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Designing Molecular Weight Distributions of Arbitrary Shape with Selectable Average Molecular Weight and Dispersity

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Abstract

While methods to control dispersity of a molecular weight distribution are slowly emerging, the question remains, how any arbitrary distribution, and more precisely distribution shape can be created in a polymer sample. Ultimately, if the aim is to create any shape form, then this can only be achieved by blending individual polymers. In here, we describe an approach to first generate molecular weight distributions of any shape with selectable average molecular weight and dispersity. With such software tool at hand, we discuss the influences of shape and dispersity on the residual structure. Molecular weight distributions are often less intuitive than anticipated, and

effects can be complex. In the next step we show how these generated distributions are automatically fitted to interpolated RAFT polymer distributions, providing a detailed instruction which polymers need to be blended in which quantity in order to obtain the desired additive distribution. The software tools required for this task are demonstrated and discussed, and are made available to the reader for download.

Introduction

In the past decades, investigations into living polymerizations and reversible deactivation radical polymerizations (RDRP) were focused on the control of functionality of a growing polymer chain, and the control of average molecular weights.^{1,2,3} The narrowness of a distribution, connected to a low dispersity value \mathcal{D} has thereby become the signature of a well-behaved process. Typically, a dispersity below 1.5 is seen as a successful controlled polymerization, and usually chemists strive to keep the value as low as 1.1 or lower if possible. Indeed, for certain applications such as self-assembly, a low dispersity had been deemed essential to reach for predictable results, even if that is not necessarily the case.⁴ On the other side, it is long known in application of polymers that low dispersities are not necessarily advantageous, and indeed for optimal polymer properties often broad distributions can be preferred.^{5,6} Surprisingly though, only little research has been applied over the years to the manipulation of \mathcal{D} , or the overall shape of molecular weight distributions. Only recently, efforts have been made to look into designer polymers with specific distribution broadness, and first results show profound influences on the properties of materials.^{5,7,8,9,10} The field has gained momentum, and next to other grand challenges in polymer chemistry, development of effective dispersity control is in the making at present.¹¹

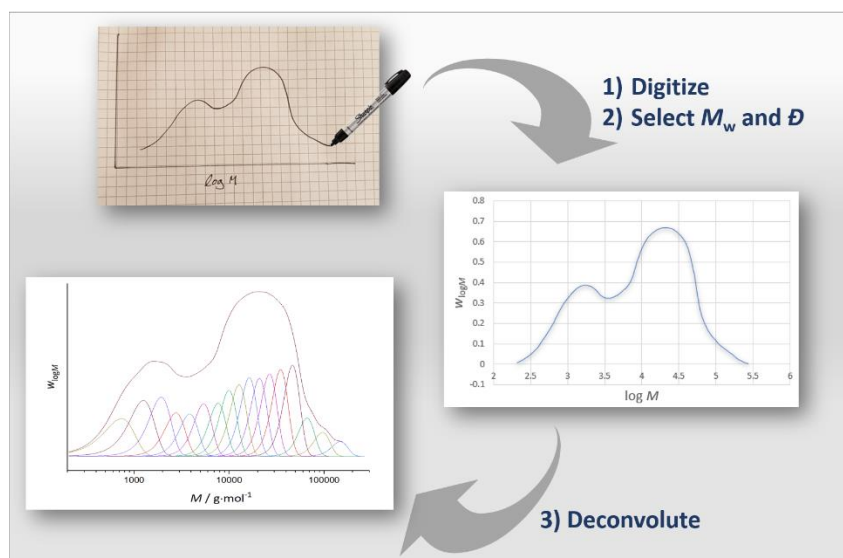
Different methods exist to influence the dispersity of a polymer from a living or RDRP process.^{11,12,13,14,15,16} In order to be able to manipulate polymers further after an initial polymerization step, high livingness is generally required for a successful dispersity-control experiment (note that broad dispersities and high livingness are not mutually exclusive as is sometimes wrongly assumed). Designer molecular weight distributions are accessible from manipulation of the reactivity of the employed control agents (or mix of control agents).^{12,16} Other possibilities are influencing the mixing efficiency of initiators at the start of polymerizations,¹³ for

example in fast anionic polymerizations. Yet, such approaches yield mostly symmetrical, or at least monomodal distributions. Dosing of initiator/control agent in a controlled manner over the period of a polymerization is another way of creating specific distributions. This concept was introduced by Fors and coworkers, who also showed that polymers with the same dispersity and average molecular weight, but different skewness of distributions can behave differently.^{7,17} This is an important observation, as it shows that average molecular weights and dispersity do not sufficiently describe a polymer distribution, even though these parameters have been used extensively over the last decades to describe polymers. Harrison noted already earlier that dispersity is a flawed value to accurately describe polymers.¹⁸ He proposed to use the standard deviation instead, as this statistical value much better represents the change in a distribution's broadness during a polymerization.

The last method to create specific polymer distributions is blending of individual polymers. In this approach, various polymers are synthesized and then mixed in the correct proportions in order to create specific distributions.^{19,20,21} This approach has the disadvantage that more than one polymerization is required to obtain a specific polymer distribution. It also suffers from a requirement of very high precision in order to mix the right polymers. Already small deviations from ideal mixtures yield ugly-shaped polymer distributions. However, we had demonstrated in the past how automated flow synthesis of polymers²² can provide the required precision and accuracy in mixing in order to solve this problem.²⁰ The advantage of the blending method is, however, directly obvious. It allows to create reliably any distribution shape, no matter how natural or non-natural it may be. Any direct polymerization method will always yield mostly monomodal distributions, even if the skewness can be varied effectively in the initiator dosing approach. In

principle, more complex distributions could be created, yet that would require sophisticated dosing profiles, and on long term become equivalent to the blending method in essence.

In the previous work on blending found in literature a significant problem is, however, eminent: How to determine optimal mixtures for a given desired polymer distribution? So far, mixtures were determined by simple serendipity, or by adjustment of parameters by hand. An approach which would allow to draw a distribution by hand and then to break it down to a list of polymers to synthesize and blend is not available yet. In this work we present a method to solve this problem and provide software tools for other researchers to create their own distributions and blended mixtures.



Scheme 1: The way to designer molecular weight distributions: First, the desired distribution is drawn or created as a function graph, then recomputed to fit a desired M_w and \mathcal{D} (in this case $M_w = 50\,000\text{ g}\cdot\text{mol}^{-1}$ and $\mathcal{D} = 3.0$), and in the last step deconvoluted into single molecular weight distributions and their additive distribution.

The concept followed is visualized in Scheme 1. First, a distribution is generated either by plotting a function or by digitizing desired shapes. This must be done with external software. In this work we either used built-in Excel functions or third party software for this purpose. Various programs

can be found providing functionality to digitize any graph or picture into a distribution plot.²³ The difficulty is though not to create a digital distribution, but to adjust it to a defined average molecular weight and overall broadness. This is achieved by an Excel Macro calculation, for which the Excel file is provided online (see below for information). In the next step, the created distribution is then deconvoluted into single sub-distributions. To reach this aim, we make use of the method used before to predict polymer blending results,^{24,25} but have significantly extended it to deconvolute and fit any given distributions. At the moment the software will create a set of RAFT polymers in distinct amounts, yet this can be easily adjusted to other polymerization methods by using the framework we have provided before. Also the deconvolution software is provided online free of charge. With this we hope to give other researchers the required software tools at hand to create designer distributions.

Software

Both the Excel macro “MWD generator” to create the distributions as well as the Python script for the deconvolution software “MWD predictor” can be found online at <https://www.polymatter.net/software>. The software tools are free to use for academic research and fall under a CC-BY-NC license. The software tools will be constantly further improved, and newer versions will be made available on the same page.

MWD generator

The provided macro works via insertion of a previously derived digitized distribution into the respective fields. The macro allows to define a desired weight-average molecular weight and dispersity. Upon running of the macro, an output is created that gives the same distribution, but

then with the correct average molecular weight and distribution broadness. The software requires to input data in a $w_{\log M}$ vs $\log M$ format, the output is given as $\log M$ -weighted, weight and number distribution (for an excellent explanation of the different distribution types, see ref²⁶). For calculation of the distribution, the macro first normalizes the input distribution to a typical logarithmic range. This allows for input data to be fully arbitrary in units. In the next step, the x-axis is stretched in order to match the desired dispersity. After this is done, the distribution is shifted to the desired average-molecular weight, which is calculated from the moments of the distribution. Note that an integral calculation is used for the moments, thus datapoints in the original distribution do not need to be evenly spaced. Then, the distribution is normalized to the area under its curve, to provide distributions that represent a constant mass, irrespective of the input data scale. Next to the three different representations of the distribution, also the average molecular weights, the dispersity and the peak maximum of the $\log M$ -weighted distribution is given. The $\log M$ -weighted distribution was chosen as main reference distribution in the macro as this representation is the most commonly used one in SEC software. It must be noted that the current way of stretching the x-axis to accommodate the desired dispersity leads to a slight skewing of the data when the chosen dispersity differs largely from the input. The normalization procedure used prevents this to some extent, but in the current version not fully. A box distribution will thus appear slightly angled when recalculated. Most curved distributions will, however, not show this effect in pronunciation. As we will show below, straight lines are difficult to approximate in molecular weight strictures in any way, hence this skewing does not have larger consequences.

Next to creating the appropriate input distributions for the second software deconvolution step, the software also can prove to be useful for teaching material, as it can be easily used to create distributions to visualize changes in dispersity relative to molecular weight, as well as providing

alternative views on weight and number distributions, which most polymer chemists are not used to examine in most cases. A view on the generated output from the macro is given in Figure 1.

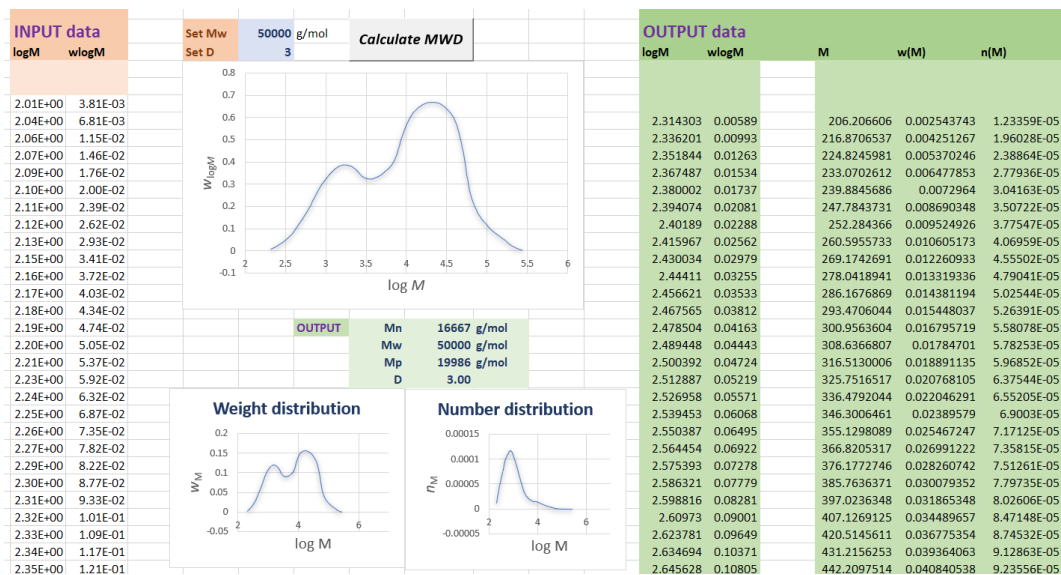


Figure 1: Screenshot of the Excel macro “MWD generator v1.0”

MWD predictor

A python script using a fitting algorithm (non-linear least-squares minimization) was programmed to deconvolute MWDs into a number of sub-distributions. The user only needs to input the target MWD and define the number of desired sub-distributions. Fitting is carried out on the number distribution. Hence, the target MWD should be entered as a number distribution and the datapoints must be spread evenly for optimal results. Performing a cubic spline is thus recommended before entering the data into the Python program. It is important to note that the excel script is based on a logarithmic scale and does not automatically interpolate. This is due to the recalculation of dispersity being processed on logarithmic data, and due to the fact that the Excel macro does not necessitate evenly spaced data inputs (as digitized shapes will typically feature non-equidistant

data). If non-interpolated data is used, more weighting is given to the low molecular weight side of the distribution (as this side contains more datapoints coming from a logarithmic axis), which can lead to unfavorable fitting results. Nevertheless, the fitting procedure can also be applied in this case, and may still result reasonable results. Yet, interpolation is recommended.

The algorithm predicts the characteristics of these additive distributions starting from a Gaussian function of which the standard deviation (σ) is correlated with the M_p of the distribution. This approach is taken from our previous work on interpolation of experimental molecular weight.²⁴ In the current version, the simulated sub-distributions will resemble experimental RAFT polymerization distributions. Yet, as described before, also other types of polymerizations can in principle be applied if the interpolation is carried out accordingly to our framework.²⁴ While the framework uses experimentally determined broadness' of the sub-distributions, the script allows to vary the sigma factor of the Gaussians in order to generate different dispersities. A factor of 1 will create the RAFT-typical natural distributions. The script will then commence varying the mean and amplitude of the individual additive distributions to reach a best total fit with the target distribution in a least-squares fitting approach. When a best fit has been found the script will create an output for the sub-distributions and create their additive distribution, both as number and $w_{\log M}$ -weighted distributions in a txt-file. A "prediction summary" file is also generated that contains a fitting report and the M_n , M_w , and D of each individual distribution and in which proportion these should be blended to yield the target MWD.

Results and Discussion

Despite the inherent flaws of the concept of dispersity, we opted to use this quantity for MWD generation, for the simple sake of using the parameters that researchers are used to. Inherently, standard deviations and skewness are better parameters to describe distributions overall, especially when discussing chain extensions in experiments. As molecular weight average, the weight average M_w was picked since polymer properties typically scale with the weight average of a material, and hence it is more interesting to model distributions according to this. Dispersity inherently describes the broadness of a distribution in relation to its average molecular weight.¹⁸ The actual spread of a distribution differs quite significantly for different distributions despite them having the same dispersity. Usage of dispersity and average molecular weight also ignores multimodality and skewness of a distribution. Even with constant average molecular weights and dispersity, quite different distributions can be obtained. The calculation tool allows to examine these effects in more detail.

Two examples for influences on molecular weight distributions is given in Figure 2. On the l.h.s. (Figure 2a) symmetrical distributions are given, which vary in dispersity while keeping the weight average molecular weight constant at $10\,000\text{ g}\cdot\text{mol}^{-1}$. On the r.h.s. in Figure 2b two skewed distributions are shown that are different in their direction of skewness, but which feature the same dispersity and average molecular weight. The dispersity series on the l.h.s. nicely shows how the whole distributions are seemingly shifted to lower molecular weight, even though its weight average remains constant. Yet, the broadness develops as one would expect for increasing values. The difficulty of dispersity is thus much better shown in Figure 2b. Both distributions (normalized to the peak maximum for better demonstration) feature exactly the same moments of distribution. Yet, they are appearing clearly different from each other. Further, the negatively skewed

distribution (dark red) appears broader in its molecular weight shape than its positively skewed counterpart (please note that before recalculation to constant M_w both distributions were mirror images of the same Weibull distribution). Both distributions still feature the same moments of distributions and hence the same dispersity value, nicely demonstrating that dispersity must be treated with care when comparing two (non-symmetrical) distributions.

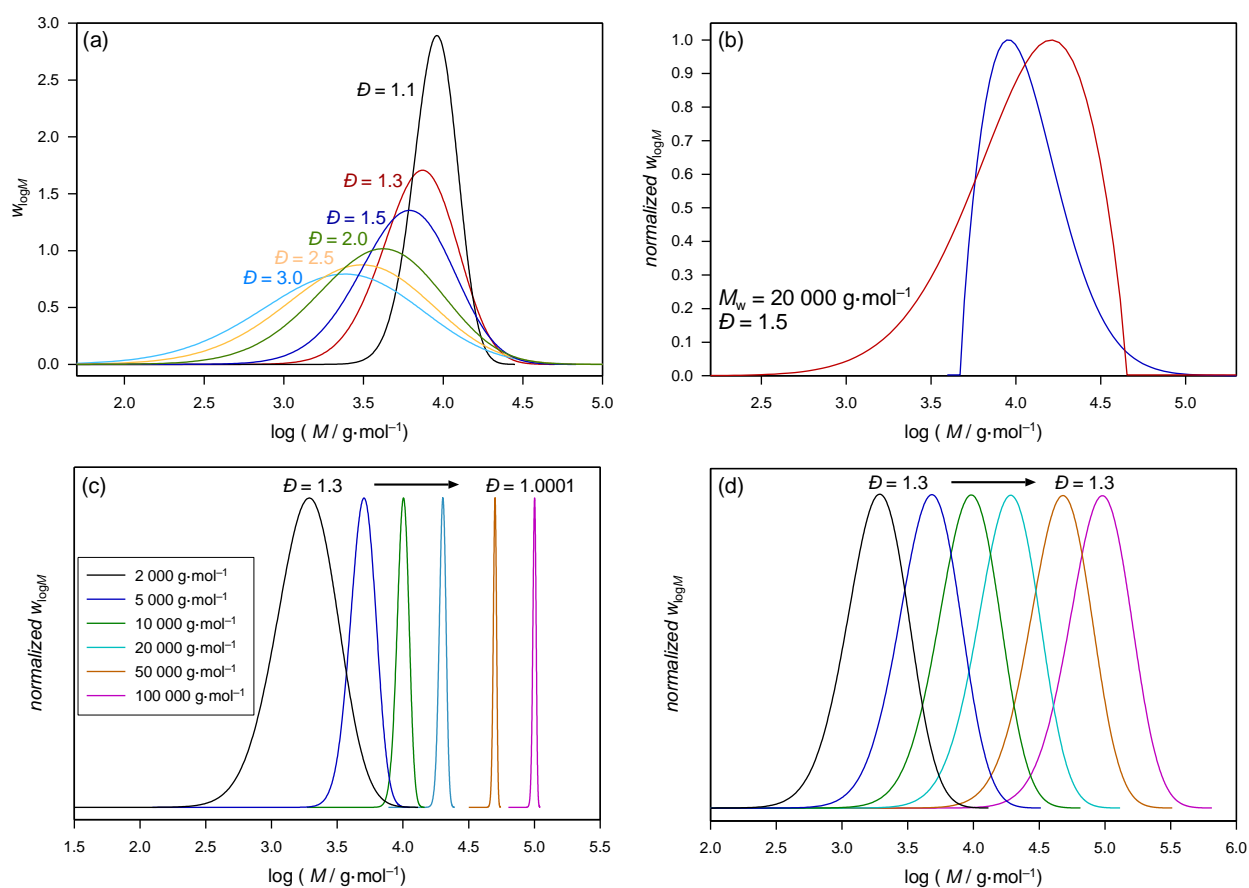


Figure 2: (a) Symmetric distributions with constant $M_w = 10\,000 \text{ g}\cdot\text{mol}^{-1}$ and decreasing dispersity and (b) positively and negatively skewed distributions with constant M_w and \mathcal{D} . (c) Distributions with increasing molecular weight and constant standard deviation and (d) with constant dispersity.

On the lower side of Figure 2, further examples are given for calculated mass distributions. The tool provided can be used to visualize progression of molecular weight distributions. In Figure 2(d), molecular weight distributions with increasing molecular weight (from 2000 g/mol to 100 000 g/mol) are given, whereby dispersity is kept constant at 1.3. This representation is often found to visualize controlled polymerizations, in fact the distributions are easily generated as the broadness on logarithmic scale does not change; the distributions are only shifted parallelly. Yet, a controlled polymerization, under absolutely perfectly living conditions, resembles a Poisson distribution that grows on the molecular weight axis. Thus, not dispersity should be constant, but the standard deviation.¹⁸ In Figure 2(c) this effect is demonstrated. Starting from the same distribution with $M_n = 2000$ g/mol and $\mathcal{D} = 1.3$ (being equivalent to a standard deviation of 1100 g/mol), progressive molecular weight distributions are given where the standard deviation is kept constant. With the moving M_n , the overall dispersity decreases rapidly. While decreasing dispersities are generally described for a successful living polymerization, the exact effect is often misinterpreted and the Excel Macro can be a good tool to display the effects precisely.

With the methodology at hand to create any desired distributions shape, and the ability to recalculate these distributions into any given weight average molecular weight and dispersity, we can examine in the next step how these distributions can be fitted to sub-distributions for blending experiments. As outline in the software section, the Excel/macro generated distributions are loaded into a Python script, and are then fitted to molecular weight distributions that are typical for RAFT polymerizations. For this aim, we used the theoretical framework that we had described before. This framework allows to interpolate MWDs as would be obtained from experiments, while allowing to choose any average molecular weight for each interpolated distribution. For the aim of this paper we stucked to the system that we had investigated before, methyl acrylate RAFT

polymerization.²⁰ As we had demonstrated that the interpolation yields distributions that are very close to what can be synthesized using automated flow synthesis.^{24,27} The framework is that validated, and should be straight forward to apply here in a theoretical approach. A practical implementation would be possible without further adjustment as the difference between our previous work and this investigation is how to determine which subdistributions are required to reach a certain overall distribution shape. The method is, however, applicable to any polymerization method that produces monomodal MWDs with increasing average molecular weights during a polymerization. It should be noted that this method is able to account for experimental inaccuracies such as termination taking place, and yielding non-ideal distributions in experiments. It thus makes a difference if random distributions are used, or if the mentioned interpolation framework is applied. For details the reader is referred to our previous study. In the following we discuss the deconvolutions of MWDs with increasing complexity.

Most researchers will be interested in monomodal distributions. Figure 3 depicts a series of symmetrical MWDs, generated from Γ -distribution functions. All distributions feature the same molecular weight, and are associate with increasing dispersity (red $\mathcal{D} = 1.5$, green $\mathcal{D} = 2.0$ and blue $\mathcal{D} = 2.5$). Each distribution is fitted using the Python script with a set number of sub-distributions. It should be noted that the bold full distribution gives the addition of the fitted sub-distributions rather than the input distribution. For further use, these distributions are referred to as additive distributions. This thus demonstrates that blending is – at least in principle - able to produce smooth monomodal additive distributions. To fit a distribution of $\mathcal{D} = 1.5$, 9 sub-distributions are required. The other two distributions require blending of a larger number of samples, in the optimized example a total of 13 sub-distributions each. It is an interesting observation that for a dispersity of 2.0 and 2.5 the same number of sub distribution suffices.

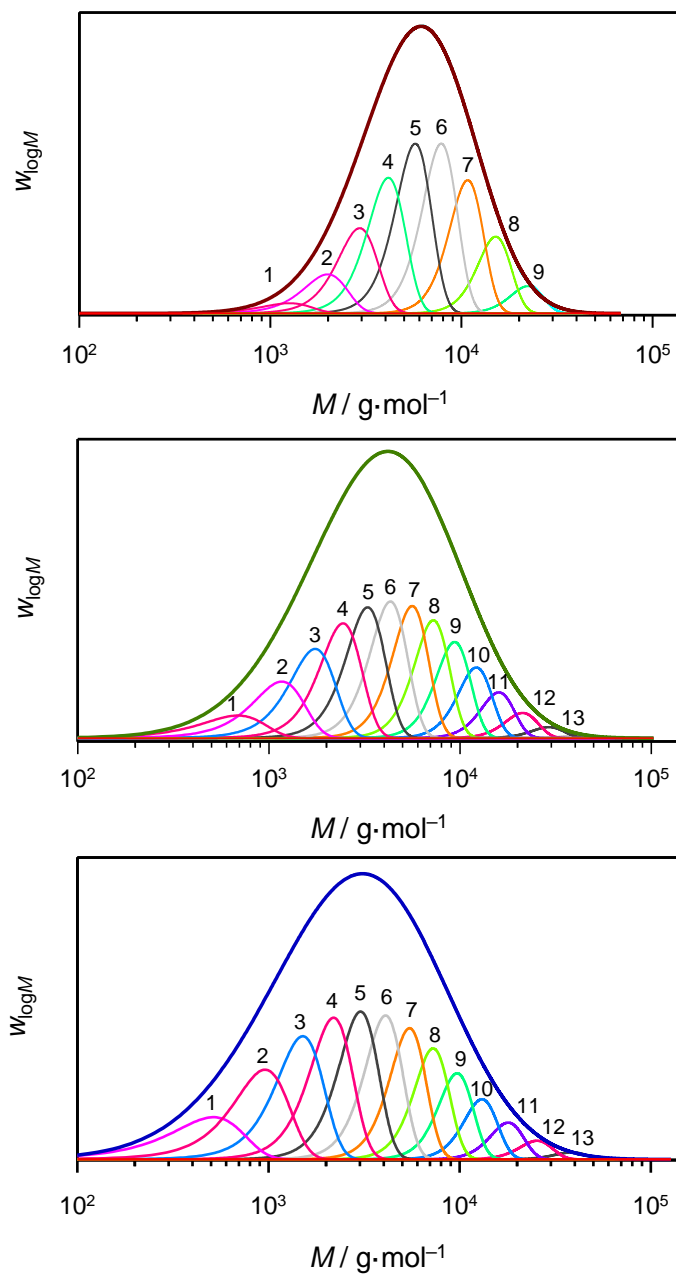


Figure 3: Symmetric distributions with constant $M_w = 10\,000\ \text{g}\cdot\text{mol}^{-1}$ and decreasing dispersity (red $D = 1.5$, green $D = 2.0$ and blue $D = 2.5$) the calculated sub-distributions.

A closer inspection of how many distributions are required to fit a specific overall MWD is made with Figure 4. Figure 4 depicts the green MWD from Figure 3, but then fitted to a different number of sub-distributions. To make the effect clearer, only the residual additive MWDs are plotted on a linear molecular weight axis (the insert gives the more common log axis). Even 7 sub-distributions are able to approximate the overall distribution relatively well. 5 sub-distributions give the overall shape also relatively well, it is, however, noticeable that the high molecular weight side of the distribution is not adequately represented. A multimodality is clearly observed for the lower number of sub-distributions. The additive distribution smooths out the more sub-distributions are allowed to be fitted. 13 distributions (as given in Figure 3) yields an additive distribution that is virtually indistinguishable from the input distribution. However, also 9 or 11 distributions would give a satisfactory result. Further, from the viewpoint of physical properties, it is debatable if smooth distributions are actually required. Polymer scientists are used to see multimodality as a negative feature of MWDs simply as multimodality usually implies occurrence of side reactions. Yet, when targeting specific polymer properties, it may make a relatively low difference if 7 or 13 sub-distributions are used to generate the additive MWD in the case of the distributions depicted in Figure 4. The software hence allows to make a manual decision for how many distributions are used, as from a practical point of view it must be doubted if the effort of creating a fully smooth distribution is worth the effort in relation to a desired aim.

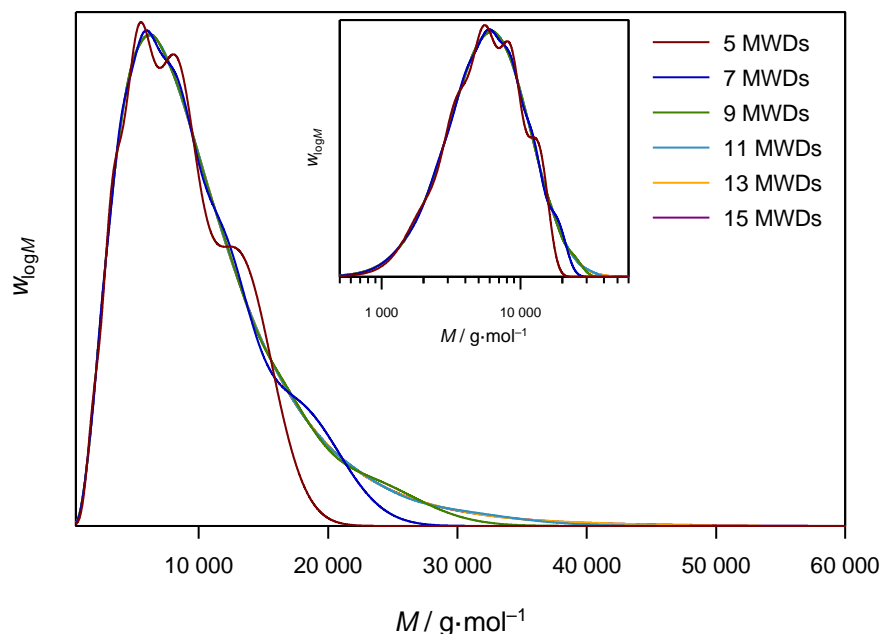


Figure 4: Additive distributions from fitting various numbers of individual distributions to a symmetric molecular weight distributions with $M_w = 10\,000 \text{ g}\cdot\text{mol}^{-1}$ and $D = 2.0$ on linear scale (large figure) and logarithmic scale (insert)

The algorithm for deconvolution was further tested on a number of monomodal distributions, and good fits can be obtained consistently with ease. It is noteworthy to add that obviously the number of sub-distributions will depend on the broadness of the individual traces. This effect on the fitting will be discussed below. Yet, of course one could use methods that yield broader molecular weight distributions^{7,12,16} to feed the interpolation algorithm, and also in this way reduce the number of samples to blend for any specific additive distribution. Yet, in order to make more complex MWD shapes, low dispersity of each individual sub-distribution is preferred.

This is exemplified on a distribution that features relatively steep edges, and mostly a plateau level of the majority of the distribution. For the sake of showing the power of the combined digitalization/fitting approach, we created a distribution that depicts the profile of the Australian Uluru monolith (see Figure 5). First, the profile is digitalized and transformed into a MWD shape

(Figure on top) with a $M_w = 20\,000\text{ g}\cdot\text{mol}^{-1}$ and $D = 3.0$. In the next step this artificial distribution is fitted to sub-distributions. 9 sub-distributions were found to give a satisfactory fit. The additive distribution is shown against the original Uluru profile in the middle of Figure 5. One can see that the overall shape is relatively well represented and the algorithm corrects even for small changes in the topology. At the same time, it is, however apparent that the algorithm is not able to fit the sharp edges of the profile. This is not a failure of the algorithm, but is rooted in the way distributions work. Any experimental distribution will require a bell shape profile of some sort, and hence a more or less vertical line can't be fitted completely, and is only approximated. The algorithm is hence not able to fit a distribution that in reality is impossible to make. It will, however, find a fit that comes the closest to the original. It should be noted that for such vertical lines, a zerofilling is recommended on the x-axis to give the least square fit method a point of reference beyond the ending of the distribution.

Another interesting observation is that the high molecular weight side is fitted more closely than the lower molecular weight side of the distribution. This effect stems again from the logarithmic nature of the molecular weight axis. This makes deviations more obvious on the low molecular weight side, and further also allows for less accurate fitting, since at a given standard deviation of a distribution, low molecular weight distributions will always be broader. Hence, the vertical feature of the Uluru distribution on the low molecular weight side can only be improved in the fitting if lower dispersity sub-distributions were assumed. Indeed, we implemented the ability to fit sub-distributions with varying dispersity into the algorithm and better additive distributions can be obtained when dispersity is varied during fitting. Yet, still a comparatively similar number of sub-distributions were required when this function was applied, and hence we believe that the added complication of needing to synthesize distributions with precisely targeted dispersity is not

worth the efficiency gain in blending accuracy. In fact, even if sub-distributions of a dispersity in the range of anionic polymerizations are assumed, still visible deviations from the Uluru shape remain. However, fitting a mixture of broad and narrow distributions may in future be more interesting, once synthetic methods to provide MWDs with precisely predefined dispersity become more available and more widespread.¹¹

The effect that low molecular weight shoulders are more difficult to fit remains even if the limit on the x-axis is shifted. On the bottom of Figure 5 a hypothetical Uluru distribution of a dispersity 1.3 is given. Also here the same deviation on the low molecular weight side is seen, even if the effect may be slightly smaller.

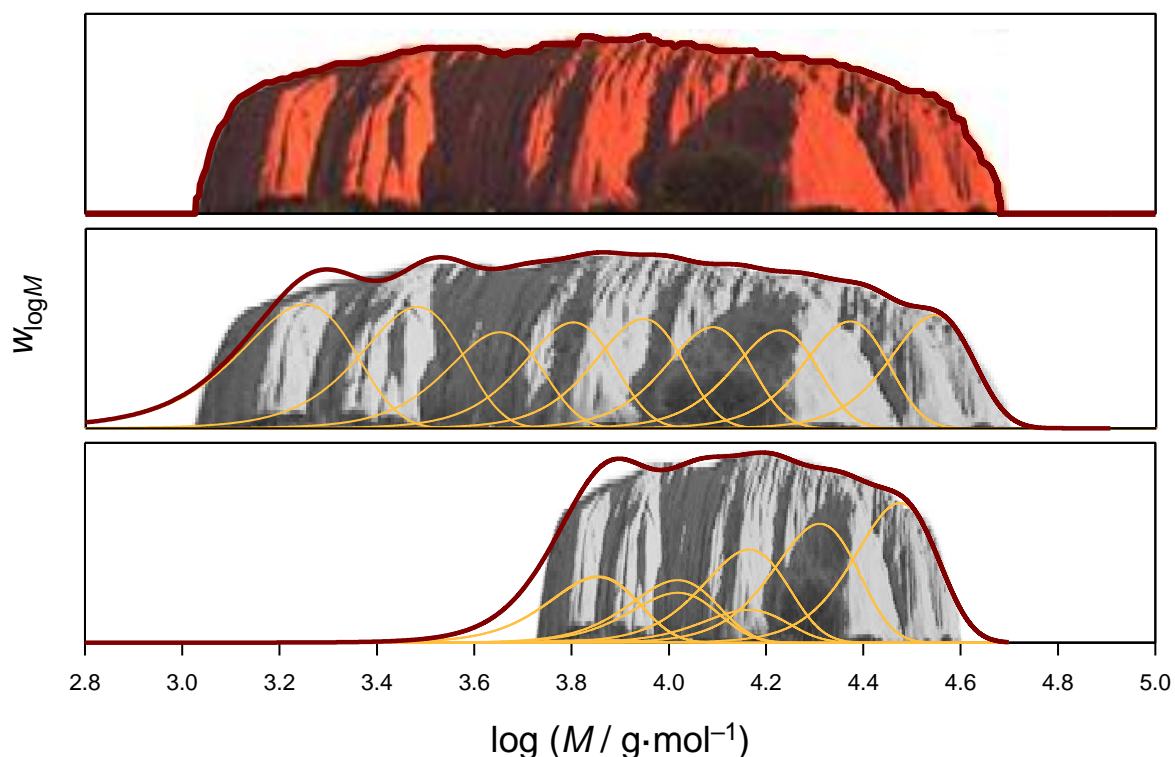


Figure 5: A molecular weight distribution in form of the Uluru monolith as a challenging example for fitting. The top figure shows a ‘Uluru MWD’ with a $M_w = 20\,000 \text{ g}\cdot\text{mol}^{-1}$ and $\mathcal{D} = 3.0$. The middle figure gives the fit of 9 distributions to the same and the bottom figure the fit of 7 distributions to a MWD of $\mathcal{D} = 1.3$.

The same can also be observed if the complexity level of the artificial molecular weight shape is further increased. Figure 6 depicts a complex distribution with vertical features, and unnaturally curvatures.²⁸ Indeed, this shape is only sufficiently well represented when more narrow sub-distributions are assumed. If all sub-distributions feature a dispersity around 1.02, hence dispersities at the very lower limit of what is synthetically achievable, a good additive distribution is obtained. For the given distribution, 25 narrow-distributions were required. Less distributions resulted in loss of shape features. Again, the high molecular weight side is somewhat better represented in the additive distribution. Yet, the overall shape is well recognizable, showing that the method presented is able to also produce complex and very sophisticated MWD shapes, even if the practical usefulness of the given distribution can probably be doubted.

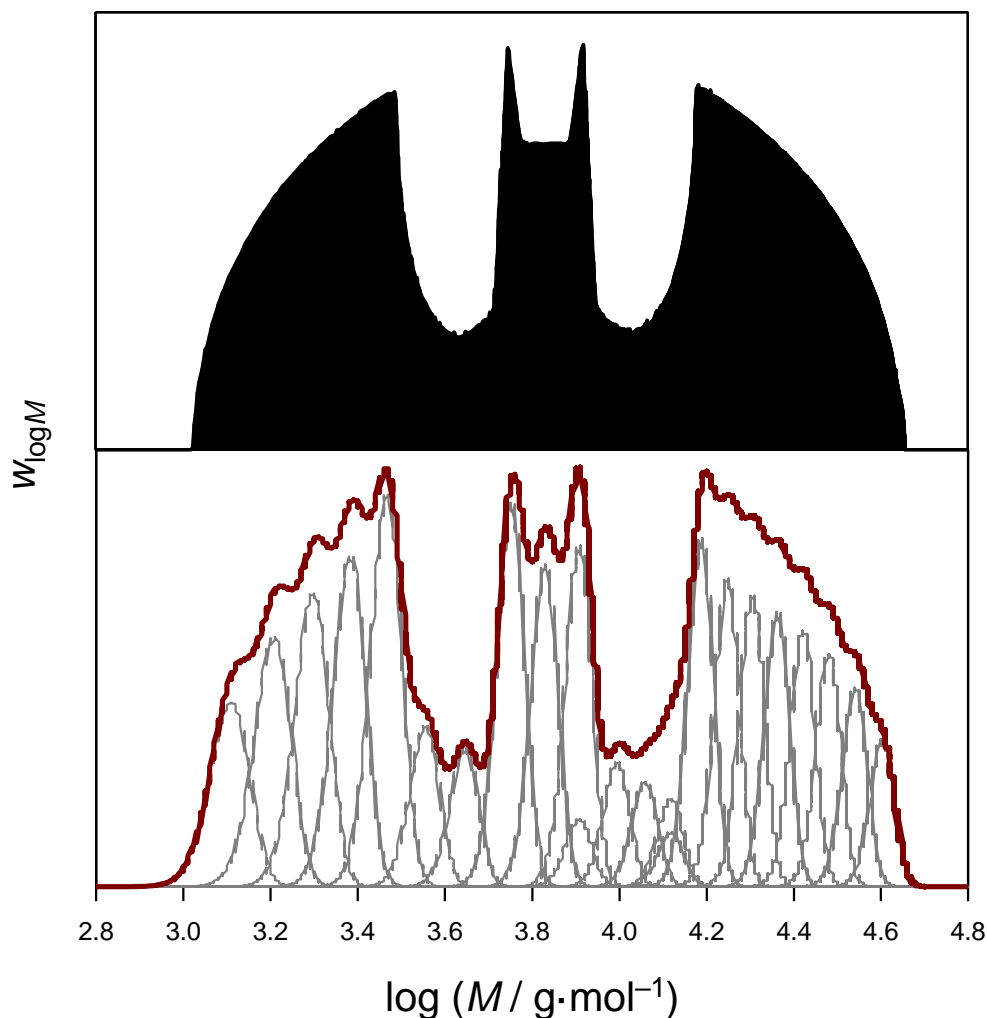


Figure 6: Stylized chiroptera anthropos distribution function (black: $M_w = 20\,000\text{ g}\cdot\text{mol}^{-1}$ and $D = 2.0$) and its fitting to 25 individual narrow MWDs (red, bottom) ($D=1.02$)

Conclusion

In summary, we have demonstrated successfully how any molecular weight distribution shape can in principle be created in a polymer blending approach. Therefore, we provide the tools to convert a given shape into a molecular weight distribution of freely chosen weight average molecular weight and overall dispersity. With a second software tool, these distributions are then fitted automatically to sub-distributions. While the current exercise is theoretical in nature, in the given

version, we base the sub-distributions on experimentally derived and interpolated MWDs that we have described before. Yet, any polymerization method can be in principle adopted as a base. We show that nearly any continuous distribution can be fitted to satisfaction. Non-natural features such as vertical shape features can only be approximated, but are overall still fairly well represented. We make both software tools available to the community via our webpage.²⁹ We believe both tools are powerful in combination, but are also independently very useful. The Excel Macro is powerful to visualize molecular weight and dispersity effects that many researchers and students in the polymer community are not familiar with. The Macro makes manipulation of distributions easy, and provides fast feedback on how a dispersity or average molecular weight change alters a distribution. The possibility to use any input further allows to sketch distributions by hand, scan them in and convert them in deconvoluted sub-distributions (as shown in Figure 1). It will be interesting to see other tools being developed to create distributions with defined skewness factors, or other distinctive features. We will provide updates to our programs as we continue to refine the algorithms, improve user friendliness and incorporation of more fitting options. The fitting program is provided as a Python script, which requires the Python framework to be installed. On our webpage we provide an instruction for installation with all required links. We have deliberately chosen for a software license that allows academic researchers to use the software at their leisure, and we hope the tools will be useful for a number of researchers.

Data Availability

The raw data required to reproduce these findings are available to download from www.polymatter.net/software

References

- [1] Mayadunne, R. T. A.; Rizzardo, E.; Chievari, J.; Chong, Y. K.; Moad, G.; Thang, S.H. *Macromolecules* **1999**, *32*, 6977.
- [2] Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.
- [3] J. Nicolas, Y. Guillaneuf, C. Lefay, D. Bertin, D. Gigmes, B. Charleux, *Prog. Polym. Sci.* **2013**, *38*, 63-235.
- [4] J. Listak, W. Jakubowski, L. Mueller, A. Plichta, K. Matyjaszewski, M. R. Bockstaller, *Macromolecules*, **2008**, *41*, 5919–5927.
- [5] D. T. Gentekos, R. J. Sifri, B. P. Fors, *Nat. Rev. Mat.* **2019**, *4*, 761–774.
- [6] A. L. Schmitt, M. H. Repollet-Pedrosa, M. K. Mahanthappa, *ACS Macro Lett.* **2012**, *1*, 300–304.
- [7] D. T. Gentekos, J. Jia, E. S. Tirado, K. P. Barteau, D. M. Smilgies, R. A. Distasio, B. P. Fors, *J. Am. Chem. Soc.*, **2018**, *140*, 4639–4648.
- [8] N. A. Lynd, M. A. Hillmyer, *Macromolecules* **2005**, *38*, 21, 8803–8810
- [9] J. J. Haven, T. Junkers, *Polym. Chem* **2019**, *10*, 679-682
- [10] M. Nadgorny, D. T. Gentekos, Z. Xiao, S. P. Singleton, B. P. Fors, L. A. Connal, *Macromol. Rapid Commun.*, **2017**, *38*, 1700352.
- [11] R. Whitfield, N. P. Truong, D. Messmer, K. Parkatzidis, M. Rolland, A. Anastasaki, *Chem. Sci.*, **2019**, *10*, 8724-8734.
- [12] R. Whitfield, K. Parkatzidis M. Rolland, N. P. Truong, A. Anastasaki, *Angew. Chem. Int. Ed.* **2019**, *131*, 13457-13462.
- [13] M. Rolland, R. Whitfield, D. Messmer, K. Parkatzidis, N. P. Truong, A. Anastasaki, *ACS Macro Lett.* **2019**, *8*, 1546-1551.
- [14] J. Morsbach, A. H. E. Müller, E. Berger-Nicoletti, H. Frey, *Macromolecules* **2016**, *49*, 5043–5050.

- [15] E.H.H. Wong, T. Junkers, C. Barner-Kowollik, *J. Polym. Sci. Polym. Chem.* **2008**, *146*, 7273-7279.
- [16] R. Whitfield, K. Parkatzidis, N. Truong, T. Junkers, A. Anastasaki, *Chem* **2020**, *in print*, doi.org/10.1016/j.chempr.2020.04.020
- [17] S. I. Rosenbloom, D. T. Gentekos, M. N. Silberstein, B. P. Fors, *Chem. Sci.* **2020**, *11*, 1361-1367.
- [18] S. Harrison, *Polym. Chem.*, **2018**, *9*, 1366–1370.
- [19] N. Corrigan, R. Manahan, Z. T. Lew, J. Yeow, J. Xu, C. Boyer, *Macromolecules*, **2018**, *51*, 4553–4563.
- [20] M. Rubens, T. Junkers, *Polym. Chem.* **2019**, *10*, 6315-6323.
- [21] J. De Neve, J.J. Haven, S. Harrison, T. Junkers, *Angew. Chem. Int. Ed.* **2019**, *131*, 14007-14011.
- [22] T. Junkers, *Macromol. Chem. Phys.* **2017**, *218*, 1600421.
- [23] We used the software GetData Graph Digitizer v2.26. www. <http://getdata-graph-digitizer.com>
- [24] M. Rubens, T. Junkers, *Polym. Chem.* **2019**, *10*, 5721-5725.
- [25] M. Rubens, J. H. Vrijssen, T. Junkers, *manuscript currently under review*.
- [26] M. Gavrilov, M.J. Monteiro, *Eur. Polym. J.* **2015**, *65*, 191–196.
- [27] M. Rubens, J.H. Vrijssen, J. Laun, T. Junkers, *Angew. Chem. Int. Ed.* **2019**, *58*, 3183-3187.
- [28] E.W. Weisstein, <https://mathworld.wolfram.com/BatmanCurve.html>
- [29] See www.polymatter.net/software

