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Characterization of Molecular Weight Distributions by the Standard Deviation

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NEW INTERPRETATIONS

Characterization of Molecular Weight Distributions by the Standard Deviation

SUMMARY

The standard deviation σ is known to be an absolute measure of Gaussian (G) distributions, because it (or multiples of it) always determines a constant fraction of the material. However, this is not true for distribution functions other than Gaussian. The weight fractions corresponding to weight standard deviations ($\pm\sigma_w$) of Schulz-Flory distributions depend on the polymolecularity index x_w/x_n, approaching a limiting value of $W(x_w \pm \sigma_w) = 86.5$ for $x_w/x_n \rightarrow \infty$. The use of weight standard deviations is meaningless for generalized logarithmic normal (LN) distributions if $x_w/x_n > 2$. The weight fractions $W(x_n \pm \sigma_n)$ around the number-average degree of polymerization of G and LN distributions first go through a maximum before decreasing with increasing x_w/x_n. The weight fractions $W(x_n \pm \sigma_n)$ decrease steadily with higher x_w/x_n.

Many parameters have been suggested to characterize the spread of molecular weights or the corresponding degrees of polymerization in a polymer sample. Most commonly used is the ratio of weight-average M_w to number-average molecular weight M_n or of the corresponding degrees of polymerization x_w and x_n, and the polymolecularity or polydispersity index $Q_{w,n}$

$$Q_{w,n} = M_w/M_n = x_w/x_n \qquad (1)$$

Similar quantities have been defined on the basis of other averages, e.g., z-average and viscosity-average ($Q_{z,w} = x_z/x_w$, $Q_{v,n} = x_v/x_n$, etc.). Other measures which have been proposed can be considered as simple derivatives from the polymolecularity index, e.g., the molecular inhomogeneity [1]

$$U_{w,n} = (x_w/x_n) - 1 = Q_{w,n} - 1 \tag{2}$$

the Δ factor [2]

$$\Delta_{w,n} = (U_{w,n})^{0.5} \tag{3}$$

or the relative dispersion factor [3]

$$f_{z,w} = (U_{z,w})^{0.5} \tag{4}$$

In addition, the standard deviation was suggested as a measure for the broadness of a molecular weight distribution (MWD) as early as 1942 [4] and later by others [5-7]. The standard deviation σ can be calculated directly from two averages of successive order without any assumption about the distribution law, e.g.,

$$\sigma_n = (x_w \cdot x_n - x_n^2)^{0.5} \tag{5a}$$

if x_n and x_w are used, and correspondingly, if x_w and x_z are known:

$$\sigma_w = (x_z \cdot x_w - x_w^2)^{0.5} \tag{5b}$$

The standard deviations σ_n and σ_w can be seen to be simply related to the parameters defined by expressions (1) to (4):

$$\sigma_n = x_n(Q_{w,n} - 1)^{0.5} = x_n(U_{w,n})^{0.5} \tag{6a}$$

$$\sigma_w = x_w(Q_{z,w} - 1)^{0.5} = x_w(U_{z,w})^{0.5} \tag{6b}$$

The standard deviation σ_w can be considered as an absolute measure for the broadness of the MWD of Gaussian weight distributions of molecular weights. This is readily visualized from the meaning of the standard deviation as the distance from the degree of polymerization at the maximum (x_w) to either inflection point of the Gaussian distribution curve. Furthermore, the area under the curve from $x = x_w - \sigma_w$ to $x = x_w + \sigma_w$ is always 68.3% of the total, irrespective of the numerical values of x_w and σ_w [8]. The areas for the ranges $x_w \pm 2\ \sigma_w$ and $x_w \pm 3\ \sigma_w$ are 95.4 and 99.7%, respectively. Because the standard deviation (or multiples of it) always determines a constant fraction of the material, it is an absolute measure for the broadness of Gaussian distributions.

The problem is whether or not the standard deviation is an absolute measure (as defined by constant fractions) for the broadness of the MWD of distributions other than Gaussian. If not, it remains to be clarified how good a measure the standard deviation is for different types of distributions.

We therefore calculated the weight fractions corresponding to unit values of σ_n or σ_w for polymer samples having either a Gaussian (G), generalized logarithmic normal (LN), or Schulz-Flory (SF) weight distribution of molecular weight (for the definition of these distributions see, e.g., Ref. 9).

The standard deviations σ_n and σ_w of a polymer sample with the number-average degree of polymerization $x_n = 10{,}000$ are listed in Table 1 for polymolecularity indices from 1.01 to 50. The weight-average degrees of polymerization x_w are given for comparison in the last column of Table 1.

As immediately seen from Eq. (5a), σ_n, for a given x_w/x_n, is independent of the type of distribution. In contrast, σ_w depends on the type of the distribution (G, LN, SF).

It should be born in mind that the calculation of the weight fraction of a polymer is meaningless for all standard deviations exceeding their corresponding averages, i.e., $\sigma_n > x_n$ and $\sigma_w > x_w$, since the lower limit of the degree of polymerization then becomes negative. These values of σ_n and σ_w are given in parantheses in Table 1. For all types of distributions, σ_n is always greater than x_n if $x_w/x_n > 2$. In the case of weight standard deviations, $\sigma_w > x_w$ for $x_w/x_n > 2$ is also found for LN weight distributions. For SF weight distributions, σ_w does not become equal to x_w even if $x_w/x_n = 50$.

The weight fractions in per cent of the total material corresponding to unit values of σ_n and σ_w are given in Tables 2, 3, and 4 for polymers with G, LN, and SF distributions, respectively. Because we are examining an asymmetric area in the weight fractions $W(x_n - \sigma_n)$, for example, from $x = x_n - \sigma_n$ to $x = x_n$, are not identical with the weight fractions $W(x_n + \sigma_n)$ from $x = x_n$ to $x = x_n + \sigma_n$. They are thus listed separately in addition to their sum $W(x \pm \sigma_n)$. Correspondingly, $W(x_w - \sigma_w) + W(x_w + \sigma_w) = W(x_w \pm \sigma_w)$. For illustration, the total weight fractions $W(x_w \pm \sigma_w)$ are plotted against x_w/x_n in Fig. 1 and the total weight fractions $W(x_n \pm \sigma_n)$ vs. x_w/x_n in Fig. 2.

The calculations for the Gaussian curve are not carried beyond the limit $x_w/x_n = 1.5$, because one tail of this curve lies in the range of negative x values. For $x_w/x_n = 2.0$ some 3% of the total area is in this negative region. The values quoted show the unexpected result that $\sigma_n > \sigma_w$.

Table 1. Standard Deviations σ_n and σ_w of a Polymolecular Material with $x_n = 10^4$ for Different x_w/x_n Values[a]

			$10^3 \sigma_w$		
x_w/x_n	$10^3 \sigma_n$	G	LN	SF	$10^4 x_w$
1.01	1.00	1.00	1.01	1.005	1.01
1.05	2.24	2.17	2.35	2.28	1.05
1.1	3.16	2.90	3.48	3.32	1.1
1.5	7.07	5.99	10.6	8.63	1.5
2.0	10.00		20.0	14.1	2.0
3.0	(14.1)		(42.3)	24.4	3.0
4.0	(17.3)		(69.2)	34.6	4.0
5.0	(20.0)		(100)	44.8	5.0
10.0	(30.0)		(300)	94.8	10.0
50.0	(70.0)		(350)	495	50.0

[a] G = Gaussian, LN = logarithmic normal, SF = Schulz-Flory distributions. Numbers in brackets indicate $\sigma_r > x_r$ (with $r = n$ or $r = w$).

For weight distributions, the Gaussian curves are symmetrical around x_w. $W(x_w \pm \sigma_w)$ is thus independent of x_w/x_n (Fig. 1). The corresponding weight fractions for SF distributions increase, however, with increasing x_w/x_n, approaching a limiting value of $W(x_w \pm \sigma_w) = 86.5\%$ for $x_w/x_n \rightarrow \infty$. The $W(x_w \pm \sigma_w)$ of LN distributions increases much faster, reaching nearly 90% for $x_w/x_n = 2$ (limit for meaningful σ_w-values for LN distributions).

For weight fractions $W(x_n \pm \sigma_n)$ around the number-average degree of polymerization, the situation is different. Interestingly, the weight fractions for G and LN distributions first go through a maximum before decreasing with increasing x_w/x_n. This result was not changed by carrying the integration in 10,000 steps instead of 5,000 steps. The weight fractions of SF distributions decrease steadily with higher x_w/x_n. All distributions reach their nonsense limit of σ_n at $x_w/x_n = 2$.

From these results it may be concluded that for narrow distributions, i.e., $Q \sim 1.0$, σ_n can be used as a good measure to characterize the width of the weight LN and SF distributions. On the other hand, σ_w is an

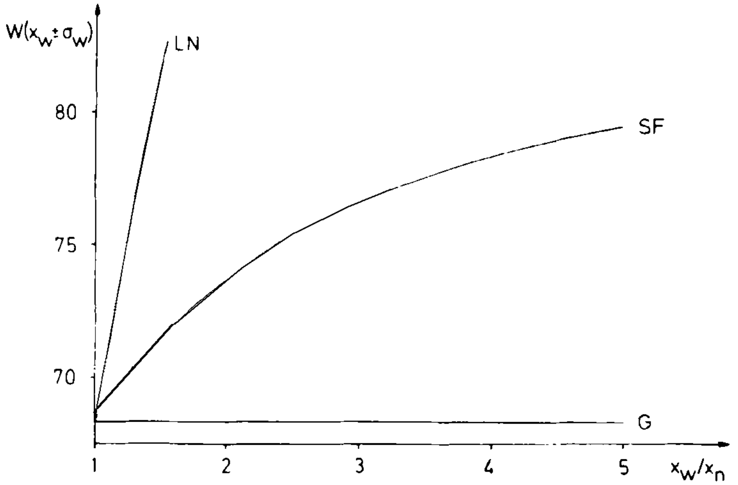

Fig. 1. Total weight fractions $W_x(x_w \pm \sigma_w)$ corresponding to unit weight standard deviations as a function of the polymolecularity index x_w/x_n for logarithmic normal (LN), Schulz-Flory (SF), and Gauss (G) weight distributions of degrees of polymerization x.

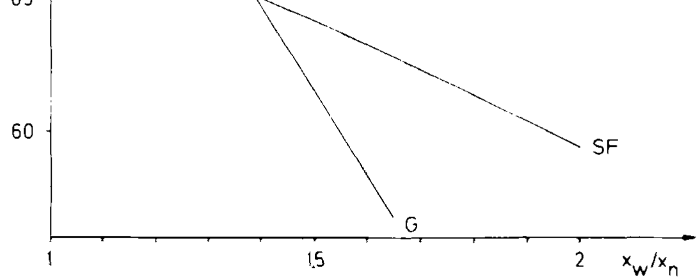

Fig. 2. Total weight fractions $W_x(x_n \pm \sigma_n)$ corresponding to unit number standard deviations as a function of the polymolecularity index x_w/x_n for logarithmic normal (LN), Schulz-Flory (SF), and Gauss (G) weight distributions of degrees of polymerization x.

Table 2. Percentage Weight Fractions for a Polymer with a Gaussian Weight MWD[a]

x_w/x_n	$W(x_n - \sigma_n)$	$W(x_n + \sigma_n)$	$W(x_n \pm \sigma_n)$	$W(x_w - \sigma_w)$	$W(x_w + \sigma_w)$	$W(x_w \pm \sigma_w)$
1.01	33.0	35.3	68.3	34.13	34.13	68.26
1.05	30.5	37.9	68.4	34.13	34.13	68.26
1.1	29.0	40.7	69.7	34.13	34.13	68.26
1.2	25.5	44.5	69.9	34.13	34.13	68.26
1.5	18.0	43.4	61.4	34.13	34.13	68.26

[a] $W(x_n - \sigma_n)$ denotes that fraction from degree of polymerization $x_n - \sigma_n$ to x_n, $W(x_n + \sigma_n)$ that from x_n to $x_n + \sigma_n$, and $W(x_n \pm \sigma_n)$ that from $x_n - \sigma_n$ to $x_n + \sigma_n$. $W(x_w - \sigma_w)$, $W(x_w + \sigma_w)$, and $W(x_w \pm \sigma_w)$ are defined correspondingly.

Table 3. Percentage Weight Fractions for a Polymer with a Logarithmic Normal Weight MWD[a]

x_w/x_n	$W(x_n - \sigma_n)$	$W(x_n + \sigma_n)$	$W(x_n \pm \sigma_n)$	$W(x_w - \sigma_w)$	$W(x_w + \sigma_w)$	$W(x_w \pm \sigma_w)$
1.01	34.6	33.7	68.3	36.3	32.3	68.6
1.05	35.2	33.3	68.5	39.4	30.3	69.7
1.1	35.6	33.0	68.6	42.7	29.0	71.7
1.33	36.4	32.5	68.9	51.5	26.2	77.7
1.4	36.4	32.5	68.9	53.9	25.7	79.6
1.5	36.3	32.4	68.7	57.1	25.1	82.2
1.66	35.8	32.3	68.1	61.8	24.4	86.2
2	33.9	32.3	66.2	66.2	23.2	89.4

[a] Meaning of the symbols as in Table 2.

Table 4. Percentage Weight Fractions for a Polymer with a Schulz-Flory Weight MWD[a]

x_w/x_n	$W(x_n - \sigma_n)$	$W(x_n + \sigma_n)$	$W(x_n \pm \sigma_n)$	$W(x_w - \sigma_w)$	$W(x_w + \sigma_w)$	$W(x_w \pm \sigma_w)$
1.1	33.0	34.5	67.5	38.6	30.4	69.0
1.25	31.8	34.4	66.2	41.3	28.8	70.1
1.33	31.4	34.2	65.6	42.4	28.2	70.6
1.4	30.9	34.1	65.0	43.1	27.8	70.9
1.5	30.1	34.0	64.1	44.1	27.4	71.5
1.66	29.1	33.6	62.7	45.5	26.8	72.3
2	26.4	33.0	59.4	47.7	26.0	73.7
3	–	–	–	51.6	24.9	76.5
5	–	–	–	55.3	24.2	79.5
10	–	–	–	58.7	23.7	82.4
30	–	–	–	61.5	23.4	84.9
50	–	–	–	62.2	23.3	85.5

[a] Meaning of symbols as in Table 2.

unsatisfactory measure for the broadness of weight distributions. In no case is the standard deviation an absolute measure of the broadness of an MWD (with the exception of σ_w for Gaussian weight distributions, of course).

The discussion was restricted to weight distributions because weight distributions will be observed in analytical work. In kinetic and mechanistic work, however, one is interested in number distributions. It is easy to show mathematically that none of the conclusions drawn above about the meaning of the standard deviations must be changed for LN and SF distributions if one switches from weight to number distributions. The values in Tables 2 and 3 as well as in Figs. 1 and 2 may thus be used for weight and number SF and LN MWD. In the case of Gaussian number distributions, σ_n is, of course, an absolute measure of the broadness of MWD.

It is easy to see that if each type of distribution possesses an absolute measure for broadness ("absolute" defined in the sense as the number standard deviation is for Gaussian number distributions or the weight standard deviation for Gaussian weight distributions), then this measure must be peculiar to the particular distribution. To our knowledge, no such absolute measures are known for logarithmic normal, Schulz-Flory, Poisson, Maxwell, or other distributions.

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