Supporting information for: Polyamides Containing a Biorenewable Aromatic Monomer Based on Coumalate Esters: From Synthesis to Evaluation of the Thermal and Mechanical Properties

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EXPERIMENTAL

Materials

4-Carboxybenzene propionic acid (98%) was purchased from Alfa Aesar. m-Xylylenediamine (99%), hexamethylenediamine (98%), sodium bicarbonate (\geq 99.7%), pentafluorophenol-d (98%D), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene (99%), sodium hypophosphite monohydrate (>99%, NaHPO₃·H₂O), polyamide 12 (PA12, T_m = 178-180 °C), 4dimethylaminopyridine (≥99%), terephthaloyl chloride (>99%), distearyl pentaerythritol diphosphite and Irganox 1330 were purchased from Sigma-Aldrich and were used as received. Isophoronediamine (99+%), p-phenylenediamine (99+%), pyridine (99,5%, extra dry.), triphenylphosphite (99%), benzoic acid (99%), hydrocinnamic acid (99%), trans-1,4diaminocyclohexane (99%), 1,1'-carbonyldiimidazole (97%), benzylamine (99.5%, extra dry), sulfuric acid (96.00%) and thionyl chloride (≥99%) were purchased from Acros organics and were used as received. D₂O (99.8%), CDCl₃ (99.8%) DMSO-d₆ (99.9%) were purchased from Cambridge Isotope Laboratories, and were used as received. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was purchased from Evochem. sodium trifluoroacetate (>98%) was purchased from TCI. N-methyl-2-pyrrolidone was dried in an M-Braun automatic distillation setup. Calcium chloride was dried at 250 °C under vacuum for 48 hours. A 10.5 wt% calcium chloride solution in NMP was prepared in a glove box under inert atmosphere prior to the polymerization. Triphenyl phosphite was dried by adding 3Å molecular sieves at least 24 hours before usage. Sulfuric acid (99.8%) for the preparation of 20 wt% and 25 wt% PA-S-5 lyotropic solutions was kindly donated by Teijin Aramid. Terephthalic acid was kindly donated by BP Geel. All other solvents were obtained from Biosolve and were used as received.

TGA

The thermal stability of the polymers was analyzed with thermogravimetric analysis (TGA) on a TA instruments Qseries, TGA Q500 with autosampler using a temperature ramp of 10 °C/min under nitrogen flow.

DSC

Differential Scanning Calorimetry (DSC) (TA instruments, Qseries, DSC Q2000) with heating and cooling rate of 10 °C/min was used to obtain information on the phase transition temperatures such as $T_{\rm g}$ and $T_{\rm m}$. The $T_{\rm g}$ was determined at the midpoint of transition. The second heating cycle was always used for interpretation and presentation. Indium was used for temperature calibration. The modulated DSC experiments were run in the temperature range from 50 °C to 200 °C with a temperature amplitude of modulation of 0.32 °C and a period of modulation of 60s, with a heating rate of 2.00 °C/min.

GPC

Gel Permeation Chromatography (GPC) was measured on a Polymer Standards Service SECcurity GPC system using 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) as the eluent with a flow rate of 0.33 mL/min. The polymers were dissolved in HFIP with 0.019% NaTFA salt. The GPC samples were

prepared by dissolving 5.0 mg of the polymer in 1.5 mL solvent. The solutions were filtered over a 0.2 μ m PTFE syringe filter before injection. The GPC apparatus was calibrated with poly(methyl methacrylate) standards. Two PFG combination medium microcolumns with 7 μ m particle size (4.6 x 250 mm, separation range 100-1.000.000 Da) and a precolumn PFG combination medium with 7 μ m particle size (4.6 x 30 mm) using a Refractive Index detector (RI) were used in order to determine molecular weight and dispersities.

For sample PA-S-5, GPC was measured with a modular HPLC set-up consisting of a pump, autosampler and UV detector. Concentrated sulfuric acid was used as eluent in combination with modified silica columns calibrated with PS standards in THF (600-7,500,000 Da). A UV detector (340 nm) was used in order to determine the molecular weight and dispersity of the polymer.

¹H and ¹³C NMR spectroscopy

NMR spectroscopy (Bruker Avance III HD Nanobay apparatus, 300 MHz for ¹H NMR and 75 MHz for ¹³C NMR spectroscopy) was used to confirm or determine chemical structure, impurities, and conversions of various compounds and to determine the polymers' monomer ratio. Compounds were dissolved in CDCl₃, DMSO- d_6 , D₂O or a 1:3 mixture of pentafluorophenol- d/CDCl_3 for semi-crystalline polymers.

Liquid chromatography-mass spectrometry (LC-MS)

LC-MS analysis was performed on a Shimadzu system equipped with a Shimadzu Nexera HPLC solvent delivery system (LC-30AD) with photo-diode array detector (PDA/SPD-M20A), evaporative light scattering detector (ELSD-LTII) and a single quadrupole mass spectrometer (LCMS 2020). The MS was attributed in a dual ionization source consisting of both electron spray ionization (ESI) and atmospheric pressure chemical ionization (APCI). The separation was performed on Vision HT Classic C18 columns with 1.5 μ m pore size (3.5 μ m, 3 mm × 75 mm) at a flow rate of 0.2 mL/min, an oven temperature of 40 °C and an injection volume of 10 μ l. A solvent gradient was applied starting from 95:5 water:methanol up to 10 minutes whereafter it was changed to a 5:95 water:methanol mixture in 50 seconds, total runtime: 20 minutes.

Melting point determination

A Mettler Toledo MP 90 melting point apparatus (heating rate 10 °C/min) was used in order to determine melting points.

Ubbelohde viscometry

The relative viscosity of polymers was determined with a Xylem Ubbelohde viscosimeter (SI analytics, type IIc with a 530 23 llc capillary) at 25 °C (with a CT 72/2 (TT)/(M) thermostat) and 0,250% (w/v) polymer dissolved in 96% sulfuric acid. The WinVisco software was used for data analysis.

Rheology

Rotational and oscillation rheometry on the PA-S-5 solutions in sulfuric acid were performed with a Haake RheoStress 600 rheometer at 85 °C. The rheometer was equipped with a CP35/2° geometry. Viscosity curves were recorded in controlled rate mode.

Tensile testing

Tensile tests were performed on a Zwick/Roell Z020 tensile tester. Tensile bars were prepared from polymer dried at 80 °C in the vacuum oven via injection molding and had dimensions of 75 mm x 12 mm (broad sides) / 4 mm (thin middle) x 2 mm. Tensile bars were elongated at 0.25 cm/min. Tensile bars were taken from a desiccator directly before measuring and were measured at room temperature. The average values reported were derived from at least three specimens.

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

MALDI-ToF-MS spectra were recorded on a Bruker UltrafleXtreme spectrometer with a 355 nm Nd:Yag laser (2 kHz repetition pulse/Smartbeam-IITM) and a grounded steel plate. All mass spectra were obtained in reflector mode. Dithranol (20 mg/mL in HFIP) was used as a matrix, NaTFA (5 mg/mL HFIP) was used as a cationating agent, and polymer samples were dissolved in HFIP (1 mg/mL). The applied ratio of polymer:matrix:salt was 20:200:10. Poly(ethylene glycol) standards with M_n equal to 5000, 10000 and 15000 g/mol were used for calibration. All data were processed using the FlexAnalysis (Bruker Daltonics) software package and mMass.

ATR-IR spectroscopy

ATR-IR analysis was performed on a PerkinElmer FTIR/NIR spectrometer Frontier with resolution 4 cm⁻¹ and 8 accumulations per spectrum. The background scan was recorded with 64 accumulations and resolution 4 cm⁻¹. All data were processed using the Spectrum (PerkinElmer) software package and SpectraGryph 1.0.3.

Polyamide dissolution in H₂SO₄

A speedmixer (DAC 150.1 FVZ-K) was used to prepare 25 wt% polymer solutions in concentrated sulfuric acid (99.8 wt%). Sulfuric acid (45.0 g) and polymer (15.0 g) were brought in a 100 mL speedmixer cup. An alternating mixing scheme of max 30 s mixing at 3000 RPM and ambient cooling was applied until a homogenous solution was obtained. The exact duration of the mixing period was determined by the temperature being allowed to reach a value of max 90 °C. The next mixing step after cooling was started as soon as a temperature of 50 °C was reached.

Polarized optical microscopy

A small amount of polymer solution (25 wt% in 99.8 wt% sulfuric acid) was brought on a microscope glass slide. The sample was covered with a glass slide cover slip, which was gently

sheared relative to the glass slide in order to homogenize the thickness of the sample layer. Subsequently the sample was observed with a Jenaval optical microscope in polarization mode.



Synthesis of ethyl 4-(3-ethoxy-3-oxopropyl)benzoate (1)

Scheme S1. Synthesis of (1) from 4CBPA.

For transamidation polycondensation, the ethyl ester of 4CBPA, ethyl 4-(3-ethoxy-3oxopropyl)benzoate was synthesized according to a modified procedure reported in literature.¹ In this study, 1 was synthesized in order to study the effect of employing the diethylester in a transamidation polycondensation instead of salt melt polycondensation. In the context of sustainability it has to be noted that this procedure does not necessarily adhere to the green chemistry principles. The procedure was as follows: a round-bottom flask equipped with reflux condenser was charged with 4CBPA (15.0 g, 0.08 mol, 1 eq), and ethanol (116 mL, 1.99 mol, 25 eq). After cooling to 0 °C in an ice bath, thionyl chloride (27.6 g, 0.23 mol, 3 eq) was added dropwise while stirring. After complete addition, the mixture was heated to reflux temperature and refluxed for two hours. Excess ethanol was removed by evaporation. To the remaining residue, 250 mL ethyl acetate and 50 mL water was added and extracted twice with ethyl acetate. The organic layer was washed with 50 mL NaHCO₃ solution and dried with magnesium sulfate. After filtration, the ethyl acetate was removed by evaporation yielding a colorless liquid. Yield: 15.45 g (80%). ¹H NMR (300 MHz), 25 °C, (DMSO- d_6) (2.50 ppm): δ = 7.86 (d, 2H, H_{Ar}), 7.39 (d, 2H, H_{Ar}), 4.28 (q, 2H, CH₂-O-), 4.02 (q, 2H, CH₂-O-), 2.92 (t, 2H, CH₂-CH₂-C=O), 2.65 (t, 2H, CH₂-C=O), 1.31 (t, 3H, CH₃), 1.14 (t, 3H, CH₃) ppm; ¹³C NMR (75 MHz), 25 °C, (DMSO-d₆) (40.04 ppm): $\delta = 172.40$ (C=O), 166.10 (C=O), 146.76 (C_{Ar}), 129.63 (2 CH_{Ar}), 129.10 (2 CH_{Ar}), 128.33 (CAr), 61.00 (-O-CH₂-CH₃), 60.34 (-O-CH₂-CH₃), 34.97 (CH₂-C=O), 30.65 (CH₂-CH₂-C=O), 14.63 (-O-CH₂-CH₃), 14.53 (-O-CH₂-CH₃) ppm.

Preparation of dibasic acid salts

Synthesis of dibasic acid salts were all performed according to a similar procedure. In a typical synthesis 4CBPA (6.0 g, 0.03 mol, 1 eq) was added to a solution of m-xylylenediamine (MXD) (4.2 g, 0.03 mol, 1 eq) in 14 mL deionized water. The mixture was heated to 80 °C until all of the diacid was dissolved. The salt was precipitated in 300 mL isopropanol, filtered and dried in a vacuum oven at 75 °C for 24 hours, which yielded white crystals. Yield: 9.76 g (96%). ¹H NMR (300 MHz), 25 °C, (D₂O) (4.75 ppm): δ = 7.70 (d, 2H, H_{Ar,4CBPA}), 7.43 (m, 4H, H_{Ar,MXD}), 7.27 (d, 2H, H_{Ar, 4CBPA}), 4.11 (s, 4H, C**H**₂-NH₃⁺), 2.86 (t, 2H, CH₂-COO⁻), 2.44 (t, 2H, C**H**₂-CH₂-COO⁻) ppm.

Salt melt polycondensation

Polyamides were synthesized according to a modified procedure reported in literature.² This procedure describes the synthesis of polyamides via salt melt polycondensation with a distinctive temperature progression. In a typical synthesis, approximately 10 g of salt was brought in a 50 mL round-bottom flask equipped with a distillation setup including Vigreux column, mechanical stirrer, and internal temperature probe. Subsequently the flask was flushed with nitrogen. In order to reduce the loss of diamine, the following temperature progression was adopted: the salt was heated quickly to 180 °C using a heating mantle, where it formed a molten boiling mixture. The released water was removed by distillation. Then, the temperature was increased by 1 °C/min to 260 °C, where it was maintained for 2 hours. Finally, a vacuum was applied for 1 hour to remove remaining condensate. The polymer was retrieved as a yellow powder without further purification.

Catalyzed salt melt polymerization

10 g of the 4CBPA and MXD monomer salt was added to an oven-dried 50 mL round-bottom flask equipped with a distillation setup including Vigreux column, mechanical stirrer, and internal temperature probe. 5 mg sodium hypophosphite monohydrate and 5 mg 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene (Irganox 1330) were added to act as a catalyst and antioxidant respectively. The reaction flask was flushed with nitrogen and the salt was heated to 220 °C, where it formed a molten boiling mixture. The released water was removed by distillation. The temperature was then raised by 1 °C/min until a temperature of 260 °C was reached. This temperature was maintained for two hours. Then a vacuum was applied for another hour to remove remaining condensate. The polymer was retrieved as a light brown, glassy material without further purification.

Transamidation polycondensation

The transamidation polycondensation was carried out in a 50 mL round-bottom flask equipped distillation setup including Vigreux column, mechanical stirrer, and internal temperature probe. In a typical synthesis **1** (7.12 g, 28.0 mmol, 1 eq), MXD (3.87 g, 28.0 mmol, 1 eq), and the antioxidant distearyl pentaerythritol diphosphite (25 mg, 0.034 mmol, 0.001 eq) were added to the flask. The flask was flushed with nitrogen and the mixture was gradually heated to 250 °C over the course of 2 hours, while ethanol was removed by distillation. The reaction was held at 250 °C, whereupon the setup was changed by removing the Vigreux column and was further held at 250 °C for 30 minutes. Subsequently, the temperature was lowered to 220 °C and a vacuum was applied for one hour. The polymer was retrieved as a light brown, glassy material without further purification.

Solution polymerization by phosphorylation

Synthesis in solution was performed via the Yamazaki-Higashi phosphorylation method.³ An initial monomer concentration of 7 mol% was used unless stated otherwise. A typical polymerization was as follows. To an oven-dried 100 mL round-bottom flask, equipped with reflux condenser and mechanical stirrer, were added 4CBPA (1.94 g, 10 mmol, 1 eq), MXD (1.36 g, 10 mmol, 1 eq), dried calcium chloride (2.5 g, 23 mmol, 2.3 eq), pyridine, (5 mL, 62 mmol, 6.2 eq),

triphenylphosphite (5.6 mL, 21 mmol, 2.1 eq), and dry NMP (22 mL) under nitrogen atmosphere. The mixture was heated in an oil bath at 100 °C for 3 hours. Then, the temperature was increased to 110 °C and reacted for another 3 hours. The cooled mixture was poured into 300 mL 0.1 M HCl and stirred vigorously. The white powder was filtered and washed with water and methanol. The obtained polymer was dried under vacuum for 24 hours at 120 °C.

Synthesis of terephthalic acid reference polymer PA(TPA,MXD)

A 100 mL round-bottom flask was oven-dried for at least 24 hours. MXD (4.29 g, 31.5 mmol, 1 eq) was added to the flask under nitrogen atmosphere. 50 mL dry NMP was added and the mixture was cooled to 0 °C. The ice bath was removed before terephthaloyl chloride (6.4 g, 31.5 mmol, 1 eq) dissolved in 43 mL dry NMP was added to the mixture. The mixture was allowed to stir for 6 hours at room temperature. The polymer was precipitated in chloroform. The solid product was filtered and washed with hexane and a solid brown powder was obtained. The polymer was dried in vacuum at 80 °C for 24 hours. The results are summarized in Table S1 of the supporting information.

Model compound *N*-hexyl-4-(3-(hexylamino)-3-oxopropyl)benzamide (2)

The synthesis of the 4CBPA hexylamine model compound is based on a modified procedure described in literature.⁴ An oven-dried 100 mL flask equipped with reflux condenser was charged with 4CBPA (2.54 g, 13.1 mmol, 1 eq), THF (75 mL), and 1,1'-carbonyldiimidazole (CDI) (4.53 g, 28.0 mmol, 2.1 eq). The mixture was stirred for one hour under nitrogen atmosphere. The evolution of carbon dioxide during the addition of CDI was observed. Hexylamine (5.1 mL, 38.8 mmol, 3 eq) and DMAP (20 mg, 0.16 mmol, 0.01 eq) were added to the mixture. The mixture was heated to reflux temperature and refluxed for 4.5 hours. Excess THF was evaporated and the compound was precipitated in hexane. The white crystals were filtered and washed with hexane and 10% HCl solution. Because NMR analysis showed the presence of carboxylic acid, the crystals were stirred in a KOH solution for 30 minutes. Subsequently the crystals were filtered, washed with water and dried at 50 °C under vacuum. The yield was 2.46 g (48%), melting point: 167.5-170.0 °C. ¹H NMR and ¹³C NMR spectra are shown in Figure S7 and S8 of the supporting information. LC-MS (in CH₃CN) one peak at 13.5 min. MS: component m/z = 360 g/mol, (M+1 = 361 g/mol H⁺ adduct, M-1 = 359 g/mol H⁻ adduct, M+23 = 383 g/mol Na⁺ adduct).

Model studies, synthesis of amides (3) and (4)

Separate model reactions that simulated the reactivity of the two reactive groups of 4CBPA were performed utilizing two different reagentia namely benzoic acid and hydrocinnamic acid together with benzylamine. For each acid a separate amidation was performed. Furthermore, two different amidation routes were simulated which were phosphorylation and thermal activation in solution giving a total of four model reactions. The first reaction was executed according to the phosphorylation method as described above. The monomers were simply replaced by the model compounds benzoic acid or hydrocinnamic acid and benzylamine. Model acid and benzylamine were added in equimolar proportions and with a concentration of 1M in NMP. The second reaction

was based on a modified procedure described in literature.⁵ In this procedure, the acid and amine were dissolved in NMP and amidation was induced by heating the mixture. The reaction of benzoic acid with benzylamine was performed as follows: to an oven-dried 50 mL flask equipped with reflux condenser were added benzoic acid (2.44 g, 0.02 mol, 1 eq), benzylamine (2.14 g, 0.02 mol, 1 eq), NMP (20 mL), and molecular sieves (2.3 g). The system was flushed with nitrogen and the mixture was heated to 100 °C. Over the course of 6 hours the reaction kinetics were followed by ¹H NMR spectroscopy. Aliquots of the reaction mixture were taken at several time intervals and immediately dissolved in deuterated chloroform.

Polymer processing via extrusion and injection molding

Prior to processing the 30/70 wt% to 70/30 wt% 4CBPA polyamide/PA12 powders were sprayed with a 0.1% 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene (Irganox 1330) antioxidant solution in acetone. The polyamides were then dried for at least 24 hours at 100 °C. After the drying, the polyamides were immediately transferred to a desiccator. Approximately 5 g of the 4CBPA or TPA polyamide/PA12 polymer mixture was fed into an Xplore MC15 twin-screw extruder equipped with a water-cooled hopper operating at 180 °C for 4CBPA based blends and 210 °C for TPA based blends. The mixture was homogenized by extruding for 2 minutes at a rotational speed of 100 rpm. Then the molten polymer blend was loaded into a pressure unit followed by evacuation into an Xplore micro-injection molding machine (injection temperature: 180 °C, mold temperature: 50 °C), where it was injected into a mold (dog bones with dimensions 75 mm x 4 mm x 2 mm for tensile tests). As a reference, the same tensile bars were prepared containing the PA(TPA,MXD)/PA12 reference polymer blends.



Figure S1. GPC analysis (RI detection) of PA-SM-1 before and after the vacuum step. Measured in HFIP against poly(methyl methacrylate) standards.



Figure S2. TGA curves of the polyamides PA-SM-1, PA-SM-3, PA-S-5, and PA-SM-4, measured under nitrogen, temperature range: 25-700 °C, heating rate was 10 °C/min.

The structure of the synthesized polyamides was confirmed with ¹H NMR and ¹³C NMR spectroscopy. The spectra are shown in Figure S3. In polymers PA-S-1 and PA-SM-4 amide (-NH) protons were observed at a chemical shift between 8 and 9 ppm. In the case of PA-S-3 the peaks shifted more upfield between 6 and 7 ppm. For polyamides PA-S-1 and PA-S-3 two carbonyl carbons could be detected in the ¹³C NMR spectrum between 165 and 175 ppm. In the case of PA-SM-4 four peaks are observed for the two carbonyl groups. This peak splitting arises from the asymmetry of IPDA, with has as result that 4CBPA can react with either the primary or secondary amine. The assigned peaks correspond well with the proposed structures.



Figure S3. ¹H NMR and ¹³C NMR spectra of polyamides (a) PA-S-3 (PFP-d/CDCl₃), (b) PA-S-1 (DMSO- d_6), and (c) PA-SM-4 (DMSO- d_6).



Figure S4. IR spectra of polymers PA-S-2, PA-S-3 and PA-S-5.



Figure S5. MALDI-ToF-MS spectrum of PA-SM-4.



Figure S6. MALDI-ToF-MS spectrum of PA-S-3.



Figure S7. ¹H NMR spectrum of model compound 2.



Figure S8. ¹³C NMR spectrum of model compound 2.

Diacid	Diamine	Scale (g)	M _n (g/mol)	Ð	T _{g,mid} (°C)	T _{deg} ^{10%} (°C)	$\eta_{rel}{}^a$
Terepthaloyl	MXD	10	_a	_a	162	270	n.a.
chloride		100	_a	_a	166	273	1.03

Table S1. Results for the synthesis of poly(TPA,MXD) reference polymer

^a Relative viscosity measured by Ubbelohde viscometry in concentrated sulfuric acid.

Table S2. Overview of the tensile behaviour of PA-S-2 and reference polymer poly(TPA,MXD) blends with PA12

wt% PA-S-2	wt% PA12	Young's modulus (MPa)	Ultimate strength σ _B (MPa)	Strain at break ε _B (%)
0	100	1400 ^a	52 ^a	250 ^a
30	70	1805 ± 64.7	39.3 ± 3.5	15.8 ± 2.8
70	30	3034 ± 183.8	33.1 ± 0.7	1.2 ± 0
wt%				
poly(TPA,MXD)				
30	70	1184 ± 94.2	23.6 ± 1.0	9.9±1.6
70	30	1985 ± 177.4	19.9 ± 0.2	1.2 ± 0.4

^a Values obtained from polymer handbook.⁶

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