# The Numerical Evaluation of Parameters in Distribution Functions of Polymers from their Molecular Weight Distributions

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## Synopsis

It has been shown that the parameters in the log-normal (LN) and generalized exponential (Gex) distributions can be evaluated if molecular weight ratiosH and $H_z$, or their equivalents, are known for a linear, unimodal homopolymer. It is suggested that better checks of observed and calculated values of $M_z$ can be obtained for such polymers as are characterized by $m \leq 0.15$, by treating them as Gex rather than LN distributions.

## INTRODUCTION

The continuum of molecular weight distributions (MWDs) proposed in reference 1 is of use to assign specific statistical distribution functions to whole, unimodal homopolymer samples for which average molecular weights $M_z$, $M_w$, and $M_n$, or corresponding $A_z$, $A_w$, and $A_n$ values from GPC, are available. Consistent data for $M_w$, $M_v$, and $M_n$ upon such samples also suit the purpose. As indicated in reference 1, the assignment of MWD consists of two elements: a value of $M_w/M_n$ for the polymer plus a statement of its position in the continuum, denoted either by stating that it follows the log-normal (LN) distribution or by giving its $m$ value if it follows a generalized exponential (Gex) distribution. As shown below, such an assignment of MWD to a polymer sample eliminates the need to assume anything about the distribution function that characterizes it. Boyer[2] stated that such assumptions were needed to describe polymer MWD curves when only $M_w/M_n$, etc., data were avaliable.

## FORMULAS FOR EVALUATING COEFFICIENTS OF DISTRIBUTION FUNCTIONS

Since the LN distribution is the broadest in the continuum of Gloor,[1] and all narrower distributions in it follow a Gex distribution, detailed formulas for evaluating coefficients are given here only for them.

### Formulas for LN Distributions

A two-parameter function, the LN frequency distribution, is given by Chiang[3] as

$$f(M) = (MB\pi^{1/2})^{-1} \exp\left[ - \left(B^{-1} \ln \frac{M}{M_m}\right)^2\right] \qquad (1)$$

who also shows the following relations for polymer average molecular weights:

$$M_n = M_m \exp(-B^2/4) \qquad (2a)$$

$$M_w = M_m \exp(B^2/4) \tag{2b}$$

$$M_z = M_m \exp(3B^2/4) \tag{2c}$$

$$M_{z+1} = M_m \exp(5B^2/4) \tag{2d}$$

where $M_m$ is the median molecular weight of the polymer sample and $B$ is related to the standard deviation of $\ln M$.

If exponent $a$ in an applicable Mark-Houwink equation for the polymer sample is known, the viscosity-average molecular weight $M_v$ is defined as

$$M_v = M_m \exp(aB^2/4) \tag{2e}$$

From these relations the following ratios of various average molecular weights in LN distributions follow:

$$(M_w/M_n)^3 = M_{z+1}/M_n \tag{3a}$$

$$(M_w/M_n)^2 = M_z/M_n \tag{3b}$$

$$M_z/M_w = M_w/M_n \tag{3c}$$

$$M_w/M_v = (M_w/M_n)^{(1-a)/2} \tag{3d}$$

Thus, by knowing test values for $M_w$ and $M_n$, the parameters $M_m$ and $B$ can be evaluated by solving eqs. (2a) and (2b) simultaneously. As a check, these parameters should be substituted into eqs. (2c) or (2e) to verify their accord with the data before acceptance as valid coefficients in eq. (1).

### Formulas for Gex Distributions

For the Gex distribution, Peebles[4] shows frequency and weight distribution relations as

$$f(r) = m y^{k/m} r^{k-1} [\exp(-yr^m)]/\Gamma(k/m) \tag{4a}$$

$$W(r) = m y^{(k+1)/m} r^k [\exp(-yr^m)]/\Gamma[(k+1)/m] \tag{4b}$$

where $r$ is the degree of polymerization (D.P.) of the polymer. In this three-parameter equation, $y$ is specific to the polymer, $k$ is related to the distribution width, and $m$ is the location parameter in the continuum. The Gex distribution embraces several distributions commonly known under other names: those in which the $m$ value is 1 (unity) are the Schulz-Zimm (S-Z) where $k > 0$; the "most probable" where $k = 1$; the Schulz, where $k > 1$; and the Poisson, where $k \gg 1$. When $m = k + 1$, the Gex distribution becomes the Tung-Weibull (T-W) distribution.

Peebles denotes average D.P. values as $\bar{r}_n$ for number-average distribution, $\bar{r}_w$ for weight-average distribution, etc. For these average D.P. values he shows

$$\bar{r}_n = \Gamma[(k+1)/m]/y^{1/m}\Gamma[k/m] \tag{5a}$$

$$\bar{r}_w = \Gamma[(k+2)/m]/y^{1/m}\Gamma[(k+1)/m] \tag{5b}$$

$$\bar{r}_z = \Gamma[(k+3)/m]/y^{1/m}\Gamma[(k+2)/m] \tag{5c}$$

$$\bar{r}_{z+1} = \Gamma[(k+4)/m]/y^{1/m}\Gamma[(k+3)/m] \tag{5d}$$

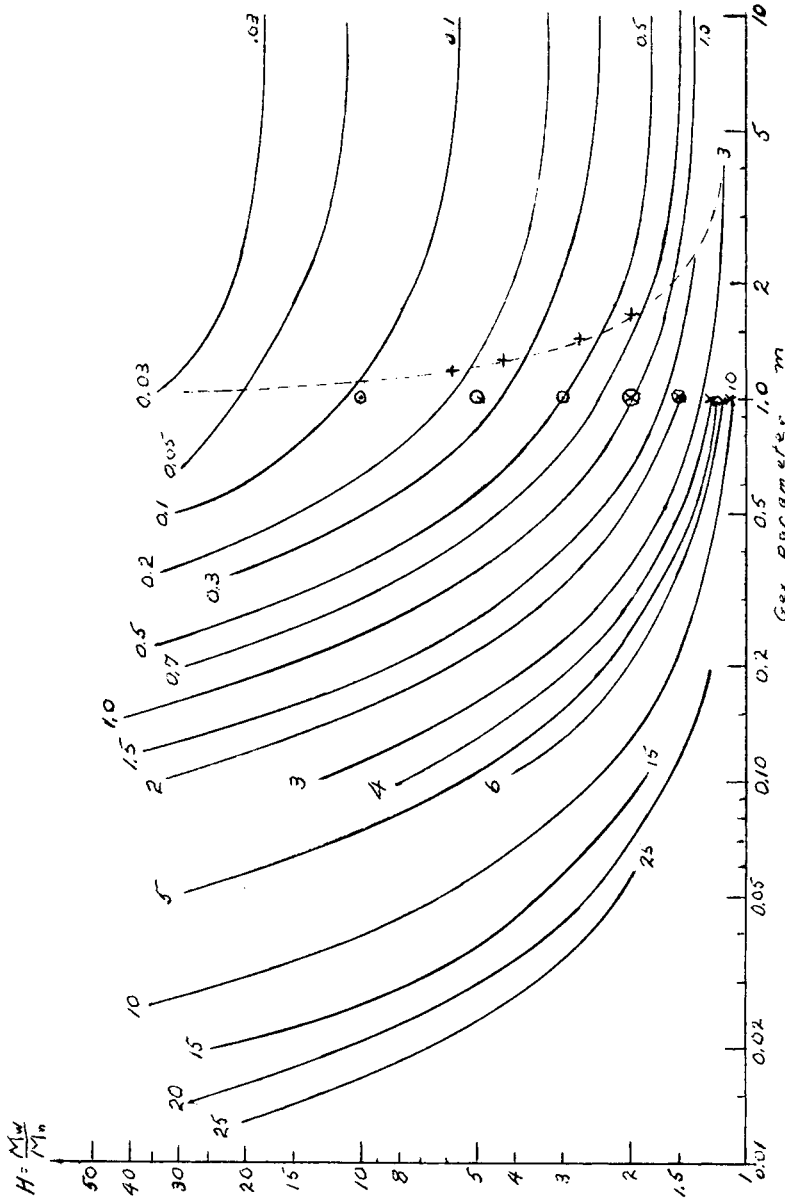For these Gex distributions, when exponent $a$ of the applicable Mark-Houwink equation is known,

Fig. 1. Lines of constant value of Gex parameter $k$ from known values of $H$ and Gex parameter $m$ of a polymer sample, using formula $H = \{\Gamma[(k + 2)/m] \cdot \Gamma[k/m] \div \{\Gamma[(k + 1)/m]\}^2$. Dashed line shows T-W distribution, in which $m = k + 1$: (X) Sibiński's points for $m = 1.0$; (O) points confirming $M_v/M_w$ of Elias, Bareiss, and Watterson for $m = 1.0$ and $a = 0.5$.

$$\bar{r}_v = \{\Gamma[(k + a + 1)/m]/y^{a/m}\Gamma[(k + 1)/m]\}^{1/a} \qquad (5e)$$

When the unit weight of monomer in the homopolymer under study is $M_0$, $\bar{r}_n M_0$ = $M_n$; $\bar{r}_w M_0 = M_w$; $\bar{r}_v M_0 = M_v$, etc., and the ratio $\bar{r}_w/\bar{r}_n = M_w/M_n$, $\bar{r}_w/\bar{r}_v =$ $M_w/M_v$, etc., and the theoretical values of the ratios of molecular weights are determined in terms of $k$ and $m$ as shown in Table 1 of reference 1.

As noted in the introduction, when $M_w/M_n$ and $m$ are known, the MWD is defined. For Gex distributions, one also needs a value of $k$ to evaluate eqs. (5a)–(5e). The relationships of these three factors are given in Figure 1, which is an elaboration of Table 2 of reference 1 and was prepared in the same way. Figure 1 not only facilitates computation but also enables one to demonstrate the validity of these relations by comparison with the literature.

For instance, Sibínski[5] gives for the Schulz distribution values of $k$ for values of $U$ between 0.1 and 1.0 (since $U + 1 = M_w/M_n$, this is plotted at 1.1–2 along that axis in Fig. 1) in exact accord with Figure 1. He also shows for the T-W distribution[6] comparisons of $b$ (in our notation, $b = m = k + 1$ for this distribution) with values of $U$ from 0.99 to 4.88 that check the T-W curve of Figure 1. For relationships involving $M_v$, values of $M_v/M_w$ for the LN and S-Z distributions, where exponent $a$ in the Mark-Houwink equation is 0.5, are given by Elias, Bareiss, and Watterson[7] for $M_w/M_n$ ratios of 1.5–10. Using the theoretical formulas of Table I of reference 1 and estimating $k$ values from Figure 1, one obtains values of $(M_w/M_v)^{-1}$ in good agreement with their values. Further, Mark-Houwink-type equations for $M_w$, $M_v$, and $M_n$, with exponents $a = 0.75$ and 0.72, proposed for polyacrylonitrile[8] and for polyamides[9] give $M_w/M_n$ of 2 and $M_w/M_v$ of 1.06. From Figure 2 of reference 1, these indicate $m = 1$; and from Figure 1, $k = 1$, in agreement with the "most probable" distribution attributed to these polymers. Thus, the relationships of Figure 1 agree with the pertinent literature.

Hence, knowing $M_w/M_n$ and $m$ for a polymer, one finds the corresponding value of $k$ in Figure 1 and solves eqs. (5a) and (5b) for $y$, to show that they give similar values. The theoretical value of $M_z$ can then be checked using eq. (5c). Equations (4a) and (4b) can then be set up using the numerical values of $k$, $m$, and $y$ to give an analytical expression for the Gex distribution functions of the polymer sample.

### Notation for Molecular Weight Ratios

As shown in reference 1 for all ratios in the continuum, the symbols $H =$ $M_w/M_n$ and $H_z = M_z/M_w$ may be found to be convenient. To be readily distinguished, the ratio $M_w/M_v$ is retained. For LN distributions, $H = H_z$, while for all Gex distributions, $H > H_z$. For *all* distributions in the continuum, $H_z$ $\times H = M_z/M_n$.

## TEST OF ASSIGNMENTS OF COEFFICIENTS USING LITERATURE DATA

The National Bureau of Standards standard sample no. 1475, a linear poly-

ethylene (HDPE), was reported to be unimodal and to be characterized[10] as follows:

| Molecular weights: | By GPC | By light scattering |
|---|---|---|
| Number-average $M_n$ | 18,310 ($\pm$360) | — |
| Weight-average $M_w$ | 53,070 ($\pm$620) | 52,000 ($\pm$2,000) |
| z-Average $M_z$ | 138,000 ($\pm$3,700) | — |

Standard deviations are shown in parentheses. From the average data, $H$ = 2.90 and $H_z$ = 2.60. At once, it appears that this sample does not follow the LN distribution exactly. A trial LN calculation indicated that coefficient $B$ = 1.459, $M_m$ = 31,173, and log $M_m$ = 4.494. Interpolated, the cumulative distribution curve[10] for this sample showed the mean log $M$ to have a value of 4.47, not a bad check. However, $M_z$ calculated for this sample using these coefficients in eq. (2c) gave $M_z$ = 153,800, outside the standard deviation limits.

The value of $H_z \times H$ = 7.54 = $M_z/M_n$ for this sample of $H$ = 2.9 indicates, from Figure 1 of reference 1, that a Gex distribution where $m$ = 0.1 would fit the data. From Figure 1, such a polymer would have, in theory, $k$ = 8.4. For HDPE, $M_0$ = 28. Hence, for this sample, $\bar{r}_n$ = 653.93 and $\bar{r}_w$ = 1895.36. From eq. (5a),

$$653.93 = \Gamma 94/[(y^{10})(\Gamma 84)] = 93!/[(y^{10})(83!)]$$

$$y = 46.255$$

From eq. (5b),

$$1895.36 = 103!/[(y^{10})(93!)]$$

$$y = 46.289$$

The two values for $y$ check, average $y$ = 46.27. From eq. (5c),

$$\bar{r}_z = 113!/[(46.27^{10}) \times (103!)] = 5015.1$$

$$M_z = 5015.1 \times 28 = 140,400$$

well within the standard deviation limits of 134,300–141,700 for $M_z$ by GPC. If $k$ is taken as 8.5, $y$ becomes 46.769 and the calculation gives theoretical $M_z$ = 138,100.

If one takes the conservative view that $M_w$ by light scattering is the only really absolute measurement and that the purpose of GPC is to give $M_z:M_w:M_n$ or $H$ and $H_z$ ratios, the standard deviation in $M_z$ ranges from 130,000 to 140,400. The $M_z$ calculated from theory for a Gex distribution where $m$ = 0.10 is also in accord with this range.

Hence, the coefficients for eqs. (4a) and (4b) for standard HDPE sample no. 1475 are: $m$ = 0.10, $k$ = 8.4, and $y$ = 46.27. Since a plot of log $M$ of its fractions on probability paper seems linear, it ostensibly follows the LN distribution. However, the Gex distribution with $m$ = 0.10 provides a better fit of $M_z$ reported.

Two other samples of HDPE, those of lowest and highest $H$ values in the series reported by Stacy and Arnett,[11] further exemplify this point. Reported data, coefficients for their Gex equations, and comparisons of their $M_z$ from LN and Gex distributions are:

**Sample 2.** Reported $H_z$ = 9, $H$ = 10.1, and $M_w$ = 82,000; hence, $M_z$ = 738,000. Coefficients: $m$ = 0.02, $k$ (by trial) = 20.64, and $y$ = 944.04. $M_z$ for LN distribution: 828,200. $M_z$ from Gex from $m$, $k$, and $y$ coefficients: 745,160.

**Sample 10.** Reported $H_z = 8$, $H = 15.7$, and $M_w = 122,000$; hence, $M_z = 976,000$. Coefficients: $m = 0.105$ (from Fig. 1 of ref. 1), $k = 2.6$ (from Fig. 1 of ref. 1), and $y = 15.97$. $M_z$ for LN distribution: 1,915,400. $M_z$ from Gex from $m$, $k$, and $y$ coefficients: 991,000. Similar agreement between Gex-based calculations of $M_z$ and data values can be shown for other samples in this series.

It is suggested that instances in the literature where polymers are reported to fit the LN distribution but where discrepancies were reported between observed and calculated values of $M_z$, as noted by Chiang,[3] may have been cases where a Gex distribution with $m \leq 0.15$ would provide better agreement. As indicated above, cumulative distribution curves are insufficiently sensitive to reflect such differences.

In the continuum of Gloor,[1] the LN distribution is its upper limit, and it is to be expected that real polymers will deviate from it slightly. Although calculations based upon LN are simple, they fail when applied to estimations of $M_z$ for polymers characterized by such small deviations.

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