Check for updates

The downside of dispersity: why the standard deviation is a better measure of dispersion in precision polymerization†

Simon Harrisson [ID]

Dispersity is firmly established as the standard measure of dispersion in molecular weight distributions. However, it can be misleading, particularly when applied to the relatively narrow molecular weight distributions obtained *via* living or reversible deactivation polymerizations. The use of the standard deviation is recommended as an alternative. In complex structures, a representative sample of chains provides a better illustration of structural variation than any single number.

Laboratoire des IMRCP, Université de Toulouse, CNRS UMR 5623, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 9, France.
E-mail: polyharrisson@gmail.com; www.twitter@polyharrisson
†Electronic supplementary information (ESI) available: Derivation of eqn (4). See DOI: 10.1039/c8py00138c

Simon Harrisson is a Chargé de Recherche at the Centre National de la Recherche Scientifique (CNRS), based in the Laboratoire des IMRCP in Toulouse. He obtained a PhD from the University of New South Wales, Australia, in 2002. After postdoctoral fellowships at the University of Warwick and Washington University in St Louis, he joined the Commonwealth Scientific and Industrial Research Organisation

Simon Harrisson

(CSIRO) in 2005. In 2010 he moved to France, working at the Institut Galénique at the Université Paris-Sud and the Solvay Research & Innovation Center Paris, before joining the CNRS in 2014. Dr Harrisson has published over 60 peer-reviewed research papers and book chapters. His research seeks to apply a fundamental understanding of polymerization kinetics and mechanisms to the development of new materials.
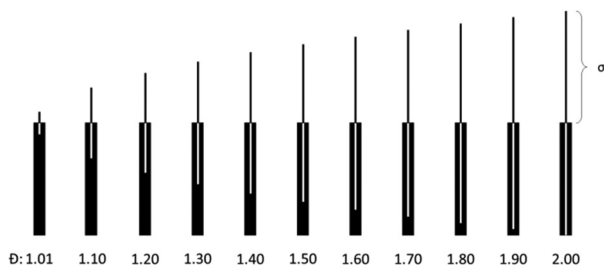
One of the essential features of synthetic polymers is that they consist of a distribution of chains covering a range of masses. Other structural features of copolymers, such as branching and composition (in copolymers), are also subject to statistical variation,[1] leading to complex populations that are extremely challenging both to characterize and to comprehend. This problem has not been helped by our choice of a measure of dispersion, the dispersity ($Đ$), that is needlessly complex.

Typically, when confronted with a distribution, we are interested in knowing not just a typical value, but also the typical range of values. For this purpose, the most commonly used measure is the standard deviation, σ, which measures the root mean square deviation of N values x_i from the mean, μ (eqn (1)).

$$\sigma = \sqrt{\frac{\sum (x_i - \mu)^2}{N}} \qquad (1)$$

The standard deviation has the same units as the quantity that is being measured, and gives an intuitive idea of the variation in the result. Faced with a result of 10 ± 2, it is natural to assume that most values fall between 8 and 12, and this intuition is usually correct. For normal distributions, approximately 70% of the sample lies within 1σ of the mean, while for any distribution, at least 75% of the values fall within 2σ of the mean.[2]

For molecular weight distributions (MWDs), however, the standard measure of dispersion is the dispersity.[3] This is defined as the ratio between weight- and number-average masses (M_w, M_n) or degrees of polymerization (DP$_w$, DP$_n$) (eqn (2)).

$$Đ = \frac{M_w}{M_n} \text{ or } \frac{DP_w}{DP_n} \qquad (2)$$

Dispersity became established because the principal techniques historically used to measure molecular weight gave either the M_n (*e.g.* osmometry, boiling point elevation, freezing point depression),[4] or M_w (ultracentrifugation,[5,6] light scatter-

Fig. 1 Relationship between standard deviation (σ) and dispersity ($Đ$) for $1.01 \leq Đ \leq 2.00$. The solid bar represents the mean of the distribution in each case.
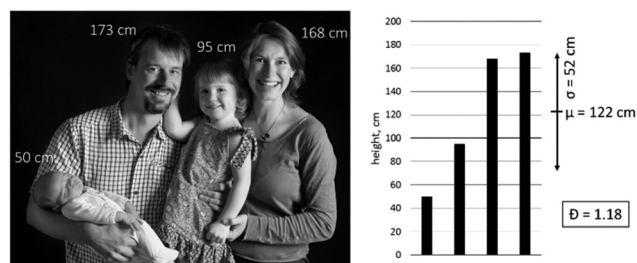

Fig. 2 Height distribution of a family of 2 adults and 2 young children with mean height of 122 cm, standard deviation of 52 cm and dispersity of 1.18.

ing[7].‡ The difference between the two average masses provided both a proof that synthetic polymers comprised a wide range of chains of different mass, and a simple measure of the breadth of the distribution.

Dispersity can equally be defined in terms of the moments of the MWD.[1] In terms of the moments of the number distribution, the dispersity is given by eqn (3), where $f(x)$ is the frequency of chains of length (or mass) x.

$$Đ = \frac{\sum x^2 f(x) \cdot \sum f(x)}{\left(\sum x f(x)\right)^2} \qquad (3)$$

This can in turn be expressed in terms of the mean and standard deviation[8] as:

$$Đ = 1 + \frac{\sigma^2}{\mu^2} \qquad (4)$$

Thus the dispersity is equivalent to one plus the square of the relative standard deviation (σ/μ) of the number distribution (a derivation of this result is given in the ESI†). This relation between $Đ$ and σ is valid for all distributions. Dispersity is thus a relative measure – a high molecular weight polymer with a given dispersity will have the same relative standard deviation as a low molecular weight polymer with the same dispersity but a larger absolute standard deviation.[9] Thus a polymer with M_n of 20 kg mol^{-1} and $Đ$ of 1.25 has a σ of 10 kg mol^{-1}, while a polymer with the same $Đ$ but M_n of 40 kg mol^{-1} has a σ of 20 kg mol^{-1}. In each case, the relative standard deviation is 50%.

Unlike the standard deviation, however, dispersity is not an intuitive measure. It varies non-linearly with the standard deviation – a polymer with a dispersity of 1.8 has a relative standard deviation only twice as large as a polymer with a dispersity of 1.2 (Fig. 1).

Secondly, polymer MWDs are typically much broader than the distributions that we encounter in everyday life. To give an example, the average height of a French adult woman in 2001 was 162 cm with a standard deviation of 6.5 cm.[10] This corresponds to a dispersity of only 1.0016. Even the seemingly broad

height distribution of a family of two adults and two young children (Fig. 2; μ = 122 cm, σ = 51 cm) gives a dispersity of only 1.18 – a value that for polymers is frequently characterized as well-controlled.

The resulting disconnect between intuition and reality leads us to underestimate the variation in molecular weight that is present even in polymers prepared using controlled or living polymerization techniques. This variation could be communicated more effectively by adding standard deviations to the average number of repeat units shown in chemical structures (Scheme 1).[11] This is particularly important when the goal is precise control over the polymer structure, for example in the preparation of polymers with a well-defined spatial arrangement of blocks or functionalities.

Turning to actual polymer MWDs, two simple distributions are strongly associated with polymerizations. The first is the geometric distribution (typically known in polymer science as the most-probable distribution[12]), which describes the distribution of a polymer chain which may either propagate or terminate (by disproportionation or chain transfer) with constant probability at each step.[13] If p is the probability of termination, then the proportion of chains of length x is given by $p(1 - p)^x$. The average chain length is $(1 - p)/p$ and the standard deviation is $(1 - p)^{0.5}/p$, giving a dispersity of $1 + 1/(1 - p)$. If the chains of length zero (those that terminated in the first step and contain no monomer units) are excluded from the MWD, $Đ$ is given by $2 - p$. In either case, $Đ$ approaches 2 for small p. This is the distribution obtained in condensation polymerizations[13] and from radical polymerizations at low conversion when termination is exclusively by disproportionation or chain transfer.[14]
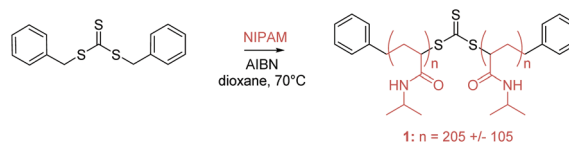
Scheme 1 Polymer structure showing number-average degree of polymerization (205) and standard deviation (105). This corresponds to a dispersity of 1.26 for each arm, and 1.13 for the entire polymer. Reproduced from ref. 11 with permission from the Royal Society of Chemistry.

---

‡Viscometry was an exception, giving an average molecular weight that depended on the Mark–Houwink–Sakurada parameters of the polymer–solvent combination in question.[39]
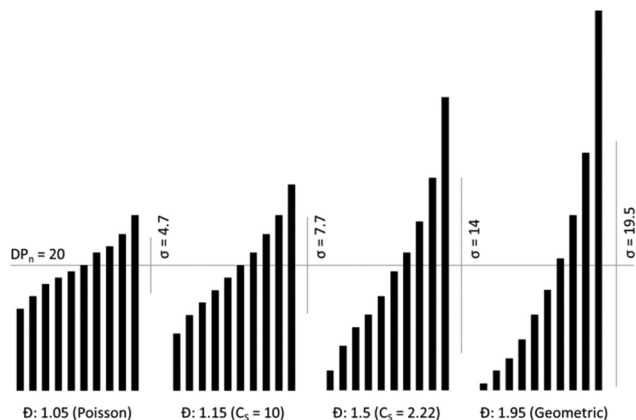
Fig. 3 Representative length distributions corresponding to an ideal living polymerization (Poisson), an ideal chain polymerization with constant monomer concentration (Geometric) and two distributions of intermediate dispersity corresponding to reversible deactivation polymerizations at full conversion with relatively high (C_S = 10) and low (C_S = 2.22) rates of deactivation. In all cases, the number average degree of polymerization is 20 and zero-length chains are excluded.

The second distribution is the Poisson distribution, which applies to polymer chains that are initiated simultaneously and propagate without terminating, as in an ideal anionic polymerization.[15,16] In this case, the proportion of chains of length x is given by $\lambda^x e^{-\lambda}/x!$, where λ is the average chain length. The standard deviation is given by $\lambda^{0.5}$, while $Ð = 1 + 1/\lambda$ and approaches 1 as λ increases.§ The relative standard deviation decreases much more slowly than the dispersity, however, while the absolute standard deviation continues to increase.[17] Fig. 3 shows a representative sample of 10 chains from a geometric distribution and a Poisson distribution with an average chain length of 20 ($Ð$ = 1.95 and 1.05 respectively). The dispersion in length that is present even in Poisson-distributed chains leads to significant structural variation in multiblock copolymers.[18]

Reversible deactivation radical polymerizations (RDRP) typically give distributions that are intermediate in dispersity between the Poisson and geometric distributions. The dispersity (including zero-length chains) for an RDRP is given by eqn (5), in which c represents the conversion, k_p and k_d rate constants of propagation and deactivation, and [P] and [D] the concentrations of dormant polymer and deactivator.[19–21]

$$Ð = 1 + 1/DP_n + \left(\frac{2-c}{c}\right)\left(\frac{k_p[P]}{k_d[D]}\right) \quad (5)$$

In reversible addition–fragmentation chain transfer (RAFT) polymerizations, the dormant polymer is itself the deactivator, and eqn (5) can be further simplified to

$$Ð = 1 + 1/DP_n + \left(\frac{2-c}{c}\right)\frac{1}{C_S} \quad (6)$$

§ If chains of length zero are excluded, $Ð = (1 - e^{-\lambda})(1 + 1/\lambda)$. The difference between the two formulas is <0.01 for $\lambda \geq 5$.

where C_S is the chain transfer constant of the dormant polymer.

The resulting dispersity is always greater than that of the Poisson distribution with the same DP_n. Sample distributions corresponding to RDRP with relatively rapid (C_S = 10) or slow (C_S = 2.22) deactivation are also shown in Fig. 3.

While dispersity is often used as a proxy for the overall success of a polymerization, it is important to note that polymers with broad molecular weight distributions may be well-controlled in the sense of having a predefined M_n and high levels of the desired chain end functionality – examples include polymers generated by catalytic chain transfer[22] or xanthate-mediated RDRP of styrene.[23] In radical polymerizations, shorter chains terminate more rapidly than longer chains.[24] Addition of a deactivating agent that reduces the dispersity by reducing the proportion of long chains can thus lead to a higher fraction of non-functional dead chains in the final polymer.[25]

Adding and subtracting dispersities

If two blocks of average degree of polymerization μ_1 and μ_2, standard deviation σ_1 and σ_2, and dispersity $Ð_1$ and $Ð_2$ are joined together, the dispersity $Ð_{1+2}$ of the resulting block copolymer is given by eqn (7).[26]

$$Ð_{1+2} = 1 + \frac{\sigma_1^2 + \sigma_2^2}{(\mu_1 + \mu_2)^2} = 1 + \frac{\mu_1^2(Ð_1 - 1) + \mu_2^2(Ð_2 - 1)}{(\mu_1 + \mu_2)^2} \quad (7)$$

This is a general result that applies to all distributions, so long as the two blocks are uncorrelated (*i.e.* there is no preference for long blocks to add to long blocks, or *vice versa*). The contribution of each block is weighted according to the square of its length, and thus even a highly disperse short block may have very little effect on the dispersity of a long block copolymer.[27] For this reason, a polymerization which undergoes a substantial loss of chain end functionality late in the reaction may maintain a low overall dispersity.[28]

Eqn (7) can be rearranged to give the dispersity of an added block ($Ð_2$) in terms of the number-average masses and dispersities of the initial (μ_1, $Ð_1$) and final (μ_{1+2}, $Ð_{1+2}$) polymers (eqn (8)).

$$Ð_2 = 1 + \frac{\mu_{1+2}^2(Ð_{1+2} - 1) - \mu_1^2(Ð_1 - 1)}{(\mu_{1+2} - \mu_1)^2} \quad (8)$$

Application of eqn (8) to the polymers generated at each step during a 24-block sulfur-free RAFT polymerization of butyl methacrylate reported by Engelis *et al.*[29] shows that while the dispersity of the overall polymer falls from 1.7 to 1.11 before slowly rising to 1.21, the apparent dispersity of each added block increases roughly exponentially from 1.4 in the first extension to 37 (!) in the last (Fig. 4). This is evident when discussed in terms of standard deviations: taking the 15th chain extension as an example (Fig. 4b), a polymer of M_n
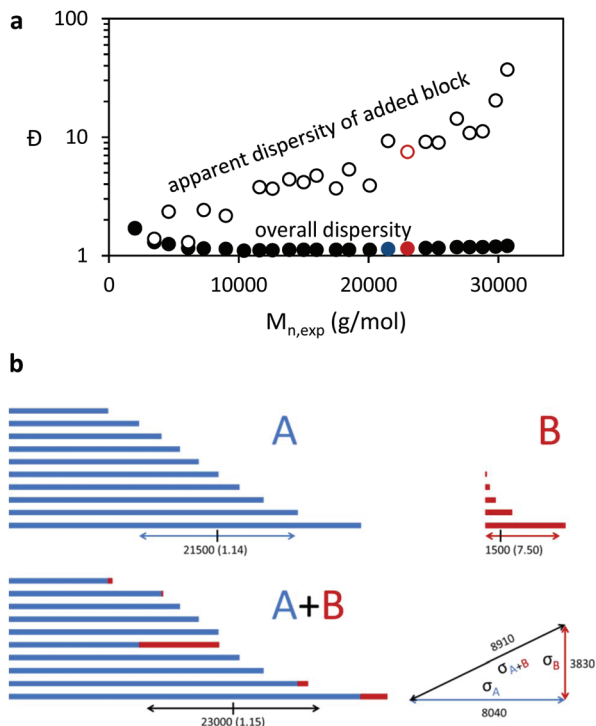
Fig. 4 a. Relationship between overall dispersity and apparent dispersity of added block for 24 successive butyl methacrylate polymerizations.[29] b. 10 sample chains with M_n of 21 500 g mol^{-1} and Đ of 1.14 (A, corresponding to the solid blue circle in a), and with M_n of 1500 g mol^{-1} and Đ of 7.50 (B, corresponding to the open red circle in a – note that 5 of the chains are shorter than 100 g mol^{-1}). The sum of the two distributions gives A + B with M_n of 23 000 g mol^{-1} and Đ of 1.15 (A + B, corresponding to the solid red circle in a). Double headed arrows under each distribution are of length 2σ and placed so as to include the greatest fraction of the distribution. The black line represents the M_n. A and B are assumed to follow Shulz-Zimm[7] molecular weight distributions.

21.5 kg mol^{-1} and dispersity of 1.14 is extended with a block of M_n 1.5 kg mol^{-1} to form a new polymer of M_n 23.0 kg mol^{-1} and dispersity 1.15. The polymers have standard deviations of 8.04 kg mol^{-1} and 8.91 kg mol^{-1}, respectively. The standard deviation of the added block is thus $(8.91^2 - 8.04^2)^{0.5}$ or 3.83 kg mol^{-1}. This is significantly greater than the length of the block itself, resulting in an apparent dispersity of 7.5.

It should be noted that these apparent dispersities are highly sensitive to errors in the determination of the mass and dispersity at each step. It is also assumed that all chains are equally reactive, and that no new chains are generated during the reaction. In reality, dead chains accumulate throughout the reaction, with the effect that long chains, which are more likely to be active, tend to get longer, while short chains, which are more likely to be dead, remain short. Additionally, in RAFT polymerizations such as the example given here, new chains are generated at each step through decomposition of the initiator. While neglecting these factors will lead to overestimation of the dispersity of the added block, they are in themselves further sources of deviation from the desired structure. In summary, the gradually rising overall dispersities seen in

many multiblock and multisite polymerizations[29–38] suggest a loss of control in the final steps which will have a significant impact on the molecular weight distributions of the final blocks and the overall fidelity of the polymer to the desired structure.

Conclusions

Dispersity is firmly established as a measure of dispersion in polymer MWDs. Its main advantage is that it is a simple ratio of M_w and M_n, and thus clearly signals the difference that is to be expected between properties that depend on M_n and those that depend on M_w. However, its utility is very limited for relatively narrow MWDs where M_w is less than twice M_n (Đ < 2). In these cases, which encompass essentially all living and reversible deactivation polymerizations, the variability in chain length is better communicated by the standard deviation (relative or absolute), which can easily be inserted into chemical structures. In multiblock copolymers, the standard deviation for each block should be supplied. This is particularly important for complex structures, which may show a low overall dispersity even when individual substructures are highly disperse. In these cases, simulation of even a small number of chains, as shown in Fig. 3 and 4, gives a better picture of the expected structural variation and is far superior to showing a single 'typical' structure.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 J. J. Thevarajah, A. T. Sutton, A. R. Maniego, E. G. Whitty, S. Harrisson, H. Cottet, P. Castignolles and M. Gaborieau, *Anal. Chem.*, 2016, **88**, 1674–1681.
2 P. Tchébychef, *J. Math. Pures Appl.*, 1867, **12**, 177–184. Accessed *via* http://sites.mathdoc.fr/JMPA/PDF/JMPA_1867_2_12_A11_0.pdf.
3 R. Stepto, *Pure Appl. Chem.*, 2009, **81**, 351–353.
4 W. H. Carothers, *Chem. Rev.*, 1931, **8**, 353–426.
5 T. Svedberg, *Chem. Rev.*, 1934, **14**, 1–15.
6 H. W. McCormick, *J. Polym. Sci.*, 1959, **36**, 341–349.
7 B. H. Zimm, *J. Chem. Phys.*, 1948, **16**, 1099–1116.
8 W. Burchard, in *Branched Polymers II*, ed. J. Roovers, Springer Berlin Heidelberg, Berlin, Heidelberg, 1999, pp. 113–194.

9 K. E. B. Doncom, L. D. Blackman, D. B. Wright, M. I. Gibson and R. K. O'Reilly, *Chem. Soc. Rev.*, 2017, **46**, 4119–4134.

10 N. Herpin, *Econ. Stat.*, 2003, **361**, 71–90.

11 L. Despax, J. Fitremann, M. Destarac and S. Harrisson, *Polym. Chem.*, 2016, **7**, 3375–3377.

12 IUPAC, *Compendium of Chemical Terminology*, ed. A. D. McNaught and A. Wilkinson, Blackwell Scientific Publications, Oxford, 1997, 2nd edn (the "Gold Book"), https://doi.org/10.1351/goldbook.M04035.

13 P. J. Flory, *J. Am. Chem. Soc.*, 1936, **58**, 1877–1885.

14 G. V. Schulz, *Z. Phys. Chem., Abt. B*, 1939, **43**, 25–46.

15 P. J. Flory, *J. Am. Chem. Soc.*, 1940, **62**, 1561–1565.

16 W. Lee, H. Lee, J. Cha, T. Chang, K. J. Hanley and T. P. Lodge, *Macromolecules*, 2000, **33**, 5111–5115.

17 G. T. Russell, in *Controlled/Living Radical Polymerization: Progress in ATRP. ACS Symposium Series*, ed. K. Matyjaszewski, American Chemical Society, Washington DC, 2009, vol. 1023, pp. 15–31.

18 G. Gody, P. B. Zetterlund, S. Perrier and S. Harrisson, *Nat. Commun.*, 2016, **7**, 10514.

19 A. Goto and T. Fukuda, *Prog. Polym. Sci.*, 2004, **29**, 329–385.

20 A. H. E. Müller, R. Zhuang, D. Yan and G. Litvinenko, *Macromolecules*, 1995, **28**, 4326–4333.

21 A. H. E. Müller, G. Litvinenko and D. Yan, *Macromolecules*, 1996, **29**, 2346–2353.

22 A. A. Gridnev and S. D. Ittel, *Chem. Rev.*, 2001, **101**, 3611–3659.

23 M. Destarac, C. Brochon, J. M. Catala, A. Wilczewska and S. Z. Zard, *Macromol. Chem. Phys.*, 2002, **203**, 2281–2289.

24 C. Barner-Kowollik and G. T. Russell, *Prog. Polym. Sci.*, 2009, **34**, 1211–1259.

25 S. Harrisson and J. Nicolas, *ACS Macro Lett.*, 2014, **3**, 643–647.

26 T. Fukuda, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4743–4755.

27 C. Barner-Kowollik, *Macromol. Rapid Commun.*, 2009, **30**, 1625–1631.

28 K. Matyjaszewski, *Macromol. Symp.*, 1996, **111**, 47–61.

29 N. G. Engelis, A. Anastasaki, G. Nurumbetov, N. P. Truong, V. Nikolaou, A. Shegiwal, M. R. Whittaker, T. P. Davis and D. M. Haddleton, *Nat. Chem.*, 2016, **9**, 171–178.

30 A. H. Soeriyadi, C. Boyer, F. Nystrom, P. B. Zetterlund and M. R. Whittaker, *J. Am. Chem. Soc.*, 2011, **133**, 11128–11131.

31 M. Zamfir and J. F. Lutz, *Nat. Commun.*, 2012, **3**, 1138.

32 G. Gody, T. Maschmeyer, P. B. Zetterlund and S. Perrier, *Nat. Commun.*, 2013, **4**, 2505.

33 G. Gody, T. Maschmeyer, P. B. Zetterlund and S. Perrier, *Macromolecules*, 2014, **47**, 3451–3460.

34 A. Anastasaki, C. Waldron, P. Wilson, C. Boyer, P. B. Zetterlund, M. R. Whittaker and D. Haddleton, *ACS Macro Lett.*, 2013, **2**, 896–900.

35 C. Bray, R. Peltier, H. Kim, A. Mastrangelo and S. Perrier, *Polym. Chem.*, 2017, **8**, 5513–5524.

36 G. Moriceau, G. Gody, M. Hartlieb, J. Winn, H. Kim, A. Mastrangelo, T. Smith and S. Perrier, *Polym. Chem.*, 2017, **8**, 4152–4161.

37 L. Xiao, W. Zhu, J. Chen and K. Zhang, *Macromol. Rapid Commun.*, 2017, **38**, 1600675.

38 T. G. McKenzie, J. M. Ren, D. E. Dunstan, E. H. H. Wong and G. G. Qiao, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, **54**, 135–143.

39 H. L. Frisch and J. L. Lundberg, *J. Polym. Sci.*, 1959, **37**, 123–129.