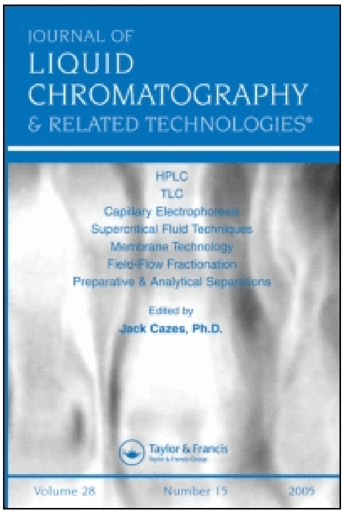

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Evaluation of a Standardless Method of Determination of Molecular Weight and Polydispersity of a Polystyrene Sample by Thermal Field-Flow Fractionation

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EVALUATION OF A STANDARDLESS METHOD OF DETERMINATION OF MOLECULAR WEIGHT AND POLYDISPERSITY OF A POLYSTYRENE SAMPLE BY THERMAL FIELD-FLOW FRACTIONATION

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ABSTRACT

The possibility of an accurate determination of polymer molecular weight and polydispersity by thermal field-flow fractionation (ThFFF) retention measurements is here discussed with reference to the use of only physicochemical data of ordinary and thermal diffusivity, but without need of prior calibration of the ThFFF system.

Special emphasis is devoted to the check of linearity conditions of retention data determination, i.e., on the proper sample loading and thermal field strength to be chosen for unbiased polymer specifications determination. Different numerical methods of determining peak profile attributes (non - linear peak fitting procedures by Edgeworth-Cramer series expansions, numerical integration, graphical determination) are compared. The approach is applied to a standard polystyrene sample, with ethylbenzene as polymer solvent and carrier liquid, as extensive physicochemical informations on this polymer-solvent system are available in the literature. In addition, it is shown that the combination of retention and plate height measurements provides an absolute and accurate method of determination of the thermal diffusion coefficient of the sample.

INTRODUCTION

The capability of the thermal field-flow fractionation (ThFFF) technique, which belongs to the family of field-flow fractionation (FFF) methods, for the determination of the molecular weight distribution (MWD) of a wide variety of organo-soluble polymers is generally recognized.[1] As compared to size-exclusion chromatography (SEC), ThFFF methods often exhibit higher separation selectivity for MWD determination.[2] For practical applications in the field of polymer characterization, the outstanding feature of ThFFF lies in the easy determination of polymer MWD from which average molecular weight (MW) and polymer polydispersity (μ) can be derived. Several methods have been suggested for these purposes. They are either based on calibration plots[3,4] or standardless methods through polymer/solvent constants.[5,6]

Giddings[7] critically considered the fundamentals of calibration and standardless method for MW determination in both SEC and ThFFF, emphasizing that ThFFF only needs physicochemical constants, but not "system" constants, such as the parameters of the calibration curve of the specific employed column, which are required in SEC. As noted by Giddings, "the calibration constants required in ThFFF are physicochemical constants describing ordinary and thermal diffusivities, which can be obtained from one thermal FFF system" or from other physicochemical measurements and "can thus be transferred to every thermal FFF system in the universe."[7] The significance of ThFFF for MW determination is thus enhanced and superior to

SEC. These appealing properties require careful experimental conditions be respected, e.g., that the experimental conditions under which the physicochemical data are employed be coherent with those under which they where originally derived.

In this paper, the standardless method of determining MW and polydispersity data, by using ordinary and thermal diffusivity data, is considered in reference to the proper check of the above mentioned experimental conditions — called here ideal conditions — which are, namely, the conditions of high dilution or the linearity conditions[8] and the control of the thermal field strength.

It is a necessary requirement that the ThFFF system behaves ideally for performing accurate ThFFF calibration-based measurements of complex samples of unknown physicochemical constants. Indeed, the standard retention equation in FFF[9] assumes especially that there are no interactions between sample molecules. This assumption is a necessary condition for a chromatographic process to be defined as linear.

It has been demonstrated that the Edgeworth-Cramèr peak shape fitting methods[10,11] are able to check linearity conditions in stochastic processes with stationary and independent increments. These methods have been applied in chromatography,[11-13] sedimentation field-flow fractionation (SdFFF),[14] and, eventually, ThFFF.[8]

In the latter work, an experimental evaluation of nonlinearity effects on ThFFF retention was performed by means of a comparison made using different methods of estimating peak parameters (i.e., mean and standard deviation).

Necessary conditions for linearity (NCL) were verified by EC series fitting for the analysis of polystyrene (PS) standards in ethylbenzene (EB) and the results established practical rules for performing ThFFF measurements under conditions of linearity.

In the present work the reported experimental conditions for measurements under linear ThFFF elutions are chosen for the estimation of the accuracy of ThFFF for MW and μ evaluations without calibration. The polymer/solvent system (PS/EB) that was already used in the previous work has been chosen because of the extensive physicochemical characterization of this system in the literature. Correction for the departure from a parabolic flow profile due to the variation in viscosity with temperature[15] was also taken into account.

THEORY

Molecular Weight Determination

For most FFF systems for which the flow profile can be assumed to be parabolic, the retention ratio, R, is exactly related to the characteristic length of the analyte layer distribution, l, which, in the high retention limit, approximates, closely, the mean layer thickness of the migrating band, and to the channel thickness, *w*, as follows:

$$\lambda = \frac{l}{w} \tag{1}$$

$$R = 6\lambda\left[\coth(1/2\lambda) - 2\lambda\right] \tag{2}$$

Nonetheless, in ThFFF, the flow profile is distorted by the temperature gradient across the channel. Whatever the degree of retention, the retention ratio was then shown to be given as:

$$R = 6\lambda\nu\left(1 - R_p\right) + R_p \tag{3}$$

where the flow distortion parameter, ν, is a constant whose value is determined by the properties of the carrier, the cold wall temperature and the field strength.[15] R_p is here referred to as the standard retention ratio expressed by Eq. 2. By means of Eqs. 2 and 3, λ can be determined through numerical methods from experimental R data andν values.

For ThFFF, λ is given to a good approximation by:

$$\lambda = \frac{D}{D_T \Delta T} \tag{4}$$

where ΔT represents the temperature difference across the channel and D and D_T are the coefficients for ordinary and thermal diffusion, respectively.[16] The relationship between the ordinary diffusion coefficient, D, and the molecular weight, M, can be expressed by:[17]

$$D = \frac{A}{M^b} \tag{5}$$

where A and b are constants for the polymer/solvent system at a given temperature, and which have been previously reported for PS/EB.[5] As D_T does not show any significant dependence on M,[16] by substituting Eq. 5 into Eq. 4 and, with the experimental values of λ from experimental retention ratios R_p, one gets M as:[18]

$$M = \left(\frac{A}{\lambda D_T \Delta T} \right)^{1/b} \tag{6}$$

It should be noted that Eq. 3, like Eq. 2, is derived on the assumption of an exponential concentration distribution of the macromolecules along the temperature gradient. In fact, the dependencies of D and D_T on temperature leads to a distortion of the concentration profile from the exponential assumption. Similarly, the temperature dependence of the thermal conductivity of the carrier liquid modifies the effective temperature difference ΔT to be used in Eq. 4. Recently developed methods are available to take into account these effects.[19,20] Although they should improve the accuracy of the MW determinations, these effects are, in the present work, considered as of second-order, and are not taken into account.

Polydispersity Determination

In ThFFF, because of the rule of additivity of the variance, the total plate height H can be expressed as the sum of individual contributions arising from independent band broadening processes. For fractionation of narrowly disperse polymers in systems for which the instrumental contribution to band broadening can be assumed negligible, the main contribution is the nonequilibrium, H_n, term. For a polydisperse polymer there is an additional term due to the tendency of high MW species to move behind the lower MW sample components. The latter term is called polydispersity contribution, H_p. The experimentally observable plate height is thus:

$$H = H_p + H_n \tag{7}$$

The polydispersity contribution can be approximately expressed in terms of the mass-based selectivity, S_M, of the separation system as:[21]

$$H_p = L S_M^2 (\mu - 1) \tag{8}$$

where $\mu = \overline{M}_w / \overline{M}_n$ is the ratio of the weight average MW to number average MW.[22] The parameter S_M is the MW-based selectivity defined as:

$$S_M = \left|\frac{d\ln R}{d\ln M}\right| = \left|\frac{d\ln R}{d\ln\lambda}\cdot\frac{d\ln\lambda}{d\ln M}\right| \qquad (9)$$

In the above expression, the term $d\ln R / d\ln\lambda$, which depends on both λ and v (see Eqs. 2 and 3) is nearly equal to 1 for highly retained samples. From Eqs. 4 and 5, it is seen that the term $d\ln\lambda / d\ln M$ is equal to -b since D_T is found to be independent of MW for most the homopolymers.[16] Since the nonequilibrium term H_n linearly depends upon the flow velocity, $<v>$, of the carrier, one gets:

$$H = H_p + C < v > \qquad (10)$$

For moderately polydispersed samples, μ can be obtained from the extrapolation at zero flow velocity of experimental total plate height H vs. linear flow velocity $<v>$ plots.[21] Furthermore, the ordinary diffusion coefficient D can be derived from the slope C as follows:

$$C = \chi w^2 / D \qquad (11)$$

provided that the dimensionless coefficient χ, which depends both on λ and v,[23] is estimated with sufficient accuracy.

MATERIALS AND METHODS

Instrumentation

The ThFFF system used in this work was the model T100 ThFFF Polymer Fractionator (FFFractionation, LLC, Salt Lake City, UT, USA) already described in previous work.[8] The channel length, breadth and thickness were, respectively, 45.6 cm, 1.9 cm and 0.0139 cm.

The sample was a linear polystyrene standard obtained from Polymer Laboratories (Church Stretton, U.K.) with a nominal μ value of 1.04 and reported MW of 170,000. The carrier liquid and polymer solvent was extrapure ethylbenzene (EB03080, Fluka Chem., Buchs, Switzerland). The solutions of

Table 1

ThFFF-based Molecular Weight Determination of PS/EB Systems*

						EC			Integration			Graphic	
% w/v	T_c[2]	ΔT[2]	Flow[1]	ν	R	λ	MW	R	λ	MW	R	λ	MW
1	30	40	0.1	-0.135	0.356	0.0779	216,929	0.356	0.0779	217,181	0.348	0.0757	228,424
1	30	40	0.15	-0.135	0.386	0.0856	182,965	0.386	0.0856	183,069	0.376	0.0829	193,890
1	30	40	0.17	-0.135	0.363	0.0797	208,366	0.363	0.0797	208,244	0.356	0.0778	217,700
1	30	40	0.2	-0.135	0.377	0.0832	192,671	0.371	0.0818	198,639	0.374	0.0824	196,245
1	30	40	0.25	-0.135	0.370	0.0815	199,908	0.370	0.0815	200,140	0.363	0.0795	209,226
1	28	35	0.2	-0.122	0.420	0.0937	197,889	0.420	0.0937	197,784	0.416	0.0926	202,287
1	31	45	0.2	-0.148	0.345	0.0759	183,970	0.344	0.0758	184,195	0.340	0.0746	189,698
1	33	50	0.2	-0.160	0.317	0.0697	177,327	0.317	0.0696	177,789	0.314	0.0689	181,066
0.5	31	45	0.2	-0.148	0.361	0.0800	166,946	0.352	0.0778	175,916	0.352	0.0778	175,916
0.5	30	40	0.2	-0.135	0.394	0.0877	175,250	0.394	0.0877	174,959	0.382	0.0847	186,515
						MW=190,222±15,723			MW=191,792±14,655			MW=198,097±16,510	

---

* PS sample MW=170,000; [1] Flow rate values are expressed in mL/min; [2] T_c and ΔT values are expressed in °C.

Table 2

Polydispersity, Molecular Weight, and Thermal Diffusion Coefficient Evaluation From Plate Height Measurements[a]

Flow[1]	Graphic H[2]	Integration H[2]	EC H[2]
0.10	0.33	0.37	0.35
0.15	0.46	0.48	0.51
0.17	0.47	0.48	0.47
0.20	0.62	0.59	0.58
0.25	0.69	0.75	0.72
	$H_p=0.0890\pm0.0491$[2]	$H_p=0.0996\pm0.0532$[2]	$H_p=0.111\pm0.059$[2]
	$\mu=1.0089\pm0.0049$	$\mu=1.0101\pm0.0054$	$\mu=1.0112\pm0.0059$
	r=0.982[3]	r=0.980[3]	r=0.974[3]
	D=2.800[4]	D=2.863[4]	D=3.008[4]
	$D_T=0.879$[5]	$D_T=0.881$[5]	$D_T=0.922$[5]
	MW=240,049[6]	MW=230,596[6]	MW=210,911[6]

---

[a] Sample 170,000 MW PS, 1% w/v sample load, $\Delta T=30°C$, nominal $\mu=1.04$;
[1] Flow values are expressed in mL/min; [2] H values are expressed in cm;
[3] r correlation coefficient; [4] *D* values determined by Eq. 11 and expressed in 10^7 cm^2s^{-1}; [5] D_T values computed by Eq. 14 and expressed in 10^7 $cm^2s^{-1}K^{-1}$;
[6] MW values obtained by Eq. 6 and Eq. 13.

polymer samples were injected by means of an injector with a 20μL loop (Rheodyne, model 7125) and relaxed as described in Ref. 8. A model 420 HPLC pump (Kontron Instruments S.p.A., Milan, Italy) was used to supply carrier flow. Peak detection was achieved with a model R410 Refractive Index Detector (Waters Associates, Milford, MA, USA). The void volume was determined, as described in Ref. 8, by injecting tetrahydrofuran 8441 for UV (J. T. Baker, Deventer, The Netherlands) as an unretained probe.

Computational

Data collection from the ThFFF system was driven by a software package from FFFractionation Inc. The routine also included a Savitzky-Golay smoothing procedure by which digitized raw fractograms were filtered. The EC series least-squares fitting routine described in Ref. 8 also included the computation of first peak moments by integration. The retention and plate height data (R, H) reported in Table 1 and Table 2 for various experimental conditions. Plate height values H were calculated from peak variance according to the definition of plate height in chromatography and related techniques as:

$$H = L\left(\frac{\sigma}{t_r}\right)^2 \tag{12}$$

where L is the channel length, t_r the retention time and σ the peak standard deviation.

There are three methods for estimating these data: a) from the experimental fractograms; b) from the computation of the first and second moments of the digitized peaks; c) from the EC-series least-squares fit of the peaks, which, among others, provides t_r and σ as parameters. In Tables 1 and 2, methods a), b) and c) are, respectively, referred to as "graphic," "integration," and "EC." Note that, in methods b) and c), t_r corresponds to peak mean retention time. In method a), which is based on simple measurements from the paper record of the fractogram, t_r is taken as the elution time of the peak maximum and σ is determined from the measurement of the peak width at half-height, $b_{0.5}$, as $\sigma = 0.425\ b_{0.5}$.

Experimental void volume and retention volumes were both corrected for the external dead volume. Indeed, because of the relatively large value of the external dead volume, resulting corrections on retention volumes are not negligible for accurate MW and μ determinations without calibration.

RESULTS AND DISCUSSION

The onset of nonlinear conditions in ThFFF has been shown to be detectable by the EC procedure even at very modest concentrations.[8] Under nonlinear elution conditions, it has been therein reported that modest increases in sample polymer load result in shifts toward higher retention volumes as well as in some additional peak broadening. Therefore, molecular weight and polydispersity determinations, which are based on peak mean and standard deviation, can be significantly affected by concentration effects. EC series fitting experiments have proved highly accurate in monitoring any peak shape difference, even for almost Gaussian profiles, by defining some convenient nonlinearity markers. The accuracy of MW and μ determinations relies on the accuracy with which retention and plate height, that is, peak mean retention time and standard deviation, can be determined. In common FFF practice, peak mean and standard deviation are measured either by a graphical approach or by integration. The EC method applied to FFF was shown to provide, not only accurate values of peak moments, but also practical rules to identify linear conditions for the elution of PS/EB systems by ThFFF.[8]

Concentration effects in thermal FFF arise from several origins. First, increasing the sample concentration, one increases the viscosity of the polymer solution in the vicinity of the accumulation wall, which tends to increase retention. Furthermore, this may lead to partial and temporary entanglement of polymeric chains, and again to increase retention as one expects two entangled chains to behave as a macromolecule of larger molar mass. On the other side, it is much likely that the gradient diffusion coefficient (which is the relevant diffusion coefficient in FFF) of polystyrene increases with increasing concentrations in ethylbenzene as it does in toluene.[24] This should result in a decreased retention (see Equation 4). The former effects are observed to be dominating the latter, in the case of polymer solutions, in contradiction with what is predicted for a hard sphere model[25] and observed for rigid particles.[26]

In this work EC fitting, graphical and integration methods are compared with respect to the level of accuracy in MW and μ determination. Specifically, the same PS sample and the same solvent (EB) that were previously used for the referred EC studies on linearity conditions are here employed. In Table 1 are reported the ThFFF-based determination for PS 170,000 MW in EB under different experimental settings for which linearity conditions for physicochemical measurements were considered as satisfyingly fulfilled.[8] The results of EC peak shape fitting, integration and graphical methods are compared. The MW values are calculated according to Eqs. 3 and 6 by taking peak means for the EC and integration methods, and peak maxima for the graphic method. The values of the A, b, and D_T constants were taken, respectively, as 2.613×10^{-4}, 0.552 and 0.95×10^{-7} (in CGS units with MW expressed in gmol^{-1}), as reported in the literature for PS/EB.[5] The ν parameter to be used in Eq. 3, accounting for the departure from a parabolic flow profile, was calculated using the procedure described in Ref. 15, which takes into account the viscosity and thermal conductivity dependencies with temperature.

It is noticeable, from Table 1, that all MW values obtained by the graphic method are larger than those obtained by the EC method, which, themselves, are generally close to those obtained by the integration method. This is due the fact that the peaks are somewhat fronting and that the peak mean times are slightly smaller than the peak maxima times as reflected by the slightly negative values of the peak skews as noted previously.[8] The first part of Table

1 reports data which were obtained in the same concentration and ΔT conditions, but at different flow rates. No systematic influence of the flow rate on retention, and, thus on MW, is apparent. The relative standard deviation of these MW values is similar for the three methods (between 6 and 7%) and appears, thus, to be some indication of the reproducibility of MW determination from ThFFF retention measurements, at least under the present experimental conditions.

This value is, however, smaller than the standard deviation of all data for PS 170,000 reported in Table 1, for which the mean molecular weight value is 14% higher than the nominal value. The difference between the overall standard deviation and that of the first part of Table 1 appears to arise from a rather distinct trend of evolution toward lower MW values on increasing ΔT. Indeed, the MW values obtained from the EC method at the flow rate of 0.2 mL/min and concentration of 1% w/v are: 197,890; 192,670; 183,970; and 177,330 for ΔT = 35°C; 40°C; 45°C; and 50°C, respectively. These data fit well the linear regression: MW = 247,783 - 1407 ΔT, with correlation coefficient $r = 0.9957$. In fact, this trend would be made more stronger if the data ($\lambda = 0.06374$, estimated MW=149,750) for ΔT = 60°C, which has been excluded from Table 1 because the EC series fitting pattern indicated a highly pronounced nonlinear behavior in that case, was added. Indeed, the intercept and negative slope of the regression would be both significantly increased (MW = 268,708 - 1921 ΔT) and the correlation coefficient worsened (r = 0.9815). This reinforces the warning of nonlinearity derived from the EC-series peak shape fitting analysis[8] and, again, indicates that data points for ΔT larger than 50°C are outliers.

Nevertheless, the systematic variation of the MW values obtained from Eqs. 3 and 6 with ΔT suggests that the influence of temperature on D and D_T, hence on the values of the constants A, b, and D_T involved in Eq. 6, should be taken into account, a topic far beyond the aims of the present treatment.

Although one cannot rule out that part of the differences between the nominal MW value and the experimentally determined data are due to inaccurate nominal specification, one may test whether the observed disagreement could be ascribed to systematic errors in retention parameter evaluation or to the effect of errors on instrumental and experimental variables. For this purpose, a plate height H vs. $\langle v \rangle$ study was performed, not only for polydispersity evaluations, but also for MW determinations. Indeed, according to Eqs. 5 and 11, M can be obtained from the diffusion coefficient derived from the slope of the plate height curve as:

$$M = \left(\frac{A\,C}{\chi\,w^2}\right)^{1/b} \qquad (13)$$

A comparison between the different methods employed for the determination of the peak parameters (t_r, σ), through which H can be evaluated, is reported in Table 2. Plate height values were measured for PS 170,000 at different flow rates and for the experimental conditions that were considered by EC fitting analysis as linear (1% w/v sample load, $\Delta T = 30°C$ field strength).[8] In Figure 1, the linear regressions of H vs. linear flow velocity $<v>$ data are plotted. Data reported in Table 2 show MW values that are even larger than those determined through ν-corrected λ values, which were discussed above and reported in Table 1.

The disagreement between MW data in Table 2 and the nominal value (170,000) is on the average 34% while the difference between MW data calculated from corrected retentions (see Table 1) was ca. 14%. Therefore, the difference between the two proposed methods of evaluation of MW is around 17% (but only 11% for the EC method). The discrepancy is not too dramatic if one notes that plate height measurements are generally less reproducible than retention measurement and, if one takes into account the effects that different experimental variables have on the accuracy, with which the slope of the H vs. $<v>$ plot (by which D is derived) can be evaluated. In fact, if one supposes, for instance, an error of 3% on the measurement of the channel thickness, this indeterminacy translates into a possible error of 11% on MW through the slope of an H vs. $<v>$ plot (see Eq. 13). Furthermore, the nonequilibrium coefficient C in Eq. 13 is highly sensitive to small variations of λ and, thus, of t_r.[23]

On the other hand, as the ratio of the thermal diffusion coefficient to the ordinary diffusion coefficient can be obtained from retention measurements and the latter from plate height determinations, this gives the possibility to determine the thermal diffusion coefficient only from ThFFF experiments. Indeed, from Eqs. 4 and 11, one gets:

$$D_T = \frac{\chi\,w^2}{\lambda\,C\,\Delta T} \qquad (14)$$

It is worth noting that thermal diffusion coefficient values D_T, determined through Eq. 14, are relatively close to the most recent published value[5] of 0.95×10^{-7} $cm^2s^{-1}K^{-1}$ which was also employed for the MW values determined from the retention ratio values discussed above and reported in Table 1. The

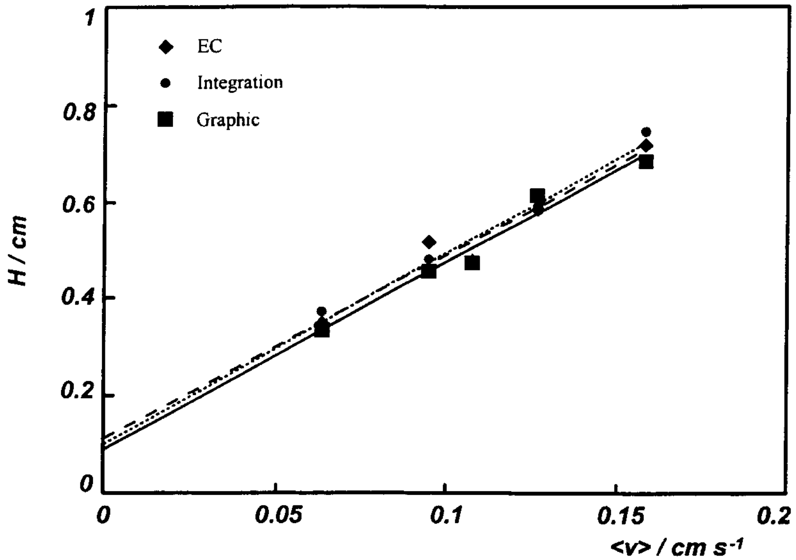

Figure 1. Polydispersity determination by linear regressions of H vs. linear flow velocity <v>; 170,000 MW PS sample. EC, Integration, Graphic corresponds to the different procedure of peak width determination (see text).

difference between the mean D_T for the three methods in Table 2 and this reference value is about 6% (it is only 3% for D_T obtained from the EC method). This finding does not contradict the previous observation of a large error on MW data from D values. Indeed, the effect of a channel thickness error on the accuracy for D_T is, for instance, smaller than the error reflected into a MW determination because of the different physical dependencies of M and D_T on the channel thickness as seen in Eqs. 13 and 14. Furthermore, the χ/λratio in Eq. 14 is less sensitive than χ in Eq. 13 to an error in t_r. Thermal diffusion coefficients have, thus far, never been determined by means of the method described here. The main advantage of the present approach lies in the fact that it does not require a separate, *à priori* knowledge of D. Altogether, this last finding enhances, *à posteriori*, the validity of the third-degree velocity profile approach for extracting physicochemical information on polymer by ThFFF.

Sample polydispersity was determined from plate height contribution H_p as expressed in Eq. 8; selectivity was derived according to Eq. 9 for the b value reported above for MW determinations and indicated in the literature for PS/EB systems at the ΔT employed in these experiments.[5] The values of $d\ln R/d\ln\lambda$ in Eq. 9, corrected for the v term accounting for the third-degree velocity profile, were computed according to the method reported in the literature (Eq. 41, Ref. 27). The resulting μ values are reported in Table 2 with their standard deviations. They appear to be much closer to unity than the nominal value.

This is not surprising. Indeed, it was already noted that very good agreement between the ThFFF-based and the nominal μ values of polymers of narrow polydispersity index, as those in Table 2, can hardly be reported since SEC, one of the most common methods thus far applied for giving nominal specifications of such polymer samples, is a technique of limited accuracy.[21] It, therefore, appears that ThFFF, by far, surpasses the possibilities of existing methods in this regard, and must be considered as a unique method of determination of polydispersity index values very close to one.

CONCLUSIONS

The molecular weight and polydispersity value of a polymer standard are evaluated, without previous calibration, from retention time parameters and polymer physicochemical constants under the necessary conditions for linearity previously determined in ThFFF by EC peak shape fitting analysis. Molecular weight determinations have been performed through retention parameters obtained by the EC method itself.

Results were compared to molecular weight and polydispersity values obtained either by integration or graphical analysis. All the proposed methods have proved to be comparable within the commonly accepted experimental error; in fact, with respect to the EC method, no differences higher than 5% have been found using either the integration method or graphical analysis.

However, with respect to the conventional methods, EC peak shape fitting had also allowed for the detection of the best experimental set-up for ThFFF elution under conditions for linearity, which are known to be necessary for unbiased ThFFF measurements of polymer physicochemical properties.

Within such conditions, standardless and relatively accurate ThFFF-based determinations of MW and μ have proved to be possible for narrowly dispersed polymer standards, provided the values of the constants to be entered in the D vs. MW relationship for the given polymer/solvent system are available and that correction for the third-degree velocity profile is performed.

Once optimized conditions for unbiased measurements are found with standard systems, they can be eventually applied to the conventional calibration procedures commonly employed in ThFFF characterization of more complex polymer/solvent systems.

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