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Influence of chemical structure on physicochemical properties and thermal decomposition of the fully bio-based poly(propylene succinate-co-butylene succinate)s

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ABSTRACT

In this work, two polyesters and four copolyesters were studied. All materials were synthesized to obtain the monomers dedicated for thermoplastic polyurethane elastomers. For this type of PUR, the monomers should characterize by appropriate selected physicochemical properties and macromolecular structure distribution, which depends on synthesis conditions. The study of chemical structure with extensive and knowledgeable analysis of formed macromolecules of synthesized bio-based copolyesters was conducted with the use of FTIR and ^{1}H NMR spectroscopy and MALDI-ToF mass spectrometry. The results allowed to propose the majority of probable chemical structures of macromolecules formed during synthesis. Moreover, the impact of the structure on the thermal stability of the obtained copolyesters was also determined with the use of thermogravimetric analysis. The temperature of the beginning of thermal decomposition equaled even 330 °C. Furthermore, the results of DSC-TG/QMS coupled method confirmed that all prepared polyesters degraded by α and β-hydrogen bond scission mechanisms.

1. Introduction

One from the most developing materials, which have a huge impact on everyday life, are polyurethanes. Due to their broad spectrum of properties they provide for quality of toys, furniture, containers, clothes, but also have importance in medicine and automotive industry. Recently, there are available chemical compounds derived from renewable resources which allowed to synthesize green polyurethane materials [1].

Polyols constitute one of the most important components in the polyurethane synthesis. Polyester polyols constitute 18 mas.% of all produced polyols for polyurethanes [2]. Polyurethane materials based on polyester polyols are usually characterized by higher mechanical, thermal and organic solvent resistance compared to polyether polyol-based PUs. Moreover, poly (ester-urethane)s are lower resistance on hydrolysis, so they are more liable on biodegradation in comparison with polyether polyol-based PUs [3]. The chemical structure of polyol determined the morphology, mechanical and thermal properties of PUs. The highest impact on above-mentioned properties, the polyol chemical structure exert in the case of thermoplastic polyurethane elastomers TPU. Moreover, the molecular mass distribution influences the industrial processes of TPU production. It is difficult to obtain a product of step-by-step polymerization method which will be characterized by designed chemical composition and narrow polydispersity [4]. Therefore, it is important to analyze the chemical structure of monomers before industrial processes. Moreover, one from the most responsive to the macromolecular structure are thermal transition temperatures and thermal stability of both, pure polyols and prepared polyurethanes. It was verified that the increasing molecular weight of polyol leads to the polyurethanes with enhanced mechanical properties and thermal stability [5]. Moreover, with increasing molecular weight polyols characterized by the increasing melting point and decreasing glass transition temperatures [6].

Sobkowicz et al. [7] investigated thermal and mechanical properties of poly (butylene succinate-co-hexamethylene succinate) copolyesters prepared with using a various molar ratio of the used glycols. All prepared materials characterized the average molecular weight in the range from 36 000 to 53 000 g/mol with polydispersity between 1.1 and 1.5. The results of the thermal analysis indicate that with increasing 1,6-hexanediol glycol content at the copolyesters macromolecular structure the increase at the thermal decomposition temperature was visible. The melting temperature for all prepared copolyesters decreased with

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increasing HDO content at the macromolecular structure. After exceeding the value of molar ratio BDO: HDO at 5:5, the melting temperature increases with growing HDO content. Mechanical properties measurements verified that the highest values of tensile strength, yield stress, and Young's modulus characterized poly (propylene succinate) and with an increasing amount of 1,6-hexanediol at the copolyesters, the value of this parameters decreases.

Papageorgiou and co-workers [8] investigated poly (butylene furanoate), poly (butylene succinate) and poly (butylene succinate-co-furanoate) which were characterized by number average molecular weight at 12 700 g/mol for PBSF and 15 200 g/mol for PBS with polydispersity 2.12 and 2.03, respectively. Authors didn't quote the value of Mn for PBF polyester. They confirmed the values of glass transition temperatures at −36 °C and 34 °C for PBS and PBF, respectively. The use of carboxylic acids mixture allowed obtaining copolyester PBSF characterized by Tg at −29 °C. Moreover, PBF polyester revealed crystallization temperature at 91 °C, when copolyester PBSF at 9 °C, which made it more favorable to use during industrial processes. PBSF copolyester featured also lower melting temperature than PBS and PBF polyesters, ca. 100, 110 and 170 °C, respectively. Authors investigated also thermal stability of all polyesters. The results indicate that the lower value of the temperature of the beginning of thermal decomposition characterized polyester PBF (325 °C) when the highest – PBS (353 °C). Copolyester PBSF revealed this temperature at 331 °C.

Loos et al. [9] investigated bio-based polyesters synthesized with the use of 2,5-bis(hydroxymethyl)furan and diacids ethyl esters of such acids as succinic, glutaric, adipic, suberic, sebacic and dodecanedioic. The results of average molecular weight measurements indicate that all polyesters characterized by Mn at ca. 2000 g/mol. Moreover, authors confirmed that with an increasing amount of methylene units in the dicarboxylic segments, increases the degree of crystallinity of polyesters. Moreover, with an increasing amount of methylene units in the dicarboxylic segments, synthesized polyesters characterized by higher values of thermal stability and melting points, which ranged from 253 to 300 °C, and from 55 to 86 °C, respectively.

In this work, six linear bio-based polyols dedicated for thermoplastic polyurethane elastomers were synthesized. Two polyesters and four copolyesters were produced with the use of succinic acid, 1,3-propanediol, and 1,4-butanediol, all with a natural origin. Due to the requirements concerning polyester polyols for thermoplastic polyurethane elastomers, the prepared bio-based polyester polyols have to be characterized by the low value of an acid number and hydroxyl number, an average molecular weight in the range from 1000 to 4000 g/mol, functionality equaled 2, and low water content. The chemical structure was analysis by FTIR and ^{1}H NMR spectroscopy. The resulted spectra confirmed the occurrence of ester groups at the macromolecular structure and shown differences in the chemical structure between polyesters and copolyesters. Moreover, the majority of probable chemical structures of macromolecules formed during synthesis were proposed based on the results of MALDI-ToF MS measurements. Thermal stability of synthesized bio-based polyester and copolyester polyols were investigated for studying the impact of the chemical structure on the thermal degradation temperature. Furthermore, the thermal decomposition mechanisms were determined with the use of DSC-TG/QMS coupled method.

2. Materials and methods

2.1. Materials

The main components used in this study constituted dicarboxylic acid which was succinic acid (SA), and two glycols: 1,3-propanediol (PDO) and 1,4-butanediol (BDO). All from the mentioned substrates were the natural origin. Succinic acid – Biosuccinium, was kindly supplied by Reverdia (Netherlands). SA characterized as a white powder with purity in the range 98–100% and the molecular weight at 118.09 g/mol. PDO – Susterra Propanediol, was obtained from DuPont Tate&Lyle Corporation Bio Products (Loudon, Tennessee, USA). This liquid component characterized purity ca. 99.98% and the molecular weight at 76.09 g/mol. BDO was kindly provided by BASF (Germany) as a liquid with the purity above 99,50%. Tetra-n-butyl titanate, $Ti(O\text{-}n\text{-}Bt)_4$ (TnBT) was used as a polycondensation catalyst and it was purchased from TCI Chemicals (India) as a liquid with the purity ca. 97% and the molecular weight at 284.22 g/mol. Other materials and solvents were used of the analytical grade for the analytical measurement methods.

2.2. Poly(propylene succinate-co-butylene succinate)s synthesis

The linear bio-based polyester and copolyester polyols were prepared with the use of succinic acid (SA), 1,3-propanediol (PDO) and 1,4-butanediol (BDO). Tetra-n-butyl titanate TnBT was used as a catalyst in the amount of 0.25 wt% as a glycol equivalent. The catalyst content was chosen according to our previous works [10–13]. All bio-based polyols were synthesized by two-step polycondensation method (Fig. 1). Six samples of the bio-based polyols were synthesized with the use of one type of glycol and glycols mixtures with various PDO: BDO molar ratio. Pure glycol or glycols mixture were always used with an excess and the molar ratio of dicarboxylic acid to glycol or glycols mixture amounted to 1:1.2. Determination of this molar ratio was due to the final molecular weight expected after full polycondensation. The designed number average molecular weight of the prepared polyols was dedicated for thermoplastic polyurethane elastomers and should equal ca. 2000 g/mol with the functionality of 2, for proving linear macromolecular chain structure. The reaction was carried out in the glass reactor, which consisted of a three-neck flask equipped with a nitrogen/vacuum inlet, mechanical stirrer, thermometer, condenser, and heating mantle. The first step, which was the esterification reaction between the succinic acid and 1,3-propanediol, 1,4-butanediol or glycols mixture, was carried out under a nitrogen atmosphere at 150 °C for 8 h. After water distillation, the second step, which was a polycondensation reaction, was started. During the polycondensation reaction, the nitrogen was stopped, the catalyst was added, the temperature was increased to 180 °C and the pressure was reduced. The acidic number was measured to track the reaction progress. After achieving the value of the acidic number ca. or preferably below 1 mg KOH/g, the polycondensation was finished.

2.3. Methods

Analytical methods were used for primary properties characterization of the synthesized bio-based polyols. Carboxyl end-group value measurements were performed in accordance with the Polish standard PN-86/C45051. Samples about 1 g of the synthesized materials were dissolved in ca. 30 cm^3 of acetone at room temperature. After that, the solutions were titrated with the use of a standard solution of potassium hydroxide KOH in distilled water (0.1 mol/dm^3). Phenolphthalein was used as an indicator.

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

For water content measurements the volumetric Karl Fischer method was used. The KF reagent used for the NIST volumetric measurements contained methanol solution of imidazole and sulfur dioxide as the organic base, J.T. Baker, HYDRA-POINT Solvent G, pyridine free, was purchased from Avantor Performance Materials Poland S.A. (Gliwice, Poland). The KF titrant for volumetric method contains methanol solution of iodine, J.T. Baker, HYDRA-POINT Titrant 5 mg H_2O/mL, was also purchased from Avantor Performance Materials Poland S.A. (Gliwice,

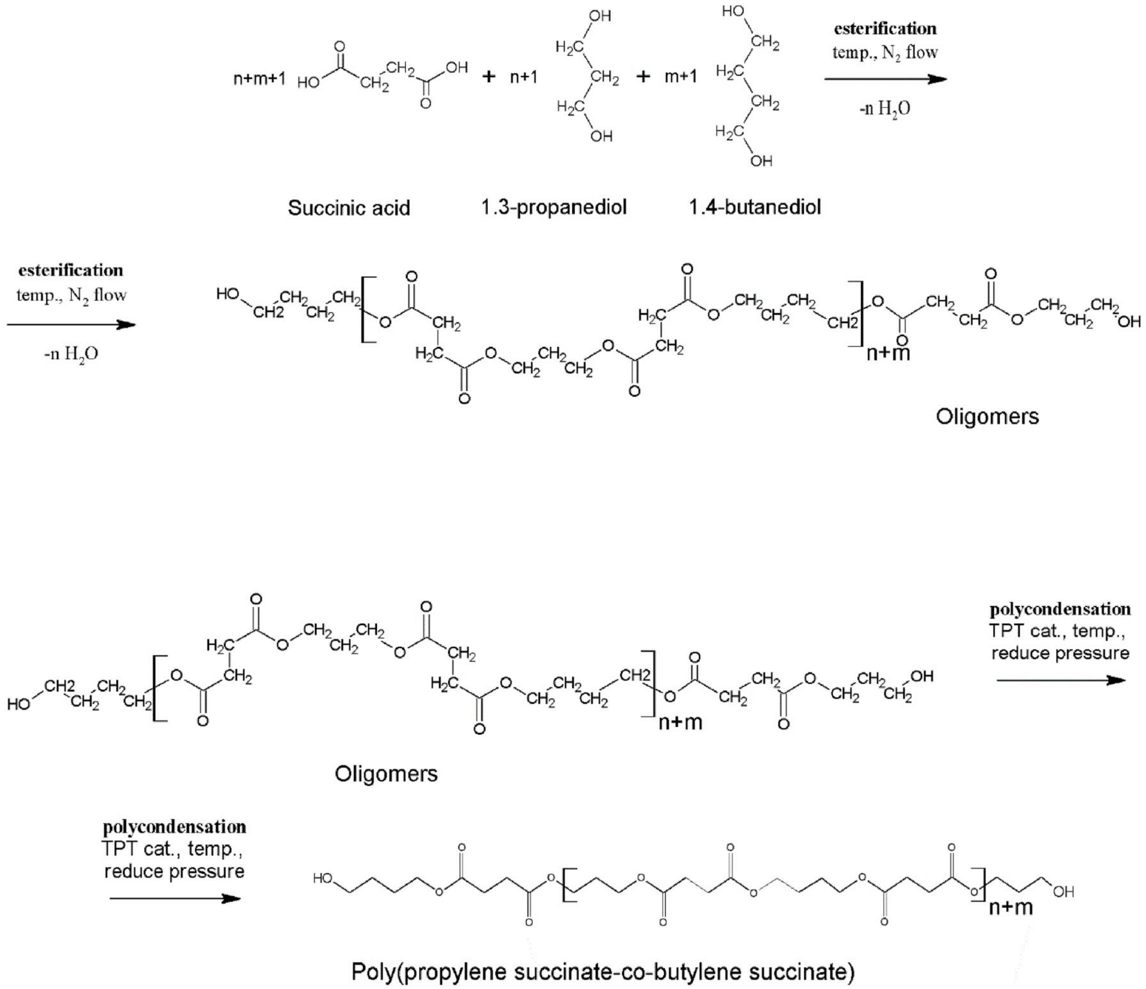

Fig. 1. Two-step polycondensation reaction of bio-based poly (propylene succinate-co-butylene succinate)s obtainment.

Poland).

Chemical structure of the obtained materials was measured by FTIR, ^1H NMR, and MALDI-ToF MS spectrometry. Fourier Transform Infrared Spectroscopy (FTIR) was used to obtain the spectra of the bio-based polyols and pure components (1.3-propanediol and succinic acid). The measurements were carried out using a Nicolet 8700 FTIR spectrometer (Thermo Electron Corporation, USA) with the use of the ATR technique. Sixty-four scans in the wavenumber range from 4500 to 500 cm^{-1} were taken with the resolution 4 cm^{-1}.

Proton nuclear magnetic resonance (^1H NMR) spectra of the prepared bio-based polyols were obtained with the use of Bruker spectrometer. The operating frequency was 400 MHz for protons. The ca. 10% w/v solutions of the sample were prepared in a $CDCl_3$ solvent at ambient temperature. The simulation and iteration of spectra were carried out using Bruker software.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was used to determine the comprehensive structure analysis all of the prepared bio-based polyols. The MALDI-TOF MS spectra were recorded on an AXIMA Assurance Linear MALDI-TOF Mass Spectrometer (Shimadzu Scientific Instruments (SSI), Kyoto, Japan) equipped with near-axis N2 laser irradiation with variable repetition rate 50 Hz in positive linear mode. Typically, 100 single-shot acquisitions were summed to give a sample mass spectrum. All data were reprocessed using the PolymerAnalysis™ software. The matrix, 2,5-dihydroxybenzoic acid (DHB), was dissolved in tetrahydrofuran (THF) (ca. 10 mg/mL). As the cationizing agent was used a potassium salt of fluoroacetic acid (CH2FCOOK) in THF. The solution of matrix, cationizing agent and the polymer solution (5 mg/mL in tetrahydrofuran) was mixed in a 1:10:5 v/v ratio. Approximately 1 μL of the final mixture was spotted onto a stainless steel MALDI plate and allowed to dry before insertion into the ion source. Mass spectrometry analysis proved to be a highly effective tool to facilitate the identification of the molecular structure distribution of the prepared bio-based polyols as well as serve as a core method to investigate the impact of the catalyst amount on the polyols structure development during synthesis.

Differential Scanning Calorimetry (DSC) of the prepared bio-based polyester polyols was used to determine the temperature of phase transitions and was carried out by using a DSC 204 F1 Phoenix Analyzer, equipped with a cooling system. In the first cycle, samples were heated at a rate of 10 °C/min from −20 to 270 °C for erasing of the polyols thermal history. Then, they were cooled down to −80 °C at a cooling rate of 5 °C/min. In the third cycle, the samples were heated up to 120 °C at a rate of 10 °C/min. All the measurements were performed under oxygen atmosphere.

In order to determine the structural properties of the obtained polyesters and co-polyesters the X-ray diffraction (XRD) was used. The measurements were conducted at Phillips X'Pert Pro diffractometer (XRD) with CuKα radiation of wavelength $\lambda = 1.540$ Å in 2θ angel in the range from 10 to 90° under 40 kV and 30 mA, at room temperature in air atmosphere.

Thermogravimetric measurements were prepared for thermal stability analysis of synthesized polyols. DSC-TG/QMS coupled method of thermogravimetric measurements was conducted using an STA 449 F1 Jupiter apparatus from NETZSCH-Feinmahltechnik GmbH. Germany.

Approximately 20 mg portions of dry samples were placed in corundum crucible and heated to 650 °C at various rates: 5, 10, 15 and 20 °C/min and under helium flow. Under these conditions, the DSC-TG experiments of bio-based polyols were sufficiently reproducible. Released gases were detected with a mass spectrometer (QMS 403C Aeolos) coupled on-line to the STA instrument. The QMS was operated with an electron impact ionizer with the energy of 70 eV. During the measurements, the mass/charge (m/z) ratio was recorded in the range from 2 to 100 amu. Based on the obtained results the main products of the prepared bio-based polyols thermal decomposition were identified.

3. Results and discussion

3.1. Bio-based polyester and copolyester polyols characterization

Table 1 shown the synthesis reaction conditions and the results of the acid and hydroxyl numbers of bio-based poly (propylene succinate), bio-based poly (butylene succinate) and bio-based poly (propylene succinate-co-butylene succinate)s. Samples named PPS and PBS represent polyols synthesized with the use of one type of glycols, PDO and BDO, respectively. Specimens called SPB 1, SPB 2, SPB 3 and SPB 4 are polyols synthesized using glycols mixture with different PDO: BDO molar ratios. All prepared polyols were designed to obtained probable monomers for thermoplastic polyurethane elastomers production. The value of acid number approximate or preferably lower than 1 mg KOH/g, hydroxyl number in the range from 20 to 100 mg KOH/g, an average molecular weight in the range from 1000 to 4000 g/mol and water content lower than 0.5 wt%, were required. The shortest reaction time characterized sample SPB 1 prepared with the use of glycol mixture in the molar ratio PDO: BDO = 0.4:0.6. Bio-based copolyester polyols synthesized with a higher amount of PDO at the glycols mixture characterized by longer II step reaction time. Moreover, with an increasing amount of PDO at the glycols mixture, samples featured a higher acid number value. The lowest values of this parameter revealed samples PPS and PBS prepared using one type of glycol. All prepared samples characterized a hydroxyl number in the designed range. In the case of polyols for thermoplastic polyurethane elastomers, it is important to control the water content. If there is the amount of water high enough in polyol or prepolymer, which can act as a foaming agent, there can be produced polyurethane foams. The highest water content revealed sample PPS, but still, it is in the range of the designed limit value.

3.2. Fourier Transform Infrared Spectroscopy results (FTIR)

Fig. 2 shows the results of the FTIR spectroscopy. All prepared bio-based polyols revealed signals at characteristic wavenumbers for this type of chemical compounds. The most visible peaks are collected in Table 2. Samples prepared with the use of glycols mixture revealed differences at the peaks intensity. Moreover, there are visible differences between wavenumbers characteristic for peaks assigned to carbonyl group stretching vibration related to the ester groups from synthesized polyols. Sample PBS, synthesized with the use of BDO as a glycol, revealed wide peak assigned to the carbony group from ester groups at the wavenumber 1710 cm^{-1}, where sample PPS, based on the pure PDO glycol, revealed sharp peak assigned to the same carbonyl groups at 1725 cm^{-1}. Sample SPB 1, SPB 2 and SPB 3 are characterized by a double peak in the range from 1750 to 1700 cm^{-1} due to the occurrence of carbonyl groups stretching vibration from ester groups formed between succinic acid and both glycols, PDO and BDO. A specimen named SPB 4 revealed one sharp peak at 1725 cm^{-1} which is characterized for sample based on pure PDO as a glycol because of the lowest content of BDO at the glycols mixture.

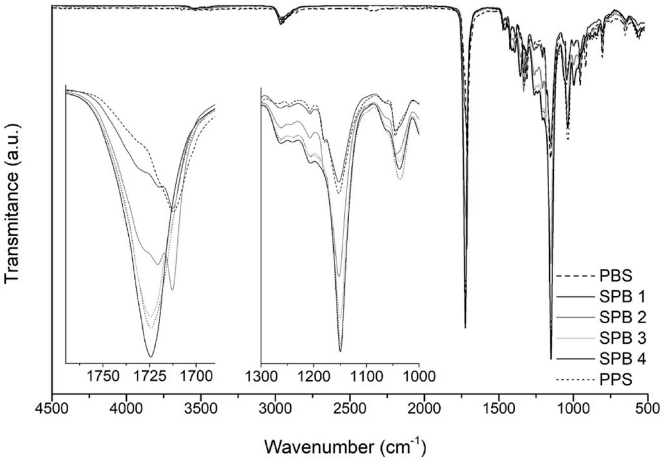

Fig. 2. The results of the FTIR spectroscopy.

Table 2
The collection of the most characteristic signals obtained from FTIR spectroscopy.

Wavenumber [cm^{-1}]	Characteristic group	Vibration type
3600–3200	-OH- from hydroxyl groups	stretching
3000–2850	-CH$_2$- from macromolecular chains	stretching
1725, 1710	-C(O)- from ester groups	stretching
1150	-C-(O)–O–C- from ester groups	stretching
1030	-C-C-O- from ester groups	stretching

3.3. Proton nuclear magnetic resonance results (^{1}H NMR)

For extensive and knowledgeable analysis of the ^{1}H NMR results, the chemical structure of the synthesized polyesters are presented in Fig. 3 presents. Fig. 4 shown ^{1}H NMR spectra all of the synthesized materials. Obtained signals at various chemical shifts were analyzed and attributed to appropriate methylene groups from macromolecular chains (Table 3). The most visible differences at signals situations revealed samples PPS and PBS. Except for the signals named ‘v’ and ‘d’, which indicate methylene protons from –CH$_2$-C(O)- derived from succinic acid, these

Table 1
Reaction conditions and primary properties of the synthesized polyols.

Bio-based polyol	Ratio of the used glycols		Catalyst content [wt. %]	Reaction temperature [oC]		Reaction time [h]		Acid number [mg KOH/g]	Hydroxyl number [mg KOH/g]	Water content [%]
	PDO	BDO		I STEP	II STEP	I STEP	II STEP			
PPS	1	0	0.25	150	180	8	8	0.96	63.40	0.49
SPB 1	0.4	0.6					5	1.03	74.00	0.36
SPB 2	0.5	0.5					8	1.08	51.30	0.18
SPB 3	0.6	0.4					6	1.52	97.50	0.13
SPB 4	0.7	0.3					6	1.54	79.20	0.14
PBS	0	1					7	0.76	50.00	ND

*ND – not defined.

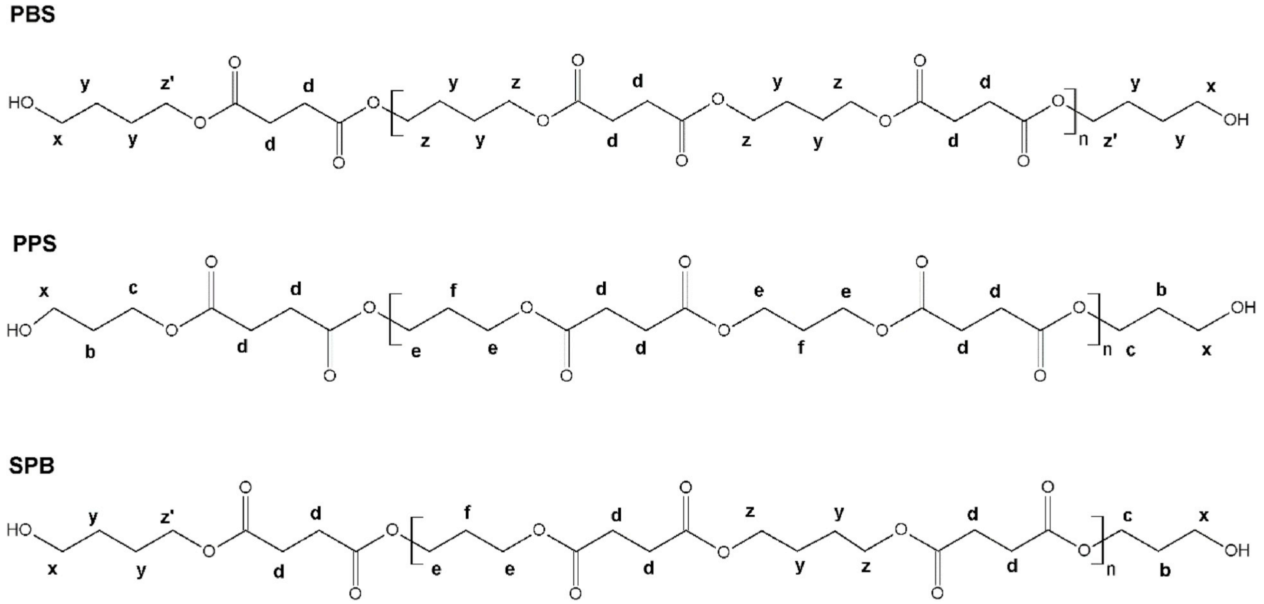

Fig. 3. Chemical structure of the synthesized polyesters.

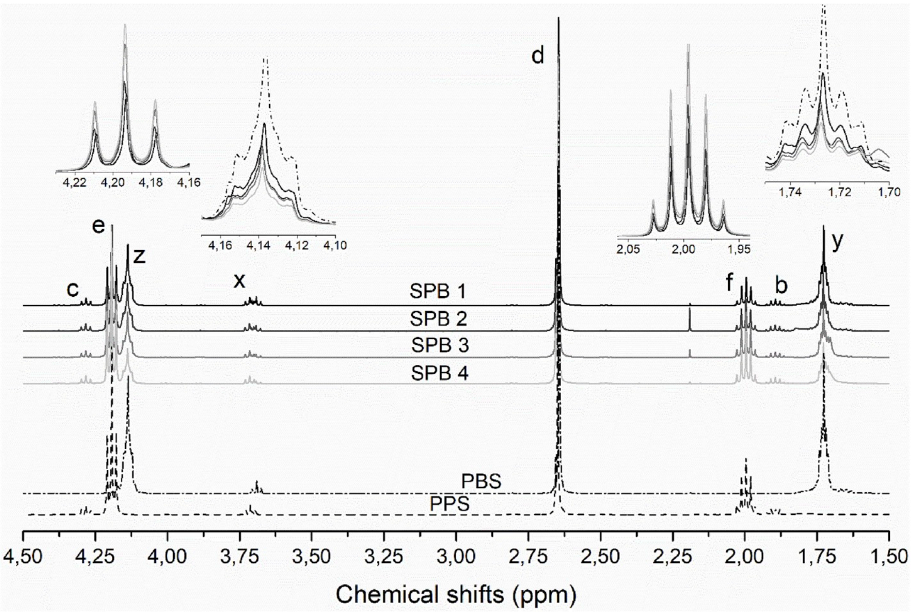

Fig. 4. ^{1}H NMR spectra of the synthesized materials.

Table 3
The collection of the most characteristic signals obtained from ^{1}H NMR spectroscopy.

Symbol	Chemical shift [ppm]	Group
y	1.47	-CH$_2$- from butylene glycol
b	1.90	-CH$_2$- from glycol terminated ends
f	2.00	-CH$_2$- from propylene glycol
d	2.63	-CH$_2$-C(O)- from succinic acid
x	3.65	-CH$_2$-OH from glycol terminated ends
z	4.10	-CH$_2$-O- from butylene glycol
e	4.20	-CH$_2$-O- from propylene glycol
c	4.35	-CH$_2$-O- from glycol terminated ends

two bio-based polyester polyols described different signals. It is characteristic for polyols synthesized with the use of different type of glycol occurred signals connected with these glycols. In the case of materials named SPB, differences are related to two different types of glycols which were used as a glycol mixture during synthesis and also with signals intensity. In the example, with an increasing amount of PDO at the glycol mixture, the intensity of signal named ‘e’, related with the methylene protons from propylene glycol, increases, when the signal named ‘y’ related with the methylene protons from butylene glycol, decreases.

According to our previous work [10] the proper equations for determination of real succinic acid to glycol or glycols mixture molar ratio (SA:GLY), PDO:BDO molar ratio at glycols mixture, polymerization degree and molecular weight are presented below.

The actual SA:GLY molar ratio of the synthesized bio-based polyols were calculated measuring the ratio of the area related with the protons from methylene groups from succinic acid and the area related with the protons from methylene groups from glycols bonded with oxygen atoms from ester groups. For SA the proper signals revealed in the main chain when for glycols the proper signals occurred in the main chain and at the end of the macromolecular chain. For determining of the actual SA:GLY molar ratio there were necessary the following assumption:

- For PPS polyol:

$$SA = d \tag{1a}$$

$$PDO = x + c + e \tag{2}$$

Where:

d - signal area related to proton from the methylene group from succinic acid in the main chain;
x – signal area related to proton from the methylene group bonded to hydroxyl group at the end of the molecular chain;
c - the area of signal from the methylene group bonded to oxygen atom at the end of the molecular chain terminated by PDO glycol;
e − the area of signal from the methylene group proton bonded to oxygen atom at the molecular main chain from PDO glycol.

- For PBS polyol:

$$SA = d \tag{1b}$$

$$BDO = x + z \tag{3}$$

Where:

d, x – as above;
z - the area of signal from the methylene group bonded to oxygen atom at the end of the molecular chain terminated by BDO glycol.

- For SPB polyols:

$$SA = d \tag{1}$$

$$GLY = x + z + c + e \tag{4}$$

Where:

d, x, z, c, e − as above.

Moreover, the differences which are visible at the intensity of particular peaks allow also calculating the actual ratio of glycols used for SPB polyols synthesis. For determining of the real PDO:BDO molar ratio there were necessary the following assumption:

$$PDO = e + c \tag{5}$$

$$BDO = z \tag{6}$$

Where:

e, c, z – as above.

The molecular weights of the synthesized bio-based polyols were calculated measuring the area from the peak in the main chain and the area from the corresponding peak at the end of the macromolecular chain. The ratio of the suitable peaks gives the information about the degree of polymerization, n, which allow determining the molecular weight of the analyzed macromolecule. It is important to the choice of good peaks, which will be considered. What is clearly visible in Fig. 4 for PPS polyol, the methylene groups of propylene glycol in the chain end and in the repeating units, bonded to the oxygen atom of ester group (peaks ‘c’ and ‘e’, respectively, Fig. 4) appeared separate to the methylene group bonded to hydroxyl group at the end of the molecular chain (peak ‘x’, Fig. 4). Moreover, the methylene groups of butylene glycol (PBS polyol) in the chain end and in the repeating units, bonded to the oxygen atom of ester group (peaks ‘z’’ and ‘z’, respectively, Fig. 4) appeared separate to the methylene group bonded to hydroxyl group at the end of the molecular chain (peak ‘x’, Fig. 4). All presented peaks correspond to methylene groups bounded with 4 hydrogen atoms due to the double occurrence at the end of the chain and in the main chain. The same hydrogen atoms are bounded with the methylene group from terminal group, peak ‘x’. Due to that the polymerization degree can be expressed:

- For PPS polyol and SA-PDO repeating units from SPB polyols:

$$(e + c) \sim (n\ 4H \text{ from repeating units} + 4H \text{ chain end}) \tag{7}$$

$$x \sim (4H \text{ terminated chain}) \tag{8}$$

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

$$n = [(e + c)-c]/x \tag{9}$$

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

$$n = e/c \tag{10}$$

- For PBS polyol:

$$(z + z') \sim (n\ 4H \text{ from repeating units} + 4H \text{ chain end}) \tag{11}$$

$$x \sim (4H \text{ terminated chain}) \tag{12}$$

$$n = [(z + z')-z']/x \tag{13}$$

$$n = z/x \tag{14}$$

- For SA-BDO repeating units from SPB polyols:

$$(z + z') \sim (n\ 4H \text{ from repeating units} + 4H \text{ chain end}) \tag{15}$$

$$x \sim (4H \text{ terminated chain}) \tag{16}$$

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

$$n = (z-z')/z' \tag{17}$$

where:

$$z = zPDO + z' \tag{18}$$

$$z' = z - zPDO \tag{19}$$

$$x = xPDO + xBDO \tag{20}$$

$$xPDO = c \tag{21}$$

$$xBDO = x - c \tag{22}$$

$$z' = xBDO \tag{23}$$

Where:

z - the area of signal from the methylene group bonded to oxygen atom at the main chain and at the end of the molecular chain,
z' - the area of signal from the methylene group bonded to oxygen atom at the end of the molecular chain terminated by BDO glycol,
zPDO - the area of signal from the methylene group bonded to oxygen atom at the end of the molecular chain terminated by PDO glycol,
x, c – as above,
xPDO – signal area related to proton from the methylene group bonded to hydroxyl group at the end of the molecular chain terminated by PDO glycol;
xBDO – signal area related to proton from the methylene group bonded to hydroxyl group at the end of the molecular chain terminated by BDO glycol.

The obtained polymerization degree from the ^{1}H NMR spectroscopy results allow to determine the molecular weight of the analyzed polyols from the equation:

$$Mn = n(Mn\ of\ the\ repeating\ unit) + Mn\ of\ the\ chain\ ends \quad (24)$$

For poly (propylene succinate) and SA-PDO repeating units from SPB, the value of molecular weight of the repeating unit amounts 158 g/mol, where the value of molecular weight of the PDO chain ends equals 76 g/mol. For poly (butylene succinate) and SA-BDO repeating units from SPB, the value of molecular weight of the repeating unit amounts 172 g/mol, where the value of molecular weight of the BDO chain ends equals 90 g/mol.

The values of real succinic acid to glycol and glycols mixture molar ratio (SA:GLY), PDO:BDO molar ratio at glycols mixture, polymerization degree and molecular weight for all synthesized polyols are shown in Table 4.

3.4. *Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry results (MALDI-ToF)*

Fig. 5 shows the results of the MALDI-ToF MS spectroscopy of bio-based poly (propylene succinate), bio-based poly (butylene succinate) and bio-based poly (propylene succinate-co-butylene succinate)s. MALDI-ToF MS is a soft ionization method which provides a huge range of information about polymers absolute molecular weights, identification of mass-resolved polymer chains including intact oligomers and simultaneous determination of end groups in polymer sample [14,15]. Moreover, MALDI-ToF measurements give information about macromolecular weight distribution. Similar to GPC results, MALDI-ToF MS spectra are the most favorable when their peak profiles have approximate Gaussian curves [4,12].

The MALDI-TOF mass spectra were obtained at the *m/z* range from 450 to maximum 9000 Da, which gave peaks with various polymerization degree from 2 to 40 and more. Presented signals correspond to the K^+ doped macromolecules. All measured materials characterized peak profiles less or more similar to the Gaussian curve with one broad spectrum with maximum intensity at various *m/z* ratios. The distance between the main peaks amounts to 158 Da for sample PPS (Fig. 5a) or 172 Da for sample PBS (Fig. 5b), which is connected with the molecular weight of the bio-based poly (propylene succinate) or poly (butylene succinate) repeating units, respectively. The maximum intense for sample PPS occurred at 2486 Da (Molecular weight (M) + potassium (K^+)), which proclaimed that the approximate polymerization degree equaled 15 ($M - K^+$) and confirmed hydroxyl-terminated macromolecules occurrence. Obtained spectra include also peaks which are related to oligomers displayed other chemical structure than designed. All calculated macromolecules from MALDI-ToF MS data corresponding to various signals are collected in Table 5. Furthermore, Fig. 6 shows the structure of all probable macromolecules calculated from obtained MALDI-TOF mass spectra. The knowledgeable analysis of the bio-based poly (propylene succinate)s were precisely described at our previous work [12]. It is visible that other samples characterized different curve curses which are caused by different glycol usage in the case of sample PPS and PBS, and different PDO: BDO molar ratios at the glycols mixture in the case of samples SPB 1, SPB 2, SPB 3 and SPB 4.

Fig. 5b presents the MALDI-ToF MS spectrum of the poly (butylene succinate). The maximum intense for this sample occurred at 1504.97 Da (Molecular weight (M) + potassium (K+)), which proclaimed that the approximate polymerization degree equaled 8 (M − K+) and confirmed hydroxyl-terminated macromolecules occurrence. Nevertheless, in Fig. 4b, we can see also peaks which are related to oligomers displayed other chemical structure than designed. Probable structure of molecules calculated from MALDI-ToF data is presented in Fig. 6.

For samples SPB (Fig. 5 c-f) there are visible more complicated MALDI-ToF spectra due to differences at the macromolecular structure in comparison with PPS and PBS. It is related to the occurrence of two kinds of monomers at the copolyesters structure. The distance between the main peaks amounts to 158 Da from PPS repeating units and 172 from PBS repeating units. The various molar ratio of both types of monomers leads to differences in the macromolecules chemical structure. The MALDI-ToF MS results confirmed the higher amount of PPS repeating units with increasing PDO content. Moreover, Fig. 6 presents the possible organization of macromolecules occurred with the highest amount at the prepared bio-based copolyesters.

Table 4
The values of real succinic acid to glycol and glycols mixture molar ratio (SA: GLY), PDO:BDO molar ratio at glycols mixture, polymerization degree and molecular weight for all synthesized polyols obtained from ^{1}H NMR results.

Polyol	SA: GLY molar ration	PDO: BDO molar ratio	Polymerization degree, n (PDO-SA repeating unit; BDO-SA repeating units)	Mn [g/mol]
PPS	1:1,04	1:0	20,9	3450
PBS	1:1,05	0:1	17,7	3220
SPB 1	1:1,09	0,39:0,61	10,0; 8,7	3240
SPB 2	1:1,07	0,48:0,52	11,7; 11,0	3900
SPB 3	1:1,05	0,63:0,37	19,5; 16,7	6100
SPB 4	1:1,06	0,73:0,27	19,0; 15,7	5900

3.5. *Differential Scanning Calorimetry (DSC)*

Polymers thermal transition temperatures as glass transition, crystallization temperature, melting point, etc., are related to the polymers chemical structure and average molecular weight. Polymers with branching at the main chain are characterized by higher glass transition temperature due to the steric hindrance which reduced chain mobility. Usually, the increasing average molecular weight of polymer increases the degree of crystallization. In consequence, the mobility of the molecular chains which constitute amorphous phase is restricted by neighboring crystals. Consequently, the glass transition shifts to lower temperatures and the melting point shifts to higher temperatures [29,30].

Fig. 7 shows the results of the DSC measurements of the prepared bio-based polyester and co-polyester polyols. The first run was carried out under air atmosphere with the heating rate of 10 °C/min at the temperature range from −20 to 270 °C to erasing polyols thermal history. For bio-based linear polyester polyols named PPS and PBS, poly (propylene succinate) and poly (butylene succinate), respectively, there are visible different melting point temperatures. PPS revealed melting temperature at 47.0 °C, when PBS at 116.5 °C (Fig. 7a). It is visible that the use of glycol mixture at co-polyester synthesis allowed to shift the melting temperatures towards lower values. For samples named SPB 1 and SPB 2 there are visible three phase transitions related to the melting point of macromolecular chains appeared in co-polyester polyols. The first step revealed at 39.8 and 39.1 °C for PPS and PBS, respectively, is related with the melting point of the macromolecules of PPS occurred at the polyol mixture. Temperatures 62.5, 58.3 and 46.0 °C for SPB 1, SPB 2 and SPB 3, respectively, characterized macromolecules of poly (propylene succinate-co-butylene succinate)s. The last phase transition temperature at 77.0, 72.2 and 75.5 °C for SPB 1, SPB 2 and SPB 3, respectively, is related with the melting point of the macromolecules of PBS occurred at the polyol mixture. Sample SPB 3 characterized two phase transition temperatures related with melting point, when sample SPB 4 which was synthesized with the use of the lowest amount of BDO glycol (0.3 wt%) revealed one melting point at 41.9 °C.

The second run was carried out with the cooling rate of 5 °C/min up to −80 °C (Fig. 7b). Only poly (butylene succinate) revealed crystallization temperature at 79.9 °C what confirmed crystalline structure of PBS. Other synthesized polyester and co-polyesters did not display crystallization despite distinct melting point occurrence at first and second heating curve courses. It is consequence of the measurements conditions, in which too fast cooling rate was used. Moreover, the

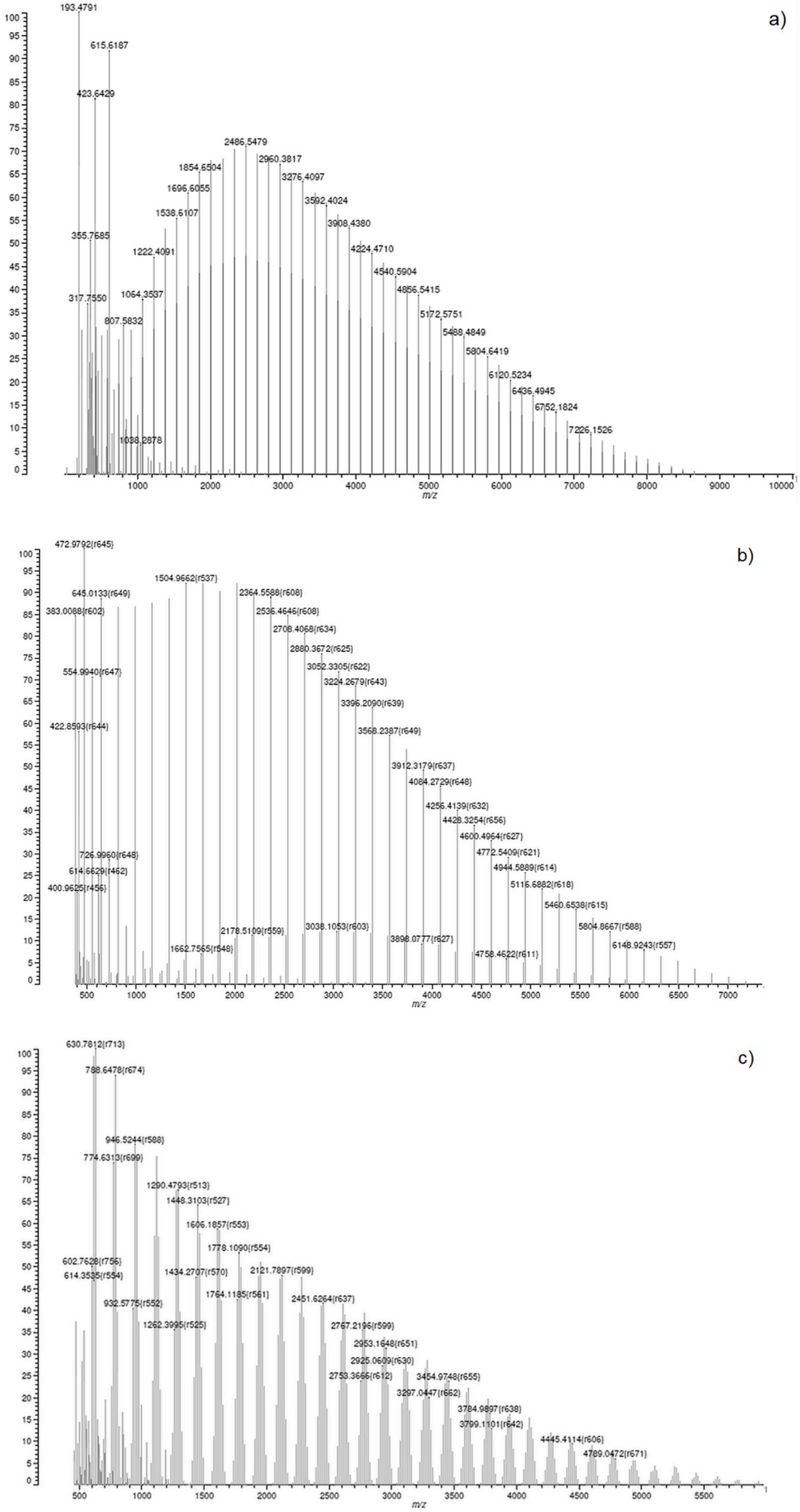

Fig. 5. MALDI-ToF MS spectra of the synthesized bio-based polyols: a) PPS, b) PBS, c) SPB 1, d) SPB 2, e) SPB 3, f) SPB 4.

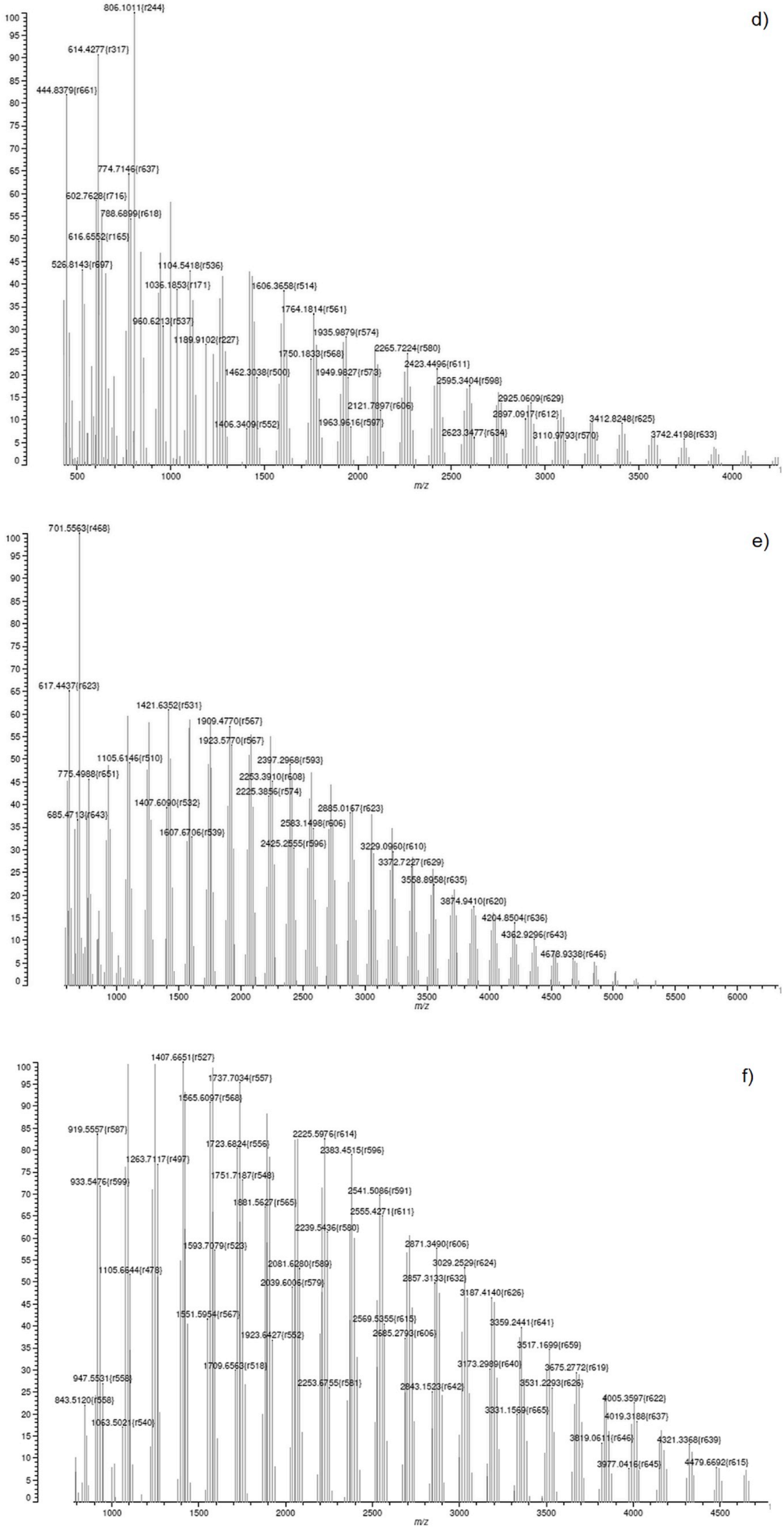

Fig. 5. (*continued*).

Table 5
Interpretation of MALDI-ToF mass spectra for obtained bio-based polyols.

Bio-based poly (propylene succinate)	Location of band (*m/z*) (M + K$^+$)	Polymerization degree (n, m)	Probable structure of molecule (M-K$^+$)	Calculated molecular weight (M + K$^+$) [g/mol]
PPS	193.48	1	A	197.17
	317.76	1	A-SA-H$_2$O	315.26
	355.77	2	A	355.24
	423.64	2	PPS	429.27
	615.62	3	A-SA	613.40
	807.58	4	ND	ND
	1038.29	6	ND	ND
	1064.35	6	PPS	1061.61
	1222.41	7	PPS	1219.62
Peaks from 1222.41 to 7226.15 Da and further are related with macromolecules PPS with higher polymerization degree (from 7 to 45 and further).				
PBS	383.01	2	PBS s.u.	383.50
	400.96	2	B	400.51
	422.86	2	B–H$_2$O	419.54
	472.98	2	PBS s.u.	473.64
	554.99	3	PBS s.u.	555.70
	614.66	3	ND	ND
	645.01	3	PBS	645.82
	727.00	4	PBS s.u.	727.90
	1504.97	8	PBS	1506.82
	1662.76	9	PBS=CH$_2$	1662.01
	2178.51	12	PBS=CH$_2$	2178.61
	2364.56	13	PBS	2367.82
	2536.46	14	PBS	2540.02
Peaks from 2536.46 to 6148.92 Da and further are related with macromolecules PBS and PBS=CH$_2$ with higher polymerization degree (from 14 to 35 and further).				
SPB 1	602.76	2	A-BDO	603.73
	614.35	3	ND	ND
	630.78	3	B-PDO	631.79
	774.63	n = 2; m = 2	SPB-PDO	775.93
	788.65	n = 2; m = 2	SPB-BDO	789.96
	932.58	n = 2; m = 3	SPB-PDO	934.10
	946.52	n = 3; m = 2	SPB-PDO	948.19
	1252.40	n = 2; m = 5	SPB-PDO	1250.44
	1290.48	n = 5; m = 2	SPB-PDO	1292.53
	1434.27	n = 4; m = 4	SPB-PDO	1436.67
	1448.31	n = 5; m = 3	SPB-PDO	1450.70
	1606.19	n = 5; m = 4	SPB-PDO	1608.87
	1764.12	n = 5; m = 5	SPB-PDO	1767.04
	1778.11	n = 5; m = 5	SPB-BDO	1781.07
	2121.79	n = 7; m = 5	SPB-BDO	2125.47
Peaks from 2121.79 to 4789.05 Da and further are related with various derivatives of SPB macromolecules with higher polymerization degree (from n = 7; m = 5 to n = 17; m = 11, even further).				
SPB 2	444.84	n = 1; m = 1	SPB-PDO	445.56
	526.81	n = 1; m = 2	SPB s.u.	527.64
	602.76	n = 1; m = 2	SPB-PDO	603.73
	614.43 and 616.66	n = 1; m = 2 or n = 2; m = 1	SPB-BDO or SPB-PDO	617.76
	774.71	n = 2; m = 2	SPB-PDO	775.93
	788.69	n = 2; m = 2	SPB-BDO	789.96
	806.10	n = 3; m = 1 or n = 1; m = 3	SPB-BDO or SPB-SA	803.99 or 803.90
	960.62	n = 3; m = 2	SPB-BDO	962.16
	1036.19	n = 2; m = 4	SPB	1034.20
	1104.54	n = 3; m = 3	SPB-PDO	1106.30
	1189.91	n = 3; m = 4	SPB s.u.	1188.38
	1406.34	n = 6; m = 2	SPB	1406.66
	1462.30	n = 5; m = 3	SPB-BDO	1464.73
Peaks from 1462.30 to 3742.42 Da and further are related with various derivatives of SPB macromolecules with higher polymerization degree (from n = 5; m = 3 to n = 11; m = 11, even further).				
SPB 3	617.44	n = 2; m = 1	SPB-PDO	617.76
	685.47	n = 1; m = 3	SPB s.u.	685.81
	701.56	n = 1; m = 3	SPB	703.83
	775.50	n = 2; m = 2	SPB-PDO	775.93
	1105.61	n = 3; m = 3	SPB-PDO	1106.30
	1407.61	n = 2; m = 6	SPB-PDO	1408.61
	1421.64	n = 3; m = 5	SPB-PDO	1422.64
	1607.67	n = 4; m = 5	SPB-BDO	1608.87
	1909.48	n = 4; m = 7	SPB-PDO	1911.18
	1923.58	n = 4; m = 7	SPB-BDO	1925.21
	2225.39	n = 4; m = 9	SPB-PDO	2227.52
	2253.39	n = 5; m = 8	SPB-BDO	2255.58
	2397.30	n = 5; m = 9	SPB-PDO	2399.72
Peaks from 2397.30 to 4678.93 Da and further are related with various derivatives of SPB macromolecules with higher polymerization degree (from n = 5; m = 9 to n = 10; m = 18, even further).				
SPB 4	843.51	n = 1; m = 4	SPB s.u.	843.98
	919.56	n = 1; m = 4	SPB-PDO	920.07
	933.55	n = 1; m = 4	SPB-BDO	934.10
	947.55	n = 2; m = 3	SPB-BDO	948.13
	1063.50	n = 4; m = 2	SPB	1062.26
	1105.66	n = 3; m = 3	SPB-PDO	1106.30
	1263.71	n = 3; m = 4	SPB-PDO	1264.47
	1407.67	n = 2; m = 6	SPB-PDO	1408.61
	1551.60	n = 5; m = 4	SPB	1550.80
	1565.61	n = 2; m = 7	SPB-PDO	1566.78
	1593.71	n = 3; m = 6	SPB-BDO	1594.84
	1709.66	n = 5; m = 5	SPB	1708.97
	1723.68	n = 2; m = 8	SPB-PDO	1724.95
Peaks from 1723.68 to 4479.67 Da and further are related with various derivatives of SPB macromolecules with higher polymerization degree (from n = 2; m = 8 to n = 9; m = 18, even further).				

*ND – not defined.
*s.u. – structural unit.
*A, A-BDO, A-SA-H$_2$O, PPS, PBS, etc. – the structure of various derivatives of macromolecules formed during measurements (see Fig. 5).
*n - polymerization degree of PBS structural units, m - polymerization degree of PPS structural units.

crystallization from melt require forming stable nuclei and growing of these nuclei. If the crystallization does not occur during the cooling cycle this may be consequence of the lack of stable nuclei [16,17].

The erasing of the polyols thermal history allowed to observe significant changes in the curve courses during the second heating run (Fig. 7c). Only two from synthesized polyesters and co-polyester polyols indicate melting temperature, PBS at 107.5 and 114.5 °C and SPB 1 at 72.2 °C. These both samples characterized also by an exothermic phase transition at 27.4 and 98.7 °C for SPB 1 and PBS, respectively. It is an exothermic crystallization process observed on heating a sample that has previously been cooled so quickly that has no time to crystallize. At temperature below the glass transition, molecular mobility is restricted and cold crystallization does not occur, but above the glass transition, small crystals are formed at relatively low temperatures [16,18,19]. Some researchers [20,21] concluded that the odd number of the carbon atoms in the co-polyesters backbone relevantly inhibits their crystallization rate. After thermal history erasing, the prepared bio-based poly (propylene succinate) polyol and poly (propylene succinate-co-butylene succinate) co-polyesters SPB 2, SPB 3 and SPB 4 revealed the lack of the melting point.

Fig. 7c presents also the effect of increasing BDO content at co-polyester polyols chemical structure on the glass transition temperatures which were shifted towards lover values from −34.4 to −37.7 °C, for SPB 4 and SPB 1, respectively. There is not visible the glass transition for PBS polyol due to the glass transition occurrence at the temperature out of the test temperature range.

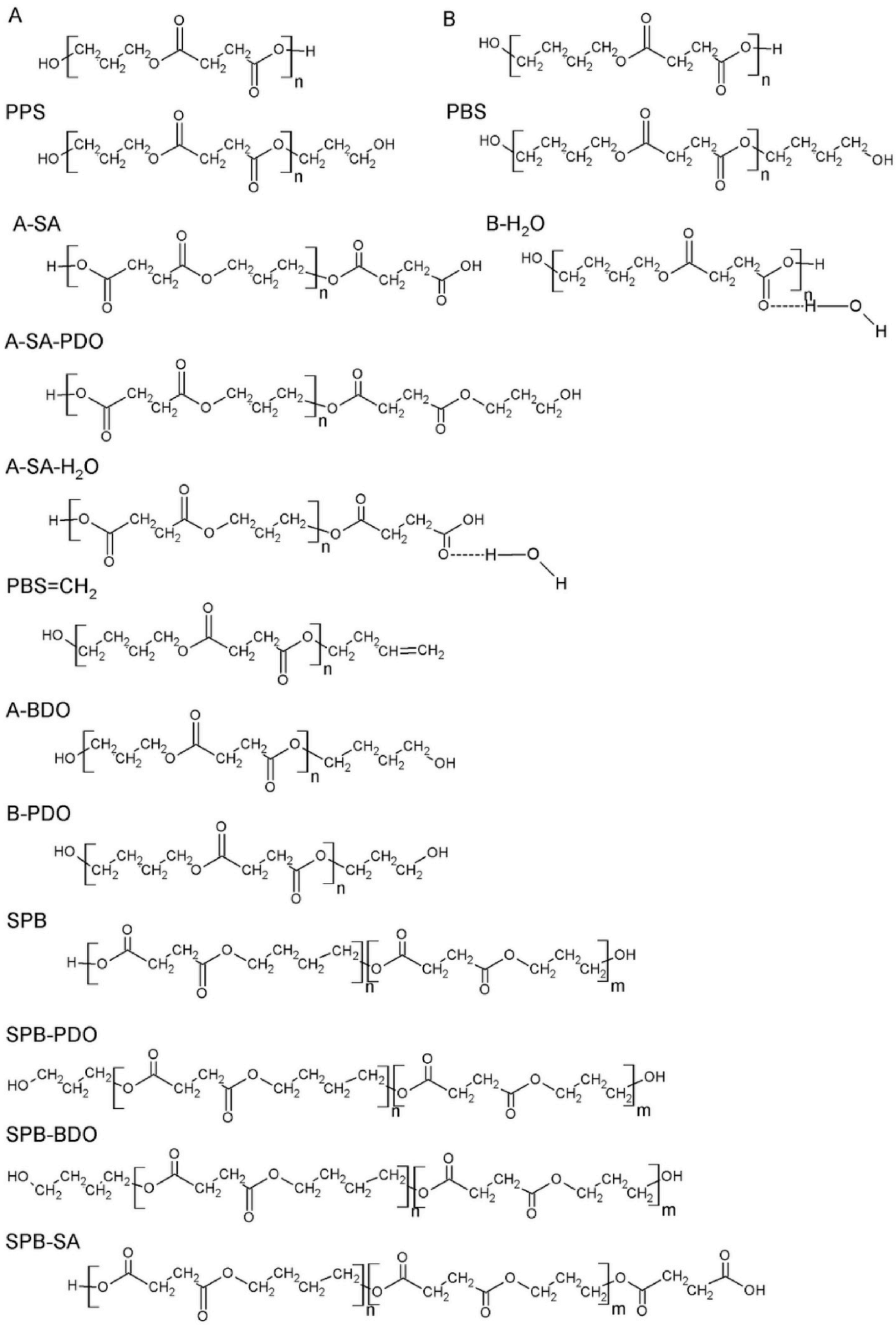

Fig. 6. Probable structure of molecules calculated from MALDI-ToF data.

3.6. *X-ray diffraction (XRD)*

The XRD results obtained for PPS, PBS, SPB 1 and SPB 4 polyester polyols are presented in Fig. 8. It was observed that PPS polyol exhibit the typical XRD pattern with the most important diffraction signals at 2θ values 19.4, 22.7, 26.2°. Polyol PBS revealed the most important diffraction signals at 2θ values 19.6, 21.9, 22.8°, which correspond to the crystal planes (020), (021), and (110), respectively [22]. For co-polyesters SPB 1 and SPB 4 there was observed the typical XRD pattern with only two the most important diffraction signals at 2θ values 19.9 and 23.2° for SPB 1 and 19.5 and 22.2° for SPB 4, respectively. All co-polyesters show a PPS type crystal phase. Moreover, it was observed that the crystalline structure of the co-polyesters increase with the increasing amount of BDO glycol employment. The XRD pattern of SPB 4 co-polyester polyol shows a broad lump between 15° and 25°, which is associated with the increase the amorphous domain at the oligomer crystal structure [23]. The addition of BDO could not change the crystalline structure but increase the crystallinity of SPB co-polyesters due to the increase in the height of the diffraction peaks. We can probably claim that the presence of PDO glycol at the macromolecular chain is responsible for disrupting chain regularity and packing in case of co-polyesters [24]. This result is agreement with the conclusions determined by DSC.

3.7. *Thermal degradation study with released gasses analysis (DSC-TG/QMS)*

Thermogravimetric measurements were conducted using DSC-TG/

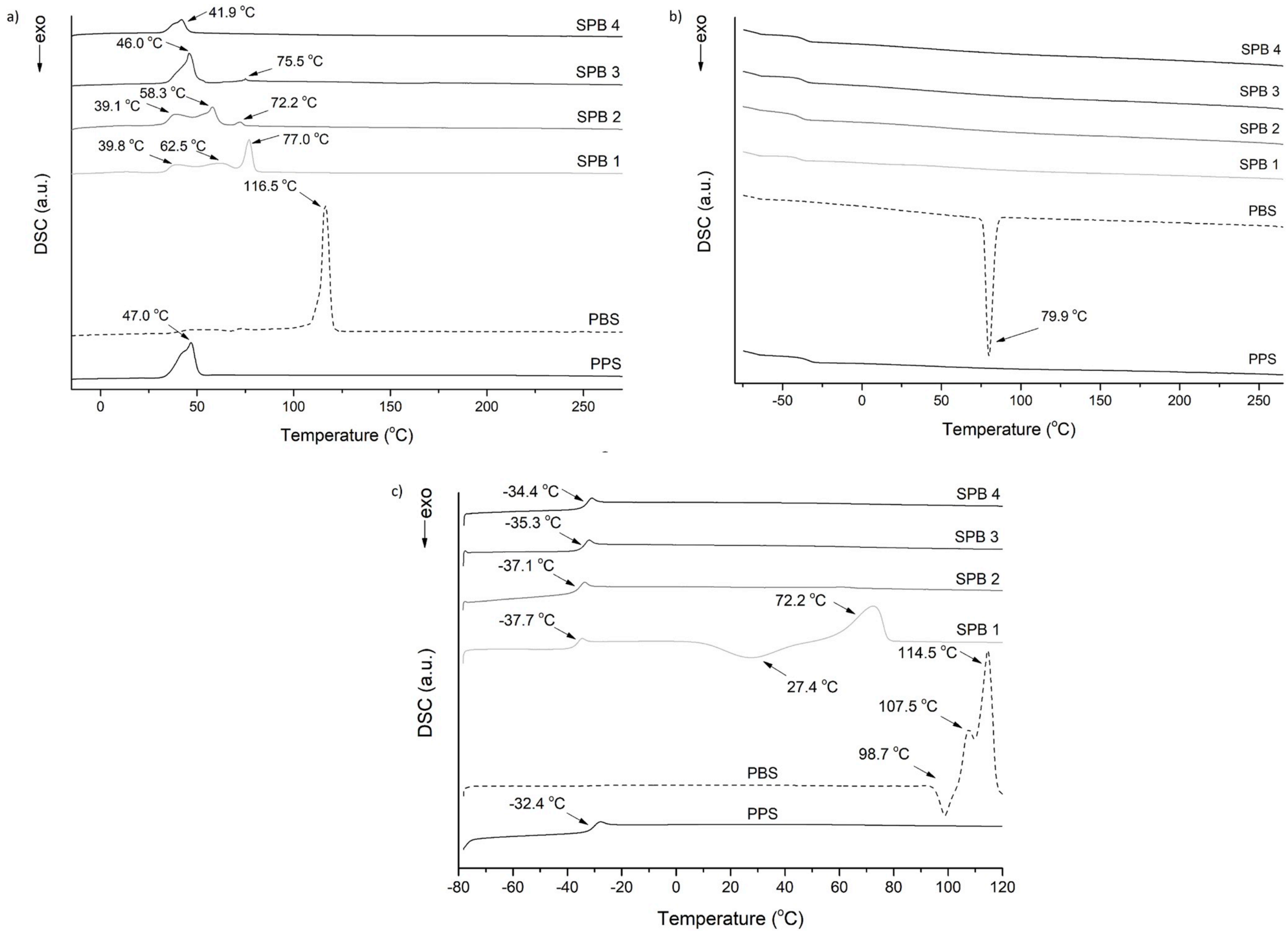

Fig. 7. The results of the DSC measurements of the prepared bio-based polyester and co-polyester polyols, where a) I heating, b) cooling, c) II heating.

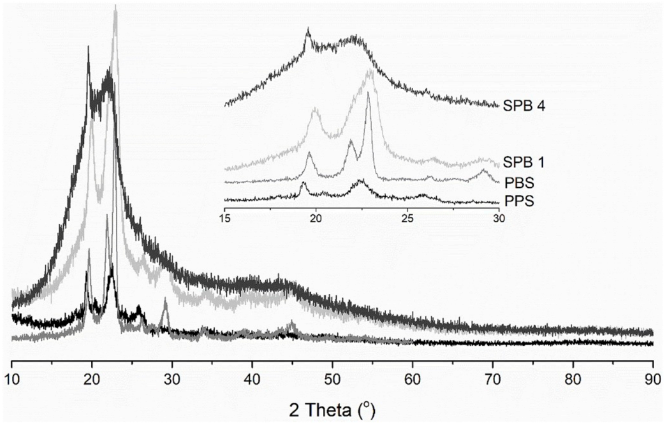

Fig. 8. The results of XRD analysis for the PPS, PBS, SPB 1 and SPB 4 polyester polyols.

QMS coupled method. Fig. 9 a and b present TG and DTG results, respectively. The results confirmed one step of thermal decomposition for all samples. There are not significant differences between thermal degradation characteristics. All of the measured bio-based polyester polyols revealed similar curve curses. There is a slightly visible impact of the glycol mixture composition on the thermal degradation temperature and the intensity of temperature of the maximum speed of weight loss at DTG graph. In order to comprehensive comparison, the relative thermal stability of polyesters, the temperatures for weight losses of 5, 50 and 90% and the temperature of a maximum speed of weight loss are presented in Table 6. With increasing PDO content at the bio-based copolyester polyols, the increase at the temperature of 5% mass loss (T5%) is visible. It confirmed that PDO content influences on thermal stability of the prepared bio-based polyester polyols. Other characteristic temperatures disclosed similar values. The quantity of the residues after tests revealed low values, even lower than 1%.

The extensive literature review allowed proposing the probable thermal degradation mechanism of fully bio-based polyester polyols. Based on the articles such researchers as Papageorgiou, Bikiaris, Chrissafis, Paraskevopoulos, and others [25–31], and also based on our previous work [10], we would like to check the bio-based monomers behavior during thermal decomposition. The above-mentioned researchers proposed two primary mechanisms different in the bond scission position. Fig. 10 presents the most probable mechanisms of the thermal degradation proposed according to the literature review information. The first reaction is the alfa hydrogen bond scission. This type takes place between oxygen atom –O- and the carboxyl group –CO- in the ester functional groups –CO-O-. Beta hydrogen bond scission takes place between the ester group –CO-O- and –CH2- a group from glycol. Thermal degradation reactions in the poly (propylene succinate-co-butylene succinate) macromolecules led to such products obtaining as 3-hydroxypropanal, 4-hydroxybutanal, 2-propenal, 3-butenal, 2-propen-1-ol, 3-buten-1-ol, allyl-succinic acid compounds, succinic acid and butylene and propylene glycols, and their derivatives. There are also produced low molecular weight compounds as water and carbon dioxide.

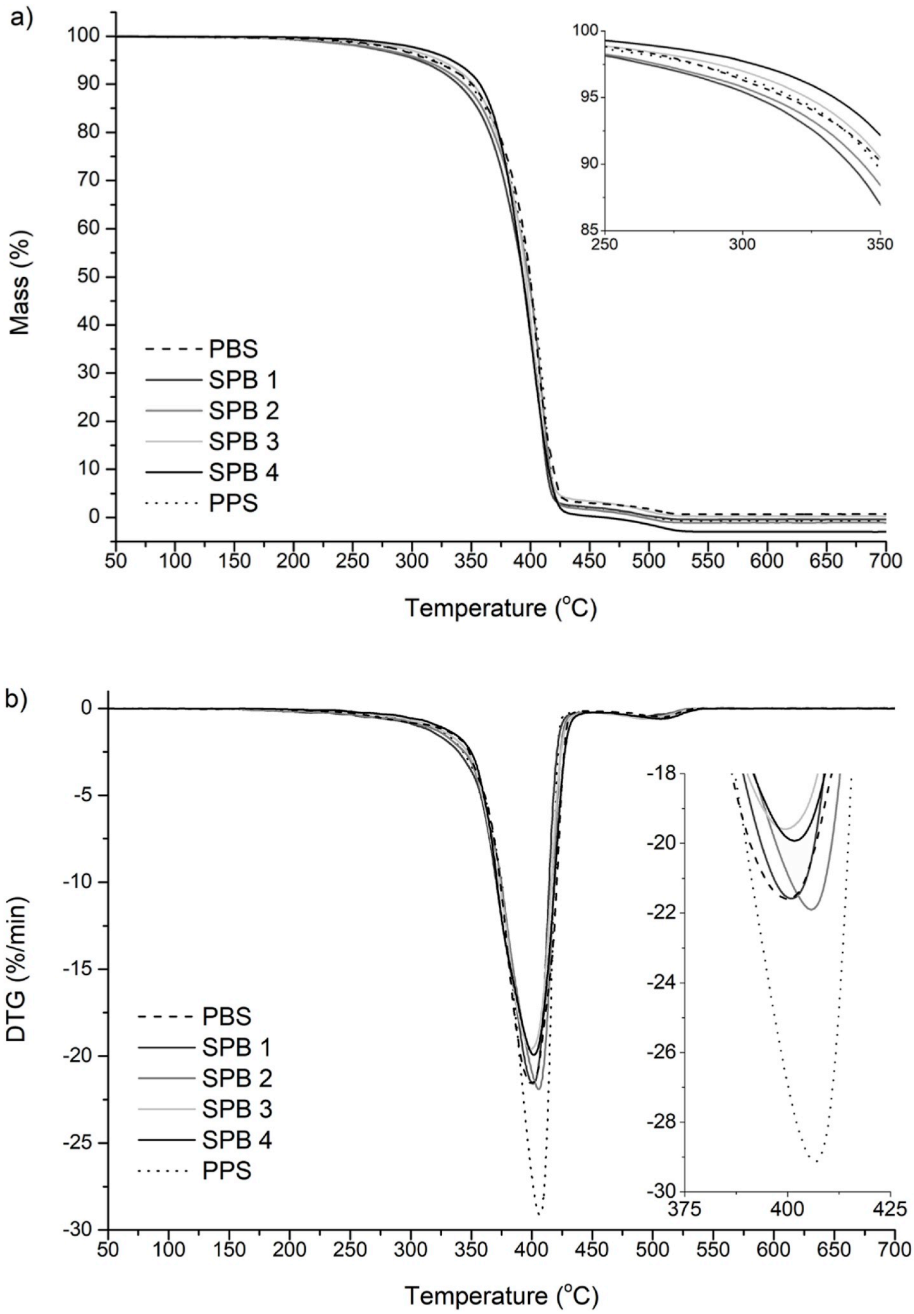

Fig. 9. a) TG and b) DTG results of the prepared bio-based polyols.

Table 6
Thermal degradation characteristics of the obtained materials.

Bio-based polyol	Thermal degradation characteristic				
	$T_{5\%}$ [°C]	$T_{50\%}$ [°C]	$T_{90\%}$ [°C]	T_{max} [°C]	Residue at 500 °C [%]
PPS	315.7	398.7	415.9	405.7	0.23
SPB 1	301.4	393.4	414.4	401.4	0.27
SPB 2	308.3	398.3	415.8	408.3	0.35
SPB 3	322.1	396.1	414.6	397.1	1.20
SPB 4	330.9	393.2	414.5	400.8	1.40
PBS	314.0	399.1	419.0	399.0	1.80

To verified the proposed mechanism the released gases during thermogravimetric measurements were detected with a quadrupole mass spectrometer (QMS 403C Aeolos) with Multiple Ion Detection (MID) mode for qualitative analysis. Fig. 11 shows the ion current intensity profiles of three gas products released during thermogravimetric analysis. Moreover, Table 7 presents the collection of mass/charge ratios and possible ions which identified proposed thermal decomposition products. The recorded QMS spectra of volatile products from poly (propylene succinate-co-butylene succinate) allowed to confirm the proposed thermal decomposition mechanism. In all samples CO_2, H_2O, 2-propenal, 2-propen-1-ol, 3-butenal, 3-buten-1-ol, 1,3-propanediol, 1,4-butanediol, succinic acid, as well as its derivatives, were detected as the main decomposition products. 2-propen-1-ol (allyl alcohol) and 2-propenal (acrolein) are toxic and strong irritant for the skin, eyes, and nasal passages chemical compounds which were used as a lachrymators. Also 4-hydroksybutanal is caustic and can provide to nausea and vomiting.

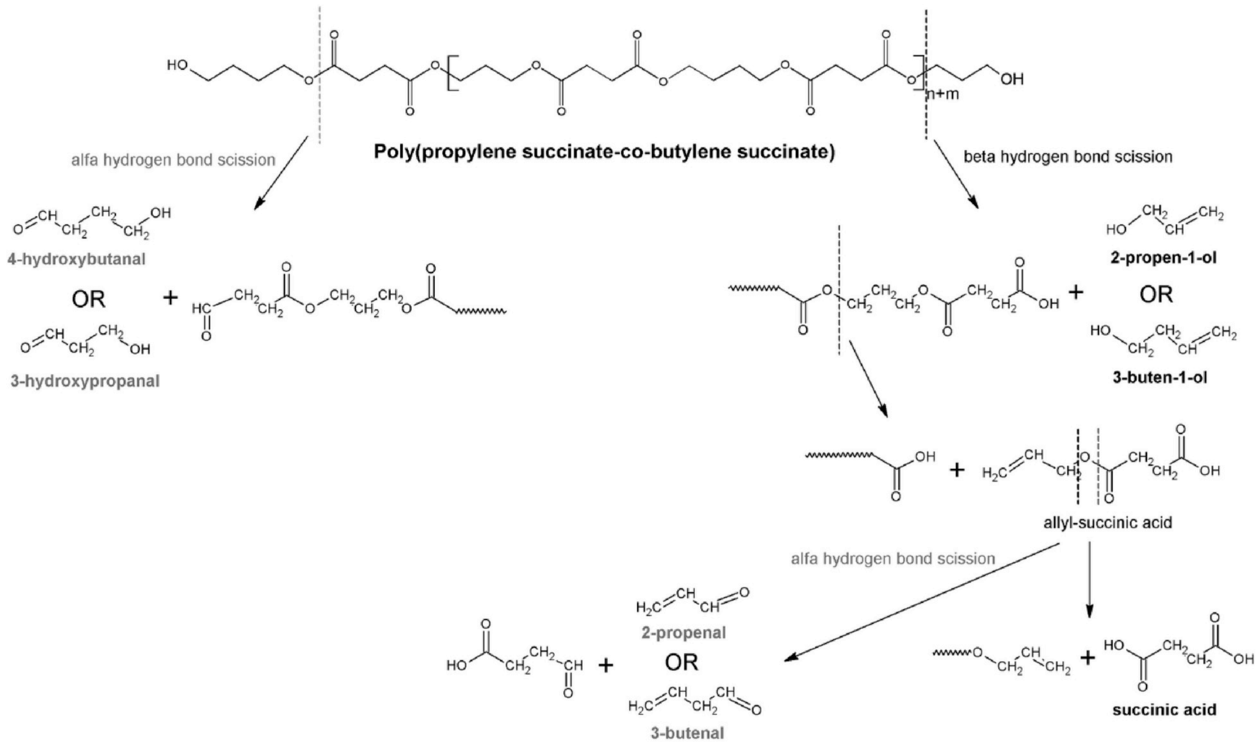

Fig. 10. Thermal decomposition mechanisms of the synthesized bio-based copolyester polyols.

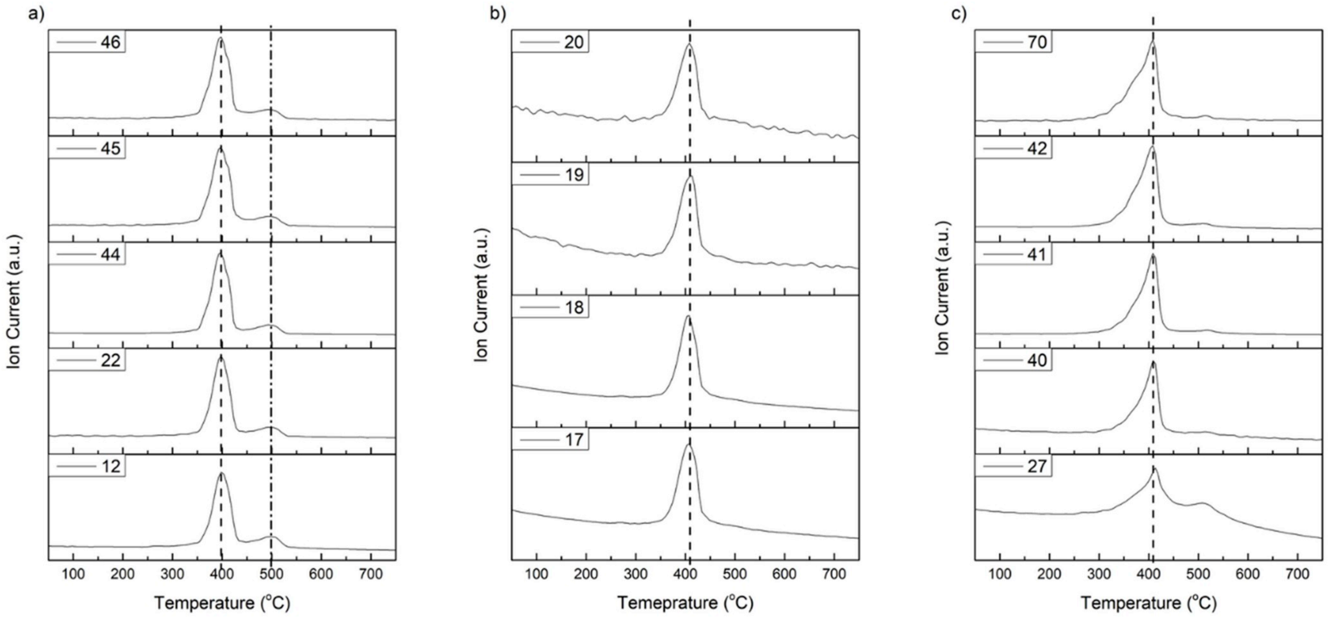

Fig. 11. QMS spectra identified examples of thermal degradation products such as a) CO_2, b) H_2O, c) 3-butenal.

4. Conclusion

In this work, two polyesters and four co-polyesters were synthesized with the use of renewable resources. All prepared bio-based materials were dedicated as polyols for thermoplastic polyurethane elastomers. The used synthesis conditions allowed to obtain polyols characterized by primary properties required for TPUs synthesis such as an acid number at ca. 1 mg KOH/g, a hydroxyl number in the range from 40 to 100 mg KOH/g, an average number molecular weight ca. 2000 g/mol and water content lower than 0.5 mas.%. The chemical structure of the prepared bio-based polyester polyols was verified and confirmed by FTIR, ^{1}H NMR, and MALDI-ToF MS methods. With the use of the last-mentioned method, the chemical structure of probable macromolecules which appeared at the polyols structure was proposed. The crystal structure of the obtained polyols were tested by XRD measurements. The results indicate that the increasing amount of the PDO glycol at the co-polyesters chemical structure increase the amorphous domain at the oligomer crystal structure. The most crystalline structure characterized PBS and SPB 1 polyols. These results confirmed the conclusion determined by DSC. Thermogravimetric analysis indicated one step of

Table 7
Degradation products identified by QMS during bio-based poly (propylene succinate) degradation under an air atmosphere.

Possible compounds	Peak (*m*/*z*)	Possible ions
Water, H_2O	16, 17, $\underline{18}$, 19	H_2O (18), OH^- (17), H_3O^+ (19)
Carbon dioxide, CO_2	12, 16, 22, 28, 29, $\underline{44}$, 45, 46	C (12), CO (28), CO_2 (44)
2-propen-1-ol, C_3H_6O	12, 15, 18, 25, 26, 27, 28, 29, 30, 31, 32, 38, 39, 40, 43, 44, 53, 55, 56, $\underline{57}$, 58, 59	$C_2H_3^+$ (27), C_2H_4 (28), $C_2H_5^+$ (29), $C_2H_6^+$ (30), $C_3H_3^+$ (39), $C_3H_5^+$ (41), $C_3H_7^+$ (43), $CH_3C{\equiv}O^+$ (43), $C_2H_4O^+$ (44), $C_3H_3O^+$ (55), $C_3H_4O^+$ (56)
3-buten-1-ol, C_4H_8O	13, 14, 15, 17, 18, 25, 26, 27, 28, 29, 30, 31, 32, 33, 36, 37, 38, 39, 40, 41, $\underline{42}$, 43, 44, 49–56, 57, 69, 70, 71, 72	$C_3H_3^+$ (39), $C_3H_5^+$ (41), $C_3H_6^+$ (42), $C_3H_7^+$ (43), $C_3H_5O^+$ (57), $C_4H_7O^+$ (71)
2-propenal, C_3H_4O	14, 16, 24, 25, 26, 27, 28, 29, 36, 37, 38, 39, 40, 52, 53, 55, $\underline{56}$	CH_4 (16), $C_2H_3^+$ (27), C_2H_4 (28), $C_2H_5^+$ (29), $C_3H_4O^+$ (56)
3-butenal, C_4H_6O	27, 29, 39, 40, $\underline{41}$, 42, 70	$C_3H_3^+$ (39), $C_3H_5^+$ (41), $C_3H_6^+$ (42)
1,3-propanediol, $C_3H_8O_2$	14, 15, 18, 25, 26, 27, $\underline{28}$, 29, 30, 31, 32, 39, 42, 43, 44, 45, 46, 47, 49, 53, 55, 57, 58, 59	$C_2H_3^+$ (27), C_2H_4 (28), $C_2H_5^+$ (29), $C_2H_6^+$ (30), $C_3H_3^+$ (39), $CH_3C{\equiv}O^+$ (43), $C_3H_5O^+$ (57), $C_3H_6O^+$ (58), $C_3H_7O^+$ (59)
1.4-butanediol, $C_4H_{10}O_2$	15, 18, 19, 25, 26, 27, 28, 29, 30, 31, 32, 33, 37, 38, 39, 40, 41, $\underline{42}$, 43, 44, 45, 46, 47, 49–51, 53–56, 57, 58–62, 69, 70, 71, 72, 73	$C_2H_3^+$ (27), $C_2H_5^+$ (29), $C_3H_3^+$ (39), $C_3H_5^+$ (41), $C_3H_6^+$ (42), $C_3H_5O^+$ (57), $C_4H_7O^+$ (71)
Succinic acid, $C_4H_6O_4$	14, 18, 19, 26, 27, 28, 29, 30, 36, 42, 45, 46, 53, $\underline{55}$, 56, 57, 72, 73, 74, 100	$C_2H_3^+$ (27), $C_3H_4O^+$ (55), $C_3H_4O^+$ (56), $C_3H_5O^+$ (57), $C_3H_5O_2^-$ (73), $C_3H_6O_2$ (74), $C_4H_4O_3^+$ (100)

thermal decomposition of all polyester and co-polyester polyols. Moreover, the impact of PDO content on thermal stability of co-polyesters were investigated. The results confirmed the increasing values of temperature of the beginning of the thermal degradation with increasing PDO content. Based on the knowledgeable analysis of the polyols chemical structure the thermal decomposition mechanisms were proposed. The results of QMS measurements confirmed thermal decomposition of poly (propylene succinate-co-butylene succinate)s, which run according to α and β hydrogen bond scissions. Though synthesized polyester polyols are fully from renewable resources, they still provide to toxic chemical compound after thermal decomposition.

Declaration of competing interest

With the submission, I would like to undertake the responsibility that the authors of the manuscript do not have any conflicts of interest.

CRediT authorship contribution statement

Paulina Parcheta: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration. **Janusz Datta:** Visualization, Project administration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2020.106337.

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