Supporting Information

Properties of Novel Polyesters Made from Renewable 1,4-Pentanediol

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Properties of novel polyesters made from renewable 1,4-pentanediol

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Supporting Information

Contents

1. General remarks ........................................................................................................................................S2
1.1 Reagents..................................................................................................................................................S2
1.2 NMR-Spectroscopy ..................................................................................................................................S2
1.3 GPC, DSC, and stress-strain tests: ........................................................................................................S2
2. Synthesis of 1,4-PDO ...................................................................................................................................S2
3. Characterization of side products in the polycondensation reactions .......................................................S3
3.1. NMR-analytics of the condensate .........................................................................................................S3
3.2. HRMS analysis of cyclic side products in the low molecular weight fraction .........................................S5
4. Characterization of 1,4-PDO polyester polyols .......................................................................................S7
4.1 NMR spectra of polyester polyols ..........................................................................................................S7
4.2 GPC traces of the polyester polyols .........................................................................................................S13
4.3 DSC traces of the polyester polyols .........................................................................................................S16
4.4 Tensile testing of 4,4’-MDI PU films of the polyester polyols .................................................................S22
1. General remarks

1.1 Reagents

\(\gamma\)-Valerolactone (98%) was obtained from Sigma Aldrich, distilled over triphenylphosphine and dried over molecular sieves prior to use. Succinic acid (99%), adipic acid (99%), azelaic acid (98%), sebacic acid (98%), 1,12-dodecanedioic acid (99%), 1,14-tetradecanedioic acid (99%) and 1,4-butanediol (99%) were purchased from TCI and used without further purification in the polycondensation reactions.

1.2 NMR-Spectroscopy

\(^1\)H-NMR and \(^{13}\)C-NMR spectra were recorded at ambient temperature on 300 MHz spectrometers (Avance 300 respectively Fourier 300) or a 400 MHz spectrometer (Avance 400) from Bruker. The chemical shifts \(\delta\) are given in ppm and referenced to the residual proton signal of the solvent used.

1.3 GPC, DSC, and stress-strain tests:

Gel permeation chromatography (GPC): Gel permeation chromatograms were measured with a 1260 Infinity GPC/SEC System from Agilent Technologies. The setup consisted of a SECcurity Isocratic Pump, SECcurity 2-Canal-Inline-Degaser, SECcurity GPC-Column thermostat TCC6000, SECcurity Fraction Collector and SECcurity Differential Refractometer detector. The measurements were performed at a constant temperature of 50 °C using three columns with a polyester co-polymer network as the stationary phase (PSS GRAM 30 Å, 10 μm particle size, 8.0 x 50 mm; PSS GRAM 30 Å, 10 μm particle size, 8.0 x 300 mm; PSS GRAM 1000 Å particle size, 8.0 x 300 mm). As the mobile phase tetrahydrofuran with a flow rate of 1 mL·min\(^{-1}\) was applied. Polystyrene standards from ReadyCal (PSS-pskitr1l-10, \(M_p = 370–2520000\) g·mol\(^{-1}\)) were used for calibration purposes.

Differential scanning calorimetry (DSC): Melting points and glass transition temperatures of polyesters were measured with a Discovery DSC from TA-Instruments using the following temperature program: -90.00 °C isothermal 5.00 min; Ramp 10.00 °C min\(^{-1}\) to 200.00 °C; Ramp 10.00 °C/min to -90.00 °C; -90.00 °C isothermal 5.00 min; Ramp 10.00 °C min to 200.00 °C; Ramp 10.00 °C/min to -90.00 °C.

Stress-strain tests: Stress-strain testing was conducted using a Z010 test system from Zwick-Roell equipped with a 500 N probe head. Specimen were SF3A-bones with the dimensions 1 x 6 x 35 mm according to DIN 53504. Speed of sample elongation was 50 mm min\(^{-1}\).

2. Synthesis of 1,4-PDO

A 300 ml autoclave (stainless steel – 316) equipped with a magnetic stirring bar was charged with GVL (200g, 2.0 mol) and the atmosphere was replaced by argon followed by the addition of RuNNS\(^{Me}\) (0.05 mol-%, 650 mg) and 16 ml of sodium pentoxide solution in toluene (c=3.33 mol l\(^{-1}\)). After this, the reactor was purged three times with hydrogen and pressurized to 60 bar of hydrogen pressure. Subsequently the stirring speed was increased slowly up to 900 rpm and the reactor heated to 80°C. Hydrogen supply was maintained via a reduction valve. After 16 hours no further hydrogen consumption was observed. After that, the pressure was carefully released and benzoic acid was added (8.0g), followed by distillation in vacuum where the first fraction boiling at 40-50°C was discarded (ca. 4-10 ml). 164 g (78%) of the product could then be collected at 80°C as colourless oil. Analytical data were in good agreement with the literature.
\(^1\text{H-NMR:}\ (300\ \text{MHz, CDCl}_3)\ \delta\ [\text{ppm}]= 3.76\ (dqd, ^3J=7.4, 6.2, 3.8\ \text{Hz}\ 1\text{H, CHCH}_3),\ 3.65–3.51\ (m, 2\text{H, CH}_2\text{OH}),\ 3.47\ (s, \text{br}, 2\text{H, OH}),\ 1.69–1.36\ (m, 4\text{H}),\ 1.13\ (d, ^3J = 6.2\ \text{Hz}, 3\text{H, CHCH}_3)\)

3. Characterization of side products in the polycondensation reactions

3.1. NMR-analytics of the condensate

The decomposition products in the aqueous distillate were identified by \(^1\text{H-}\) and HMBC-NMR spectra after addition of D2O. Revealing the major compound to be water and traces of GVL, 5-hydroxypentan-2-one, 2-MeTHF and 1,4-PDO.

Figure S1: \(^1\text{HNMR of the condensate of a 1,4-PDO polyester synthesis}\)
Figure S2: HMBC-NMR of the sample from above
3.2. HRMS analysis of cyclic side products in the low molecular weight fraction

To determine the presence of cyclic by-products HR-ESI-MS was carried out in the range of m/z = 110-1500, as it was anticipated that cyclics would mostly occur in the lower molecular weight fraction. This fraction roughly contains 4% percent of the molecular weight fraction as shown in figure S3.

![SEC-Trace](image)

**Figure S3**: SEC-Trace of the polyester polyol obtained from 1,4-PDO and succinic acid. The red area corresponds to 4% and represents the part of the molecular weight distribution from 100 to 1000 g/mol.

Prior to the MS-measurement the following derivatization procedure was carried out to aid the distinction between cyclic and linear oligomers:

Phenyl isocyanate derivatization: 500 mg (OH-N; 30 mg KOH/g) of the polyester obtained from 1,4-PDO and succinic acid was placed in a 4 ml vial equipped with a magnetic stirring bar and subsequently vacuum was applied (0.02 mbar) through a cannula. After that, the sample was heated to 80°C and stirred vigorously for 1 hour to ensure dewatering of the polyester polyol. For the next step the vial was repressurized with an argon atmosphere followed by the addition of phenyl isocyanate (30µl, 2.2 eq.). After that, the mixture was stirred for another 2 hours and finally allowed to cool to room temperature. 10 mg of this product were then dissolved in 1 ml of acetonitrile and measured by HR-ESI-MS.

**Figure S4** shows a) the repeating unit and the smallest cyclic respective linear chain found and b) the obtained mass spectrum. Here cyclics containing 2,3,4 and 5 repetition units can be found besides linear chains of the same repeating units. Since there is no deviation from the targeted OH number and in view of the fact that it is possible to obtain solid films, these cyclic impurities most likely only exist in the low molecular weight fraction (itself only 4% of the total) and thus the overall concentration of cyclics is rather low.
Figure S 4: a) Repeating unit and structures of the smallest cyclic and linear oligomers b) ESI-MS showing the cyclic (O) and linear oligomers (L)
4. Characterization of 1,4-PDO polyester polyols
4.1 NMR spectra of polyester polyols

Figure S5: $^1$H-NMR of poly(2-methyl-butylene-succinate)

Figure S6: $^{13}$C-NMR of poly(2-methyl-butylene-succinate)
Figure S7: $^1$H-NMR of poly(2-methyl-butylene-adipate)

Figure S8: $^{13}$C-NMR of poly(2-methyl-butylene-adipate)
Figure S9: $^1$H-NMR poly(2-methyl-butylene-azelate)

Figure S10: $^{13}$C-NMR poly(2-methyl-butylene-azelate)
Figure S11: $^1$H-NMR poly(2-methyl-butylene-sebacate)

Figure S12: $^{13}$C-NMR poly(2-methyl-butylene-sebacate)
Figure S13: $^1$H-NMR of Poly(2-methyl-butylene-1,12-dodecanedioate)

Figure S14: $^{13}$C-NMR of poly(2-methyl-butylene-1,12-dodecanedioate)
Figure S 15: $^1$H-NMR of poly(2-methyl-butylene-tetradecanedioate)

Figure S 16: $^{13}$C-NMR of poly(2-methyl-butylene-tetradecanedioate)
4.2 GPC traces of the polyester polyols

Figure S17: GPC poly(2-methyl-butylene-succinate)

Figure S18: GPC poly(2-methyl-butylene-adipate)
Figure S19: GPC poly(2-methyl-butylene-azelate)

Figure S20: GPC poly(2-methyl-butylene-sebacate)
Figure S21: GPC poly(2-methyl-butylene-1,12-dodecanedioate)

Figure S22: GPC poly(2-methyl-butylene-1,14-tetradecanedioate)
4.3 DSC traces of the polyester polyols

Figure S23: DSC of poly(2-methyl-butylene-succinate)

Figure S24: DSC of poly(2-methyl-butylene-adipate)
Figure S25: DSC of poly(2-methyl-butylene-azole)

Figure S26: DSC of poly(2-methyl-butylene-sebacate)
Figure S 27: DSC of poly(2-methyl-butylene-1,12-dodecanedioate)

Figure S 28: DSC of poly(butylene-1,14-tetradecanedioate)
Figure S 29: DSC of poly(butylene-succinate)

Figure S 30: DSC of poly(butylene-adipate)
Figure S 31: DSC of poly(butylene-azeolate)

Figure S 32: DSC of poly(butylene-sebacate)
Figure S33: DSC of poly(butylene-1,12-dodecanedioate)

Figure S34: DSC of 4,4'-MDI crosslinked poly(2-methyl-butylene-1,12-dodecanedioate)
4.4 Tensile testing of 4,4’-MDI PU films of the polyester polyols

![Stress vs. strain of the MDI crosslinked film of poly(2-methyl-butylene-succinate). The observed inhomogenities are most likely caused by the relative high acid number of 10 mg g⁻¹ of the oligomer.](image1.png)

Figure S35: Stress vs. strain of the MDI crosslinked film of poly(2-methyl-butylene-succinate). The observed inhomogenities are most likely caused by the relative high acid number of 10 mg g⁻¹ of the oligomer.

![Stress vs. strain of the MDI crosslinked film of poly(2-methyl-butylene-adipate). The higher deviation of the individual traces is caused by inhomogeneities in the obtained film, however the result follows still the observed trend.](image2.png)

Figure S36: Stress vs. strain of the MDI crosslinked film of poly(2-methyl-butylene-adipate). The higher deviation of the individual traces is caused by inhomogeneities in the obtained film, however the result follows still the observed trend.
Figure S 37: Stress vs. strain of the MDI crosslinked film of poly(2-methyl-butylen-azelate)

Figure S 38: Stress vs. Strain of the MDI crosslinked film of poly(2-methyl-butylen-sebacate)

Figure S 39: Stress vs. strain of the MDI crosslinked film of poly(2-methyl-butylen-1,12-dodecanedioate)
Figure S40: Stress vs. strain of the MDI crosslinked film of poly(butylene-succinate). The exact determination of the elongation at break is not possible due to the high brittleness of the film.

Figure S41: Stress vs. strain of the MDI crosslinked film of poly(butylene-adipate)
Figure S42: Stress vs. strain of the MDI crosslinked film of poly(butylene-azelate)

Figure S43: Stress vs. strain of the MDI crosslinked film of poly(butylene-sebacate)

Figure S44: Stress vs. Strain of the MDI crosslinked film of poly(butylene-1,12-dodecandioate)