

**γ -Valerolactone-based organic electrolyte solutions: a benign approach
to polyaramid dissolution and processing**

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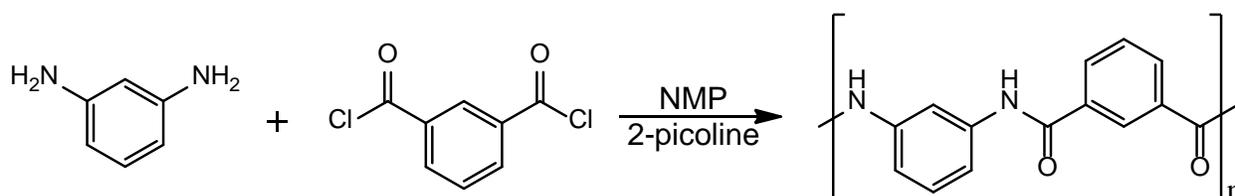
Electronic Supplementary Information (ESI)

1. Synthesis and characterisation of polyaramids

1.1 Purification of diamine monomers

m-Phenylenediamine was received as a black powder. It was purified simply 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 very clear 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.

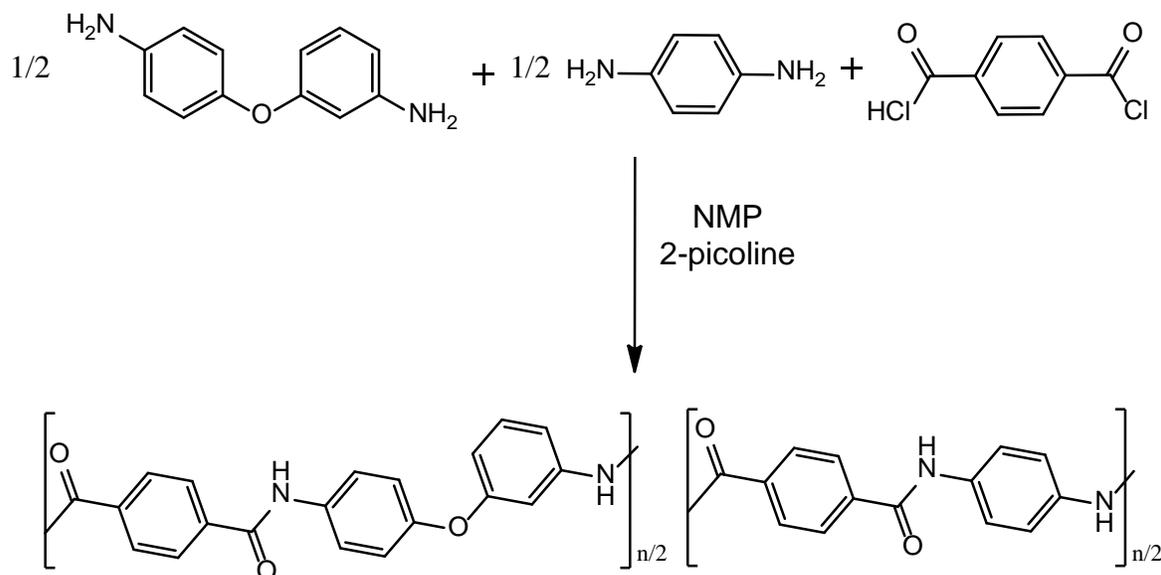
1.2 Synthesis of Poly-*m*-phenyleneisophthalamide (PMIA)



Dry NMP (20 g) was added to a dried 3-neck flask flushed with N₂. *m*-Phenylenediamine (1.0 eq, 19.4 mmol, 2.09 g) was added under a gentle N₂ flow. The monomer was dissolved by shaking for roughly 10 min. The solution was then put on an ice bath and 2-picoline (2.1 eq, 40.7 mmol, 3.79 g) was added using a syringe. An overhead stirrer (4 cm collapsible two-blade impeller fitted in a Cowie universal stirrer guide) was then placed on the flask under N₂ flow, and the reaction mixture

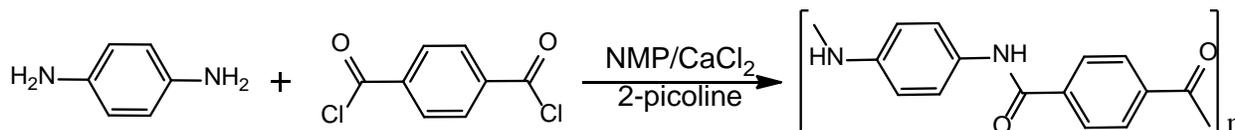
was stirred at a rate of 200 rpm. The ice bath was replaced with a cooling bath containing dry ice and isopropanol, and the stirring rate was increased to 500 rpm. Isophthaloyl chloride (1.0 eq, 19.4 mmol, 3.94 g) was added under a N₂ flow. The viscosity of the reaction mixture rapidly increased, creating a thick white gel. The stirring rate was further increased to 1000 rpm, and stirring continued for 15 min. Water was added to precipitate the polymer, which was removed from the 3-neck flask and subsequently washed with water and briefly dried in a vacuum oven at 50 °C. The polymer chunks were redissolved in 100 mL of NMP at 50 °C. When dissolution was complete, the polymer was again precipitated by adding water dropwise to the solution while under heavy stirring. This way, a fine white powder could be obtained. The polymer powder was filtrated, washed with water, further purified via 12 h of Soxhlet extraction with methanol and finally dried overnight in a vacuum oven at 50 °C. The yield was quantitative. The inherent viscosity, using a PMIA/sulfuric acid (96%) solution with a concentration of 0.5 g dL⁻¹, was determined to be 2.11 dL g⁻¹.

1.3 Synthesis of Copoly(p-phenylene/3,4'-diphenylether terephthalamide) (ODA/PPTA)



Dry NMP (40 g) was added to a dried 3-neck flask flushed with N₂. *p*-Phenylenediamine (0.5 eq, 4.25 mmol, 0.46 g) and 3,4-oxydianiline (0.5 eq, 4.25 mmol, 0.85 g) were added under a gentle N₂ flow. The monomers were dissolved by shaking for roughly 20 min. The solution was then put on an ice bath and 2-picoline (2.1 eq, 17.8 mmol, 1.66 g) was added using a syringe. An overhead stirrer (4 cm collapsible two-blade impeller fitted in a Cowie universal stirrer guide) was then placed on the flask under N₂ flow, and the reaction mixture was stirred at a rate of 200 rpm. The solution was allowed to cool down for another 10 minutes. The stirring rate was increased to 500 rpm and terephthaloyl chloride (1.0 eq, 8.50 mmol, 1.73 g) was added under N₂ flow. The viscosity of the reaction mixture gradually increased, creating a light yellow gel. The stirring continued for another 3 hours. Water was added to precipitate the polymer, which was removed from the 3-neck flask and subsequently washed with water and briefly dried in a vacuum oven at 50 °C. The polymer chunks were redissolved in 100 mL of NMP at 50 °C. When dissolution was complete, the polymer was again precipitated by adding water dropwise to the solution while under heavy stirring. This way, a fine light yellow powder could be obtained. The polymer powder was filtrated, washed with water, further purified via 12 h of Soxhlet extraction with methanol and finally dried overnight in a vacuum oven at 50 °C. The yield was quantitative. The inherent viscosity, using a ODA/PPTA / sulfuric acid (96%) solution with a concentration of 0.5 g dL⁻¹, was determined to be 2.45 dL g⁻¹.

1.4 Synthesis of Poly-*p*-phenylene terephthalamide (PPTA)



Calcium chloride dihydrate (CaCl₂·2H₂O; 2.91 g, 19.8 mmol) and dry NMP (40 g) were added to a 3-neck flask. The excess water was distilled off by fractionated distillation on a vacuum line at 75 °C. Additional dry NMP was added to compensate for solvent losses during distillation. The solvent was dried until the water content was below 200 ppm. *p*-Phenylenediamine (1.0 eq, 13.5 mmol, 1.46 g) was added under a gentle N₂ flow. The monomer was dissolved by shaking for roughly 20 min. The solution was then put in an ice bath and 2-picoline (2.1 eq, 28.4 mmol, 2.64 g) was added using a syringe. An overhead stirrer (4 cm collapsible two-blade impeller fitted in a Cowie universal stirrer guide) was then placed on the flask under N₂ flow, and the reaction mixture was stirred at a rate of 200 rpm. The solution was allowed to cool down for another 10 minutes. The stirring rate was increased to 500 rpm and terephthaloyl chloride (1.0 eq, 13.5 mmol, 2.74 g) was added under N₂ flow. The viscosity of the reaction mixture rapidly increased, turning into a yellow gel. The stirring rate was further increased to 1000 rpm, and stirring continued for 10 more minutes until the reaction mixture turned into a solid crumble. The crumble was transferred to a beaker filled with water and broken up into a powder using an immersion blender. The polymer powder was thoroughly washed with water, further purified via 12 h of Soxhlet extraction with methanol and finally dried overnight in a vacuum oven at 50 °C. The inherent viscosity, using a PPTA/sulfuric acid (96%) solution with a concentration of 0.5 g dL⁻¹, was determined to be 5.17 dL g⁻¹.

1.5 Inherent viscosity measurements

The inherent viscosities of PMIA, PPTA and ODA/PPTA were all measured using the same procedure. Dried polyaramid (0.1 g) was dissolved in 20 mL of concentrated sulfuric acid (96 %) to obtain a solution with a concentration (c) of 0.5 g dL⁻¹. An Ubbelohde capillary viscometer, placed in a water bath at 25°C, was used to measure the flow times of pure sulfuric acid (t_{solvent}) and of the polyaramid/sulfuric acid solution (t_{solution}). From these flow times, the relative viscosity of the solution (η_{rel}), and subsequently the inherent viscosity (η_{inh}) were calculated as a measure for the molecular weight of the polyaramid (eq. 1-2). The inherent viscosities for the polymers used in these studies were 2.11 dL.g⁻¹ for PMIA, 2.45 dL.g⁻¹ for ODA/PPTA and 5.17 dL.g⁻¹ for PPTA, which are on par with the industrial standard for each polyaramid.

$$\eta_{inh} = \frac{\ln \eta_{rel}}{c} \quad (1)$$

$$\eta_{rel} = \frac{t_{solution}}{t_{solvent}} \quad (2)$$

2. Tables and equations

2.1 Polymer solubility

The composition of the solvents is reported in IL molar fraction x_{IL} (eq. 3). The solubility is reported in total weight percent wt% (eq. 4).

$$x_{IL} = \frac{n_{IL}}{n_{IL} + n_{co-solvent}} \quad (3)$$

$$wt\% = \frac{m_{polyaramid}}{m_{IL} + m_{co-solvent} + m_{polyaramid}} \quad (4)$$

Table S1: Solubility of PMIA and ODA/PPTA in selected OESs. PPTA was omitted from this table due to general insolubility.

Ionic Liquid	Co-Solvent	x_{IL}	Solubility PMIA (wt%)	Solubility ODA/PPTA (wt%)
\	GVL	0.00	0.0	0.0
[C ₈ MIm][Cl]	GVL	0.05	9.9	0.0
[C ₈ MIm][Cl]	GVL	0.10	18.0	2.0
[C ₈ MIm][Cl]	GVL	0.20	23.7	6.5
[C ₈ MIm][Cl]	GVL	0.40	23.1	7.4
[C ₈ MIm][Cl]	GVL	0.60	21.9	5.7
[C ₈ MIm][Cl]	GVL	0.80	20.6	4.8
[C ₈ MIm][Cl]	\	1.00	20.0	5.3
[P ₁₄₆₆₆][Cl]	GVL	0.05	8.3	0.0
[P ₁₄₆₆₆][Cl]	GVL	0.10	15.3	2.0
[P ₁₄₆₆₆][Cl]	GVL	0.20	18.0	3.8
[P ₁₄₆₆₆][Cl]	GVL	0.40	13.8	2.9
[P ₁₄₆₆₆][Cl]	GVL	0.60	1.0	0.0
[P ₁₄₆₆₆][Cl]	GVL	0.80	0.0	0.0
[P ₁₄₆₆₆][Cl]	\	1.00	0.0	0.0
[C ₄ MIm][NTf ₂]	GVL	0.05	0.0	0.0
[C ₄ MIm][NTf ₂]	GVL	0.10	0.0	0.0
[C ₄ MIm][NTf ₂]	GVL	0.20	0.0	0.0
[C ₄ MIm][NTf ₂]	GVL	0.40	0.0	0.0
[C ₄ MIm][NTf ₂]	GVL	0.60	0.0	0.0
[C ₄ MIm][NTf ₂]	GVL	0.80	0.0	0.0
[C ₄ MIm][NTf ₂]	\	1.00	0.0	0.0
\	ACN	0.00	0.0	0.0
[C ₈ MIm][Cl]	ACN	0.05	5.7	0.0
[C ₈ MIm][Cl]	ACN	0.10	10.7	0.0
[C ₈ MIm][Cl]	ACN	0.20	16.0	1.0
[C ₈ MIm][Cl]	ACN	0.40	19.4	2.9
[C ₈ MIm][Cl]	ACN	0.60	20.0	3.8
[C ₈ MIm][Cl]	ACN	0.80	20.0	4.3
\	EtOH	0.00	0.0	0.0

[C ₈ MIm][Cl]	EtOH	0.05	0.0	0.0
[C ₈ MIm][Cl]	EtOH	0.10	0.0	0.0
[C ₈ MIm][Cl]	EtOH	0.20	0.0	0.0
[C ₈ MIm][Cl]	EtOH	0.40	13.0	0.0
[C ₈ MIm][Cl]	EtOH	0.60	16.0	0.0
[C ₈ MIm][Cl]	EtOH	0.80	17.4	0.5

2.2 Kamlet-Taft parameters

The Kamlet-Taft parameters were then calculated using eq. 5-9.^{1,2} Note that eq. 7-9 use the peak maxima expressed in kilokaiser (kK) with 1 kK = 10000/ λ_{\max} (nm).

$$E_t(30) = \frac{28591.5}{\lambda_{\max(RD)}(nm)} \quad (5)$$

$$E_t^N = \frac{E_t(30) - 30.7}{32.4} \quad (6)$$

$$\pi^* = \frac{\lambda_{\max(DENA)}(kK) - 27.52}{-3.182} \quad (7)$$

$$\alpha = \frac{E_t^N - 0.009 - 0.415\pi^*}{0.465} \quad (8)$$

$$\beta = \frac{1.035 * \lambda_{\max(DENA)}(kK) - \lambda_{\max(NA)}(kK) + 2.64}{2.8} \quad (9)$$

Table S2: Kamlet-Taft data for selected OESs.

Ionic Liquid	Co-Solvent	x_{IL}	E_t^N	α	β	π^*
\	GVL	0.00	0.41	0.06	0.51	0.89
[C ₈ MIm][Cl]	GVL	0.05	0.51	0.27	0.93	0.91
[C ₈ MIm][Cl]	GVL	0.10	0.51	0.26	0.94	0.93
[C ₈ MIm][Cl]	GVL	0.20	0.53	0.26	0.95	0.95
[C ₈ MIm][Cl]	GVL	0.40	0.54	0.28	0.98	0.96
[C ₈ MIm][Cl]	GVL	0.60	0.56	0.32	0.94	0.97
[C ₈ MIm][Cl]	GVL	0.80	0.57	0.33	0.92	0.98
[C ₈ MIm][Cl]	\	1.00	0.58	0.34	0.93	0.99
[P ₁₄₆₆₆][Cl]	GVL	0.05	0.45	0.12	1.02	0.9
[P ₁₄₆₆₆][Cl]	GVL	0.10	0.43	0.11	1.13	0.9
[P ₁₄₆₆₆][Cl]	GVL	0.20	0.43	0.12	1.14	0.88
[P ₁₄₆₆₆][Cl]	GVL	0.40	0.44	0.14	1.23	0.88
[P ₁₄₆₆₆][Cl]	GVL	0.60	0.41	0.08	1.25	0.87
[P ₁₄₆₆₆][Cl]	GVL	0.80	0.40	0.07	1.28	0.87
[P ₁₄₆₆₆][Cl]	\	1.00	0.40	0.06	1.28	0.88
[C ₄ MIm][NTf ₂]	GVL	0.05	0.50	0.24	0.47	0.91
[C ₄ MIm][NTf ₂]	GVL	0.10	0.50	0.25	0.46	0.91
[C ₄ MIm][NTf ₂]	GVL	0.20	0.52	0.28	0.44	0.92
[C ₄ MIm][NTf ₂]	GVL	0.40	0.54	0.32	0.39	0.93
[C ₄ MIm][NTf ₂]	GVL	0.60	0.56	0.34	0.33	0.94
[C ₄ MIm][NTf ₂]	GVL	0.80	0.56	0.33	0.29	0.95
[C ₄ MIm][NTf ₂]	\	1.00	0.56	0.34	0.26	0.95
\	ACN	0.00	0.47	0.27	0.37	0.8
[C ₈ MIm][Cl]	ACN	0.05	0.55	0.41	0.95	0.86
[C ₈ MIm][Cl]	ACN	0.10	0.56	0.39	0.96	0.88
[C ₈ MIm][Cl]	ACN	0.20	0.56	0.36	0.97	0.93
[C ₈ MIm][Cl]	ACN	0.40	0.57	0.34	0.96	0.96
[C ₈ MIm][Cl]	ACN	0.60	0.57	0.33	0.93	0.99
[C ₈ MIm][Cl]	ACN	0.80	0.57	0.32	0.93	0.99
\	EtOH	0.00	0.66	0.80	0.71	0.71
[C ₈ MIm][Cl]	EtOH	0.05	0.72	0.80	0.81	0.81
[C ₈ MIm][Cl]	EtOH	0.10	0.70	0.71	0.79	0.79
[C ₈ MIm][Cl]	EtOH	0.20	0.70	0.69	0.83	0.83

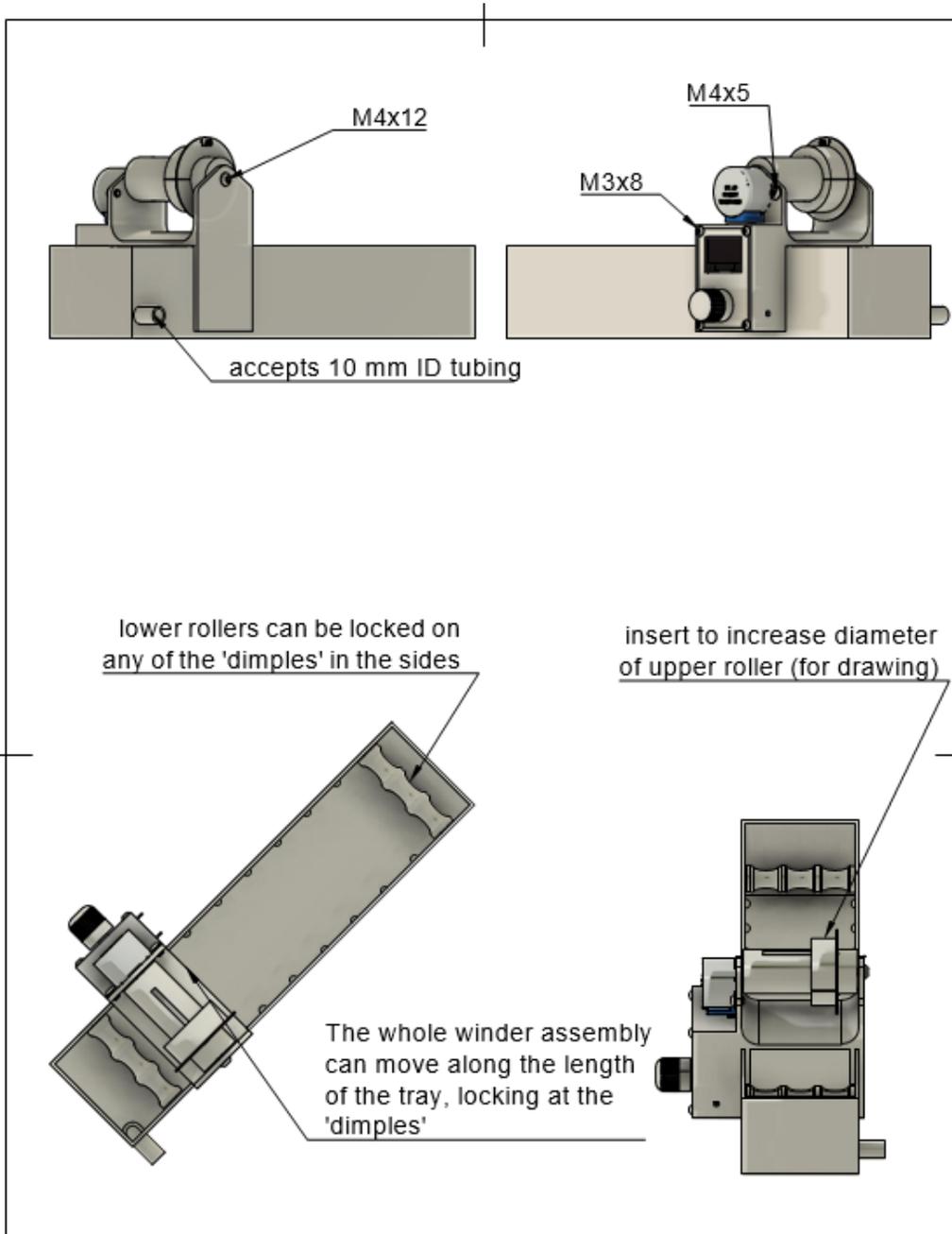
[C ₈ MIm][Cl]	EtOH	0.40	0.65	0.54	0.87	0.87
[C ₈ MIm][Cl]	EtOH	0.60	0.63	0.47	0.89	0.89
[C ₈ MIm][Cl]	EtOH	0.80	0.59	0.38	0.93	0.93

3. 3D-printed spinning setup

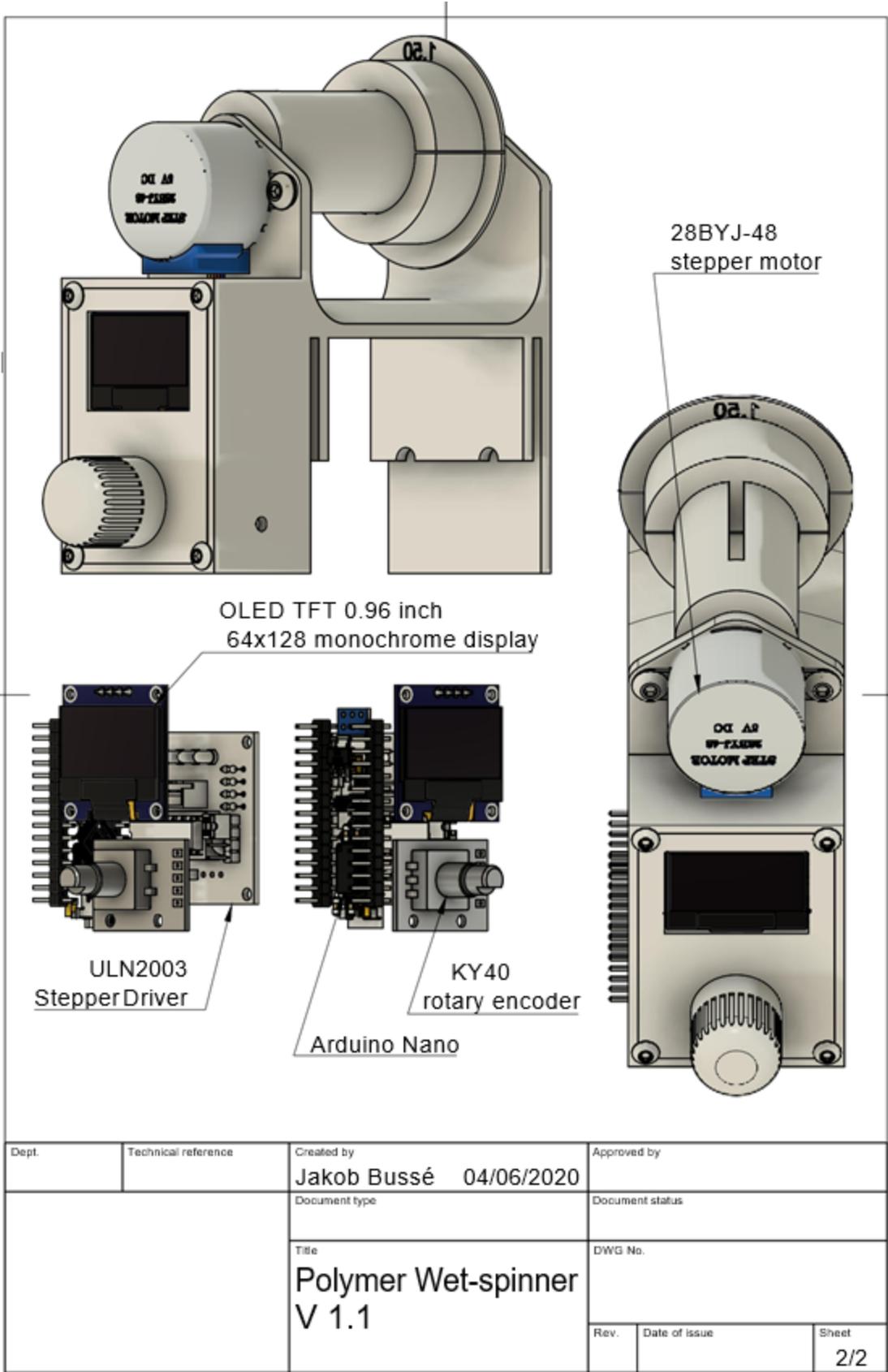
3.1 Print settings:

The polymer wet spinner was printed on an intamsys funmat HT enhanced in 'BASF Ultrafuse PRO1 filament - Natural white' PLA filament with an 0.4mm 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.

3.2 Device schematics



Dept.	Technical reference	Created by Jakob Bussé 04/06/2020	Approved by
		Document type	Document status
		Title Polymer Wet-spinner V 1.1	DWG No.
		Rev.	Date of issue
			Sheet 1/2



3.3 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.

4. References

1. Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, 98 (2), 377-383.
2. Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, 48 (17), 2877-2887.