

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

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

23 Keywords: Bio-based polyester polyols; Kinetics study; Functional group approach; <sup>1</sup>H NMR; GPC;  
24 Thermal stability

## 25 1. Introduction

26 The growing interest in the field of the bioresources for the polymers synthesis caused the  
27 increasing focus on the biorenewables in the polyurethane synthesis. The reduction of energy  
28 consumption and the greenhouse gasses production, CO<sub>2</sub> emission reduction, the economic volatility  
29 reduction by the decrease in the fossil fuel stocks utilization and the decrease in the production costs

30 with increasing production scale represent the major advantages which contribute to the increasing  
31 interest in the utilization of biorenewables in chemical syntheses [1,2].

32 It is well-known that the petrochemical-based components have more impurities, which are  
33 consisted of the different chemical compounds. The scientists from Genomatica Company [3]  
34 investigated the variation in the purity of the bio-based 1,4-butanediol and other, commonly used,  
35 petrochemical-based 1,4-butanediol. The results confirmed differences between samples composition.  
36 The various contaminants can lead to the different reaction mechanisms during the polymer synthesis,  
37 therefore it is necessary to find out the contaminants impact on the synthesis pathways.

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

47 Another reaction type, which is more popular for the kinetics investigation constitutes thermal  
48 degradation reaction. He et al. [5] described the results of the thermal decomposition kinetics novel  
49 polyester containing bithiazole rings. It was established that the decomposition of the polyester is a  
50 complex multi-step mechanism with the activation energy of 146.9 kJ/mol. Tsanaktsis and co-workers  
51 [6] investigated three novel aliphatic polyesters based on the 2,5-furandicarboxylic acid and low  
52 molecular weight aliphatic diols. It was found that butanediol-based polyester, PBF, was less stable  
53 thermally, than the other two polyesters (propanediol, PPF, and ethanediol-based, PEF). The activation  
54 energy revealed 121, 159 and 162 kJ/mol for PBF, PPF, and PEF, respectively.

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

59 The kinetics of the three succinic acid-based polyesters synthesis was studied by Bikiaris and  
60 co-workers [8,9]. The researchers found that the use of different glycols does not influence much the  
61 number average degree of polymerization values of the oligomers produced. Nevertheless, different  
62 glycols slightly affect esterification rates towards lower amounts of CH<sub>2</sub> groups at the molecular chain,  
63 namely: poly(butylene succinate)(PBS) > poly(propylene succinate)(PPS) > poly(ethylene  
64 succinate)(PES). Moreover, with larger catalyst molar ratio, polymers with bigger average molecular  
65 weight were obtained. Finally, it was found that although higher initial ratios of glycol to succinic acid  
66 were used to increase the esterification rate, they lowered the degree of polymerization of the oligomers.  
67 [8] In their second work, it was found that when ethylene glycol is used as a reactant, both esterification  
68 and transesterification reaction rates are promoted. However, the transesterification reaction rate  
69 constant of PPS is much lower compared to PBS. Moreover, the esterification rate constant was  
70 estimated always to be much larger compared to the rate constant of the transesterification reaction,  
71 meaning that the former reaction proceeds much faster compared to the later, resulting thus in very low  
72 values of the carboxyl end groups compared to corresponding hydroxyl end groups. Activation energies  
73 of the esterification reaction (1 step of polycondensation) equaled 47, 52 and 59.5 kJ/mol for PBS, PPS  
74 and PES, respectively.

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

80 The aim of this work was the profound investigation of kinetics characteristics with activation  
81 energy determination of fully bio-based poly(propylene succinate)s prepared under different reaction  
82 temperature conditions. Products were synthesized via well-known two-step polycondensation reaction  
83 and tetraisopropyl orthotitanate as a catalyst. Functional group approach was chosen for establishing  
84 the framework for the kinetics of the reaction. Based on the results, orders of reaction (divided into first  
85 and second step), rate constants and activation energy of the first step of the reaction were determined.  
86 For macromolecular structure changes characteristics and the progress of the chemical reaction  
87 monitoring, Fourier Transform Infrared Spectroscopy and Proton Nuclear Magnetic Resonance were  
88 used and described. Moreover, <sup>1</sup>H NMR spectra allowed determining changes in the degree of

89 polymerization over the reaction time. Gel Permeation Chromatography allowed characterizing the  
90 molecular weight distribution of the prepared bio-based polyols. Furthermore, thermal stability was  
91 investigated with the use of TGA measurement.

## 92 2. Material and methods

### 93 2.1. Materials

94 The series of the fully bio-based poly(propylene succinate) syntheses were carried out with the  
95 use of two fully bio-based components. The used dicarboxylic acid was succinic acid (SA) obtained from  
96 BioAmber Sarnia Inc. (Ontario, Canada). The SA purity was in the range 98-100%. The molecular weight  
97 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  
98 employed glycol constituted Susterra Propanediol (1,3-propanediol) which was obtained from DuPont  
99 Tate&Lyle Corporation Bio Products (Loudon, Tennessee, USA). This liquid component revealed purity  
100 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>.  
101 Furthermore, water content by Karl Fischer equaled 12.1 ppm and a dynamic viscosity at 20°C was 52  
102 mPas. As a catalyst was used the Tetraisopropyl orthotitanate, Ti(O-i-Pr)<sub>4</sub> (TPT). It was purchased from  
103 TCI Chemicals (India) as a liquid component with the purity ca. 97%. The molecular weight amounts to  
104 284.22 g/mol. The catalyst was used in an amount of 0.25 wt.% as a glycol equivalent every time in the  
105 second step of the polycondensation. For water content measurements the volumetric Karl Fischer  
106 method was used. The KF reagent used for the NIST volumetric measurements contained methanol  
107 solution of imidazole and sulfur dioxide as the organic base, J.T. Baker, HYDRA-POINT Solvent G,  
108 pyridine free, was purchased from Avantor Performance Materials Poland S.A. (Gliwice, Poland). The  
109 KF titrant for volumetric method contains methanol solution of iodine, J.T. Baker, HYDRA-POINT Titrant  
110 5mg H<sub>2</sub>O/mL, was also purchased from Avantor Performance Materials Poland S.A. (Gliwice, Poland).  
111 The other materials and solvents were used of the analytical grade for the analytical measurement  
112 methods.

113

### 114 2.2. Bio-based polyesters synthesis

115 The linear bio-based polyester polyols were prepared with the use of succinic acid SA and 1,3-  
116 propanediol PDO. Catalyst, tetraisopropyl orthotitanate TPT, was used as a glycol equivalent in the  
117 amount of 0.25 wt.%. The catalyst content was determined according to our previous work. All bio-based  
118 poly(propylene succinate)s were synthesized by two-step polycondensation method (see Figure 1 in

119 reference [10]). Glycol was always used with an excess and the molar ratio SA:PDO amounted to 1:1.2.  
120 Determination of this molar ratio was ordered by the final molecular weight expected after full  
121 polycondensation. The designed number average molecular weight of the prepared polyols was  $M_n$   
122 = 2000 g/mol with functionality equaled 2, for proving linear macromolecular chain structure. The  
123 reaction was carried out in the glass reactor, which consisted of a three-neck flask equipped with a  
124 nitrogen/vacuum inlet, mechanical stirrer, thermometer, condenser, and heating mantle. The first step  
125 was represented by the esterification reaction between a succinic acid (SA) and 1,3-propanediol (PDO)  
126 which was carried out under a nitrogen atmosphere. The bio-based components mixtures were stirring  
127 at three different temperatures, exactly 140, 150 and 160°C. During the first step of the synthesis, the  
128 mixtures were kept for 10 hours at the suitable temperature without catalyst presence, according to the  
129 patent application in the Polish Patent Office (no. P.418808). After water distillation, the second step  
130 was started. During the polycondensation reaction, the nitrogen was stopped, the catalyst was added,  
131 and the temperature was increased. The second step was carried out under reduced pressure at three  
132 different temperatures for all three various temperatures from the first step. The temperatures of the  
133 second step amounted to 160, 180, 190 and 200°C according to the first step. The acidic number was  
134 measured to track the reaction progress. After achieving the value of the acidic number ca. or preferably  
135 below 1 mg KOH/g, the polycondensation was finished.

136

### 137 2.3. Polymer characterization methods

#### 138 2.3.1. Acid number

139 Carboxyl end-group value measurements were performed by the Polish standard PN-  
140 86/C45051. Samples about 1 g of the prepared polyesters were dissolved in ca. 30 cm<sup>3</sup> of acetone at  
141 room temperature. After that, the solutions were titrated with the use of a standard solution of potassium  
142 hydroxide KOH in distilled water (0.1 mol/dm<sup>3</sup>) and phenolphthalein as an indicator.

#### 143 2.3.2. Hydroxyl number

144 Hydroxyl end-group determination was prepared by the Polish standard PN-88/C-89082.  
145 Sample about ca. 0.5 g of polyester was dissolved in 5 cm<sup>3</sup> of the acetic anhydride solution. The solution  
146 was refluxed for 30 minutes. Subsequently, 1 cm<sup>3</sup> of pyridine was added and heating for 10 minutes.  
147 After that, 50 cm<sup>3</sup> of distilled water was added, the mixture was cool to room temperature and titrated

148 with the use of a standard solution of potassium hydroxide KOH in distilled water (0.5 mol/dm<sup>3</sup>) and  
149 phenolphthalein as indicator.

### 150 2.3.3. Dynamic viscosity

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

### 157 2.3.4. Fourier Transform Infrared Spectroscopy (FTIR)

158 Fourier Transform Infrared Spectroscopy was used to obtain the spectra of the bio-based  
159 polyester polyols and pure components (1,3-propanediol and succinic acid). The FTIR spectra were also  
160 investigated to track the reaction progress. The measurements were carried out using a Nicolet 8700  
161 FTIR spectrometer (Thermo Electron Corporation, USA) with the use of the ATR technique. Sixty-four  
162 scans in the wavenumber range from 4500 to 500 cm<sup>-1</sup> were taken with the resolution 4 cm<sup>-1</sup>. The  
163 kinetics of the reaction between dicarboxylic acid and glycol was followed using FTIR spectroscopy by  
164 investigation of the selective spectra absorbance changes at a various time.

### 165 2.3.5. Nuclear Magnetic Resonance (<sup>1</sup>H NMR)

166 Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra of the prepared bio-based polyester  
167 polyols were studied for molecular structure analysis. The resulted spectra allowed to determine the  
168 degree of the polymerization and the approximative molecular weight of the synthesized polyols, ipso  
169 facto. The <sup>1</sup>H NMR data were obtained with the use of Bruker spectrometer. Operating frequency was  
170 400 MHz for protons. The ca. 10% w/v solutions of the poly(propylene succinate) polyesters were  
171 prepared in a CDCl<sub>3</sub> solvent at ambient temperature. The simulation and iteration of spectra were carried  
172 out using Bruker software.

### 173 2.3.6. Gel permeation chromatography (GPC)

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

#### 184 2.3.7. Thermogravimetric analysis

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

### 190 3. Results and discussion

#### 191 3.1. Bio-based poly(propylene succinate)s

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

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

202

203 3.2. Kinetics study

204 3.2.1. Approach and reactions

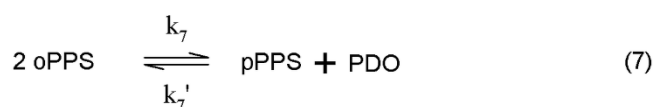
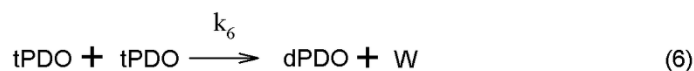
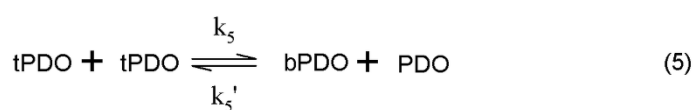
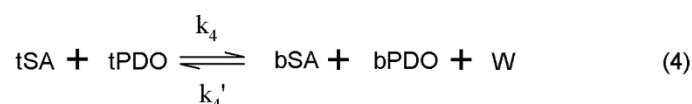
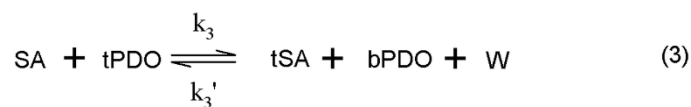
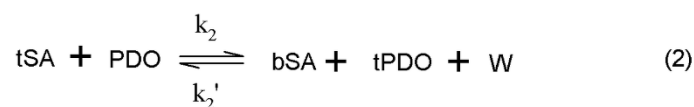
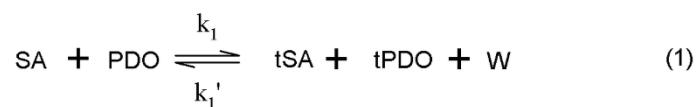
205 There are two main approaches which allowed establishing the framework for the kinetics of the  
 206 reaction: the functional group model and molecular species model. The second model, as mentioned,  
 207 give more comprehensive information about the reaction but involves also more complicated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

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



221 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 <sub>2</sub> -CH <sub>2</sub> -COOH
PDO	Propylene glycol	HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH
Products		
W	Water	H <sub>2</sub> O
pPPS	Poly(propylene succiate)	HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> [-O-C(O)-CH <sub>2</sub> -CH <sub>2</sub> -C(O)-O-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> ] <sub>n</sub> -OH
Oligomers		
tSA	SA end group	HOOC-CH <sub>2</sub> -CH <sub>2</sub> -CO-
tPDO	PDO end group	HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-
bSA	SA repeating unit	-OC-CH <sub>2</sub> -CH <sub>2</sub> -CO-
bPDO	PDO repeating unit	-O-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-
dPDO	Dipropylene glycol repeating unit	-O-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-
oPPS	Oligomeric PPS terminated PDO	~CH <sub>2</sub> -OH
cPPS	Oligomeric PPS terminated SA	~CH <sub>2</sub> -COOH



222

223 Figure 1 Scheme of the possible reactions during two-step polycondensation between succinic acid and  
 224 1,3-propanediol.

225

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

232 All presented reactions are described by the 15 kinetics rate constants, where  $k_j$  ( $j=1, 8$ ) and  $k_j'$   
 233 ( $j=1, 8$ , without 6) refer to appropriate elementary reactions. Based on the calculated rate constants the  
 234 mole number and thereby the amount of all components presented in the reaction mixture can be

235 evaluated as a function of the polycondensation time. The extensive literature review on the kinetics  
236 study of the polycondensation has not provided any experimental data and equations which allowed to  
237 determine the values of all of the kinetic rate constants. Therefore, some assumptions are necessary  
238 for the research development.

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

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

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

$$257 k_1 = k_2 = 2k_3 = 2k_4.$$

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

$$259 k_5 = 0.$$

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

263

264 3.2.2. The progress of the reaction

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

$$268 \quad S_{1,2,\dots,n} = S_0 - [A_1 * S_0 / A_0] \quad (1)$$

$$269 \quad Y_{1,2,\dots,n} = [S_0 - S_{1,2,\dots,n}] / 100 \quad (2)$$

270 Where:

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

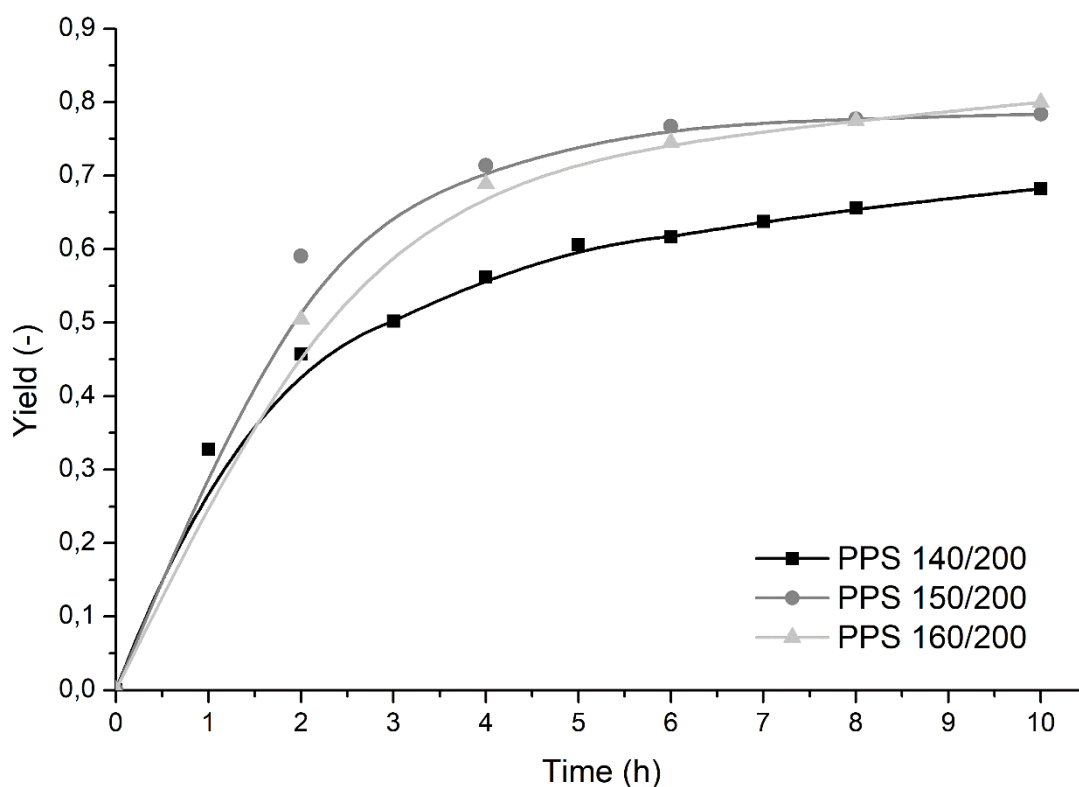
272  $S_{1,2,\dots,n}$  – means how much dicarboxylic acid molecules are bonded after approximate reaction time  $t_1$ ,  
 273  $t_2, \dots, t_n$ , [%]

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

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

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

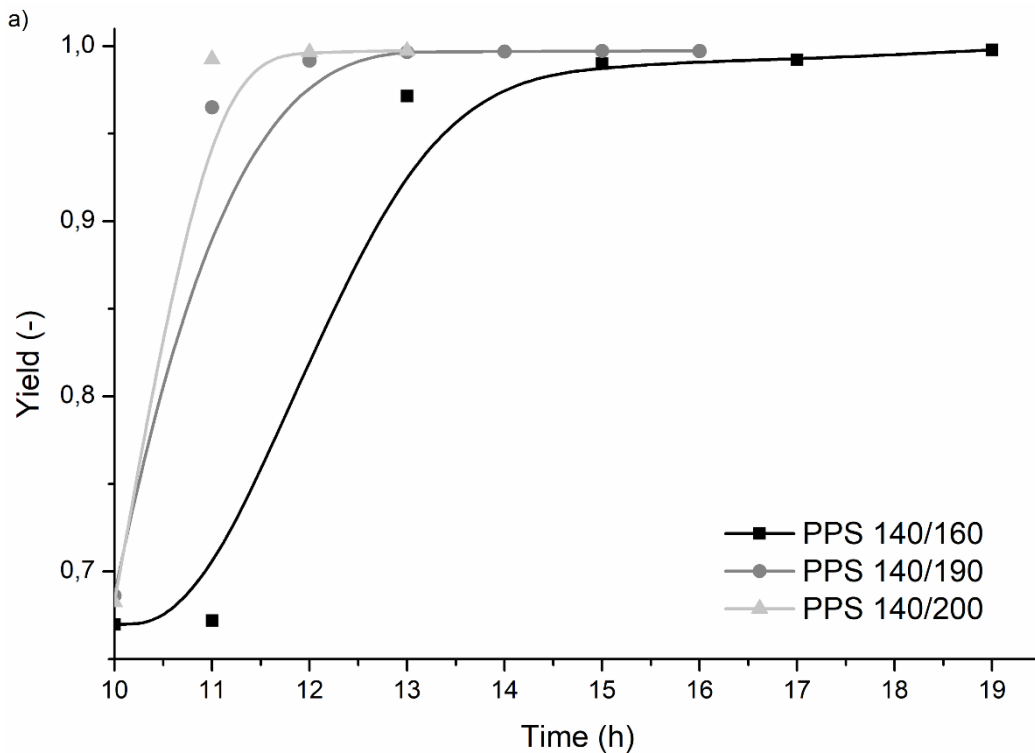
277 Figure 2 and 3 show changes in the reaction yield in the reaction time during the first and second steps.



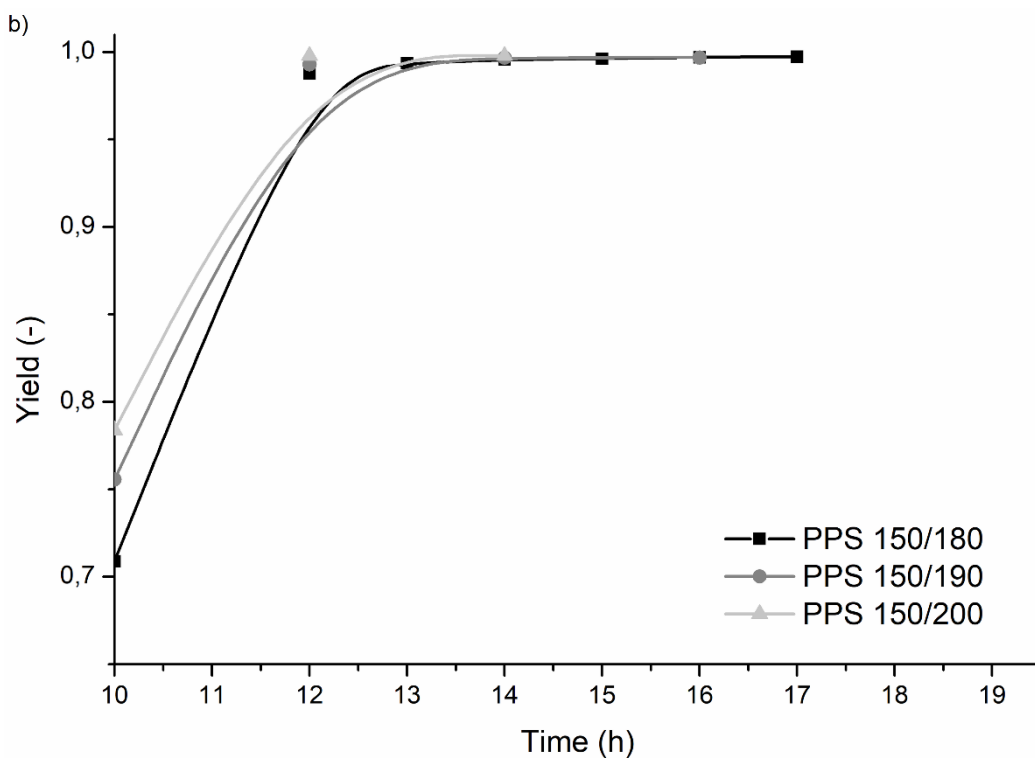
278  
 279 Figure 2 Effect of various temperatures on the yield of the first step.

280  
 281 Figure 2 presents the effect of the temperature conditions on the yield of the first step. The  
 282 controlled reaction progress indicated that with the growing temperature during the reaction led to a

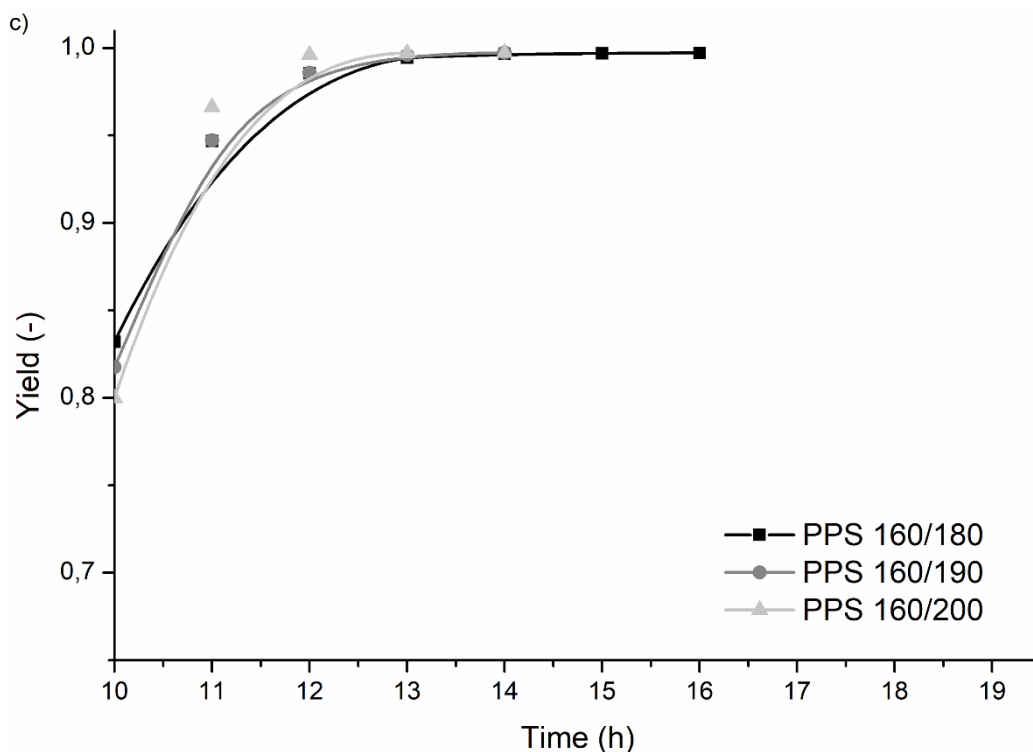
283 higher yield of the reaction. The lowest value characterized samples prepared at 140°C, when polyols  
284 synthesized at higher temperatures disclosed similar yield ca. 0.8.



285



286



287

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

290

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

304

305 3.2.3. Reaction order

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

$$312 \quad f(t) = \log(1-Y_{1,2,\dots,n})^{-1} \quad (3)$$

$$313 \quad f(t) = (1-Y_{1,2,\dots,n})^{-1} \quad (4)$$

$$314 \quad f(t) = (1-Y_{1,2,\dots,n})^{-2} \quad (5)$$

315 Usually, one of this function has the linear curve course. The linear relationship of the function  $f(t)=at+b$ ,  
316 characterized by the highest correlation coefficient verifying the reaction order. For two-step  
317 polycondensation method used in this study, there is necessary to divide the data into two steps. The  
318 results confirmed two different reaction orders for all syntheses, III order of the first step and I order of  
319 the second step. A collection of math equations of the reaction orders for all syntheses is shown in Table  
320 3. It is related to the amount of the various macromolecules which can react together. During the first  
321 step, the molecules of succinic acid and 1,3-propanediol react with each other and formed low molecular  
322 weight esters, hydroxyl and carboxyl-terminated. These esters constitute the third component, which  
323 concentration is constantly increasing over the reaction time. The confirmation of this reaction order was  
324 also described based on the  $^1\text{H}$  NMR spectra (please, see Chapter 3.4 Nuclear Magnetic Resonance  
325 ( $^1\text{H}$  NMR), section 3. Results and Discussion, Table 5). I order of the reaction during the second step is  
326 related to the catalyst employment. The polycondensation catalyst leads to the oligomerization between  
327 low molecular weight esters at the beginning and polymerization between oligomers at the end of the  
328 reaction. This reaction order was also proved via  $^1\text{H}$  NMR results.

329

#### 330 3.2.4. Reaction rate constants

331 Several publications have appeared in recent years documenting the reaction rate constants for  
332 polycondensation as a function of the rate of the end-group changes [15,17,18]. Based on the acid  
333 number changes over the reaction time, the reaction yield had been calculated. The resulted calculation  
334 allow verifying similar reaction yield for all synthesis, which values in the range from 0.9968 to 0.9978  
335 (Table 3). Moreover, the graphical method of the reaction order determination allowed assigning the

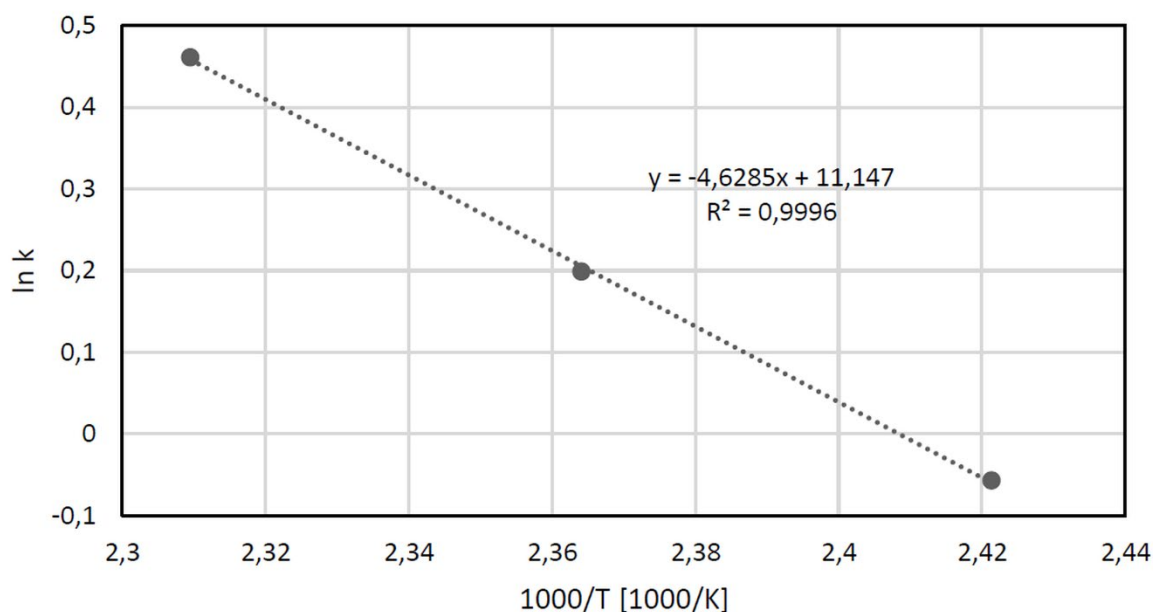
336 math equation of the reaction order, from which the reaction rate constant,  $k$ , can be established. The  
 337 slope of the curves for III order of the first step and I order of the second step of the synthesis constitutes  
 338 the values of the reaction rate constants.

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

344 Table 3 Kinetics characteristic of the esterification and polycondensation reactions.

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





345

346 Figure 4 Arrhenius plot of the esterification reaction.

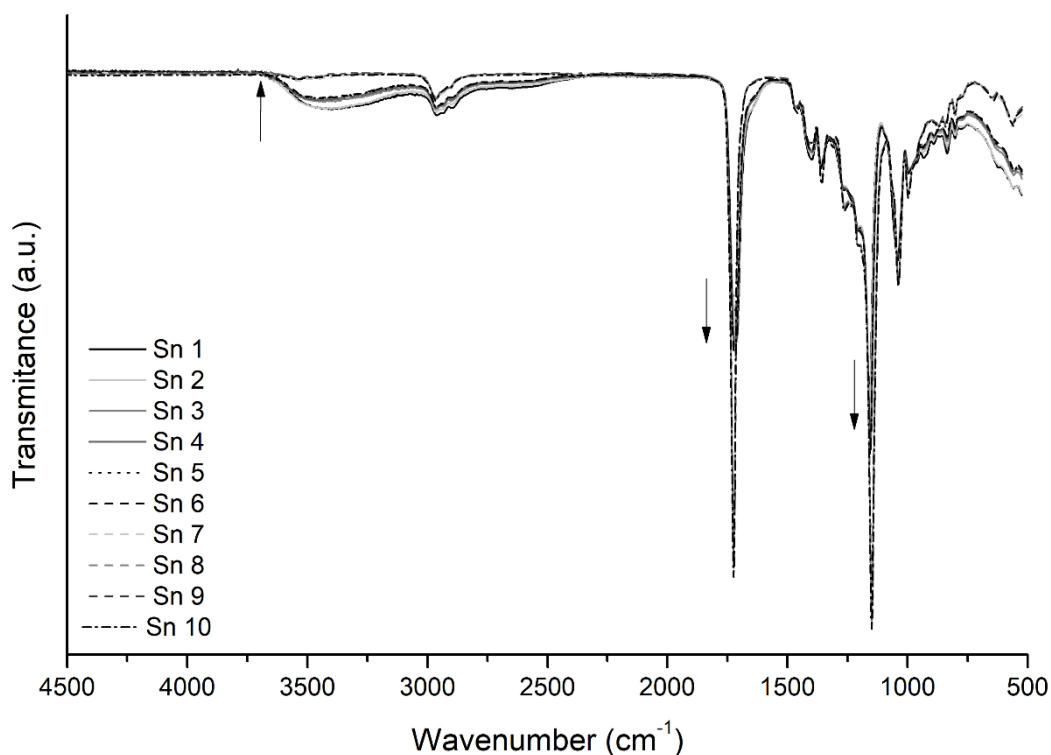
347

348 The activation energy,  $E_a$ , values for the considered reactions were also determined from  
 349 measurements taken at different temperatures. Figure 4 shows the relationship between the reaction  
 350 rate constant and temperature for esterification promoted without catalyst employment. Figure 4  
 351 indicates that 'ln k' against 1000/T plot is linear. The fitting equation and its correlation coefficient ( $R^2$ )  
 352 is obtained and shown on the graph. Based on the equation, the activation energy value of 38.5 kJ/mol  
 353 and the logarithm of the pre-exponential or frequency factor A value of 11.147, are determined for the  
 354 first step of the bio-based polyols synthesis. This investigation verified the lower value of the activation  
 355 energy of the bio-based polyester polyols synthesis than their petrochemical-based counterparts which  
 356 equaled ca. 50 kJ/mol [9]. This is due to the differences in monomer purity. The biotechnological process  
 357 of the 1,3-propanediol production allows obtaining monomer with purity even higher than 99.98%, when  
 358 its petrochemical equivalent characterized purity ca. 99.70%. Even this little differences can affect  
 359 reaction kinetics and, in the sequel, a different value of the activation energy. It can be concluded that  
 360 with the increase in monomer pollution, the value of the activation energy of the reaction increases. For  
 361 the second step of the polycondensation reaction, conducted measurement results made it impossible  
 362 to calculate the activation energy value. It was due to the irregular value of the reaction rate constant,  
 363 'k'. For this study, it is important to replicate the equal synthesis and pulling out the average of the  
 364 second step reaction rate constant, 'k' results. It is seen in Table 3, standard deviations between reaction  
 365 rate constant revealed increasing values with growing temperature of the first step of the

366 polycondensation reaction. The various reaction rate constant values without express increasing trend  
367 with the growing temperature of the second step confirmed the necessity of the repeatability  
368 investigation of bio-based sources usage in the two-step polycondensation method.

### 369 3.3. Fourier Transform Infrared Spectroscopy (FTIR)

370 The structure analysis was performed using Fourier Transform Infrared Spectroscopy. This  
371 method allows to track changes at the macromolecular structure of the polyols during synthesis Figure  
372 5 shows exemplary FTIR spectra of a polyol PPS 140/160, where different curves are collected together  
373 to show characteristic changes during the polycondensation reaction. Samples from Sn 1 to Sn 10  
374 characterize reaction mixture during synthesis from the beginning to the end of the synthesis. They were  
375 taken to the testing every two hours. Samples from Sn 1 to Sn 5 represent the first step of the reaction  
376 when samples from Sn 6 to Sn 10 – second step. All characteristic peaks were precisely described in  
377 our previous article [10,19]. The arrows on the graph show the direction of changes in the intensity of  
378 the peaks.

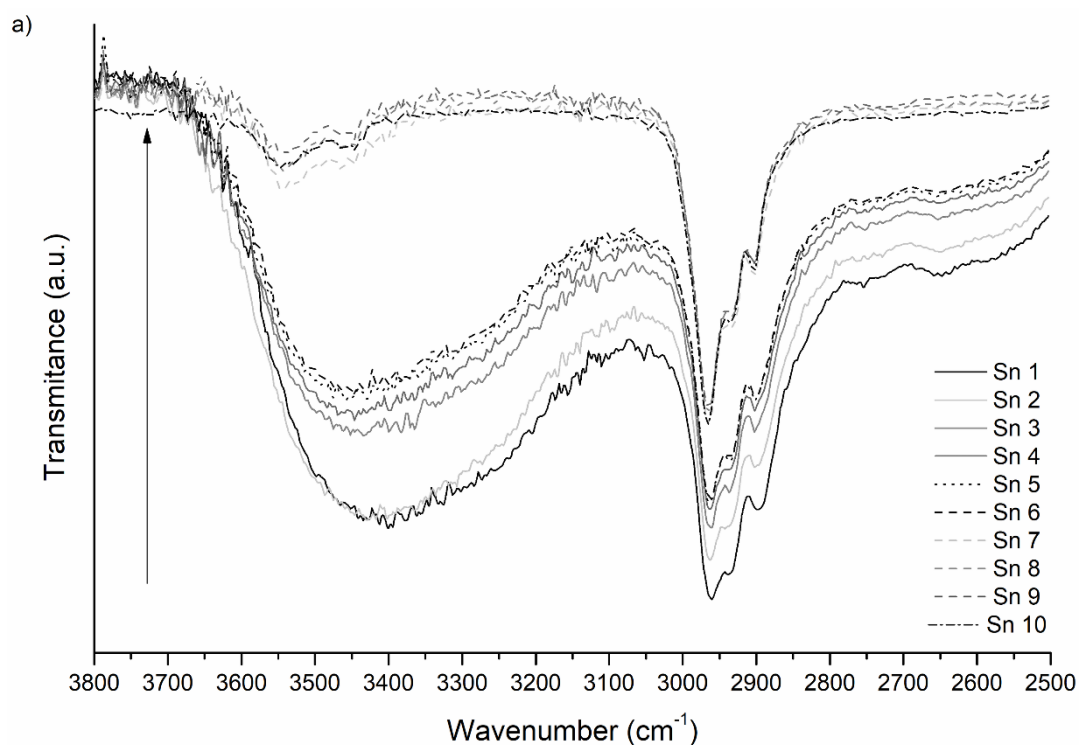


379  
380 Figure 5 FTIR spectra of PPS 140/160.

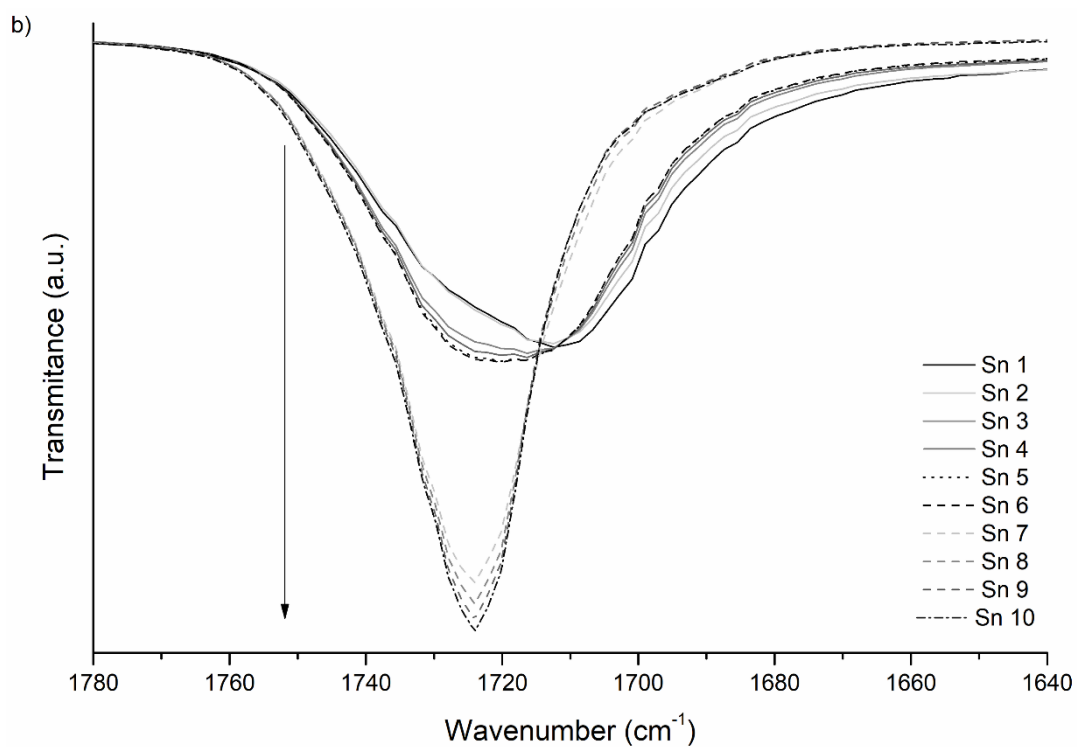
381  
382 Figure 5 shows the differences in the curve courses during both steps of polycondensation. The  
383 most visible changes are related to the peak intensity. The broad peak in the wavelength range between

384 3700 and 2500  $\text{cm}^{-1}$  is attributable to the stretching vibrations of hydrogen-bonded hydroxyl groups. The  
385 characteristic for the 1,3-propanediol spectrum in the wavelength range between 3570 and 3170  $\text{cm}^{-1}$   
386 assigns to the stretching vibrations of hydrogen-bonded hydroxyl groups. For the succinic acid spectrum,  
387 the peak assigned to the hydrogen-bonded carboxyl groups stretching vibration appeared as the broad  
388 peak centered at 3300-2500  $\text{cm}^{-1}$ . The peaks at 3000-2850  $\text{cm}^{-1}$  are assigned to the methylene groups  
389 which are visible for glycol and polyesters spectra. The most intensive peaks identifying ester groups  
390 formation are visible at 1725  $\text{cm}^{-1}$  and 1150  $\text{cm}^{-1}$ .

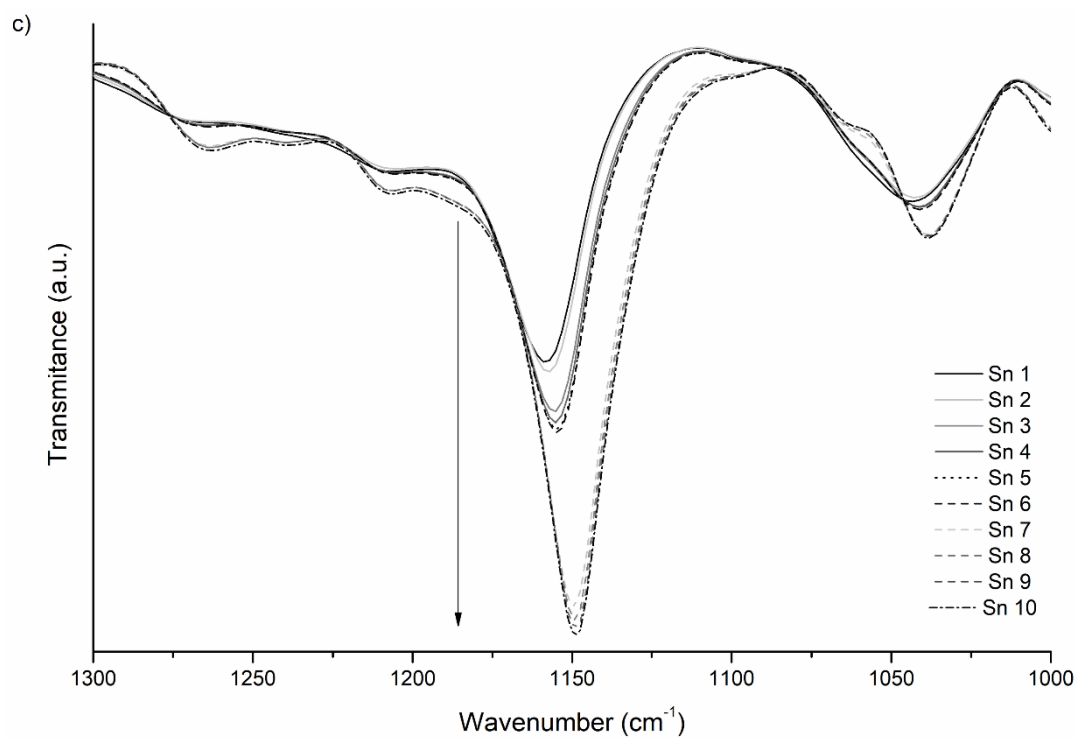
391 Figure 6 presents, more precisely, changes that occur during synthesis on the example of three  
392 main peaks. During polycondensation reaction, water as a by-product is eliminated from the reaction  
393 mixture and the hydroxyl groups from glycol react with carboxyl groups from a dicarboxylic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



397



398



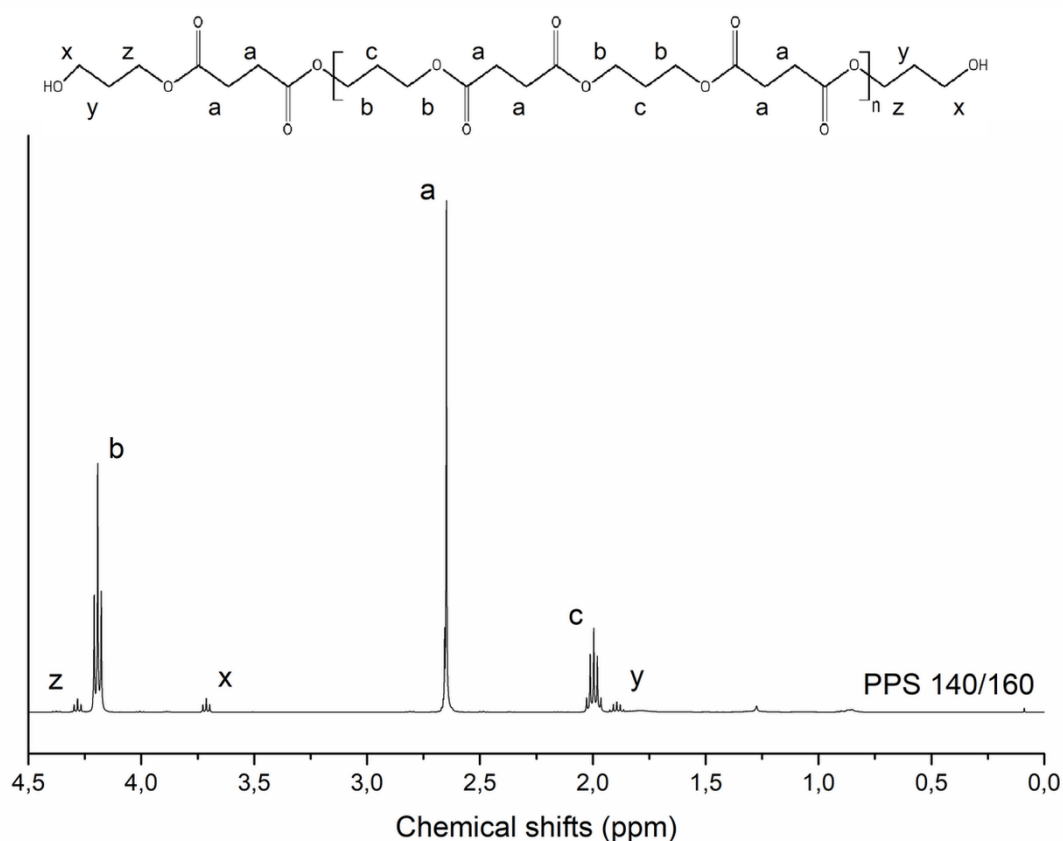
399

400 Figure 6 Peaks intensity changes monitored during synthesis at wavenumber range from a) 3800 to  
 401 2500  $\text{cm}^{-1}$ , b) 1780 to 1640  $\text{cm}^{-1}$ , c) 1300 to 1000  $\text{cm}^{-1}$ .

402

403 3.4. Nuclear Magnetic Resonance ( $^1\text{H}$  NMR)

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



417  
 418 Figure 7  $^1\text{H}$  NMR spectrum of PPS 140/160.

419



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

$$427 \quad (b + z) \sim (n \cdot 4H_{\text{from repeating units}} + 4H_{\text{chain end}}) \quad (6)$$

$$428 \quad x \sim (4H_{\text{terminated chain}}) \quad (7)$$

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

$$430 \quad n = [(b+z)-z]/x \quad (8)$$

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

$$432 \quad n = b/z \quad (9)$$

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

$$435 \quad M_n = n(M_n \text{ of the repeating unit}) + M_n \text{ of the chain ends} \quad (10)$$

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

440 Table 4 Degree of polymerization and average molecular weight of the synthesized polyester polyols  
 441 obtained from  $^1\text{H}$  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

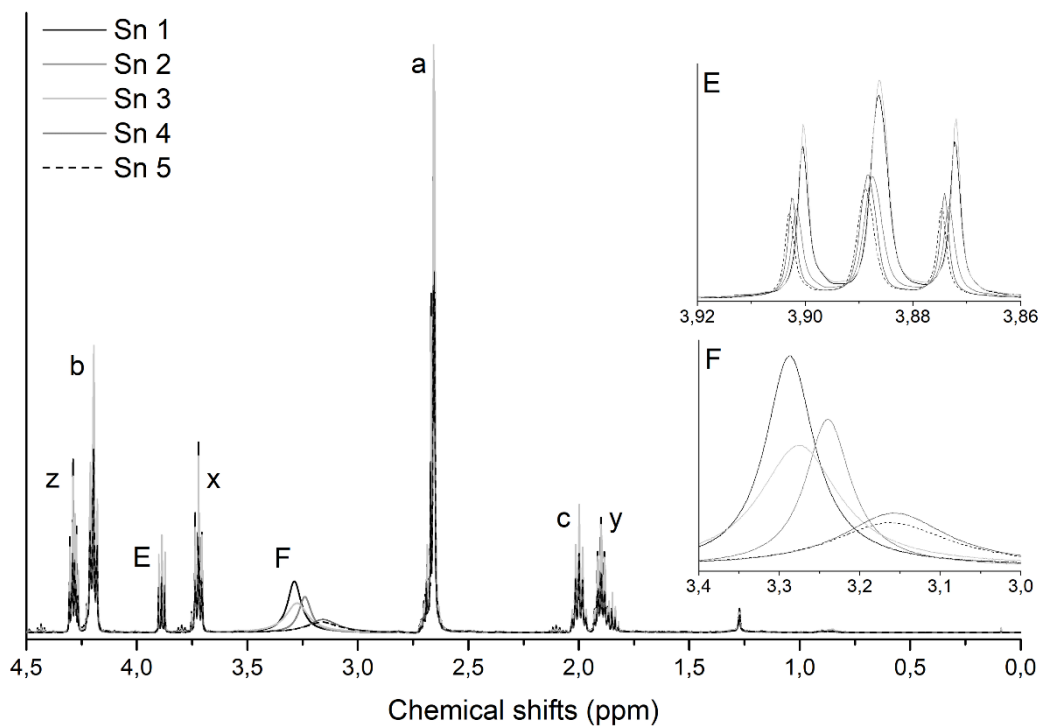
PPS 160/180	25,1	4046
PPS 160/190	19,3	3123
PPS 160/200	20,0	3243

442

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

447 Based on the above-mentioned assumptions, <sup>1</sup>H NMR measurements allow determining  
 448 estimated reaction progress over time. Therefore, the sample PPS 140/160 was submitted for this  
 449 analysis. Figure 8 and Figure 9 present <sup>1</sup>H NMR spectra prepared for PPS 140/160 during synthesis  
 450 over reaction time. Figure 8 shows <sup>1</sup>H NMR spectra for different samples, which were taken from the  
 451 reaction mixture during the first step of the synthesis. Characteristic peaks named 'x', 'y' and 'z' (Figure  
 452 7, 8 and 9) during the first step of the polycondensation revealed higher intensity than resulted polyols.  
 453 These peaks are characterized by the hydroxyl-terminated end groups of the macromolecules. It is  
 454 related to the macromolecular structure development over reaction time, which leads to the higher  
 455 amount of macromolecules characterized by higher average molecular weight. Furthermore, the results  
 456 indicate the appearance of the two new peaks 'E' and 'F', which were not detected on the <sup>1</sup>H NMR  
 457 spectra of the synthesized polyol PPS 140/160 (Figure 7). The intensity of these peaks decrease with  
 458 reaction time and after catalyst addition to the reaction mixture, they are disappeared (Figure 9). The  
 459 extensive and profound research allow determining the probable chemical compound from which these  
 460 two peaks are visible. This chemical is a 1,3-propylene glycol, with the chemical structure: HO-CH<sub>2</sub>-CH<sub>2</sub>-  
 461 CH<sub>2</sub>-OH. Peak named 'E' is related with a triple peak corresponding to methylene protons which are  
 462 adjoined to hydroxyl groups: HO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OH. The characteristic intensive single peak named 'F'  
 463 is attributed to protons derived from hydroxyl groups: HO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OH. The last peaks  
 464 corresponding to the multiple peaks related to methylene protons from propylene glycol: HO-CH<sub>2</sub>-CH<sub>2</sub>-  
 465 CH<sub>2</sub>-OH overlap with some of those derived from hydroxyl-terminated macromolecules (the peak named  
 466 'y'). These two peaks, 'E' and 'F', identify the presence of the unreacted glycol, which amounts decrease  
 467 with the time of the synthesis. The prepared investigation confirmed also the autocatalytic character of  
 468 the succinic acid during synthesis due to the absence of peaks related with the free hydroxyl groups

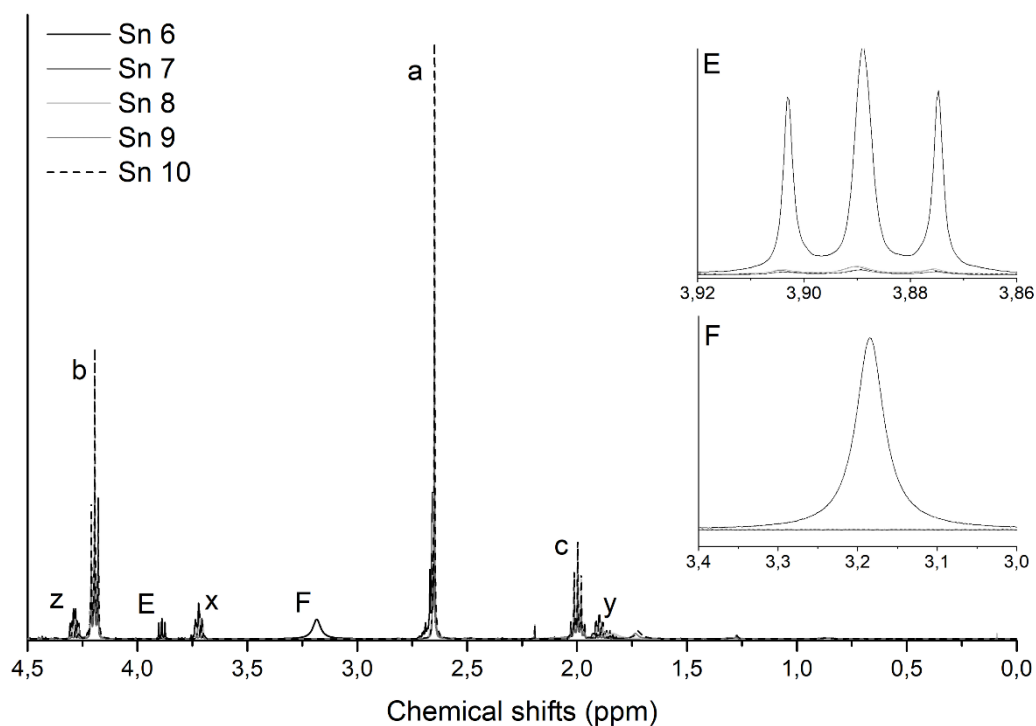
469 from carboxylic groups, which chemical shift should be visible from 10 to 12 ppm. This observation  
470 suggests that firstly in the reaction mixture reacts molecules of the succinic acid. One molecule of the  
471 succinic acid bonding with two molecules of 1,3-propylene glycol. Due to the excess of the used glycol,  
472 the peaks 'E' and 'F' are visible during the first step of the polycondensation and disappeared during the  
473 second step, after the catalyst employment.



474

475 Figure 8  $^1\text{H}$  NMR spectra of PPS 140/160 during the first step of the synthesis.





476

477 Figure 9  $^1\text{H}$  NMR spectra of PPS 140/160 during the second step of the synthesis.

478

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

488 Table 5 Polymerization degree with average molecular weight determination over reaction time for PPS  
 489 140/160.

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

490

491 3.5. Gel Permeation Chromatography (GPC)

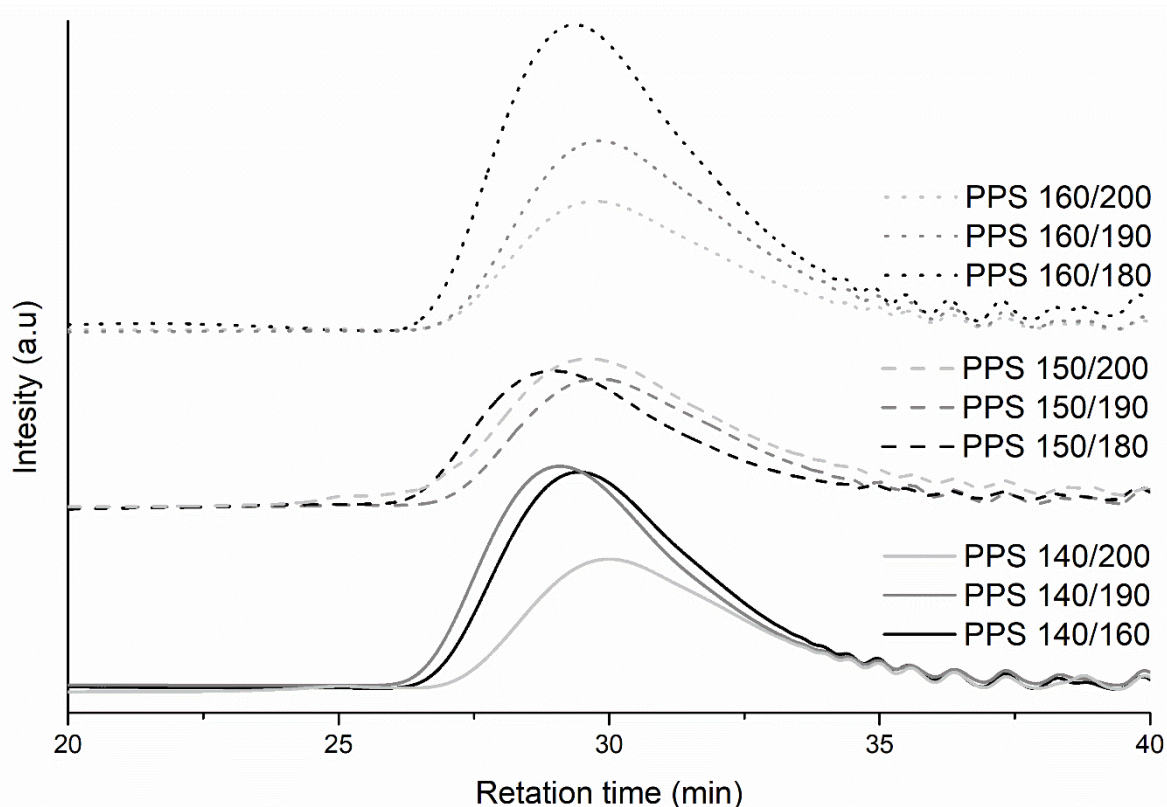
492 One of the most important information about polyol macromolecular structure, besides the  
 493 average molecular weight, indicates polydispersity, PD. For the PD characterization, the Gel Permeation  
 494 Chromatography of the synthesized bio-based polyester polyols was carried out. This feature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

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

BIO-BASED POLYESTER POLYOL	Max. retention 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

500 PD – polydispersity

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



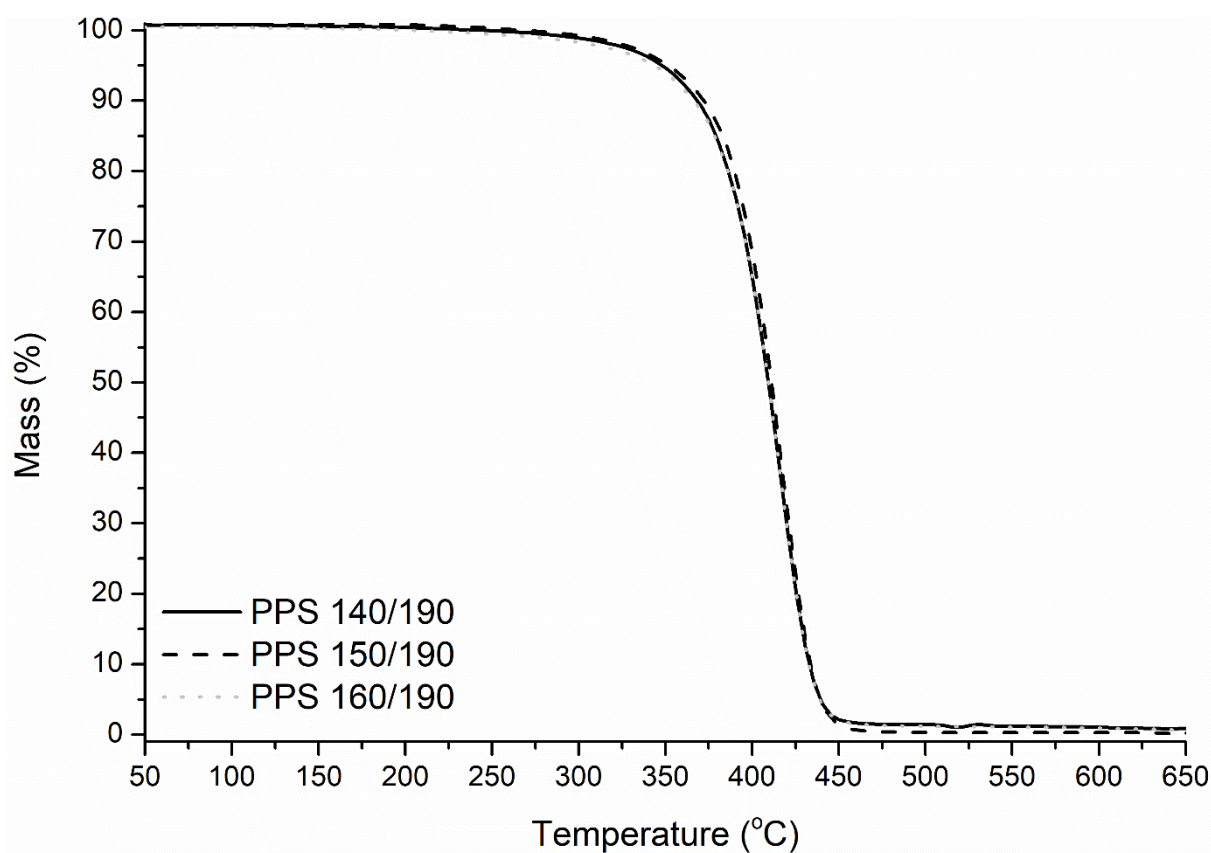
512  
513 Figure 10 The GPC spectra of the synthesized bio-based polyester polyols.

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

517

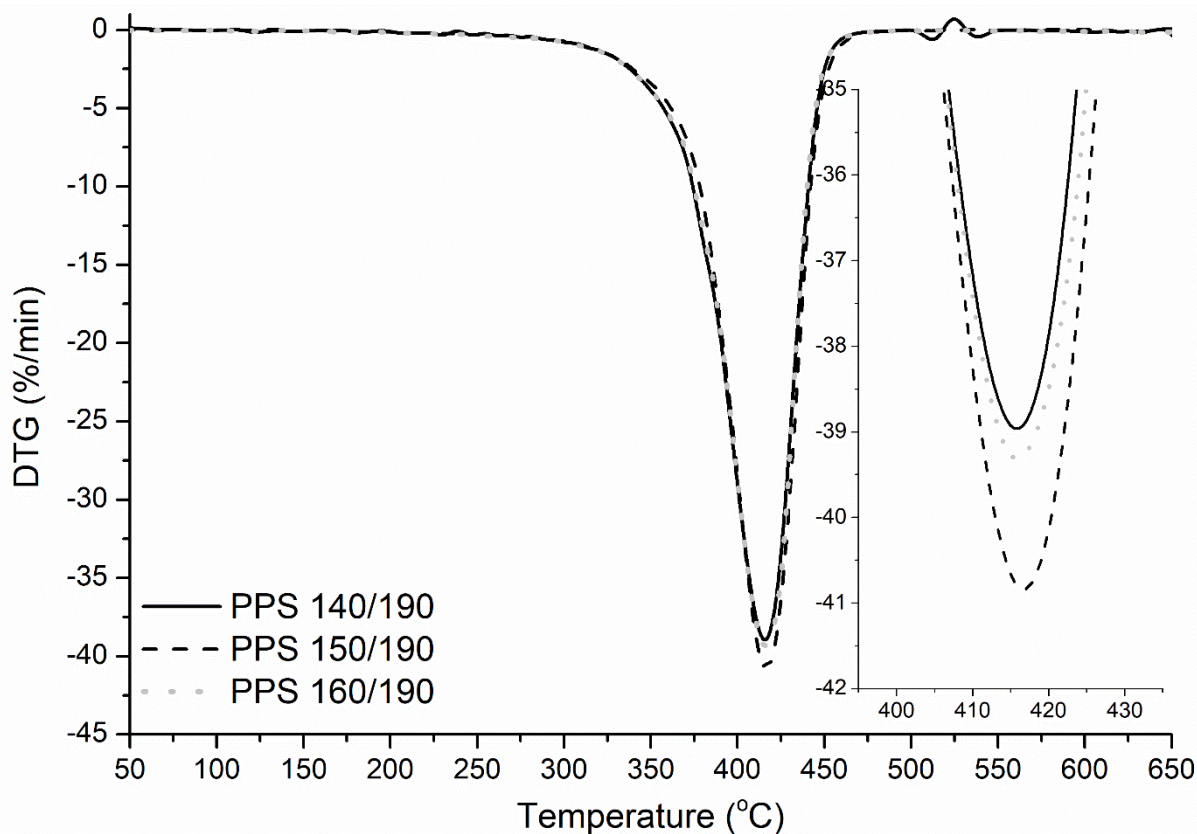
518 3.6. Thermogravimetric analysis (TGA)

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



526

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



528

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

530 4. Conclusions

531 The main aim of this work was to precisely and profoundly determined and described the kinetics  
 532 characteristic of the two-step polycondensation reaction between fully bio-based monomers. The series  
 533 of bio-based poly(propylene succinate)s were synthesized under different temperature conditions which  
 534 allowed calculate the reaction rate constants and energy activation. The conducted investigation  
 535 confirmed the impact of the temperature conditions on the reaction rate constants for both steps of the  
 536 reaction. Based on the results the energy activation for the first step of the reaction was calculated and  
 537 equaled ca. 38.5 kJ/mol, which is the slightly lower value with the energy activation of the polyols  
 538 synthesis based on the petrochemical monomers (ca. 50 kJ/mol). Nevertheless, the uncertain  
 539 repeatability of the second step precludes the energy activation determination for the second step of the  
 540 synthesis. Based on the FTIR and  $^1\text{H}$  NMR spectra for samples collected for investigation over the  
 541 synthesis time, the profound research about macromolecular structure development during both steps  
 542 of the synthesis was precisely described. In this work, the approximate average molecular weight of the  
 543 formed during synthesis macromolecules over time were calculated. The results confirmed low  
 544 polymerization degree values during the first step of the reaction, in the range from 1.7 to 2.4, and

545 increasing value of polymerization degree after polycondensation catalyst employment (second step)  
546 from 2.4 to 25.7, which allowed obtaining polyester polyols with an average molecular weight  
547 approximately 3000 g/mol. The GPC measurements allowed obtaining the polydispersity of the samples.  
548 The lowest values revealed samples PPS 150/190 and PPS 160/200, with equaled 1.587 and 1.616,  
549 respectively. The results of the TGA analysis confirmed the high thermal stability of the prepared bio-  
550 based polyester polyols which equaled ca. 418°C. This value is comparable to the thermal stability of  
551 commercially used petrochemical polyester polyols.

552

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- 622 Caption of Figures
- 623 Figure 1 Scheme of the possible reactions during two-step polycondensation between succinic acid and
- 624 1,3-propanediol.
- 625 Figure 2 Effect of various temperatures on the yield of the first step.
- 626 Figure 3 Effect of various temperatures on the yield of the second step after the first step conducted at
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- 628 Figure 4 Arrhenius plot of the esterification reaction.
- 629 Figure 5 FTIR spectra of PPS 140/160.
- 630 Figure 6 Peaks intensity changes monitored during synthesis at wavenumber range from: a) 3800 to
- 631 2500  $\text{cm}^{-1}$ , b) 1780 to 1640  $\text{cm}^{-1}$ , c) 1300 to 1000  $\text{cm}^{-1}$ .
- 632 Figure 7  $^1\text{H}$  NMR spectrum of PPS 140/160.
- 633 Figure 8  $^1\text{H}$  NMR spectra of PPS 140/160 during the first step of the synthesis.
- 634 Figure 9  $^1\text{H}$  NMR spectra of PPS 140/160 during the second step of the synthesis.
- 635 Figure 10 The GPC spectra of the synthesized bio-based polyester polyols.
- 636 Figure 11 The TGA curves of the PPS 140/190, PPS 150/190 and PPS 160/190 polyols.
- 637 Figure 12 The DTG curves of the PPS 140/190, PPS 150/190 and PPS 160/190 polyols.

- 638 Caption of Tables
- 639 Table 1 Preparation and properties of the obtained bio-based polyester polyols.
- 640 Table 2 Components used during the synthesis and the semi-product and product of the synthesis.
- 641 Table 3 Kinetics characteristic of the esterification and polycondensation reactions.
- 642 Table 4 Degree of polymerization and average molecular weight of the synthesized polyester polyols
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- 644 Table 5 Polymerization degree with average molecular weight determination over reaction time for PPS
- 645 140/160.
- 646 Table 6 GPC results of the synthesized bio-based polyester polyols.