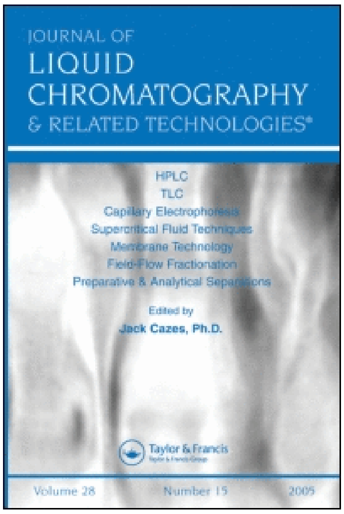

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A NEW METHOD OF THE PEAK SPREADING CORRECTION IN GPC BY MEANS OF WESSLAU'S AND TUNG'S MOLECULAR WEIGHT DISTRIBUTION FUNCTIONS

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ABSTRACT

Peak spreading correction by means of model molecular weight distribution functions, such as Wesslau's and Tung's, were described by using the method of the dimensionless parameters. The methods are convenient and simple. Peak shift for the peak skew distribution has also been found and a method of correcting the peak shift has been proposed. Procedures of the correction method are described.

INTRODUCTION

Like any other type of chromatography, the resolution of GPC is not unlimited. Hence, one of the important problems associated with the determination of the molecular weight distribution (MWD) of polymers by GPC is the correction of imperfect resolution due to peak spreading. Numerous methods for the peak spreading correction in GPC have already been proposed, such as Fourier transform method (1-5), the gradient method

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(6, 7), the method of singular value decomposition (8) and the iteration method (9-12). Some of them are feasible and effective, but unfortunately tedious and complicated.

In this paper, we propose to carry out the peak spreading correction in GPC by means of model MWD functions (13), such as Wesslau's and Tung's. The proposed methods are simple and convenient. Since the method of dimensionless parameters was used in treating the problem, the present method should have broader universality.

The continuous experimental GPC chromatogram f(x) is related to the peak spreading function G(x,y) and the true MWD function W(y) by the integral equation after Tung (14):

$$\int_{-\infty}^{\infty} G(x,y)\, W(y)\, dy = f(x), \qquad x,y \in (-\infty,\infty) \tag{1}$$

where x and y are the elution volumes, but y is associated with the integral. Assume G(x,y) to be a Gaussian function, we have

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

where h is the resolution factor in GPC column and f(x) and W(y) are normalized with respect to area under the chromatogram curve.

1. **The** case of normal distribution:

If the MWD of polymers can be represented by Wesslau's distribution (15) and the calibration curve is linear, the GPC chromatogram will be of the normal distribution. Wesslau's molecular weight distribution can be shown as follows,

$$W_w(M) = (\sqrt{2\pi}\,\sigma_1 M)^{-1} \exp\left\{(-1/2)[(\ln M - \ln M_1)/\sigma_1]^2\right\} \tag{3}$$

where M is the molecular weight, M_1 is the molecular weight at the peak position and σ_1 is the peak width parameter. The linear calibration curve is,

$$M = D_1 \exp(-D_2\, y) \tag{4}$$

which can be obtained by calibration with standards. From eq. (3) and eq. (4), we can obtain Wesslau's distribution with respect to the elution volume as follows:

$$W_w(y) = (h_1/\sqrt{\pi})\exp(-h_1^2 (y-y_1)^2) \tag{5}$$

$$\text{where } h_1 = D_2/(\sqrt{2}\,\sigma_1), \qquad y_1 = (1/D_2)\ln(D_1/M_1) \tag{6}$$

h_1 is the peak width parameter and y_1 is the elution volume at the peak position. Substituting eq. (2) and (5) into eq. (1), integrating and computing extreme value of f(x) with respect to x, the following formulae can be obtained,

$$f_{max} / h = u_1 \left(\pi \left(1 + u_1 \right)^2 \right)^{1/2} \tag{7}$$

and

$$f_{max} / h_1 = 1 / \left(\pi \left(1 + u_1^2 \right) \right)^{1/2} \tag{8}$$

where

$$u_1 = h_1 / h = \sigma / \sigma_1 \quad , \quad \sigma = D_2 / (\sqrt{2}\ h) \tag{9}$$

u_1 is the peak width ratio between the width of the column spreading in GPC and the width of MWD. σ is the width parameter of the column spreading in GPC. f_{max} is the peak height of the chromatogram. The relationships between f_{max}/h and f_{max}/h_1 and u_1 are shown in Fig. 1. It can be seen that f_{max}/h and f_{max}/h_1 are merely the function of the sole parameter u_1. Similar property exists in Lansing-Kraemer molecular weight distribution function.

Now we make the dimension analysis on f_{max}/h, f_{max}/h_1 and u_1. Because f(x) is normalized with respect to area, then

$$[f] = [f^p] / ([f^p][x]) = 1 / [x] \tag{10}$$

of course $[f_{max}] = 1 / [x]$, and

$$[h_1] = 1 / [x] \quad , \quad [h] = [h_1] \tag{11}$$

where $[f^p]$ has the dimension of f^p, and f^p is the height of the primitive chromatogram. $[x]$ has the dimension of the elution volume x. Hence f_{max}/h , f_{max}/h_1 and u_1 are dimensionless parameters. Therefore, even if various dimensions are used, the application of eq. (7) and (8) will not be confined. Their application in GPC will be discussed later.

2. The case of the peak skew distribution:

Since it is known that Tung's distribution (16) is very useful for the fitting in the peak skew MWD of polymers, we will expect that an analogous relationship, such as eq. (7) and (8), also exist for the Tung's distribution. Tung's distribution

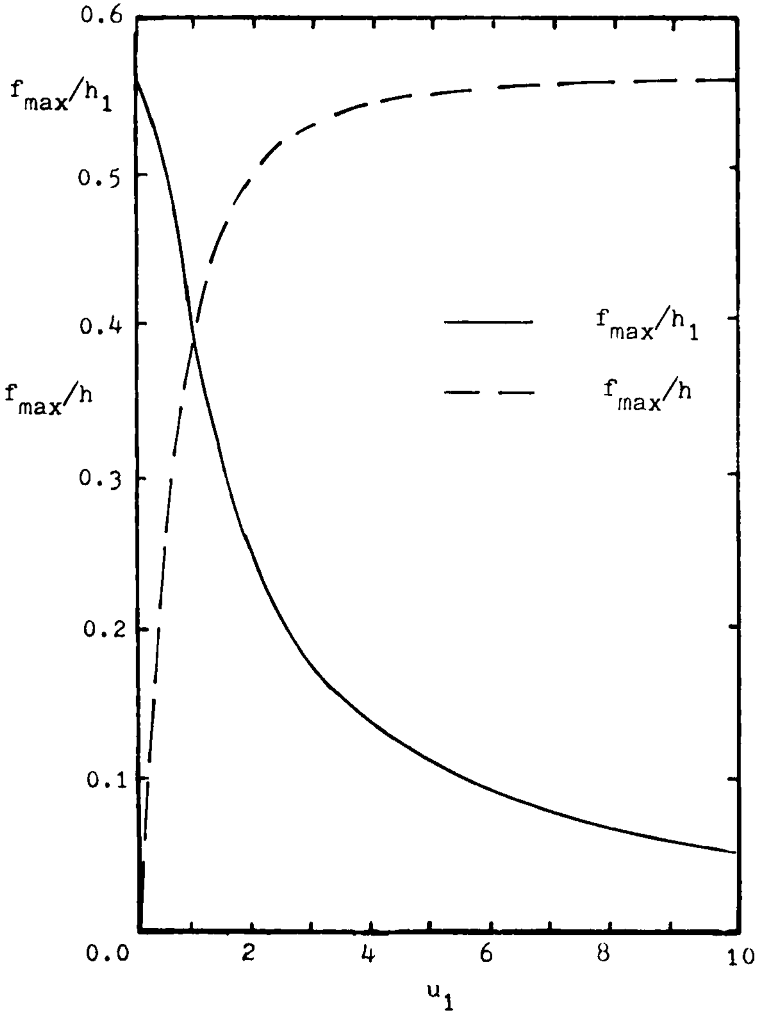

Fig.1 The relationship between f_{max}/h, f_{max}/h_1 and u_1 for the Wesslau's MWDF.

can be expressed as follows:

$$W_t(M) = (M\sigma_4)^{-1}(M/M_4)^{1/\sigma_4}\exp(-M/M_4)^{1/\sigma_4} \qquad (12)$$

where M_4 is the molecular weight at the peak position and σ_4 is the peak width parameter. We will see that these two parameters can be obtained from GPC. By using linear calibration curve, we can obtain Tung's distribution with respect to the elution volume from eq. (12) as follows:

$$W_t(y) = \sqrt{2}\,h_4\exp\left[-\sqrt{2}\,h_4(y-y_4)\right]\exp\left\{-\exp\left[-\sqrt{2}h_4(y-y_4)\right]\right\} \qquad (13)$$

where

$$h_4 = D_2/(\sqrt{2}\,\sigma_4), \qquad y_4 = (1/D_2)\ln(D_1/M_4) \qquad (14)$$

h_4 is the peak width parameter for Tung's MWD function in GPC and y_4 is the elution volume at the peak position for Tung's distribution eq. (13). Substituting eq. (2) and (13) into eq. (1), transfering independent variables x and y into X and Y and calculating the extreme value of f (X) with respect to X, the following formulae can be obtained:

$$f_{max}/h = u_4\,F(X_{max}, u_4) \qquad (15)$$

and

$$f_{max}/h_4 = F(X_{max}, u_4) \qquad (16)$$

where

$$u_4 = h_4/h = \sigma/\sigma_4 \qquad (17)$$

$$Y = h_4(y-y_4), \qquad X = h_4(x-y_4) \qquad (18)$$

and

$$X_{max} = h_4(x_4-y_4), \qquad X_{max}/u_4 = h(x_4-y_4) \qquad (19)$$

u_4 is the peak width ratio; x_4 and y_4 are the elution volumes at the peak positions of f (x) and W_t (y) for Tung's MWD function. We note that x_4 is not equal to y_4 for Tung's MWD function. X_{max} can be called the peak shift factor and $x_4 - y_4$ is called the peak shift.

$$F(X, u_4) = \sqrt{2/\pi}\,u_4^{-1}\int_{-\infty}^{\infty}\exp(-u_4^{-2}(X-Y)^2 - \sqrt{2}Y - \exp(-\sqrt{2}Y))\,dY \qquad (20)$$

To calculate the extreme value of F (X, u_4), from $dF(X,u_4)dX = 0$, we can finally obtain:

$$X_{max} = \bar{F}(X_{max}, u_4) / F(X_{max}, u_4) \qquad (21)$$

where

$$\bar{F}(X_{max}, u_4) = \sqrt{2/\pi}\, u_4^{-1} \int_{-\infty}^{\infty} Y \exp(-u_4^{-2}(X_{max}-Y)^2 - \sqrt{2}Y - \exp(-\sqrt{2}Y))dY \qquad (22)$$

$F(X_{max}, u_4)$ is expressed as eq. (20). X_{max} and X_{max}/u_4 can be determined by the iteration method for a given u_4 through eq. (21). We note that X_{max} and X_{max}/u_4 are also the functions of u_4 only. Thus, f_{max}/h_4 and f_{max}/h can also be determined by u_4 only. It is an important property of Tung's MWD function. Such property does not exist in Schulz-Zimm MWD function (17). The relationship between f_{max}/h_4, f_{max}/h, X_{max}, X_{max}/u_4 and u_4 for Tung's distribution are shown in Fig. 2. These relationships will be used to correct the peak spreading in GPC later.

From eq. (19) we can see that $x_4 - y_4$ is directly proportional to X_{max} for a given h_4. However, for the given h_4, X_{max} monotonously decreases as h increases as shown in Fig. 2, thus $x_4 - y_4$ will monotonously decrease with h. From the second equation of eq. (19) and Fig. 2 for a given h, $x_4 - y_4$ monotonously increases as h_4 increases when $u_4 < 1$. When $u_4 > 1$, $x_4 - y_4$ monotonously decreases with h_4 as shown in Fig. 3. Thus, the peak shift $x_4 - y_4$ will arrive at maximum when h_4 (or σ_4), the peak width parameter of MWD of the polymer, is the same as that of GPC column h (or σ).

We can also obtain the expression of M_4 through eq. (14) and the first equation in eq. (19) as follows:

$$M_4 = M_4' \exp(D_2 X_{max}/h_4), \quad M_4' = D_1 \exp(-D_2 x_4) \qquad (23)$$

The parameters on the right side of eq. (23) can all be determined by GPC. M_4' is the molecular weight at the peak position of the experimental chromagram f (x). The factor $\exp(D_2 X_{max}/h_4)$ is the ratio of the corrected MW at the peak position to the uncorrected one. The relationship between $\exp(D_2 X_{max}/h_4)$ and u_4 is shown in Fig. 4. We can see that the peak shift correction is quite important.

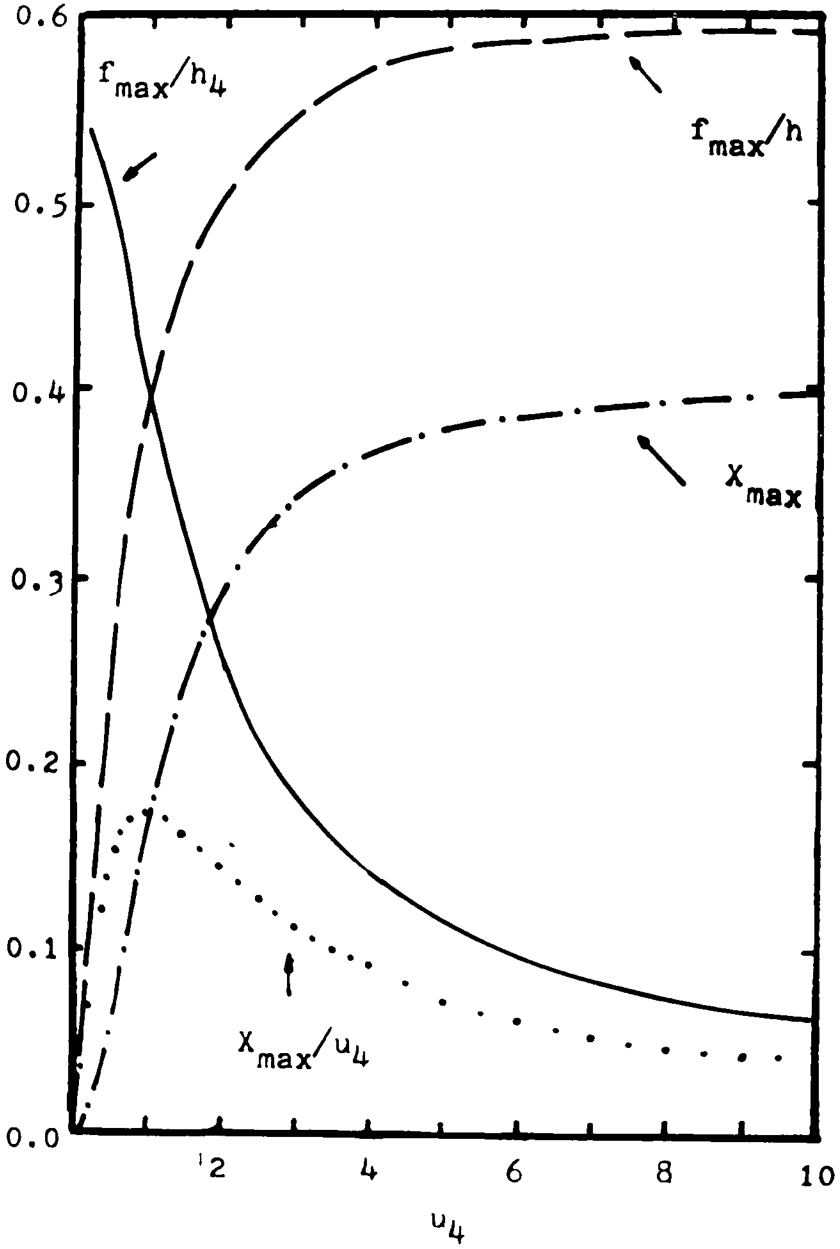

Fig.2 f_{max}/h, f_{max}/h_4, X_{max}, X_{max}/u_4 versus u_4 for Tung's MWDF

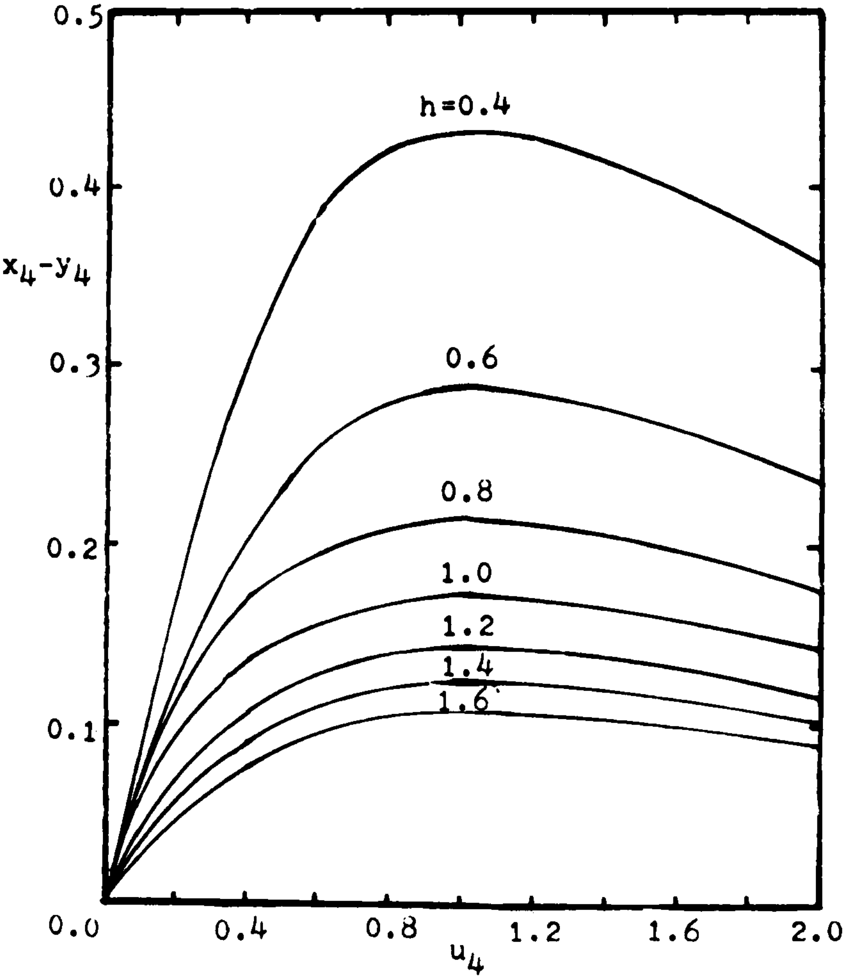

Fig.3 x_4-y_4 versus u_4 for Tung's MWDF

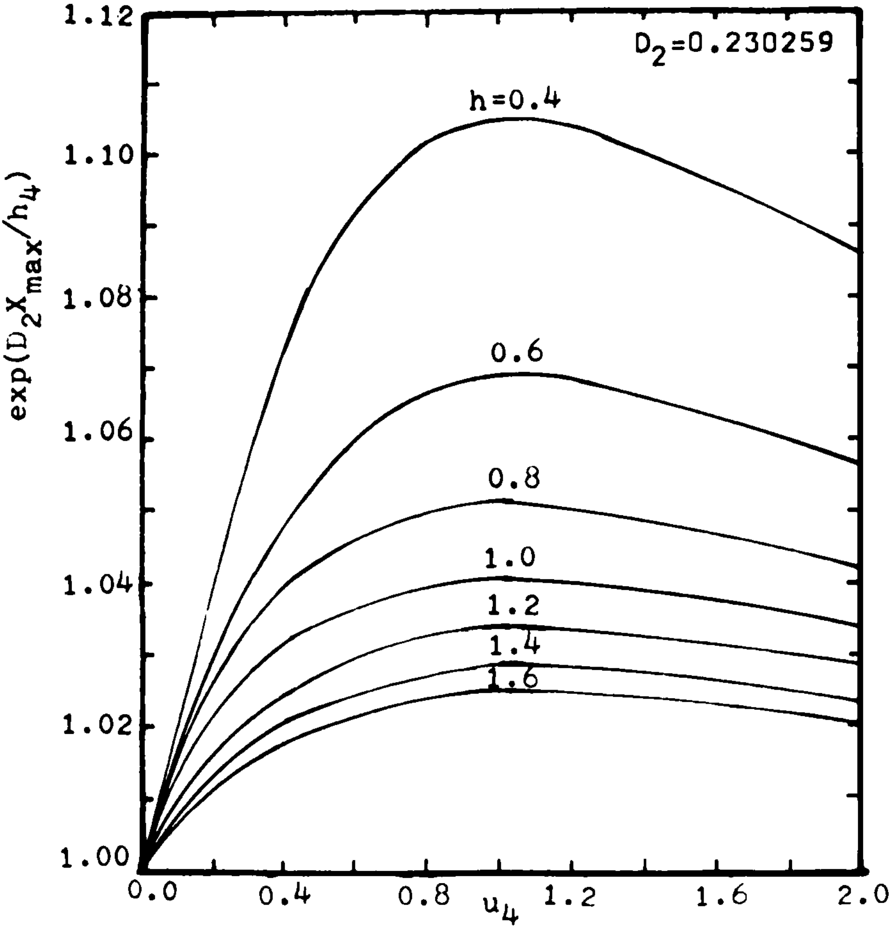

Fig.4 $\exp(D_2X_{max}/h_4)$ versus u_4 for Tung's MWDF

In conclusion, the procedures of the peak spreading correction suggested in this paper are:

(1) The determination of h: Given D_2 and the polydispersity ratio of the standard sample d, ($d = M_w / M_n) = \exp \sigma_1^2$ for Wesslau's MWD function and $d = \pi \sigma_4 / \sin (\pi \sigma_4)$ for Tung's MWD function) , σ_1 (or σ_4) can be determined, and hence h_1 (or h_4) for the standard sample from eq. (6) or eq. (14) respectively. Knowing the value of f_{max} of the standard sample from GPC, f_{max} / h_1 (or f_{max} / h_4) can be obtained. By using the relationship f_{max} / h_1 and u_1 (or f_{max} / h_4 and u_4) in Fig. 1 (or Fig. 2), u_1 (or u_4) can be determined and hence h from the first equation of eq. (9) (or eq. (17)). We can finally obtain σ from the second equation of eq. (9).

(2) The determination of σ_1 (or σ_4) and M_1 (or M_4): Given h by (1) and f_{max} by GPC for an unknown sample and using

TABLE 1
Various Averages for Wesslau's and Tung's Distribution

Items	Wesslau's	Tung's
M_n	$M_1 \exp(-\sigma_1^2/2)$	$M_4 / \Gamma(1-\sigma_4)$
M_w	$M_1 \exp(\sigma_1^2/2)$	$M_4 \Gamma(1+\sigma_4)$
M_w/M_n	$\exp \sigma_1^2$	$\pi \sigma_4 / \sin(\pi \sigma_4)$
M_z	$M_1 \exp(\frac{3}{2}\sigma_1^2)$	$M_4 \frac{\Gamma(1+2\sigma_4)}{\Gamma(1+\sigma_4)}$
M_{z+1}	$M_1 \exp(\frac{5}{2}\sigma_1^2)$	$M_4 \frac{\Gamma(1+3\sigma_4)}{\Gamma(1+2\sigma_4)}$
M_v	$M_1 \exp(\frac{\alpha}{2}\sigma_1^2)$	$M_4 [\Gamma(\alpha\sigma_4+1)]^{1/\alpha}$
$[\eta]$	$K M_1^{\alpha} \exp(\frac{\alpha^2}{2}\sigma_1^2)$	$K M_4^{\alpha} \Gamma(1+\alpha\sigma_4)$

the relationship between f_{max} / h and u_1 (or f_{max} / h and u_4), we can then obtain u_1 (or u_4), and hence h_1 (or h_4) from the first equation of eq. (9) (or from eq. (17)). Finally, knowing h_1 (or h_4), σ_1 (or σ_4) can be obtained by the first equation of eq. (6) (or eq. (14)). We note that $X_{max} = 0$ for Wesslau's MWD function, then $x_1 = y_1$. Knowing x_1 from GPC, hence y_1, finally M_1 can be determined by the second equation of eq.(6). According to the relationship between X_{max} and u_4 as shown in Fig. 2, we can obtain X_{max} for the known value of u_4 for Tung's MWD function. x_4 can be obtained too. Thus, M_4 can be obtained through eq. (23) for Tung's MWD function as shown in Fig. 4.

(3) Knowing σ_1 (or σ_4) and M_1 (or M_4), we can obtain the various average molecular weight, MWD and the integral distribution of molecular weight of polymer as shown in Table 1.

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