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; ^{1}H NMR; GPC;

24   Thermal stability

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_2 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 alipharomatic 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_3 and C_5 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_2 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 (I 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,   ^{1}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^{3}. 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^{3}.

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)$_4$ (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$_2$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 Mn

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^3 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^3) 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^3 of the acetic anhydride solution. The solution

146 was refluxed for 30 minutes. Subsequently, 1 cm^3 of pyridine was added and heating for 10 minutes.

147 After that, 50 cm^3 of distilled water was added, the mixture was cool to room temperature and titrated

5

148 with the use of a standard solution of potassium hydroxide KOH in distilled water (0.5 mol/dm^3) and

149 phenolphthalein as indicator.

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^{-1}, 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^{-1} or pumping 10 – 300 s^{-1} [11,12].

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^{-1} were taken with the resolution 4 cm^{-1}. 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.

2.3.5. Nuclear Magnetic Resonance (^{1}H NMR)

166 Proton nuclear magnetic resonance (^{1}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 ^{1}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$_3$ solvent at ambient temperature. The simulation and iteration of spectra were carried

172 out using Bruker software.

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 µm 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 µm pore

182   size. Number-average molecular weight, Mn, weight- average molecular weight, Mw 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 [°C]		REACTION TIME [h]		ACID NUMBER [mg KOH/g]	HYDROXYL NUMBER [mg KOH/g]	VISCOSITY [80°C; Pas]
	I step	II step	I step	II step			
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

3.2. Kinetics study

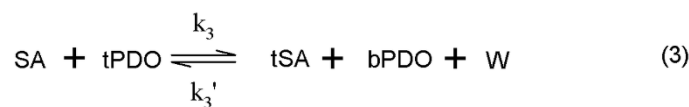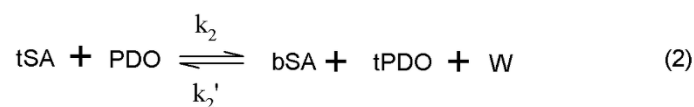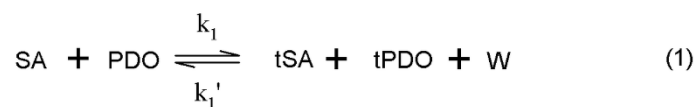#### 3.2.1. Approach and reactions

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.

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	$HOOC-CH_2-CH_2-COOH$
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	$\sim CH_2-COOH$

9

$$SA + PDO \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} tSA + tPDO + W \qquad (1)$$

$$tSA + PDO \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} bSA + tPDO + W \qquad (2)$$

$$SA + tPDO \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} tSA + bPDO + W \qquad (3)$$

$$tSA + tPDO \underset{k_4'}{\overset{k_4}{\rightleftharpoons}} bSA + bPDO + W \qquad (4)$$

$$tPDO + tPDO \underset{k_5'}{\overset{k_5}{\rightleftharpoons}} bPDO + PDO \qquad (5)$$

$$tPDO + tPDO \overset{k_6}{\longrightarrow} dPDO + W \qquad (6)$$

$$2\ oPPS \underset{k_7'}{\overset{k_7}{\rightleftharpoons}} pPPS + PDO \qquad (7)$$

$$oPPS + cPPS \underset{k_8'}{\overset{k_8}{\rightleftharpoons}} pPPS + W \qquad (8)$$
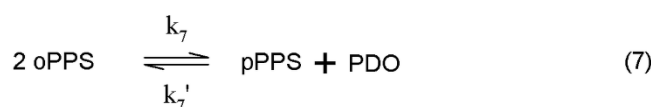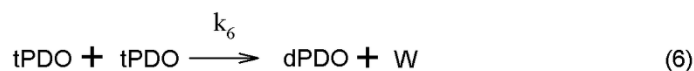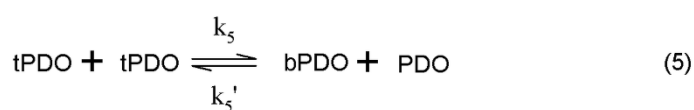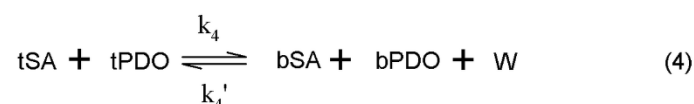
222

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 kj (j=1, 8) and kj'

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

10

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

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

270   Where:

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

272    $S_{1,2,...,n}$ – means how much dicarboxylic acid molecules are bonded after approximate reaction time t_1,

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

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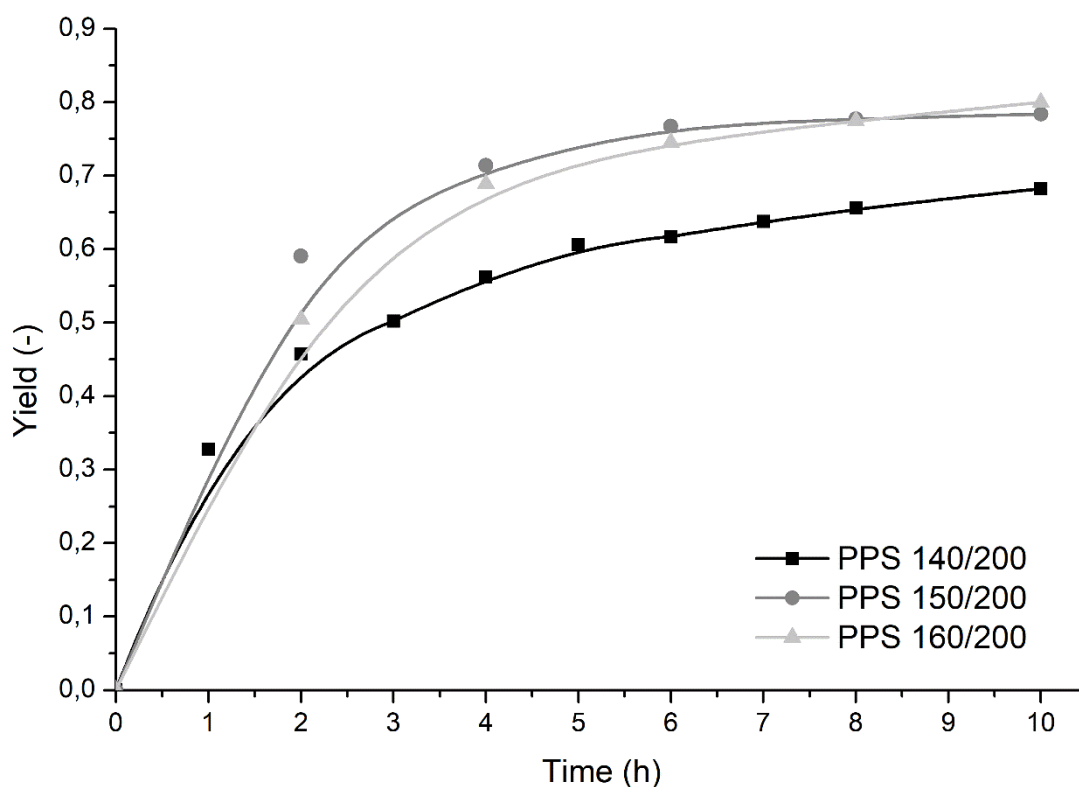

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279   Figure 2 Effect of various temperatures on the yield of the first step.

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
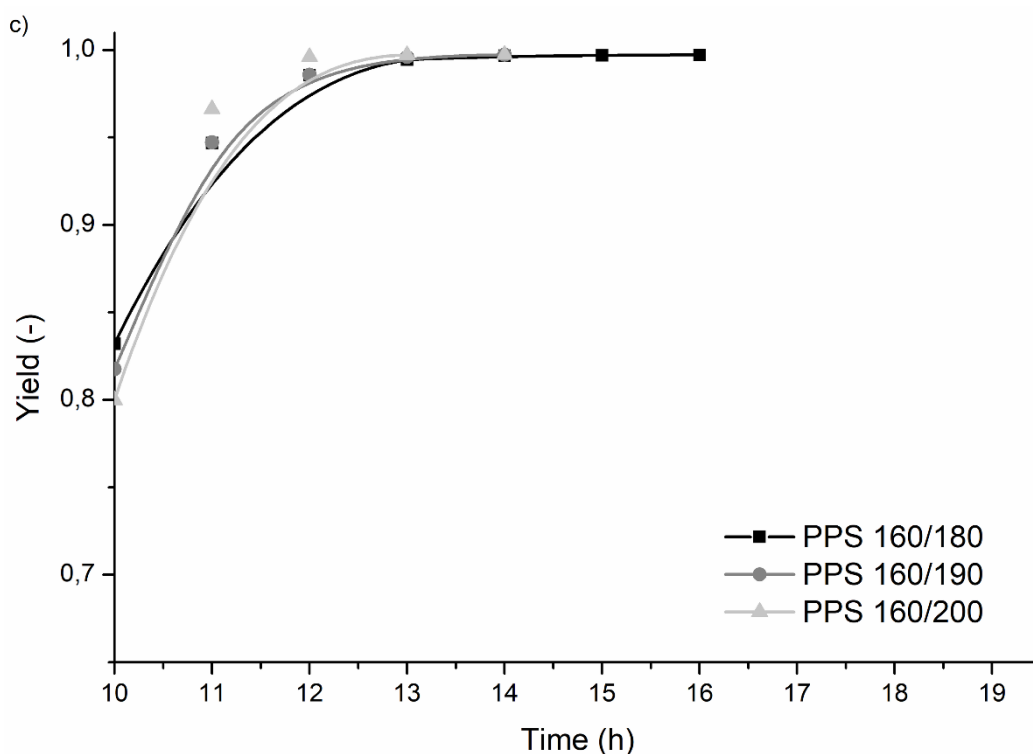
283　higher yield of the reaction. The lowest value characterized samples prepared at 140°C, when polyols

284　synthesized at higher temperatures disclosed similar yield ca. 0.8.

a)

285

b)

286

13

c)
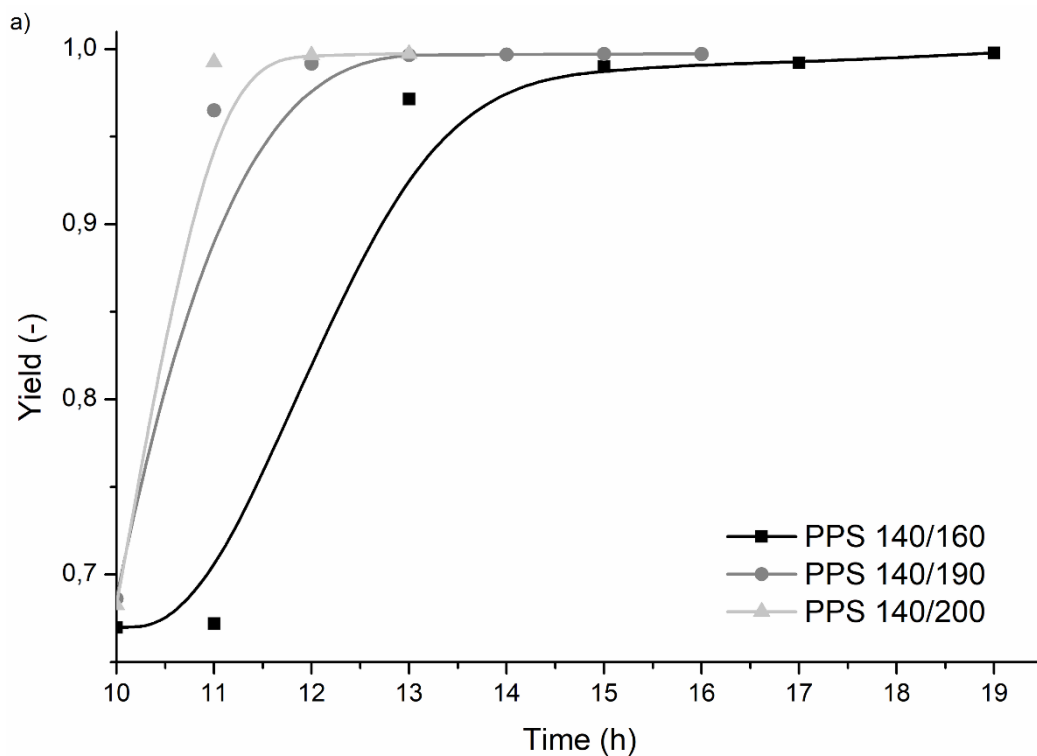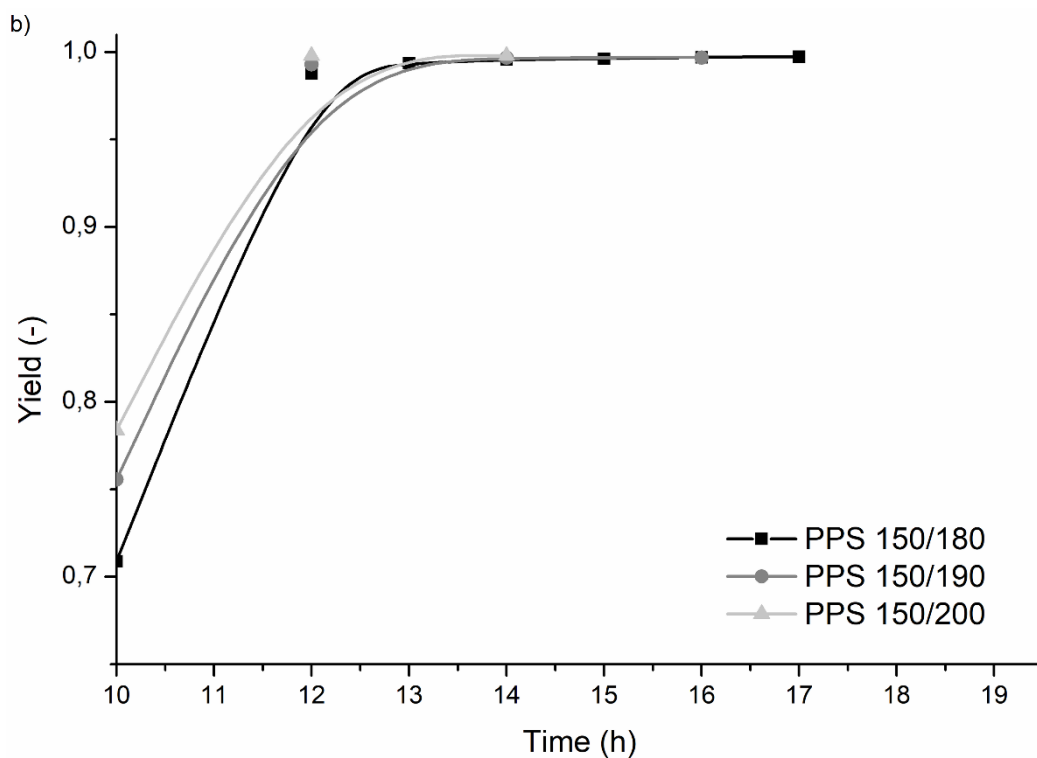
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288   Figure 3 Effect of various temperatures on the yield of the second step after the first step conducted at

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 (Ti(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

14

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

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

314    $f(t) = (1-Y_{1,2,...,n})^{-2}$ (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}H NMR spectra (please, see Chapter 3.4 Nuclear Magnetic Resonance

325   (^{1}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}H NMR results.
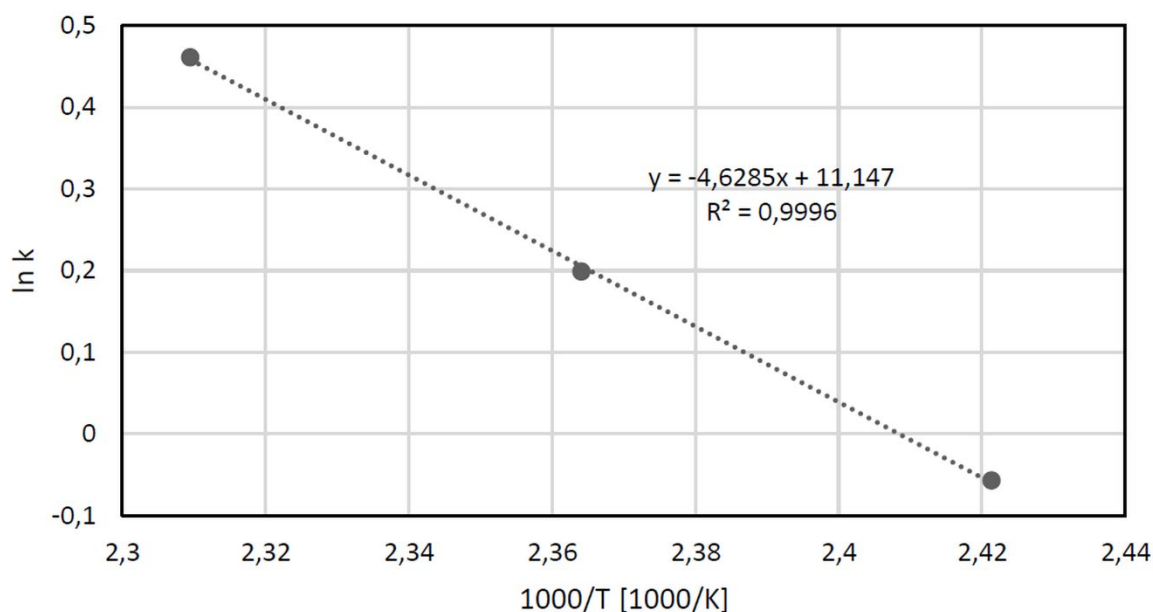
329

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

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.

POLYOL	REACTION YIELD	MATH EQUATION OF THE REACTION ORDER, 'y=ax+b'		REACTION RATE CONSTANT, 'k' [kg/(mol*h)]			CORRELATION COEFFICIENT, R^2	
	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

17

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.
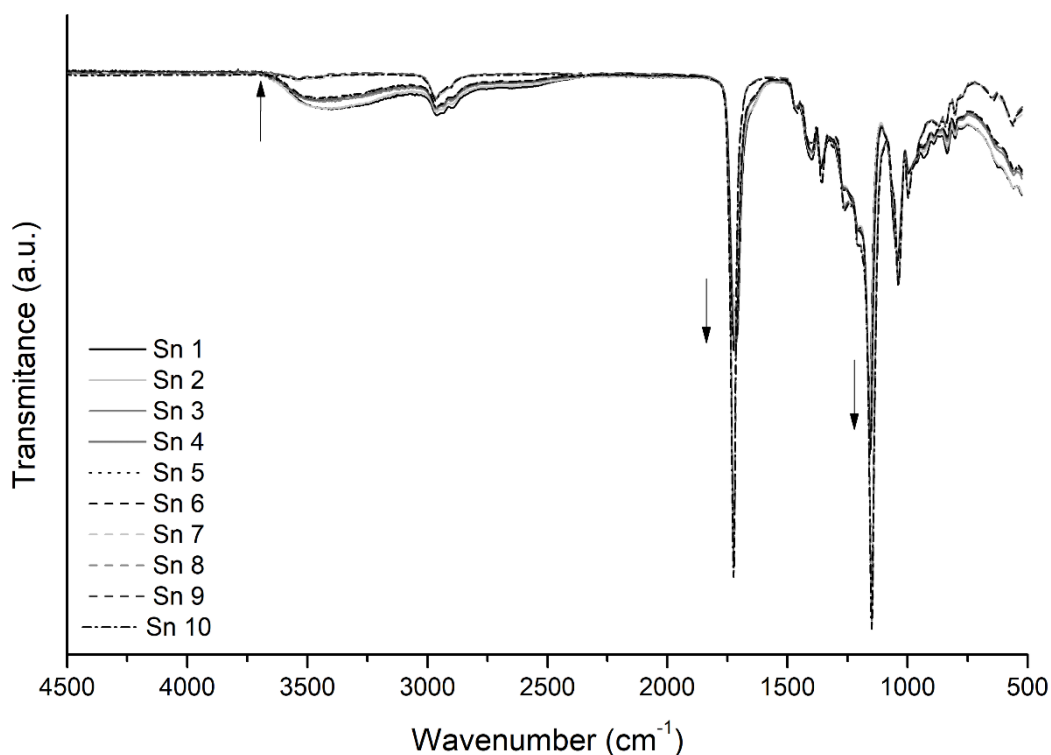
379

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

18

384   3700 and 2500 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 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 cm^{-1}. The peaks at 3000-2850 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 cm^{-1} and 1150 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 cm^{-1} decreases with the

395   increasing reaction time. In the same time, the intensity of peaks at 1725 cm^{-1} and 1150 cm^{-1} increases,

396   what confirms increasing concentration of the ester groups of the reaction mixture.


397

b)

c)
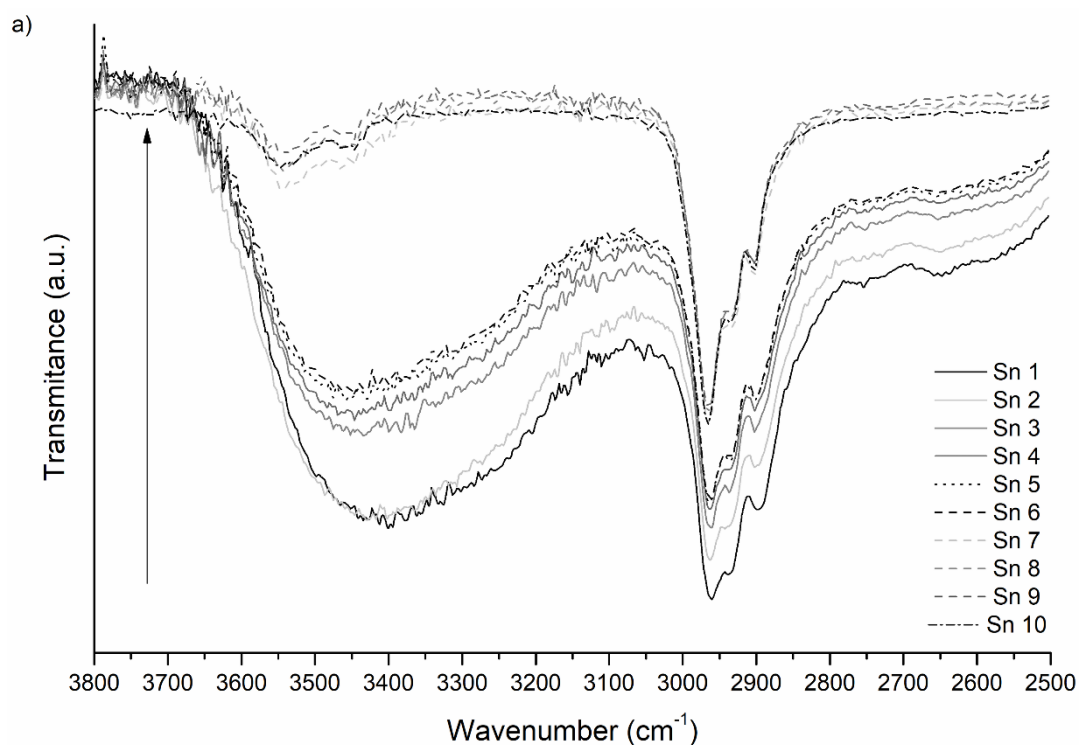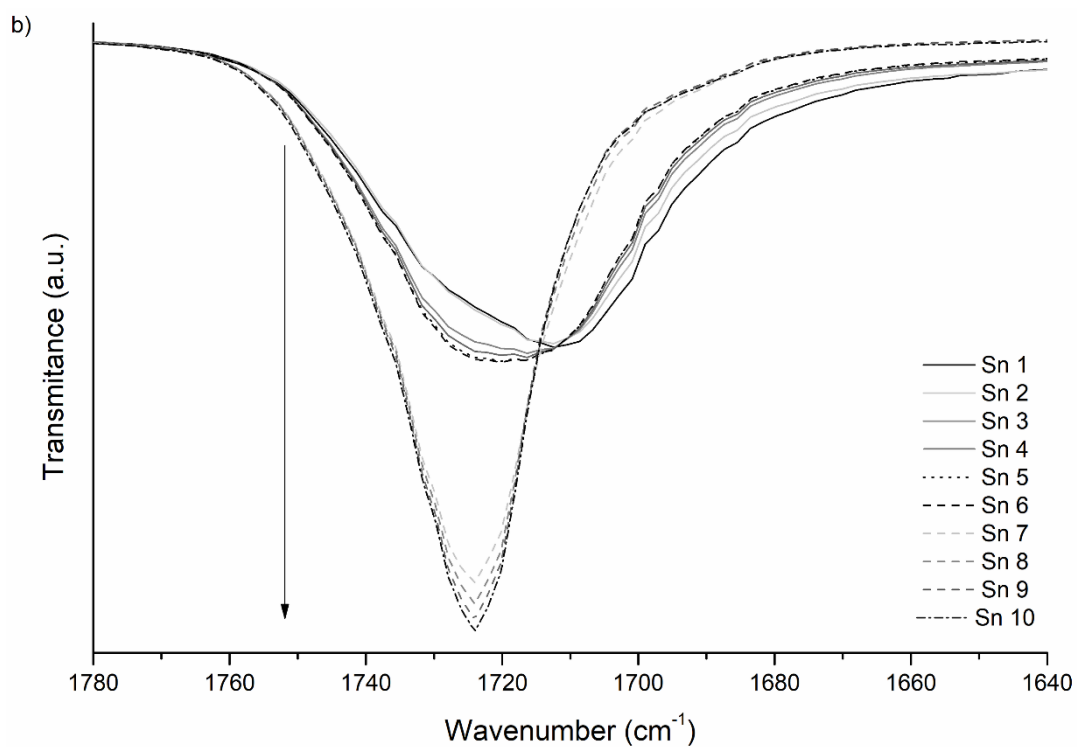
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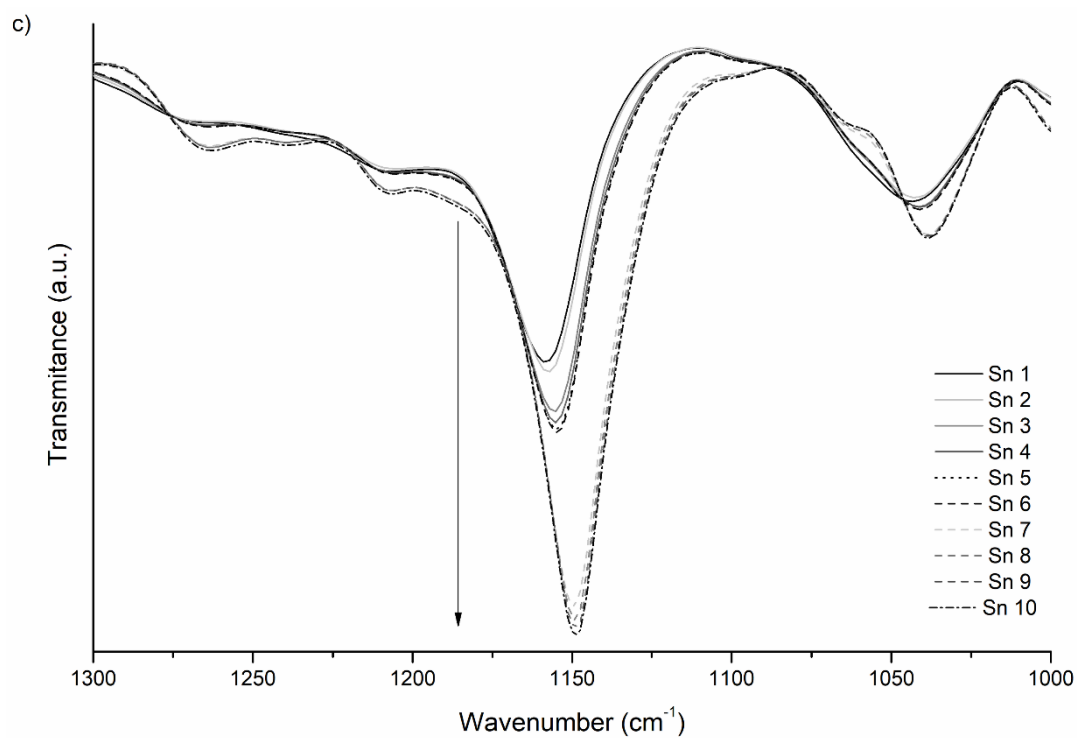
399

400 Figure 6 Peaks intensity changes monitored during synthesis at wavenumber range from a) 3800 to

401 2500 cm^{-1}, b) 1780 to 1640 cm^{-1}, c) 1300 to 1000 cm^{-1}.

402

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

404   The various peaks on ^{1}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}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.
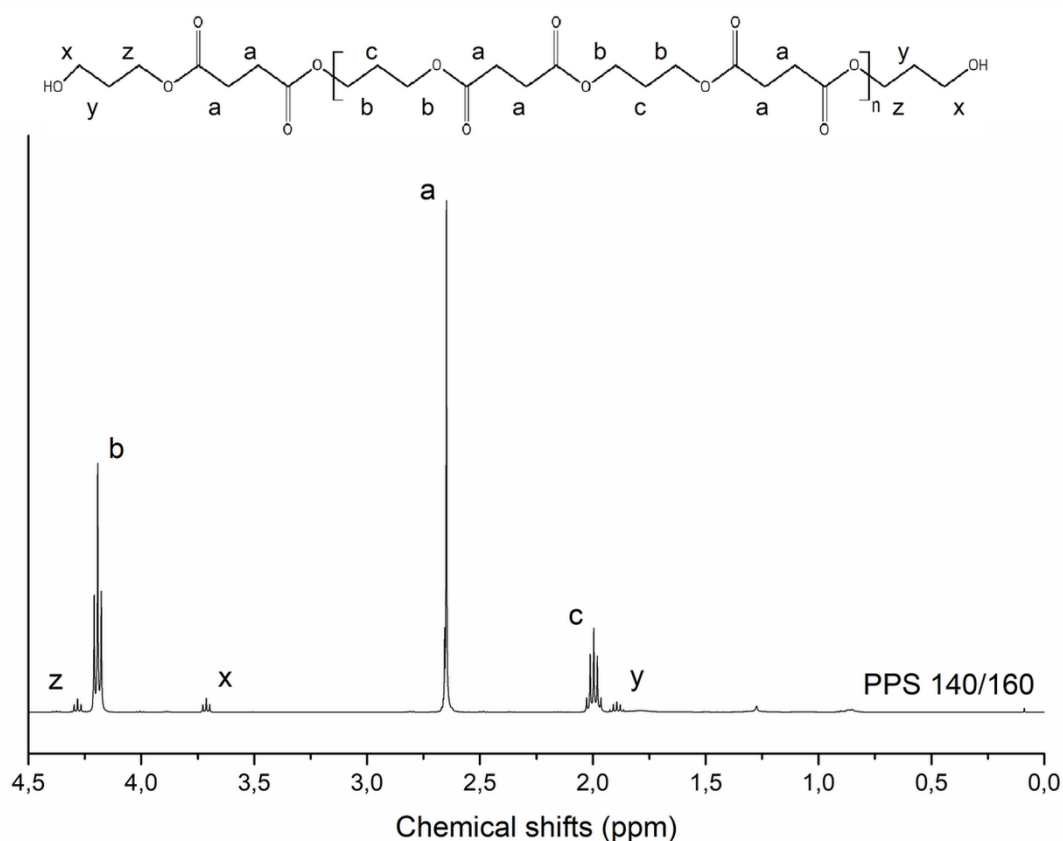
417

418   Figure 7 ^{1}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    $(b + z) \sim (n\ 4H_{from\ repeating\ units} + 4H_{chain\ end})$ (6)

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

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

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

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

432    $n = b/z$ (9)

433   The obtained polymerization degree from the ^{1}H NMR spectroscopy results allow to determine

434   the molecular weight of the analyzed polyols from the equation 10 [20]:

435    $M_n = n(M_n\ of\ the\ repeating\ unit) + M_n\ of\ the\ chain\ ends$ (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}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: $HO\text{-}C\underline{H_2}\text{-}CH_2\text{-}C\underline{H_2}\text{-}OH$. The characteristic intensive single peak named 'F' is attributed to protons derived from hydroxyl groups: $\underline{H}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\underline{H}$. The last peaks corresponding to the multiple peaks related to methylene protons from propylene glycol: $HO\text{-}CH_2\text{-}C\underline{H_2}\text{-}CH_2\text{-}OH$ 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

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.
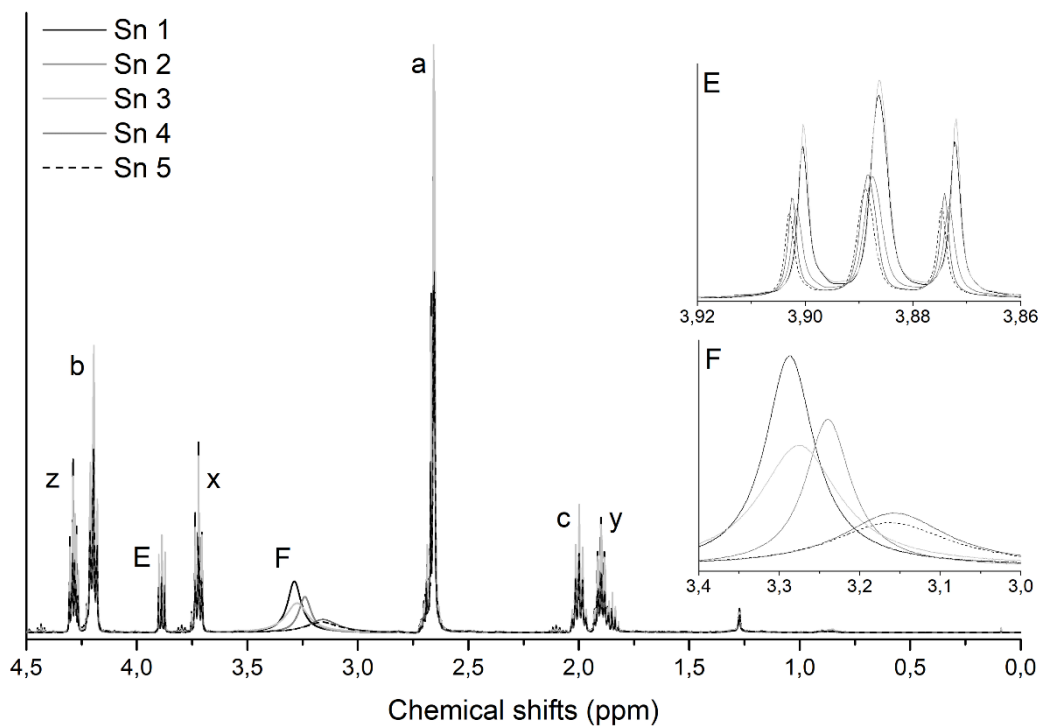
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475   Figure 8 ^{1}H NMR spectra of PPS 140/160 during the first step of the synthesis.
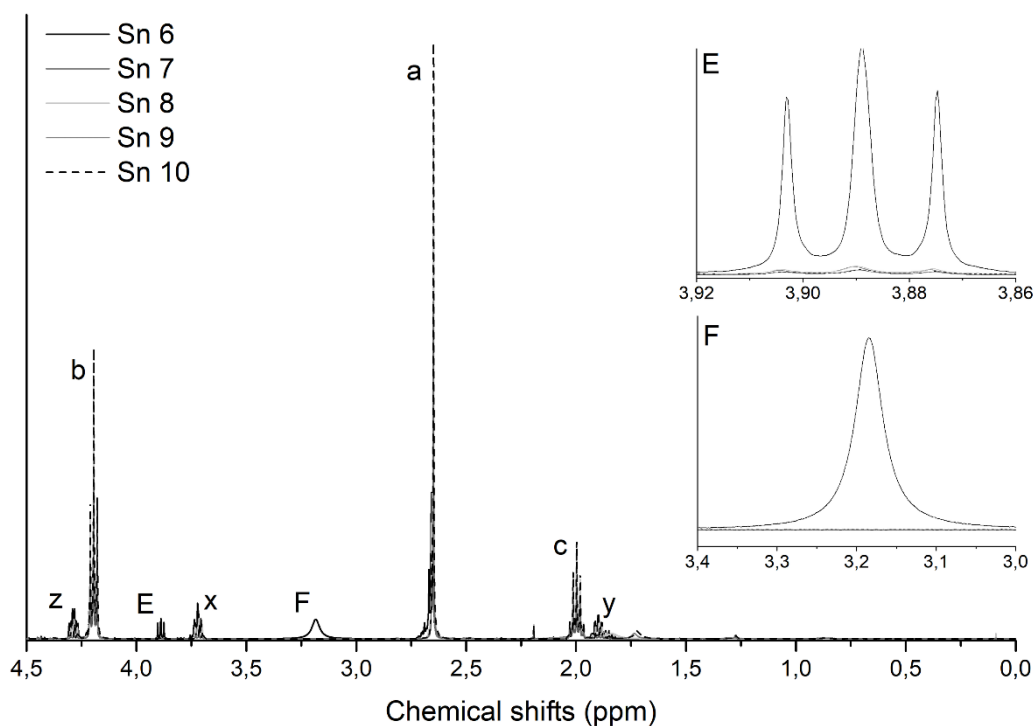
476

477   Figure 9 ^{1}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 [-]	M_n [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. 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

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.
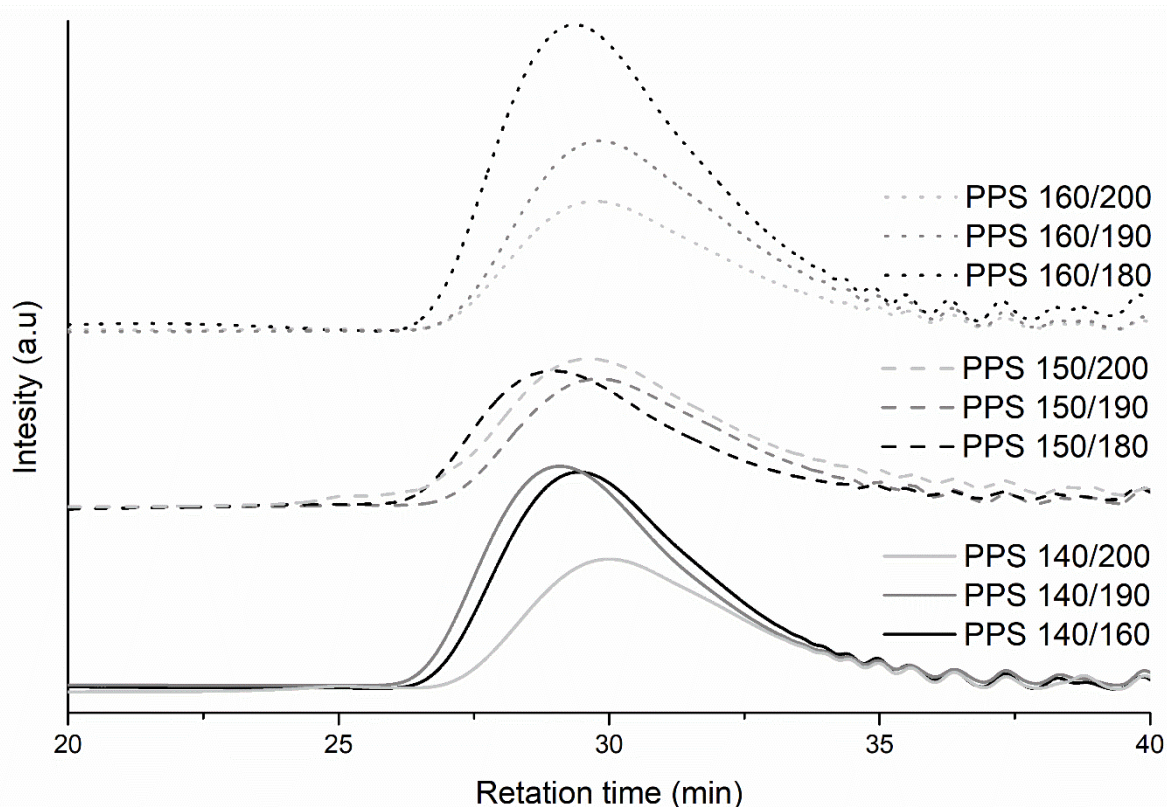
512

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}H NMR and GPC (M_w).

517

27

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.
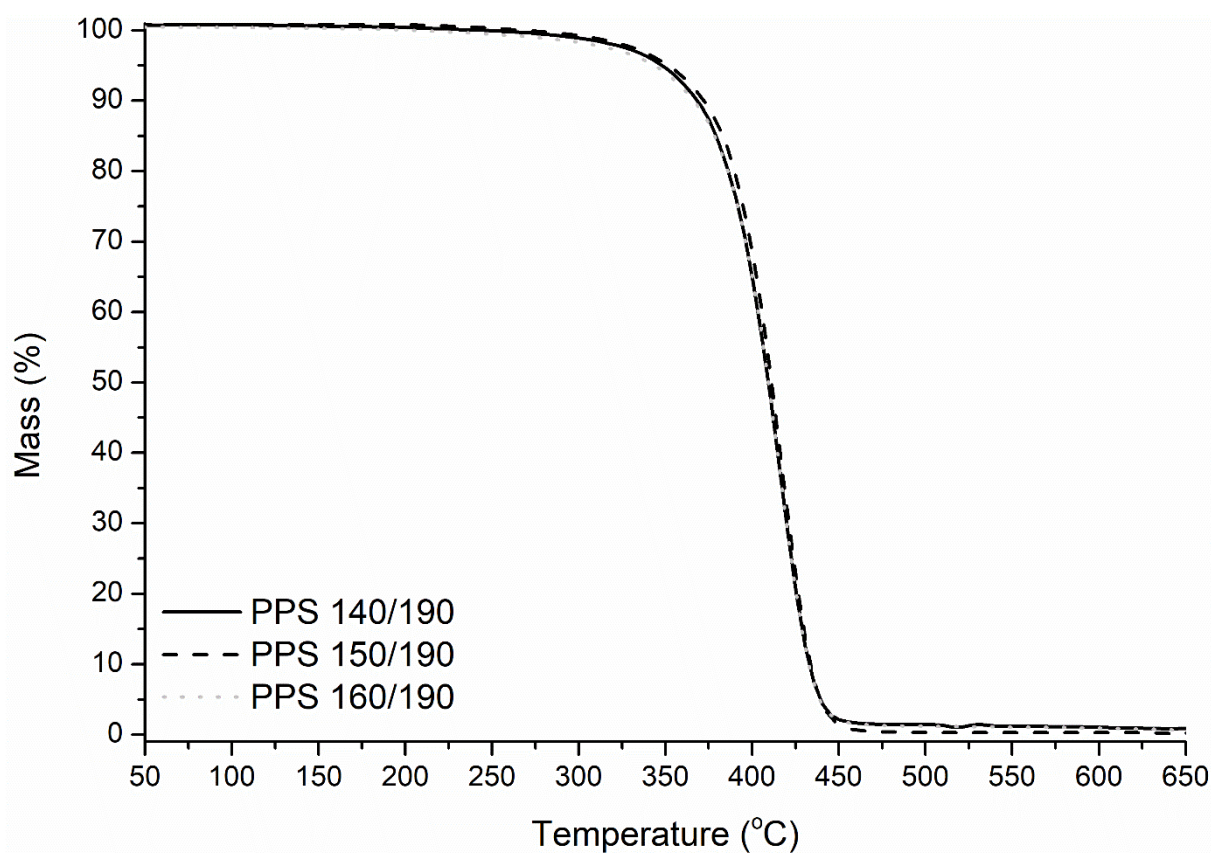
526

527   Figure 11 The TGA curves of the PPS 140/190, PPS 150/190 and PPS 160/190 polyols.
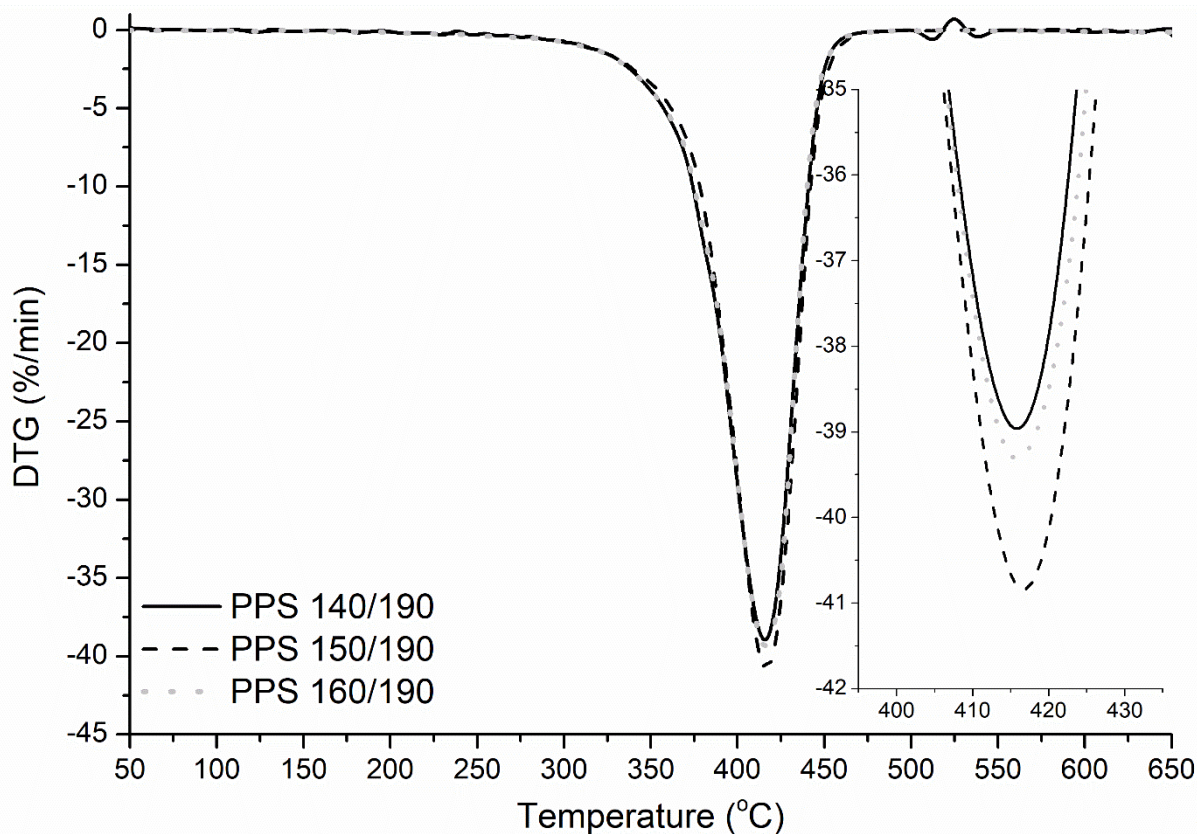
Figure 12 The DTG curves of the PPS 140/190, PPS 150/190 and PPS 160/190 polyols.

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

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

553 Funding

556

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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 cm^{-1}, b) 1780 to 1640 cm^{-1}, c) 1300 to 1000 cm^{-1}.

632   Figure 7 ^{1}H NMR spectrum of PPS 140/160.

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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.

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638   Caption of Tables

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

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645   140/160.

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