JOURNAL OF APPLIED POLYMER SCIENCE VOL. 21, 501–514 (1977)

Gel Permeation Chromatography: Dispersion Effects on Molecular Weight Monitor-Installed Gel Permeation Chromatograph

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Synopsis

Computer simulation was carried out to examine the performance of a molecular weight (MW) monitor-installed gel permeation chromatograph (GPC), by taking account of the effects of limited column resolution according to Tung's phenomenological scheme. Efficiency of GPC fractionation was discussed also in the same light. For simulated GPC fractionation results of model polymers having log-normal distribution, various average MW's and MWD functions were calculated from the data obtained by the MW monitor method as well as the conventional MW calibration methods, and compared with the given true values. The MW monitor method generally tends to predict narrower distributions than the true ones, as opposed to the conventional calibration methods which usually predict broader distributions. For certain simple cases, semiquantitative relation between the extent of column resolution and these deduced average MW's was derived. The efficiency of GPC fractionation (as judged, for example, by the polydispersity of recovered fractions) is limited by such factors as fraction size, column resolution, and polydispersity of the original sample itself.

INTRODUCTION

A recent significant advance in gel permeation chromatography (GPC) is undoubtedly the installation of molecular weight detectors,[1-6] which enables one to monitor molecular weights of GPC effluents. Particularly, a low-angle laser light-scattering (LALLS) system[7] developed and combined with GPC by Ouano[1,2] allows one to determine weight-average molecular weights M_w of the effluents in a continuous fashion. Then, the average molecular weights and the molecular weight distribution (MWD) can be determined directly rather than through a log (molecular weight M) versus elution volume v calibration, as is done by conventional GPC methods. Use of narrow-distribution standards is, therefore, unnecessary, and this widens the applicability of GPC methods to virtually any polymer systems for which such standards are not available.

However, even in such a molecular weight monitor-installed GPC unit, the basic separation mechanism is all the same as any other conventional GPC units. The outcome is then subject to the dispersion effect or to the band-broadening effects due to the limited resolution of GPC units.[8-10] We have carried out a computer simulation of GPC fractionation, being based on Tung's phenomenological scheme,[8,11] to examine the dispersion effects on a molecular weight

monitor-installed GPC unit. Assuming certain model polymer samples, we have calculated average molecular weights and MWD function reconstructed from such molecular weight monitor data as well as apparent values through the conventional log M versus v calibration method. These results were compared with the true values. Particularly, we considered a GPC unit which has a permeability limit and a distorted calibration curve. We will discuss the results here, in the hope of shedding light on interpreting GPC data from such a molecular weight monitor-installed GPC unit.

COMPUTER SIMULATION METHOD

GPC Chromatograms

The principle and procedures of the simulation here are the same as those in our previous paper.[11] We assume a log M versus v calibration with a permeability limit v_L as follows:

$$v = f(\log M) \tag{1}$$

where all the species with $M \geqq M_L$ should be eluted at v_L which equals to $f(\log M_L)$. Suppose a sample which has the log MWD function $w(\log M)$. First, using eq. (1), we fractionate the sample to construct a hypothetical chromatogram $F(v_i)\delta v$, which would be the chromatogram obtained if the GPC unit had unlimited resolution but the permeability limit v_L:

$$F(v_L)\delta v = \sum_{M_j \geqq M_L} w(\log M_j)\delta \log M \tag{2a}$$

$$F(v_i)\delta v = \sum_{\delta v} w(\log M_i)\delta \log M = \sum_{\delta v} C_2^{-1} w(\log M_i)\delta v \tag{2b}$$

$$C_2 = (dv/d \log M)_{M=M_j} \qquad (\delta v \to 0) \tag{2c}$$

Then, assuming that each fraction $F(v_i)\ \delta v$ would give a Gaussian-shape chromatogram with the dispersion parameter h_i, as suggested by Tung,[8] we construct the chromatogram as

$$G(v_k)\delta v = \sum_{i}^{\text{all}} F(y_i)(h_i/\pi)^{1/2} \exp[-h_i(v_k - y_i)^2]\delta y \delta v \tag{3}$$

where v_k and y_i are elution volumes. The parameter h may depend on v, and therefore is designated as h_i.

For the computer experiments, we assumed certain model polymers which have a log-normal MWD function:

$$w(M)d \log M = (2.3026/\beta\pi^{1/2}) \exp[-(1/\beta^2) \ln^2(M/M_0)]d \log M \tag{4a}$$

$$M_n = M_0 \exp(-\beta^2/4) \tag{4b}$$

$$M_w = M_0 \exp(\beta^2/4) \tag{4c}$$

where M_0 is the peak molecular weight and β is related to the polydispersity. In most cases, we further assumed the parameter $h_i \equiv h$ being constant, independent of elution volume v. Employing adequate values of h and log M versus v calibration, we calculated various average molecular weights and MWD functions

such as defined in the following sections, in order to compare them with molecular weight monitor-installed GPC data.

Average Molecular Weights

Generally the α-average molecular weight $M_\alpha{}^k$ of the effluent eluted at $v_k \sim v_k + \delta v$ may be defined as follows:

$$M_\alpha{}^k = \frac{\sum_i^{\text{all}} M_i{}^\alpha F(y_i)(h_i/\pi)^{1/2} \exp[-h_i(v_k - y_i)^2]\, \delta y,}{\sum_i^{\text{all}} M_i{}^{\alpha-1} F(y_i)(h_i/\pi)^{1/2} \exp[-h_i(v_k - y_i)^2]\, \delta y} \tag{5a}$$

where M_i is the true molecular weight of the ith fraction which appears at $y_i \sim y_i + \delta y$ in the hypothetical chromatogram $F(y_i)\, \delta y$. If we take $\alpha = 0$, the result is the number-average $M_n{}^k$; if $\alpha = 1$, the weight-average $M_w{}^k$ results; and so on. The LALLS monitoring system[1,2] would give the $M_w{}^k$ in a continuous fashion, while the viscometric monitoring system of Ouano[6] would give a more complicated viscosity-average $M_\eta{}^k$:

$$M_\eta{}^k = \frac{\sum_i^{\text{all}} M_i{}^a F(y_i)(h_i/\pi)^{1/2} \exp[-h_i(v_k - y_i)^2]\, \delta y}{\sum_i^{\text{all}} F(y_i)(h_i/\pi)^{1/2} \exp[-h_i(v_k - y_i)^2]\, \delta y} \tag{5b}$$

where a is the Mark-Houwink exponent.

If we collect effluents within a certain elution volume interval Δv, we can determine the various averages of each fraction by a batchwise manner rather than by a continuous fashion. Such is the case for a preparatory GPC, and also for a GPC with a batch-type viscometric monitor.[3-5] For such averages, the averages must be taken over the given elution volume interval Δv:

$$M_\alpha{}^\Delta = \frac{\sum_k^{\Delta v} M_\alpha{}^k G(v_k)\, \delta v}{\sum_k^{\Delta v} M_{\alpha-1}{}^k G(v_k)\, \delta v} \tag{5c}$$

where $M_\alpha{}^k$ and $M_{\alpha-1}{}^k$ are those defined by eqs. (5a) and (5b).

On the other hand, if we use a continuous M_w monitor such as Ouano's[1,2] LALLS system, we can establish a chromatogram $G(v_k)$ as a function of $M_w{}^k$. Then, using such chromatogram, we can calculate average molecular weights of the sample as a whole, which we temporarily refer to as the "reconstructed" averages, $M_n{}^{\text{rec}}$, $M_w{}^{\text{rec}}$, $M_z{}^{\text{rec}}$, etc.:

$$M_n{}^{\text{rec}} = \left[\sum_k G(v_k)\, \delta v\right] \Big/ \left[\sum_k (M_w{}^k)^{-1} G(v_k)\, \delta v\right] \tag{6a}$$

$$M_w{}^{\text{rec}} = \left[\sum_k (M_w{}^k) G(v_k)\, \delta v\right] \Big/ \left[\sum_k G(v_k)\, \delta v\right] \tag{6b}$$

$$M_z{}^{\text{rec}} = \left[\sum_k (M_w{}^k)^2 G(v_k)\, \delta v\right] \Big/ \left[\sum_k (M_w{}^k) G(v_k)\, \delta v\right] \tag{6c}$$

Here it should be noted that the "reconstructed" weight-average $M_w{}^{rec}$ should be always equal to the true weight-average M_w of the sample, while other averages are not so, unless the GPC has unlimited resolution. These "reconstructed" averages will coincide with one another when the sample is indeed monodisperse or when the GPC has no resolution whatsoever.[1,2] In the latter case, the $M_w{}^k$ values which the monitor measures are always equal to M_w, and then $M_w = M_n{}^{rec} = M_w{}^{rec} = M_z{}^{rec}$, etc.

As the column resolution becomes poorer, the M_w monitor data would give a result as if the sample distribution is narrower than it actually is. This is to be contrasted with the behavior of the apparent averages, $M_n{}^{app}$, $M_w{}^{app}$, $M_z{}^{app}$, etc., which are obtained by conventional calibration methods:

$$M_n{}^{app} = \left[\sum_k G(v_k)\,\delta v\right] \Big/ \left[\sum_k (M_e{}^k)^{-1} G(v_k)\,\delta v\right] \tag{7a}$$

$$M_w{}^{app} = \left[\sum_k (M_e{}^k) G(v_k)\,\delta v\right] \Big/ \left[\sum_k G(v_k)\,\delta v\right] \tag{7b}$$

$$M_z{}^{app} = \left[\sum_k (M_e{}^k)^2 G(v_k)\,\delta v\right] \Big/ \left[\sum_k (M_e{}^k) G(v_k)\,\delta v\right] \tag{7c}$$

where $M_e{}^k$ is the molecular weight value of the effluent at v_k determined from the calibration curve as $v_k = f(\log M_e{}^k)$. The apparent weight-average $M_w{}^{app}$ is usually larger and the apparent number-average $M_n{}^{app}$ smaller than the respective true values (unless the sample is eluted in the region near the v_L limit). As opposed to the M_w monitor method, as the column resolution becomes poorer, the conventional GPC methods predict as if the sample distribution were much broader than it actually is.

MWD Functions

Chromatograms of the form $G(v_k)$ versus $M_w{}^k$ or of the form $G(v_k)$ versus $M_e{}^k$ may be further interpreted as the MWD function. From the former, we obtain the integral and differential "reconstructed" MWD functions, respectively, as follows:

$$I^{rec}(M_w{}^k) = \sum_k^{M_w{}^j \le M_w{}^k} G(v_j)\,\delta v = \int^{M_w{}^k} G(v)\,dv \tag{8a}$$

$$W^{rec}(M_w{}^k) = dI^{rec}/d\,\log M_w{}^k = G(v_k)(dv/d\,\log M_w{}^k) \tag{8b}$$

while, from the latter, we obtain the apparent MWD functions as

$$I^{app}(M_e{}^k) = \sum_j^{M_e{}^j \le M_e{}^k} G(v_j)\,\delta v = \int^{M_e{}^k} G(v)\,dv \tag{9a}$$

$$W^{app}(M_e{}^k) = dI^{app}/d\,\log M_e{}^k = G(v_k)C_2(v_k) \tag{9b}$$

where $C_2(v_k)$ is the slope of the log M versus v calibration at v_k as defined by eq. (2c). The differential functions are given on the common logarithmic scale. We expect that the "reconstructed" MWD function is always narrower, while the apparent MWD function is broader than the true one (unless the sample contains a substantial amount of components beyond the v_L limit).

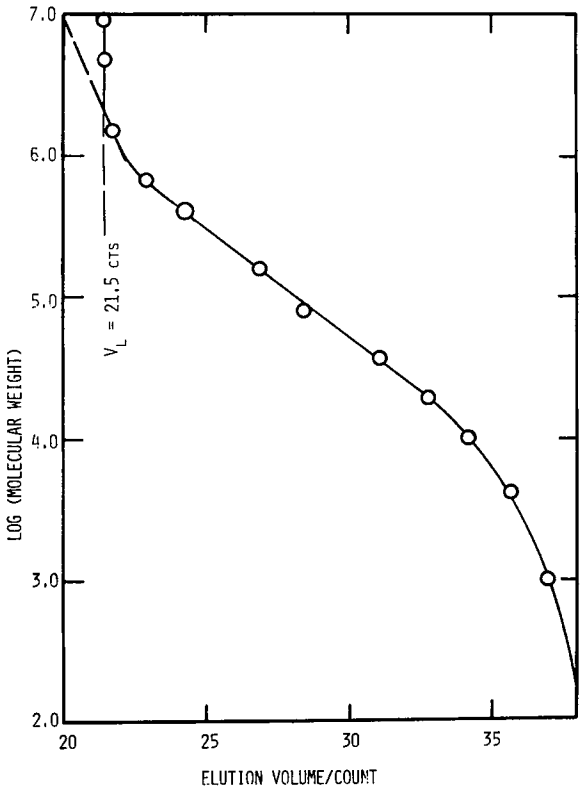

Fig. 1. Typical example of log M-vs.-v calibration curve constructed with narrow distribution polystyrene standards. Straight-line portion is approximated by $v = 60.98 - 6.557 \log M$.

RESULTS AND DISCUSSION

Average Molecular Weights

We consider two GPC units: One is an ordinary GPC which has a permeability limit v_L, which we assume as 21.5 count (1 count = 5 ml elution volume) and a somewhat distorted calibration curve such as shown in Figure 1. The other is an ideal GPC which has unlimited permeability and a logarithmic straight-line calibration:

$$v = C_1 - C_2 \log M \tag{10}$$

Here we employ $C_1 = 60.98$ and $C_2 = 6.557$, which are the values of the straight-line portion of the calibration curve in Figure 1.

First, we examine the behavior of the "reconstructed" averages with varying h parmeter. Figure 2 shows the plots of M_n^{rec}/M_n, M_w^{rec}/M_w, and Y^{rec}/Y ($Y = M_w/M_n$) versus h relations. As we have anticipated, the M_w^{rec}/M_w ratios are always unity, while the M_n^{rec}/M_n ratio (>1) approaches the true M_w/M_n and Y^{rec}/Y (<1) approaches $1/Y$ as h tends to zero. The relations between these ratios and h are somewhat dependent on the type of MWD of the sample, on the calibration curve, and on the h-versus-v relation (although here we assume constant h).

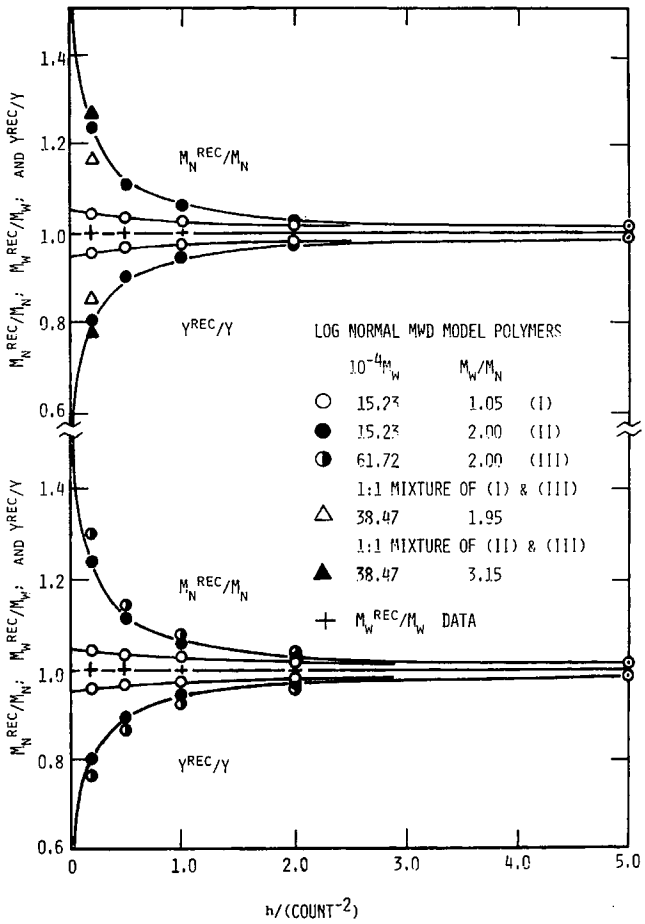

Fig. 2. Plots of $M_w{}^{rec}/M_n$, $M_w{}^{rec}/M_w$, and Y^{rec}/Y vs. h obtained by the ideal GPC unit (above) with logarithmic straight line calibration and by the conventional GPC unit (below), whose calibration is shown in Fig. 1. In the latter, solid curves are those of the ideal GPC unit.

Figure 3 shows the similar ratios for the apparent averages on an ideal GPC unit, which are

$$M_n{}^{app}/M_n = \exp(-D_2{}^2/4h) \tag{11a}$$

$$M_w{}^{app}/M_w = \exp(D_2{}^2/4h) \tag{11b}$$

$$Y^{app}/Y = \exp(D_2{}^2/2h) \tag{11c}$$

with $D_2 = 2.3026/C_2$ being constant. As anticipated, the $M_n{}^{app}/M_n$ is always smaller than unity, while the $M_w{}^{app}/M_w$ and Y^{app}/Y are always larger than unity. On such an ideal GPC unit, these ratios are the functions of only $D_2{}^2/h$ and do not depend on the type of the sample's MWD function. This feature enables one to construct, in principle, simultaneously the log M-versus-v calibration as well as the calibration for column resolution, i.e., the h-versus-v relation with a single broad distribution sample (of any MWD type) of known average molecular weights, as suggested earlier by Hamielec et al.[12] On the other hand,

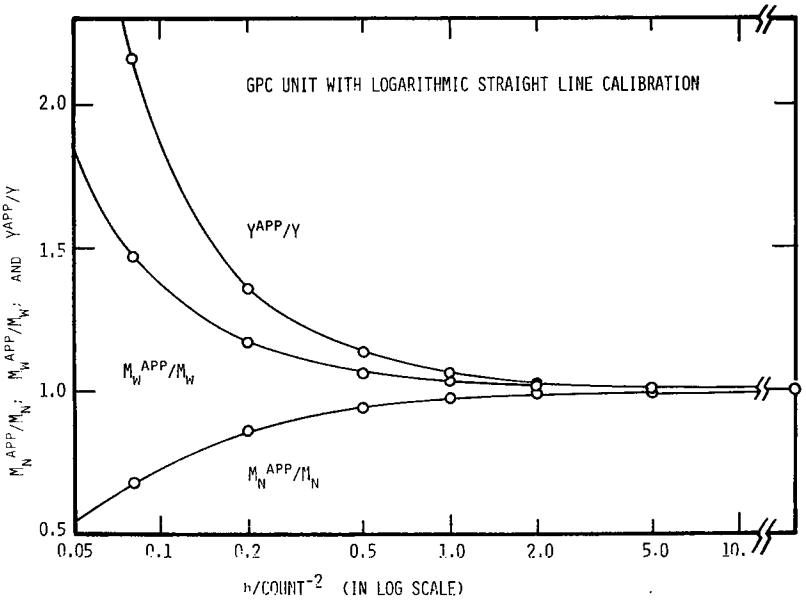

Fig. 3. Plots of M_n^{app}/M_n, M_w^{app}/M_w, and Y^{app}/Y vs. log h obtained by the ideal GPC unit.

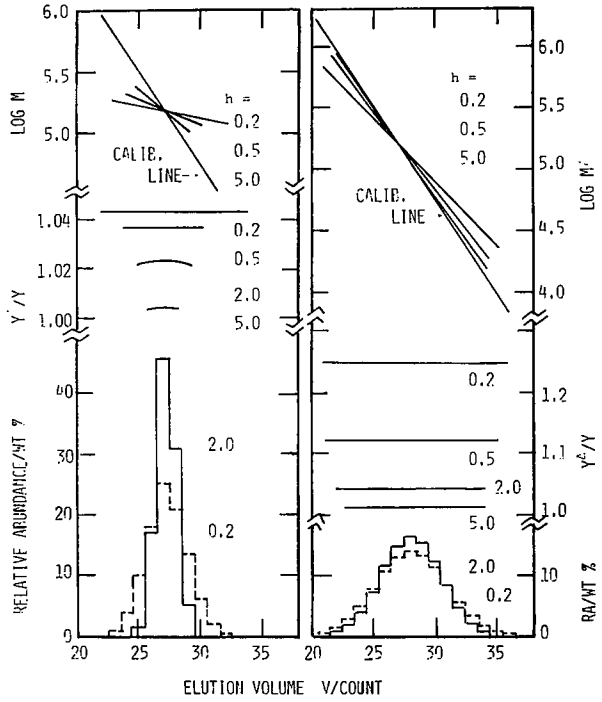

Fig. 4. Results of fractionation by the ideal GPC unit indicate plots of M_w^{Δ}, Y^{Δ}, and weight % vs. elution volume v of each fraction (size = 1 count interval) from log-normal MWD model polymers ($10^{-4} M_w = 15.23$) of narrow ($Y = 1.05$, left) and of broad ($Y = 2.00$, right) distributions. Several constant h values are assumed as indicated.

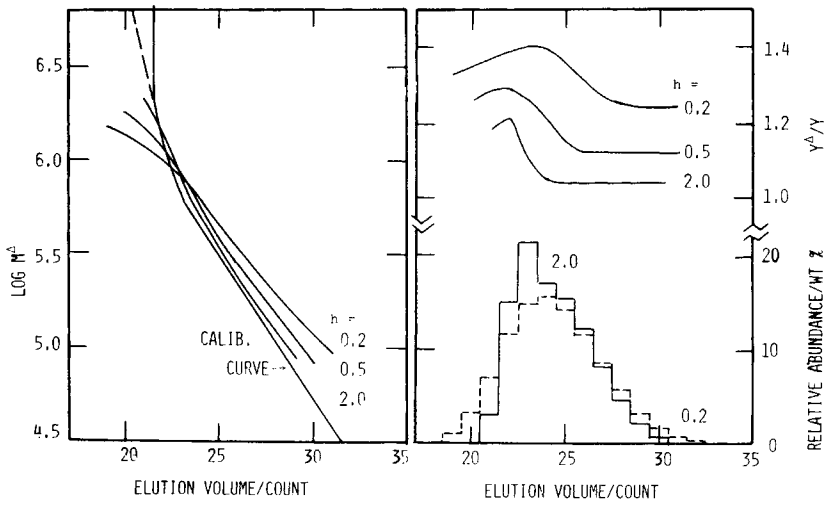

Fig. 5. Results of fractionation by the conventional GPC unit. For symbols, see Fig. 4. Polymer has $10^{-4} M_w = 61.72$ and $Y = 2.00$.

because of the net resolution being related with the factor D_2^2/h, these ratios are highly sensitive to even a slight distortion of the log M-versus-v calibration and become dependent on the feature of the sample's MWD. The simple relations of eq. (11) and, hence, the Hamielec method of killing two birds with one stone would become invalid for such practical GPC units. However, if the sample has sufficiently narrow distribution (say, $Y < 1.20$), the approximation assuming a monodisperse model sample appears to be sufficient to describe these ratios. The resulting equations are

$$M_n^{\text{app}}/M_n = \frac{\sum_k \exp[-h_e(v_k - v_e)^2]}{\sum_k (M_e/M_k) \exp[-h_e(v_k - v_e)^2]} \tag{12a}$$

$$M_w^{\text{app}}/M_w = \frac{\sum_k (M_k/M_e) \exp[-h_e(v_k - v_e)^2]}{\sum_k \exp[-h_e(v_k - v_e)^2]} \tag{12b}$$

etc., where M_k and M_e are, respectively, the molecular weights determined from the calibration $v = f(\log M)$ at a given elution volume v_k and at the peak elution volume v_e of the sample. These equations can be used to establish the calibration for column resolution if standard samples with narrow distribution are available.[11]

Efficiency of GPC Fractionation

Suppose we have collected GPC effluents at a certain elution volume interval and separately characterized each of these fractions. The average molecular weights of such fractions can be readily calculated by eqs. (5a)–(5c). Figure 4 summarizes the characteristics of the fractions from certain model polymers

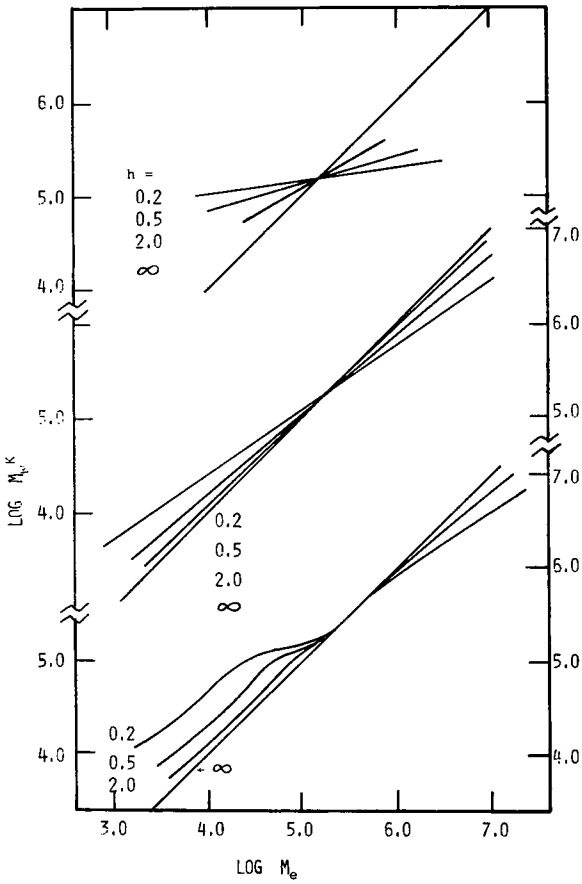

Fig. 6. Continuous M_w monitor data by the ideal GPC unit plotted as log $M_w{}^k$ vs. log $M_e{}^k$ with several constant h values as indicated. Log-normal MWD model polymers fractionated are (from top) $10^{-4} M_w = 15.23$ with $Y = 1.05$ with $Y = 2.00$, and 1:1 mixture of $10^{-4} M_w = 15.23$ with $Y = 1.05$ and $10^{-4} M_w = 61.72$ with $Y = 2.00$.

fractionated by the ideal GPC unit. The figure shows the plots of M_w, M_w/M_n, and weight % value of each fractions as functions of elution volumes. Here, we assume that the fractions are collected at every 1-count (= 5 ml elution volume) interval. Apparently, if the sample is monodisperse, the $M_w{}^\Delta$ values of all the fractions are the same, whereas, if the sample has broad distribution but the GPC unit has no resolution, again the $M_w{}^\Delta$ values are the same as the sample's M_w value. As the resolution has been improved, the plot of $M_w{}^\Delta$ versus v approaches more and more closely the log M-versus-v calibration. However, as we are collecting the effluents within a finite Δv interval, these fractions cannot be monodisperse, even when the column resolution is infinitely high. Usually, the level of $h = 2.0$ is perhaps the best we can hope for any practical GPC units. Then, the level of $Y = 1.02 \sim 1.05$ is the best we can expect by using such GPC units. Depending on the level of the GPC resolution ($\sim D_2{}^2/h$), the best attainable fractionation efficiency is automatically limited to a certain level such as mentioned above. Fractionation of a narrow distribution sample beyond such a limit is virtually impossible.

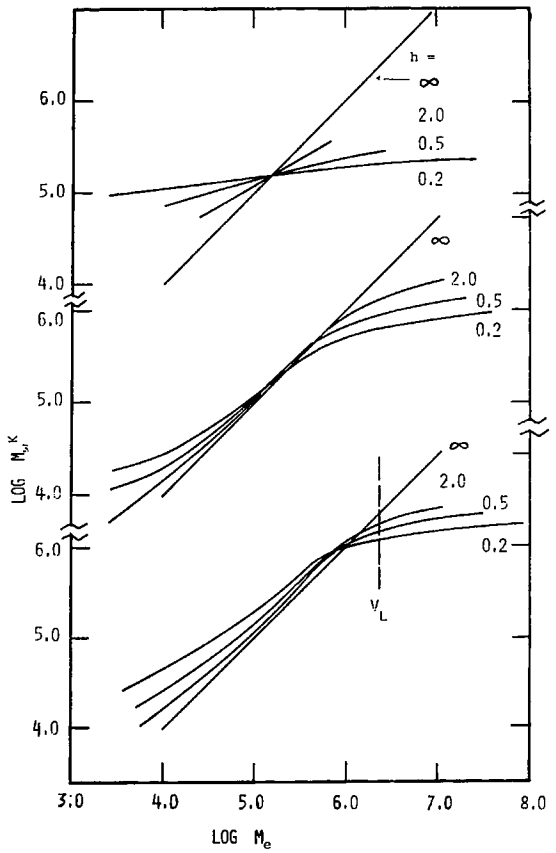

Fig. 7. Continuous M_w monitor data by the conventional GPC unit. Log-normal MWD model polymers fractionated are (from top) $10^{-4} M_w = 15.23$ with $Y = 1.05$ and $Y = 2.00$, and $10^{-4} M_w = 61.72$ with $Y = 2.00$ (see Fig. 6).

Figure 5 illustrates similar results obtained on the conventional GPC unit whose calibration curve is shown in Figure 1. Here, we consider a fairly high molecular weight model polymer, which contains a substantial amount of components beyond the v_L limit. As anticipated, the fractionation efficiency is very poor in the region near the v_L limit.

Therefore, it is advisable to calibrate gpc unit for the net resolution to be able to estimate its performance. For this purpose, Tung et al.[9] proposed a "reverse flow" technique. This can also be done by our method suggested before,[11] which consists of examining the behavior of a series of narrow distribution standards.

MWD Function From Chromatogram

We now turn our attention to the performance of continuous M_w monitor-installed GPC units. Figures 6 and 7 illustrate some examples of log $M_w{}^k$ versus log $M_e{}^k$ plots obtained, respectively, with the ideal and conventional GPC units. The behavior of such plots is essentially the same as that of the log $M_w{}^\Delta$ versus v plots in Figures 4 and 5. For model polymers having log-normal MWD tested

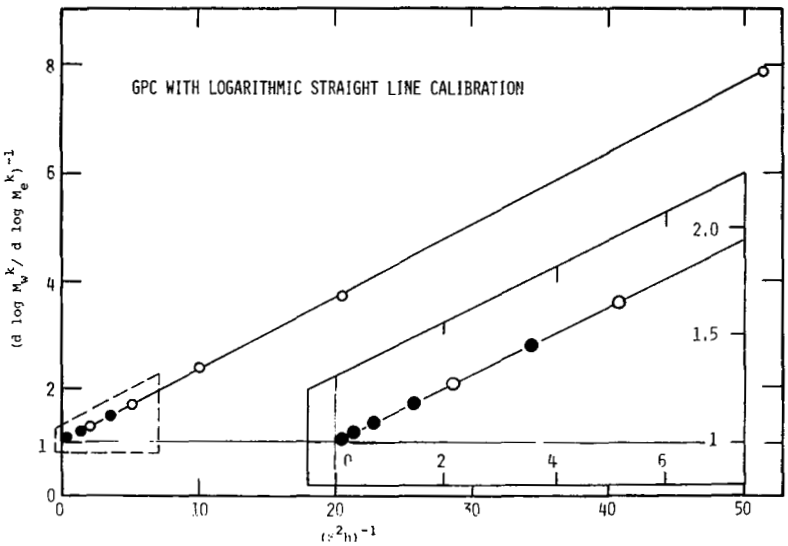

Fig. 8. Reciprocal slopes of the plots in Fig. 6 vs. $(\beta^2 h)^{-1}$ for log-normal MWD model polymers with $10^{-4} M_w = 15.25$ and $Y = 1.05$ (open circles), $10^{-4} M_w = 15.25$ and $Y = 2.00$ (closed circles), and $10^{-4} M_w = 61.72$ and $Y = 2.00$ (triangles). Plots are independent of M_w and Y as far as for log-normal MWD model polymers are concerned.

on the ideal GPC unit, the slope of the log $M_w{}^k$ versus log $M_e{}^k$ plots may be written simply as

$$\frac{d \log M_w{}^k}{d \log M_e{}^k} = \left[1 + \frac{D_2{}^2}{\beta^2 h}\right]^{-1} \tag{13}$$

Figure 8 shows an example of the reciprocal slope versus $(\beta^2 h)^{-1}$ plots. Since, for the log-normal MWD model polymers, we have $\beta^2 = 2 \ln (M_2/M_n)$, the slope tends to zero as M_w/M_n tends to unity; and also the slope varies from zero to unity, as the column resolution becomes better and better from zero (no resolution) to infinity (perfect resolution). Of course, if the sample's MWD is skewed (on logarithmic scale) and/or the calibration curves (i.e., either one or both of log M and h versus v) are distorted, the situation is more complicated (cf. Figs. 6c and 7). Nevertheless, the factor $(D_2{}^2/\beta^2 h)$ would roughly reflect the slope of such plots, which in turn is a measure for the net resolution of the GPC unit.

According to the above discussion, it is again clear that the use of a M_w monitor tends to predict a narrower distribution, whereas use of conventional calibration methods tends to predict a broader distribution than the true distribution. Figure 9 illustrates two examples of the comparison between the "reconstructed" versus apparent MWD functions calculated, respectively, by eqs. (8) and (9) obtained on the ideal GPC unit. Tung's statement[8,9] that the correction for the imperfect resolution of the GPC unit is important when the distribution is narrow, but minor when the distribution is broad appears to be true for the "reconstructed" MWD function as well.

We should emphasize that the statement is true when the MWD functions are directly compared and when a certain MWD parameter such as the peak width is compared.[13] However, when some other parameters such as $M_n{}^{app}/M_n$,

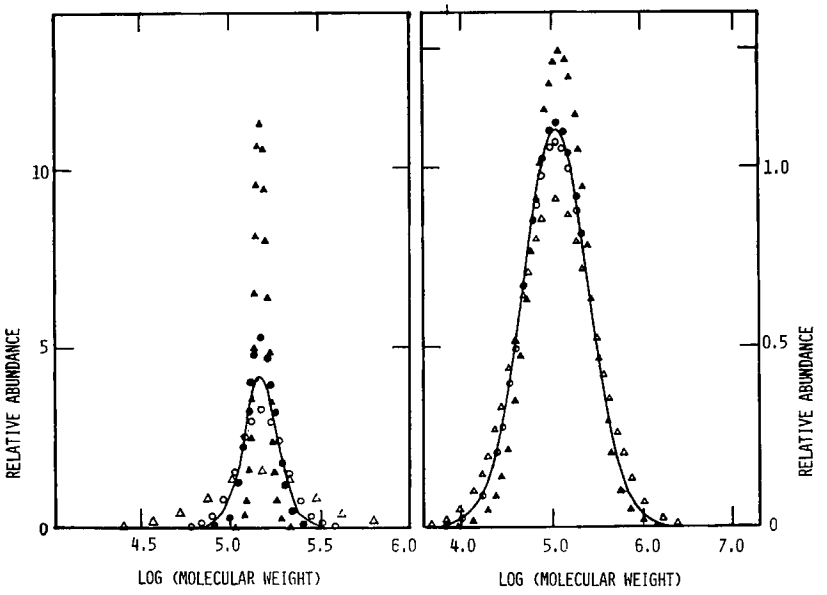

Fig. 9. Apparent (open symbols) and "reconstructed" (closed symbols) MWD functions derived from the ideal GPC data for log-normal MWD model polymers ($10^{-4} M_w = 15.23$) of narrow ($Y = 1.05$, left) and broad ($Y = 2.00$, right) distributions. Solid curves are original MWD functions, and two h values, 0.20 (triangles) and 2.00 (circles), are assumed.

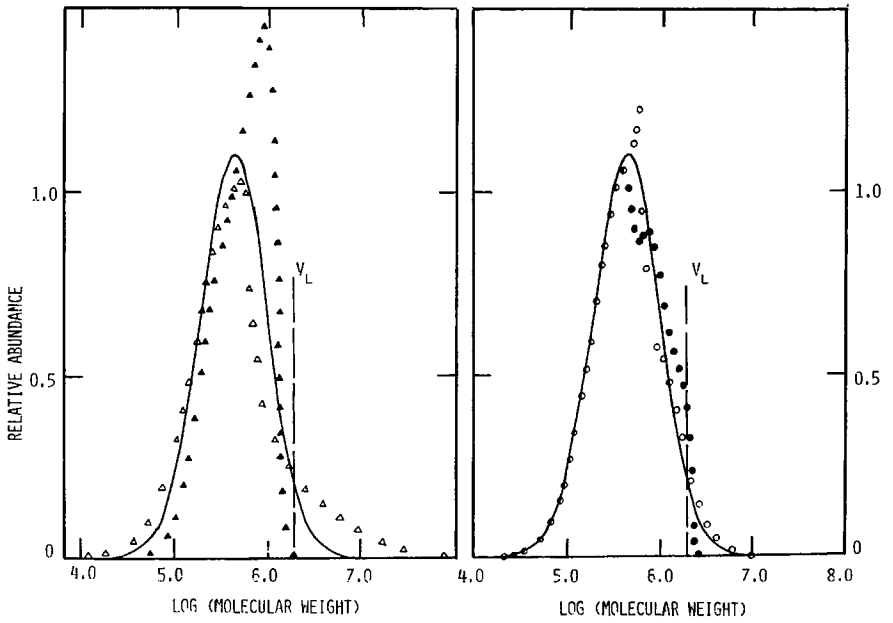

Fig. 10. Apparent and "reconstructed" MWD functions derived from the conventional GPC data for a high molecular weight ($10^{-4} M_w = 61.72$) and broad ($Y = 2.00$) distribution log-normal MWD model polymer. For symbols, see Fig. 9.

M_w^{app}/M_w, and M_n^{rec}/M_n are compared, the corrections depend on the factor D_2^2/h and not essentially on the MWD. In other words, the correction is important for broad MWD samples as well. Rather, we should say that if the calibration curve is distorted, the correction becomes much more difficult for broad MWD samples than for narrow MWD samples, since the approximation of logarithmic straight line calibration is better applicable to the latter. To demonstrate this point, we give an example in Figure 10 of the "reconstructed" and apparent MWD functions obtained for the conventional GPC unit. Here, we assumed a high molecular weight log-normal MWD sample, which contains a substantial amount of components beyond the v_L limit. We see severe distortion in both of the MWD functions, and even artificial shoulders in the MWD functions simulated for the GPC of high resolution. Apparently such artifacts have arisen from the existence of the v_L limit (or of the highly distorted region) in the calibration curve.

CONCLUSIONS

Data from a M_w monitor-installed GPC unit are also inevitably affected by the imperfect resolution. The best advantages of using such a GPC are undoubtedly that (i) use of narrow distribution standards is not an absolute requirement; and (ii) the M_w^{rec} values are always equal to the true M_w values within the accuracy of any absolute method of M_w determination, say, the light-scattering method. As opposed to the conventional molecular weight calibration method, (iii) use of a M_w monitor always tends to predict narrower distributions than the true ones: If the GPC unit has zero resolution, it predicts any sample as if it were monodisperse with a molecular weight equal to the true M_w values. Efficiency of GPC fractionation is also limited in the same way. (iv) The distribution of each fraction is affected, besides by the fraction size, by the net resolution of the GPC unit: a narrow distribution sample cannot be further fractionated beyond a certain limit, which is governed by the factor D_2^2/h. Because of these reasons, it is desirable even for a M_w monitor-installed GPC unit to calibrate it for the imperfect resolution just to know how large the corrections would be.

This analysis was inspired by a discussion with Dr. Benoit who visited us at Uji in May 1975. The author is greatly indebted also to Dr. Ouano of the IBM San Jose Laboratory for showing the results of his LALLS-installed GPC unit and many stimulating discussions. A part of this work was reported at a 1975 GPC seminar held at Pittsburgh, Pa., during October 15–17, 1975. The computer simulation was carried out with a Facom 230-48 digital computer (Fujitsu Ltd., Tokyo, Japan) of the Computer Laboratory of this Institute.

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Received January 28, 1976