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A simple method to determine unperturbed dimensions of polymers using size exclusion chromatography and multiangle light scattering

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Abstract

A very simple method to obtain unperturbed dimensions from measurements of just one sample of a polydisperse polymer, using differential refractive index and multiangle laser light scattering detectors in size exclusion chromatography is presented. Poly(methyl methacrylate)s of broad molecular weight distribution have been measured, in a good solvent, in order to obtain the scaling law between the radius of gyration and the molecular weight. The unperturbed dimensions have been calculated using three different mathematical procedures for the extrapolation and compared with data found in the literature. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Size exclusion chromatography; Multiangle laser light scattering detector; Poly(methyl methacrylate)

1. Introduction

Size exclusion chromatography (SEC) has become a widely employed tool for routine polymer characterization [1,2]. In SEC it is assumed that there is an absence of interaction between the macromolecules and the gel contained in the columns, and consequently, the elution volumes of macromolecules depend on their size. With a suitable calibration curve, constructed from adequate standard polymers of known molar masses, elution volumes can be related to molar mass and hence molecular weight distribution (MWD) of polymers can be obtained. The necessity of calibration has recently been overcome by the use of molecular weight-sensitive detectors such as light-scattering detectors. The use of both a multiangle laser light scattering (MALLS) detector, and a concentration sensitive detector such as the conventional one based on refractive index changes, DRI, allows us to obtain the absolute molecular weight distribution for the polymer, from which different averaged molecular weights can be computed [3,4]. Moreover, the combination of these techniques permits us to also obtain a useful size-dependent property namely the mean square radius of gyration [5–7] $\langle s^2 \rangle$. The unperturbed value of the mean square radius of gyration, $\langle s^2 \rangle_0$, occurs when the macromolecular chain is not disturbed by the excluded volume effects arising from intermolecular and long range intramolecular interactions. The polymer is then said to be in theta conditions [7,8]. The evaluation of the unperturbed value $\langle s^2 \rangle_0$ for any given polymer is important for two reasons. In the first place, this is the value usually obtained by theoretical calculations and therefore it is used for comparison between theory and experiment. Moreover the value of $\langle s^2 \rangle$ is solvent-dependent while $\langle s^2 \rangle_0$ depends only on the polymer and temperature (in fact, the same value of $\langle s^2 \rangle_0$ is obtained in theta solution than in solid amorphous state), consequently $\langle s^2 \rangle_0$ is more suitable than $\langle s^2 \rangle$ for comparison of the molecular dimensions of different polymers. A number of methods can be used for the direct determination of unperturbed dimensions of polymer chains, for instance light scattering or viscosity measurements of polymer solutions at θ conditions. However, very often the experimental attainment of the theta conditions is difficult and unperturbed dimensions can only be obtained through an indirect method, from viscosity or light scattering measurements performed in good solvents followed by a mathematical extrapolation algorithm [9,10]. This second procedure is usually tedious and time consuming since, several samples of the polymer of different molecular weight had to be measured; these samples must be monodisperse or the results corrected for the polydispersity [11,12]. Moreover, the preparation (either from synthesis or from fractionation) of adequate samples for the extrapolation procedure, is a difficult task for some polymers [13].

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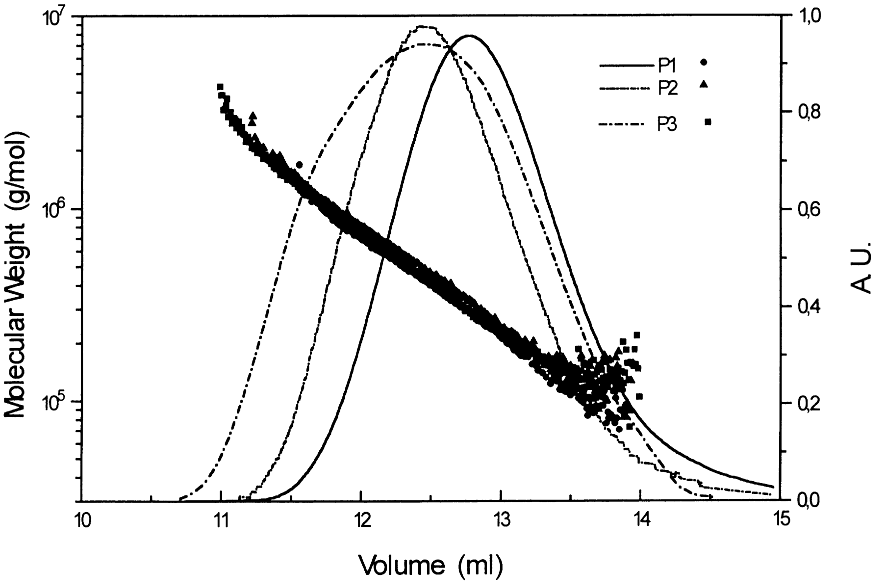

Fig. 1. Logarithm of molecular weight versus elution volume for three different samples of poly(methylmethacrylate). The corresponding DRI signals, in arbitrary units, are also shown.

In the present study we propose a very simple method to obtain unperturbed dimensions with just one sample of a polydisperse polymer. Poly(methyl methacrylate) (PMMA) is studied as a test case. Thus, samples of PMMA having broad molecular weight distribution, in a good solvent, have been analyzed by SEC coupled with MALLS and DRI detectors. The relationship between the radius of gyration with molecular weight, i.e. the scaling law [14] has been obtained, and the unperturbed dimensions have been extrapolated using three different mathematical procedures. The results are in good agreement with those, calculated by more conventional methods, found in the literature.

2. Experimental

The absolute molecular weight distribution and radius of gyration were determined by SEC, combined with MALLS. A Waters Associates differential refractive index detector Model 410 was used as the concentration detector and a Dawn-DSP-F laser photometer operating at 632.8 nm from Wyatt Technology Corp. was the molecular weight and size detector used. A Model 510 pump, a U6K injector (Waters Associates) and two columns PLgel mixed B (Polymer Laboratories) in series completed the equipment. Tetrahydrofuran, THF, freshly distilled from sodium and benzophenone, filtered through a 0.2 μm Fluoropore filter and degassed, was used as the eluent at a flow rate of 1.0 ml/min.

The calibration of the Dawn was done with spectrometric grade toluene freshly distilled from sodium and benzophenone, and the normalization of the detectors was performed with standard monodisperse polystyrene of low molecular weight which did not show angular dependence on the light scattering signal. Standard monodisperse polystyrene was also used to determine the interdetector volume using the “spider” plot method [3].

PMMA samples P1 and P2 were synthesized by radical chain polymerization of methyl methacrylate in toluene using benzoyl peroxide as initiator in a sealed evacuated tube at 80–85°C for 6 h. The initiator concentration, 8×10^{-3} mol/dm^3, was the same for both polymers, whereas the concentrations of the monomers were 1.6 and 2.2 mol/dm^3, respectively. Sample P3 was obtained from Aldrich (Ref. 18,226-5).

3. Results and discussion

3.1. Molecular weight distributions of polymers

The use of a multiangle light scattering detector enables the average molar mass and the mean square radius of gyration $\langle s^2 \rangle$ to be calculated for each fraction eluted. Fig. 1 shows the molecular weight calculated from the scattered light for the three samples of PMMA plotted versus the elution volume, i.e. absolute calibration curves for SEC. The signals from the differential refractive index detector, proportional to the concentration, have also been plotted. As can be seen in this figure, the results for the different samples are consistent. The uncertainties in the tails or heads of the molecular weight distributions are much more easily discernible from the plot of the calibration curve than from the raw chromatograms.

Fig. 2 presents the absolute MWD of the polymers calculated from the combined measurements of molecular weight (MALLS detector) and concentration (DRI detector) using

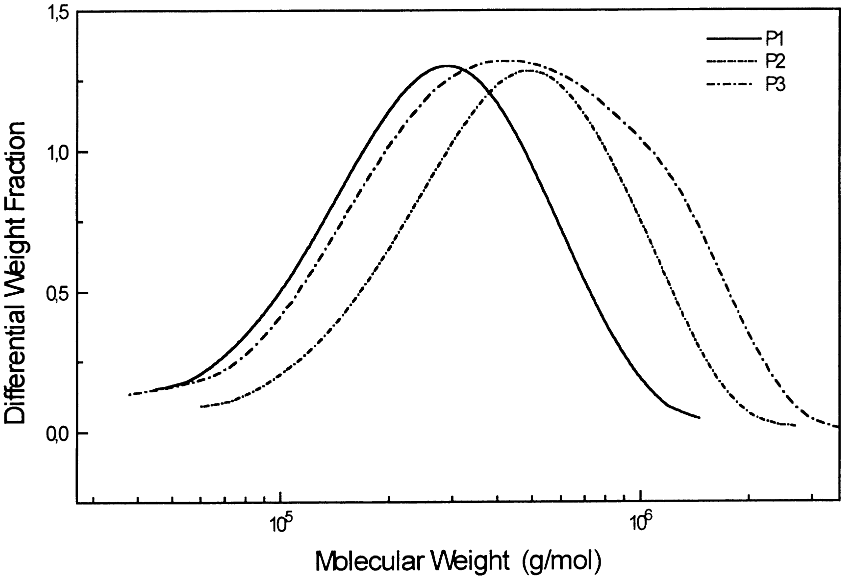

Fig. 2. Differential molecular weight distributions of the PMMA samples.

ASTRA software [3,15] version 4.2. The different averaged molecular weights are easily calculated assuming that each slice of the chromatogram contains molecules of a single molecular weight or at least very narrow distributions of molecular weight [3]. Mean values of molecular weight and polydispersities, with their standard deviation calculated using ASTRA, are listed in Table 1. Sample P3 presents the broadest MWD and highest molecular weights whereas samples P1 and P2 show similar MWD but at a different range of molecular weights.

3.2. Dimensions

The z average root mean square radius $\langle s^2\rangle^{1/2}$ can be derived from the angular dependence of the intensity of the scattered light. The calculation of the values for $\langle s^2\rangle^{1/2}$ is independent of both $\mathrm{d}n/\mathrm{d}c$ (assumed constant), and M_w and therefore, assuming that the normalization constants of the different detectors have been measured with care, it offers an excellent form to study the dimensions of the polymer. The only problem is that dimensions must be greater than $\lambda/20$, λ being the wavelength of the incident light in the medium, in order to observe the angular dependence of the scattered light intensity [16]. Thus, the accuracy of the radius of gyration obtained in the region of low molecular weights begins to deteriorate rapidly. Fig. 3 shows the root mean square radius of gyration versus the elution volume for poly(methylmethacrylate); the signals from the differential refractive index detector are also shown. The dimensions diminish as the elution volume increases, as expected, the reason is that the radius of gyration is proportional to the hydrodynamic ratio [7,17] and thus to the product $([\eta]M)^{1/3}$. The values of the z average root mean square radius and their standard deviation for the three samples, calculated using ASTRA software, are listed in the sixth column of Table 1. It is interesting to note the comparison between the plots of molecular weight (Fig. 1) and radius of gyration (Fig. 3) versus elution volume; the dispersion of the points is larger for the radius of gyration, especially at high elution volumes and for sample P1, which is the one with the lowest molecular weight.

There is a direct relationship between the mean square radius of gyration and the molecular weight which is often formulated as a scaling law of the form $\langle s^2\rangle^{1/2} = QM^q$ where the value of the exponent q may provide a hint about the shape of the polymeric chain. Thus, values of $q \simeq 0.3$ are expected for globular polymers, $q \simeq 0.5$ would indicate theta conditions and $0.5 < q \leq 0.6$ are obtained for random coil polymers in good solvents [14]. Fig. 4 shows the log–log plot of radius of gyration versus molecular weight, that is the scaling law, for the three samples. The values of the q coefficients obtained by linear regression analysis and their standard deviation are shown in the last column of Table 1. They indicate that the polymer behaves

Table 1
Averaged molecular weights, polydispersities and root mean square radii of gyration

Polymer	$10^{-5}M_\mathrm{n}$ (g/mol)	$10^{-6}M_\mathrm{w}$ (g/mol)	$10^{-6}M_z$ (g/mol)	M_w/M_n	$\langle s^2\rangle_z^{1/2}$ (nm)	q
P1	2.2 ± 0.1	3.3 ± 0.1	4.8 ± 0.6	1.5 ± 0.1	22 ± 3	0.57 ± 0.02
P2	3.5 ± 0.2	5.4 ± 0.1	8.1 ± 0.3	1.5 ± 0.1	33 ± 2	0.58 ± 0.01
P3	3.1 ± 0.3	6.1 ± 0.2	10.2 ± 0.1	1.9 ± 0.2	36 ± 2	0.590 ± 0.005

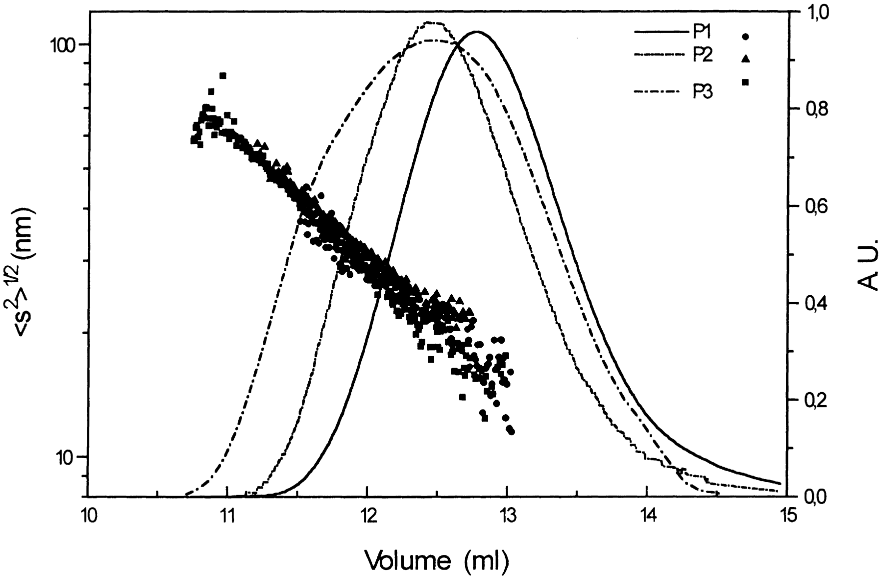

Fig. 3. Logarithm of root mean squared radius of gyration versus elution volume for the PMMA samples. The corresponding DRI signals are also shown.

as a random coil chain in a good solvent, in accordance with the literature value [9] of the Mark–Houwink parameter $a = 0.72$ for PMMA in THF at 25°C. Moreover, these scaling laws are consistent with the assumption that a good SEC resolution has been achieved.

As can be seen in Fig. 4, most values of the radius of gyration for sample P1 are lower than $\lambda/20$ ($\lambda/20 \simeq \lambda_0/20n \simeq 23$ nm where λ_0 is the wavelength in vacuo, 633 nm and n the refractive index of the medium $\simeq$ refractive index of solvent THF = 1.40) and, for the reason stated above, this sample is not adequate for extrapolating to unperturbed dimensions. All the calculations presented below were performed for the broadest sample P3, which overlaps the results for the narrower sample P2. Thus the broad peak in SEC corresponding to a single sample of PMMA (P3) has been divided in slices and, even eliminating the head and tail of the chromatogram, the measurement provides molecular weights and radius of gyration of 175 almost monodisperse samples, in a wide range of molecular weights.

3.3. Unperturbed dimensions

Unperturbed dimensions can be evaluated from measurements of dimensions of the polymers as a function of molecular weight in a good solvent, using several extrapolation procedures. Thus, the 175 experimental values of M and the z-average mean square radius of gyration $\langle s^2\rangle$ of the lowest panel on Fig. 4 have been used to evaluate $\langle s^2\rangle_0$. Considering the slices of the chromatogram as monodisperse samples, the z and weight averages are similar, $\langle s^2\rangle_z = \langle s^2\rangle_w$ and no correction for polydispersities is required.

The unperturbed dimensions have been computed using three different extrapolation procedures. The first one, due to Fixman [18], is defined in Eq. (1), which obtains $\langle s^2\rangle_0/M$ as the intercept on a $\langle s^2\rangle/M$ versus $M^{1/2}$ plot:

$$\frac{\langle s^2\rangle}{M} = \frac{\langle s^2\rangle_0}{M} + 0.0299B\left(\frac{\langle s^2\rangle_0}{M}\right)^{-1/2} M^{1/2}. \qquad (1)$$

The second procedure used is similar to the extrapolation of Stockmayer and Fixman [19] for viscosity measurements. Since the perturbed and unperturbed mean square radius of gyration are related through the chain expansion factor, α:

$$\langle s^2\rangle = \alpha^2\langle s^2\rangle_0, \qquad (2)$$

and the expansion factor is related to the molecular weight M by [19]

$$\alpha^3 = 1 + CM^{1/2} \qquad (3)$$

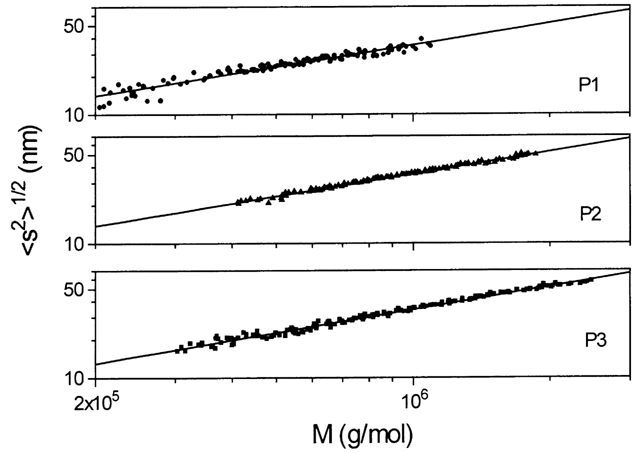

Fig. 4. Log–log plot of root mean squared radius of gyration versus molecular weight for the three PMMA samples.

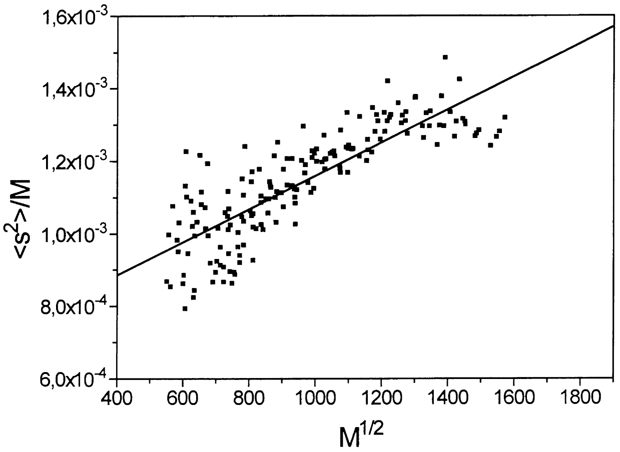

Fig. 5. Fixman extrapolation.

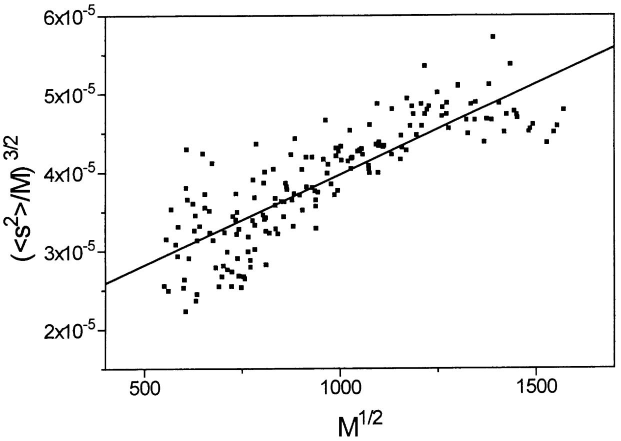

Fig. 6. Stockmayer–Fixman extrapolation.

the extrapolation equation may be written as:

$$\left(\frac{\langle s^2\rangle}{M}\right)^{3/2} = \left(\frac{\langle s^2\rangle_0}{M}\right)^{3/2}(1 + CM^{1/2}) \tag{4}$$

and the intercept provides $(\langle s^2\rangle_0/M^{3/2})$.

The last equation used is due to Kurata et al. [20]:

$$\frac{\langle s^2\rangle}{M} = \frac{\langle s^2\rangle_0}{M} + 0.0286Bg(\alpha)\left(\frac{M}{\langle s^2\rangle^{1/2}}\right). \tag{5}$$

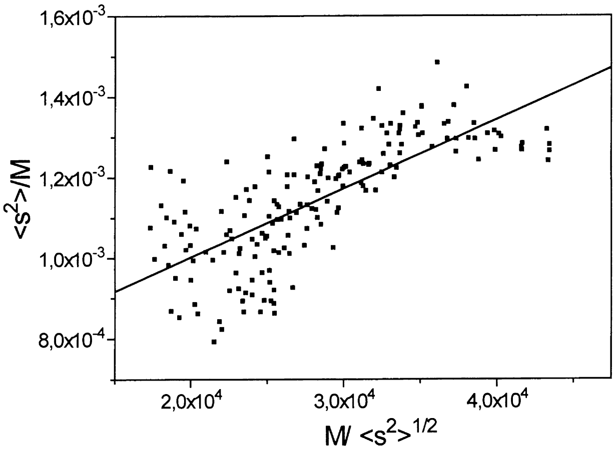

Fig. 7. Kurata, Stockmayer, Roig extrapolation.

The three plots are represented in Figs. 5–7. The derived values of $\langle s^2\rangle_0/M$, in nm^2 mol g^{-1}, are listed in Table 2. It is worth noting that, despite the points dispersion, the errors in the intercepts are not too large and there is good concordance between both the three extrapolations and with the values obtained by light scattering measurements of several samples of PMMA in a theta solvent [21].

Viscometric measurements provide an other magnitude from which the dimensions of the polymer chain can be obtained as the unperturbed value of the mean square end to end distance $\langle r^2\rangle_0$ which for random coil chains is [7,8] $\langle r^2\rangle_0 = 6\langle s^2\rangle_0$. Thus, the last column of Table 2 has been calculated in order to compare our results with those obtained from viscosity measurements.

The characteristic ratio C_n is defined as the ratio of the real unperturbed value of the mean square end to end distance $\langle r^2\rangle_0$ to the value it would have if the units of the chain were freely-jointed (i.e.$\langle r^2\rangle_f = nl^2$ and can be calculated from the extrapolated values of $\langle s^2\rangle_0/M$ as:

$$C_n = \frac{\langle r^2\rangle_0}{nl^2} = \frac{6M_0}{2l^2}\frac{\langle s^2\rangle_0}{M} \tag{6}$$

where n is the number of skeletal bonds, M_0 is the molecular weight of the repetitive unit which contains two C–C bonds of length $l = 0.154$ nm. A value of $C_n = 8.8$ is obtained with the mean of the three extrapolations ($\langle s^2\rangle_0/M = 7.0 \times 10^{-4}$).

Table 2
Unperturbed dimensions for PMMA as obtained by different extrapolations

Reference	Method	$10^4\langle s^2\rangle_0/M$ (nm^2 mol/g)	$10^4\langle r^2\rangle_0^{1/2}/M^{1/2}$ (nm mol$^{1/2}$ g$^{-1/2}$)
This work	Fixman	7.0 ± 0.2	648 ± 9
This work	SF	7.3 ± 0.3	662 ± 13
This work	KSR	6.6 ± 0.3	629 ± 14
[21]	Light scattering in θ conditions, uncorrected	7.81 ± 0.14	684
[21]	Light scattering in θ conditions, corrected	6.32	616
[9]	Viscosity in various solvents	–	640 ± 60

This result is in very good agreement with the value expected for a random coil polymer and with literature data [9]. The uncertainties in Table 2 are the standard deviations and can be used as a measure of the statistical consistence of the data.

Finally, we want to stress the point that unperturbed values of chain dimensions can be obtained with experimental results of SEC for a single sample in a good solvent, provided both MALLS and DRI detectors are used.

Acknowledgements

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