Electronic Supplementary Material (ESI) for Digital Discovery.

Supporting Information

Operator-Independent High-Throughput Polymerization Screening Based on Automated Inline NMR and Online SEC

Joren Van Herck[a], Iyomali Abeysekera[a], Axel-Laurenz Buckinx[a], Kewei Cai[a], Jordan Hooker[a], Kirti Thakur[a], Emma Van de Reydt[a], Pieter-Jan Voorter[a], Dries Wyers[a] and Tanja Junkers[a]

[a] Polymer Reaction Design Group, School of Chemistry, Monash University, 19 Rainforest Walk, Clayton, Victoria 3800, Australia

Contents

Materials

Chemicals

The monomers methyl acrylate (MA, 99% Merck), ethyl acrylate (EA, 99% Sigma-Aldrich), propyl acrylate (PA, 95% Thermo Scientific), isobutyl acrylate (*iso*BA, >99.0% TCI), *n*-butyl acrylate (*n*BA, Merck), 2-ethylhexyl acrylate (EHA, Merck), cyclohexyl acrylate (cHA, Chem-Supply) and dodecyl acrylate (DA, >98.0 % TCI) were deinhibited over a column of activated basic alumina prior to use. 2-(Dodecylthiocarbonothioylthio)propionic acid (DOPAT) was synthesized according to literature.[1] The reagents and chemicals that were used for the synthesis of DOPAT were purchased from Sigma Aldrich or VWR. 1,1'-azobis(isobutyronitrile) (AIBN, 98% Sigma-Aldrich) was recrystallized twice from methanol prior to use. Butyl acetate (Merck) and THF (Sigma-Aldrich) was used as received.

Reactor Setup

Gastight syringe (100MR-LL-GT 10ML, SGE) and a syringe pump (Fusion 100, Chemyx) were used to feed the reactor mixture the flow reactor. PFA tubing (1/16'' x 0.75 mm ID) was used for all flow segments of the setup. A peristaltic pump (SF-10, Vapourtec) diluted the flow stream prior to SEC analysis. A 6-port switch valve (VICI VALCO EUDA-C6W) controlled the column injections.

Table S 1 *Overview of flow parts used in setup*

	IDEX XP-230	Flangeless Fitting Natural, PEEK, 1/4-28 Flat-Bottom, for 1/16" OD
	IDEX F-120	One-Piece Fingertight 10-32 Coned, for 1/16" OD Natural
	IDEX P-629	Luer Adapter Female Luer x 10-32 Female, Tefzel™ (ETFE) Natural
	IDEX P-702	Union Assembly PEEK .020 thru hole, for 1/16" OD"
	IDEX P-512	Y Assembly PEEK 1/4-28 .020in

Characterisation

Inline NMR reaction monitoring was accomplished by recording ^{1}H spectra (acquisition bandwidth 5 kHz: 83 ppm; 90 pulse width: 7 microseconds; dwell time: 200 microseconds; number of points: 32,768; acquisition time: 6.554 seconds; repetition time: 17 seconds), using a low field benchtop 60 MHz NMR (Magritek, Spinsolve 1.19.0). A Powershim (40min) was performed at the start of the day. The reaction monitor protocol (RMX) was used for data acquisition. All spectra were auto-phased in the Spinsolve software prior to analysis.

SEC was performed on a custom designed PSS system, operated by PSS WinGPC software, equipped with a PSS SDV analytical 3.0 µm guard column (50 x 8 mm), followed by one PSS SDV analytical 3.0 µm particles with porosity of 1000 Å (300 x 8 mm) and an evaporative light scattering detector (ELSD) ELS1300 using THF as eluent at 40 °C with a flow rate of 1 $mL \cdot min^{-1}$ using an isocratic PSS SECcurity pump. The SEC system was calibrated using linear narrow polystyrene standards ranging from 474 – 7.5 x 106 g mol^{-1} ($K = 14.1 \times 10^{-5}$ dL g^{-1} and $\alpha = 0.70$)[2]. Molar masses and dispersity values were calculated against the Mark-Houwink (MHKS) parameters of the various monomers when available (pMA[3]: $K = 10.2 \times 10^{-5}$ $dL \cdot g^{-1}$ and $\alpha = 0.740$, pEA[4]: $K = 12.2 \times 10^{-5}$ $dL \cdot g^{-1}$ and $\alpha = 0.700$, pBA[4]: $K = 12.2 \times 10^{-5}$ $dL \cdot g^{-1}$ and $\alpha = 0.700$, pEHA: $K = 12.2 \times 10^{-5}$ $dL \cdot g^{-1}$ and $\alpha = 0.700$). If MHKS parameters were not available, values for pBA were used.

Reactor Setup

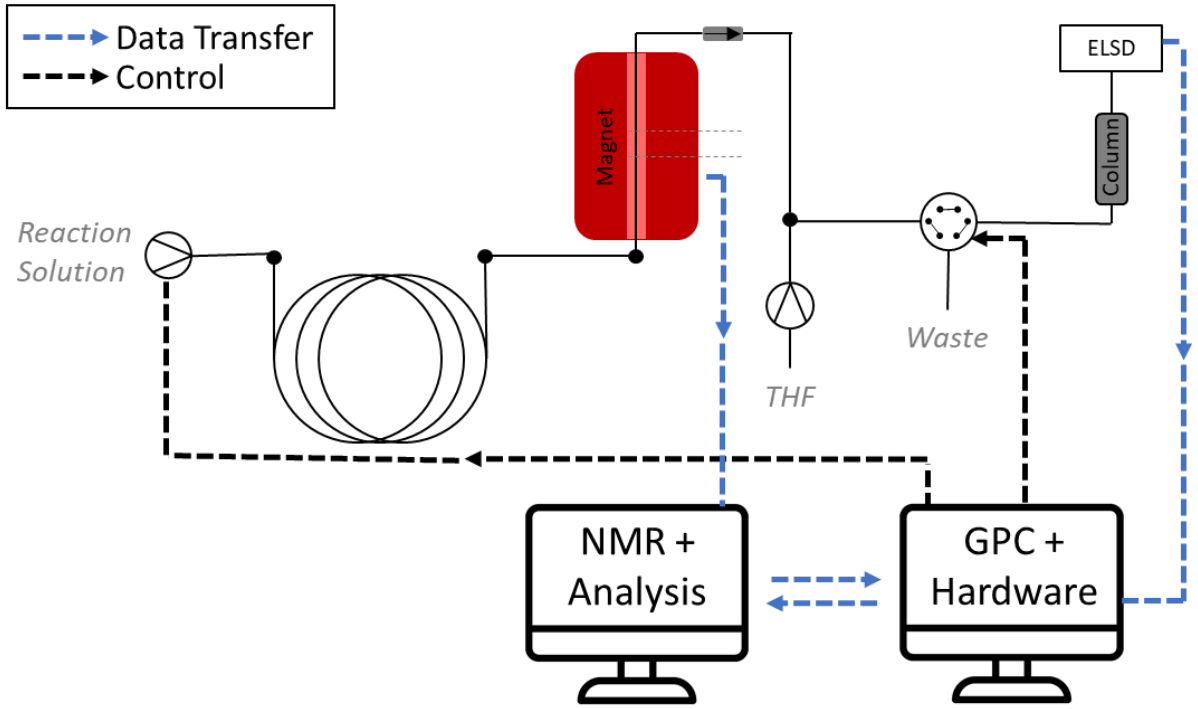


Figure S 1 *Automated screening platform. One PC is responsible for reaction initialisation, NMR data acquisition and analysis. Another PC collects SEC data and controls the hardware, i.e. pumps and switch valve.*

Reaction solutions were transferred to a 10 mL gastight syringe and placed in the holder of the syringe pumps. The syringes pump (software controlled) delivered the reagent solution to the flow reactor ($V_{reactor}$ = 0.4 mL), which was placed in an isothermal oil bath (80°C). The outlet of the reactor was extended to pass through the benchtop NMR. The dead volume ($V_{dead,\,1}$) between the outlet of the reactor and the measuring area of the benchtop NMR was 0.32mL. When exiting the NMR, the stream was diluted with filtered THF, delivered by a peristaltic pump, through a static y-shaped mixer. An inline check valve was placed before the dilution mixer to ensure a correct flow direction. The dead volume ($V_{dead,\,2}$) between the measuring area of the NMR and the mixer was 0.17mL. Diluted samples were injected into the SEC column via a computer-steered switch valve (**Figure S 2**). The dead volume ($V_{dead,\,3}$) between the mixer and the SEC column was 0.17mL.

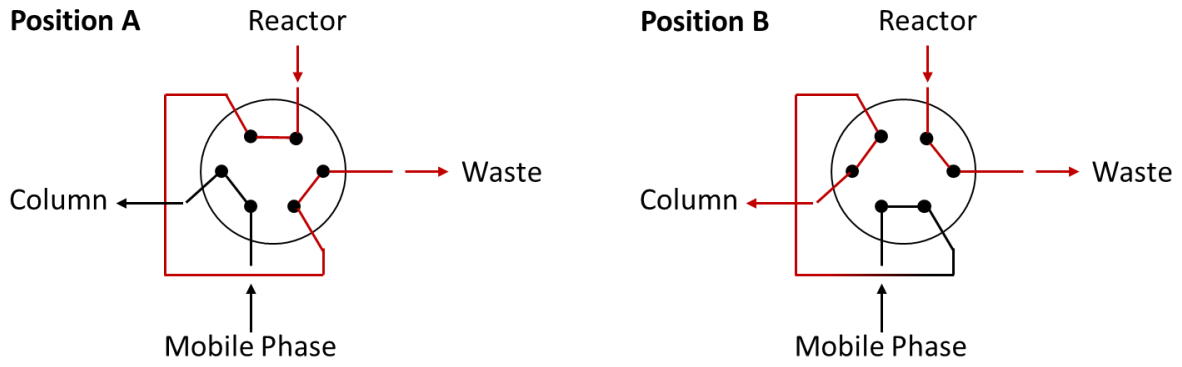


Figure S 2 *Switch valve position for column injections. When in position A, a 5µL sample loop was loaded with reactor solution and directed to the waste. A brief switch (500ms) to position B injects the sample onto the column.*

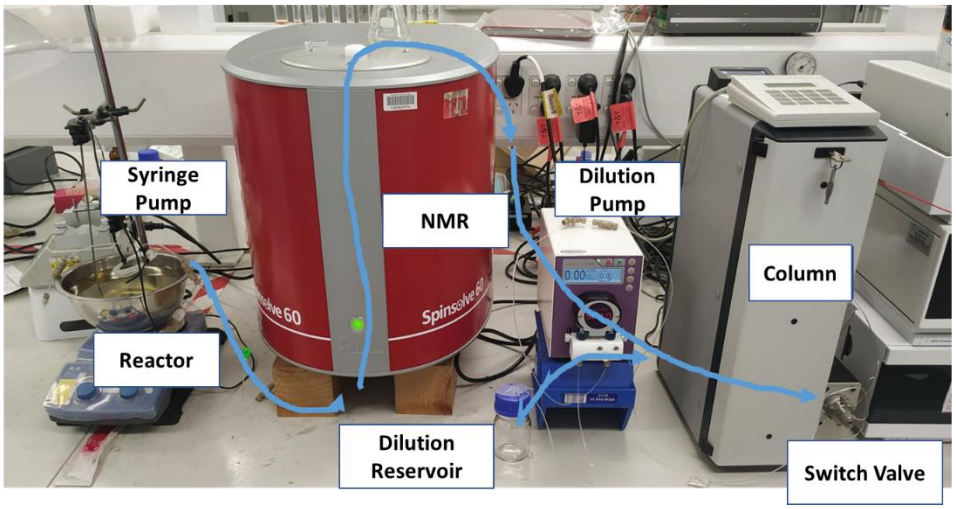


Figure S 3 *Automated screening platform in lab.*

Polymerization Procedures

In a typical procedure, the RAFT-agent DOPAT, the thermal initiator AIBN, the monomer and solvent butyl acetate were added in a glass vial. The monomer was screened in three different concentration; 1M, 2M and 4M. Due to the high molecular weight of the monomer dodecyl acrylate, a 4M screening was not possible and 0.5M was chosen as an alternative. For all reaction, the ratio [monomer]:[DOPAT] (*DP*) was 50 and the concentration of AIBN was set to 0.005 M. (See **Table S 2-Table S 9** for detailed reaction solutions). The glass vial was sealed with a rubber septum and the solution was purged with nitrogen (N_2) for 5 minutes. Next, the reaction solution was transferred to a 10 mL gastight syringe, prepurged with N_2 (3x), and placed in the holder of the syringe pumps. The flow reactor was manually flushed with butyl acetate before each new reaction. After the syringe was connected to the flow reactor, the pump was started to ensure the block of the pump is against the plunger. Once the reaction solution was moving in the tubing, the pump was manually paused and the user could initiate the experiment via the software. All reactions were performed at 80 ^{o}C.

Table S 2 *Reaction solution for the 1M, 2M and 4M methyl acrylate (MA) screening.*

Methyl Acrylate								
1M MA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.070		0.0002	0.0200	1.00
monomer	MA	86.09	0.95	0.864	0.91	0.0100	1.0038	50.30
initiator	AIBN	164.21		0.008		0.0000	0.0049	0.24
solvent	Butyl Acetate	116.16	0.882	8.021	9.094	0.0691	6.9023	345.84
2M MA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.140		0.0004	0.040	1.00
monomer	MA	86.09	0.95	1.720	1.81	0.0200	1.998	50.02
initiator	AIBN	164.21		0.008		0.0000	0.005	0.12
solvent	Butyl Acetate	116.16	0.882	7.222	8.188	0.0622	6.218	155.69
4M MA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.280		0.0008	0.0799	1.00
monomer	MA	86.09	0.95	3.439	3.62	0.0399	3.9967	50.02
initiator	AIBN	164.21		0.008		0.0000	0.0049	0.06
solvent	Butyl Acetate	116.16	0.882	5.623	6.375	0.0484	4.8429	60.61

Table S 3 *Reaction solution for the 1M, 2M and 4M ethyl acrylate (EA) screening.*

Ethyl Acrylate								
1M EA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.036		0.0001	0.0205	1.00
monomer	EA	100.11	0.94	0.498	0.53	0.0050	0.9953	48.47
initiator	AIBN	164.21		0.004		0.0000	0.0049	0.24
solvent	Butyl Acetate	116.16	0.882	3.943	4.47	0.0339	6.7881	330.54
2M EA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.140		0.0004	0.040	1.00
monomer	EA	100.11	0.94	2.002	2.13	0.0200	2.000	50.09
initiator	AIBN	164.21		0.008		0.0000	0.005	0.12
solvent	Butyl Acetate	116.16	0.882	6.941	7.87	0.0598	5.976	149.65
4M EA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.139		0.0004	0.0793	1.00
monomer	EA	100.11	0.94	2.002	2.13	0.0200	4.0000	50.45
initiator	AIBN	164.21		0.004		0.0000	0.0049	0.06
solvent	Butyl Acetate	116.16	0.882	2.531	2.87	0.0218	4.3584	54.97

Table S 4 *Reaction solution for the 1M, 2M and 4M propyl acrylate (PA) screening.*

Propyl Acrylate								
1M PA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.036		0.0001	0.0205	1.00
monomer	PA	114.14	0.92	0.580	0.63	0.0051	1.0118	49.45
initiator	AIBN	164.21		0.004		0.0000	0.0050	0.24
solvent	Butyl Acetate	116.16	0.882	3.871	4.389	0.0333	6.6399	324.55
2M PA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.072		0.0002	0.041	1.00
monomer	PA	114.14	0.92	1.136	1.235	0.0100	1.987	48.34
initiator	AIBN	164.21		0.004		0.0000	0.005	0.12
solvent	Butyl Acetate	116.16	0.882	3.330	3.775	0.0287	5.721	139.19
4M PA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.140		0.0004	0.0794	1.00
monomer	PA	114.14	0.92	2.302	2.502	0.0202	4.0125	50.50
initiator	AIBN	164.21		0.005		0.0000	0.0061	0.08
solvent	Butyl Acetate	116.16	0.882	2.226	2.524	0.0192	3.8131	47.99

Table S 5 *Reaction solution for the 1M, 2M and 4M butyl acrylate (BA) screening.*

Butyl Acrylate								
1M BA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.042		0.0001	0.0200	1.00
monomer	BA	128.17	0.89	0.765	0.86	0.0060	0.9960	49.85
initiator	AIBN	164.21		0.005		0.0000	0.0051	0.25
solvent	Butyl Acetate	116.16	0.882	4.530	5.136	0.0390	6.5039	325.54
2M BA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.086		0.0002	0.041	1.00
monomer	BA	128.17	0.89	1.540	1.73	0.0120	2.002	48.97
initiator	AIBN	164.21		0.005		0.0000	0.005	0.13
solvent	Butyl Acetate	116.16	0.882	3.766	4.27	0.0324	5.404	132.18
4M BA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.168		0.0005	0.0798	1.00
monomer	BA	128.17	0.89	3.079	3.46	0.0240	4.0016	50.14
initiator	AIBN	164.21		0.005		0.0000	0.0051	0.06
solvent	Butyl Acetate	116.16	0.882	2.244	2.544	0.0193	3.2173	40.31

Table S 6 *Reaction solution for the 1M, 2M and 4M isoButyl acrylate (iBA) screening.*

isoButyl Acrylate								
1M iBA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.043		0.0001	0.0202	1.00
monomer	isoBA	128.17	0.89	0.765	0.86	0.0060	0.9961	49.26
initiator	AIBN	164.21		0.005		0.0000	0.0051	0.25
solvent	Butyl Acetate	116.16	0.882	4.529	5.135	0.0390	6.5037	321.64
2M iBA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.084		0.0002	0.040	1.00
monomer	isoBA	128.17	0.89	1.540	1.73	0.0120	2.001	50.14
initiator	AIBN	164.21		0.005		0.0000	0.005	0.13
solvent	Butyl Acetate	116.16	0.882	3.768	4.272	0.0324	5.404	135.39
4M iBA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.168		0.0005	0.0797	1.00
monomer	isoBA	128.17	0.89	3.071	3.45	0.0240	3.9927	50.08
initiator	AIBN	164.21		0.005		0.0000	0.0055	0.07
solvent	Butyl Acetate	116.16	0.882	2.249	2.55	0.0194	3.2270	40.48

Table S 7 *Reaction solution for the 1M, 2M and 4M ethylhexyl acrylate (EHA) screening.*

Ethylhexyl Acrylate								
1M EHA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.042		0.0001	0.0200	1.00
monomer	2EHA	184.28	0.885	1.106	1.25	0.0060	1.0005	50.11
initiator	AIBN	164.21		0.005		0.0000	0.0051	0.25
solvent	Butyl Acetate	116.16	0.882	4.190	4.75	0.0361	6.0111	301.07
2M EHA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.086		0.0002	0.041	1.00
monomer	2EHA	184.28	0.885	2.213	2.5	0.0120	2.001	49.23
initiator	AIBN	164.21		0.005		0.0000	0.005	0.12
solvent	Butyl Acetate	116.16	0.882	3.087	3.5	0.0266	4.429	108.97
4M EHA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.168		0.0005	0.0799	1.00
monomer	2EHA	184.28	0.885	4.425	5	0.0240	4.0021	50.11
initiator	AIBN	164.21		0.005		0.0000	0.0051	0.06
solvent	Butyl Acetate	116.16	0.882	0.882	1	0.0076	1.2655	15.85

Table S *8 Reaction solution for the 1M, 2M and 4M cyclohexyl acrylate (cHA) screening.*

Cyclohexyl Acrylate								
1M cHA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.070		0.0002	0.0199	1.00
monomer	cycloHA	154.21	0.975	1.538	1.5777	0.0100	0.9987	50.10
initiator	AIBN	164.21		0.008		0.0000	0.0049	0.25
solvent	Butyl Acetate	116.16	0.882	7.418	8.41	0.0639	6.3936	320.75
2M cHA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.141		0.0004	0.040	1.00
monomer	cycloHA	154.21	0.975	3.088	3.167	0.0200	2.002	49.97
initiator	AIBN	164.21		0.008		0.0000	0.005	0.12
solvent	Butyl Acetate	116.16	0.882	6.029	6.8354	0.0519	5.189	129.51
4M cHA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.280		0.0008	0.0799	1.00
monomer	cycloHA	154.21	0.975	6.161	6.3186	0.0399	3.9978	50.02
initiator	AIBN	164.21		0.008		0.0000	0.0049	0.06
solvent	Butyl Acetate	116.16	0.882	3.241	3.6743	0.0279	2.7919	34.93

Table S 9 *Reaction solution for the 0.5M,1M and 2M dodecyl acrylate (DA) screening.*

Dodecyl Acrylate								
0.5M DA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.021		0.0001	0.0100	1.00
monomer	Dodecyl-A	240.38	0.884	0.725	0.82	0.0030	0.5023	50.35
initiator	AIBN	164.21		0.005		0.0000	0.0051	0.51
solvent	Butyl Acetate	116.16	0.882	4.572	5.184	0.0394	6.5560	657.16
1M DA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.042		0.0001	0.020	1.00
monomer	Dodecyl-A	240.38	0.884	1.441	1.63	0.0060	0.999	50.04
initiator	AIBN	164.21		0.005		0.0000	0.005	0.25
solvent	Butyl Acetate	116.16	0.882	3.853	4.369	0.0332	5.530	276.92
2M DA								
class	**name**	**M**	**density**	**mass (g)**	**V (mL)**	**moles (mol)**	**Molar (M)**	**eq**
RAFT	DoPAT	350.6		0.086		0.0002	0.0409	1.00
monomer	Dodecyl-A	240.38	0.884	2.882	3.26	0.0120	1.9998	48.87
initiator	AIBN	164.21		0.005		0.0000	0.0051	0.12
solvent	Butyl Acetate	116.16	0.882	2.412	2.735	0.0208	3.4640	84.66

Graphic User Interface & Metadata Storage

A self-written python script controlled the experiment flow. A graphic user interface (GUI) was created with the python library tkinter to make the software easy to use. Besides the initialisation of the experiment via the GUI, the python script was also responsible for data analysis. A LabView script controlled the pumps and switch valve. The LabView interface gives the operator a visual overview of reaction progress (**Figure S 5**). Moreover, since the LabView script is independent of the Python script, reactions were not lost when a bug occurred in the development phase of the platform.

In general, a *communication folder* is responsible for metadata transfer between the GUI and the LabView Control script. A standardized csv file with reaction parameters is created by Python and read out by LabView. Right before the reaction is started, an *experiment folder* is initialized by the GUI. A new directory in a dedicated folder is created in the form of "*year/month/day/time_ExperimentCode*". Since all the data is stored on the school drive, reaction progress can be followed from personal devices. Additionally, a dated template of the directory makes experiments easy to find. After the reaction is started, the LabView script performs the reaction autonomously and independent from the Python GUI. The Python software extracts the NMR and SEC data from the respective folders and updates the experiment folder in real-time (**Figure S 4**).

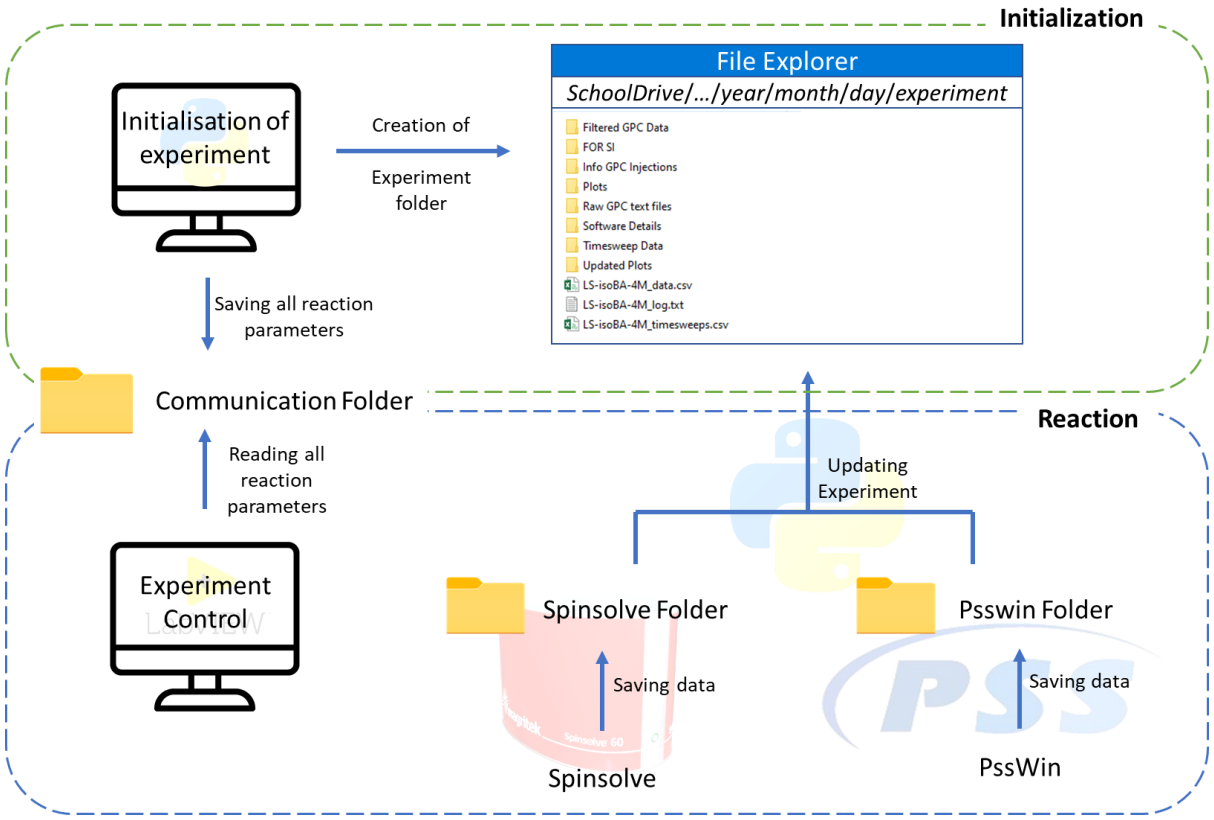


Figure S 4 *General software structure of the screening platform.*

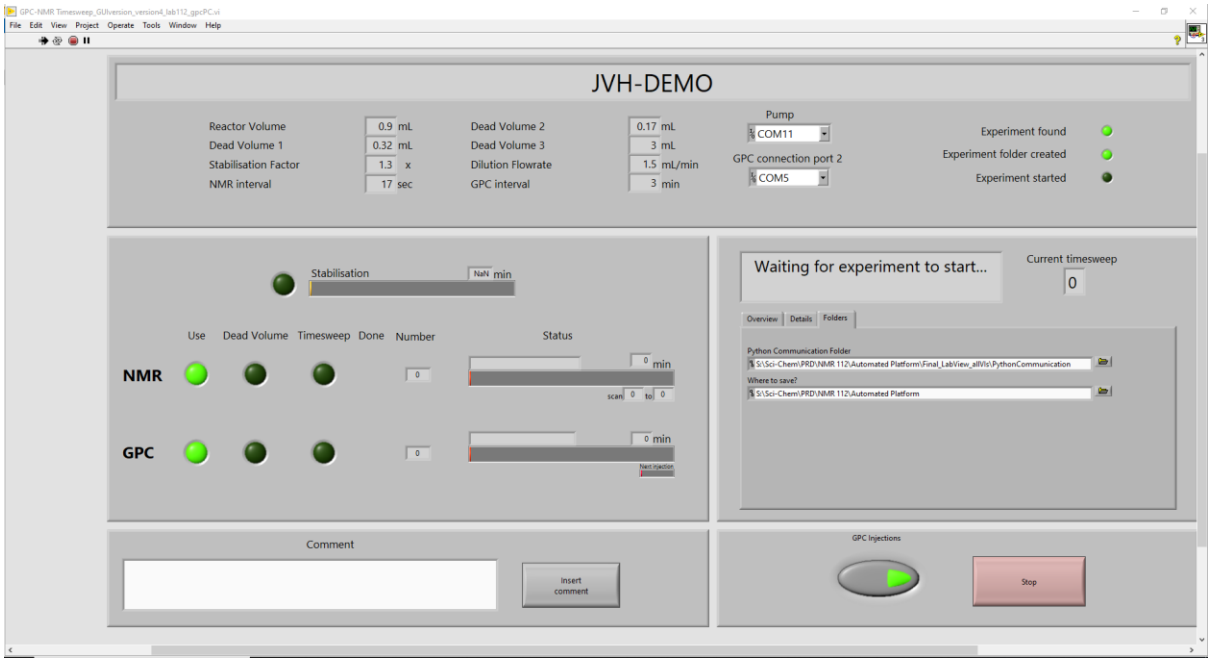


Figure S 5 *Screenshot of the LabView interface.*

Once started, the reaction progress can be followed on the LabView interface (**Figure S 5**). The top window displays the parameters of the current reaction. Green lights and progress bars (middle – left window) gives the operator a visual indication of the time and phase of the experiment, e.g. timesweep or dead volume and scan numbers. Status and software details are given in the middle - right window. Real-time comments can be entered (bottom – left window) and are saved with a timestamp in the log text file of the experiment. Lastly, if abnormalities in the reactor setup (e.g. leaks) are observed in the setup, SEC injections can be cancelled while still continuing with NMR data collection (bottom – right window).

Mode of Operation

In a first step, the operator can choose the mode of operation: A reaction screening with only the benchtop NMR or a screening using the benchtop NMR and SEC measurements (**Figure S 6**). Besides the extra GPC data collection and analysis in the latter, the two option are based on the same script. In this work, all reactions are performed in the *NMR-GPC* mode. Additionally, the saving folders can be altered by the operator and are saved in a standardized csv file (**Table S 10**).

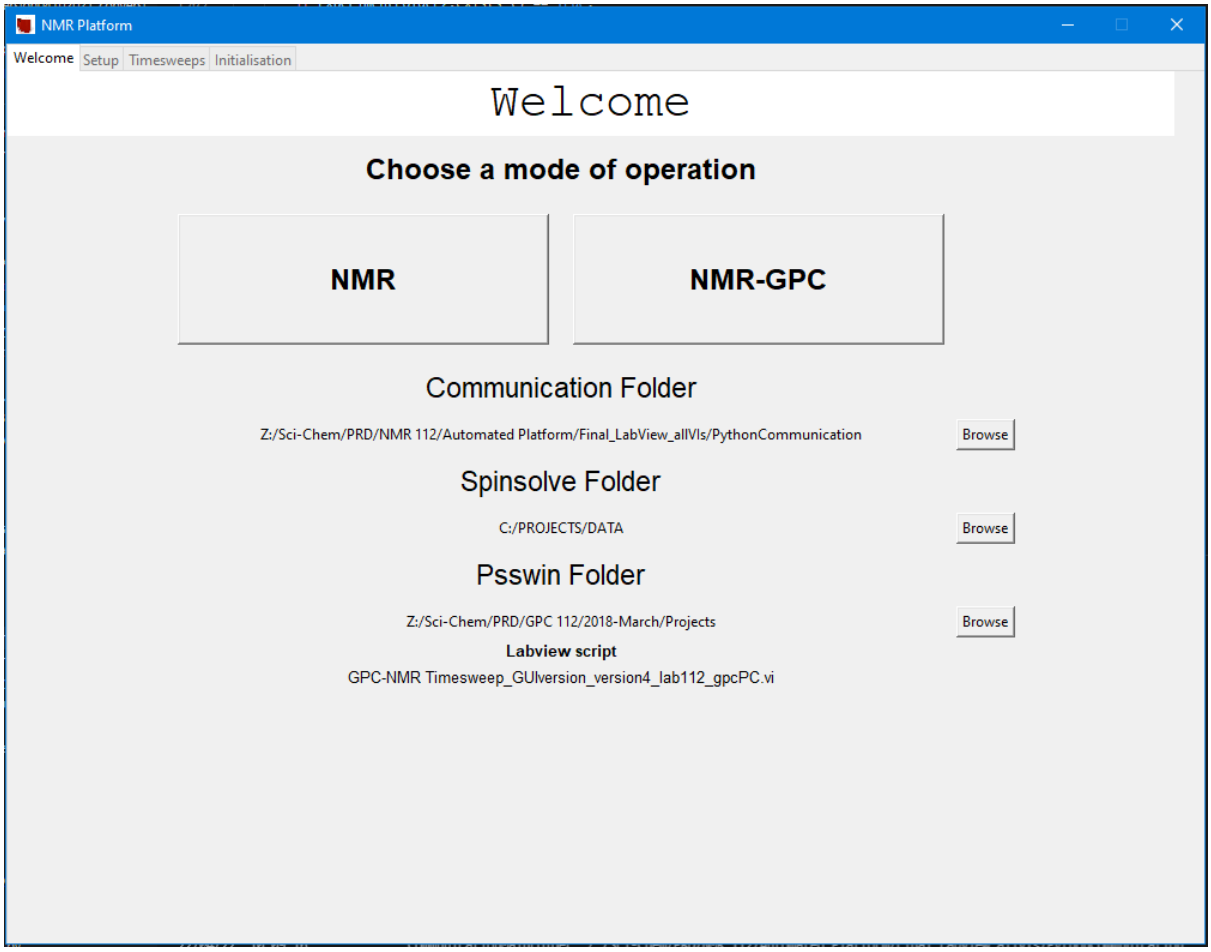


Figure S 6 *Screenshot of 'Start' tab of the GUI.*

Table S 10 *Overview of parameters in the initialisation tab of the software.*

Communication Folder	Folder that serves as a communication between the Python script (initialisation and data analysis) and LabView (Experiment Control)
Spinsolve Folder	Folder where NMR data is saved
Psswin Folder	Folder where SEC data is saved
LabView script	LabView script used for the experiment

Reactor Setup

Next, the reactor setup needs to be described (**Figure S 7**). Even though default parameters are displayed in the GUI, every value can be changed by the operator. This feature makes the software versatile and not limited to one setup and/or reaction. In an extra pop up window, the reaction solution can be specified. Chemicals can be chosen from the dropdown menus and volumes/masses can be given in the dedicated entry fields. Upon confirming, both the reactor parameters and the reaction solution are saved as standardized csv files in the experiment folder (**Figure S 8**).

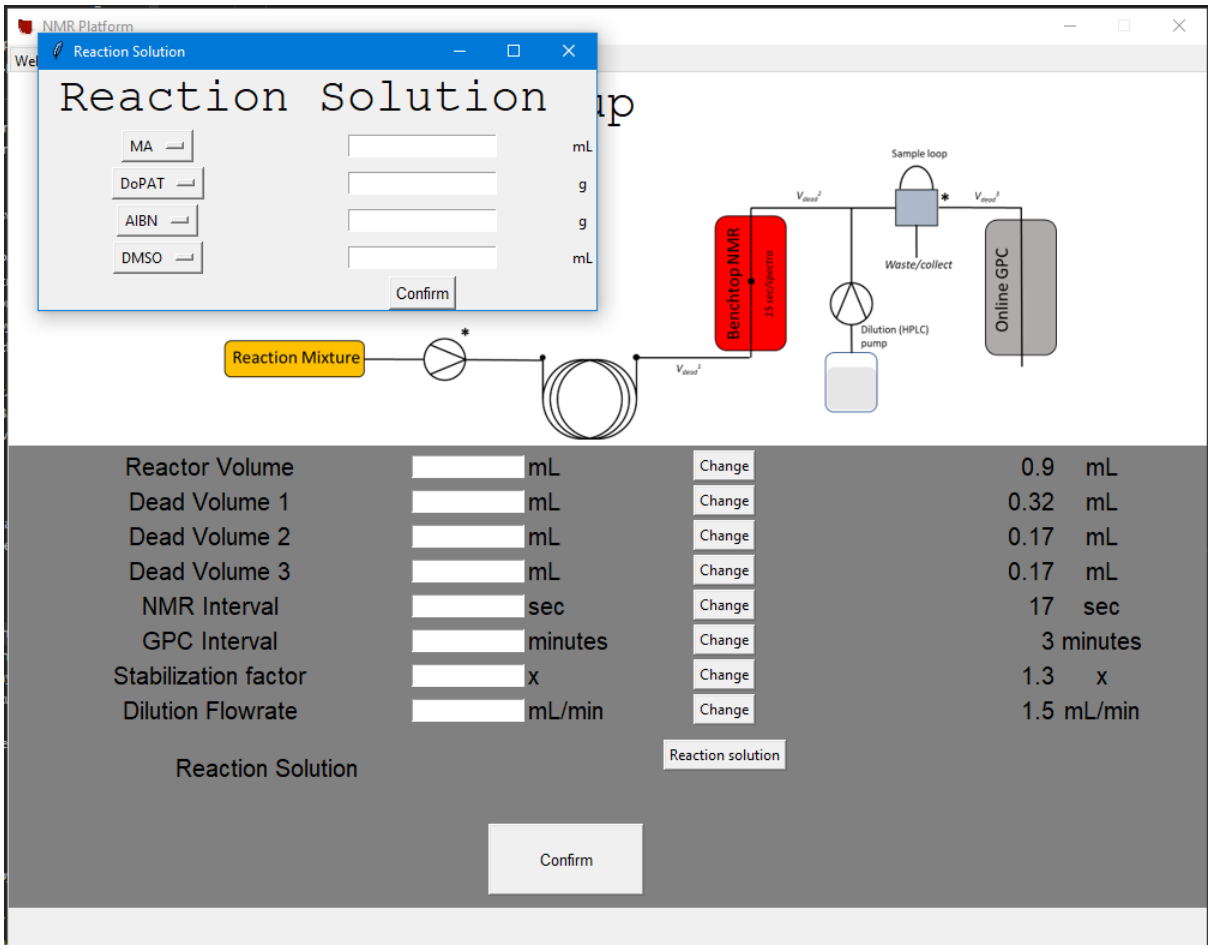


Figure S 7 *Screenshot of 'Reactor Setup' tab of the GUI. Default values are displayed on the right-hand side but can be changed by the operator.*

ReactionSolution_*code*.csv

	A	B	C	D	E	F	G	H	I	J	K	L
1		class	name	abbreviati	molecular	density	mass (g)	volume (n	moles (m	Molar (M)	eq	
2	0	RAFT	2-(Dodecy	DoPAT	350.6		0.139		0.000396	0.079293	1	
3	1	monomer	Ethyl Acry	EA	100.11	0.94	2.0022	2.13	0.02	4	50.44604	
4	2	initiator	Azobisisol	AIBN	164.21		0.004		2.44E-05	0.004872	0.061441	
5	3	solvent	Butyl Acet	Butyl Acet	116.16	0.882	2.53134	2.87	0.021792	4.358368	54.9656	
6												

Figure S 8 *Screenshot of standardized csv file of the reaction solution.*

Table S 11 *Overview of parameters saved in the 'ReactionSolution.csv' file.*

class	class of chemical (RAFT, monomer, initiator, solvent)
name	full name of chemical
abbreviation	short name of chemical
molecular mass	molecular mass of chemical in $g \cdot mol^{-1}$ (hardcoded for available chemical)
density	if applicable, density of chemical in $mL \cdot g^{-1}$ (hardcoded for available chemical; else *empty*)
mass (g)	mass of chemical in g; as given or calculated as 'volume · density'
V (mL)	if applicable, volume of chemical in mL; as given (else *empty)*
moles (mol)	moles of chemical in mol; calculated as 'mass · molecular $mass^{-1}$'
Molar (M)	concentration in M of chemical; calculated as 'moles · $total\ volume^{-1}$
eq	equivalent of chemical with respect to RAFT agent

Timesweep Experiment

In a third tab, the timesweep parameters are requested. Timesweep experiments are an excellent tool for collecting high-density data.[5] Standard screenings were performed with 2 consecutive timesweeps, i.e. from 3 to 12 minutes and from 12 to 30 minutes. In previous work, we showed that the combination of two smaller range timesweeps gives more reliable data as compared to one wide-range timesweep, e.g. directly from 3 to 30 minutes.[6] From the given timesweep and the setup parameters (see section Reactor Setup), the flowrates and reaction progress are calculated. Again, all the given and calculated parameters are stored in a standardized csv file (**Figure S 10**).

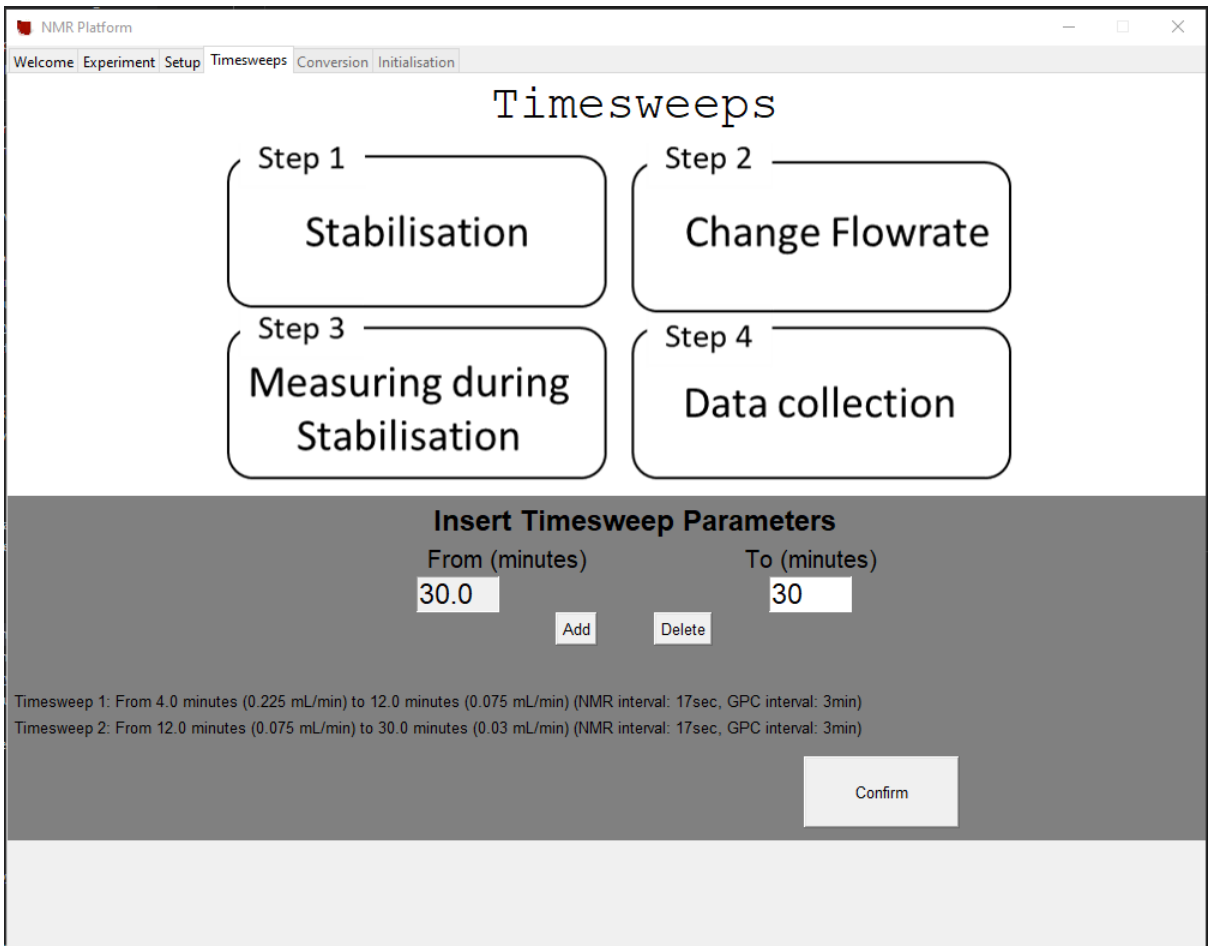


Figure S 9 *Screenshot of 'Timesweep' tab of the GUI. Entries need to be given in minutes. Upon adding, the timesweep parameters are displayed. Timesweeps can be deleted in the GUI.*

Parameters_*code*.csv

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
1		Start	Stop	volume	StartFR	StopFR	stabilisati	dead volu	Dead Volu	GPC Inten	Dead Volu	Dilution F	DeadVolu	DeadVolu	DeadVolu	NMR inter	mode	
2	0	3	12	0.4	0.133333	0.033333	1.3	0.32	0.17	3	0.17	1.5	9.6	5.1	0.113333	17	GPCandNMR	
3	1	12	30	0.4	0.033333	0.013333	1.3	0.32	0.17	3	0.17	1.5	24	12.75	0.113333	17	GPCandNMR	
4																		

Figure S 10 *Screenshot of standardized csv file of the reactor and timesweep parameters.*

Table S 12 *Overview of parameters saved in the 'Parameters.csv' file.*

Start	Start of timesweep in minutes; as given
Stop	Stop of timesweep in minutes; as given
volume	Volume of reactor in mL; as given
StartFR	Start flowrate of timesweep in mL·min^{-1}; calculated as 'volume·Start^{-1}'
StopFR	Stop flowrate of timesweep in mL·min^{-1}; calculated as 'volume·Stop^{-1}'
stabilisation time	Stabilisation time in minutes; calculated as 'volume · factor (as given)'
Dead Volume 1	Dead Volume 1 (reactor - NMR) in mL
Dead Volume 2	Dead Volume 2 (NMR - dilution) in mL
GPC Interval	GPC injection interval in minutes; as given
Dead Volume 3	Dead Volume 3 (dilution - GPC) in mL
Dilution FR	Dilution flow rate in n mL·min^{-1}; as given
DeadVolume1 (min)	Time for Dead Volume 1 in minutes; calculated as 'Dead Volume 1·StopFR^{-1}'
DeadVolume2 (min)	Time for Dead Volume 2 in minutes; calculated as 'Dead Volume 2·StopFR^{-1}'
DeadVolume3 (min)	Time for Dead Volume 2 in minutes; calculated as 'Dead Volume 2·StopFR^{-1}'
NMR interval	NMR measuring interval in seconds; as given
Mode	mode of operation; 'GPCandNMR' or 'NMR'

An important aspect of the platform is the synchronisation of reaction progress and data collection (**Figure S 11**). As NMR data is continuously measured in a known (as given) interval, the scan number serves as an excellent time unit. Based on the reactor volume, the dead volumes and the start time of data acquisition, i.e. after stabilisation of the reactor, the exact start and stop scan of each timesweep can be calculated before the actual start of the experiment (**Table S 13**). Similarly, a residence time for every SEC injection can be determined.

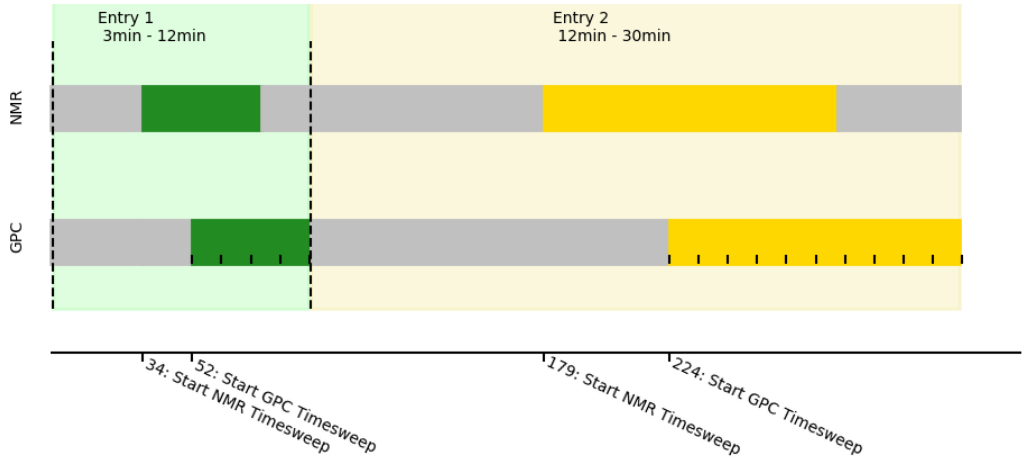


Figure S 11 *Visualisation of the reaction progress of a standard screening. Timesweeps are from 3 to 12 minutes and from 12 to 30 minutes. Calculations are based on* $V_{reactor}$ *= 0.4mL,* $V_{dead,1}$*= 0.32mL,* $V_{dead,2}$*= 0.17mL,* $V_{dead,\ 3}$ *= 0.17mL, NMR interval of 17 sec, SEC injection interval of 3 minutes, stabilisation factor of 1.3 x* $V_{reactor}$*.*

Table S 13 *Detailed overview for reaction progress as calculated in the software. Timesweeps are from 3 to 12 minutes and from 12 to 30 minutes. Calculations are based on $V_{reactor}$ = 0.4mL, $V_{dead,1}$= 0.32mL, $V_{dead,2}$= 0.17mL, $V_{dead,3}$ = 0.17mL, NMR interval of 17 sec, SEC injection interval of 3 minutes, stabilisation factor of 1.3 x $V_{reactor}$.*

Flowrate (mL · min^{-1})	***NMR***					***GPC***				
	Status	**Time (min)**	**Cum. Time (min)**	**Scans**	**Cum. Scans**	**Status**	**Time (min)**	**Cum. Time (min)**	**Scans**	**Cum. Scans**
Entry 1: 3min - 12min										
0.133	Stabilisation	3.9	3.9	NA		Stabilisation	3.9	3.9	NA	
0.033	Flowrate Change			0	0	Flowrate Change			0	0
	Dead Volume 1	9.6	13.5	34	**34**	Dead Volumes 1 + 2 + 3	14.7	18.6	52	**52**
	Timesweep	12	25.5	42	**76**					
	Waiting for GPC	5.1	30.6	18	94	Timesweep	12	30.6	42	94
Entry 2: 12min - 30min										
0.013	Flowrate Change	0	30.6	0	94	Flowrate Change	0	30.6	0	94
	Dead Volume 1	24	54.6	85	**179**	Dead Volumes 1 + 2 + 3	36.8	67.4	130	**224**
	Timesweep	30	84.6	106	**285**					
	Waiting for GPC	12.8	97.4	45	330	Timesweep	30	97.4	106	330

Conversion Determination

The csv output file of Spinsolve, i.e. the benchtop NMR software, contains absolution integral values. It is therefore necessary to specify the methodology for conversion calculation (**Figure S 12**). The operator can choose between three pre-programmed methods:

Internal Standard – The conversion will be based on the vinyl integral with respect to an internal standard integral. 4-hydroxy benzaldehyde is set as the internal standard. By giving the initial concentrations of both chemicals, the conversion can be calculated without the need of physically taking a t_0 sample.

Monomer – For now, this option is only available for MA in DMSO. Since there is no peak overlap in this system, the conversion can be calculated directly form the vinyl and methyl peak of the monomer.

Solvent (Butyl Acetate) – When using butyl acetate as the solvent, a peak overlap requires a concentration correction for accurate conversion calculation. Since this was the used method in our lab screening, a detailed explanation is given in the next section.

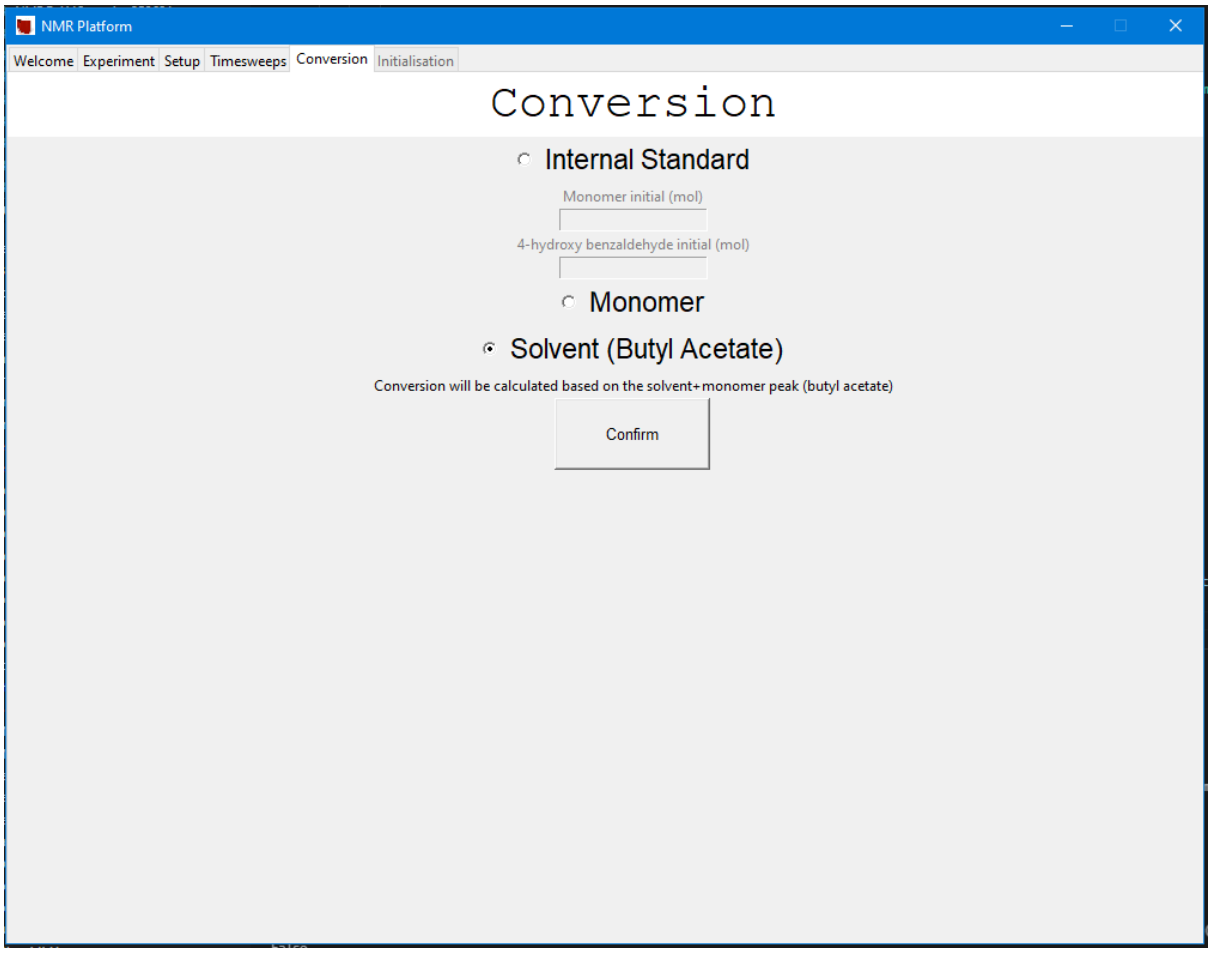


Figure S 12 *Screenshot of 'Conversion' tab of the GUI.*

Conversion Calculation – Solvent (Butyl Acetate)

Since the solvent peak overlaps with the monomer peak, a concentration correction needed to be made for proper conversion calculation (**Figure S 13**).

Both the $moles_{monomer}$ and $moles_{solvent}$ can be extracted from the solution csv file of the experiment. The concentration correction factor can therefore be calculated as,

$$Correction\ Factor = \frac{moles_{monomer}}{moles_{solvent}}$$

With this factor, a concentration corrected relative t_0 integration can be calculated for both the I0 integration and the I1 integration, representing the vinyl protons and reference proton, respectively:

$$I1_{rel,reference} = \#protons_{solvent} + (\#protons_{monomer} * Correction\ Factor)$$

$$I0_{rel,t_0} = \#protons_{vinly} * Correction\ Factor$$

With $\#protons_{vinly}$ is 3, $\#protons_{solvent}$ is 2 and $\#protons_{monomer}$ refers to the reference protons on the monomer and is thus dependent on the monomer used (3 for MA, 1 for cHA and 2 for EA, PA, nBA, isoBA, 2EHA and DODA).

Next, the relative integration of the measured sample can be calculated from the absolute integration value, given by the Spinsolve Software.

$$\frac{I0_{rel,sample}}{I0_{abs,sample}} = \frac{I1_{rel,reference}}{I1_{abs,reference}}$$

$$I0_{rel,sample} = \frac{I1_{rel,reference}}{I1_{abs,reference}} * I0_{abs,sample}$$

Finally, the conversion can be calculated via:

$$Conversion = 1 - \left(\frac{I0_{rel,sample}}{I0_{rel,t_0}}\right) x\ 100$$

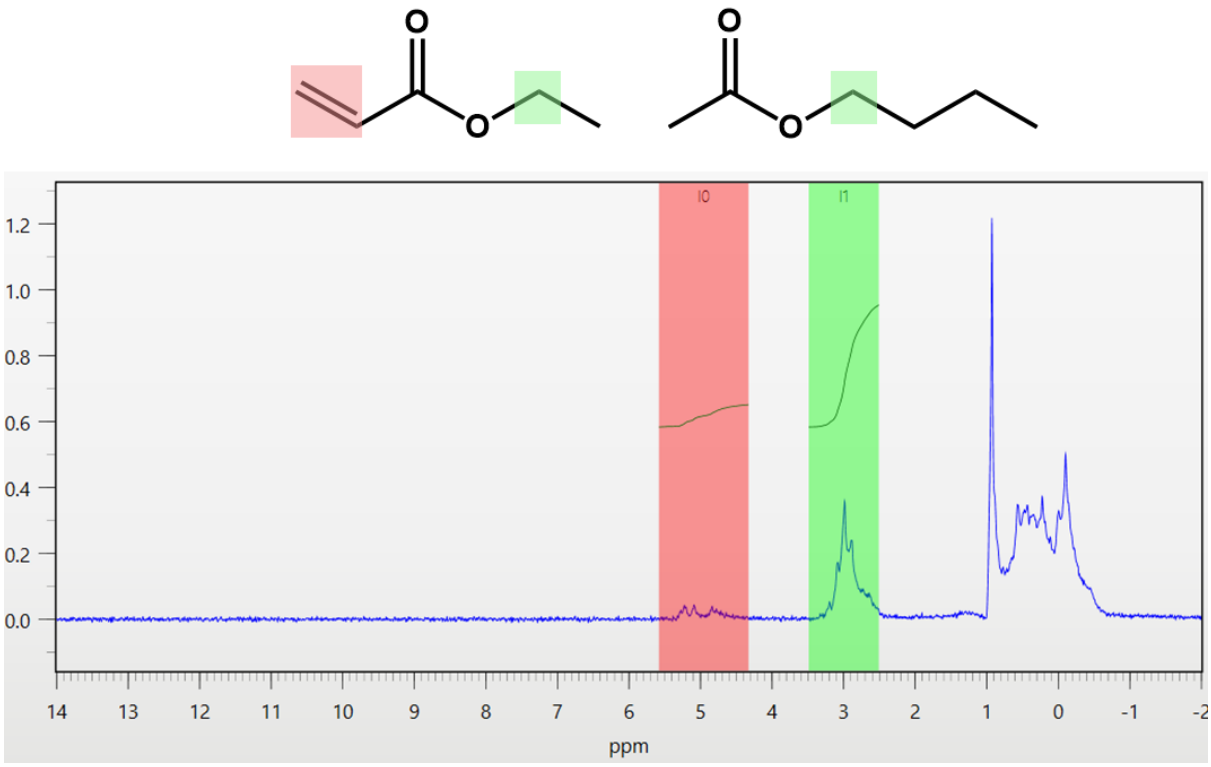


Figure S 13 *Raw spectra from Spinsolve software. Scan 370 from 2M ethyl acrylate screening. I0 (red): vinyl protons; I1 (green): reference peak from both ethyl acrylate and butyl acetate. With I0 = 16.63, I1 = 89.387,* $n_{monomer}$ *= 0.02 moles and* $n_{solvent}$*= 0.06, a monomer conversion of 50.5% was calculated.*

Software communication initialisation

As a last step, all the software needs to be initialized for proper data collection (**Figure S 14**). The experiment code has a central role in this task. After this is given, all the metadata required for running the reaction is communicated to the LabView program. A successful transfer is confirmed by the 'Communication folder found' message in the GUI. Next, output text files of the PSSwin software (SEC) need to be named as the given experiment code. While the experiment is running, the software searches for the files with the exact same code. Similarly, the name of the Spinsolve (NMR) experiment will be the given experiment code. As an optional feature, a short overview of the data can be sent via email at the end of the experiment.

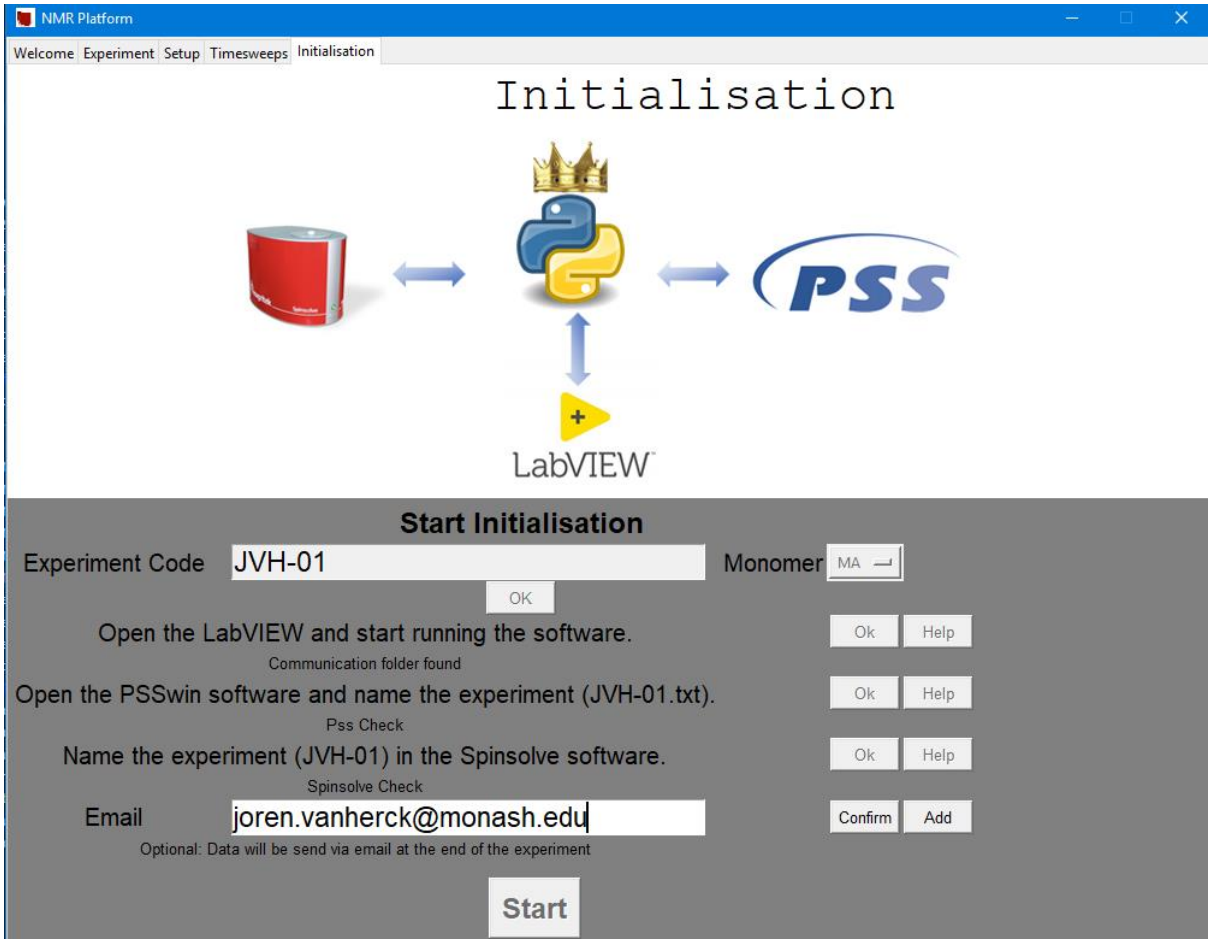


Figure S 14 *Screenshot of 'Initialisation' tab of the GUI.*

Data Collection

Based on the given reaction parameters, the exact start and stop scan of every phase of the experiment can be calculated. At the start of the experiment, a standardized csv file is created in the experiment folder (**Figure S 15**). As new data (NMR and SEC) is detected and collected, this file is updated in real-time.

Experiment_*code*.csv

Scannumb	Timeswee	Status	I0(5.581|4	I1(3.487|2	conversio	treaction	tres	GPC_num	Mn	Mw	D	tres_GPC	Mn theory
171	2	No	24.169	87.978	0.269651								
172	2	No	23.86	88.106	0.280036								
173	2	No	24.461	88.217	0.26283								
174	2	No	24.427	87.893	0.261141								
175	2	No	24.48	87.785	0.258626								
176	2	No	24.242	87.713	0.265232								
177	2	No	23.977	88.28	0.277931								
178	2	Timeswee	24.087	88.119	0.273293	0	12	6	2284	2394	1.048	12	1721
179	2	Timeswee	24.592	88.004	0.257088	17	12.17						
180	2	Timeswee	24.195	88.117	0.270018	34	12.34						
181	2	Timeswee	23.747	88.146	0.283771	51	12.51						
182	2	Timeswee	23.41	87.943	0.292305	68	12.68						
183	2	Timeswee	23.673	88.04	0.285143	85	12.85						
184	2	Timeswee	23.924	87.988	0.277136	102	13.02						
185	2	Timeswee	23.95	87.77	0.274553	119	13.19						
186	2	Timeswee	24.32	88.205	0.266979	136	13.36						
187	2	Timeswee	23.898	87.921	0.277372	153	13.53						
188	2	Timeswee	23.223	88.451	0.30199	170	13.7						
189	2	Timeswee	23.731	87.877	0.282062	187	13.87	7	2360	2490	1.055	13.8	1765
190	2	Timeswee	23.367	88.22	0.295823	204	14.04						
191	2	Timeswee	23.313	87.526	0.29188	221	14.21						

Figure S 15 *Screenshot of standardized csv file experiment data.*

Table S 14 *Overview of parameters saved in the 'experiment.csv' file.*

Scannumber	Scan number of data point; as calculated
Timesweep	Number of timesweep
Status	Status of data point; "Timesweep" or "No" for dead volumes
I0	Absolute integral of vinyl region; borders are given in header
I1	Absolute integral of reference region; borders are given in header
conversion	Monomer conversion in 10^{-2} %; as calculated
treaction	Reaction time of timesweep phase in seconds
tres	Residence time of datapoint in minutes; as calculated[5]
Mn	M_n of SEC injection in g·mol^{-1}
Mw	M_w of SEC injection in g·mol^{-1}
D	Dispersity of SEC injection
tres_GPC	Residence time of SEC injection in minutes
Mn_theory	Theoretical M_n of SEC injected; as calculated from conversion

Inline NMR

Once the experiment is started, NMR scans are continuously taken at the given NMR interval (17 seconds in this work). The operator has to set the relevant integration borders and ensure the 'update to csv' option is selected. These manual steps are unavoidable for the automated generation of the integral file in the Spinsolve folder. The Python software extracts the absolute integration borders and calculates the conversion accordingly (**Figure S 16**).

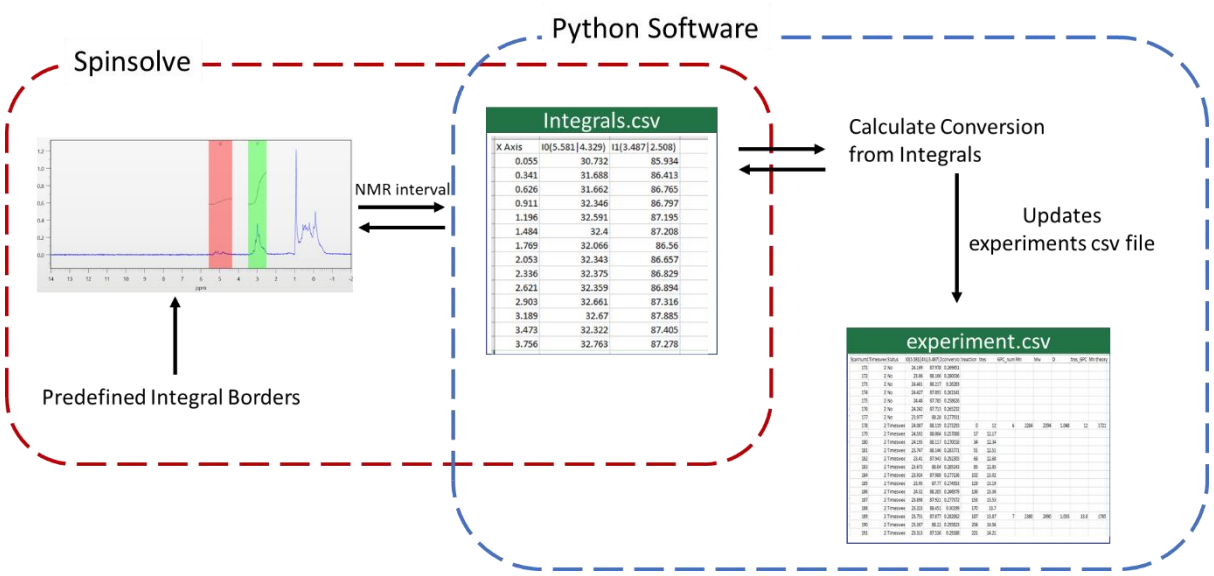


Figure S 16 *Overview of NMR data collection.*

Online GPC

In contrast to the continuous NMR data collection, SEC injections are only programmed in the timesweep phases of the experiment. Once a timesweep start (as calculated from the setup parameters), the LabView script triggers a brief switch to position B of the switch valve and thus a sample injection in column. This injection process is repeated at the given GPC interval (3 minutes in this work). The measuring time of a sample is 12 minutes. Thereafter, a standardized text file (by Psswin software) is created containing all the relevant data. Note here, that the integration borders are pre-defined at the start of the reaction. Consequently, raw molecular weight distributions can be calculated and saved incorrectly. Such abnormalities can later be detected by a data cleaning algorithm (see next section). Nevertheless, the Python software extracts the data from the text files and updates the experiment folder/csv file accordingly (**Figure S 17**).

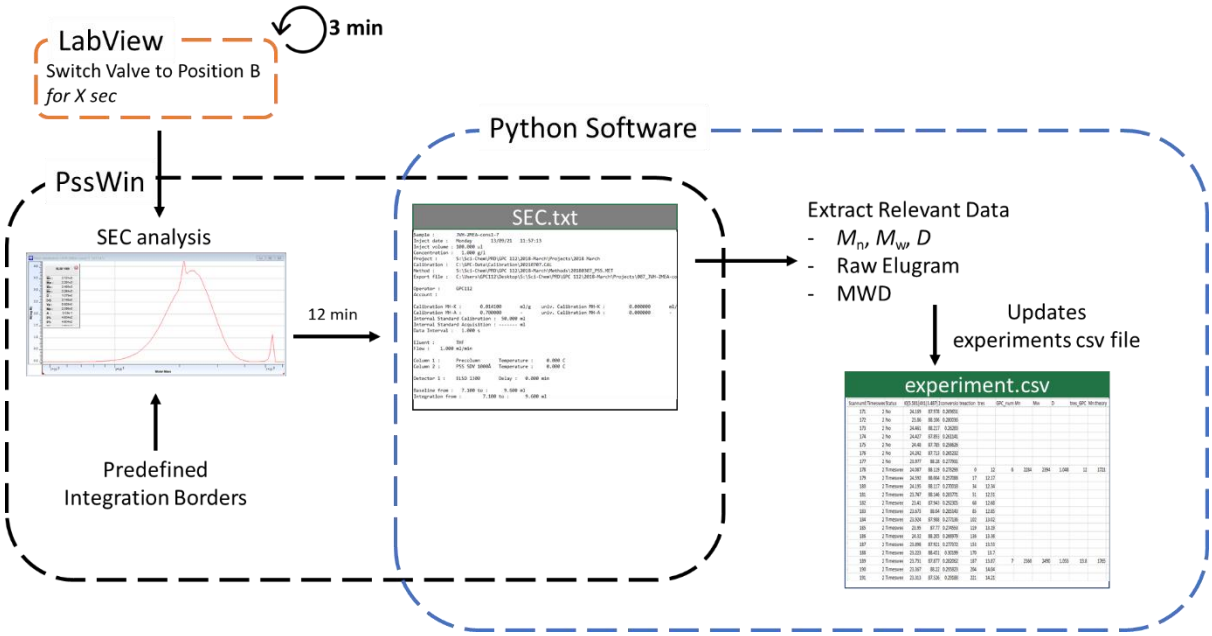


Figure S 17 *Overview of SEC data collection.*

Real-time data visualisation

From the experiment csv file, overview plots are created and saved in experiment folder (**Figure S 18**). This feature allows the operator to follow the reaction remotely. Irregularities can easily be detected so failed reactions can be stopped prematurely. Note that these are raw datapoints. For instance, outliers in SEC data gives the operator a first indication to manually check and correct the data.

Scan-Integral – Plot of absolute integral values of the predefined integration regions on the NMR spectra (Here: I0(5.581|4.329) for vinyl region and I1(3.487|2.508) for reference region). Blue and red data indicates dead volume and timesweep data, respectively.

Scan-Conversion – Plot monomer conversion values, as calculated from the absolute integrals. Blue and red data indicates dead volume and timesweep data, respectively.

tres-Conversion – Kinetic conversion plot of the combined timesweeps. Different colours indicate different timesweeps (Here: green for 3 to 12 minutes and yellow for 12 to 30 minutes.).

tres-Mn – Kinetic M_n plot of the combined timesweeps. Different colours indicate different timesweeps (Here: green for 3 to 12 minutes and yellow for 12 to 30 minutes. Outliers in the beginning of the experiment are a result of incorrect integral borders and thus need manual correction.). Grey datapoints are the theoretical M_n as calculated from monomer conversion.

Conversion-Mn – Kinetic plot of the combined timesweeps. Different colours indicate different timesweeps (Here: green for 3 to 12 minutes and yellow for 12 to 30 minutes. Outliers in the beginning of the experiment are a result of incorrect integral borders and thus need manual correction.). Grey datapoints are the theoretical M_n as calculated from monomer conversion.

Raw SEC trace – Raw data of SEC injection as extracted from the output text file of the PSSwin software. The legend displays M_n, M_w and dispersity ($Đ$). All SEC traces are saved in a separate subfolder.

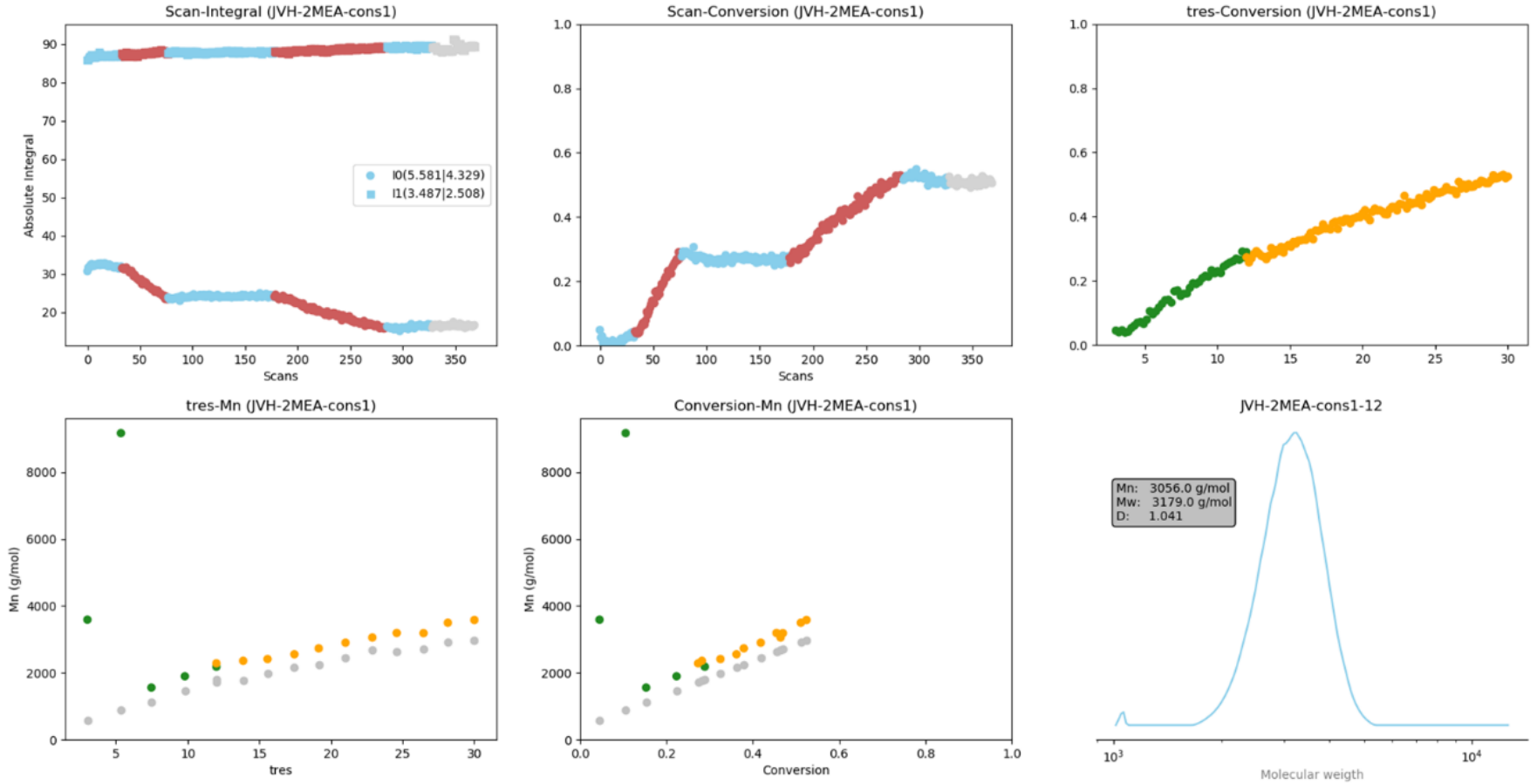


Figure S 18 *Overview of raw data plots created by the software for real-time monitoring of reaction progress.*

Data Cleaning

A Python script is written to detect outliers and other abnormalities in data collection and analysis (**Figure S 19**-**Figure S 22**). The only input that needs to be given by the user is the experiment folder. The script is able to extract all relevant data from the csv files, highlighting the importance of standardized data formats and storing of metadata. Overview plots are saved in the experiment folder. A detailed explanation of the data cleaning algorithm is given in the main paper.

NMR data

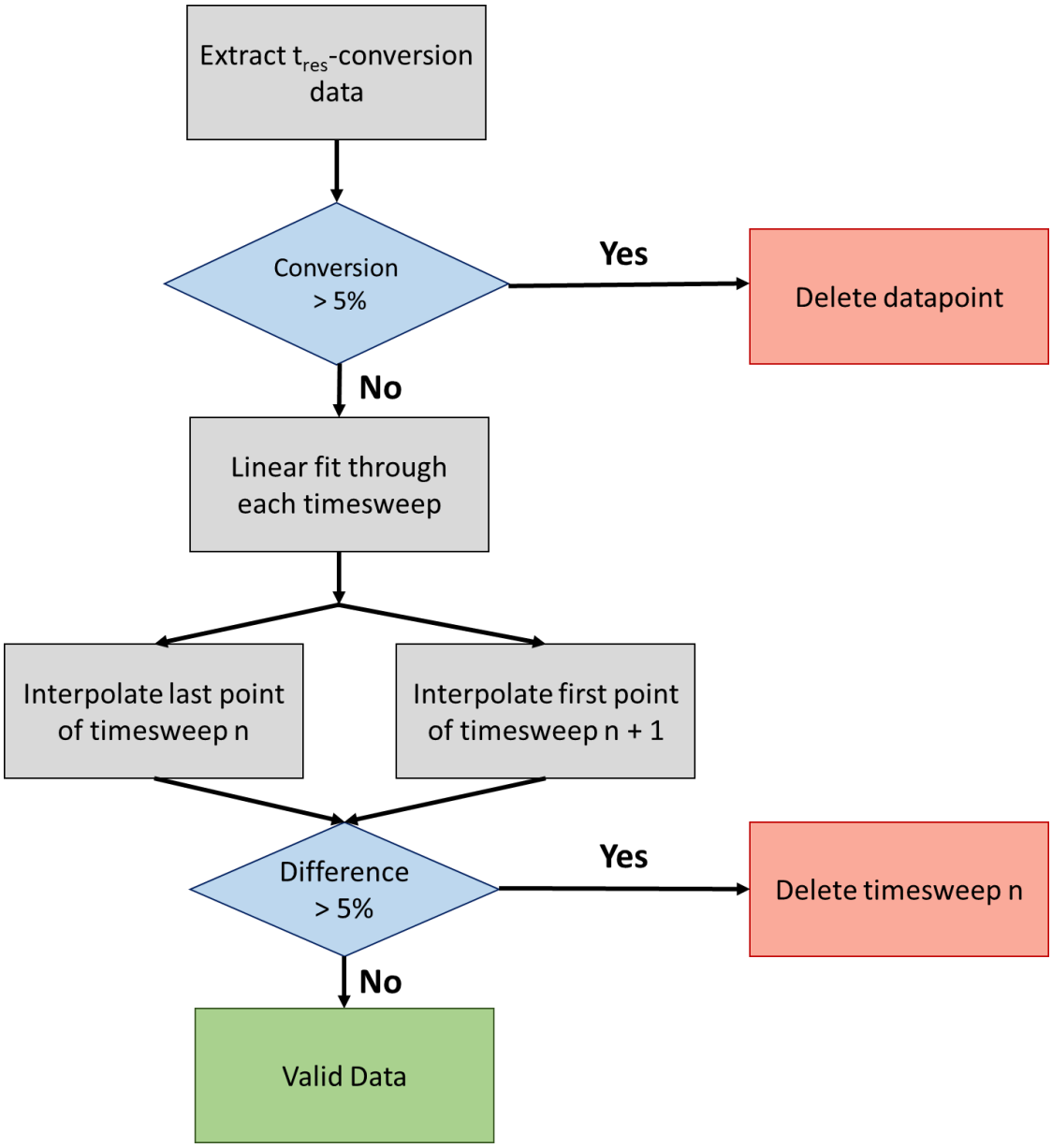


Figure S 19 Flow chart of NMR data cleaning algorithm as described in main paper.

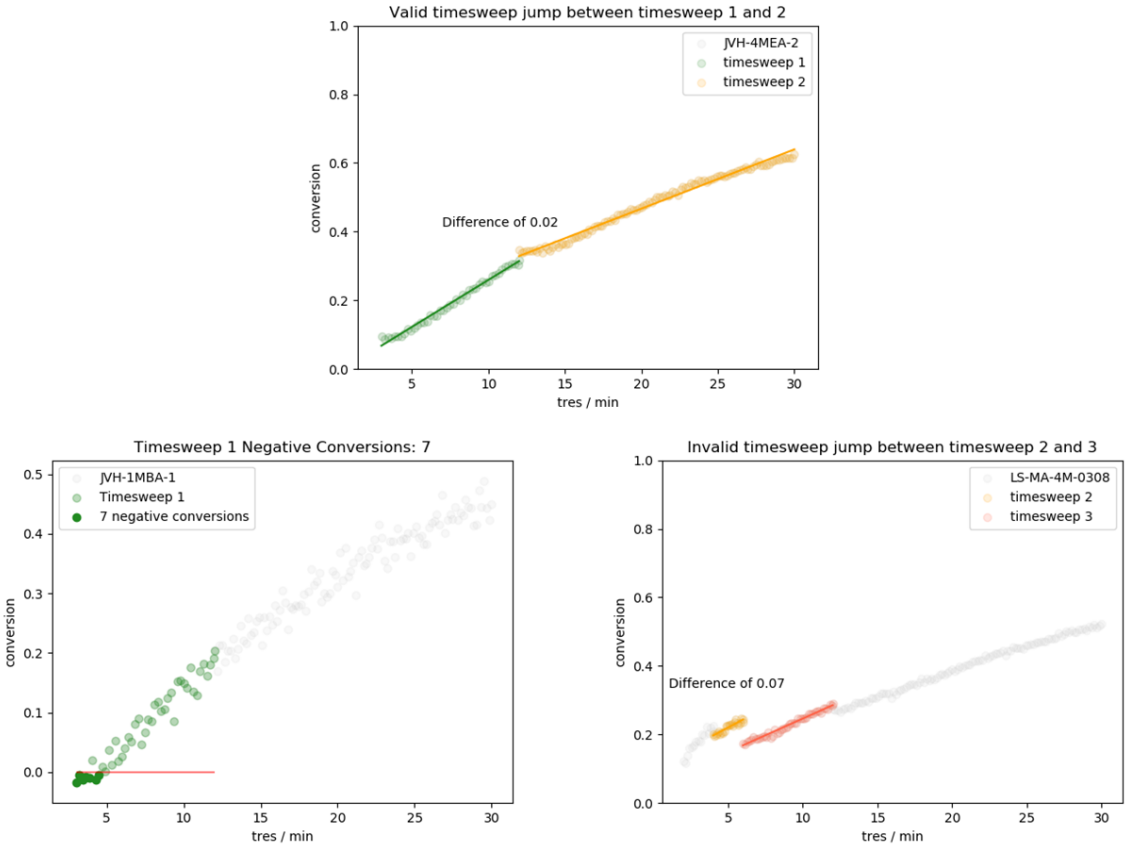


Figure S 20 *Raw output plots generated by the cleaning algorithm. Top: Valid kinetic plot with timesweep jump of 2% and no negative conversion. Bottom – left: Negative Conversion (7 datapoints) detected by the algorithm. Bottom – right: Invalid timesweep jump of 7% conversion detected by the algorithm.*

Table S 15 *Detailed overview of the data cleaning algorithm for timesweep jumps.*

Timesweep n	4 minutes to 6 minutes	3 minutes to 12 minutes
Timesweep n+1	6 minutes to 12 minutes	12 minutes to 30 minutes
Fit Timesweep n	y = 2.3 x + 10.3	y = 2.7 x – 1.4
Fit Timesweep n+1	y = 1.9 x + 5.1	y = 1.7 x + 12.1
Last on timesweep n	24	31
First on timesweep n+1	17	33
Difference	7	2
Threshold	5	5
Validation	INVALID; delete timesweep n	VALID

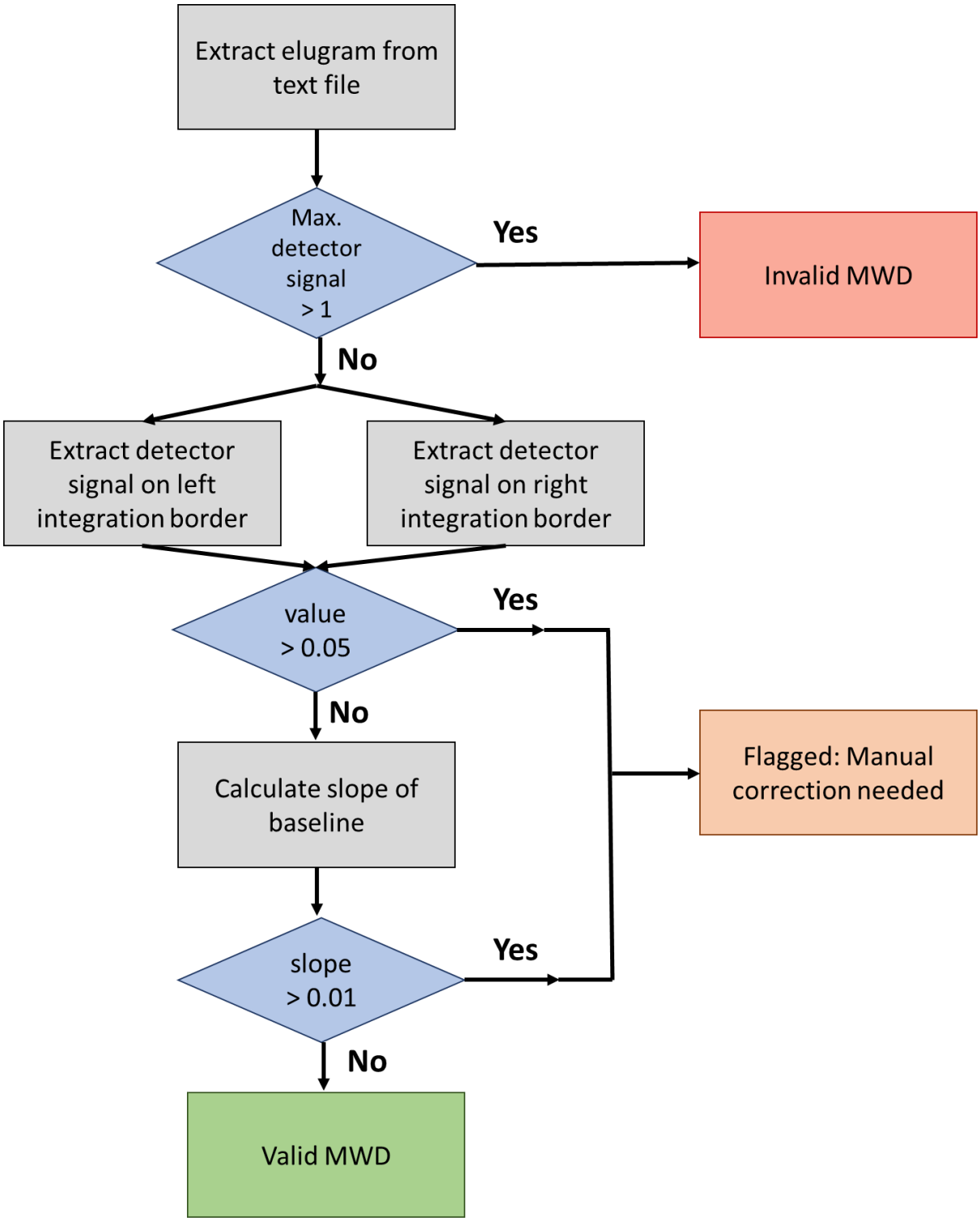


Figure S 21 Flow chart of SEC data cleaning algorithm as described in main paper.

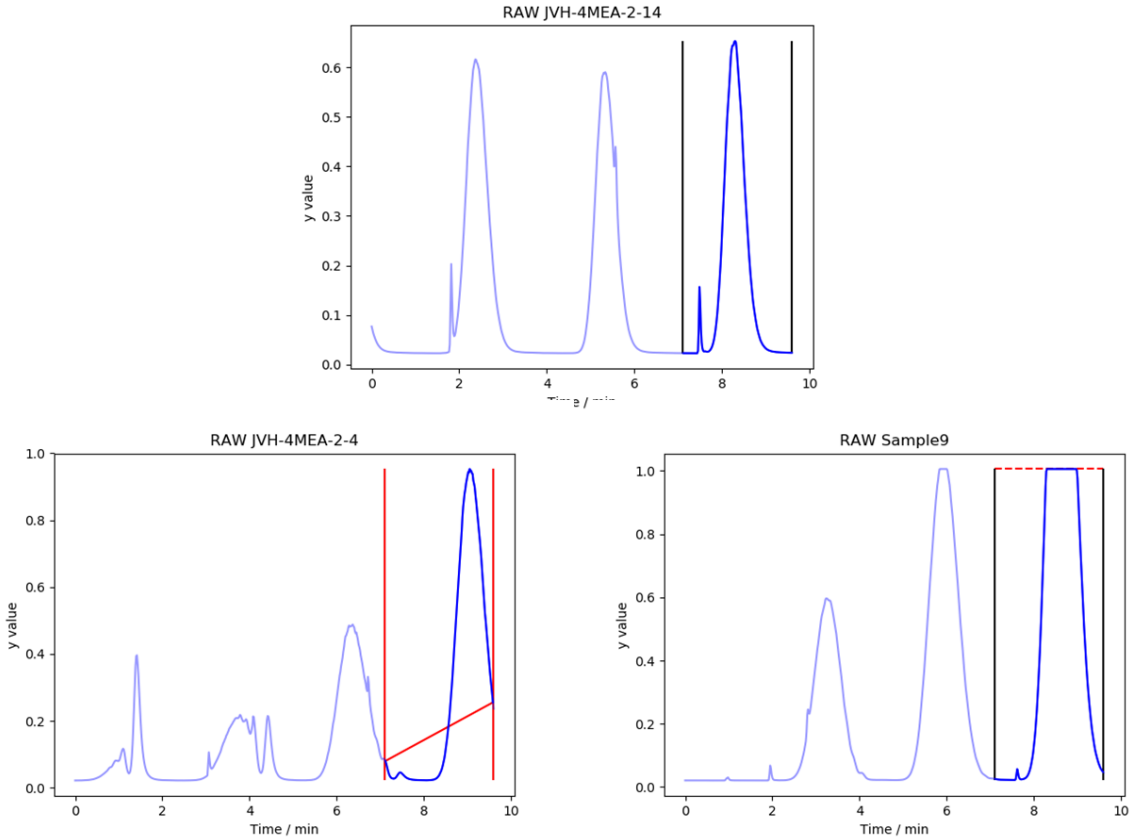


Figure S 22 *Raw output plots generated by the cleaning algorithm. Top: Valid MWD with correct integration borders and no saturation of detector. Bottom – left: Invalid MWD with incorrect integration borders and thus inaccurate baseline detected by the algorithm and flagged for manual correction. Bottom – right: Invalid MWD with saturation of the detector detected by the algorithm and deleted from the data set.*

Overview of data

After data cleaning and manual correction of flagged datapoints, the final dataset can be presented in three summary plots. Similar to the data cleaning algorithm, the developed Python script only asks for the experiment folder as input parameter and is able to extract all relevant data from the saved csv files. With one click, summary plots and quantitative analysis of >250 datapoints is provided. This allows the operator the interpreted a large set of data on the spot.

The 'Data Overview' algorithm was used for all the individual screening reactions (**Figure S 23**-**Figure S 30**). Three plots are generated:

SEC Overview – Overlay of all molecular weight distributions. Different colours indicate different timesweeps**.** A clear in increase in molecular weight is observed in all reactions, indicating a successful polymerization.

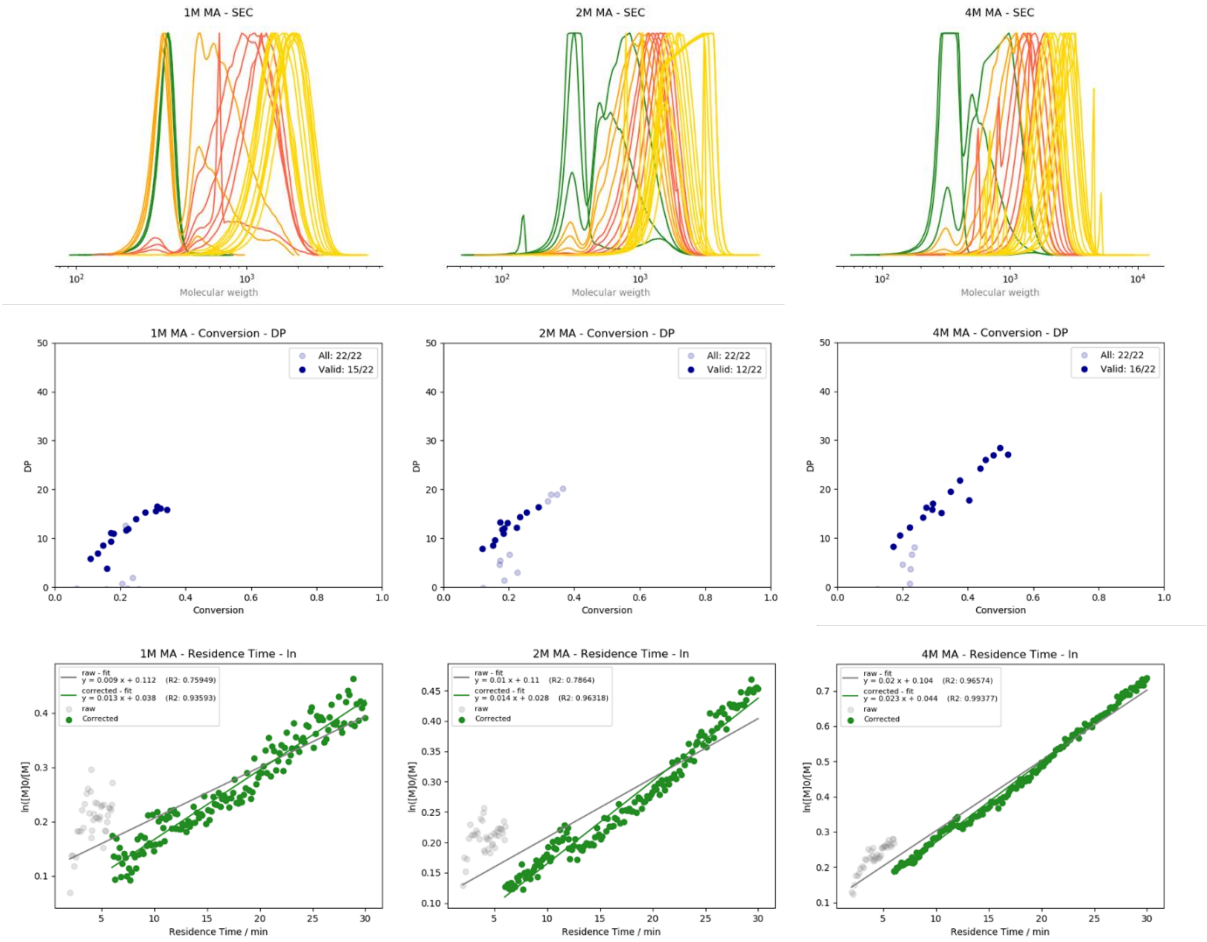
Conversion-DP – Summary conversion-DP plot. Degree of polymerisation (DP) values are calculated from the corrected M_n and the molecular weight of the monomer and RAFT agent, as extracted from the solution csv file. Invalid datapoints are shaded and only valid data is highlighted (full purple in plots). As DP 50 was targeted in all polymerizations, ideally, a linear fit through the valid data points should extrapolate to (1,50), i.e. DP50 at 100% conversion. Fits are saved in a separate text file.

First order plot – First order plots visualize the kinetics of the polymerisation. Each datapoint is therefore converted via:

$$\ln([M]_0/[M]) = \ln(1/1 - conversion)$$

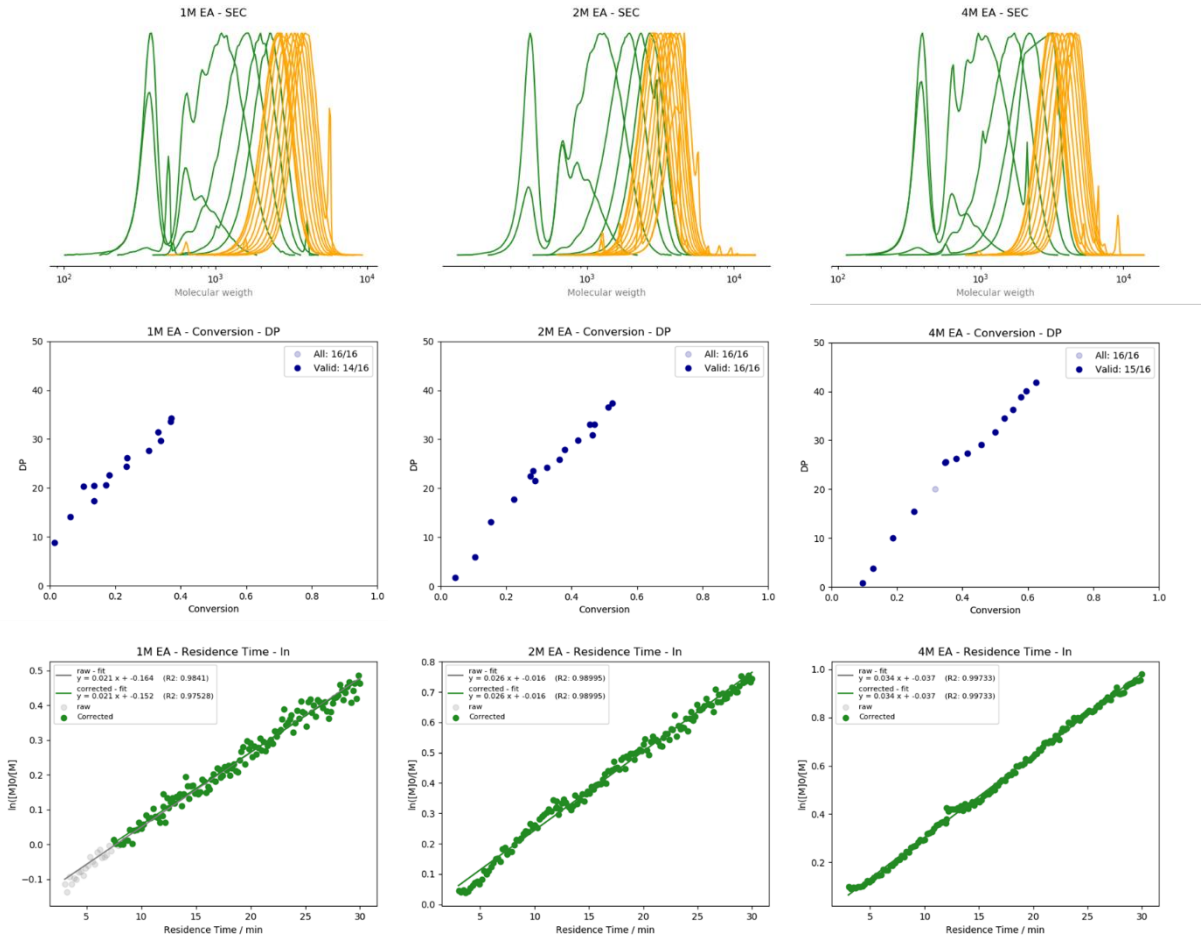
Invalid datapoints are shaded and only valid data is highlighted (full green in plots). In addition to a raw linear fit of all the data, a corrected linear fit is calculated based only on the valid data points. Both fits are saved in separate text files.

Finally, all the slopes of the corrected first order plots are manually summarized to plot the final carbon chain length dependence on the rate of polymerization (**Figure S 31**).


1M MA - SEC
2M MA - SEC
4M MA - SEC
Molecular weigth
1M MA - Conversion - DP
2M MA - Conversion - DP
4M MA - Conversion - DP
All: 22/22
Valid: 15/22
Valid: 12/22
Valid: 16/22
DP
Conversion
1M MA - Residence Time - ln
2M MA - Residence Time - ln
4M MA - Residence Time - ln
raw - fit
y = 0.009 x + 0.112 (R2: 0.75949)
corrected - fit
y = 0.013 x + 0.038 (R2: 0.93593)
y = 0.01 x + 0.11 (R2: 0.7864)
y = 0.014 x + 0.028 (R2: 0.96318)
y = 0.02 x + 0.104 (R2: 0.96574)
y = 0.023 x + 0.044 (R2: 0.99377)
raw
Corrected
ln([M]0/[M]
Residence Time / min

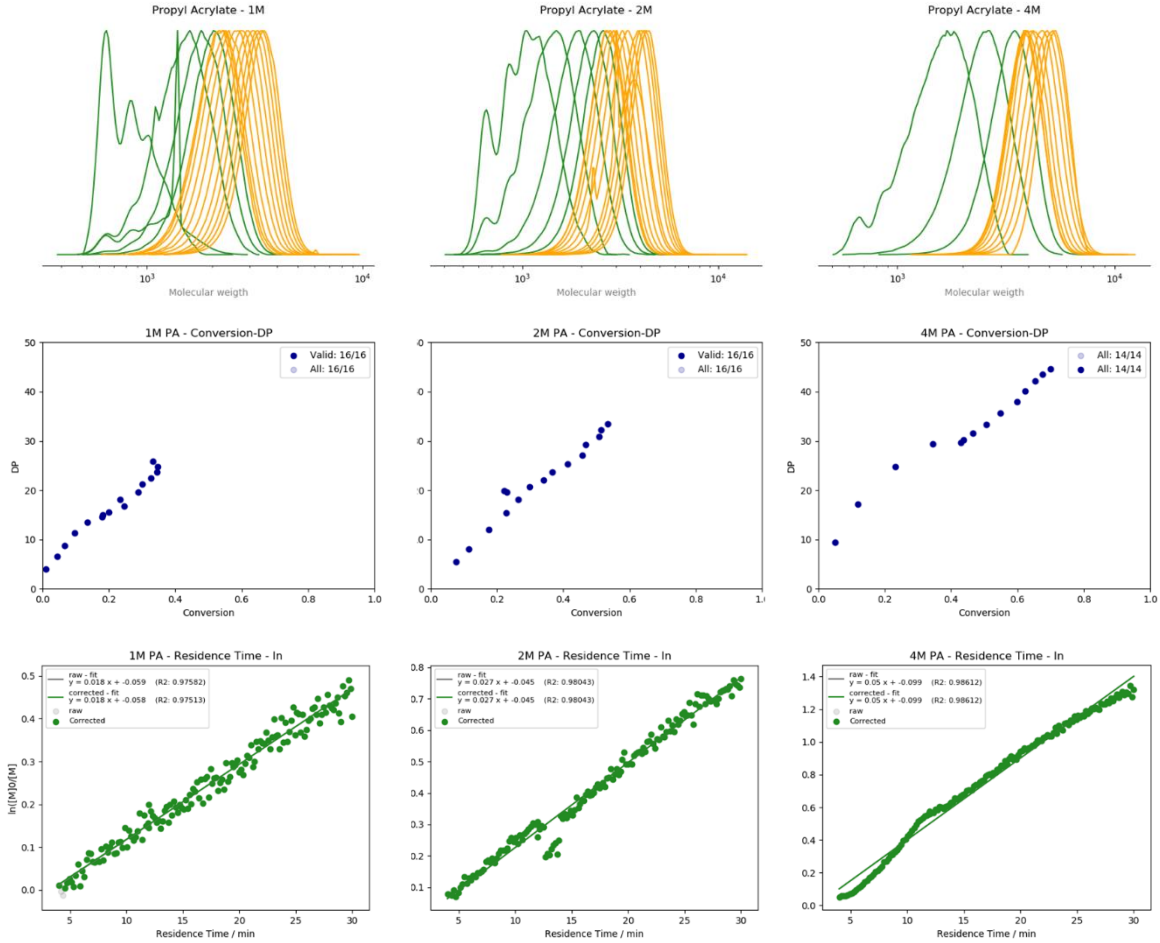
	1M		2M		4M	
t_{res} (min.)	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})
2	6.7	312	12.1	329.8	12.2	298.9
3.5583	22.2	310.3	18.5	450.6	22.2	391.7
4	25.7	306.1	22.6	584.2	22.5	641.6
4	15.7	307.2	17.1	727.6	20	730
5.0389	20.6	397.2	17.4	800.5	22.8	897.8
6	23.8	491.1	20.2	899.3	23.5	1032
6	16	660.1	11.9	1004	17.2	1038
7.5583	10.8	831.3	15.1	1061	19.2	1234
8.975	13.2	926.5	15.7	1160	22.2	1381
10.5333	14.7	1058	18.2	1270	26.1	1555
12	17.1	1135	18.6	1366	29.1	1693
12	17.1	1283	17.3	1475	27.3	1732
13.87	17.9	1274	17.9	1345	29.2	1803
15.57	21.8	1327	19.6	1456	31.8	1642
17.44	22.4	1360	22.4	1376	34.6	2011
19.14	21.5	1416	23.4	1566	37.5	2216
21.01	24.7	1527	25.4	1654	40.4	1857
22.88	27.6	1653	29	1747	43.7	2431
24.58	31.3	1761	31.8	1846	45.3	2581
26.45	30.9	1672	32.8	1965	47.9	2672
28.15	34.3	1702	34.7	1972	49.9	2805
30	32.3	1718	36.4	2077	52.1	2683

Figure S 23 *Automated screening of methyl acrylate polymerization (0.005M AIBN, 80°C, DP_{target} = 50, butyl acetate as solvent). Data was acquired via timesweeps of 2 to 4, 4 to 6, 6 to 12 and 12 to 30 minutes.*



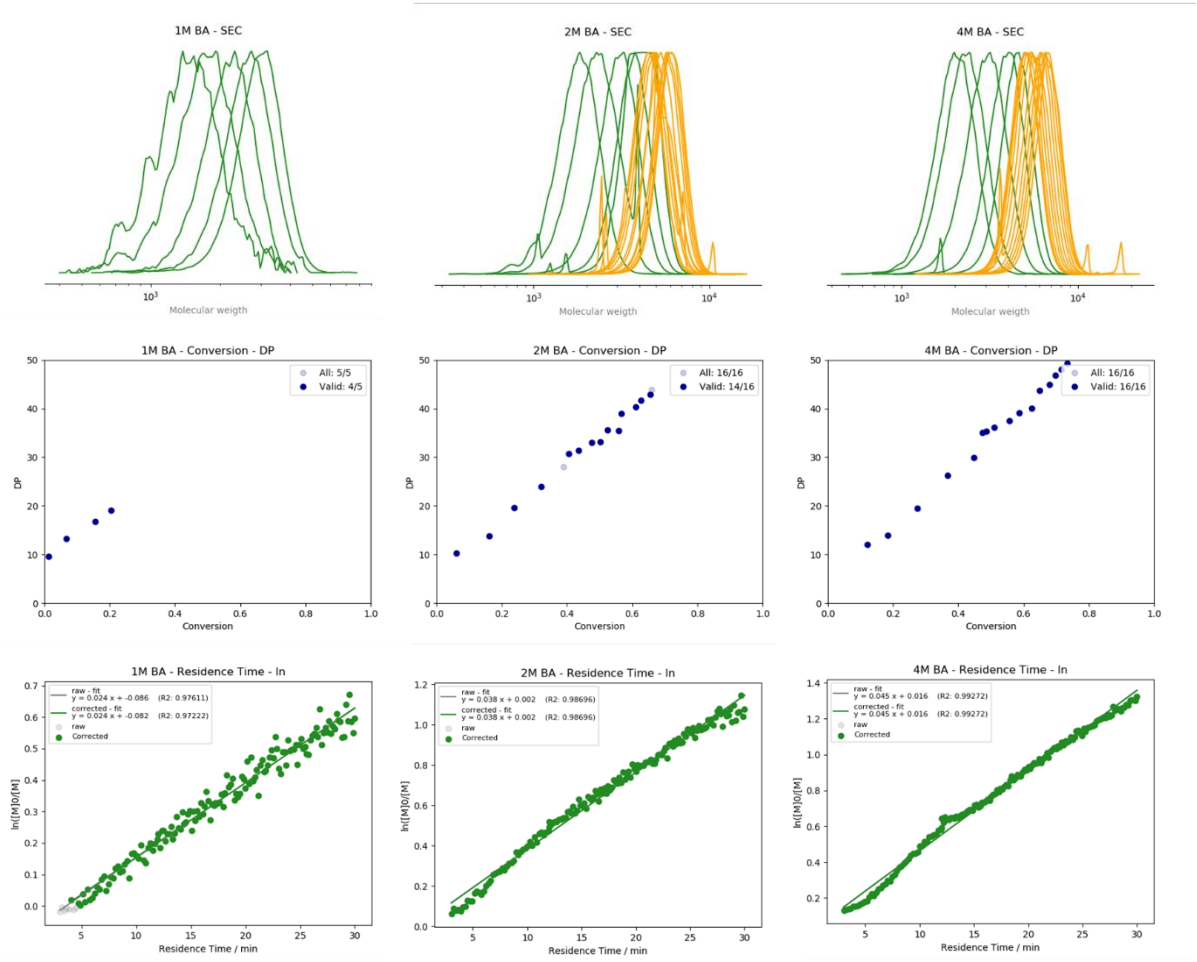
	1M		2M		4M	
t_{res} (min.)	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})
4	-12	365.3	4.5	441.3	9.5	360.4
6	-3.6	598.6	10.5	792.9	12.8	604.7
8	1.5	1038	15.3	1423	18.7	1142
10	6.2	1504	22.3	1826	25.2	1623
12	13.5	1791	28.9	2154	31.6	2029
12	10.3	2056	27.3	2243	34.6	2504
13.8	13.6	2069	28.2	2343	34.9	2525
15.6	17.1	2071	32.5	2402	38.1	2578
17.4	18.1	2250	36.2	2545	41.6	2681
19.2	23.5	2411	37.9	2728	45.7	2836
21	23.7	2568	41.8	2896	50	3066
22.8	30.2	2699	46.4	2993	52.8	3325
24.6	33.8	2889	45.5	3192	55.3	3474
26.4	33.1	3042	47	3182	57.9	3714
28.2	36.8	3238	51.1	3497	59.4	3824
30	37	3301	52.4	3578	62.4	3973

Figure S 24 *Automated screening of ethyl acrylate polymerization (0.005M AIBN, 80°C, DP_{target} = 50, butyl acetate as solvent). Data was acquired via timesweeps of 4 to 12 and 12 to 30 minutes.*



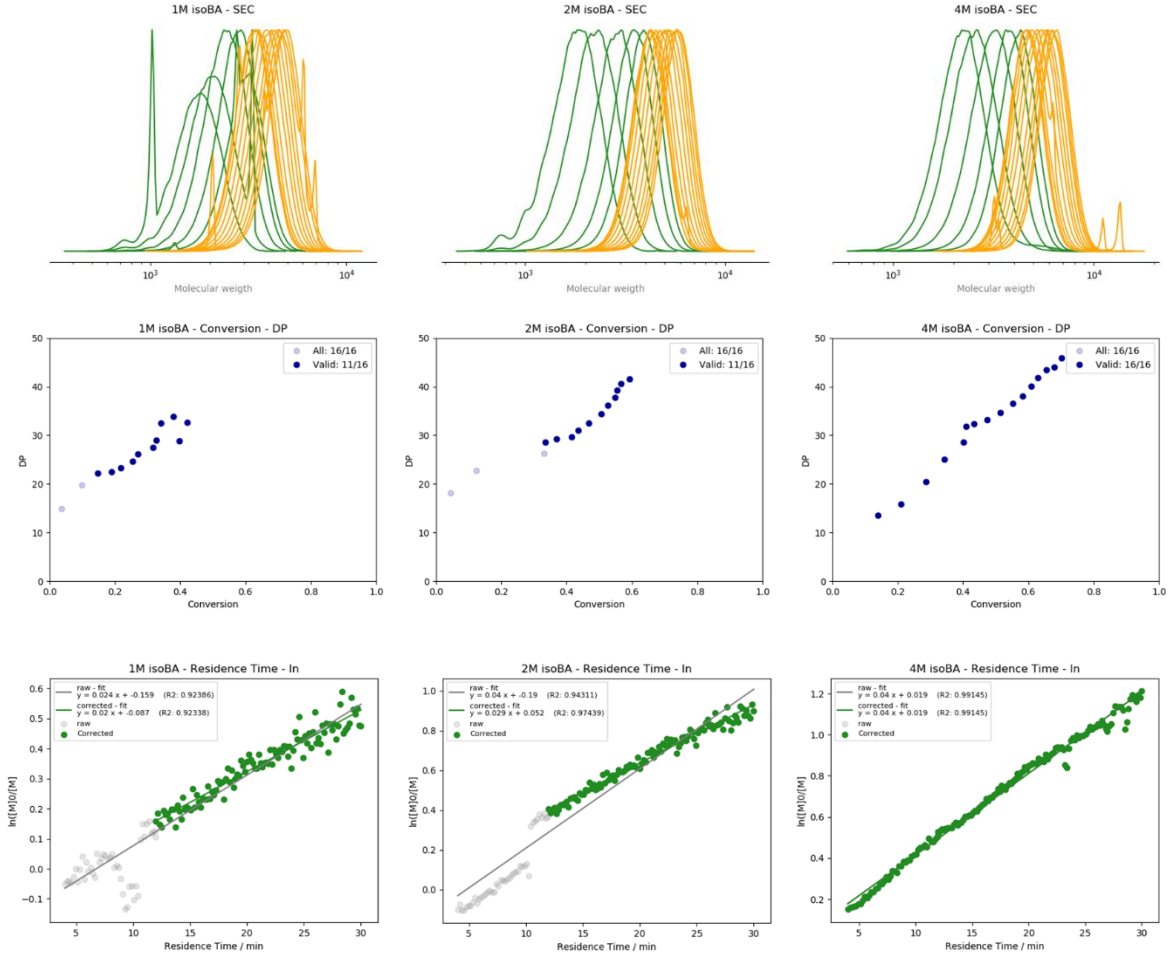
	1M		2M		4M	
t_{res} (min.)	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})
4	1	668.7	7.6	824.8	5.1	NA
6	4.4	929.8	11.5	1072	11.9	NA
8	6.8	1148	17.6	1465	23.3	1205
10	9.6	1404	22.7	1805	34.6	1992
12	13.6	1611	26.5	2083	42.9	2755
12	18	1723	22.9	2237	43.7	3231
13.8	18.1	1765	22.1	2255	46.6	3251
15.6	20	1819	29.8	2341	50.7	3317
17.4	24.7	1949	34	2478	54.8	3451
19.2	23.3	2079	36.7	2643	59.8	3631
21	28.8	2228	41.2	2816	62.4	3875
22.8	30.1	2392	45.7	2998	65.2	4110
24.6	32.7	2520	46.8	3220	67.5	4334
26.4	34.5	2644	50.9	3379	70	4539
28.2	34.7	2759	51.4	3524	71.4	4679
30	33.3	2874	53.4	3643	73.2	4794

Figure S 25 *Automated screening of propyl acrylate polymerization (0.005M AIBN, 80°C, DP_{target} = 50, butyl acetate as solvent). Data was acquired via timesweeps of 4 to 12 and 12 to 30 minutes.*



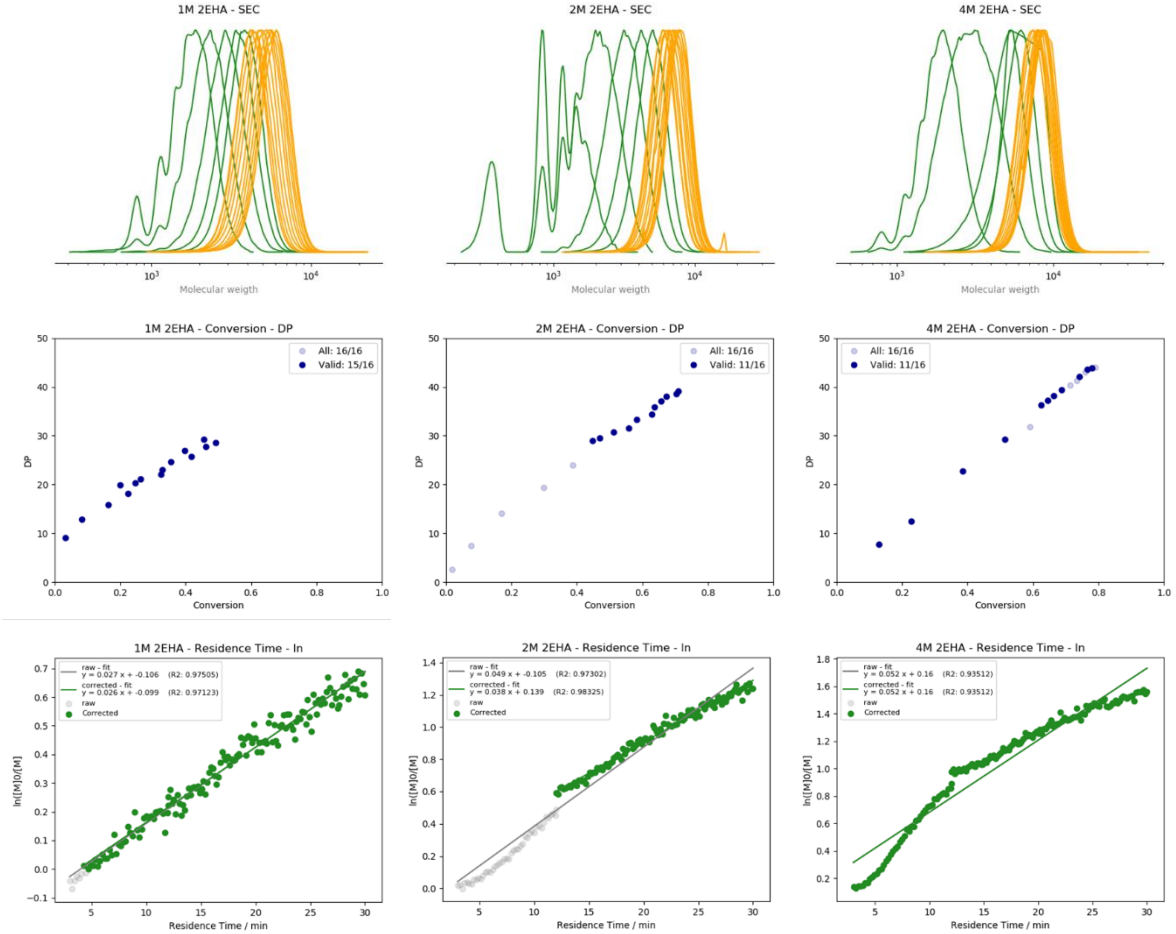
	1M		2M		4M	
t_{res} (min.)	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})
4	-1.8	1133	6	1425	12.2	1626
6	1.2	1340	16	1821	18.4	1835
8	6.7	1764	23.8	2474	27.5	2465
10	15.4	2155	32.1	2974	36.7	3240
12	20.4	2416	38.8	3444	44.7	3662
12	20.4	NA	40.5	3753	47.5	4249
13.8	22	NA	43.6	3836	48.6	4294
15.6	26.1	NA	47.5	4015	51.1	4385
17.4	27.8	NA	50.2	4030	55.6	4545
19.2	30	NA	52.5	4318	58.6	4725
21	35.1	NA	55.8	4299	62.4	4831
22.8	39.4	NA	56.6	4715	64.8	5260
24.6	40.1	NA	61	4875	67.9	5399
26.4	43.3	NA	62.7	5031	69.7	5632
28.2	43	NA	65.4	5173	71.6	5762
30	45	NA	65.9	5274	73.4	5918

Figure S 26 *Automated screening of butyl acrylate polymerization (0.005M AIBN, 80°C, DP_{target} = 50, butyl acetate as solvent). Data was acquired via timesweeps of 4 to 12 and 12 to 30 minutes.*



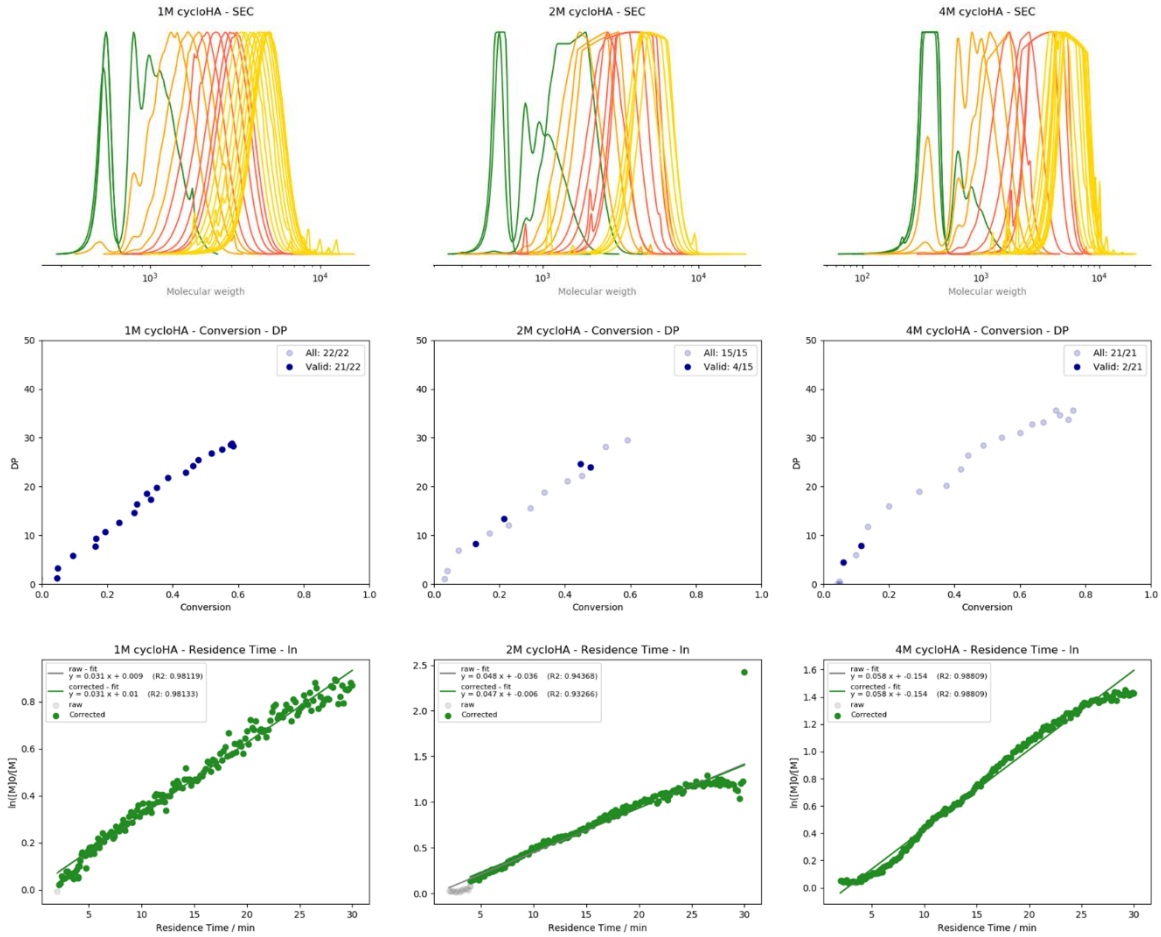
	1M		2M		4M	
t_{res} (min.)	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})
4	-5.3	1288	-10.7	1409	14	1789
6	-0.8	1654	-3.9	1774	21	2048
8	3.7	1939	4.5	2318	28.6	2566
10	-10.9	2266	12.2	2839	34.3	3094
12	9.9	2499	33.1	3233	40.1	3510
12	14.7	2770	33.4	3507	41	3887
13.8	19	2804	36.9	3578	43.4	3937
15.6	21.8	2901	41.6	3635	47.4	4035
17.4	25.4	3048	43.5	3785	51.5	4201
19.2	27.1	3221	46.7	3963	55.2	4423
21	31.6	3381	50.5	4177	58.3	4607
22.8	32.7	3556	52.6	4386	60.9	4834
24.6	39.7	3536	54.9	4571	63	5037
26.4	34.1	3963	55.4	4739	65.6	5229
28.2	42.2	3981	56.8	4894	67.9	5297
30	37.8	4120	59.3	5016	70.2	5522

Figure S 27 *Automated screening of isobutyl acrylate polymerization (0.005M AIBN, 80°C, DP_{target} = 50, butyl acetate as solvent). Data was acquired via timesweeps of 4 to 12 and 12 to 30 minutes.*



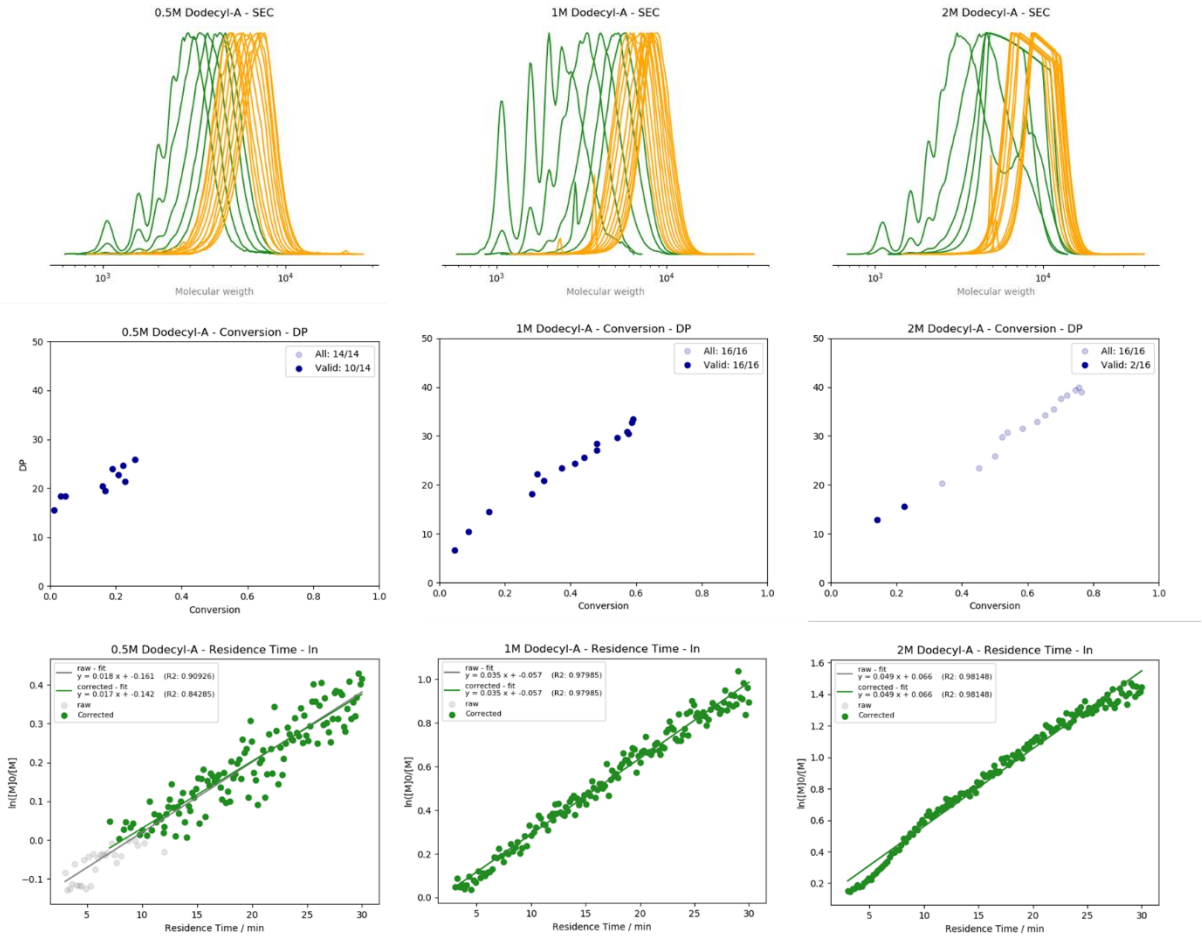
	1M		2M		4M	
t_{res} (min.)	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})
4	-4	1413	1.8	728.3	12.9	1555
6	3.3	1779	7.7	1520	22.8	2350
8	8.2	2405	16.9	2602	38.6	4041
10	16.4	2898	29.8	3479	51.4	5123
12	22.4	3270	38.7	4235	59	5558
12	19.9	3573	44.7	5068	62.4	6285
13.8	24.5	3638	47	5160	64.5	6438
15.6	26.2	3779	51.2	5364	66.4	6608
17.4	32.4	3929	55.8	5507	68.7	6803
19.2	32.8	4088	58.3	5792	71.3	6977
21	35.5	4351	63	5986	73.5	7134
22.8	41.8	4538	63.7	6214	74.3	7261
24.6	39.7	4732	65.7	6428	76.1	7425
26.4	46.2	4873	67.3	6579	76.6	7506
28.2	49.3	5011	70.4	6671	77.9	7562
30	45.5	5128	71.1	6771	79	7570

Figure S 28 *Automated screening of 2-ethylhexyl acrylate polymerization (0.005M AIBN, 80°C, DP_{target} = 50, butyl acetate as solvent). Data was acquired via timesweeps of 4 to 12 and 12 to 30 minutes.*


1M cycloHA - SEC
2M cycloHA - SEC
4M cycloHA - SEC
Molecular weigth
1M cycloHA - Conversion - DP
2M cycloHA - Conversion - DP
4M cycloHA - Conversion - DP
All: 22/22
Valid: 21/22
All: 15/15
Valid: 4/15
All: 21/21
Valid: 2/21
DP
Conversion
1M cycloHA - Residence Time - ln
2M cycloHA - Residence Time - ln
4M cycloHA - Residence Time - ln
raw - fit
corrected - fit
raw
Corrected
ln([M]0/[M]
Residence Time / min

	1M		2M		4M	
t_{res} (min.)	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})
2	-0.6	441.8	3.1	423.7	5.1	284.9
3.5	4.7	441.2	4.1	635.2	4.3	282.9
4	4.8	719.5	7.5	1202	4.7	350.3
4	9.5	1048	12.7	1388	6	576.3
5	16.4	1320	16.9	1679	9.9	868.5
6	16.4	1532	22.8	1901	11.5	1083
6	19.3	1708	21.4	2078	13.5	1330
7.5	23.6	1967	29.5	2382	20	1858
9	28.2	2251	33.8	2833	29.3	2427
10.5	28.9	2489	40.8	3148	37.6	2842
12	33.3	2620	45.1	3297	41.9	3006
12	32	2795	44.8	3625	44.2	3482
13.8	35.2	2959	47.8	3534	48.8	3873
15.6	38.5	3231	52.4	4118	54.4	4153
17.4	43.9	3378	59.1	4310	60	4392
19.2	46.2	3583	61	4561	63.7	4524
21	47.7	3752	63.5	NA	67.2	4760
22.8	51.8	3940	65.8	NA	70.9	4821
24.6	55.1	4053	69.3	NA	72.1	5164
26.4	58.5	4140	72.5	NA	74.9	5021
28.2	57.7	4169	69.9	NA	76.2	4892
30	58.1	4214	91.1	NA	76	5164

Figure S 29 *Automated screening of cyclohexyl acrylate polymerization (0.005M AIBN, 80°C, DP_{target} = 50, butyl acetate as solvent). Data was acquired via timesweeps of 2 to 4, 4 to 6, 6 to 12 and 12 to 30 minutes.*



	0.5M		1M		2M	
t_{res} (min.)	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})	Conv. (%)	M_n (g·mol^{-1})
4	-8.8	2174	4.6	1660	14.1	2994
6	-12.5	2574	8.8	2462	22.3	3581
8	-3.9	3089	15.2	3361	33.8	4606
10	1.3	3568	28.1	4126	45.2	5291
12	-3.1	3904	31.8	4726	50	5834
12	3.3	4184	29.9	5033	52.2	6690
13.8	4.5	4204	37.3	5280	53.8	6880
15.6	16.7	4419	41.4	5491	58.5	7078
17.4	15.9	4627	44.1	5769	63	7367
19.2	22.8	4843	48	6093	65.3	7676
21	20.7	5150	48	6374	67.9	7935
22.8	18.9	5419	54.1	6656	70.1	8408
24.6	22.2	5567	57.3	6912	71.9	8563
26.4	25.8	5832	57.7	6847	74.6	8811
28.2	31.2	6012	58.7	7343	75.6	8926
30	34	6129	59.1	7488	76.5	8731

Figure S 30 *Automated screening of dodecyl acrylate polymerization (0.005M AIBN, 80°C, DP_{target} = 50, butyl acetate as solvent). Data was acquired via timesweeps of 4 to 12 and 12 to 30 minutes.*

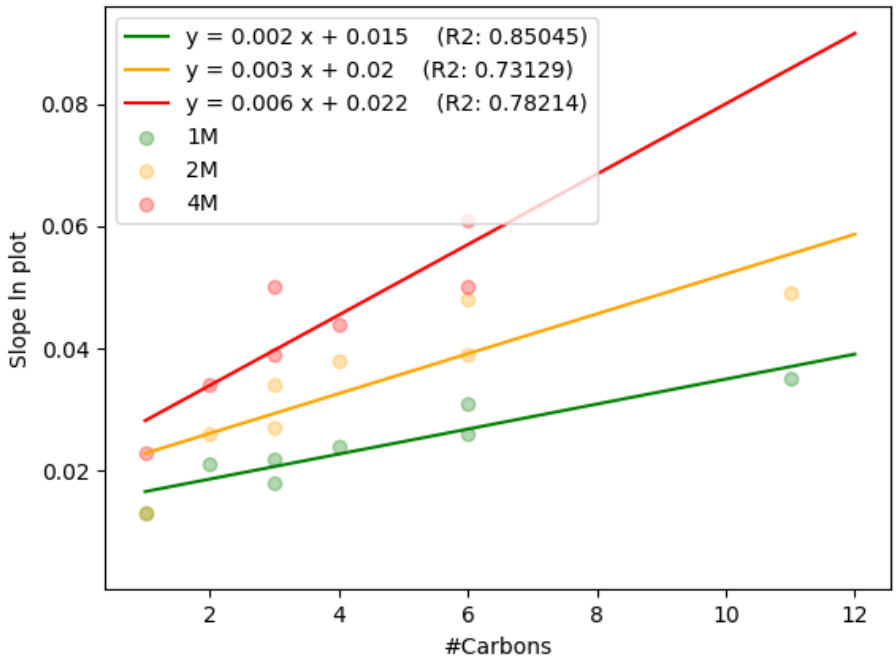


Figure S 31 *Raw overview plot of meta-analysis.*

Table S 16 *Raw data of meta-analysis.*

Monomer	# carbons	Rate of Polymerization		
		1 Molar	2 Molar	4 Molar
Methyl acrylate	1	0.013	0.013	0.023
Ethyl Acrylate	2	0.021	0.026	0.034
Propyl Acrylate	3	0.018	0.027	0.05
n-butyl Acrylate	4	0.024	0.038	0.044
Iso-butyl Acrylate	4	0.021	0.03	0.039
2 ethyl hexyl acrylate	6	0.026	0.039	0.05
Cyclohexyl acrylate	6	0.031	0.048	0.061
Dodecyl acrylate	11	0.035	0.049	*NA*

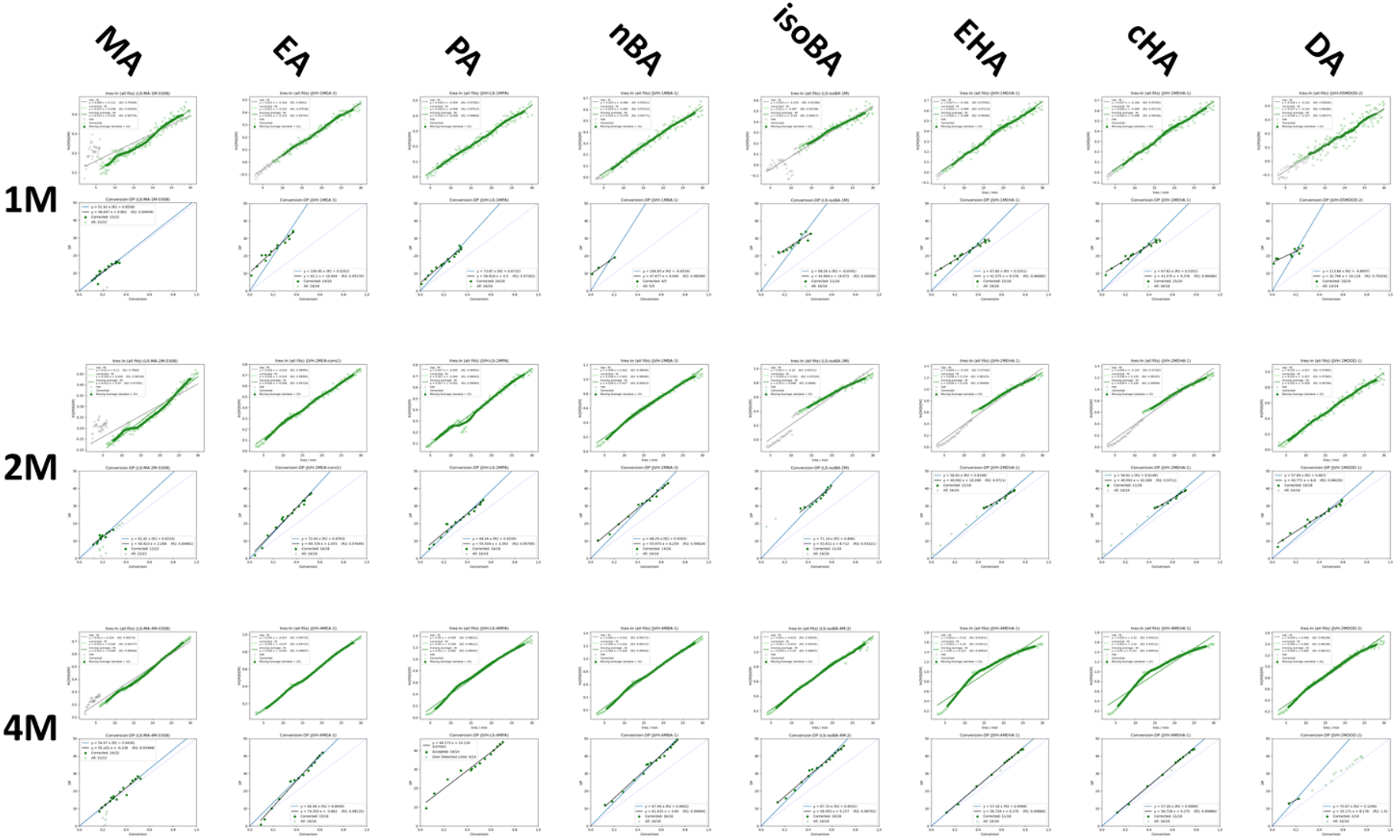


Figure S 32 *Overview of the lab-wide polymerization screening.*

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