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J. Janca[a]; K. Kleparnik[a]
[a] INSTITUTE OF ANALYTICAL CHEMISTRY CZECHOSLOVAK ACADEMY OF SCIENCES, BRNO, CZECHOSLOVAKIA

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Determination of Molecular Weight Distribution of Polymers by Thermal Field-Flow Fractionation

J. JANCA and K. KLEPARNIK

INSTITUTE OF ANALYTICAL CHEMISTRY
CZECHOSLOVAK ACADEMY OF SCIENCES
61142 BRNO, CZECHOSLOVAKIA

ABSTRACT

The Thermal Field-Flow Fractionation method was used to determine average molecular weights for standard polystyrene samples with narrow distribution whose molecular weight ranged from 3600 to 867000. An effective calibration method was proposed and verified, and through the use of this method experimental fractograms could be interpreted in terms of sample molecular weight. Results were obtained by measuring at three temperature differentials (ΔT = 10°, 15°, and 40°C). The average molecular weights calculated from the fractograms were in very good agreement with the data given for these polystyrene standards by the supplier, and with the results calculated from size exclusion chromatography data. Polydispersity indices were calculated from the fractograms without corrections for longitudinal zone broadening. In view of the potential experimental errors associated with any measurement of polydispersity such corrections do not appear necessary for proper evaluation of data collected even in channels of standard efficiency. A substantial increase in efficiency can be reached e.g., by reducing the thickness of the channel by a factor of two.

Results presented in this paper confirm the prospects offered by the Field-Flow Fractionation method for determinations of molecular weights, and eventually also molecular weight distributions for polymers. The method used to analyze the experimental results indicates that the Field-Flow Fractionation technique may be used as a standard high efficiency method for characterizing polymers.

INTRODUCTION

Reliable determinations of average molecular weights and molecular weight distributions (MWD) of polymers are matters of permanent interest to polymer chemists and physicists. Classic absolute methods, such as osmometry or light-scattering, make it possible to determine average molecular weights of polymers; the distribution of molecular weights can then be determined by examination of the various fractions of the initial polymer sample, which result from application of some classic fractionation method such as precipitation fractionation. During the past fifteen years chromatographic methods have been developed to such a degree of refinement that today's polymer molecular weights and molecular weight distributions are routinely determined from chromatographic data. Size exclusion chromatography (SEC) has in this respect gained a dominant position. Recently even other liquid chromatographic techniques, such as adsorption or partition methods, have found a place beside those methods which rely on simple steric exclusion for polymer characterization. In comparison with SEC, adsorption chromatography suffers from certain drawbacks with respect to universal applicability, in that different polymers will require different sorbent types and mobile phases for proper fractionation. Experimental results are often difficult to interpret because of a separation mechanism which is complicated and at times poorly understood. On the other hand, adsorption chromatography has an advantage over SEC in its wide range of pratical achievable retentions. The separation range of SEC is determined exclusively by the pore volume of the employed gel packing, i.e. it lies between the dead volume of the column V_o and the sum of volumes $V_o + V_i$, where V_i, the internal volume of the pores in the gel, is usually approximately equal to V_o.

In this situation a search for new alternatives to existing separation methods which would permit polymer fractionation is obviously very important. Thermal Field-Flow Fractionation (TFFF) is one such promising alternative (1,2). Some of the theoretical and experimental aspects of this technique which are associated

with retention and dispersion have already been studied by Giddings and co-workers (3,4). The applicability of the TFFF method to measurements of thermal diffusion factors (5) has been demonstrated. A theoretical comparison of SEC with TFFF for the separation of polymers (6) pointed at a number of advantages inherent in the latter technique of which the most important is its superior fractionating power. TFFF was also used to study the thermal diffusion of polystyrene (PS) in diverse solvents differing in thermodynamic quality (7). In a number of other studies experimental factors were investigated which have bearing on the TFFF technique, and which once optimized have improved its performance. The use of a pressurized system permits extension of the working range of temperatures across the channel with resulting effective separation of PS with molecular weights of several hundreds. On the other hand this method was also shown (9) to have potential for fractionation of polymers with extremely high molecular weights (up to 10^{12}). Programming of the temperature gradient (10), and even of the flow rate (11), made it possible to improve fractionation to such an extent that PS samples covering a wide range of molecular weights could be separated with retentions which were acceptable both from the standpoint of experimental arrangement and time. Miniaturization of the TFFF channel and some other design changes permitted a time of analysis of around one minute (12). Further studies were oriented towards a theoretical elucidation of factors influencing peak broadening in TFFF (13), such as non-equilibrium and polydispersity effects. The possibility of performing accurate determinations of polymer polydispersity by measuring peak width at various linear velocities of the solvent (14) has also been explored. In this treatment one determines the velocity independent residue in the plate height expression by extrapolation to zero carrier velocity thus eliminating contributions due to non-equilibrium processes.

Enhancement of the TFFF can also be reached by using the thermogravitational effects, i.e. by relying on the thermal convection in a non-horizontal channel to produce a complicated, non-

parabolic velocity profile (15). In all the above listed studies the polymer sample consisted of polystyrene. Just recently work has been published which decisively shows that the TFFF technique is applicable also to the fractionation of polymers other than PS (16).

Up to the present time no work has been published concerning determinations of molecular weight distributions and average molecular weights for polydisperse polymer samples by means of the TFFF method, i.e. dealing with objective quantitative evaluation based on molecular parameters of a given polymer. This kind of study is the subject of the present paper. Commonly available PS standards with narrow molecular weight distributions were selected as the sample best suited for the study. The selection was motivated by certain advantages provided by PS standards. On the one hand they are commonly characterized by miscellaneous methods, both absolute and chromatographic in nature, and a comparison between results obtained by the various methods can easily be made. On the other hand, molecular parameters for PS are highly reliable for the very reason that they are being studied so frequently. Finally, in consideration of the narrow MWD (polydispersity index M_w/M_n is for the most part 1.05) these samples represent the case of highly sophisticated fractionation from the viewpoint of both precision and accuracy.

EXPERIMENTAL

A dual hairpin TFFF column used in this work is in principle identical to the columns used by Giddings et al. in the experimental work cited above. The 0.2 mm thick spacer determined the channel thickness w. The total volume of the channel was 2.283 ml which gave a ratio of thickness to width amounting to 1:50. The temperature gradient across the channel was 10°, 15° or 40°C depending on the range of PS molecular weights for which efficient separation was to be carried out. Even under the highest experimental temperature differential the temperature of the hot wall was several degrees below the boiling point of the solvent, which

eliminated the necessity for working at an elevated column pressure.

Solutions of the samples of PS standards were injected with the aid of a 6-port injection valve (Rheodyne Inc., Berkeley, Ca. U.S.A.). The volume of the sampling loop was 20 μl which is less than 1% of the total volume of the TFFF channel.

A differential UV detector with a constant wavelength of 254 nm (Development Workshops of the Czechoslovak Academy of Sciences, Czechoslovakia) was used for the detection.

A constant solvent flow of 2.287 ml/h was maintained by a home-made syringe pump. The corresponding linear velocity <v> of solvent through the channel was 0.032 cm/s. Under the above conditions the influence of relaxation processes is negligible, and therefore the flow was not switched off for zone equilibration following injection.

The carrier liquid was tetrahydrofuran (THF), which had been purified prior to use by distillation from copper(I) chloride and potassium hydroxide.

PS standards (Waters Associates, Inc., Milford, Mass., U.S.A.) with narrow molecular weight distribution were used for this study. M_w/M_n was less than 1.05 in the majority of cases; a few samples showed M_w/M_n in excess of 1.1. The supplier's data on average molecular weights for these PS standards are presented in Table 1. Solutions of the various PS standards were injected in concentrations amounting to 0.1%, 0.5%, and 1.0% on a weight per volume basis.

The elution volume for a nonretained solute, which is required for calculation of the retention ratio R, was determined by means of additions of small amounts of benzene to the sample solutions and subsequent careful monitoring of the elution position of this inert marker. In some instances it was unnecessary to add a marker to the solution, since the void volume was indicated by the elution of oxidation products of THF whose content in the sample differed from the content in the solvent or mobile phase.

TABLE 1

Molecular Weights of Polystyrene Standards Certified by the Supplier and Measured by Size Exclusion Chromatography (22)

Standard	Supplier's Data			SEC Data		
	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
PS 1	3.6[a]		not given	5.28	4.42	1.19
PS 2	10.0	9.6	1.042		not measured	
PS 3	17.5[a]		not given	18.0	15.8	1.14
PS 4	20.8	20.0	1.040	23.7	19.6	1.21
PS 5	36.0	33.0	1.091		not measured	
PS 6	51.0	49.0	1.041	59.1	51.9	1.14
PS 7	111.0	111.0	1.000	108	93	1.16
PS 8	200.0	193.0	1.036	206	174	1.18
PS 9	411.0	392.0	1.048	398	360	1.11
PS 10	498.0	404.0	1.233	526	458	1.15
PS 11	867.0	773.0	1.122	921	760	1.21

a) The supplier certifies only one value of the molecular weight

RESULTS AND DISCUSSION

Polymers are often characterized by their molecular weight distribution and their average molecular weights, where the latter parameters are defined by the various statistical moments of this distribution. The weight average molecular weight M_w, and the number average molecular weight M_n are the most commonly used averages since these parameters are easily measured experimentally through observations of light-scattering (M_w) and osmometry (M_n). These average molecular weights are defined by the following relationships

$$M_w = \int_0^\infty M f_w(M)\ dM \Big/ \int_0^\infty f_w(M)\ dM \tag{1}$$

and

$$M_n = \int_0^\infty f_w(M)\ dM \Big/ \int_0^\infty M^{-1}\ f_w(M)\ dM \tag{2}$$

where M is a discrete value of the molecular weight which for a given distribution corresponds to the value of the unnormalized weight distribution function $f_w(M)$. If the distribution function is normalized, the following relationship applies

$$\int_0^\infty f_w(M)\ dM = 1 \tag{3}$$

By using fractionation methods that permit the separation of molecular species according to their molecular weights, it is possible with a suitable interpretation of experimental data to obtain both the distribution and the average values of the molecular weights. Thermal FFF is such a method. The fractogram, obtained as a dectector response to continuously eluting molecular species of the fractionated polymer, is in principle defined by a certain type of differential distribution curve in non-standard coordinates. If the detector response is proportional to the weight amount of the polymer fraction in the eluting solution, and if the relationship between elution volume and molecular weight is known the fractogram can be interpreted to yield an unnormalized

differential distribution curve. Such a curve can then easily be used to calculate average molecular weights according to relationships 1-3.

With aid of the above procedure it is possible to interpret the fractogram only under ideal conditions with no axial dispersion effects contributing to the peak broadening. However, even the fractogram of an ideally monodisperse polymer will have a final width. This broadening is responsible for the fact that the eluate from the column at any given moment is not a strictly monodisperse fraction, but a mixture of macromolecular species with molecular weights both above and below the theoretical value corresponding to the particular elution position. The resulting fractogram thus provides the information on both fractionation and dispersion and can be described quantitatively by Tung's integral equation (17)

$$F(v) = \int_{-\infty}^{+\infty} W(y)G(v,y)\, dy \qquad (4)$$

where function F(v) describes the uncorrected chromatogram in units of elution volume v. Function W(y) is the corrected chromatogram, and G(v,y) denotes the spreading function whose physical meaning can be explained as the broadening which is caused by a particular separation system during passage of a unit amount of a given polymer fraction. This fraction is assumed to be injected in an infinitely small volume, and its molecular weight corresponds to elution volume y. Function G(v,y) is usually approximated by a Gaussian function in the case of SEC.

A number of methods are described in the literature which make it possible to solve Equation 4 for SEC, and to correct the resulting chromatograms. A review of these methods can be found elsewhere (18). The same type of corrections to the experimental fractogram can be used in the case of TFFF. However, in each case it is necessary to establish whether or not such corrections are truly needed. The agreement between average molecular weight values for standard polymer samples which are on the one hand calculated from experimental fractograms without corrections, and

on the other hand measured by independent (e.g. absolute) methods can serve best as a criterion to determine the necessity for a correction. As long as the difference between the two values lies within the range of experimental errors inherent in respective method the correction is unnecessary.

If, for the sake of simplicity, one neglects the contribution of axial dispersion to the shape of the fractogram the MWD can be calculated on the basis of the following considerations:

The retention ratio R is the experimental parameter which is accessible directly from the fractogram.

$$R = \frac{\langle v \rangle}{v} \tag{5}$$

where v stands for the elution volume of a given macromolecular species, and <v> is the average elution volume of a non-retained solute. Let us notice that for practical reasons we have introduced a notation which is rather different than the one used in the works by Giddings and co-workers; the physical meaning of retention R, however, remains unchanged. The dependence of R on molecular parameters of the fractionated polymer (e.g. the molecular weight) has so far been described by a strictly empirical relationship due to the fact that the physical process which leads to a concentration distribution of macromolecules in a thermal field (4) is as yet poorly understood. In an earlier paper (16) it was shown experimentally that the dependence of retention R on molecular weight varies with polymer type.

At the present state of knowledge it is necessary to find a separate empirical relationship between R and M for every polymer type with the aid of well defined standards, and to use the calibration function thus obtained for interpretation of the fractogram of an unknown polymer sample of the same chemical composition and general structure. An alternate route, which from the view point of experiment is more exacting and expensive, is to equip the TFFF channel with a detector which directly monitors molecular weight or a quantity proportional to it. Suitable detectors for this purpose are e.g. automatic flow-through viscometers (19) or monitors of

low-angle light scattering (20).

The performance of an SEC column is most commonly calibrated through use of well defined standard polymers. An exhaustive review of various calibration procedures can be found elsewhere (21). In the present case of TFFF we selected a calibration function of the following polynomial type

$$M = \sum_{i=0}^{n} a_i R^i \qquad (6)$$

where M is the molecular weight corresponding to a given retention R. As a first iterative step, virial coefficients a_o to a_n of the above polynomial were calculated by non-linear regression using M_w values and their corresponding empirical average retentions R_{ave} for a set of PS standards. R_{ave} in turn is defined by the following relationship

$$R_{ave} = \int_{R(v_b)}^{R(v_a)} R\, f_w(R)\, dR \Big/ \int_{R(v_b)}^{R(v_a)} f_w(R)\, dR \qquad (7)$$

where v_a and v_b are elution volumes corresponding to the end and beginning of an eluting zone. This first calibration function was used to analyze the TFFF fractograms, which were recorded for each of the PS standards, thereby determining a molecular weight distribution function for each sample. This sample mass spectrum was then used as base for determination of the sample's experimental M_w and M_n by means of Equations 1 and 2. Each experimental M_w value was subsequently identified with its corresponding R value through use of the first calibration function (Eqn. 6). In this manner a new set of R values was obtained which could be related to the original (manufacturer's) values for M_w for fitting to a second calibration function (Eqn. 6) through non-linear regression. This iterative procedure was repeated until variations in the calculated values for the average molecular weights were within the range of the experimental errors. In this manner it was possible to obtain a so-called effective calibration dependence.

In this work the degree of the polynomial in Equation 6 was not predetermined, but was increased stage by stage starting from a linear function. At the moment when further increase in the degree of the polynomial did not lead to enhancement of the results of the effective calibration, the procedure was discontinued. In cases of all experimental data presented here (collected at temperature differentials of 40°, 15°, and 10°C respectively) a third degree polynomial:

$$M = a_o + a_1R + a_2R^2 + a_3R^3 \qquad (8)$$

was sufficient to yield highly reliable approximations with deviations in the calculated values of M_w for observed retentions which were comparable in magnitude to the experimental errors.

By using the calibration functions thus obtained, values for M_w and M_n were determined as described above. In carrying out this procedure no attempt was made to correct for zone broadening due to nonequilibrium effects. Already the first approximate calibration function (Eqn. 8) provided M_w and M_n values within the range of experimental errors, which made further iterative steps unnecessary. The results are summarized in Tables 2, 3 and 4 for temperature gradients ΔT = 40°, 15° and 10°C, respectively. As follows from the comparison of the values of M_w and M_n calculated from the TFFF fractograms (Tables 2, 3 and 4) with the values reported by the supplier (Table 1), the average difference between these values is within the range 5-10% rel. for both average molecular weights. With regard to all possible experimental errors of all procedures for the determination of molecular weights of polymers (21), this agreement can be considered as very good. Even under the given experimental conditions, which have not by far been considered as high-resolution TFFF (12), the correction for longitudinal broadening is obviously not necessary. This is proved not only by the above agreement of M_w and M_n values but, in the first place, by the fact that the polydispersity indices, M_w/M_n, that are calculated from TFFF fractograms are, in the majority of cases, lower than the values of M_w/M_n calculated from SEC

TABLE 2

Retentions and Molecular Weights Calculated from Fractograms Obtained by TFFF at $\Delta T = 40°C$

Standard	R_{ave}	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
PS 1	0.960[a]	- [b]	- [b]	-
PS 2	0.880	11.2	- [b]	-
PS 3	0.831	18.6	15.4	1.20
PS 4	0.822	19.9	17.2	1.16
PS 5	0.737	34.0	31.4	1.08
PS 6	0.657	48.3	44.6	1.08
PS 7	0.493	102.7	99.9	1.03

a) peak maximum volume
b) unresolved peak

TABLE 3

Retentions and Molecular Weights Calculated from Fractograms Obtained by TFFF at $\Delta T = 15°$

Standard	R_{ave}	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
PS 7	0.821	125.0	97.0[a]	1.29
PS 8	0.745	182.3	169.9	1.07
PS 9	0.574	414.5	374.3	1.11
PS 10	0.510	564.5	482.3	1.17
PS 11	0.420	854.5	815.4	1.05

a) unresolved peak

TABLE 4

Retentions and Molecular Weights Calculated from Fractograms Obtained by TFFF at $\Delta T = 10°C$

Standard	R_{ave}	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
PS 7	0.909	129.8	- [a]	-
PS 8	0.860	199.1	125.3[a]	1.59
PS 9	0.740	415.9	315.6[a]	1.32
PS 10	0.712	503.8	368.9	1.37
PS 11	0.571	824.3	719.5	1.15

a) unresolved peak

data and very close to the values reported by the suppliers (±3% rel. on average). In the case of some PS standards, indicated in Tables 2, 3 and 4, the values of the polydispersity indices, M_w/M_n, obviously are higher than those given by the supplier. In all these cases determinations were based on fractograms with an imperfect separation of the polymer from the peak corresponding to non-retained solutes in the low-molecular weight range. This means that in this section of the fractogram it was necessary to extrapolate the calibration function into the range of molecular weights or retentions which were not measurable experimentally. The poorer the resolution of peaks in this range, the higher was the discrepancy between the values of M_n calculated from TFFF fractograms and those given by the supplier. Consequently, also the agreement between M_w/M_n was poorer. It is thus obvious that for the exact interpretation of the TFFF data by using the described method of effective calibration, good separation in the low-molecular weight range of the fractogram should necessarily be reached in order to calculate the values of M_n with a sufficient reliability.

It follows from the above results that the TFFF method is well suited for determining both molecular weights of polymers and their distribution. In consideration of the fact that all the results were obtained by using the standard TFFF channel, the assumption is justified that the potential applications of this method for characterizing polymers have, by far, not been exhausted.

REFERENCES

1. G.H. Thompson, M.N. Myers and J.C. Giddings, Sep. Sci. 2, 797 (1967).

2. G.H. Thompson, M.N. Myers and J.C. Giddings, Anal. Chem. 41, 1219 (1969).

3. M.E. Hovingh, G.H. Thompson and J.C. Giddings, Anal. Chem. 42, 195 (1970).

4. M.N. Myers, K.D. Caldwell and J.C. Giddings, Sep. Sci. 9, 47 (1974).

5. J.C. Giddings, M.E. Hovingh and G.H. Thompson, J. Phys. Chem. 74, 4291 (1970).

6. J.C. Giddings, Y.H. Yoon and M.N. Myers, Anal. Chem. 47, 126 (1975).

7. J.C.Giddings, K.D. Caldwell and M.N. Myers, Macromolecules 9, 106 (1976).

8. J.C. Giddings, L.K. Smith and M.N. Myers, Anal. Chem. 47, 2389 (1975).

9. J.C. Giddings, J. Chromatogr. 125, 3 (1976).

10. J.C. Giddings, L.K. Smith and M.N. Myers, Anal. Chem. 48, 1587 (1976).

11. J.C. Giddings, K.D. Caldwell, J.F. Moellmer, T.H. Dickinson, M.N. Myers and M. Martin, Anal. Chem. 51, 30 (1979).

12. J.C.Giddings, M. Martin and M.N. Myers, J. Chromatogr., 158, 419 (1978).

13. L.K. Smith, M.N. Myers and J.C. Giddings, Anal. Chem. 49, 1750 (1977).

14. M. Martin, M.N. Myers and J.C. Giddings, J. Liq. Chromatogr. 2, 147 (1979).

15. J.C. Giddings, M. Martin and M.N. Myers, Sep. Sci. Technol. 14, 611 (1979).

16. J.C. Giddings, M.N. Myers and J. Janča, J. Chromatogr. 186, 37 (1979).

17. L.H. Tung, J. App. Polym. Sci. 10, 375 (1966).

18. N. Friis and A.E. Hamielec, Adv. Chromatogr. 13, 41 (1975).

19. G. Meyerhoff, Makromol. Chem. 118, 265 (1968).

20. A.C. Ouano and W. Kaye, J. Polym. Sci., Polym. Chem. Ed. 12, 1151 (1974).

21. J. Janča, Adv. Chromatogr. 19, 37 (1980).

22. J. Janča, M. Kolínský, and L. Mrkvičková, J. Chromatogr. 121, 23 (1976).