Electronic Supplementary Material (ESI) for Polymer Chemistry.


**Supporting Information**

# A predictive framework for mixing of low dispersity polymer samples to design custom molecular weight distributions"

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**Content**

**Materials**

Methyl acrylate (MA) (Acros, 99%) was deinhibited over a column of activated basic alumina, prior to use. 1,1'-azobis(isobutyronitrile) (AIBN) (Sigma-Aldrich, 98%) was recrystallized twice from methanol prior to use. The RAFT agent, 2-(dodecylthiocarbonothioylthio)propionic acid (DoPAT)) was synthesized according to a literature procedure.[1] n-Butyl acetate (Chem-Supply) was used as received.

**Characterization**

Analysis of the molecular weight (distributions) of the samples was performed on a PSS SECcurity$^2$ GPC system operated by PSS WinGPC software, equipped with a SDV 5.0 µm guard column (50 x 8 mm), followed by three SDV analytical 5.0 µm columns with varying porosity (1000 Å, 100000 Å and 1000000 Å) (50 x 8 mm) and a differential refractive index detector using THF as the eluent at 40°C with a flow rate of 1 mL·min$^{-1}$. The SEC system was calibrated using linear narrow polystyrene standards ranging from 682 to 2.52 x $10^6$ g·mol$^{-1}$ PS (K = 14.1 x $10^{-5}$ dL·g$^{-1}$ and α = 0.70). Molar masses and dispersity values were calculated against the Mark-Houwink (MHKS) parameters of the various monomers when available (PMA[2]: K = 10.2 x 10–5 dL·g$^{-1}$ and α = 0.740, PBA[3]: K = 12.2 x 10–5 dL·g$^{-1}$ and α = 0.700). For block copolymers always the MHKS of the first polymer block was applied to approximate the true molecular weight as good as possible.

**RAFT polymerization**

In a typical polymerization, methyl acrylate monomer (4M, eq. degree of polymerization) is weighted in a septum closed glass vial together with the right equivalent of RAFT agent (DOPAT, 1 eq.) and thermal initiator AIBN (0.1 eq). Afterwards, the solvent, n-butyl acetate is added and the solution is flushed with a nitrogen ($N_2$) stream for 5 minutes to remove all residual oxygen. The mixture is transferred to a 10 mL gastight syringe and placed in a Chemyx syringe pump (Fusion 100) attached to a 0.25 ml flow reactor PFA tubing( I.D. 0.5 mm) at 90 °C . The targeted number average molecular weight ($M_n$) is reached with the help of a self-optimizing flow reactor with online SEC. [4]

**Calibration curve**

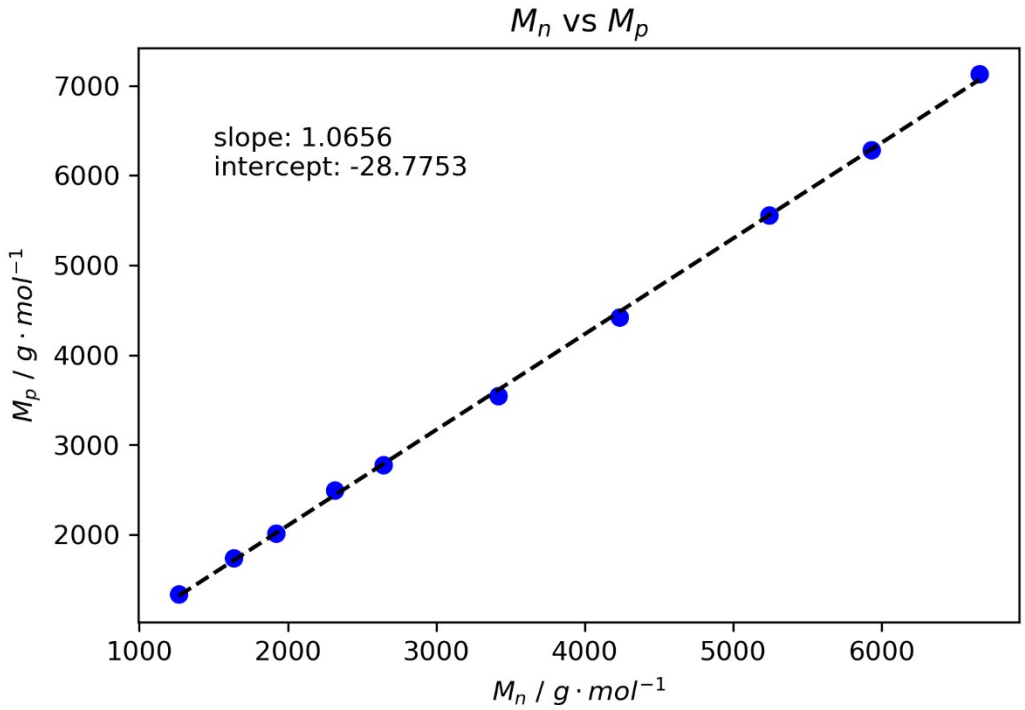



Figure S1: Correlation between $M_n$ SEC and $M_p$ Gaussian

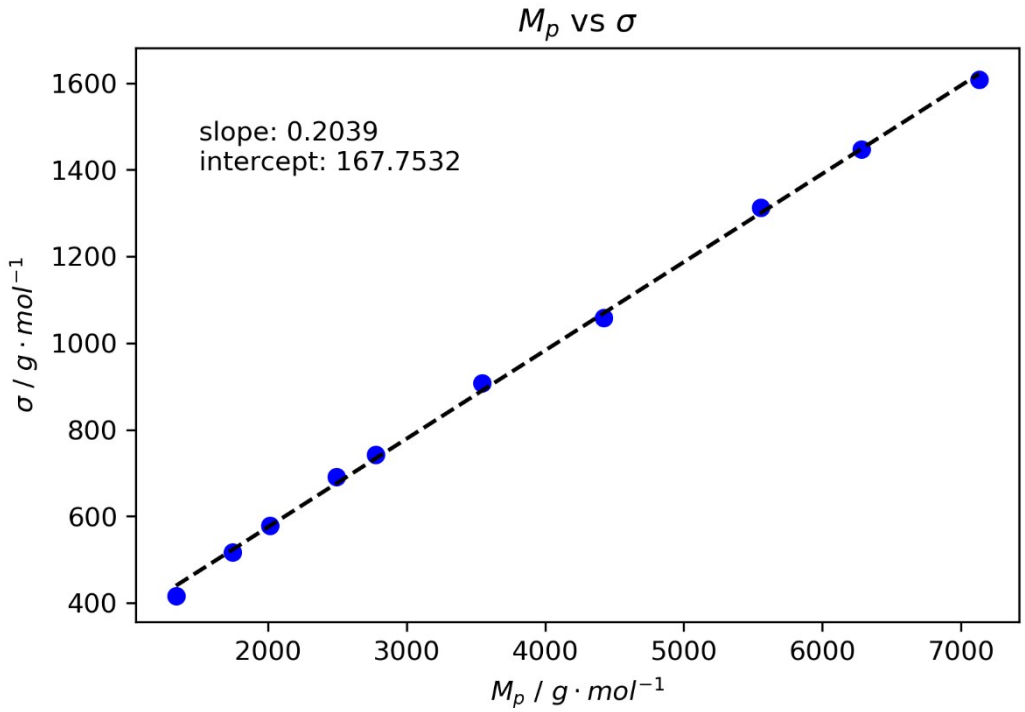



Figure S2: Correlation between $M_p$ and sigma (Gaussian)

Twelve different pMA samples are synthesized according to the procedure discussed above. DP's of 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90 and 100 are targeted and analyzed with SEC. The raw MWD data is processed by the Juypter Notebook script "Fitting Gaussian Distribution to GPC

data.ipynb" to obtain the fitted gaussian distributions. The gaussian distributions are used to find strong correlations between $M_n$ and $M_p$ and $M_p$ and sigma (Figure S1 and S2). With these parameters we can simulate any pMA in the DP range 10 to 100.

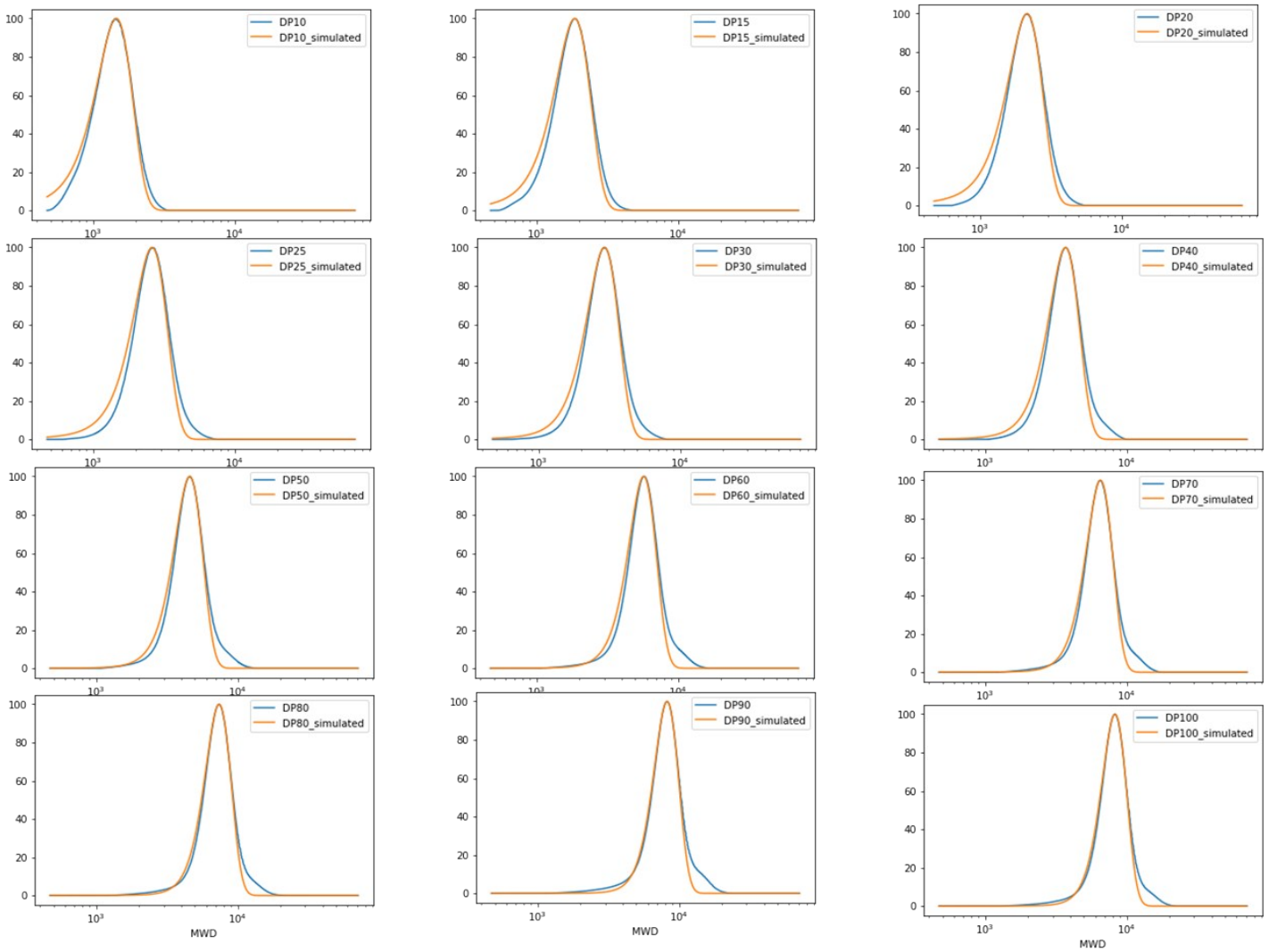



Figure S3: Experimental pMA distributions versus simulated Gaussian distributions

**Synthesis of simulated MWD**

*MWD 1*

Seven pMA samples of DP 10, 15, 20, 25, 30, 35 and 40 are synthesized with predetermined $M_n$ according to the procedure mentioned above and afterwards mixed together. See Table S1 for fractions and Figure S4 .

Table S1: Degree of polymerization (DP) and amount required of 7 pMA polymer samples to attain simulated MWD.

| *Entry* | *DP* | *n* (µmol) |
|---|---|---|
| **1** | *10* | 34.06 |
| **2** | *15* | 18.55 |
| **3** | *20* | 11.64 |
| **4** | *25* | 7.89 |
| **5** | *30* | 5.81 |
| **6** | *35* | 4.42 |
| **7** | *40* | 3.47 |

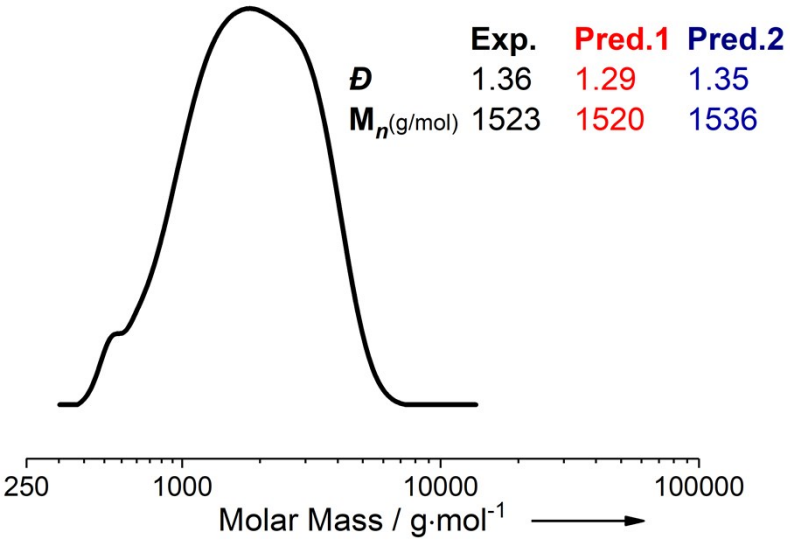



Figure S4: Experimental MWD of equal double molecular weight intensity with $M_n$ of 1500 g·mol$^{-1}$ and D of 1.35 as target.

*MWD 2*

Eight pMA samples of DP 12.5, 17.4, 21.6, 27.4, 36.5, 44.6, 56 and 69.5 are synthesized with predetermined $M_n$ according to the procedure mentioned above and afterwards mixed together. See Table S2 for fractions and Figure S5 .

Table S2: Degree of polymerization (DP) and amount required of 8 pMA polymer samples to attain simulated MWD.

| *Entry* | *DP* | *n* (µmol) |
|---|---|---|
| **1** | *12.5* | 31.2 |
| **2** | *17.4* | 24.8 |
| **3** | *21.6* | 20.4 |
| **4** | *27.4* | 17.2 |
| **5** | *36.5* | 9.2 |
| **6** | *44.6* | 5.54 |
| **7** | *56* | 3.5 |
| **8** | *69.5* | 2.74 |

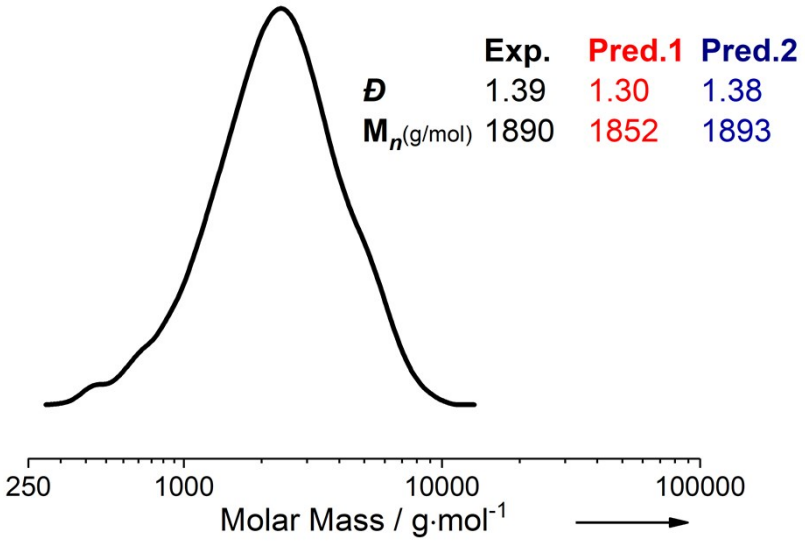



Figure S5: Experimental MWD of equal double molecular weight intensity with $M_n$ of 1900 g·mol$^{-1}$ and D of 1.40 as target.

*MWD 3*

Three pMA samples of DP 10, 20 and 30 are synthesized with predetermined $M_n$ according to the procedure mentioned above and afterwards mixed together. See Table S3 for fractions and Figure S6 .

Table S3: Degree of polymerization (DP) and amount required of 3 pMA polymer samples to attain simulated MWD.

| *Entry* | *DP* | *n* (µmol) |
|---|---|---|
| **1** | *10* | 17.033 |
| **2** | *20* | 5.821 |
| **3** | *30* | 2.906 |

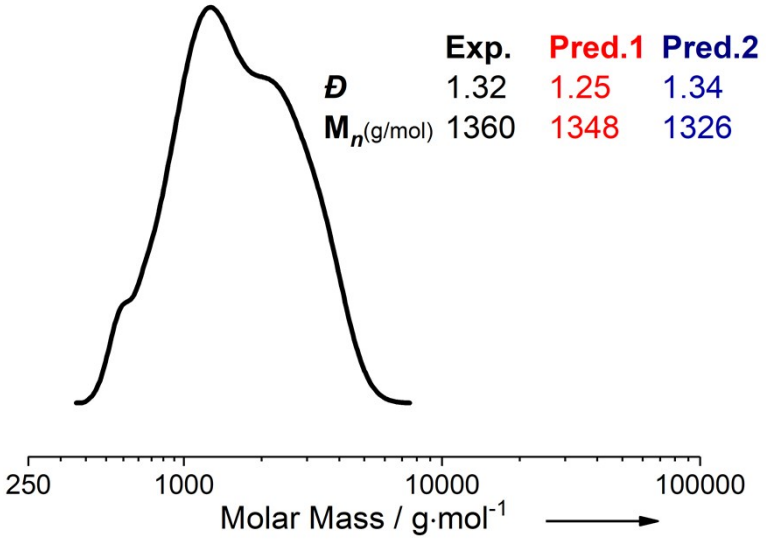



Figure S6: Experimental MWD with high molecular weight shoulder feature , $M_n$ of 1360 g·mol$^{-1}$ and D of 1.32 as target.

*MWD 4*

Three pMA samples of DP 7, 23, 46, 64 and 83 are synthesized with predetermined $M_n$ according to the procedure mentioned above and afterwards mixed together. See Table S4 for fractions and Figure S7 .

Table S4: Degree of polymerization (DP) and amount required of 3 pMA polymer samples to attain simulated MWD.

| *Entry* | *DP* | *n* (µmol) |
|---|---|---|
| **1** | *7* | 5 |
| **2** | *23* | 2.5 |
| **3** | *46* | 1 |
| **4** | *64* | 0.5 |
| **5** | *83* | 0.25 |

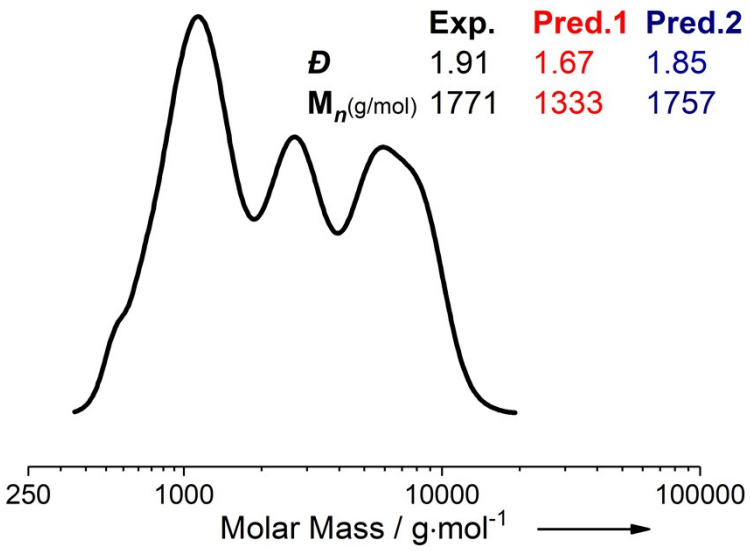



Figure S7: Experimental multimodal MWD with three distinct features , $M_n$ of 1750 g·mol$^{-1}$ and D of 1.91 as target.

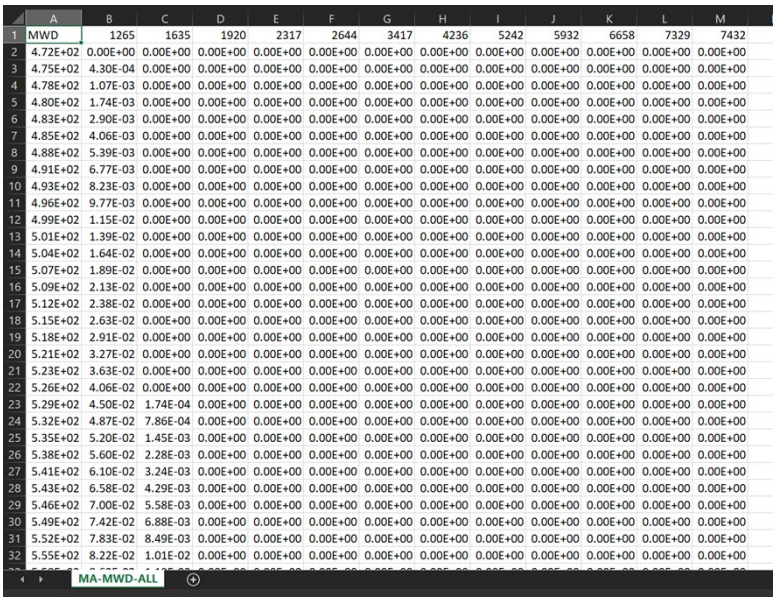
**Juypter Notebook**

Juypter notebooks are a web-based interactive computational environment for a dozen or so programming languages.[5] All relevant code and scripts of this work are written in the Python programming language and are made available as a Juypter notebook. Juypter notebooks provide an easy sharable way to distribute interactive code and is widely used in data engineering and data sciences.

Juypter notebooks and the Python language are best installed with Anaconda.[6] Anaconda is a free and open-source distribution of the Python programming language, including the most common packages and libraries used in scientific computing. These packages are best installed through anaconda.[7] The following additional packages are required to run the code in this work.

- lmfit
- pandas
- matplotlib
- numpy
- ipywidgets
- IPython
- scipy.stats
- pathlib

**Juypter Notebook "Fitting Gaussian Distribution to GPC data.ipynb"**



| | A | B | C | D | E | F | G | H | I | J | K | L | M |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | MWD | 1265 | 1635 | 1920 | 2317 | 2644 | 3417 | 4236 | 5242 | 5932 | 6658 | 7329 | 7432 |
| 2 | 4.72E+02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 3 | 4.75E+02 | 4.30E-04 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 4 | 4.78E+02 | 1.07E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 5 | 4.80E+02 | 1.74E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 6 | 4.83E+02 | 2.90E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 7 | 4.85E+02 | 4.06E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 8 | 4.88E+02 | 5.39E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 9 | 4.91E+02 | 6.77E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 10 | 4.93E+02 | 8.23E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 11 | 4.96E+02 | 9.77E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 12 | 4.99E+02 | 1.15E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 13 | 5.01E+02 | 1.39E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 14 | 5.04E+02 | 1.64E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 15 | 5.07E+02 | 1.89E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 16 | 5.09E+02 | 2.13E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 17 | 5.12E+02 | 2.38E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 18 | 5.15E+02 | 2.63E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 19 | 5.18E+02 | 2.91E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 20 | 5.21E+02 | 3.27E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 21 | 5.23E+02 | 3.63E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 22 | 5.26E+02 | 4.06E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 23 | 5.29E+02 | 4.50E-02 | 1.74E-04 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 24 | 5.32E+02 | 4.87E-02 | 7.86E-04 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 25 | 5.35E+02 | 5.20E-02 | 1.45E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 26 | 5.38E+02 | 5.60E-02 | 2.28E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 27 | 5.41E+02 | 6.10E-02 | 3.24E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 28 | 5.43E+02 | 6.58E-02 | 4.29E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 29 | 5.46E+02 | 7.00E-02 | 5.58E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 30 | 5.49E+02 | 7.42E-02 | 6.88E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 31 | 5.52E+02 | 7.83E-02 | 8.49E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 32 | 5.55E+02 | 8.22E-02 | 1.01E-02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |

MA-MWD-ALL

Figure S8: Example of experimental MWD format for " Fitting Gaussian Distribution to GPC data " script.

The first Juypter notebook offers an easy way to find the Gaussian fits of experimental MWDs. The raw MWD data needs to be saved as a *comma-separated-value* file with extension *.csv*. The file needs to be saved in the same folder as the notebook and the file name *xxx.csv* needs to be added to the script (see comment in the third cell of the notebook). The raw MWD data needs to be strictly formatted as the example to guarantee compatibility with the script (Figure S8). In short, the first column needs the title 'MWD' and following columns need the $M_n$ as title.

The notebook contains six cells with code. The first cell defines the gaussian function. The second cell imports the required libraries. The third cell reads in the .csv file with the experimental data. The forth computes the gaussian fit to the experimental data and saves it in a pandas DataFrame. The fifth cell calculates the correlation between the experimental $M_n$ and the gaussian average ($M_p$). The data is plotted and saved as png image file with name "Mn_vs_Mp.png" in the same folder as the notebook. The final cell calculates the correlation between the gaussian average ($M_p$ ) and the standard deviation of the fitted gaussian distribution. The data is plotted and saved as png image file with name "Mn_vs_sigma.png" in the same folder as the notebook.

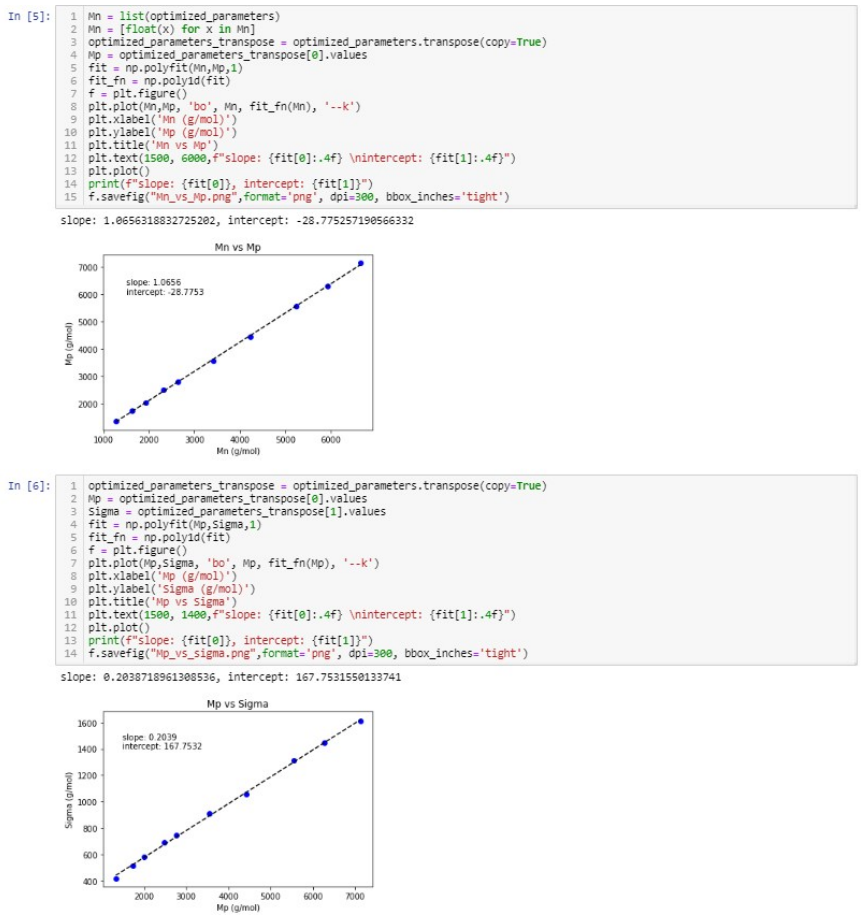



Figure S9: Last two output cells of Fitting Gaussian Distribution to GPC data notebook.

**Juypter Notebook "Distribution_simulator.ipynb"**

The second Jupyter notebook gives the user the ability to simulate the same distribution as shown in the paper. The notebook hides all the cell with code and only shows a click-and-point user interface. All the code can be shown by clicking the top button "Show code". The user interface consists out of 4 separate tabs containing multiple functions:

- Distributions
    - Up to 10 distributions can be mixed. Only the number average chain length (or targeted DP) is required as input parameter
- Concentrations
    - For each distribution a concentration is required. Concentration zero is the concentration of Distribution zero and so forth.
- Type of Distribution
    - Distribution
        - Theoretical Gamma Distribution (method 1 of paper).
        - Experimental Calibrated Distributions (method 2 of paper) and requires the fits of the Gaussian distributions to the experimental data.
    - Analysis
        - Theoretical versus Experimental MWD. The experimental broad MWD can be loaded and compared to the computed theoretical MWD. The file path of .csv file containing the experimental data is required in the settings tab. The .csv file with experimental data needs to be strictly formatted with 'MWD' and 'Experimental' as title of first and second column respectively. (Figure S11)
        - Residual Analysis MWD. The difference between the theoretical and experimental MWD.
        - Residual Analysis Number. The difference between the theoretical and experimental number.
        - Plot button: Plots the theoretical distribution in the notebook
        - Save button: Saves the theoretical distribution as a .csv file in the same folder as the notebook.
        - Analysis button. Plots the chosen analysis in the notebook

- Save Analysis button. Saves the chosen analysis as a .csv file in the same folder as the notebook.

- Monomer and RAFT agent
  - The molar mass of the raft agent and monomer is set in g $mol^{-1}$. Also the slope and intercept of both the "$M_n$ vs $M_p$" and "$M_p$ vs sigma" correlation is required if the Gaussian method is used.
- Settings

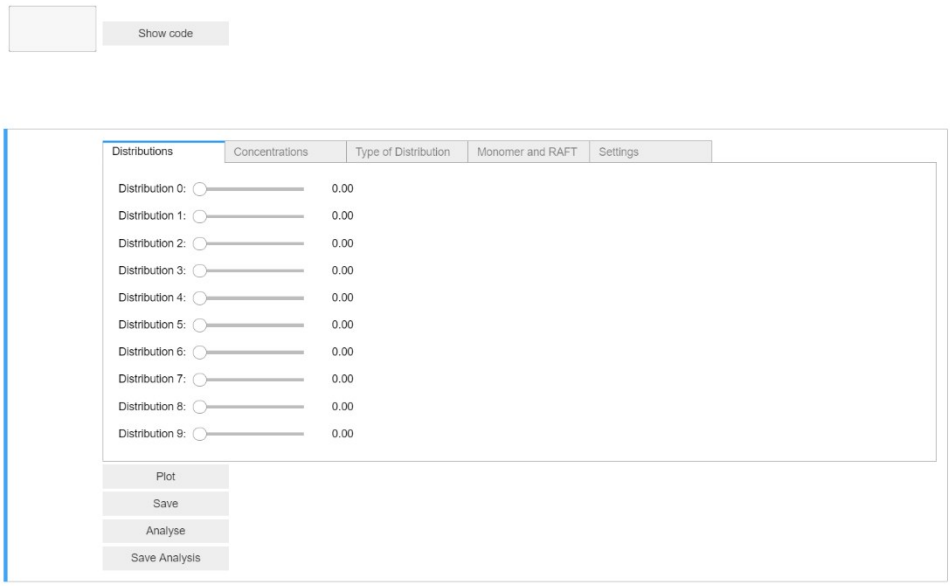



Figure S10: User interface for simulating distributions by method 1 and 2.

  - The name of the saved files and the path of the experimental broad MWD for comparison is required.

| | A | B | C |
|---|---|---|---|
| 1 | MWD | Experimental | |
| 2 | 5.08E+02 | 2.78E-18 | |
| 3 | 5.14E+02 | 2.76E-02 | |
| 4 | 5.19E+02 | 3.98E-02 | |
| 5 | 5.24E+02 | 4.00E-02 | |
| 6 | 5.29E+02 | 2.66E-02 | |
| 7 | 5.34E+02 | 1.06E-02 | |
| 8 | 5.40E+02 | 0.00E+00 | |
| 9 | 5.45E+02 | 0.00E+00 | |
| 10 | 5.50E+02 | 0.00E+00 | |
| 11 | 5.56E+02 | 0.00E+00 | |
| 12 | 5.61E+02 | 0.00E+00 | |
| 13 | 5.67E+02 | 0.00E+00 | |
| 14 | 5.73E+02 | 0.00E+00 | |
| 15 | 5.78E+02 | 0.00E+00 | |
| 16 | 5.84E+02 | 0.00E+00 | |

Figure S11: Example .csv file for experimental data

**References**

[1] C. J. Ferguson, R. J. Hughes, , D. Nguyen, B. T. T. Pham, R. G. Gilbert , A. K. Serelis, C.H. Such and B.S. Hawkett, *Macromolecules* **2005**, 38, 2191- 2204

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[4] M. Rubens, J. H. Vrijsen, J. Laun, T. Junkers, *Angew. Chem. Int. Ed*. **2019**, 58, 3183

[5] https://jupyter.org

[6] https://www.anaconda.com/

[7] https://docs.anaconda.com/anaconda/user-guide/tasks/install-packages/