LETTER TO THE EDITORS

An Analytical Solution to Tung's Axial Dispersion Equation

Tung's axial dispersion equation[1] sometimes referred to as his integral dispersion equation, corrects for Gaussian axial dispersion which occurs when a finite pulse is injected into the solvent stream which flows through the packed columns of the gel permeation chromatograph (GPC). A solution of the integral equation provides a differential molecular weight distribution (MWD) and molecular weight averages corrected for symmetrical axial dispersion. Previous workers[1,2] have attempted to solve for the corrected chromatogram numerically. These numerical solutions were not completely satisfactory in all cases. For example, when corrections for axial dispersion were appreciable, artificial maxima in the corrected MWD were present. Such maxima could lead to incorrect chromatogram interpretation and hence cannot be tolerated. The molecular weight averages obtained from these corrected MWD's appeared reasonable, however. When solving a set of ordinary differential equations of polymerization kinetics, it is usually a much easier task to solve for the molecular weight averages than for the explicit MWD itself. This suggested that an attempt to first solve for the dispersion corrected molecular weight averages from the chromatogram using the integral equation might be more rewarding than an attempt to solve for the corrected differential distribution.[3] Molecular weight averages (both corrected and uncorrected for symmetrical axial dispersion) obtained by Duerksen and Hamielec[4] using Tung's hermite polynomial method and by Balke and Hamielec[3] using Pierce and Armonas method showed an interesting symmetry, and correlated with a simple algebraic equation. This suggested that an analytical solution was possible and motivated the present investigation.

If we assume that chain length is a continuous variable, then the molecular weight averages may be expressed by

$$\frac{M_K(h)}{M_K(\infty)} = \frac{\int_{V_a}^{V_b} W(v)M(v)^{K-1}dv \Big/ \int_{V_a}^{V_b} W(v)M(v)^{K-2}dv}{\int_{V_a}^{V_b} F(v)M(v)^{K-1}dv \Big/ \int_{V_a}^{V_b} F(v)M(v)^{K-2}dv} \tag{1}$$

$$\text{with } K = 1, 2, \ldots$$

where:

$M_1(h) \equiv$ dispersion corrected number average chain length
$M_1(\infty) \equiv$ uncorrected number average chain length
$M_2(h) \equiv$ dispersion corrected weight average chain length
$M_2(\infty) \equiv$ uncorrected weight average chain length
$F(v) \equiv$ normalized GPC chromatogram uncorrected for dispersion
$W(v) \equiv$ normalized GPC chromatogram corrected for dispersion
$M(v) \equiv$ true molecular weight calibration curve
$V_a \equiv$ initial elution volume
$V_b \equiv$ final elution volume

It is well known that the calibration curve or segments of the curve can be represented by

$$V = C_1 - C_2 \log_{10} M(v) \quad C_1, C_2 > 0 \tag{2}$$

or alternatively

$$M(v) = D_1 \exp(-D_2 v) \quad D_1, D_2 > 0 \tag{3}$$

There is no loss in generality if we let $V_a \to -\infty$, $B_3 \to \infty$, so that eq. (1) becomes

$$\frac{M_1(h)}{M_1(\infty)} = \frac{\int_{-\infty}^{\infty} F(v) \exp(D_2 v) dv}{\int_{-\infty}^{\infty} W(v) \exp(D_2 v) dv} = \frac{\bar{F}(-D_2)}{\bar{W}(-D_2)} \tag{4}$$

$$\frac{M_2(h)}{M_2(\infty)} = \frac{\int_{-\infty}^{\infty} W(v) \exp(-D_2 v) dv}{\int_{-\infty}^{\infty} F(v) \exp(-D_2 v) VD} = \frac{\bar{W}(D_2)}{\bar{F}(D_2)} \tag{5}$$

and so on.

Where $\bar{F}$ and $\bar{W}$ are the bilateral Laplace transforms of F and W, respectively. In order for these transforms to exist it is sufficient that $F(v)$ and $W(v)$ satisfy

$$\lim_{v \to \infty} \{F(v)\, e^{|D_2|v}\} < \infty \tag{6}$$

$$\lim_{v \to \infty} \{W(v)\, e^{|D_2|v}\} < \infty$$

Fortunately, we can claim these conditions to be satisfied from the physical shape of the chromatogram and calibration curve.

Tung's axial dispersion eq. (1) then is

$$F(v) = \left(\frac{h}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} W(y) \exp\{-h(v-y)^2\} dy \tag{7}$$

which can be considered the convolution integral of the bilateral Laplace transformation. Hence

$$\bar{F}(s) = \bar{W}(s) \left(\frac{h}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \exp\{-hv^2\} \exp\{-sv\} dv \tag{8}$$

$$= \bar{W}(s) \left(\frac{h}{\pi}\right)^{1/2} \exp\left\{\frac{s^2}{4h}\right\} \int_{-\infty}^{\infty} \exp\{-hx^2\} dx \tag{9}$$

where the integrals are assured of existence for all s and $h > 0$. The last integral on the right is $(\pi/h)^{1/2}$ so that

$$\bar{F}(s) = \bar{W}(s) \exp\left\{\frac{s^2}{4h}\right\} \tag{9}$$

Applying this result to eq. (4) and (5) we get

$$\frac{M_1(h)}{M_1(\infty)} = \exp\left\{\frac{(D_2)^2}{4h}\right\} \tag{10}$$

$$\frac{M_2(h)}{M_2(\infty)} = \exp\left\{\frac{-(D_2)^2}{4h}\right\} \tag{11}$$

$$\frac{M_K(h)}{M_K(\infty)} = \exp\{(3 - 2K)(D_2)^2/4h\} \tag{12}$$

$$K = 1, 2, \ldots$$

The ratios of corrected to uncorrected moments may be expressed as

$$\frac{Q_K(h)}{Q_K(\infty)} = \exp(-D_2{}^2/4h) \prod_{j=0}^{K-1} \exp\{(3 - 2(K - j))D_2{}^2/4h\} \tag{13}$$

where Q_K is the Kth moment of the distribution.

A next stage could be the calculation of the MWD from the corrected moments. A procedure suggested by Bamford et al.[5] is to use Laguerre polynomials $L_m(\rho)$

$$\frac{L_m(\rho)}{m!} = \sum_{i=0}^{m} \binom{m}{i} \frac{(-\rho)^i}{i!} \tag{14}$$

where $\rho = r/M_1(h)$ and $r = $ number of monomer units in the chain.

P_r, the concentration of polymer molecules containing r units is expanded in the form

$$P_r = \frac{\exp(-\rho)}{(M_1(h))^2} \sum_{m=0}^{\infty} \gamma_m \frac{L_m(\rho)}{m!} \tag{15}$$

The coefficients γ_m may be expressed in terms of the corrected moments as

$$\gamma_m = \sum_{i=0}^{m} \binom{m}{i} (-1)^i \left(\frac{Q_i(h)}{i!(M_1(h))^{i-1}} \right) \tag{16}$$

We cannot guarantee that this procedure for constructing the differential molecular weight distribution from the corrected moments will be free of artificial maxima. In fact it should be possible to show that solution through Laguerre polynomials is equivalent to that through Hermite polynomials as used by Tung.[1] Before any definite statements about the advantages of either method can be made, it would be necessary to make a comprehensive investigation of the method suggested by Bamford et al.[5]

Thus we have found an analytic solution for the ratio of corrected to uncorrected moments and molecular weight averages in terms of GPC parameters D_2 and h. For examples of its application to a variety of GPC operating conditions including situations where the calibration curve is not logarithmic and where the resolution factor varies significantly with elution volume, see the work of Balke and Hamielec.[3]

References

1. L. H. Tung, *J. Appl. Polym. Sci.*, **10**, 375 (1966).
2. P. E. Pierce and J. E. Armonas, *J. Polym. Sci.*, **23** (1968).
3. S. T. Balke and A. E. Hamielec, Paper presented at the 6th International GPC Seminar, Miami Beach, October (1968) and accepted for publication in the *J. Appl. Polym. Sci.*, November (1968).
4. J. H. Duerksen and A. E. Hamielec, *J. Polym. Sci.*, **83** (1968).
5. Bamford, Barb, Jenkins, and Onyon, *The Kinetics of Vinyl Polymerization by Radical Mechanisms*, Butterworths (1958) p. 292.

A. E. HAMIELEC
W. H. RAY

McMaster University, Canada
University of Waterloo, Canada