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

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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.

Keywords: Bio-based polyester polyols; Kinetics study; Functional group approach; $^1$H NMR; GPC; Thermal stability

## 1. Introduction

The growing interest in the field of the bioresources for the polymers synthesis caused the increasing focus on the biorenewables in the polyurethane synthesis. The reduction of energy consumption and the greenhouse gasses production, $CO_2$ 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 biorenewables 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 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. Tsanaktsis and co-workers [6] investigated three novel alipharomatic 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 $C_3$ and $C_5$ 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 $CH_2$ 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 Ea for different reaction types. It was presented that the synthesis reactions as polycondensation, polymerization, characterized Ea values lower than 100 kJ/mol, where thermal decomposition reactions featured higher values of Ea, 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, $^1H$ 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$^3$. 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$^3$. 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, $Ti(O\text{-}i\text{-}Pr)_4$ (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 5mg $H_2O$/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 Figure 1 in reference [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 Mn = 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$^{o}$C. During the first step of the synthesis, the mixtures were kept for 10 hours 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$^{o}$C according to the first step. The acidic number was measured to track the reaction progress. After achieving the value of the acidic number ca. or preferably below 1 mg KOH/g, the polycondensation was finished.

## 2.3. Polymer characterization methods

### 2.3.1. Acid number

Carboxyl end-group value measurements were performed by the Polish standard PN-86/C45051. Samples about 1 g of the prepared polyesters were dissolved in ca. 30 cm$^3$ of acetone at room temperature. After that, the solutions were titrated with the use of a standard solution of potassium hydroxide KOH in distilled water (0.1 mol/dm$^3$) and phenolphthalein as an indicator.

### 2.3.2. Hydroxyl number

Hydroxyl end-group determination was prepared by the Polish standard PN-88/C-89082. Sample about ca. 0.5 g of polyester was dissolved in 5 cm$^3$ of the acetic anhydride solution. The solution was refluxed for 30 minutes. Subsequently, 1 cm$^3$ of pyridine was added and heating for 10 minutes. After that, 50 cm$^3$ of distilled water was added, the mixture was cool to room temperature and titrated with the use of a standard solution of potassium hydroxide KOH in distilled water (0.5 mol/dm$^3$) and phenolphthalein as indicator.

### 2.3.3. Dynamic viscosity

Dynamic viscosity measurements were performed with the use of rotary rheometer R/S-CPS+ produced by Brookfield Company, USA. The viscosity values at 80$^o$C and shear rate 100 s$^{-1}$, were defined with the use of computer program Rheo3000. Measurements were conducted with controlled shear rate (CSR). Justification of choice the temperature is occurring temperature ranges in some industrial processes. The shear rate program was chosen due to occurring shear rate ranges also in some industrial processes, e.g. mixing 10 - 500 s$^{-1}$ or pumping 10 – 300 s$^{-1}$ [11,12].

### 2.3.4. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy was used to obtain the spectra of the bio-based polyester polyols and pure components (1.3-propanediol and succinic acid). The FTIR spectra were also investigated to track the reaction progress. The measurements were carried out using a Nicolet 8700 FTIR spectrometer (Thermo Electron Corporation, USA) with the use of the ATR technique. Sixty-four scans in the wavenumber range from 4500 to 500 cm$^{-1}$ were taken with the resolution 4 cm$^{-1}$. The kinetics of the reaction between dicarboxylic acid and glycol was followed using FTIR spectroscopy by investigation of the selective spectra absorbance changes at a various time.

### 2.3.5. Nuclear Magnetic Resonance ($^1$H NMR)

Proton nuclear magnetic resonance ($^1$H NMR) spectra of the prepared bio-based polyester polyols were studied for molecular structure analysis. The resulted spectra allowed to determine the degree of the polymerization and the approximative molecular weight of the synthesized polyols, ipso facto. The $^1$H NMR data were obtained with the use of Bruker spectrometer. Operating frequency was 400 MHz for protons. The ca. 10% w/v solutions of the poly(propylene succinate) polyesters were prepared in a $CDCl_3$ solvent at ambient temperature. The simulation and iteration of spectra were carried out using Bruker software.

### 2.3.6. Gel permeation chromatography (GPC)

The molecular weight distribution of the synthesized bio-based polyester polyols was determined with the use of Gel permeation chromatography, GPC. Measurements were performed using a Thermo Scientific chromatograph, equipped with an isocratic Dionex UltiMate 3000 pump and a RefractoMax 521 refractive index detector. Four Phenogel GPC columns, produced by Phenomenex, were used with 5 μm particle size and 105,103, 100 and 50Å porosities, respectively, located in an UltiMate 3000 thermostatic column compartment. The separation was carried out at 30 °C. Tetrahydrofuran (THF) was used as mobile phase at a flow rate of 1 mL/min. Bio-Based polyester polyol specimens were prepared by dissolving in THF at 1 wt.% and filtering using nylon filters with 2 μm pore size. Number-average molecular weight, Mn, weight- average molecular weight, Mw and polydispersity, PD were determined as polystyrene standards.

### 2.3.7. Thermogravimetric analysis

Thermogravimetric analysis of selected specimens of the bio-based poly(propylene succinate)s was conducted using DSC-TG/QMS coupled method. An STA 449 F1 Jupiter apparatus from NETZSCH-Feinmahltechnik GmbH Germany was used. Approximately 20 mg portions of dry samples were placed in a corundum crucible and heated to 650°C under helium flow. The heating rate of measurements equaled 20$^{o}$C/min.

## 3. Results and discussion

### 3.1. Bio-based poly(propylene succinate)s

Table 1 collected the synthesis conditions and selected properties all of the obtained polyols. Higher temperature conditions allow reducing the time of the synthesis while the designed properties are kept. The shortest synthesis time of 13 hours revealed polyol PPS 140/200. The same sample characterized also the lowest viscosity (2.76 Pas), which is one of the most desirable properties for the polyurethane industry. The value of acid and hydroxyl numbers, and in the sequel, viscosity, are related to the optimization of the water elimination (by-product formed during synthesis) from the reaction mixture. Since the uncombined glycol macromolecules can be emitted with the water, it is significant to return the glycol to the reaction mixture. Due to the questionable matter of the repeatability of the synthesis, the synthesized polyols revealed incoherent trends at the properties presented in Table 1.

Table 1 Preparation and properties of the obtained bio-based polyester polyols.

| POLYOL | TEMPERATURE [$^{o}$C] |  | REACTION TIME [h] |  | ACID NUMBER [mg KOH/g] | HYDROXYL NUMBER [mg KOH/g] | VISCOSITY [80$^{o}$C; Pas] |
|---|---|---|---|---|---|---|---|
|  | I step | II step | I step | II step |  |  |  |
| PPS 140/160 | 140 | 160 | 10 | 9 | 0.83 | 51.50 | 3.43 |
| PPS 140/190 |  | 190 |  | 6 | 1.05 | 58.51 | 4.66 |
| PPS 140/200 |  | 200 |  | 3 | 1.02 | 77.43 | 2.76 |
| PPS 150/180 | 150 | 180 |  | 7 | 0.96 | 63.37 | 7.41 |
| PPS 150/190 |  | 190 |  | 6 | 1.15 | 48.72 | 3.47 |
| PPS 150/200 |  | 200 |  | 4 | 0.80 | 70.35 | 3.38 |
| PPS 160/180 | 160 | 180 |  | 6 | 1.05 | 79.00 | 4.76 |
| PPS 160/190 |  | 190 |  | 4 | 1.00 | 64.70 | 5.77 |
| PPS 160/200 |  | 200 |  | 4 | 1.02 | 71.78 | 4.34 |

### 3.2. Kinetics study

#### 3.2.1. Approach and reactions

There are two main approaches which allowed establishing the framework for the kinetics of the reaction: the functional group model and molecular species model. The second model, as mentioned, give more comprehensive information about the reaction but involves also more complicated calculations. It is due to the independent approach for all unique polymer macromolecule existing in the mixture [13].

According to the literature on the kinetics of the two-step polycondensation reaction, the functional group approach was used to modeling the reactions of the bio-based poly(propylene succinate) synthesis. The kinetics of the esterification (I step) and the main polycondensation (II step) reaction were determined accordingly to the following literature [8,9,13,14]. The functional group approach regarded the polycondensation reaction as a reaction between two different functional groups. Based on the equations and the indications proposed by the researchers the reactions scheme of our work are presented below (Figure 1). For simplification of the depicted mechanisms, some acronyms were used. Table 2 shows the main information about the components used during the synthesis and the semi-product and product of the synthesis. The acronyms ‘t’, ‘b’ and ‘d’ were used for distinguishing the five different oligomeric segments where the appropriate term describe the terminal functional groups, bound monomeric repeating units and di-glycol repeating units, respectively.

Table 2 Components used during the synthesis and the semi-product and product of the synthesis.

| Symbol | Chemical appellation | Molecular structure |
|---|---|---|
| Monomers | | |
| SA | Succinic acid | $HOOC-CH_2-CH_2-COOH$ |
| PDO | Propylene glycol | $HO-CH_2-CH_2-CH_2-OH$ |
| Products | | |
| W | Water | $H_2O$ |
| pPPS | Poly(propylene succiate) | $HO-CH_2-CH_2-CH_2[-O-C(O)-CH_2-CH_2-C(O)-O-CH_2-CH_2-CH_2]_n-OH$ |
| Oligomers | | |
| tSA | SA end group | $HOOC-CH_2-CH_2-CO-$ |
| tPDO | PDO end group | $HO-CH_2-CH_2-CH_2-O-$ |
| bSA | SA repeating unit | $-OC-CH_2-CH_2-CO-$ |
| bPDO | PDO repeating unit | $-O-CH_2-CH_2-CH_2-O-$ |
| dPDO | Dipropylene glycol repeating unit | $-O-CH_2-CH_2-CH_2-O-CH_2-CH_2-CH_2-O-$ |
| oPPS | Oligomeric PPS terminated PDO | $\sim CH_2-OH$ |
| cPPS | Oligomeric PPS terminated SA | $\sim CH_2-COOH$ |

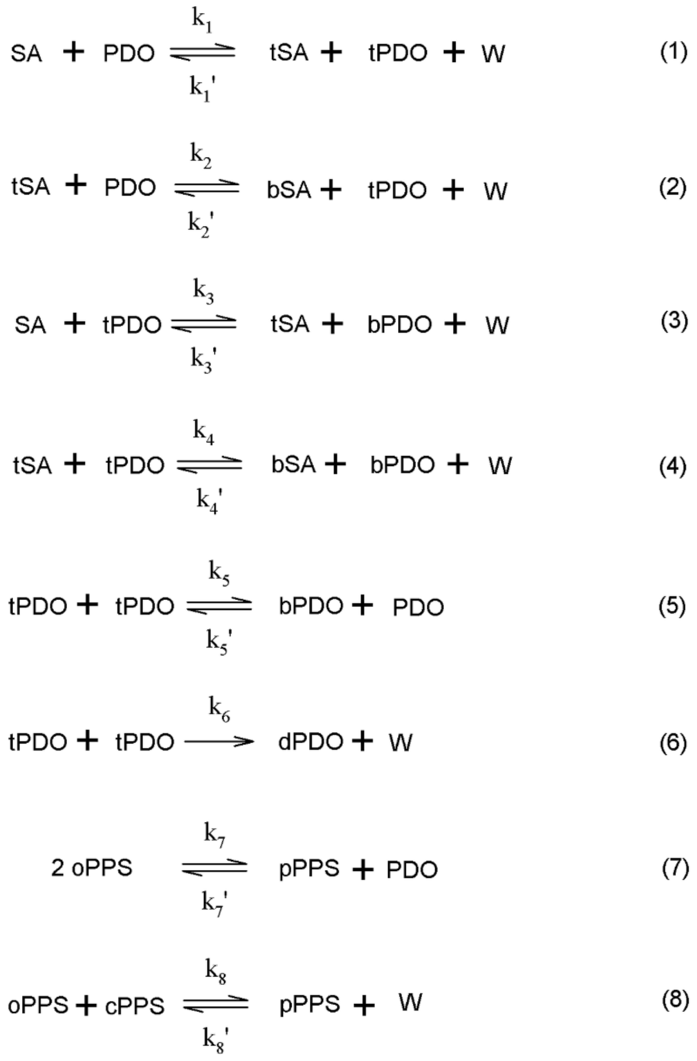


Figure 1 Scheme of the possible reactions during two-step polycondensation between succinic acid and 1,3-propanediol.

The reaction (1)-(5) represent the typical mechanism of the esterification which constitutes the first step of the synthesis. The reaction (6) refers to the side reaction between glycol units resulting in the ether linkages in the macromolecular chain. The mechanism of the main polycondensation reaction (second step of the prepared bio-based polyols synthesis) is described by the reaction (7) and (8). The first of the mentioned, represent the transesterification or polycondensation with the glycol producing. The reaction (8) shown the esterification mechanism with water production as a by-product [9].

All presented reactions are described by the 15 kinetics rate constants, where kj (j=1, 8) and kj' (j=1, 8, without 6) refer to appropriate elementary reactions. Based on the calculated rate constants the mole number and thereby the amount of all components presented in the reaction mixture can be evaluated as a function of the polycondensation time. The extensive literature review on the kinetics study of the polycondensation has not provided any experimental data and equations which allowed to determine the values of all of the kinetic rate constants. Therefore, some assumptions are necessary for the research development.

Several publications have appeared in recent years documenting that the following assumptions are needed for improving kinetics study of the described synthesis:

- The length of the polymer chain has not influenced the kinetic rate constants.
- All produced water is removed from the reaction.
- All vaporized propylene glycol is returned to the reaction. So, the reaction (7) will not be evaluated.
- Kinetics rate constants (ipso facto polymer end-group reactivity) are independent of the polymer chain length.
- During the synthesis, the side reactions as formation the dipropylene glycol or ester degradation do not appear. So, the reaction (6) will not be evaluated.
- The backward reactions (7) and (8) are eliminated when the water and glycol are absent in the mixture.
- The limitations of the volatile compounds diffusion are neglected.

Kang and co-workers [15], Karayannidis and co-workers [16] and others, investigated that the differences between the various end-group reactivity. The results indicate that the acid end-group in the used terephthalic acid revealed the same reactivity as the acid end-group in the oligomers. Furthermore, the researchers indicated that the hydroxyl end-group from glycol (which was ethylene glycol) revealed twice of the reactivity compared to hydroxyl terminated oligomers. Based on the literature, for simplifying the kinetics study, it was assumed that:

$k_1 = k_2 = 2k_3 = 2k_4$.

Moreover, according to the results presented by Bikiaris and co-workers [8], it was assumed that:

$k_5 = 0$.

Bikiaris et al. [8] affirmed also that the reverse reaction rates totaled zero, whereupon the rate constants $k_1' - k_5'$ of the reverse reactions (1) – (5) need not be evaluated. Based on the assumptions, the rate constants which need to be evaluated are $k_1$ (**I** step) and $k_8$ (**II** step).

### 3.2.2. The progress of the reaction

During all of the synthesis, the progress of the reaction was measured with the use of an analytical method (determination of changes in the acid number). The yield of the prepared synthesis, divided into first and second steps, was measured based on the equations 1 and 2:

$$S_{1,2,\ldots,n} = S_0 - [A_1 * S_0 / A_0] \quad (1)$$

$$Y_{1,2,\ldots,n} = [S_0 - S_{1,2,\ldots,n}]/100 \quad (2)$$

Where:

$S_0$ – means that the 100% of the dicarboxylic acid molecules are unreacted in the reaction mixture, [%]

$S_{1,2,\ldots,n}$ – means how much dicarboxylic acid molecules are bonded after approximate reaction time $t_1$, $t_2$, …, $t_n$, [%]

$A_0$ – acid number of the reaction mixture before the synthesis beginning, [mg KOH/g]

$A_1$ - acid number after approximate reaction time $t_1$, [mg KOH/g]

$Y_{1,2,\ldots,n}$ – the yield of the reaction after approximate reaction time $t_1$, $t_2$, …, $t_n$, [-]

Figure 2 and 3 show changes in the reaction yield in the reaction time during the first and second steps.

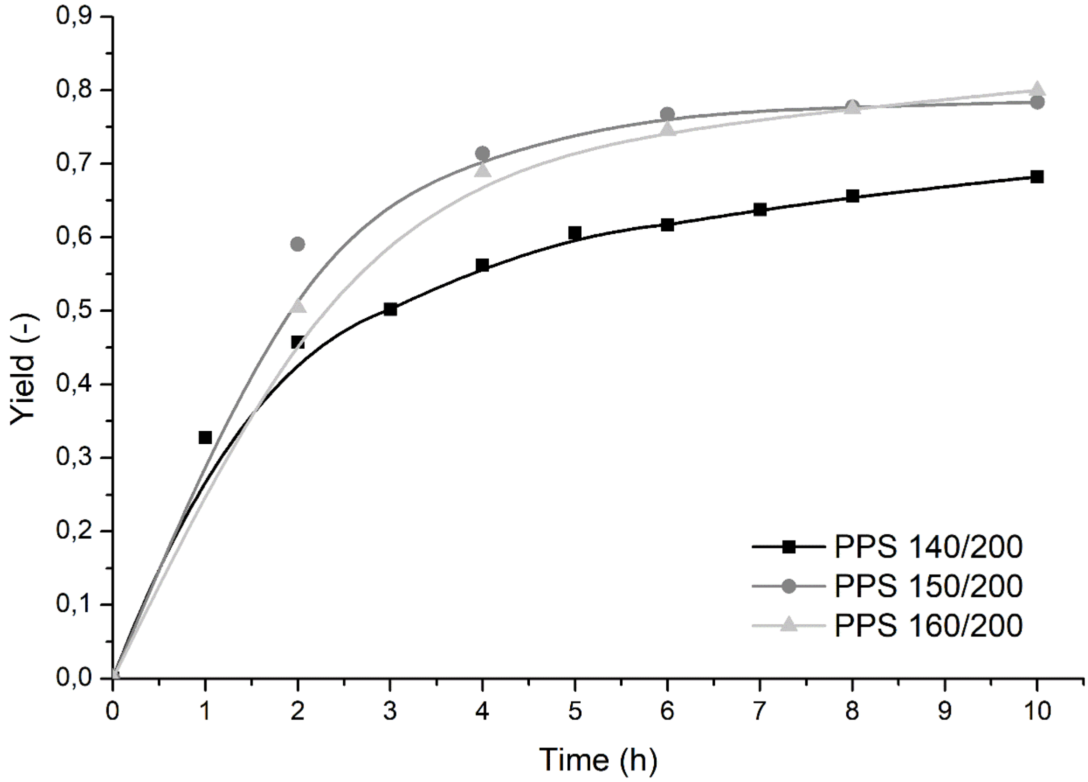
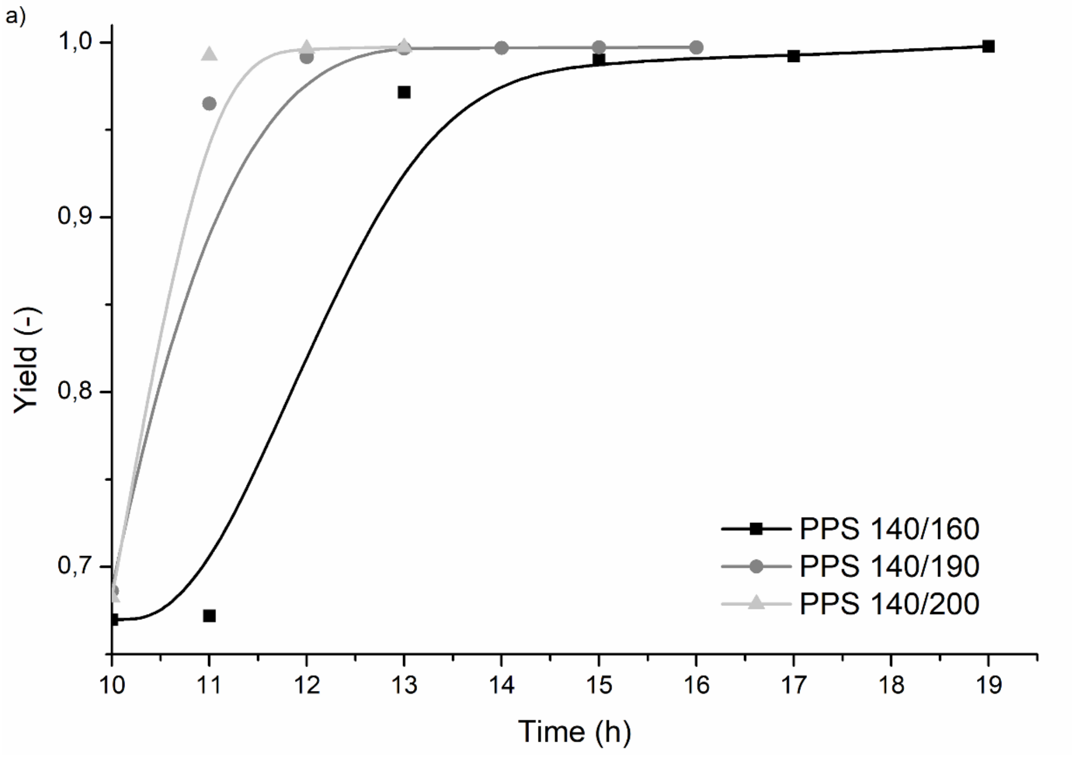
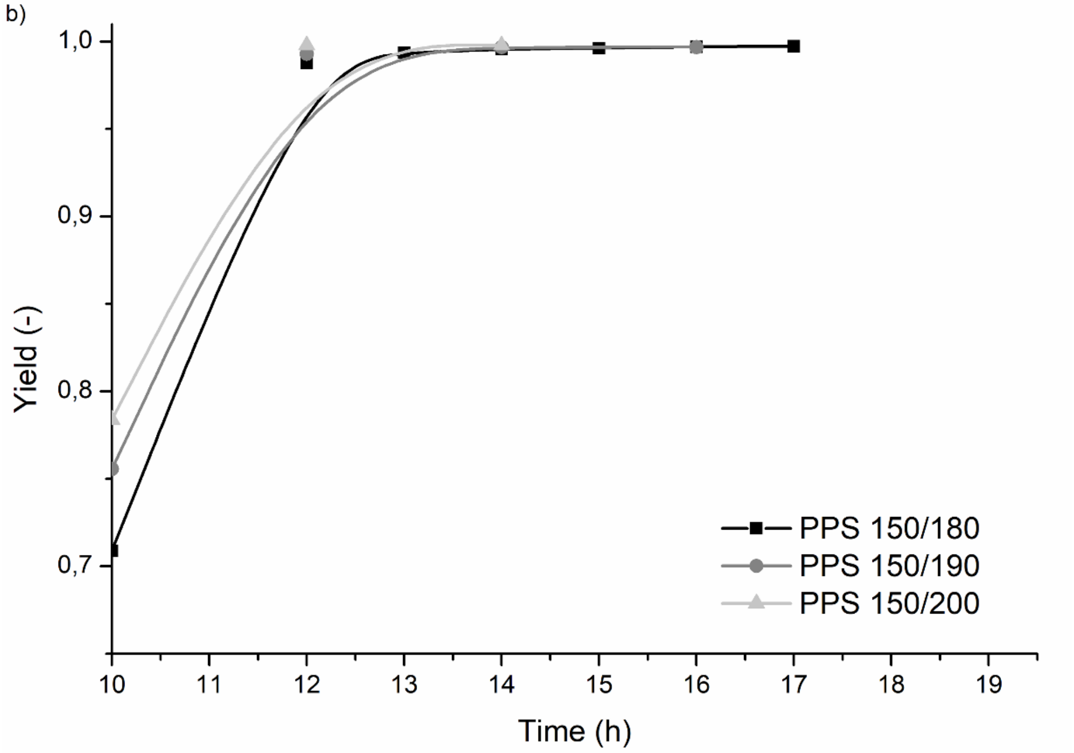


Figure 2 Effect of various temperatures on the yield of the first step.

Figure 2 presents the effect of the temperature conditions on the yield of the first step. The controlled reaction progress indicated that with the growing temperature during the reaction led to a higher yield of the reaction. The lowest value characterized samples prepared at 140°C, when polyols synthesized at higher temperatures disclosed similar yield ca. 0.8.





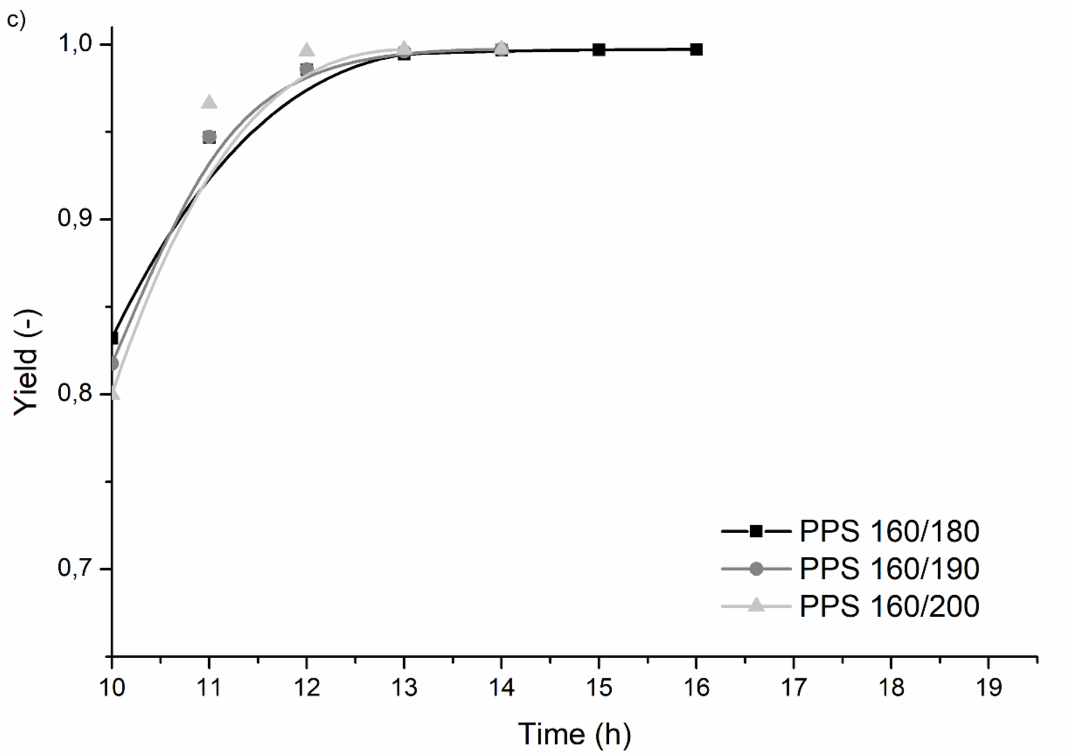


Figure 3 Effect of various temperatures on the yield of the second step after the first step conducted at a) 140°C, b) 150°C, c) 160°C.

Figure 3 shows the profile of the yield of the second step. The origin of the continuous curves is related to the finish of the first step of the synthesis. For synthesis where the first step was conducted at 140°C the yield of the reaction finished at ca. 0.65 value. For synthesis at 150 and 160°C at the first step, the yield lines finished at ca. 0.7-0.8 and above 0.8, respectively. The same yield values constitute the beginning of the curves on Figure 3 a, b and c. Higher temperature during the first step of the synthesis allows for starting the second step when the highest values of the reaction yield were obtained. There is also visible the impact of the temperature conditions on the reaction time. The shortening of the synthesis time can be associated with the intensity of water elimination from the reaction mixture, which, in the sequel, support the catalyst activity. During synthesis conducted under higher temperature conditions the higher amount of water as a by-product, was eliminated from the reaction mixture. It is known that the tetraisopropyl orthotitanate ($Ti(O\text{-}i\text{-}Pr)_4$, TPT), which was used as a polycondensation reaction catalyst during the second step of the synthesis, is sensitive to water chemical compound. Even the lowest water content in the reaction mixture can lead to the catalyst deactivation by decomposition.

### 3.2.3. Reaction order

Based on the acid number changes over the reaction time, the progress of the reaction had been calculated (reaction yield). The results allow for reaction order determining based on the graphical method. The dependence of the reagents concentration changes over the reaction time should give the straight line. Based on the equations 3, 4 and 5, the reaction order can be determined. These equations are results of the kinetics equations integration. The following linear relationships are characterized by the first (equation 3), second (equation 4) and third (equation 5) reaction orders.

$$f(t) = \log(1-Y_{1,2,\ldots,n})^{-1} \qquad (3)$$

$$f(t) = (1-Y_{1,2,\ldots,n})^{-1} \qquad (4)$$

$$f(t) = (1-Y_{1,2,\ldots,n})^{-2} \qquad (5)$$

Usually, one of this function has the linear curve course. The linear relationship of the function f(t)=at+b, characterized by the highest correlation coefficient verifying the reaction order. For two-step polycondensation method used in this study, there is necessary to divide the data into two steps. The results confirmed two different reaction orders for all syntheses, III order of the first step and I order of the second step. A collection of math equations of the reaction orders for all syntheses is shown in Table 3. It is related to the amount of the various macromolecules which can react together. During the first step, the molecules of succinic acid and 1,3-propanediol react with each other and formed low molecular weight esters, hydroxyl and carboxyl-terminated. These esters constitute the third component, which concentration is constantly increasing over the reaction time. The confirmation of this reaction order was also described based on the $^1$H NMR spectra (please, see Chapter 3.4 Nuclear Magnetic Resonance ($^1$H NMR), section 3. Results and Discussion, Table 5). I order of the reaction during the second step is related to the catalyst employment. The polycondensation catalyst leads to the oligomerization between low molecular weight esters at the beginning and polymerization between oligomers at the end of the reaction. This reaction order was also proved via $^1$H NMR results.

### 3.2.4. Reaction rate constants

Several publications have appeared in recent years documenting the reaction rate constants for polycondensation as a function of the rate of the end-group changes [15,17,18]. Based on the acid number changes over the reaction time, the reaction yield had been calculated. The resulted calculation allow verifying similar reaction yield for all synthesis, which values in the range from 0.9968 to 0.9978 (Table 3). Moreover, the graphical method of the reaction order determination allowed assigning the math equation of the reaction order, from which the reaction rate constant, k, can be established. The slope of the curves for III order of the first step and I order of the second step of the synthesis constitutes the values of the reaction rate constants.

The determined reaction rate constant values identified growing trend with the increasing temperature during the first step. Nevertheless, values obtained for synthesis conducted under higher temperatures revealed higher deviation. For the second step of the polycondensation, the reaction rate constants revealed lower values than kinetic rate constants for the first step, what confirmed theoretical postulates.

Table 3 Kinetics characteristic of the esterification and polycondensation reactions.

| | REACTION YIELD | MATH EQUATION OF THE REACTION ORDER, 'y=ax+b' | | REACTION RATE CONSTANT, 'k' [kg/(mol*h)] | | | CORRELATION COEFFICIENT, $R^2$ | |
|---|---|---|---|---|---|---|---|---|
| POLYOL | Step: | I | II | I | | II | I | II |
| | | III order | I order | $k_1=k_2$ | $k_3=k_4$ | $k_8$ | $k_1=2k_3$ | $k_8$ |
| PPS 140/160 | 0.9978 | y = 0.8520x + 1.1623 | y = 0.5634x - 4.4078 | 0.8520 | 1.7040 | 0.5634 | 0.9875 | 0.9067 |
| PPS 140/190 | 0.9971 | y = 0.8969x + 1.5843 | y = 0.4498x - 0.8696 | 0.8969 | 1.7938 | 0.4498 | 0.9791 | 0.7178 |
| PPS 140/200 | 0.9972 | y = 0.8847x + 1.4445 | y = 0.5049x - 0.5903 | 0.8847 | 1.7694 | 0.5049 | 0.9893 | 0.9302 |
| PPS 150/180 | 0.9973 | y = 1.0311x + 1.9151 | y = 0.2827x + 1.249 | 1.0311 | 2.0622 | 0.2827 | 0.9692 | 0.9076 |
| PPS 150/190 | 0.9968 | y = 1.5617x + 1.5642 | y = 0.1981x + 2.6926 | 1.5617 | 3.1234 | 0.1981 | 0.9892 | 0.75 |
| PPS 150/200 | 0.9978 | y = 2.153x + 2.4334 | y = 0.0123x + 5.9624 | 2.1530 | 4.3060 | 0.0123 | 0.9403 | 0.9611 |
| PPS 160/180 | 0.9972 | y = 3.3527x + 0.118 | y = 0.5675x - 2.7033 | 3.3527 | 6.7054 | 0.5675 | 0.9921 | 0.8300 |
| PPS 160/190 | 0.9973 | y = 2.8695x + 1.3639 | y = 1.0177x - 8.0688 | 2.8695 | 5.7390 | 1.0177 | 0.981 | 0.9564 |
| PPS 160/200 | 0.9972 | y = 2.4542x + 0.3121 | y = 0.7826x - 4.6252 | 2.4542 | 4.9084 | 0.7826 | 0.9951 | 0.7192 |

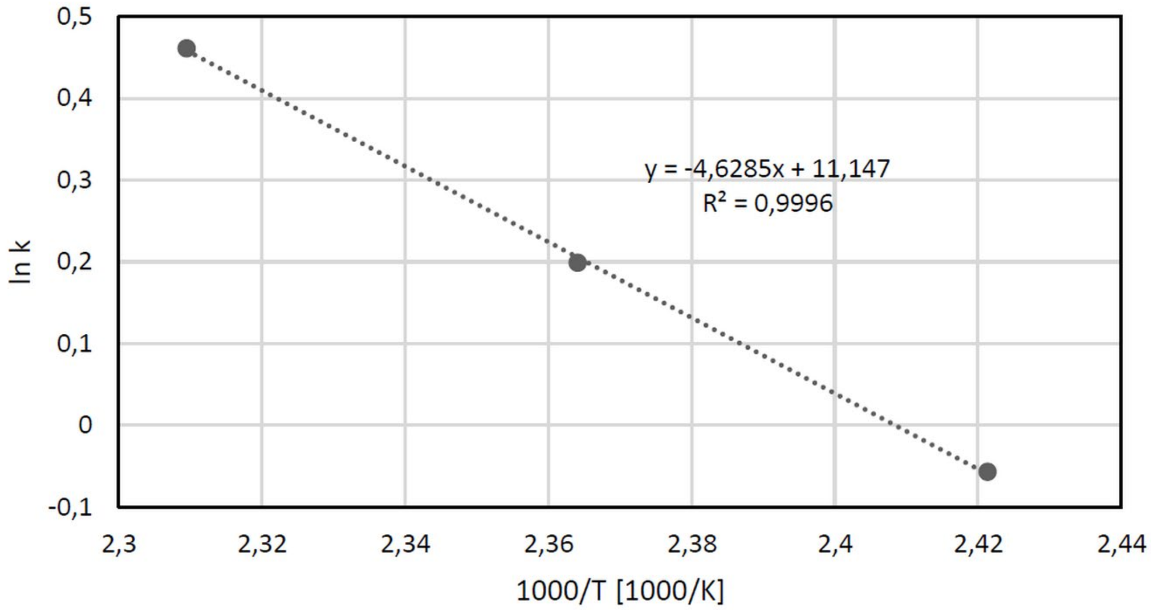


Figure 4 Arrhenius plot of the esterification reaction.

The activation energy, Ea, values for the considered reactions were also determined from measurements taken at different temperatures. Figure 4 shows the relationship between the reaction rate constant and temperature for esterification promoted without catalyst employment. Figure 4 indicates that 'ln k' against 1000/T plot is linear. The fitting equation and its correlation coefficient ($R^2$) is obtained and shown on the graph. Based on the equation, the activation energy value of 38.5 kJ/mol and the logarithm of the pre-exponential or frequency factor A value of 11.147, are determined for the first step of the bio-based polyols synthesis. This investigation verified the lower value of the activation energy of the bio-based polyester polyols synthesis than their petrochemical-based counterparts which equaled ca. 50 kJ/mol [9]. This is due to the differences in monomer purity. The biotechnological process of the 1.3-propanediol production allows obtaining monomer with purity even higher than 99.98%, when its petrochemical equivalent characterized purity ca. 99.70%. Even this little differences can affect reaction kinetics and, in the sequel, a different value of the activation energy. It can be concluded that with the increase in monomer pollution, the value of the activation energy of the reaction increases. For the second step of the polycondensation reaction, conducted measurement results made it impossible to calculate the activation energy value. It was due to the irregular value of the reaction rate constant, 'k'. For this study, it is important to replicate the equal synthesis and pulling out the average of the second step reaction rate constant, 'k' results. It is seen in Table 3, standard deviations between reaction rate constant revealed increasing values with growing temperature of the first step of the polycondensation reaction. The various reaction rate constant values without express increasing trend with the growing temperature of the second step confirmed the necessity of the repeatability investigation of bio-based sources usage in the two-step polycondensation method.

### 3.3. Fourier Transform Infrared Spectroscopy (FTIR)

The structure analysis was performed using Fourier Transform Infrared Spectroscopy. This method allows to track changes at the macromolecular structure of the polyols during synthesis Figure 5 shows exemplary FTIR spectra of a polyol PPS 140/160, where different curves are collected together to show characteristic changes during the polycondensation reaction. Samples from Sn 1 to Sn 10 characterize reaction mixture during synthesis from the beginning to the end of the synthesis. They were taken to the testing every two hours. Samples from Sn 1 to Sn 5 represent the first step of the reaction when samples from Sn 6 to Sn 10 – second step. All characteristic peaks were precisely described in our previous article [10,19]. The arrows on the graph show the direction of changes in the intensity of the peaks.

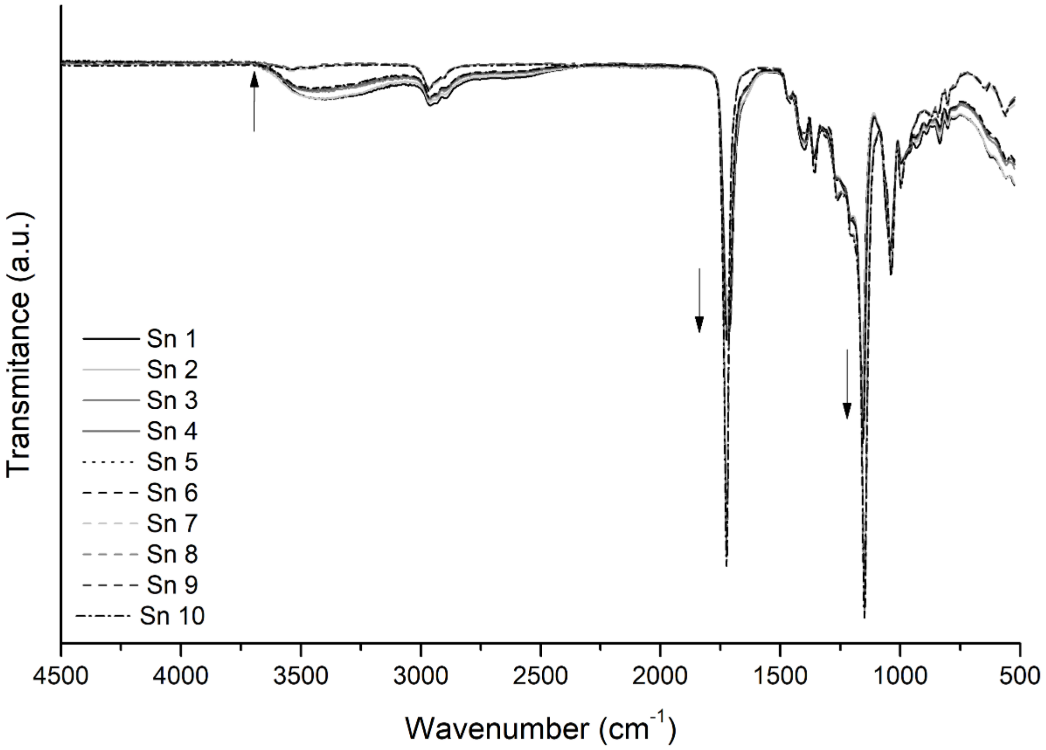
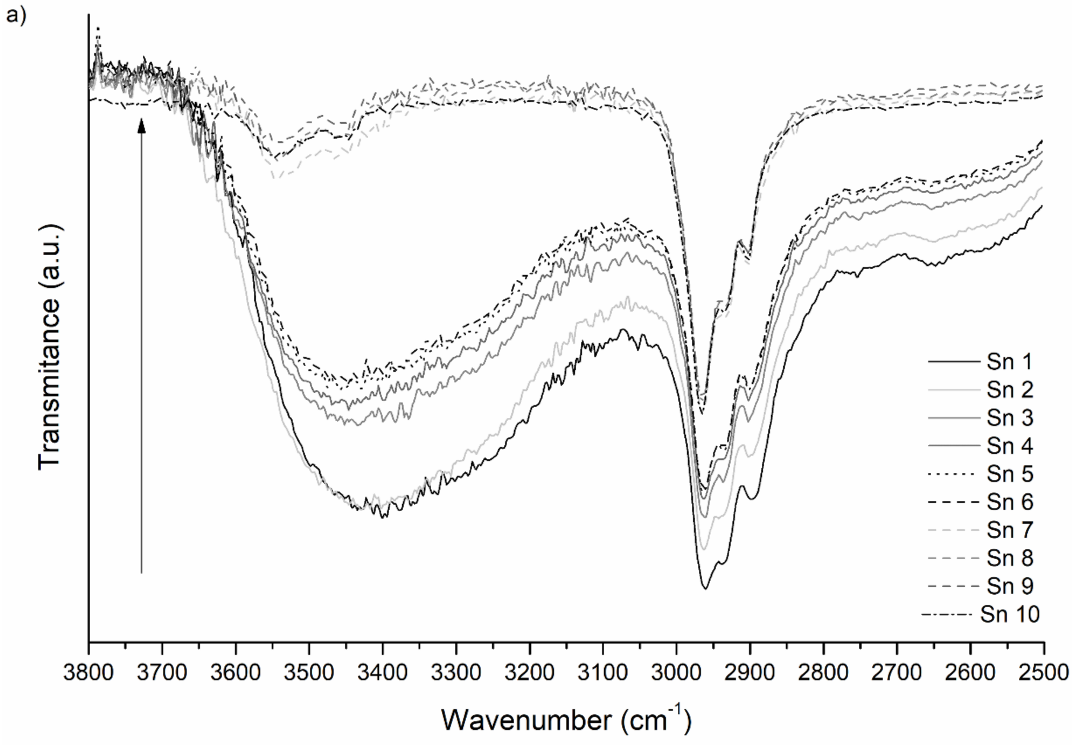


Figure 5 FTIR spectra of PPS 140/160.

Figure 5 shows the differences in the curve courses during both steps of polycondensation. The most visible changes are related to the peak intensity. The broad peak in the wavelength range between

3700 and 2500 cm$^{-1}$ is attributable to the stretching vibrations of hydrogen-bonded hydroxyl groups. The characteristic for the 1.3-propanediol spectrum in the wavelength range between 3570 and 3170 cm$^{-1}$ assigns to the stretching vibrations of hydrogen-bonded hydroxyl groups. For the succinic acid spectrum, the peak assigned to the hydrogen-bonded carboxyl groups stretching vibration appeared as the broad peak centered at 3300-2500 cm$^{-1}$. The peaks at 3000-2850 cm$^{-1}$ are assigned to the methylene groups which are visible for glycol and polyesters spectra. The most intensive peaks identifying ester groups formation are visible at 1725 cm$^{-1}$ and 1150 cm$^{-1}$.

Figure 6 presents, more precisely, changes that occur during synthesis on the example of three main peaks. During polycondensation reaction, water as a by-product is eliminated from the reaction mixture and the hydroxyl groups from glycol react with carboxyl groups from a dicarboxylic acid. Therefore, the intensity of the broad peak in the range from 3700 to 2500 cm$^{-1}$ decreases with the increasing reaction time. In the same time, the intensity of peaks at 1725 cm$^{-1}$ and 1150 cm$^{-1}$ increases, what confirms increasing concentration of the ester groups of the reaction mixture.



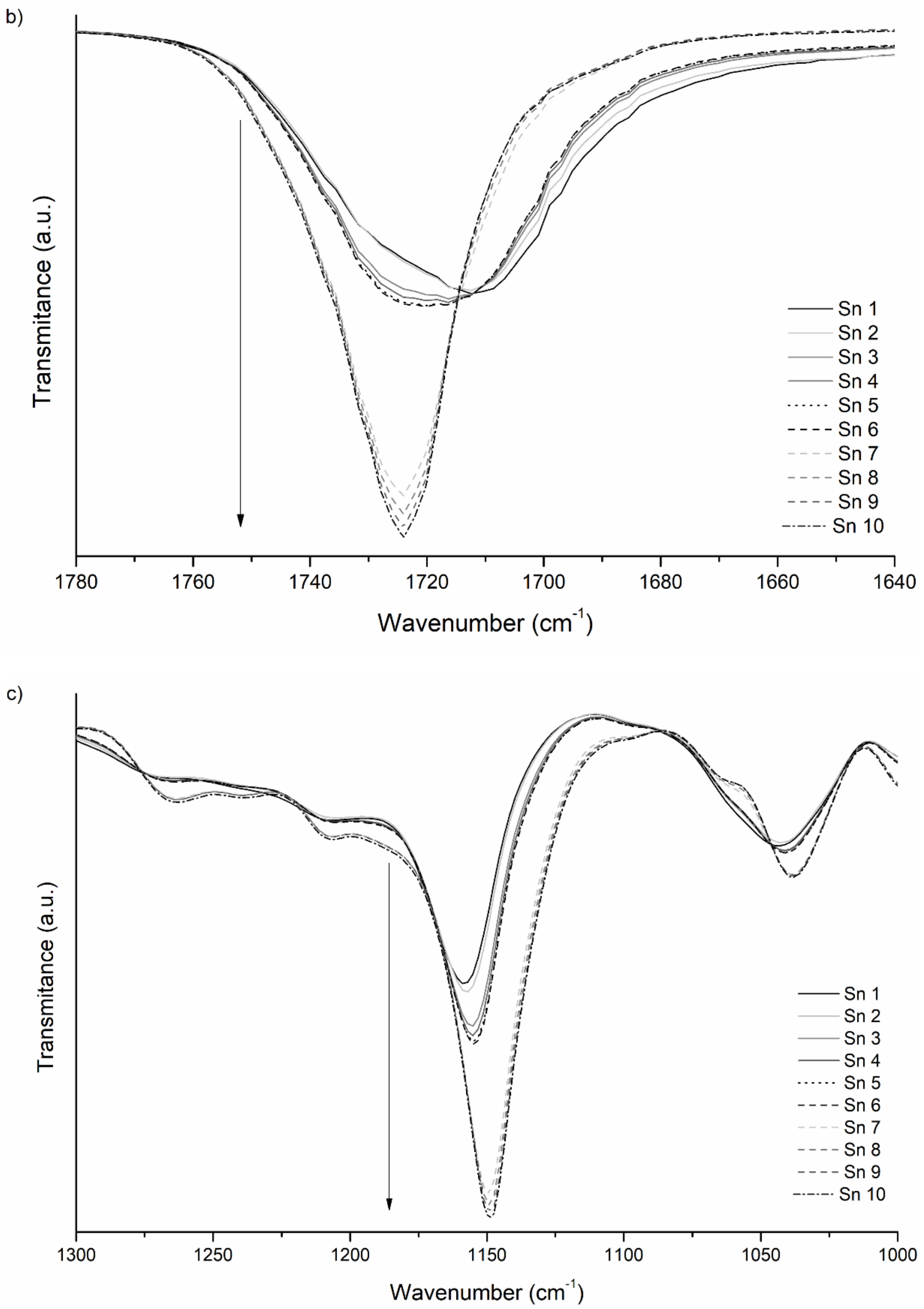


Figure 6 Peaks intensity changes monitored during synthesis at wavenumber range from a) 3800 to 2500 cm$^{-1}$, b) 1780 to 1640 cm$^{-1}$, c) 1300 to 1000 cm$^{-1}$.

### 3.4. Nuclear Magnetic Resonance ($^1$H NMR)

The various peaks on $^1$H NMR spectra represent the different groups appeared in the molecular structure. The particular signals revealed different intensity what indicate the various molecular weight of them [20]. Figure 7 shows the exemplary $^1$H NMR spectrum of one of the synthesized polyols, where the particular groups are assigned to the appropriate chemical shifts. The expanded and knowledgeable description of the individual peaks origin in the bio-based poly(propylene succinate) molecular structure can be found in references [10,19]. All of the investigated bio-based poly(propylene succinate)s revealed congruity at the chemical shift appearance. The differences were visible at the intensity of particular peaks. These differences allow calculating the degree of polymerization and molecular weight of the analyzed polymer macromolecule. The molecular weights of the synthesized bio-based polyols were calculated measuring the area from the peak in the main chain and the area from the corresponding peak at the end of the macromolecular chain. The ratio of the suitable peaks gives the information about the degree of polymerization, *n*, which allow determining the molecular weight of the analyzed macromolecule [21]. It is important to the choice of good peaks, which will be considered.

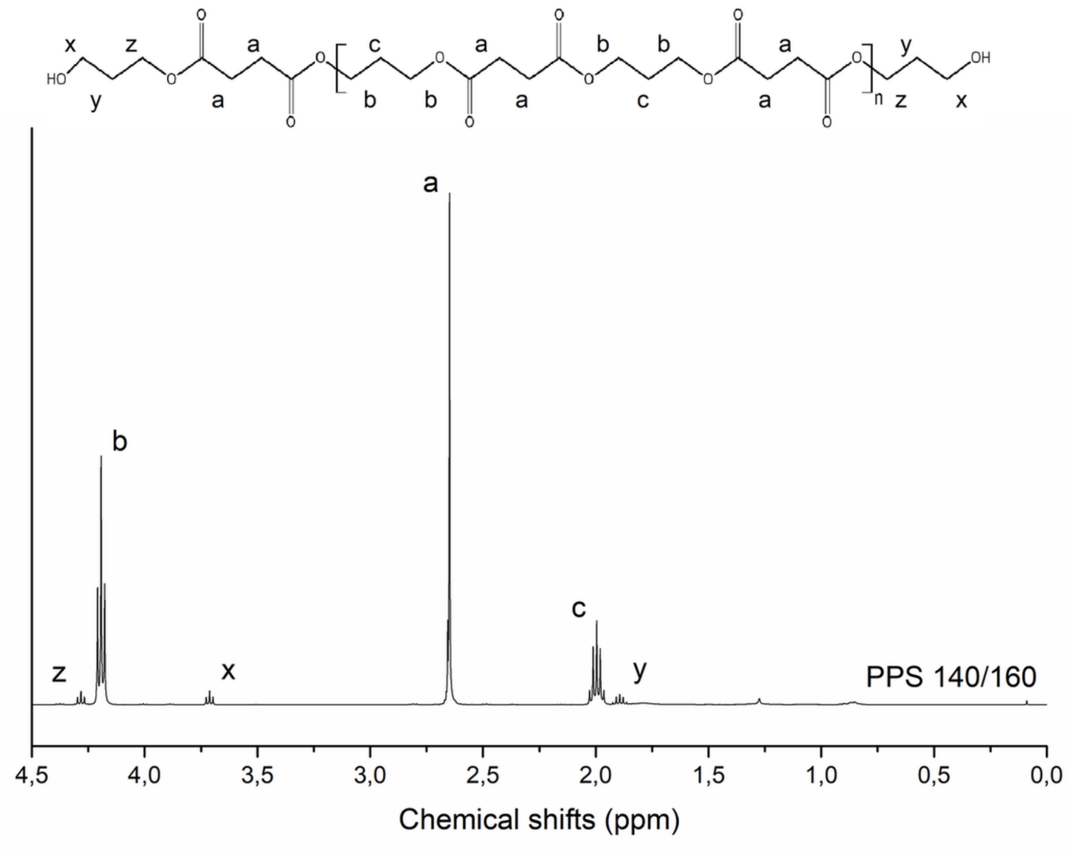


Figure 7 $^1$H NMR spectrum of PPS 140/160.

What is clearly visible in Figure 7, the methylene groups of propylene in the chain end and in the repeating units, bonded to the oxygen atom of ester group (peaks ‘z’ and ‘b’, respectively, Figure 7) appeared separate to the methylene group bonded to hydroxyl group at the end of the molecular chain (peak ‘x’, Figure 7). Both peaks, ‘z’ and ‘b’, correspond to methylene groups bounded with 4 hydrogen atoms due to the double occurrence at the end of the chain and in the main chain. The same hydrogen atoms are bounded with the methylene group from terminal group, peak ‘x’. These can be expressed as equation 6 and 7:

$$(b + z) \sim (n\ 4H_{\text{from repeating units}} + 4H_{\text{chain end}}) \tag{6}$$

$$x \sim (4H_{\text{terminated chain}}) \tag{7}$$

Based on the defined dependents, the degree of polymerization can be calculated from the equation 8:

$$n = [(b+z)-z]/x \tag{8}$$

where the assumption: $x = z$, is necessary. After transformation:

$$n = b/z \tag{9}$$

The obtained polymerization degree from the $^1$H NMR spectroscopy results allow to determine the molecular weight of the analyzed polyols from the equation 10 [20]:

$$M_n = n(M_n \text{ of the repeating unit}) + M_n \text{ of the chain ends} \tag{10}$$

For poly(propylene succinate) the value of molecular weight of the repeating unit amounts 158 g/mol, where the value of molecular weight of the chain ends equals 76 g/mol. The values of the average degree of polymerization and corresponding molecular weight for all synthesized polyols are shown in Table 4.

Table 4 Degree of polymerization and average molecular weight of the synthesized polyester polyols obtained from $^1$H NMR results.

| POLYOL | Degree of polymerization, n [-] | Average molecular weight, Mn [g/mol] |
|---|---|---|
| PPS 140/160 | 24,3 | 3912 |
| PPS 140/190 | 26,2 | 4217 |
| PPS 140/200 | 16,4 | 2667 |
| PPS 150/180 | 26,9 | 4322 |
| PPS 150/190 | 19,2 | 3105 |
| PPS 150/200 | 20,2 | 3274 |

| | | |
|---|---|---|
| PPS 160/180 | 25,1 | 4046 |
| PPS 160/190 | 19,3 | 3123 |
| PPS 160/200 | 20,0 | 3243 |

The used conditions under polyols synthesis allow obtaining bio-based polyesters with polymerization degree in the range from 16 to 27. Hence, the range of the average molecular weight revealed from 2600 to 4400 g/mol. The lowest polymerization degree characterized polyol PPS 140/200 which suggested also the most akin to designed average molecular weight which equaled 2667 g/mol.

Based on the above-mentioned assumptions, $^1$H NMR measurements allow determining estimated reaction progress over time. Therefore, the sample PPS 140/160 was submitted for this analysis. Figure 8 and Figure 9 present $^1$H NMR spectra prepared for PPS 140/160 during synthesis over reaction time. Figure 8 shows $^1$H NMR spectra for different samples, which were taken from the reaction mixture during the first step of the synthesis. Characteristic peaks named ‘x’, ‘y’ and ‘z’ (Figure 7, 8 and 9) during the first step of the polycondensation revealed higher intensity than resulted polyols. These peaks are characterized by the hydroxyl-terminated end groups of the macromolecules. It is related to the macromolecular structure development over reaction time, which leads to the higher amount of macromolecules characterized by higher average molecular weight. Furthermore, the results indicate the appearance of the two new peaks ‘E’ and ‘F’, which were not detected on the $^1$H NMR spectra of the synthesized polyol PPS 140/160 (Figure 7). The intensity of these peaks decrease with reaction time and after catalyst addition to the reaction mixture, they are disappeared (Figure 9). The extensive and profound research allow determining the probable chemical compound from which these two peaks are visible. This chemical is a 1,3-propylene glycol, with the chemical structure: $HO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$. Peak named ‘E’ is related with a triple peak corresponding to methylene protons which are adjoined to hydroxyl groups: $HO\text{-}C\underline{\mathbf{H_2}}\text{-}CH_2\text{-}C\underline{\mathbf{H_2}}\text{-}OH$. The characteristic intensive single peak named ‘F’ is attributed to protons derived from hydroxyl groups: $\underline{\mathbf{H}}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\underline{\mathbf{H}}$. The last peaks corresponding to the multiple peaks related to methylene protons from propylene glycol: $HO\text{-}CH_2\text{-}C\underline{\mathbf{H_2}}\text{-}CH_2\text{-}OH$ overlap with some of those derived from hydroxyl-terminated macromolecules (the peak named ‘y’). These two peaks, ‘E’ and ‘F’, identify the presence of the unreacted glycol, which amounts decrease with the time of the synthesis. The prepared investigation confirmed also the autocatalytic character of the succinic acid during synthesis due to the absence of peaks related with the free hydroxyl groups from carboxylic groups, which chemical shift should be visible from 10 to 12 ppm. This observation suggests that firstly in the reaction mixture reacts molecules of the succinic acid. One molecule of the succinic acid bonding with two molecules of 1,3-propylene glycol. Due to the excess of the used glycol, the peaks ‘E’ and ‘F’ are visible during the first step of the polycondensation and disappeared during the second step, after the catalyst employment.

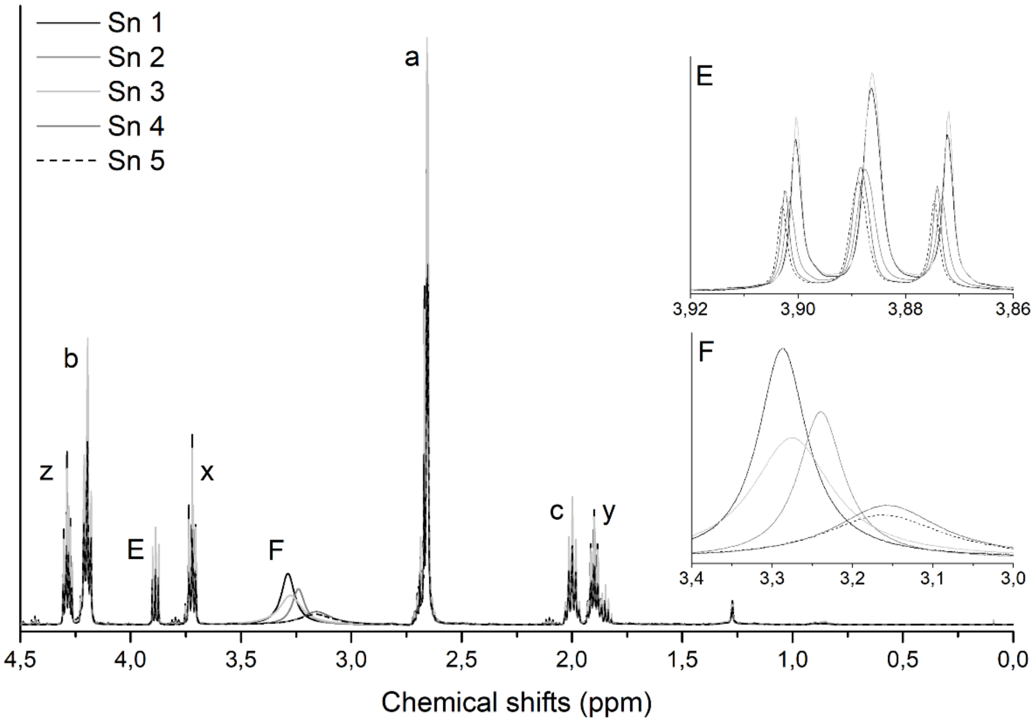


Figure 8 $^1$H NMR spectra of PPS 140/160 during the first step of the synthesis.

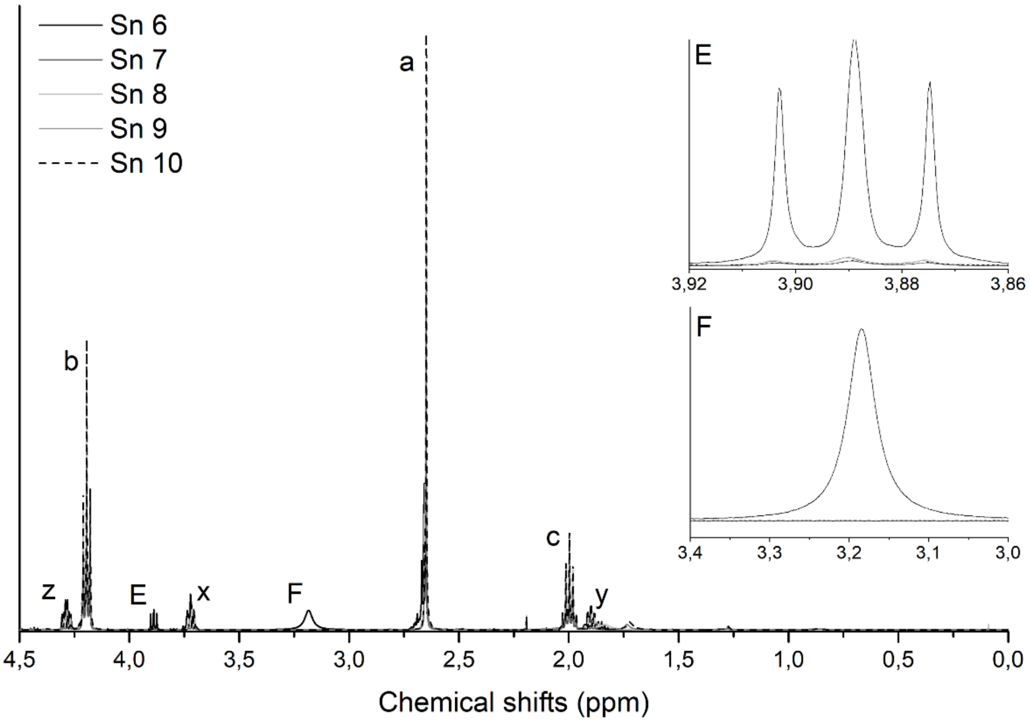


Figure 9 $^1$H NMR spectra of PPS 140/160 during the second step of the synthesis.

Conducted measurements allowed determining estimated reaction progress over time based on the approximate average molecular weight of the formed during synthesis macromolecules. The obtained results confirmed the above-mentioned statement about the autocatalytic character of the succinic acid. Table 5 shows the results of the polymerization degree with average molecular weight determination over reaction time for PPS 140/160. The results confirmed a low polymerization degree during the first step of the reaction and increasing value of polymerization degree after catalyst addition (second step). The average molecular weight during the first step ranged from 269 to 372 g/mol when after catalyst addition these values radically increased and ranged from 1641 to 4067 g/mol (from Sn 6 to Sn 8, see Table 5).

Table 5 Polymerization degree with average molecular weight determination over reaction time for PPS 140/160.

| Sample number | Reaction time [h] | n [-] | Mn [g/mol] |
|---|---|---|---|
| Sn 1 | 2 | 1.71 | 269.4 |
| Sn 2 | 4 | 1.84 | 290.7 |
| Sn 3 | 6 | 2.07 | 326.3 |

| | | | |
|---|---|---|---|
| Sn 4 | 8 | 2.17 | 343.2 |
| Sn 5 | 10 | 2.30 | 363.4 |
| Sn 6 | 11 | 2.36 | 372.2 |
| Sn 7 | 13 | 10.39 | 1641.3 |
| Sn 8 | 15 | 16.23 | 2564.0 |
| Sn 9 | 17 | 22.40 | 3539.4 |
| Sn 10 | 19 | 25.74 | 4067.2 |

### 3.5. Gel Permeation Chromatography (GPC)

One of the most important information about polyol macromolecular structure, besides the average molecular weight, indicates polydispersity, PD. For the PD characterization, the Gel Permeation Chromatography of the synthesized bio-based polyester polyols was carried out. This feature gives information about molecular weight distribution at the polyol structure, what affects the reaction proceedings during polyurethane materials synthesis. Furthermore, GPC measurement allows determining the weight and number average molecular weights ($M_w$ and $M_n$, respectively). Table 6 shows the results of the prepared measurements.

Table 6 GPC results of the synthesized bio-based polyester polyols.

| BIO-BASED POLYESTER POLYOL | Max. retation time (min) | $M_n$ (g/mol) | $M_w$ (g/mol) | PD (-) |
|---|---|---|---|---|
| PPS 140/160 | 29.49 | 2578.3 | 4644.4 | 1.801 |
| PPS 140/190 | 29.16 | 2534.1 | 5168.7 | 2.039 |
| PPS 140/200 | 30.00 | 2047.7 | 3518.2 | 1.718 |
| PPS 150/180 | 28.97 | 3413.6 | 5845.9 | 1.713 |
| PPS 150/190 | 29.79 | 2555.9 | 4054.6 | 1.587 |
| PPS 150/200 | 29.61 | 1744.7 | 4486.9 | 2.572 |
| PPS 160/180 | 29.36 | 2678.4 | 4800.8 | 1.793 |
| PPS 160/190 | 29.83 | 2305.8 | 3955.2 | 1.715 |
| PPS 160/200 | 29.74 | 2523.1 | 4077.0 | 1.616 |

PD – polydispersity

The results of the GPC measurement shows that values of $M_w$ are higher than $M_n$ values. The ratio of this two features informs about polydispersity. The lowest PD characterized polyols PPS 150/190 and PPS 160/200, with values at 1.587 and 1.616, respectively. These polyols characterize by molecular weight distribution in the similar range, which proclaims better feature for polyurethane materials synthesis. The highest values of polydispersity revealed specimens PPS 140/190 and PPS 150/200, equaled 2.039 and 2.572, respectively. These polyols characterize by molecular weight distribution in the broad range, which hinders the reaction proceedings during polyurethane materials synthesis. Besides the weight and number average molecular weight ratio values, the shape of the Gaussian curves obtained from GPC measurements, also proclaimed about polydispersity. Figure 10 shows the GPC spectra of the synthesized bio-based polyester polyols. The narrow shape of the Gaussian curve proclaims lower polydispersity of sample than the sample with broad curve course.

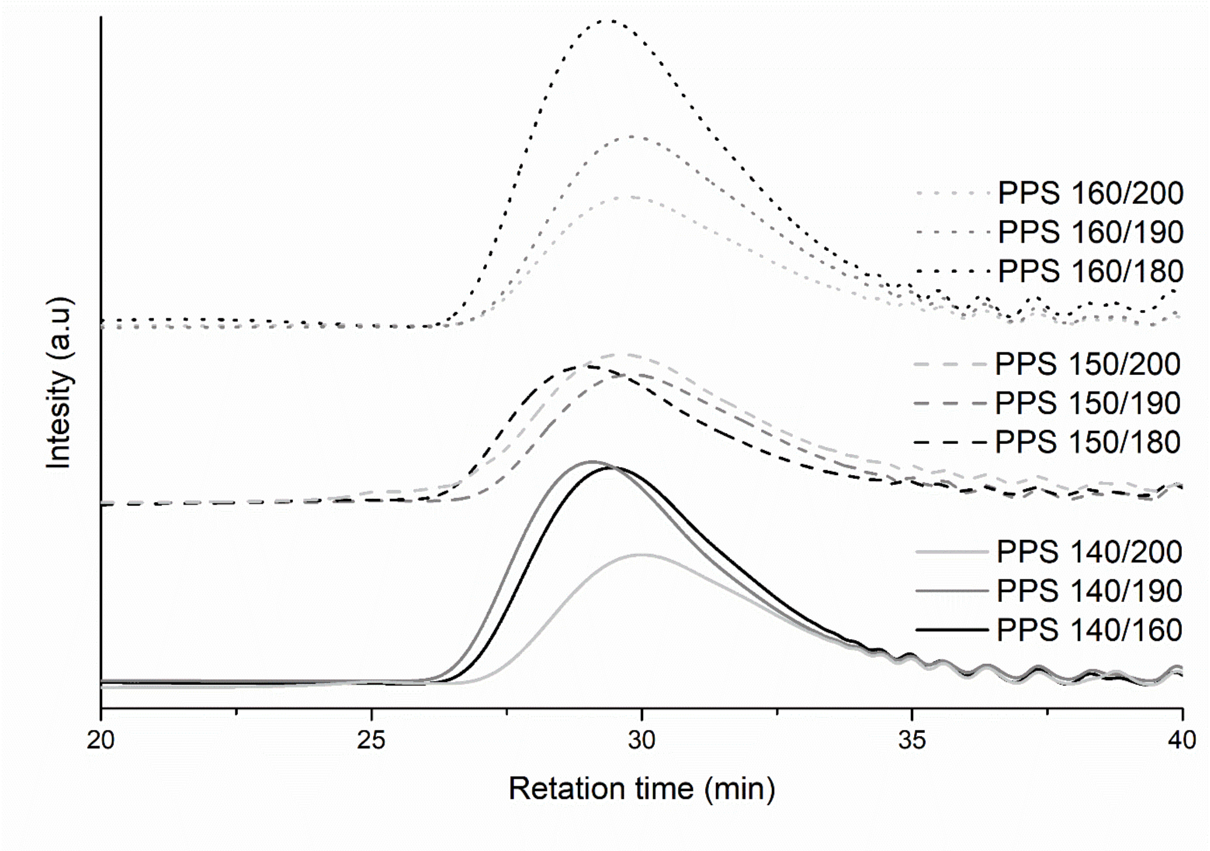


Figure 10 The GPC spectra of the synthesized bio-based polyester polyols.

It is well known, that the different measurement methods of the average molecular weight determination, give different results. Nevertheless, there is visible the similar trend in the relationship of the temperature conditions and average molecular weight results obtained from $^1$H NMR and GPC ($M_w$).

### 3.6. Thermogravimetric analysis (TGA)

The thermogravimetric analysis allowed to characterize the thermal stability of the selected synthesized bio-based polyester polyols. For the analysis, the samples PPS 140/190, PPS 150/190 and PPS 160/190 were chosen. Figure 11 and 12 present the TGA and DTG curves, respectively. The results confirmed their high thermal stability, comparable to the thermal stability of commercially used petrochemical polyester polyols [22]. All of the measured samples revealed the temperature of the maximum speed of weight loss at ca. 418$^{o}$C under a heating rate of measurements equaled 20$^{o}$C/min. The sole difference is related to the intensity of the peaks of the speed of weight loss.

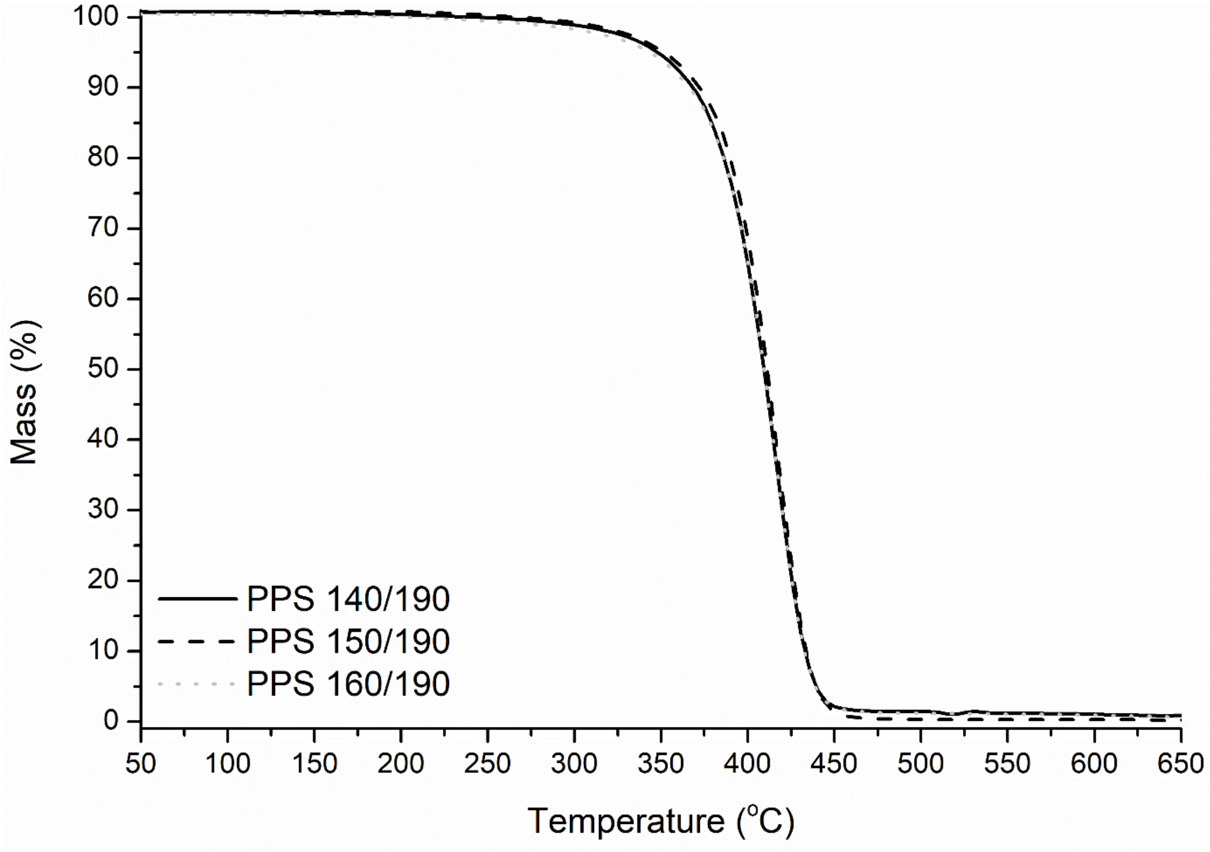


Figure 11 The TGA curves of the PPS 140/190, PPS 150/190 and PPS 160/190 polyols.

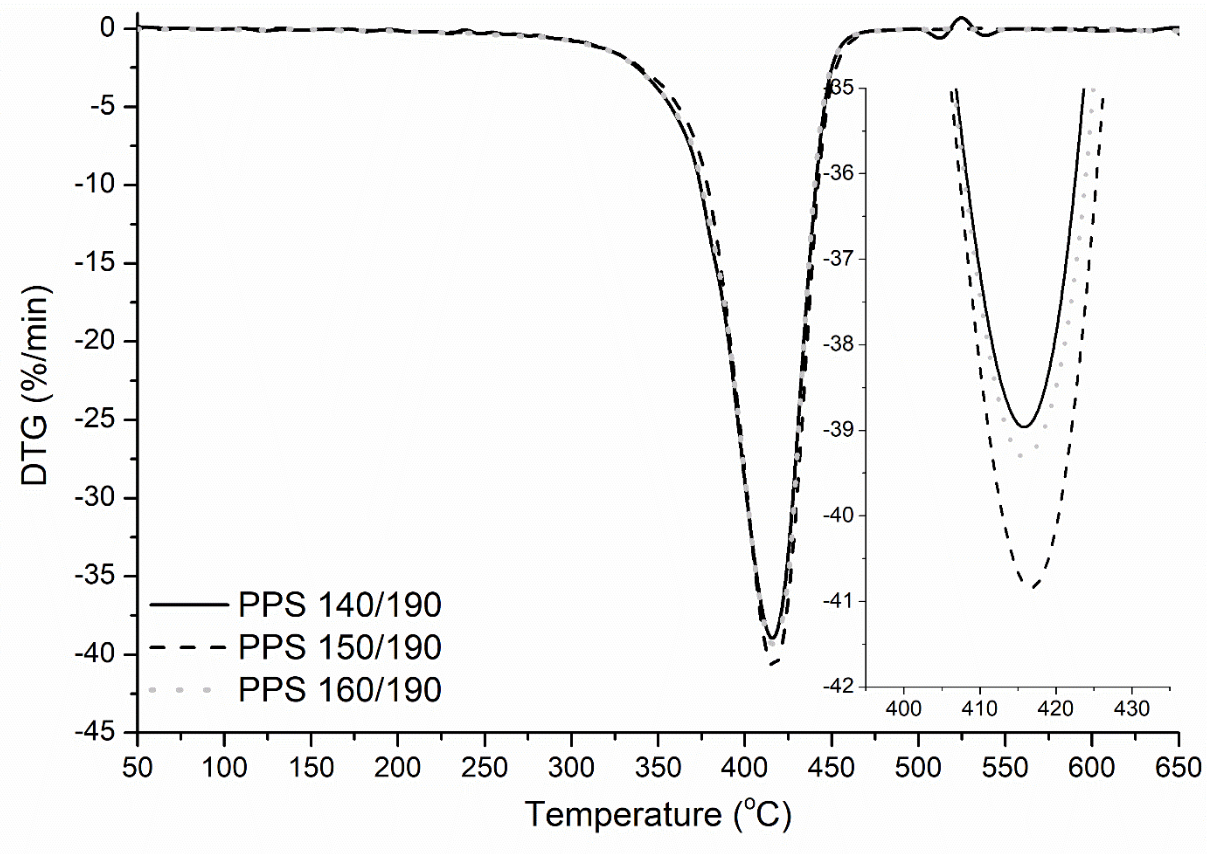


Figure 12 The DTG curves of the PPS 140/190, PPS 150/190 and PPS 160/190 polyols.

## 4. Conclusions

The main aim of this work was to precisely and profoundly determined and described the kinetics characteristic of the two-step polycondensation reaction between fully bio-based monomers. The series of bio-based poly(propylene succinate)s were synthesized under different temperature conditions which allowed calculate the reaction rate constants and energy activation. The conducted investigation confirmed the impact of the temperature conditions on the reaction rate constants for both steps of the reaction. Based on the results the energy activation for the first step of the reaction was calculated and equaled ca. 38.5 kJ/mol, which is the slightly lower value with the energy activation of the polyols synthesis based on the petrochemical monomers (ca. 50 kJ/mol). Nevertheless, the uncertain repeatability of the second step precludes the energy activation determination for the second step of the synthesis. Based on the FTIR and $^{1}$H NMR spectra for samples collected for investigation over the synthesis time, the profound research about macromolecular structure development during both steps of the synthesis was precisely described. In this work, the approximate average molecular weight of the formed during synthesis macromolecules over time were calculated. The results confirmed low polymerization degree values during the first step of the reaction, in the range from 1.7 to 2.4, and increasing value of polymerization degree after polycondensation catalyst employment (second step) from 2.4 to 25.7, which allowed obtaining polyester polyols with an average molecular weight approximately 3000 g/mol. The GPC measurements allowed obtaining the polydispersity of the samples. The lowest values revealed samples PPS 150/190 and PPS 160/200, with equaled 1.587 and 1.616, respectively. The results of the TGA analysis confirmed the high thermal stability of the prepared bio-based polyester polyols which equaled ca. 418°C. This value is comparable to the thermal stability of commercially used petrochemical polyester polyols.

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Caption of Figures

Figure 1 Scheme of the possible reactions during two-step polycondensation between succinic acid and 1,3-propanediol.

Figure 2 Effect of various temperatures on the yield of the first step.

Figure 3 Effect of various temperatures on the yield of the second step after the first step conducted at a) 140$^{o}$C, b) 150$^{o}$C, c) 160$^{o}$C.

Figure 4 Arrhenius plot of the esterification reaction.

Figure 5 FTIR spectra of PPS 140/160.

Figure 6 Peaks intensity changes monitored during synthesis at wavenumber range from: a) 3800 to 2500 cm$^{-1}$, b) 1780 to 1640 cm$^{-1}$, c) 1300 to 1000 cm$^{-1}$.

Figure 7 $^1$H NMR spectrum of PPS 140/160.

Figure 8 $^1$H NMR spectra of PPS 140/160 during the first step of the synthesis.

Figure 9 $^1$H NMR spectra of PPS 140/160 during the second step of the synthesis.

Figure 10 The GPC spectra of the synthesized bio-based polyester polyols.

Figure 11 The TGA curves of the PPS 140/190, PPS 150/190 and PPS 160/190 polyols.

Figure 12 The DTG curves of the PPS 140/190, PPS 150/190 and PPS 160/190 polyols.

Caption of Tables

Table 1 Preparation and properties of the obtained bio-based polyester polyols.

Table 2 Components used during the synthesis and the semi-product and product of the synthesis.

Table 3 Kinetics characteristic of the esterification and polycondensation reactions.

Table 4 Degree of polymerization and average molecular weight of the synthesized polyester polyols obtained from $^1$H NMR results.

Table 5 Polymerization degree with average molecular weight determination over reaction time for PPS 140/160.

Table 6 GPC results of the synthesized bio-based polyester polyols.