Post-print of: Parcheta P., Datta J.: Structure-rheology relationship of fully bio-based linear polyester polyols for polyurethanes - Synthesis and investigation. POLYMER TESTING. Vol. 67, (2018), p. 110-121. DOI: 10.1016/j.polymertesting.2018.02.022

Structure-rheology relationship of fully bio-based linear polyester polyols for polyurethanes - synthesis and investigation

Paulina Parcheta[1], Janusz Datta[1,*]

[1] Gdańsk University of Technology, Faculty of Chemistry, Department of Polymers Technology, G. Narutowicza St. 11/12, 80-233 Gdańsk, Poland

* Corresponding author (J. Datta): janusz.datta@pg.gda.pl

ABSTRACT: The synthesis of polyols from renewable substances as an alternative for petrochemical-based polyols play important matter in the polyurethane industry. In this work, the fully bio-based linear polyester polyols with different catalyst amounts were synthesized via two-step polycondensation method. The effect of various catalyst content on the structure and rheological behavior were established. Fourier Transform Infrared Spectroscopy, Nuclear Magnetic Resonance, Gel Permeation Chromatography and Matrix-Assisted Laser Desorption/Ionization Time-of-Flight mass spectrometry allowed confirming the impact of the catalyst amount during synthesis on the molecular structure of the resulted polyols. Through the hyphenation of these sophisticated polymer characterization techniques, information on the molecular weight distribution was obtained. Moreover, it was found that the obtained polyols are non-Newtonian fluids. According to conducted measurements, it was observed that the poly(propylene succinate)s prepared with the use of the 0.25 wt.% and 0.30 wt.% catalyst revealed the structures and selected properties the most akin to design.

KEYWORDS

Bio-based poly(propylene succinate); Macromolecular structure; Rheological behavior; MALDI-ToF mass spectrometry; Gel permeation chromatography.

1. Introduction

Currently, clearly visible is the growing interest of using biorenewables as a primary component at the polymer synthesis. This trend is determined by the unfavorable oil consumption forecasts when the increasing demand for the polymer materials utilization performs on the global market. Recently, the bio-components have become readily accessible which allow producing biopolymers, including polyester polyols even in 100% from bio-resources [1,2]. The biotechnological process consisting of the corn crops fermentation allow obtaining bio-based glycols and dicarboxylic acids. Such microorganisms as fungi, yeasts or bacteria [3–6] lead to the formation of the proper product during fermentation processes.

The major advantages which contribute to the increasing interest in the utilization of biorenewables in chemical syntheses [7] represent the reduction of energy consumption, the decrease of the greenhouse gasses production and CO_2 emission reduction. Moreover, the economic volatility reduction by the decrease in the fossil fuel stocks utilization and the decline in the production costs with increasing production scale made a contribution to develop the research on the biorenewables utilization.

The initial reaction, which leads to the polyester polyols obtainment, is a two-step polycondensation reaction. The first step constitutes the esterification or transesterification reaction between carboxylic acid or carboxylic acid esters, respectively, and the excess of the glycols. During the esterification, water or alcohols are formed, respectively, as by-products which hindered the main reaction. The capability of the by-product elimination from reaction mixture affected the reaction

kinetics and productivity. After the by-product elimination, second step – polycondensation reaction, can be started [8].

It is characteristic for this type of polycondensation to run at high temperatures, sometimes exceeding 200°C. However, the choice of temperature depends on the thermal stability of both substrates and the main product. The disadvantages of these methods are often the side reactions to which the oxidation reaction takes place. To prevent these reactions, polycondensation is carried out under inert gas (eg, nitrogen, argon) or under reduced pressure. In addition, the use of both reaction conditions facilitates the removal of the by-product from the reaction medium, thereby shifting the reaction to the main product. It is well-known that the reaction kinetics are also affected by the amount of the catalyst, the chemical structure of the catalyst and monomers, monomer concentration, by the temperature during both steps, reaction time, and removal rate of the low molecular by-products [9]. By manipulating these parameters, we can optimize the polycondensation process to accelerate the formation of the main product [10].

Among the industrial properties such as hydroxyl and acidic number and viscosity, the macromolecular structure has also a huge impact on the polyurethane synthesis and properties of resulted materials. Thereby, it is necessary to explore the macromolecular structure of the polyols before polyurethane material synthesis. Recently, the huge interest gained molecular weight distribution study with the use of Matrix-Assisted Laser Desorption/Ionization Time-of-Flight mass spectrometry [11–15]. This method allows obtaining information about absolute molecular weights, identification of mass-resolved polymer chains including intact oligomers, and simultaneous determination of end groups in a polymer sample. Many scientists have used this method to determine the molecular structure of the various type of polymers.

Król and Pilch-Pitera [16,17] used this method for structure investigation of urethane oligomers for polyurethane elastomers. The researchers used this method to proposed the majority of molecular structure presented in the materials. They affirmed that not all of obtained bands could be identified in this method but the GPC findings could be confirmed.

One of the most important properties which verify polyols possibility to industrial processes is their rheological behavior. Furthermore, rheology can inform about the dynamic viscosity of the fluids, which is important properties during preparation at the used temperature and pressure. The rheological behavior and viscosity are also connected with the structure of the polymer chains [18]. Proposed rheological models, as an optimal individual function, described the fluids rheological behavior. There is two primary behavior delineated the liquids, namely, Newtonian and non-Newtonian. The Newtonian model characterizes the ideal fluids, which performed linear curve course in the rheograms, which show the shear stress via shear rate (dynamic viscosity stay constant for all point of the curve). This model is described by the equation (1):

$$\tau = \eta * \gamma \quad (1)$$

Where: τ – shear stress [Pa], γ – shear rate [s^{-1}], η – viscosity [Pas].

Non-Newtonian fluids are described by a large number of models. This type of fluids does not show the linearity of the curve course in the rheograms. The non-Newtonian liquids exhibit the complex structure, and due to the various deformation effects, they can be characterized as pseudoplastic fluids, viscoplastic, dilatant or thixotropic liquids. There are several mathematical models which allow describing the information about the non-Newtonian fluids rheological behavior. There are three

mostly applied models: Herschel, Bulkley, Ostwald-de Waele and Bingham models [19]. For the test analysis, two of them will be characterized.

The Herschel, Bulkley model, describe the fluids with a nonlinear rheograms. The model is expressed by the equation (2):

$$\tau = \tau_0 + K * \gamma^n \quad (2)$$

Where: τ – shear stress [Pa], τ_0 – yield stress [Pa], γ – shear rate [s^{-1}], K – consistency index [-], which gives an idea of the fluid viscosity, n – flow behavior index [-], which should be similar to comparative study of the different fluids. The 'τ_0' and 'n' values give information about fluids behavior as follows:

$\tau_0 = 0$, $n = 1$ – means that the Herschel, Bulkley mathematical model describes the Newtonian behavior of the fluids;

$\tau_0 = 0$, $n > 1$ – the Herschel, Bulkley mathematical model describes the dilatant behavior (shear thickening);

$\tau_0 = 0$, $n < 1$ – the Herschel, Bulkley mathematical model describes the behavior of the pseudoplastic fluid (shear thinning);

$\tau_0 > 0$, $n = 1$ – the Herschel, Bulkley mathematical model describes the Bingham plastics, which are the fluids with the linear viscosity curve above the yield stress [19].

The Ostwald-de Waele describe the shear thinning fluids without a yield stress. The model is expressed by the equation (3):

$$\tau = K * \gamma^{(n-1)} \quad (3)$$

Where: τ – shear stress [Pa], γ – shear rate [s^{-1}], K – consistency index [-] gives an idea of the fluid viscosity, n – flow behavior index [-] which give information about fluids behavior as follows:

n < 1 – pseudoplastic,

n = 1 – Newtonian fluids,

n > 1 – dilatant fluids [19].

Schrock and co-workers [20] investigated the structure, thermal phase transition temperatures and viscosity of few polyester polyols prepared based on succinic acid, adipic acid and various glycols. Materials were synthesized with planned average molecular structure at ca. 1000 and 2000 Da. They explored that the poly(propylene succinate)s polyesters and co-polyester with other glycols revealed high viscosity even at elevated temperature. Schrock investigated that the viscosity value of pure poly(propylene succinate) at 80^{o}C revealed ca. 1000 mPas. Our work presents the impact of the catalyst employment during synthesis on the viscosity of poly(propylene succinate) and other properties.

In this work, the synthesis of fully bio-based poly(propylene succinate)s via well-known two-step polycondensation method is described. The polycondensation catalyst, tetraisopropyl orthotitanate TPT, was used to find the catalyst impact on the structure and rheological behavior. Six poly(propylene succinate)s were analyzed by Fourier Transform Infrared Spectroscopy and Nuclear Magnetic Resonance. The structure was also verified by Gel Permeation Chromatography, which characterizes the impact of the catalyst amount on the molecular weight distribution. Moreover, for more detailed investigation, the study of the molecular weight distribution was

expanded about results of the Matrix-Assisted Laser Desorption/Ionization Time-of-Flight mass spectrometry. The influence of the catalyst amount on the rheological behavior was determined with the use of rotary rheometer. The choice of the measurements temperature ranges and shear rates were done due to the temperature conditions for industrial processes during preparation and production of polyurethane materials [18].

2. Materials and methods

2.1. Materials

The main components used in this study:

Bio-based succinic acid (SA) was obtained from BioAmber Sarnia Inc. (Ontario, Canada) as a solid-state component with purity in the range 98-100%. The molecular weight was 118.09 g/mol and relative density at 20^{o}C was 0.900 g/cm^{3}.

Susterra Propanediol (1.3-propanediol) was obtained from DuPont Tate&Lyle Corporation Bio Products (Loudon, Tennessee, USA) as a liquid component with purity ca. 99.98%. The molecular weight was 76.09 g/mol, and relative density at 20^{o}C was 1.053 g/cm^{3}. Moreover, water content by Karl Fischer equaled 12.1 ppm and a dynamic viscosity at 20^{o}C was 52 mPas.

Tetraisopropyl orthotitanate, Ti(O-i-Pr)$_4$ (TPT) was purchased from TCI Chemicals (India) as a liquid with the purity ca. 97% and the molecular weight: 284.22 g/mol and was used as a catalyst with four different amount.

For the analytical measurement methods, other materials and solvents were used of analytical grade.

2.2. Bio-based polyesters synthesis

Aliphatic bio-based polyester polyols – poly(propylene succinate)s, were prepared with the use of succinic acid SA and 1.3-propanediol PDO, both with a natural origin. Catalyst, tetraisopropyl orthotitanate TPT, was used as a glycol equivalent in five different amount, namely, 0.1 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 reference sample was prepared without catalyst employment (PPS-0.00). All aliphatic bio-based polyester polyols were synthesized by two-step polycondensation method, which scheme is shown in Figure 1. 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 and the molar ratio SA: PDO amounted to 1:1.2. Determination of this molar ratio was ordered by the final molecular weight expected after full polycondensation. The expected number average molecular weight of the prepared bio-based polyester polyols was Mn = 2000 g/mol with functionality equaled 2, for proving linearity in the molecular structure. The reaction was carried out in the glass reactor, which consisted of a three-neck flask equipped with nitrogen/vacuum inlet, mechanical stirrer, thermometer, condenser, and heating mantle. The first step of the reaction was carried out under a nitrogen atmosphere. The bio-based component mixture was stirring at 140^{o}C and after water distillation, the second step was started according to the patent application in the Polish Patent Office (no. P.418808). During the polycondensation reaction, the nitrogen was stopped, the appropriate amount of catalyst was added, and the temperature was increased up to 160^{o}C under reduced pressure. 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.

Figure 1 Two-step polycondensation method for poly(propylene succinate) obtainment.

2.3. Polymer characterization

2.3.1. Acidic and hydroxyl number

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

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

2.3.2. 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 70 and 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. Fourier Transform Infrared Spectroscopy (FTIR)

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

2.3.4. Nuclear magnetic resonance (^{1}H NMR)

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

2.3.5. Gel permeation chromatography (GPC)

Molecular weight distribution of the synthesized bio-based polyester polyols was determined with the use of Gel permeation chromatography, GPC. Measurements were performed using a Thermo Scientific chromatograph, equipped with an isocratic Dionex UltiMate 3000 pump and a RefractoMax 521 refractive index detector. Four Phenogel GPC columns, produced by Phenomenex, were used with 5 μm particle size and 10^5, 10^3, 100 and 50 Å porosities, respectively, located in an UltiMate 3000 thermostatic column compartment. The separation was carried out at 30^{o}C. Tetrahydrofuran (THF) was used as mobile phase at a flow rate of 1 mL/min. Bio-Based polyester polyol specimens were prepared by dissolving in THF at 1 wt.% and filtering using nylon filters with 2 μm pore size. Number-average molecular weight, Mn,

weight-average molecular weight, Mw and polydispersity, PD were determined as polystyrene standards.

2.3.6. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS)

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 polyester 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 N_2 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 cationizing agent was used a potassium salt of fluoroacetic acid (CH_2FCOOK) 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 polyester polyols as well as serve as a core method to investigate the impact of the catalyst amount on the polyols structure development during synthesis.

2.3.7. Rheological behavior

Rheological measurements were performed with the use of rotary rheometer R/S-CPS+ produced by Brookfield Company, USA. The machine was equipped with

the cone/plate system. The rheological models and parameters were defined and calculated with the use of computer program Rheo3000. Measurements were conducted with controlled shear rate (CSR). All samples were tested by the program where first the increasing shear rate was conducted from 0 to 100 s^{-1} for 120 s, in the next step the constant shear rate for 120 s was applied and at the end, the decreasing shear rate from 100 to 0 s^{-1} for 120 s were carried out. Based on the rheological measurements, the viscosity and flow curves of synthesized bio-based polyester polyols and commercially used polyester polyol POLIOS 55/20 (Purinova Sp. Z o.o., Bydgoszcz, Poland) were plotted at temperatures 60, 70 and 80^{o}C. Justification of the conditions choice is occurring shear rate ranges and processing temperatures in some industrial processes [18,21]. Moreover, it gave the possibility to more comprehensive comparative study between particular samples.

3. Results and Discussion

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

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. After minimum 60% of 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 [22]. Table 1 shows the preparation condition and properties of the obtained bio-based polyester polyols.

Table 1 Preparation and properties of the obtained bio-based polyester polyols and POLIOS 55/20.

POLYOL	PPS-0.00	PPS-0.10	PPS-0.15	PPS-0.20	PPS-0.25	PPS-0.30	POLIOS 55/20
MOLAR RATIO SA: PDO	1:1.2						ND
CATALYST CONTENT [wt.%]	0.00	0.10	0.15	0.20	0.25	0.30	ND
ESTERIFICATION REACTION TIME [h]	10						ND
POLYCONDENSATION REACTION TIME [h]	170	35	15	10	9	10	ND
ACID NUMBER [mg KOH/g]	1.16	0.97	0.84	0.92	0.83	0.91	0.30
HYDROXYL NUMBER [mg KOH/g]	44.6	64.2	50.4	61.8	51.5	74.9	58.0
VISCOSITY [80°C, Pas]	100*	4.35	6.17	8.87	3.43	2.88	2.20

ND – not defined; * Dynamic viscosity measured at 90°C

The final properties of the synthesized polyester polyols showed the significant impact of the catalyst usage. With the growing catalyst amount, the polycondensation reaction time was decreased up to 0.25 wt.% catalyst usage. The lack of the second step time reduction was visible for the sample with the highest catalyst content (PPS-0.30). Nevertheless, sample PPS-0.30 characterized viscosity value more akin to commercially used polyester polyols POLIOS 55/20.

The value of the hydroxyl number confirmed similarity of the prepared bio-based polyester polyols to the commercially used synthetic polyester polyols proposed for flexible and thermoplastic polyurethane materials (e.g.: POLIOS 55/20, PURINOVA Sp. Zoo, Bydgoszcz, Poland) [22].

The viscosity of the synthesized polyester polyols also verified the influence of the catalyst employment on the polyol final properties. Without catalyst usage, the synthesized polyester polyol revealed the highest viscosity, 100 Pas at 90°C (Table 1).

This viscosity level disenables PPS-0.00 usage in the industrial processes. With the growing catalyst usage during poly(propylene succinate)s synthesis, the increasing tendency at the viscosity until 0.20 wt.% catalyst content was observed. For polyols prepared with the use of 0.25 and 0.30 wt.% catalyst content, the viscosity was decreased. The lowest value revealed sample containing the highest catalyst content (PPS-0.30: 2.88 Pas at 80^{o}C), but the polycondensation reaction time was longer than the PPS-0.25 polyol.

3.2. Structure analysis

The structure analysis was performed using the FTIR and ^{1}H NMR measurements. The Fourier Transform Infrared spectra of the poly(propylene succinate)s and pure component used for polyesters synthesis (1.3-propanediol and succinic acid) are shown in Figure 2. The broad peak characteristic for the 1.3-propanediol spectrum in the wavelength range between 3570 and 3170 cm^{-1} was attributable to the stretching vibrations of hydrogen-bonded hydroxyl groups. For the succinic acid spectrum, the peak assigned to the hydrogen-bonded carboxyl groups stretching vibration appeared as the broad peak centered at 3300-2500 cm^{-1}. The peaks at 3000-2850 cm^{-1} were assigned to the methylene groups which are visible for glycol and polyesters spectra. Two intensive peaks visible for poly(propylene succinate) spectrum at 1725 cm^{-1} and 1150 cm^{-1} indicated ester groups [23]. The peak at 1725 cm^{-1} is assigned to carbonyl group stretching vibration related to the ester groups from synthesized polyester polyols. The peak at 1690 cm^{-1} visible on the succinic acid spectrum also indicated the –C=O stretching vibration but assigned to the carboxyl group. The absorption at 1150 cm^{-1} is related to the C(O)-O-C stretching vibration from the formed ester groups. The two clearly visible peaks at 1380 and 1400

318 cm^{-1} ascribed the -OH bending vibration derived from succinic acid. The peaks at 1170
319 cm^{-1} on the glycol spectrum and 1200 cm^{-1} on the succinic acid spectrum are attributed
320 to the -C-O group stretching vibration [24]. The bond in the wavenumber at 1030 cm^{-1}
321 indicated -C-O stretching vibration from synthesized polyesters and 1.3-propanediol
322 [25].

323 In the case of analyzed poly(propylene succinate)s, the intensity of the peaks,
324 which are assigned to the ester groups (wavenumber: 1725 cm^{-1} and 1150 cm^{-1}), is
325 similar. The results allowed confirming that the content of the catalyst nonsignificantly
326 influenced on the macromolecular structure of the synthesized polyols.

327

328 Figure 2 FTIR spectra of the used succinic acid, 1.3-propanediol, and selected
329 poly(propylene succinate)s.

330

331 ^{1}H NMR spectra were used to study the structure of the synthesized polyesters
332 (Figure 3). Based on the spectra of the poly(propylene succinate)s prepared with the
333 0.15, 0.20 and 0.25 wt.% catalyst employment, the chemical shifts of the protons were
334 investigated. The characteristic intensive single peak at 2.63 ppm is attributed to
335 methylene protons ‘d’ from succinic acid (-CH_2-C(O)-) [26,27]. Peaks marked ‘e’ (-CH_2-
336 O-) and ‘f’ (-CH_2-) at 4.20 and 2.00 ppm, respectively, are connected with a triple and
337 multiple peaks corresponding to methylene protons from propylene glycol (1.3-
338 propanediol) [28,29]. At the sample spectra are also visible other peaks in lower
339 intensity which can indicate the end groups of oligomers. The little triple peak at 3.65
340 ppm named ‘a’ attributed to methylene protons from hydroxyl-terminated ends (-CH_2-

OH) of polyester macromolecules [30]. The peak at 4.35 ppm named ‘c’ is attributed to the triple peak corresponding to methylene protons (-CH_2-O-) from glycol terminated ends group. Peak named ‘b’ at ca. 1.90 ppm is connected to methylene protons also from glycol terminated ends group (-CH_2-). Chrissafis and co-workers [28] explain that these little shifts at the 1.90, 3.68 and 4.35 ppm can correspond to the low molecular weight of the synthesized polyester polyols. These peaks verified the intensity of the polyester macromolecules end-groups occurrence. At the ^{1}H NMR spectra of the high molecular weight polyesters, these shifts are not visible.

Figure 3 ^{1}H NMR spectrum of the synthesized poly(propylene succinate)s samples.

3.3. Gel permeation chromatography measurements

Molecular weight distribution depended on the reaction condition such as used temperature, pressure, stirring but also on the molar ratio of the components and the used catalyst. The gel permeation chromatography was measured to characterize the number average molecular weight and polydispersity of the synthesized polyester polyols. The impact of the catalyst amount on the molecular structure is shown in Figure 4. Table 2 presents the statement of the GPC results. For better results exposition the POLIOS 55/20 was used as a reference sample [31]. It is commercially used synthetic polyester polyol proposed for the flexible and thermoplastic polyurethane materials (PURINOVA Sp. Zoo, Bydgoszcz, Poland). POLIOS 55/20 reveals number average molecular weight at ca. 2000 g/mol. The distinct peaks at similar retention time for all measured polyols are visible on the graph. It is seen that with the catalyst amount during the polycondensation reaction the synthesized polyols

revealed more akin to designed average molecular weight and lower polydispersity. With the growing catalyst content, the prepared materials exhibit the retention time similar to the reference sample – POLIOS 55/20 and thereby more coterminous average molecular weight.

Polyol named PPS-0.00, which was prepared without catalyst employment exhibited the sharp peak at the shortest retention time. It verified the highest average molecular weight of prepared bio-based polyester polyols. Although the single peak at the graph (Figure 4), PPS-0.00 revealed the highest polydispersity which indicates the high dispersion of molecular weight on the polyol structure. The polydispersity of PPS-0.00 amounts to 3.5235. The usual level of the molecular weight dispersion should be equaled ca. 1.05-2.0. It can be account for the lower molecular weight macromolecules distribution in the sample. The smaller macromolecules reveal higher retention time and thereby they are unseen at the used retention time range on the graph.

In the case of the PPS-0.10 polyol where the 0.10 wt.% of TPT was used, the final polyol revealed double-peak at the graph of the average molecular weight distribution. It indicates the long chain macromolecules distribution on the sample and high polydispersity level. The first peak indicates the M_n at ca. 18 000 g/mol, when the second peak – ca. 2500 g/mol. The polydispersity at the second peak equaled 1.9640 which is also very high. It confirmed the above-mentioned assumptions involved PPS-0.00 polyol. This catalyst amount is deficient for polyol with good polydispersity and planned average molecular weight preparation.

The catalyst addition above 0.10 wt.% allowed the polyester polyol synthesis with the beneficial molecular weight distribution. Polyols PPS-0.15, PPS-0.20, PPS-0.25 and PPS-0.30, revealed coterminous number average molecular weight with the

expected (2000 g/mol). Nevertheless, polyols prepared with the 0.15 and 0.20 wt.% catalyst content exhibited high polydispersity level, above 2.0. Bio-based poly(propylene succinate) synthesized with the 0.30 wt.% catalyst content revealed the best molecular weight distribution with the ca. 1.8 polydispersity level and ca. 2000 g/mol number average molecular weight. It can be explained as catalyst content which shifts the reaction towards a product with planned average molecular weight with the best efficiency from measured polyols. A detailed study of the structures of the different polyols detected by GPC was performed by MALDI-TOF MS in order to identify the eventual side reactions producing differences in the molecular weight distribution.

Figure 4 GPC spectra of the synthesized poly(propylene succinate)s.

Table 2 The results of the GPC measurements.

BIO-BASED POLYESTER POLYOL	M_n	M_w	PDI
PPS-0.00	4615	16261	3.524
PPS-0.10	18270/2524	18903/4957	1.035/1.964
PPS-0.15	22705/2050	24527/4752	1.080/2.318
PPS-0.20	1727	4466	2.586
PPS-0.25	2578	4644	1.801
PPS-0.30	2158	3808	1.765
POLIOS 55/20*	2000	3349	1.675

*reference sample – commercially used linear synthetic polyester polyol proposed for the flexible and thermoplastic polyurethane materials, PURINOVA Sp. zoo, Bydgoszcz, Poland

3.4. MALDI-ToF mass spectrometry

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectrometry is a powerful method for the characterization of polymers [12,16,32].

MALDI-ToF MS as a soft ionization method provides measurements of absolute molecular weights, identification of mass-resolved polymer chains including intact oligomers and simultaneous determination of end groups in polymer sample [33]. Four representatives bio-based poly(propylene succinate) samples were measured with the use of MALDI-ToF mass spectrometry. The study of their structure was investigated in terms of the presence and possible domination of a specific oligomer, polymerization degree and end groups. Moreover, MALDI-ToF measurements give information about macromolecular weight distribution. Similar to GPC, there is an ideal situation when MALDI-ToF spectra (peak profiles) have approximate Gaussian curve [17].

The MALDI-TOF mass spectra were obtained at the m/z range from 450 to 9000 Da, what gave peaks with various polymerization degree from 2-3 even to 40 and more (Figure 5). Presented signals correspond to the K+ doped macromolecules. The distance between the main peaks amount to 158 Da, which is connected with the molecular weight of the bio-based poly(propylene succinate) repeating units. Obtained spectra include also peaks which are related to oligomers displayed other chemical structure than designed. It is visible that all of the measured polyols revealed differences in the curve courses. Due to the various catalyst amounts during the polycondensation process between succinic acid and the excess of the 1,3-propanediol, the various molecular mass distributions are observed.

Figure 5 MALDI-ToF spectra of the bio-based poly(propylene succinate)s: a) PPS-0.00, b) PPS-0.10, c) PPS-0.15, d) PPS-0.20, e) PPS-0.25, f) PPS-0.30.

Sample PPS-0.00 (Figure 5 a) is characterized by peak profile with two broad spectra with maximum intense at 1147 Da, within 39 Da from K^+ ($M+K^+$) which indicate polymerization degree 7 (n=7), and 4704 Da (n=29, $M+K^+$) in the m/z range from 500 to 6000 Da. Furthermore, a lot of peaks are visible in the m/z range from 500 to 2500 Da. These peaks are related to different molecular chain structure, specifically, with various end groups of the synthesized oligomers in the polyol PPS-0.00. The spectrum course departs from Gaussian distribution, thus the results of the MALDI-ToF measurements confirmed the macromolecular weight distribution from the GPC, exactly, high polydispersity. Bio-based poly(propylene succinate) prepared with the catalyst usage at 0.10 wt.% revealed more similar spectrum to Gaussian curve (Figure 5 b) in the m/z range from 500 to 8500 Da. This sample has a maximum at 1696 Da (n=10, $M+K^+$), but the most intensive peak is visible at 615 Da (n=3, $M+K^+$) which is connected with molecules terminated by acid-end groups. Samples PPS-0.15 and PPS-0.30 (Figure 5 c and f) revealed similar spectra shape. The first from above-mentioned polyols characterized peaks in the m/z range from 500 to ca. 6500 Da, second polyols - from 500 to ca. 6000 Da. The most intensive peaks in both cases are at 747 and 746 Da (n=4, $M+K^+$), respectively. The difference is related to the carbon isotope occurrence at the polyol macromolecules. These peaks confirmed macromolecules formation with hydroxyl-terminated end groups. Sample PPS-0.30 has more complicated structure due to peaks occurrence in the m/z range from 500 to 1000 Da (Figure 5 f). PPS-0.20 is characterized by the most similar peak profile to Gaussian curve (Figure 5 d). The maximum intense at 2486 Da (n=15, $M+K^+$) confirms hydroxyl-terminated macromolecules occurrence. Polyol PPS-0.25 has similar peak profile to PPS-0.20 but with a visible double maximum at 1853 (n=11, $M+K^+$) and 5966 Da (n=37, $M+K^+$). Theoretical bio-based poly(propylene succinate) should have

polymerization degree ca. 12 for obtaining designed macromolecular weight. More precise spectra interpretation of selected polyol samples is presented in Table 3.

Table 3 Interpretation of MALDI-ToF mass spectra for obtained bio-based polyester polyols.

Bio-based poly(propylene succinate)	Location of band (m/z) ($M+K^+$)	Polymerization degree (n)	Probable structure of molecule ($M-K^+$)	Calculated molecular weight ($M+K^+$) [g/mol]
PPS-0.00	513.97	3	A	513.31
	582.58	3	PPS	587.34
	672.27	4	A	671.38
	830.54	5	A	829.45
	906.94	5	PPS	903.48
	976.48	5	ND	ND
	988.82	6	A	987.52
	1147.03	7	A	1145.59
	1305.11	8	A	1303.66
	1323.02	7	A-SA-PDO	1321.77
	1363.30	8	ND	ND
	1463.10	9	A	1461.73
	1538.96	9	PPS	1535.76
	1621.04	10	A	1619.80
	1638.94	9	A-SA-PDO	1637.91
	1696.91	10	PPS	1693.83
	1854.91	11	PPS	1851.90
Peaks from 2012.95 to 4704.99 Da and further are related to macromolecules PPS with higher polymerization degree (from 12 to 29 and further).				
PPS-0.20	193.48	1	A	197.17
	317.76	1	$[A-SA-H_2O]^-$	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 to macromolecules PPS with higher polymerization degree (from 7 to 45 and further).				
PPS-0.25	354.99	2	A	355.24
	422.88	2	PPS	429.27
	430.92	2	PPS	429.27
	747.09	4	PPS	745.41
	905.22	5	PPS	903.48
	1063.30	6	PPS	1061.61
	1221.32	7	PPS	1219.62
	1303.37	8	A	1303.66
	1379.50	8	PPS	1377.69
Peaks from 1379.50 to 8023.62 Da and further are related to macromolecules PPS with higher polymerization degree (from 8 to 50 and further).				

*ND – not defined;

*A, A-SA, A-SA-PDO, $[A\text{-}SA\text{-}H_2O]^-$, PPS– structures of macromolecules (see Figure 6).

Table 3 shows the precise interpretation of MALDI-ToF spectra of three selected poly(propylene succinate)s. All of the peaks at characteristic m/z ranges represent macromolecules with a specific structure and specific end-groups. From obtained data, it was possible to calculate the polymerization degree (n) and molecular weight of the probable structure of a molecule for several peak locations. All defined structures are coded and presented in Figure 6. At all of the prepared bio-based poly(propylene succinate)s it was desirable to obtain the highest amount of the PPS structures throughout the sample volume. These macromolecules are hydroxyl-terminated from both sides. Structure A is related to macromolecules terminated by both, an acid-end group as well as an hydroxyl-end group. A-SA-PDO describe features when hydroxyl-terminated macromolecules are formed but during ionization differently detected macromolecules are formed. Structure A-SA depicts macromolecules terminated by acid-end groups from both sides. MALDI-ToF measurements can lead to complex structure formation, even with residual water which can be presented in the sample. This possible situation described probable structure coded A-SA-H_2O. It is

476 characteristic that the most ordered structure (the most approximate to designed)
477 revealed sample PPS-0.25. The results of the MALDI-ToF mass spectrometry
478 confirmed the results obtained from GPC measurements. Sample PPS-0.25 revealed
479 the lowest polydispersity and the most ordered and approximate to designed,
480 macromolecular structure.

481

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

483

484 3.5. Rheological behavior

485 The rheological measurements allowed characterizing the mathematical model
486 and rheological behavior of the synthesized bio-based poly(propylene succinate)s. The
487 tests were prepared at 60, 70 and 80^{o}C and the share rate at the range from 0 to 100
488 s^{-1}. The justification for the temperature and share rate choice is due to the usually
489 used conditions during industrial processes. Figures 7 and 8 show the viscosity and
490 flow curves of the prepared polyester polyols, respectively. Moreover, Tables 4 and 5
491 present the mathematical models of the prepared polyols rheological behavior. For
492 more comprehensive results interpretation, rheological behavior of the POLIOS 55/20
493 was also investigated and presented in the figures and tables.

494

495 Figure 7 The viscosity curves of the synthesized bio-based polyester polyols and
496 POLIOS 55/20 at a) 60^{o}C, b) 70^{o}C, c) 80^{o}C.

497

The viscosity curves showed the relationship between polyols viscosity and shear rate. The results confirmed the non-Newtonian character of the measured materials. In Figure 7, the initial viscosity trend behavior with increasing shear rate indicates the pseudoplastic behavior of the measured polyols. The macromolecular chain orientation caused by flow field can explain the observed shear thinning behavior. In the flow field, the molecules are changing their direction by rotation. After achieving the parallel position to the flow direction, the viscosity stays constant. The obtained viscosity curves confirmed the decrease of the synthesized polyols viscosity with the increasing temperature. Only POLIOS 55/20 viscosity stays approximately with the same values at different temeratures. Interesting is the fact that the initial viscosity trend behavior with increasing shear rate for POLIOS 55/20 increase with the growing temerature. The highest viscosity, at all three temperatures, revealed polyols PPS-0.15 and PPS-0.20, when the lowest POLIOS 55/20 and PPS-0.30. The sample PPS-0.25 revealed similar viscosity value to PPS-0.10 at 60 and 70^{o}C and clearly lower, similar to PPS-0.30, at 80^{o}C.

Figure 8 The flow curves of the synthesized bio-based polyester polyols and POLIOS 55/20 at a) 60^{o}C, b) 70^{o}C, c) 80^{o}C. The black line means the rising curves and the gray line means falling curves.

Fluids exhibited the non-linear flow curves are described as non-Newtonian liquids. The changes in the viscosity value can be observed as the variation of the tangent of the curve slope angle [34] at the flow curves. It is expressed by the equation (4):

$$\tan \alpha = \eta_0 \quad (4)$$

All measured polyols revealed the decreasing angle α with increasing temperatures. The obtained results verified the decreasing viscosity of the prepared bio-based polyester polyols with the growing temperature. It also confirmed that the shear stress decreases with the increasing temperature. The highest value of the shear stress disclosed the polyol samples PPS-0.15 at 60°C and PPS-0.20 at 70°C which equaled ca. 1500 Pa for both polyols (Figure 8). Specimen PPS-0.20 exhibited molecular structure which disenabled the rheological measurement with 100 s^{-1} of the shear rate at 60°C. The obtained results are related to the viscosity of the sample. What is seen in Table 1, polyol PPS-0.20 exhibited one of the higher viscosity, above 14.5 Pas (at 70°C), from the measured polyols. The viscosity incidents to the dispersion of the molecular weight (polydispersity) of the sample. The highest value of the polydispersity (above 2.5 for PPS-0.20, Table 2) confirmed that the PPS-0.20 featured a lot of the macromolecules with the differential molecular weights. Furthermore, the peak location for PPS-0.20 in Figure 4 suggests that the prepared polyol shows the higher content of the macromolecules with larger molecular weight than designed. Its caused that the polyol is more sticky at the same temperature compared to other measured polyols (except the PPS-0.00).

The lowest shear stress occurred for all synthesized polyols at 80°C and equaled 885 Pa for PPS-0.20, 615 Pa for PPS-0.15, 435 Pa for PPS-0.10, 341 Pa for PPS-0.25, 282 Pa for PPS-0.30, and 233 Pa for POLIOS 55/20, respectively. Nevertheless, for this temperature, the flow curves for all polyol samples disclosed the most visible no overlapping curves courses. This phenomenon is related to the thixotropic behavior which occurs with irreversible decreasing shear stress with time for the constant shear rate. At this time the hysteresis loops are observed. The

thixotropic fluids are the non-Newtonian liquids which characterized the decreasing viscosity with the constant shear rate. It is caused by a progressive decomposition of the fluid's structure. Due to the irreversible character of the thixotropic fluids, the state of balance can be achieved after the structure reconstruction. The small hysteresis is visible for all samples in the initial part of the curves courses. For the higher value of the shear rate, the flow curves exhibited the linear behavior. This observation caused difficulties with the unequivocal ascertainment of the pseudoplastic behavior of the measured polyols (Figure 8). Nevertheless, the rheological measurements allowed characterizing the mathematical models of the synthesized bio-based polyester polyols, which clearly determined the pseudoplasticity of the polyols (Table 4 and 5).

Except for the temperature influence on the thixotropic behavior, the addition of the catalyst have also an impact on this phenomenon. It is visible that the biggest hysteresis loops exhibited samples with 0.15 and 0.20 wt.% of the catalyst employment during synthesis. For sample PPS-0.25 and PPS-0.30, the hysteresis loops are smaller which result in the decreasing of the thixotropic behavior. The observed hysteresis is due to the polydispersity of the obtained bio-based polyols. The high level of the molecular weight macromolecules distribution hindered the macromolecules reversion to the state before the test. Nevertheless, observed hysteresis loops are small enough to the nonsignificant impact on the industrial processes.

569 Table 4 The Herschel, Bulkley functions based on the rheological data from prepared bio-based polyols and POLIOS 55/20.

POLYESTER POLYOL	TEMPERATURE [^oC]	FUNCTION	YIELD STRESS, τ_0 [Pa]	CONSISTENCY INDEX, μ_{om} [Pas^n]	THE FLOW INDEX, n [-]	STABILITY INDEX, R^2 [-]	BEHAVIOR
PPS-0.00	90	$y = 0+99.3391*x^{1.0008}$	0	99.3391	1.0008	0.9999	Newtonian
PPS-0.10	60	$y = 0+9.6411*x^{1.0079}$	0	9.6411	1.0079	0.9999	Dilatant
	70	$y = 0+5.4014*x^{1.0060}$	0	5.4014	1.0060	0.9999	Dilatant
	80	$y = 0+4.1753*x^{1.0093}$	0	4.1753	1.0093	0.9999	Dilatant
PPS-0.15	60	$y = 54.5411+15.8369*x^{0.9858}$	54.5411	15.8369	0.9858	0.9996	Bingham plastic
	70	$y = 78.2383+9.0299*x^{0.9822}$	78.2383	9.0299	0.9822	0.9978	Bingham plastic
	80	$y = 115.1738+4.4440*x^{1.0244}$	115.1738	4.4440	1.0244	0.9925	Bingham plastic
PPS-0.20	60	-	-	-	-	-	-
	70	$y = 16.6613+14.8832*x^{0.9958}$	16.6613	14.8835	0.9958	0.9999	Bingham plastic
	80	$y = 16.1543+9.1918*x^{0.9874}$	16.1543	9.1918	0.9874	0.9874	Bingham plastic
PPS-0.25	60	$y = 8.5405+9.5392*x^{0.9960}$	8.5405	9.5392	0.9960	0.9999	Bingham plastic
	70	$y = 14.2074+5.1267*x^{1.0067}$	14.2074	5.1267	1.0067	0.9995	Bingham plastic
	80	$y = 24.1504+2.8562*x^{1.0226}$	24.1504	2.8562	1.0226	0.9966	Bingham plastic
PPS-0.30	60	$y = 13.8697+6.2816*x^{1.0062}$	13.8697	6.2816	1.0062	0.9997	Bingham plastic
	70	$y = 27.4123+3.2987*x^{1.0204}$	27.4123	3.2987	1.0204	0.9977	Bingham plastic
	80	$y = 76.472+1.2952*x^{1.1036}$	76.4720	1.2952	1.1036	0.9892	Bingham plastic
POLIOS 55/20	60	$y = 83.6282+0.6145*x^{1.1687}$	83.6282	0.6145	1.1687	0.9025	Bingham plastic
	70	$y = 129.0917+0.0752*x^{1.4844}$	129.0917	0.0752	1.4844	0.5949	Bingham plastic
	80	$y = 165.6580+0.0188*x^{1.6719}$	165.6580	0.0188	1.6719	0.3510	Bingham plastic

570 y – shear stress [Pa], x – shear rate [s^{-1}]

571

572 Table 5 The Ostwald-de Waele functions based on the rheological data from prepared bio-based polyols and POLIOS 55/20.

POLYESTER POLYOL	TEMPERATURE [^{o}C]	FUNCTION	CONSISTENCY INDEX, K [Pas^{n}]	THE FLOW INDEX, n [-]	STABILITY INDEX R^2 [-]	BEHAVIOR
PPS-0.00	90	$y = 98.5614*x^{1,0044}$	98.5614	1.0044	0.9999	Newtonian
PPS-0.10	60	$y = 9.5418*x^{1,0094}$	9.5418	1.0094	0.9999	Dilatant
	70	$y = 5.1120*x^{1,0191}$	5.1120	1.0191	0.9999	Dilatant
	80	$y = 3.9225*x^{1,0242}$	3.9225	1.0242	0.9999	Dilatant
PPS-0.15	60	$y = 124.3603*x^{0.4950}$	124.3603	0.495	0.9660	Pseudoplastic
	70	$y = 105.1657*x^{0.4262}$	105.1657	0.4262	0.9696	Pseudoplastic
	80	$y = 127.6615*x^{0.2980}$	127.6615	0.2980	0.9677	Pseudoplastic
PPS-0.20	60	-	-	-	-	
	70	$y = 67.9241*x^{0,6034}$	67.9241	0.6034	0.9605	Pseudoplastic
	80	$y = 41.7221*x^{0.6025}$	41.7221	0.6025	0.9659	Pseudoplastic
PPS-0.25	60	$y = 40.9889*x^{0.6437}$	40.9889	0.6437	0.9776	Pseudoplastic
	70	$y = 36.0143*x^{0.5436}$	36.0143	0.5436	0.9679	Pseudoplastic
	80	$y = 9.0573*x^{0.7791}$	9.0573	0.7791	0.9981	Pseudoplastic
PPS-0.30	60	$y = 47.641*x^{0.4867}$	47.6410	0.4867	0.9376	Pseudoplastic
	70	$y = 11.1922*x^{0.7527}$	11.1922	0.7527	0.9965	Pseudoplastic
	80	$y =34.5608*x^{0.4277}$	34.5608	0.4277	0.9910	Pseudoplastic
POLIOS 55/20	60	$y =83.7755*x^{0.1451}$	83.7755	0.1451	0.9639	Pseudoplastic
	70	$y =82.6236*x^{0.1806}$	82.6236	0.1806	0.9779	Pseudoplastic
	80	$y =154.6387*x^{0.0478}$	154.6387	0.0478	0.9878	Pseudoplastic

573 y – shear stress [Pa], x – shear rate [s^{-1}]

574 The mathematical models for all measured bio-based polyester polyols, at all
575 three temperatures, as an optimal function with the highest stability index, were defined
576 and collected in Table 4 and 5. The rheological models were determined for measured
577 polyols as Herschel, Bulkley, and Ostwald-de Waele. The first model from above-
578 mentioned described fluids with the yield stress, the second model – without yield
579 stress. Although more appropriate for polyurethane industry are fluids without yields
580 stress, the obtained results confirmed possibility to the synthesized polyester polyols
581 industry employment.

582 Table 4 presents the functions of the Herschel, Bulkley model. The bio-based
583 polyester polyol PPS-0.00 was measured at 90^{o}C due to the high viscosity which
584 hindered the measurements at a lower temperature. This reference polyol exhibited
585 the Newtonian model of liquids. PPS-0.10 revealed the dilatant behavior at all three
586 temperatures. These behavior types were determined due to the zero yield stress and
587 the flow index, which was higher than 1. The Herschel, Bulkley model described the
588 pseudoplastic behavior of the fluid revealed the yield stress above 1. The yield stress
589 of bio-based polyester polyols with higher catalyst content than 0.10 wt.% increases
590 with the growing temperature. Only PPS-0.20 revealed approximately constant value
591 ca. 16 Pa. The lowest value of the yield stress from all measured polyols at 60 and
592 70^{o}C exhibited PPS-0.25, which totaled ca. 8.5 and 14.2 Pa, respectively. At 80^{o}C this
593 value for PPS-0.25 amounted to ca. 24 Pa. The consistency index is a measure of the
594 viscosity. The value of consistency index decreased with the temperature growing
595 except for this value for PPS-0.15, PPS-0.30 and POLIOS 55/20 at 80^{o}C (Table 4).

596 The Ostwald-de Waele models, which are presented in Table 5 also confirmed
597 the Newtonian fluid behavior for PPS-0.00 and dilatant behavior for PPS-0.10. The
598 other measured polyols revealed pseudoplastic behavior due to the flow index value,

599 which was lower than 1 at all temperatures. Furthermore, the differences in the
600 behavior appellation for polyols from PPS-0.15 to PPS-0.30 in Table 4 and Table 5 are
601 related to the appropriate model character. The Bingham plastic behavior (Table 4)
602 describes fluids with the yield stress (Hershel, Bulkley model). The pseudoplastic
603 behavior depicts fluids without yield stress (Ostwald-de Waele model, Table 5).

604 The obtained results of the rheological measurements confirmed the most
605 desirable rheological behavior from the synthesized bio-based polyester polyols as a
606 polyol with the use of 0.25 wt.% of the catalyst.

607 4. Conclusion

608 The fully bio-based polyester polyols for polyurethane materials were
609 successfully synthesized via two-step polycondensation method. The optimization of
610 polycondensation process was based on the verification of the catalyst amount, which
611 led to the molecular structure characteristics and selective properties the most akin to
612 designed. The structure analysis via FTIR method confirmed that the content of the
613 catalyst nonsignificantly influenced on the macromolecular structure of the synthesized
614 polyols. The ^{1}H NMR measurements allowed verifying obtainment of the designed low
615 molecular weight polyesters as an occurrence of the little peaks named ‘a’, ’b’, ‘c’ on
616 the ^{1}H NMR spectra of the synthesized poly(propylene succinate)s. The GPC analysis
617 confirmed that the fully bio-based polyols synthesized with the 0.25 wt.% and 0.30
618 wt.% catalyst content revealed the most desirable molecular weight distribution with
619 the ca. 1.8 polydispersity level and ca. 2500 g/mol number average molecular weight.
620 Mass spectrometry analysis proved to be a highly effective tool to facilitate the
621 identification of the molecular structure distribution of the prepared bio-based polyester
622 polyols as well as serve as a core method to investigate the impact of the catalyst
623 amount on the polyols structure development during synthesis. Through the

hyphenation of these sophisticated polymer characterization techniques, information on the molecular heterogeneity of the obtained bio-based polyester polyols, showing a complex variety of possible distributions, was obtained. Matrix-Assisted Laser Desorption/Ionization Time-of-Flight mass spectrometry allowed confirming the impact of the catalyst amount during synthesis on the molecular structure of the resulted polyols. Moreover, it was found that the obtained polyols are non-Newtonian fluids, which can be described as an optimal function by Herschel, Bulkley and Ostwald-de Waele models. The obtained results of the rheological measurements confirmed the desirable rheological behavior for the bio-based polyester polyol synthesized with the use of 0.25 wt.% and 0.30 wt.% of the catalyst. These polyols revealed pseudoplasticity with the lowest value of the yield stress at 60, 70 and 80^{o}C. The conducted investigations confirmed similarity of the prepared bio-based polyester polyols to the commercially used synthetic polyester polyols proposed for flexible and thermoplastic polyurethane materials.

Acknowledgments

Authors acknowledged the DuPont Tate&Lyle BioProducts (Loudon, Tennessee, USA) for supplying the glycol (1.3-propanediol) samples used in this study. Moreover, Authors gratefully acknowledge also receiving the samples of succinic acid employed in this study from BioAmber Sarnia Inc. (Sarnia, Ontario, Canada).

Thanks are also due to Mrs. Professor Arantxa Eceiza and her research team from the Department of Chemical and Environmental Engineering at the University of the Basque Country for the Gel Permeation Chromatography measurements of the bio-based polyester polyols described in this work.

The sincere acknowledgments are directed to the PURINOVA Sp. Z o.o. (Bydgoszcz, Poland) for the Matrix-Assisted Laser Desorption/Ionization Time-of-Flight mass spectrometry measurements of the bio-based polyester polyols described in this work. Tests were conducted during the scientific and technological internship.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

REFERENCES

[1] J.C. de Haro, J.F. Rodriguez, A. Perez, M. Carmona, Incorporation of azide groups into bio-polyols, J. Clean. Prod. 138 (2016) 77–82. doi:10.1016/j.jclepro.2016.05.012.

[2] R. Miller, Evaluating the Properties and Performance of Susterra® 1, 3 Propanediol and Biosuccinium™ Sustainable Succinic Acid in TPU Applications, in: CPI Polyurethanes 2012 Tech. Conf., 2012: pp. 1–19. http://www.reverdia.com/wp-content/uploads/Article-PUMI-Biosuccinium_and_Susterra_03-2013.pdf.

[3] C. Delhomme, D. Weuster-Botz, F.E. Kühn, Succinic acid from renewable resources as a C4 building-block chemical—a review of the catalytic possibilities in aqueous media, Green Chem. 11 (2009) 13. doi:10.1039/b810684c.

[4] I. Bechthold, K. Bretz, S. Kabasci, R. Kopitzky, A. Springer, Succinic acid: A new platform chemical for biobased polymers from renewable resources, Chem. Eng. Technol. 31 (2008) 647–654. doi:10.1002/ceat.200800063.

[5] S. V. Kamzolova, A.I. Yusupova, E.G. Dedyukhina, T.I. Chistyakova, T.M. Kozyreva, I.G. Morgunov, Succinic acid synthesis by ethanol-grown yeasts, Food Technol. Biotechnol. 47 (2009) 144–152.

[6] N. Nghiem, B. Davison, B. Suttle, G. Richardson, Production of succinic acid by Anaerobiospirillum succiniciproducens, Apply Biochem. Biotechnol. 63/65 (1997) 565–576. http://www.ncbi.nlm.nih.gov/pubmed/24409768.

[7] L. Montero de Espinosa, M. Meier, J. Ronda, M. Galia, V. Cadiz, Phosphorus-Containing Renewable Polyester-Polyols via ADMET Polymerization: Synthesis, Functionalization, and Radical Crosslinking, J. Polym. Sci. Part A Polym. Chem. 48 (2010) 1649–1660. doi:10.1002/pola.

[8] J. Djonlagic, M.S. Nicolic, Chapter 6: Biodegradable polyesters: Synthesis and Physical Properties, in: A Handb. Appl. Biopolym. Technol. Synth. Degrad. Appl., Royal Society of Chemistry, United Kingdom, 2011: pp. 149–196.

[9] D.N. Bikiaris, D.S. Achilias, Synthesis of poly(alkylene succinate) biodegradable polyesters, Part I: Mathematical modelling of the esterification reaction, Polymer (Guildf). 47 (2006) 4851–4860. doi:10.1016/j.polymer.2008.06.026.

[10] M. Ionescu, Chemistry and Technology of Polyols for Polyurethane, First Edit, Rapra Technology Limited, United Kingdom, 2005. doi:10.1002/pi.2159.

[11] N.E. Alexander, J.P. Swanson, A. Joy, C. Wesdemiotis, Sequence analysis of cyclic polyester copolymers using ion mobility tandem mass spectrometry, Int. J. Mass Spectrom. (2017). doi:10.1016/j.ijms.2017.07.019.

[12] A.P. Gies, S.M. Stow, J.A. McLean, D.M. Hercules, MALDI-TOF/TOF CID study of poly(1,4-dihydroxybenzene terephthalate) fragmentation reactions, Polymer (Guildf). 64 (2015) 100–111. doi:10.1016/j.polymer.2015.03.021.

[13] R. Medimagh, S. Mghirbi, A. Saadaoui, A. Fildier, M. Desloir-Bonjour, G. Raffin, H.R. Kricheldorf, S. Chatti, Synthesis of biosourced polyether-amides from 1,4-3,6-dianhydrohexitols: Characterization by NMR and MALDI-ToF mass spectrometry, Comptes Rendus Chim. 16 (2013) 1127–1139. doi:10.1016/j.crci.2013.05.004.

[14] H. Ben Abderrazak, A. Fildier, S. Marque, D. Prim, H. Ben Romdhane, H.R. Kricheldorf, S. Chatti, Cyclic and non cyclic aliphatic-aromatic polyesters derived from biomass: Study of structures by MALDI-ToF and NMR, Eur. Polym. J. 47 (2011) 2097–2110. doi:10.1016/j.eurpolymj.2011.07.009.

[15] L. Chikh, M. Tessier, A. Fradet, NMR and MALDI-TOF MS study of side reactions in hyperbranched polyesters based on 2,2-bis(hydroxymethyl)propanoic acid, Polymer (Guildf). 48 (2007) 1884–1892. doi:10.1016/j.polymer.2007.02.019.

[16] P. Król, B. Pilch-Pitera, Urethane oligomers as raw materials and intermediates for polyurethane elastomers. Methods for synthesis, structural studies and analysis of chemical composition, Polymer (Guildf). 44 (2003) 5075–5101. doi:10.1016/S0032-3861(03)00431-2.

[17] P. Król, B. Pilch-Pitera, Study on the synthesis of urethane oligomers as intermediate products for the production of linear polyurethanes, Eur. Polym. J. 37 (2001) 251–266. doi:10.1016/S0014-3057(00)00116-6.

715 [18] E. Głowińska, J. Datta, A mathematical model of rheological behavior of novel
716 bio-based isocyanate-terminated polyurethane prepolymers, Ind. Crops Prod.
717 60 (2014) 123–129. doi:10.1016/j.indcrop.2014.06.016.

718 [19] A. Björn, P. Segura, D. La Monja, A. Karlsson, J. Ejlertsson, B.H. Svensson,
719 Rheological Characterization, Intech. (2012) 64–76. doi:10.5772/32596.

720 [20] A.K. Schrock, H.S.C. Hamilton, B.D. Thompson, K. Ulrich, C. del Rosario, C.J.
721 Saint-Louis, W.D. Coggio, Development of structure–property relationships that
722 allow independent control of glass transition temperature, melting temperature,
723 and rheology in a library of bio-based succinate polyester polyols, Polymer
724 (Guildf). 114 (2017) 103–112.
725 doi:http://dx.doi.org/10.1016/j.polymer.2017.02.092.

726 [21] N. Triantafillopoulos, Measurement of Fluid Rheology and Interpretation of
727 Rheograms, Second Edi, Kaltec Scientific, Inc., Novi, Michigan, USA, 1988.

728 [22] PURINOVA, http://www.purinova.com/, (2017).

729 [23] L. Zheng, C. Li, D. Zhang, G. Guan, Y. Xiao, D. Wang, Multiblock copolymers
730 composed of poly (butylene succinate) and poly (1 , 2-propylene succinate):
731 Effect of molar ratio of diisocyanate to polyester-diols on crosslink densities ,
732 thermal properties , mechanical properties and biodegradability, Polym.
733 Degrad. Stab. 95 (2010) 1743–1750.
734 doi:10.1016/j.polymdegradstab.2010.05.016.

735 [24] S.S. Umare, A.S. Chandure, R.A. Pandey, Synthesis, characterization and
736 biodegradable studies of 1,3-propanediol based polyesters, Polym. Degrad.
737 Stab. 92 (2007) 464–479. doi:10.1016/j.polymdegradstab.2006.10.007.

738 [25] X. Ma, P.R. Chang, J. Yu, N. Wang, Preparation and properties of
739 biodegradable poly (propylene carbonate)/ thermoplastic dried starch
740 composites, Carbohydr. Polym. 71 (2008) 229–234.
741 doi:10.1016/j.carbpol.2007.05.033.

742 [26] D.N. Bikiaris, G.Z. Papageorgiou, D.S. Achilias, Synthesis and comparative
743 biodegradability studies of three poly(alkylene succinate)s, Polym. Degrad.
744 Stab. 91 (2006) 31–43. doi:10.1016/j.polymdegradstab.2005.04.030.

745 [27] D.N. Bikiaris, G.Z. Papageorgiou, D.J. Giliopoulos, C.A. Stergiou, Correlation
746 between Chemical and Solid-State Structures and Enzymatic Hydrolysis in
747 Novel Biodegradable Polyesters . The Case of Poly (propylene
748 alkanedicarboxylate) s, Macromol. Boscience. 8 (2008) 728–740.
749 doi:10.1002/mabi.200800035.

750 [28] K. Chrissafis, K.M. Paraskevopoulos, D.N. Bikiaris, Thermal degradation
751 kinetics of the biodegradable aliphatic polyester, poly(propylene succinate),
752 Polym. Degrad. Stab. 91 (2006) 60–68.
753 doi:10.1016/j.polymdegradstab.2005.04.028.

754 [29] K. Chrissafis, K.M. Paraskevopoulos, D.N. Bikiaris, Thermal degradation
755 mechanism of poly(ethylene succinate) and poly(butylene succinate):
756 Comparative study, Thermochim. Acta. 435 (2005) 142–150.
757 doi:10.1016/j.tca.2005.05.011.

758 [30] L. Zheng, C. Li, W. Huang, X. Huang, Synthesis of high-impact biodegradable
759 multiblock copolymers comprising of poly (butylene succinate) and
760 hexamethylene diisocyanate as chain extender, Polym. Adv. Technol. 22

(2011) 279–285. doi:10.1002/pat.1530.

[31] P. Kopczyńska, J. Datta, Single-phase product obtained via crude glycerine depolymerisation of polyurethane elastomer: Structure characterisation and rheological behaviour, Polym. Int. 65 (2016) 946–954. doi:10.1002/pi.5128.

[32] N.O. Pretorius, K. Rode, J.M. Simpson, H. Pasch, Analysis of complex phthalic acid based polyesters by the combination of size exclusion chromatography and matrix-assisted laser desorption/ionization mass spectrometry, Anal. Chim. Acta. 808 (2014) 94–103. doi:10.1016/j.aca.2013.07.030.

[33] J.C. Soutif, N.T.H. Doan, V. Montembault, Determination by MALDI-TOF MS of the structures obtained from polytransesterification of diethyl 2,6-pyridinedicarboxylate and poly(ethylene glycol), Eur. Polym. J. 42 (2006) 126–132. doi:10.1016/j.eurpolymj.2005.07.026.

[34] K. Wilczyński, Reologia w przetwórstwie tworzyw sztucznych, Wydawnictwo Naukowo-Techniczne, Warszawa, 2001.

Caption of Figures

Figure 1 Two-step polycondensation method for poly(propylene succinate) obtainment.

Figure 2 FTIR spectra of the used succinic acid, 1.3-propanediol, and selected poly(propylene succinate)s.

Figure 3 ^{1}H NMR spectrum of the synthesized poly(propylene succinate)s samples.

Figure 4 GPC spectra of the synthesized poly(propylene succinate)s.

Figure 5 MALDI-ToF spectra of the bio-based poly(propylene succinate)s: a) PPS-0.00, b) PPS-0.10, c) PPS-0.15, d) PPS-0.20, e) PPS-0.25, f) PPS-0.30.

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

Figure 7 The viscosity curves of the synthesized bio-based polyester polyols and POLIOS 55/20 at a) 60^{o}C, b) 70^{o}C, c) 80^{o}C.

Figure 8 The flow curves of the synthesized bio-based polyester polyols and POLIOS 55/20 at a) 60^{o}C, b) 70^{o}C, c) 80^{o}C. The black line means the rising curves and the gray line means falling curves.

Caption of Tables

Table 1 Preparation and properties of the obtained bio-based polyester polyols and POLIOS 55/20.

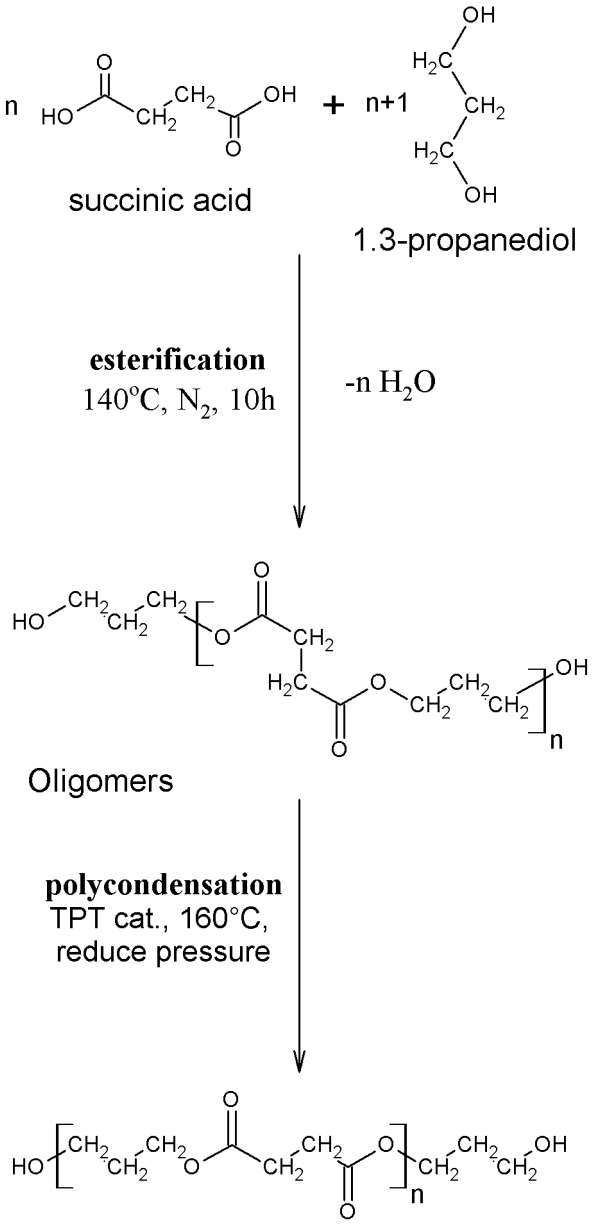
Table 2 The results of the GPC measurements.

Table 3 Interpretation of MALDI-ToF mass spectra for obtained bio-based polyester polyols.

Table 4 The Herschel, Bulkley functions based on the rheological data from prepared bio-based polyols and POLIOS 55/20.

Table 5 The Ostwald-de Waele functions based on the rheological data from prepared bio-based polyols and POLIOS 55/20.

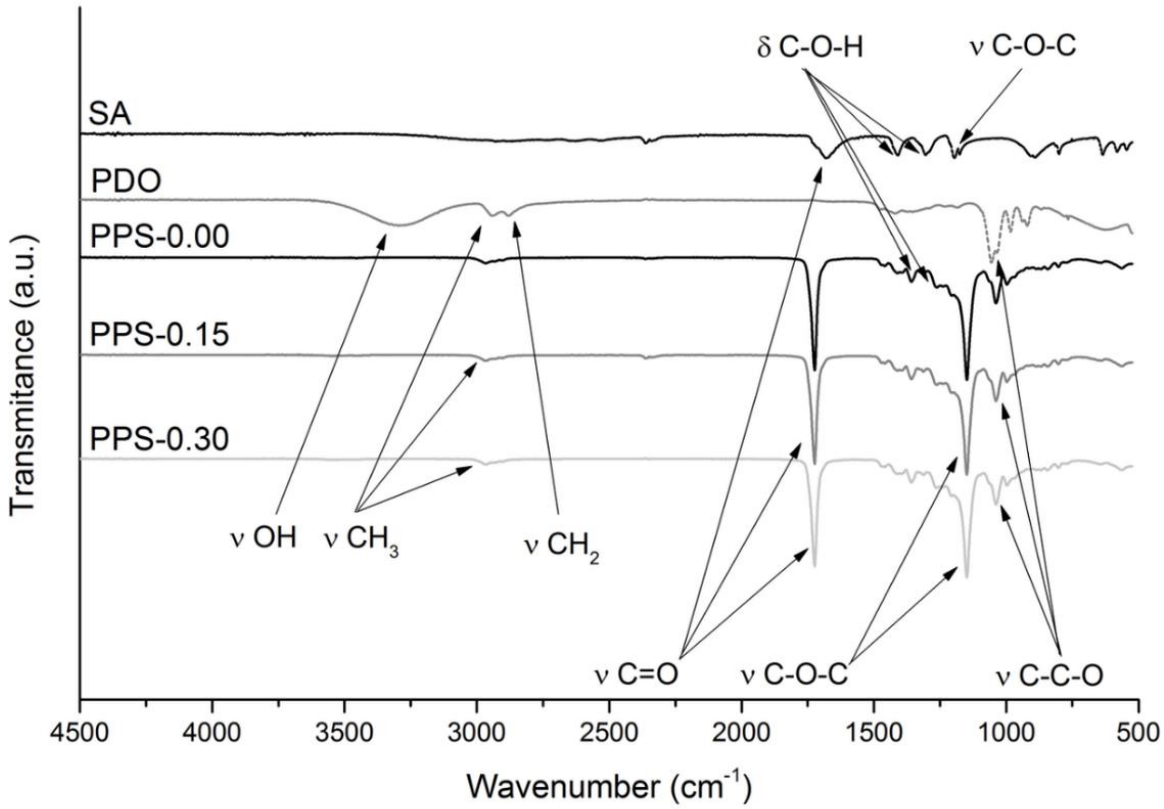
804 Figure 1



805 **Poly(propylene succinate)**

806

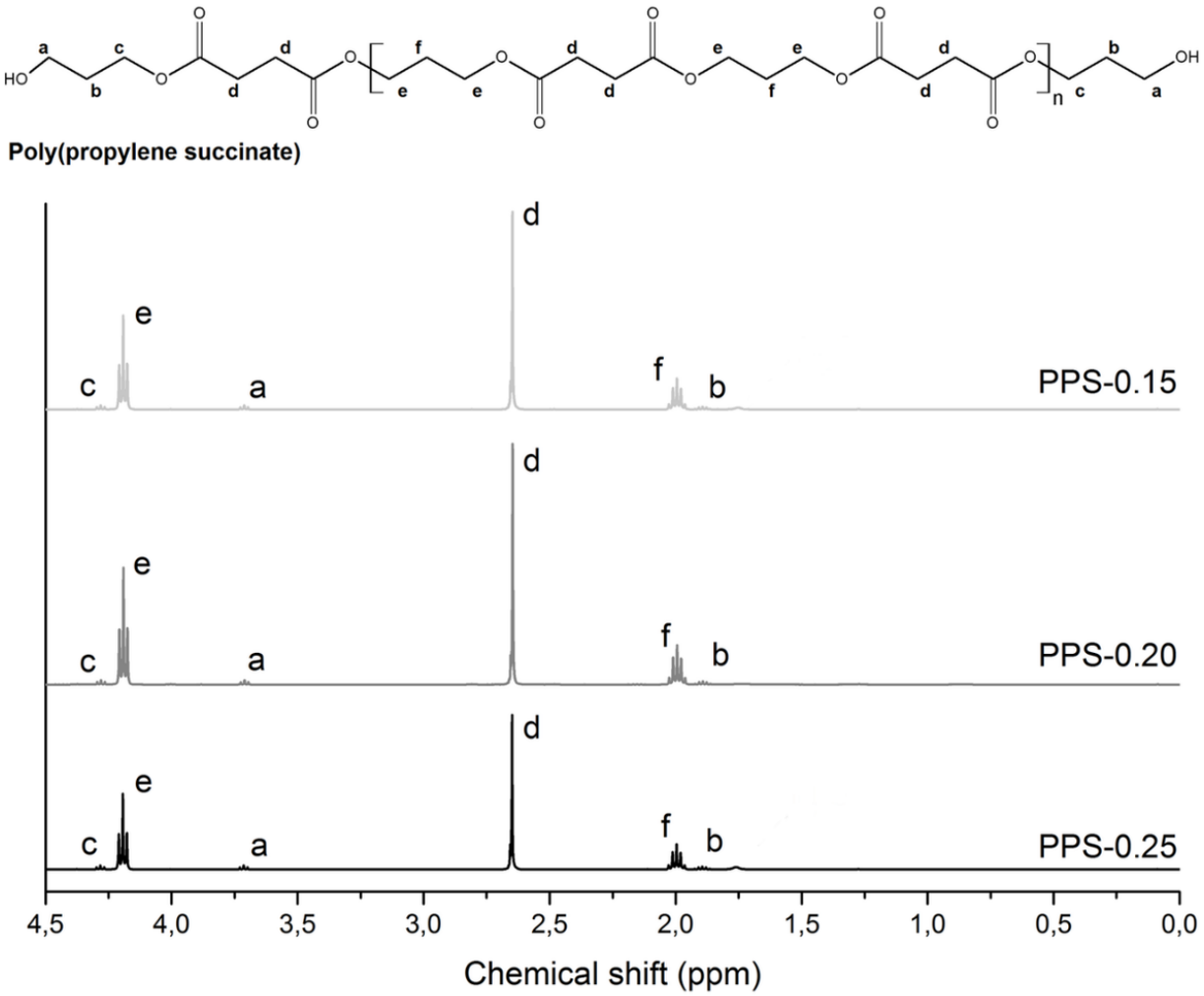
807 Figure 2



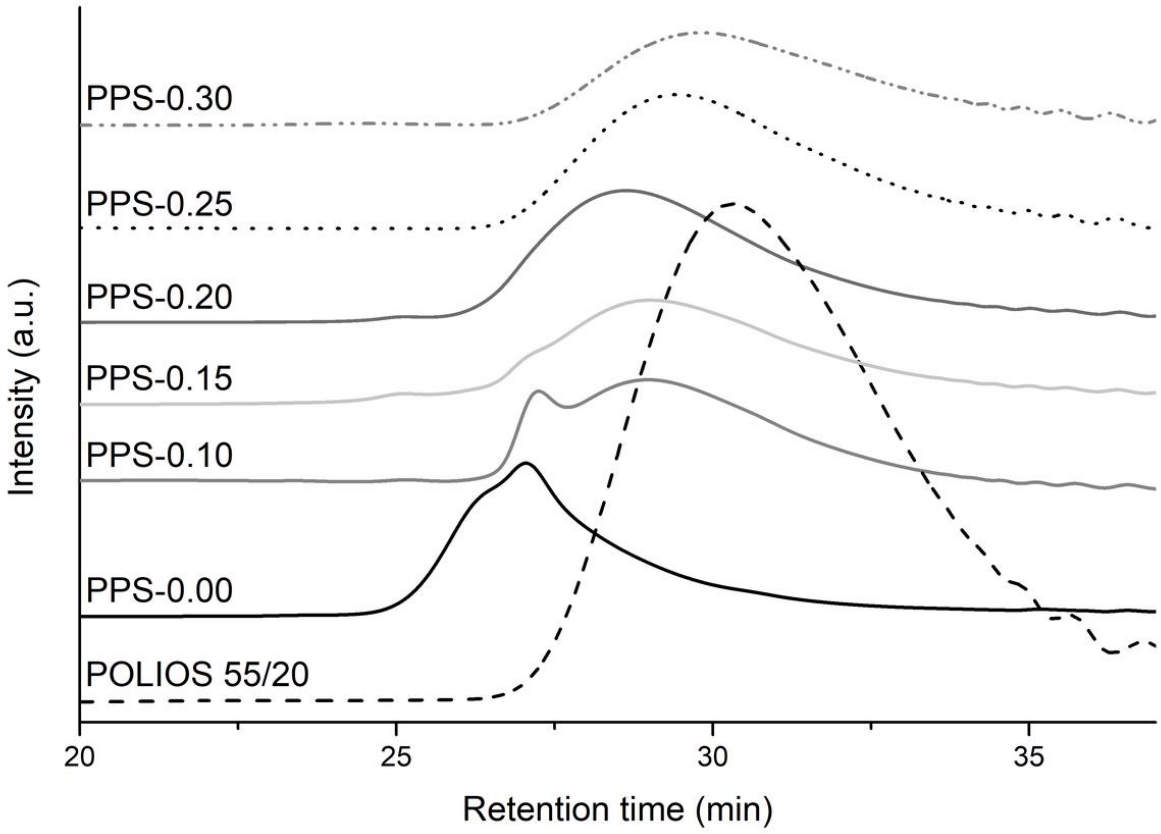
808

809

Figure 3



813 Figure 4

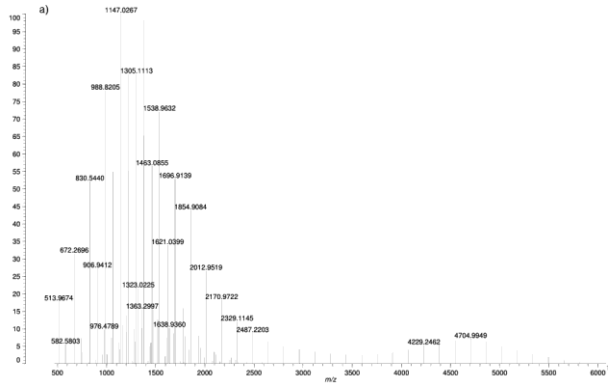


814

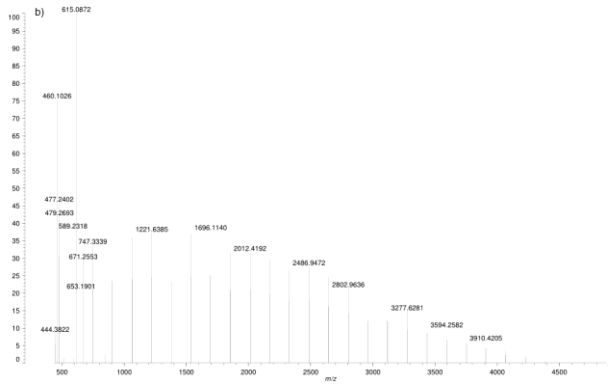
815

816 Figure 5

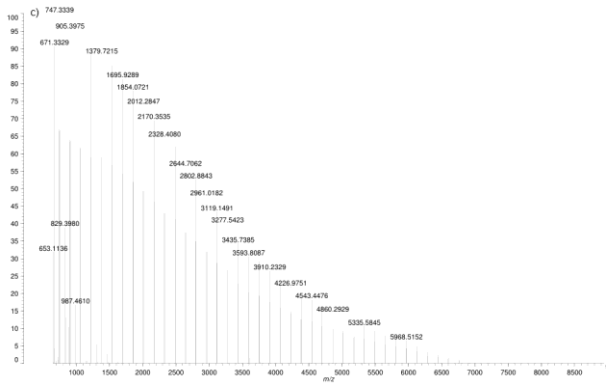
817



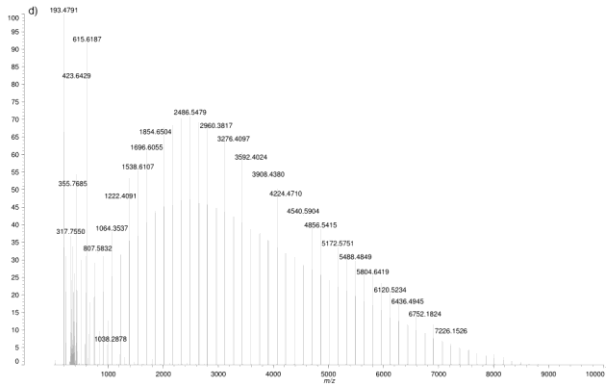
818



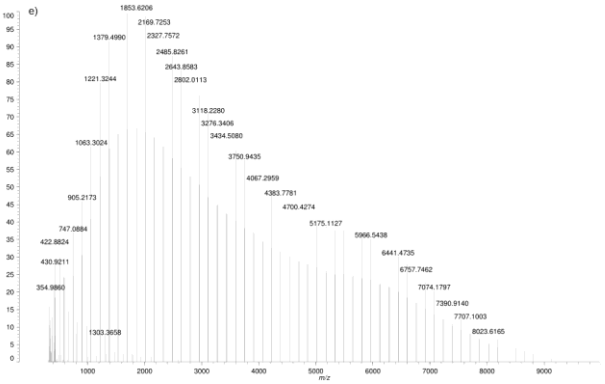
819



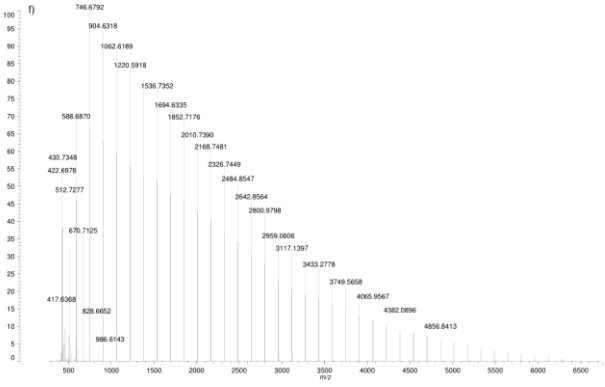
820



821

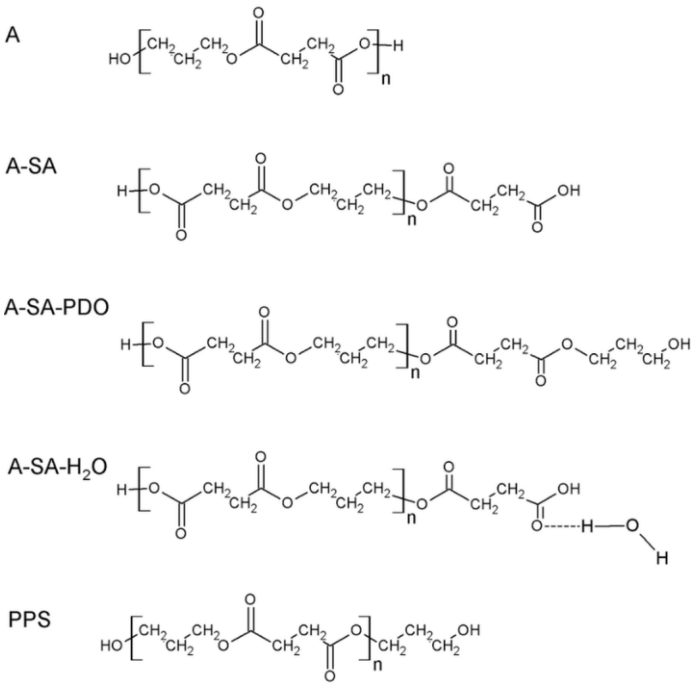


822



823

824 Figure 6

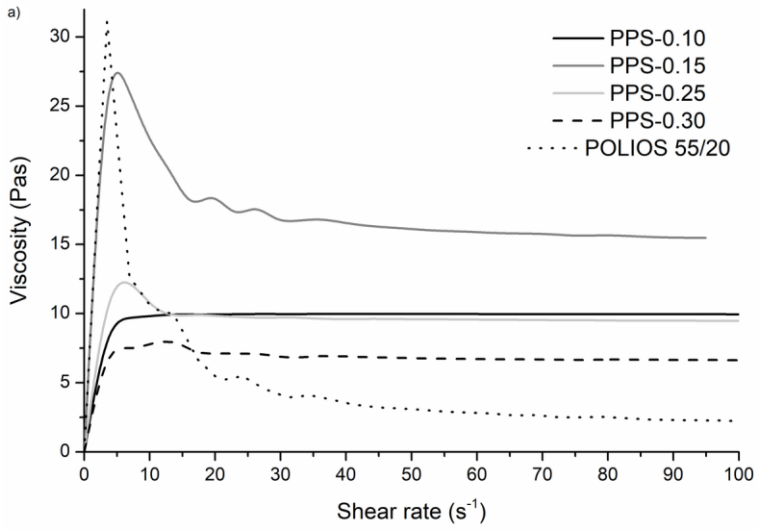


825

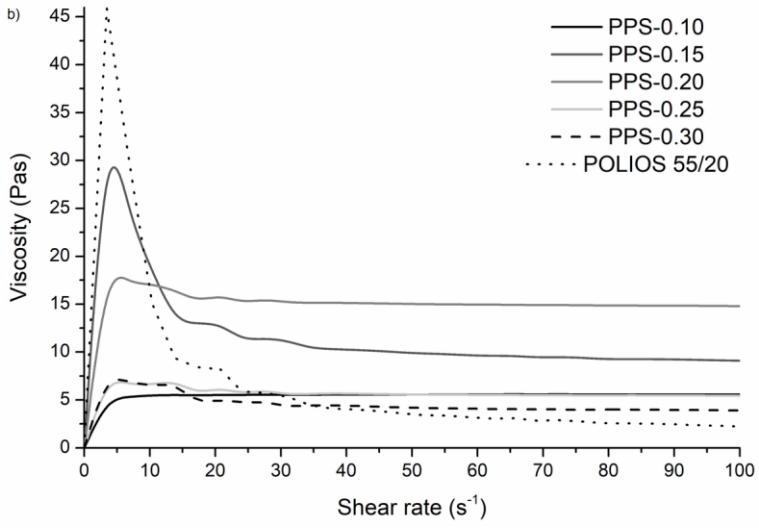
826

827 Figure 7

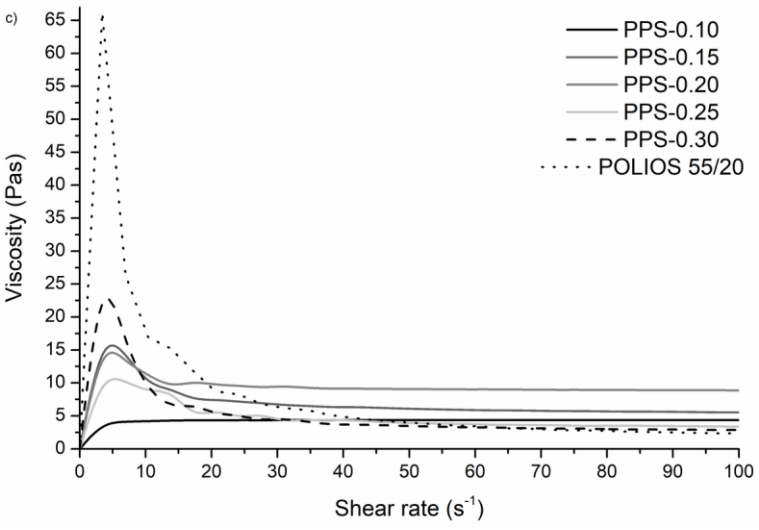
828



829

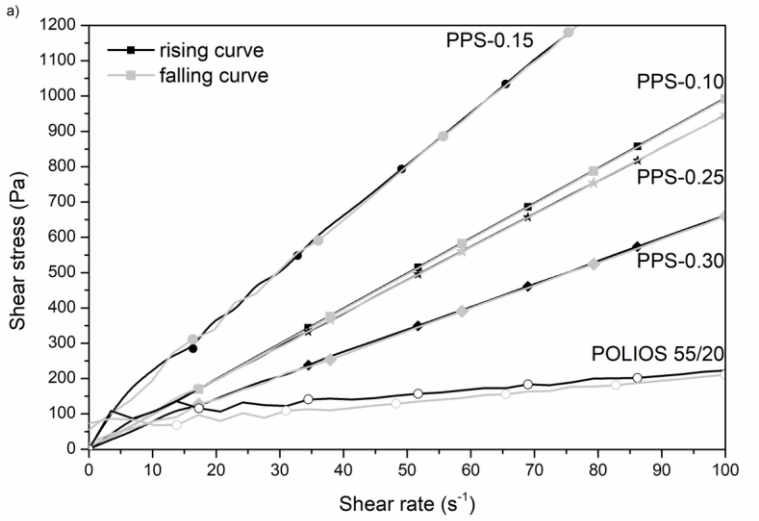


830

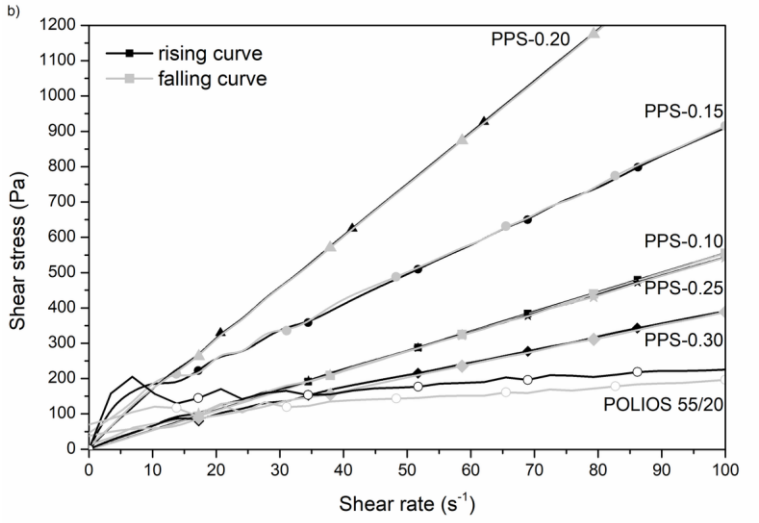


831

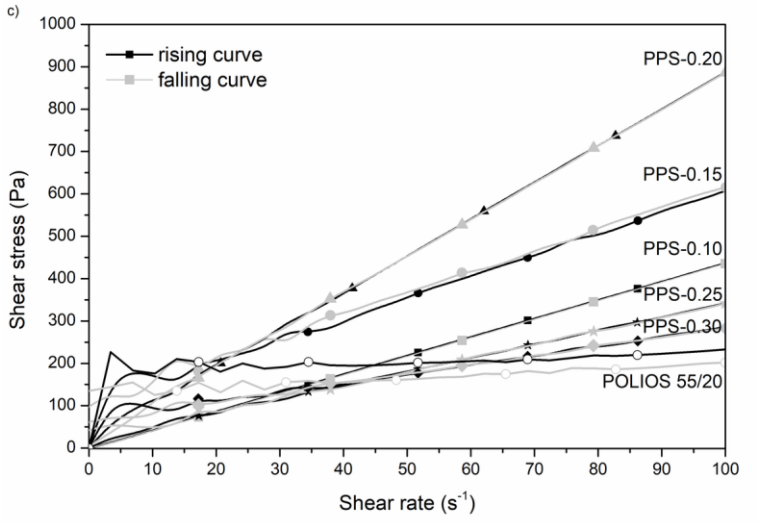
832 Figure 8



833



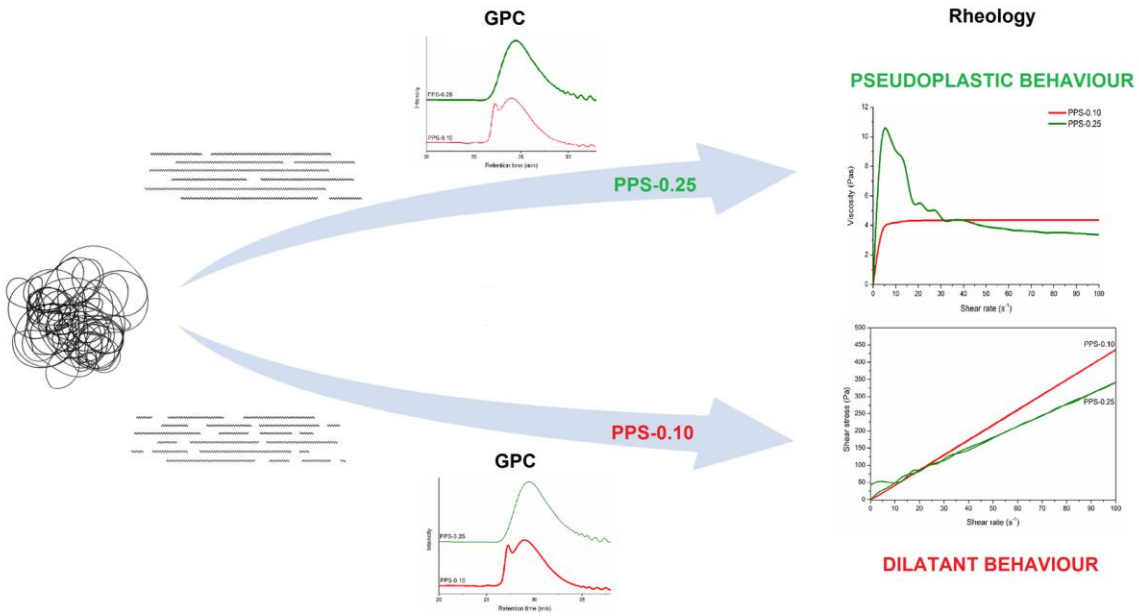
834



835

836

837 Graphical Abstract



838