CHROM. 6145

THE DETERMINATION OF THE INSTRUMENTAL SPREADING FUNCTION IN GEL PERMEATION CHROMATOGRAPHY

N. G. TAGANOV, D. D. NOVIKOV, G. V. KOROVINA AND S. G. ENTELIS
Institute of Chemical Physics, Academy of Sciences, Moscow (U.S.S.R.)

(First received September 3rd, 1971; revised manuscript received March 1st, 1972)

SUMMARY

At present, gel permeation chromatography (GPC) is often used for the determination of the molecular weight distribution of polymers. To obtain the quantitative molecular weight distribution parameters, it is necessary to take into account the spreading of the sample during its passage through the column and connecting tubes (instrumental spreading). The existing methods of correction for instrumental spreading give different results, depending on which instrumental spreading function is used for the calculations. Nevertheless, the literature on the interpretation of gel permeation chromatography data does not describe methods that permit the precise determination of the instrumental spreading function. A new method of determining the instrumental spreading function is suggested in this paper.

INTRODUCTION

To interpret gel permeation chromatography (GPC) data, instrumental spreading should be taken into account. Previous methods[1-4] of determining the instrumental spreading function (ISF) do not give reliable results. For instance, the reverse flow method[1] excludes the possibility of determining ISF skewing, which affects the results obtained: the values of the average molecular weight calculated with the use of such a correction are often too low. Other methods[2-4] are indirect and their accuracy depends greatly on the precision of the determination of the average molecular weight of standard samples and on the accuracy of the calibration curve.

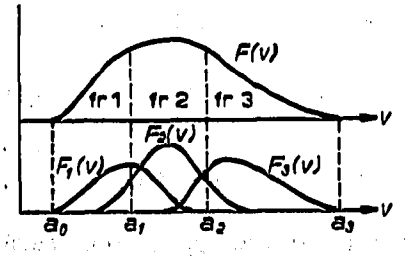

Fig. 1. Gel permeation chromatogram, $F(v)$, of the initial sample. $F_1(v)$, $F_2(v)$ and $F_3(v)$ are chromatograms of fractions 1, 2 and 3, respectively; a_0, a_1, a_2 and a_3 are values of the eluent volumes corresponding to the limits of fraction collection.

EXPERIMENTAL

We have developed a new method for determining the ISF, based on the analysis of the correlations between the corrected gel permeation chromatograms of the initial sample and of the fractions of this sample obtained by running it through the column. The polymer sample is collected as a number of consecutive fractions at the exit of the column. Fraction i contains the part of the initial sample that leaves the column during the elution interval between elution volumes a_{i-1} and a_i (Fig. 1). These fractions also run through the column. Their gel permeation chromatograms are additive, and the following correlation therefore holds:

$$F(v) = \sum_{i=1}^{N} F_i(v) \tag{1}$$

where $F(v)$ is the chromatogram of the initial sample, $F_i(v)$ is the chromatogram of the fraction, N the number of the fractions received. Correlation between the chromatogram $F_i(v)$ and the corrected chromatogram $W_i(v)$ is determined by the following equations.

For fraction i:

$$F_i(v) = \int_{-\infty}^{+\infty} W_i(y)\,G(v,y)\,\mathrm{d}y, \qquad i = 1,2,\ldots N \tag{2}$$

For the initial sample:

$$F(v) = \int_{-\infty}^{+\infty} W(y)\,G(v,y)\,\mathrm{d}y \tag{3}$$

where $G(v,y)$ is normalized, *i.e.*, $\int_{-\infty}^{+\infty} G(v,y)\,\mathrm{d}v = 1$.

As shown below, when the chromatograms of the total polymer and of its fractions are obtained under the same experimental conditions, one obtains the following simple correlation between $W_i(y)$ and $W(y)$ for each fraction:

$$W_i(y) = W(y)\int_{a_{i-1}}^{a_i} G(v,y)\,\mathrm{d}v, \qquad i = 1,2,\ldots N \tag{4}$$

These correlations can be explained with the help of Fig. 2. The corrected

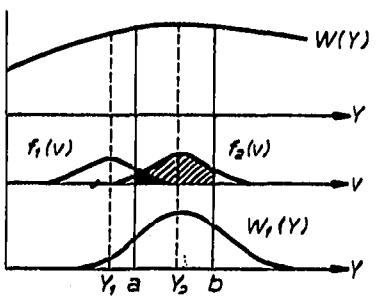

Fig. 2. Corrected gel permeation chromatogram, $W(y)$ of the initial sample. $f_1(v)$ and $f_2(v)$ are the contributions of polymer homologues corresponding to values of y equal to y_1 and y_2 to the chromatogram of the initial sample; a and b are limits of fraction collection; $W_f(y)$ is the corrected chromatogram of the fraction collected during the eluent interval between a and b.

chromatogram of the initial sample, $W(y)$, is shown in the upper part of the figure. The concentrations of the polymer homologues corresponding to y_1 and y_2 eluent volumes are proportional to $W(y_1)$ and $W(y_2)$ values, respectively. The contribution of these polymer homologues to the actual chromatogram is represented by curves $f_1(v)$ and $f_2(v)$, shown in the middle part of the figure, and can be described as follows:

$$f_k(v) \approx W(y_k)G(v,y_k), \qquad k = 1,2 \tag{5}$$

The fraction collected during the elution volume interval between a and b does not contain the whole of the polymer homologue 2, but only the part of it that corresponds to the shaded area under the $f_2(v)$ curve. This fraction also contains the part of polymer homologue 1 that corresponds to the shaded area under the $f_1(v)$ curve.

The corrected chromatogram of the fraction $W_f(y)$ is represented in the lower part of Fig. 2. The ratios of function W to W_f in y_1 and y_2 points are proportional to the concentration ratios of polymer homologues corresponding to these y values in the initial sample and the fraction. Hence,

$$W(y_k)/W_f(y_k) = \int_{-\infty}^{+\infty} f_k(v)\,\mathrm{d}v \Big/ \int_a^b f_k(v)\,\mathrm{d}v, \qquad k = 1,2 \tag{6}$$

and, from eqn. 5,

$$W(y_k)/W_f(y_k) = \int_{-\infty}^{+\infty} G(v,y_k)\,\mathrm{d}v \Big/ \int_a^b G(v,y_k)\,\mathrm{d}v, \qquad k = 1,2 \tag{7}$$

Eqn. 7 therefore proves that eqn. 4 is correct, as the $G(v,y)$ function is normalized and the choice of the y_1 and y_2 values is arbitrary.

DISCUSSION

The system of eqns. 2–4 for each fixed i can be used for the determination of the ISF parameters and their dependence on the molecular volume. For this purpose, a suitable mathematical expression for ISF, $G(v, y, c_1, \ldots, c_n)$, should be used (it must approximate well the chromatograms of individual species and of extra-narrow polymer samples ($M_w/M_n < 1.1$) under sets of values of parametres $c_1, \ldots, c_n$, and a set of values, under which the minimum of the following expression can be reached, should be sought:

$$\int_{-\infty}^{+\infty} \left[W_i(y,c_1,\ldots,c_n) - W(y,c_1,\ldots,c_n) \int_{a_{i-1}}^{a_i} G(v,y,c_1,\ldots,c_n)\,\mathrm{d}v \right]^2 \mathrm{d}y \tag{8}$$

Functions W_i and W of the previous expression are the solutions of the equations:

$$F_i(v) = \int_{-\infty}^{+\infty} W_i(y)\,G(v,y,c_1,\ldots,c_n)\,\mathrm{d}y, \qquad i = 1,2,\ldots,N \tag{9}$$

and

$$F(v) = \int_{-\infty}^{+\infty} W(y)\,G(v,y,c_1,\ldots,c_n)\,\mathrm{d}y \tag{9a}$$

respectively, *i.e.*, they also appear to be the functions of parameters $c_1, \ldots, c_n$. Determination of the set of $c_1^*, \ldots, c_n^*$ values, which minimize eqn. 8, can be carried out by means of one of the schemes described by PITHA AND JONES[5]. To obtain the dependence of the parameters $c_1^*, \ldots, c_n^*$ on the co-ordinate y, *i.e.*, on the molecular volume, one should obtain sets of $c_1^*, \ldots, c_n^*$ values for every fraction and correlate them with the eluent volumes that correspond to the maximum of the corrected chromatograms of these fractions.

Experimental results[6] indicate the universality of these dependences for a wide range of polymers.

It should be noted that the above discussion is based on the assumption of a weak dependence of $c_1^*, \ldots, c_n^*$ on y in the range of elution volumes where $W_i(y)$ is significantly greater then zero and where this dependence can be neglected. Therefore, to increase the accuracy of the determination, of the ISF parameters, it is necessary that the intervals of the fraction collection should be as narrow as possible.

To test the suggested method, the following model test was carried out. Arbitrary values of the function $W(y)$ and the eluent volume values corresponding to the limits of the fraction collection (a_i; $i = 0,1,2, \ldots, N$) were taken. The following function was chosen for ISF:

$$G(v,y,c) = \sqrt{\frac{c}{\pi}} \exp\{-c(v-y)^2\} \qquad (10)$$

where the model value of c was c'. Then $F_i(v)$ and $F(v)$ were modelled by means of eqns. 2–4 and 9. Then, knowing the values of $F(v)$ and sets of $F_i(v)$ and a_i values a digital computer was used to determine the value of the parameter c^*, minimizing eqn. 8. Eqns. 2 and 3 were solved by CHANG AND HUANG's method[7]. The difference between the values of c^* obtained in this way and c' appear to be within the limits of 2% of the c' value. This error may be significantly decreased at the expense of increasing the time of the calculation.

CONCLUSION

The suggested method thus permits the direct determination of the ISF parameters and their dependence on the molecular volume. It is particularly important that by using this method of determining the ISF parameters one can avoid both the necessity of using only narrow polymer fractions and the errors connected with determination of the average molecular weight of standard samples.

REFERENCES

1 L. H. TUNG, J. C. MOORE AND G. W. KNIGHT, *J. Appl. Polym. Sci.*, 10 (1966) 1261.
2 A. E. HAMIELEC AND W. H. RAY, *J. Appl. Polym. Sci.*, 13 (1969) 1319.
3 T. PROVDER AND E. M. ROSEN, *Sep. Sci.*, 5 (1970) 437.
4 D. D. NOVIKOV, N. G. TAGANOV, G. V. KOROVINA AND S. G. ENTELIS, *J. Chromatogr.*, 53 (1970) 117.
5 J. PITHA AND R. N. JONES, *Can. J. Chem.*, 44 (1966) 3031.
6 L. H. TUNG AND J. R. RUNYON, *J. Appl. Polym. Sci.*, 13 (1969) 2397.
7 K. S. CHANG AND R. J. M. HUANG, *J. Appl. Polym. Sci.*, 13 (1969) 1459.