Notes to the Editor

Generalized exponential distribution as an adequate description of the molecular weight distribution of many polymers

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The recent paper of van Krevelen, Goedhart, and Hoftijzer[2] provides g.p.c. data which give M_{z+1} values for 14 polymer samples, as well as the more commonly reported values for M_z, M_w, and M_n. The first such report with a critical analysis of these data, concluded that, within the accuracy of measuring average molecular weights, only M_w and (M_w/M_n) are needed to characterize an unblended polymer for descriptions of its flow or mechanical properties. Further, the g.p.c. data were used to calculate the quotients (M_w/M_n), (M_z/M_w), (M_{z+1}/M_z), and $(M_zM_{z+1}/M_w{}^2)$ which correspond to quotients H, H_z, H_{z+1}, and $(H_{z+1}H_z{}^2)$, respectively, of the writer's earlier papers[2,3]. Ref 1 states that none of the 14 samples could be described by any of the theoretical molecular weight distribution (*MWD*) functions commonly used, such as the Lansing–Kraemer (a log–normal distribution), Schulz–Flory, Tung, or Poisson, etc. distributions. A need was expressed for a new theoretical approach.

Since the continuum[2] of *MWD*s embraces all the above named distributions, either as log–normal (*LN*) or a myriad of Generalized Exponential (*Gex*) distributions, it seemed useful to evaluate the data of ref 1 to see how it fits into the continuum.

The expression for the frequency distribution of a polymer which follows a *Gex MWD* is often given as:

$$F_{m,k,y}(r) = my^{k/m}r^{k-1} \times [\exp(-yr^m)]/\Gamma(k/m)$$

The corresponding expression for weight distribution, $W_{m,k,y}(r)$, is the same except that, on the right-hand side of the equation, the parameter k is replaced by $(k + 1)$. In both expressions, r signifies the degree of polymerization (*DP*) of the polymer. The average *DP* of a polymer that follows a *Gex MWD* are, in general:

$$\bar{r}_i = \Gamma[(k+i)/m]/y^{1/m} \times \Gamma[(k+i-1)/m]$$

where $i = 1, 2, 3$, and 4 for $\bar{r}_n$, $\bar{r}_w$, $\bar{r}_z$, and $\bar{r}_{z+1}$, respectively. For any polymer made up of monomers of unit weight M_0 and for which the average molecular weights M_n, M_w, M_z, etc. are known, $M_n = M_0\bar{r}_n$, $M_w = M_0\bar{r}_w$, etc. In dealing with the quotients H, H_z and H_{z+1} for the linear, unimodal homopolymers of the continuum[2], the *Gex* y parameter disappears, so only m and k are needed to evaluate the quotients and define the *Gex* distribution which defines the polymer.

Using the method given in refs 2 and 3, the *Gex* parameters m and k were assigned to each polymer sample, and from these the theoretical values were found for quotients H, H_z, H_{z+1}, and $(H_{z+1}H_z{}^2)$. *Table 1* compares the values of these quotients based on the g.p.c. measurements with those given by assuming that the *Gex* parameters apply. It is necessary to determine whether the agreements shown are within the accuracy of g.p.c. methodology.

Ref 1 indicates that the average spread between the results of two investigations measuring quotient H may be approximated by the relation:

$$\log H - \log[(H + H_0)/2] \approx 0.12$$

where H is the high value and H_0 the low value found. The difference between the log values is symbolized in *Table 1* as 'Δ log'; if the difference is smaller than 0.12, the inaccuracy is less than that due to experimental error. The following relation is indicated for H_z:

$$\log H_z - \log[(H_z + H_{z0})/2] \approx 0.18$$

In more familiar terms when $\{\log x - \log[(x + x_0)/2]\}$ takes the values given below, the percentage differences between $(x + x_0)/2$ and x or x_0 *and* between x and x_0 are as given in columns 2 and 3 of the Table below.

	Difference between	
Log x – log $[(x + x_0)/2]$	$(x + x_0)/2$ and x or x_0	x and x_0
0.026	~ ± 5	~ 10
0.046	~ ±10	~ 20
0.12	~ ±16	~ 32
0.18	~ ±25	~ 50

The uncertainties reported for narrow *MWD* polypropylene from g.p.c. measurements by Atkinson and Dietz[4], of ±8% in M_n and ±10% in M_w lead to percentage differences between H and H_0 of ~35%, in accord with this interpretation.

Scrutiny of *Table 1* shows that no value of 'Δ log' for H, H_z, or H_{z+1} exceeds 0.059, meaning that all the values estimated using the *Gex* parameters fall within the accuracy limits for H. The values for sample 5, poly(vinyl acetate), while showing that it does not follow any *Gex MWD*, merely indicate that the *LN MWD* gives a better description of it. Since the accuracy limits for H_{z+1}, though unknown, must be greater than those shown above for H and H_z, it seems fair to say that the agreement between these measurements and g.p.c. data is well within the limits of experimental error.

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Table 1 Comparisons of values of H, H_z, H_{z+1}, and $(H_{z+1}H_z^2)$ from g.p.c. data[1] and those calculated using the *Gex* parameters m and k estimated for each sample

	Gex parameters					
Sample	m	k	H	H_z	H_{z+1}	$(H_{z+1}H_z^2)^a$
1-Poly(isobutylene):						
Reported[1] by g.p.c.			3.5	2.9	2.9	24.3
Calculated from m and k	0.12	5.7	3.525	2.99	2.63	23.5
$\Delta \log^b$			0.002	0.007	0.020	(3.2%)
. . -Poly(isobutylene):						
Reported[1] by g.p.c.			6.0	3.2	2.2	23.3
Calculated from m and k	0.30	1.1	5.985	3.16	2.345	23.5
$\Delta \log$			0.001	0.003	0.025	(0.9%)
2-Polystyrene:						
Reported[1] by g.p.c.			2.2	1.8	1.58	5.3
Calculated from m and k	0.45	2.05	2.23	1.80	1.589	5.14
$\Delta \log$			0.003	0	0.004	(2.0%)
3-Poly(vinylidene fluoride):						
Reported[1] by g.p.c.			2.6	2.1	1.68	7.7
Calculated from m and k	0.40	1.90	2.58	1.98	1.716	6.7
$\Delta \log$			0.002	0.013	0.005	(13%)
4-Poly(vinyl alcohol):						
Reported[1] by g.p.c.			4.5	3.2	1.96	20.1
Calculated from m and k	0.2	2.48	4.49	3.16	2.55	25.5
$\Delta \log$			0.001	0.003	0.048	(27%)
5-Poly(vinyl acetate):						
Reported[1] by g.p.c.			2.8	3.0	2.9	25.8
Sample does not follow *Gex* distribution, because $H_z > H$						
Assuming log-normal distribution	–	–	2.8	2.8	2.8	21.95
$\Delta \log$			0	0.015	0.008	(18%)
6-Poly(vinyl pyrrolidone):						
Reported[1] by g.p.c.			2.5	2.3	1.85	9.4
Calculated from m and k	0.10	10.9	2.42	2.25	2.12	10.7
$\Delta \log$			0.005	0.001	0.048	(11.4%)
7-Poly(methyl methacrylate):						
Reported[1] by g.p.c.			1.9	1.6	1.56	4.0
Calculated from m and k	0.55	2.10	1.92	1.62	1.46	3.8
$\Delta \log$			0.003	0.002	0.017	(5.0%)
8-Polyacrylonitrile:						
Reported[1] by g.p.c.			3.1	2.1	1.63	7.5
Calculated from m and k	0.45	1.35	3.04	2.09	1.73	7.6
$\Delta \log$			0.004	0.003	0.015	(1.3%)
9-Poly(butadiene):						
Reported[1] by g.p.c.			3.1	2.4	1.6	9.6
Calculated from m and k	0.25	2.70	3.11	2.41	2.057	11.7
$\Delta \log$			0.002	0.002	0.059	(22%)
10-Poly(2,6-dimethyl-1,4-phenylene oxide):						
Reported[1] by g.p.c.			2.2	1.6	1.33	3.3
Calculated from m and k	0.80	1.05	2.21	1.71	1.346	3.9
$\Delta \log$			0.001	0.014	0.003	(18%)
11-Poly(2,6-diphenyl-1,4-phenylene oxide):						
Reported[1] by g.p.c.			1.9	1.6	1.51	3.8
Calculated from m and k	0.60	2.0	1.88	1.60	1.429	3.65
$\Delta \log$			0.002	0.003	0.012	(4.0%)
12-Poly(ethylene terephthalate):						
Reported[1] by g.p.c.			2.3	1.9	1.71	6.0
Calculated from m and k	0.36	2.50	2.34	1.91	1.615	5.85
$\Delta \log$			0.002	0.002	0.025	(2.5%)
13-Poly(6-aminohexanoic acid):						
Reported[1] by g.p.c.			2.4	2.0	1.59	6.2
Calculated from m and k	0.34	2.56	2.41	1.96	1.731	6.6
$\Delta \log$			0.001	0.006	0.019	(6.4%)

[a] Figures in parentheses give the % difference between values of $(H_{z+1}H_z^2)$ reported[1] and those found from *Gex* calculations. [b] '$\Delta \log$' symbolizes the difference between $\log H$ and $\log[(H+H_0)/2]$, where H is the highest value and H_0 the lowest shown for each sample; H_z and H_{z+1} were handled similarly.

From the work of Rudin[5] one can show that the breadth of any number or mol% distribution is a function of H, while its statistical coefficient of asymmetry can be shown to be a function of an expression containing (H_zH^2). Thus, the *Gex* parameters m and k appear to give reasonable descriptions of the breadth and shape of the number distributions of 13 of the 14 samples.

The breadth of any weight distribution is a function[5] of H_z, and its statistical coefficient of asymmetry is a function[6] of an expression containing $(H_{z+1}H_z^2)$. It can be said that the *Gex* parameters m and k provide an adequate description of the breadth of the weight distribution of 13 samples, but one must consider the degree of accord between values of $(H_{z+1}H_z^2)$ with respect to the shape of weight distributions. The percentage difference between the values for this measure on sample 5, assuming it follows the *LN* distribution, is 18%, and it is stated in ref 1 that no sample follows *LN*; thus one infers that any difference ⩾ 18% is not well described. From *Table 1*, samples 4, 9 and 10 equal or surpass this limit, leaving 10 samples for which the *Gex* distribution gives an adequate portrayal of the shape of their weight distributions.

Table 2 compares the values of M_n, M_w, M_z, and M_{z+1} reported[1] by g.p.c. with those calculated for a *Gex* distribution. In effect, if all values agree closely, it means that the *Gex* function is a good model of the experimental distribution, since in obtaining the *Gex* parameter y one uses the experimental values for M_n and M_w, and averages the result to obtain the model values of M_z and M_{z+1}. The agreements in M_z seem acceptable, all being within 11% of one another, while the greatest differences are for M_{z+1} in samples 4, 6 and 9. Hence the *Gex* distribution gives an acceptable model for 10 of the 14 samples of ref 1.

The m values found for the 13 samples whose number distributions are well described by the *Gex MWD* range between 0.1 and 0.8, indicating that none should be well described by the distributions named in ref 1. For an *LN MWD*, $m \rightarrow 0$, and for the Schulz–Flory, Poisson, and Tung distributions, $m \geqslant 1$. It is often stated that polyacrylonitrile and condensation polymers such as linear polyesters and polyamides follow the 'most probable' distribution, a form of *Gex* where $m = k = 1$, and for which $H = 2$. The samples reported[1]: numbers 8. 12 and 13 which fall into this category do not confirm the statement; however, one does note that samples 12 and 13 have H values in the range 2.3–2.4, and the products of their k and m parameters approach a value of 0.9. The k and m parameters

Table 2 Average molecular weights reported[1] for each sample and its *Gex* model given by parameters *m*, *k*, and y^a

Sample	Molecular weights × 10^3			
	M_n	M_w	M_z	M_{z+1}
1-Polyisobutylene (M_0 = 56.1):				
Reported[1] from g.p.c.	171	597	1730	5012
Model, y = 19.4499	176.1	620.8	1854	4873
. . Polyisobutylene:				
Reported[1] from g.p.c.	565	3382	10 930	24 372
Model, y = 0.2987	565	3381	10 695	25 083
2-Polystyrene (M_0 = 104.1):				
Reported[1] from g.p.c.	74	165	304	479
Model, y = 0.26733	74	165.1	296.9	461.9
3-Poly(vinylidene fluoride) (M_0 = 64):				
Reported[1] from g.p.c.	75	191	409	689
Model, y = 0.32406	74.6	192.1	380.5	653.4
4-Poly(vinyl alcohol) (M_0 = 44):				
Reported[1] from g.p.c.	66	294	941	1846
Model, y = 3.3216	65.7	295.1	933.3	2376
5-Poly(vinyl acetate):				
Reported[1] from g.p.c.	217	611	1821	5287
Not *Gex*; (if *LN*, H = 2.8)	(217)	(611)	(1715)	(4800)
6-Poly(vinyl pyrrolidone) (M_0 = 111):				
Reported[1] from g.p.c.	10	24	54	100
Model, y = 66.7324	9.86	24.5	56.6	122.5
7-Poly(methyl methacrylate) (M_0 = 100):				
Reported[1] from g.p.c.	252	481	766	1196
Model, y = 0.05676	250.8	483.3	780.9	1141
8-Polyacrylonitrile (M_0 = 53):				
Reported[1] by g.p.c.	38	116	249	405
Model, y = 0.17914	38	116	239.6	417.4
9-Polybutadiene (M_0 = 54):				
Reported[1] by g.p.c.	142	443	1076	1745
Model, y = 1.71021	142.3	442.2	1067	2195
10-Poly(2,6-dimethyl-1,4-phenylene oxide) (M_0 122):				
Reported[1] by g.p.c.	26	56	88	117
Model, y = 0.01969	25.7	56.7	97	130.5
11-Poly(2,6-diphenyl-1,4-phenylene oxide) (M_0 = 246):				
Reported[1] by g.p.c.	297	550	875	1319
Model, y = 0.051843	295.1	553.6	872.7	1247
12-Poly(ethylene terephthalate) (M_0 192):				
Reported[1] by g.p.c.	27	62	116	198
Model, y = 2.1549	26.8	62.3	119.6	202.3
13-Poly(6-aminohexanoic acid) (M_0 = 113):				
Reported[1] by g.p.c.	50	118	233	371
Model, y = 1.2649	49.5	118.6	231.7	399.8

[a] For each sample, the parameters *m* and *k* given in *Table 1* were used with the value of *y* estimated for its model.

of sample 12, a poly(ethylene terephthalate), are close in value to those of several samples of this polymer reported by Browning and Overton[7]. These authors gave g.p.c. data on 30 samples of this polyester; of these 27 could be assigned *Gex* parameters.

It is suggested that since the *Gex* distributions offer adequate descriptions of many of the polymers of ref 1, they may provide the new theoretical approach sought by its authors.

From *Tables 1* and *2*, one notes that the quotients and models of average molecular weights provided by the *Gex* distribution agree quite well with the g.p.c. data of ref 1 for these economically important polymers: polyisobutylene, polystyrene, poly(methyl methacrylate), polyacrylonitrile, and poly(ethylene terephthalate). The greatest deviations were found for poly(vinyl acetate) and its chemical derivative, poly(vinyl alcohol). It has already been shown[2,3] that the *Gex* distribution describes many polyolefins.

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Turbulent flow characteristics of solutions of hydroxylpropylmethyl cellulose

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INTRODUCTION

The phenomenon of turbulent drag reduction by means of polymer additives has recently been reviewed by Hoyt[1,2], Virk[3], and Little *et al.*[4]. A disadvantage associated with effective drag-reducing polymers, such as poly(ethylene oxide), is the occurrence of rapid diminuation of the drag-reducing efficiency of the polymer as a result of shear degradation. Recently, considerable effort has been put in by researchers to search for shear-resistant polymers which can be used in recirculatory pipe flows. In the present Note, results from a study of the friction-reducing properties of a new polymer belonging to the cellulose family are reported.

The polymer used in the present investigation is hydroxylpropylmethyl cellulose – a commercial product of the Imperial Chemical Industries, UK. This polymer is marketed as Methofas. Methofas is a non-ionic methyl cellulose derivative modified by the inclusion of a small percentage of the hydroxylpropyl

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