

## Molecular Weights from Fractionation Data by a Simplified Log-Normal Treatment

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### Synopsis

A simplified procedure is presented to estimate the two adjustable parameters in a log-normal distribution function. From values of these parameters, the weight distribution function,  $W(M)$ , as well as various molecular weight averages can be calculated. The method was applied to fractionation data selected at random for several polymers. The agreement between calculated and reported values appears to be good.

### INTRODUCTION

Although the estimation of molecular weights from polymer fractionation data often involves discrete functions (summation methods), polymer molecular weights may also be estimated employing continuous functions. A decided advantage of continuous over discrete functions is that once certain parameters have been calculated, a differential molecular weight distribution (MWD) curve may readily be constructed, however, a chief disadvantage of continuous over discrete functions is that the calculation of parameters is often difficult if not tedious. Thus, consider several MWD functions which have been proposed; some were theoretically derived, whereas others were devised empirically to fit the experimental data.

One MWD function was derived by Schulz<sup>1</sup> for chain coupling vinyl polymerization,

$$W(M) = \frac{(-\ln a)^{b+2}}{(b+1)!} M^{b+1} a^M \quad (1)$$

where  $W(M)$  denotes a differential distribution function,  $M$  is molecular weight, and  $a$  and  $b$  are parameters. A method of estimating parameters  $a$  and  $b$  in eq. (1) was given by Boyer.<sup>2</sup> He selected appropriate values of  $a$  and  $b$  and numerically calculated the integral distribution function [ $I(M) = \int_0^M W(M) dM$ ]. Graphs were then constructed for various sets of values of  $a$  and  $b$ . The abscissa involved degree of polymerization rather than molecular weight  $M$ , while the ordinate involved some probability function

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of  $I(M)$  which was devised so that a linear relationship would be obtained for a particular set of values of  $a$  and  $b$ .

A second MWD function involves an empirical relation used by Tung<sup>3,4</sup>

$$W(M) = yz M^{z-1} \exp(-yM^z) \quad (2)$$

where  $y$  and  $z$  are parameters. Equation (2) can be integrated analytically to yield the integral distribution form,

$$I(M) = 1 - \exp(-yM^z). \quad (2a)$$

From eq. (3), a double log plot may be constructed<sup>4</sup> to afford values of  $y$  and  $z$ . Then values of weight-average and number-average molecular weights may be calculated (as well as  $W(M)$ ) from the expressions

$$\bar{M}_w = y^{-1/z} \Gamma(1 + 1/z) \quad (2b)$$

$$\bar{M}_n = [y^{1/z} \Gamma(1 - 1/z)]^{-1} \quad (2c)$$

However,  $z$ -values are often less than unity so that  $\bar{M}_n$  in eq. (2c) possesses a physically unrealistic negative value.

Another often used MWD function is the log-normal distribution,<sup>4,5</sup>

$$W(M) = (\beta\sqrt{\pi}M)^{-1} \exp\left(\frac{-1}{\beta^2} \ln^2 \frac{M}{M_0}\right) \quad (3)$$

where  $\beta$  and  $M_0$  are adjustable parameters. For polymers conforming to eq. (3), it has been shown<sup>6</sup> that a plot of  $I(M)$  versus  $M$  on log-probability graph paper will yield a straight line. The parameters  $\beta$  and  $M_0$  can then be estimated from the slope and position of the straight line. Subsequently, molecular weights can be calculated from the expressions

$$\bar{M}_w = M_0 \exp(\beta^2/4) \quad (3a)$$

$$\bar{M}_n = M_0 \exp(-\beta^2/4) \quad (3b)$$

$$\bar{M}_v = M_0 \exp(\alpha\beta^2/4) \quad (3c)$$

where  $\bar{M}_v$  is viscosity-average molecular weight and  $\alpha$  is the exponent in the Mark-Houwink equation.

From the preceding, it can be seen that in eqs. (1) and (3), values of the adjustable parameters may be estimated after rather tedious and specialized plots are constructed. While parameters in eq. (2) may be readily obtained by a double log plot, values obtained for  $\bar{M}_n$  are often unrealistic. The purpose of this paper is to demonstrate that a rather simple plot involving eq. (3) may be made which will readily afford values of  $\beta$  and  $M_0$  and consequently values of  $\bar{M}_n$  and  $\bar{M}_v$ . These latter values were obtained from such simple plots to be described and were compared with corresponding values reported. Fractionation data for various polymers were selected at random from the literature.

## RESULTS AND DISCUSSION

If we substitute the expression for  $W(M)$  in eq. (3) in the expression for  $I(M)$ , there is obtained

$$I(M) = \int_0^M W(M) dM = (\beta\sqrt{\pi})^{-1} \int_0^M M^{-1} \exp\left(-\frac{1}{\beta^2} \ln^2 \frac{M}{M_0}\right) dM. \quad (4)$$

Further, letting  $u = (\sqrt{2}/\beta) \ln M/M_0$ , eq. (4) becomes

$$I(M) = \text{erf}(u) \quad (5)$$

where  $\text{erf}$  denotes error function and  $\text{erf}(u) = (1/\sqrt{2\pi}) \int_{-\infty}^u e^{-u^2/2} du$ . Values of  $\text{erf}(u)$  for various values of  $u$  have been tabulated.<sup>7</sup> From such tabulated values, theoretical plots of  $I^n(M)$  versus  $u$  were constructed for  $n = 1/2, 1$ , and  $3$  (cf. Fig. 1). From least-squares treatment, the following was obtained ( $r$  denotes linear correlation coefficient):

$$I^{1/2}(M) = 0.2897u + 0.6960 \quad (6)$$

$$(r = 0.9992, -1.8 \leq u \leq 0.63)$$

$$I^1(M) = 0.3504u + 0.5000 \quad (7)$$

$$(r = 0.9985, -1.13 \leq u \leq 1.13)$$

$$I^3(M) = 0.4544u + 0.1175 \quad (8)$$

$$(r = 0.9969, -0.13 \leq u \leq 1.8)$$

The limits for  $u$  over which eqs. (6)–(8) are valid are listed after these equations as well as in Figure 1. From eqs. (6)–(8), plots of  $I^n(M)$  versus  $\ln M$  should yield linear relationships (between the appropriate limits of  $u$ ) whose slopes will afford values of  $\beta$  and whose intercepts, values of  $M_0$ . Thus, for example, eq. (7) may be expanded to give

$$I^1(M) = K \ln M + 0.5000 - K \ln M_0 \quad (7a)$$

TABLE I  
Summary of Results from Simplified Log-Normal Equations (6)–(8)

Polymer	$\bar{M}_w \times 10^{-4}$		$\bar{M}_n \times 10^{-4}$		$\bar{M}_v \times 10^{-4}$		Ref.
	Calcd	Reptd	Calcd	Reptd	Calcd	Reptd	
PE	8.38	8.40	1.10	1.03	—	—	3
PIB	5.73	4.85 <sup>c</sup>	2.25	1.99 <sup>c</sup>	—	—	8
PVCl/PVAc	4.61	—	3.09	2.80	4.38	4.1	9
PVAc	19.1	18.1	13.6	11.3	18.0	17.1	10
PSt#666	29.1	25.0	12.7	12.0	—	—	11
PSt#69	55.8	—	55.6	—	55.8	55.8	11
PPr <sup>a</sup>	—	—	—	—	15.7	16.5	12
PIBM <sup>b</sup>	8.83	8.24	5.72	5.19	—	—	13

<sup>a</sup> Fractionation utilizing coacervate extraction.

<sup>b</sup>  $\bar{A}_w$  and  $\bar{A}_n$  values given (angstrom-size averages).

<sup>c</sup> These values were calculated by the authors using summation methods.

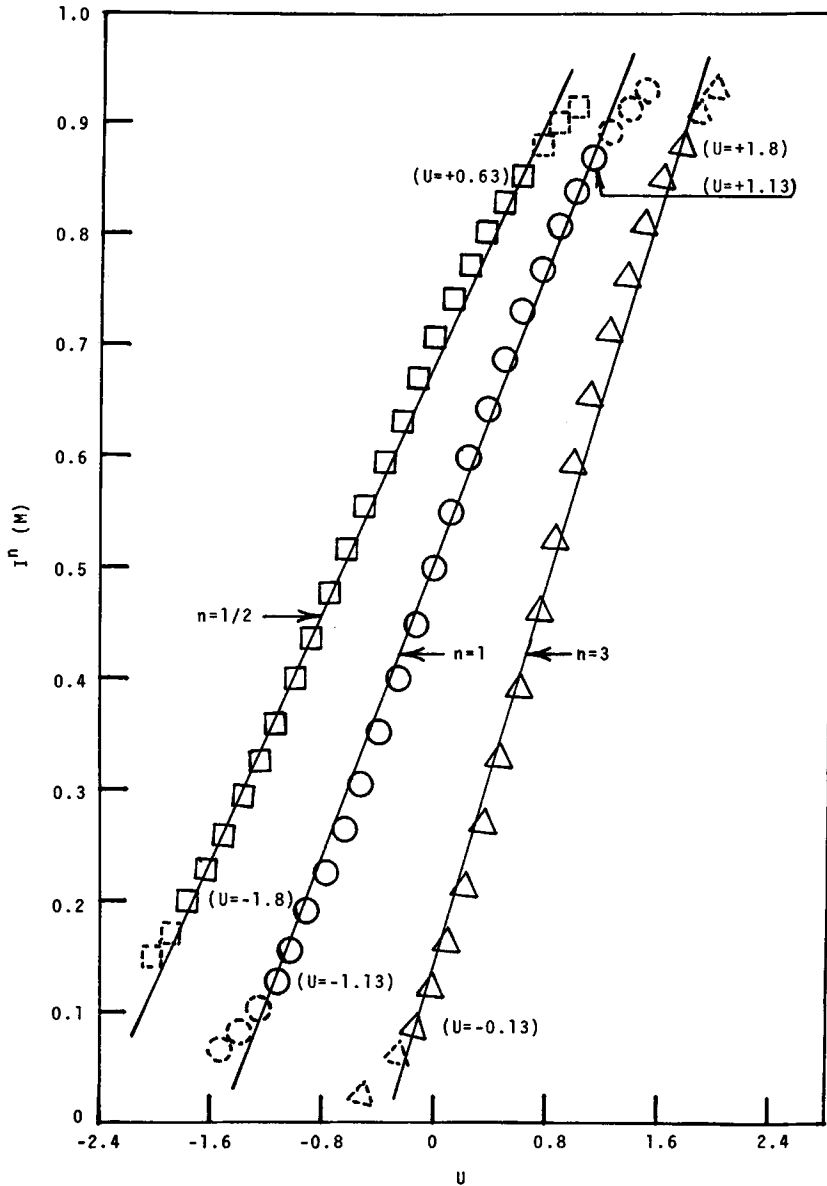


Fig. 1. Theoretical plots of  $I^n(M)$  vs.  $u$  for values of  $n = 1/2, 1,$  and  $3$ .

where  $K = 0.3504\sqrt{2}/\beta$ . Thus, a plot of  $I^1(M)$  versus  $\ln M$  will provide a linear relation whose slope is equal to  $K$  and whose intercept is equal to  $0.5000 - K \ln M_0$ . Thus,  $\beta$  and  $M_0$  can be obtained readily as well as values of  $u$  for corresponding values of  $M$ . Equations (6) and (8) may be treated similarly. In Figure 2 are shown plots of  $I^n(M)$  ( $n = 1$  and  $3$ ) versus  $\ln M$  for polyethylene (PE).<sup>3</sup> For a least-squares treatment, the  $I^1(M)$  and  $I^3(M)$  plots gave the following values:  $\beta = 2.02 \pm 0.02$ ,  $\bar{M}_w =$

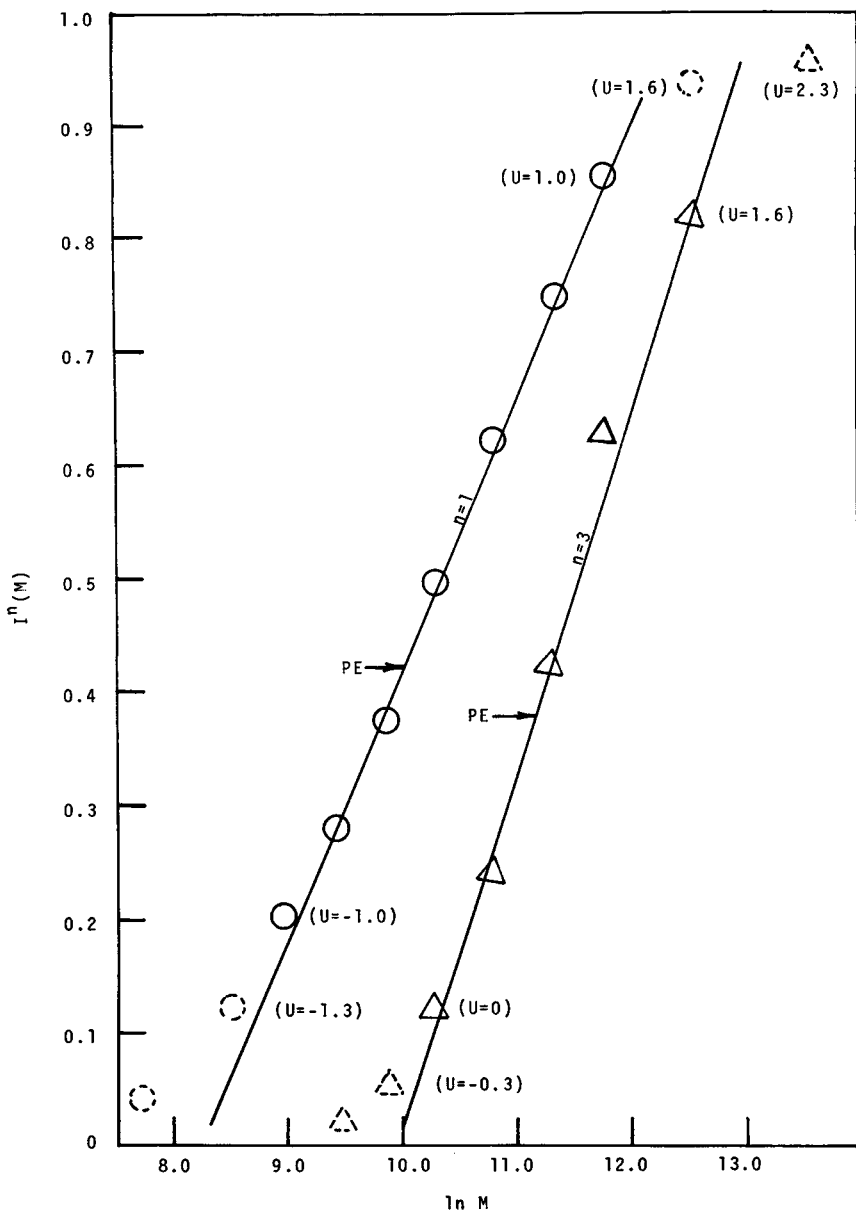


Fig. 2. Plot of  $I^n(M)$  vs.  $\ln M$  for polyethylene (PE) for values of  $n = 1$  and 3.

$(8.38 \pm 0.07) \times 10^4$ , and  $\bar{M}_n = (1.10 \pm 0.05) \times 10^4$ . These and reported values are in good agreement (cf. Table I). The advantage of employing more than an  $I^1(M)$  plot is that an  $I^3(M)$  plot may involve data (within the proper limits of  $u$ ) that were not utilized in the  $I^1(M)$  plot. When an  $I^1(M)$  plot employs a large percentage of the fractionation data, it is obviously not necessary to employ other  $I^n(M)$  plots. In Figures 3 and 4 are

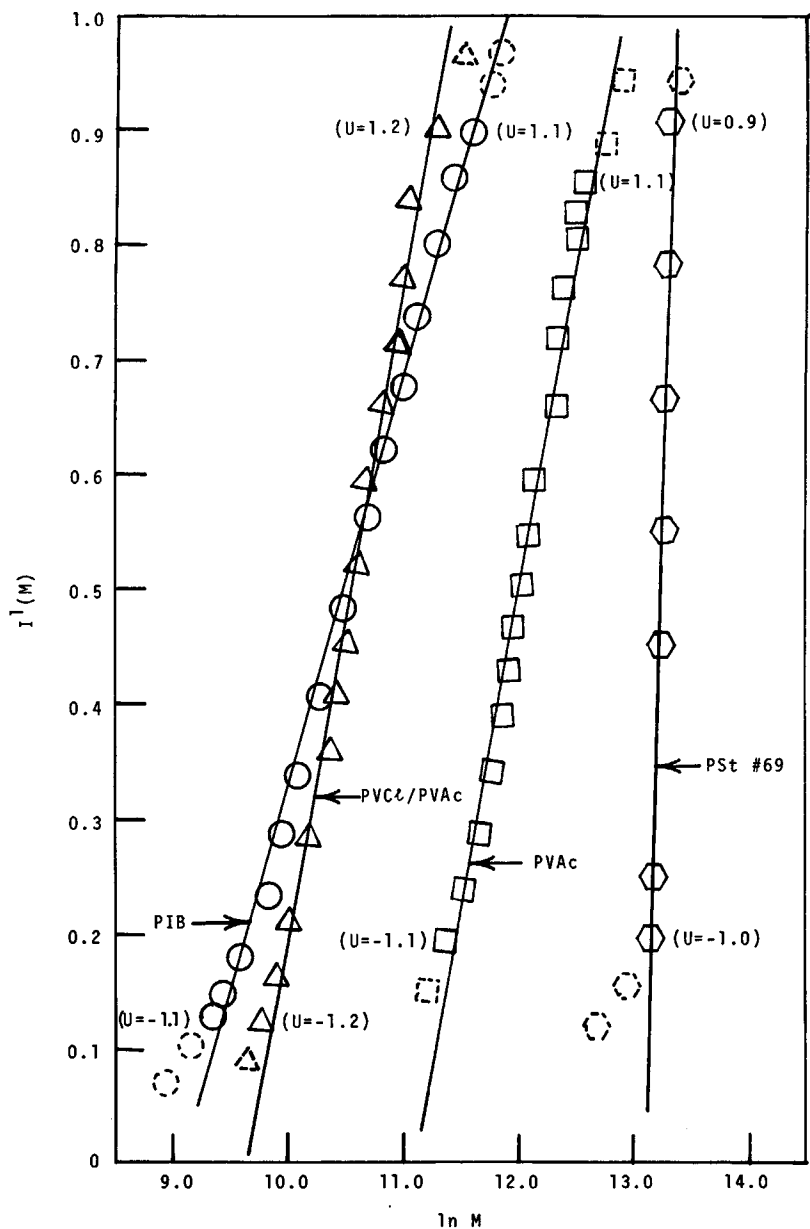


Fig. 3. Plot of  $I^1(M)$  vs.  $\ln M$  for polyisobutylene (PIB), poly(vinyl chloride)-poly(vinyl acetate) copolymer (PVCt-PVAc), poly(vinyl acetate) (PVAc), and polystyrene (PSt).

depicted plots of  $I^1(M)$  versus  $\ln M$  for various polymers. Thus, polyisobutylene<sup>8</sup> (PIB), poly(vinyl chloride)-poly(vinyl acetate) copolymer<sup>9</sup> (PVCt/PVAc), poly(vinyl acetate)<sup>10</sup> (PVAc), polystyrene<sup>11</sup> (PSt), polypropylene<sup>12</sup> (PPr), and poly(isobutyl methacrylate)<sup>13</sup> (PIBM) are listed in the figures. In all cases, least-squares treatment was utilized to estimate

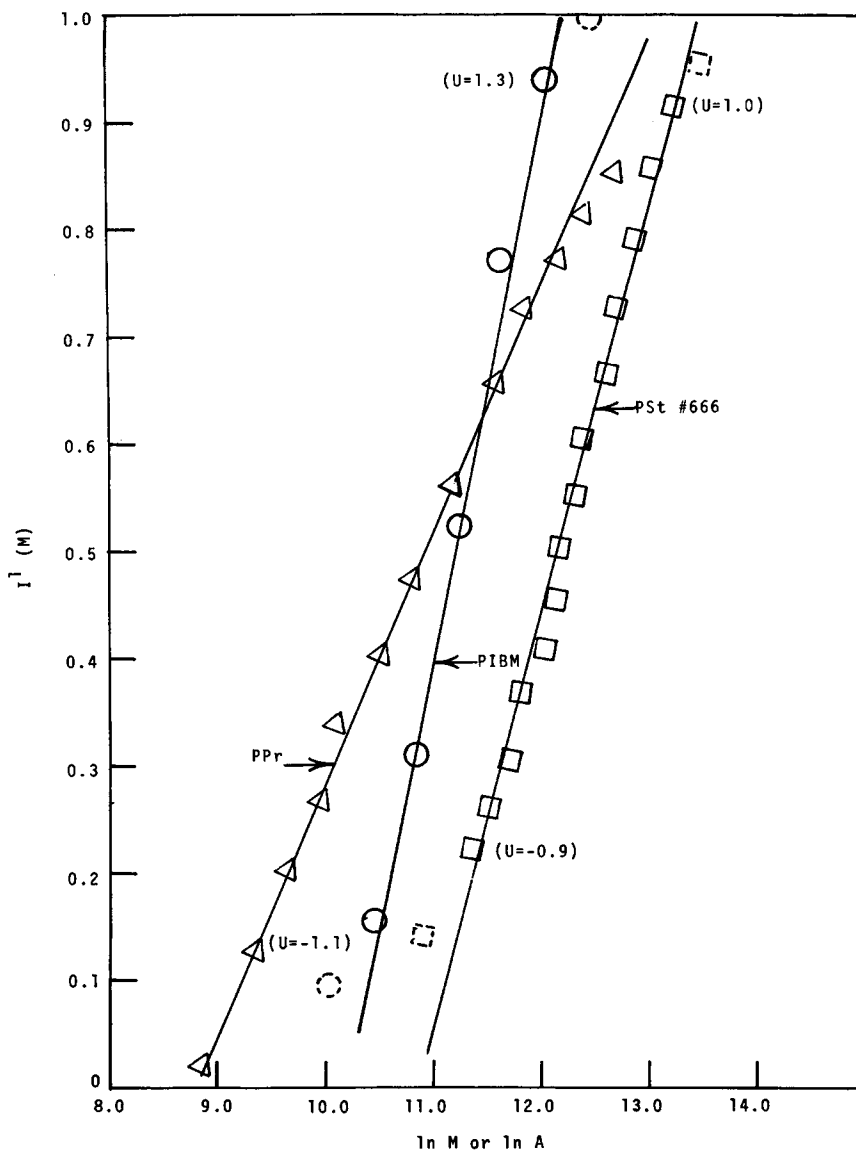


Fig. 4. Plot of  $I^1(M)$  vs.  $\ln M$  or  $\ln A$  for polypropylene (PPr), poly(isobutyl methacrylate) (PIBM) and polystyrene (PSt).

the values given in Table I. In obtaining the values in Table I,  $I(M)$  was assumed to be equal to the Schulz<sup>14</sup> cumulative weight function  $C(M)$ , where,  $C(M) = w_i/2 + \sum_{j=1}^i w_j$ , and  $w$  = weight fraction. From this table, it can be seen that the agreement between calculated and reported values is good.<sup>15</sup> Thus, the average deviations are: for  $\bar{M}_w$ , +8%; for  $\bar{M}_n$ , +10%; and for  $\bar{M}_v$ ,  $\pm 4\%$ . From the preceding, the simplified method for estimating  $\beta$  and  $M_0$  (and consequently  $\bar{M}_w$ ,  $\bar{M}_n$ , and  $\bar{M}_v$ ) can be employed to

give, in a relatively facile manner, fairly reliable estimates of various molecular weight averages. Of course, the differential weight distribution function,  $W(M)$ , may also be calculated.

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