Electronic Supporting Information

A modular low-cost automated synthesis machine demonstrated by Ring-Opening Metathesis Polymerization†

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Technical drawings

The following sections contain the technical drawings for the ASM modules. Further information can be found on our gitgub repository, where drawings, CAD files (.stl and .ipt), and demonstrations of the ASM can be accessed. [1]

S1 CAD Stirring module

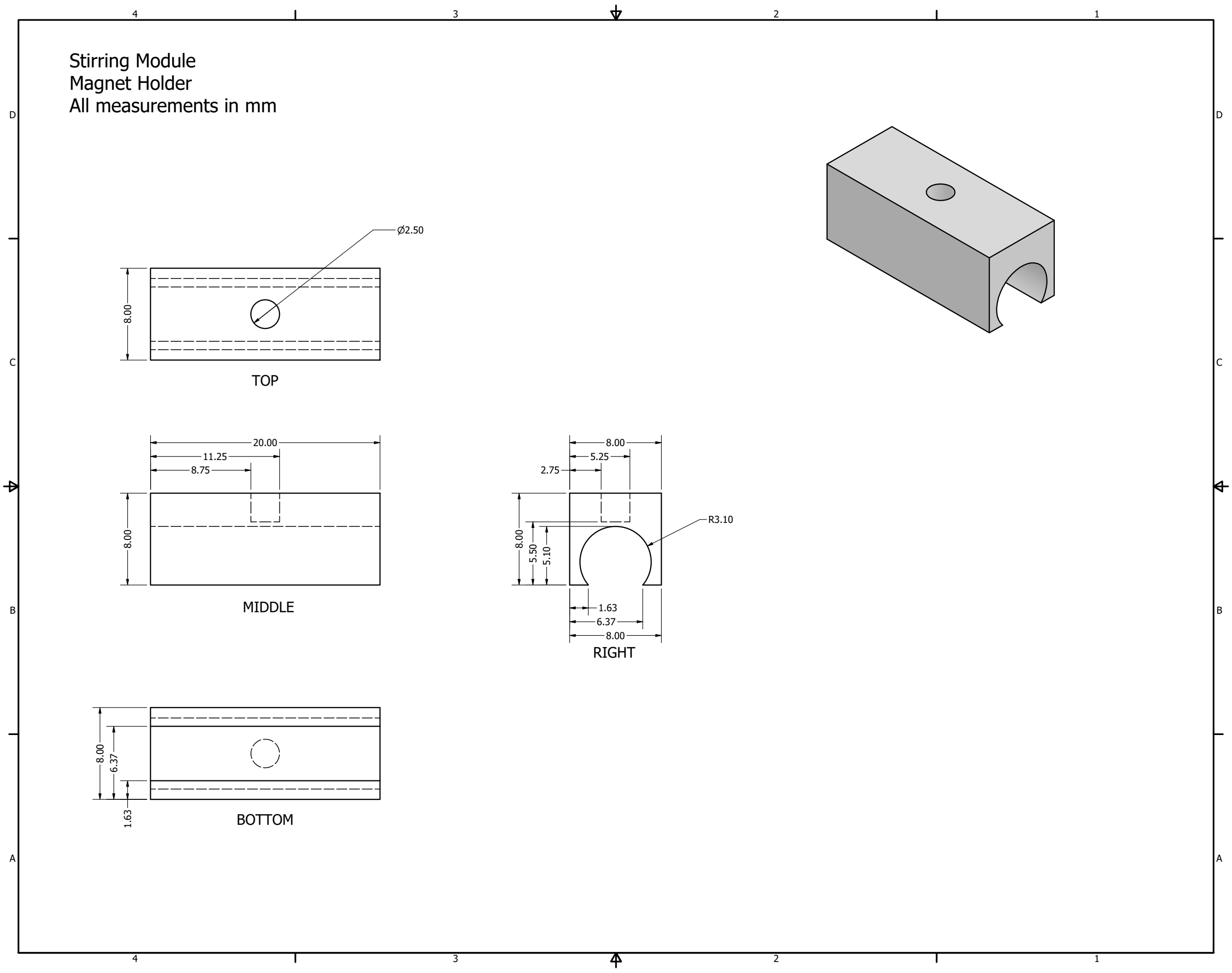


Figure S1: CAD drawing of the magnet stir bar holder used to finish the stirring module. The design fits onto the DC motor driving axes and holds a magnetic stir bar.

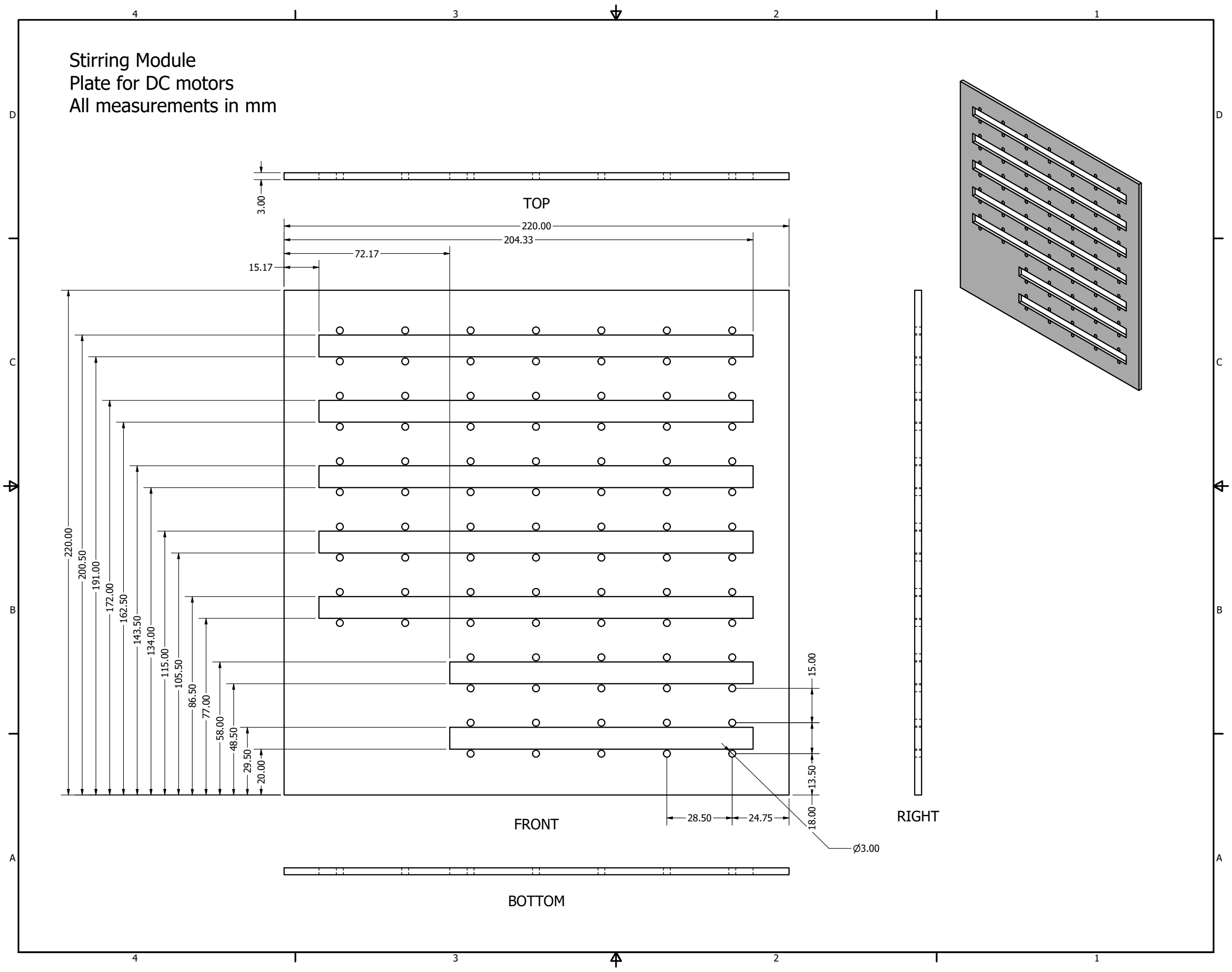


Figure S2: CAD drawing of the base plate for the stirring module, used to mount and subsequently connect the DC motors on in blocks.

S2 CAD Atmospheric control module

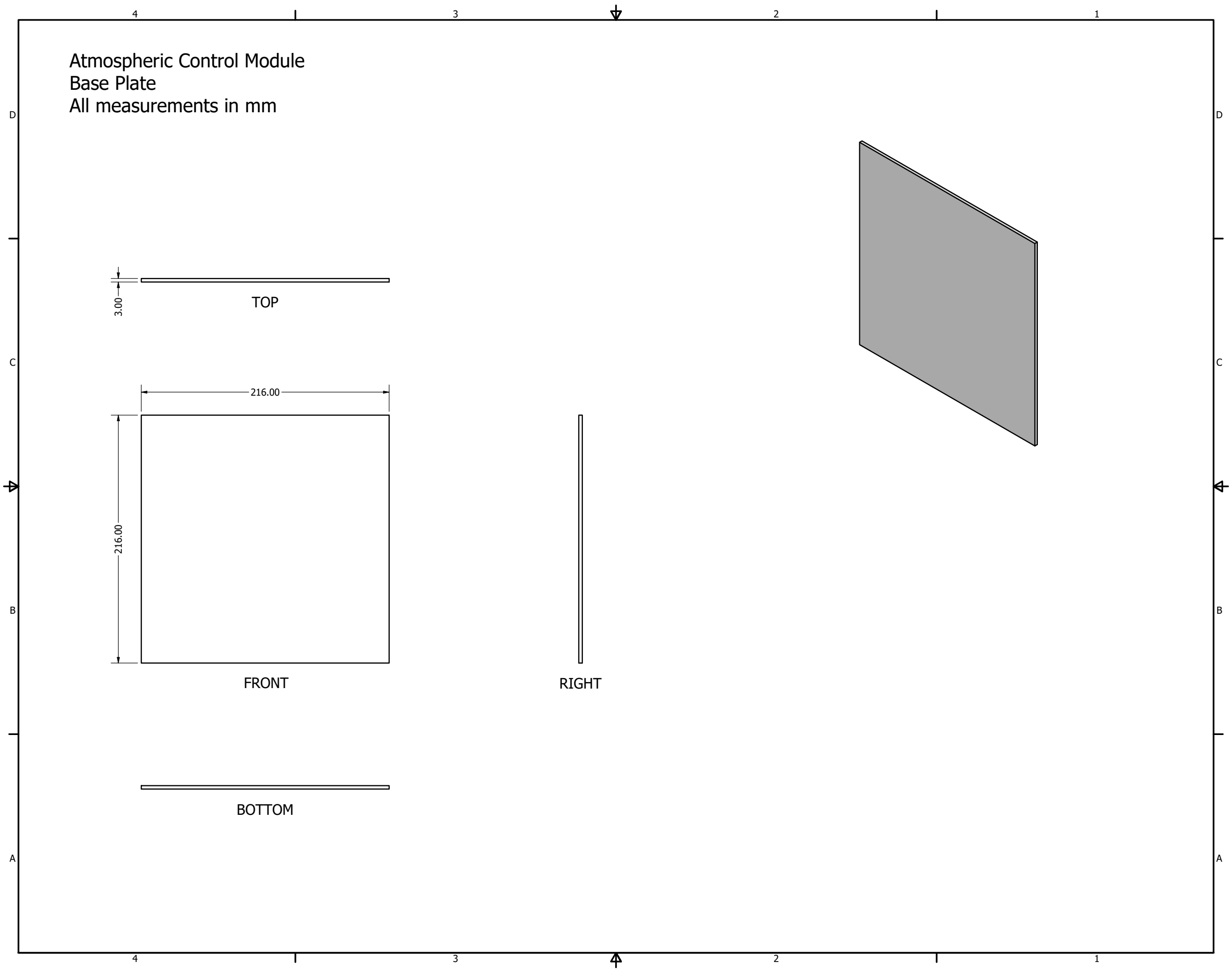


Figure S3: CAD drawing of the base plate used in the atmospheric control box.

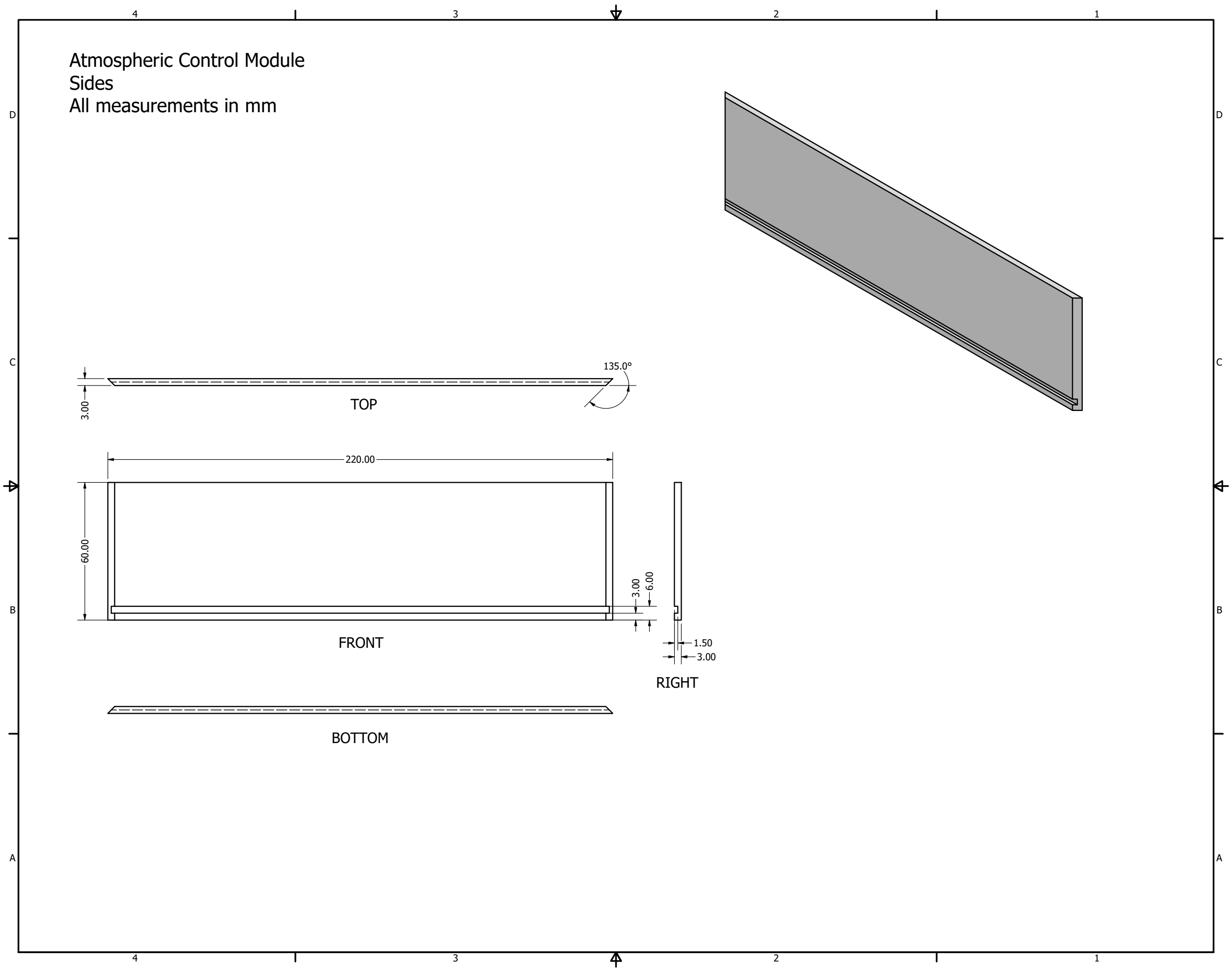


Figure S4: CAD drawing of the sides used for the atmospheric control module.

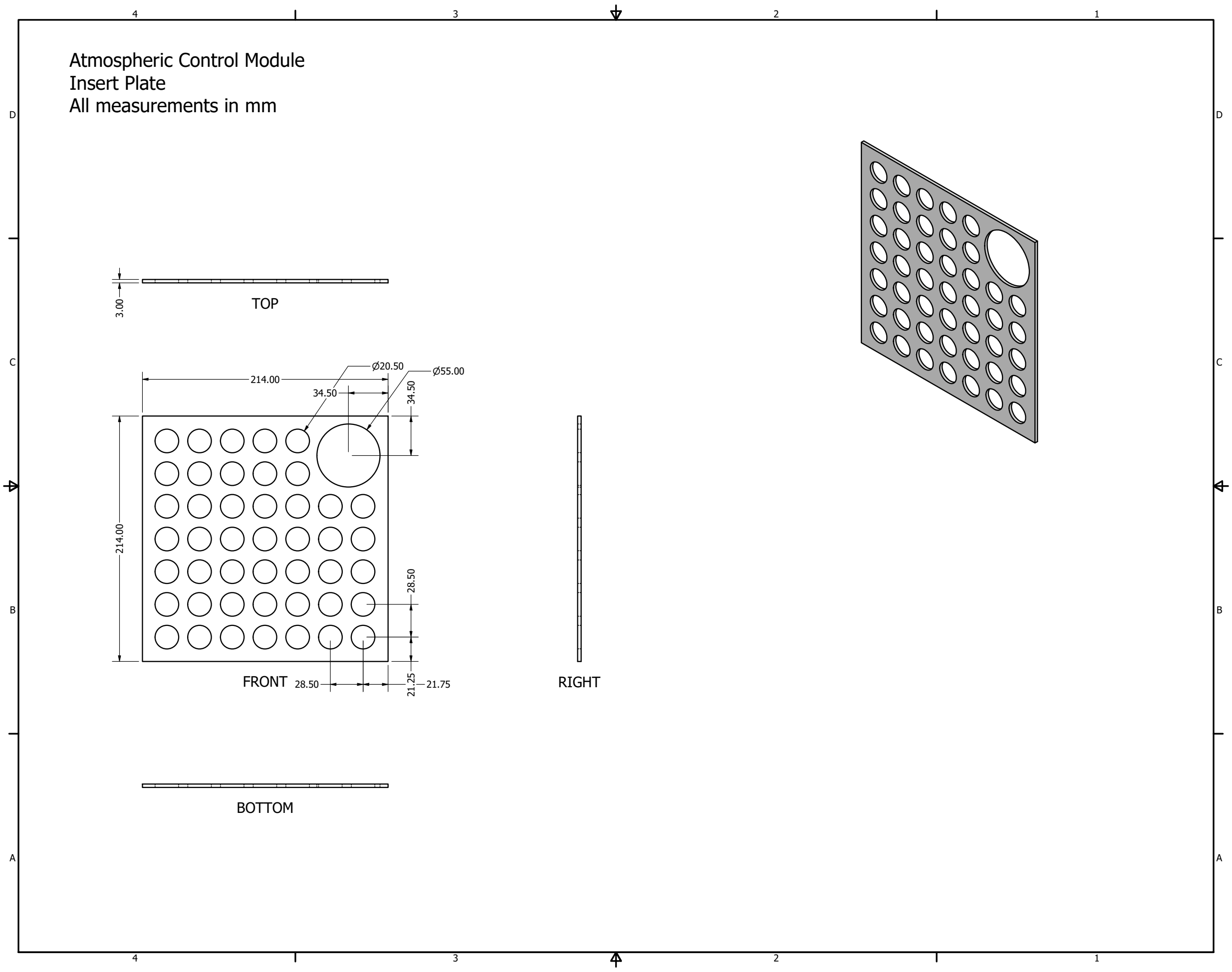


Figure S5: CAD drawing of the insert designed for the atmospheric control module. Each hole is designed to fit a 5 mL snap cap vial, and the large hole to fit a waste beaker.

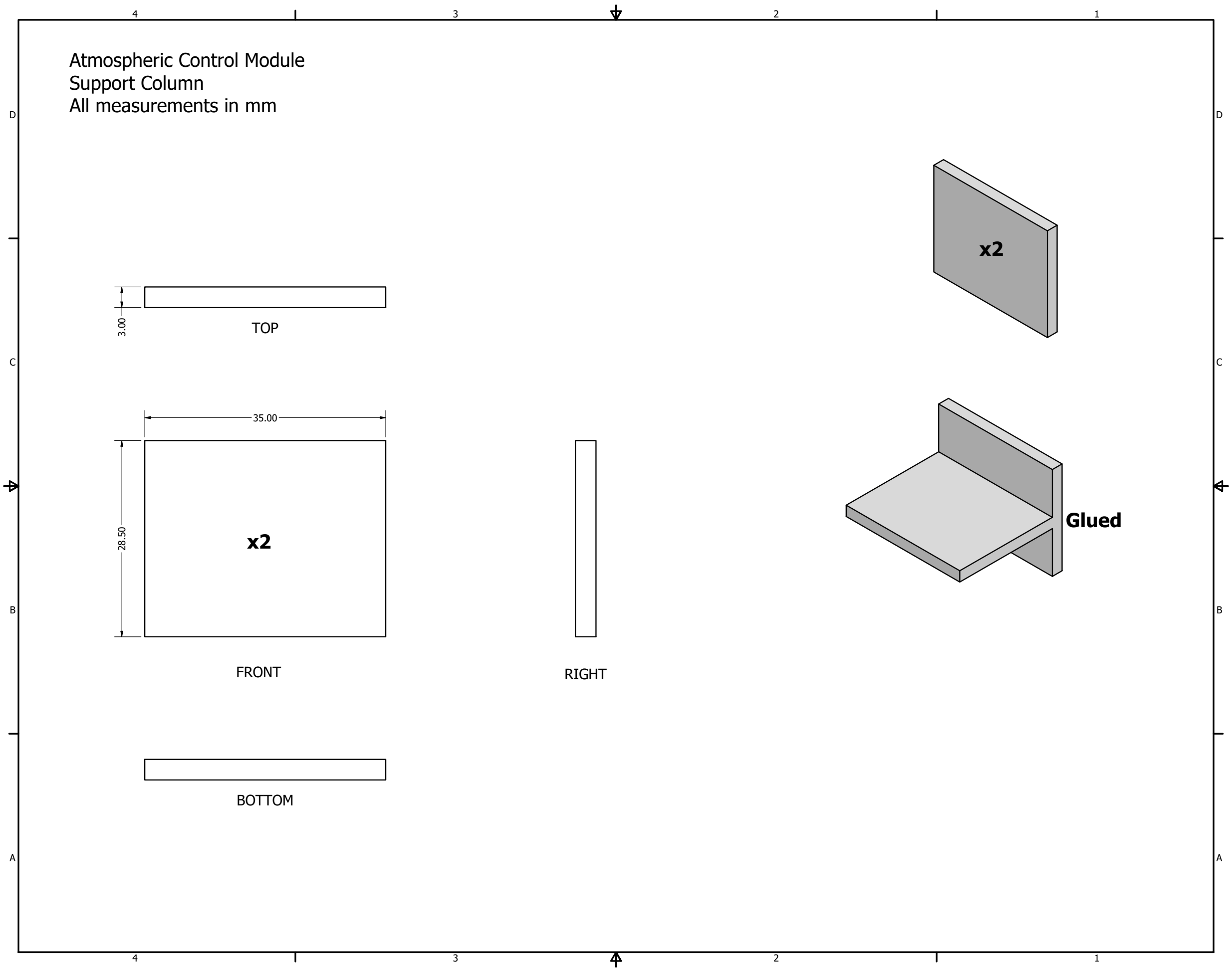


Figure S6: CAD drawing of the feet for the atmospheric control insert.

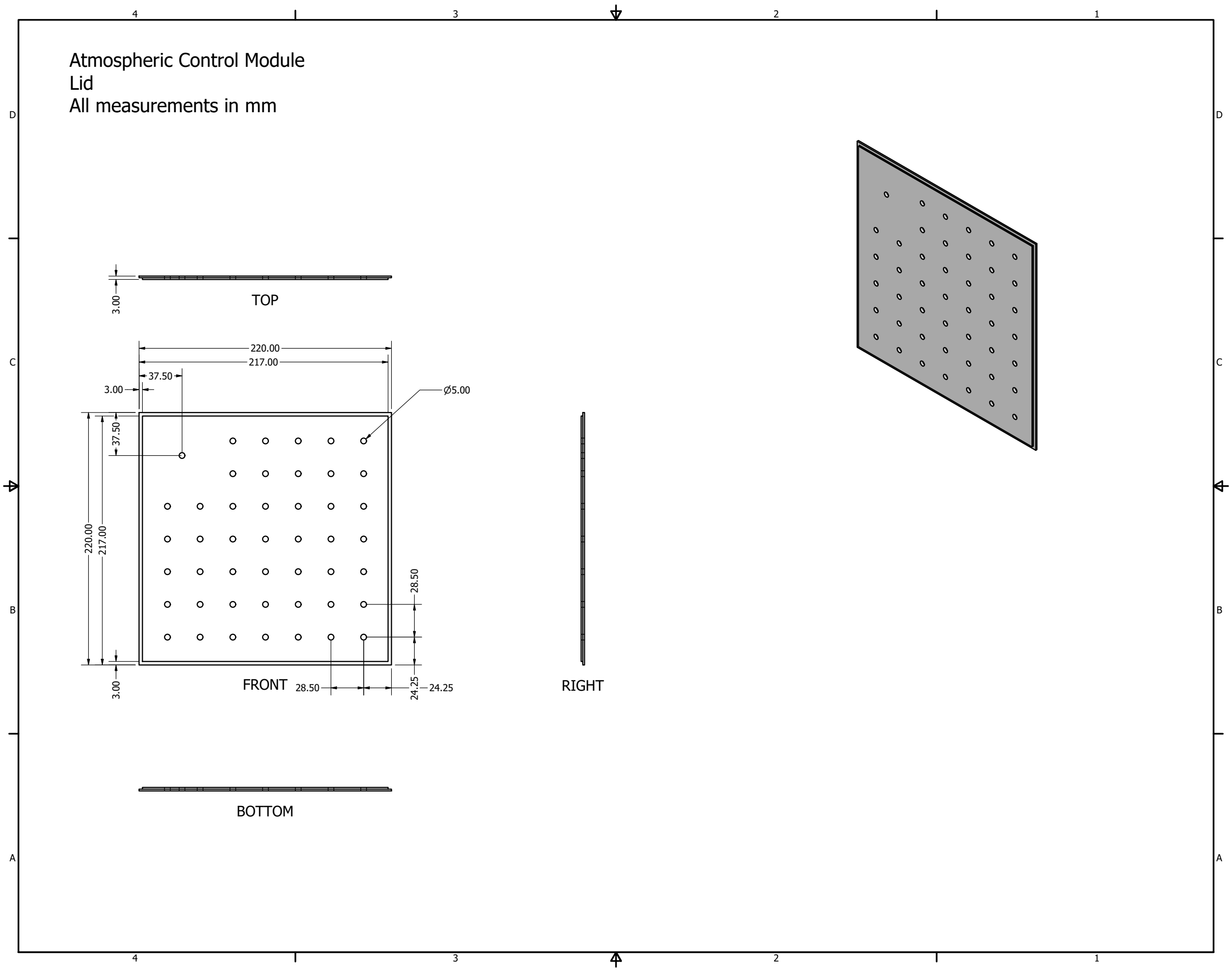


Figure S7: CAD drawing of the lid used for the atmospheric control module.

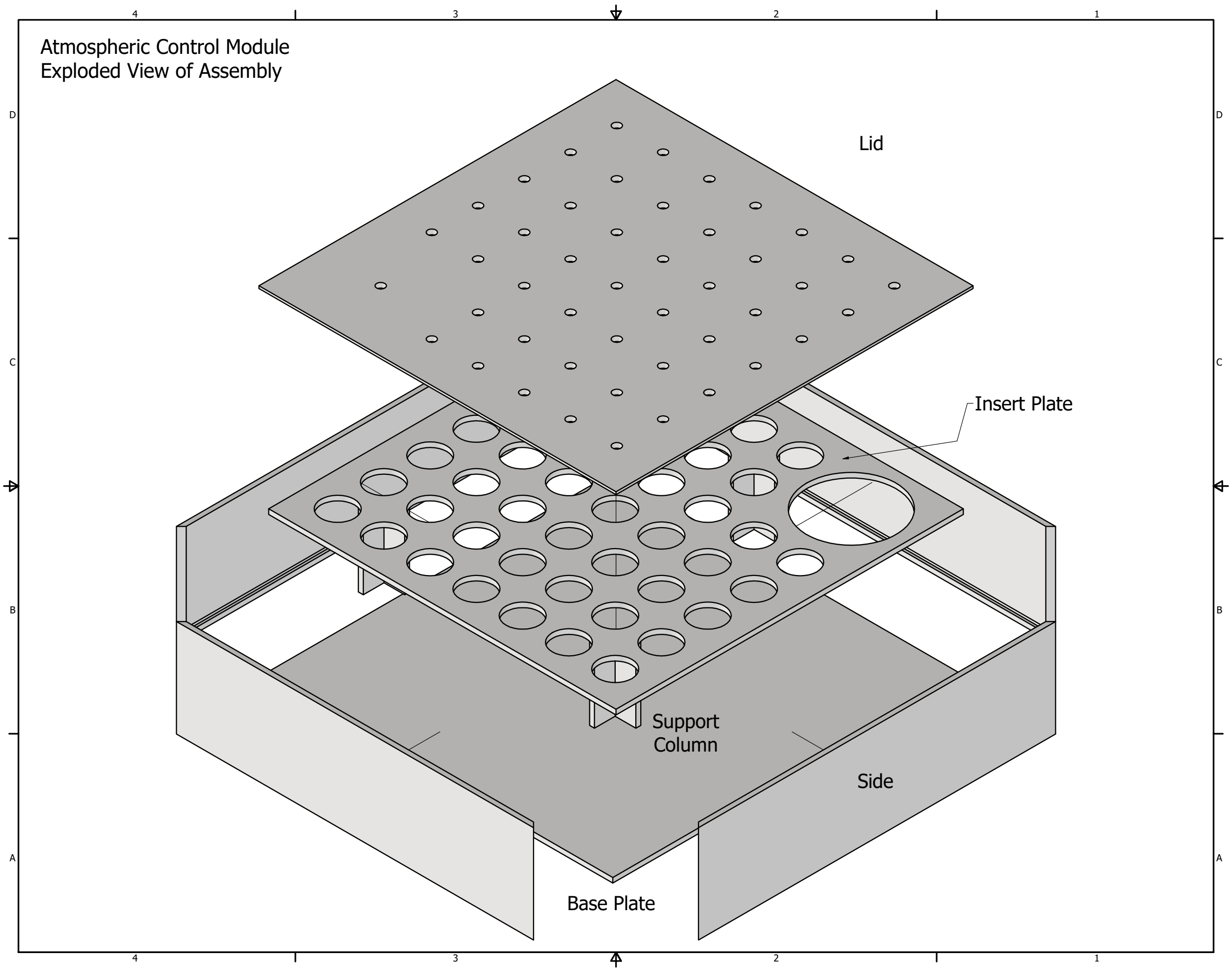


Figure S8: Exploded view of the assembled atmospheric control module.

S3 CAD Dosing module

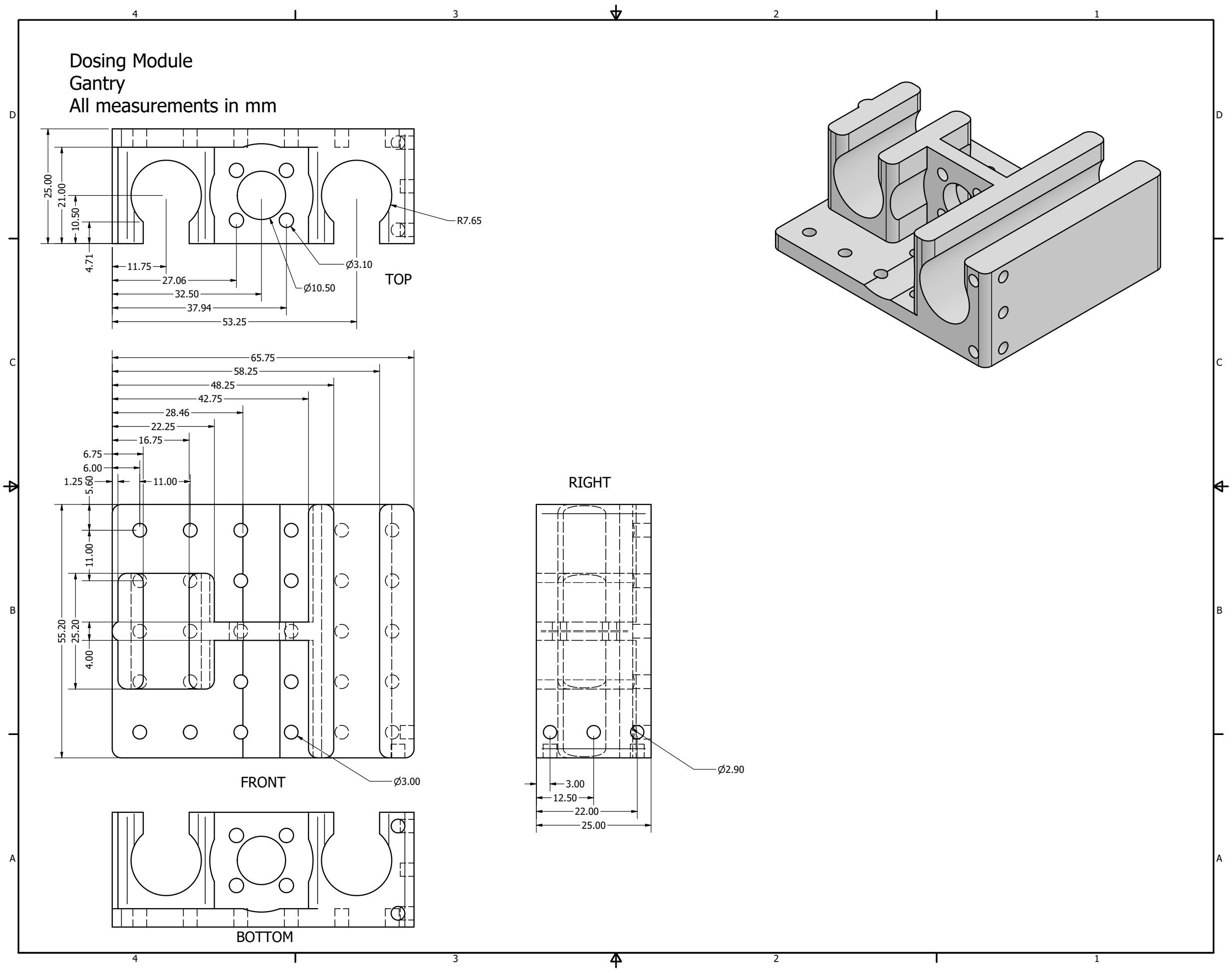


Figure S9: CAD drawing of the X-axis carriage used in the dosing module.

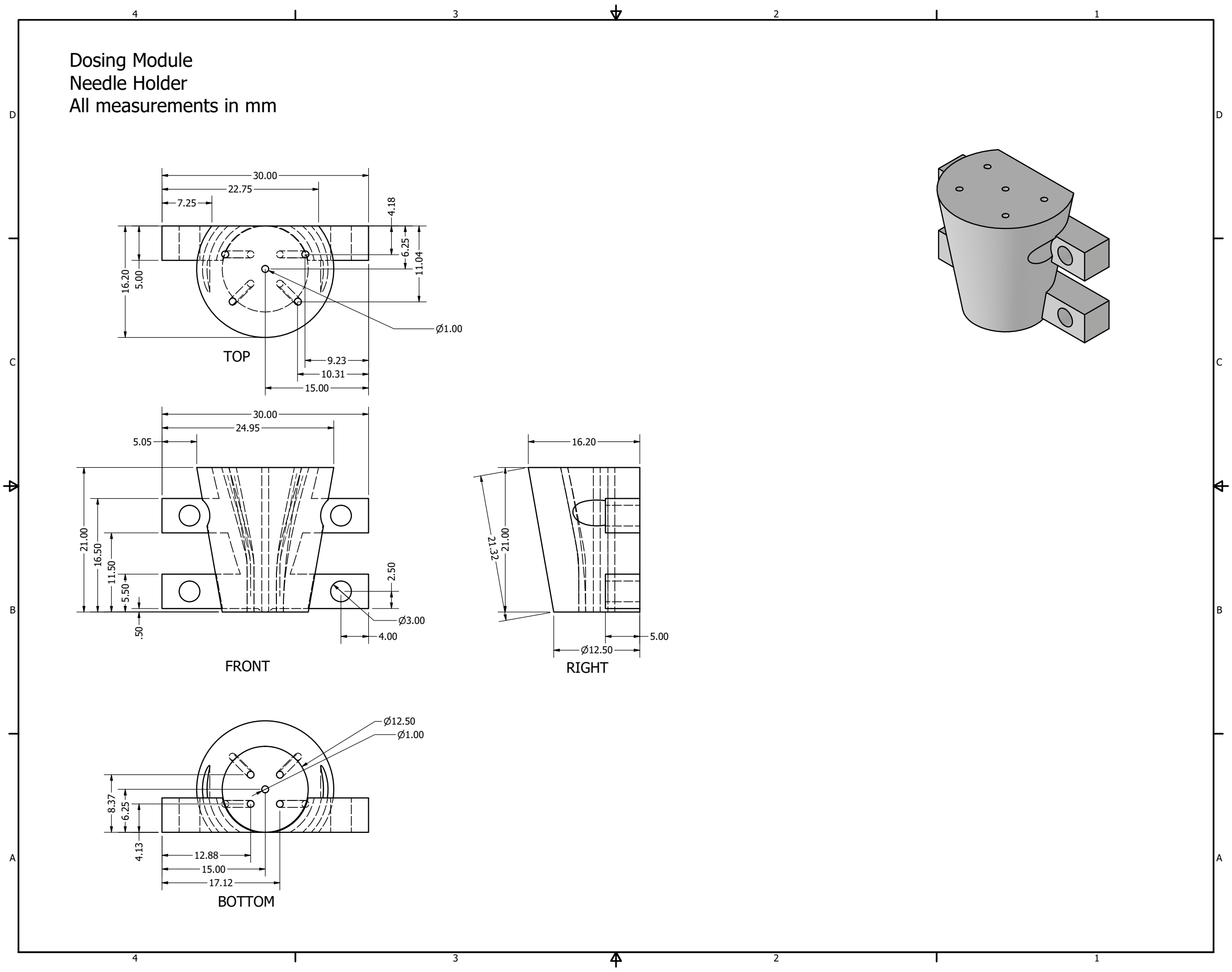


Figure S10: CAD drawing of the needle holder used in the dosing module.

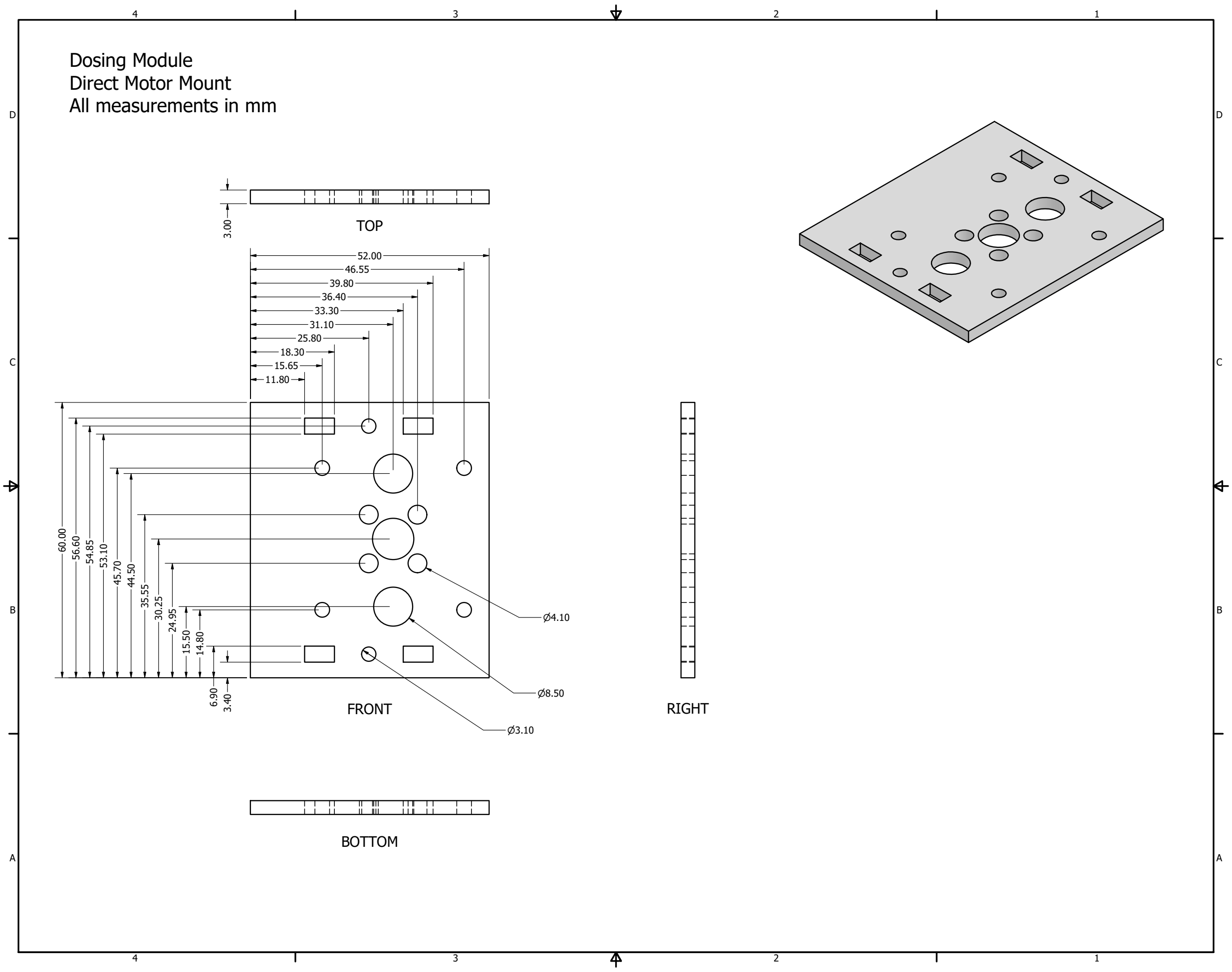


Figure S11: CAD drawing of a plate as a modification to the pump system shown in [2]. The modification allows for mounting the stepper motor directly on the driving thread instead of through gearing.

Machine precision

S4 Experiment order

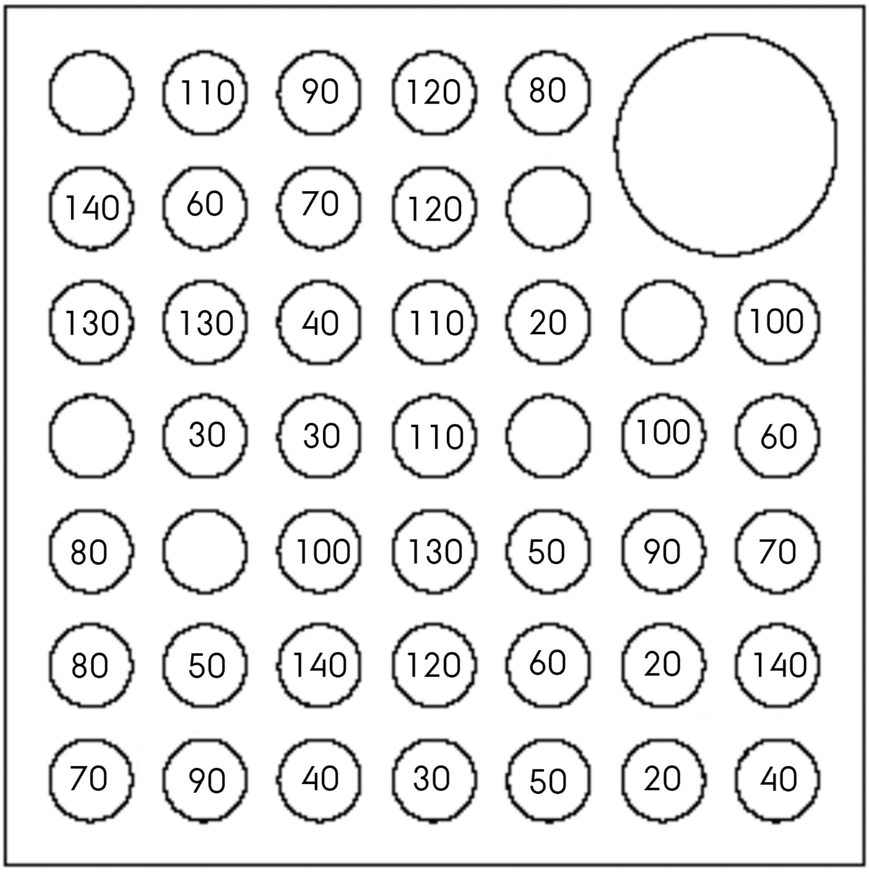


Figure S12: Image summarizing the experimental order after randomization and triplication. Each circle represents a vial on the experimental printer bed, with the numbers indicating the target degree of polymerization in each vial.

S5 Dosing calibration

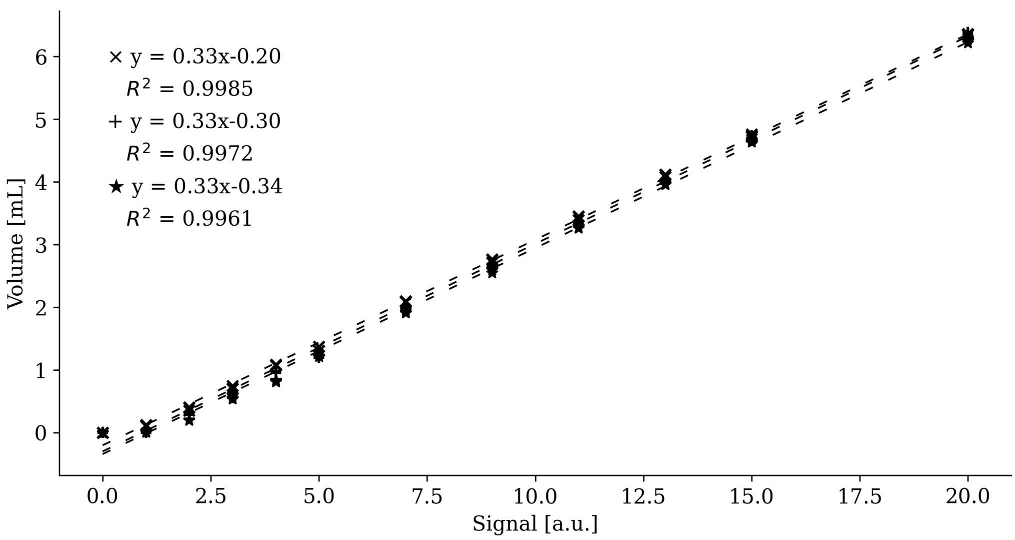


Figure S13: Calibrations of the pump module using toluene as the dispensed liquid.

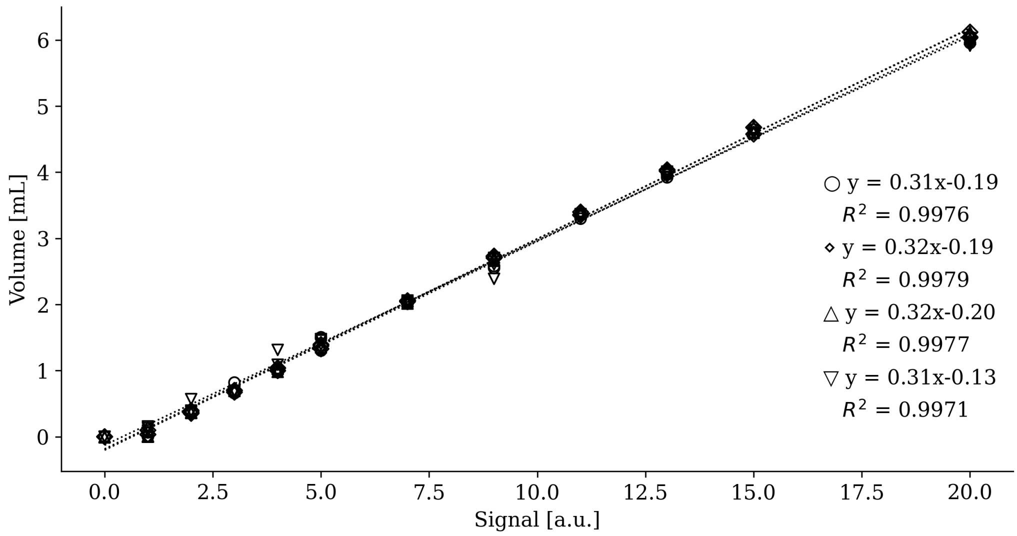
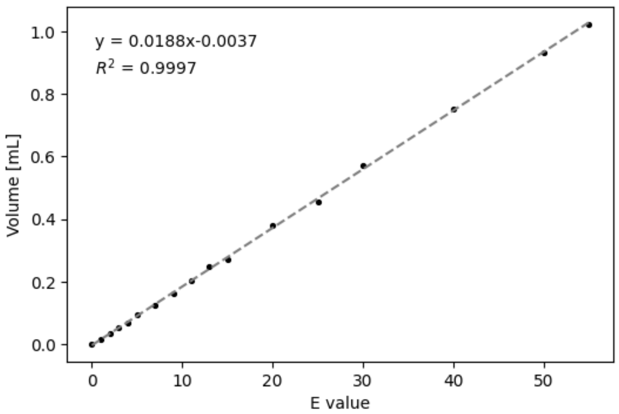
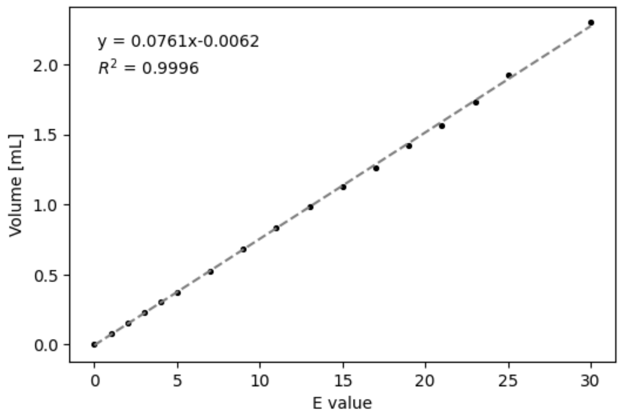


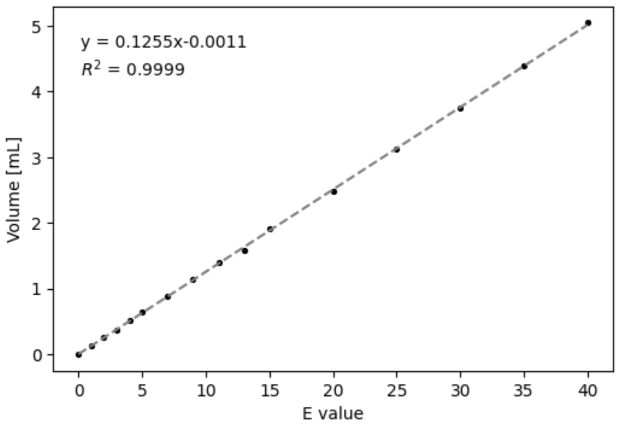
Figure S14: Calibrations of the pump module using water as the dispensed liquid.



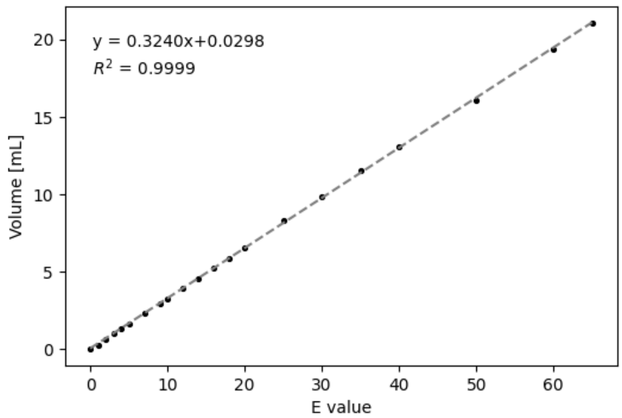
Calibration of the pump module using a 1 mL syringe



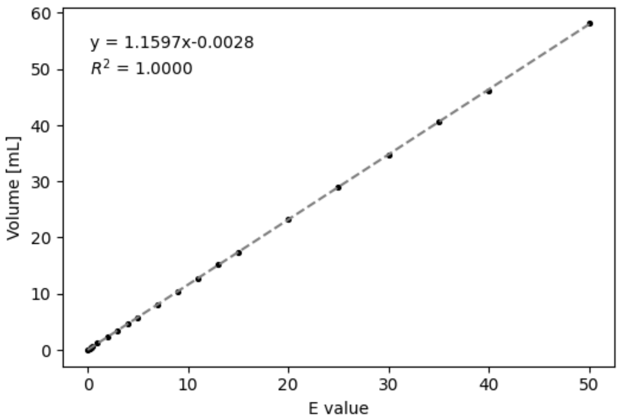
Calibration of the pump module using a 2 mL syringe



Calibration of the pump module using a 5 mL syringe



Calibration of the pump module using a 20 mL syringe



Calibration of the pump module using a 50 mL syringe

Figure S15: Calibration of various syringe sizes on a previous dosage module iteration. Each calibration was done by dispensing water.

Table S1: Summary of the calibration accuracy and precision. Each measurement was made as a triplicate and the order of dosing was randomized.

Target volume [mL]	Actual volume [mL]	Deviation [mL]
0.75	0.467 ± 0.014	0.297
1.50	1.240 ± 0.004	0.260
3.00	2.712 ± 0.045	0.288
4.00	3.729 ± 0.036	0.271
5.00	4.752 ± 0.014	0.248

Chemistry and Analysis

S6 ATR-FTIR and NMR of synthesised monomer

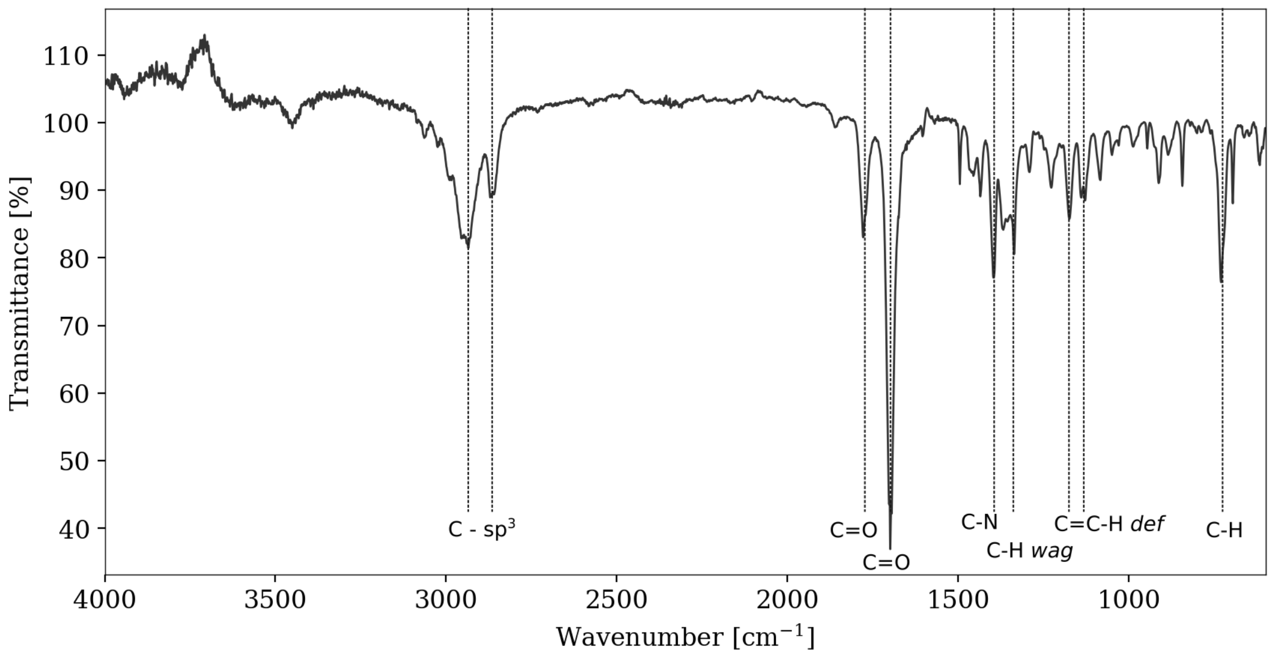


Figure S16: ATR-FTIR of the synthesised monomer.

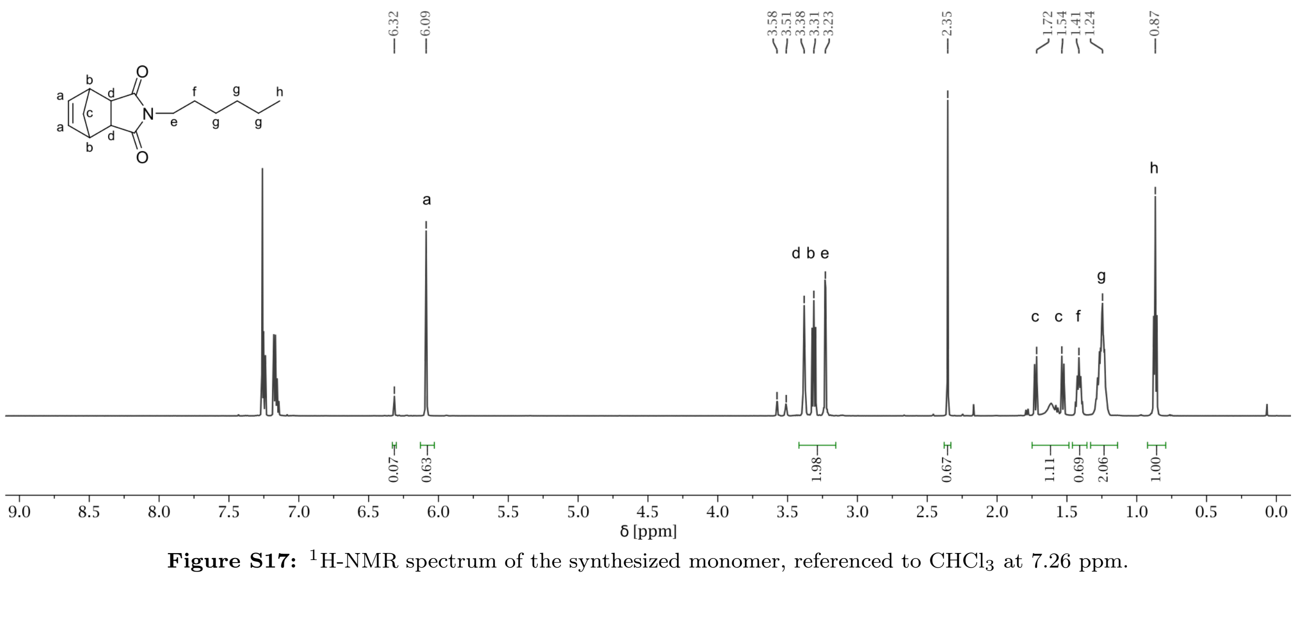


Figure S17: ^{1}H-NMR spectrum of the synthesized monomer, referenced to $CHCl_3$ at 7.26 ppm.

S7 Grubbs catalyst

The Grubbs 3rd Generation initiator was made by reacting Grubbs 2nd Generation with pyridine. The conversion was based on the color change from red/brown (Figure S18, left) to bright green (Figure S18, right), and the yield was determined to 97.9 %.

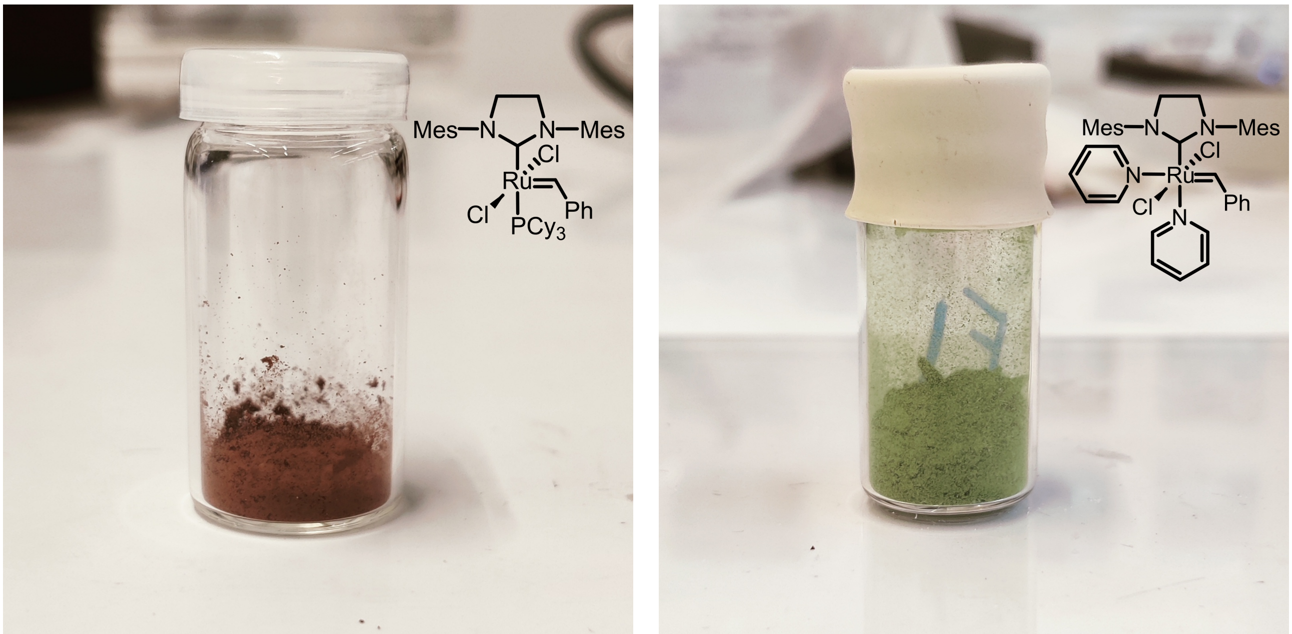


Figure S18: Images of the Grubbs 2nd generation catalyst (left) and the 3rd generation (right) after reaction with pyridine.

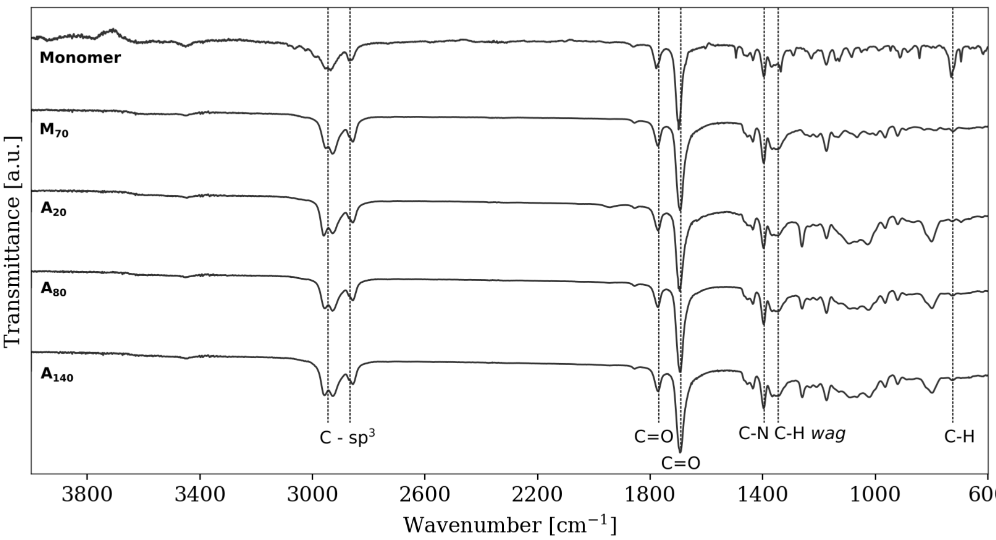


Figure S19: ATR-FTIR spectra of the monomer, the manual polymer $\mathbf{M_{70}}$ and the automatically produced polymers $\mathbf{A_{20}}$, $\mathbf{A_{80}}$, and $\mathbf{A_{140}}$, which represents the entire range.

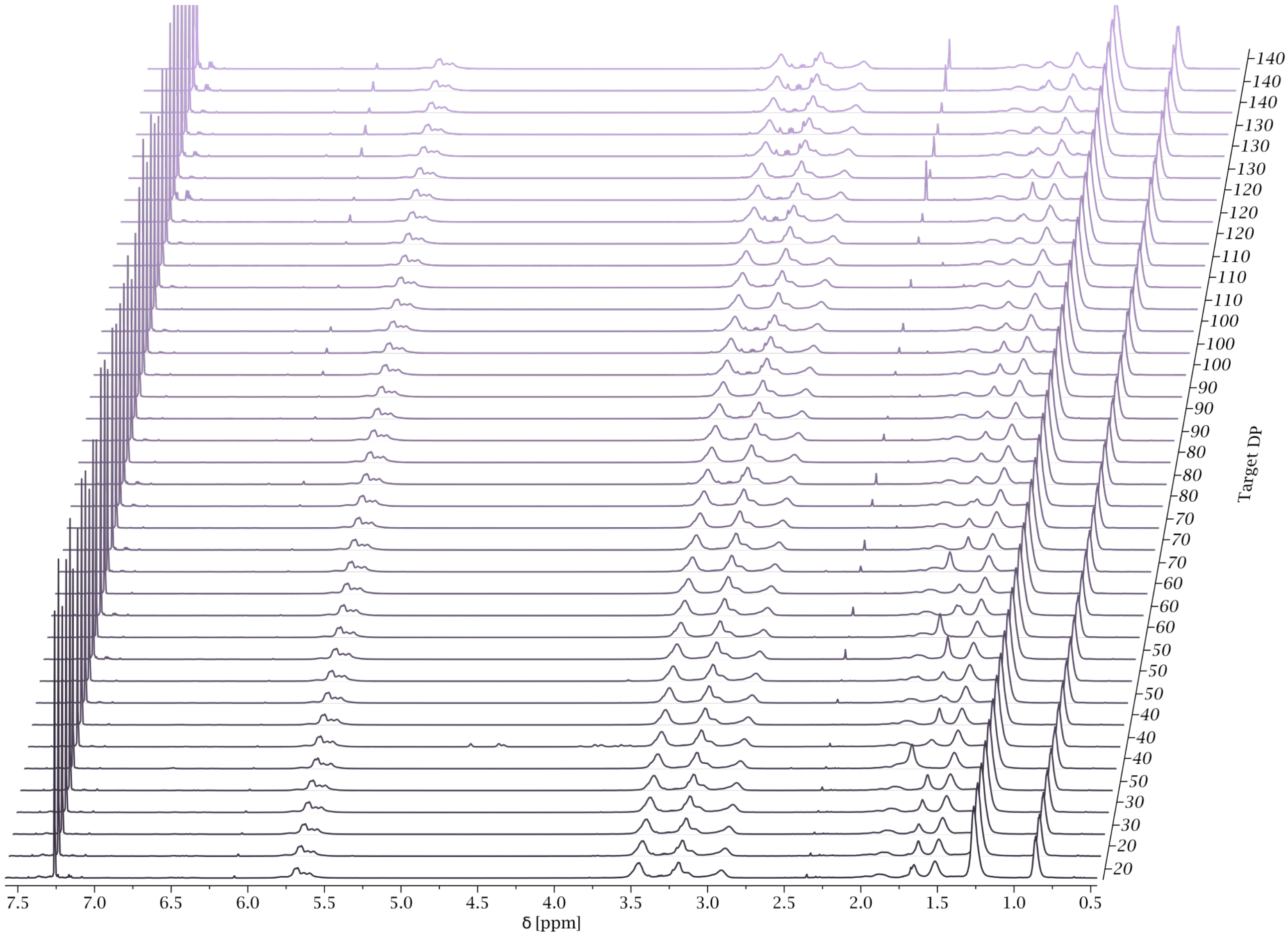


Figure S20: [1]H-NMR spectra of each 3x13 polymers automatically synthesized. Residuals from the deuterated solvent is seen at 7.26 ppm and impurities from toluene is present at 7.20 and 2.30 ppm.

S8 Gel Permeation Chromatography

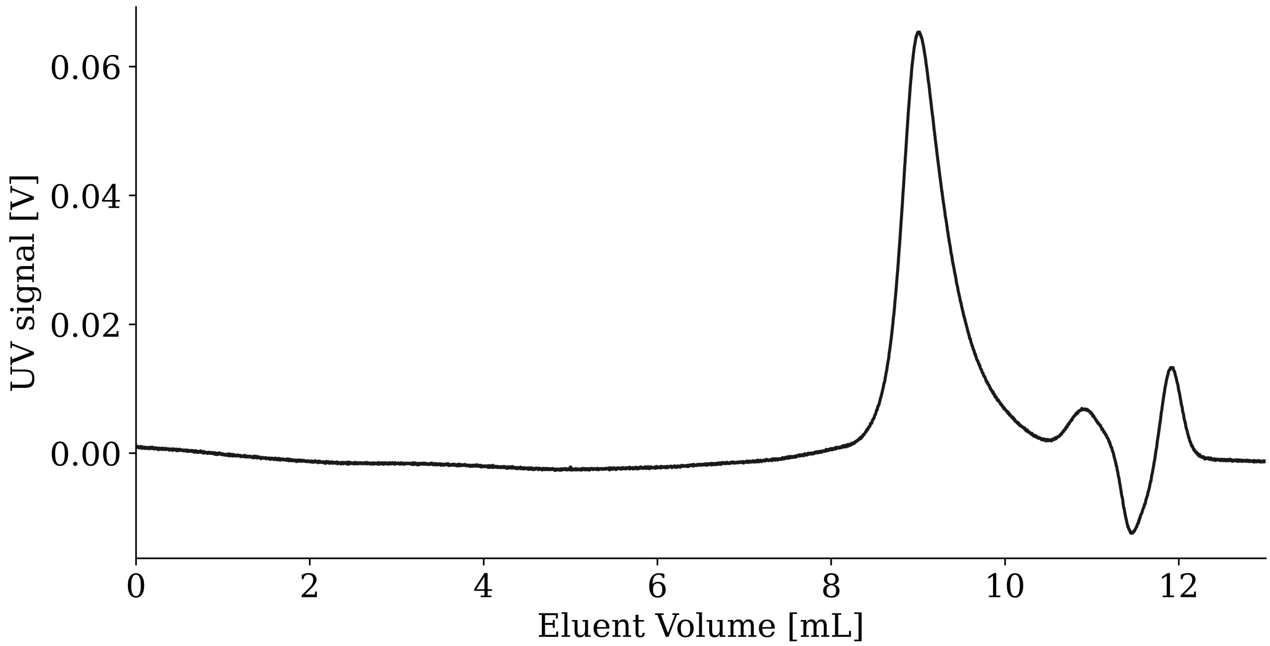


Figure S21: GPC chromatogram of M_{70}.

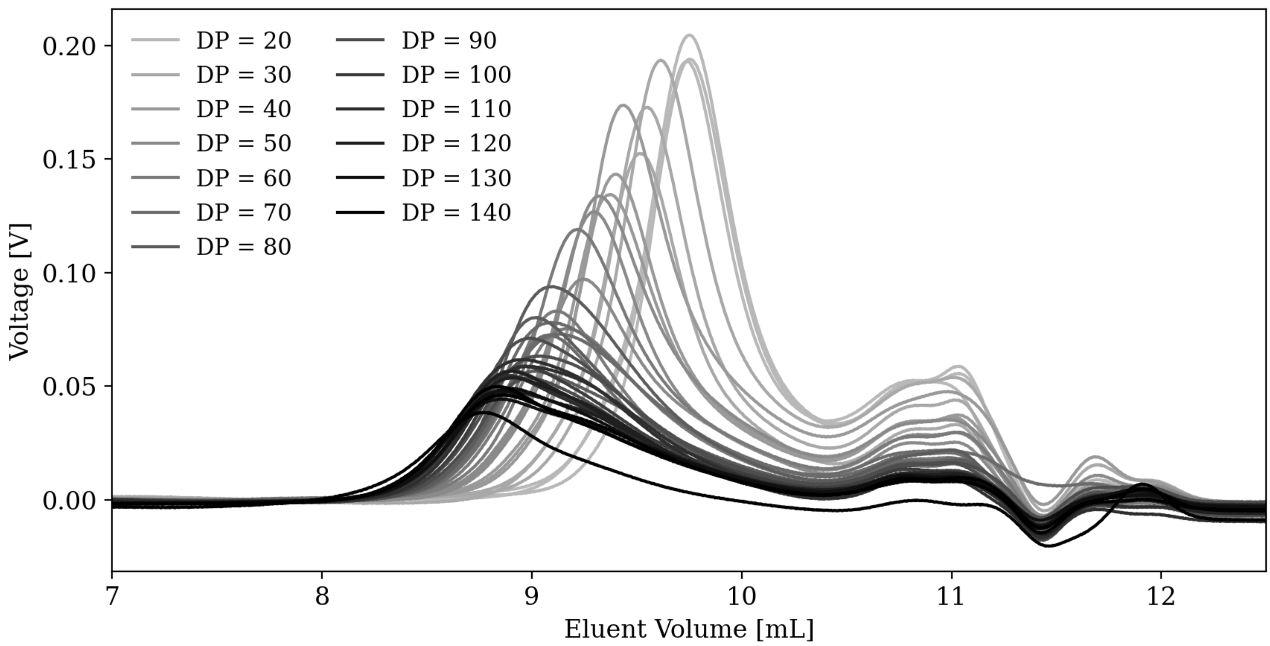


Figure S22: GPC chromatograms of all polymers synthesized by the ASM.

Table S2: The number and weight average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) and the dispersity ($Đ$) of the automatically synthesized polymers are determined according to polystyrene standards. Each target $\overline{DP}$ is given as an average of the triplicates. M_t denotes the theoretical mass of each polymer and the molecular weights.

DP	M_t [kDa]	$\overline{M}_n$ [kDa]	$\overline{M}_w$ [kDa]	$Đ$	Conversion [%]
20	5.67	7.99 ± 0.10	9.60 ± 0.26	1.20 ± 0.02	98.36
30	8.15	11.61 ± 0.79	14.39 ± 1.02	1.24 ± 0.01	99.01
40	10.62	15.33 ± 0.93	19.49 ± 1.41	1.27 ± 0.02	99.38
50	13.09	19.24 ± 1.09	25.65 ± 1.82	1.33 ± 0.02	99.67
60	15.57	23.68 ± 1.80	32.03 ± 2.62	1.35 ± 0.02	99.50
70	18.04	26.88 ± 1.12	38.11 ± 1.16	1.42 ± 0.02	99.34
80	20.51	28.36 ± 1.87	40.04 ± 3.03	1.41 ± 0.03	99.01
90	22.99	31.33 ± 1.07	46.11 ± 1.94	1.47 ± 0.02	99.01
100	25.46	34.51 ± 1.02	51.33 ± 1.96	1.49 ± 0.01	96.77
110	27.93	36.01 ± 2.69	54.97 ± 4.25	1.53 ± 0.02	99.34
120	30.41	36.81 ± 0.17	55.95 ± 1.61	1.52 ± 0.04	97.09
130	32.88	39.27 ± 0.94	60.78 ± 1.71	1.55 ± 0.02	95.54
140	35.35	46.44 ± 7.55	75.01 ± 14.61	1.61 ± 0.06	95.85

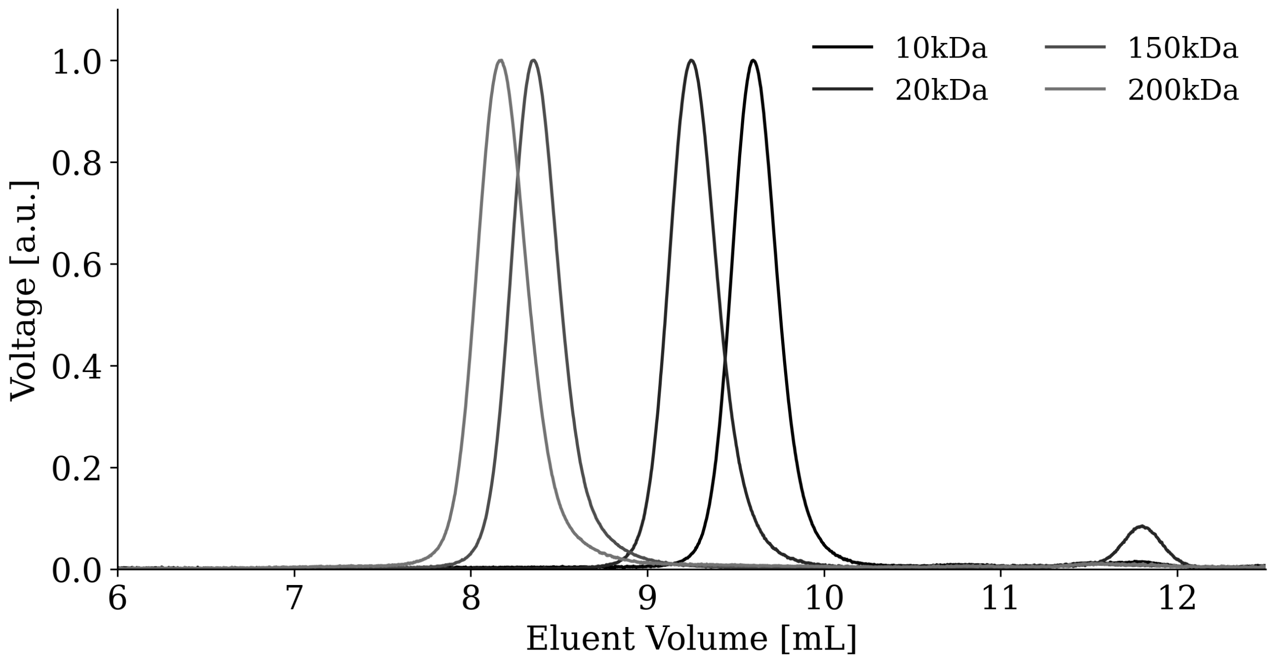


Figure S23: GPC chromatograms of the polystyrene standards used for calibration. The signals are normalized relative to the highest peak. All standards were obtained from Sigma Aldrich; 10 kDa ($Đ = 1.04$), 20 kDa ($Đ = 1.05$), 150 kDa ($Đ = 1.03$), and 200 kDa ($Đ = 1.03$)

Table S3: The number and weight average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) and the dispersity ($Đ$) of the polystyrene standard. M_t denotes the mass reported by the producer. Additionally, the table reports the conversion of the monomer calculated through ^{1}H-NMR

M_t [kDa]	$\overline{M}_n$ [kDa]	$\overline{M}_w$ [kDa]	$Đ$
10	9.28	10.05	1.08
20	18.94	20.83	1.10
150	126.65	139.93	1.10
200	188.81	209.05	1.11

Bill of Materials

Table S4: Bill of materials

Description	Quantity	Location	Notes	Cost [DKK]
General				
3D printer	1		We used a Prusa i3 clone with an Arduino Mega and a Ramps 1.4 shield attached [3]	3500
1.75 mm PLA filament	1 spool (1000 g)		For production of various parts and pieces	170
Wires	A lot	All over		36

RampsXB	1	Attachment to the Ramps 1.4 shield	RampsXB is an expired product, similar boards can be used (e.g. Ramps stepper expander)	-
M3 screws	A lot	All threads are made for M3 screws in various lengths	Get a set from 3 to 20 mm	150
Mechanical end-stop	1	Replaces the induction sensor for the Z-axis		80
Polycarbonate sheets, 3mm	About 1 m^2	Stirring and inert modules		299
Dosage module				
Custom pump	1-5	Attaches to the machine	Similar pump systems can be used	500 per pump
Bükert three-way solenoid valve	1 per pump	Placed on the pump	Controls the flow direction	1,061
Tube fittings	3 per valve	Fits the ports on the valve		66
Silicone tubing 4 mm ID	A lot	Pump module	Connects stock solutions to the machine	450 for 7.6 m
BlueCap flask 250 mL	1 per pump	Connected to the valve	Contains stock solution	25 per flask
Special cannula	1 per pump	Connects the blue cap to tubing		20 per needle
Rubber septum	1 per pump	BlueCap lid	Seals the modified BlueCap lid	20 per septum
50 x 0.8 mm 21g sterile syringe	1 box (100 pcs)	In the needle module	Different needles can be used with slight modifications	34
Stirring module				
12 DC motors	45	Stirring module		1750
Teflon coated magnets 20x6 mm	45	Stirring module		608
Teflon coated magnets 15x4.5 mm	45	Stirring module		428
PWM controller	3	Stirring module		300

ABS box	1	Stirring module	Holds the PWM controller	79
Atmosphere control module				
Luer lock male and female set	10 sets	In the silicone tubing and for gas inlet in the atmosphere control module		100
Total cost	With 1 pump			9,676 $\approx 1,300$ EUR
	With 5 pumps			16,439 $\approx 2,205$ EUR

References

[1] T. B. Jensen, J. R. Saugbjerg, and M. L. Henriksen, *Information and documentation on the automatic synthesis machine via github repository*, 2023. [Online]. Available: `https://gitfront.io/r/user-2909906/5ykxNBqEmKoo/ASM-v1.0/`.

[2] [Online]. Available: `https://osf.io/qcnjt/`, 02/03/2023.

[3] [Online]. Available: `http://prusa.samle.dk/`.