

# Comparison of molecular weight distribution models for polymers characterized by g.p.c.

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A semi-empirical model which employs polynomials based on general free radical polymerization kinetics, is developed to describe the molecular weight distribution data as well as to evaluate the average molecular weights of a variety of commercial thermoplastics including polystyrene, poly(methyl methacrylate) and low density polyethylene. These novel expressions are equally applicable to a natural rubber sample with a bimodal distribution. Least-squares methods for the classical Schulz and Flory distribution functions are introduced to handle the g.p.c. data of the above polymers. Comparison of the results collected from various analyses indicates clearly that the polynomial model is the most versatile one in the sense that it can be utilized to smooth out satisfactorily the molecular weight distribution data of many polymers. In general, the Wesslau distribution function is particularly good for the highly branched polyolefin and the Schulz model is fairly effective for the addition polymers of moderately sharp molecular weight distribution, presumably with  $\overline{M}_w/\overline{M}_n=3.0$ . However, the Flory and Tung distributions are found to be rather inferior in the present studies. On the basis of the current findings, a new procedure is suggested to facilitate the computations of the true average molecular weights from g.p.c. data directly.

(Keywords: molecular weight distribution; polynomial function; least-squares analysis; molecular weight averages; gel permeation chromatography)

## INTRODUCTION

Since the inception of gel permeation chromatography (g.p.c.) in the early 60's<sup>1-3</sup>, it has been routinely used to determine the molecular weight distribution of high polymers in many laboratories. This method has been recently improved by the coupling of a low-angle laser light scattering photometer<sup>4,5</sup>. In spite of the rapid development of this particular experimental technique, the amount of work reported on the mathematical description of the molecular weight distribution data from g.p.c., which is of theoretical and practical importance, is rather scarce. Nevertheless, several classical models have been commonly applied to deal with the data obtained from the conventional fractionation experiments<sup>6a,7</sup>. The Flory<sup>8</sup> and Schulz<sup>9</sup> models can be derived theoretically but the Wesslau<sup>10,11</sup> and Tung<sup>12</sup> distribution functions were devised empirically to suit some specific systems. These models are defined by one or two parameters and often describe less adequately the observed molecular weight distribution of most polymers. Thus analytical expressions that contain more than two parameters are postulated to cope with these involved situations.

It has been reported that a polymer may be considered as a blend of several components with known distributions<sup>13,14</sup>. As such its molecular weight distribution can be specified by a linear function of the simple models that fit the individual components. This analysis hinges on the accuracy in differentiating the cumulative distribution curves. A second established multiparameter distribution function rests on a series that involves either Laguerre polynomials<sup>15-17</sup> or Hermite polynomials<sup>18</sup>. The coef-

ficients of these polynomials are evaluated from the moments of distributions which in many cases are difficult to estimate accurately, particularly the higher moments. In this paper, we derive a semi-empirical polynomial model which can readily be applied to analyse distribution data directly by means of a non-linear regression procedure. The effectiveness of these novel functions is tested using g.p.c. data which are also interpreted by various simple models.

### *Molecular weight distribution of free radical polymerization*

The free radical polymerization of a monomer would produce an addition polymer of final molecular weight distribution depending predominantly on the rates of the individual kinetic steps involved as well as the duration of reaction. It may be described by a general kinetic scheme which includes four distinct elementary processes, viz. initiation, propagation, termination (combination and disproportionation) and chain transfer (to a monomer and/or a chain transfer agent) with their respective rate constants designated as  $k_i$ ,  $k_p$ ,  $k_t$  (combination),  $k_t'$  (disproportionation),  $k_{tr}$  (transfer to monomer) and  $k_{tr}'$  (transfer to chain transfer agent). If the instantaneous concentrations of the two essential reactants; monomer and chain transfer agent are denoted by  $[M]$  and  $[S]$  respectively at time  $t$ , then the rate of formation of  $X$ -mer<sup>6b</sup> expressed by the first derivative of the concentration of  $X$ -mer  $[P_x]$  with respect to time  $t$ , is given by,

$$\frac{d[P_x]}{dt} = (\phi\theta\psi + \phi^2\theta^2k_tX/2)\exp(-\theta X) \quad (1)$$

where the variables  $\phi$ ,  $\theta$  and  $\psi$  are independent of the number of monomer units incorporated into the inactive chain  $P_x$ , and are defined respectively by,

$$\phi = [I'/(k_i + k'_i)]^{1/2} \quad (1a)$$

$$\theta = \frac{k_{tr}[M] + k'_{tr}[S] + [I'(k_i + k'_i)]^{1/2}}{k_p[M]} \quad (1b)$$

$$\psi = k_{tr}[M] + k'_{tr}[S] + k'_i\phi \quad (1c)$$

Hereafter, we use the symbols  $I'$  and  $X$  to stand for the rate of initiation and the number of repeating units in the  $X$ -mer respectively. Two main assumptions are made in formulating equation (1), these are the steady-state approximation applied to the radicals and the independence of the rate constants of the size of the reactive species.

By using the Taylor series expansion, we can express the variable  $\theta$  in the following form

$$\theta = \theta_0 + \sum_{i=1}^m \theta_i t^i \quad (2)$$

where the first term on the right hand side is independent of  $t$  and the constant  $\theta_i$  is related to the  $i^{\text{th}}$  derivative of  $\theta$  evaluated at  $t=0$ . Equation (1) now becomes,

$$\frac{d[P_x]}{dt} = (\phi\theta\psi + \phi^2\theta^2k_iX/2)\exp(-\theta_0X)\exp\left(-X\sum_{i=1}^m\theta_it^i\right) \quad (3)$$

By expanding the exponential function  $\exp(-X\sum_{i=1}^m\theta_it^i)$  in series, we obtain from the foregoing equation,

$$\frac{d[P_x]}{dt} = (\phi\theta\psi + \sum_{i=1}^n F_i(t)X^i)\exp(-\theta_0X) \quad (4)$$

where the coefficients  $F_i s'$  are functions of  $t$  and are intimately related to the variables  $\phi$ ,  $\theta$ ,  $\psi$  and constants  $k_i$  and  $\theta_i s'$ . Integration of equation (4) results in,

$$[P_x] = (G(t) + \sum_{i=1}^n H_i(t)X^i)\exp(-\theta_0X) \quad (5)$$

where

$$G(t) = \int_0^t \phi\theta\psi dt \quad (5a)$$

$$H_i(t) = \int_0^t F_i(t) dt \quad (5b)$$

It follows that the number distribution functions  $N'(X)$  may be written as,

$$N'(X) = \frac{\partial[P_x]}{\partial X} \quad (6)$$

$$= \left(E + \sum_{i=1}^n L_i X^i\right)\exp(-\theta_0X) \quad (7)$$

where

$$E = H_1 - \theta_0 G \quad (7a)$$

$$L_i = (i+1)H_{i+1} - \theta_0 H_i; \quad i=1,2,\dots,n-1 \quad (7b)$$

$$L_n = -\theta_0 H_n \quad (7c)$$

Then the differential distribution function  $W(X)$  is equal to a polynomial,

$$W(X) = \left(\sum_{i=1}^n R_i X^i\right)\exp(-\theta_0 X) \quad (8)$$

where

$$R_1 = E / \int_0^\infty X N'(X) dX \quad (8a)$$

$$R_i = L_i / \int_0^\infty X N'(X) dX; \quad i=2,3,\dots,n \quad (8b)$$

To convert equation (8) into a useful form, we proceed to derive the integral distribution function,

$$I(X) = \int_0^X W(X) dX \quad (9)$$

$$= K - \left(K + \sum_{i=1}^n A_i X^i\right)\exp(-\theta_0 X) \quad (10)$$

where

$$K = \sum_{i=1}^n \frac{i! R_i}{\theta_0^{i+1}} \quad (10a)$$

$$A_i = \frac{1}{\theta_0} \sum_{s=i}^n \frac{s! R_s}{i! \theta_0^{s-i}} \quad (10b)$$

Normalization of function  $W(X)$  leads to,

$$I(y) = 1 - \left(1 + y + \sum_{i=2}^n N_i y^i\right)\exp(-y) \quad (11)$$

where

$$y = \theta_0 X \quad (11a)$$

$$N_i = \sum_{j=i}^n \left(\frac{A_j - (j+1)A_{j+1}}{K}\right) \frac{j!}{i!} \quad (11b)$$

$$A_{1+n} = 0 \quad (11c)$$

Consequently, equation (8) becomes,

$$W(X) = \frac{\partial I(X)}{\partial X} \quad (12)$$

$$= \left\{ \theta_0 \sum_{i=1}^n [N_i - (i+1)N_{i+1}] y^i \right\} \exp(-y) \quad (13)$$

with  $N_1 = 1$  and  $N_{1+n} = 0$ . Eventually, the  $a^{\text{th}}$  moment of

the distribution  $W(X)$  is equal to,

$$U_a = \int_0^{\infty} X^a W(X) dX \quad (14)$$

$$= \theta_0^{-a} \sum_{l=1}^n [N_l - (l+1)N_{l+1}] \Gamma(1+a+l) \quad (15)$$

where  $\Gamma(1+a+l)$  is a gamma function of the variable  $(1+a+l)$ . Equations (11), (13) and (15) are used to analyse the molecular weight distribution data.

In practice, it is desirable to recast equation (11) to

$$\{[1 - I(y)] \exp(y) - 1 - y\} = \sum_{l=2}^n N_l y^l \quad (16)$$

where the degree of the polynomial  $n$  should depend on circumstances. The value of the expression on the left hand side can be computed for each chain length  $X$  or experimental datum  $I(y)$  provided that the constant  $\theta_0$  has been preset at a particular value. In the present analysis, the least-squares method is employed to determine the polynomial coefficients  $N_l$ 's. Together, we also compute the standard error of estimate of  $I(y)$  on  $y$  defined by,

$$\overline{SE} = \left\{ \frac{\sum_y \left[ I(y) - 1 + \left( 1 + y + \sum_{l=2}^n N_l y^l \right) \exp(-y) \right]^2}{N'' - 2} \right\}^{1/2} \quad (17)$$

where  $N''$  is the total number of data points  $y$  or  $X$ . This computation cycle is repeated many times by varying the input value of  $\theta_0$  until a minimum  $\overline{SE}$  is achieved.

#### Least-squares analyses for Schulz and other distribution models

The Schulz distribution function is one of the classical molecular weight distribution functions and is widely used particularly for vinyl polymerization terminated by coupling. This differential distribution function  $W(M)$  consists of two adjustable parameters  $\alpha$  and  $b$  and is given as

$$W(M) = \frac{(-\ln \alpha)^{b+2}}{\Gamma(b+2)} M^{b+1} \alpha^M \quad (18)$$

It describes the integral weight fraction of molecular weight  $M$  by an expression,

$$I(M) = f(\alpha, b) \cdot g(\alpha, b) \quad (19)$$

where

$$f(\alpha, b) = \frac{(-\ln \alpha)^{b+2}}{\Gamma(b+2)} \quad (19a)$$

$$g(\alpha, b) = \int_0^M M^{b+1} \alpha^M dM \quad (19b)$$

The integral function  $g(\alpha, b)$  may be conveniently evaluated by a numerical method if the values of  $\alpha$  and  $b$  are known. Boyer<sup>19</sup> and Mussa<sup>20</sup> have introduced two

different graphical methods for determining the constants  $\alpha$  and  $b$ . Here, we resort to a least-squares treatment for solving these two parameters.

A difference formula is first defined as,

$$D = \sum_M [I(M) - f(\alpha, b) \cdot g(\alpha, b)]^2 \quad (20)$$

of which a minimum value would offer the best-estimates of  $\alpha$  and  $b$  designated respectively as  $\alpha'$  and  $b'$ . This implies that

$$F' = \left( \frac{\partial D}{\partial \alpha} \right)_{\alpha'} = 0 \quad (21)$$

$$G' = \left( \frac{\partial D}{\partial b} \right)_{b'} = 0 \quad (22)$$

where

$$F' = \sum_M \{ [I(M) - f(\alpha', b') \cdot g(\alpha', b')] [f_{\alpha'} g(\alpha', b') + f(\alpha', b') \cdot g_{\alpha'}] \} \quad (21a)$$

$$G' = \sum_M \{ [I(M) - f(\alpha', b') \cdot g(\alpha', b')] [f_{b'} g(\alpha', b') + f(\alpha', b') \cdot g_{b'}] \} \quad (22a)$$

The various derivatives are,

$$f_{\alpha'} = \left( \frac{\partial f}{\partial \alpha} \right)_{\alpha'} = \left( \frac{b'+2}{\alpha' \ln \alpha'} \right) f(\alpha', b') \quad (23)$$

$$f_{b'} = \left( \frac{\partial f}{\partial b} \right)_{b'} [\ln(-\ln \alpha') - \mu(b'+1)] f(\alpha', b') \quad (24)$$

$$g_{\alpha'} = \frac{1}{\alpha'} \int_0^M M^{b'+2} \alpha'^M dM \quad (25)$$

$$g_{b'} = \int_0^M (\ln M) \cdot M^{b'+1} \alpha'^M dM \quad (26)$$

where  $\mu(X)$  is a digamma function of  $X^{21}$ . The integrations in equation (25) and (26) are carried out numerically in this work. Equations (21) and (22) can be rearranged to obtain (respectively)

$$\alpha' = \exp \left\{ - \left[ \frac{\Gamma(b'+2) \sum_M I(M) [f_{\alpha'} g(\alpha', b') + f(\alpha', b') g_{\alpha'}]}{\sum_M g(\alpha', b') [f_{\alpha'} g(\alpha', b') + f(\alpha', b') g_{\alpha'}]} \right]^{1/(b'+2)} \right\} \quad (27)$$

$$b' = \frac{1}{\ln(-\ln \alpha')} \ln \left[ \frac{\Gamma(b'+2) \sum_M I(M) [f_{b'} g(\alpha', b') + f(\alpha', b') g_{b'}]}{\sum_M g(\alpha', b') [f_{b'} g(\alpha', b') + f(\alpha', b') g_{b'}]} \right] - 2 \quad (28)$$

An iterative method is applied to equations (27) and (28) to generate a series of approximate values of  $\alpha'$  and  $b'$ . For each pair of these values, we also calculate the cor-

responding function values of  $F'$  (equation (21a)),  $G'$  (equation (22a)) and  $S'$ , where

$$S' = F'^2 + G'^2 \quad (29)$$

Practically, we select the best values of  $\alpha'$  and  $b'$  as the pair that yields the smallest  $S'$  value. It will be illustrated that this is in fact an accurate and simple approach to evaluate the best-fit Schulz distribution curve. The standard error of estimate of  $I(M)$  on  $M$  is equal to,

$$\overline{SE} = [D/N'' - 2]^{1/2} \quad (30)$$

where  $D$  is computed by equation (20) based on the final-selected values of  $\alpha'$  and  $b'$ , which also produce the  $a^{\text{th}}$  moment of  $W(M)$ ,

$$U_a = \left( \frac{1}{-\ln \alpha'} \right)^a \frac{\Gamma(a+b'+2)}{\Gamma(a+b')} \quad (31)$$

The Flory<sup>8</sup> distribution function was first derived for the linear condensation polymers. In this case the differential distribution function for the  $X$ -mer is,

$$W(X) = X(\ln P)^2 P^X \quad (32)$$

where  $P$  is a probability constant. By analogy, we have the integral distribution function of the  $X$ -mer,

$$I(X) = 1 + XP^X \ln P - P^X \quad (33)$$

and a deviation function defined as,

$$D = \sum_X (I(X) - 1 - XP^X \ln P + P^X)^2 \quad (34)$$

In the least-squares sense, the best value of  $P$  denoted by  $P'$  should satisfy the relationship,

$$\left( \frac{\partial D}{\partial P} \right)_{P'} = 0 \quad (35)$$

An effective algorithm to a root of the foregoing equation is the Newton iteration method which obtains the successive approximations by,

$$P'_q = P'_{q-1} - \frac{h(P'_{q-1})}{h'(P'_{q-1})} \quad (36)$$

where the subscript  $q$  is for the  $q^{\text{th}}$  repetition and the functions,

$$h(P) = \sum_X [I(X) - 1 - XP^X \ln P + P^X] X^2 P^X \quad (36a)$$

$$h'(P) = \frac{\partial h(P)}{\partial P} = \sum_X (I(X) - 1 - XP^X \ln P + P^X) X^3 P^{X-1} - \sum_X X^4 P^{2X-1} \ln P \quad (36b)$$

The  $a^{\text{th}}$  moment of the distribution is,

$$U_a = \Gamma(2+a)/(1-P)^a \quad (37)$$

while the standard error of estimate of  $I(X)$  on  $X$  may also be computed by equation (30), but here  $D$  refers to equation (34).

Tung<sup>6a</sup> has discussed data treatment using the Wesslau and Tung distribution models. The Wesslau distribution function contains two parameters  $M_0$  and  $\beta$ ; the latter increases with the increase of the breadth of distribution. This unique feature is implicitly exhibited by the following equations:

$$W(M) = \frac{1}{\beta \sqrt{\pi}} \frac{1}{M} \exp\left(-\frac{1}{\beta^2} \ln^2 \frac{M}{M_0}\right) \quad (38)$$

$$I(M) = \frac{1}{2} \left[ 1 + \operatorname{erf}\left(\frac{1}{\beta} \ln \frac{M}{M_0}\right) \right] \quad (39)$$

$$U_a = M_0^a \exp(a^2 \beta^2 / 4) \quad (40)$$

where  $\operatorname{erf}(X)$  is an error function of  $X^2$ .

The Wesslau parameters  $\beta$  and  $M_0$  are evaluated by finding the inverse transform of the error function using equation (39) and a relevant mathematical table<sup>22</sup>, i.e.

$$\operatorname{erf}^{-1}\left(\frac{1}{\beta} \ln \frac{M}{M_0}\right) = \frac{1}{\beta} \ln M - \frac{1}{\beta} \ln M_0 \quad (41)$$

Hence a plot of  $\operatorname{erf}^{-1}(1/\beta \ln M/M_0)$  against  $\ln M$  should produce a straight line whose gradient and intercept result in  $\beta$  and  $M_0$  respectively. Analogously, we get,

$$\overline{SE} = \left\{ \frac{\sum_M \left[ I(M) - \frac{1}{2} - \frac{1}{2} \operatorname{erf}\left(\frac{1}{\beta} \ln \frac{M}{M_0}\right) \right]^2}{N'' - 2} \right\}^{1/2} \quad (42)$$

As far as the data analysis is concerned, the most advantageous model is perhaps the one postulated by Tung who has studied the molecular weight distribution of polyethylene using the equations listed below:

$$W(M) = YZM^{Z-1} \exp(-YM^Z) \quad (43)$$

$$I(M) = 1 - \exp(-YM^Z) \quad (44)$$

$$U_a = Y^{-a/Z} \Gamma(1+a/Z) \quad (45)$$

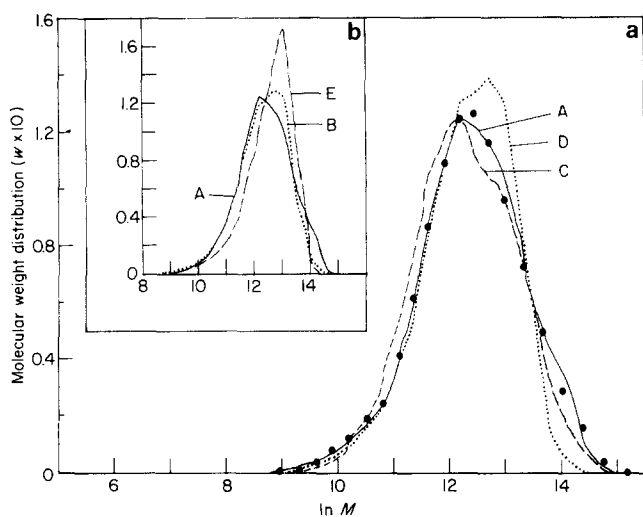
where  $Y$  and  $Z$  are two adjustable parameters. Equation (44) can be readily rearranged to,

$$\ln \ln [1 - I(M)]^{-1} = \ln Y + Z \ln M \quad (46)$$

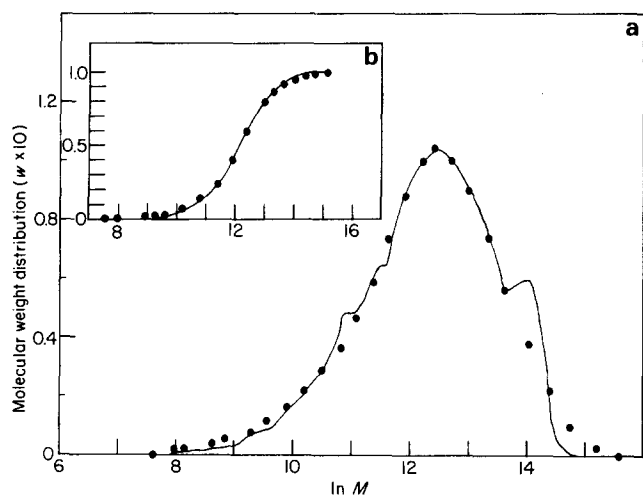
Once the parameters  $Y$  and  $Z$  are determined from the above linear plot, we can compute the

$$\overline{SE} = \left\{ \frac{\sum_M [(M) - 1 + \exp(-YM^Z)]^2}{N'' - 2} \right\}^{1/2} \quad (47)$$

This statistical parameter  $\overline{SE}$  is consistently<sup>47</sup> employed to indicate the goodness of fit of a particular integral distribution function to the observed cumulative weight fractions. Least-squares methods are applied to equations (41) and (46).



**Figure 1** Plots of molecular weight distribution with  $w \times 10$  against  $\ln M$  for sample S1. The data points are obtained from experiments and the curves are predicted theoretically: Curve A; polynomial model, curve B; Schulz model, curve C; Wesslau model, curve D; Flory model, and curve E; Tung model



**Figure 2** (a) Plot of molecular weight distribution with  $w \times 10$  against  $\ln M$  for sample S2. (b) Integral distribution curve with  $I(M)$  against  $\ln M$  for sample S2. The data points are obtained from experiment and the curves are predicted by the polynomial model

## EXPERIMENTAL

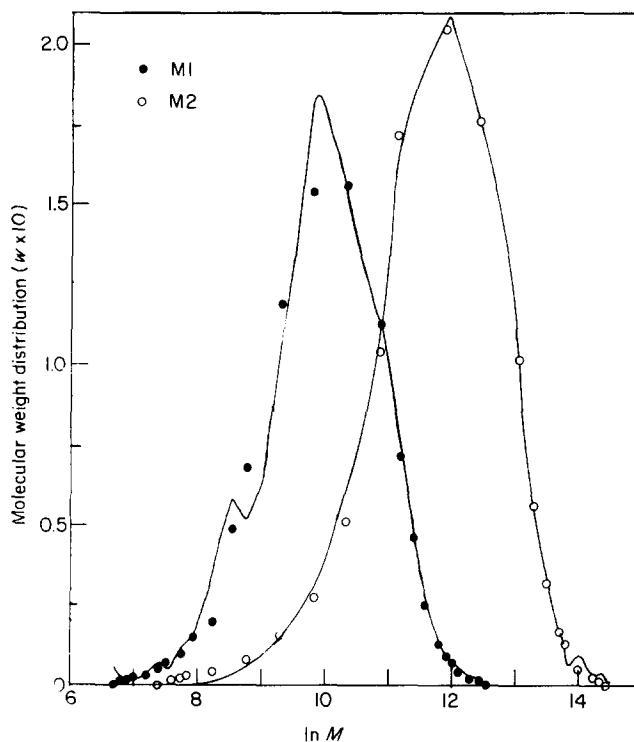
Six commercial thermoplastic samples and two biopolymer samples were studied altogether. These samples were designated as S1 and S2 for polystyrene, M1 and M2 for poly(methyl methacrylate), E1 and E2 for low density polyethylene, and N1 and N2 for natural rubber. Rudin *et al.*<sup>23</sup> have reported the molecular weight distribution data of the same pair of poly(methyl methacrylate) samples (originally coded as samples A and C) recently. The g.p.c. data of the natural rubber samples (previously quoted as samples RRIM 703 and PB5/51) from different clones were acquired from the work of Subramanian<sup>24</sup>.

Samples S1, S2, E1 and E2 were analysed by the Polymer Supply and Characterization Centre of RAPRA, England. The g.p.c. columns which were calibrated by the polystyrene standards, were eluted with tetrahydrofuran at 25°C for polystyrene samples and with  $\sigma$ -dichlorobenzene plus 1% Ionox 330 as antioxidant at 138–140°C for the low density polyethylene samples.

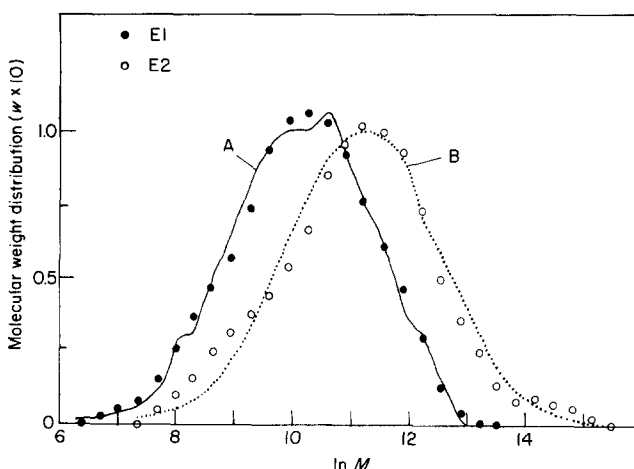
Mathematical calculations were performed on a Univac 1100/11 computer system.

## RESULTS AND DISCUSSION

The raw data are displayed in *Figures 1–5*; (plotting weight fraction,  $w$ , against logarithm of molecular weight  $M$ ). Though the observed data points of the samples are not connected for the sake of simplicity, they all do obviously exhibit distinct unimodal distributions except sample N1 which is particularly chosen to represent the bimodal distribution. Moreover, sample N2 is conspicuously skewed to the high molecular weight region. In the ensuing analyses, various distribution functions will be applied to match these experimental data.



**Figure 3** Plots of molecular weight distribution with  $w \times 10$  against  $\ln M$  for samples M1 and M2. The points are obtained from experiments and the curves are predicted by the polynomial model



**Figure 4** Plots of molecular weight distribution with  $w \times 10$  against  $\ln M$  for samples E1 and E2. The data points are obtained from experiments and the curves A and B are predicted by the polynomial and Wesslau models respectively

It can be demonstrated that the constant  $\theta_0 = 1/X_n$ , where  $X_n$  is the hypothetical number-average degree of polymerization at  $t=0$ . Hence the computation cycle using equations (16) and (17) is started with the first approximation of  $\theta_0$  taken as the reciprocal of  $X_n$  estimated by

$$\bar{X}_n = \left[ \bar{M}_0 \sum_{i=1}^{N'} w_i/M_i \right]^{-1} \quad (48)$$

where  $w_i$  is the weight fraction of the  $i^{\text{th}}$  species of molecular weight  $M_i$  and  $\bar{M}_0$  is the molecular weight of a

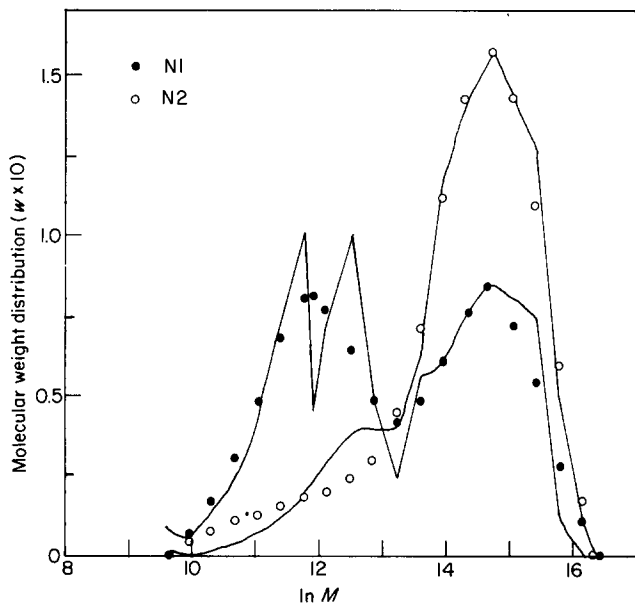


Figure 5 Plots of molecular weight distribution with  $w \times 10$  against  $\ln M$  for samples N1 and N2. The data points are obtained from experiments and the curves are predicted by the polynomial model

repeating unit. The  $\theta_0$  values is then successively decreased or increased until a smallest  $\overline{SE}$  is produced. In any case the degree of  $n$  may be effectively kept below 10. The results obtained for all the samples are shown in Table 1.

Equations (27) and (28) are executed to create new sets of  $\alpha'$  and  $b'$ . The first approximations of  $\alpha'$  and  $b'$  are computed by,

$$b' = \frac{2 - \Delta'}{1 - \Delta'} \quad (49)$$

$$\alpha' = \exp \left[ -\frac{(b' + 2)}{M'_w} \right] \quad (50)$$

where the polydispersity index,

$$\Delta' = \overline{M'_w} / \overline{M'_n} \quad (49a)$$

Here, the apparent number-average and weight-average molecular weight are given respectively as:

$$\overline{M'_n} = \left[ \sum_{i=1}^{N'} w_i/M_i \right]^{-1} \quad (49b)$$

$$\overline{M'_w} = \sum_{i=1}^{N'} w_i M_i \quad (49c)$$

Figure 6 illustrates the variations of functions  $F'$  (equation (21a)) and  $G'$  (equation (22a)) with the iteration sequence  $\bar{N}$  for sample S1. Since the function  $F'$  is more responsive than the function  $G'$  to the parameter  $\bar{N}$ , the iterates that tend to vanish the former function are interpolated from the Figure. We have detected from the Figure that when  $\bar{N}$  increases from 12 to 13, the value of  $\ln \alpha'$  stays at  $-6.8694 \times 10^{-6}$ , but the values of both parameters  $b'$  and

Table 1 Parameters of various molecular weight distribution models

No.	Model	Parameter	Sample							
			S1	S2	M1	M2	E1	E2	N1	N2
1	Polynomial	$\theta_0 \times 10^3$	0.6628	1.1920	8.9686	1.3075	1.9015	0.7366	0.2305	0.1378
		$-N_2$	0.4713	0.4756	0.7015	0.7675	1.0641	1.3485	2.8039	0.6931
		$N_3$	0.1269	0.8050	0.4138	0.9515	1.2188	1.7228	3.4578	0.1519
		$-N_4 \times 10$	0.0243	3.6510	-0.0947	4.9332	5.5213	8.7428	16.71	7.8181
		$N_5 \times 10$	-	0.9160	-0.5237	1.2979	1.3809	2.3622	4.1806	2.0285
		$N_6 \times 10^2$	-	1.084	-1.7335	1.4648	1.668	3.071	4.976	2.225
		$N_7 \times 10^4$	-	6.0396	-21.104	6.4246	8.5159	16.244	24.19	9.6621
		$N_8 \times 10^5$	-	-	9.3217	-	-	-	-	-
		$\overline{SE} \times 10^2$	0.26	0.76	1.09	0.62	0.64	1.76	1.19	1.22
2	Schulz	$-\ln \alpha' \times 10^6$	6.8694	4.7609	60.067	7.3965	38.50	11.843	1.6168	0.5662
		$-b' \times 10$	2.7902	7.3933	6.1037	7.3480	7.3422	9.2018	9.6616	7.8429
		$\overline{SE} \times 10^2$	1.62	1.67	3.76	2.13	3.24	3.35	9.65	1.88
3	Flory	$-\ln p' \times 10^4$	8.5926	8.8773	101.53	13.432	19.338	7.4339	-	-
		$\overline{SE} \times 10^2$	2.17	4.76	5.29	4.01	6.52	7.44	-	-
4	Wesslau	$\beta$	1.2151	1.6573	1.3369	1.6099	1.5004	1.8327	1.6996	1.6942
		$M_0 \times 10^{-5}$	1.7494	1.4268	0.1567	0.7362	0.1954	0.6201	4.0772	8.4316
		$\overline{SE} \times 10^2$	2.72	5.05	2.70	6.89	3.51	1.60	8.16	11.1
5	Tung	$Z$	1.5637	1.0885	1.3610	1.1720	1.1449	-	-	1.0214
		$Y \times 10^9$	2.302	841.9	588.3	506.9	4731.0	-	-	345.0
		$\overline{SE} \times 10^2$	6.89	5.98	8.53	4.72	6.08	-	-	2.22

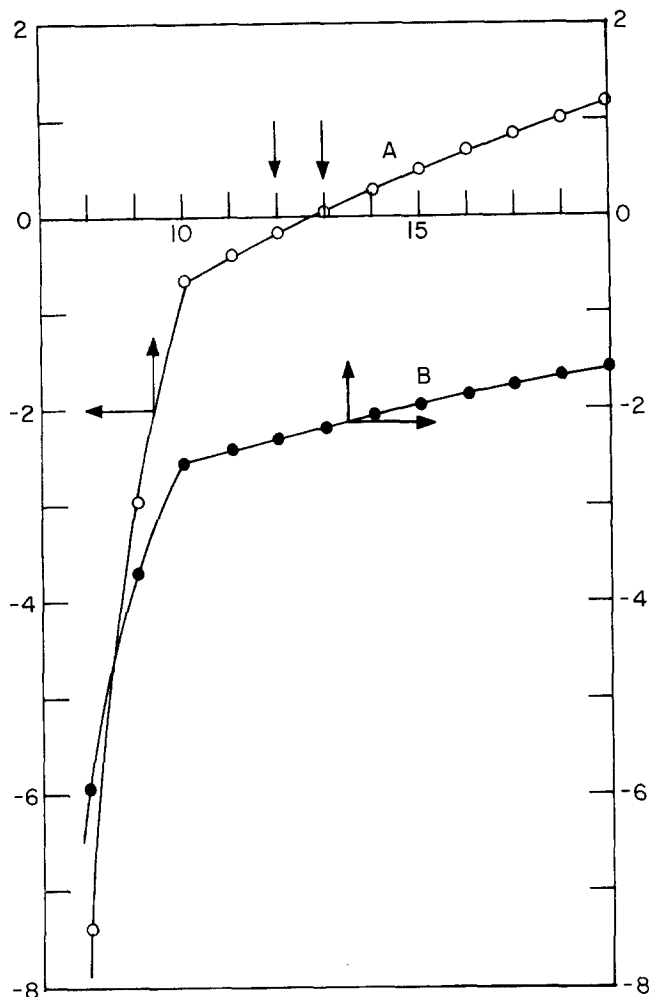


Figure 6 Iterative method applying to solve the Schulz parameters for sample S1; curve A:  $F' \times 10^{-2}$  against  $N$  and curve B:  $G' \times 10$  against  $N$

$S'$  drop from  $-0.27889$  to  $-0.27907$  and from  $266.0$  to  $46.6$ , respectively. Then appropriate combinations of  $\alpha'$  and  $b'$  values are chosen within the above specified ranges and substituted into equations (27), (28) and (29). The smallest  $S' = 0.0013$  decides the values of  $\ln \alpha' = -6.8694 \times 10^{-6}$  and  $b' = -0.27902$ , which are considered as the best solutions to equations (21) and (22). These results are shown in Table 1 together with those obtained by the same algorithm for other samples. It should be noted that the determining function  $S'$  is sensitive to at least the fourth decimal place of  $\ln \alpha'$  and  $b'$ . Besides, this iterative procedure is relatively simple in that it does not require a good first approximation.

To compute the best value of the Flory parameter  $P'$ , we use equation (36). The calculation exercise is initiated by the first approximation  $P' = 0.9990$ , a value which makes the algorithms converge rapidly for all samples except N1 and N2, that do not yield convergent values at all. Table 1 includes the  $\ln P'$  values and also results obtained from the Wesslau (equation (41)) and Tung (equation (46)) models. The Tung distribution function does not hold for samples E2 and N1 because the parameter  $Z < 1^{25}$ .

Using the information provided in Table 1, equations (11), (19), (33), (39) and (44) would predict the cumulative weight fraction of any polymer species. The theoretical weight fraction  $w_i$  of an observed  $M_i$  is then readily computed by treating the function

$I(X)$  or  $I(M)$  as a discrete variable, and hence we have  $w_i = I(X_i) - I(X_{i-1}) = I(M_i) - I(M_{i-1})$ , where  $X_i$  is the number of repeating units of the species  $M_i$ . Some of these results are compared with those measured in Figures 1–5. Figure 1 shows that the polynomial distribution function (equation (11)) is the most suitable one for sample S1 and this coincides with the fact that it does give the smallest  $SE$  value. In fact, these Figures are constructed to magnify the differences between the theoretical and experimental weight fractions over the whole molecular weight range covered in each case. Figure 2(a) confirms that such a plot is more informative than the conventional integral distribution curve (Figure 2(b)) which tends to compress the data points. Here the polynomial curve fits the observed data satisfactorily only when the molecular weight is neither too high nor too low, i.e. it holds over  $11.0 < \ln M < 13.5$ . This explains the enormous deviations between the predictions and measurements of the low- and high-order average molecular weights for sample S2 as will be touched on later. The Wesslau model is most compatible with sample E2 and so it is presented in Figure 4. Other curves in Figures 3–5 are produced according to the polynomial distribution equation which fits these systems best.

In the present context, accordance between the estimates and measurements has to be accomplished with respect to the average molecular weights which are based on a continuous frequency function, viz. the differential distribution function defined by equation (12). In terms of molecular weight  $M$ , we have

$$W(M) = \frac{\partial I(M)}{\partial M} \quad (12a)$$

$$U_a = \int_0^{\infty} M^a W(M) dM \quad (14a)$$

which correspond to equations (12) and (14) respectively. Equations (15), (31), (37), (40) and (45) are invoked to compute the various theoretical moments of distribution which in turn report the average molecular weights<sup>26</sup>. To evaluate the average molecular weights from the experimental data, we estimate the derivative  $W(M)$  numerically. This is done by a least-squares fit of 3 adjacent data points to a parabola one at a time, i.e.

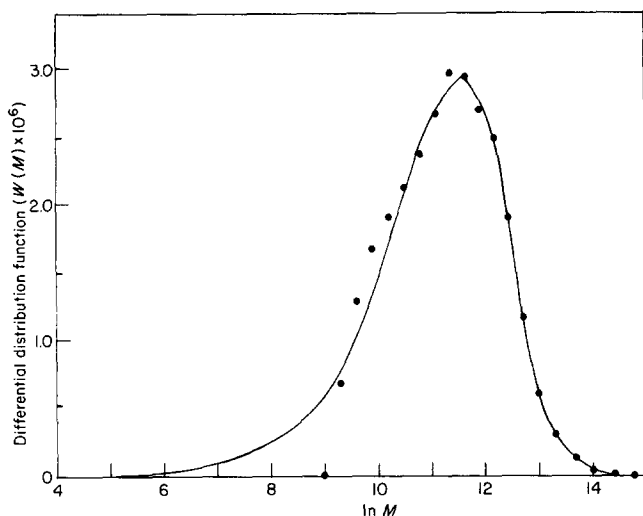
$$I_i(M) = a_i + b_i \ln M + c_i (\ln M)^2 \quad (51)$$

where the empirical constants  $a_i$ ,  $b_i$  and  $c_i$  are determined by the integral weight fractions  $I(M_{i-1})$ ,  $I(M_i)$  and  $I(M_{i+1})$ . These data points are arranged in the ascending order, i.e. the molecular weights  $M_{i-1} < M_i < M_{i+1}$ . It follows that, the experimental  $a^{\text{th}}$  moment of distribution

$$U_a = \sum_{i=2}^{N'} \int_{M_{i-1}}^{M_i} M^a W_i(M) dM \quad (52)$$

where  $W_i(M)$  is the differential distribution function pertaining to the species  $M_i$  and it is equal to,

$$W_i(M) = \frac{b_i}{M} + \frac{2c_i \ln M}{M} \quad (53)$$



**Figure 7** Differential distribution functional with  $W(M) \times 10^6$  against  $\ln M$  for sample S1. The data points are derived from g.p.c. data and the curve is predicted by the polynomial model

As *Figure 7* is very similar to *Figure 1*, it illustrates that the  $W(M)$  curve predicted by the polynomial model (equation (13)) is compatible with the data points calculated by equation (53) for sample S1. *Table 2* summarizes the values of the average molecular weights for all the samples. Obviously the polynomial model predictions are quite consistent with measurements for samples S1, M1, E1, M2 and N2, except that there are some noticeable discrepancies in the  $\bar{M}_n$  values for the last two samples, as is also shown in *Figure 3* and *5*. In these two *Figures*, the theoretical curves do not conform to the experimental data at the low molecular weight ends. Although for sample S2, considerable disagreement between some of the average molecular weight data from the polynomial model and experiment is encountered, as mentioned earlier, the values of  $\bar{M}_v$  and  $\bar{M}_w$  from the two sources are indeed in agreement.

The competency of this new model is also examined by a polyisoprene sample (N1) whose molecular weight distribution manifests two definite peaks at molecular weights around  $1.5 \times 10^5$  and  $2.3 \times 10^6$  (*Figure 5*). Surpris-

**Table 2** Estimated average molecular weights based on continuous distribution

No.	Estimated Average Molecular Weight	Model	Sample							
			S1	S2	M1	M2	E1	E2	N1	N2
1	$\bar{M}_n^a \times 10^{-5}$	Expt.	1.244	0.756	0.097	0.481	0.105	0.232	1.581	4.134
		Polynomial	1.163	0.840	0.082	0.589	0.104	0.254	1.416	5.257
		Wesslau	1.209	0.718	0.100	0.383	0.111	0.268	1.980	4.114
		Schulz	1.050	0.548	0.065	0.359	0.069	0.067	0.209	3.810
		Flory	1.211	1.172	0.099	0.745	0.145	0.377	—	—
		Tung	1.354	0.323	0.111	0.369	0.060	—	—	0.450
2	$\bar{M}_v^b \times 10^{-5}$	Expt.	2.326	2.403	0.223	1.537	0.306	0.944	7.301	17.16
		Polynomial	2.308	2.318	0.222	1.544	0.308	0.847	6.967	17.00
		Wesslau	2.104	2.011	0.196	1.018	0.259	0.944	5.850	12.07
		Schulz	2.171	2.181	0.194	1.410	0.271	0.728	5.060	17.57
		Flory	2.140	2.071	0.175	1.317	0.256	0.666	—	—
		Tung	2.676	2.987	0.299	1.846	0.354	—	—	16.66
3	$\bar{M}_w^c \times 10^{-5}$	Expt.	2.804	3.172	0.291	1.993	0.412	1.551	11.44	20.98
		Polynomial	2.762	2.922	0.293	1.989	0.410	1.170	10.54	20.51
		Wesslau	2.530	2.835	0.245	1.407	0.343	1.436	8.394	17.28
		Schulz	2.505	3.744	0.231	1.711	0.329	0.912	0.394	21.47
		Flory	2.422	2.344	0.198	1.490	0.290	0.754	—	—
		Tung	3.005	3.688	0.346	2.225	0.431	—	—	21.04
4	$\bar{M}_z^d \times 10^{-5}$	Expt.	5.569	8.340	0.674	4.498	1.038	8.765	33.78	35.85
		Polynomial	5.216	5.906	0.701	4.447	0.982	2.996	27.12	34.07
		Wesslau	5.290	11.19	0.599	5.142	1.057	7.700	35.58	72.58
		Schulz	3.961	4.748	0.398	3.063	0.589	1.756	12.58	39.12
		Flory	3.633	3.516	0.297	2.235	0.435	1.130	—	—
		Tung	4.288	6.807	0.538	3.856	0.761	—	—	41.22
5	$\bar{M}_{z+1}^e \times 10^{-5}$	Expt.	9.249	16.69	1.034	7.053	1.762	19.01	49.26	47.36
		Polynomial	8.178	8.562	1.116	6.866	1.510	4.447	35.35	44.67
		Wesslau	11.08	44.19	1.463	18.79	3.260	4.129	150.8	304.9
		Schulz	5.417	6.849	0.564	4.414	0.848	2.601	18.77	56.80
		Flory	4.843	4.688	3.960	2.980	0.580	1.507	—	—
		Tung	5.391	9.805	0.707	5.377	1.072	—	—	61.18
6	$\bar{M}_w/\bar{M}_n$	Polynomial	2.37	3.48	3.55	3.38	3.95	5.36 <sup>f</sup>	7.44	3.90

<sup>a</sup>Number-average molecular weight

<sup>b</sup>Viscosity-average molecular weight under theta conditions

<sup>c</sup>Weight-average molecular weight

<sup>d</sup>Z-average molecular weight

<sup>e</sup>(Z+1)-average molecular weight

<sup>f</sup>Value estimated by Wesslau model



ingly, Table 2 indicates that the values of  $\bar{M}_n$ ,  $\bar{M}_v$ , and  $\bar{M}_w$  can be estimated reasonably well by the polynomial method (equation (11)). The theoretical curve drawn in Figure 5 is considered to be acceptable in view of the complicated feature of the distribution as well as the small  $SE = 0.0119$  (Table 1) obtained.

The Wesslau distribution function which best accounts for the g.p.c. data of sample E2 (Figure 4), furnishes comparable values of  $\bar{M}_v$ ,  $\bar{M}_w$  and  $\bar{M}_{z+1}$  as quoted in Table 2.

The overall performance of the four simple models is also demonstrated by the  $SE$  data (Table 1) and average molecular weights (Table 2). As far as the curve-fitting of  $I(M)$  data is concerned, the Schulz function is definitely superior to the other three for addition polymers with moderate polydispersity while the Wesslau function appears to be the most suitable one for polymers with broad molecular weight distribution, particularly polyolefins. When the data on average molecular weights are examined, it is evident that the Schulz and Wesslau distributions reproduce the observed low-order molecular weights  $\bar{M}_n$ ,  $\bar{M}_v$  and  $\bar{M}_w$ , and high-order molecular weights  $\bar{M}_w$ ,  $\bar{M}_z$  and  $\bar{M}_{z+1}$  reasonably well, respectively. In any event, the Flory and Tung distributions do not afford satisfactory predictions in the present investigations. These findings have some practical implications as explained below.

First of all, we will establish a distribution model which fits the g.p.c. data best by referring to the smallest value of  $SE$ . In this connection, it is not unreasonable to assume that the polynomial model is the choice as has been demonstrated in the majority of the cases. Under this specific condition, equation (16) is employed to deal with the experimental data. Now if the difference between the estimated and observed average molecular weights is within the experimental error which usually is not exceeding 10% at low molecular weights, then equation (15) will ultimately lead to the true values of various average molecular weights. This operation has an advantage in that it does not involve the approximate derivative  $W(M)$ , which is estimated either numerically (see equation (53)) or graphically. Unfortunately, both algorithms are tedious and would inherently introduce considerable error in the final values of the average molecular weights. Thus, we have proposed a relatively simple approach to assess the average molecular weights accurately. Applications of this method to various commercial thermoplastics and a bimodal polymer have proved to be fruitful.

Incidentally, the values of absolute  $\bar{M}_n$  determined by osmometry, have been reported to be  $0.193 \times 10^5$  and  $1.10 \times 10^5$  for samples M1 and M2 respectively<sup>23</sup>. These figures are substantially higher than those deduced from the g.p.c. measurements (Table 2), reflecting partially the approximate nature of the algorithm involved in estimating the derivative  $W(M)$ , particularly in the low molecular weight region as also witnessed in Figure 7 for sample S2. It has been commented that the overestimate from the osmometric data may be due to the experimental conditions that allow the low molecular weight fractions to pass through undesirably the membrane<sup>27</sup>.

Table 2 also reports the values of the polydispersity index  $\Delta$ . Recently, we have investigated the polydispersity effects on a particular property of polymer solutions<sup>28</sup>. The present work justifies the use of Schulz distribution function for our purposes in those particular studies.

An immense amount of work has been done on the mathematical prediction of the molecular weight distribution in terms of the various kinetic parameters<sup>7,29,30</sup>. However, to evaluate the relevant absolute rate constants from a set of a known molecular weight distribution data is a formidable task<sup>31</sup>. Preliminary investigations indicate that the present technique may be used to determine transfer constants via the coefficient  $\theta_0$ , which is inversely proportional to  $\bar{M}_n$ , as stated. Nevertheless, the relationships between the rate constants and the polynomial parameters  $N_i$  and  $\theta_0$  are too complicated to be dealt with even for a simple system such as the bulk polymerization of styrene initiated by 2,2'-azobisisobutyronitrile under controlled conditions. Furthermore, these rate constants are hardly mathematically separable from one another, except the one associated with the initiation step. This implies that the rate constant  $k_i$ , which can be determined rapidly from the polymerization kinetic data by a method proposed by us recently<sup>32</sup>, may also be derived from the molecular weight distribution data of the polymer.

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#### NOMENCLATURE

$a$	order of the moment $U_a$
$a_i$	empirical constant associated with $I_i(M)$
$b$	Schulz parameter
$b'$	approximate value of $b$
$b_i$	empirical constant associated with $I_i(M)$
$c_i$	empirical constant associated with $I_i(M)$
$f(\alpha, b)$	function defined by equation (19a)
$f_x$	function defined by equation (23)
$f_b$	function defined by equation (24)
$g(\alpha, b)$	function defined by equation (19b)
$g_x$	function defined by equation (25)
$g_b$	function defined by equation (26)
$h(P)$	function defined by equation (36a)
$h'(P)$	function defined by equation (36b)
$i$	summation index for power of $t$
$j$	summation index
$k_p$	rate constant for propagation reaction
$k_t$	rate constant for combination reaction
$k'_t$	rate constant for disproportionation reaction
$k_{tr}$	rate constant for transfer reaction to monomer
$k'_{tr}$	rate constant for transfer reaction to chain transfer agent
$l$	summation index or power of $X$
$m$	degree of Taylor series for $\theta$
$n$	degree of various polynomials with argument $X$ or $y$
$q$	subscript for $q^{\text{th}}$ repetition
$s$	summation index
$t$	time
$w_i(w)$	weight fraction (normalized) of $M_i(M)$ or $X_i(X)$
$y$	variable defined by equation (11a)

$A_i$  variable defined by equation (1b)  
 $D$  difference parameter  
 $E$  function defined by equation (7a)  
 $F_i(t)$  complex function of  $t$  and other variables  
 $F'$  function defined by equation (21a)  
 $G(t)$  function defined by equation (5a)  
 $G'$  function defined by equation (22a)  
 $H_i(t)$  function defined by equation (5b)  
 $I'$  initiation rate  
 $I(M)$  integral distribution function of  $M$   
 $I_i(M)$  empirical integral distribution function over a limited range of  $M$  around  $M_i$   
 $I(X)$  integral distribution function of  $X$   
 $I(y)$  integral distribution function of  $y$   
 $K$  constant defined by equation (10a)  
 $L_i$  function defined by equation (7a)  
 $L_n$  function defined by equation (7c)  
 $M$  molecular weight of polymer  
 $M_i$  molecular weight of  $i^{\text{th}}$  polymer species  
 $M_0$  Wesslau parameter  
 $\bar{M}_0$  molecular weight of a repeating unit  
 $\bar{M}_n$  number-average molecular weight  
 $\bar{M}_n'$  apparent number-average molecular weight  
 $\bar{M}_v$  viscosity-average molecular weight under theta conditions  
 $\bar{M}_w$  weight-average molecular weight  
 $\bar{M}_w'$  apparent weight-average molecular weight  
 $\bar{M}_z$  z-average molecular weight  
 $\bar{M}_{z+1}$   $(z+1)$  average molecular weight  
 $[M]$  instantaneous monomer concentration  
 $N_i$  variable defined by equation (11b)  
 $N'(X)$  number distribution function of  $X$   
 $N''$  total number of g.p.c. data points  
 $\bar{N}$  integer indicating  $N^{\text{th}}$  iteration  
 $P$  Flory parameter  
 $P'$  approximate value of  $P$   
 $[P_x]$  concentration of  $X$ -mer  
 $R_i$  function defined by equations (8a) and (8b)  
 $S'$  function defined by equation (29)  
 $SE$  standard error of estimate  
 $[S]$  instantaneous chain transfer agent concentration  
 $U_a$   $a^{\text{th}}$  moment of distribution  
 $W(M)$  differential distribution function of  $M$   
 $W(X)$  differential distribution function of  $X$   
 $W_i(M)$  empirical differential distribution function over a limited range of  $M$  around  $M_i$   
 $X$  number of repeating units of  $X$ -mer  
 $X_i$  number of repeating units in  $M_i$   
 $\bar{X}_n$  hypothetical number-average degree of polymerization at  $t=0$   
 $Y$  Tung parameter  
 $Z$  Tung parameter  
 $\alpha$  Schulz parameter

$\alpha'$  approximate value of  $\alpha$   
 $\beta$  Wesslau parameter  
 $\theta$   $X$ -independent parameter defined by equation (1b)  
 $\theta_0$  constant equal to  $\theta$  at  $t=0$   
 $\theta_i$   $i^{\text{th}}$  coefficient of Taylor series for  $\theta$   
 $\mu(x)$  digamma function of  $x$   
 $\phi$   $X$ -independent parameter defined by equation (1a)  
 $\psi$   $X$ -independent parameter defined by equation (1c)  
 $\Gamma(x)$  gamma function of  $x$   
 $\Delta$  polydispersity index

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