

Determination of polymer polydispersity by gel permeation chromatography

M. B. TENNIKOV*

Institute of Analytical Instrumentation, Academy of Science of U.S.S.R., Ogorodnikova 26, 193024 Leningrad (U.S.S.R.)

A. A. GORBUNOV

All-Union Research Institute for Highly Pure Biopreparations, Pudozhskaya 7, 197110 Leningrad (U.S.S.R.)

and

A. M. SKVORTSOV

Chemical-Pharmaceutical Institute, Prof. Popova 14, 197022 Leningrad (U.S.S.R.)

ABSTRACT

A gel permeation chromatographic method for the determination of polymer polydispersity without the need for preliminary calibration with standards is proposed. Only the chromatogram of the sample under study is required, so the method is convenient for polydispersity investigations of new synthetic polymer materials. The universal dependence of the slope of the calibration graph on the distribution coefficient is used. For verification of the method, polystyrene standards were preliminarily mixed in certain proportions so that the polydispersities of these mixtures could be calculated initially, and then chromatograms of these mixtures were obtained for cross-checking. The proposed method was found to give satisfactory determinations of M_z/M_w , *i.e.*, polymer polydispersity.

INTRODUCTION

The polydispersity of a polymer, U , is usually characterized by the ratio of different average molecular weights, *e.g.*, $U_n = M_w/M_n$ or $U_w = M_z/M_w$. The polydispersity, U_i , is related to the average value of the molecular weight of the sample, M_i ($i = n$ or w), and to its dispersion, σ_i^2 , as follows¹:

$$U_i = 1 + (\sigma_i/M_i)^2 \quad (1)$$

The usual method of determining the polydispersity by gel permeation chromatography (GPC) is as follows¹. First the calibration dependence is obtained, *i.e.*, the relationship between the retention volume, $V_R = V_o + V_p K$, and the molecular weight of the polymer under study is determined, where V_o and V_p are

volumes of the mobile and stationary phases, respectively, and K is the distribution coefficient. Normally narrow fractions are used to obtain such a relationship (Fig. 1 shows an example of a calibration dependence for the system of polystyrene and silica gel SW-3000 with a pore diameter $2d = 15$ nm). Next the chromatogram of the sample under investigation is obtained and corrected if necessary by elimination of the instrumental broadening. Then, using the calibration the chromatogram is transformed to the weight function of the molecular weight distribution (MWD), $f_w(M)$ and subsequently the moments of the function

$$M_w = \int_0^{\infty} f_w(M) M dM \quad (2)$$

$$M_z = (M_w)^{-1} \int_0^{\infty} f_w(M) M^2 dM$$

are calculated and U_w is determined.

The need for preliminary calibration is a disadvantage of this procedure because narrow-MWD fractions (standards) are not generally available.

In this paper we propose a method for the determination of M_z/M_w that does not require any calibration and is based exclusively on the use of the chromatogram of the sample under study.

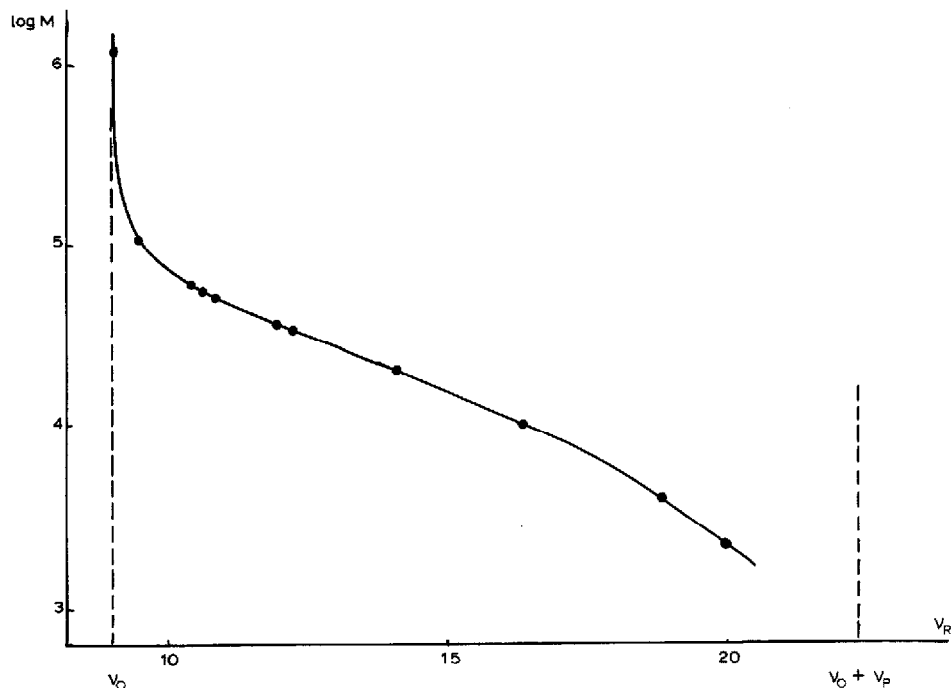


Fig. 1. Calibration dependence for polystyrene and silica gel SW-3000 with pore diameter $2d = 15$ nm, $V_0 = 9.0$ ml, $V_0 + V_p = 22.45$ ml.

GENERAL THEORY AND INTERNAL STANDARD IN GPC

First we shall show that it is not necessary to obtain a calibration graph of V_R vs. $\ln M$ in order to determine U_w , it being sufficient just to know the slope of the calibration graph:

$$\psi(K) = \frac{1}{V_p} \cdot \frac{\partial V_R}{\partial \ln M} = \frac{\partial K}{\partial \ln M} \quad (3)$$

Let σ_v be the width of the chromatogram, and assume that the calibration graph is approximately linear within σ_v . It follows that

$$\sigma_v = \left| \frac{dV_R}{d \ln M} \right| \sigma_{\ln M} \approx V_p \cdot \frac{\sigma_w}{M_w} \cdot \psi \quad (4)$$

where $\sigma_{\ln M}$ is the width of the molecular weight logarithmic distribution function. It follows from eqn. 4 that

$$U_w = 1 + (\sigma_w/M_w)^2 \approx 1 + \left(\frac{\sigma_v}{\psi V_p} \right)^2 \quad (5)$$

Hence to determine U_w it is sufficient to know: (a) the chromatographic column characteristics, *i.e.*, the total pore volume, V_p , and the dead volume, V_0 ; (b) the first and the second moments of the chromatogram, *i.e.*, the distribution coefficient K , and the width of the chromatogram of the sample under study, σ_v ; and (c) the slope of the calibration graph, $\psi(K)$, which corresponds to this value of K .

We shall now show that the value of ψ is determined by the value of K only and is independent of both the type of polymer and the type of adsorbent involved.

Let us consider the behaviour of the function $\psi = \partial K / \partial \ln M$, which is inversely proportional to the slope of the calibration graph. Fig. 2 shows normalized calibration graphs in the coordinates $\log M$ versus K for polystyrene standards and porous silica gel SW-3000, and for narrow disperse dextrans and porous glasses (with different pore diameters). The calibration graphs are similar for these different polymers and adsorbents.

The value of $\psi(K)$ first increases from $\psi(0) = 0$ to a certain value and then decreases to $\psi(1) = 0$. The distribution coefficient for a flexible-chain macromolecule under GPC conditions is known^{2,3} to be determined by the ratio of the chain size (average radius of gyration, R) to the pore radius, d . The theory of GPC² based on the model of a Gaussian chain in a slit-like pore shows that

$$K \approx \begin{cases} 1 - \frac{2}{\sqrt{\pi}} \cdot g, & \text{if } R < d \\ \frac{8}{\pi^2} \exp \left[- \left(\frac{\pi}{2} \cdot g \right)^2 \right], & \text{if } R > d \end{cases} \quad (6)$$

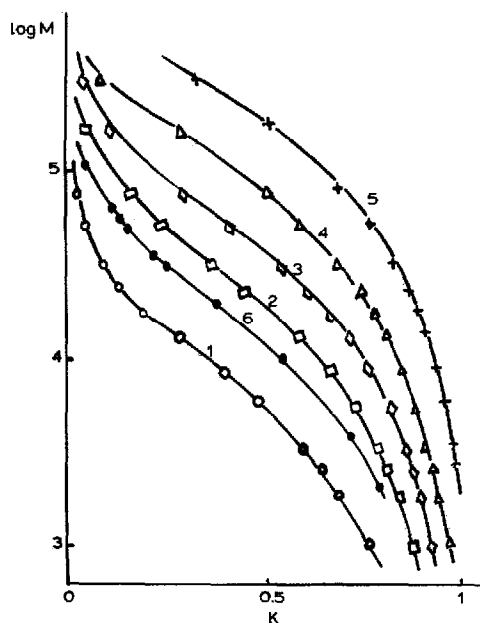


Fig. 2. Normalized calibration dependences for narrow disperse dextrans and porous glasses with pore diameter $2d =$ (1) 8.4, (2) 15.9, (3) 22.7, (4) 31.4 and (5) 51.7 nm⁴ and for polystyrene standards and modified silica gel SW-3000 with $2d = 15$ nm.

where $g = R/d$. For Gaussian chains the relationship

$$\psi = \frac{\partial K}{\partial \ln M} = \frac{g}{2} \cdot \frac{\partial K}{\partial g} \quad (7)$$

is valid, and therefore from eqns. 6 and 7 it follows³ that

$$|\psi| \approx \begin{cases} (1 - K)/2, & \text{if } K > 0.5 \\ K \ln\left(\frac{8}{\pi^2 K}\right), & \text{if } K < 0.5 \end{cases} \quad (8)$$

An analysis proves³ that eqn. 8 remains valid for pores of various shapes. Hence the dependence $\psi(K)$ is universal for any monodisperse sorbent.

Fig. 3 shows dependence $\psi(K)$ calculated by use of eqn. 8 (solid line). It shows also the experimental data⁴ for dextran molecules and porous glasses of various pore diameters and the data for polystyrene and silica gel SW-3000, all these data being obtained by numerical differentiation of the calibration graphs in Fig. 2. It can be seen that universal dependence of the slope of the calibration graph on the distribution coefficient really does exist for various polymers and adsorbents. We shall call this universal dependence an "internal standard" in the GPC of polymers. Experimental corroboration of such a "standard" is shown in Fig. 3.

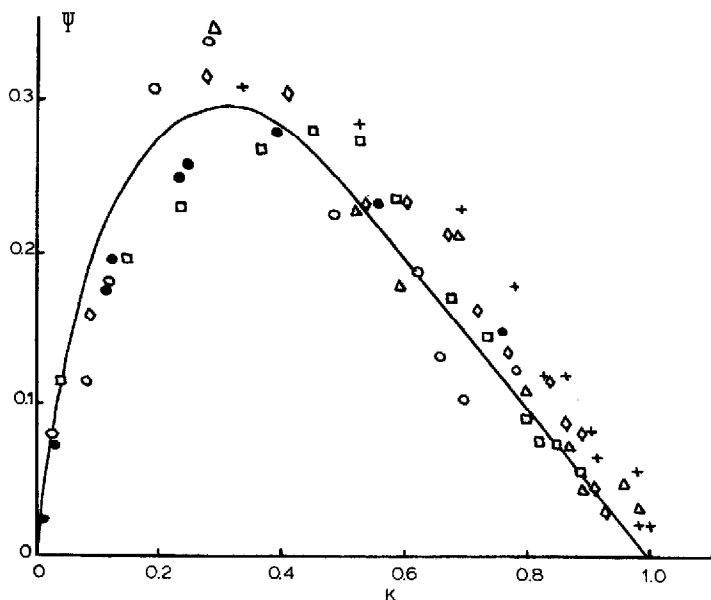


Fig. 3. Slope of calibration graph, $\psi = \partial K / \partial \ln M$, as a function of the distribution coefficient, K , the dependence being obtained by numerical differentiation of the curves in Fig. 2. Symbols as in Fig. 2. The solid line shows the theoretical dependence (eqn. 8).

Hence the procedure for the determination of polydispersity by the proposed method consists in the following: from the value of the distribution coefficient of the sample under study (the first moment of the chromatogram), the value of $\psi = \psi(K)$ is calculated by means of eqn. 8. Subsequently, using both the $\psi(K)$ and the measured value of the chromatogram width σ_v (the second moment), the ratio M_z/M_w is calculated by means of eqn. 5.

EXPERIMENTAL VERIFICATION OF THE METHOD FOR DETERMINATION OF POLYMER POLYDISPERSITY

The proposed method was tested using a Model Triotar SR2 high-performance liquid chromatograph (Jasco, Tokyo, Japan) with UV detection at 254 nm. A 600×7.5 mm I.D. column (LKB, Bromma, Sweden) packed with SW-3000 sorbent (Toyo Soda, Tokyo, Japan) was used with tetrahydrofuran as the eluent. The sorbent is a porous modified silica gel with a particle size of $10 \mu\text{m}$ and a pore diameter of ca. 15 nm. Polystyrene standards with $M = 2 \cdot 10^3 - 1.11 \cdot 10^5$ (Waters Assoc., Milford, MA, U.S.A.) were investigated. The sample volume (sampling loop) was $20 \mu\text{l}$, the polymer concentration in the sample was 1–2 mg/ml, the elution rate was 1 ml/min and all experiments were carried out at ambient temperature (ca. 22°C). The quasi-equilibrium character of the process under study and the exclusion mode of the chromatography were verified by checking the constancy of the retention volumes when the elution rate was varied from 0.3 to 2 ml/min and temperature from 10°C to 50°C . The efficiency of the column was ca. 12 000 theoretical plates for toluene.

TABLE I
COMPOSITIONS AND MOLECULAR AND CHROMATOGRAPHIC CHARACTERISTICS OF THE MODEL MIXTURES OF POLYSTYRENE STANDARDS

| Mixture No. | Weight-average molecular weights of polystyrene standards, $M \cdot 10^{-3}$ | | | | | | Characteristics calculated on the basis of mixture composition | | | | Characteristics of samples (mixtures) under study measured experimentally | | | | | | | | |
|---|--|------|------|-------|-------|-------|--|-------|-------|-------|---|-------|-------|-------|-------|------------|-----------|-------|-------|
| | 2.4 | 4 | 10 | 20.8 | 34 | 36 | 51 | 54 | 60 | 111 | M_z | M_w | M_z | M_w | K | σ_b | $\psi(K)$ | M_z | M_w |
| Distribution coefficients of polystyrene standards, K_i | | | | | | | | | | | | | | | | | | | |
| — | 0.80 | 0.55 | 0.40 | 0.245 | 0.227 | 0.152 | 0.123 | 0.111 | 0.037 | 0.037 | 0.037 | 0.037 | 0.037 | 0.037 | 0.037 | 0.037 | 0.037 | 0.037 | 0.037 |
| Mixture composition (% v/v) | | | | | | | | | | | | | | | | | | | |
| 1 | | | | | 40 | | 40 | 20 | | | 54.2 | 52.1 | 1.04 | 1.04 | 0.14 | 0.65 | 0.25 | 1.04 | 1.04 |
| 2 | | | | 20 | | 20 | 20 | 30 | 50 | | 93 | 84.5 | 1.10 | 1.10 | 0.09 | 0.766 | 0.20 | 1.08 | 1.08 |
| 3 | | | 20 | | 20 | 20 | 20 | 10 | 10 | | 61.1 | 52.2 | 1.17 | 1.17 | 0.16 | 0.964 | 0.262 | 1.075 | 1.075 |
| 4 | | 20 | 20 | 10 | 10 | 10 | 10 | 10 | 10 | | 61.3 | 40.6 | 1.51 | 1.51 | 0.29 | 2.49 | 0.298 | 1.38 | 1.38 |
| 5 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | | 64 | 38 | 1.67 | 1.67 | 0.35 | 3.60 | 0.294 | 1.8 | 1.8 |

Correction for the instrumental broadening was performed with the reversed-flow method (Tung's method⁵) as follows. At the moment when the retention volume reached half its maximum value the column was reversed, causing the direction of flow to be reversed. This resulted in the width of the chromatogram being independent of the sample MWD and to be dependent on the instrumental broadening only. For all the samples studied the instrumental broadening was within the range $(\sigma_v)_{\text{approx.}} \approx 0.19\text{--}0.22$ ml. The distribution coefficients were calculated as follows:

$$K = (V_R - V_o)/V_p$$

A dead volume of $V_o = 9.0$ ml and a pore volume of $V_p = 13.45$ ml were obtained on the basis of the retention volumes of polystyrene with $M = 1.5 \cdot 10^6$ and toluene. All retention volumes were calculated as the first moments of the corresponding chromatograms.

An investigation of samples with exactly known polydispersities was conducted. These samples were prepared by mixing polystyrene standards in certain preliminarily chosen proportions. The characteristics of the standards and the mixtures prepared are given in Table I. Fig. 4 shows the chromatograms of some mixtures.

The experimental values of the distribution coefficient, K , and the chromatogram widths, σ_v , for all the mixtures investigated are also given in Table I, together with the

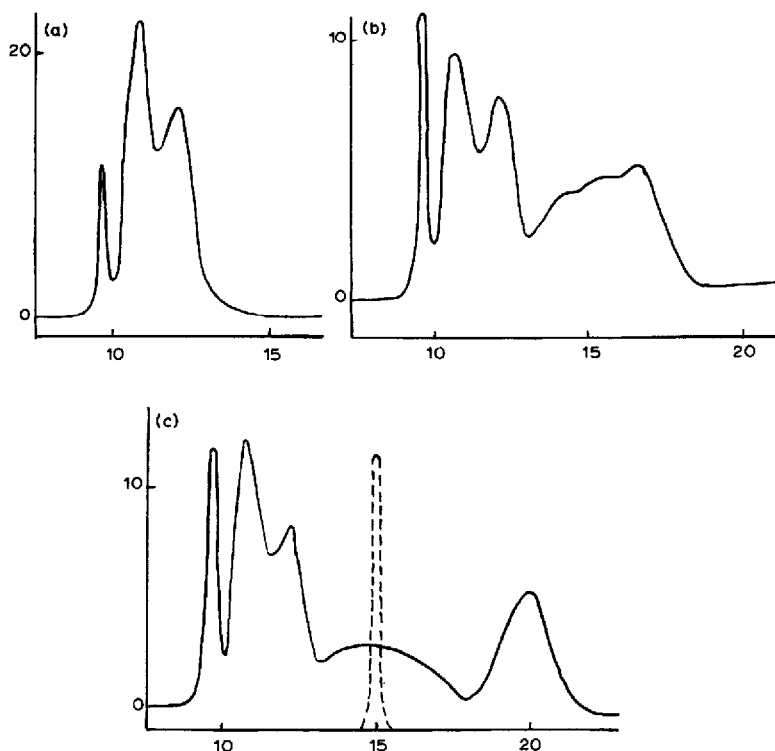


Fig. 4. Experimental chromatograms of mixtures (a) 2, (b) 4 and (c) 5 in Table I. Dashed line shows the instrumental broadening measured by Tung's method⁵.

values of $\psi(K)$ determined by means of eqn. 1 and the values of $(M_z/M_w)_{\text{exp}}$ calculated by means of eqn. 2.

As can be seen from Table I, the polydispersities obtained experimentally from chromatograms are close to the precise values of M_z/M_w which were calculated previously for all the samples involved.

It should be noted that the proposed procedure requires no preliminary information about the polymer under study.

When verifying the method experimentally, mixtures with a wide range of MWDs were prepared and the chromatograms were of complex shape (see Fig. 4). It is concluded that the method will be useful in both laboratory and industrial practice for the rapid analysis of new synthetic polymer materials.

DISCUSSION

The basis of the proposed method is the concept of internal calibration, *i.e.*, the universal dependence $\psi = \psi(k)$. Eqn. 8, which describes this dependence, follows directly from Casassa and Tagami's theory², which is rigorously valid for thermodynamically ideal solvents (so called θ -solvents) with $v_\theta = 1/2(R^2 = CM^{2v})$. In practice, good solvents with values of v between 0.5 and 0.6 are used. In this case

$$\psi = \frac{dK}{d \ln M} = \frac{\partial}{\partial \theta} \psi_\theta = 2v\psi_\theta \quad (9)$$

An important assumption in the derivation of eqns. 8 was monodispersity of the adsorbent, *i.e.*, all the pores are of equal width. With adsorbents with wide pore-size distribution, eqns. 8 can be considered to be approximate. If greater accuracy is to be achieved the experimental dependence $\psi(K)$ should be obtained previously using polymer standards (*e.g.*, polystyrene standards).

It follows from eqns. 8 that ψ reaches its maximum value $\psi_{\text{max}} \approx 0.3$ at $K \approx 0.3$. For sorbents with slit-like pores this corresponds to $R^* \approx 2d/\pi$. It is useful to change from consideration of the average pore diameter $2d$ to the specific surface area, $\Sigma = d^{-1}$, which is equal to the ratio of the area of all the pores, S_p , to the total volume, V_p . Then

$$R^* \approx \frac{2}{\pi}(\Sigma)^{-1} \approx 0.64V_p/S_p \quad (10)$$

Eqn. 10 determines the dependence of the point of inflection of the calibration graph on the pore sorbent characteristics and allows the pore specific surface area to be obtained. The experimental data are described⁶ by the empirical relationship $R^* \approx 0.7(\Sigma)^{-1}$, and this is in good accordance with eqn. 10.

REFERENCES

- 1 B. G. Belenky and L. Z. Vilenchik, *Khromatografiya Polimerov*, Khimiya, Moscow, 1978.
- 2 E. F. Casassa and Y. Tagami, *Macromolecules*, 2 (1969) 14.
- 3 A. A. Gorbunov and A. M. Skvortsov, *Vysokomol. Soedin., Ser. A*, 29 (1987) 920.
- 4 W. Haller, *Macromolecules*, 10 (1977) 202.
- 5 L. H. Tung, *J. Appl. Polym. Sci.*, 10 (1966) 375.
- 6 D. Berek, I. Novak, Z. Grubisic-Gallot and M. Benoit, *J. Chromatogr.*, 53 (1970) 55.