

## A Three-Parameter Equation for Molecular Weight Distribution of Low-Density Polyethylene

J. MILTZ and A. RAM, *Department of Chemical Engineering,  
Technion—Israel Institute of Technology, Haifa, Israel*

### Synopsis

A new three-parameter distribution function is proposed

$$W(M) = AM^a \exp[-b \ln^c(M)]$$

which fits best the experimental molecular weight distribution curves of branched low-density polyethylenes. The data were interpreted from GPC measurements, and a special computer program was utilized in order to derive the best values of the empirical constants  $a$ ,  $b$ , and  $c$ .

### INTRODUCTION

Previous publications<sup>1,2</sup> have dealt with molecular weight distribution (MWD) curves obtained for samples of low-density polyethylene (LDPE) from GPC data, with the effect of long-chain branches on the hydrodynamic volume of the chains taken into consideration. A suitable distribution function is proposed in this paper.

Of the two-parameter distribution functions, those introduced by Wesslau<sup>3</sup> and by Tung<sup>4</sup> (hereafter referred to as the WE and TU equations, respectively) were tried first. The WE equation (also known as "the log-normal distribution equation") reads:

$$W(M) = \frac{1}{\beta\sqrt{\pi}} \frac{1}{M} \exp\left(-\frac{1}{\beta^2} \ln^2\left(\frac{M}{M_0}\right)\right) \quad (1)$$

where  $W(M)$  is the weight fraction per unit molecular weight and the adjustable parameters  $\beta$  and  $M_0$  are obtainable from molecular weight averages.

The TU equation,

$$W(M) = abM^{b-1} \exp(-aM^b) \quad (2)$$

with the parameters  $a$  and  $b$  again related to the molecular weight averages, yields the integral distribution function

$$I(M) = \int_0^M W(M)dM = 1 - \exp(-aM^b). \quad (3)$$

More details about these functions are to be found in Tung.<sup>5</sup>

Kubin<sup>6</sup> proposed recently a three-parameter distribution function (hereafter referred to as the K1 equation):

$$W(M) = \frac{|s| t^{(u+1)/s}}{\Gamma[(u+1)/s]} M^u \exp(-tM^s), \quad (4)$$

subsequently<sup>7</sup> relating the parameters  $s$ ,  $t$ , and  $u$  nomographically to the number-, weight-, and  $z$ -average molecular weights:

$$\bar{M}_n = \frac{1}{t^{1/s}} \frac{\Gamma[(u+1)/s]}{\Gamma[u/s]} \quad (5)$$

$$\bar{M}_w = \frac{1}{t^{1/s}} \frac{\Gamma[(u+2)/s]}{\Gamma[(u+1)/s]} \quad (6)$$

$$\bar{M}_z = \frac{1}{t^{1/s}} \frac{\Gamma[(u+3)/s]}{\Gamma[(u+2)/s]}. \quad (7)$$

Unfortunately, the two-parameter distribution functions cannot properly describe the MWD of LDPE.<sup>8,9</sup> Thus, the present study was undertaken with a view to confirming the validity of a three-parameter function for branched polyethylene.

### PROCEDURE

The proposed new distribution function (subsequently referred to as MR) is

$$W(M) = AM^a \exp[-b \ln^c(M)] \quad (8)$$

where  $A$  is a normalizing parameter, obtained by

$$\int_0^\infty W(M) dM = 1. \quad (9)$$

It is obvious that the WE equation (1) is a particular case of MR, with  $c = 2$  and  $a = -1$ .

First, the IBM DFMFP subroutine (which minimizes a multidimensional function) was used in an attempt to minimize the sum of squares of weight-fraction differences between eq. (8) and data derived from GPC measurements, but no conversion was obtained.

The next attempt consisted in reducing the problem from three unknown parameters ( $a$ ,  $b$ ,  $c$ ) to one; once the first parameter is known, the other two follow directly.

Differentiating eq. (8) and equating the derivative to zero,

$$\frac{\partial W}{\partial M} = A \{ aM^{a-1} \exp[-b \ln^c(M)] - bcM^{a-1} \ln^{c-1}(M) \exp[-b \ln^c(M)] \} = 0, \quad (10)$$

we have

$$a = bc \ln^{c-1}(M)_{w_{\max}} \quad (11)$$

where  $(M)_{W_{\max}}$  (or  $M'$  for short) is the value of  $M$  at the maximum of  $W$ . Substituting in eq. (8), we find

$$W = AM^{bc \ln^{c-1}(M')} \cdot \exp [-b \ln^c(M)] \quad (12)$$

$$\ln W = \ln A + bc \ln^{c-1}(M') \cdot \ln(M) - b \ln^c(M) \quad (13)$$

Since  $M = M'$  for  $W = W_{\max}$ , we have

$$\ln W_{\max} = \ln A + bc \ln^c(M') - b \ln^c(M'). \quad (14)$$

Hence,

$$\ln A = \ln W_{\max} + b \ln^c(M')(1 - c). \quad (15)$$

Combining eqs. (13) and (14),

$$\ln \frac{W}{W_{\max}} = b \ln^c(M') \left\{ 1 + c \left( \frac{\ln(M)}{\ln(M')} - 1 \right) - \left[ \frac{\ln(M)}{\ln(M')} \right]^c \right\} \quad (16)$$

and defining

$$x_i = \frac{\ln(M_i)}{\ln(M')} \quad (17)$$

$$z_i = \ln \left( \frac{W_i}{W_{\max}} \right) \quad (18)$$

$$q = b \ln^c(M') \quad (19)$$

where  $i$  denotes the individual value of  $W$  or  $M$  in the series of GPC readings (a total of 20–30 values depending on the width of the distribution curve) at intervals of 2.5 cc elution volume (i.e., halfcounts), eq. (16), for a given species, becomes

$$z_i = q[c(x_i - 1) + 1 - x_i^c]. \quad (20)$$

Choosing a point on the MWD curve and denoting its  $z$  by  $T$  and its  $x$  by  $S$ , we obtain

$$T = q[c(S - 1) + 1 - S^c]. \quad (21)$$

The next step is to minimize the expression

$$\min \sum_i \left[ T \frac{c(x_i - 1) + 1 - x_i^c}{c(S - 1) - S^c + 1} - Z1_i \right]^2 \quad (22)$$

where  $Z1_i = \ln(W1_i/W_{\max})$  and  $W1_i$  denotes the measured weight fraction of species  $i$ .

This minimization yields the optimal value of  $c$ . Consequently,

$$q = \frac{T}{c(S - 1) + 1 - S^c} \quad (23)$$

$$b = \frac{q}{\ln^c(M')} = \frac{T}{\ln^c(M')[c(S - 1) + 1 - S^c]} \quad (24)$$

$$a = \frac{q \cdot c}{\ln(M')} = \frac{T \cdot c}{\ln(M')[c(S - 1) + 1 - S^c]} \quad (25)$$

## RESULTS AND DISCUSSION

Of the six polymer samples studied, three (PE-75, 76, and 77) were provided by courtesy of F. W. Billmeyer Jr., and three (A, B, and C) were from the Israel Petrochemical Corp.

Calculated values of the MW averages and distribution indices are given in Table I, and the distribution curves according to the various equations are compared in Figures 1 and 2.

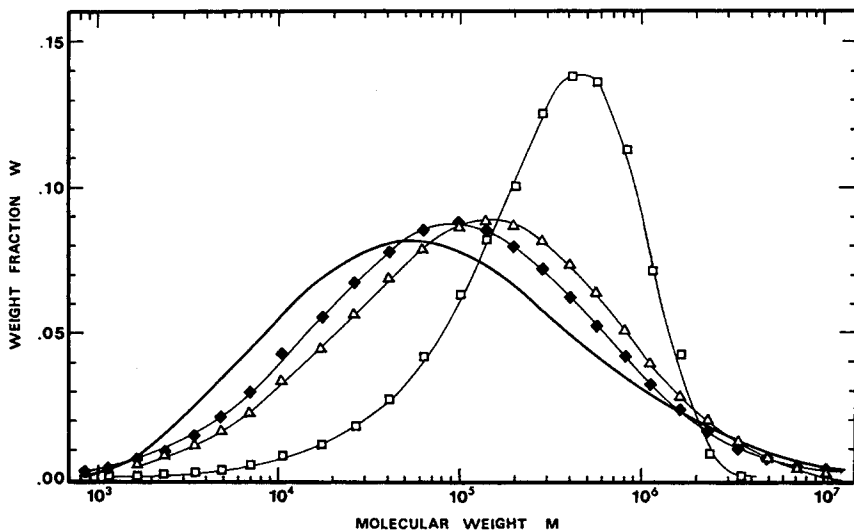


Fig. 1. MWD curves of PE-77: (—) true curve; (◆—◆) WE; (△—△) KI; (□—□) TU.

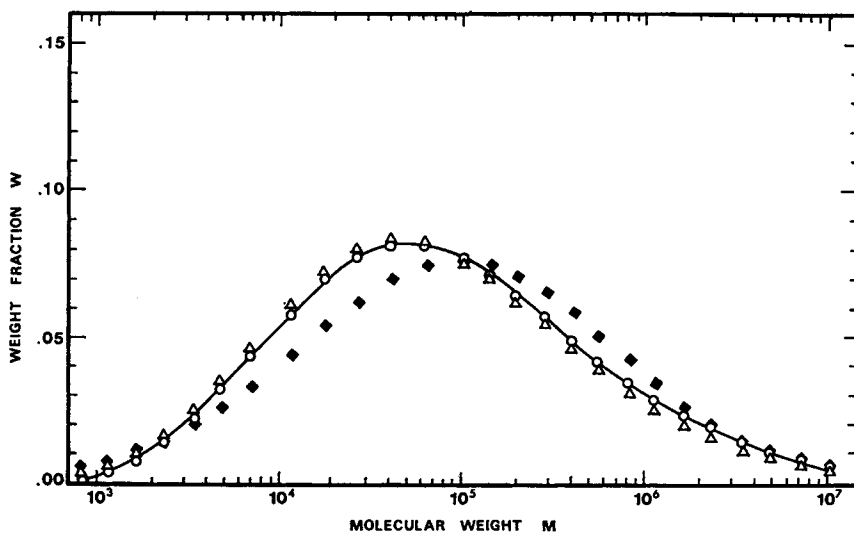


Fig. 2. MWD curves of PE-77: (—) true curve; (△) K2; (○) MR; (◆) WE2.

TABLE I  
Molecular Weight Parameters

Polymer	$10^{-4} \times \bar{M}_n$	$10^{-4} \times \bar{M}_w$	$10^{-4} \times \bar{M}_z$	$D_n = \frac{\bar{M}_w}{\bar{M}_n}$	$D_w = \frac{\bar{M}_z}{\bar{M}_w}$
PE-75	1.33	43.1	329	32.4	7.63
PE-76	1.44	24.1	239	16.7	9.93
PE-77	1.90	45.7	404	24.1	8.84
A	2.06	32.1	212.5	15.6	6.62
B	2.38	19.1	78.6	8.1	4.11
C	2.21	14.0	47.4	6.3	3.38

TABLE II  
Parameters for Distribution Functions

Polymer	Distribution K1			Distribution K2			Distribution MR		
	<i>u</i>	<i>t</i>	<i>s</i>	<i>u'</i>	<i>t'</i>	<i>s'</i>	<i>a</i>	<i>b</i>	<i>c</i>
PE-75	—	—	—	-0.541	84.9	-0.400	-1.557	124.7	-0.970
PE-76	3.6	1.43	0.083	-1.156	85.8	-0.297	-2.758	191.4	-0.341
PE-77	1.6	4.27	1.3	-1.198	66.3	-2.415	-1.221	298.7	-1.477
A	1.52	2.41	0.16	2.10	2.96	0.141	1.738	$2.35 \times 10^{-4}$	3.235
B	1.43	1.04	0.21	1.63	0.27	0.27	1.822	$2.30 \times 10^{-4}$	4.113
C	0.9	0.21	0.3	1.22	0.022	0.42	1.633	$1.62 \times 10^{-6}$	5.092

Only one polymer (PE-77) was described in these figures, as the others verified similar behavior. In Figure 1, the measured MWD curve (as derived from the GPC data and corrected for long-chain branching) is compared to the calculated WE, TU, and K1 functions. These calculations were based on parameters derived from the molecular weight averages. Figure 2 describes the MWD curves of the proposed distribution function MR, as well as the recalculated functions WE2 and K2 compared to the original curve. WE2 and K2 were obtained by exploiting the above-mentioned regression procedure to the equations of Wesslau, eq. (1), and Kubin, eq. (4), respectively. It is clearly shown that the recalculated functions offer an improved fit to the measured MWD curve, however inferior to the MR function. On the other hand, by using the regression technique, some of the parameters are forced to deviate from the values obtained directly by analytical methods based on molecular weight averages. This is shown in Table II, wherein two sets of parameters (*u*, *s*, *t* for K1 and *u'*, *s'*, *t'* for K2) are given. These parameters differ strongly both in magnitude and sign. In the case of WE2, the parameter  $\beta$  was calculated by the regression technique, while  $M_0$  was directly obtained (as in WE) from the molecular weight averages. Trying to obtain  $M_0$  from  $(M)_{w_{\max}}$  and the best value of  $\beta$  provided extremely high values that strongly distorted the MWD curves.

Tung's function did not show any significant improvement by recalculation and therefore was not described in Figure 2.

It is clearly shown that the MR three-parameter distribution function describes best the MWD of six commercial LDPE samples. The other mentioned two- or three-parameter functions are inadequate when based on parameters derived from molecular weight averages.

The authors wish to thank Mr. J. Regev for valuable discussions, and Dr. M. Kubin for his cooperation. This paper is partly based on the Sc.D. work of Joseph Miltz.

### References

1. J. Miltz and A. Ram *Polymer*, **12**, 685 (1971).
2. A. Ram and J. Miltz, *J. Appl. Polym. Sci.*, **15**, 2639 (1971).
3. H. Wesslau, *Macromol. Chem.*, **20**, 111 (1956).
4. L. H. Tung, *J. Polym. Sci.*, **20**, 495 (1956).
5. L. H. Tung, in *Polymer Fractionation*, M. J. R. Cantow, Ed., Academic Press, New York, 1967, Chap. E.
6. M. Kubin, *Collect. Czech. Chem. Commun.*, **32**, 1505 (1967).
7. M. Kubin, *Collect. Czech. Chem. Commun.* **34**, 703 (1969).
8. N. Nakajima, *J. Polym. Sci. C*, **21**, 153 (1968).
9. N. S. Schneider, R. T. Traskos, and A. S. Hoffman, *J. Appl. Polym. Sci.*, **12**, 1567 (1968).

Received February 7, 1972

Revised March 29, 1972