Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Selective chemical disassembly of elastane fibres and polyurethane coatings in textiles

Martin B. Johansen[a†], Bjarke S. Donslund[b†], Martin L. Henriksen[c], Steffan K. Kristensen*[a], Troels Skrydstrup*[d]

Corresponding authors
Email: skk@inano.au.dk
Email: ts@chem.au.dk

[a]Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Gustav Wieds Vej 14, 8000 Aarhus C, Denmark.

[b]Carbon Dioxide Activation Center (CADIAC), Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, Gustav Wieds Vej 14, 8000 Aarhus C, Denmark.

[c]Department of Biological and Chemical Engineering, Aarhus University, Aabogade 40, 8200 Aarhus N, Denmark.

[d]Carbon Dioxide Activation Center (CADIAC), Novo Nordisk Foundation CO_2 Research Center, Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, Gustav Wieds Vej 14, 8000 Aarhus C, Denmark.

[†]Contributed equally.

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SI-1. General Information

Unless otherwise stated, all reactions were set-up in an oven-dried 30 mL PTFE inlay fitted into a 45 mL autoclave cell under ambient atmosphere. The pressure vessels were heated in aluminium blocks specifically designed to fit the vessels. Flash column chromatography was performed on the Interchim Puriflash XS520plus automated column system using Interchim Puriflash prepacked 25 g columns with 30 µm spherical silica (PF-30SIHP-F0025). NMR analysis was performed on a Bruker Ascend 400 spectrometer, where ^{1}H NMR and ^{13}C NMR were recorded at 400 MHz and 101 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent signal of the deuterated solvent. Abbreviations of multiplicity patterns in NMR spectra are reported as followed: s = singlet, bs = broad singlet, br. t = broad triplet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sep = septet, m = multiplet, dd = double doublet, dt = double triplet, ddd = double double doublet. HRMS spectra were recorded on a Bruker Maxis Impact Spectrometer (TOF, ESI). GC experiments were performed using an Agilent 8890 GC System (Column: HP-5 5% Phenyl methyl siloxane, 30 m x 250 µm x 0.25 µm). Specifications on the method: Inlet: 170 ºC, Detector: FID 300 ºC; Carrier gas: He. Flow 2 mL/min. Oven: 50 ºC, hold 0.5 min; 35 ºC/min to 300 ºC, hold 1.7 min. Calibration curve for determining GC yields was obtained by using standard solutions of the analyte (4,4'-methylenedianiline) in EtOAc. Differential Scanning Calorimetry (DSC) was performed under nitrogen atmosphere in a DSC 8500 (PerkinElmer, USA) controlled by Pyris (v. 11.1.0.0488, PerkinElmer, USA). Samples (5-10 mg) were sealed (Universal Crimper Press, PerkinElmer, USA) into aluminium pans (Pans and covers type: 02190041) prior to measurement. All samples were run through the following program. 1) Heating from 20.0 °C to 290.0 °C at 10.0 °C min^{-1}, 2) Cooling from 290.0 °C to 20.0 °C at 60.0 °C min^{-1}, 3) Heating from 20.0 °C to 290.0 °C at 10.0 °C min^{-1}, 4) Cooling from 290.0 °C to 0.0 °C at 60.0 °C min^{-1}, 5) Holding for 1.0 min at 0.0 °C, 6) StepScan of step size 1.0 °C from 0.0 to 300.0 °C at 5.0 °C min^{-1}. The reported values are based on the StepScan. Thermogravimetric Analysis (TGA) was performed on a TG 209 F1 Libra (Netzsch, GE). Samples (5-10 mg) were heated at 10 °C min^{-1} from 35 °C to 500 °C in either nitrogen or laboratory atmosphere; subsequently changed into laboratory air and held isotherm for 10 min at 500 °C, and heated at 10 °C min^{-1} from 500 °C to 600 °C. The derivative was found via a Savitzy-Golay filter (25 points average, 2nd order, 1st derivative) and is indicated with a dotted line. Fourier Transformed Infrared Spectroscopy (FTIR) of the samples were collected in an Attenuated Total Reflection (ATR) mode on an iS5 spectrophotometer (Thermo Fisher Scientific, USA) fitted with a ZnSe crystal (iD5, Thermo Fisher Scientific, USA). Background (n=16) and sample measurement (n=16) were measured with a resolution of 2 cm^{-1} from 600 to 4000 cm^{-1}. For SI-15 and SI-16, FTIR was measured on a Bruker Alpha II system with ATR fitted with a diamond crystal. Background (n=24) and sample measurement (n=24) were measured with a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1}.

SI-2. Description of Pressure Vessels

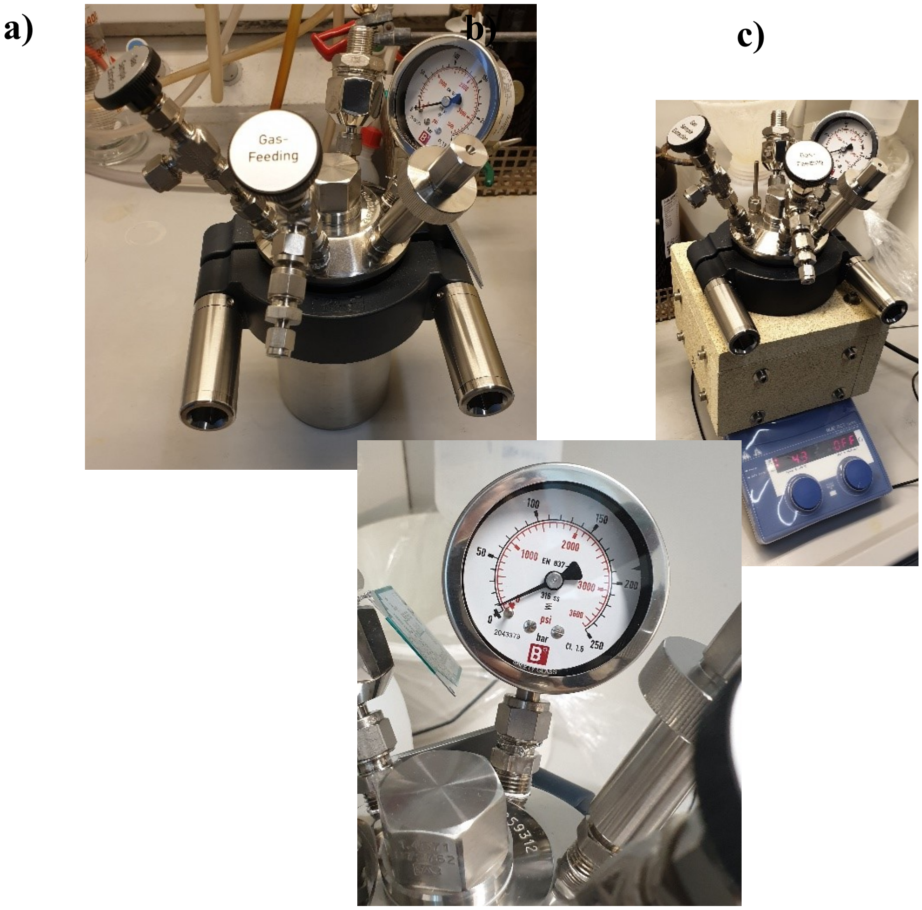
“Small autoclave”

45 mL pressure vessels made from T316 stainless steel alloy, designed to handle a temperature range: -10–300 ˚C. The head consists of a single inlet/outlet valve fitted for 5000 Multi Reactor System (Parr®), thermowell for thermocouple insertion, removable PTFE gasket, screw cap and six stainless steel compression bolts for sealing the contents of the reaction well. Unless otherwise noted, all reactions were set up using a 30 mL PTFE inlay along with a PTFE coated magnet.

a) Parts of a pressure vessel: 1 – vessel head, 2 – 45 mL reaction well, 3 – magnetic stirring bar, 4 – 30 mL PTFE inlay, 5 – hex key for fastening bolts; b) assembled pressure vessel.

“Large autoclave”

Berghof BR-300 High Pressure Reactor with an internal volume of appr. 390 mL made of Stainless Steel 316Ti. A heating block that is adaptable to common heating- and stirring plates was made in-house.



a) Assembled autoclave. b) Autoclave in heating block on stirring plate. c) Manometer for pressure read-out.

SI-3. Procedures

General Procedure A: Deconstruction of PU containing Textiles or Elastane

To a PTFE inlay fitted with a stir bar was added textile sample or elastane (250 mg), KOH (1.9 mg, 0.033 mmol), and *tert*-amyl alcohol (5 mL) in an argon-filled glovebox. The PTFE inlay was placed in an autoclave reactor, which was sealed and fastened using a hex key. The reactor was placed in a pre-heated aluminium block at 225 °C for 4.5 h at 800 rpm stirring rate. The reactor was then cooled to room temperature before it was opened and the thermowell was washed with EtOAc. The content of the reactor was transferred washing with EtOAc to a round-bottomed flask or a vial in which mesitylene (50 µL) was previously added as an internal standard (exact mass of mesitylene was noted). An aliquot of 250 µL was transferred to a vial and the mixture was filtered through a small cotton and celite plug (3–5 mm of celite in a glass pipette) followed by additional EtOAc into a 2 mL vial suited for GC-MS. The sample was analysed using the GC method described under General Information. The GC yield of dianilines was determined using pre-made calibration curves.

The aliquot was returned to the main crude mixture. If the sample did not contain leftover fabric, the mixture was purified by automated flash column chromatography using an EtOAc/heptane eluent system from 1:9 to pure EtOAc. Following elution of the anilines, the polyol fraction was collected by flushing the column with MeOH. If the sample contained leftover fabric, the crude reaction mixture was filtered and washed with excess EtOAc. The leftover fabric was dried *in vacuo* overnight. The filtrate was purified by column chromatography as described above.

General Procedure B: Deconstruction of PU Textiles (1 g, benchtop)

On the benchtop, a PTFE inlay fitted with a stir bar was added textile sample (1 g), KOH (1.9 mg, 0.033 mmol), and *tert*-amyl alcohol (5 mL). The PTFE inlay was placed in an autoclave reactor, which was sealed under ambient atmosphere and fastened using a hex key. The reactor was placed in a pre-heated aluminium block at 225 °C for 4.5 h at 800 rpm stirring rate. The reactor was then cooled to room temperature before it was opened and the thermowell was washed with EtOAc. The content of the reactor was filtered and washed with excess EtOAc. The leftover fabric was dried *in vacuo* overnight. The filtrate was concentrated onto celite under reduced pressure and purified by automated flash column chromatography using an EtOAc/heptane eluent system going from 1:9 to pure EtOAc. Following elution of the anilines, the polyol fraction was collected by flushing the column with MeOH.

General Procedure C: Deconstruction of PU Textiles (1 g, benchtop)

On the benchtop, a PTFE inlay fitted with a stir bar was added textile sample (1 g), KOH (1.9 mg, 0.033 mmol), and *tert*-amyl alcohol (5 mL). The PTFE inlay was placed in an autoclave reactor, which was sealed under ambient atmosphere and fastened using a hex key. The reactor was placed in a pre-heated aluminium block at 225 °C for 4.5 h at 800 rpm stirring rate. The reactor was then cooled to room temperature before it was opened and the thermowell was washed with EtOAc. The content of the reactor was filtered and washed with excess EtOAc. The leftover fabric was dried *in vacuo* overnight. The filtrate was concentrated under reduced pressure and purified by silica plug filtration on an automated flash column chromatography using an EtOAc/heptane eluent system of 3:1 (200 mL) to remove impurities (by-products) after which the plug was flushed with MeOH (200 mL) to collect the polyol fraction.

General Procedure D: Deconstruction of PU Textiles, Precipitation of Anilines (1 g, benchtop)

On the benchtop, a PTFE inlay fitted with a stir bar was added textile sample (1 g), KOH (1.9 mg, 0.033 mmol), and *tert*-amyl alcohol (5 mL). The PTFE inlay was placed in an autoclave reactor, which was sealed under ambient atmosphere and fastened using a hex key. The reactor was placed in a pre-heated aluminium block at 225 °C for 4.5 h at 800 rpm stirring rate. The reactor was then cooled to room temperature before it was opened and the thermowell was washed with EtOAc. The content of the reactor was filtered and washed with excess EtOAc. The leftover solid was dried *in vacuo* overnight. The filtrate was concentrated and redissolved in toluene or EtOAc followed by addition of HCl (0.5 mL, 3 M in CPME). The 4,4'-MDA·2HCl was washed thoroughly with EtOAc. The filtrate (polyol fraction) was concentrated *in vacuo* to afford polyol. The sticky 4,4'-MDA·2HCl was flushed into a flask with methanol and concentrated *in vacuo*.

SI-4. Solvolysis of Elastane/Spandex Fibre (Virgin)

The elastane fibre/thread was of the brand: Creoara

The fibre was used as received.

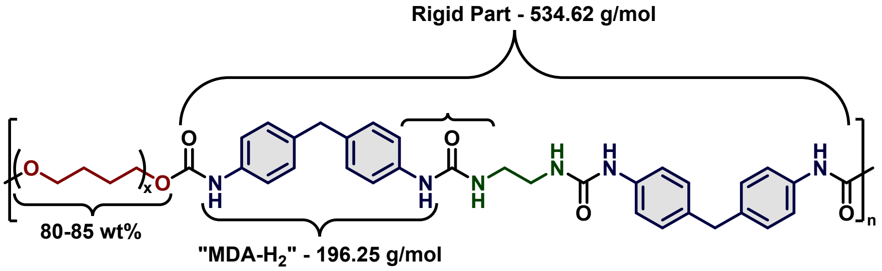
The PU (run 1: 253.8 mg; run 2: 256.3 mg) was deconstructed as described in General Procedure A to afford 4,4'-MDA (run 1: 35.5 mg; run 2: 31.1 mg) as an off-white solid in an average yield of 33.3 mg, and a polyol fraction (run 1: 179.1 mg; run 2: 193.6 mg) as a viscous yellow oil in an average yield of 186.4 mg.

Back-of-the-envelope calculation for the estimation of 4,4'-MDA theoretical yield

Assume mass of 250 mg elastane fibre.

Assume 80-85 wt% polyol (x_{polyol}).

Assume following repeating unit of elastane:



The ratio of "MDA-H$_2$" in the rigid part of the repeating unit is 0.73:

$$\frac{M_{"MDA-H_2"}}{M_{rigid\ part}} = \frac{392.5\frac{g}{mol}}{534.62\frac{g}{mol}} = 0.73$$

The ratio of molar mass between MDA and "MDA-H$_2$" is 1.01:

$$\frac{M_{MDA}}{M_{"MDA-H_2"}} = \frac{198.27\frac{g}{mol}}{196.25\frac{g}{mol}} = 1.01$$

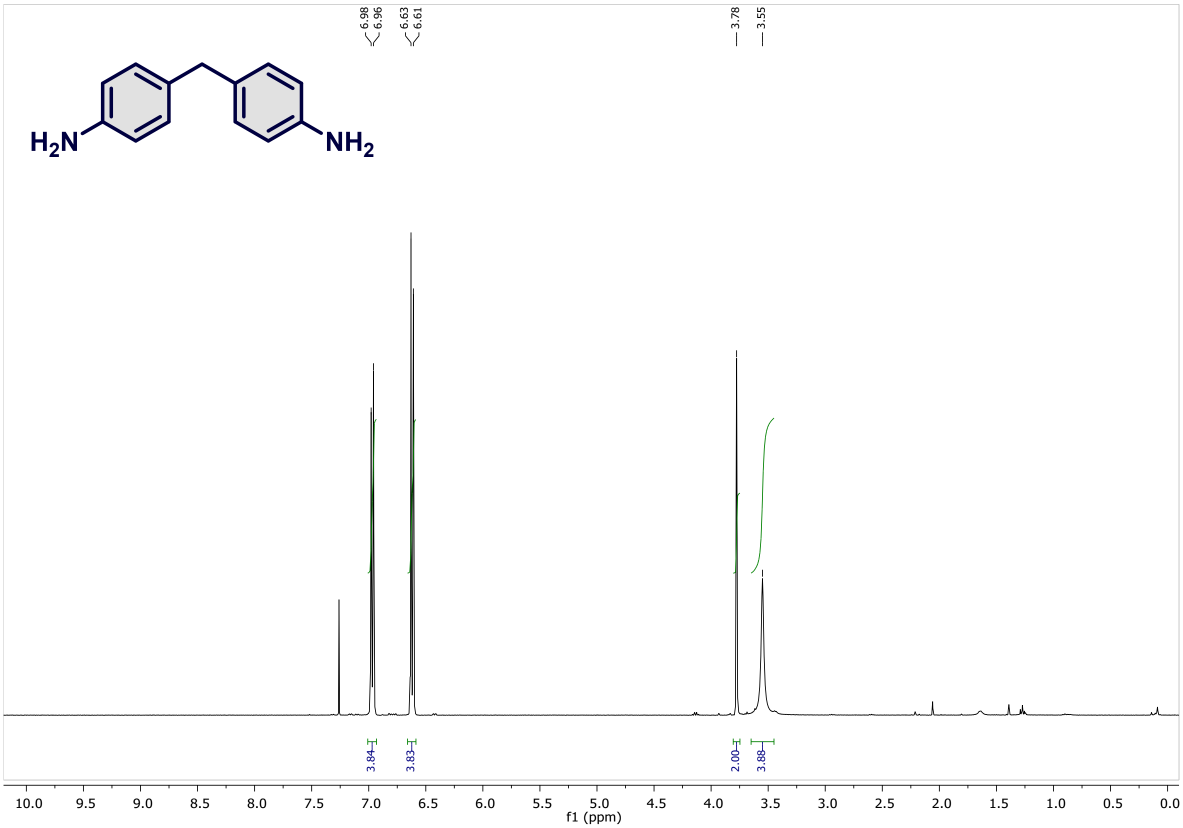
Lower theoretical MDA mass:

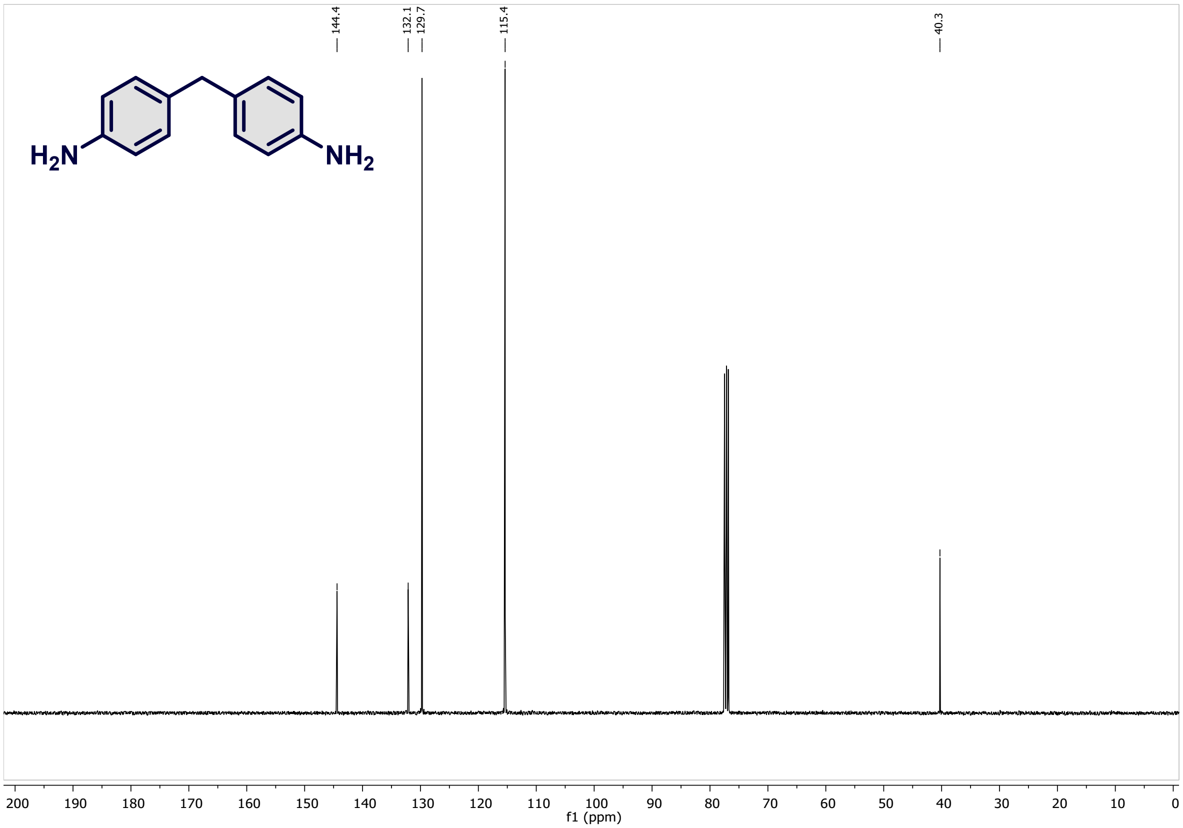
$$m_{low\,MDA} = m_{elastane} \cdot (1 - x_{polyol,high}) \cdot \frac{M_{"MDA-H_2"}}{M_{rigid\,part}} \cdot \frac{M_{MDA}}{M_{"MDA-H_2"}} = 250\ mg \cdot (1 - 0.85) \cdot 0.73 \cdot 1.01 = 27.7\ mg$$

Higher theoretical MDA mass:

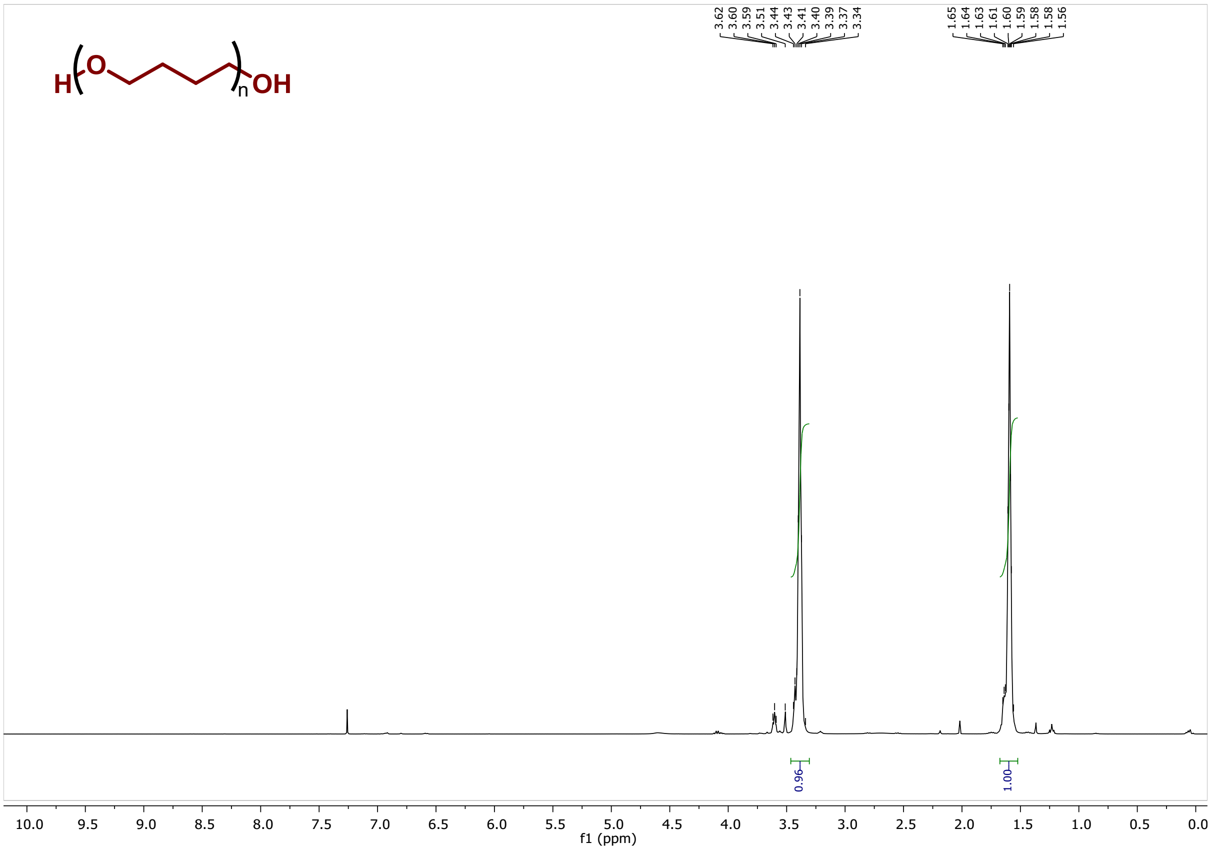
$$m_{high\,MDA} = m_{elastane} \cdot (1 - x_{polyol,low}) \cdot \frac{M_{"MDA-H_2"}}{M_{rigid\,part}} \cdot \frac{M_{MDA}}{M_{"MDA-H_2"}} = 250\ mg \cdot (1 - 0.80) \cdot 0.73 \cdot 1.01 = 36.9\ mg$$

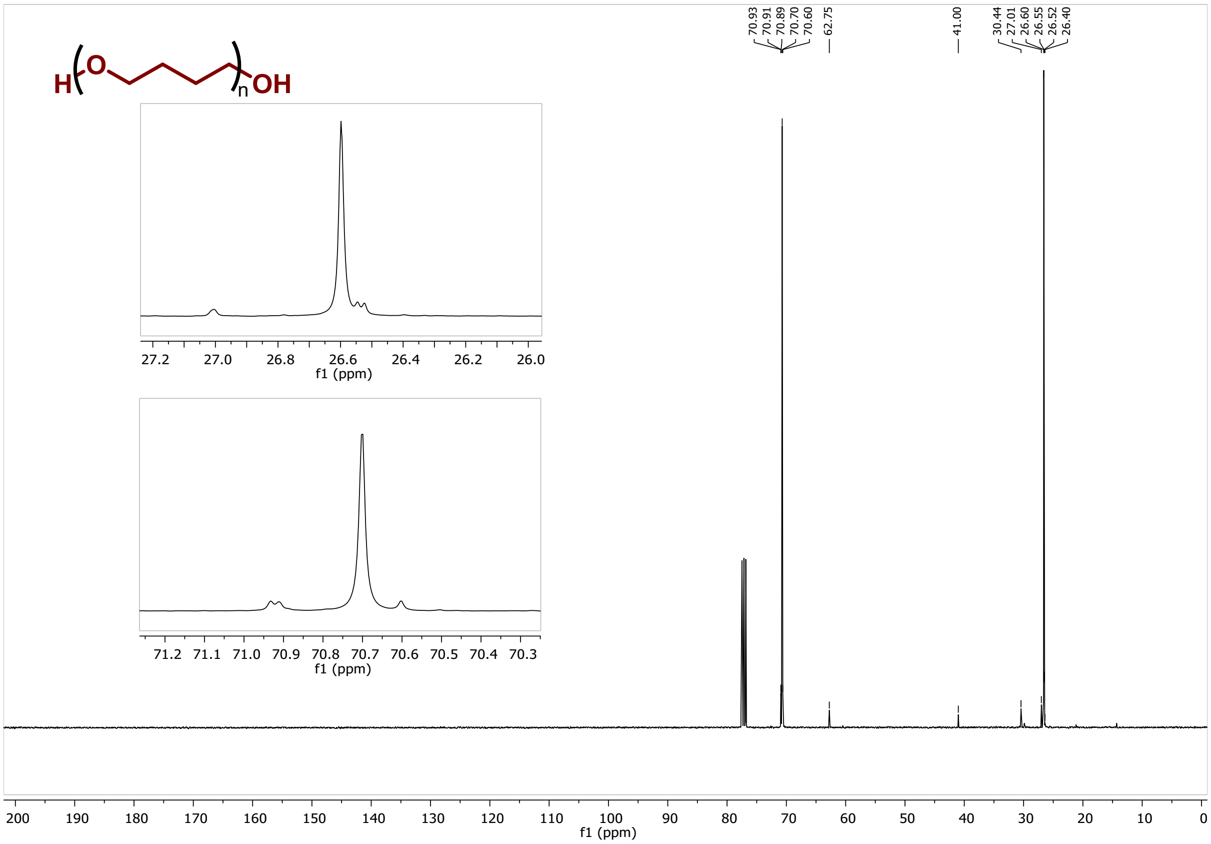
NMR Spectra of MDA fraction



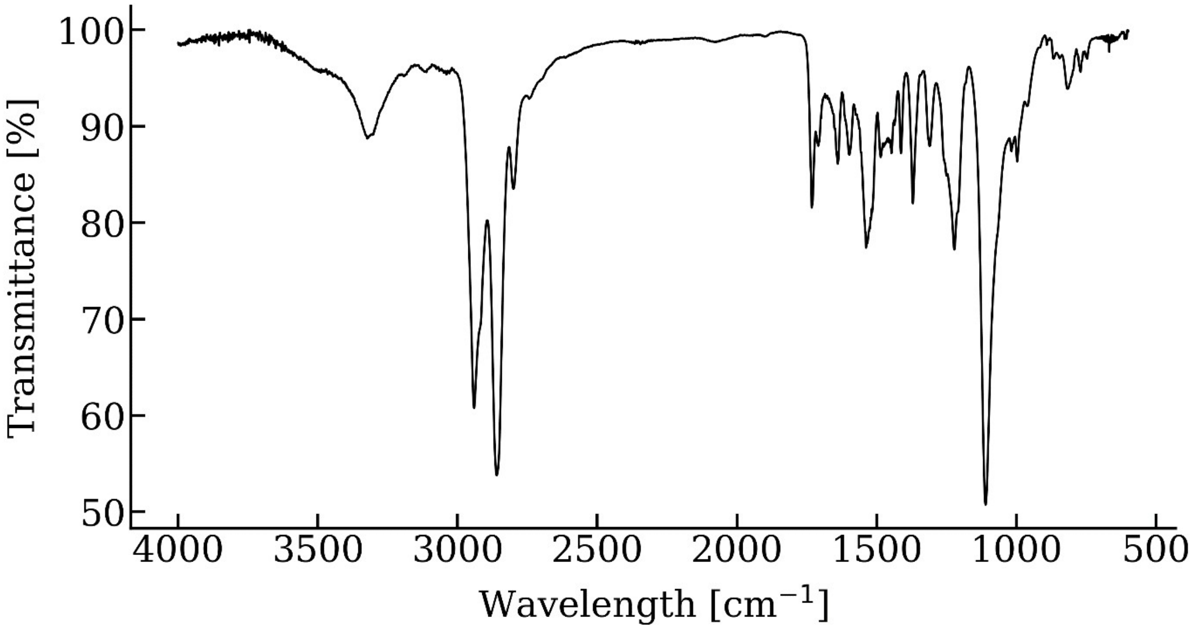


NMR Spectra of Polyol Fraction

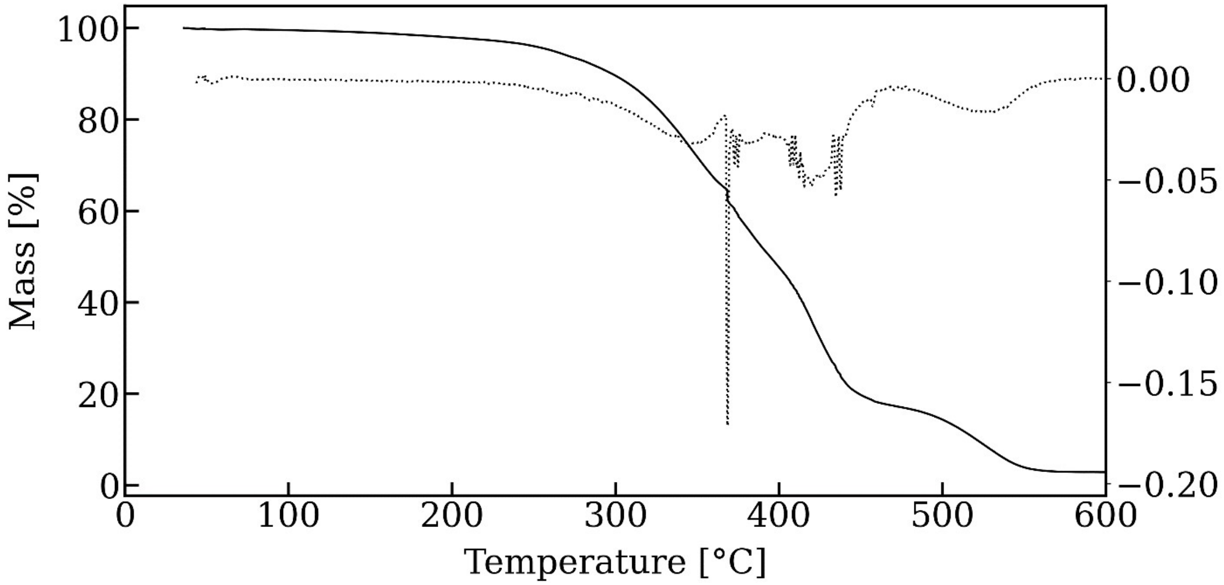


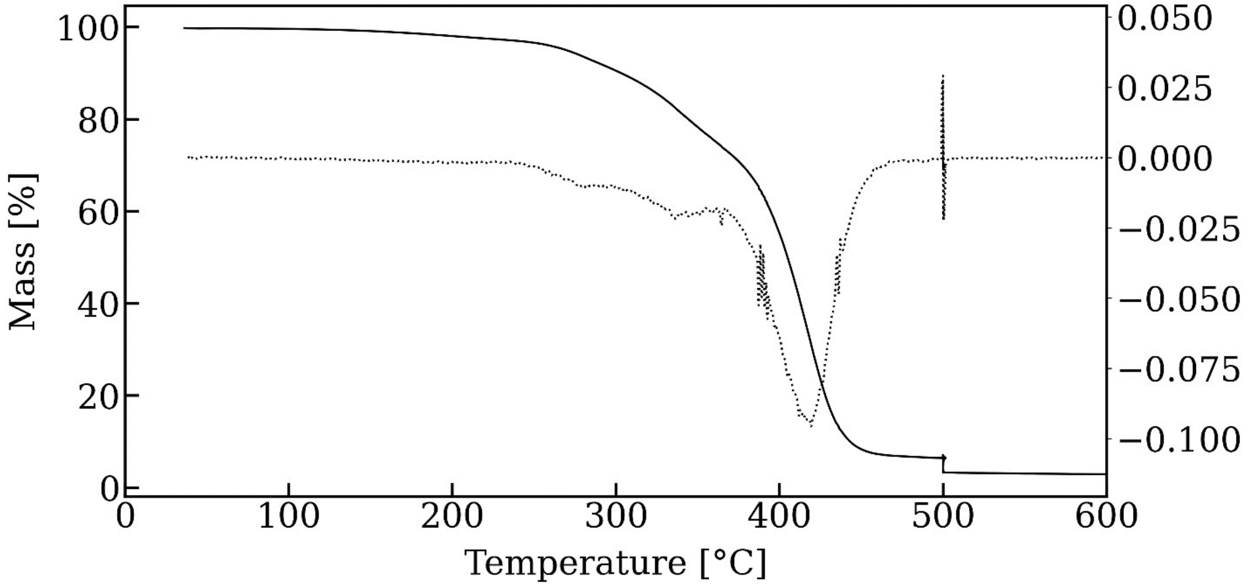


FTIR Spectrum of Creoara Elastane Fibre

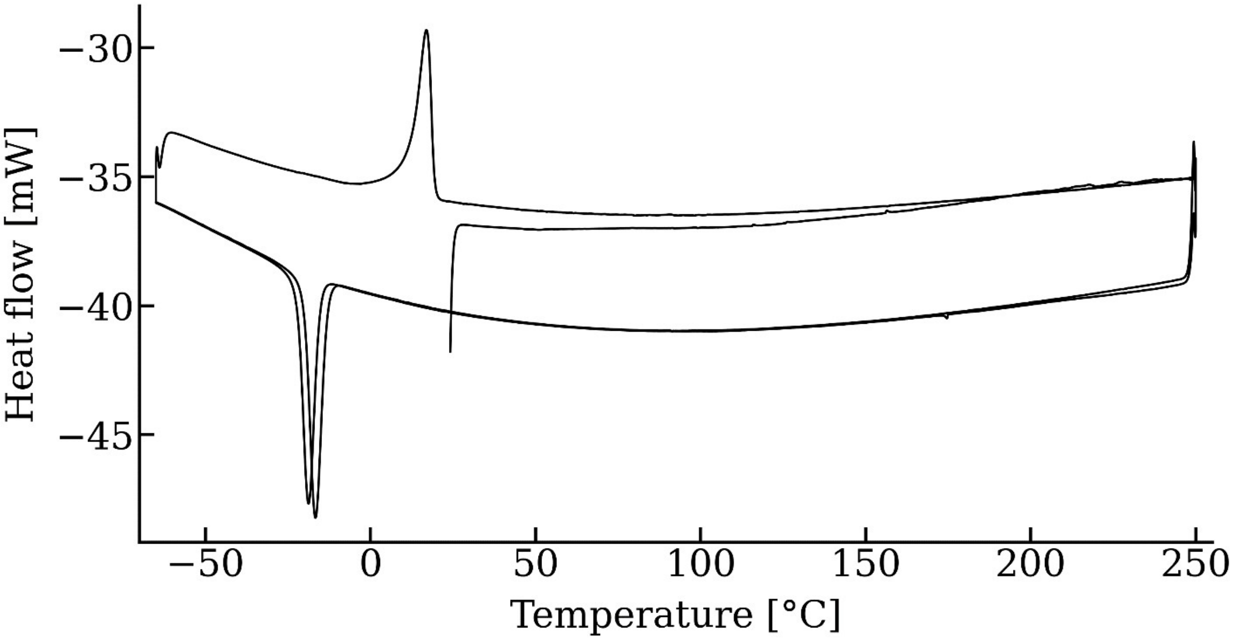


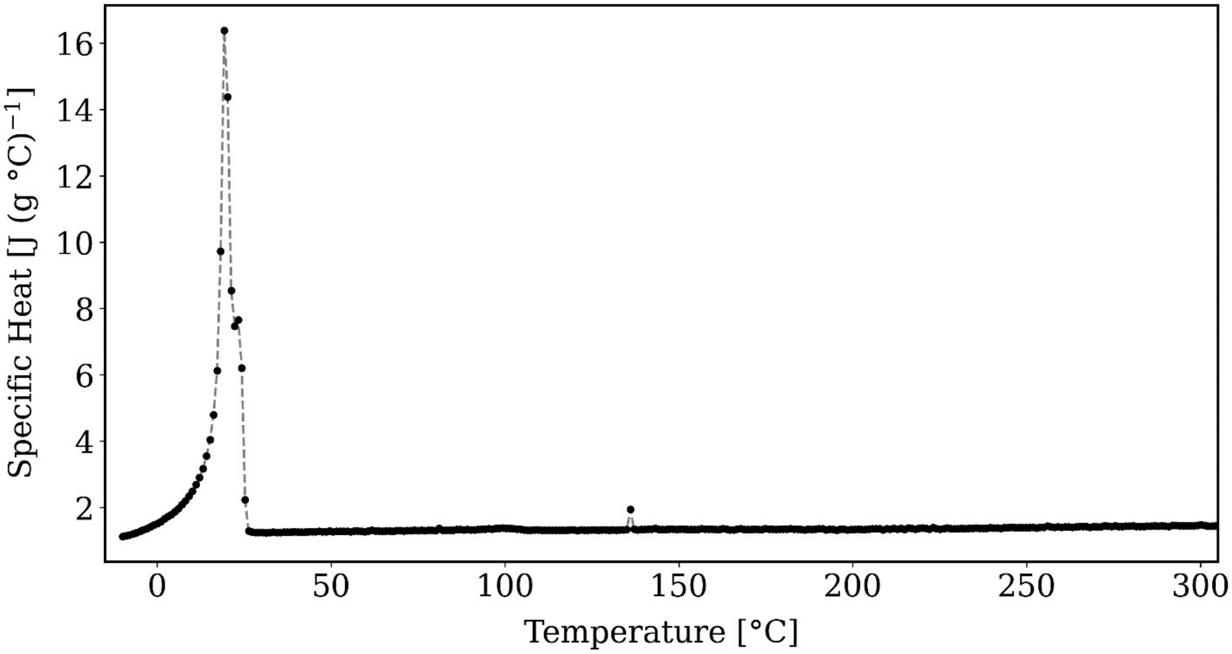
TGA Spectra of Creoara Elastane Fibre Recorded in Laboratory Air (Top) and Nitrogen Atmosphere (Bottom)





DSC of Creoara Elastane Fibre with two Heating-Cooling Cycles (top) and DSC StepScan (bottom)





SI-5. Solvolysis of Nylon Tights (250 mg scale)

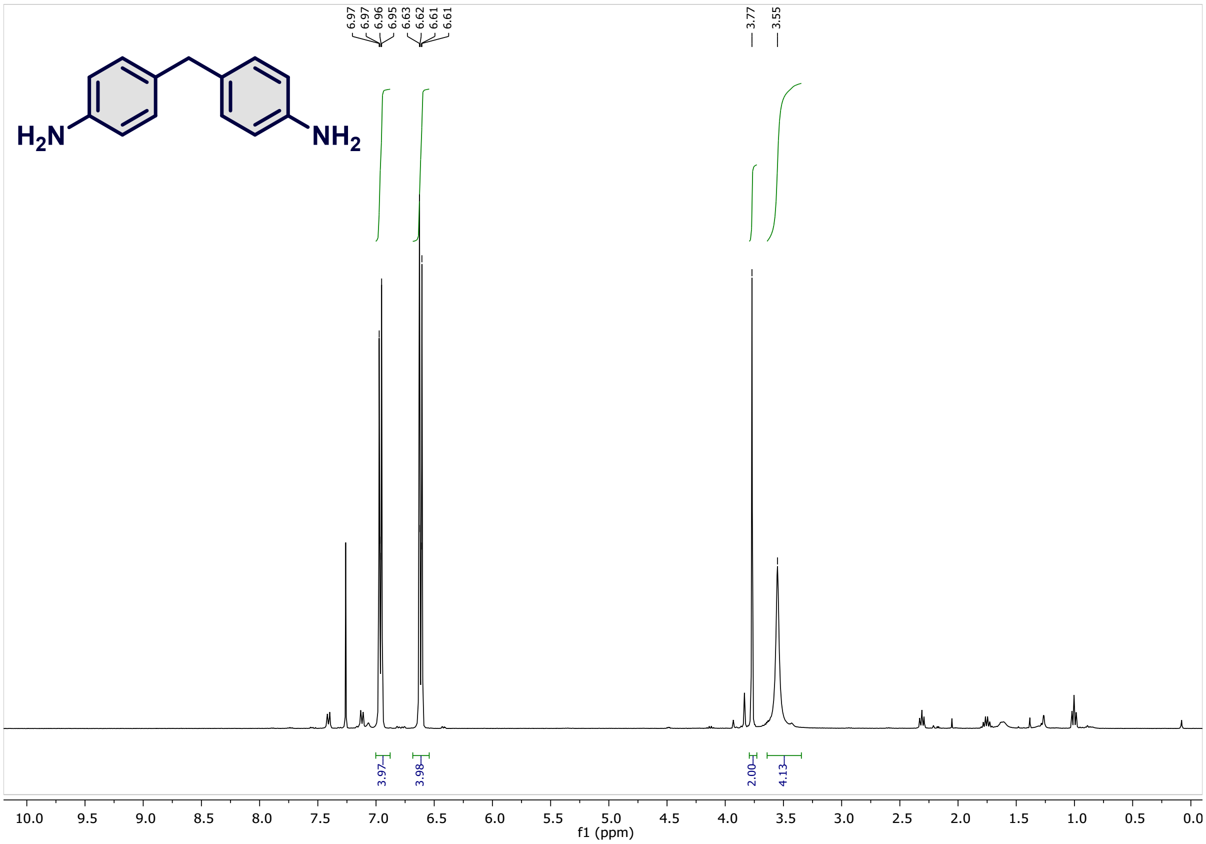
The tights (brand: VRS, 10 denier, black, “Løbefri Strømpebukser”, 27% elastane and 73% polyamide) were acquired in a local supermarket.

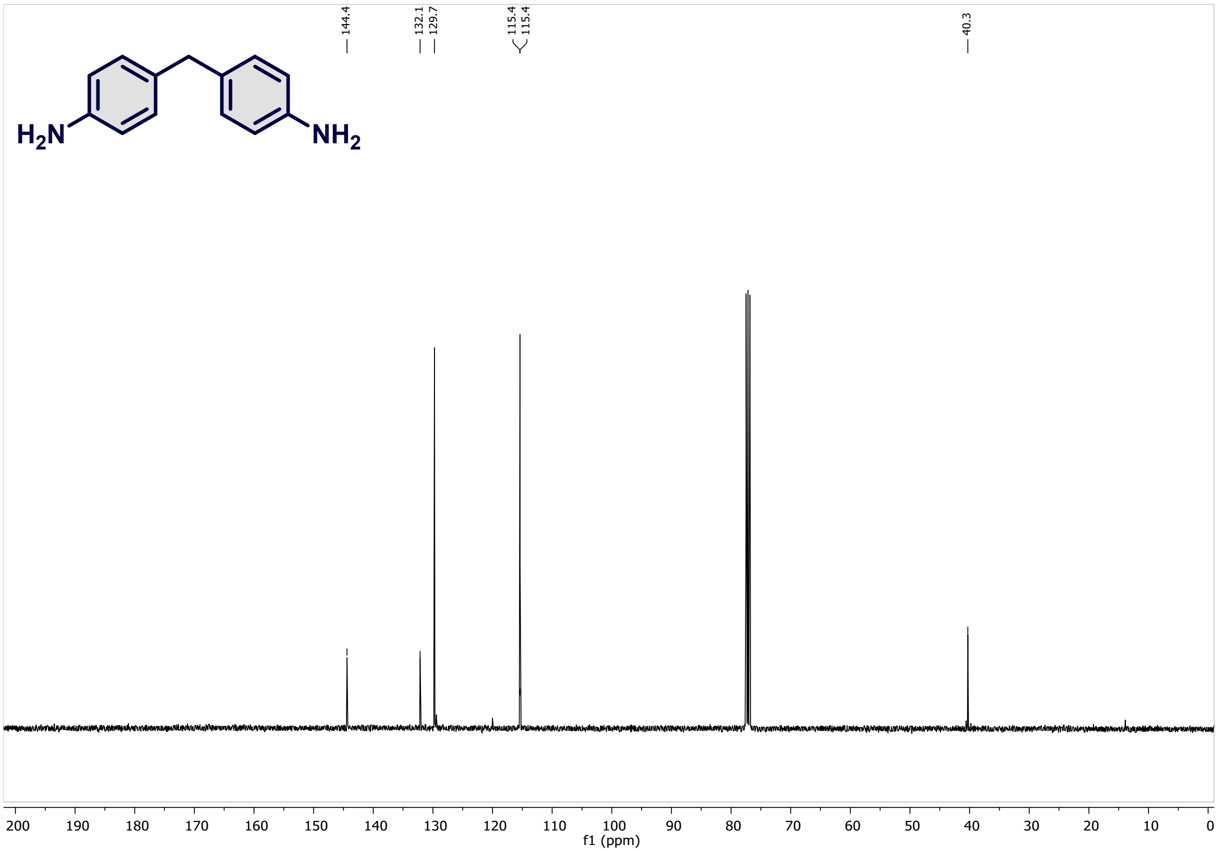
The tights were cut into smaller pieces with a pair of scissors.

The PU (run 1: 252.5 mg; run 2: 255.2 mg) was deconstructed as described in General Procedure A to afford 4,4’-MDA (run 1: 11.3 mg; run 2: 12.0 mg)* in an average yield of 11.7 mg, an unknown mixture of by-products (run 1: 17.3 mg; run 2: 2.9 mg) as an off-white solid in an average yield of 10.1 mg, a polyol fraction (run 1: 46.4 mg; run 2: 63.0 mg) as a viscous yellow oil in an average yield of 54.7 mg, and a leftover black fabric (run 1: 163.7 mg; run 2: 166.9 mg) in an average mass of 165.3 mg.

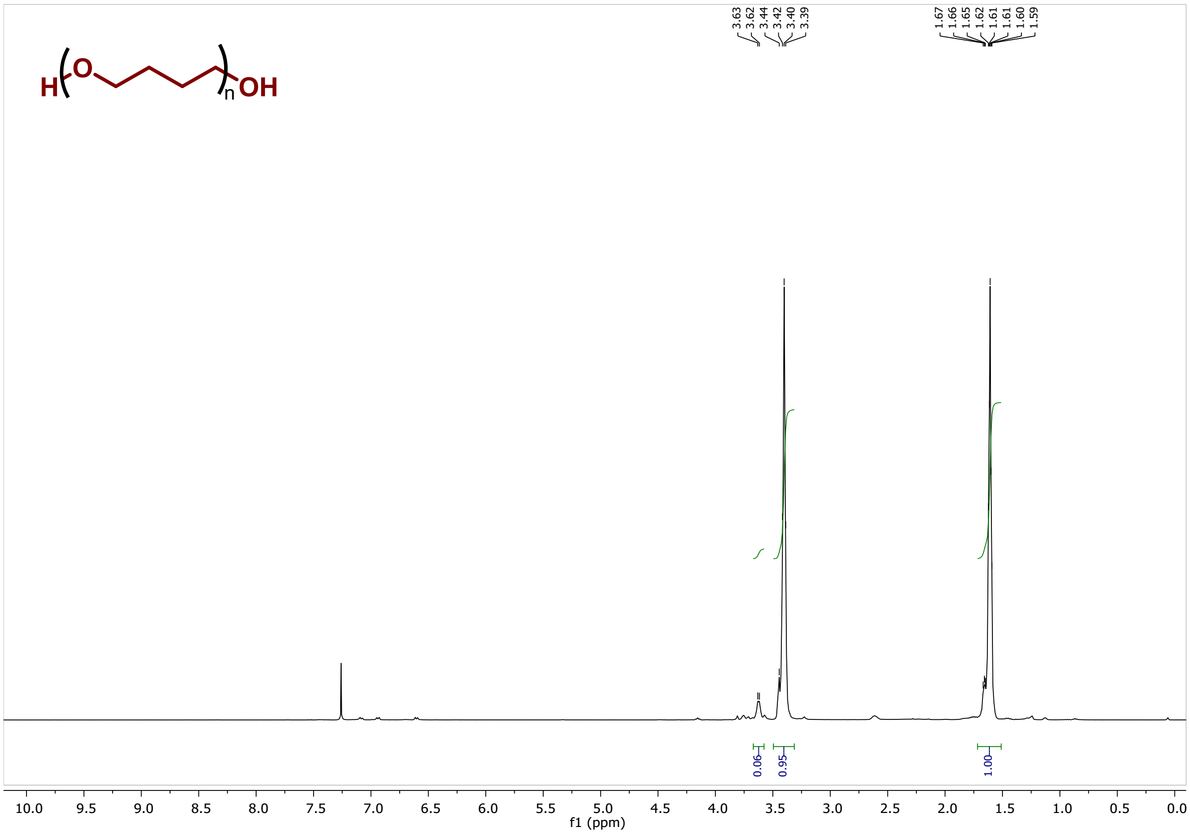
*The 4,4’-MDA fraction contains a minor impurity.

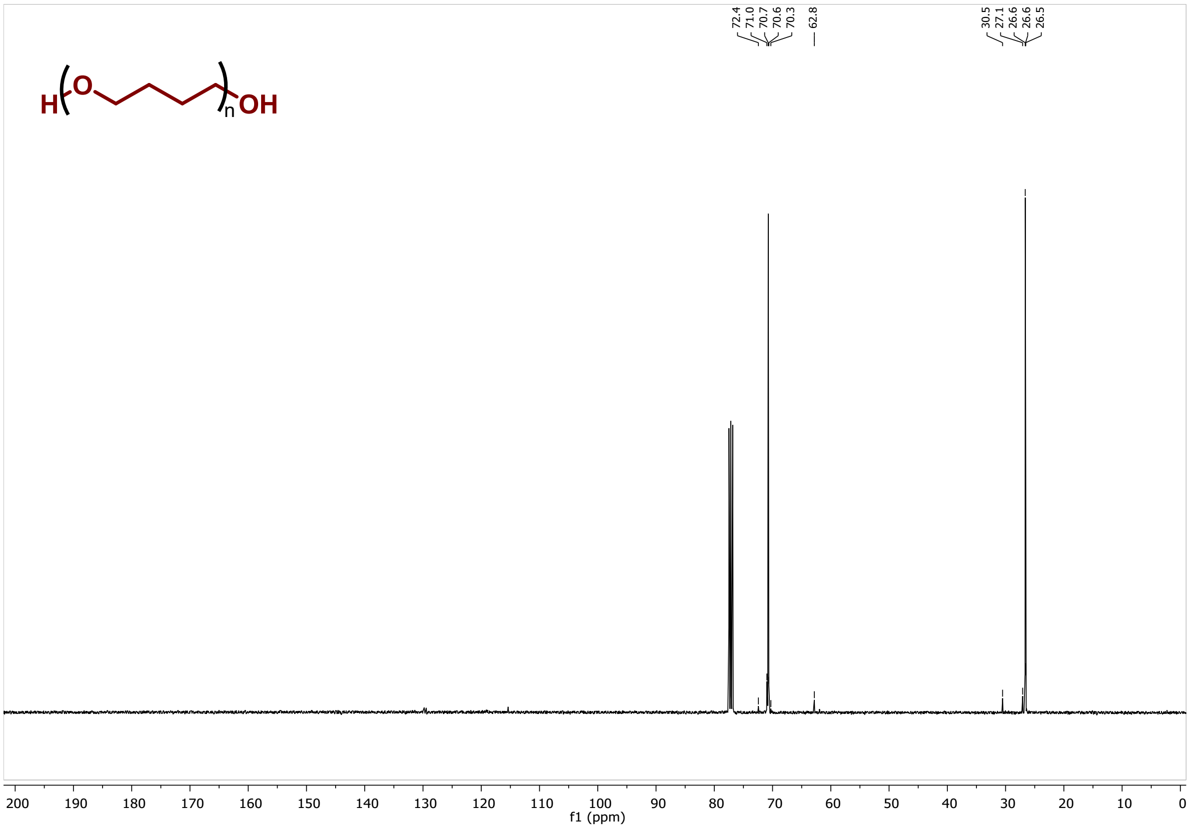
NMR Spectra of MDA Fraction



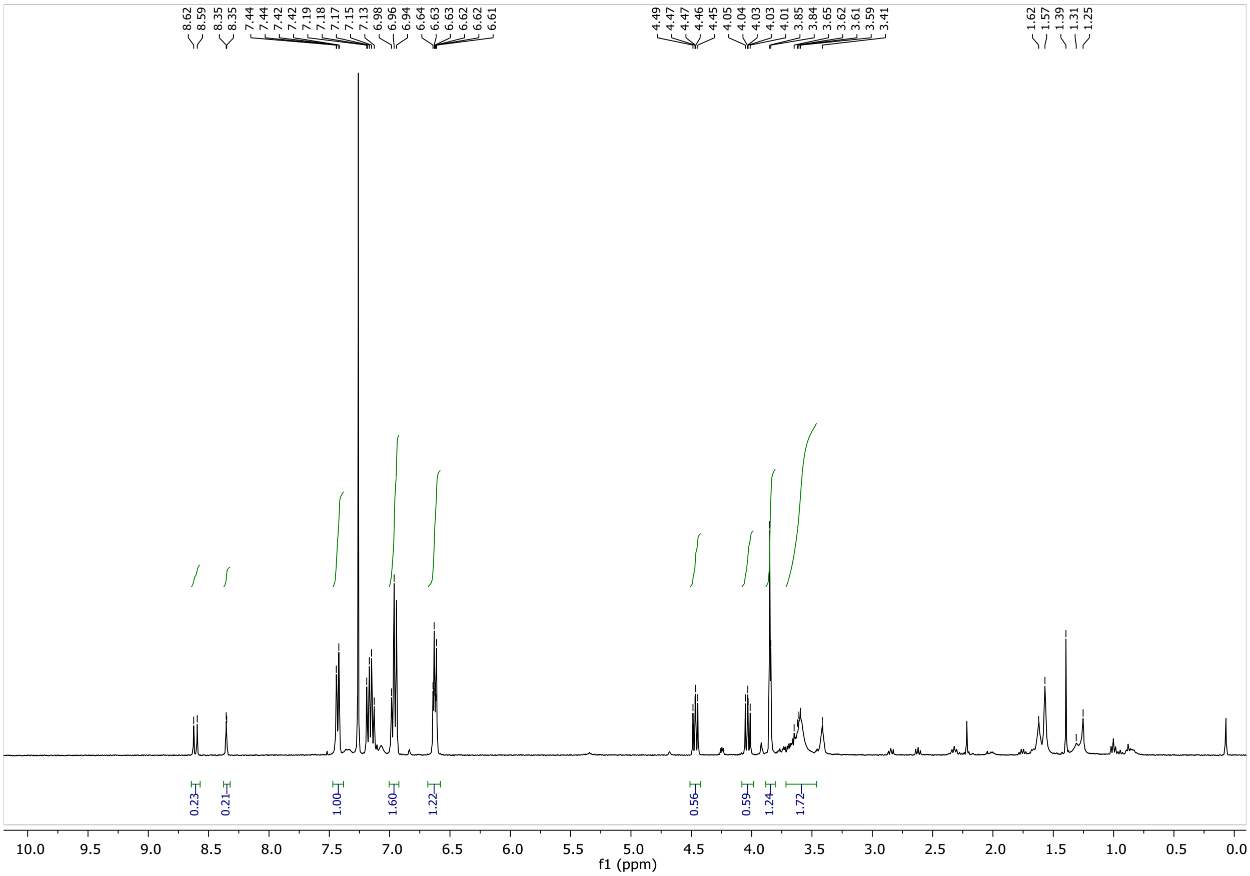


NMR Spectra of Polyol Fraction





^{1}H NMR Spectrum of Unknown By-Products



SI-6. Solvolysis of Nylon Tights (1.0 g scale)

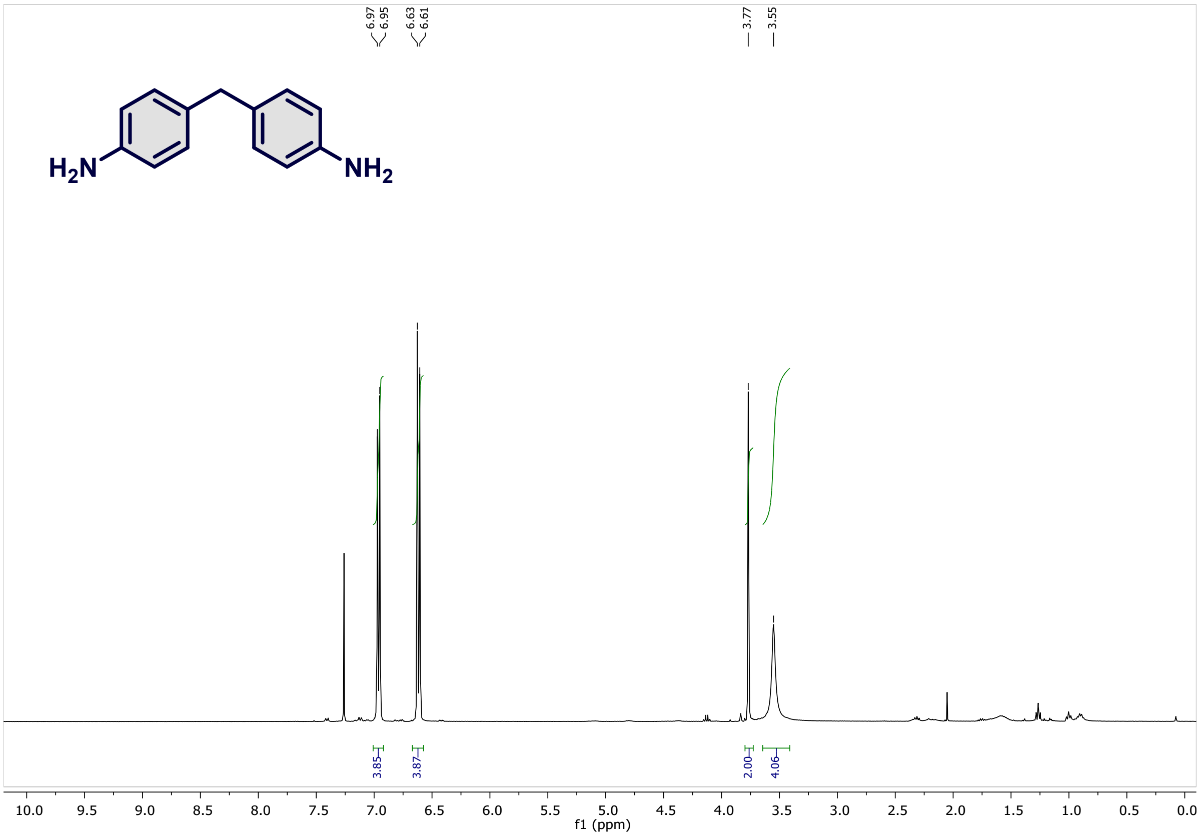
The tights (brand: VRS, 10 denier, black, “Løbefri Strømpebukser”, 27% elastane and 73% polyamide) was acquired in a local supermarket.

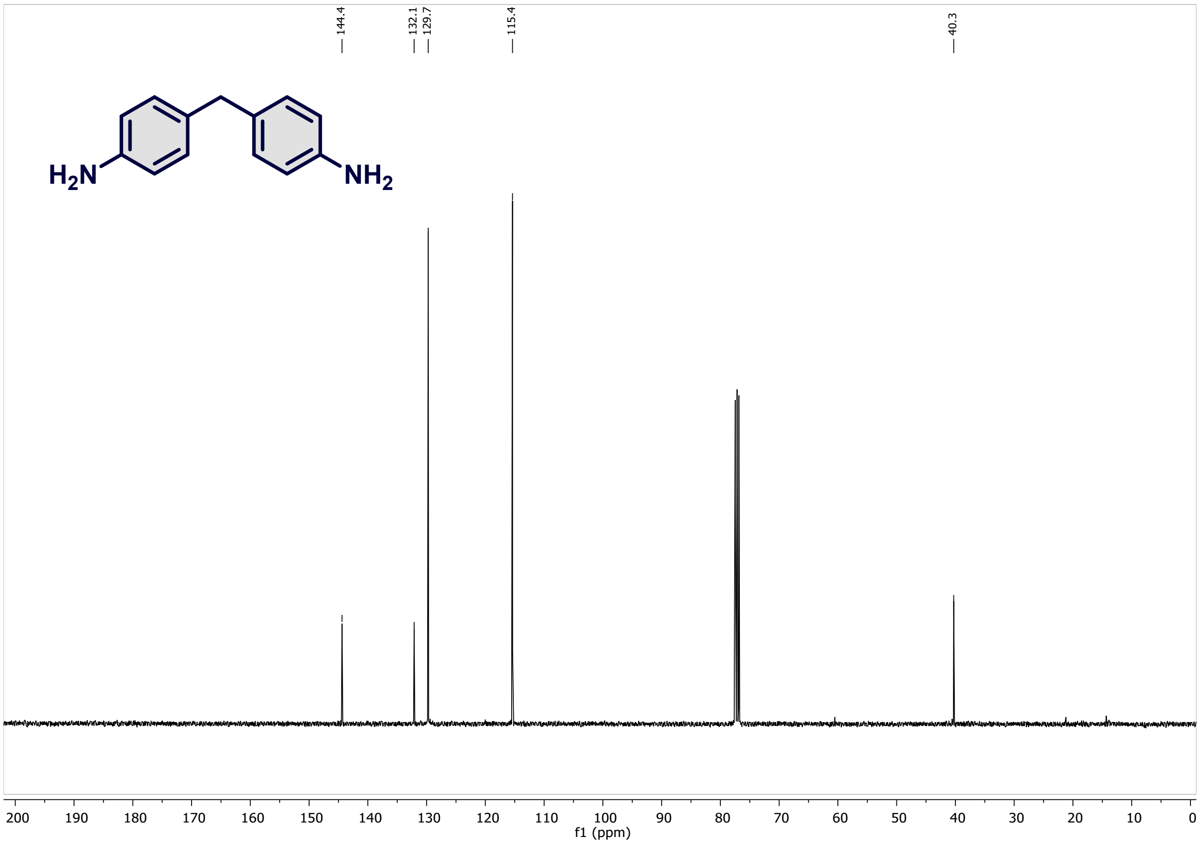
The tights were cut into smaller pieces with a pair of scissors.

The PU (run 1: 1.04 g; run 2: 1.07 g) was deconstructed as described in General Procedure B to afford 4,4’-MDA (run 1: 39.1 mg; run 2: 62.6 mg)* as a yellow solid in an average yield of 50.9 mg, an unknown mixture of by-products (run 1: 7.4 mg; run 2: 6.3 mg) as a yellow solid in an average yield of 6.9 mg, a polyol fraction (run 1: 260 mg; run 2: 272 mg) as a viscous yellow oil in an average yield of 266 mg, and a leftover black fabric (run 1: 689 mg; run 2: 708 mg) in an average mass of 698 mg.

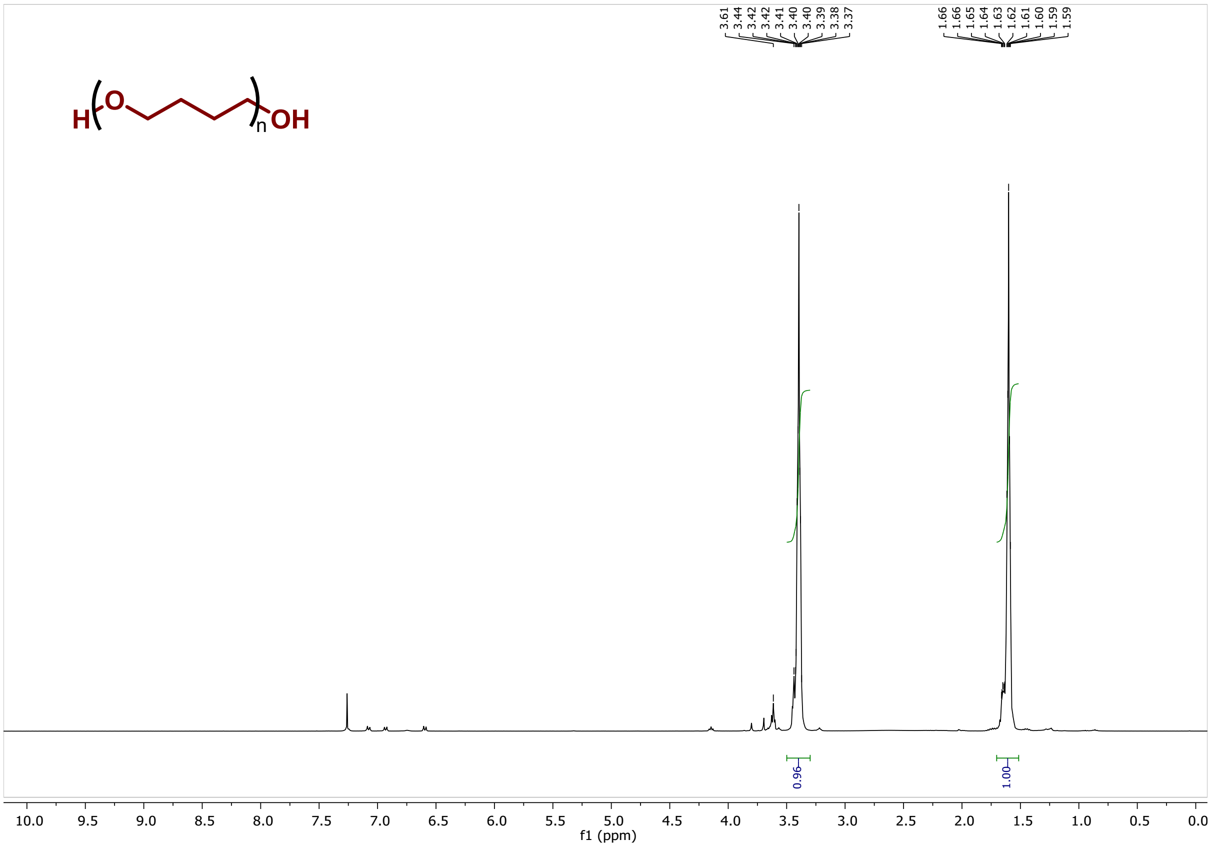
*The 4,4’-MDA fraction contains a minor impurity.

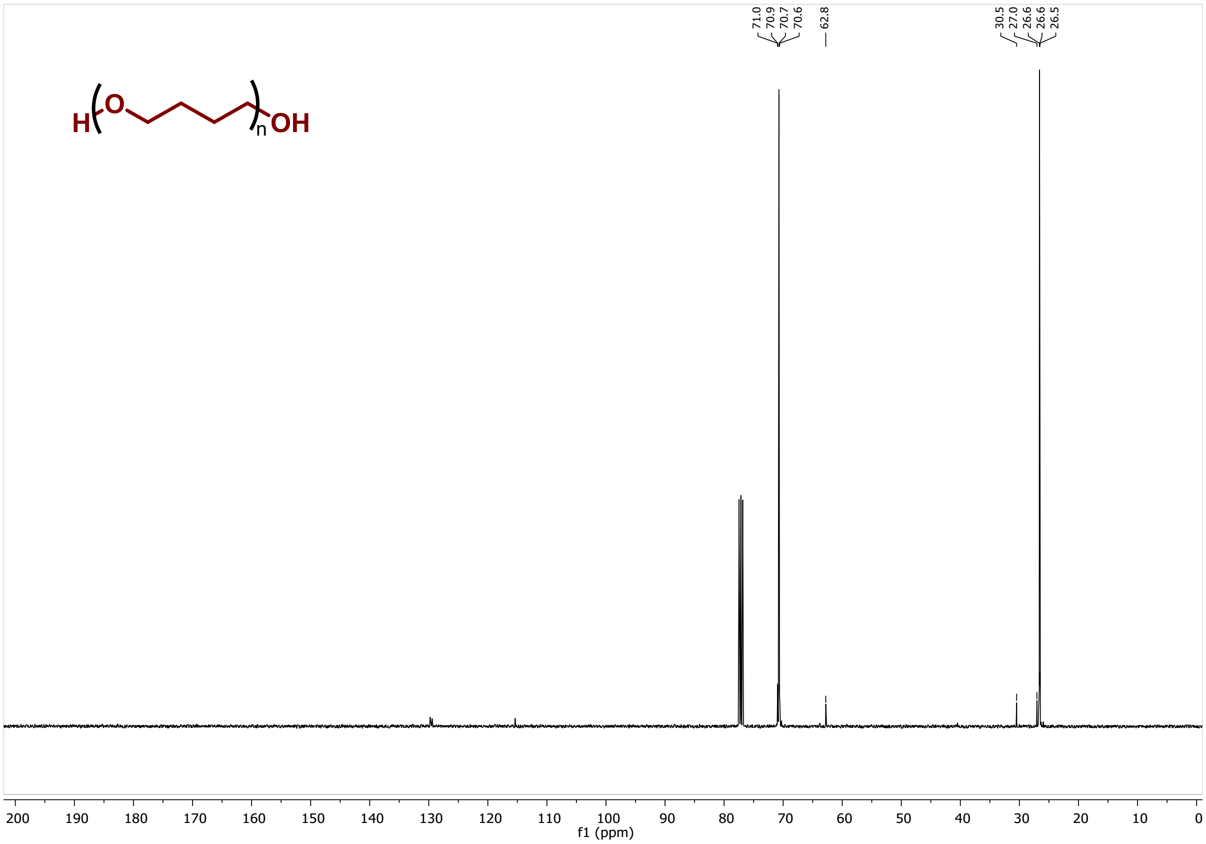
NMR Spectra of MDA Fraction



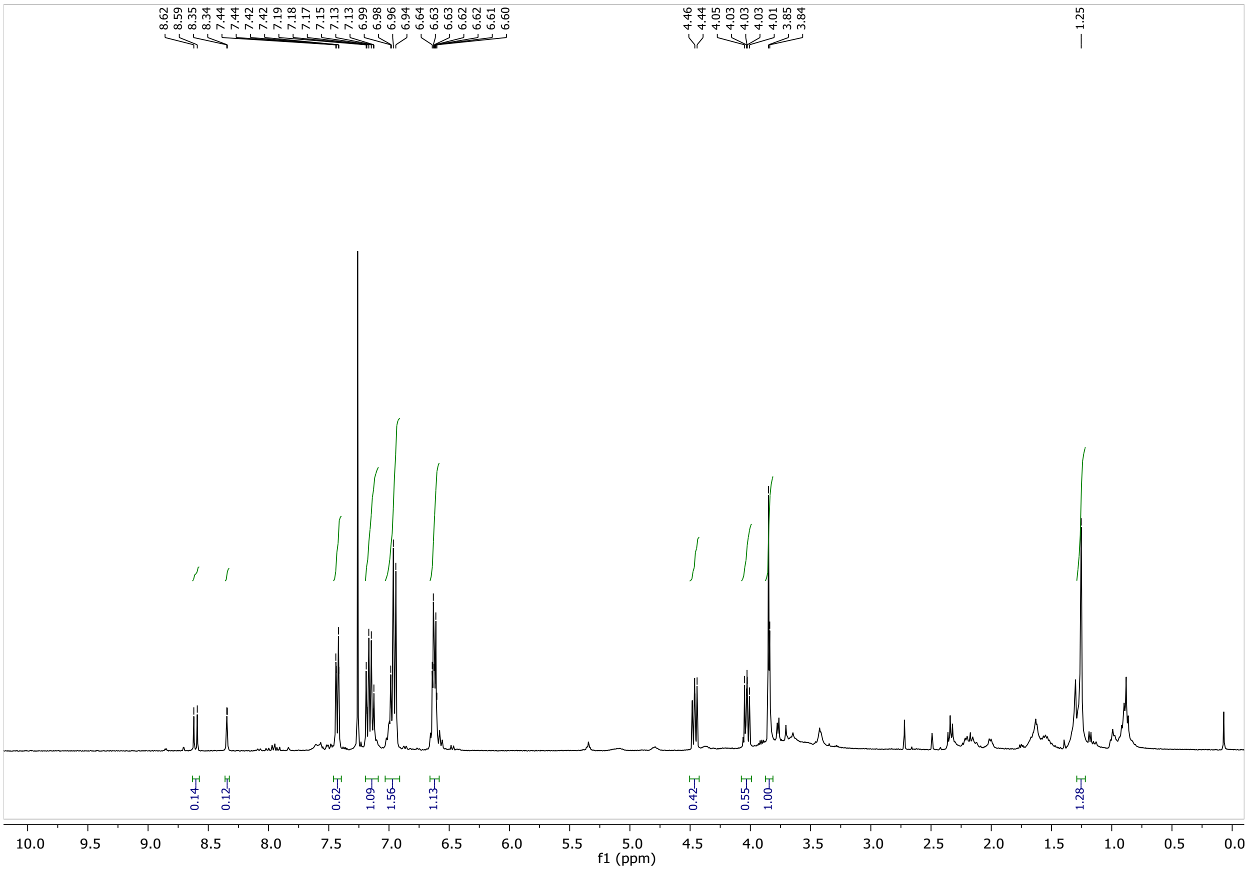


NMR Spectra of Polyol Fraction

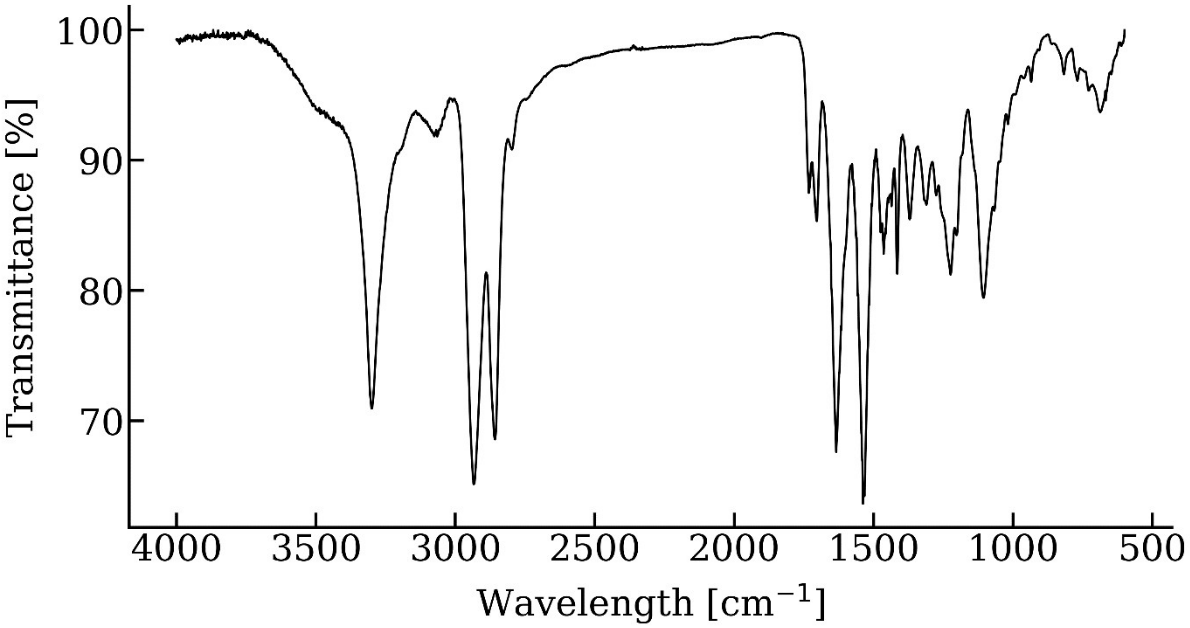


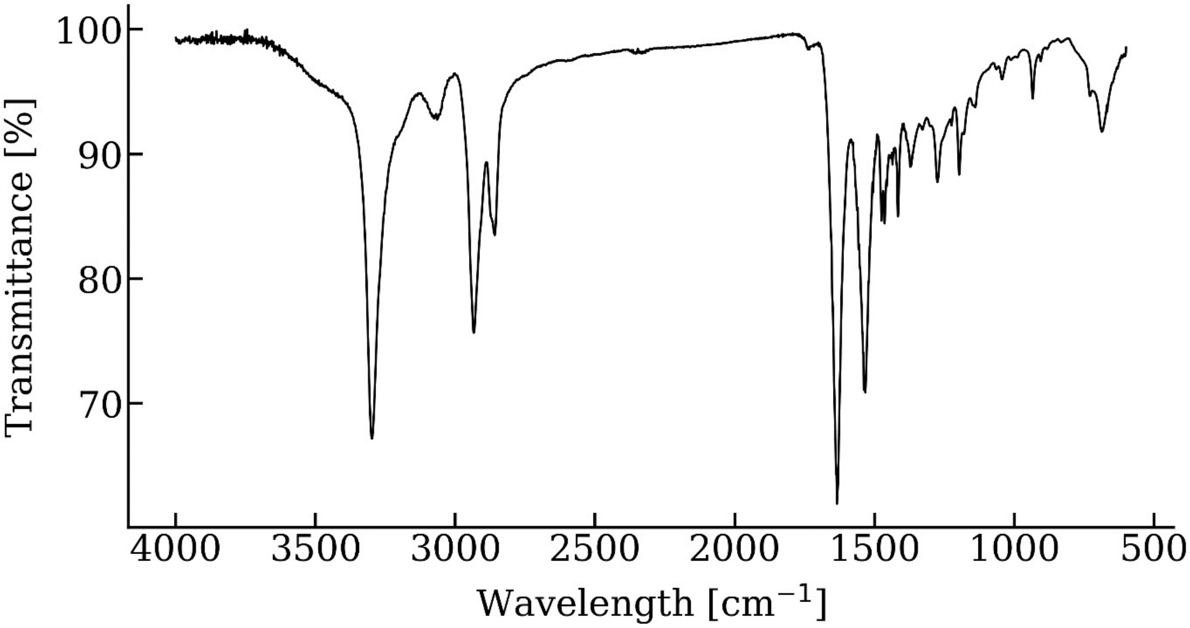


^{1}H NMR Spectrum of Unknown By-Products

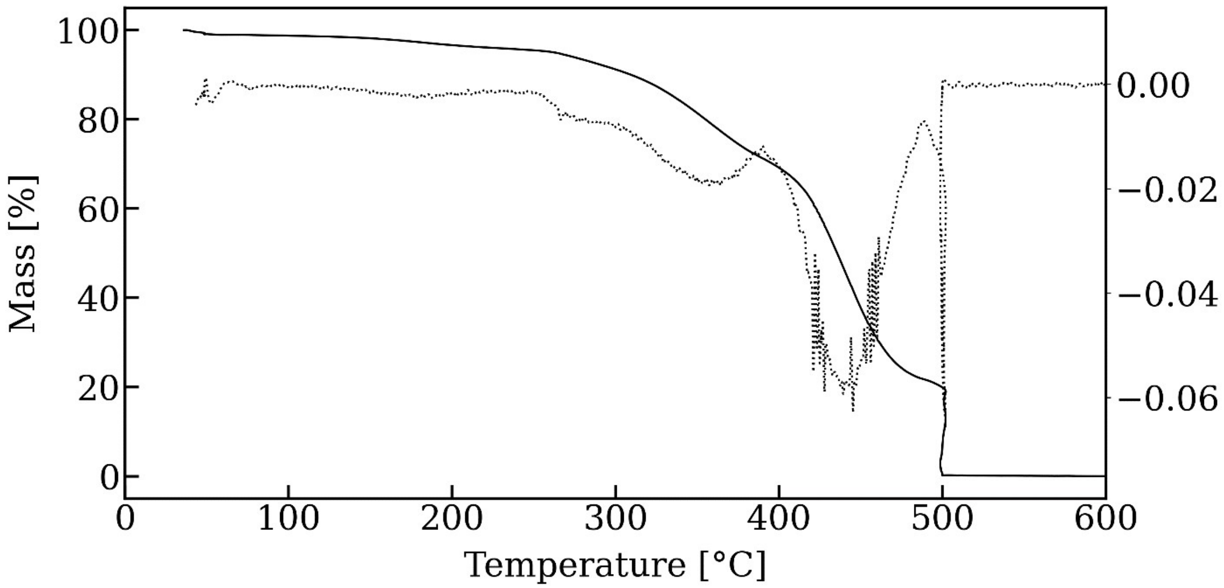


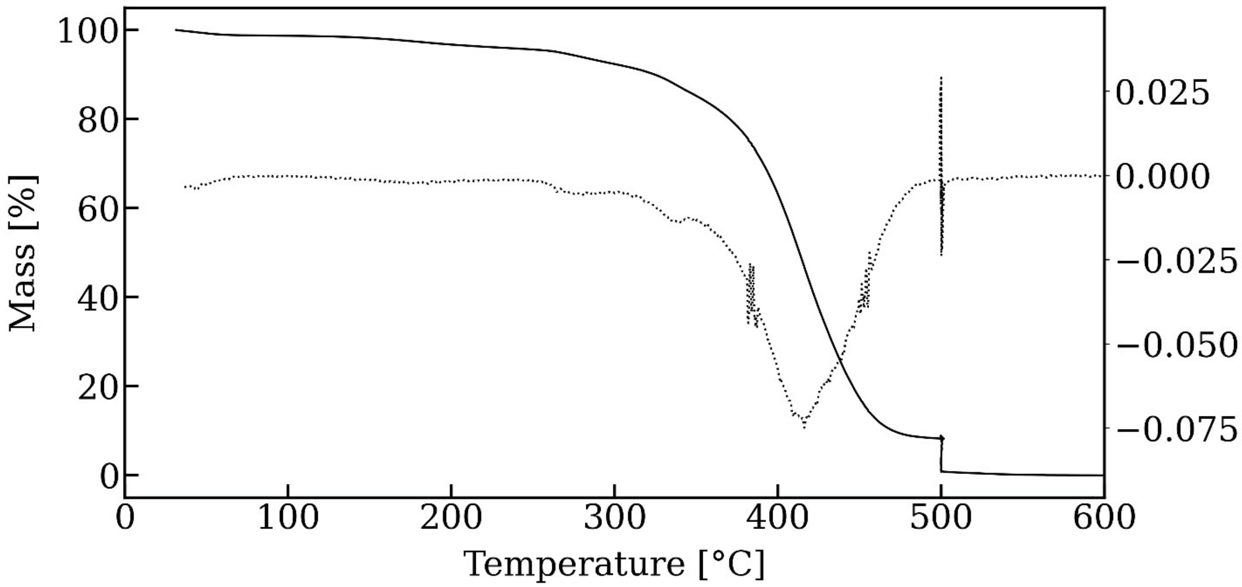
FTIR Spectra of Tights (Top) and Leftover Fabric from Solvolysis (Bottom)



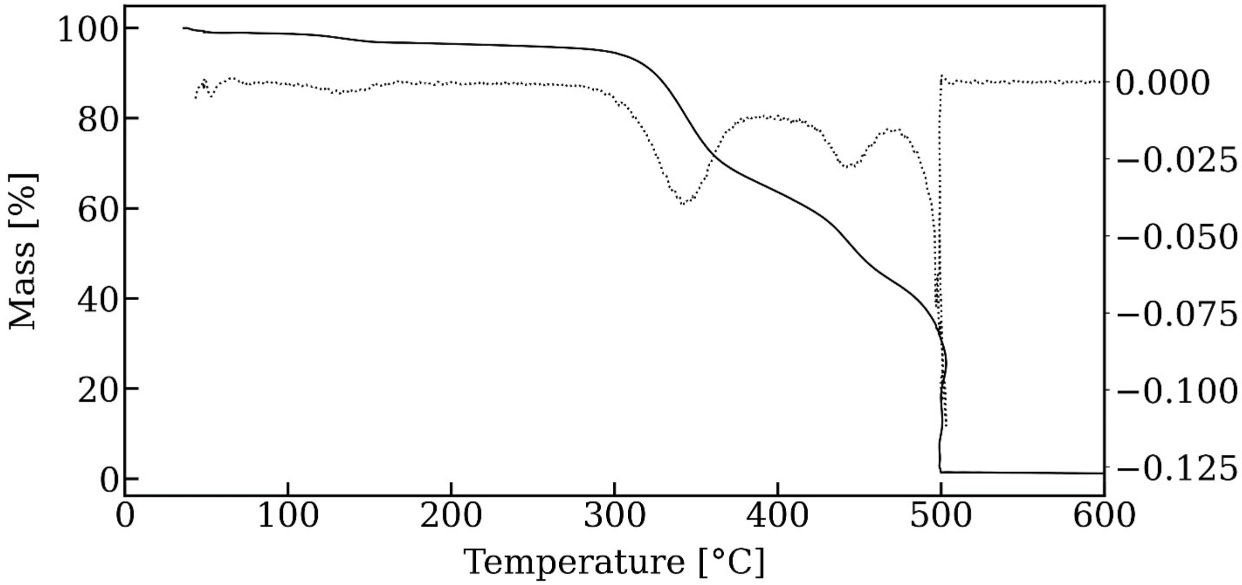


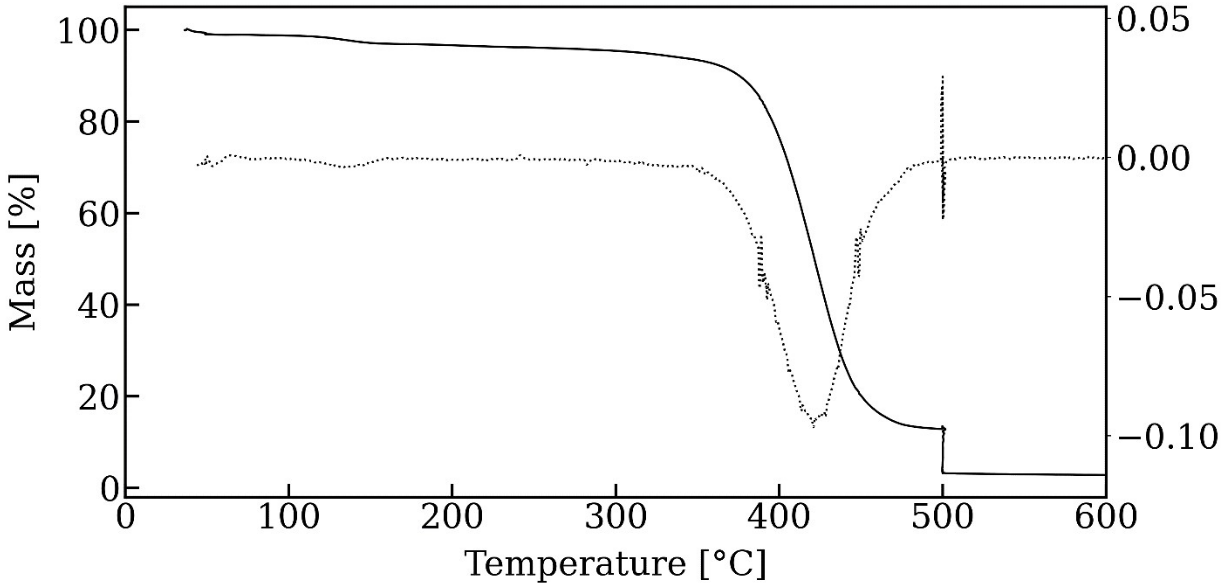
TGA Spectra of Tights Recorded in Laboratory Air (Top) and Nitrogen Atmosphere (Bottom)



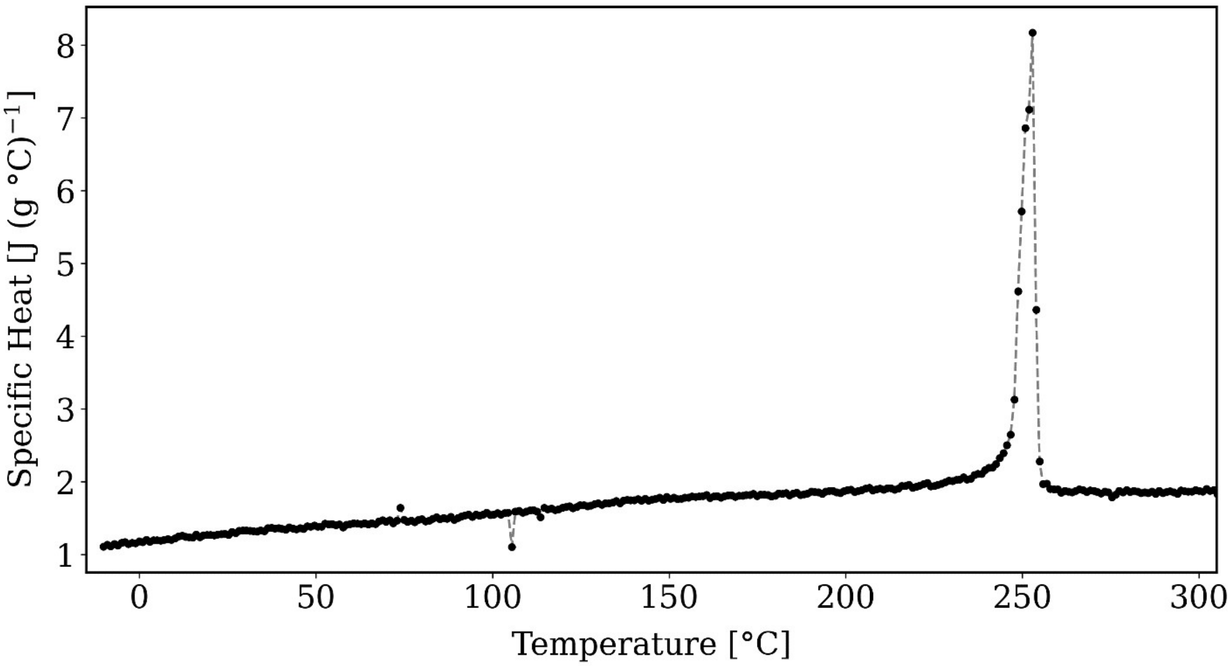


TGA Spectra of Leftover Fabric from Tights from Solvolysis in Laboratory Air (Top) and Nitrogen Atmosphere (Bottom)

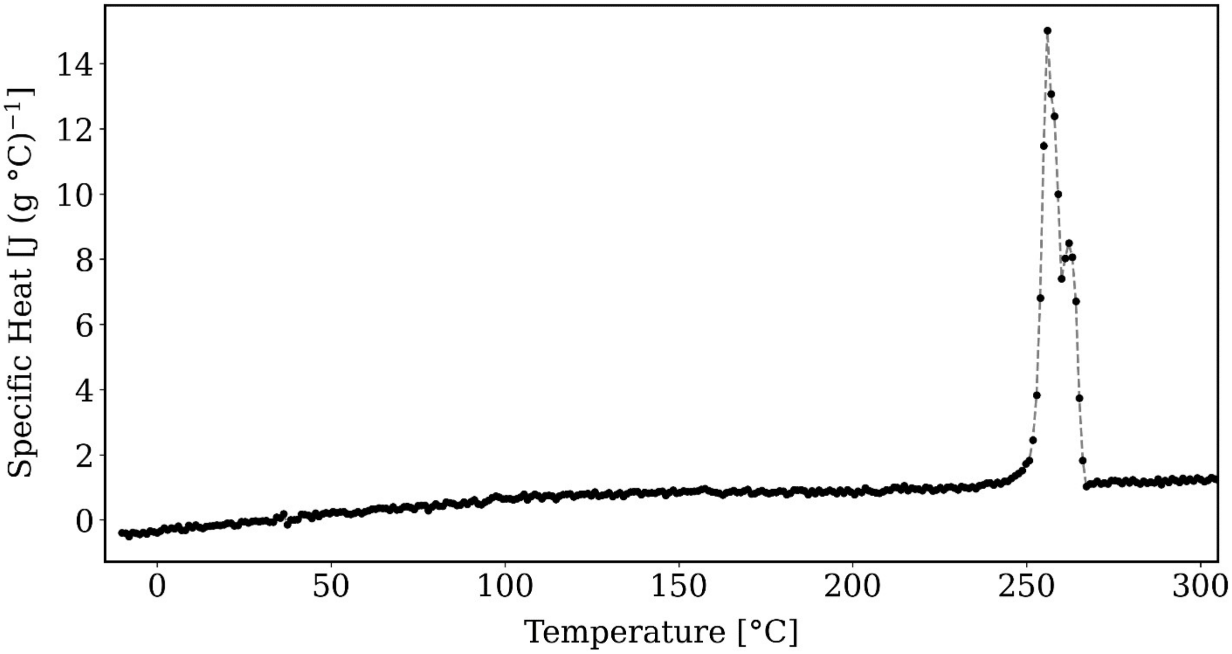




DSC of Tights with Two Heating-Cooling Cycles (top) and DSC StepScan (bottom)



DSC of Leftover Fabric from Tights with Two Heating-Cooling Cycles (top) and DSC StepScan (bottom)



SI-7. Solvolysis of Nylon Tights (Two Pair, 33 g scale)

The nylon tights (beige) (brand: VRS, 10 denier, size S/M, beige colored, "Løbefri Strømpebukser", 27% elastane and 73% polyamide) were acquired in a local supermarket.

The two pairs of tights were not processed before solvolysis reaction.

On the benchtop, a Berghof BR-300 High Pressure Reactor was charged with a stir bar, two pairs of tights (33.1 g in total), KOH (0.06 g, 1.1 mmol), and *tert*-amyl alcohol (165 mL). The autoclave was sealed under atmospheric air and slowly heated from room temperature to 225 °C. The desired temperature was reached after 60 minutes, from which the 4.5 h reaction time started. From here, the reaction was allowed to cool slowly overnight. It was observed that the fabric had soaked all the liquid in the vessel and that a piece of the fabric had disintegrated/melted at the bottom of the vessel. The product mixture was filtered and the leftover fabric was washed with excess EtOAc (6 x 300 mL) before drying *in vacuo* to afford the leftover fabric (24.7 g, 75 wt%). The filtrate was concentrated and to the mixture 1 M HCl (40 mL), water (200 mL), and brine (10 mL) were added. The mixture was extracted with CH_2Cl_2 (6 x 150 mL), the combined organic phases were dried over anhydrous Na_2SO_4, filtered, and dried *in vacuo* to provide a polyol fraction as an amorphous blue, viscous oil (6.85 g, 21 wt%). The acidic aqueous phase was basified with 4 M NaOH till pH reached 12. The aqueous phase was extracted with CH_2Cl_2 (5 x 150 mL) and the combined organic phases were dried over anhydrous Na_2SO_4, filtered, and dried *in vacuo* to yield 4,4'-MDA as a brown solid (0.87 g, 3 wt%).

The internal pressure was recorded using an analog manometer (10 bar intervals) during the reaction:

0 h (225 °C reached): 5 bar

1 h: 10-15 bar

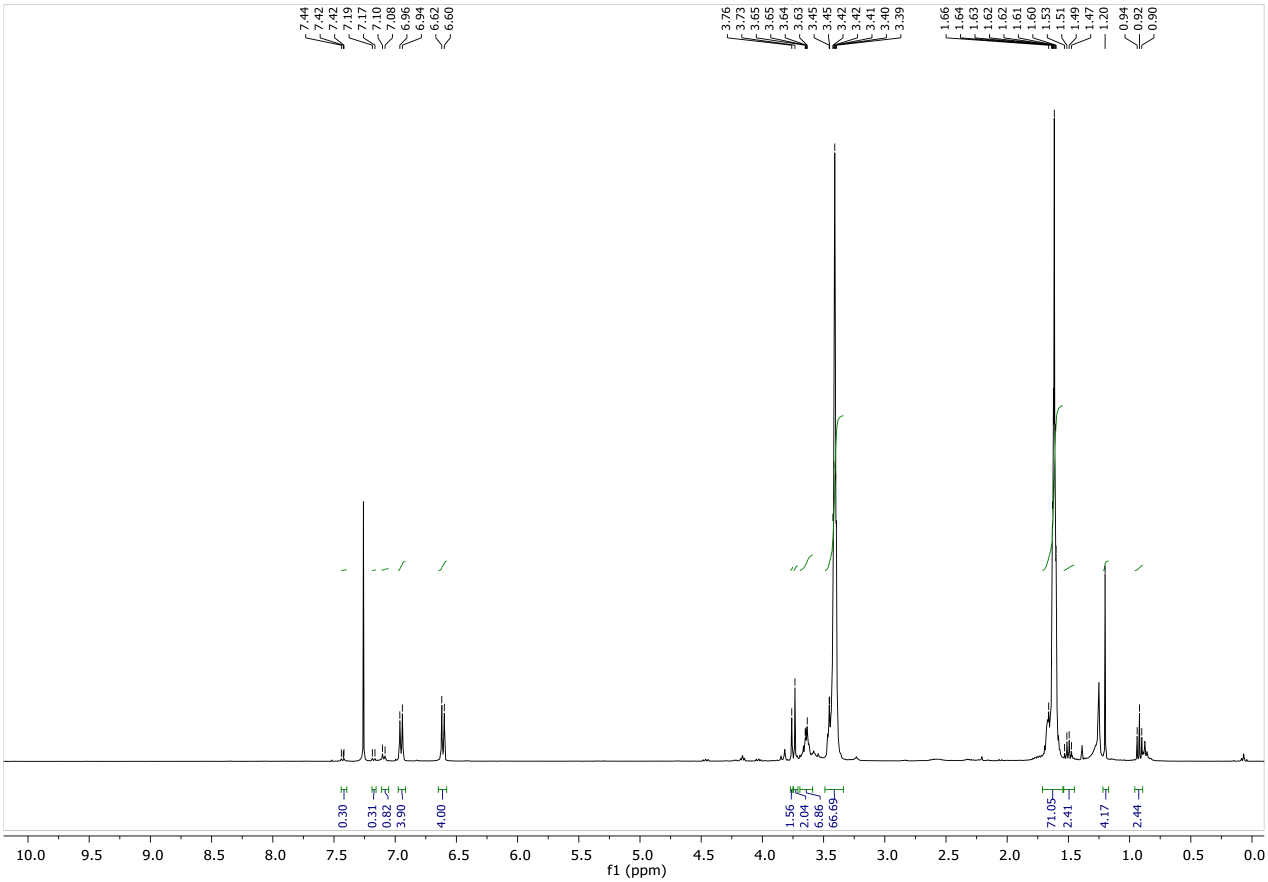
2 h: 10-15 bar

4.5 h: 10-15 bar

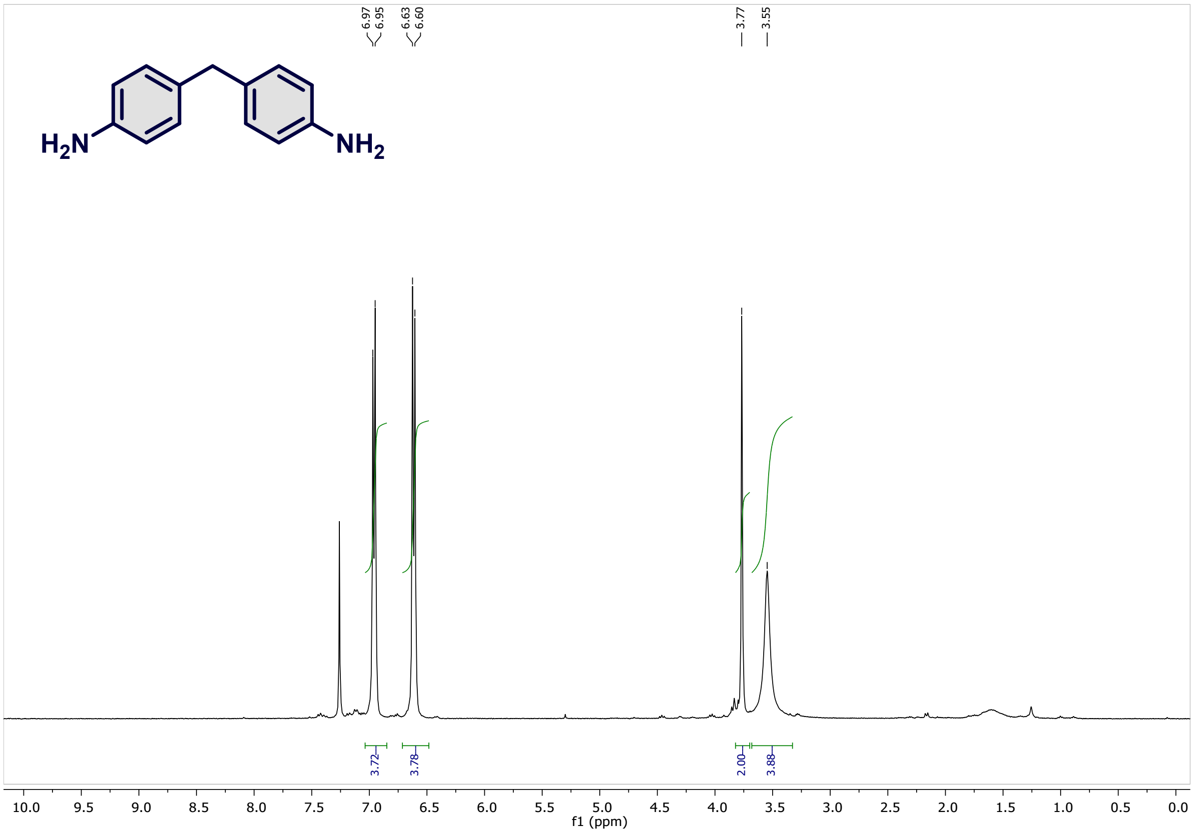
After cooling to room temperature: 1-3 bar – no significant reading on pressure gauge

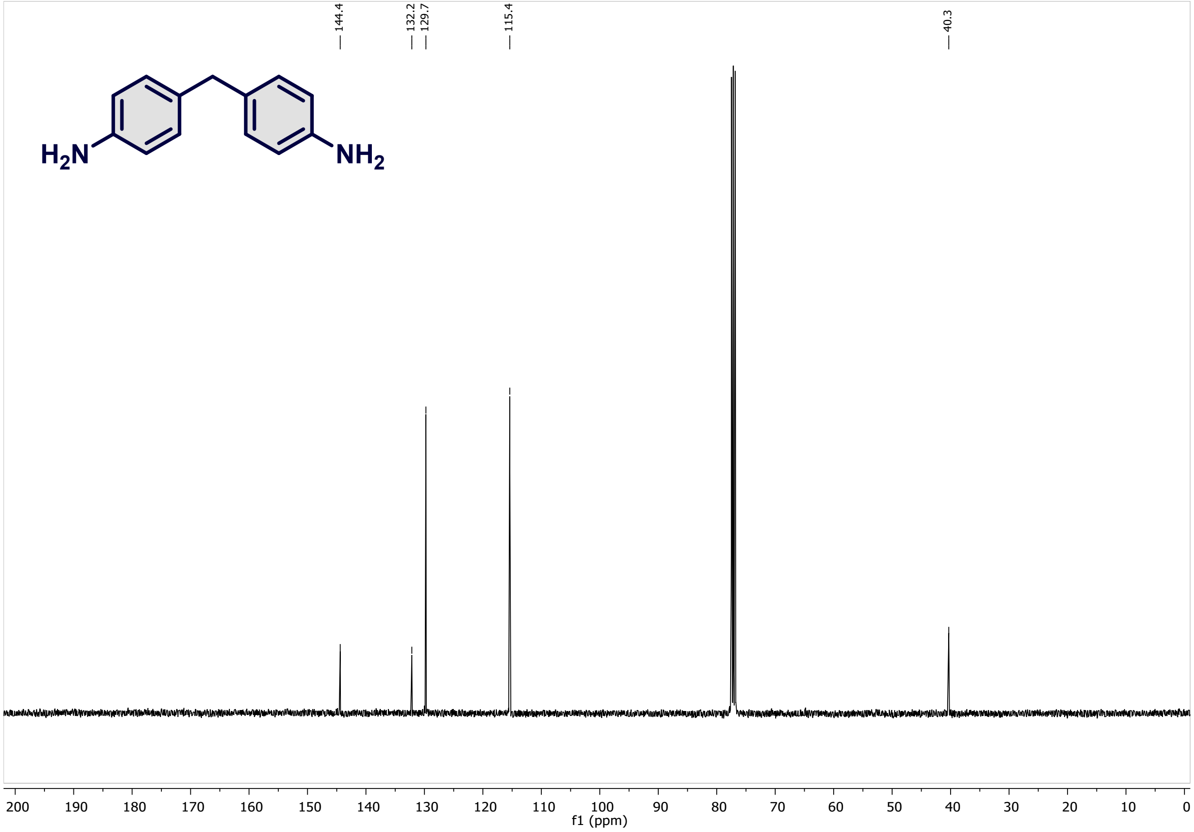

Gas Sample Extraction
Gas Feeding
Remember to clean up

^{1}H NMR Spectrum of Crude Reaction Mixture

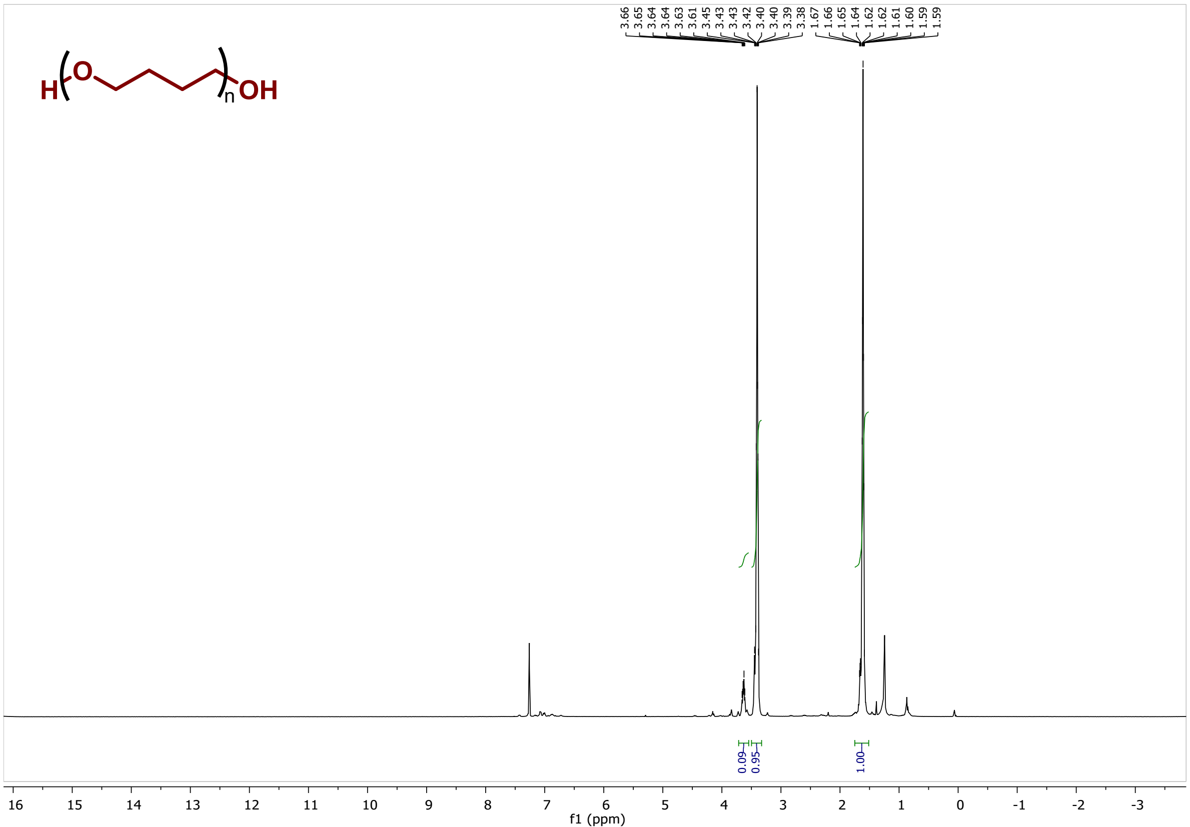


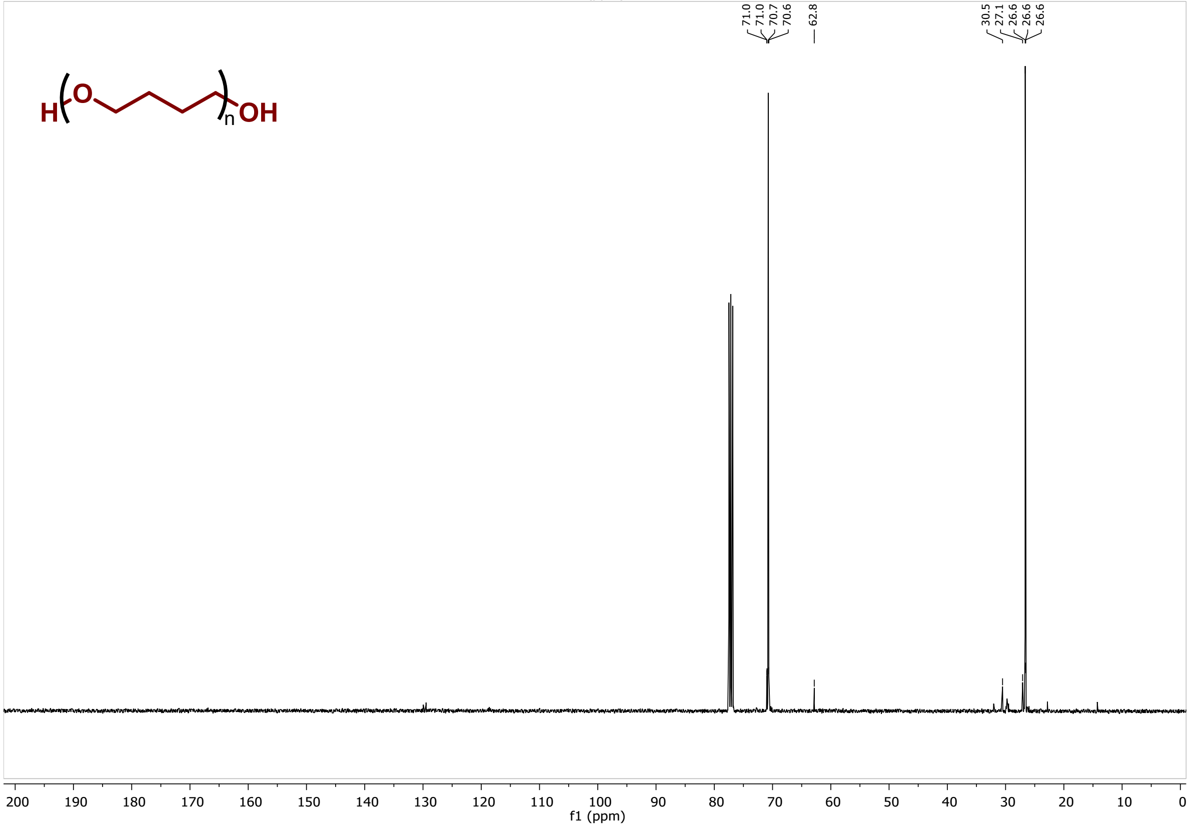
NMR Spectra of 4,4’-MDA



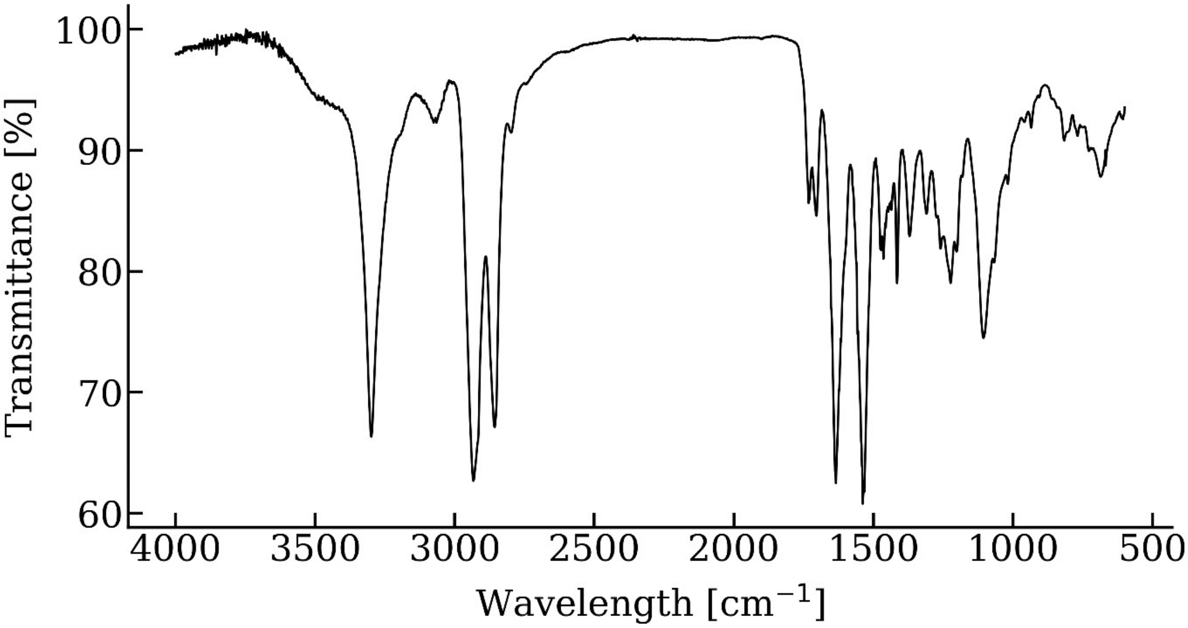


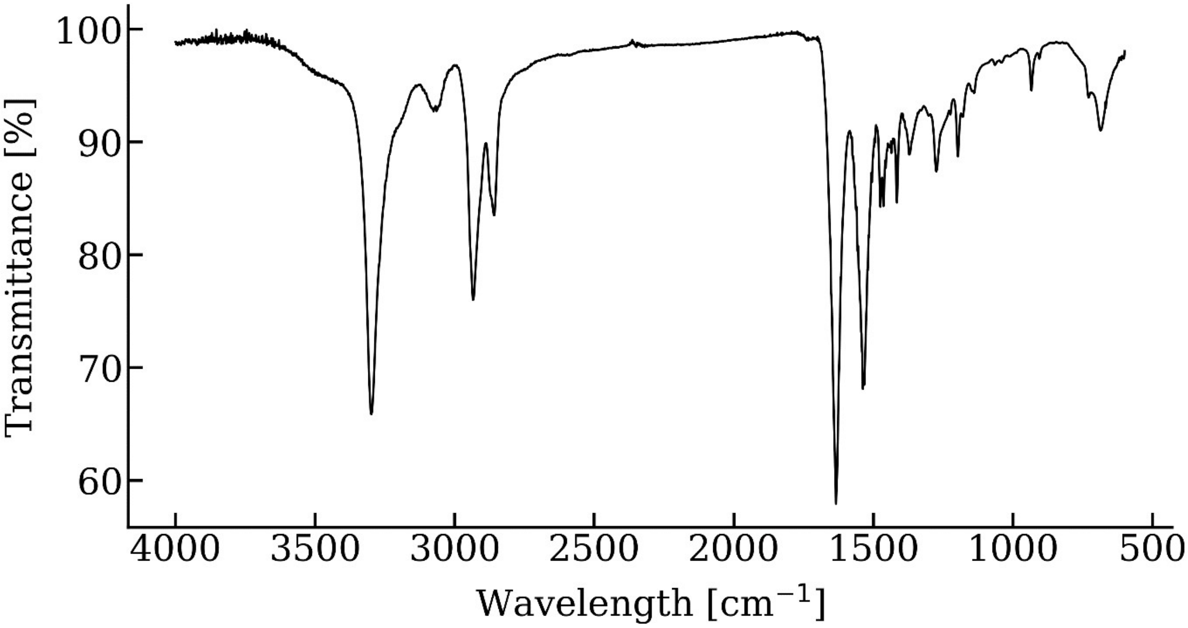
NMR Spectra of Polyol Fraction



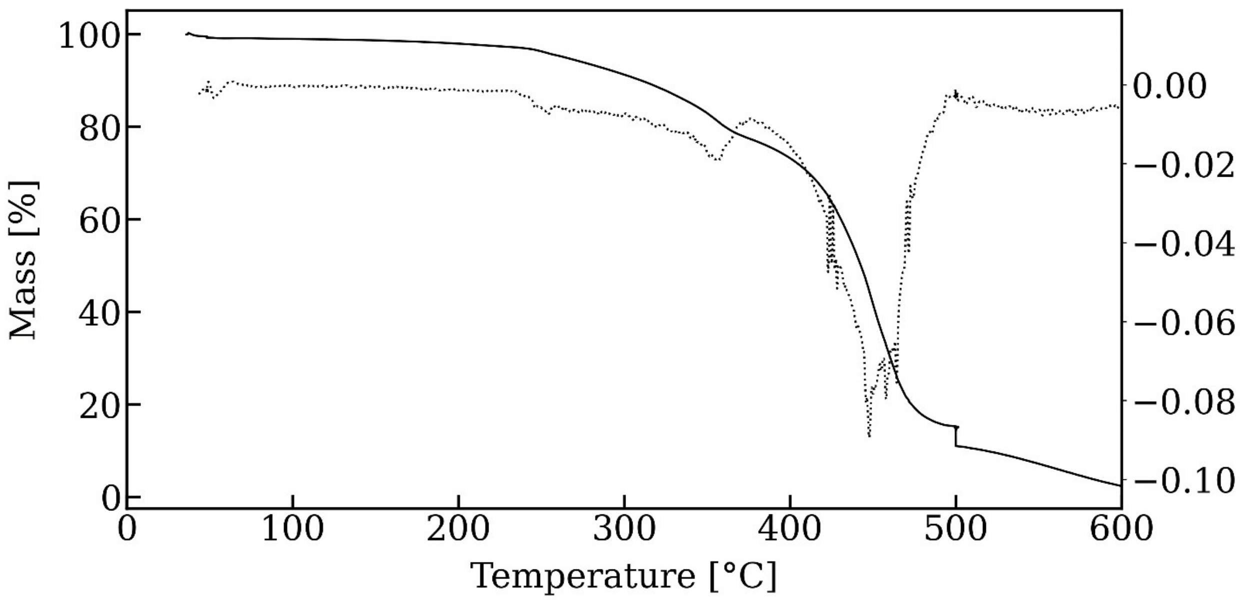


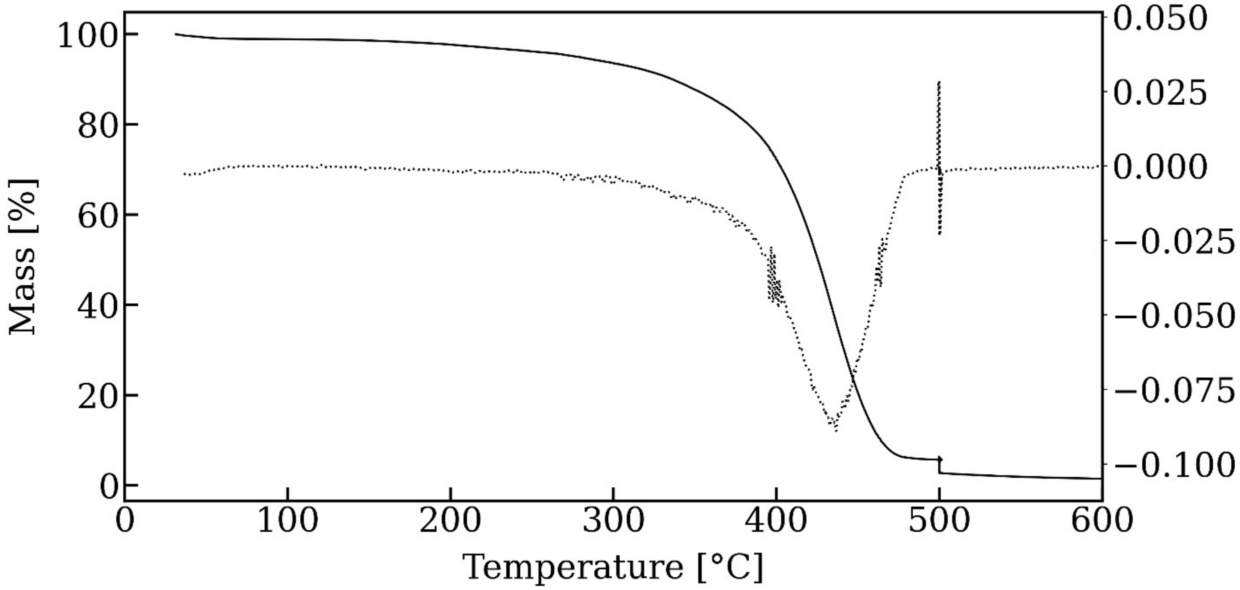
FTIR Spectra of Tights (Top) and Leftover Fabric from Solvolysis (Bottom)


Transmittance [%]
100
90
80
70
60
4000
3500
3000
2500
2000
1500
1000
500
Wavelength [cm^{-1}]

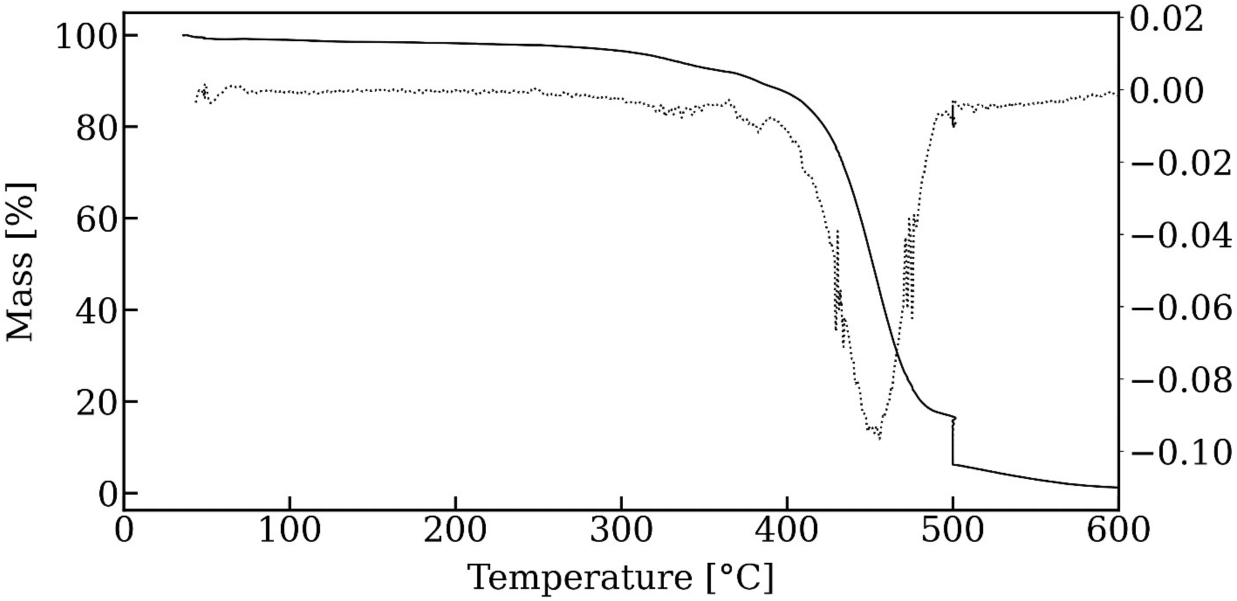

Transmittance [%]
100
90
80
70
60
4000
3500
3000
2500
2000
1500
1000
500
Wavelength [cm^{-1}]

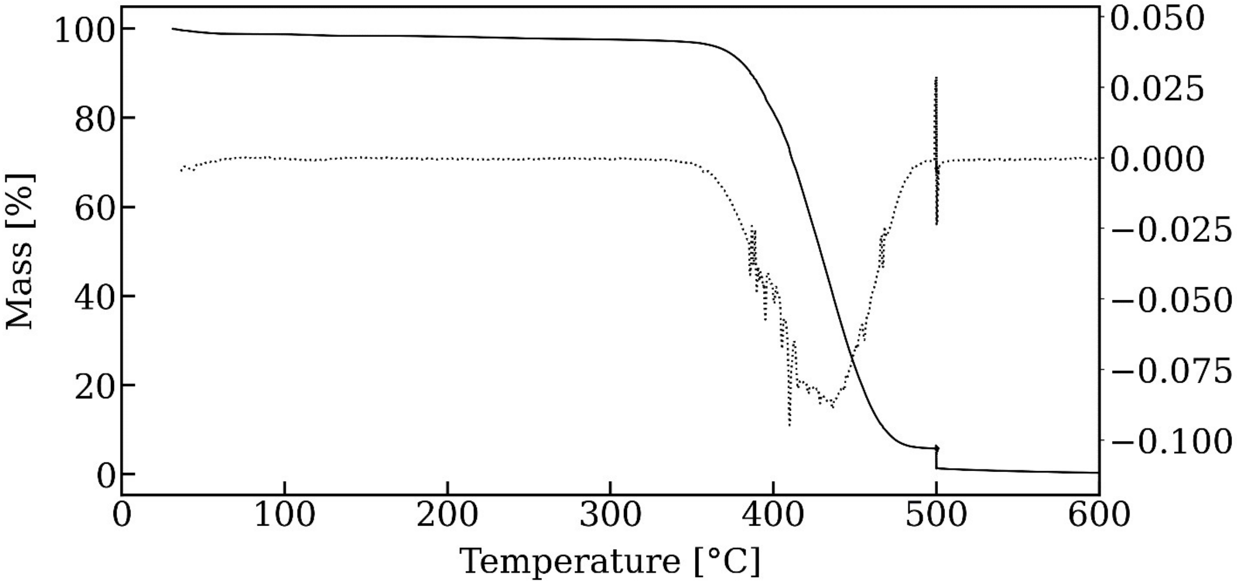
TGA Spectra of Tights Recorded in Laboratory Air (Top) and Nitrogen Atmosphere (Bottom)



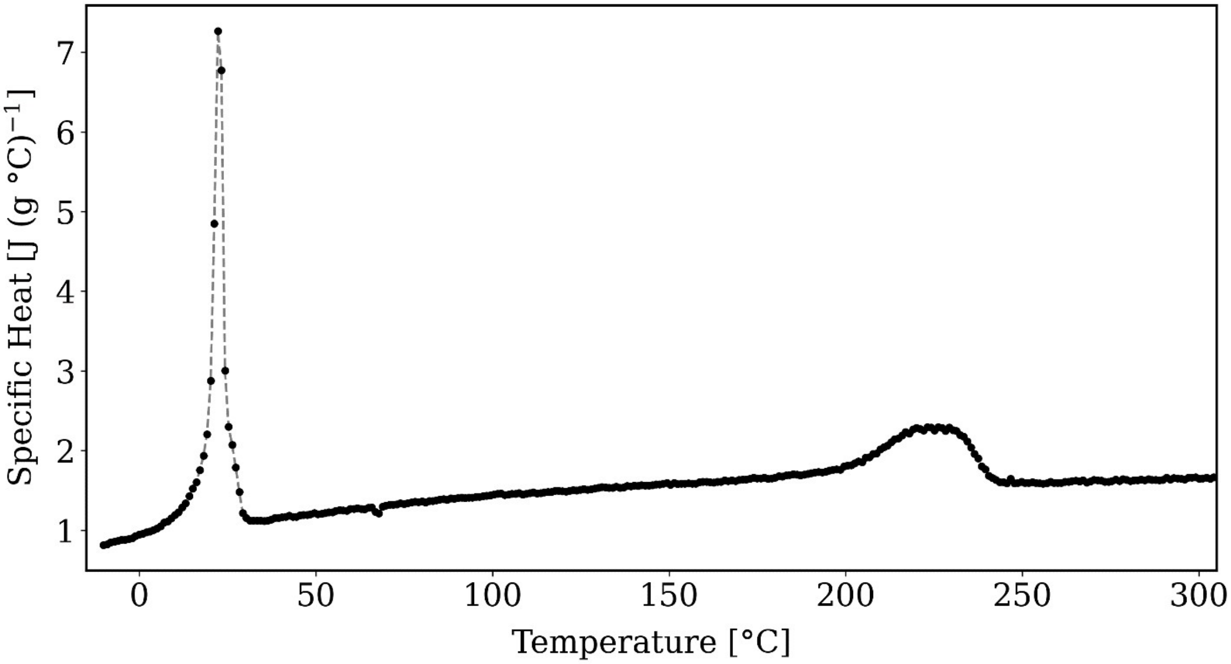


TGA Spectra of Leftover Fabric from Tights From Solvolysis in Laboratory Air (Top) and Nitrogen Atmosphere (Bottom)

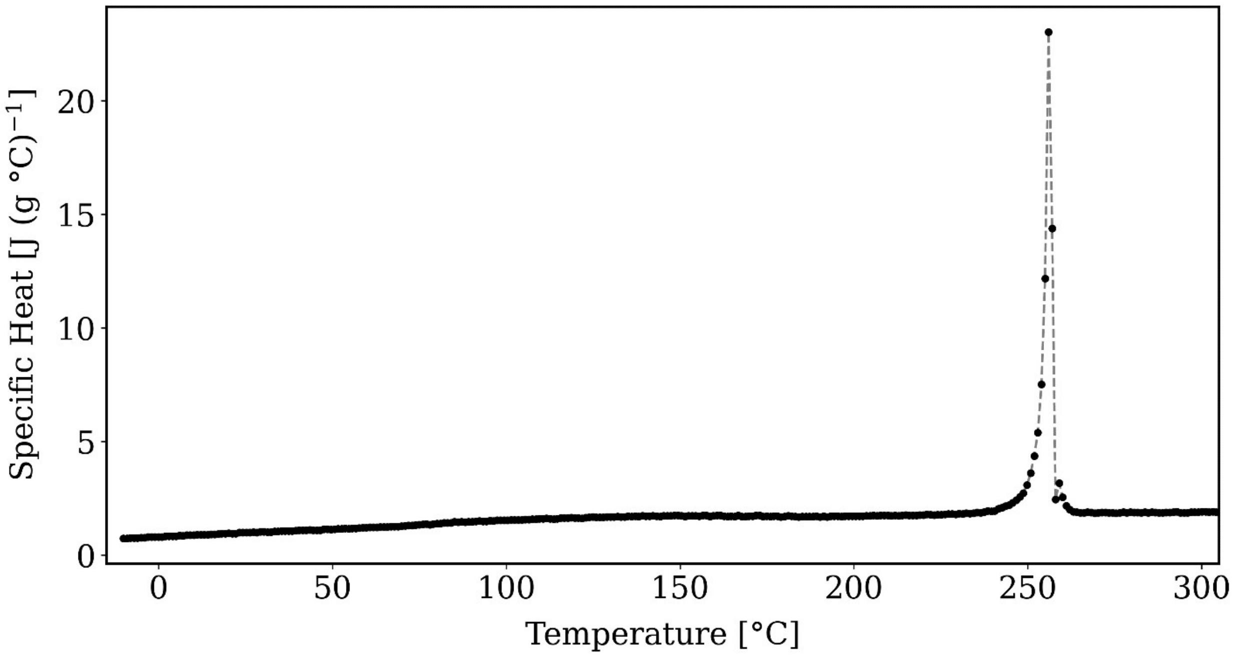




DSC of Tights with Two Heating-Cooling Cycles (top) and DSC StepScan (bottom)



DSC of Leftover Fabric from Tights with Two Heating-Cooling Cycles (top) and DSC StepScan (bottom)



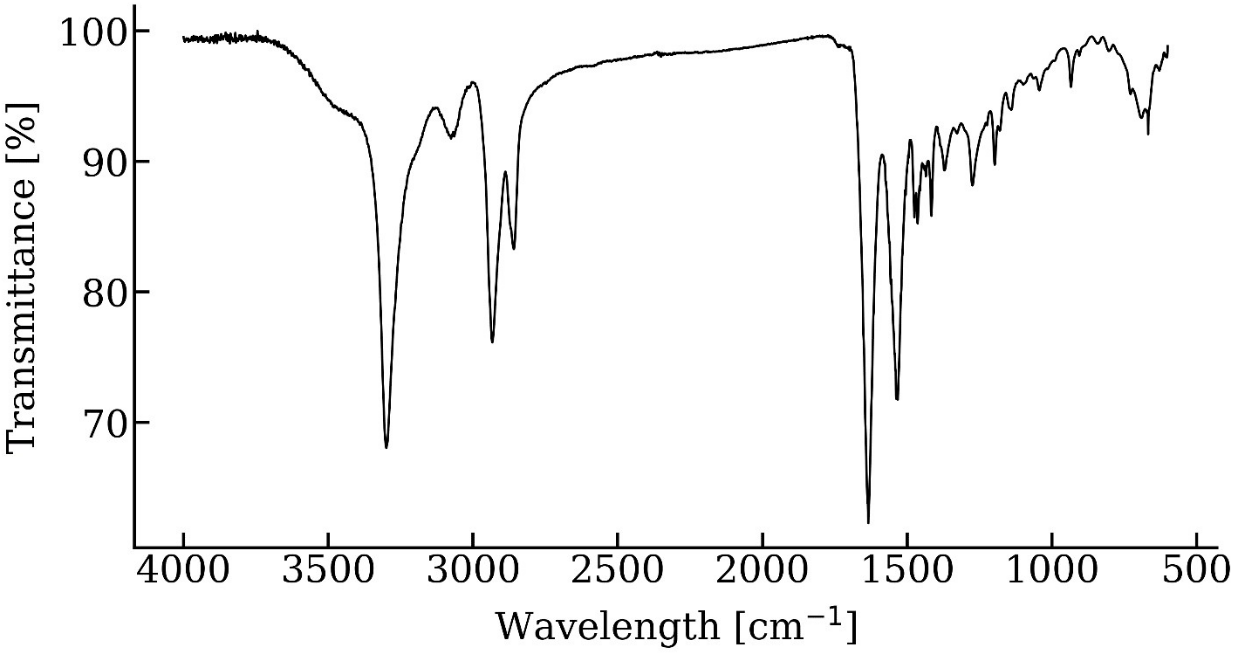
SI-8. Dissolution of Elastane From Nylon Tights

The tights (VRS, 10 denier, black, “Løbefri Strømpebukser”, 27% elastane and 73% polyamid) were acquired in a local supermarket (Føtex). The tights were cut into smaller pieces with a pair of scissors.

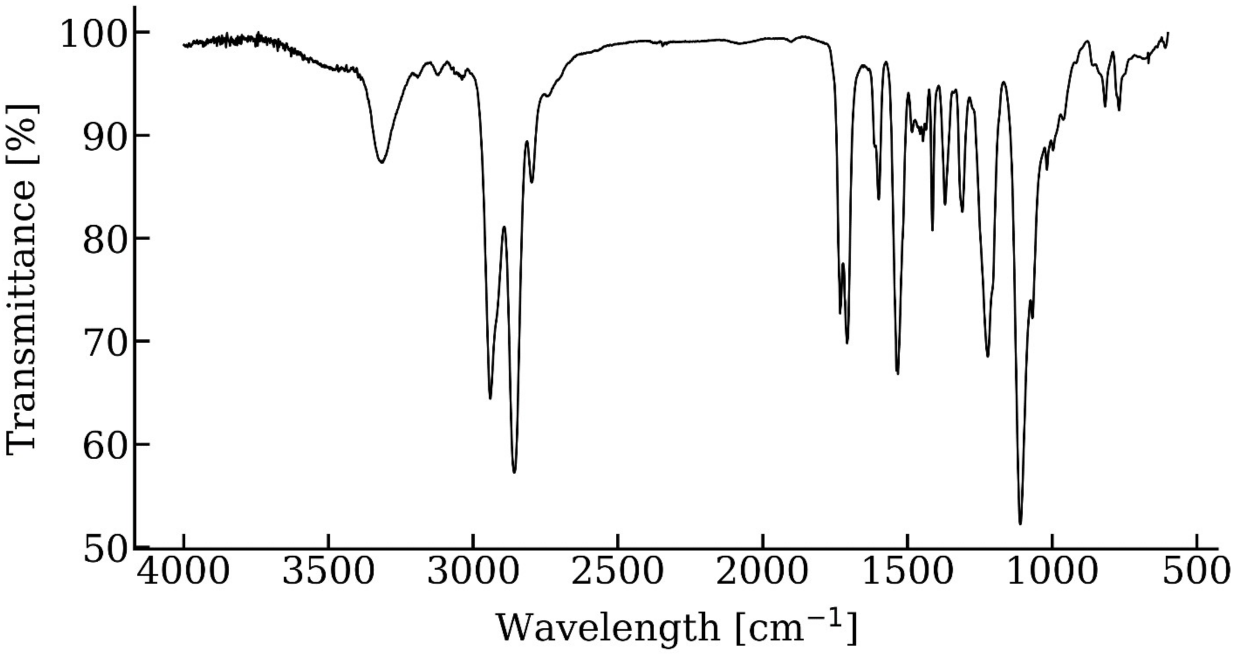
The procedure was modified from literature procedures.[1,2]

In an argon-filled glovebox, pieces of tights (5.10 g) and DMF (100 mL) were charged to a 250 mL round-bottomed flask equipped with an oval stir bar. The flask was sealed with a septum and taken out of the glovebox. The flask was allowed to stir at 70 °C with a stirring rate of 800 rpm for 4 days. The cooled reaction mixture was filtered and the leftover fabric was washed with excess DMF and EtOAc before it was dried *in vacuo* at 80 °C overnight to afford a black fabric (3.11 g, 61 wt%). The filtrate was concentrated and redissolved in DMF (35 mL) by gentle heating. The black solution was added to a stirring solution of water (75 mL) using a glass pipette. The porous precipitate was filtered, washed with excess water and EtOH, dried *in vacuo* at 80 °C overnight to afford an elastic black/grey solid (1.66 g, 33 wt%). The total mass recovery was 94%.

FTIR Spectrum of Leftover Fabric from Extraction



FTIR Spectrum of Extracted Elastane

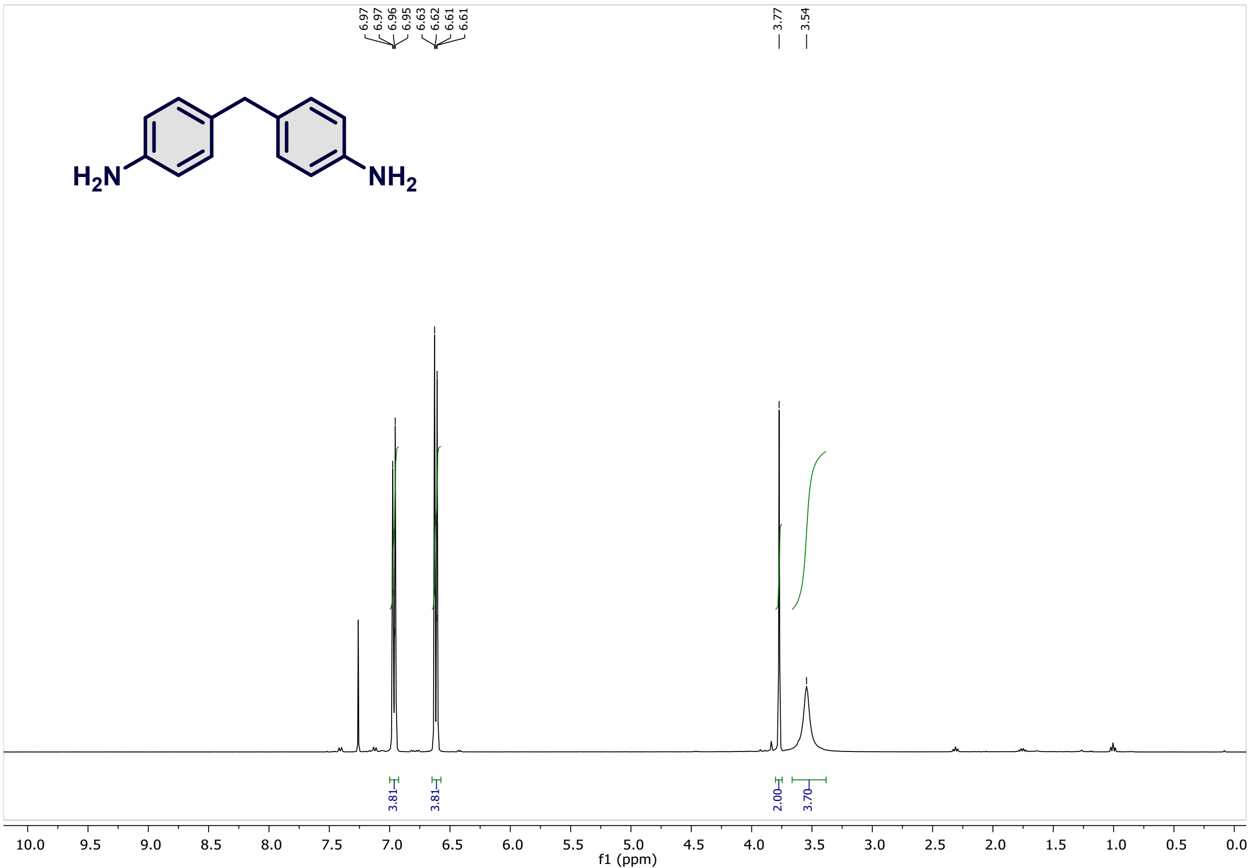


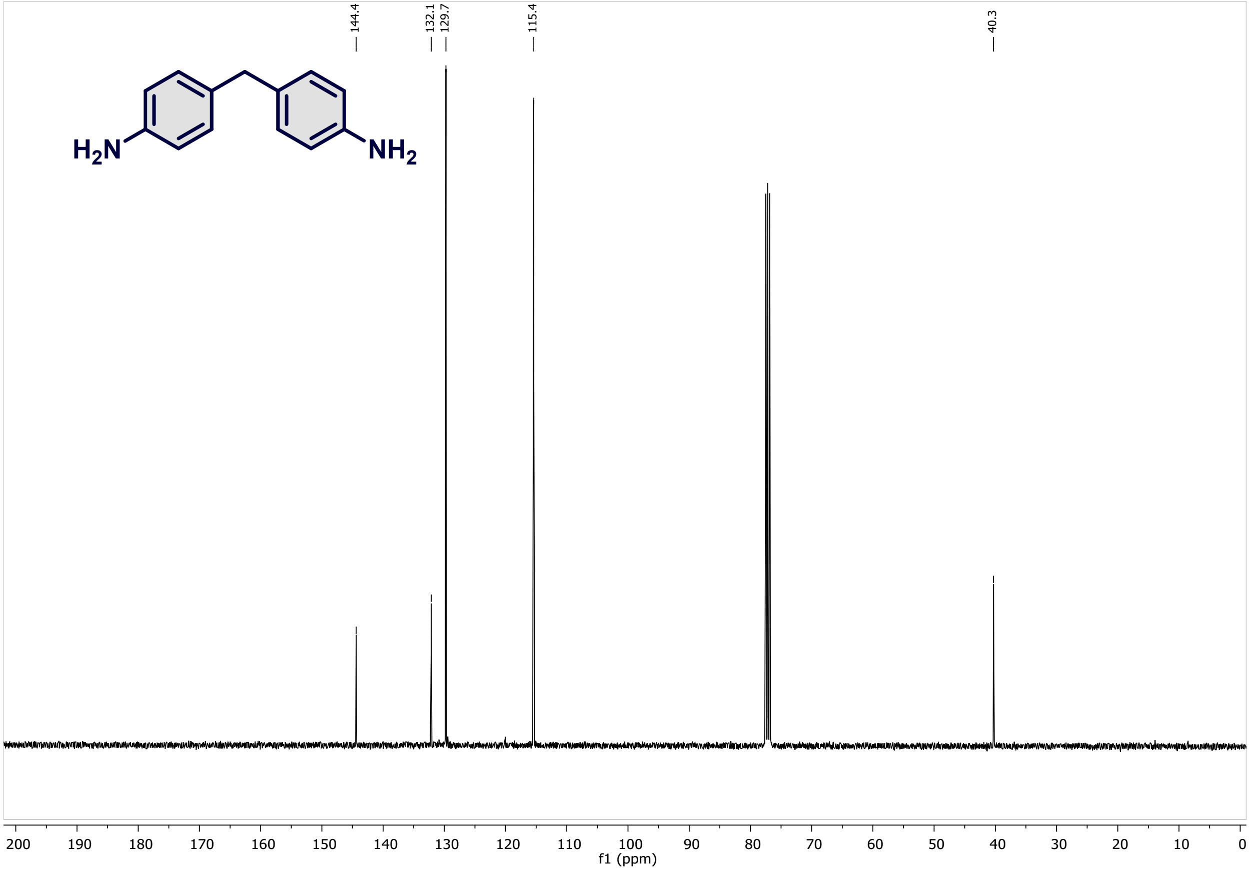
SI-9. Solvolysis of Elastane Extracted by Dissolution from Nylon Tights

The material was extracted from a pair of tights with DMF as described.

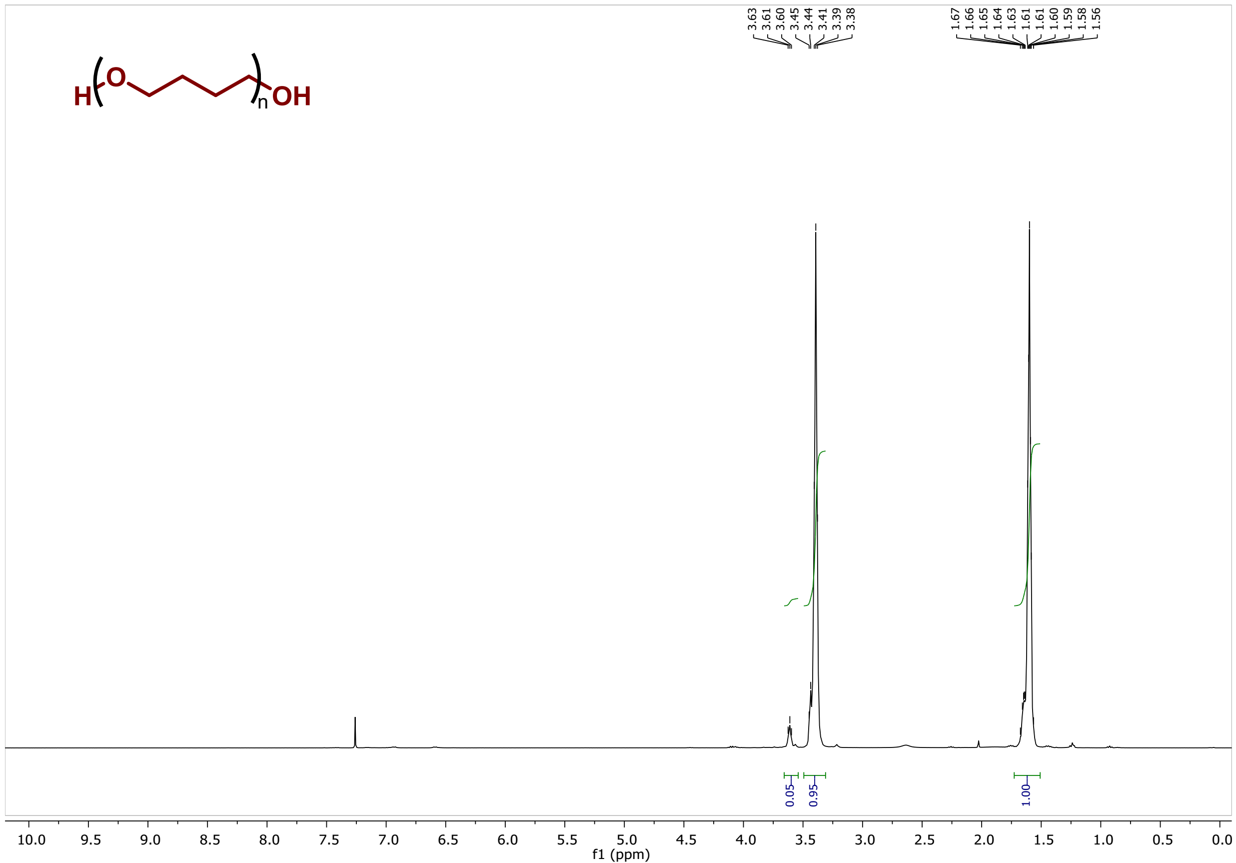
The extract (run 1: 256 mg; run 2: 254 mg) was deconstructed as described in General Procedure A with elongated reaction time to a total of 4.5 h to afford 4,4'-MDA (run 1: 29.5 mg; run 2: 29.8 mg) as a yellow solid in an average yield of 29.7 mg, an unknown by-product (run 1: 14.5 mg; run 2: 12.7 mg) as an off-white solid in an average yield of 13.6 mg, a second unknown by-product (run 1: 4.9 mg; run 2: 4.6 mg) as an off-white solid in an average yield of 4.8 mg, and a polyol fraction (run 1: 180 mg; run 2: 187 mg) as a viscous, yellow oil/solid in an average yield of 183 mg.

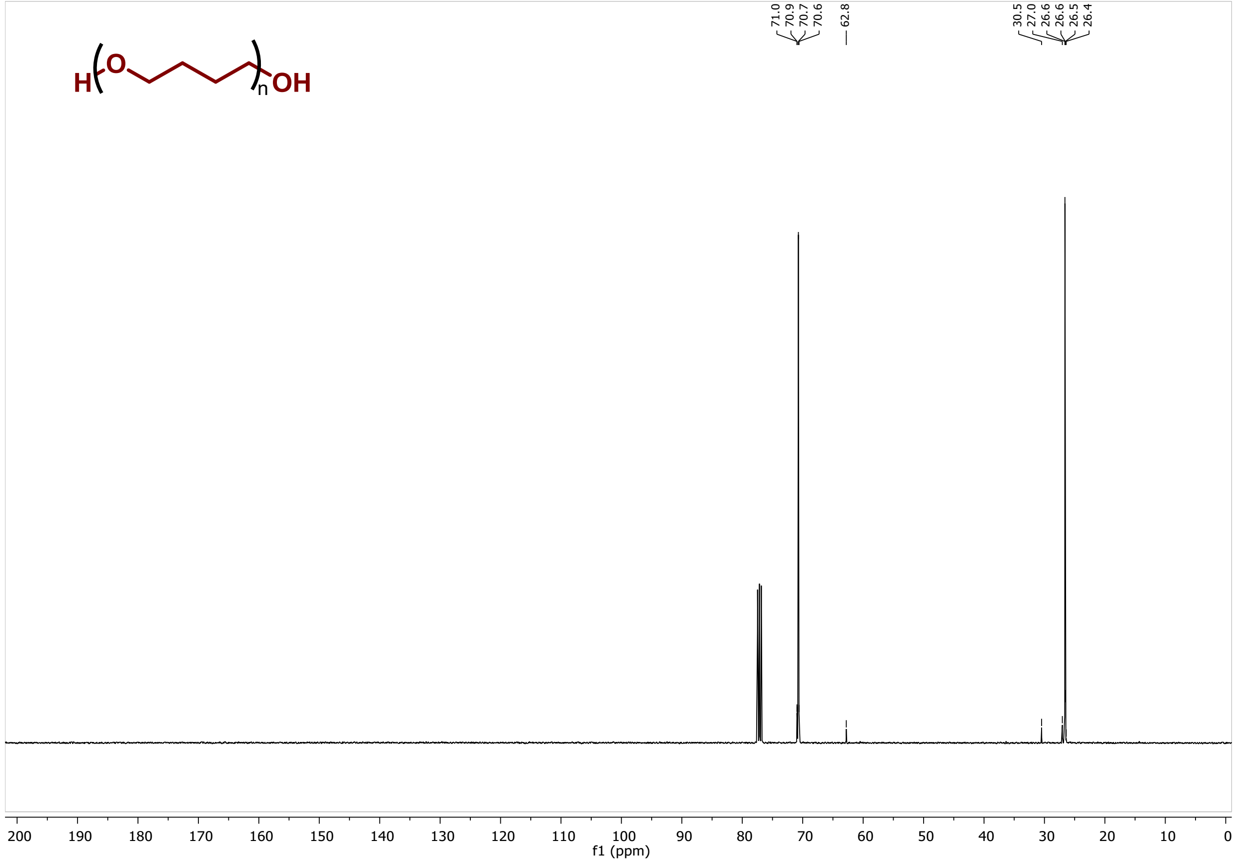
NMR Spectra of MDA Fraction



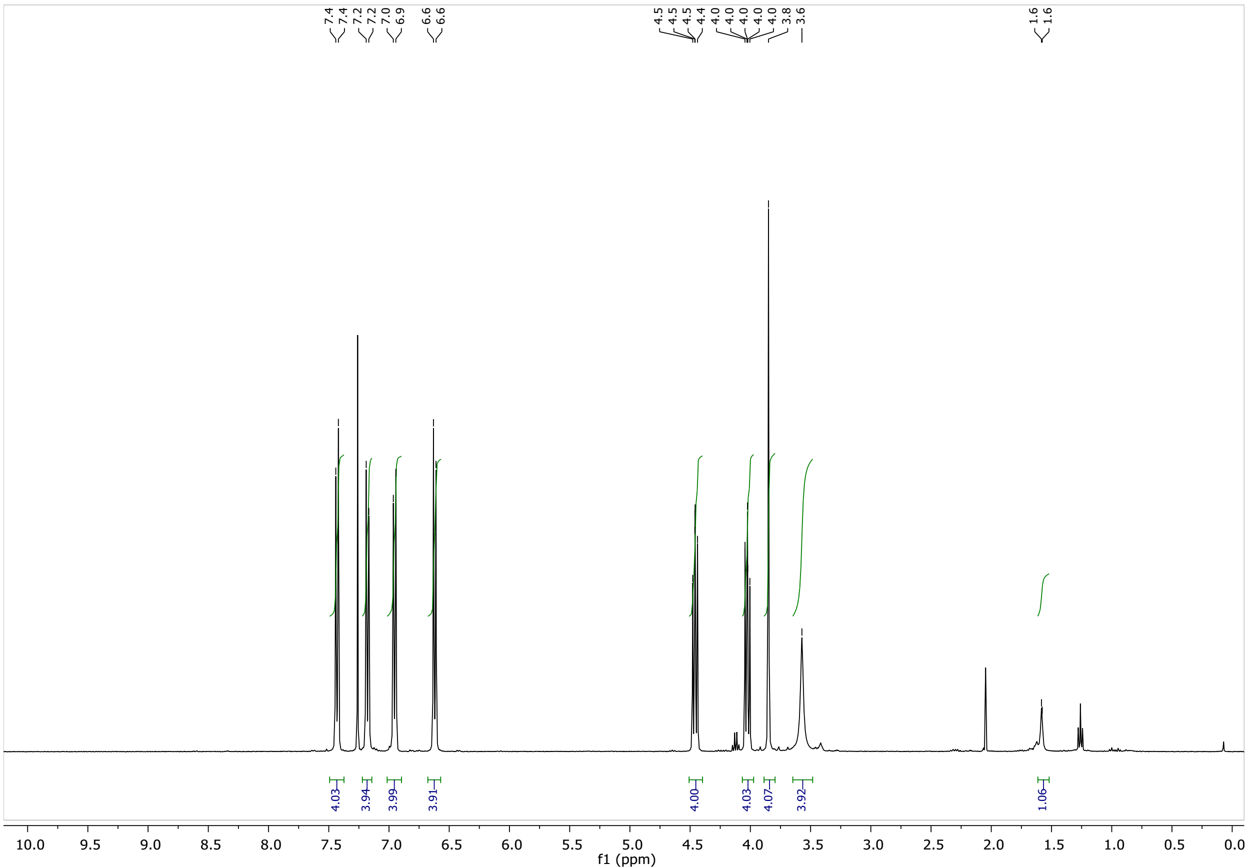


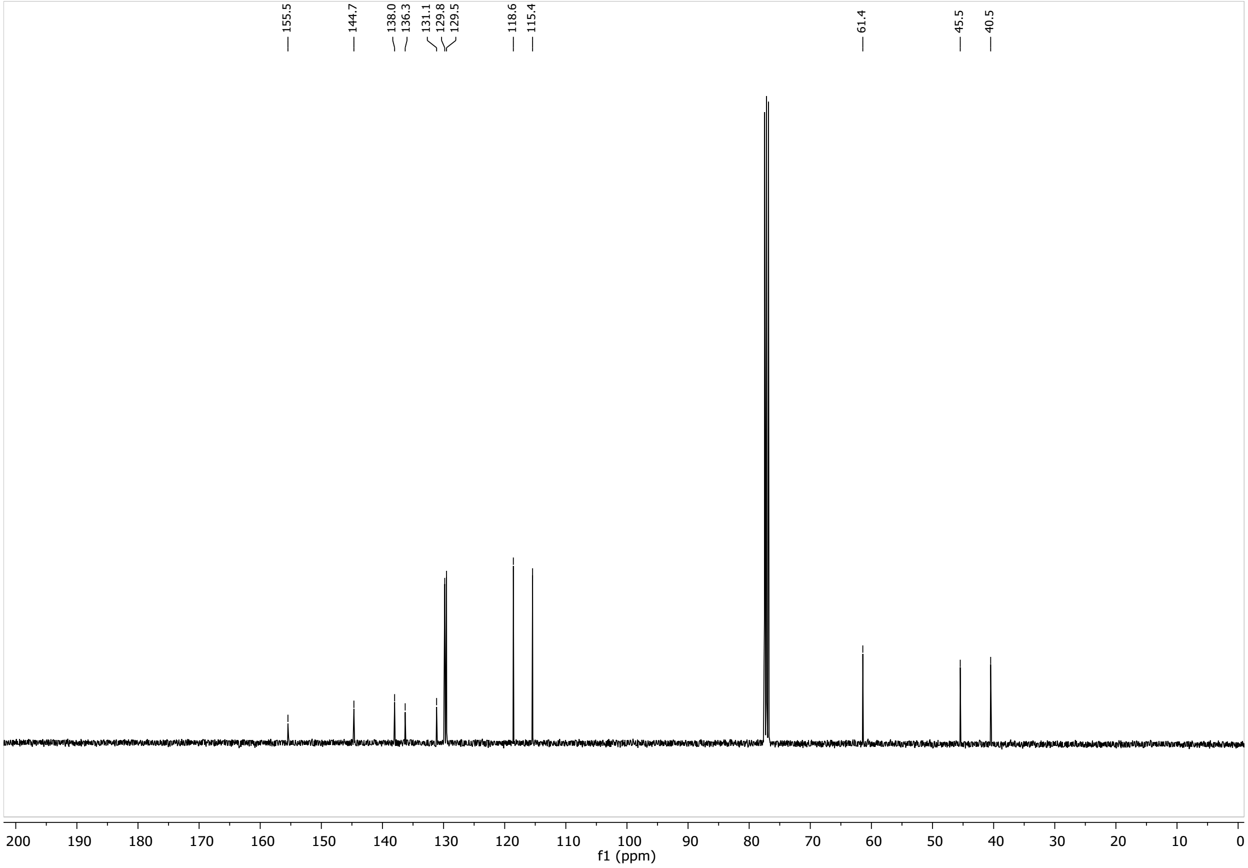
NMR Spectra of Polyol Fraction



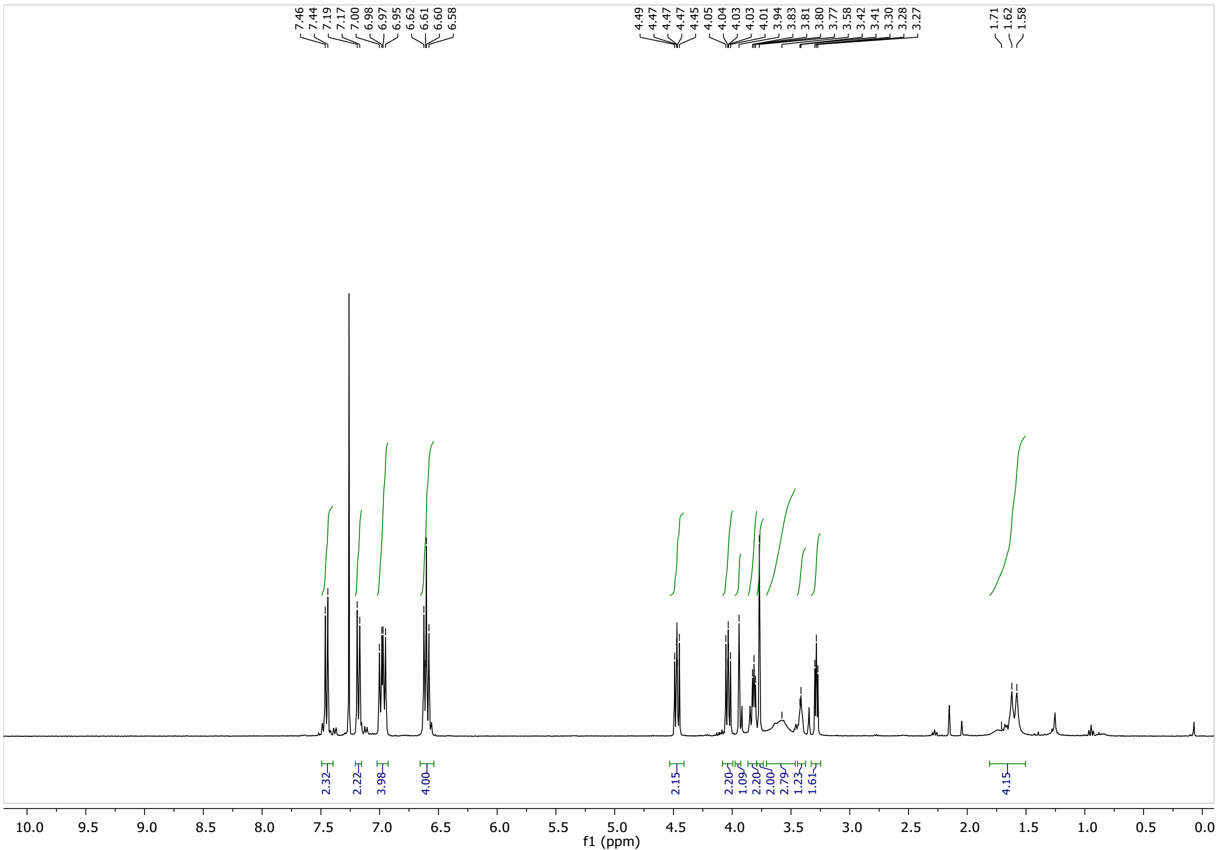


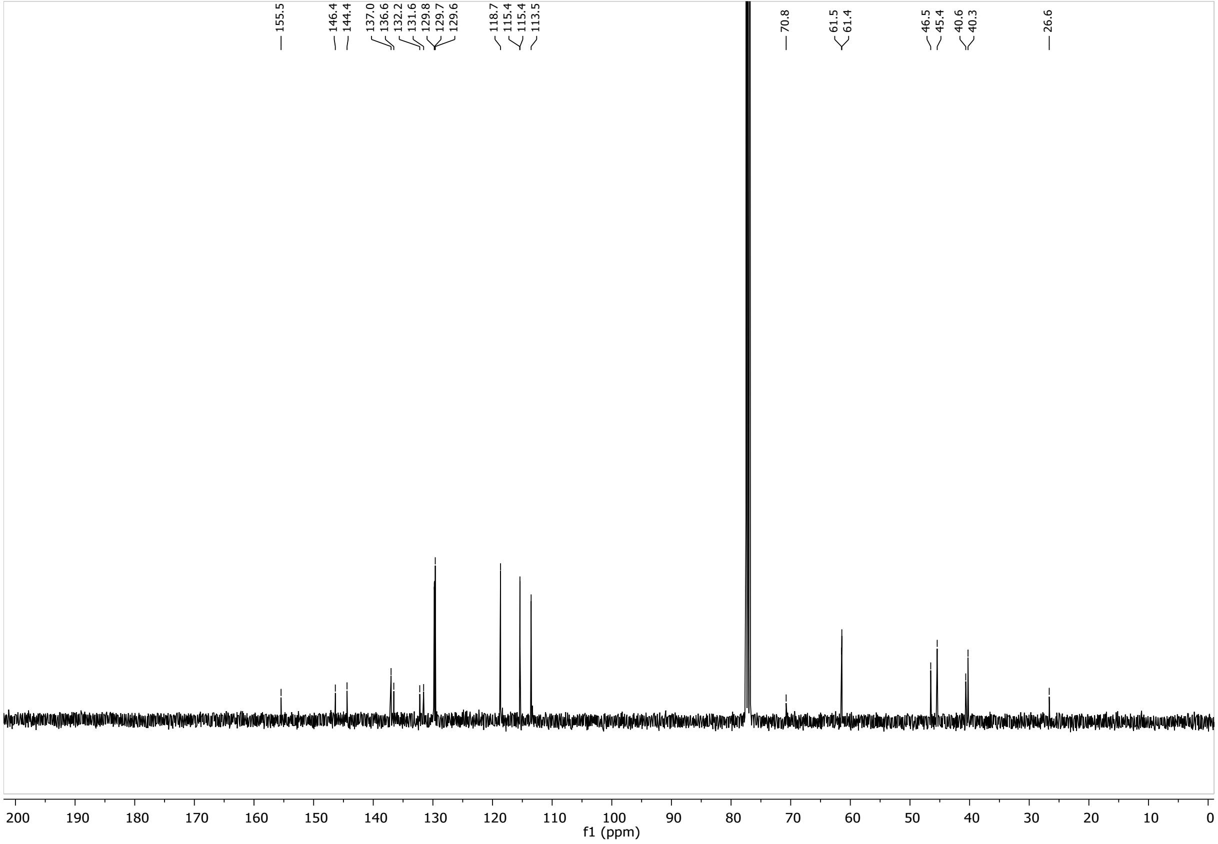
NMR Spectra of the First Unknown By-Product





NMR Spectra of the Second Unknown By-Product





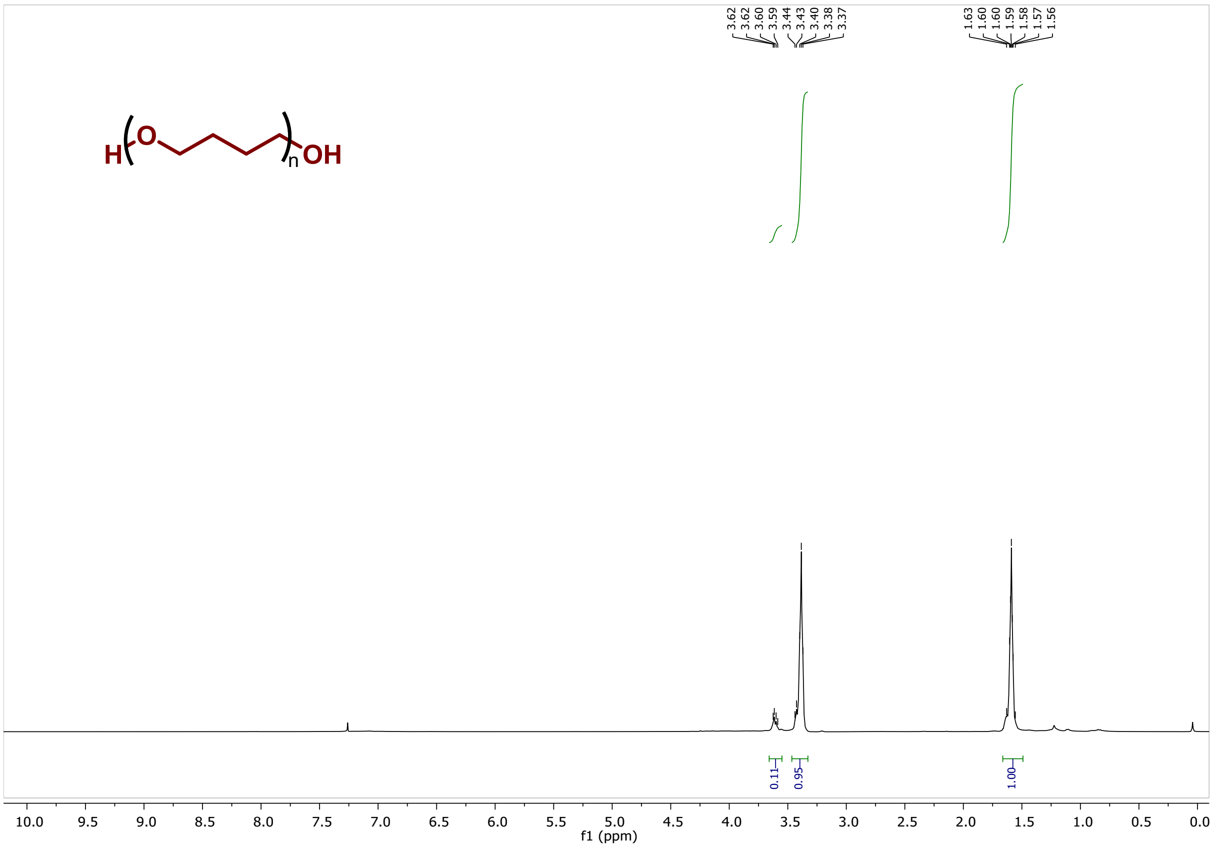
SI-10. Solvolysis of Elastane-Cotton Fabric

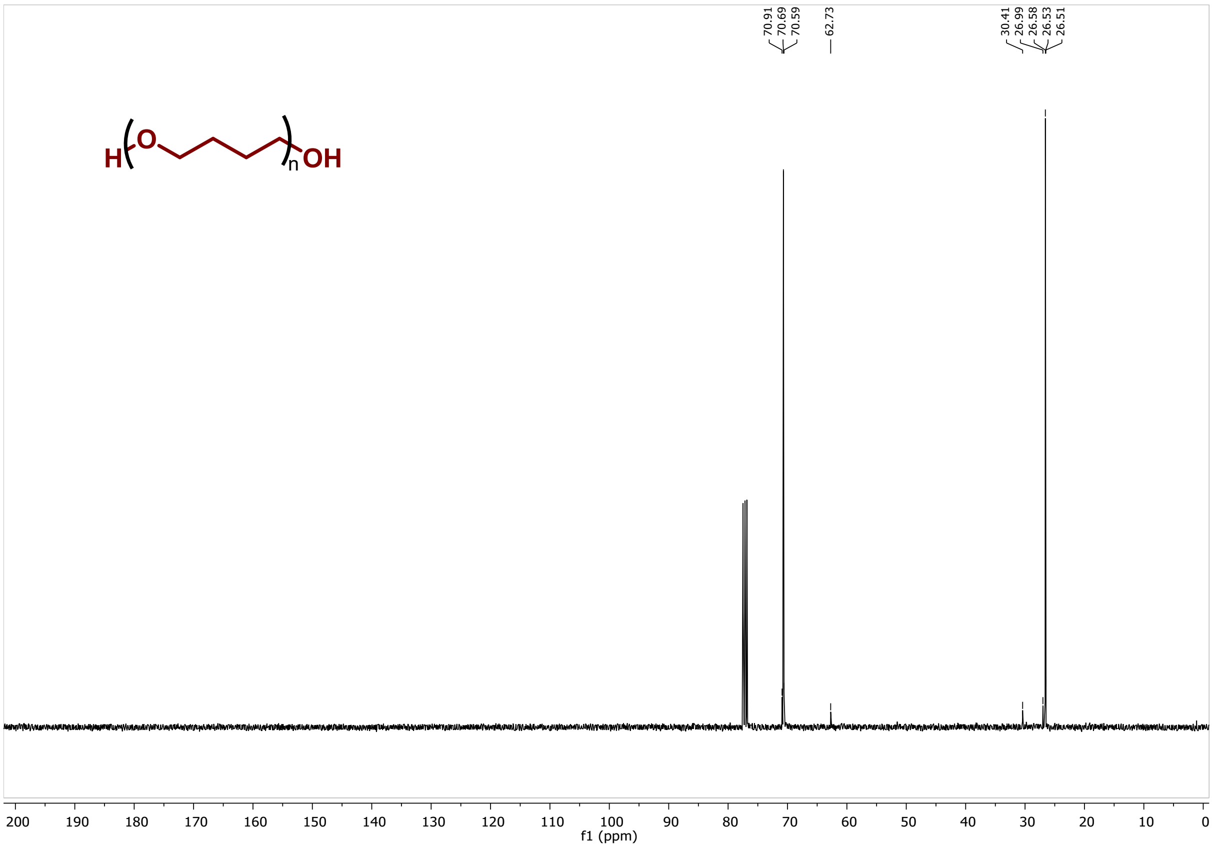
The fabric (“Organic stretch jersey with checks and cars”; article no. 272886; 8% elastane and 92% organic cotton) was acquired from www.stofogstil.dk.

The fabric was cut into smaller pieces with a pair of scissors.

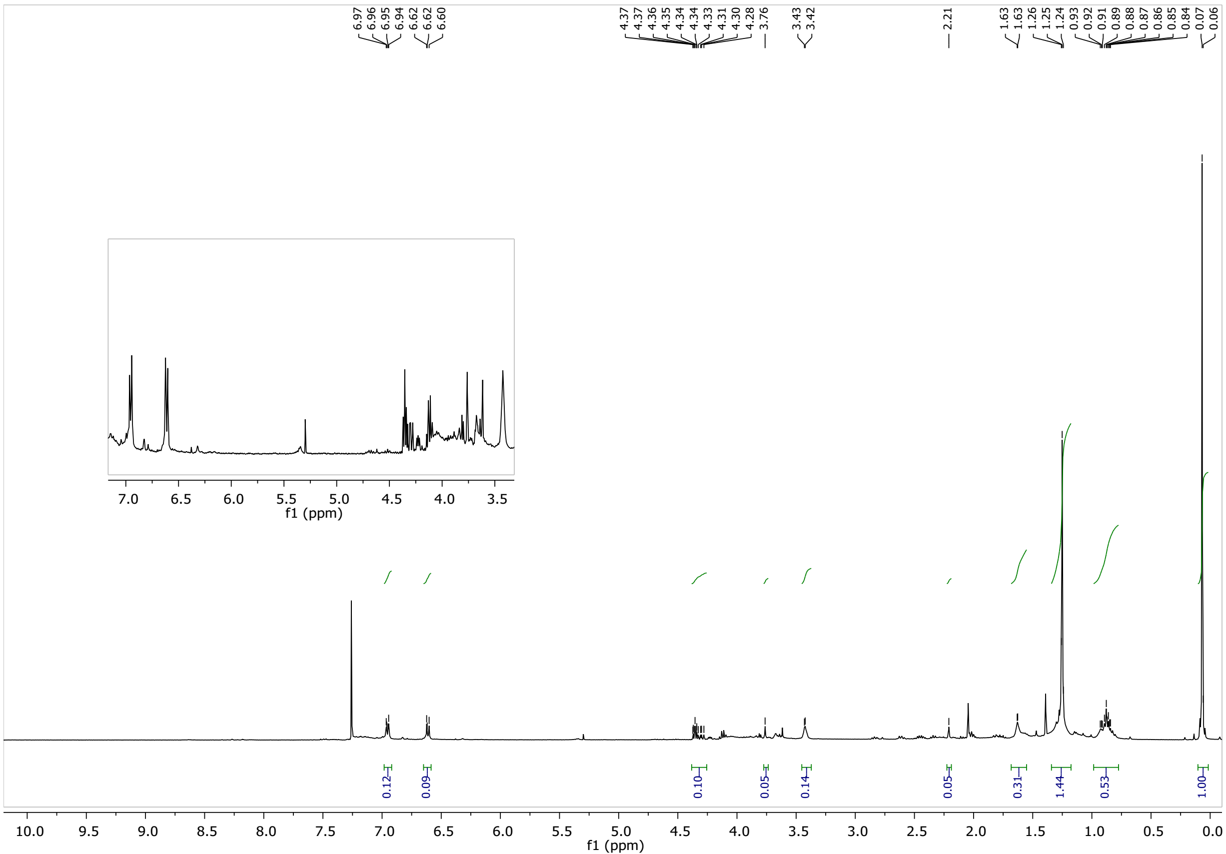
The material (run 1: 1.01 g; run 2: 1.01 g) was deconstructed as described in General Procedure C to afford a mixture of comprising mostly of polyol with traces of 4,4’-MDA (only isolated for run 2: 28.4 mg) as a yellow solid, a polyol fraction (run 1: 69.0 mg; run 2: 68.0 mg) as a brown amorphous solid in an average yield of 68.5 mg, and leftover brown pieces of fabric (run 1: 0.86 g; run 2: 0.86 g) in an average mass of 0.86 g.

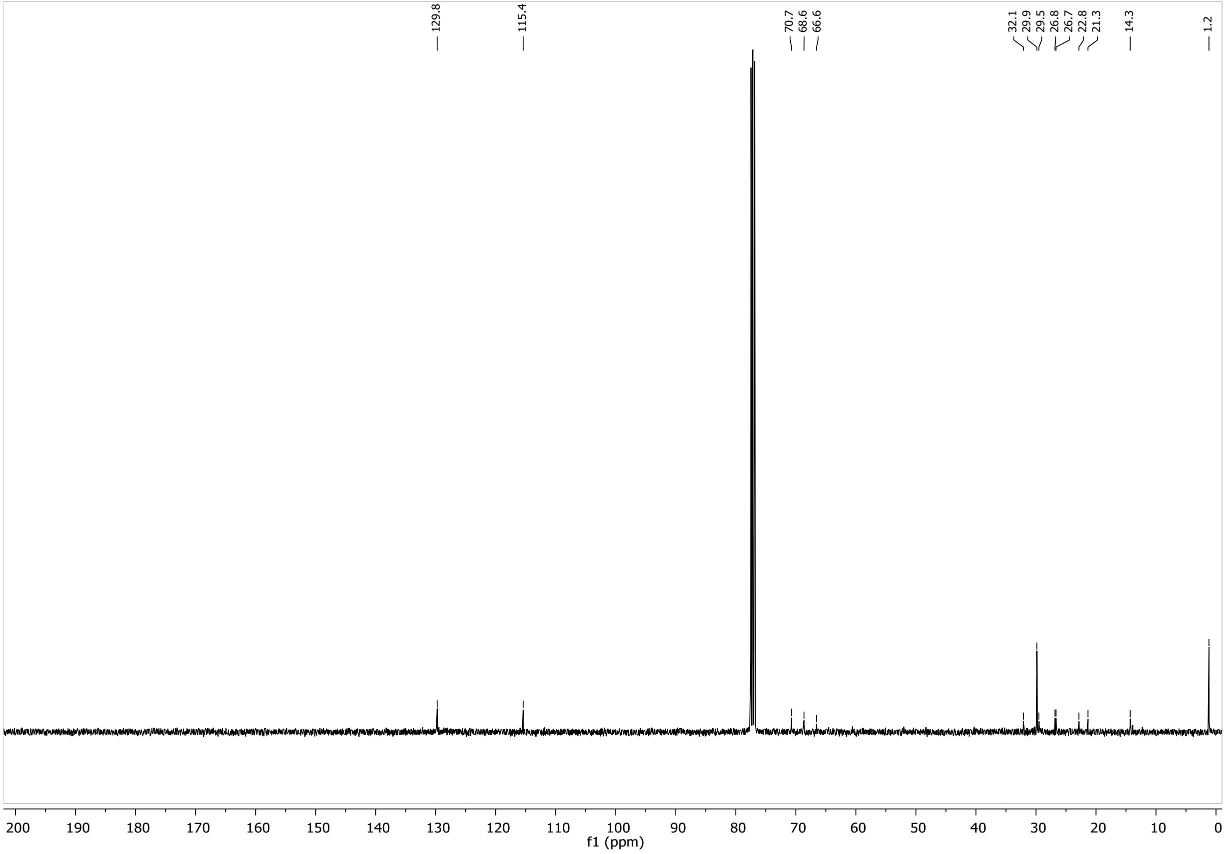
NMR Spectra of Polyol Fraction



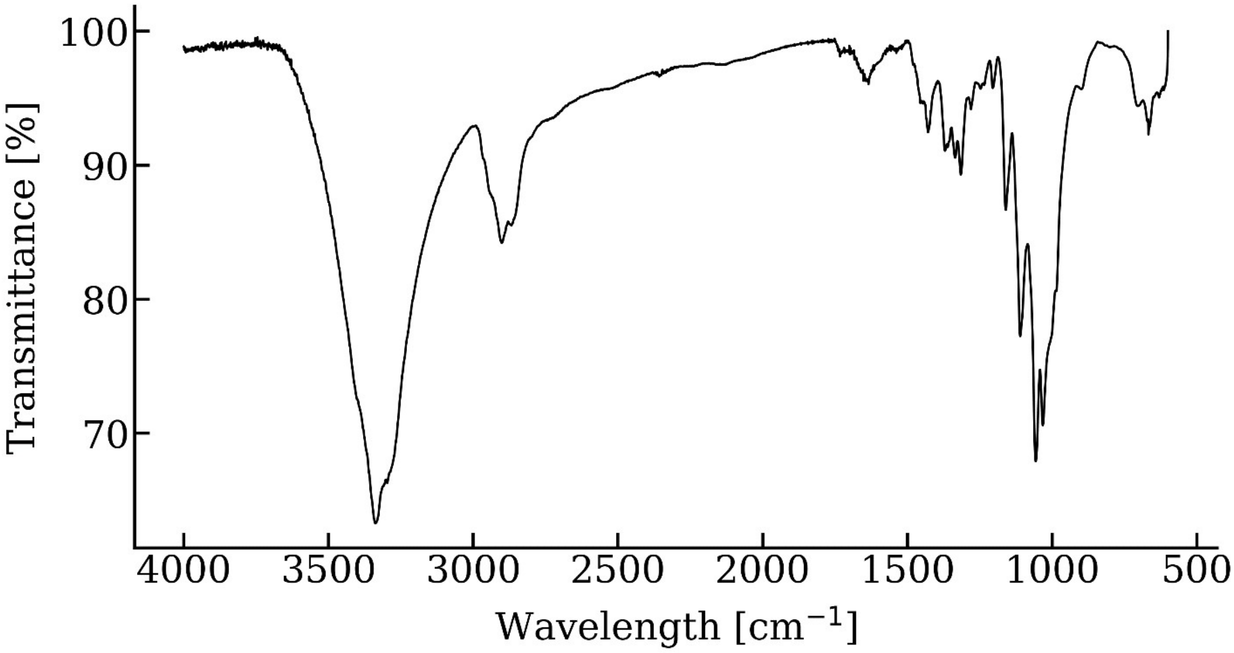


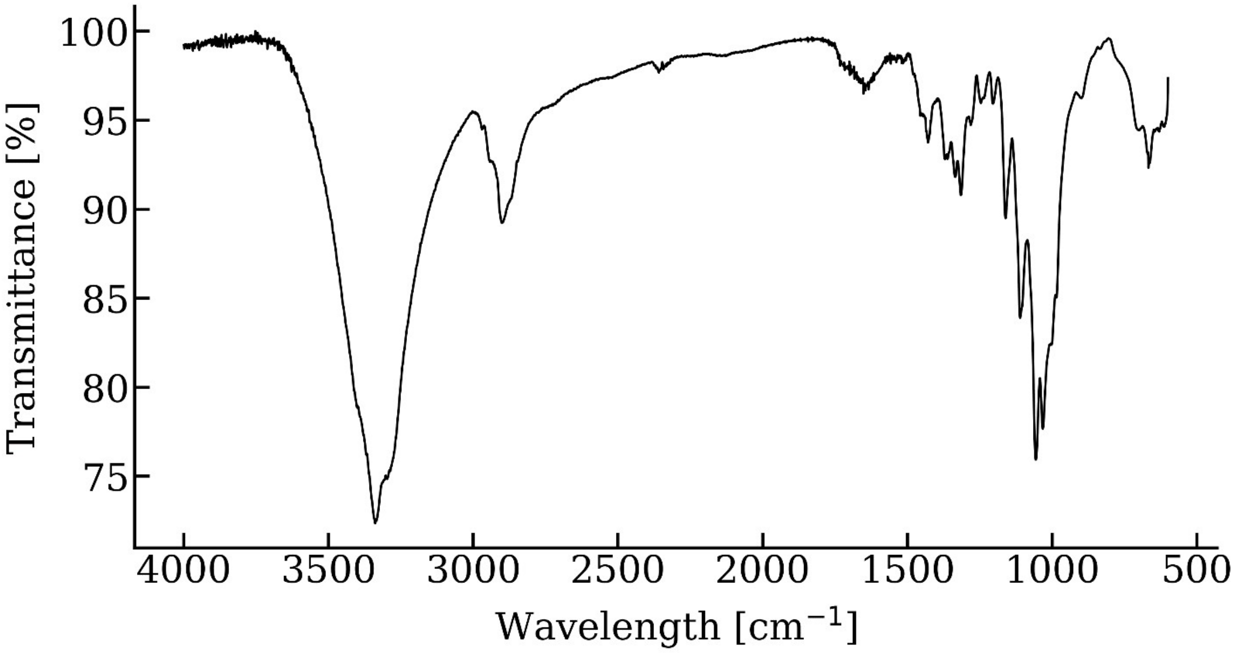
NMR Spectra of Fraction with Trace 4,4’-MDA and By-Products



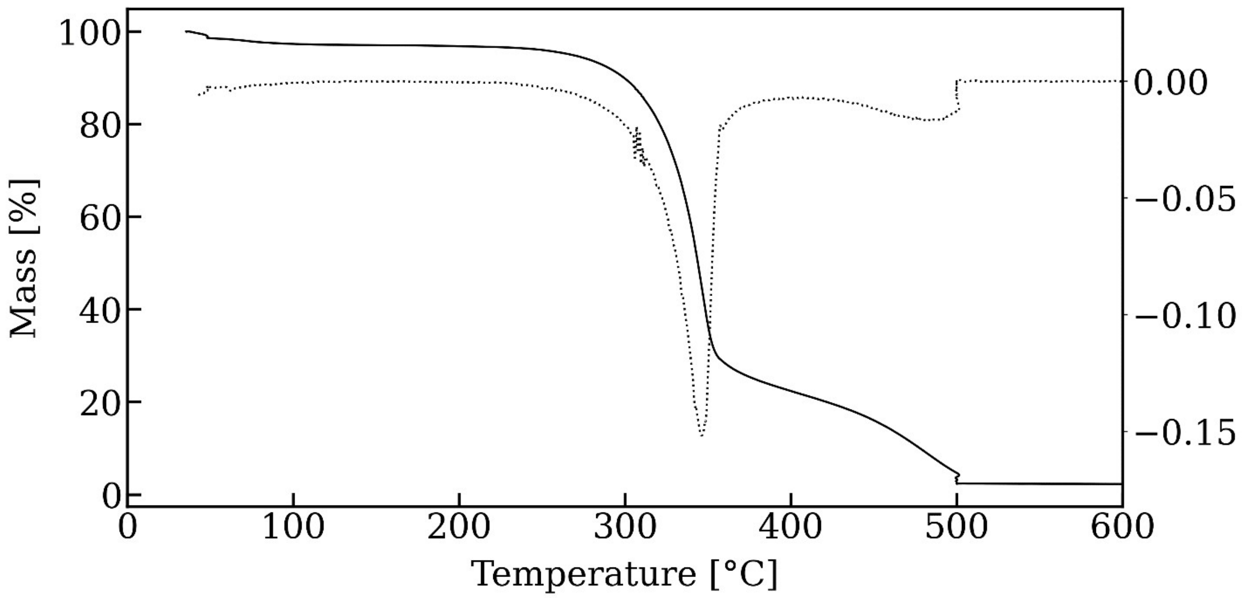


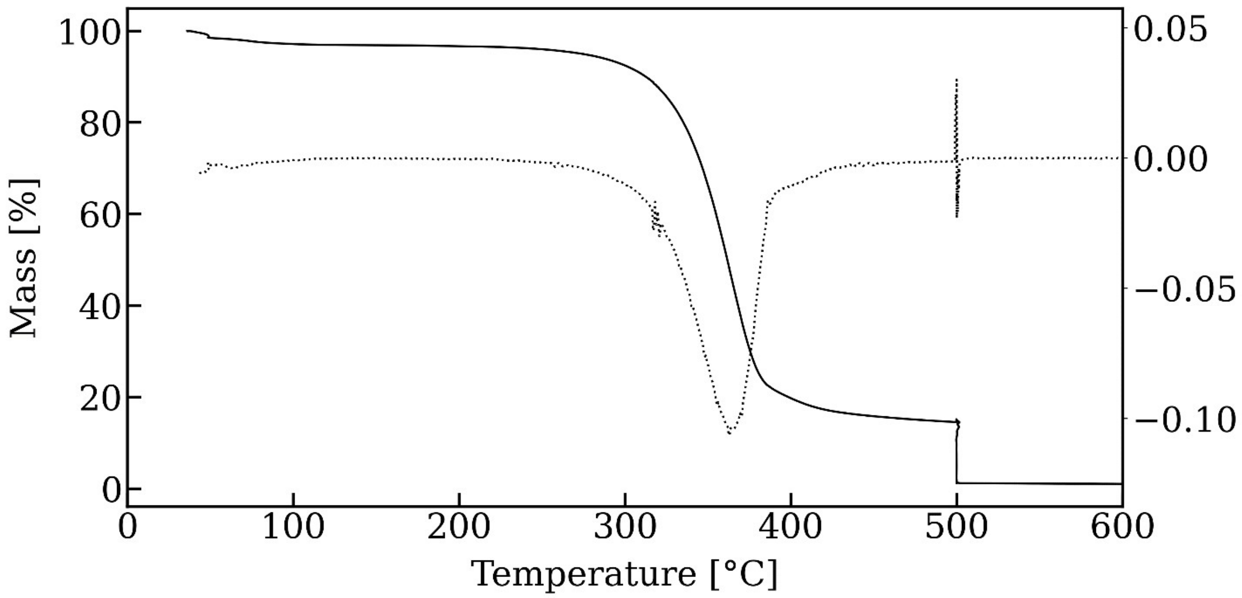
FTIR Spectra of Cotton (Top) and Leftover Fabric from Solvolysis (Bottom)



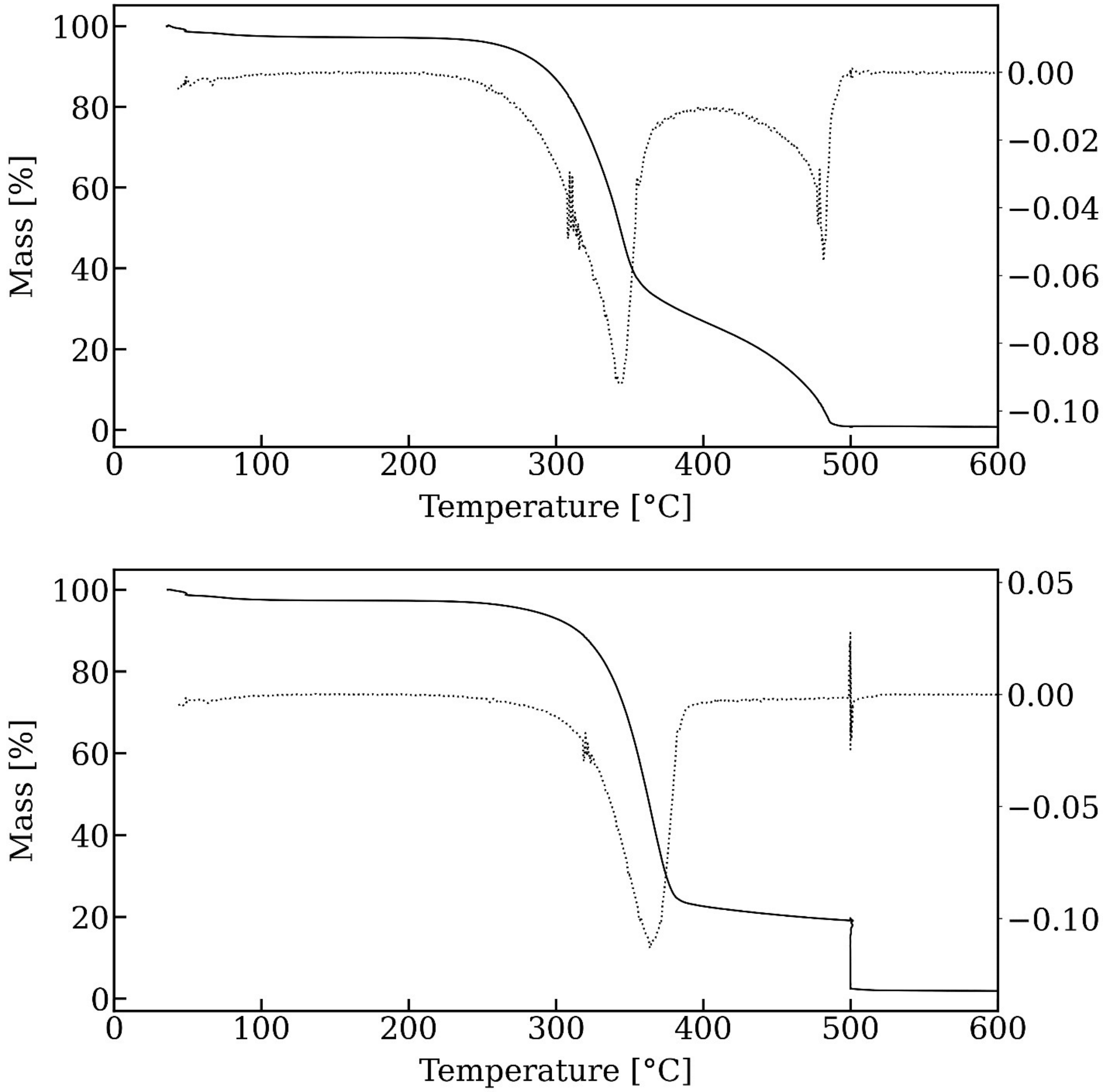


TGA Spectra of Cotton Recorded in Laboratory Air (Top) and Nitrogen Atmosphere (Bottom)

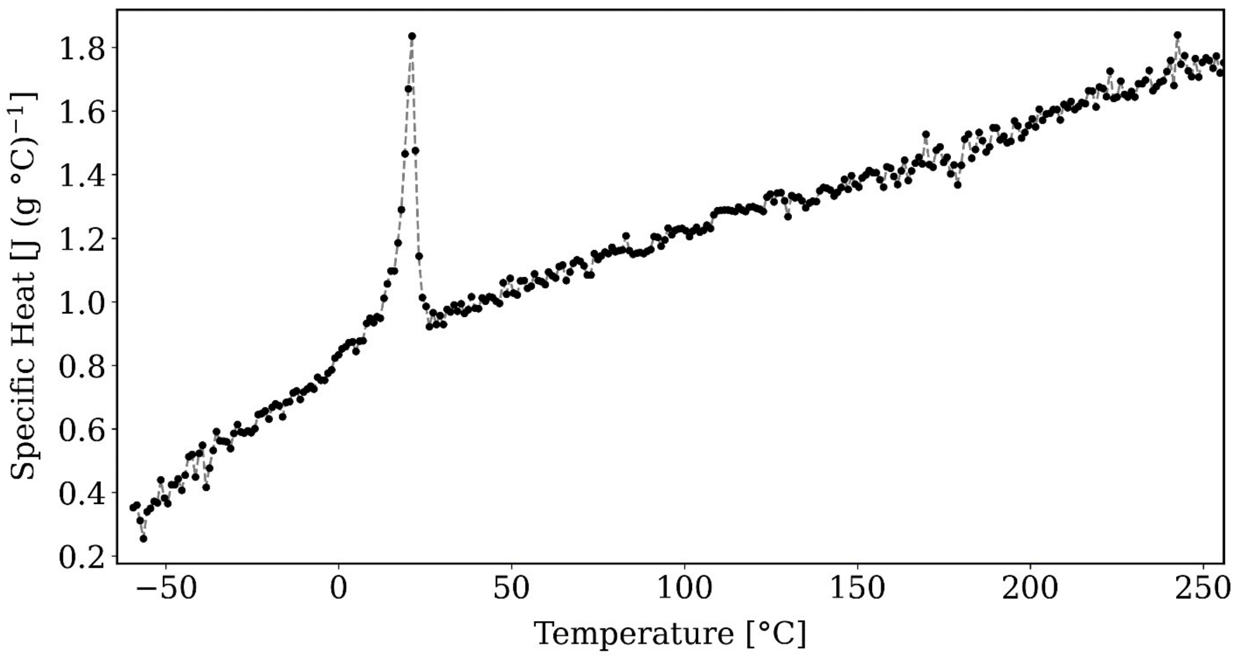




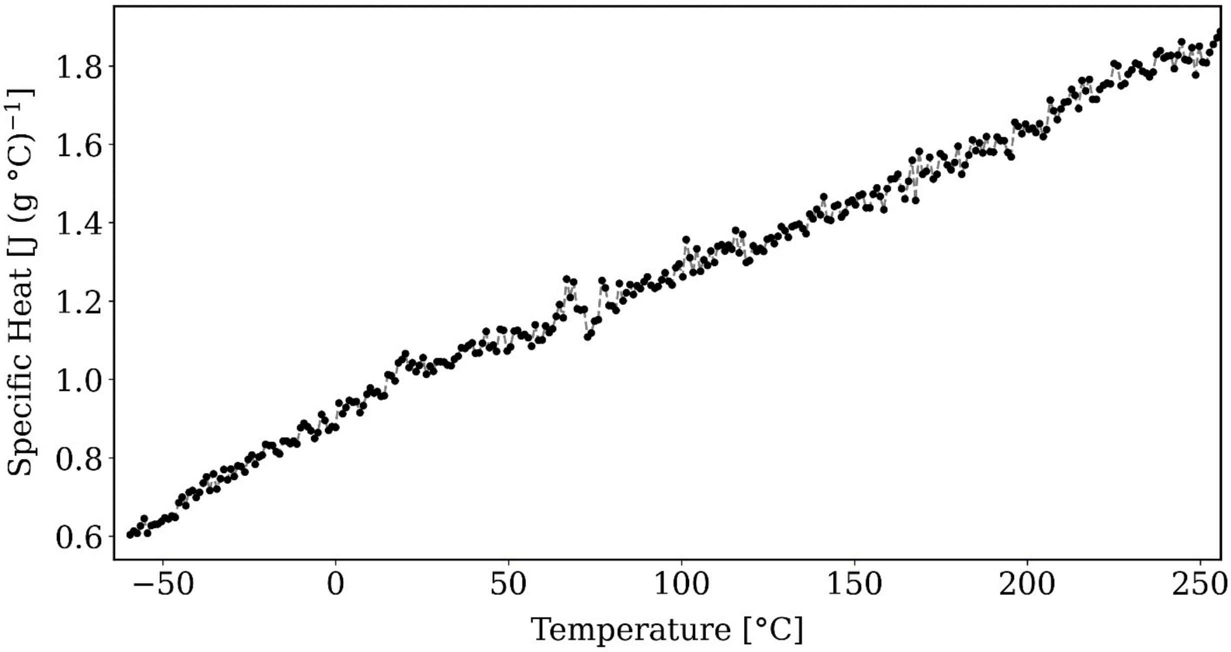
TGA Spectra of Leftover Fabric from Cotton From Solvolysis in Laboratory Air (Top) and Nitrogen Atmosphere (Bottom)



DSC of Tights with Two Heating-Cooling Cycles (top) and DSC StepScan (bottom)



DSC of Leftover Fabric from Tights with Two Heating-Cooling Cycles (top) and DSC StepScan (bottom)

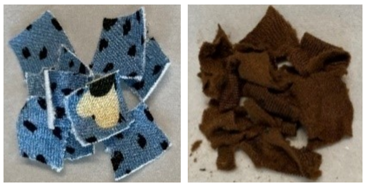


SI-11. Solvolysis of Viscose-Elastane Fabric

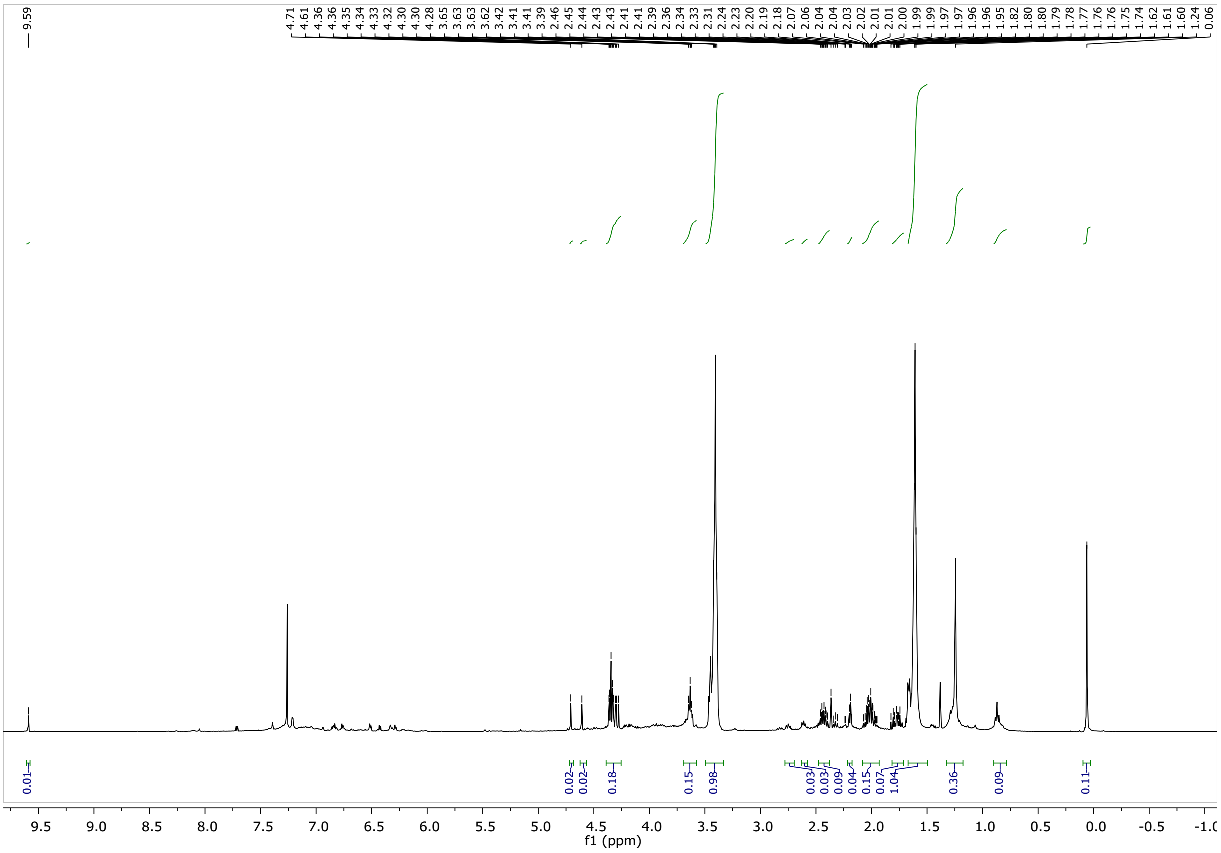
The fabric (“Viscose stretch jersey blue with hearts”; article no. 272890; 9% elastane and 91% viscose) was acquired from www.stofogstil.dk.

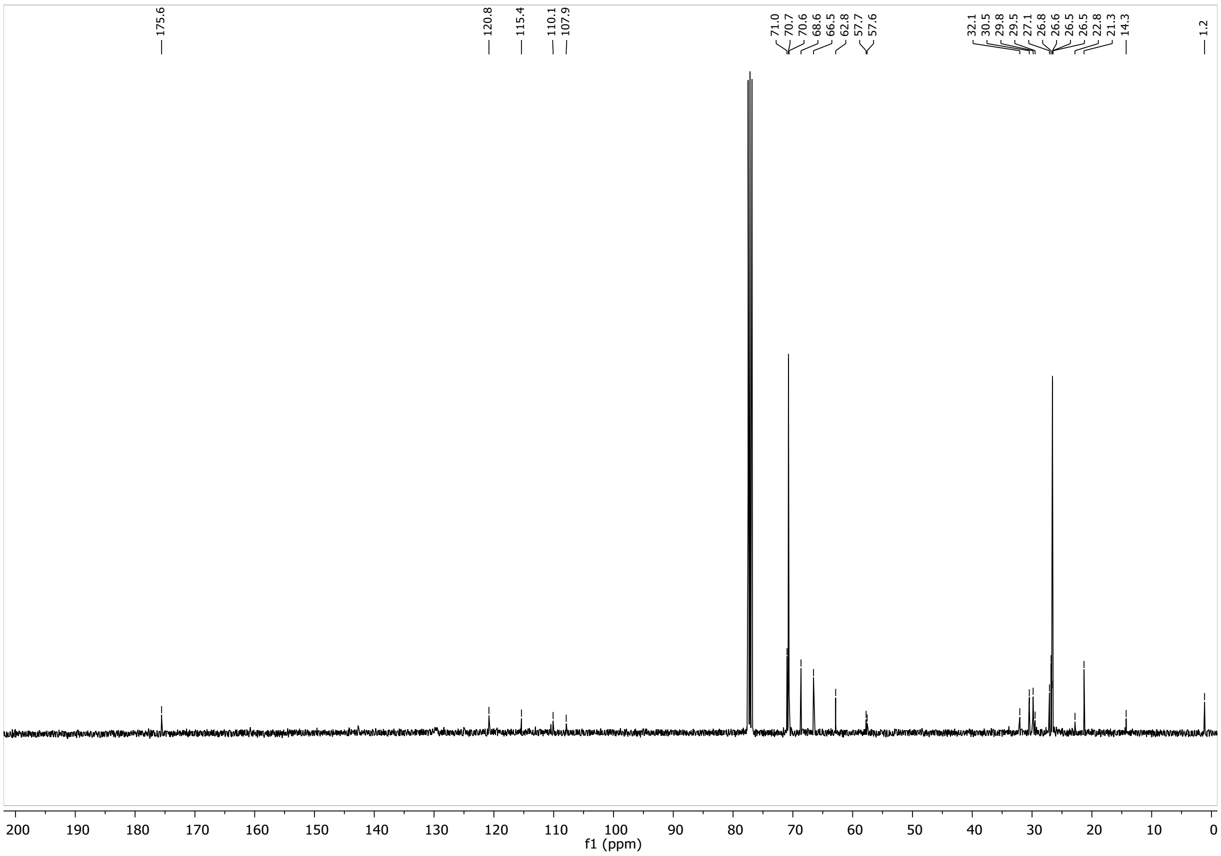
The fabric was cut into smaller pieces with a pair of scissors.

The sample (run 1: 1.00 g; run 2: 1.01 g) was deconstructed as described in General Procedure C to afford a mixture of compounds (run 1: 38.8 mg; run 2: 79.3 mg) as a brown oil in an average yield of 59.1 mg, a polyol fraction (run 1: 78.8 mg; run 2: 89.7 mg) as a brown amorphous solid in an average yield of 84.1 mg, and crumbling leftover brown pieces of fabric (run 1: 0.67 g; run 2: 0.63 g) in an average mass of 0.65 g.

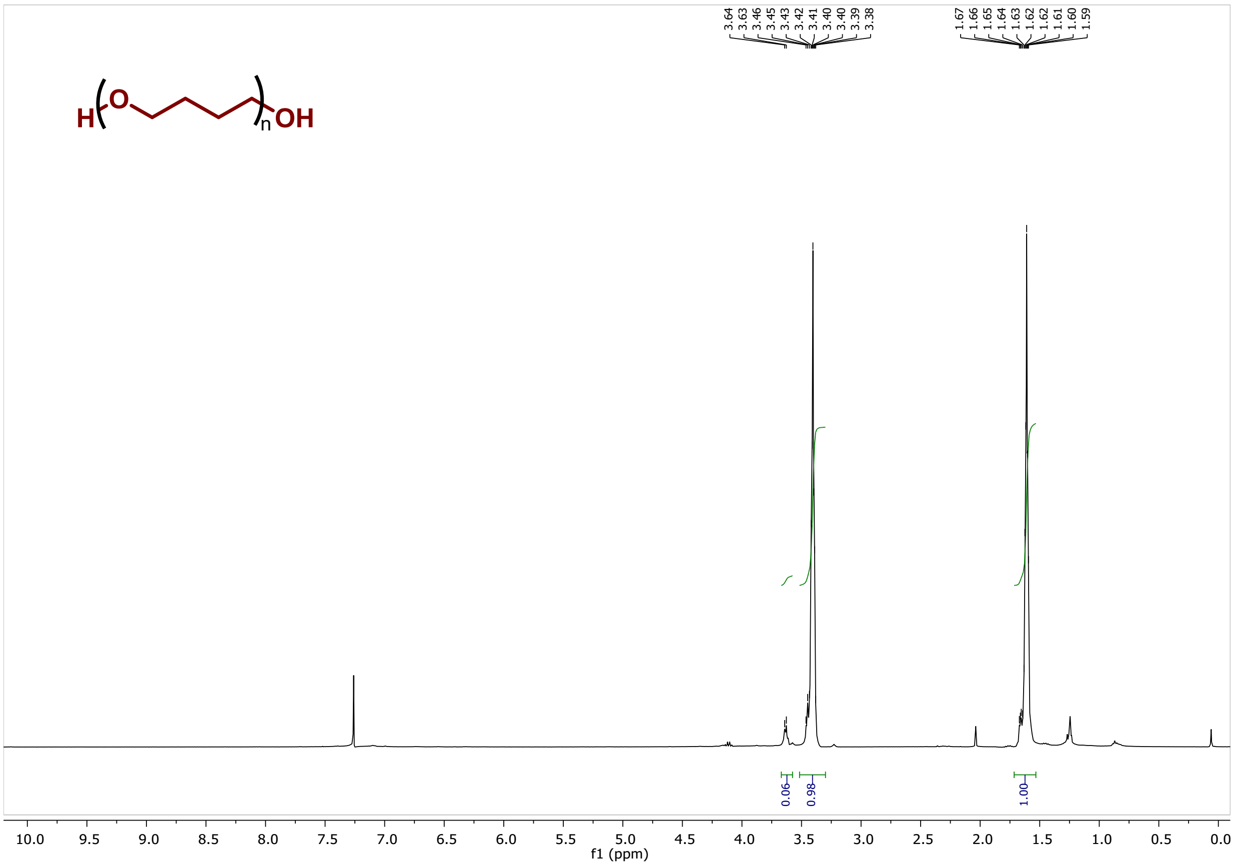


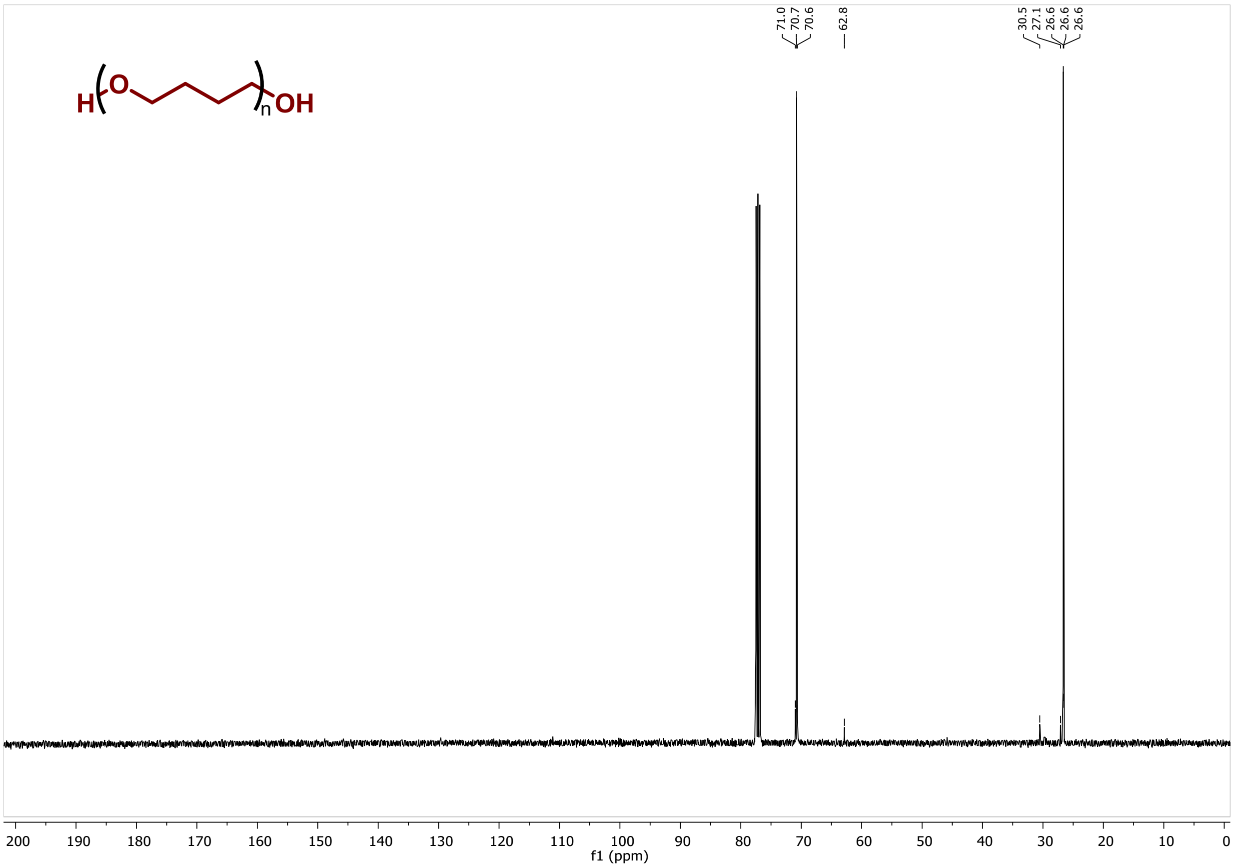
NMR Spectra of Mixture of By-Products



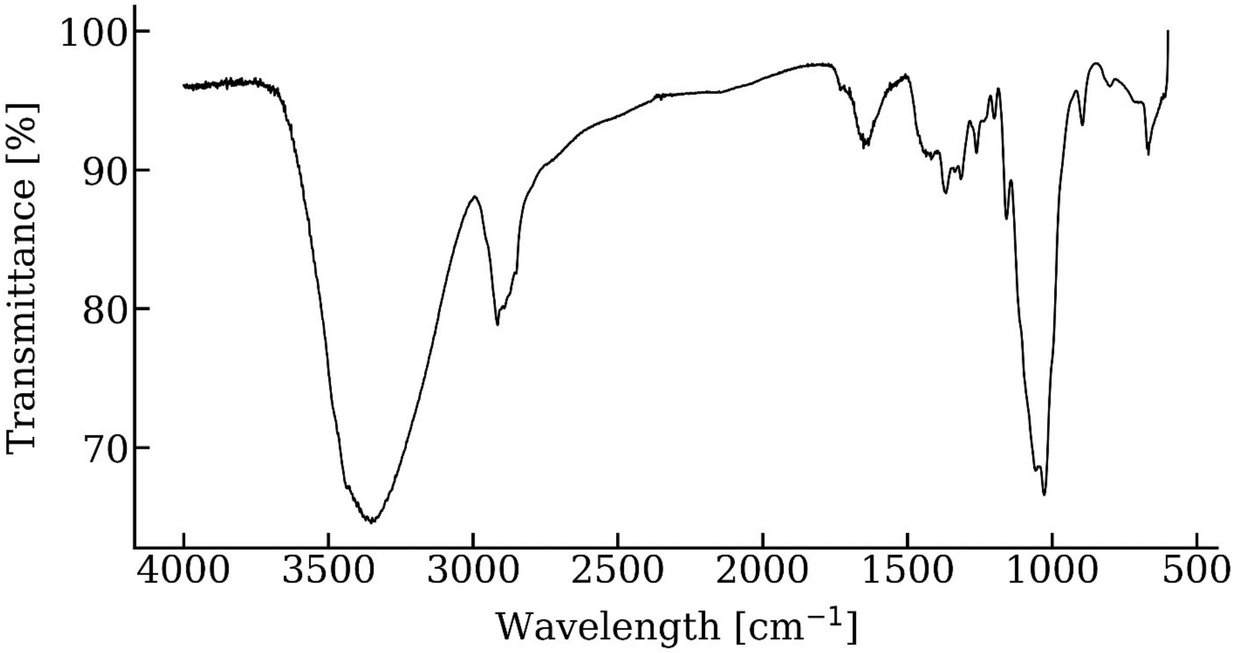


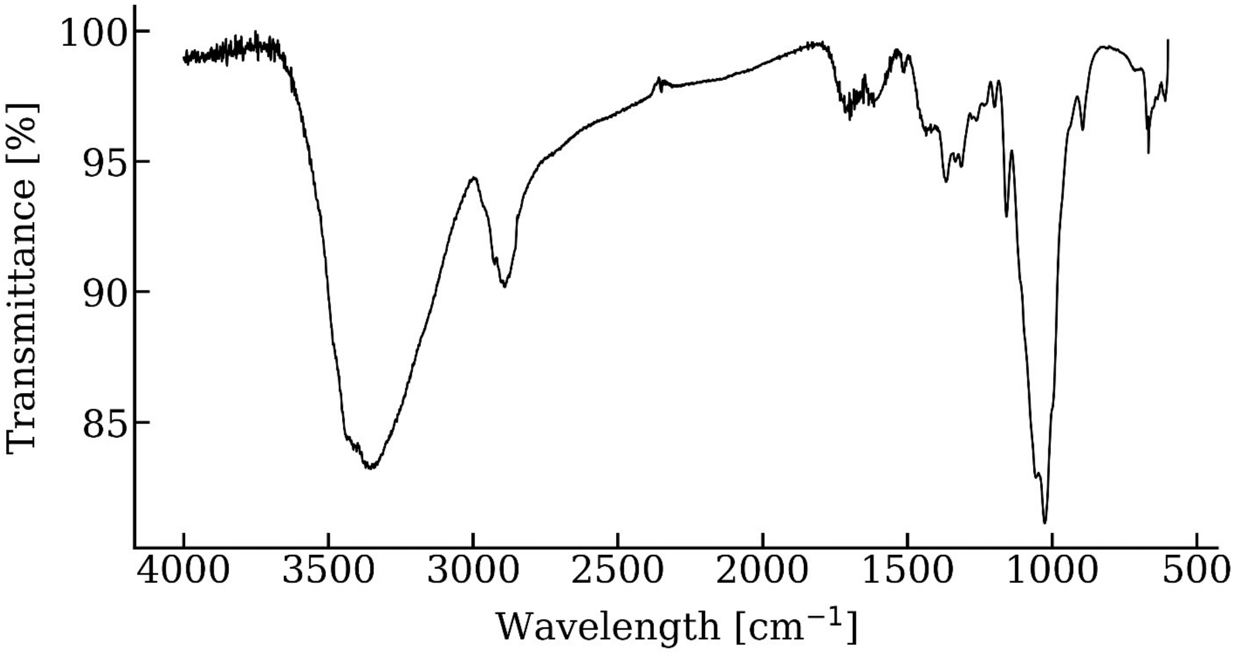
NMR Spectra of Polyol Fraction





FTIR Spectra of Viscose (top) and Leftover Solid from Solvolysis (Bottom)





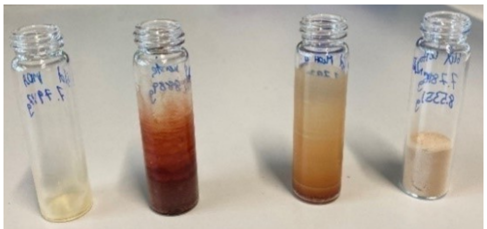
SI-12. Solvolysis of Satin (Elastane-Polyester Fabric)

The fabric ("Duchess satin with stretch Bordeaux"; article no. 620514; 14% elastane and 86% polyester) was acquired from www.stofogstil.dk.

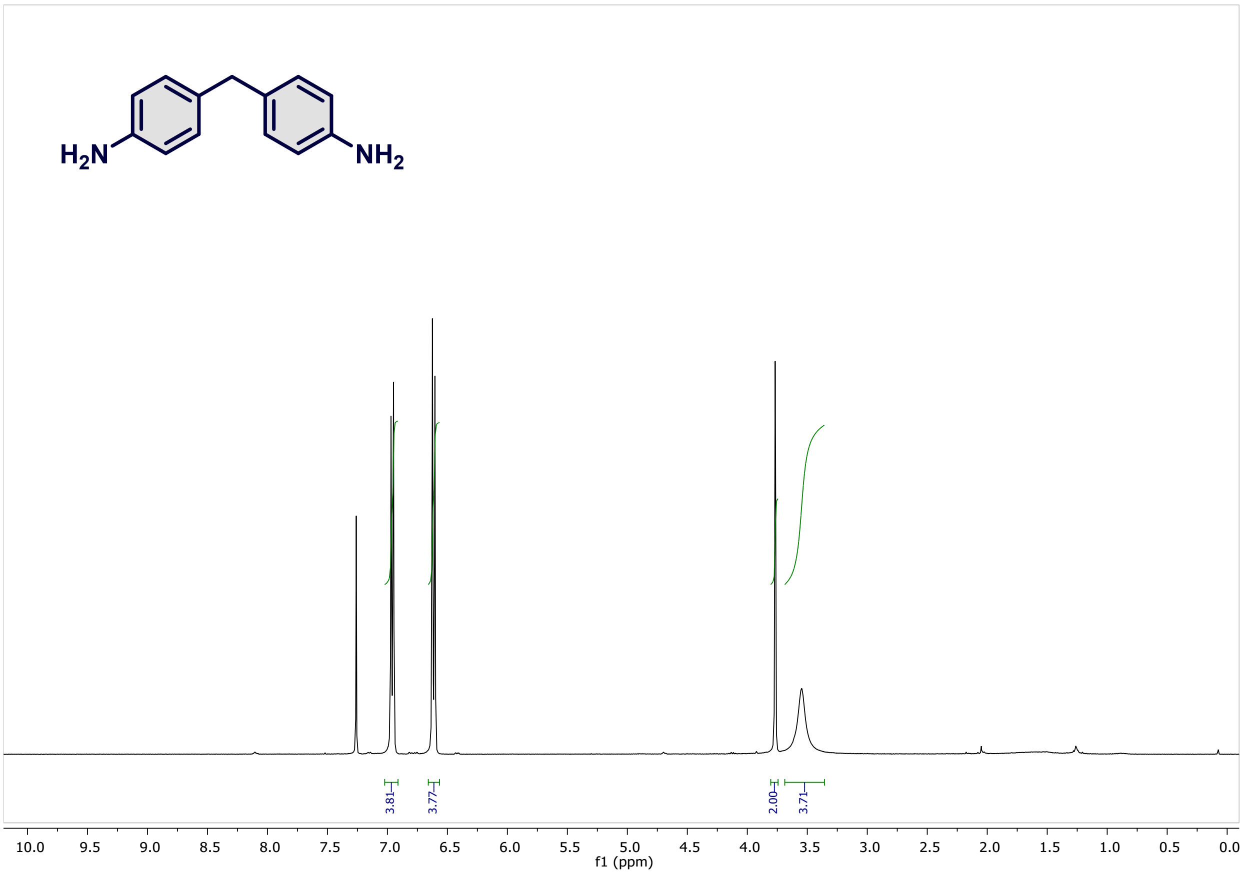
The fabric was cut into smaller pieces with a pair of scissors.

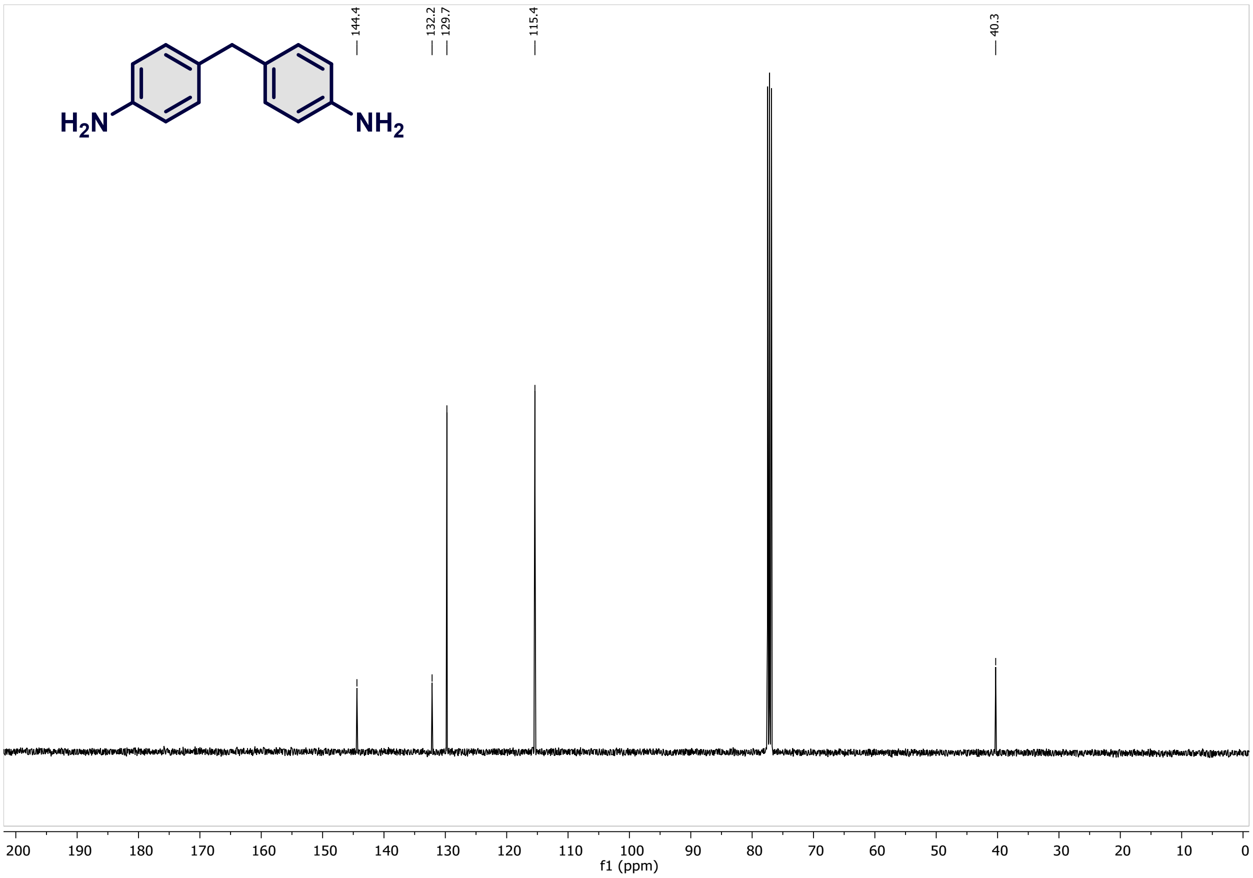
The sample (run 1: 1.01 g; run 2: 1.01 g) was deconstructed as described in General Procedure B to afford 4,4'-MDA* (run 1: 5.6 mg; run 2: 5.6 mg) as a yellow solid in an average yield of 5.6 mg, an unknown mixture of by-products (run 1: 30.2 mg; run 2: 54.1 mg) as a red solid in an average yield of 42.2 mg, a polyol fraction (run 1: 0.11 g; run 2: 0.11 g) as a brown amorphous solid in an average yield of 0.11 g, and leftover fluffy yellow powder (run 1: 0.76 g; run 2: 0.75 g) in an average mass of 0.76 g.

*4,4'-MDA fraction from column chromatography was further purified by an acid-base wash to remove non-basic impurities: The impurity was removed by dissolving the sample in 1 M HCl/brine (1:1, 2 mL) and extracting the aqueous phase with CH_2Cl_2 (5 x 2 mL). For the recovery of 4,4'-MDA, the aqueous phase was basified with 4 M NaOH to pH of 10-11 and extracted with CH_2Cl_2 (5 x 2 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, filtered, concentrated, and dried *in vacuo* overnight to afford 4,4'-MDA.

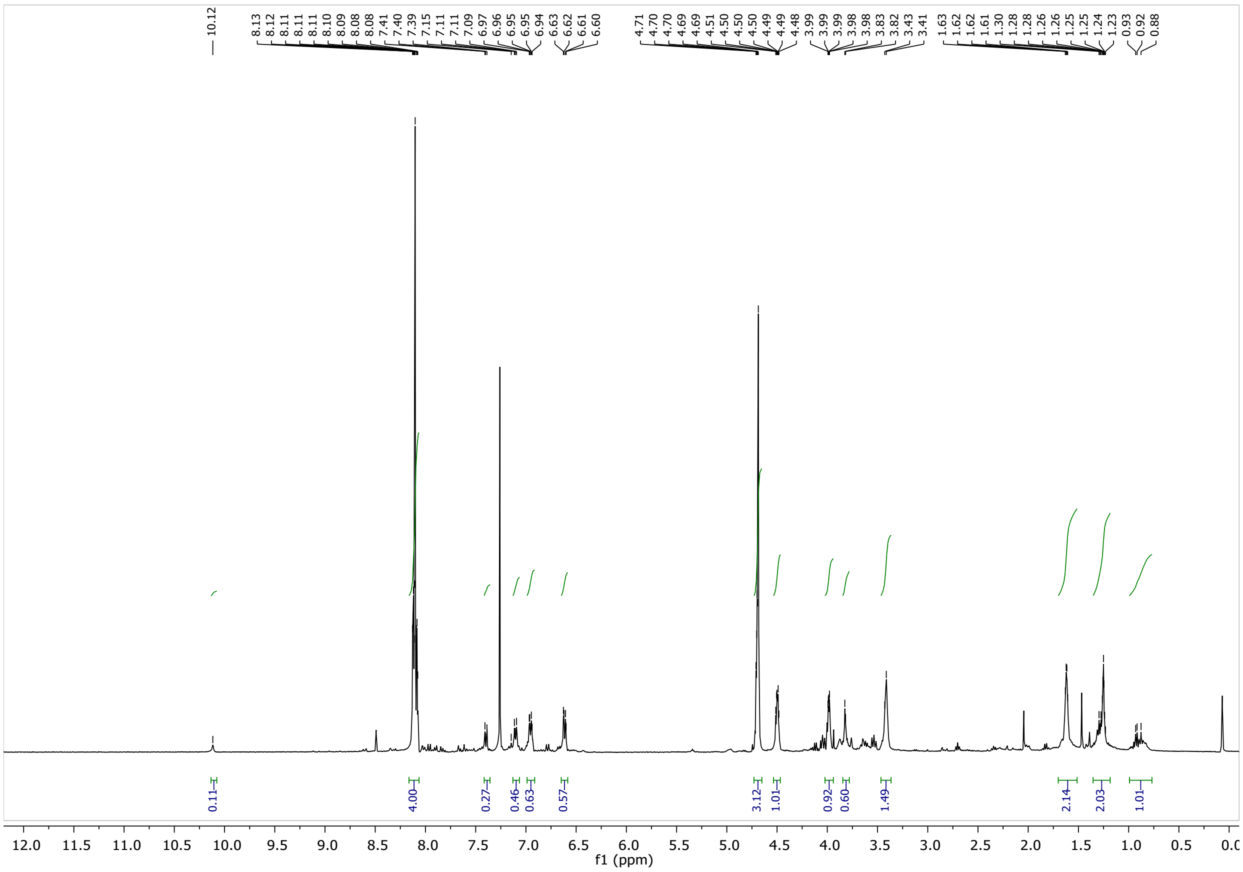


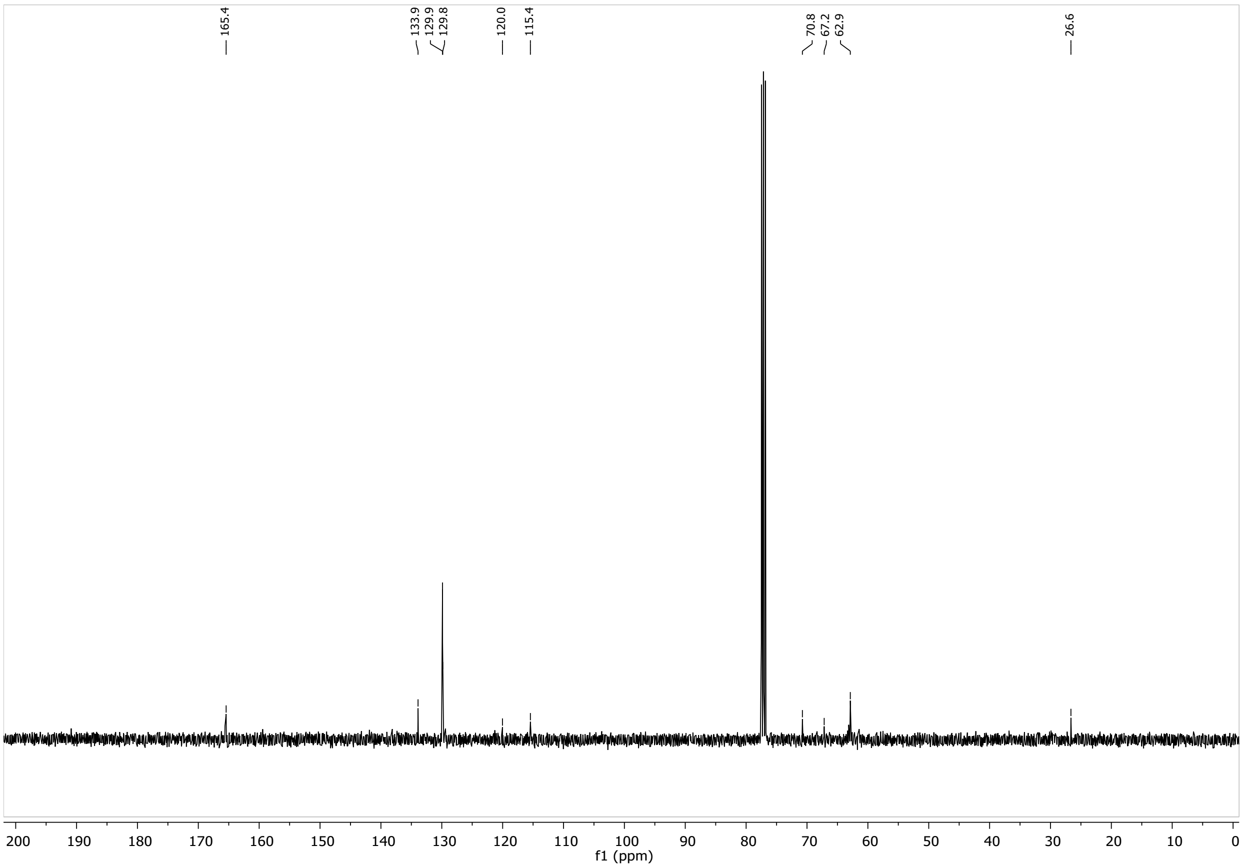
NMR Spectra of 4,4’-MDA



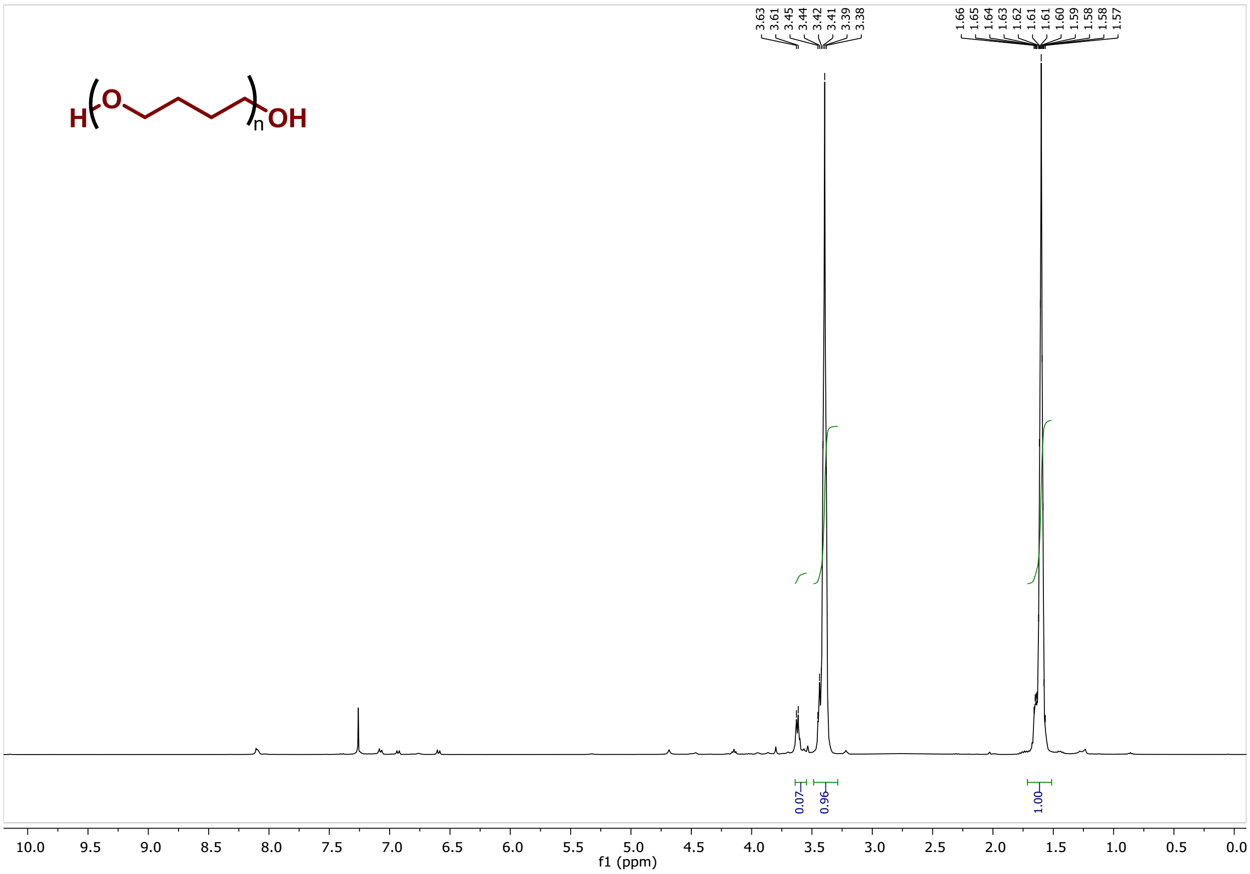


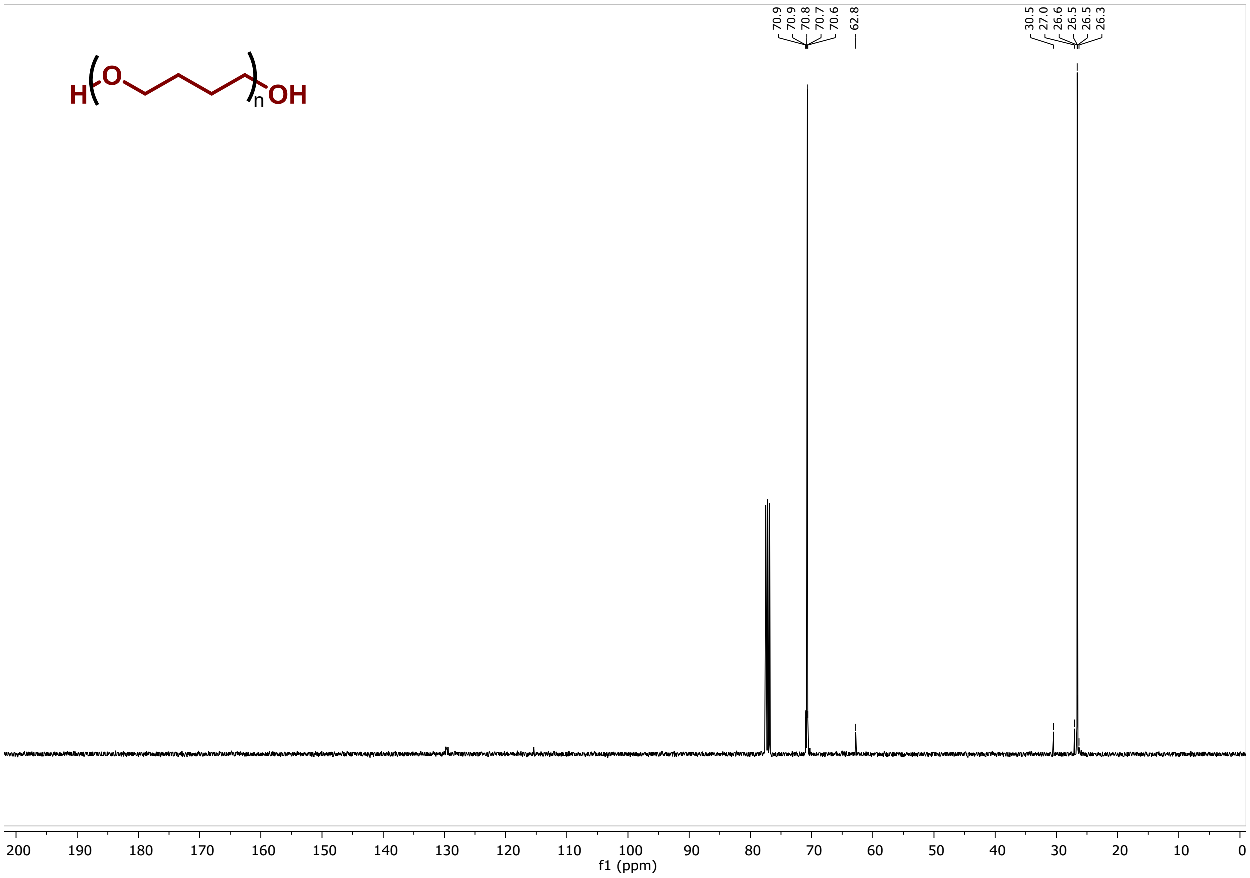
NMR Spectra of By-Products



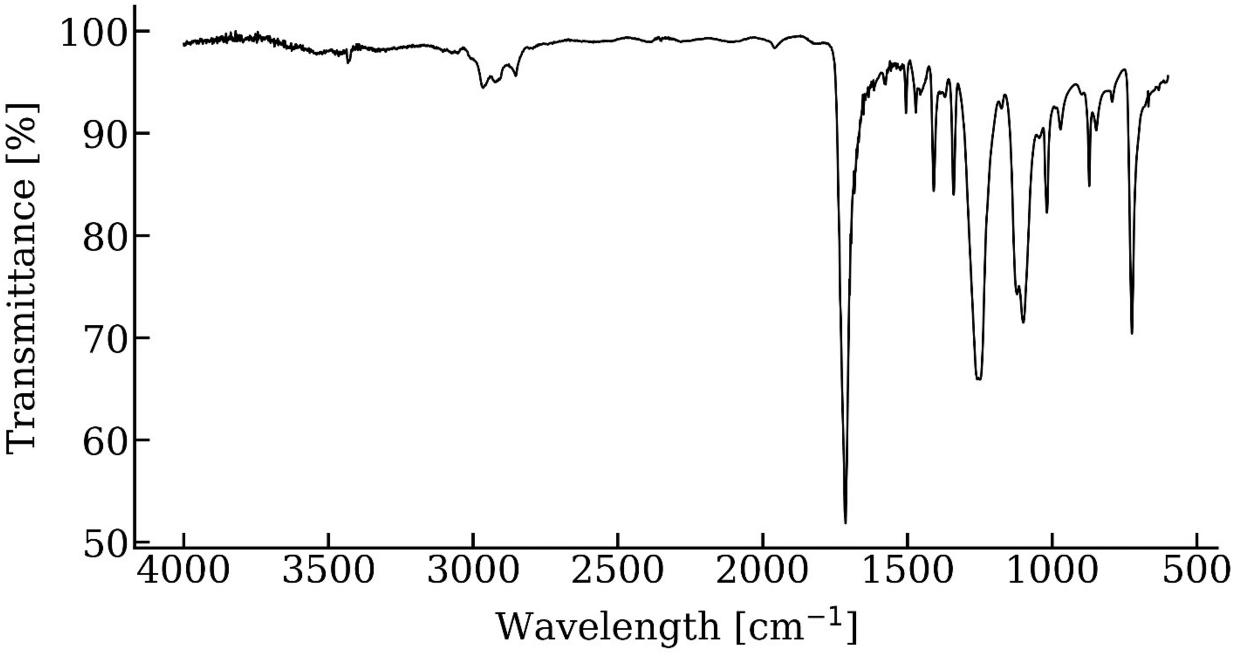


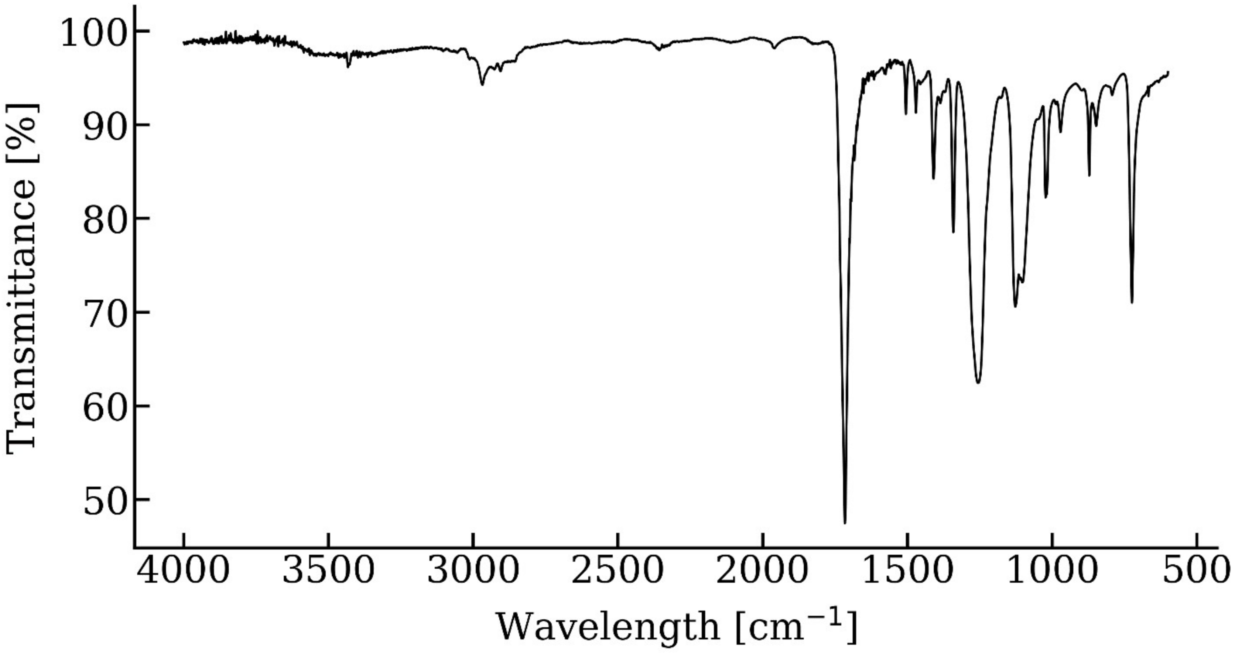
NMR Spectra of Polyol Fraction





FTIR Spectra of PET Satin (top) and Leftover Solids from Solvolysis (bottom)

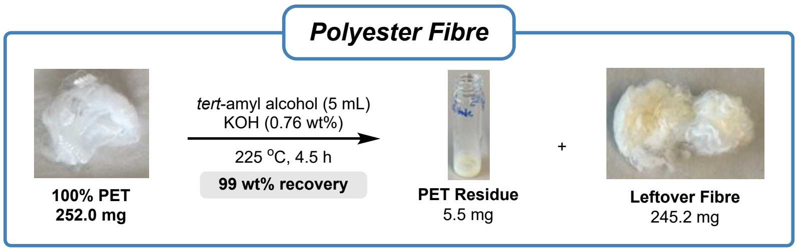




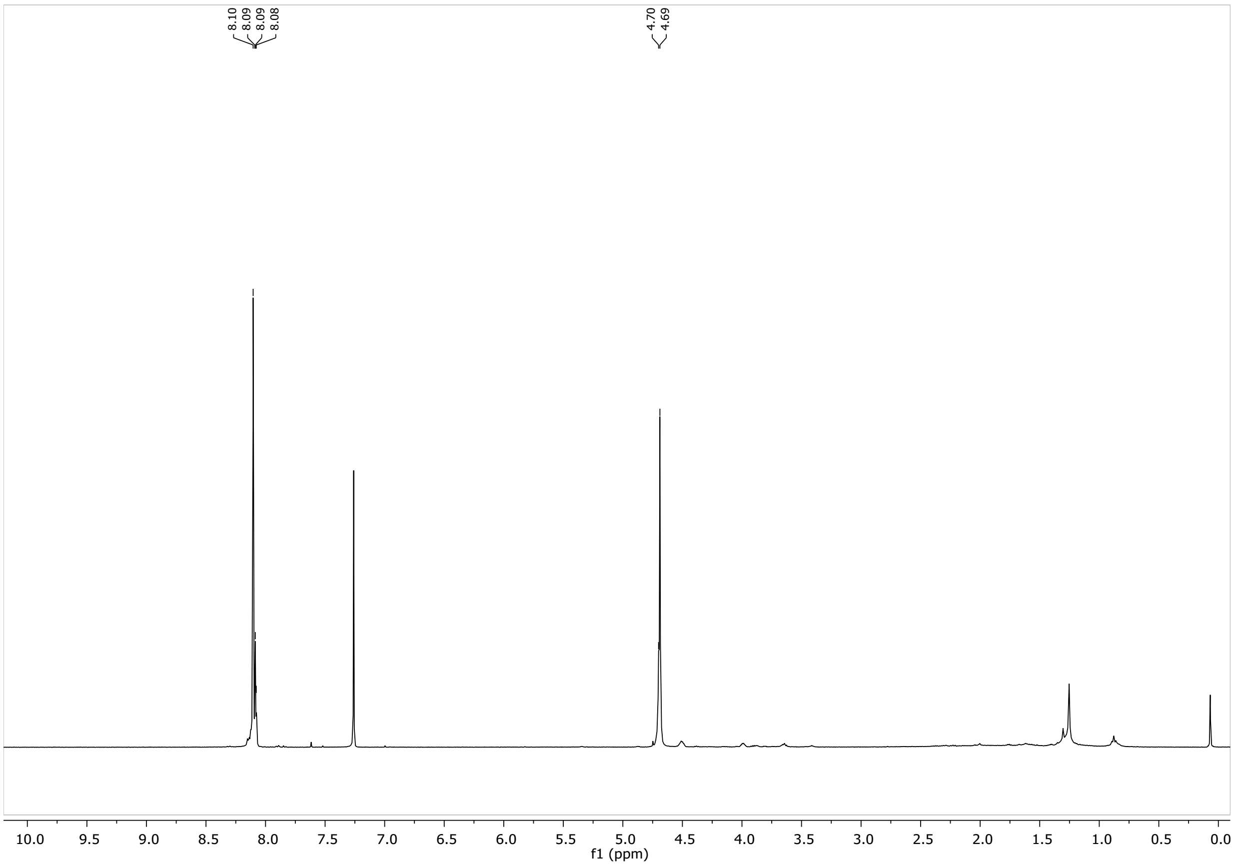
SI-13. Solvolysis of Virgin Polyester Fibre

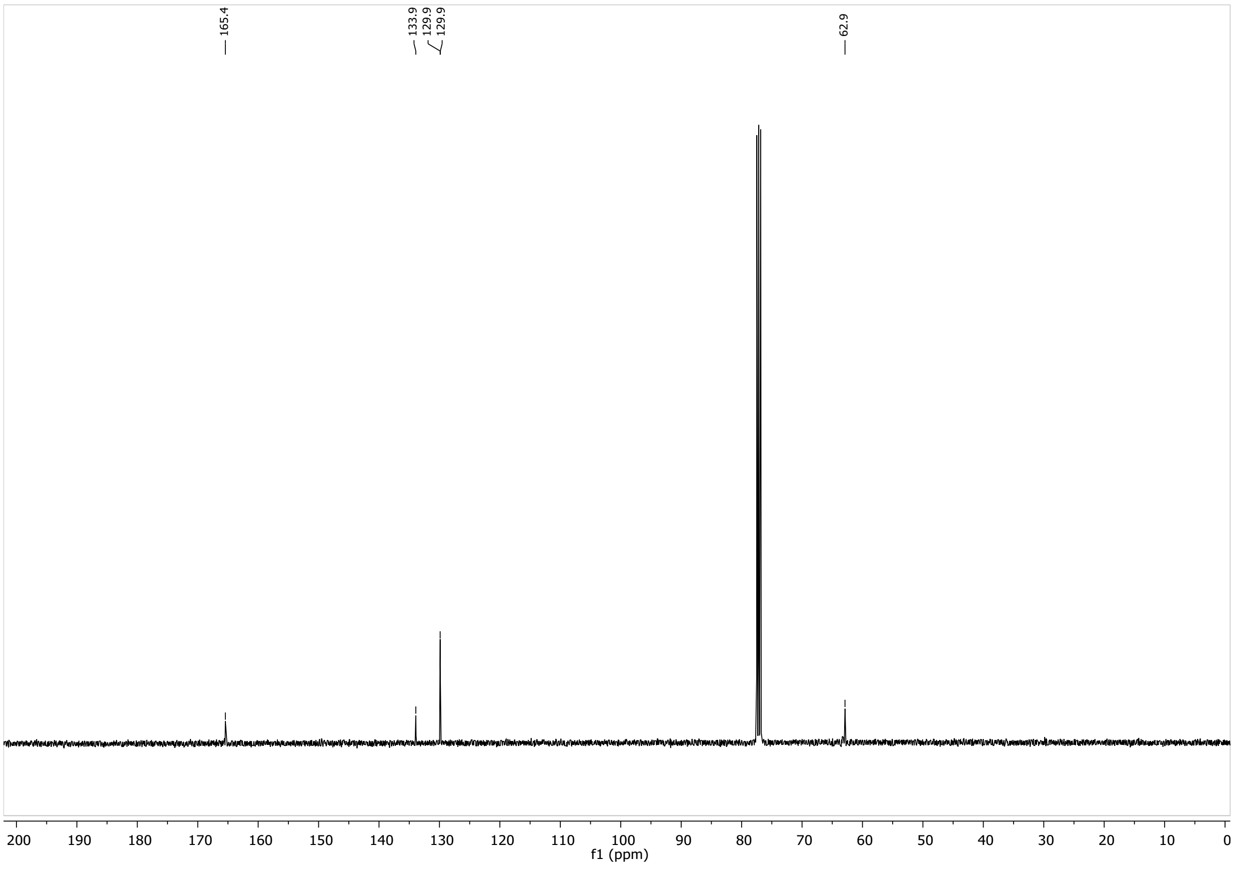
The polyester fibre was of the brand: ICI Polyester

The fibre (252.0 mg) was reacted as described in General Procedure A without any purification besides filtration to afford a PET residue fraction from the filtrate (5.5 mg) as a yellow solid and a leftover fibre fraction (245.2 mg).



NMR of PET Residue



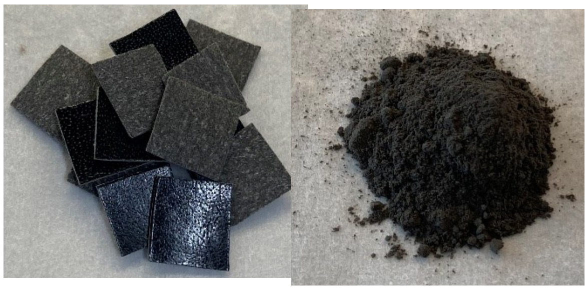


SI-14. Solvolysis of PU Leather

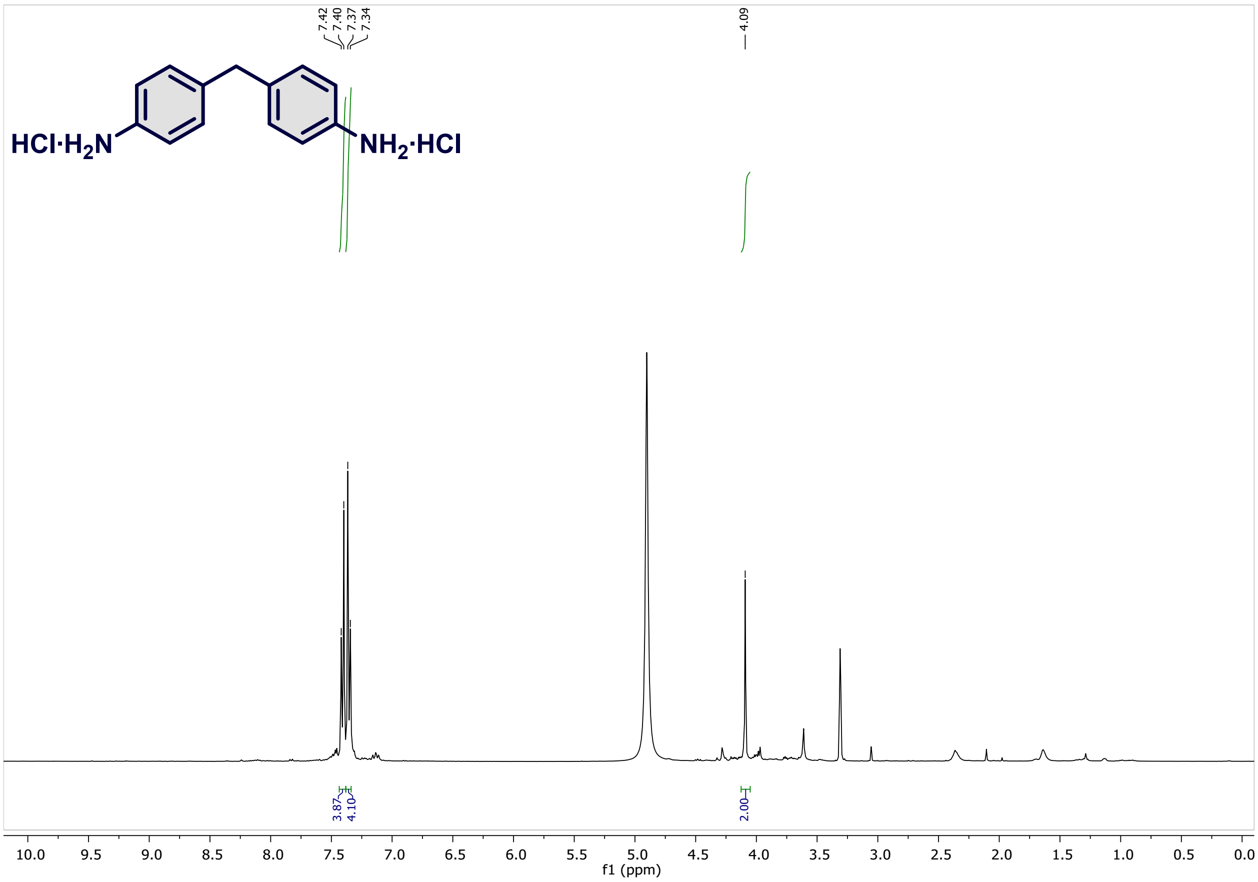
The fabric (“Lederimitat Lackoptik - schwarz”; article no. 214_poso_n21_134; “100% polyurethane”) was acquired from www.stofkiosken.dk.

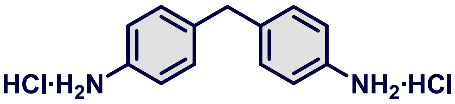
The fabric was cut into smaller pieces with a pair of scissors.

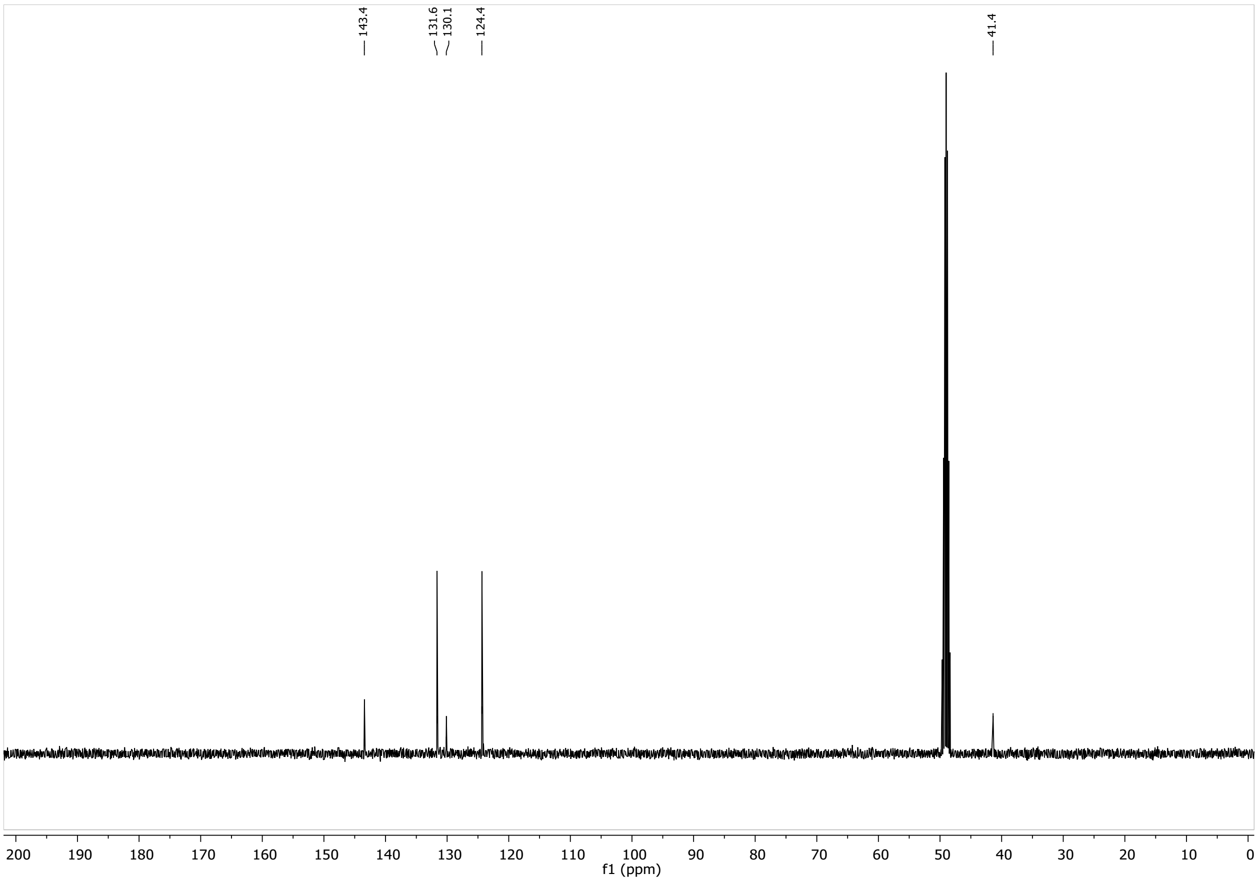
The PU (run 1: 1.02 g; run 2: 1.02 g) was deconstructed as described in General Procedure D to afford 2HCl·4,4’-MDA (run 1: 85.2 mg; run 2: 82.5 mg) as a sticky salt in an average yield of 83.9 mg, and a polyol fraction with minor impurities of suspected PET (run 1: 0.20 g; run 2: 0.24g) as a brown amorphous solid in an average yield of 0.22 g, and leftover black solid (run 1: 0.66 g; run 2: 0.64 g) in an average mass of 0.65 g.



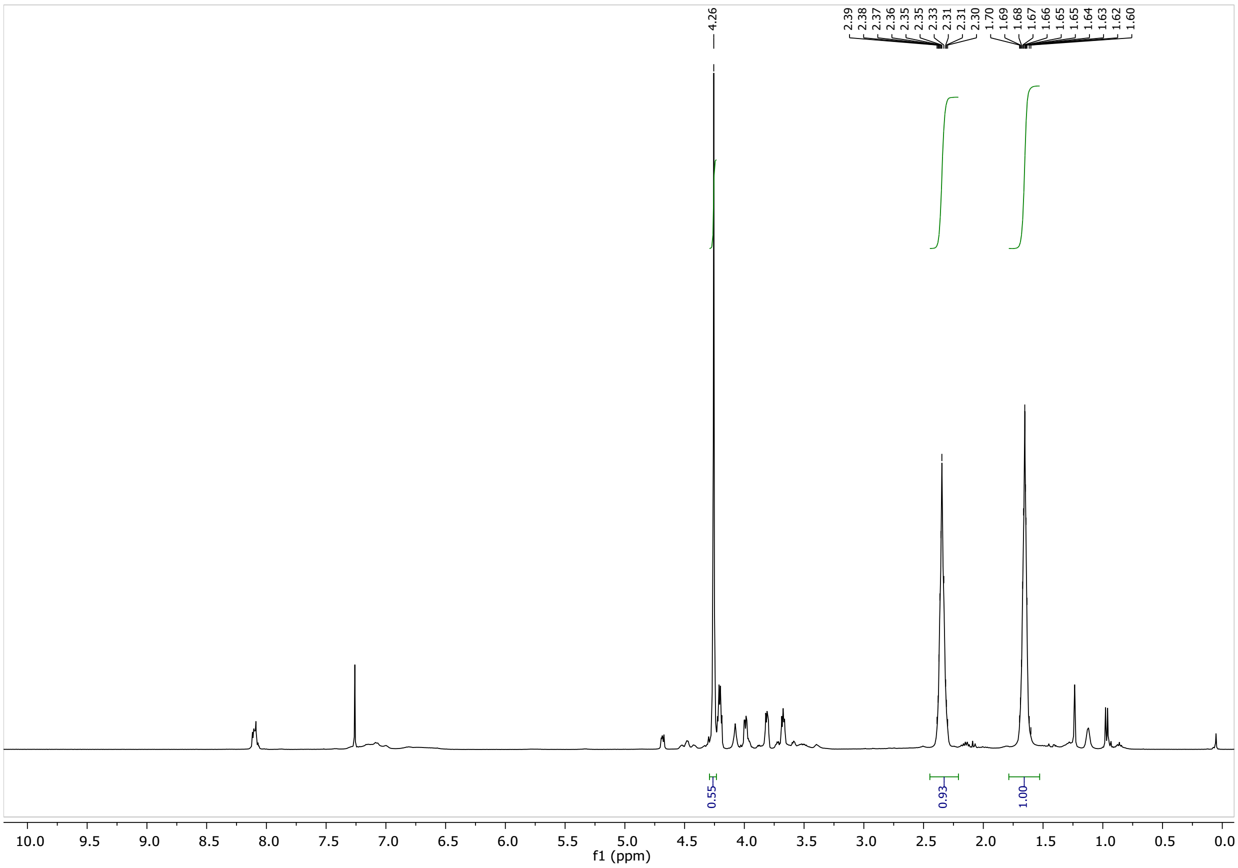
NMR Spectra of 2HCl·4,4’-MDA (in MeOD-*d4*)

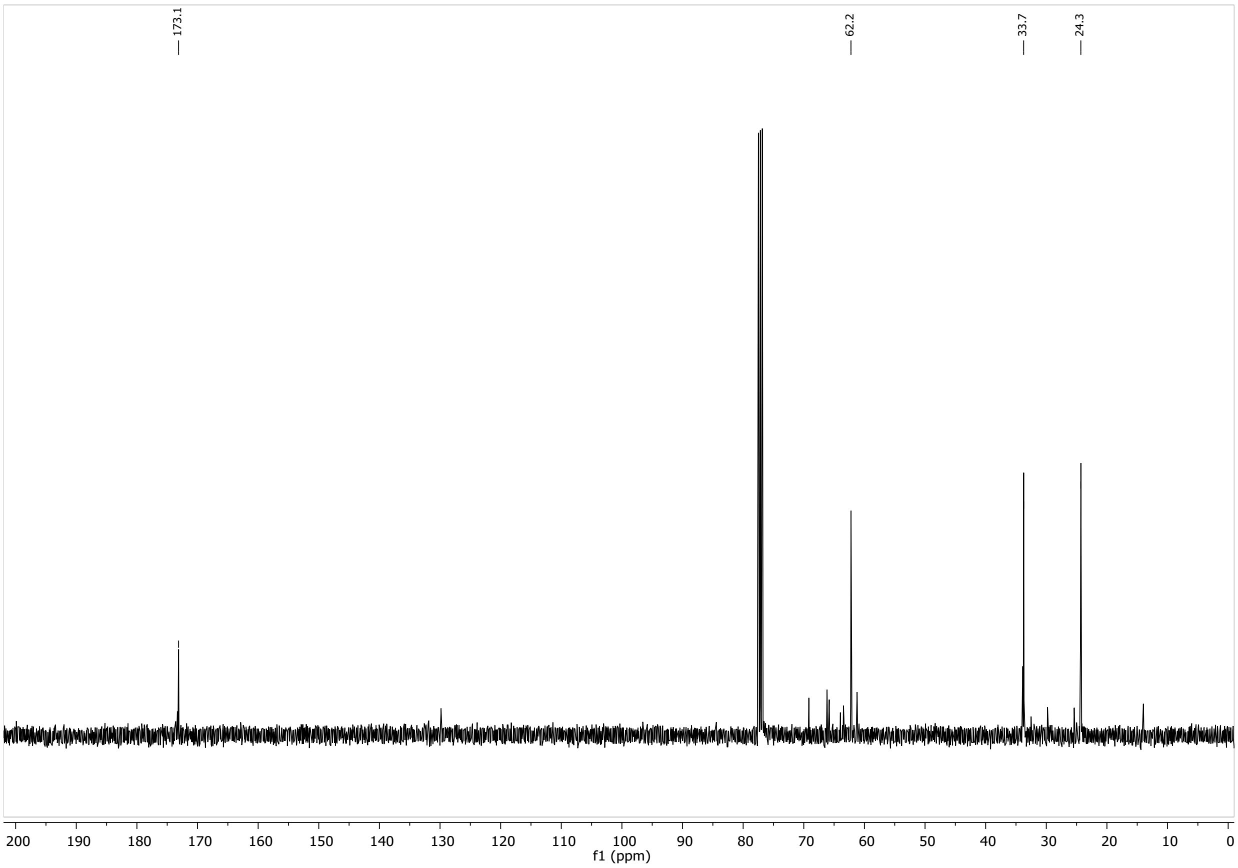




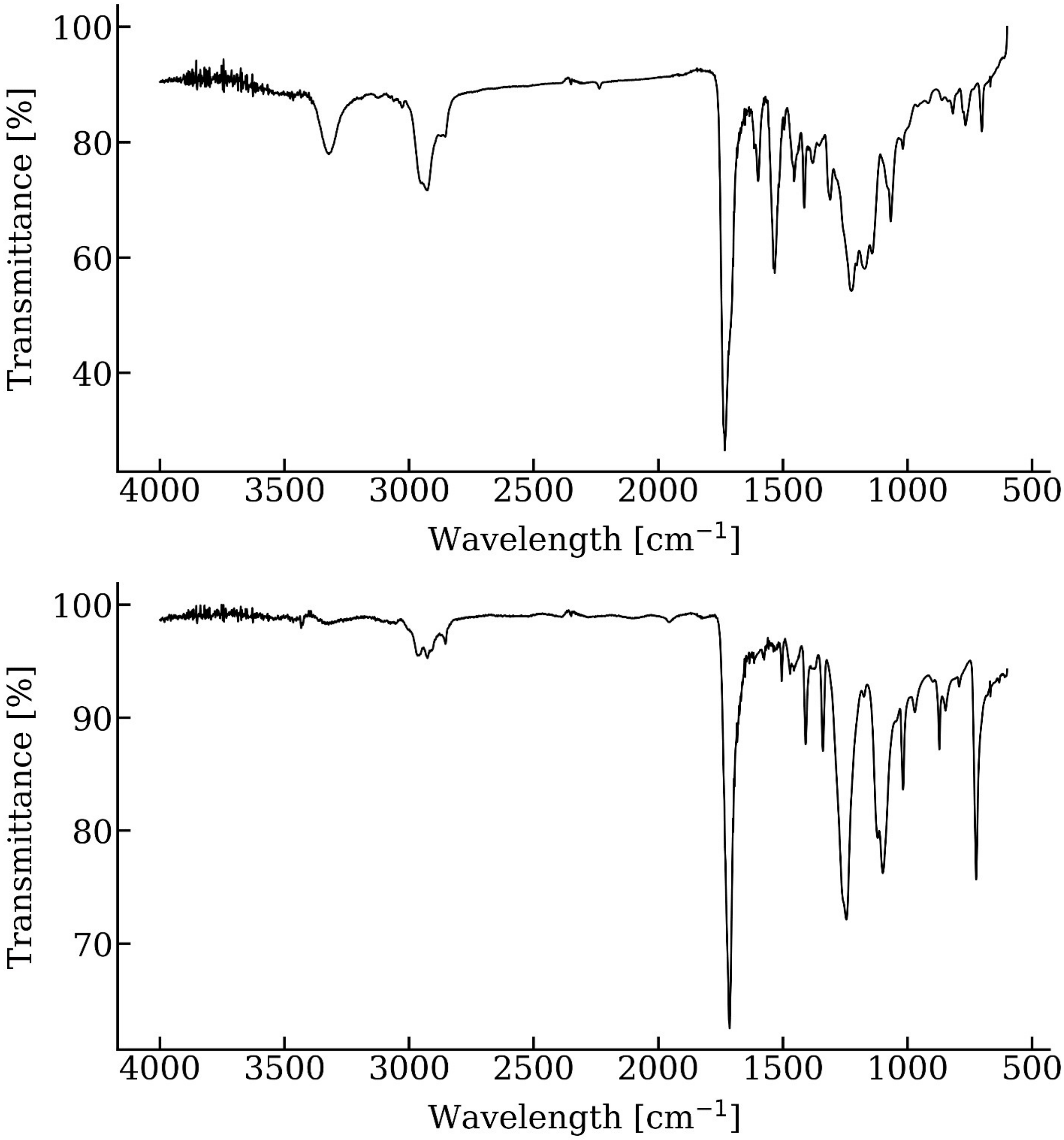

143.4
131.6
130.1
124.4
41.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

NMR Spectra of Polyol Fraction

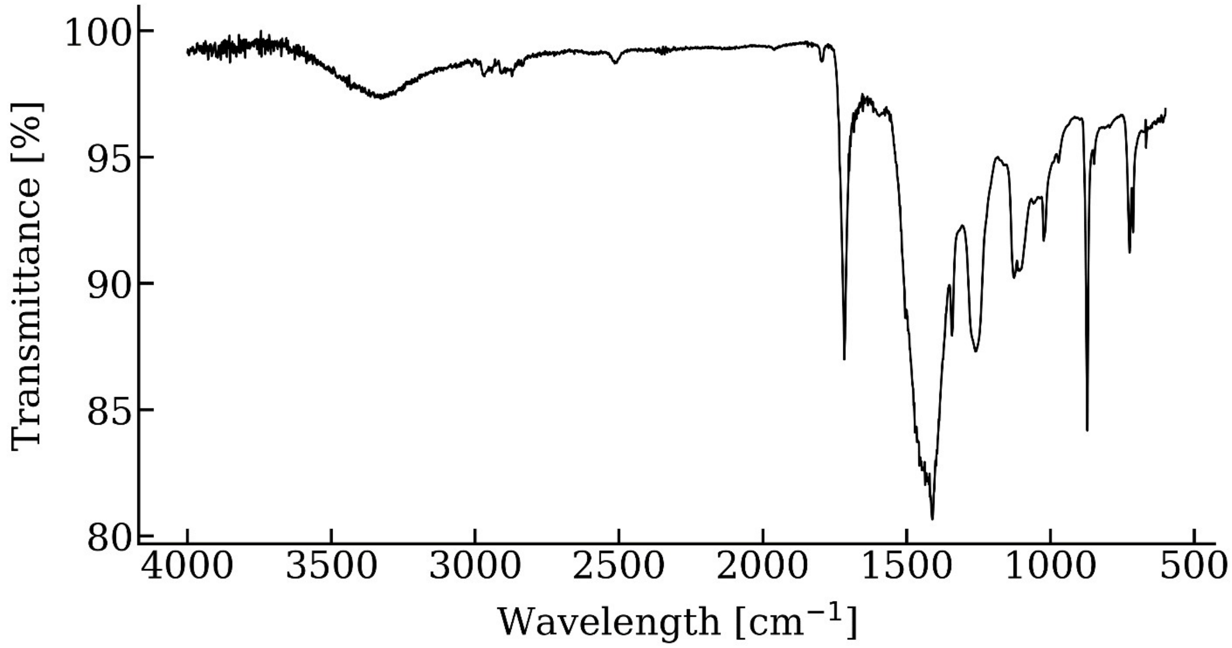




FTIR Spectra of to the Blank (top) and the Rough Side (bottom) of the PU Leather



FTIR Spectrum of Leftover Solid from PU Leather



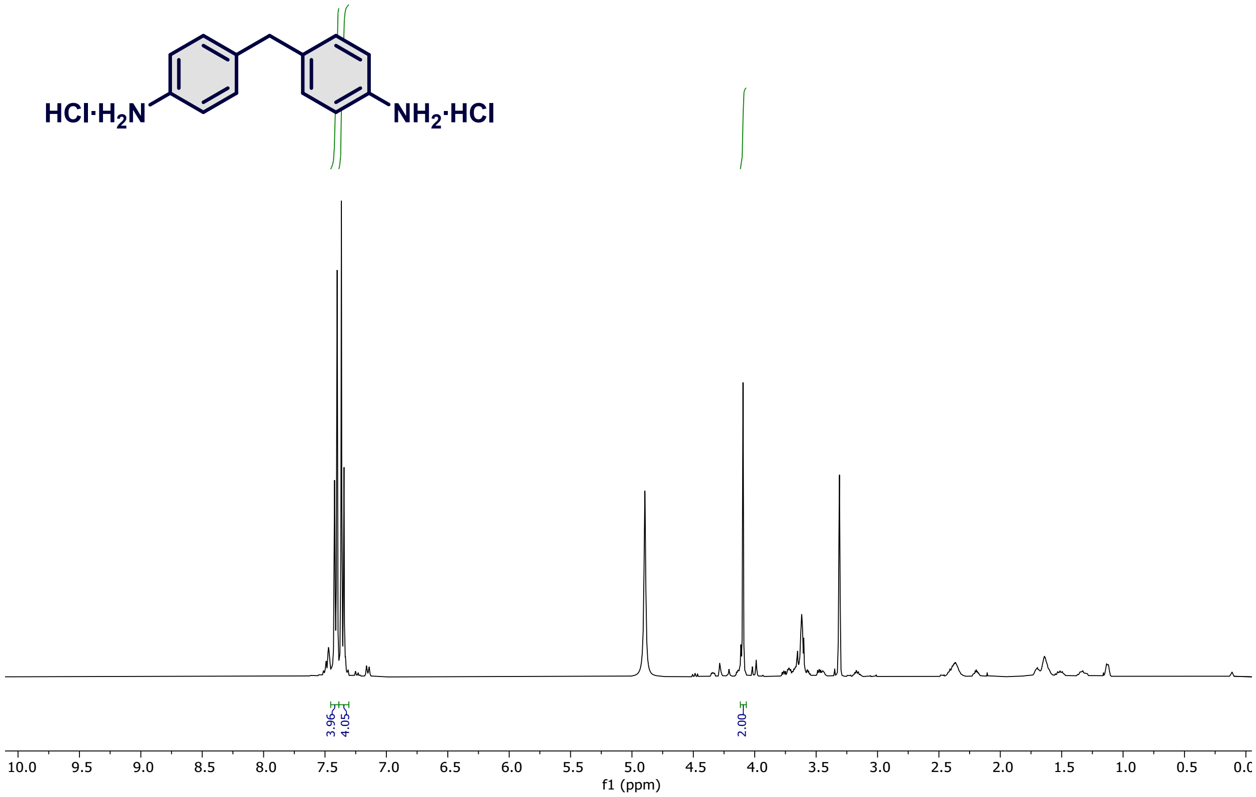
SI-15. Solvolysis of Coated gloves

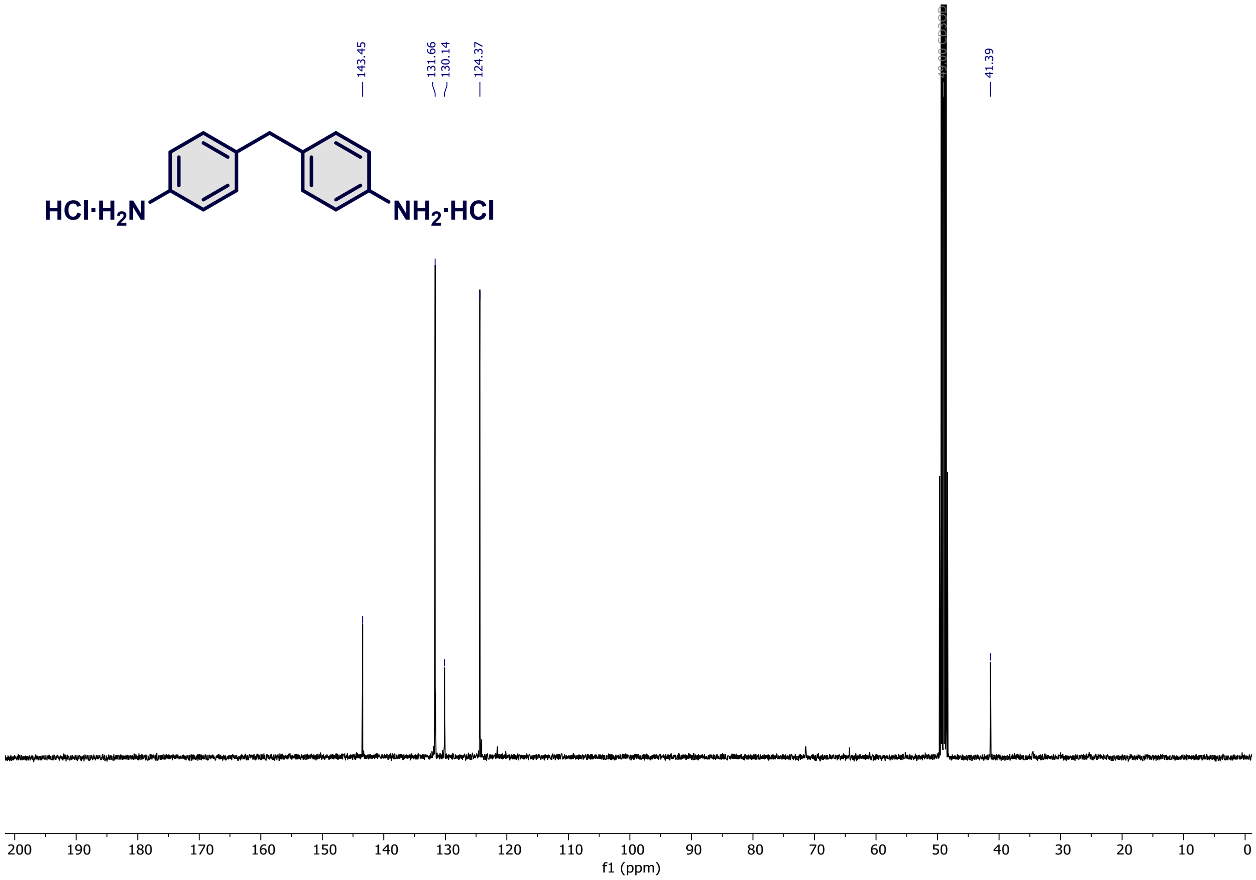
HyFlex 48-102 gloves from Ansell acquired from Avantor. According to label: Knitted polyamide liner dipped in polyurethane.

Approximately 1 g of thumb was cut from two gloves.

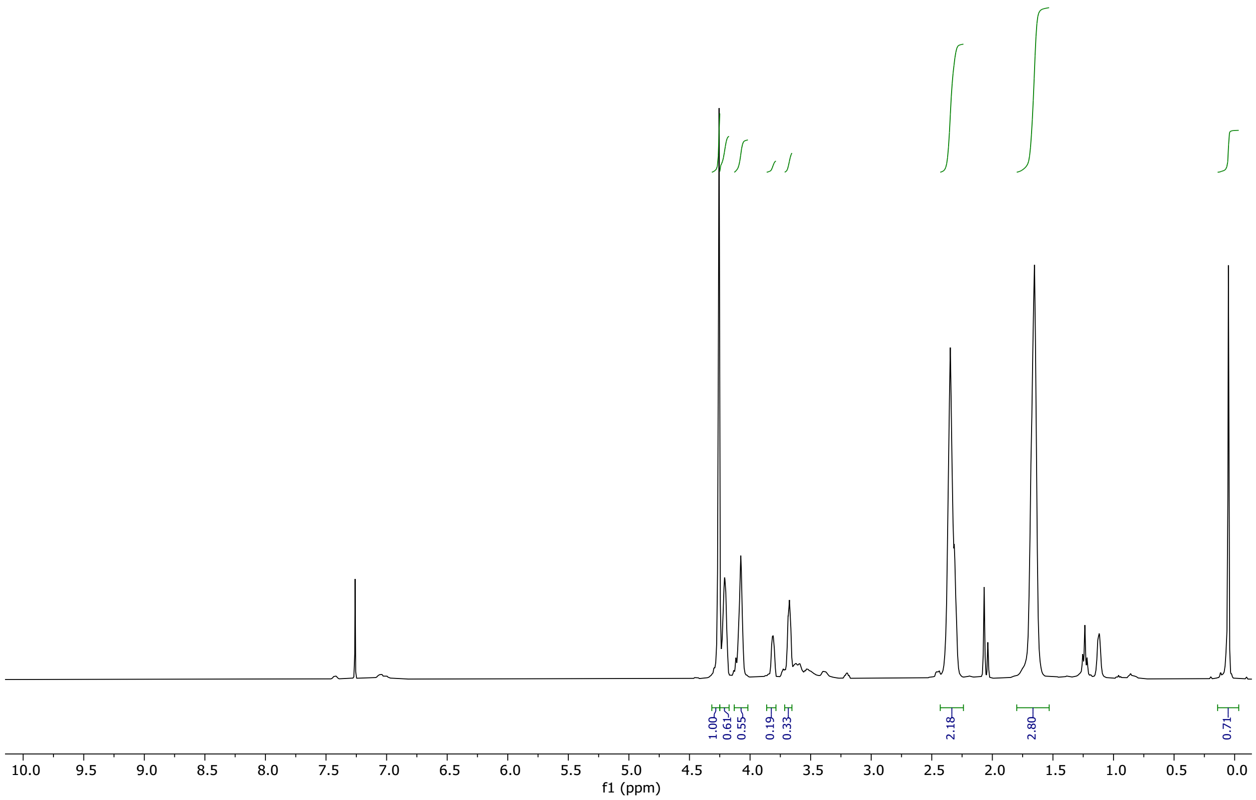
The PU (run 1: 1.05 g; run 2: 1.06 g) was deconstructed as described in General Procedure D to afford 2HCl·4,4'-MDA (run 1: 77.1 mg; run 2: 66.2 mg) as a yellow salt in an average yield of 71.7 mg containing small amounts of polyol, and a polyol fraction with an impurity of suspected silicon-based surfactant (run 1: 0.26 g; run 2: 0.27 g) as a light brown oil in an average yield of 0.27 g. The nylon was recovered as a remoulded grey lump which was melted again to release trapped solvent residues from the material (run 1: 0.62 g; run 2: 0.67 g) in an average mass of 0.65 g. Since the nylon melted at 225 °C it is likely to be nylon-6.

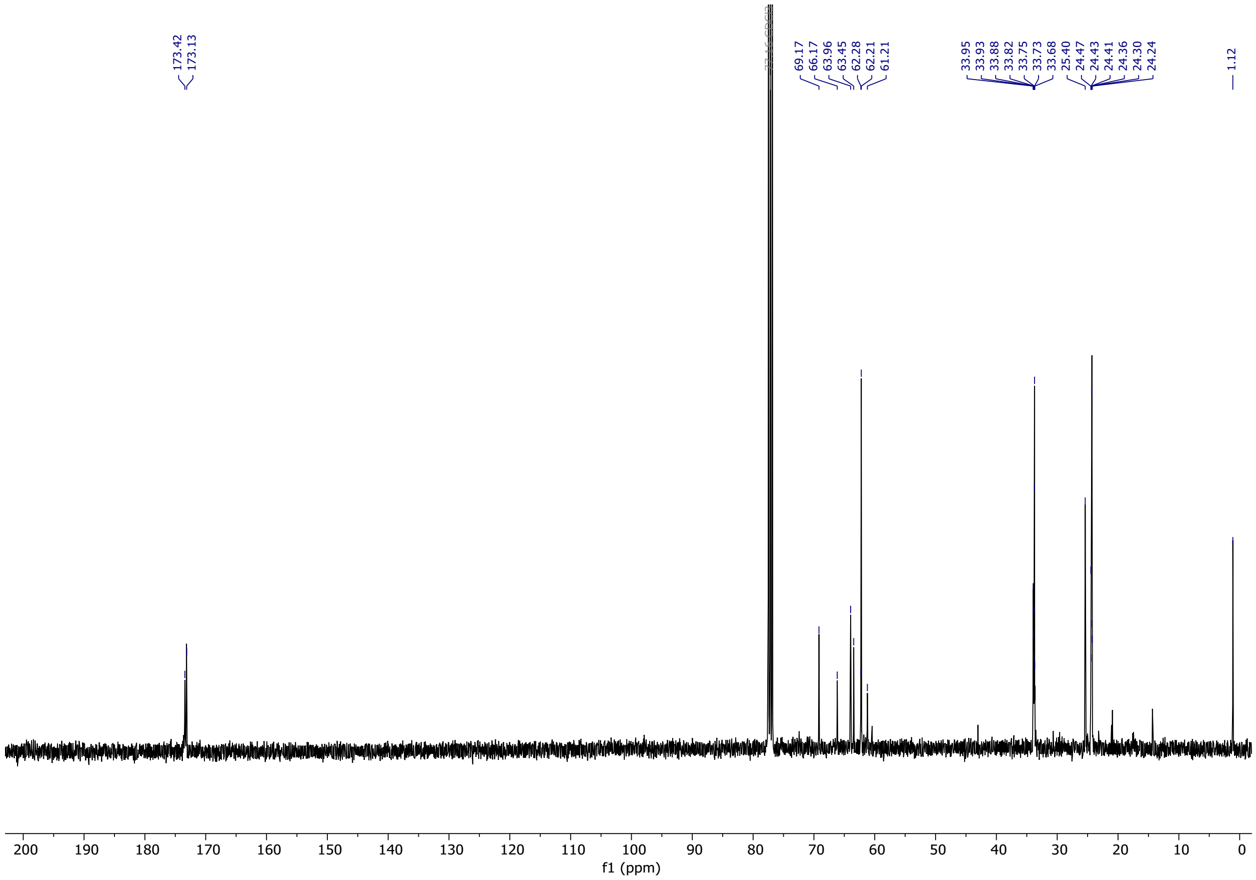
NMR spectra of 2HCl·4,4’-MDA (in MeOD-*d4*)



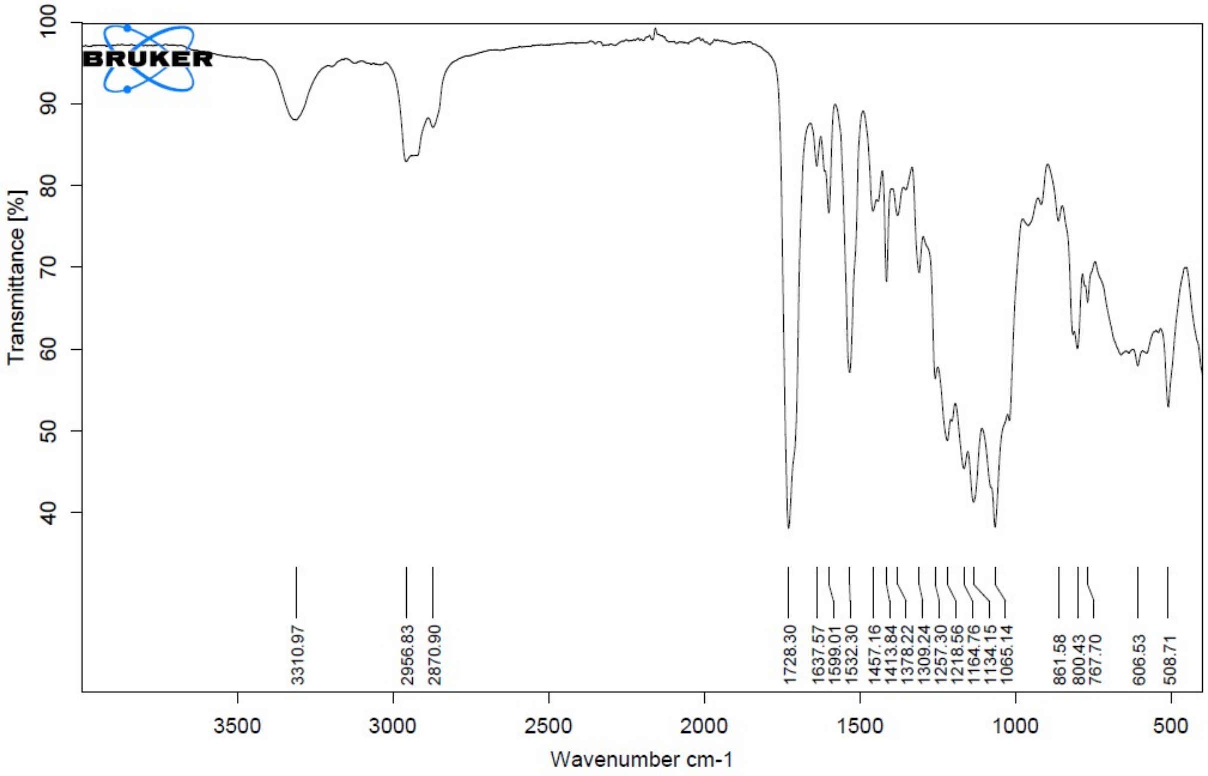


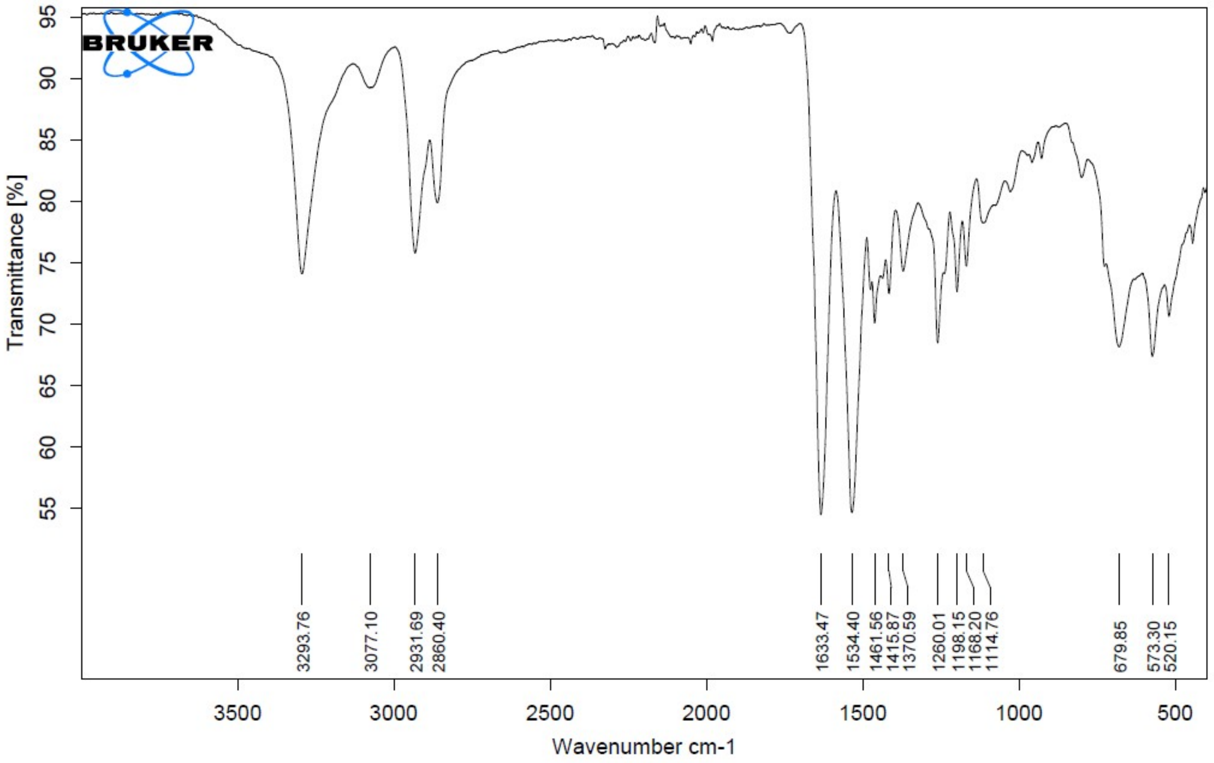
NMR Spectra of Polyol Fraction



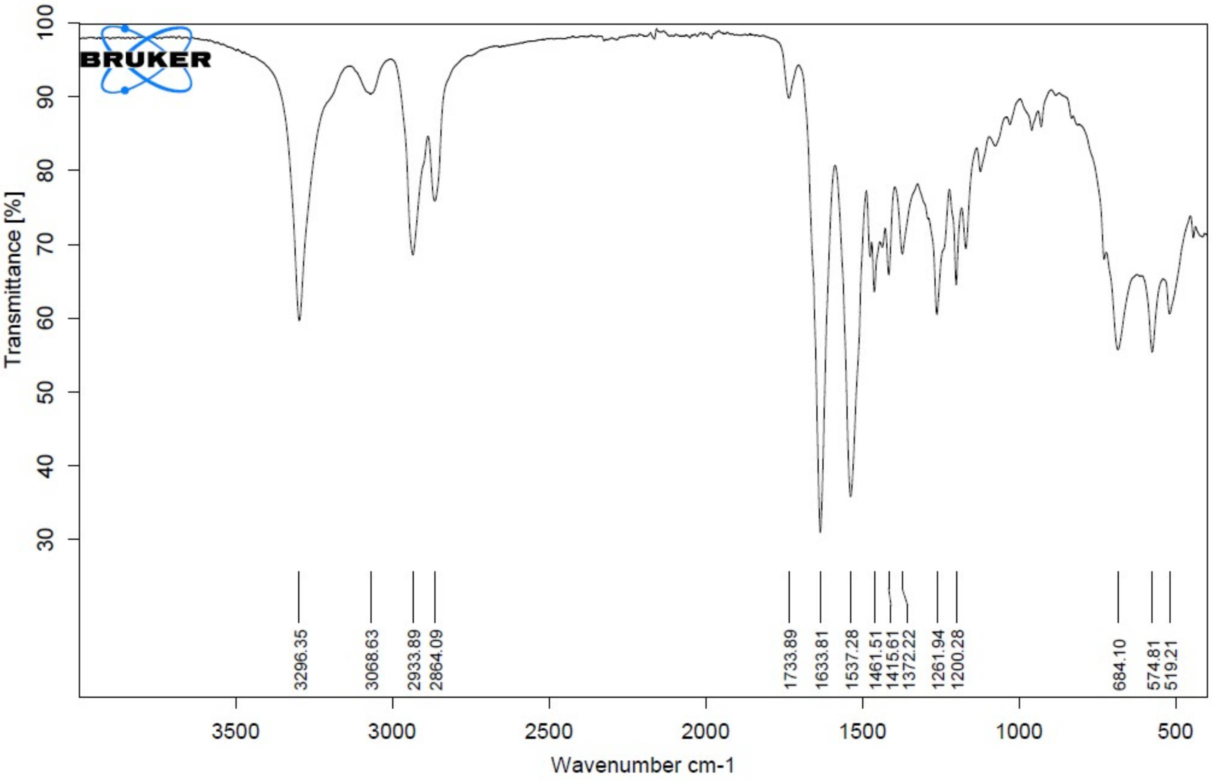


FTIR Spectra of PU-Coating on Glove (top) and Polyamide Knitting (bottom)





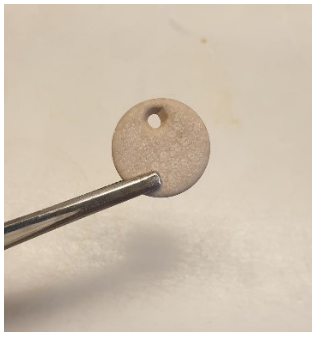
FTIR Spectrum of Leftover Solid



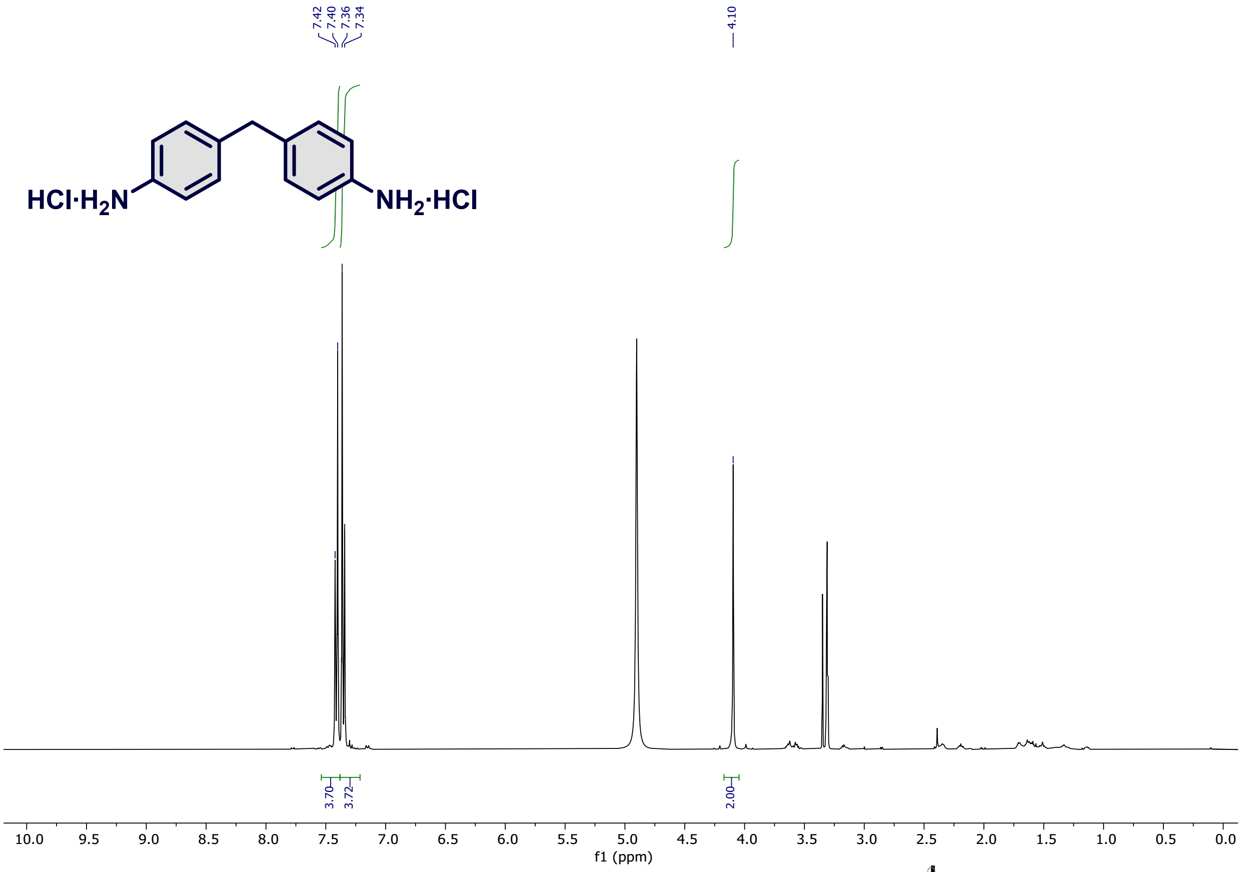
SI-16. Solvolysis of Rain Jacket

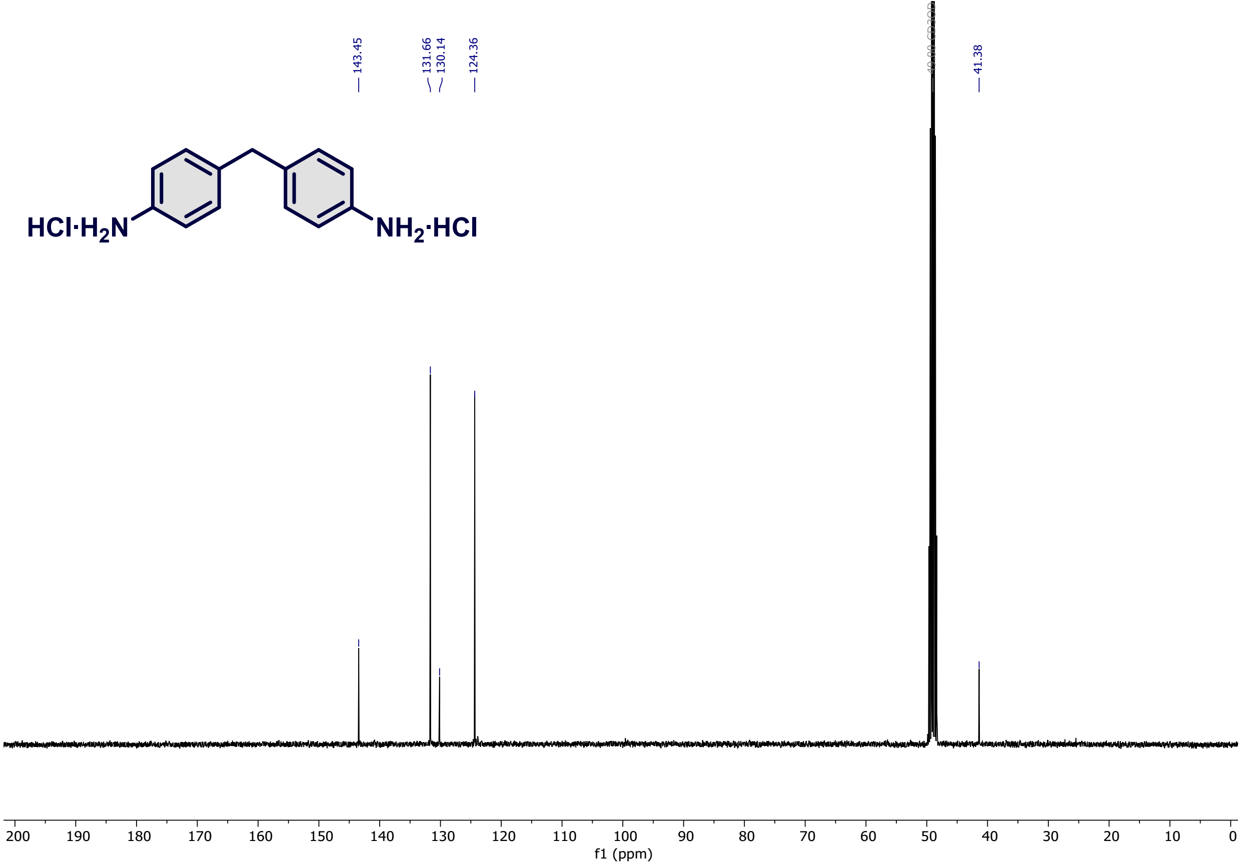
4391 Morgat white rain jacket in Flexothane KLEEN from Sioen acquired from Avantor. According to vendors homepage: 100% polyamide 6.6 knitting with PU coating

The PU (run 1: 1.02 g; run 2: 1.03 g) was deconstructed as described in General Procedure D to afford 2HCl·4,4'-MDA (run 1: 0.11 g; run 2: 0.07 g) as a yellow salt in an average yield of 0.09 g, and a polyol fraction (run 1: 0.31 g; run 2: 0.31 g) as a light brown oil in an average yield of 0.31 g. The nylon was recovered as a remoulded grey disc shaped by the bottom of the reactor (run 1: 0.61 g; run 2: 0.64 g) in an average mass of 0.62 g. Since the nylon melted at 225 °C it is likely to be nylon-6.

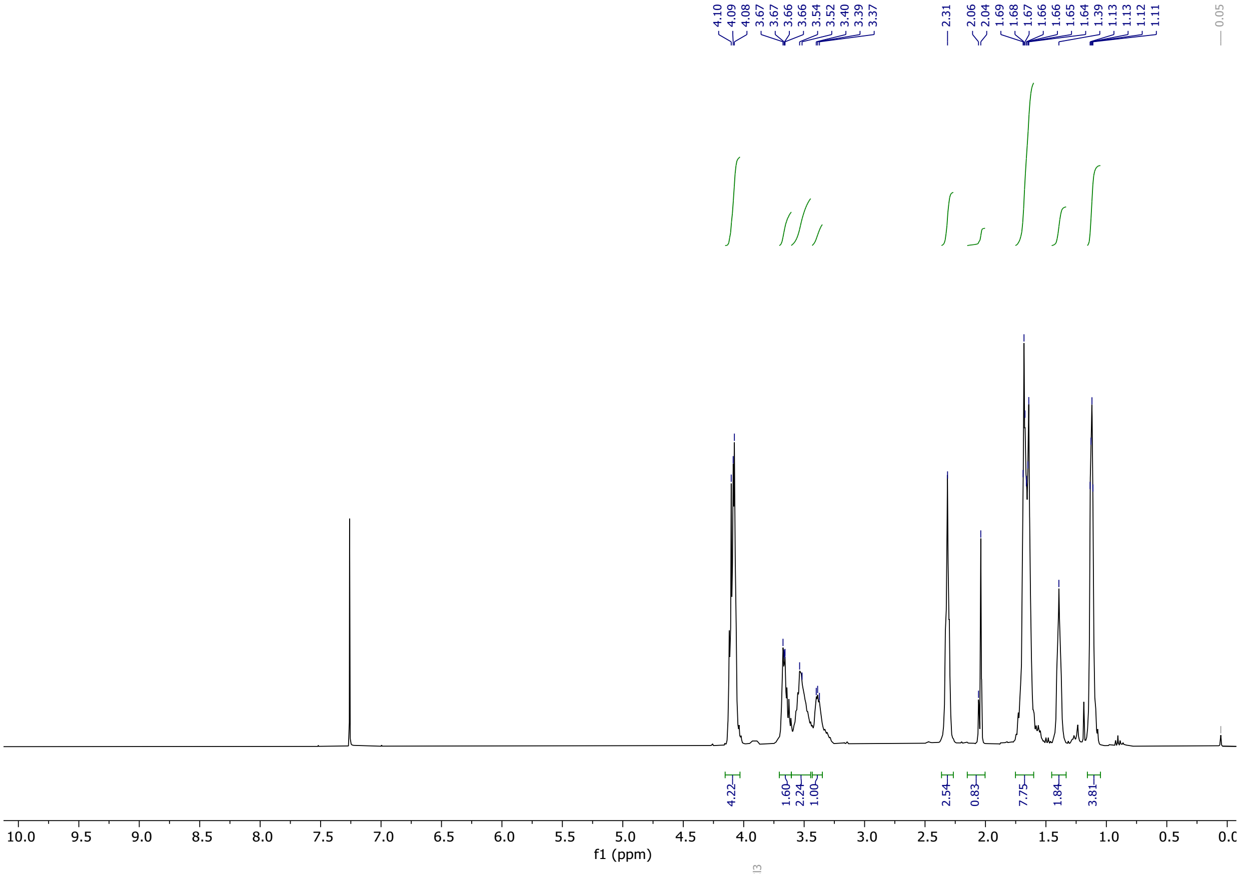


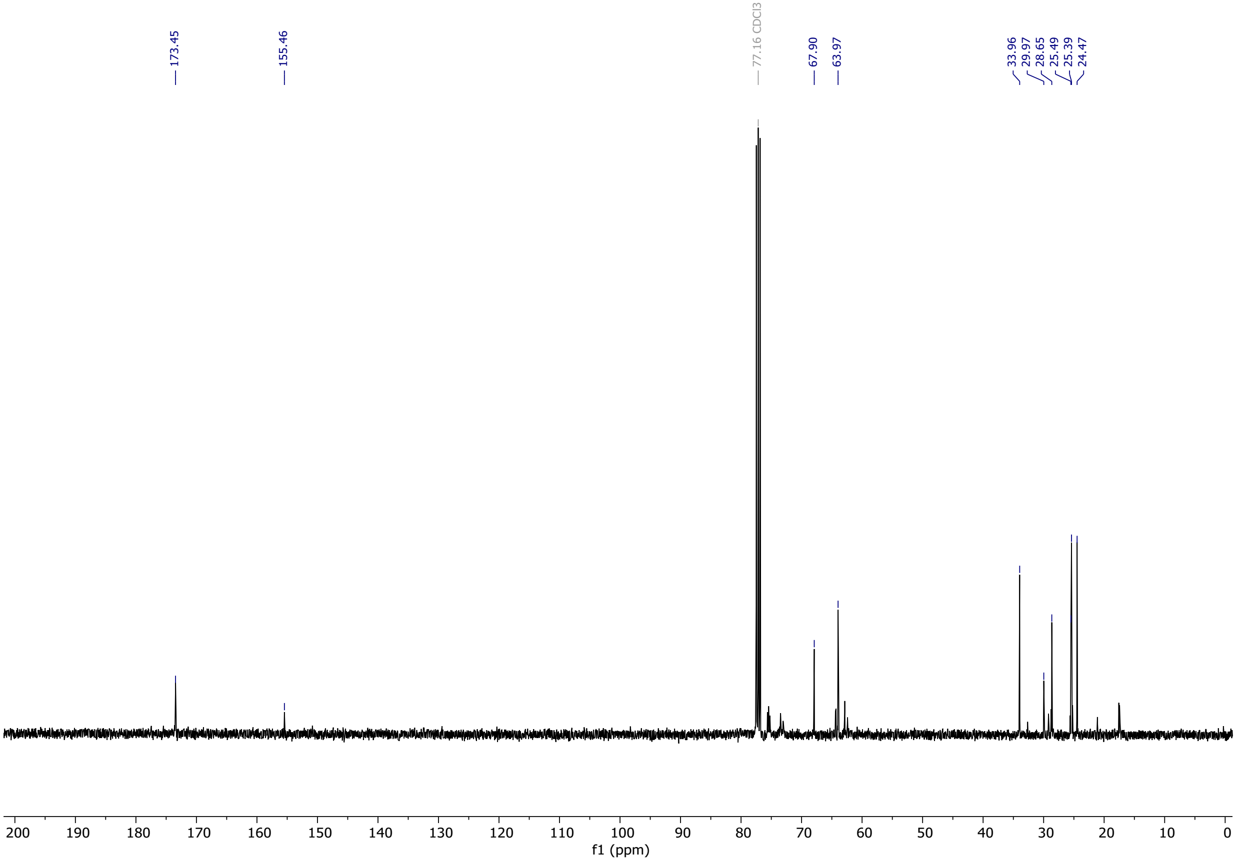
NMR Spectra of 2HCl·4,4’-MDA (in MeOD-*d4*)



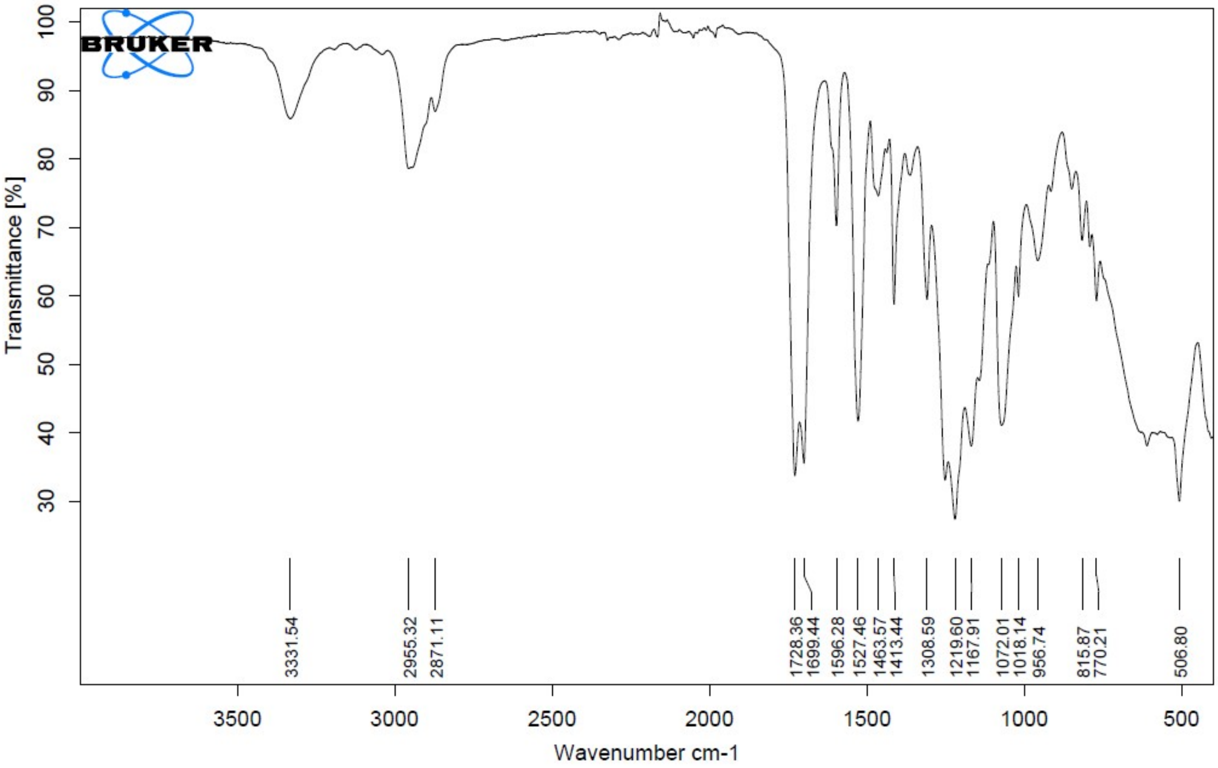


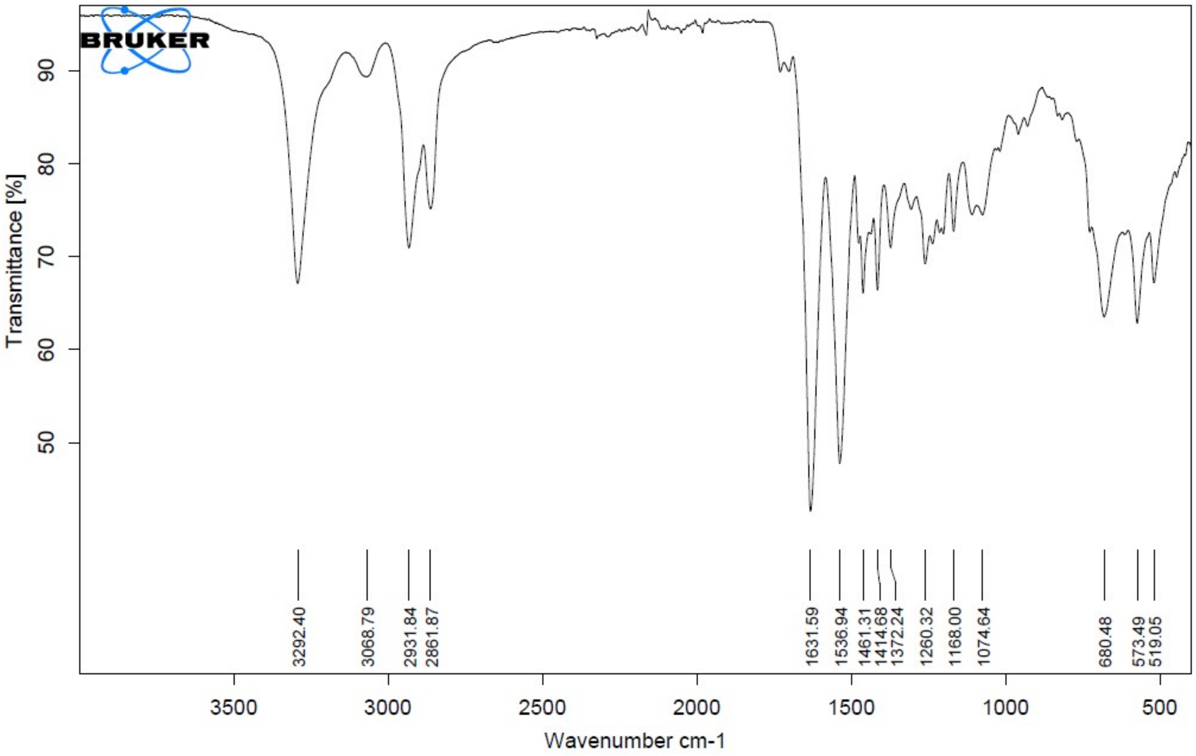
NMR Spectra of Polyol Fraction



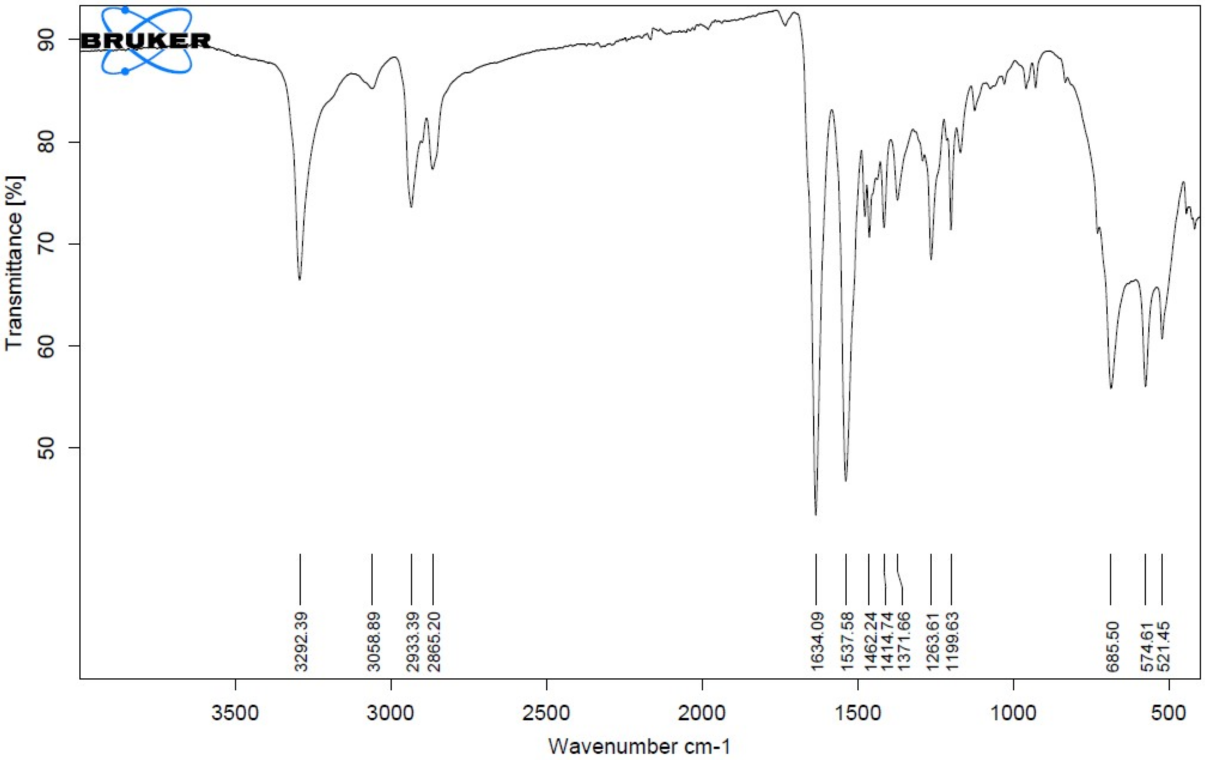


FTIR Spectra of PU-coating on the Outer Side of the Jacket (top) and Polyamide Knitting on the Inside (bottom)





FTIR Spectrum of Leftover Solid



SI-17 References

1. Y. Yin, D. Yao, C. Wang, Y. Wang, *Text. Res. J.* 2014, **84**, 16−27.
2. C. Gong, K. Zhang, C. Yang, J. Chen, S. Zhang, C. Yi, *Text. Res. J.*, 2021, **91**, 18−27.