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A Continuum of Molecular Weight Distributions Applicable to Linear Homopolymers

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Synopsis

An array or continuum of molecular weight distributions was set up, based upon the numerical solutions found for the theoretical log-normal (LN) and generalized exponential(Gex) distribution functions, for a range of $M_w/M_n = H$ ratios. For the Gex distributions, $m > 0$ in the continuum, and the theoretical Schulz–Zimm and Tung–Weibull distributions, in which $m \geq 1$ for $H \leq 31$, are located within the continuum. The LN distribution is the broadest, and the Gex-related distributions become narrower as the numerical value of m increases. From literature data for polystyrene, poly(vinyl chloride), linear polyethylene, and polypropylene, one can assign to these polymers specific molecular weight distributions that fall within the continuum.

Several known distribution functions can be assembled into an array or continuum of molecular weight distributions (MWD's) by comparing the numerical solutions of theoretical formulas for certain ratios based on average molecular weights. Literature data giving such molecular weight data for a number of homopolymers fit into the continuum. This defines the specific MWD pertaining to each of the homopolymers.

The first step in developing the continuum was to find theoretical formulas for M_z, M_w, M_v, and M_n, values for which are usually given by reports characterizing polymers, and then to set up, in consistent symbols, formulas for M_w/M_n, M_z/M_w, M_z/M_n, and M_w/M_v. For convenience, the first two of these ratios will hereafter be designated as H and H_z, respectively, and $M_z/M_n = H \times H_z$.

In the form of the generalized exponential (Gex) distribution function given by Peebles,[1] the three parameters k, m, and y are considered to be related to distribution breadth, location, and the specific polymer, respectively. When $m = 1$, the Gex distribution becomes that of Schulz-Zimm; when $m = k + 1$, it is equivalent to the Tung-Weibull distribution. These are all unimodal distributions. Formulas for M_z, M_w, and M_n are given by Peebles[1] and Tung[2] in terms of the three parameters. These authors also give formulas for M_v using the three parameters plus a, the exponent in the Mark-Houwink equation linking intrinsic viscosity of a polymer with its M_v.

When the ratios H and H_z are set up in terms of the three parameters, the polymer-specific y cancels out, giving H and H_z in terms of k and m; for M_w/M_v, only k, m, and a remain in the formulas, as shown in Table I.

TABLE 1

Formulas for Ratios H, M_w/M_v, and H_s in Terms of k and m for Gex-related MWD's[a]

MWD	Gen. exponential	Schulz–Zimm, $m = 1$	Tung–Weibull, $m = k + 1$
Ratios			
H	$\dfrac{\Gamma[(k+2)/m] \times \Gamma[k/m]}{\{\Gamma[(k+1)/m]\}^2}$	$(k+1)/k$	$\Gamma[(k+2)/(k+1)] \times \Gamma[k/(k+1)]$
M_w/M_v	$\dfrac{\Gamma[(k+2)/m]/\Gamma[(k+1)/m]}{\left\{\dfrac{\Gamma[(k+a+1)/m]}{\Gamma[(k+1)/m]}\right\}^{1/a}}$	$\dfrac{(k+1)}{\left\{\dfrac{\Gamma[(k+a+1)]}{\Gamma[(k+1)]}\right\}^{1/a}}$	$\dfrac{\Gamma[(k+2)/(k+1)]}{\{\Gamma[(k+a+1)/(k+1)]\}^{1/a}}$
H_s	$\dfrac{\Gamma[(k+3)/m] \times \Gamma[(k+1)/m]}{\{\Gamma[(k+2)/m]\}^2}$	$\dfrac{(k+2)}{(k+1)}$	$\dfrac{\Gamma[(k+3)/(k+1)]}{\Gamma[(k+2)/(k+1)]}$

[a] $\Gamma[\cdot]$ denotes gamma function of bracketed expression. For these distributions, $H_s < H$.

TABLE II
Values of Gex Parameter k Calculated for Various Distributions and Combinations of Gex Parameter m and H

Distribution	$H = 2$	$H = 3$	$H = 6$	$H = 11$	$H = 21$	$H = 31$
Gex, $m = 0.2$	6.3	3.7	1.95	1.25	0.85	0.67
$m = 0.5$	2.15	1.14	0.49	0.27	0.14	0.095
$m = 1.0$	1.0	0.50	0.20	0.10	0.05	0.033
Tung–Weibull	0.67	0.38	0.175	0.094	0.049	0.033
Gex, $m = 10.$	0.43	0.23	0.098	0.05	0.025	0.017

TABLE III
Values of H_z/H and $H_z \times H = M_z/M_n$ Calculated from Log-Normal and Gex Distribution Formulas Using k from Table II

	$H = 2$	$H = 3$	$H = 6$	$H = 11$	$H = 21$	$H = 31$
			A. H_z/H			
Log-normal	1.0	1.0	1.0	1.0	1.0	1.0
Gex, $m = 0.2$	0.91	0.83	0.61	0.45	0.30	0.23
$m = 0.5$	0.83	0.67	0.42	0.26	0.14	0.10
$m = 1.0$	0.74	0.56	0.305	0.173	0.092	0.064
Tung–Weibull	0.62	0.47	0.275	0.168	0.092	0.064
Gex, $m = 10.$	0.58	0.42	0.22	0.12	0.063	0.043
			B. $H_z \times H$ or M_z/M_n			
Log-normal	4	9	36	121	441	961
Gex, $m = 0.2$	3.6	7.3	22	55	132	218
$m = 0.5$	3.4	6.1	14.8	30	64	96
$m = 1.0$	3.0	5.0	11.2	21	41	61.6
Tung–Weibull	2.5	4.3	9.7	19.2	38.3	59.7
Gex, $m = 10.$	2.45	3.8	7.8	14.5	27.5	40.5

When these formulas are evaluated systematically using a series of numerical values of m, H, or k as called for, Table II can be set up giving the theoretical value of k for each pair of assigned values of H and m. The formulas for H_z and for M_w/M_v can then be evaluated using the theoretical value of k pertaining to each pair of H and m values.

For the log-normal MWD, H is usually known from experiment, $H_z = H$, and $M_w/M_v = H^{(1-a)/2}$ as shown by Chiang.[3]

To set up the continuum for polymers whose M_v is not known, the theoretical values of H and H_z in the log-normal and Gex distributions are calculated, the ratio H_z/H and the product $H \times H_z$ are found, and these measures are tabulated against H over the range of MWD forms considered, as shown in Table III. Since some polymer characterizations report $M_z:M_w:M_n$, Figure 1 shows a log–log plot of the theoretical values for $H \times H_z$ versus H in more complete form, illustrating the range of the continuum of MWD's.

Rudin[4] published formulas relating known M_z, M_w, and M_n of a polymer to its characterization in terms of skewness and asymmetry of its distribution. Log–log plots of these two measures for a series of hypothetical

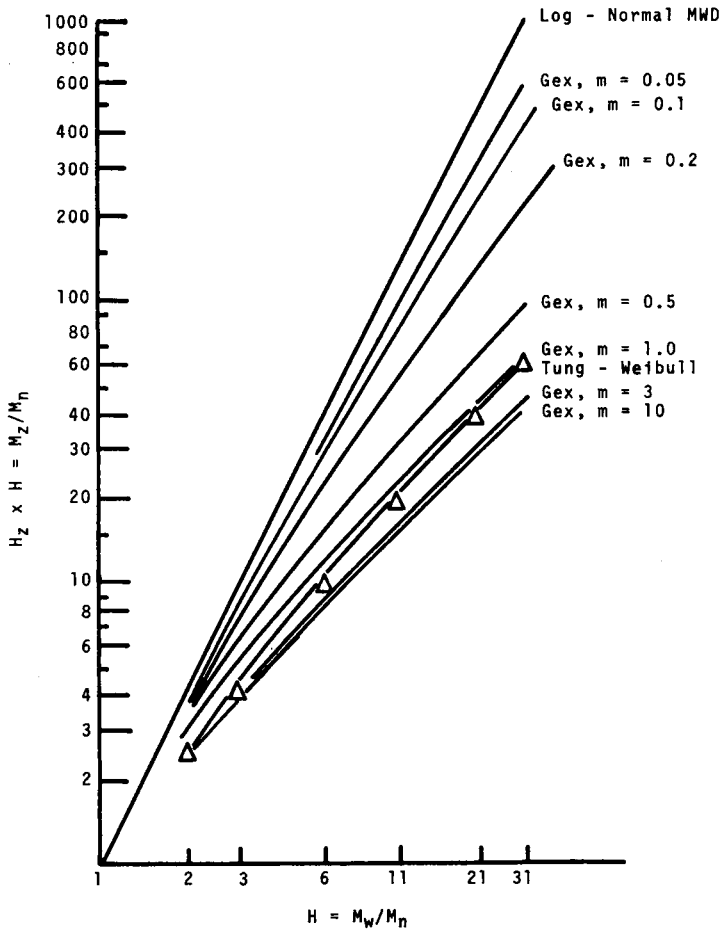

Fig. 1. Theoretical relations between M_z/M_n and H for various molecular weight distributions (MWD's).

polymers of constant M_n following the various distributions show a strong resemblance to Figure 1 with respect to position, linearity, and deviations of the lines for the Gex-related MWD's from log normal as H increases.

Theoretical values for M_w/M_v using several values of a also were calculated; for each value of a, log–log plots of M_w/M_v versus H gave straight lines for the log-normal MWD, while the Gex-related MWD's again gave lines concave to the abscissa, departing more from log-normal as m increases, as shown in Figure 2. These relations are useful to establish a distribution when M_z is unknown, or to check the accord between fractionation and viscometric data in assigning an MWD to a polymer. Each group of lines calculated for a specific value of a in Figure 2 represents the continuum for that value a only.

Using this approach, it is possible to assign a specific MWD to many whole homopolymers using literature values of their average molecular

TABLE IV
Assignment of MWD to Polymers from Literature Data Given for Them

Sample	Assigned using M_z/M_n		Assigned using M_w/M_v	
	m	MWD	m	MWD
IUPAC,[a] PS[5]	1.1	S–Z[b]	0.8	near S–Z
IUPAC, PVC[5]	1.0	S–Z	~0.2	near L–N[c]
NBS 1475, HDPE[6]	0.07	L–N	0.05	L–N
HDPE No. 2[7]	0.03	L–N	0.26	near L–N
PP sample C[8]	0.10	near L–N	no data on M_v shown	
IUPAC broad HDPE[5]	no M_z reported		0.08	L–N
HDPE No. 6[9]	no M_z reported		1.7	near T–W[d]
HDPE No. 9[9]	no M_z reported		0.23	near L–N
PP sample E-1[10]	no M_z reported		~7	Gex
PP sample E-2[10]	no M_z reported		0.6	Gex
PP sample E-4[10]	no M_z reported		0.05	L–N

[a] Study of MWD of commercial polymers by International Union of Pure and Applied Chemistry.
[b] Schulz–Zimm MWD.
[c] Log–normal MWD.
[d] Tung–Weibull MWD.

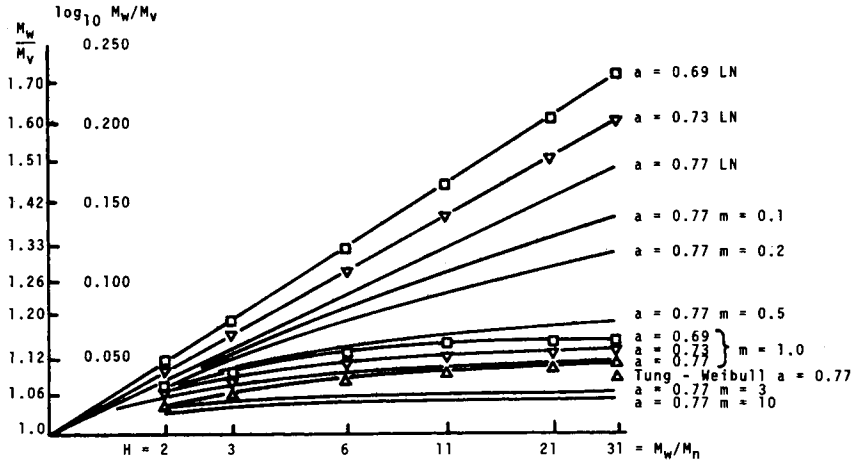

Fig. 2. Theoretical relations between M_w/M_v and H for various molecular weight distributions (MWD's).

weights. Table IV gives a few such assignments using M_z, M_w, and M_n or H_z/H as reported for polystyrene (PS),[5] poly(vinylchloride) (PVC),[5] linear polyethylene (HDPE),[6,7,9] and polypropylene (PP).[8,10] The assignments using M_z data gave the anticipated distributions: Schulz-Zimm for PS and PVC, and near log-normal for the polyolefins. Except for PVC, the assignments made using M_v were similar; agreement was even poorer for the nonlinear poly(vinyl acetate) reported in reference 5. As an example of an assignment, the PS sample had $M_z:M_w:M_n = 5.7:3.4:1$; at $H = 3.4$ of Figure 1, M_z/M_n of 5.7 is just below the line $m = 1$, leading

to the assignment of $m = 1.1$ to this sample. Data upon other polymers for which only H and M_v were given illustrate the range of distributions found in the data surveyed.

Noteworthy are the HDPE samples 6 and 9 of Wesslau,[9] made using Ti ester and Ti halide catalysts, respectively, which conform to the Tung-Weibull and log-normal MWD's attributed to them by that author. The PP samples E-1, E-2, and E-4 made by Yamaguchi[10] in the presence of different amounts of hydrogen follow quite different MWD's. Yamaguchi described their MWD's by means of the f-factor correction to the log-normal distribution of Davis, Tobias, and Peterli,[11] reporting f-factors of 1.28, 1.05, and 1.0, respectively, for them. The values of m shown for them in Table IV follow the same trend. The usual measure of polymer heterogeneity H reported for samples E-1 and E-2 was 7.4 and 6.7; it is of interest to calculate polydispersity g; from Hosemann and Schramek,[12] for them. Tung[2] gives this in a form equivalent to $g = (H_z - 1)^{1/2}$, which takes MWD into account. The MWD assignments for the two samples in Table IV and their H values enable us to estimate their $H \times H_z$ values, from which H_z values of 1.22 and 2.32 result, their polymolecularities g becoming 0.47 and 1.15, quite the reverse of the usual measures.

The various forms of the continuum shown above enable one to assign specific MWD's to several linear homopolymers that follow unimodal distribution functions. It indicates that the log-normal MWD is broader than Gex-related MWD's where $m > 0$ and that, as m increases, these distributions narrow. It enables one to assign a specific Gex MWD of parameter m to such polymers, fills the gaps in the continuum between the log-normal, Schulz-Zimm, and Tung-Weibull distributions, and extends beyond them. It provides a definite picture of the interrelationships of the three distributions named. Application of the continuum to real polymers suggests that it offers (1) a simple way of characterizing many polymers, (2) a simpler way of characterizing deviations from the log-normal MWD than do f-factors, (3) a way of following the effect of polymerization conditions upon the heterogeneity of the product, and (4) a better way of comparing distribution breadth of polymers which do not follow the same MWD.

We hope to publish a more complete description of the material outlined in this note.

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