Estimation of Molecular Weight Distribution Parameters for Free-Radical Polymerization

LEO REICH,* *Polymer Research Branch, Picatinny Arsenal, Dover, New Jersey 07801* and S. S. STIVALA, *Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030*

Synopsis

A method is described which allows the precise estimation of molecular weight distribution parameters p and A which pertain to free-radical polymerizations. Thus, expressions are developed which allow the estimation of $(1 - p)$ by means of a programmable calculator using molecular weight distribution data derived from GPC. Values of A may subsequently be calculated by means of a plot of one of the expressions given. Values of $(1 - p)$ and A obtained in this paper were checked using theoretical values as well as by a comparison between calculated and observed values. The agreement between calculated and theoretical or experimental values indicates that the method presented for the estimation of $(1 - p)$ and A is both reliable and relatively rapid. Previously reported methods for the estimation of $(1 - p)$ and A have involved curve-fitting trial calculations as well as more precise interpolation procedures. However, the latter are based on single-peak maximum values.

INTRODUCTION

The molecular weight distributions of polymers formed by free-radical polymerizations are known to be functions of the mechanism of formation. Thus, we may write, based on a kinetic analysis (assuming low conversions and high degrees of polymerization),[1,2]

$$W(X) = A(1 - p)^2 X e^{-X(1-p)} + 0.5(1 - A)X^2(1 - p)^3 e^{-X(1-p)} \quad (1)$$

where $W(X)$ = weight fraction of the polymer with X-mer units; A = fraction of radical termination by disproportionation and transfer as opposed to termination by combination; and p = probability of radical addition to monomer as opposed to termination. The molecular weight distribution parameters p and A may be estimated from eq. (1) once the molecular weight distribution has been experimentally determined. Once these parameters have been accurately estimated, various kinetic parameters may also be obtained.[3,4] Thus, parameters p and A may be employed to estimate values of k_t/k^2_p and chain transfer constants. Gel permeation chromatography (GPC) may be utilized to obtain accurate plots of $W(X)$

---

* Affiliate Professor of Chemistry, Stevens Institute of Technology, Hoboken, New Jersey 07030.

versus X^{2-4}. However, no precise methods of estimating parameters p and A from molecular weight distribution data have been reported. Thus, Smith and co-workers[2] attempted to estimate values of p and A by utilizing values of k_t/k^2_p reported in the literature. However, the literature reported several values of k_t/k^2_p for the same system at the same temperature. Thus, several trial calculations were carried out in order to obtain values of p and A which gave a good fit to the molecular weight distribution data. Smith and co-workers[2] indicated, however, that the agreement between calculated points and the GPC curve could be improved by a better set of parameters p and A. Subsequently, Smith and May[3,4] found, based on theoretical plots of $W(X)$ versus X, that the variation of p or A (while the other is held constant) leads to regular variations in the distribution. Further, the loci of the peak maxima were found to be smooth functions. These smooth peak functions were compared with peak values of replotted GPC curves in order to estimate values of p and A. However, this procedure often involves interpolation and emphasizes single-peak values. This may lead to small changes in p which may affect values of A dramatically.

The purpose of this paper is to present a method of obtaining precise values of p (based upon precise molecular weight distribution data) and subsequently of A.

THEORY

From eq. (1), we may readily obtain the expression

$$\frac{W(X)X_1e^{X(1-p)} - W(X_1)Xe^{X_1(1-p)}}{XX_1(X - X_1)} = \frac{(1 - A)}{2}(1 - p)^3 \equiv K. \quad (2)$$

Since K = constant for a particular free-radical polymerization, eq. (2) leads to

$$W(X)e^{X(1-p)}\left[\frac{X_1 - X_2}{(X - X_1)(X - X_2)}\right] + \frac{W(X_2)e^{X_2(1-p)}X}{X_2(X - X_2)} = \frac{W(X_1)e^{X_1(1-p)}X}{X_1(X - X_1)}.$$

$$(3)$$

From eq. (3), it can be seen that only the parameter p is involved. Utilizing these sets of data, i.e., X, X_1, and X_2 and the corresponding $W(X)$, $W(X_1)$, and $W(X_2)$, and a programmable calculator (Hewlett-Packard Model 9100 A), values of $1 - p$ could be readily calculated using a trial-and-error program. Generally, five or more sets of $W(X)$–X data were selected and the various different combinations were utilized (thus, five sets of data gave ten different combinations of three sets of data). The points were selected prior to the $W(X)$ versus X peak, near the peak, and after the peak. From each different combination of data, two values of $1 - p$ were obtained. The lower value afforded unrealistic values of A (>1), whereas the higher value gave realistic values of A (between 0 and 1). The latter values of

$1 - p$ were averaged, and this value was employed in the following expression to obtain values of A:

$$\frac{W(X)e^{X(1-p)}}{X} = A(1 - p)^2 + \frac{(1 - A)}{2}(1 - p)^3X. \qquad (4)$$

From eq. (4), it can be seen that a plot of the left-hand side versus X should afford a linear relation from whose slope and intercept values of A can be calculated. The two values of A thus obtained were averaged, and this average value along with the average $(1 - p)$ were employed in eq. (1) to calculate values of $W(X)$ so that these values could be compared with experimental values.

Expressions may also be derived from eq. (1) which allow the estimation of $(1 - p)$ and A from cumulative weight-fraction data, $I(X)$. Thus, we may write

$$I(X) = \int_0^W dW(X) = \int_0^X W(X)dX. \qquad (5)$$

Upon substituting eq. (1) into eq. (5) and integrating, there is obtained after some manipulation

$$\frac{[1 - I(X)]e^{X(1-p)} - 1}{X(1 - p)} = 1 + \frac{(1 - p)(1 - A)}{2}X. \qquad (6)$$

Thus, once $(1 - p)$ has been estimated, eq. (6) may be utilized to estimate A from a plot of the left-hand side of eq. (6) versus X. From the resulting linear relation, A may be calculated from the values of the slope and $(1 - p)$.

The value of $(1-p)$ may be estimated from cumulative weight-fraction data using expression developed in the following. From eq. (6), we may readily obtain

$$\frac{[1 - I(X)]e^{X(1-p)}X_1 - [1 - I(X)]_1e^{X_1(1-p)}X + (X - X_1)}{XX_1(X - X_1)} = C \qquad (7)$$

where $C = $ constant $= K/(1 - p)$. Since $C = $ constant for a particular free radical polymerization, eq. (7) leads to, cf. eq. (3),

$$\frac{(X - X_2)}{X}\left[\frac{[1 - I(X)]e^{X(1-p)}}{(X - X_1)(X - X_2)} - \frac{1}{X_1X_2}\right] + \frac{[1 - I(X)]_2e^{X_2(1-p)}}{X_2(X - X_2)}$$
$$= \frac{[1 - I(X)]_1e^{X_1(1-p)}}{X_1(X - X_1)}. \qquad (8)$$

As in eq. (3), it can be seen that eq. (8) involves only one parameter, p. Utilizing three sets of data, i.e., X, X_1, and X_2 and corresponding $(1 - I(X))$, $(1 - I(X))_1$, and $(1 - I(X))_2$ and a programmable calculator (Hewlett-Packard Model 9100 A), values of $(1 - p)$ could be readily estimated using a trial-and-error program. As observed in the case of $W(X)$-versus-X data, the $(1 - I(X))$-versus-X data also afforded two values of $(1 - p)$. Again, the lower value gave unrealistic values of A (>1), whereas the higher value

gave realistic values of A (between 0 and 1). The latter values of $(1 - p)$ were averaged, and this value employed in eq. (6) to obtain values of A.

RESULTS AND DISCUSSION

In order to check the accuracy of the method proposed in this paper, $W(X)$-versus-X data were selected from theoretical plots[3] which were calculated using $(1 - p) = 1.5 \times 10^{-3}$ and $A = 0.5$. Table I shows ten different combinations, which resulted from the selection of five points on the theoretical $W(X)$-X curve. For each combination, two values of $(1 - p)$ were estimated by the programmable calculator using eq. (3). The averages of these values were then employed in eq. (4) to estimate A. Figure 1 shows a plot of eq. (4). A least-squares treatment gave values of $A = 2.6 \pm 0.2$ for the lower value of $(1 - p) = 0.71 \times 10^{-3}$ and a value of 0.52 ± 0.00 for the higher value of $(1 - p) = (1.49 \pm 0.08) \times 10^{-3}$. The

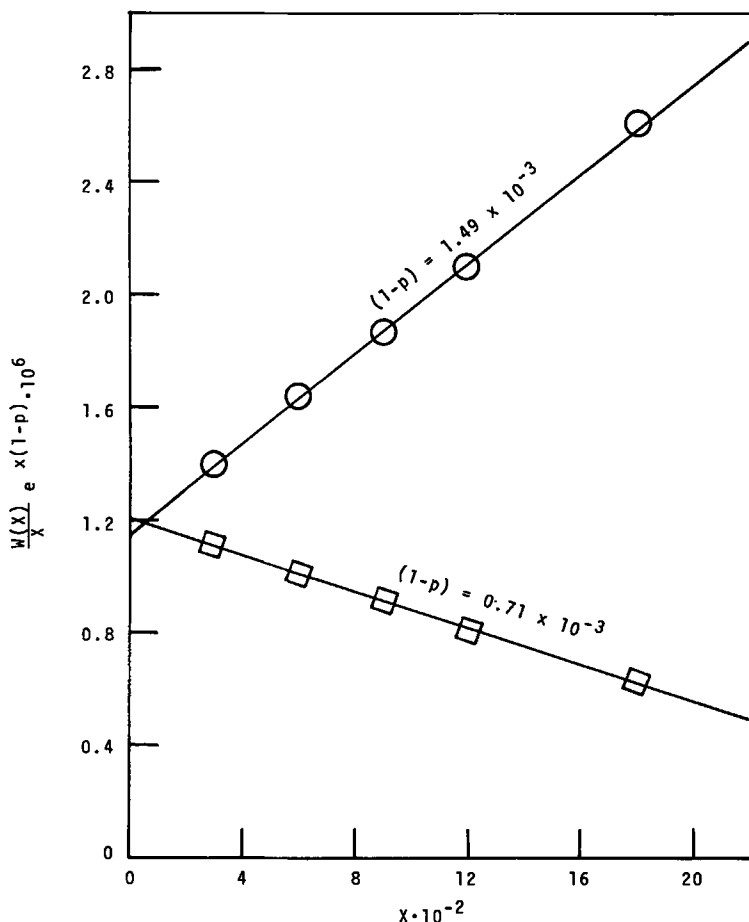

Fig. 1. Plot of eq. (4) using $(1 - p)$ values calculated from data obtained from a theoretical plot of $W(X)$ vs. X.

TABLE I
Estimation of Parameters $(1 - p)$ and A from Theoretical Plots
$[(1 - p) = 1.50 \times 10^3, A = 0.50]$

$X \times 10^{-2}$	$X_1 \times 10^{-2}$	$X_2 \times 10^{-2}$	$W(X) \times 10^4$	$W(X_1) \times 10^4$	$W(X_2) \times 10^4$	$(1 - p) \times 10^3$
3	6	9	2.69	4.00	4.38	0.58, 1.51
9	12	18	4.38	4.16	3.16	1.06, 1.25
3	6	12	2.69	4.00	4.16	0.58, 1.55
3	6	18	2.69	4.00	3.16	0.66, 1.51
3	9	12	2.69	4.38	4.16	0.58, 1.59
3	9	18	2.69	4.38	3.16	0.70, 1.51
3	12	18	2.69	4.16	3.16	0.78, 1.43
6	9	12	4.00	4.38	4.16	0.58, 1.63
6	9	18	4.00	4.38	3.16	0.74, 1.51
6	12	18	4.00	4.16	3.16	0.85, 1.39

$(1 - p) \times 10^3$ (av.) $= 0.71 \pm 0.11, 1.49 \pm 0.08$

TABLE II
Estimation of Parameter $(1 - p)$ from Experimental Data Obtained
From Plots of $W(X)$ Versus X for Poly(methyl Methacrylate)[2]

$X \times 10^{-3}$	$X_1 \times 10^{-3}$	$X_2 \times 10^{-3}$	$W(X) \times 10^4$	$W(X_i) \times 10^4$	$W(X_2) \times 10^4$	$(1 - p) \times 10^4$
1	3	4	1.75	1.81	1.36	3.94, 7.19
4	5	7	1.36	1.00	0.444	3.94, 7.39
1	3	5	1.75	1.81	1.00	4.51, 6.44
1	3	7	1.75	1.81	0.444	4.51, 6.62
1[a]	4	5	1.75	1.36	1.00	—
1	4	7	1.75	1.36	0.444	4.90, 6.27
1	5	7	1.75	1.00	0.444	4.64, 6.62
3[a]	4	5	1.81	1.36	1.00	—
3[a]	4	7	1.81	1.36	0.444	—
3	5	7	1.81	1.00	0.444	4.64, 6.81

$(1 - p) \times 10^4$ (av.) $= 4.44, 6.76 \pm 0.31$

[a] The values in these combinations were not sufficiently accurate to afford closed values of $(1 - p)$.

latter values are in excellent agreement with the theoretical values considering that the selected values in Table I were extracted from a theoretical plot.

Table II lists different combinations of data which were selected from experimental plots of $W(X)$ versus X for poly(methyl methacrylate).[2] The average value of $(1 - p) \times 10^4 = 6.76 \pm 0.31$. This value was employed in the plot in Figure 2 to obtain $A = 0.60 \pm 0.00$ (using a least-squares treatment). These values were inserted into eq. (1) to give the following calculated values of $W(X) \times 10^4$ (the experimental values follow in parentheses): 1.71 (1.75), 1.81 (1.81), 1.39 (1.36), 0.99 (1.00), 0.44 (0.44). The agreement between calculated and observed values is seen to be very good. The values reported[2] for $(1 - p) \times 10^4$ and A were, respectively, 6.0 and 0.85.
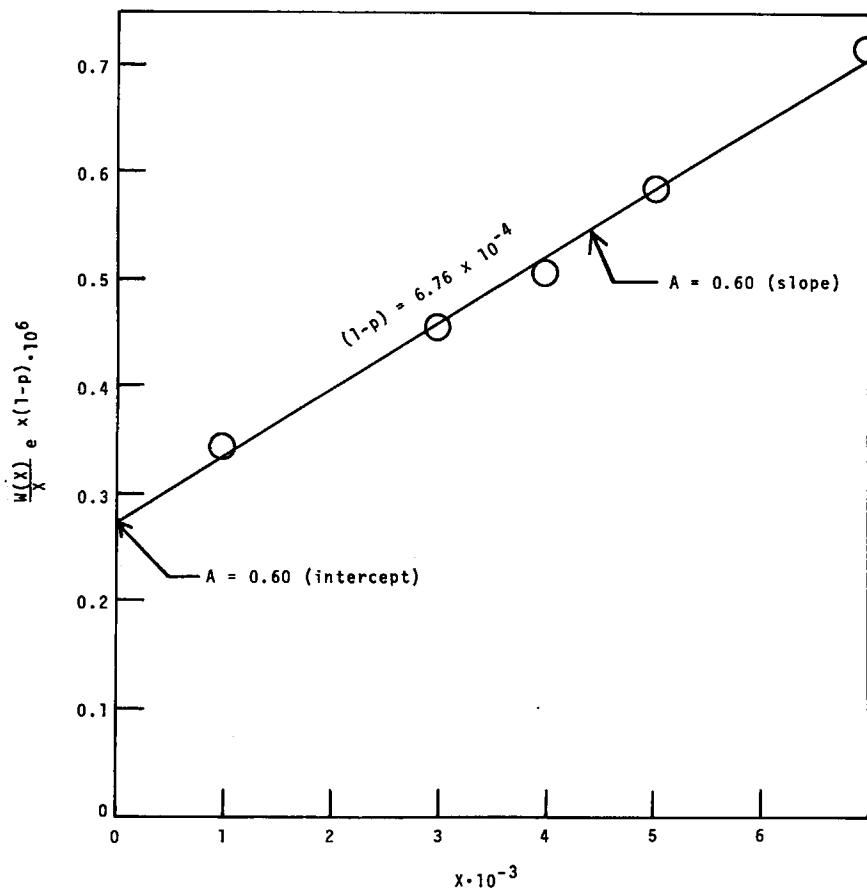
Fig. 2. Plot of eq. (4) for poly(methyl methacrylate) using $(1 - p)$ values calculated from an experimental plot of $W(X)$ vs. X.

However, these values were obtained by several trial calculations in order to fit the experimental data.[2]   It may be noted in Table II that only 70% of the different combinations afforded closed values of $1 - p$.   In the remaining cases, the extracted data were not sufficiently accurate to afford closed values of $1 - p$.   (Thus, the programmable calculator was stopped after it had revealed values of $(1 - p) > 10^3$ in these cases.)

As a final check on the method presented in this paper, eight pairs of experimental values of $W(X)$–X were selected from a GPC-derived curve for polystyrene.[3]   From the 56 possible combinations, the data in 13 cases were insufficiently accurate to afford realistic $(1-p)$ values.   The remaining 43 combinations (77% of all the combinations possible) afforded the physically real value of $(1 - p) \times 10^3 = 2.56 \pm 0.17$.   Using this value, a plot was carried out as previously described to give $A = 0.60 \pm 0.00$ using a least-squares treatment.   These values were inserted into eq. (1) to give the following calculated values of $W(X) \times 10^4$ (the experimental values are

also listed in parentheses): 5.50 (5.72), 7.54 (7.31), 7.62 (7.59), 7.26 (7.38), 4.37 (4.41), 2.86 (2.76), 1.25 (1.24), 0.61 (0.62). Values of $(1 - p) \times 10^3$ and A reported[3] were, respectively, 2.46 and 0.75. These latter values were estimated by an interpolation procedure previously mentioned.

In order to check the reliability of the procedure employing $I(X)$-versus-X data, a theoretical plot of $W(X)$ versus X was constructed using eq. (1) and $A = 0.5$ and $(1 - p) = 1.5 \times 10^{-3}$. From this plot, values of $I(X)$ were estimated for corresponding values of X by means of graphic integration. From such values, different combinations of $(1 - I(X))$-X data were employed in eq. (8). Thus, from five sets of $(1 - I(X))$-X values (ten different combinations as previously indicated), eq. (8) gave $(1-p) \times 10^{-3}$ (av.) $= 0.90 \pm 0.06$ and 1.49 ± 0.02. From the latter value (the former value gave an unrealistic value of A) and eq. (6), a plot was constructed which afforded a value of $A = 0.47$. These values agree well with theoretical values and the values reported previously using $W(X)$-X data. [It may be mentioned here that relatively small changes in $W(X)$ or $I(X)$ data can result in relatively large changes in p- and A-values.]

It may be pertinent to note here that during the free-radical polymerization of methyl methacrylate, termination has been reported[1] to involve both disproportionation and combination simultaneously and to be influenced by polymerization temperature. Further, in the case of free-radical polymerization of styrene, there have been discordant views as to the mode of termination.[1,5] Thus, both disproportionation and combination have been advocated.

References

1. C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, *The Kinetics of Vinyl Polymerization by Radical Mechanism*, Academic Press, New York, 1958, pp. 274ff.
2. W. B. Smith, J. A. May, and C. W. Kim, *J. Polym. Sci. A-2*, **4**, 365 (1966).
3. J. A. May and W. B. Smith, *J. Phys. Chem.*, **72**, 216 (1968).
4. J. A. May and W. B. Smith, *J. Phys. Chem.*, **72**, 2993 (1968).
5. G. M. Guzman, *J. Polym. Sci.*, **19**, 519 (1956).