Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Pyun, C. W.(1973) 'The Logarithmic Normal Distribution of Degrees of Polymerization and Molecular Weights', Journal of Macromolecular Science, Part A, 7: 8, 1721 — 1725
To link to this Article: DOI: 10.1080/00222337308066386
URL: http://dx.doi.org/10.1080/00222337308066386

J. MACROMOL. SCI.—CHEM., A7(8), pp. 1721-1725 (1973)

The Logarithmic Normal Distribution of Degrees of Polymerization and Molecular Weights

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ABSTRACT

The reason why two generalized logarithmic normal distributions with the same set of two average molecular weights are interconvertible is discussed. The generalized distribution, however, appears in polymer chemistry in a different context.

Let W(x) be a continuous distribution function of the degrees of polymerization (DP) such that W(x) dx is the mass or weight fraction of the polymer molecules with the DP between x and x + dx. The logarithmic normal DP distribution function is given by [1, 2]

$$W(x) = (\sqrt{2\pi\sigma x})^{-1} \exp\{-(\ln x - \ln x_m)^2/2\sigma^2\} \tag{1}$$

which contains two parameters x_m and σ. A generalized logarithmic distribution function of order s (s being a real number) may be written [3]

$$W_s(x) = A_s x^s \exp\{-(\ln x - \ln x_s)^2/2\sigma_s^2\} \qquad (2)$$

where

$$A_s = \{\sqrt{2\pi}\sigma_s x_s^{s+1} \exp[(s+1)^2\sigma_s^2/2]\}^{-1}$$

is the normalization constant. $W_s(x)$ contains three parameters: σ_s, x_s, and s. For the special case of $s = -1$, Eq. (2) reduces to Eq. (1).

Recently, Watterson [4] has shown that if we require two logarithmic distributions of different order $W_s(x)$ and $W_r(x)$ to have the same set of the number- and weight-average DPs,

$$\bar{x}_n(s) = \bar{x}_n(r) \quad \text{and} \quad \bar{x}_w(s) = \bar{x}_w(r) \qquad (3)$$

then we can show that $W_s(x)$ and $W_r(x)$ are identical to each other. Here $\bar{x}_n(s)$, for example, stands for the number-average DP of $W_s(x)$.

The purpose of this communication is 1) to point out that Honig [5] has previously reached a similar conclusion, 2) to indicate the relationship between Honig's and Watterson's works, and 3) to discuss briefly the significance of their conclusion.

We first note that the i-th average DP of $W_s(x)$ is given by [6]

$$\bar{x}_i(s) = x_s \exp(s\sigma_s^2) \exp[(i - 1/2)\sigma_s^2] \qquad (4)$$

where $i = 1, 2, 3, \ldots$. The first three averages are the number-, weight-, and z-average DPs: $\bar{x}_1 = \bar{x}_n$, $\bar{x}_2 = \bar{x}_w$, and $\bar{x}_3 = \bar{x}_z$. In addition, the viscosity-average DP of $W_s(x)$ may be expressed by

$$\bar{x}_v(s) = x_s \exp(s\sigma_s^2) \exp[(1 + a/2)\sigma_s^2] \qquad (5)$$

Here, a is the positive exponent appearing in the intrinsic viscosity formula for long flexible polymer molecules

$$[\eta] = K(\bar{x}_v)^a$$

If we put $s = -1$ in Eqs. (4) and (5), we recover various average DPs of the logarithmic normal distribution (Eq. 1).

Substituting $\bar{x}_1$ and $\bar{x}_2$ of Eqs. (4) into Eqs. (3), Watterson obtains

$$\sigma_s^2 = \sigma_r^2 \tag{6}$$

which may be denoted by σ^2, dropping the subscripts, and

$$x_s \exp (s\sigma^2) = x_r \exp (r\sigma^2) \tag{7}$$

By the use of Eq. (7), $W_r(x)$ is converted to $W_s(x)$ [4] and vice versa. Watterson concludes that there is, therefore, only one logarithmic normal distribution.

Honig has previously shown [5] that Eq. (2), after a little rearrangement, can be put into the form of Eq. (1) with $\ln x_s + (s + 1)\sigma^2$ playing the role of $\ln x_m$. Therefore, if we adopt the definition

$$x_m = x_s \exp [(s + 1)\sigma_s^2] \tag{8}$$

then Eq. (2) transforms to Eq. (1). Honig concludes that there is no need to introduce a set of $W_s(s)$ other than Eq. (1), since separate determination of x_s and s by experiment seems impossible.

The meaning of Honig's definition (Eq. 8) becomes clear in view of Watterson's relation (Eq. 7): Eq. (8) is a special case of Eq. (7) for $r = -1$. Also implicit in Honig's treatment is an assumption corresponding to Eq. (6), equating σ and σ_s. Therefore, Eq. (8) may be interpreted as a consequence of the conditions expressed by Eqs. (3) with $r = -1$. This indicates that Honig's and Watterson's works are essentially equivalent.

In this connection, the conditions given by Eqs. (3) are not unique; if $W_s(x)$ and $W_r(x)$ have the same set of any two DP averages from Eqs. (4) and (5), then we get Eqs. (6) and (7) which in turn guarantee the interconvertibility of $W_s(x)$ and $W_r(x)$.

Inspection of the forms of the DP averages given by Eqs. (4) and (5) leads us immediately to the conclusion that if Eqs. (6) and (7) hold, then all the DP averages of $W_s(x)$ are equal to those of $W_r(x)$. This is, of course, expected, since two identical distributions have the same set of moments or averages. Under ordinary circumstances the reverse would also be true: Two distributions with the same set of moments or averages are identical to each other. However, the distributions expressed by Eqs. (1) and (2) are exceptional in this regard. The reader is referred to Moran [7] for a simple proof that the logarithmic normal distribution is not uniquely determined by its moments. His method is equally applicable to the distributions given by Eq. (2).

On the other hand, if a three-parameter distribution function is given or assumed, then it is in general completely determined by specification of its three moments or averages. However, for the distribution given by Eq. (2), specification of only two averages is sufficient, since specification of any two averages determines a third (and all the other averages) as seen in the above. This is apparently due to the form of the averages as given by Eqs. (4) and (5) where the parameters x_s and s occur in the same combination of $x_s \exp(s\sigma_s^2)$ and in no other way. Therefore, specification of the value of this combination (and not separate specification of the values of x_s and s), together with the value of σ_s, is sufficient as noted by Honig previously.

Thus $W_s(x)$ and $W_r(x)$ are identical if their two DP averages are given or specified. And this distribution can always be expressed by an identical logarithmic normal distribution of Eq. (1). In terms of the parameters themselves, $W_s(x)$ is not completely determined by specification of two parameters only. For example, even if $\sigma_s = \sigma_r$ and $x_s = x_r$, $W_s(x)$ and $W_r(x)$ are different as long as $s \neq r$. In this case they do not share even a single DP average in common. We can, however, easily find two logarithmic normal distributions (Eq. 1), one of which is identical to $W_s(x)$ and the other identical to $W_r(x)$. In this sense, introduction of the third parameter s in the logarithmic normal distribution as in Eq. (2) is superfluous, as pointed out by Honig and Watterson.

We observe, however, that $W_s(x)$ of Eq. (2) appears quite naturally in polymer chemistry in a different context. Suppose that W(x) of Eq. (1) is the weight fraction DP distribution function of a certain polymer sample. Then the corresponding mole fraction DP distribution function F(x) of the same polymer is given by

$$
\begin{aligned}
F(x) &= x^{-1} W(x) \Big/ \int_0^\infty x^{-1} W(x)\,dx \\
&= \frac{x_m \exp(-\sigma^2/2)}{\sqrt{2\pi}\,\sigma x^2} \exp\left\{-\frac{(\ln x - \ln x_m)^2}{2\sigma^2}\right\}
\end{aligned}
$$

Here F(x) dx gives the mole or number fraction of the molecules with the DP between x and x + dx. The above F(x) can immediately be recognized as $W_{-2}(x)$ with $\sigma_{-2} = \sigma$ and $x_{-2} = x_m$. In general, $W_k(x;\sigma,x_m)$, which is $W_k(x)$ with $\sigma_k = \sigma$ and $x_k = x_m$, may be interpreted as the distribution function associated with the (k + 3)rd average DP of the polymer sample. In other words, we have

$$x_k = \int_0^\infty x\, W_{k-3}(x;\sigma,x_m)\, dx$$

where k = 1, 2, 3, ...

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Accepted by editor December 20, 1972
Received for publication February 14, 1973