

Extending the Continuum of Molecular Weight Distributions Based on the Generalized Exponential (Gex) Distributions

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Synopsis

Literature data on the average molecular weights M_n , M_w , M_z , and/or M_v for several polymers indicated that they fell outside the continuum originally proposed to model molecular weight distribution (MWD), where the log-normal (LN) distribution, or positively valued Gex parameters m and k , define the continuum. Following the papers of Kubin, it is possible to embrace these polymers in an extended continuum by including these parameters, *both* negatively valued, in it. To the extent that $m \geq -1$ and $k < -5$, the extended continuum models average molecular weights through M_{z+2} . The correspondence of Gex models of MWD of a polymer obtained from data on its M_n , M_w , and M_z with that obtained from data on its M_n , M_v , and M_w is indicated, using published data. The numerical value of the m parameter in a Gex model is of use in polymerization kinetics; when m values are obtained for each analysis from multiple analyses upon a given polymer, their consistency indicates the concordance of the three average molecular weights from each test run. The Gex parameters based upon M_n , M_w , and M_v or M_z can be used to estimate values for higher average molecular weights of linear, unimodal homopolymers. This is of use in interpreting rheological data on such polymers.

INTRODUCTION

A survey of data for more than 140 different homopolymer samples, upon which the literature gives sufficient average molecular weight values, found that several samples fall outside the continuum of molecular weight distributions (MWDs) based on the generalized exponential (Gex) distribution studied by the writer.¹⁻³ In these studies, the log-normal (LN) distribution was taken as the upper limit for Gex distributions, in which both the parameters k and m , which define the distribution, have positive values. The exceptions were found to have average molecular weights M_n , M_w , M_z , or M_v , which suggested that their m and k parameters might be negatively valued.

The work of Kubin⁴ was called to my attention by the reviewer of an unpublished paper. This led to the finding of another work by Kubin⁵ that, except for an area subject to mathematical limitations, showed that the use of such negatively valued parameters extends the range of applicability of the Gex MWD. In this extension, the LN distribution becomes the boundary between Gex distributions for which *both* parameters m and k are *positive* and those for which *both* have *negative* values.

It is the purpose of this paper to determine whether such an extension of Gex theory is applicable to the above-mentioned exceptions, and to indicate limits of applicability of Gex MWD analysis as a mathematical model of MWD of linear homopolymers.

The Gex distribution function in its normalized form, for differential weight

distributions of a homopolymer^{4,5} is

$$w(M) = \frac{mt^{(k+1)/m}}{\Gamma[(k+1)/m]} M^k \exp(-tM^m)$$

In this three-parameter function, the parameter m defines the Gex distribution that describes the polymer, the parameter k defines the polydispersity of the polymer, assuming that it follows the Gex distribution denoted by m , and the parameter t is related to molecular weight M of the polymer and always positive in value.

For the i th statistical moment μ'_i about zero⁵ in this distribution

$$\mu'_i = \frac{1}{t^{i/m}} \frac{\Gamma[(k+i+1)/m]}{\Gamma[(k+1)/m]}$$

so that when $i = 0$, $\mu'_0 = 1$. For weight distributions, $M_n = \mu'_0/\mu - 1 = 1/\mu'_{-1}$, and $M_w = \mu'_1$, and $M_z = \mu'_2/\mu'_1$, leading to eqs. (1)–(3) in the following section.

FITTING A GEX MODEL TO MWD DATA UPON A HOMOPOLYMER

Experimental data for M_n , M_w , M_z , or M_v are needed to model the MWD of a homopolymer by Gex theory. These values are most frequently found in polymer literature, and are usually those which can be measured most accurately. Standard fractionation techniques (elution, precipitation, GPC, etc.) yield integral and differential weight-distribution curves for a linear homopolymer sample. The Gex analysis is applicable only if the differential curve is essentially unimodal. For such normalized distributions one evaluates the successive moments of the differential distributions to obtain values for molecular weights which are related to Gex parameters m , k , and t :

$$M_n = \Gamma[(k+1)/m]/t^{1/m} \Gamma[k/m] \quad (1)$$

$$M_w = \Gamma[(k+2)/m]/t^{1/m} \Gamma[(k+1)/m] \quad (2)$$

$$M_z = \Gamma[(k+3)/m]/t^{1/m} \Gamma[(k+2)/m] \quad (3)$$

as shown by Kubin.^{4,5} To these can be added

$$M_{z+1} = \Gamma[(k+4)/m]/t^{1/m} \Gamma[(k+3)/m] \quad (4)$$

$$M_{z+2} = \Gamma[(k+5)/m]/t^{1/m} \Gamma[(k+4)/m] \quad (5)$$

as shown by Peebles⁶ and Kotliar.⁷

The last-named authors indicate that the two-parameter distribution function of Schulz and Flory is a Gex distribution for which $m = 1$, and the Tung or Tung-Weibull distribution has $m = k + 1$, with $k > 0$ in both cases. Kubin⁴ adds the Pearson distribution for which $m = -1$. Kotliar indicates that the Poisson distribution is also a special case of Gex where $m = 1$ and $k \gg 1$; Lechner⁸ gives $m \approx 2$ and $k \gg 1$ for this; Kubin does not mention the Poisson distribution.

When one has data upon a whole polymer for M_n by osmotic (Os) or ebulliometric methods, on M_w by light-scattering (LS) or ultracentrifuge (UC) methods, and for M_z , etc., by UC, such data also are useful for Gex analyses.

As shown below, our evaluation of Γz requires that z be positively valued. In

eqs. (1)–(5), the parameter t and the molecular weights are always positively valued. In cases where *both* parameters m and k are negatively valued, the evaluation of parameter m requires that $k < -3$. Extrapolation to higher molecular weights M_{z+1} or M_{z+2} require that the k that best corresponds to the data must have values smaller than -4 or -5 , respectively. If $k = -6$, m remaining negatively valued, eqs. (1)–(5) are true, but the next higher molecular weight, M_{z+3} , would have zero value. This is one limitation of Gex models, but in practice one seldom finds molecular weights higher than $z + 1$. Cases where m and k are of opposite sign often lead to negatively valued molecular weights, and are not considered here.

Some reports characterize their polymeric materials by giving M_n , M_w , and the intrinsic viscosity (IV) for the samples. In such cases, when one can establish a Mark–Houwink relation $IV = K(M_v)^a$ for the sample, where K and the exponent a are constants dependent on temperature, with solvent and units used to report IV for the conditions used to measure IV, and the relation

$$M_v = \frac{1}{t^{1/m}} \left\{ \frac{\Gamma[(1+k+a)/m]}{\Gamma[(k+1)/m]} \right\}^{1/a} \quad (6)$$

applies for the Gex distribution as set forth by Peebles.⁶

Finally, the molecular weight data for a polymer sample enables one to set up quotients for a Gex MWD, as follows:

$$H = (M_w/M_n) = \Gamma[(k+2)/m] \times \Gamma[k/m] / \Gamma^2[(k+1)/m] \quad (7)$$

$$H_z = (M_z/M_w) = \Gamma[(k+3)/m] \times \Gamma[(k+1)/m] / \Gamma^2(k+2)/m] \quad (8)$$

$$H_{z+1} = (M_{z+1}/M_z) = \Gamma[(k+4)/m] \times \Gamma(k+2)/m] / \Gamma(k+3)/m] \quad (9)$$

$$H_{z+2} = (M_{z+2}/M_{z+1}) = \Gamma[(k+5)/m] \times \Gamma(k+3)/m] / \Gamma(k+4)/m] \quad (10)$$

$$(M_w/M_v) = \frac{\Gamma[(k+2)/m]}{\Gamma[(k+1)/m]} \div \left\{ \frac{\Gamma[(k+1+a)/m]}{\Gamma[(k+1)/m]} \right\}^{1/a} \quad (11)$$

By assuming various numerical values for k and m , including negative values for both parameters, Gex theoretical values for the quotients were calculated, including that for H_z/H . A plot of H vs. H_z/H for Gex theoretical values is shown in Figure 1.

Applied to the average molecular weight data for a linear homopolymer having a unimodal differential distribution, one can evaluate H and H_z/H from the data, and estimate the values of parameters k and m for it from Figure 1. The choice of H_z/H as the ordinate of Figure 1 enables one to plot values for $\pm k$ and $\pm m$ on the same chart with reasonable spacing. This has already been done by Ho and Liu⁹ for seminormal distributions. Numerical checks and adjustments should be made for these estimated parametric values to minimize errors in reading and interpolation using Figure 1, until values of k and m are found that agree with the H and H_z values found for the the polymer. Together, H and H_z also depend on 4 moments of a distribution. Evaluation of Gex parameter m is of interest for polymerization kinetics work, as indicated above. Distributions are skewed to the right when $m \leq 1$; depending upon the value of H or k , they are skewed to the left when $m > 1-3$. Agreements of results from round-robin or replicate testing may also be compared by estimating m values from data reported by participants.

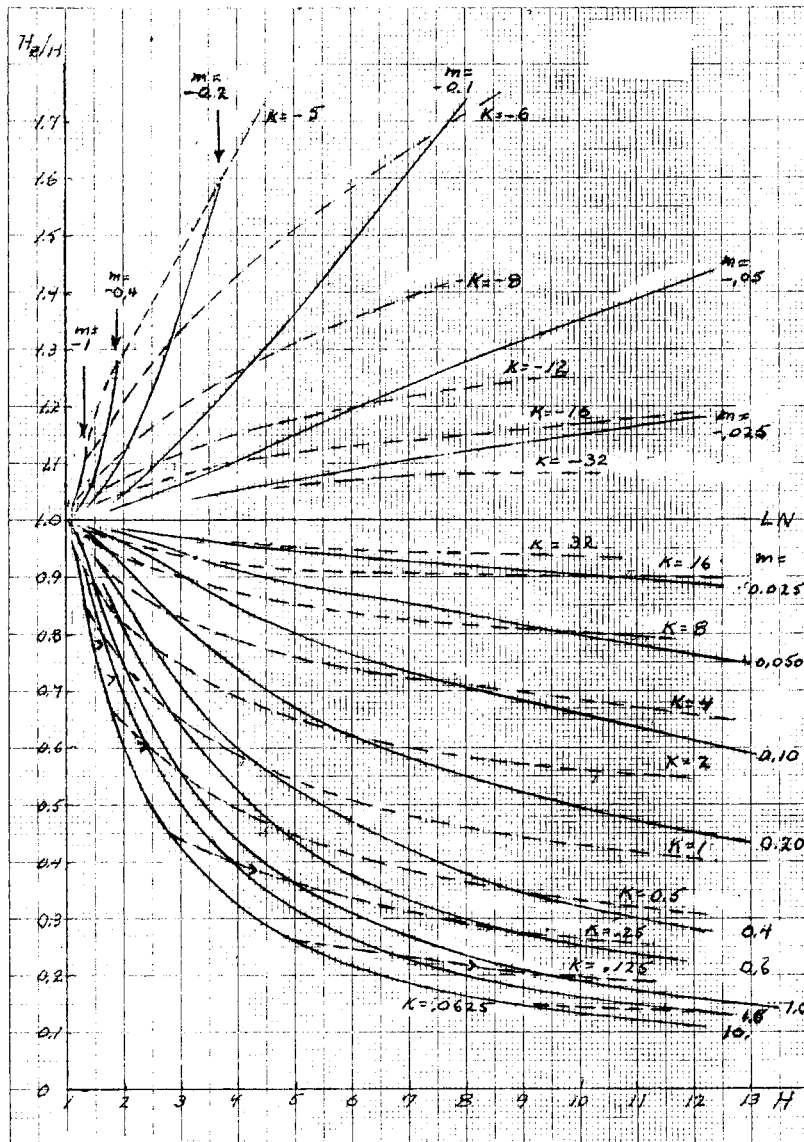


Fig. 1. Theoretical Gex relations of H to H_z/H , showing lines of constant value for Gex parameters m (—) and k (---). Points for the Tung-Weibull MWD are shown by \triangleright .

RESULTS FROM THE LITERATURE

(a) Application to poly(vinyl acetate) of van Krevelen et al.¹⁹: This report gives data for the sample by GPC enabling one to calculate $H = 2.8$, $H_z = 3.0$, $H_{z+1} = 2.9$ for it; hence $H_z/H = 1.071$. From Figure 1 one estimates $m \approx -0.064$, $k \approx -17$. By trial, the best fit was found to be $m = -0.62$, $k = -16.7$ which by Gex theory gives $H = 2.801$, $H_z = 3.005$, and $H_{z+1} = 3.258$, and $H_z/H = 1.073$. Except for H_{z+1} , which is 12% higher, the agreement of these Gex theoretical values with the data is quite satisfactory.

(b) Application to high-density polyethylene, NBS standard Sample 1475, data of Bersted¹¹: From GPC data given for this sample, one finds $H = 2.9$ and $H_z = 3.1$, whence $H_z/H = 1.069$. From Figure 1 for a Gex MWD, one estimates $m = -.055$, $k = -18$. Used in eqs. (7) and (8), these parameters yield $H = 2.92$ and $H_z = 3.13$, whence $H_z/H = 1.072$, which are satisfactory checks for Bersted's data. It should be noted that the GPC data of the original NBS report of Hoeve, Wagner, and Verdier¹² has been found² to be characterized by Gex parameters $m = 0.10$ and $k = 8.4-8.5$, with a good check for M_z reported. The data of Ross and Shank¹³ on nine different GPC tests of pellets of this sample give m values of 0.15-0.3; in their work, the experimental values of M_n , M_w , and H are within 2.5% at the 95% confidence level, while those for M_z are at 5.1% at this level.

The difference between the results from Bersted's data and that of the other authors seems to stem from differences in the experimental techniques used.

(c) Application to some other linear polyethylenes in Bersted¹¹: The data and its Gex analysis are summarized in Table I. Samples A and C are modelled reasonably well by Gex distributions having positively and negatively valued parameters m and k , respectively; sample F obviously follows a LN model.

(d) Application to linear polyethylene sample tested by several participants in an IUPAC working party, report by Strazielle¹⁴: Several laboratories reported values for M_n , M_w , and IV on a homogenized commercial sample of unfractionated HDPE. For this sample, the Mark-Houwink relation $IV = 0.007 M_v^{0.67}$ is given¹⁴ for the range of molecular weights studied, [with IV in dL/g, using 135°C TCB (trichlorobenzene) solvent. GPC tests were also conducted using TCB. One participant also measured M_n by Os method, and M_w by LS and UC methods. Thus, H and M_w/M_v can be evaluated from the data of this report.

For the estimation of Gex parameters for the samples, one first constructs a table, calculating H and M_w/M_v from various assumed values of k and m , keeping $a = 0.67$ constant, via eq. (11). Figure 2 was constructed from this table, enabling one to estimate a value of m for the results of each participant. The corresponding value of k can then be obtained from Figure 1. After trial and necessary adjustments, results of the Gex analysis were as given in Table II. All H values from GPC data reported for M_w and M_n except for note a from Os and LS and note b from Os and UC; M_v is from IV data; the quotient M_w/M_v is from GPC, except for notes a and b. The value of M_v for the Gex MWD of each participant was calculated from the parameters and estimating parameter t by use of eq. (2) and M_w is reported by the data, thus facilitating the solution of eq. (6).

The GPC data from the seven participants showed that only nos. 7, 9, and 10 could be considered as giving Gex distributions in poor accord with that of the average reported in (14); the reports of 3, 4, and 8 agree reasonably well in m values, even though the data of 3 require negatively valued parameters for its

TABLE I

Sample	From data			Best fit Gex		Calculated from eqs. (7), (8)		
	H	H_z	H_z/H	m	k	H	H_z	H_z/H
A	12.2	9.6	0.787	0.0435	8.24	12.16	9.52	0.783
C	5.7	5.9	1.035	-0.0125	-46.95	5.71	5.93	1.038
F	13.6	13.6	1.000	LN distribution, $H = H_z$ by inspection				

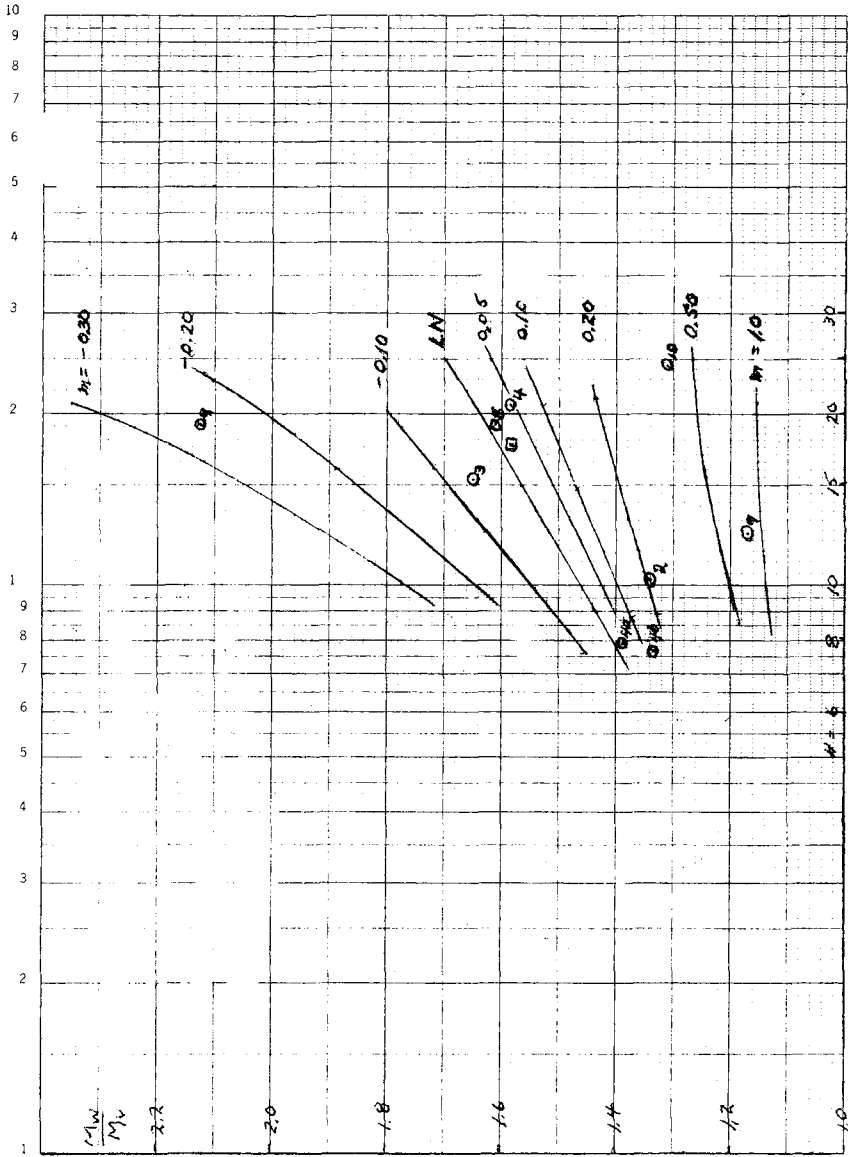


Fig. 2. Theoretical relations of M_w/M_n to H for $\alpha = 0.67$ showing lines of constant value of Gex parameter m . Points locate results of IUPAC participants: (□) average of all tests; (○) test of each participant as numbered. Data from Strazielle.¹⁴

TABLE II

Participant	Evaluated from data			Best fit Gex		% Deviation from data in Gex values of:		
	H	$M_v \times 10^{-3}$	M_w/M_v	m	k	H	M_v	M_w/M_v
2	10.16	94.6	1.342	0.20	1.328	0.04	-0.4	0.4
3	15.4	112.0	1.652	-0.06	-7.15	0.0	0.7	-0.7
4	20.9	120.0	1.583	0.05	5.63	0.0	-0.2	0.2
4 ^a	7.95	120.0	1.392	0.04	11.2	-0.2	0.4	-0.5
4 ^b	7.62	120.0	1.333	0.115	3.38	-0.1	-0.7	0.8
7	12.4	111.0	1.171	0.80	0.113	0.0	-0.3	0.6
8	19.1	130.0	1.615	0.02	15.98	-0.2	0.8	-0.9
9	19.1	94.6	2.125	-0.26	-2.56	0.4	-0.7	0.9
10	24.4	126.0	1.317	0.40	0.19	0.3	0.8	-0.5
Average	17.62	112.0	1.589	0.02	16.45	0.0	-0.5	-0.5

Gex model. The negatively valued parameters that model the data of report 9 lead to negative values of M_z in that model, however.

The m values for reports 4^a and 4^b, based on average molecular weights obtained on the whole polymer by methods other than GPC, show rather good accord with those from GPC, despite the differences found in their H values. The validity of these Gex analyses is indicated by the fact that the % differences between the Gex values for H , M_v , and M_w/M_v are all within $\pm 1\%$ of those found from the experimental data.

(e) Application to data on polystyrenes of Pearson and Garfield¹⁵: These authors give M_n , M_w , M_z , and M_{z+1} data from GPC on four commercial samples, and indicate that all are unimodal. The comparison of values of the quotients obtained from reported data and from those of the best fit Gex distribution are given in Table III. The deviations of the Gex models in this case are less than 2%, 4%, and 7% for H , H_z , and H_{z+1} , respectively, and are within expectations.

Because one of the aims of Ref. 15 was to show the effect of MWD on polymer melt rheology, it is of interest to compare the values of Graessley's ratio,¹⁶ $M_z M_{z+1}/M_w^2$, a measure of the onset of non-Newtonian flow in polymer melts, from the data and from the Gex quotients, since, from eqs. (7)–(9), it equals $H_z^2 \times H_{z+1}$. The values of Graessley's ratio are given in Table IV. The Gex values model Graessley's ratio, despite the 7% deviations found above in H_{z+1} .

(f) Applications to polypropylenes of Minoshima, White, and Spruiell¹⁷: This work gives characterization data for M_w , $M_w/M_n = H$, $M_z/M_w = H_z$, and M_v

TABLE III

Sample designation	Quotients from reported data			Best fit Gex parameters		Quotients from Gex theory by eqs. (7)–(9)		
	H	H_z	H_{z+1}	m	k	H	H_z	H_{z+1}
KTPL 5	2.20	1.82	1.58	0.375	2.62	2.20	1.83	1.64
PSR 3/8	2.80	2.15	1.675	0.375	1.82	2.82	2.10	1.79
8D	2.72	2.05 ₅	1.62	0.45	1.50	2.74	1.99	1.69
685	5.31	1.93	1.59	0.825	0.28	5.41	1.96	1.54

Range of % deviation from reported data: 0 to 1.8–3.3 to 1.3–3.3 to 6.9.

TABLE IV

Sample	From mol wt data	From quotients based on data	From quotients of best fit Gex	% Deviation
KTPL 5	5.269	5.23	5.49	5.0
PSR 3/8	7.754	7.74	7.89	1.9
8 D	6.805	6.84	6.69	-2.0
685	5.923	5.92	5.92	0

upon eight commercial polypropylenes, and investigates the influence of their MWDs upon their rheological properties. Gex models of MWD from H and H_z data are given in Table V, using Figure 1. The Gex models give quotients and their ratios that agree within 1% of those reported. It is suggested that the m -parameters found for each sample give a numerical designation of their breadth of distribution, rather than the qualitative indications of the designation of the samples from Ref. 17.

Also of importance, in view of the use of H and M_v to evaluate the Gex parameters of application (d) above, is the effort to see how the reported values of M_w , M_v , and their ratio M_w/M_v fit into the Gex models established for the samples of Ref. 17. It is assumed that H will be the same as reported, and that the m and k values established will apply; thus, only values for Mark-Houwink exponent a are missing for solutions of eq. (11). From charts like Figure 2—or Figure 2 of Ref. 1—where the Gex relations between H , M_w/M_v , and parameter m are established for values of exponent a ranging between $a = 0.67$ and $a = 0.73$, one can select trial values of a , giving values of M_w/M_v , that bracket the value that pertains to a given sample at its characterizing H . By linear interpolation one can thus select the proper value of a for the sample, and use it to solve eq. (11). Using the value of M_w/M_v thus obtained, and given M_w from the data, a value of M_v results. As a crosscheck, eq. (2) was solved, using the M_w value from the data, to evaluate the term $(1/m \log t)$ for each sample. This enables one to evaluate M_v for each sample using the three Gex parameters k , m , and t , by eq. (6).

In Table VI, the true values of M_w and of M_v are divided by 10^5 for ease of tabulation; only one value for M_v by Gex analysis is shown because the results from eqs. (6) and (11) are practically identical. Using the interpolated values of a , Gex theory gives close agreements in M_w/M_v and M_v with those reported.

TABLE V

Sample	From data of Ref. 17			Best fit Gex		Quotients from Eqs. (7), (8)		H_z/H by Gex
	H	H_z	H_z/h	m	k	H	H_z	
PP-H-N	6.4	2.59	0.405	0.49	0.48	6.415	2.565	0.400
PP-H-R-B	9.0	3.57	0.397	0.315	0.71	9.072	3.582	0.395
PP-H-B-R	7.7	3.54	0.460	0.29	0.93	7.707	3.543	0.460
PP-M-N	4.7	2.81	0.598	0.305	1.35	4.690	2.835	0.604
PP-M-R	7.8	4.82	0.618	0.15	2.37	7.808	4.789	0.613
PP-M-B	9.0	4.46	0.496	0.21	1.355	8.938	4.431	0.496
PP-L-N	4.6	2.47	0.537	0.44	0.82	4.561	2.446	0.536
PP-L-R-N	6.7	3.18	0.475	0.32	0.90	6.709	3.208	0.478

TABLE VI

Sample	Reported by Ref. 17			Inter- polated <i>a</i>	By Gex analysis		<i>H</i> / <i>m</i> log <i>t</i> , eq. (2)
	<i>M_w</i>	<i>M_v</i>	<i>M_w</i> / <i>M_v</i>		<i>M_w</i> / <i>M_v</i> , eq. (11)	<i>M_v</i> , Eqs. (6) or (11)	
PP-H-N	2.84	2.40	1.18 ₃	0.718	1.1827	2.401	-4.35017
PP-H-R-B	3.03	2.42	1.25 ₂	0.702	1.2523	2.419	-2.90986
PP-H-B-R	3.39	2.71	1.25 ₁	0.697	1.2508	2.710	-2.44994
PP-M-N	2.32	1.92	1.20 ₈	0.684	1.2077	1.921	-2.26913
PP-M-R	2.79	2.13	1.310	0.687	1.3116	2.127	3.90030
PP-M-B	2.68	2.07	1.295	0.696	1.2949	2.069	-0.11944
PP-L-N	1.79	1.52	1.17 ₈	0.690	1.1786	1.520	-3.71779
PP-L-R-N	2.02	1.66	1.21 ₇	0.712	1.2167	1.660	-2.67446

The average *a* values for all eight samples is $0.697 \pm .021$. If one assumes that the reported values of *M_v* were all based upon a Mark-Houwink equation using $a = 0.697$, samples PP-H-N and PP-M-N (for which the highest and lowest *a* values were found) give *M_v* values by eq. (6) of 2.37×10^5 and of 1.94×10^5 , respectively, both within 1.3% of the datum for each.

Hence, for practical purposes, Gex MWD models based on *H* vs. *H_z*/*H* data, or on *H* vs. *M_w*/*M_v* data, are in agreement. In such models, it is implied that *M_v* represents the ratio of the *a*th moment to the zeroth moment of the differential weight distribution curve of a polymer.

From Figures 1 and 2 of Ref. 17 there are differences in the melt flow behavior of PP-H-N, PP-M-R, and PP-M-B, which have similar values of *M_w*. In Figure 2 of Ref. 17 charting principal normal stress differences as a function of shear rate in 180°C melts, sample PP-H-N shows smaller stress differences than the other two, with the line for PP-M-R crossing that for PP-M-B at a shear rate of 0.1 s^{-1} and continuing at higher stress differences at higher shear rates. Since in application (e) it is shown that the Gex model enables one to get *H_{z+1}* values and thus to evaluate Graessley's ratio, the Gex parameters *m* and *k* for these samples were used to estimate this quotient and the corresponding Graessley ratio for these three samples (Table VII). The Graessley ratios seem to account for the different flow behavior of the three samples; so do the *m* values, where lower values indicate broader distributions.

DISCUSSION

The extension of the continuum concept to unimodal differential weight distributions of linear homopolymers characterized by Gex MWDs for which both *m* and *k* parameters are negatively valued is demonstrated in applications (a)-(d). The extended continuum enables one to define Gex models that ade-

TABLE VII

	PP-H-N	PP-M-R	PP-M-B
<i>H_z</i> from above	2.565	4.789	4.431
<i>H_{z+1}</i> from <i>m</i> and <i>k</i>	2.38	3.55	2.28
Graessley H_z^2/H_{z+1}	15.7	81.4	44.8
<i>m</i> Value	0.49	0.15	0.21

quately describe many such homopolymers in all instances where $m \geq -1$, $k > 0$, or $k < -5$. For integral values of $m \leq -2$, the Γ functions of eqs. (1)–(5) become indeterminate in value,¹⁸ hence the continuum is broken in this region.

The Gex models, derived from molecular weight data, are of value because their m parameters can be related to polymerization kinetics, as indicated in Ref. 4 and in the section on fitting data to a model. The m parameters also let one view in a new way the molecular weight data obtained by different workers upon the same polymer sample, as indicated in application (b) above on a linear polyethylene, or in application (d) using data from a "round-robin" test conducted by an IUPAC working party. The Gex models enable one to compare not only the molecular weights reported, but to put them together in a way that compares the consistency of the MWD characteristic of each test report.

The Gex parameters, based on the measures M_n , M_w , M_v , or M_z which are most accurately determined, can be used to estimate, using eqs. (4) and (9), values of M_{z+1} or H_{z+1} if needed. These estimated values are in good accord with the data, as in application (e) above, and in nine of 13 samples studied in Ref. 3. The poor check of application (a) above is attributed to the fact that poly(vinyl acetate) is usually not a linear polymer, but is branched in structure.

Additionally, application (e) illustrates how the modeling of MWD using Gex parameters can give values of Graessley's ratio, useful in accounting for rheological behavior of polymers on a molecular basis. Application (f) uses Gex parameters to evaluate all the quotients, not reported, needed to estimate this ratio.

NOTE ON CALCULATIONS

All gamma functions in eqs. (1)–(11) are evaluated by the Stirling expansion given by Korn and Korn,¹⁸ as expressed in the form:

$$\log \Gamma z = -z \log e + (z - 0.5) \log z + \frac{1}{2} \log 2\pi + \log \left(1 + \frac{1}{12z} + \frac{1}{288z^2} - \frac{139}{57,840z^3} - \frac{571}{2,488,320z^4} \right)$$

This was programmed on a TI 59 desk calculator for ease of computation. The Stirling expansion is useful with large positive real numbers; the form used provides checks within 0.00001 for $\log \Gamma z$ when $z \geq 1.4$ and for $\log (z!)$ through $z = 300$. It is also valid for positive numbers consisting of an integer and a decimal fraction, as often occurs in this work. All computations of gamma functions and their ratios were carried out using five-place common logarithms. The antilogarithm corresponding to a result was expressed to the number of places called for by the starting data. Best fit trials for m and k were carried out only to a degree consistent with the experimental accuracy of the data on which Gex models were based, usually 1–2% for M_n and M_w , and ~5% for M_z .

In Figure 1, note that, at any $H > 1$, the Gex parameter m follows a continuous function through its negative values, while the Gex parameter k is discontinuous as it approaches the LN line, which fills the Gex discontinuity where $m \rightarrow 0$ and k approaches $\pm \infty$. The empty spaces above the line $k = -5$ represents the area where eqs. (1)–(5) and (7)–(10) may result in indeterminate solutions.

References

1. W. E. Gloor, *J. Appl. Polym. Sci.*, **19**(1), 273-9 (1975).
2. W. E. Gloor, *J. Appl. Polym. Sci.*, **22**, 1172-82 (1978).
3. W. E. Gloor, *Polymer*, **19**(8), 984-6 (1978).
4. M. Kubin, *Coll. Czech. Chem. Commun.*, **32**, 1505-17 (1967).
5. M. Kubin, *Coll. Czech. Chem. Commun.*, **34**, 703-7 (1969).
6. L. H. Peebles, *Molecular Weight Distribution in Polymers*, Wiley-Interscience, New York, 1971, pp. 15-27.
7. A. M. Kotliar, *J. Polym. Sci., Part A*, **2**, 4303-25 (1964).
8. M. D. Lechner, *J. Polym. Sci. Polym. Symp.*, **61**, 63-71 (1977).
9. F.-C. Ho and L.-P. Liu, *Kao Feng Tzu T'ung Hsun*, **1**(2), 23-9 (1979) (original gives name as GAOFENZI TONGZUN).
10. D. W. van Krevelen, D. J. Goedhart, and P. J. Hoftijzer, *Polymer*, **18**, 751 (1977).
11. B. H. Bersted, *J. Appl. Polym. Sci.*, **19**, 2167-77 (1975).
12. C. A. J. Hoeve, H. L. Wagner, and P. Verdier, *J. Res. Natl. Bur. Stand.*, **76a**(2), 137 (1972).
13. J. H. Ross, Jr., and R. L. Shank, *Polymer Molecular Weight Methods*, M. Ezrin, Ed., Adv. in Chem Series 125, Am. Chem. Soc., Washington, D.C., 1973, pp. 108-16.
14. C. Strazielle, *Pure Appl. Chem.*, **42**(4), 615-25 (1975).
15. G. H. Pearson and L. J. Garfield, *Polym. Eng. Sci.*, **18**(7), 583-589 (1978).
16. W. W. Graessley and L. Segal, *AIChE J.*, **16**, 261 (1970).
17. W. Minoshima, J. L. White, and J. E. Spruiell, *Polym. Eng. Sci.*, **20**(17), 1166-75 (1980).
18. Korn and Korn, *Handbook of Mathematics*, McGraw-Hill, New York, 1969, pp. 697-9.

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