JOURNAL OF APPLIED POLYMER SCIENCE VOL. 15, PP. 2321–2333 (1971)

GPC Calibration for Polymers of Unknown Composition and Structure Using a Real-Time Computer

GÉRARD BRAUN, *Esso Research S.A., 1920 Diegem, Belgium*

Synopsis

A computer technique ultimately yielding, from GPC data, both differential and integral molecular weight distributions of macromolecular products with unknown composition and structure has been worked out, based on a "universal" calibration method previously proposed by other authors to calculate average molecular weights. The technique involves as sole assumption the validity of the "universal" calibration for the kind of sample under investigation. The GPC output data are handled through a real-time computer program and punched on paper tape. Together with two experimental parameters of the polymer (average molecular weights, limiting flow number) and the "universal" calibration of the columns set, the tape is used as input for the off-line programming. Examples are presented, showing the accuracy which can be expected.

INTRODUCTION

The use of gels as a means of separating solutes differing in molecular size was already known as early as 1954,[1] and commercially available gels were introduced for this purpose in 1959.[3] Various kinds of gels are nowadays displayed on the market so that almost any separation problem can be successfully tackled whether large or small molecules are involved. Yet, although the need for a better method of determining the molecular weight distribution (MWD) of organic polymers was the reason for the tremendous development of gel permeation chromatography (GPC),[4] the interpretation of the chromatograms remains beset with difficulties. One of the major ones resides in the understanding of the exact mechanism of the GPC size-sorting process, already discussed by a number of authors[5] but not yet satisfactorily resolved.

In the meantime, however, the chromatograph columns need to be calibrated, and the literature provides considerable information on this subject. Three calibration methods are generally proposed[6] using (a) narrow molecular weight-distributed standards,[7–14] (b) the so-called "universal" calibration (hydrodynamic volumes or unperturbed dimensions of the solute),[15–25] (c) broad molecular weight-distributed standards.[26–31]

The main disadvantage of the first method (a) is the difficulty of preparing standards of narrow MWD for most polymers. Only polystyrene is commercially available over the whole range of molecular weights; and

it is now well known that relying on a molecular-weight (or size) calibration performed with a given polymer to interpret the chromatograms of other polymers leads to serious errors.

The "universal" calibration method (b), although it has proved to be applicable to a wide range of different molecular species, yields a calibration in hydrodynamic volumes (or in unperturbed dimensions) rather than in molecular weights. To overcome this weakness, measurements of the intrinsic viscosity of a large number of eluted fractions are necessary unless the two Mark-Houwink equation parameters are known.*

The third calibration method (c) seems to be the most useful in practical applications. Broad molecular weight-distributed samples are always readily available. However, in some cases, the approximations or hypotheses involved drastically reduce the generality of the method.

This paper presents a computer technique which ultimately gives both differential and integral MWD of any sample versus the logarithm of the molecular weight [$dw/d(\log M) = f(\log M)$ and $w = f(\log M)$]. The computation is based on the "universal" calibration method proposed by Weiss and Cohn-Ginsberg[20] and dealing with hydrodynamic volumes. It necessitates the determination of the number-average molecular weight ($\bar{M}_n$) and the weight-average molecular weight ($\bar{M}_w$) of the sample. Alternatively, either one of these molecular parameters is sufficient if the intrinsic viscosity of the sample in the eluting solvent, at the elution temperature, is known. No attempt was made to correct the data for axial dispersion, imperfect resolution, or diffusional phenomena.

BASIC APPROACH

The basic approach of our computation considers as valid the "universal" calibration method for the kind of sample being dealt with. This assumption means that the calibration curve of $M_i[\eta]_i$ versus v_i (where M_i is the molecular weight and $[\eta]_i$ is the limiting viscosity number of a species i eluting at volume v_i) obtained with any narrow molecular weight-distributed standards is valid for the sample under evaluation over the whole elution range. This assumption could be erroneous for low molecular weight species where solute–solvent as well as gel–solute interactions are relatively more significant than they are for high molecular weight species, which is not likely, however, to occur for polymers.

If $f(M)$ is the normalized distribution function so that

$$\int_0^\infty f(M)dM = 1 \tag{1}$$

* After preparation of the manuscript, the author was informed of the existence of a newly developed automatic viscometer. This viscometer can be installed downstream to the syphon of the GPC apparatus and is specially designed for measuring the flow time of the 5-ml solution contained in the syphon.[32]

the intrinsic viscosity $[\eta]$, the number-average molecular weight $\bar{M}_n$, and the weight-average molecular weight $\bar{M}_w$ can be written as follows:

$$[\eta] = K \int_0^\infty M^\alpha f(M) dM \tag{2}$$

$$\bar{M}_n = \left[\int_0^\infty M^{-1} f(M) dM \right]^{-1} \tag{3}$$

$$\bar{M}_w = \int_0^\infty M f(M) dM \tag{4}$$

K and α being the constant parameters of the Mark-Houwink equation relating the intrinsic viscosity to the viscosity-average molecular weight $\bar{M}_v$,

$$[\eta] = K \bar{M}_v^\alpha. \tag{5}$$

Although these parameters are not strictly constant over the entire molecular weight range, their values as considered here can be taken as average ones.

From eq. (5) and for monodisperse polymers where $\bar{M}_v = M_i$ for molecular species i,

$$M_i = K^{-1/\alpha} [\eta]_i^{1/\alpha} = J_i [\eta]_i^{-1} \tag{6}$$

where

$$J_i = M_i [\eta]_i, \tag{7}$$

it follows that

$$[\eta]_i = J_i^{\alpha/(1+\alpha)} K^{1/(1+\alpha)} \tag{8}$$

and

$$M_i = J_i^{1/(1+\alpha)} K^{-1/(1+\alpha)}. \tag{9}$$

Substituting this value of M in eqs. (2) to (4) gives

$$[\eta] = K^{1/(1+\alpha)} \int_0^\infty J^{\alpha/(1+\alpha)} f(M) dM \tag{10}$$

$$\bar{M}_n = K^{-1/(1+\alpha)} \left[\int_0^\infty J^{-1/(1+\alpha)} f(M) dM \right]^{-1} \tag{11}$$

$$\bar{M}_w = K^{-1/(1+\alpha)} \int_0^\infty J^{1/(1+\alpha)} f(M) dM. \tag{12}$$

The parameter K can be eliminated so that only α remains as unknown, thus:

$$[\eta] \bar{M}_n = \left[\int_0^\infty J^{\alpha/(1+\alpha)} f(M) dM \right] \left[\int_0^\infty J^{-1/(1+\alpha)} f(M) dM \right]^{-1} \tag{13}$$

$$[\eta]\bar{M}_w = \left[\int_0^\infty J^{\alpha/(1+\alpha)} f(M)dM\right]\left[\int_0^\infty J^{1/(1+\alpha)} f(M)dM\right] \quad (14)$$

$$\bar{M}_w/\bar{M}_n = \left[\int_0^\infty J^{1/(1+\alpha)} f(M)dM\right]\left[\int_0^\infty J^{-1/(1+\alpha)} f(M)dM\right]. \quad (15)$$

The computer programs presented here allow the evaluation of the value of α which minimizes the difference between both sides of eqs. (13) to (15). Subsequently, a value of K can then be derived from any of eqs. (10) to (12), depending on the experimental properties measured.

At this step of the computation, both parameters K and α of the Mark-Houwink eq. (5) are known for the sample under evaluation together with the "universal" calibration curve of the instrument, $J_i = f(v_i)$. Utilizing eq. (9), any J_i value can then be replaced by its corresponding M_i value so that a calibration curve $M_i = f(v_i)$ is obtained for the sample. The accuracy of the calculated values K and α, and consequently that of the calibration curve $M = f(v)$, obviously depends on the precision of the experimental determination of $[\eta]$, $\bar{M}_n$, and $\bar{M}_w$.

METHOD OF COMPUTATION

On a gel permeation chromatogram such as put out by a Waters instrument, the ordinate is proportional to the difference between the solution and solvent refractive indexes, while the eluted volume of solution after sample injection is measured on the abscissa.

It is known that for low concentrations, as is the case at the output of the columns, the ratio dn/dc, or refractive index increment, is concentration independent. It is also generally assumed that the value of dn/dc is constant over the whole molecular range for a given sample and that the ordinate of the chromatogram therefore can be considered as a measure of the relative concentration of the eluting species. Here again, the assumption could be erroneous for low molecular weight species. If the chromatogram is normalized to unit area, it can be thought of as a representation of the function

$$\frac{dw}{dv} = f(v) \quad (16)$$

where w is the weight fraction of the polymer eluted up to elution volume v. Since

$$f(M)dM = \frac{dw}{dM}\,dM = \frac{dw}{dv}\,dv = f(v)dv, \quad (17)$$

eqs. (1) and (10) to (12) can be rewritten in a discontinuous form for discrete values of v:

$$\sum_{v_1}^{v_2} f(v_i)\Delta v = 1 \quad (1')$$

$$[\eta] = K^{1/(1+\alpha)} \sum_{v_1}^{v_2} J_i^{\alpha/(1+\alpha)} f(v_i)\Delta v \tag{10'}$$

$$\bar{M}_n = K^{-1/(1+\alpha)} \left[\sum_{v_1}^{v_2} J_i^{-1/(1+\alpha)} f(v_i)\Delta v \right]^{-1} \tag{11'}$$

$$\bar{M}_w = K^{-1/(1+\alpha)} \sum_{v_1}^{v_2} J_i^{1/(1+\alpha)} f(v_i)\Delta v, \tag{12'}$$

v_1 and v_2 being the elution volume limits of the chromatogram ($v_1 > v_2$); and Δv, the constant interval between two values, v_i.

If $h_i = f(v_i)\Delta v_i$, the relations (13) to (15) used for computation are

$$[\eta]\bar{M}_n = \left[\sum_{v_1}^{v_2} J_i^{\alpha/(1+\alpha)} h_i \right] \left[\sum_{v_1}^{v_2} J_i^{-1/(1+\alpha)} h_i \right]^{-1} \tag{13'}$$

$$[\eta]\bar{M}_w = \left[\sum_{v_1}^{v_2} J_i^{\alpha/(1+\alpha)} h_i \right] \left[\sum_{v_1}^{v_2} J_i^{1/(1+\alpha)} h_i \right] \tag{14'}$$

$$\bar{M}_w/\bar{M}_n = \left[\sum_{v_1}^{v_2} J_i^{1/(1+\alpha)} h_i \right] \left[\sum_{v_1}^{v_2} J_i^{-1/(1+\alpha)} h_i \right]. \tag{15'}$$

The values h_i are calculated from the chromatogram, and J_i from the "universal" calibration, both a function of the elution volume v_i, thus allowing computation of α and hence K.

The molecular weight distribution existing in a given polymer can be conveniently visualized by plotting $f(M)$ versus M. However, the large range of molecular weights encountered in unfractioned commercial polymers requires a plot of $\varphi(M) = M f(M)$ versus log M for adequate scaling.

Multiplying the chromatogram output h_i by dv_i/d (log M_i), the reciprocal of the slope of the calibration curve of log $M_i = \varphi(v_i)$, one obtains $\psi(M) = \varphi(M)\Delta v$ for each value of log M.[33]

COMPUTER PROGRAMMING

The programs as developed consist of two separate parts. The first program, for on-line data acquisition and reduction, has been written in ASSEMBLY language and fits in the general on-line data handling program serving the laboratory (Hewlett-Packard 2116-C computer).

The second program exists in two languages, BASIC and FORTRAN; it is intended for the calculation leading to the normalized MWD representations:

$$\psi(M_i) = f(\log M_i) \quad \text{and} \quad \sum_{v_1}^{v_i} \psi(M_i) = f(\log M_i).$$

The guiding principles in compiling these programs were (a) to gather the GPC data on-line and reduce the information to a compact format compatible with further off-line processing; (b) to further process the information off-line (e.g., on a time-sharing computer).

Systems Approach

As soon as the sample is injected, the computer samples the refractometer signal at constant time intervals. Each data point is actually a voltage proportional to the relative refractive index of solution and solvent flowing through the differential refractometer unit. At each "count" (emptying of the 5-ml syphon) and at each sample injection, a trigger pulse superimposes an additional voltage at the recorder input. This trigger pulse indicates to the computer the occurrence of a count or of an injection.

Since the total volume of a GPC column set available to a given molecule is at least the interstitial volume V_0 of the gel and at most V_0 plus the internal volume V_i of the gel, neither the data corresponding to an elution volume $v_i < V_0$ nor those corresponding to $v_i > V_0 + V_i$ will be interesting. Therefore, the program will provide for two counts, C_1 and C_2, corresponding to elution volumes respectively slightly smaller than V_0 and slightly larger than $V_0 + V_i$. From sample injection up to count C_1, the data sampled will be rejected at each count. Then, data acquisition and reduction take place until count C_2. The program can deal simultaneously with several overlapping sample injections; waiting for complete elution of a sample before injecting the next one is unnecessary.

After count C_2 has been reached, a punched tape is output with the reduced data. This tape is ready for use for the second group of programs (off-line computation). Besides the data provided by the tape, only five additional input data are required: (a) the values of two counts used for baseline evaluation; (b) two of the three values $[\eta]$, $\bar{M}_n$, and $\bar{M}_w$; (c) identification of the particular set of columns used to chromatograph sample.

The off-line calculations proceed until both differential and integral MWD are printed out.

Programs

On-Line Data Acquisition and Handling

Under computer clock control, data points are read in every 3 sec. Between counts C_1 and C_2, these data points pass one by one through a chain of decision, as shown in Figure 1. The trigger pulse arising from a count is recorded independently from the data points on a second input channel. After each one of these pulses, the interval between the two last counts is divided into ten equal subintervals and the data are averaged in each of these subintervals. These average data points are stored until the printout. If two counts are detected successively within a 1-min time interval, the first one is taken as count zero of the next sample and the second one, as an injection pulse.

After count C_2, the averaged data are punched on a paper tape giving the relative height values of the chromatogram for every decimal count between C_1 and C_2.

Program for MWD Calculations

The tape as output by the on-line computer serves as input information for the off-line BASIC or FORTRAN program. An additional step is to feed the computer with the five above-mentioned data. The calculation can then start according the scheme outlined in Figure 2, the "universal" calibration curve having already been stored in the computer memory. A straight line is computed between the two counts used for baseline evaluation, and at every decimal count its value is subtracted from the corresponding collected on-line data. This calculation assumes baseline linearity during sample elution. If negative values arise from this calculation (baseline value higher than corresponding data point at a given decimal count, due to appearance of negative peaks of impurities or dissolved gases), these values are increased to zero. Consequently, at this step of the program, all the heights of the chromatogram, stored for every decimal count for which a calibration value in hydrodynamic volume is known, are either positive or zero.

The second part of the program is the most critical. Chromatogram heights are normalized to obtain $f(v_i)$ and to obey eq. (1′). Then, with the aid of the hydrodynamic volume values, the difference between both sides of either eq. (13′), (14′), or (15′) is computed for successively increasing positive integer values of α. Each difference is compared to the previous one. If it is smaller, the computer takes the next α-value; if not, starting from the antipenultimate value of α, the difference is computed again for successive decimal values of α. The process continues until an optimum value of α is obtained with three decimal digits. This last value is then printed out together with the corresponding mean value of K computed from two out of the three equations (10′) to (12′). Once these two parameters K and α are known, eq. (9) allows the calculation of a calibration

$$\log M = \varphi(v) \tag{18}$$

curve for which the reciprocal slope value (Mdv/dM) is computed at every decimal count. Multiplying by the corresponding h_i value and normalizing to unity for the sake of uniformity, $\psi(M)$ is obtained for every decimal count. A teletype then prints out the MWD data.

The last part of the off-line program consists in the computation of $[\eta]$, $\bar{M}_n$, $\bar{M}_v$, and $\bar{M}_w$ from eqs. (2) to (5). These values are output together with the polydispersity index $\bar{M}_w/\bar{M}_n$.

CONCLUSIONS

The presented calibration procedure for GPC leads to a possibility of MWD representation as a function of molecular weight for polymeric materials. It is of course clearly felt that the MWD thus obtained can only be a crude approximation of the reality (see Appendix), the accuracy being limited by a series of factors among which can be enumerated (1) the accuracy of molecular weight-average and limiting viscosity number deter-

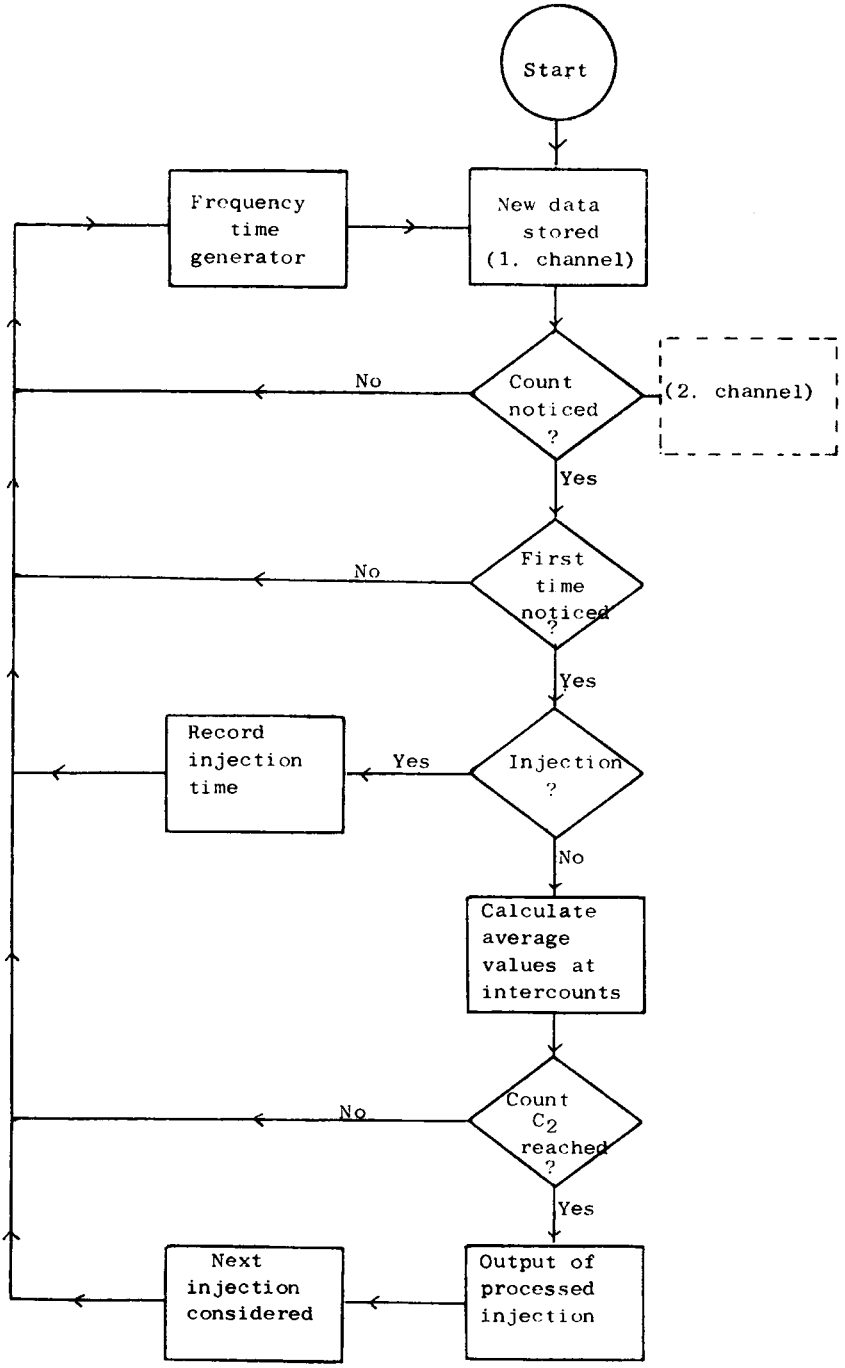

Fig. 1. Data evaluation flow chart.

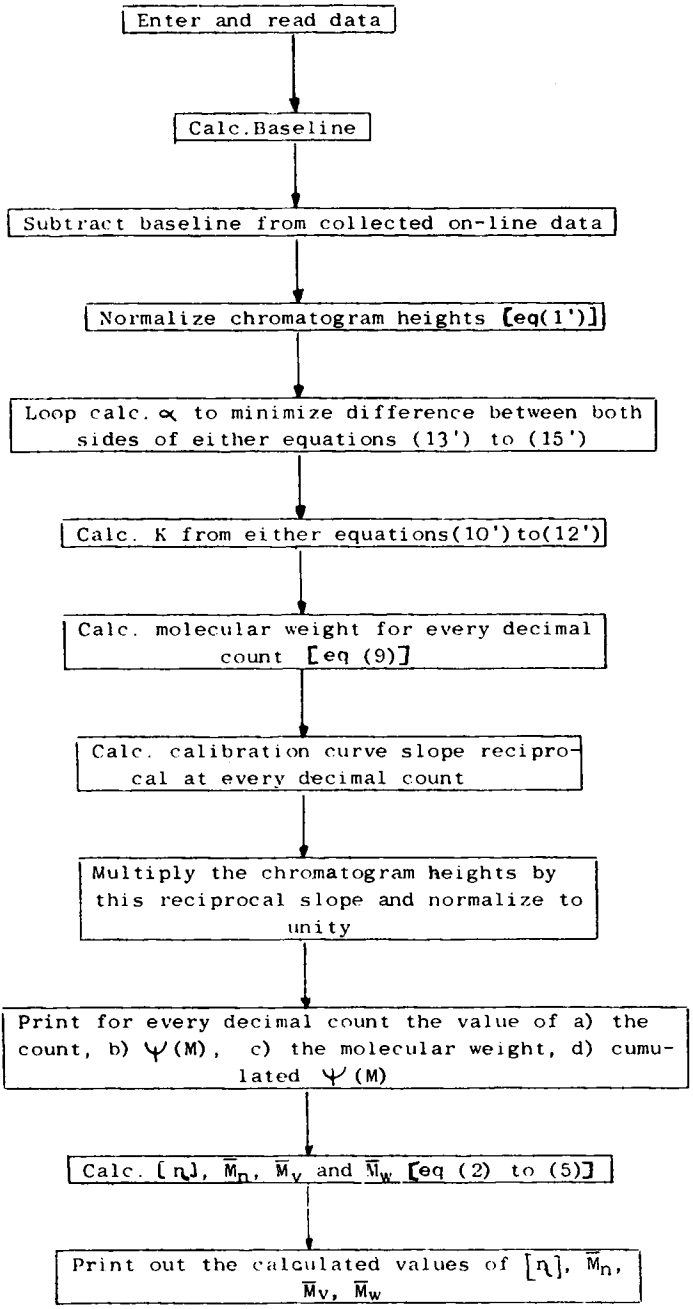

Fig. 2. Off-line calculations.

minations; (2) the reproducibility and accuracy of the chromatogram; (3) the detection device sensitivity to pick up high and low molecular weight species present in small amounts; (4) the well-known inherent limitations, both mechanical and theoretical, of the gel permeation approach to fractionation of polydisperse materials.[5]

However, the sole assumption implied is the validity of the "universal" calibration for the sample dealt with; the method is therefore useful when monodisperse standards are not available, which is frequently the case for most commercial macromolecular products.

Appendix

The National Bureau of Standards (NBS) Standard Sample 706, which is a broad molecular weight-distributed polystyrene, was used to check the accuracy of the computerized mathematical data treatment presented. From the GPC data, the MWD of the sample was computed by using (1) the narrow molecular weight-distributed standards calibration and (2) the "universal" calibration.

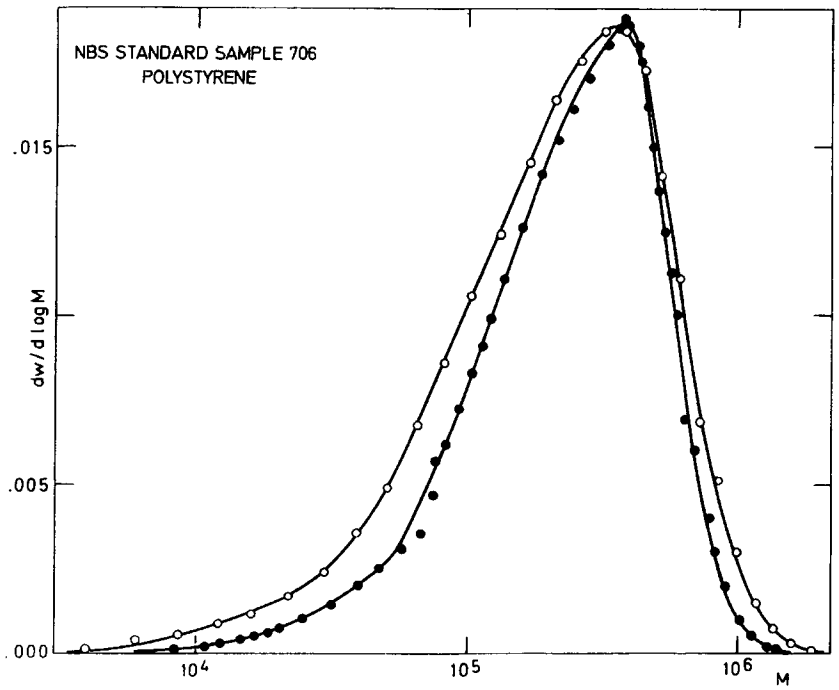

Fig. 3. MWD of NBS Sample 706 obtained by "classical" (○) and by "computer" (●) conversion of GPC chromatogram.

Both calibrations were established for a set of five Styragel columns with respective maximum nominal pore size of 10^7, 3×10^6, 5×10^4, 1.5×10^4, and 5×10^3 Å. Fifteen narrow molecular weight-distributed polystyrene were used, the nominal molecular weights of which ranged from 104 (styrene) up to 860,000. The limiting flow number $[\eta]$ of each calibration polystyrene standard was measured in tetrahydrofuran (THF)

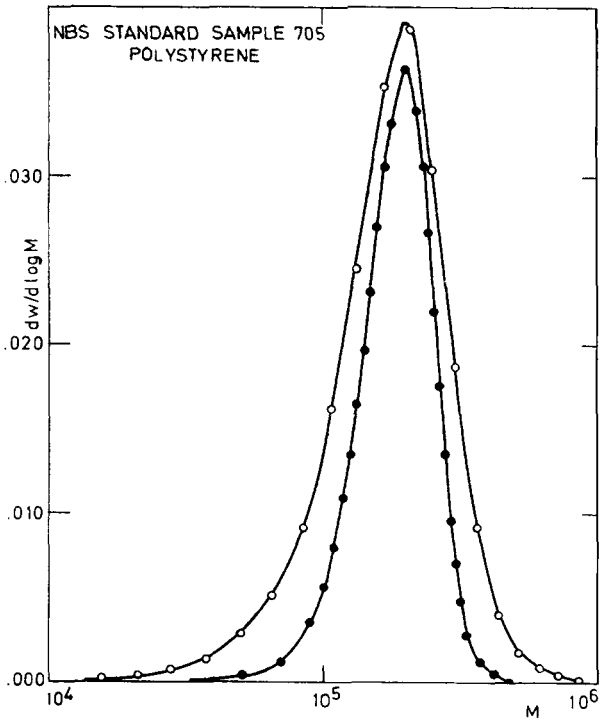

Fig. 4. MWD of NBS Sample 705 obtained by "classical" (○) and by "computer" (●) conversion of GPC chromatogram.

at 25°C, and the relation thus obtained between $[\eta]$ and M was used to calibrate the column set for "universal" calibration (hydrodynamic volumes).

The chromatogram obtained was then converted to the corresponding MWD (1) by applying the procedure suggested by Yau and Fleming[33] and (2) by subjecting the chromatogram to the treatment described in this paper. Figure 3 shows the results of both conversions. It can be seen that although procedure (1) gives a broader distribution than treatment (2), there is a good correlation between the two MWD curves obtained, especially if the approximations and limitations of both computations are kept in mind.

The theoretical characteristics of Sample 706 as given on the NBS certificate are: $\bar{M}_w$ (light scattering) = 257,800; $\bar{M}_w$ (sedimentation equilibrium) = 288,100; $\bar{M}_n$ (osmotic pressure) = 136,500; $\bar{M}_w/\bar{M}_n$ (fractionation) = 2.1. The limiting viscosity number measured in THF at 25°C was found to be 1.046 dl/g. With inputting $[\eta]$ and $\bar{M}_n$ as experimental data in the computer, the recalculated data from the MWD thus obtained were $[\eta]$ = 1.046; $\bar{M}_n$ = 136,500; $\bar{M}_w$ = 290,400; $\bar{M}_w/\bar{M}_n$ = 2.1. The theoretical and recalculated $\bar{M}_w$ values are most likely fortuitously close to one another. However, the same order of magnitude obtained for the MWD given by two different data treatment is a comforting result.

The same procedure was followed with the NBS Standard Sample 705, which is a narrow molecular weight-distributed polystyrene. Its theoretical characteristics as given on the NBS certificate are: $\bar{M}_w$ (light scattering) = 179,300; $\bar{M}_w$ (sedimentation equilibrium) = 189,800; $\bar{M}_n$ (osmotic pressure) = 170,900; $\bar{M}_w/\bar{M}_n$ (fractionation) = 1.07. The limiting viscosity number measured in THF at 25°C was found to be 0.746 dl/g. When inputting $\bar{M}_n$ (170,900) and $\bar{M}_w$ (189,800) as experimental data, the recalculated

data from the MWD thus obtained were $\bar{M}_n$ = 170,900; $\bar{M}_w$ = 189,800; $[\eta]$ = 0.862; $\bar{M}_w/\bar{M}_n$ = 1.11. Figure 4 compares the MWD obtained (1) by applying the "classical" procedure[33] and (2) by subjecting the chromatogram to the computer treatment. Here again, a good correlation between both MWD curves is observed.

The method was also applied to two lots of low molecular weight resins. The molecular structure of the polymers was the same for all the resins inside a lot but differed from one lot to the other. Using a set of five Styragel columns with respective maximum nominal pore size of 10^3, 700, 250, 100, and 80 Å, two average calibrations were established from about four to five resins in each lot. These calibrations were subsequently used to obtain MWD for other resins in these two series. The accuracy of the calibrations was checked by comparing the number-average molecular weights obtained by direct measurement (vapor pressure "osmometry") with those recalculated from the MWD curves for the resins which were not used for calibration. As can be seen from Table A-I, the differences observed are, except for one case, less than 10%.

TABLE A-I
Comparison of Number-Average Molecular Weights
Obtained by Direct Measurement and From MWD Curves

Sample	$\bar{M}_n$ measured directly	$\bar{M}_n$ from MWD	Differences
A4	560	540	−3.6%
A5	580	615	+6.0%
B5	545	585	+7.3%
C5	585	595	+1.7%
B4	435	515	+18.4%
C4	265	270	+1.9%
D5	680	615	−9.6%
E5	660	605	−8.3%

I would like to express my appreciation to Professor H. Benoit for having critically reviewed the manuscript.

References

1. P. Deuel and H. Neukom, quoted in P. Flodin (see below).
2. P. Flodin, *Dextra Gels and their Applications in Gel Filtration*, Pharmacia, Uppsala, 1962.
3. J. Porath and P. Flodin, *Nature*, **183**, 1657 (1959).
4. J. C. Moore, *J. Polym. Sci. C*, **21**, 1 (1968).
5. K. H. Altgelt and J. C. Moore, *Polymer Fractionation*, Academic Press, New York, 1967.
6. Waters Associates Technical Information Bulletin, GPC-TIB-968/1, Framingham, Mass.
7. N. S. Schneider, *J. Polym. Sci. C*, **8**, 253 (1965).
8. J. C. Moore and J. G. Hendrickson, *J. Polym. Sci. C*, **8**, 233 (1965).
9. D. J. Harmon, *J. Polym. Sci. C*, **8**, 243 (1965).
10. L. E. Maley, *J. Polym. Sci. C*, **8**, 253 (1965).
11. J. G. Hendrickson and J. C. Moore, *J. Polym. Sci. A-1*, **4**, 167 (1966).
12. W. B. Smith, J. A. May, and C. W. Kim, *J. Polym. Sci. A-2*, **4**, 365 (1966).
13. M. E. Pickett, M. J. R. Cantow, and J. F. Johnson, *J. Appl. Polym. Sci.*, **10**, 917 (1966).
14. R. D. Law, *J. Polym. Sci. C*, **21**, 225 (1968).
15. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci. B*, **5**, 753 (1967).

16. H. Coll and L. R. Prusinowski, *J. Polym. Sci. B*, **5**, 1153 (1967).
17. J. V. Dawkins, *J. Macromol. Sci. Phys.*, *B2*, 623 (1968).
18. K. A. Boni, F. A. Sliemers, and P. B. Stickney, *J. Polym. Sci. A-2*, **6**, 1579 (1968).
19. E. A. DiMarzio and C. M. Guttman, *J. Polym. Sci. B*, **7**, 267 (1969).
20. A. R. Weiss and E. Cohn-Ginsberg, *J. Polym. Sci. B*, **7**, 379 (1969).
21. J. V. Dawkins, R. Denyer, and J. W. Maddock, *Polymer*, **10**, 154 (1969).
22. J. V. Dawkins, *Chem. Ind.* (London), (**4**), 118 (1970).
23. H. Coll and D. K. Gilding, *J. Polym. Sci. A-2*, **8**, 89 (1970).
24. J. V. Dawkins, *Eur. Polym. J.*, **6**, 831 (1970).
25. E. A. DiMarzio and C. M. Guttman, *Macromolecules*, **3**, 131 (1970).
25a. H. Coll, *Separ. Sci.*, **5**, 273 (1970).
25b. F. H. Verhoff and N. D. Sylvester, *J. Macromol. Sci.*, *A4*, 979 (1970).
26. J. R. Purdon Jr. and R. D. Mate, *J. Polym. Sci. A-1*, **6**, 243 (1968).
27. F. C. Frank, I. M. Ward, and T. Williams, *J. Polym. Sci. A-2*, **6**, 1357 (1968).
28. S. T. Balke, A. E. Hamielec, B. P. Leclair, and S. L. Pearce, *Ind. Eng. Chem., Prod. Res. Develop.*, **8**, 54 (1969).
29. S. T. Balke and A. E. Hamielec, *J. Appl. Polym. Sci.*, **13**, 1381 (1969).
30. R. Y. M. Huang and R. G. Jenkins, *Tappi*, **52**, 1503 (1969).
31. A. R. Weiss and E. Cohn-Ginsberg, *J. Polym. Sci. A-2*, **8**, 148 (1970).
32. D. Goedhart and A. Opschoor, *J. Polym. Sci. A-2*, **8**, 1227 (1970).
33. W. W. Yau and S. W. Fleming, *J. Appl. Polym. Sci.*, **12**, 2111 (1968).

Received April 27, 1971
Revised June 3, 1971