Electronic Supplementary Material (ESI) for Green Chemistry.

Synthesis of polyaramids in γ–valerolactone-based organic electrolyte solutions

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Electronic Supplementary Information (ESI)

Purification procedures of diamine monomers

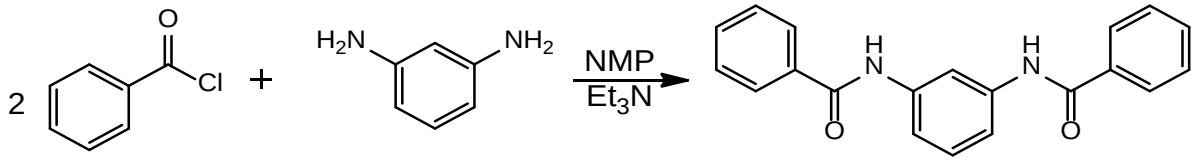
These purification procedures have been performed as described in our previous work.[1] *m*-Phenylenediamine was received as a black powder. It was purified by vacuum sublimation at 60 °C, yielding clear white crystals. *p*-Phenylenediamine was received as dark purple-black crystals. Purification started with a vacuum sublimation at 90 °C, yielding yellow crystals. These crystals were again purified by recrystallization from heptane/chloroform, resulting in pink crystals. The final step was another vacuum sublimation at 90 °C, this time yielding transparent white crystals. 3,4-Oxydianiline was received as a black powder and was purified by a sequence of 3 recrystallizations from heptane/chloroform. The resulting crystals turned more white with each subsequent recrystallization, ultimately yielding bright white crystals.

1. Winters, J.; Dehaen, W.; Binnemans, K. *Green Chem.* **2020**, *22* (18), 6127-6136.

Synthesis procedures of *m*-aramid oligomers

These synthetic procedures have been described in our previous paper.[2]

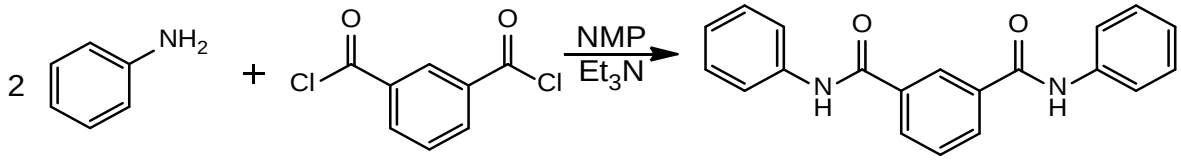
m-Trimer N (MTN)



Triethylamine (2.1 eq, 77.7 mmol, 7.86 g) and *m*-phenylenediamine (1.0 eq, 37.0 mmol, 4.0 g) were dissolved in 60 mL of dry NMP in a dried 3-neck flask flushed with N_2. The solution was put in an ice bath and benzoyl chloride (2.1 eq, 78.6 mmol, 10.9 g) was added dropwise under stirring. After 30 min, water was added to precipitate the product. The solid *m*-trimer N was

isolated via filtration, washed with water and dried in a vacuum oven at 50 °C overnight, yielding a white solid. Yield: 11.3 g, 97%. ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 10.3 (2H, s), 8.34 (1H, t, *J* = 2.0 Hz), 7.96 (4H, m), 7.54 (8H, m), 7.32 (1H, m). ^{13}C NMR (100 MHz, DMSO-d_6, δ/ppm): 166.0, 139.8, 135.4, 132.0, 128.8, 128.6, 128.2, 116.5, 113.4. FTIR (ATR, ν_{max}/cm^{-1}): 3267 (N-H stretch), 3129, 3060, 3029 (C-H stretch), 1639 (amide I), 1518 (amide II), 792, 710. Melting point: 248 °C.

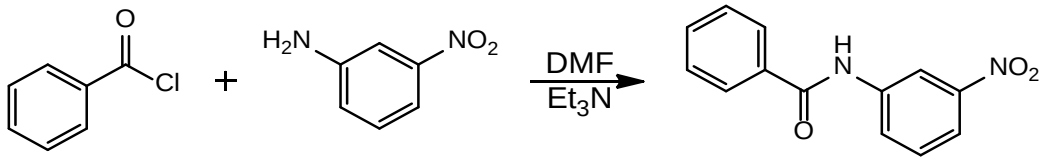
m-Trimer O (MTO)



Triethylamine (2.1 eq, 41.4 mmol, 4.18 g) and isophthaloyl chloride (1.0 eq, 19.7 mmol, 4.0 g) were dissolved in 60 mL of dry NMP in a dried 3-neck flask flushed with N_2. The solution was put in an ice bath and aniline (2.5 eq, 49.3 mmol, 4.58 g) was added dropwise under stirring. After 30 min, water was added to precipitate the product. The solid *m*-trimer O was isolated via filtration, washed with water and dried in a vacuum oven at 50 °C overnight, yielding a white solid. Yield: 5.9 g (95%). ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 10.44 (2H, s), 8.53 (1H, t, *J* = 1.6 Hz), 8.14 (2H, dd, *J* = 7.8 , *J* = 1.7 Hz), 7.79 (4H, m), 7.70 (1H, t, *J* = 7.8 Hz), 7.38 (4H, m), 7.12 (2H, m). ^{13}C NMR (100 MHz, DMSO-d_6, δ/ppm): 165.5, 139.5, 135.7, 131.1, 129.2, 129.1, 127.5, 124.3, 120.8. FTIR (ATR, ν_{max}/cm^{-1}): 3256 (N-H stretch), 3130, 3061, 3041 (C-H stretch), 1638 (amide I), 1545 (amide II), 1028, 688. Melting point: 291 °C.

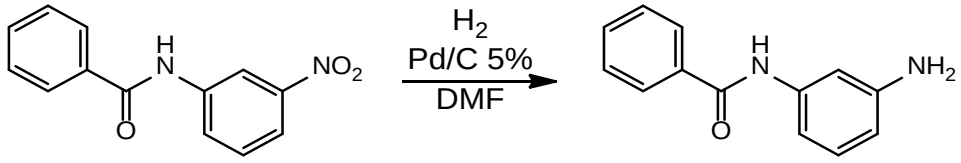
PMIA pentamer model compound (PTN)

Step 1:



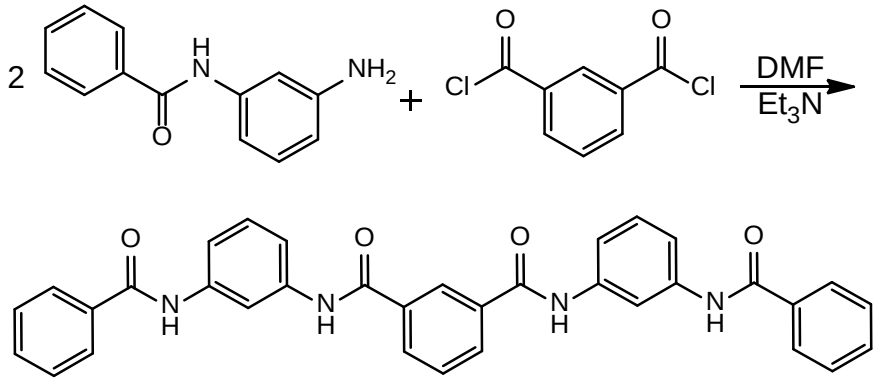
Triethylamine (1.0 eq, 36.2 mmol, 3.66 g) and 3-nitroaniline (1.0 eq, 36.2 mmol, 5.0 g) were dissolved in 60 mL of dry NMP in a dried 3-neck flask flushed with N_2. The solution was put in an ice bath and benzoyl chloride (1.0 eq, 36.2 mmol, 5.09 g) was added dropwise under stirring. After 30 min, water was added to precipitate the product. The white solid was isolated via filtration, washed with water and dried in a vacuum oven at 50 °C overnight. Yield: 8.6 g (98%). ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 10.71 (1H, s), 8.82 (1H, t, J = 2.1 Hz), 8.20 (1H, m), 7.99 (3H, m), 7.61 (4H, m). Melting point: 158 °C.

Step 2:



The product from step 1 (2.3 g) was dissolved in 20 mL of dry DMF in a dried 3-neck flask flushed with N_2. The catalyst Pd/C (5%) (0.1g) was added, and the flask was again flushed with N_2. A balloon filled with H_2 was attached, and the reaction mixture was stirred at 80 °C for 24h. The reaction was considered complete due to the disappearance of signals of the starting product in the crude ^{1}H NMR spectrum of the reaction mixture. The solution was filtered using a syringe filter (pore size 0.45 μm), and the flask and filter washed again using 10 mL of dry DMF. The filtered solution was used directly for step 3.

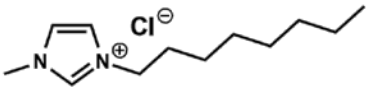
Step 3:

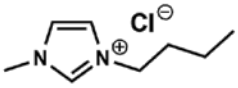


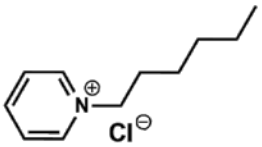
An aliquot of 20 mL containing the product of step 2 (2.2 eq, 9.49 mmol, 2.01 g) was added to a dried 3-neck flask flushed with N_2. Triethylamine (2.2 eq, 9.49 mmol, 0.96 g) was added and the solution was put on an ice bath. Isophthaloyl chloride (1.0 eq, 4.32 mmol, 0.88 g) was added under N_2 flow. The reaction mixture was stirred for 1 h, and precipitated with water. The solid pentamer model compound was isolated by filtration, washed with water and cold acetone. The product was further purified by recrystallization from NMP/H_2O and finally dried overnight in a vacuum oven at 50 °C, resulting in a yellow powder. Yield: 1.6 g (67%). ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 10.50 (2H, s), 10.34 (2H, s), 8.55 (1H, s), 8.36 (2H, s), 8.16 (2H, d, *J* = 7.0 Hz), 7.98 (4H, d, *J* = 7.0 Hz), 7.70 (1H, t, J = 7.0 Hz), 7.54 (10H, m), 7.34 (2H, t, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6, δ/ppm): 166.0, 165.6, 139.9, 139.7, 135.6, 135.4, 132.0, 131.2, 129.1, 129.0, 128.8, 128.2, 127.6, 116.7, 116.5, 113.4. FTIR (ATR, ν_{max}/cm^{-1}): 3316 (N-H stretch), 1645 (amide I), 1532 (amide II), 687. Melting point: 332 °C.

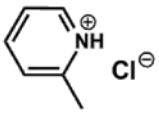
2. Winters, J.; Dehaen, W.; Binnemans, K. *Phys. Chem. Chem. Phys.* **2019,** *21* (7), 4053-4062.

Chemical structures of Ionic Liquids

[C_8MIm][Cl] 

[C_4MIm][Cl] 

[C_6Pyr][Cl] 

[2-Me-HPyr][Cl] 

Spinning setup

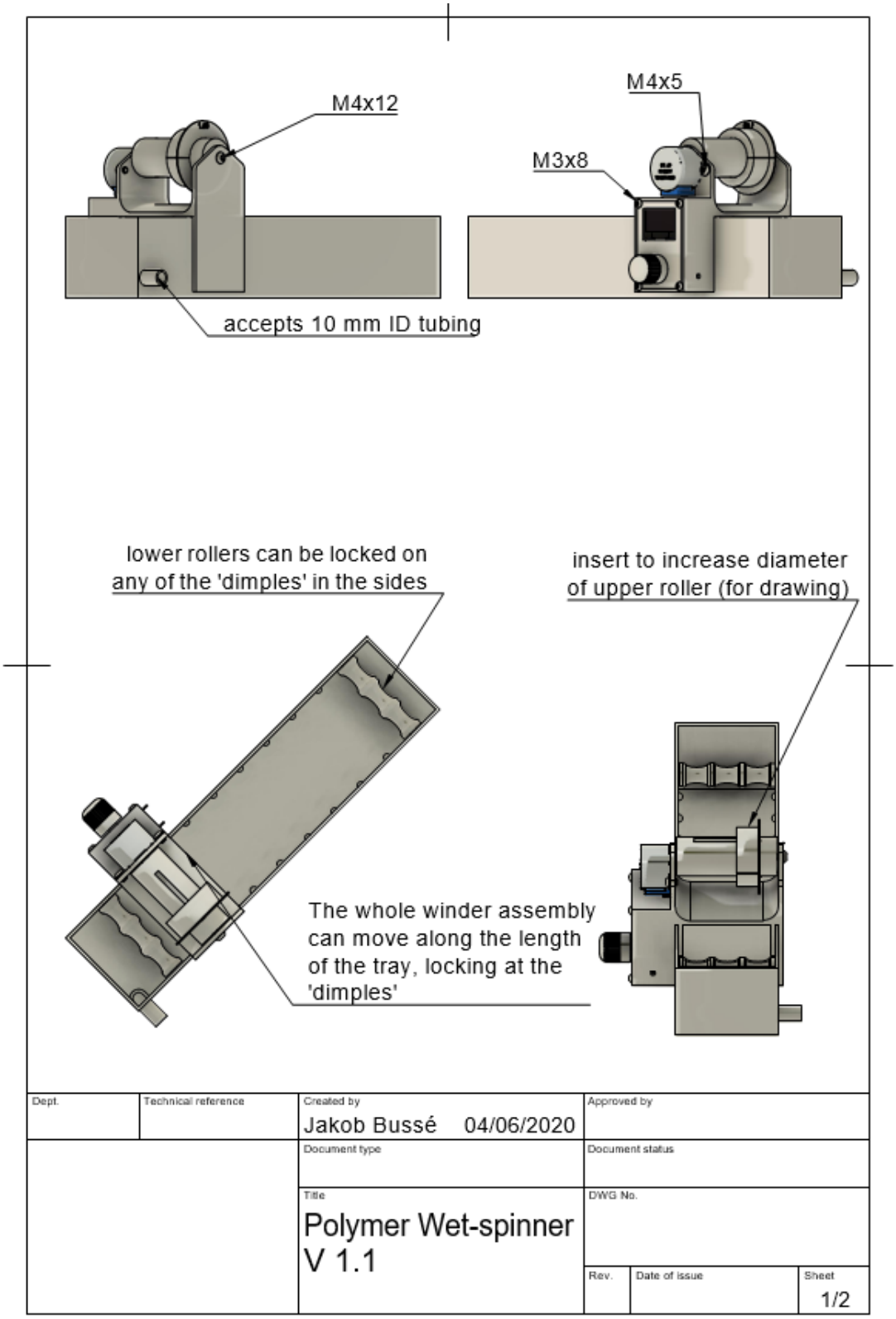
Print settings:

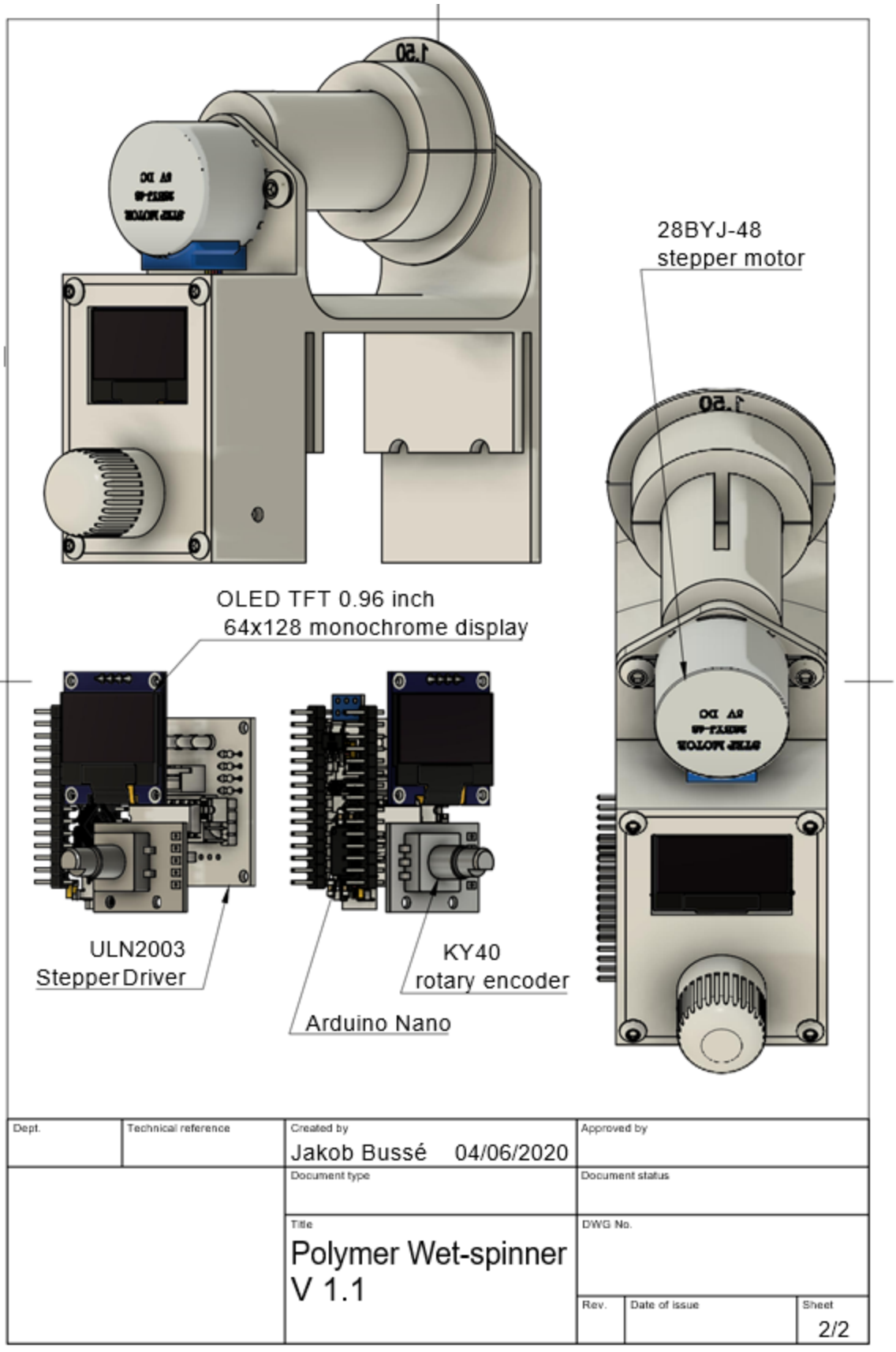
The polymer wet spinner was printed on an Intamsys Funmat HT enhanced in 'BASF Ultrafuse PRO1 filament - Natural white' PLA filament with an 0.4 mm nozzle operating at 210 °C and 0.1 mm layer height on a 60 °C bed. The G-code was generated with Cura_SteamEngine 4.5.0. Other relevant print settings were: 25% infill (triangles), 5 perimeters, 5 top layers, 5 bottom layers, 60 mm/s print speed.

Spinning parameters

The PMIA solutions were ejected by the syringe pump at a rate of 10 mL/h, with a needle diameter of 0.8 mm, and pulled from the water bath by the winder rotating at 14 RPM. The fibers were washed and drawn 25 % simultaneously by unwinding the fibers, running them through the water bath, and rewinding on a section of the upper roller with increased diameter. The ODA/PPTA solutions were ejected by the syringe pump at a rate of 15 mL/h, with a needle diameter of 0.8 mm, and pulled from the water bath by the winder rotating at 7 RPM. The fibers were washed and drawn 10 % simultaneously by unwinding the fibers, running them through the water bath, and rewinding on a section of the upper roller with increased diameter.

Device schematics





Dept.	Technical reference	Created by	Approved by
		Jakob Bussé 04/06/2020	
		Document type	Document status
		Title: Polymer Wet-spinner V 1.1	DWG No.
			Rev. / Date of issue / Sheet: 2/2