Polymer Bulletin 10, 478–481 (1983)

Polymer Bulletin

© Springer-Verlag 1983

Analytical Solution of the Effect of Axial Dispersion in the Analysis of a Polymer with the Log-Normal Distribution by Gel Permeation Chromatography with a Molecular Weight Detector

Miloš Netopilík

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, CS-162 06 Prague 6, Czechoslovakia

Summary

Integral equations describing the effect of axial dispersion on data of the scattering cell and on-line viscometer which serve as the molecular weight detector of the gel permeation chromatography apparatus can be solved in a special case (distribution curve of the polymer satisfies the log-normal distribution, calibration dependence of the column is linear) not only for the record of the concentration detector (TUNG, 1966), but also for the record obtained with the molecular weight detector. Due to axial dispersion, calibration dependence of the column calculated using the detector data is turned around the point whose coordinates on the elution volume axis lies just half-between modes of the records of the two detectors; the dependence remains however linear.

Introduction

The effect of axial dispersion on the data of a gel permeation chromatograph (GPC), provided in addition to the concentration detector also with a so-called molecular weight detector (automatic viscometer, scattering cell), has been described mathematically (KOTAKA, 1977; BERGER, 1978), and the problem of correction of data obtained by the GPC apparatus in the given arrangement has in principle been solved. It has been shown in a preceding communication (NETOPILÍK, 1982) that the problem of correction of the molecular weight detector record can be transformed into one that is mathematically equivalent to the correction of the concentration detector data, which means that the problem can be solved by employing identical mathematical procedures.

In this study it is shown that in a special case where the calibration dependence of the column is linear, the distribution curve of the polymer satisfies the log-normal distribution and the assumed function of spreading has the shape of the Gaussian normal distribution, an analytical relation can be found between the experimental and corrected quantities not only for the concentration record (TUNG, 1966) but also for the molecular weight detector record.

Theory

The relation between the experimentally accessible chromatogram $F(V)$ as a function of the elution volume V and the so-called corrected chromatogram $W(y)$ as a function of the retention volume is described by the equation (TUNG, 1966)

$$F(V) = \int_{V_1}^{V_2} W(y)\,G(V,y)\,dy \tag{1}$$

where V_1, V_2 are limiting values of the chromatogram on the elution volume axis and $G(V,y)$ is the so-called spreading function, which is assumed to have the form

$$G(V,y) = \sqrt{h/\pi}\,\exp\left[-h(V-y)^2\right] \tag{2}$$

where h is the spreading factor.

The corrected molecular weight $M(y)$ and the uncorrected value $\bar{M}(V)$ are related by (KOTAKA, 1977)

$$\bar{M}^a(V) = \frac{1}{F(V)} \int_{V_1}^{V_2} M^a(y)\,W(y)\,G(V,y)\,dy \tag{3}$$

where a is the exponent of the Mark-Houwink equation $[\eta] = K\,M^a$ ($[\eta]$ is intrinsic viscosity) for the viscometric detector, and $a = 1$ applies to the scattering cell. The products $\bar{M}^a(V)\,F(V)$ $M^a(y)\,W(y)$ respectively are the uncorrected and corrected records of the molecular weight detector (NETOPILÍK, 1982).

For a polymer with a molecular weight distribution curve which satisfies the log-normal distribution

$$w(M) = (1/\beta\sqrt{\pi}\,M)\,\exp\left[(-1/\beta^2)\,\ln^2(M/M_o)\right] \tag{4}$$

with parameters M_o and $\beta = \sqrt{2\,\ln M_w/M_n}$, and for which the calibration dependence of the column is given by

$$y = C_1 - \ln M\ C_2 \tag{5}$$

we obtain, using the relation

$$W(y) = -(M/C_2)\,w(M) \tag{6}$$

a corrected chromatogram corresponding to the distribution curve of the polymer as

$$W(y) = (1/C_2\beta\sqrt{\pi})\,\exp\left[-(1/C_2^2\beta^2)(y-y_o)^2\right] \tag{7}$$

where

$$y = C_1 - \ln M_o\ C_2 \tag{8}$$

By substituing the functions $W(y)$ and $G(V,y)$ from equations (2) and (7) in equation (1) $F(V)$ can be calculated (TUNG, 1966)

$$F(V) = \sqrt{\frac{h}{\pi(1 + C_2^2\beta^2 h)}}\ \exp\left[-\frac{h(V - y_o)^2}{1 + C_2^2\,{}^2 h}\right] \tag{9}$$

In this case, the functions W(y) and F(V) have the form of the Gaussian normal distribution.

Equations (5) and (7) allow us to express $M^a(y)W(y)$ which appears in equation (3). After rearrangement, we obtain

$$M^a(y)W(y) = \frac{M_o^a}{C_2\beta\sqrt{\pi}}\exp\left[\frac{a^2\beta^2}{4}\right]\exp\left[-\frac{1}{C_2^2\beta^2}\left(y_o - \frac{a\,C_2\beta^2}{2} - y\right)^2\right] \qquad (10)$$

After normalization (dividing by $M_o^a\exp\left[a^2\beta^2/4\right]$), this function differs from the function W(y) only by a displacement towards lower y values by the factor $aC_2\beta^2/2$. On substituting from equations (10) and (2) into equation (3), the integral on the right-hand side of this equation may be calculated by employing a procedure similar to that used in the calculation of F(V)

$$\bar{M}^a(V) = M_o^a\exp\left[a^2\beta^2/4\right]\exp\left[\frac{aC_2\beta^2 h}{1 + C_2^2\beta^2 h}\left(y_o - \frac{a\,C_2\beta^2}{4} - V\right)\right] \qquad (11)$$

By taking a logarithm and dividing a, we obtain the final relation for the calibration dependence calculated from the GPC detectors data which have been affected by spreading

$$\ln\bar{M}(V) = \frac{C_2^2\beta^2 h}{1 + C_2^2\beta^2 h}\,\frac{y_o - a\,C_2\beta^2/4 - V}{C_2} + \frac{a\beta^2}{4} + \ln M_o \qquad (12)$$

Discussion

For various values of the spreading factor h, equation (12) obviously represents a system of straight lines which pass through a point having the coordinates $y_o - aC_2\beta^2/4$ and $\ln M_o + a\beta^2/4$; in the limit $h \longrightarrow \infty$ (i.e. for an ideal column with an infinite resolution power) it represents equation (5). The y coordinate of the interesection of these straight lines lies in half-between modes of the curves determined by equations (9) and (10). Thus, axial dispersion leads to a revolution of the calibration dependence calculated from the detectors data, but linearity of the calibration dependence for the polymer with the log-normal distribution remains unchanged. This conclusion holds however only under the simplifying assumptions mentioned here: model calculations (KOTAKA, 1977; NETOPILÍK, 1982) have shown that with a different type of molecular weight distribution of the analyzed polymer the effect of axial dispersion leads to a curvature in the dependence of $\ln\bar{M}$ as a function of V. Hence, the use of relation (12) is restricted to polymers with a narrow molecular weight distribution, where approximation of the log-normal distribution can be applied.

Equation (12) makes possible a graphic determination of the spreading factor h, by comparing the course of the functions ln $\bar{M}(V)$ and ln M)y). In order to compare both calibration dependences, we shall rewrite equation (12) in the form

$$V = y_o - (C_2/A) \ln M/\bar{M}_o \tag{13}$$

where

$$A = C_2^2 \beta^2 h/(1 + C_2^2 \beta^2 h) \tag{14}$$

and

$$\bar{M}_o = M_o \exp\left[(a\beta^2/4)(1 - A)\right] \tag{15}$$

Obviously, the spreading factor h can be determined from the difference (reflected in the factor A) in the slopes of the two calibration lines. Another graphic procedure is based on a calculation which uses equation (9) from the variance σ^2 of the function F(V) (Gaussian normal distribution) (KENDRICK, 1969). The relation for h may be written as

$$h = 1/(2\sigma^2 - C_2^2 \beta^2) \tag{16}$$

A comparison between the h values determined under the above assumptions may be used, e.g., in checking the correctness of determination of the transport lag between the two detectors, which can considerably affect the accuracy of calculation of the function ln $\bar{M}(V)$.

Let us now compare the distribution functions correspoding to the spread chromatogram F(V). First we consider the distribution calculated from the data of the two detectors. As the calibration line (cf. Eq. (13)) is rotated due to spreading, the modus $\bar{M}_o$ of this distribution is shifted and is given by equation (15), as is easily proved by inserting $V = y_o$ into equation (12). If β_d given by

$$\beta_d = \beta\sqrt{A} \tag{17}$$

is substituted into equation (9) and the latter is then compared with equation (7), we see that $\beta_d = \sqrt{2 \ln (M_w/M_n)_d}$ is the second parameter of the distribution. The subscript d indicates that the values are evaluated from the data of the two detectors.

If the molecular weight detector is not used and the distribution is calculated from the known calibration dependence, equation (5), the value of parameter M_o does not change and the quality $\beta_c = \sqrt{2 \ln (M_w/M_n)_c}$ is given by

$$\beta_c = \beta/\sqrt{A} \tag{18}$$

By comparing the last two equations, we see that

$$(M_w/M_n)_d = (M_w/M_n)_c^A \tag{19}$$

This equation may also be used for checking the correct evaluation of the data of the two detectors.

References

BERGER, K.C., Makromol. Chem. 179, 719 (1978).
KENDRICK, T.C., J. Polym. Sci. Part A-2, 7, 297 (1969).
KOTAKA, T., J. Appl. Polym. Sci. 21, 501 (1977).
NETOPILÍK, M., Polymer Bull. 7, 575 (1982).
TUNG, L.H., J. Appl. Polym. Sci. 10, 375 (1966).

Accepted July 21, 1983