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Fully bio-based poly(propylene succinate) synthesis and investigation of thermal degradation kinetics with released gases analysis

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ABSTRACT: One of the most important information about polyesters is their thermal stability and phase transition temperatures. These characteristics give information about the promising behavior of the polyester during processing. In this work, linear bio-based polyester polyols were prepared with the use of succinic acid and 1.3-propanediol (both with natural origin). As a polycondensation catalyst was used tetraisopropyl orthotitanate (TPT), which different amount was employed. The thermogravimetric analysis allowed to observe high thermal stability and one step of the thermal decomposition. This analysis affirmed also that the catalyst content did not influence the thermal degradation characteristics of the prepared polyols. Nevertheless, it has huge importance in the context of thermal degradation kinetics. It was determined with the use of Ozawa, Flynn, and Wall and Kissinger's methods to verifying catalyst impact on the thermal degradation kinetics. Moreover, probable mechanism of the prepared bio-based polyols thermal degradation was proposed based on the QMS results.

KEYWORDS: Poly(propylene succinate); Bio-based polyester polyol; Thermal degradation kinetics; Ozawa, Flynn and Wall method; Kissinger method; Released gases analysis

1. INTRODUCTION

Polyols constitute one of the major components for the polyurethane synthesis. They are usually liquid, reactive substances mostly terminated by the hydroxyl or partially amine groups [1], which are responsible for the reaction with isocyanates [2]. Polyester polyols represent the second most important group (besides polyether polyols) with around 18 % of the polyols global usage [3]. The polyurethane materials obtained with the use of polyester polyols are less resistant to hydrolysis compared to the polyether polyols. However, it makes them more favorable due to the biodegradability [4–6]. Polyurethanes based on the polyester polyols have better thermal and fire resistance than the polyether-based PUR and superior solvent resistance. The greatest value of polyester polyols application is the polyurethane elastomers (ca. 43 %), flexible foams (ca. 15-18 %), adhesives, coating, etc.. Furthermore, polyesters give major possibilities to the biorenewable PUR material obtaining [3].

Currently, readily accessible are the bio-components which allow producing polyester polyols even in 100% consisting from bio-resources [7]. One of the most important bio-based monomer for the polyester polyols synthesis is the succinic acid (SA), which consists of the C4 building blocks [8]. Commercially available are also glycols, which constitute second monomer taking part in the two-step

polycondensation reaction during polyester polyols preparation. Bio-based glycol with the highest global usage and the first widely available in the industry, represent 1.3-propanediol (PDO) (Susterra, DuPont) [9]. Other bio-based glycols commonly available constitute also bio-based 1.4-butanediol (bio-BDO) and ethylene glycol (bio-EG). Currently, the research on the bio-based 1.6-hexanediol (bio-HDO) and adipic acid (bio-AA) are carried out [10–12]. The various type of the impurities which occurrence at the bio-based substrates compared to corresponding petrochemical-based substrates for polyols synthesis can lead to the different reaction mechanism and in the sequel – different product properties. So, it is necessary to find the contaminants impact on the synthesis pathways, mechanical and thermal properties of the fully bio-based polyols.

One of the most important information about polyesters is their thermal stability and phase transition temperatures. This characteristic gives information about the promising behavior of the polyester during processing. Papageorgiou and Bikiaris [13] carried out the comparative study about crystallization and melting behavior of three polyesters based on the succinic acid, namely, poly(ethylene succinate), PES, poly(propylene succinate), PPS and poly(butylene succinate), PBS. All measured polymers revealed the same molecular weight. They indicated that the slowest crystallization rate and the lowest crystallinity degree, among these polyesters, exhibited poly(propylene succinate). The results of the differential scanning calorimetry allowed to find the equilibrium melting points of PES, PPS, and PBS at 114, 58 and 133.5^{o}C. A lower melting point confirmed superior promising behavior during industrial processes for poly(propylene succinate), where the higher melting points for PES and PBS limited their practical application. Another thermal property with high impact on the polyesters practical employment is glass transition temperature. Bikiaris et al. [14] indicated that the highest glass transition temperature exhibited PES at ca. -11^{o}C, where the PPS and PBS exhibited this temperature at ca. -35^{o}C and -44^{o}C, respectively. Similar results have been obtained also by the Qiu and co-workers [15] and Liu at al. [16]. Chrissafis and co-workers [17] measured thermal decomposition temperature of the poly(propylene succinate) by thermogravimetric measurements. In the results, PPS revealed a very high thermal stability, which confirmed the thermal decomposition temperature at 404^{o}C. The same researchers indicated that PES and PBS decomposed at 413 and 399^{o}C, respectively [18]. This temperature can be compared to the degradation temperatures of the aromatic polyesters and they are higher than thermal decomposition temperatures of other aliphatic polyesters.

Due to thermal degradation stability measurements prepared with various conditions, the thermal degradation kinetics can be determined. There are some methods which allow measuring the kinetics of the thermally activated reactions. The first method which allows for determining the activation energy E_a during thermal decomposition is the Kissinger's method [17]. This method makes it possible to determine the activation energy E without the precise knowledge about the mechanism of the reaction in accordance with the equation (1):

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{RT_p} + const \qquad (1)$$

Where: β – heating rate (^{o}C/min), T_p – temperature corresponding to the inflection point (maximum reaction rate) of the thermal degradation curves (^{o}C), R – gas constant (8.314x10^{-3} kJ mol^{-1} K^{-1}).

Activation energy E of the decomposition can be also calculated by the isoconventional method of Ozawa, Flynn, and Wall (OFW). This method assumes that the conversion function f(α) stay constant for all values of conversion α with the alteration of the heating rate β. This method consists of temperature measurements, which are attributable to the constant value of conversion α from experiments carried out at different heating rate β. Plotting ln(β) against 1/T according to the equation (1) allows determining the activation energy E. After Arrhenius equation implementation, taking into account the constant heating rate and conducting mathematical transformations, the equation (2) takes a form of equation (3).

$$\ln(\beta) = \ln(\frac{Af(\alpha)}{\frac{d\alpha}{dT}}) - \frac{E}{RT} \quad (2)$$

$$\ln(\beta) = -1{,}0516\frac{E}{RT} + const \quad (3)$$

Where: β – heating rate (°C/min), A – pre-exponential factor, that is assumed to be temperature-independent, f(α) – conversion function, α – conversion value, T – temperature (°C), R – gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}).

Ozawa, Flynn and Wall plot should give the straight lines which slope is proportional to the activation energy (-E/R). The existence of the single-step reaction can be verified if the determined activation energy E is the same for the different α conversion values. When the activation energy E increases with the increase of the conversion degree, the complex reaction mechanism can be confirmed [17–19].

Ozawa, Flynn and Wall method requires knowledge of probable conversion function, f(α) during decomposition reaction. There are a lot of kinetics models of conversion function, f(α). The most used are presented in Table 1.

Table 1 Mathematical form of preselected kinetic models describing the degradation process [20].

Model	Symbol	Conversion function, f(α)
1st order reaction	F1	$(1-\alpha)$
nth order reaction	Fn	$(1-\alpha)^n$
nth order reaction with autocatalysis	Cn	$(1-\alpha)^n(1+K_{cat.}\alpha)$
Johnsos-Mehl-Avrami	JMA	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
2D growth of nuclei (Avrami)	A2	$2[-\ln(1-\alpha)^{1/2}](1-\alpha)$
3D growth of nuclei (Avrami)	A3	$3[-\ln(1-\alpha)^{2/3}](1-\alpha)$
nD nucleation (Avrami-Erofeev)	An	$n[-\ln(1-\alpha)^n](1-\alpha)$
1D diffusion	D1	$1/2\alpha$
2D diffusion	D2	$1/[-1(1-\alpha)]$
3D diffusion (Jander)	D3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$
3D diffusion (Ginstling-Brounshtein)	D4	$3/2[(1-\alpha)^{-1/3}-1]$
Prout-Tompkins equation	Bna	$(1-\alpha)^n\alpha^n$

For linear polyesters, the most used models are F1, Fn, Cn, and Bna [21,22].

In cases where some uncertainty over baselines of the thermal analysis data exists or where the accuracy of determination of transformation rates is limited, model-free type of degradation kinetics study are preferred than methods with the necessity of kinetics models knowledge. Model-free isoconversion methods are the most reliable methods for the calculation of activation energies of thermally activated reactions [22,23]. Ozawa, Flynn, and Wall developed also a model-free method for degradation kinetics study with the use of TG data [24]. This isoconversional method uses the following equation (4):

$$\ln(\beta) = \ln(\frac{AE_{app}}{Rg(\alpha)}) - 0.4567\ \frac{E_{app}}{RT} - 2.315 \quad (4)$$

Where: g(α) is the integral reaction model and E_{app} is the approximate activation energy. At each fixed degree of conversion α, plotting log β against 1/T creates linear trends. The slope of the plot's best-fit line is proportional to the approximate activation energy, according to the relation (5):

$$\text{slope} = -0.4567\ \frac{E_{app}}{R} \quad (5)$$

The error approximate activation energy can surpass even 10 %, depending on the value of E_{app}/RT. So, it is necessary to clarify this method to improve accuracy through a reevaluation accordingly with steps described in [24].

It is well-known that the thermal degradation kinetics can be affected by the amount of the catalyst used during synthesis, the chemical structure of the catalyst and monomers [25,26], monomer concentration, by the decomposition temperature [22], average molecular weight and the amount and chemical structure of the end group [27]. Chrissafis et al. [21] investigated the thermal degradation kinetics of the biodegradable polyesters: poly(propylene sebacate) (PPSeb) and poly(propylene azelate)

(PPAz) with the use of two main methods: Friedman and Ozawa, Flynn, and Wall (OFW). Researchers indicated that both of polyesters revealed differences in the energy activation of the thermal degradation. They verified highest energy activation value for poly(propylene sebacate). Moreover, based on the thermal degradation kinetics results they indicated that both polyesters are characterized by complex decomposition reaction mechanisms. The same researchers studied thermal degradation kinetics of the poly(propylene sebacate) nanocomposites with the use of Friedman [23] and Kissinger methods [28]. They investigated that the addition of nanoparticles enhances the thermal stability of the nanocomposites, the beginning of degradation is more difficult than in pure PPSeb but it progresses in a similar way. With the use of TG-GC/MS coupled method, they also proposed probable degradation reaction mechanism with released gasses analysis. Bikiaris et al. [22] explored the catalyst amount influence on the biodegradable poly(propylene succinate) thermal stability and mechanism of the decomposition reaction. They prepared sample largely based on petrochemical sources and used tetrabutyl orthotitanate (TBT) as a catalyst in three different amount as a succinic acid equivalent (which indicates other synthesis conditions than described in this work). It was shown that poly(propylene succinate) thermal decomposition takes place in two stages, indicating the existence of at least two decomposition mechanisms. The catalyst amount has not impact on the overall decomposition mechanism but increases the rate of poly(propylene succinate) decomposition. Chrissafis and co-workers [29], in their another work, analyzed the impact of the molecular weight of the poly(ethylene succinate) on the thermal degradation mechanism. They concluded that the molecular weight of polyesters achieved during polycondensation is strongly related to thermal stabilities of initial oligomers. Degradation of samples with low molecular weight is more complex that of polyesters having high molecular weights. For the kinetic description of the mass loss of all samples three different mechanisms must be used. The first corresponds to a very small mass loss, the second for the main degradation stage and the third—at elevated temperatures—that has the lowest rate is due to the decomposition of very small mass. These stages are attributed to different decomposition mechanisms and activation energies. The values of the activation energy for the two groups of samples—with different molecular weight—are similar, regarding the first two mechanisms, while there is an alteration in the case of the third mechanism.

Currently, there are available apparatuses which allow proposed a probable mechanism of the polymer thermal degradation based on the release gasses analysis. One of the methods is a DSC-TG/QMS coupled method. A mass spectrometer, additional equipment to thermal degradation analyzers, make it possible to release gasses analysis during the test. Furthermore, thermogravimetric analysis extended by GC/MS detector also allow for degradation mechanism determination. Chrissafis and co-workers [21,28] elucidated the thermal degradation kinetics mechanisms of PPSeb and PPAz with the use of TG-gas chromatography-mass spectrometry system. They determined that the main thermal degradation reaction products are 2-propenal, 2-propenol, 3-hydroxypropanal, and 1,3-propanediol, which were detected at low retention times. Sebacic and azelaic acids as well as, their allyl and diallyl compounds were also detected, at higher retention times.

In the present work, series of the linear bio-based aliphatic polyester polyols were synthesized with the use of two-step polycondensation method. The thermal decomposition characteristic was described to find out the catalyst impact on the thermal decomposition kinetics, which was determined by using Ozawa, Flynn and Wall and Kissinger method. Moreover, DSC-TG/QMS coupled method allowed proposed probable mechanism of thermal decomposition study with released gasses analysis. The obtained poly(propylene succinate)s were also characterized by structure analysis with the use Fourier Transform Infrared Spectroscopy and Proton Nuclear Magnetic Resonance, which results were presented in our previous article [30].

2. MEASUREMENTS

2.1. Materials

Bio-based succinic acid (SA) (solid, molecular weight: 118.09 g/mol, purity: 98-100%, relative density at 20°C: 0.900 g/cm^3) used in this study was obtained from BioAmber Sarnia Inc. (Ontario, Canada). Susterra Propanediol (1.3-propanediol) (liquid, molecular weight: 76.09 g/mol, purity: 99.98%, water content by Karl Fischer: 12.1 ppm, relative density at 20°C: 1.053 g/cm^3, dynamic viscosity at 20°C: 52 mPas) was obtained from DuPont Tate&Lyle Corporation Bio Products (Loudon, Tennessee, USA). Tetraisopropyle orthotitanate, Ti(O-i-Pr)$_4$ (TPT) (liquid, molecular weight: 284.22 g/mol, purity: 97%) was used as a catalyst with four different amount. The catalyst was purchased from TCI Chemicals (India). All other materials and solvents used for the analytical measurement methods for prepared bio-based polyester polyols characterization were of analytical grade.

2.2. Bio-based polyesters synthesis

Aliphatic bio-based polyester polyols were prepared with the use of dicarboxylic acid, which was succinic acid, and glycol, which was 1.3-propanediol. Both used components were of a natural origin. Catalyst was used in different amounts, namely, 0.10 wt% (PPS-0.10), 0.15 wt% (PPS-0.15), 0.2 wt% (PPS-0.20), 0.25 wt% (PPS-0.25) and 0.30 wt% (PPS-0.30). The catalyst mass was calculated as a glycol equivalent. Poly(propylene succinate) was also prepared without catalyst employment (PPS-0.00). All linear bio-based polyester polyols were synthesized in the bulk by two-step polycondensation method (esterification and polycondensation) (Figure 1 in reference [30]). The first step was represented by the esterification reaction between a succinic acid (SA) and 1.3-propanediol (PDO). Glycol was always used with an excess. The molar ratio SA:PDO was determined considering the final molar mass expected after full polycondensation (approximately number average molecular weight: Mn = 2000 g/mol and functionality: f = 2). Both of the steps were carried out in the glass reactor, which consisted of three neck flask equipped with nitrogen/vacuum inlet, mechanical stirrer, thermometer, and condenser. The glass reactor was placed into a heating mantle. The first step of the reaction was carried out under a nitrogen atmosphere. Succinic acid and 1.3-propanediol mixture (without catalyst) were stirring at 140°C and kept at this temperature, until water elimination (application for patent in the Polish Patent Office, no. P.418808). After the water distillation, the second step, which was the main polycondensation reaction, was carried out. The nitrogen was stopped, the appropriate amount of catalyst was added to reaction mixture and the temperature was increased up to 160°C under reduced pressure. During

polycondensation, the acidic number was measured. After achieving the value of the acidic number ca. or preferably below 1 mg KOH/g, the polycondensation was finished.

2.3. Polymer characterization

2.3.1. Acidic and hydroxyl number

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

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

2.3.2. Dynamic viscosity

Dynamic viscosity measurements were performed with the use of rotary rheometer R/S-CPS+ produced by Brookfield Company, USA. The viscosity values at 80^{o}C were defined with the use of computer program Rheo3000. Measurements were conducted with controlled shear rate (CSR). Justification of choice the temperature is occurring temperature ranges in some industrial processes.

2.3.3. Thermal analysis

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 700^{o}C at various rates: 5, 10, 15 and 20^{o}C/min and under continues helium flow. Under these conditions, the DSC-TG experiments of bio-based polyester polyols were sufficiently reproducible.

Released gases were analyzed on 403 Aeolos quadrupole mass spectrometry (QMS) module coupled on-line to the STA instrument (NETZSCH-Feinmahltechnik GmbH, Germany). 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. For qualitative analysis of released gases Multiple Ion Detection (MID) mode was used. Based on the obtained results the main products of the prepared bio-based polyols thermal decomposition were identified.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of the obtained poly(propylene succinate)

All prepared polyester polyols were synthesized with the use of well-known two-step polycondensation method. The first step was the esterification reaction, which was conducted for 10 hours for all of the prepared polyester polyols without catalyst used. It was ordered due to the fact that

the water, a by-product formed during the esterification reaction, revealed higher purity than water from esterification conducted with the use of a catalyst. After water removal, the catalyst was added. The second step, which was the main polycondensation reaction, was carried out by individual time for all synthesized polyesters until achievement the acid number ca. or preferably lower than 1 mg KOH/g. Justification of choice the end-point of the polycondensation reaction was the carboxyl end-group value due to the acid number occurring in some synthetic polyester polyols commonly used in the polyurethane industry. Table 2 shows properties of the prepared polyols.

Table 2 Properties of the prepared polyester polyols.

POLY-(PROPYLENE SUCCINATE)	CATALYST CONTENT [wt.%]	REACTION TIME [h]	ACID NUMBER [mg KOH/g]	HYDROXYL NUMBER [mg KOH/g]	VISCOSITY [80°C, Pas]
PPS-0.00	0	180	1.16	44.60	100*
PPS-0.10	0.10	45	0.97	64.20	4.37
PPS-0.15	0.15	26	0.84	50.41	6.18
PPS-0.20	0.20	25	0.75	72.90	8.85
PPS-0.25	0.25	18	0.83	51.50	3.43
PPS-0.30	0.30	20	0.91	74.90	2.88

* Viscosity was measured at 90°C

The series of the conducted synthesis allow for determining the catalyst amount which led to a resulted product with the most akin to designed properties. It was determined based on the lowest acid value obtaining in the shortest time. Moreover, this bio-based polyol should be characterized by one of the lowest viscosity values. Based on these assumptions, the 0.25 wt.% and 0.30 wt.% of the catalyst as glycol equivalent results in the best polycondensation reaction condition [30].

3.2. Thermal degradation kinetics

The first method which was used to thermal degradation kinetics determination was Kissinger's method. This model allows determining the activation energy without precise knowledge about the reaction mechanism. With the known temperatures of the inflection point according to the maximum reaction rate of the thermal degradation curves received at different heating rates, the Kissinger's model can be calculated. Table 3 presents the results of the thermal degradation kinetics determined by Kissinger's method. The plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for all synthesized polyesters are given in Figure 1. The correlation coefficient ranged from 0.8925 to 0.9937.

Table 3 Activation energy of the prepared poly(propylene succinate)s determined by Kissinger's method.

Poly(propylene succinate)	Activation energy by Kissinger's method, [kJ/mol]	Correlation coefficient, R^2
PPS-0.00	149.3	0.9561
PPS-0.10	126.0	0.9741
PPS-0.15	180.1	0.8925
PPS-0.20	180.2	0.9844
PPS-0.25	188.3	0.9937
PPS-0.30	179.5	0.9679

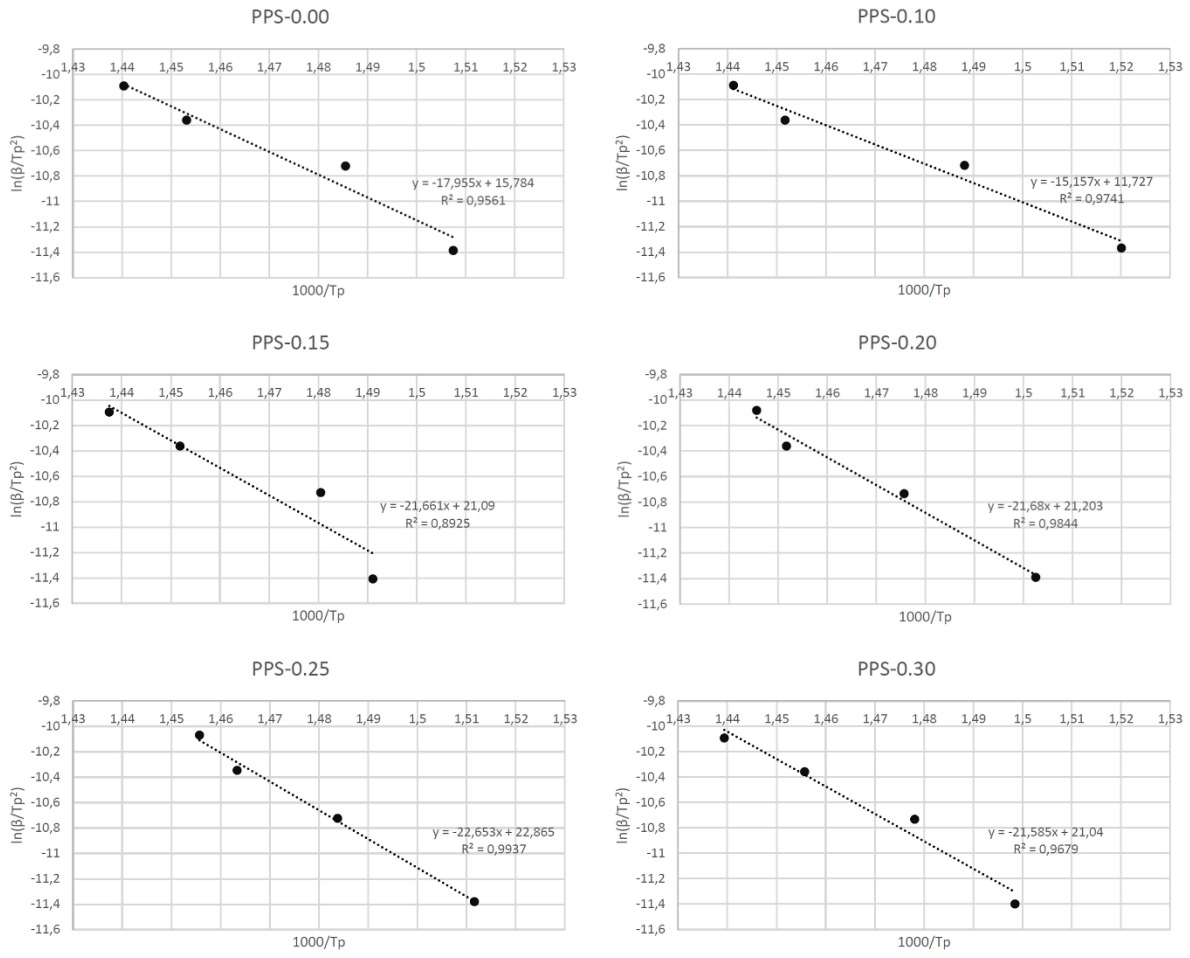


Figure 1 Kissinger plots of synthesized polyesters.

The highest activation energy, E_a with the highest correlation coefficient, characterized polyester PPS-0.25 (188.3 kJ/mol). The obtained results attest to the best thermal stability for this material. Other prepared bio-based polyester polyols degraded at lower activation energy values. Moreover, the increasing catalyst amount led to the highest E_a excepted for PPS-0.10 and PPS-0.30. Sample PPS-0.10 revealed the lowest activation energy, 126.0 kJ/mol, from all prepared bio-based polyester polyols. The results are related to the macromolecular structure and polydispersity of the polyol. Polydispersity

delineated molecular mass distribution, therefore, polyols with a high value of polydispersity can degrade when lower activation energy was provided. Figure 2 presents the dependence of the activation energy (E_a) on the relative extent of degradation (mass conversion) (α), as calculated with Kissinger method.

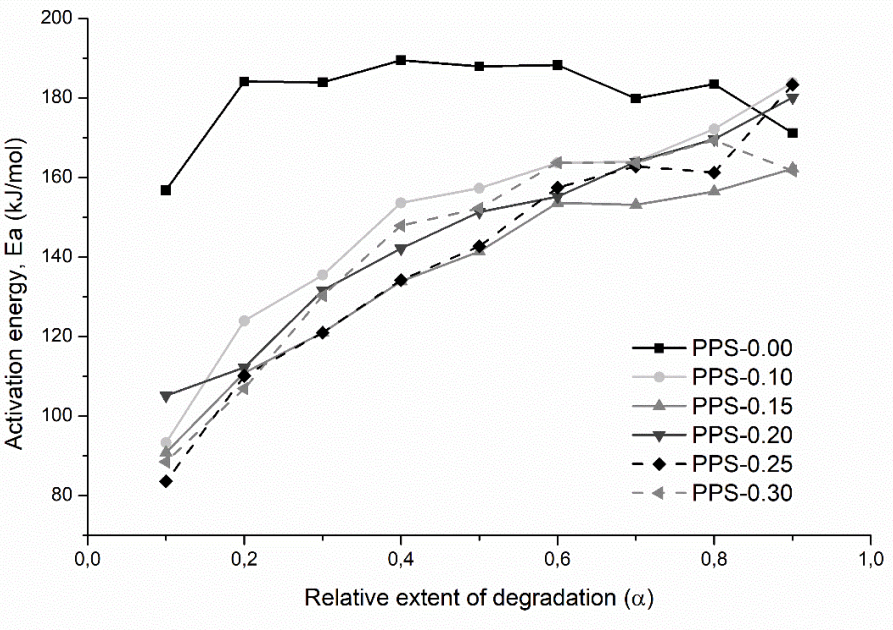


Figure 2 Dependence of the activation energy (E_a) on the relative extent of degradation (α), as calculated with Kissinger method.

From Figure 2, the dependence of the mean value of the calculated E_a on mass conversion α can be observed. This dependence can be separated into three and two distinct regions for PPS-0.00 and PPS-0.30, respectively, and one, approximately linear curve course for the other prepared polyester polyols. For the PPS-0.00 sample, in the first region, till α=0.2, a small increase of the activation energy is observed, while in the second one, for 0.2<α<0.8, the activation energy can be considered as having a constant value. In the third region for α>0.8, a small increase of the activation energy is observed. For the PPS-0.30 sample, in the first region, till α=0.8, a small increase of the activation energy is shown, while in the second one, for α>0.8, a small decrease of the activation energy is presented. For samples PPS-0.10, PPS-0.15, PPS-0.20 and PPS-0.25 an increase of the activation energy are observed on the all relative extent of degradation (α). The results indicate that activation energy increased with the increase of the conversion degree which confirmed the complex degradation reaction mechanism.

In this article model-free Ozawa, Flynn and Wall method was used for activation energy verification with Kissinger method results. Figure 3 presents the obtained plots of synthesized polyesters. Moreover, Figure 4 shows the dependence of the activation energy (E_a) on the relative extent of degradation (α), as calculated with Kissinger and OFW methods for three from prepared polyols. The comparison confirmed similarity at the curve courses for all plots. The activation energy determined by OFW method revealed higher values than obtained with the use of Kissinger method, what is also visible in Table 4 and 5.

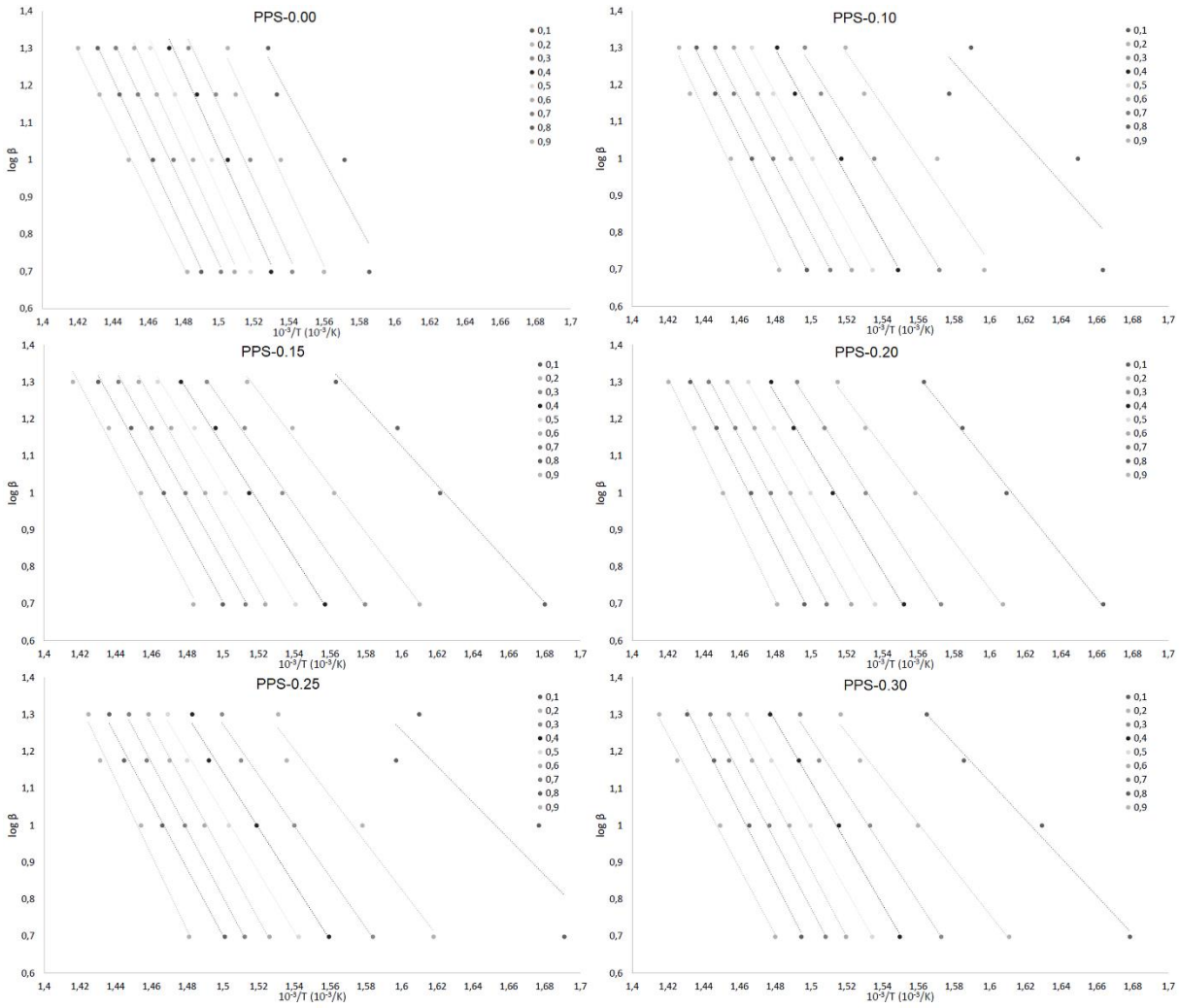


Figure 3 Ozawa, Flynn and Wall plots of synthesized polyesters.

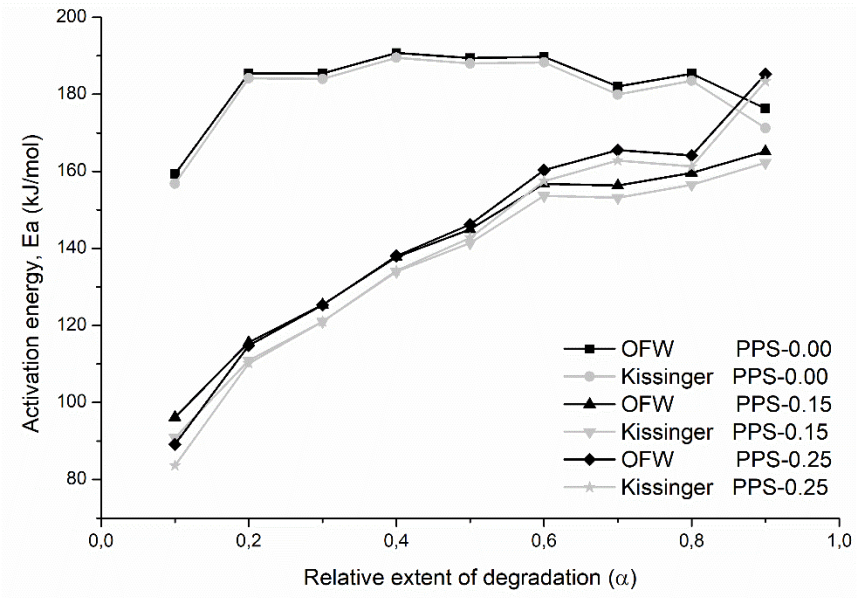


Figure 4 Dependence of the activation energy (E_a) on the relative extent of degradation (α), as calculated with Kissinger and OFW methods for three from prepared polyols.

Table 4 Activation energy of polyols thermal degradation determined by Kissinger method.

relative extent of degradation (α)	Poly(propylene succinate)					
	PPS-0.00	PPS-0.10	PPS-0.15	PPS-0.20	PPS-0.25	PPS-0.30
	E_a [kJ/mol]					
0.1	156.8	93.3	90.9	105.1	83.6	88.5
0.2	184.1	124.0	110.9	112.2	110.2	106.9
0.3	184.0	135.5	121.0	131.7	121.0	130.3
0.4	189.5	153.6	133.9	142.2	134.2	147.9
0.5	188.0	157.3	141.4	151.4	142.7	152.3
0.6	188.3	163.7	153.7	155.2	157.5	163.7
0.7	179.9	164.0	153.1	164.0	162.8	163.7
0.8	183.5	172.2	156.5	169.6	161.3	169.4
0.9	171.2	183.9	162.2	180.1	183.3	161.7
E_a	149.3	126.0	180.1	180.2	188.3	179.5

Table 5 Activation energy of polyols thermal degradation determined by Ozawa, Flynn, and Wall method.

relative extent of degradation (α)	Poly(propylene succinate)					
	PPS-0.00	PPS-0.10	PPS-0.15	PPS-0.20	PPS-0.25	PPS-0.30
	E_a [kJ/mol]					
0.1	159.3	98.5	96.1	109.8	89.1	93.9
0.2	185.4	128.8	115.6	116.8	114.8	111.8
0.3	185.4	139.1	125.4	135.5	125.3	134.2
0.4	190.7	156.5	137.8	145.6	138.0	151.1
0.5	189.4	160.1	145.0	154.5	146.2	155.4
0.6	189.7	166.2	156.7	158.7	160.3	166.3
0.7	182.0	166.6	156.3	166.6	165.5	166.4
0.8	185.3	174.5	159.6	172.1	164.1	171.9
0.9	176.3	185.7	165.2	182.2	185.2	164.2
E_a	152.7	130.5	182.0	182.1	189.7	181.4

All prepared bio-based polyester polyols characterized activation energy higher than 100 kJ/mol. The highest E_a, 188.3 and 189.7 kJ/mol, by Kissinger and OFW, respectively, revealed poly(propylene succinate) prepared with 0.25 wt.% catalyst employment. Both thermal degradation kinetics methods confirm that the lowest value characterized PPS-0.10. Conducted investigation allowed determining the impact of the catalyst amount on the thermal degradation kinetics of the obtained materials.

3.3. Released gases analysis

The extensive literature review allowed proposing probable degradation reaction mechanisms for fully bio-based poly(propylene succinate)s synthesized with different catalyst employment. Based on the articles such researchers as Papageorgiou, Bikiaris, Chrissafis, Paraskevopoulos and other cited in this work, 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. Figure 5 presents the most probable mechanism for poly(propylene succinate) thermal degradation proposed according to the literature review information. The first reaction is 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 ester group –CO-O- and $–CH_2$- group from glycol. Thermal degradation reactions in the poly(propylene succinate)s macromolecules can lead to such products obtaining as 3-hydroxypropanal, 2-propenal, 2-propen-1-ol, allyl-succinic acid compounds, succinic acid and propylene glycol and its derivatives. There are also produced low molecular weight compounds as water and carbon dioxide [21,28].

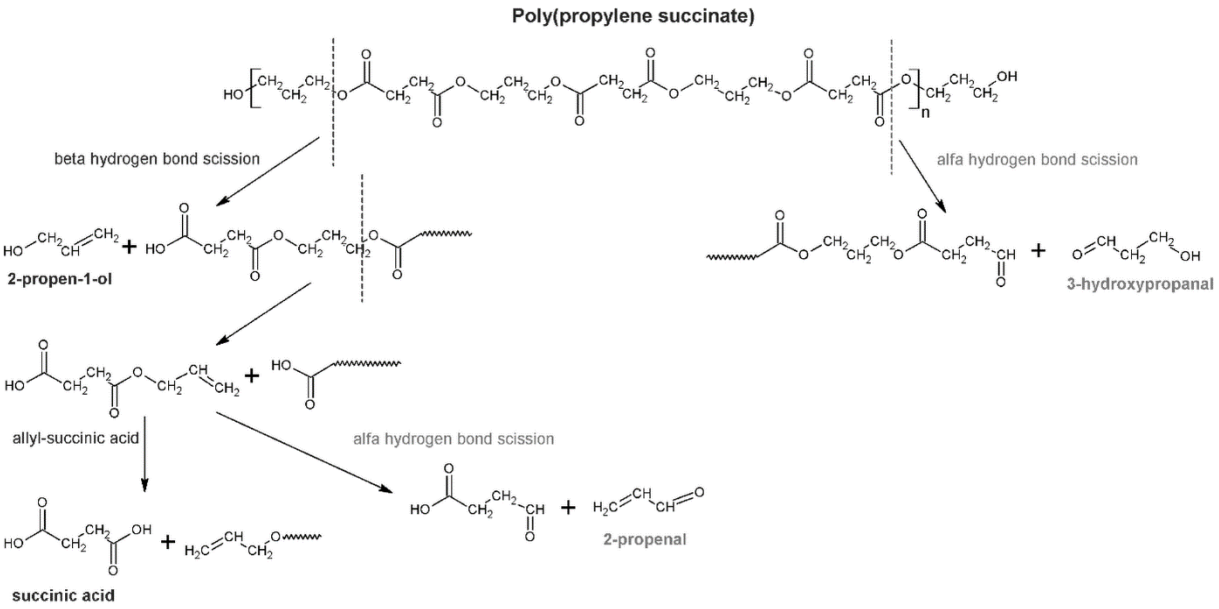


Figure 5 Probable mechanism of poly(propylene succinate) thermal degradation reaction.

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. During the measurements, the mass/charge (m/z) ratio was recorded in the range from 2 to 100 amu. The analysis allow discovered characteristic peaks which occurred for the different mass/charge (m/z) ratio. These peaks are typical for the ions arisen during measurement. They were characterized by similar curve courses which identified the representative mass spectrum for each of thermal degradation products. The results were compared with the mass spectra of the pure compounds proposed as thermal degradation products with the use of NIST database [31].

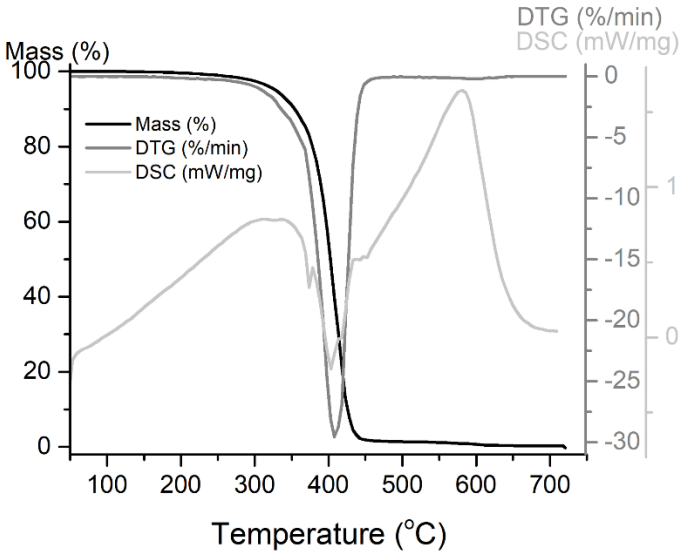
The exemplary graphs with the obtained peaks from the released gasses mass spectrometry are presented in Figures 6-8. For more comprehensive interpretation of the results, the TGA, DTG and

DSC curves obtained for polyol PPS-0.25 at 20 K heating rate under nitrogen flow were added. Figure 6 presents the dependence of the ion current intensity and temperature for characteristic ions for water, H_2O. The most intensive peaks characteristic for mass spectra at 16, 17, 18 and 19 mass/charge (m/z) ratio are appeared at ca. 400^{o}C which is thermal degradation temperature. There is also visible little peak for all presented m/z ratios at ca. 100^{o}C attributed to the boiling point of water residue which should be eliminated during synthesis. This step is not visible on the TGA and DTG curves.

Figure 7 shows the QMS spectra of carbon dioxide CO_2. Based on the NIST database, the primary m/z ratios for this compound should be at 12, 16, 22, 28, 29, 44, 45 and 46 amu. In the figure, there are visible differences in the curve courses. It is related to the peaks overlapping derived from other degradation products. The most similar curve courses characterized at 12, 22, 44, 45 and 46 revealed two peaks at ca. 400 and 600^{o}C. The second temperature is attributed to the burning temperature emitted during measurement gases.

The next figure presents the dependence of the ion current intensity and temperature for succinic acid identified as one from thermal degradation products (Figure 8). The characteristic ions should gave peaks at 14, 18, 19, 26, 27, 28, 29, 30, 36, 42, 45, 46, 53, 55, 56, 57, 72, 73, 74, 100 amu. Due to the peaks overlapping, there are two characteristic similar curve courses at 56 and 100 m/z ratios. Table 6 accumulates the obtained results from the QMS measurements for all identified thermal degradation products with possible ions determination.

Conducted measurements allowed confirming the proposed thermal degradation mechanism where the probable gases were released. The measurements affirmed that fully bio-based polyols can degrade at thermal decomposition experiments with the same mechanism as petrochemical substitutes.



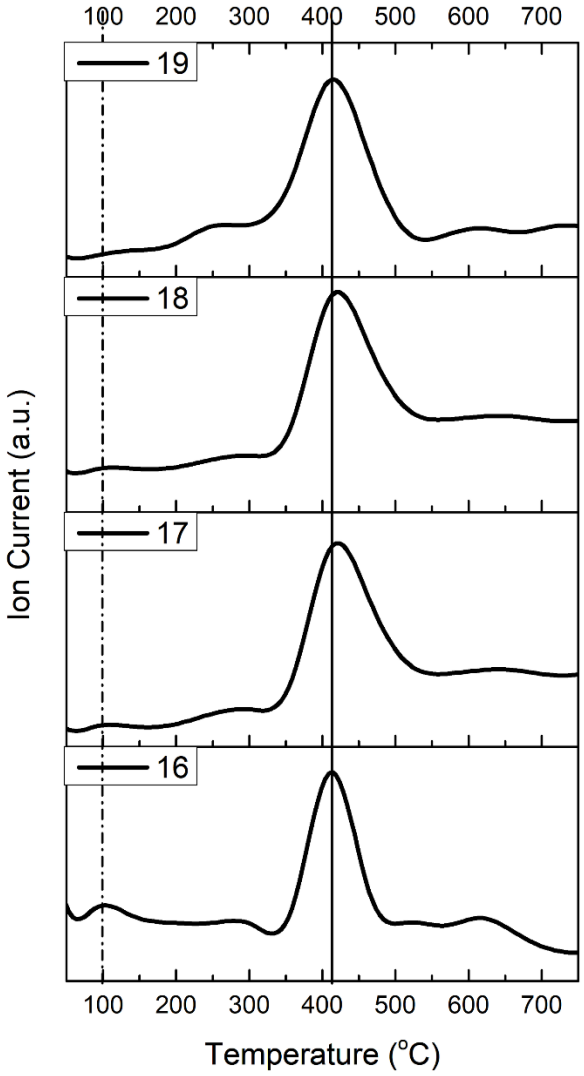
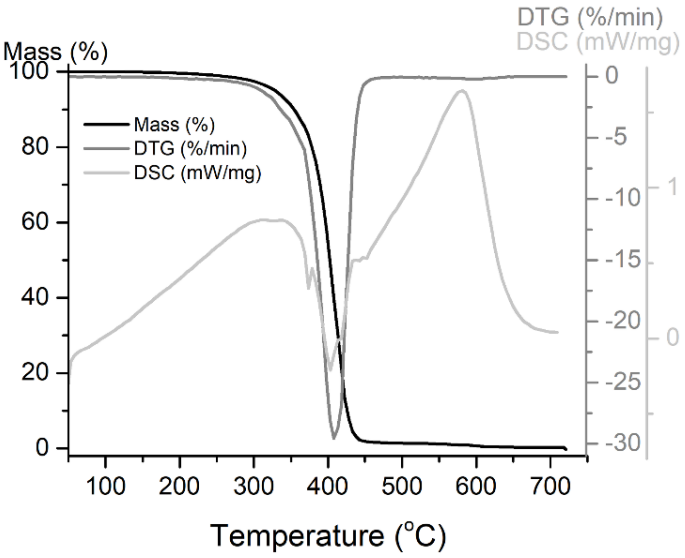


Figure 6 QMS spectra of water as a thermal degradation product.



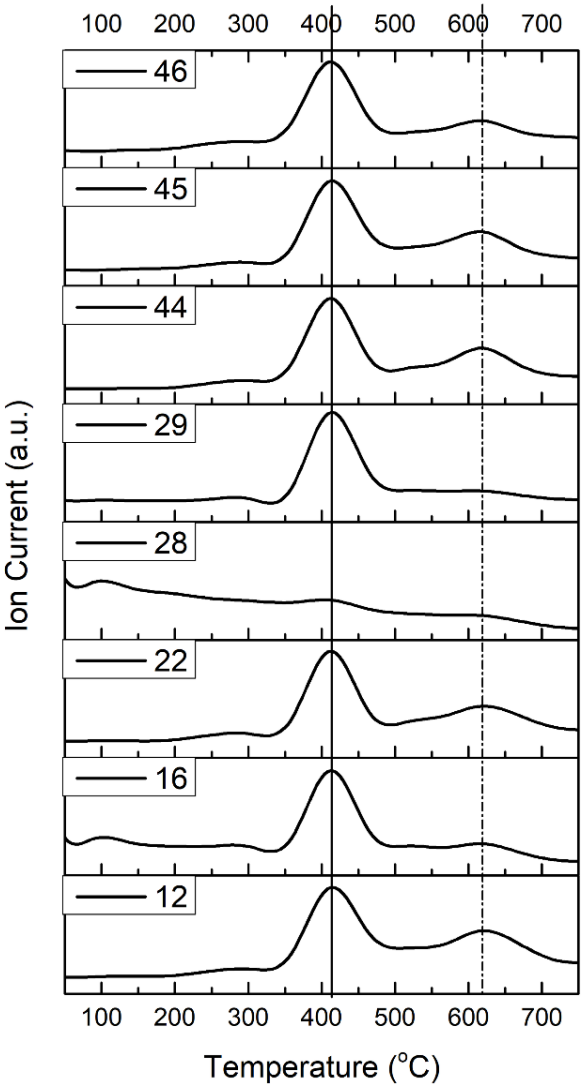
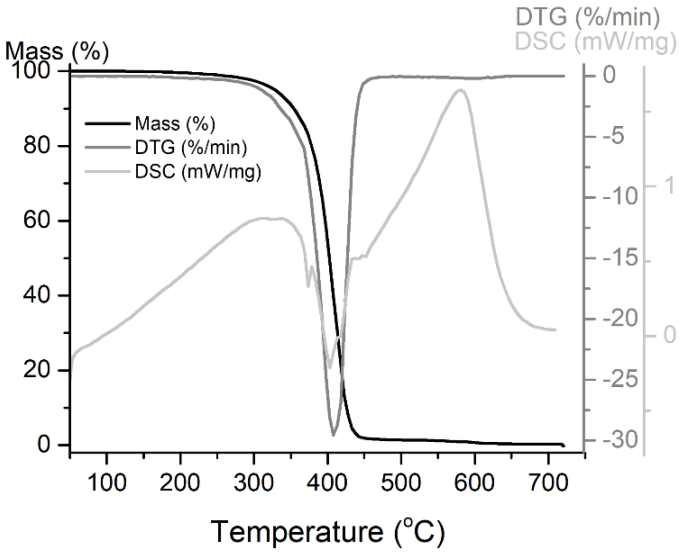


Figure 7 QMS spectra of carbon dioxide as a thermal degradation product.



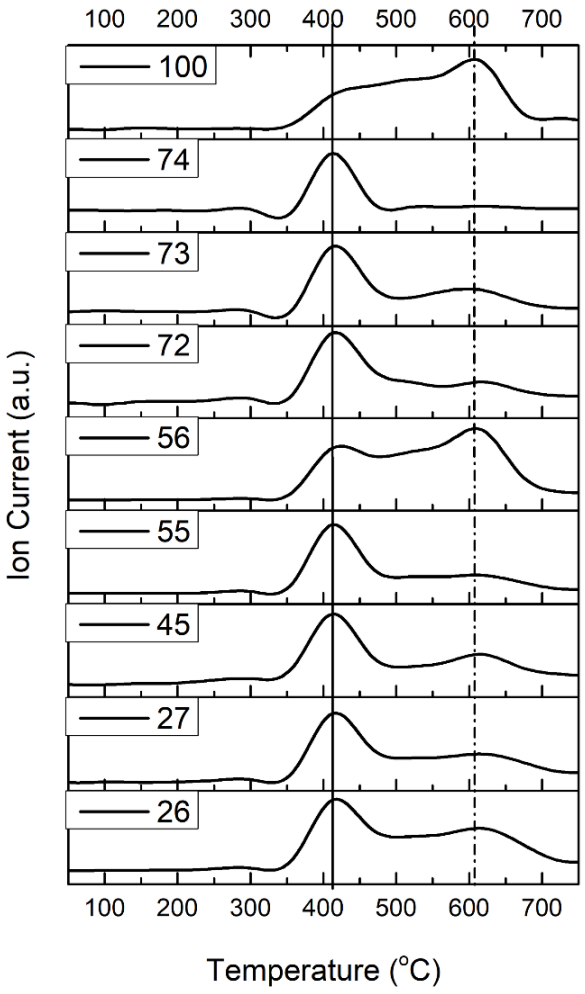


Figure 8 QMS spectra of succinic acid as a thermal degradation product.

Table 6 Degradation products identified by QMS during bio-based poly(propylene succinate) degradation under an inert atmosphere.

Possible compounds	Peak (m/z)	Possible ions
Water, H_2O	**16, 17, 18**, 19	H_2O (18), OH^- (17), H_3O^+ (19)
Carbon dioxide, CO_2	**12, 16**, 22, **28**, 29, **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, 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), $C_3H_7^+$, $CH_3C{=}O^+$ (43), $C_2H_4O^+$ (44), $C_3H_3O^+$ (55), $C_3H_4O^+$ (56)
2-propenal, C_3H_4O	14, 16, 24, **25, 26, 27, 28, 29, 36, 37, 38**, 39, 40, 52, 53, 55, **56, 57**	CH_4 (16), $C_2H_3^+$ (27), C_2H_4 (28), $C_2H_5^+$ (29), $C_3H_4O^+$ (56), $C_3H_5O^+$ (57)
1,3-propanediol, $C_3H_8O_2$	14, 15, 18, 25, **26, 27, 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), $CH_3C{=}O^+$ (43), $C_3H_5O^+$ (57), $C_3H_6O^+$ (58), $C_3H_7O^+$ (59)
Succinic acid, $C_4H_6O_4$	14, 18, 19, **26, 27,** 28, 29, 30, 36, 42, **45,** 46, 53, **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)

CONCLUSION

The series of the linear bio-based polyester polyols were synthesized with planned molecular structure and functionality. The designed poly(propylene succinate)s were characterized by number average molecular weight ca. 2000 g/mol and functionality, which was 2. The chosen properties were created in accordance with the requirements of the thermoplastic polyurethane industries. The extensive thermal stability measurements and thermal degradation reactions were investigated. Determined activation energy affirmed impact of the catalyst amount on the bio-based polyester polyols thermal decomposition. The highest value characterized poly(propylene succinate) synthesized with the use of 0.25 wt.% catalyst, 188.3 and 189.7 kJ/mol, by Kissinger and OFW, respectively. During measurements, the release gasses were detected with the use of mass spectrophotometry. Conducted measurement allowed exploring impact of the catalyst employment during synthesis on the thermal characteristics of the resulted bio-based polyester polyols. Moreover, the proposed mechanism of the thermal degradation was confirmed by released gasses analysis. Investigation affirmed alfa and beta hydrogen bond scissions occurrence during thermal degradation. Identified gas products are 2-propenal, 2-propen-1-ol, allyl-succinic acid compounds, succinic acid and propylene glycol and its derivatives. There are also produced low molecular weight compounds as water and carbon dioxide.

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