and catalyst. The composition of cooligomer i.e., average number of lactic acid per MDI units was determined by NMR spectroscopy.

On the basis of NMR, it was concluded that the reaction product was a mixture containing the cooligomers with similar ratio of LA-MDI units but different microstructures. In order to find out the microstructures of the cooligomers formed, MALDI-TOF MS experiments were performed. As a result of our studies we determined the mechanism of LA-MDI reaction. **[4]**

4. Linear-chain polymers were synthetized with the reaction between biodegradable polylactic acid (PLA) and diisocyanates (MDI and TDI). For optimisation of the reaction conditions, the following parameters were systematically investigated: reaction temperature, reaction time, molar ratio of the reagents and the type of catalyst.

The products were yellow-white powders and their average molecular weights were 20000-30000 g/mole. The melting points of copolymers were 260-280 °C. These products don't have thermoplastic properties but they have active isocyanate end-groups, and hence they can react with proper reagent to get new type polymers. **[1, 2]**

5. Since the PLA based urethanes have active isocyanate end-groups, further chemical reactions are possible and thus we can synthetize new type linear-chain multiblock copolymers.

With on excess of TDI, PEG or PPG was added to the reaction mixture at the end of the reaction to obtain the PLA-TDI-PEG/PPG block copolymer. The polyols were varied in wide range of molecular weight (400-8000 g/mole).

The reaction parameters were optimised. The structure of products was investigated by IR and NMR methods. The average molecular weight of multiblock copolymers was 40000-60000 g/mole by SEC.

In this work, the synthesis and mechanical properties of these products were also studied. The reaction parameters have significant influence on the properties of products. With the variation of reaction parameters soft and hard polymers can be prepared.

Based on a comparison with standards (polyvinyl chloride, low density polyethylene and polyurethane elastomers), biodegradable copolymers were produced with higher tensile strength and good mechanical properties.

Experiments were also performed in which we reinforced the PLA-TDI-PEG/PPG copolymers with carbon fiber. We got reinforced composites, which possess better mechanical properties.

Due to environmental issues, the synthesis of polylactic acid–toluilene diisocyanate–polyethylene glycol/polypropylene glycol multiblock copolymers is also very important. They have very good elastic properties. **[2, 6]**

IV. Some aspects of possible applications of the results

The importance of biodegradable polymers is continuously increasing nowadays. In many fields one of the main goal is the synthesis of biodegradable and biocompatible polymers and the introduction of practical applications of these materials.

The polylactic acid based polymers meet the expectations of our time from this point of view and they can get more applications on several fields of our life.

The PLA-TDI-PEG/PPG multiblock copolymers are potentially biodegradable. In the future we will plan to test these materials for agricultural and food industrial applications where they will meet the new expectations.

VI. Tudományos közlemények / Scientific publications

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