Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Berger, K. C. and Schulz, G. V.(1971) 'Apparent and Real Distribution in GPC (Experiments with PMMA Samples)', Separation Science and Technology, 6: 2, 297 — 303
To link to this Article: DOI: 10.1080/00372367108058963
URL: http://dx.doi.org/10.1080/00372367108058963

SEPARATION SCIENCE, 6(2), pp. 297–303, April, 1971

Apparent and Real Distribution in GPC (Experiments with PMMA Samples)*

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Summary

Molecular weight distribution curves obtained by GPC are broadened if concentration and flow rate are fixed in the usual range. Therefore, the apparent nonuniformity U_{app} of the samples is larger than the real nonuniformity $U = (M_w/M_n) - 1$. For a number of fractionated and unfractionated samples of polymethyl methacrylate we determined M_n and M_w by osmotic, light-scattering, and viscosity measurements. Thus, the real value of U can be compared to U_{app} obtained by GPC at different concentrations and flow rates, v. The excess nonuniformity U_{exc} is evaluated as function of concentration c, polydispersity, molecular weight, and flow rate. For $c = 0$ and $v = 0$, U_{exc} is not far from zero. For standard conditions one certain value of the excess standard deviation of the elution volume allow calculation of U_{exc} for narrow and broader distributions and the obtaining of nearly correct values for the real nonuniformity U.

INTRODUCTION

The aim of this contribution is to determine experimentally the broadening effect of a GPC column. The best method for this purpose would be to pump samples with known molecular weight distribution through the column and to compare the uncorrected distribution curves with the known distributions. Unfortunately, there are no polymer samples for which the real distribution is precisely known. Therefore, we propose a simplified procedure which may be regarded as an approach.

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* Presented at the ACS Symposium on Gel Permeation Chromatography sponsored by the Division of Petroleum Chemistry at the 159th National Meeting of the American Chemical Society, Houston, Texas, February, 1970.

The average values $\bar{M}_n = M_0\bar{P}_n$ and $\bar{M}_w = M_0\bar{P}_w$ of given samples are directly measured by osmotic pressure and light scattering or viscometry, respectively. On the other hand, these values of the samples are calculated from the elution curves by the so-called strip method: The elution curve is divided into small strips and, by using a calibration curve, the molecular weight averages are calculated according to the equations

$$\bar{P}_n = 1/\sum_i (m_i/P_i) \tag{1a}$$

and

$$\bar{P}_w = \sum_i (m_iP_i) \tag{1b}$$

m_i and P_i are the weight fraction and the degree of polymerization (DP) of the ith fraction, respectively. Comparison of the different values of $\bar{P}_n$ and $\bar{P}_w$ obtained by the two methods yields a direct measure of the broadening effect. For a quantitative comparison we introduce the nonuniformity (Uneinheitlichkeit) defined by (*1*)

$$U = (\bar{P}_w/\bar{P}_n) - 1 \tag{2}$$

Table 1 shows the directly measured values of $\bar{P}_n$ and $\bar{P}_w$ of 4 fractions and 1 unfractionated polymethyl methacrylate obtained by radical polymerization. The real values of the unfractionated sample, Polymer III, may be a little higher than listed in Table 1 because the osmotically determined value of $\bar{M}_n$ is too high, though by no more than 5–10%. Other samples of PMMA (see Table 2) were fractionated by the Baker-Williams technique in combination with the GPC technique. They have nonuniformity values between 0.95 and 1.00.

TABLE 1

Nonuniformity Data of PMMA Samples, as Determined by Osmotic Pressure ($\bar{P}_n$), Light-Scattering, and Viscosity Measurements ($\bar{P}_w$)

Sample	$\bar{P}_n \times 10^3$	$\bar{P}_w \times 10^3$	U, Eq. (2)
C.1 (fraction)	1.74	2.33	0.34
C.2 (fraction)	1.98	2.40	0.21
B.1 (fraction)	3.54	4.46	0.26
B.2 (fraction)	5.47	5.96	0.09
III (unfractionated)	1.73	3.25	0.9

FORMAL RELATIONS

If the experimental elution curve is Gaussian with the variance σ_v and the calibration curve is given by

$$\ln P = A - BV_e \qquad (3)$$

(V_e = elution volume), the molecular weights follow a log-normal distribution with the variance $\sigma_P = B\sigma_v$. In this case U is given by (*2*)

$$U = \exp(\sigma_P^2) - 1 \qquad (4)$$

The direct measurements of $\bar{P}_n$ and $\bar{P}_w$ allow calculation of the *real* values of U and σ_P according to Eqs. (1), (2), and (4). The strip method gives an *apparent* value U_{app}

$$U_{app} = \exp(B\sigma_v)^2 - 1 \qquad (5)$$

which includes the broadening effect of the column.

Let $\sigma_{v,0}$ be the variance of the elution curve corresponding to the molecular weight distribution and $\Delta\sigma_v$ the contribution of the broadening effect of the column (axial dispersion), then

$$\sigma_{v,0}^2 = \sigma_v^2 - \Delta\sigma_v^2 \quad \text{and} \quad \sigma_P = B\sigma_{v,0} \qquad (6a,b)$$

It follows from Eqs. (4), (5), and (6) that

$$\ln(1 + U_{app}) = \ln(1 + U) + (B\Delta\sigma_v)^2 \qquad (7)$$

One can assume that the treatment of experimental errors as proposed here for Gaussian distributions is at least approximately correct for other distribution functions (*3*). To prove that assumption, the following experiments were performed.

EXPERIMENTS

We used a Waters GPC apparatus equipped with the following set of columns: 10^6, 10^5, 2×10^4, and 10^3. Figure 1 shows the calibration curves of 3 fractions with approximately the same values of U. Each sample was run at 5 concentrations. Figure 1 shows the considerable effect of the concentration on the position of the elution curves. Obviously, to obtain accurate values for the DP, the concentration must be standardized. It will be shown later that it is best to choose zero concentration.

As can be seen from Fig. 2, the elution curves of the fractions are much more sensitive to changes in concentration than those of the un-

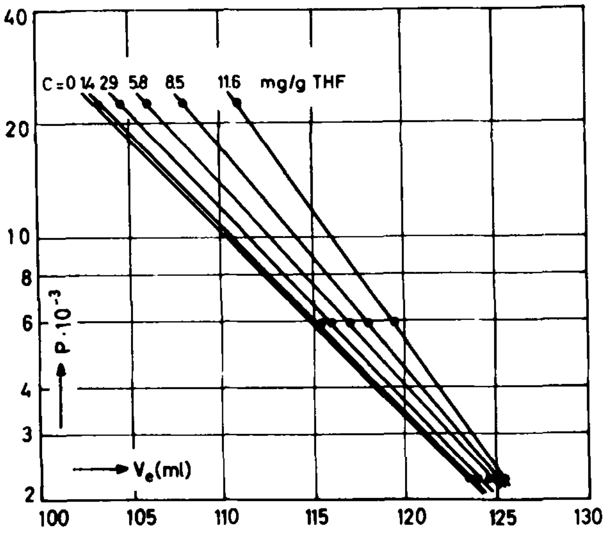

FIG. 1. Concentration dependence of calibration curves (3 fractions of PMMA).

fractionated samples. Obviously, due to their narrow distribution, the fractions migrate through the columns with comparatively high concentrations. They undergo greater dispersion which results in a wider spread of the elution curve. Therefore the concentration, c_m, at the maximum of the elution curve must be taken into account. Moreover, one can see from Fig. 2 that at higher concentrations the maximum of the elution curve is shifted to higher elution volumes and the curves are broadened. To obtain well defined values for both DP and U, an extrapolation is necessary.

A linear extrapolation of the DP (maxima of the curves) to $c = 0$ can be achieved by plotting log DP vs. concentration. The slope of the straight lines is a function of DP and U.

Figure 3 shows that the plot of $\log(1 + U_{app})$ vs. c^2 gives straight lines down to zero concentration. This plot corresponds to the equation

$$\log(1 + U_{app}) = \log(1 + U^0_{app}) + k_u c^2 \qquad (8)$$

where k_u depends on the DP and the nonuniformity. It increases with increasing DP and decreasing U.

Comparing Eqs. (8) and (7), one could assume that the value U^0_{app} is identical with U and that $\Delta\sigma_v$ is proportional to c. As Table 2 shows, this is not true. The extrapolated values U^0_{app} are higher than the directly

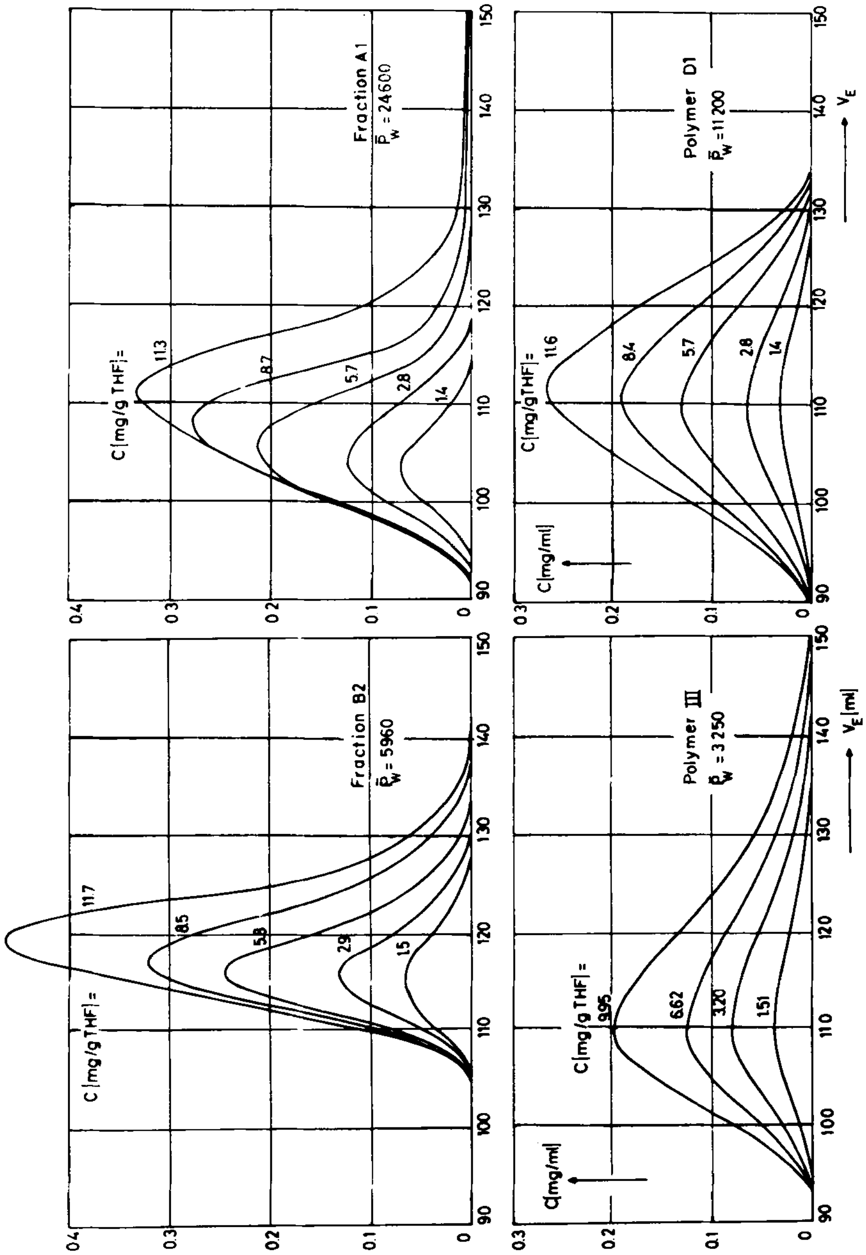

FIG. 2. Elution curves for 2 fractions and 2 unfractionated polymers of PMMA.

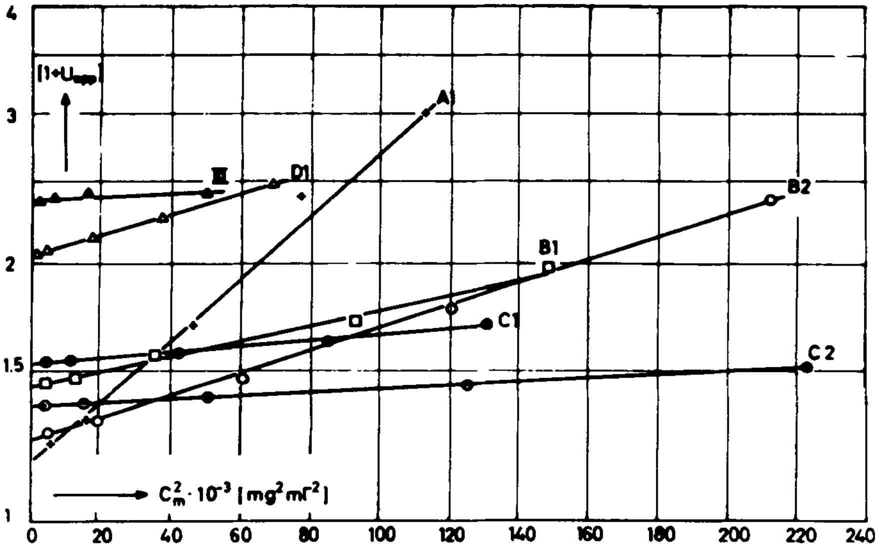

FIG. 3. Nonuniformity as a function of concentration.

measured values. However, the additional variance $\Delta\sigma_v$ is approximately constant regardless of the nonuniformity and of the molecular weight. Thus it is possible to determine the broadening effect of a combination of columns if some samples of known nonuniformity are available.

TABLE 2

Comparison of U^0_{app} (GPC) and U (determined by light scattering and osmotic pressure)

Sample	$\bar{P}_w \times 10^3$	U	U^0_{app}	$\Delta\sigma_v$ (ml)
C.1 (fraction)	2.33	0.34	0.53	3.08
C.2 (fraction)	2.40	0.21	0.37	3.19
B.1 (fraction)	4.46	0.26	0.44	3.19
B.2 (fiaction)	5.96	0.09	0.25	3.29
				$\Delta\sigma_v = 3.2$
III.1 (polymer)	3.25	0.95	1.36	3.85
Mo.1 (polymer)	4.06	0.95	1.36	3.68
Mo.2 (polymer)	6.99	0.95	1.26	3.40
II.1 (polymer)	11.26	0.95	1.28	3.49
I.1 (polymer)	21.03	0.95	1.29	3.49
				$\Delta\sigma_q = 3.6$

The additional variance $\Delta\sigma_v$ comes close to zero by extrapolating the flow rate to zero as some preliminary experiments suggest (*4*). It seems that the extrapolated value $U_{app\ c} = 0/\text{flow rate} = 0$ is not far from the correct value of U.

A more detailed report has been published in *Die Makromolekulare Chemie* (*5*).

Acknowledgment

This work was supported by the Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AIF).

REFERENCES

1. G. V. Schulz, *Z. Phys. Chem.* (*B*), **43,** 25 (1939).

2. H. Wesslau, *Monatsh. Chem.*, **20,** 111 (1956).

3. L. H. Tung, *J. Appl. Polym. Sci.*, **10,** 375 (1966).

4. G. Meyerhoff, *J. Polym. Sci., Part C*, **21,** 67 (1968). W. W. Yau, H. L. Suchan, and C. P. Malone, *J. Polym. Sci., Part A-2*, **6,** 1349 (1968). W. W. Yau, *J. Polym. Sci., Part A-2*, **7,** 483 (1969).

5. K. C. Berger and G. V. Schulz, *Makromol. Chem.*, **136,** 221 (1970).

Received by editor July 15, 1970