



# Kinetics study of the fully bio-based poly(propylene succinate) synthesis. Functional group approach

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## ARTICLE INFO

### Article history:

Received 28 May 2018

Received in revised form

16 July 2018

Accepted 28 July 2018

Available online 30 July 2018

### Keywords:

Bio-based polyester polyols

Kinetics study

Functional group approach

<sup>1</sup>H NMR

GPC

Thermal stability

## ABSTRACT

Currently, the increasing importance of the bio-based chemical compounds development is visible in the polymer chemistry, chemical engineering and materials science. It is well-known that the various purity level and different contaminants characterize petrochemical-based compounds compared to their bio-based counterparts. Therefore, it is necessary to find out the contaminants impact on the bio-based monomers synthesis. One of the most important information about the reaction pathway gave the kinetics study. In this work, the fully bio-based poly (propylene succinate)s were synthesized under various temperature conditions via two-step polycondensation reaction. The kinetics studies were investigated with the use of a functional group approach. The first step of the polycondensation reaction was autocatalytic esterification reaction. During the second step, the polycondensation catalyst was used. For macromolecular structure characteristics and the progress of the chemical reaction monitoring, Fourier Transform Infrared Spectroscopy, Proton Nuclear Magnetic Resonance, and Gel Permeation Chromatography were conducted. The activation energy value of 38.5 kJ/mol was determined for the first step of the bio-based polyols synthesis. The results of the investigations verified that the activation energy for the bio-based poly (propylene succinate) synthesis revealed lower value than the same polyester synthesis based on the petrochemical monomers. Thermal analysis by TGA measurements allowed confirmed the high thermal stability of the prepared bio-based polyols equaled ca. 418 °C.

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## 1. Introduction

The growing interest in the field of the bioresources for the polymers synthesis caused the increasing focus on the bio-renewables in the polyurethane synthesis. The reduction of energy consumption and the greenhouse gasses production, CO<sub>2</sub> emission reduction, the economic volatility reduction by the decrease in the fossil fuel stocks utilization and the decrease in the production costs with increasing production scale represent the major advantages which contribute to the increasing interest in the utilization of bioresources in chemical syntheses [1,2].

It is well-known that the petrochemical-based components have more impurities, which are consisted of the different chemical compounds. The scientists from Genomatica Company [3] investigated the variation in the purity of the bio-based 1,4-butanediol and other, commonly used, petrochemical-based 1,4-butanediol. The results confirmed differences between samples composition.

The various contaminants can lead to the different reaction mechanisms during the polymer synthesis, therefore it is necessary to find out the contaminants impact on the synthesis pathways.

One of the most extensive information about pathways of the various reaction types gives the kinetics study. The dependence of the reaction kinetics on such parameters as type and amount of the used catalyst, temperature conditions and time of the reaction has not been reported frequently in the literature. One of the most interesting information form the kinetics characteristics constitute activation energy. Rubén López-Fonseca and co-workers [4] investigated the kinetics of glycolysis of poly (ethylene terephthalate) wastes with ethylene glycol to give highly pure bis(2-hydroxyethyl terephthalate). Different reaction conditions were used for kinetics characterization as temperature, mean particle size, stirring rate, reaction time and catalyst type and concentration. Based on the results the determined activation energy values of 185 kJ/mol.

Another reaction type, which is more popular for the kinetics investigation constitutes thermal degradation reaction. He et al. [5] described the results of the thermal decomposition kinetics novel

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polyester containing bithiazole rings. It was established that the decomposition of the polyester is a complex multi-step mechanism with the activation energy of 146.9 kJ/mol. Tsanaktis and co-workers [6] investigated three novel aliphatic polyesters based on the 2,5-furandicarboxylic acid and low molecular weight aliphatic diols. It was found that butanediol-based polyester, PBF, was less stable thermally, than the other two polyesters (propanediol, PPF, and ethanediol-based, PEF). The activation energy revealed 121, 159 and 162 kJ/mol for PBF, PPF, and PEF, respectively.

Gandini et al. [7] studied the acid-catalyzed polycondensation of 2-acetoxymethylthiophenes and its C<sub>3</sub> and C<sub>5</sub> methylated homologs. Different synthesis conditions such as temperature, solvent, and acidic catalyst concentration were used. The results confirmed that all reactions followed as a first-order reaction with activation energies around 50 kJ/mol.

The kinetics of the three succinic acid-based polyesters synthesis was studied by Bikiaris and co-workers [8,9]. The researchers found that the use of different glycols does not influence much the number average degree of polymerization values of the oligomers produced. Nevertheless, different glycols slightly affect esterification rates towards lower amounts of CH<sub>2</sub> groups at the molecular chain, namely: poly (butylene succinate) (PBS) > poly (propylene succinate) (PPS) > poly (ethylene succinate) (PES). Moreover, with larger catalyst molar ratio, polymers with bigger average molecular weight were obtained. Finally, it was found that although higher initial ratios of glycol to succinic acid were used to increase the esterification rate, they lowered the degree of polymerization of the oligomers [8]. In their second work, it was found that when ethylene glycol is used as a reactant, both esterification and transesterification reaction rates are promoted. However, the transesterification reaction rate constant of PPS is much lower compared to PBS. Moreover, the esterification rate constant was estimated always to be much larger compared to the rate constant of the transesterification reaction, meaning that the former reaction proceeds much faster compared to the later, resulting thus in very low values of the carboxyl end groups compared to corresponding hydroxyl end groups. Activation energies of the esterification reaction (I step of polycondensation) equaled 47, 52 and 59.5 kJ/mol for PBS, PPS and PES, respectively.

Conducted literature review verified the impact of the reaction type on the kinetics and degree of the activation energy. The above-mentioned exemplars allowed to verify the degree of E<sub>a</sub> for different reaction types. It was presented that the synthesis reactions as polycondensation, polymerization, characterized E<sub>a</sub> values lower than 100 kJ/mol, where thermal decomposition reactions featured higher values of E<sub>a</sub>, for polyesters even higher than 180 kJ/mol.

The aim of this work was the profound investigation of kinetics characteristics with activation energy determination of fully bio-based poly (propylene succinate)s prepared under different reaction temperature conditions. Products were synthesized via well-known two-step polycondensation reaction and tetraisopropyl orthotitanate as a catalyst. Functional group approach was chosen for establishing the framework for the kinetics of the reaction. Based on the results, orders of reaction (divided into first and second step), rate constants and activation energy of the first step of the reaction were determined. For macromolecular structure changes characteristics and the progress of the chemical reaction monitoring, Fourier Transform Infrared Spectroscopy and Proton Nuclear Magnetic Resonance were used and described. Moreover, <sup>1</sup>H NMR spectra allowed determining changes in the degree of polymerization over the reaction time. Gel Permeation Chromatography allowed characterizing the molecular weight distribution of the prepared bio-based polyols. Furthermore, thermal stability was investigated with the use of TGA measurement.

## 2. Material and methods

### 2.1. Materials

The series of the fully bio-based poly (propylene succinate) syntheses were carried out with the use of two fully bio-based components. The used dicarboxylic acid was succinic acid (SA) obtained from BioAmber Sarnia Inc. (Ontario, Canada). The SA purity was in the range 98–100%. The molecular weight of this solid-state component was 118.09 g/mol and relative density at 20 °C was 0.900 g/cm<sup>3</sup>. The employed glycol constituted Susterra Propanediol (1,3-propanediol) which was obtained from DuPont Tate&Lyle Corporation Bio Products (Loudon, Tennessee, USA). This liquid component revealed purity ca. 99.98%. The molecular weight was 76.09 g/mol, and relative density at 20 °C was 1.053 g/cm<sup>3</sup>. Furthermore, water content by Karl Fischer equaled 12.1 ppm and a dynamic viscosity at 20 °C was 52 mPas. As a catalyst was used the Tetraisopropyl orthotitanate, Ti(O-*i*-Pr)<sub>4</sub> (TPT). It was purchased from TCI Chemicals (India) as a liquid component with the purity ca. 97%. The molecular weight amounts to 284.22 g/mol. The catalyst was used in an amount of 0.25 wt.% as a glycol equivalent every time in the second step of the polycondensation. For water content measurements the volumetric Karl Fischer method was used. The KF reagent used for the NIST volumetric measurements contained methanol solution of imidazole and sulfur dioxide as the organic base, J.T. Baker, HYDRA-POINT Solvent G, pyridine free, was purchased from Avantor Performance Materials Poland S.A. (Gliwice, Poland). The KF titrant for volumetric method contains methanol solution of iodine, J.T. Baker, HYDRA-POINT Titrant 5 mg H<sub>2</sub>O/mL, was also purchased from Avantor Performance Materials Poland S.A. (Gliwice, Poland). The other materials and solvents were used of the analytical grade for the analytical measurement methods.

### 2.2. Bio-based polyesters synthesis

The linear bio-based polyester polyols were prepared with the use of succinic acid SA and 1,3-propanediol PDO. Catalyst, tetraisopropyl orthotitanate TPT, was used as a glycol equivalent in the amount of 0.25 wt.%. The catalyst content was determined according to our previous work. All bio-based poly (propylene succinate)s were synthesized by two-step polycondensation method (see Fig. 1 in Ref. [10]). Glycol was always used with an excess and the molar ratio SA:PDO amounted to 1:1.2. Determination of this molar ratio was ordered by the final molecular weight expected after full polycondensation. The designed number average molecular weight of the prepared polyols was M<sub>n</sub> = 2000 g/mol with functionality equaled 2, for proving linear macromolecular chain structure. The reaction was carried out in the glass reactor, which consisted of a three-neck flask equipped with a nitrogen/vacuum inlet, mechanical stirrer, thermometer, condenser, and heating mantle. The first step was represented by the esterification reaction between a succinic acid (SA) and 1,3-propanediol (PDO) which was carried out under a nitrogen atmosphere. The bio-based components mixtures were stirring at three different temperatures, exactly 140, 150 and 160 °C. During the first step of the synthesis, the mixtures were kept for 10 h at the suitable temperature without catalyst presence, according to the patent application in the Polish Patent Office (no. P.418808). After water distillation, the second step was started. During the polycondensation reaction, the nitrogen was stopped, the catalyst was added, and the temperature was increased. The second step was carried out under reduced pressure at three different temperatures for all three various temperatures from the first step. The temperatures of the second step amounted to 160, 180, 190 and 200 °C according to the first step. The acidic number was measured to track the reaction progress. After

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