

Isotactic Polystyrene Characterization by Gel Permeation Chromatography in Tetrahydrofuran

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Synopsis

Isotactic polystyrene fractions were characterized by gel permeation chromatography (GPC) in tetrahydrofuran (THF) at 25°C. From the universal calibration method, a viscosity law has been established allowing determination of the correspondence between the molecular weight GPC calibration laws for APS and IPS. The validity of characterization of IPS by this method was confirmed with light scattering and osmometry.

INTRODUCTION

Isotactic polystyrenes (IPS) prepared by Ziegler-Natta catalysts are usually of high average molecular weight and present the disadvantage of a very broad molecular weight distribution. In a small-angle neutron-scattering (SANS) experiment as in light scattering measurements, well-defined samples are needed in order to obtain more precise information about the molecular conformation. In this frame, and especially with the final aim of studying IPS conformations in the bulk by SANS, we have prepared hydrogenated as well as deuterated IPS. In the SANS measurements, the limitations imposed by the available scattering vectors q ($2 \times 10^{-3} \text{ \AA}^{-1} \leq q \leq 10^{-2} \text{ \AA}^{-1}$)¹ require particles whose dimensions are smaller than 500 Å. Therefore, molecular weights less than 500,000 are needed.

Taking into account these limitations, it has been necessary to adjust the polymerization conditions in order to obtain molecular weight distributions in a range suitable for SANS and then to proceed with fractionation of the crude polymer. The need for a precise characterization of the fractions required a fast and accurate method. For this purpose, gel permeation chromatography was used in THF at room temperature. It was certainly due to the fact that the highest molecular weights of the crude polymer did not exceed 10^6 that no problem of solubilization of IPS in THF was encountered.

However, IPS does not have exactly the same solution behavior as atactic polystyrene (APS). Thus, a new calibration law had to be determined.

One of the interesting points of this work is that it is sufficient to know the constants of the viscosity law of IPS and the molecular weight calibration law of the set of columns for APS to deduce that of IPS by a simple transformation.²

TABLE I
Quantities Used for Synthesis of Samples

Sample	AlEt ₃	TiCl ₄	Heptane	Styrene
IPS 1	9.3 cc	2.9 cc	28.3 cc	32.3 cc
IPS 2	37.2 cc	11.7 cc	56.7 cc	38.3 cc
IPSD3	27.9 cc	8.8 cc	56.7 cc	38.3 cc ^a

^a Perdeuterated styrene.

EXPERIMENTAL

Synthesis, Characterization, and Fractionation of IPS

Synthesis

Isotactic polystyrenes were prepared according to the classical method proposed by Natta.³ Three samples were prepared and are referred to as IPS 1, IPS 2, and IPSD 3, where IPSD 3 is a perdeuterated (99%) IPS (the monomer was provided by the "Service des Molécules Marquées," C.E.A. Saclay, France). The complex obtained by mixture of 0.4 mole AlEt₃ (aluminium triethyl) and 0.16 mole TiCl₄ (*titanium tetrachloride*) dispersed in *n*-heptane was used as catalyst. After addition of hydrogenated or deuterated monomer (purified by distillation) the medium was heated for 12 hr at 80°C after the reaction is completed. In Table I are listed the quantities used for the synthesis of the three samples.

As the average molecular weight of IPS 1 was in a range not suitable for our SANS experiments ($M_w \sim 10^6$), the catalyst concentration used for IPS 2 and IPSD 3 were increased in order to shift the distribution toward smaller molecular weights.

As will be shown later, the tacticity of the polymer was not modified by these different synthesis conditions. The polymer obtained by this procedure contains an appreciable amount of atactic polystyrene (10%) which can be extracted, according to a method proposed by Utiyama,⁴ by washing the polymer for 12 hr in boiling heptane (98°C). Then, the insoluble part is washed by a large excess of MEK in order to extract the remaining nonisotactic polymer.

Characterization

The three polymers prepared were at first characterized by light scattering in monochlorobenzene solution. The dissolution of the polymer was achieved in monochlorobenzene at its boiling temperature (130°C) during 2 hr. The polymer remains in solution at room temperature for several days allowing light scattering measurements at 25°C.

Refractive index increments were measured in this solvent on a Brice Phoenix differential refractometer. Results are listed in Table II. Light scattering molecular weight values are listed in Table III.

It was possible to obtain a complete solubilization of IPS 2 and IPSD 3 in THF and to characterize them by gel permeation chromatography (GPC) in this solvent at room temperature (25°C). Figure 1 gives the chromatogram of IPS 2 before extraction of the amorphous part (a) and the chromatogram of IPSD 3 (b). In Figure 2, the chromatograms are given for IPS 2 after atactic polymer

TABLE II
Refractive Index Increment (cm^3/g) for IPS and IPSD at 5460 Å and 4360 Å

Sample	$\lambda = 5460 \text{ \AA}$	$\lambda = 4360 \text{ \AA}$
IPS	0.08	0.084
IPSD	0.076	0.076

TABLE III
Molecular Weights Obtained by Light Scattering
in Monochlorobenzene Solutions for Isotactic Samples

Sample	M_w
IPS 1'	1,800,000
IPS 2	300,000
IPSD3	350,000

extraction (a) and for the extracted part (b). The latter is essentially made of low molecular weights, showing that the smallest molecular weights are less stereoregular than the highest, assuming that the method of separation is correct.

Fractionation

As revealed by the chromatograms, the molecular weight distribution of the initial polymer is quite broad. A fractionation of the hydrogenated samples was achieved according to a method proposed by Nakajima et al.⁵ using paradichlorobenzene - PEO 400 at 50°C as solvent-nonsolvent system and by operating

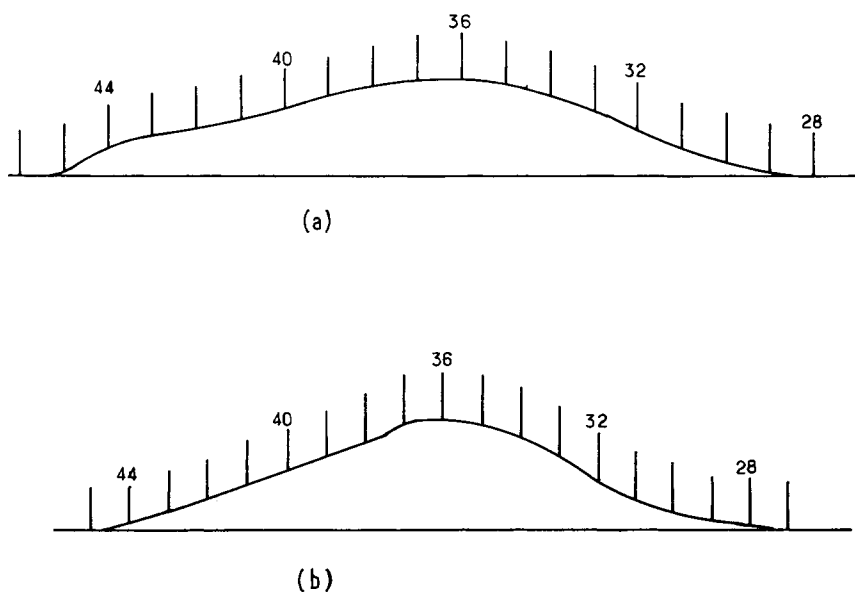


Fig. 1. (a) GPC chromatogram of IPS 2 in THF at 25°C before treatment in boiling heptane. (b) GPC chromatogram of IPSD 3 in THF at 25°C.

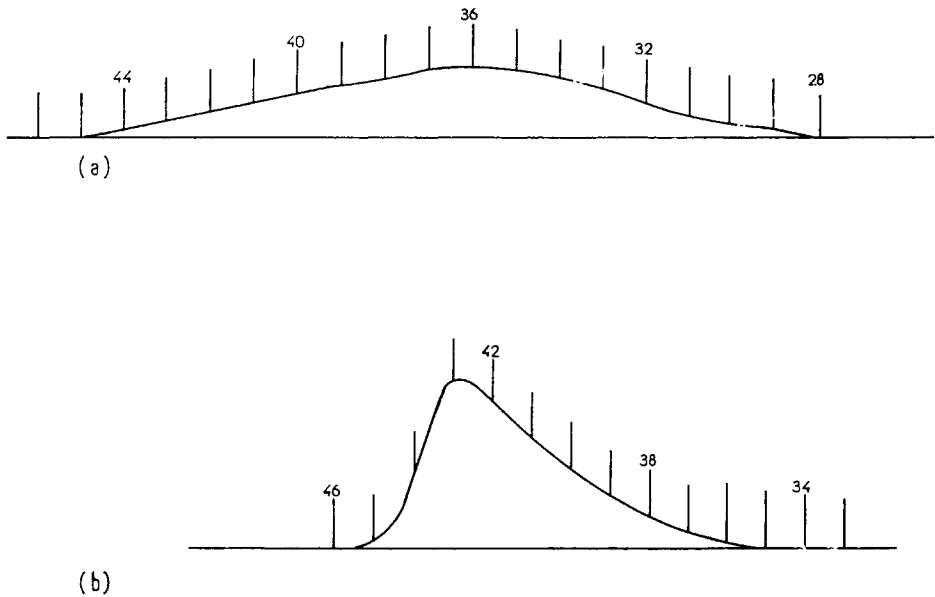
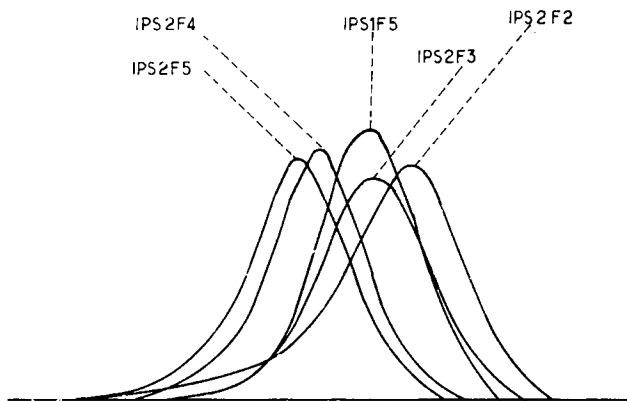


Fig. 2. (a) GPC chromatogram of IPS 2 in THF at 25°C after treatment in boiling heptane. (b) GPC chromatogram of extracted material of IPS 2.



CHROMATOGRAMS OF IPSH FRACTIONS

Fig. 3. Chromatograms of the analyzed fractions

in a device designed by Tung.⁶ The interest of the method is to form a coacervate less dense than the solution which can be recovered by flotation. This procedure is, however, not very efficient and gives fractions of broad molecular weights distribution (Fig. 3) ($M_w/M_n = 1.8$). Moreover, this method is not suitable for perdeuterated isotactic polystyrene because its highest density (8% higher) prevents the flotation of the coacervate. For the fractionation of this polymer, we have used a more classical solvent–nonsolvent system, i.e., toluene–ethanol at 50°C. The results are quite satisfactory as revealed by the chromatograms of Figure 4 ($1.20 \leq M_w/M_n \leq 1.3$).

Moreover, fractions obtained by the first method were used for viscosity law characterization of IPS in THF, and the results will be discussed later. The two

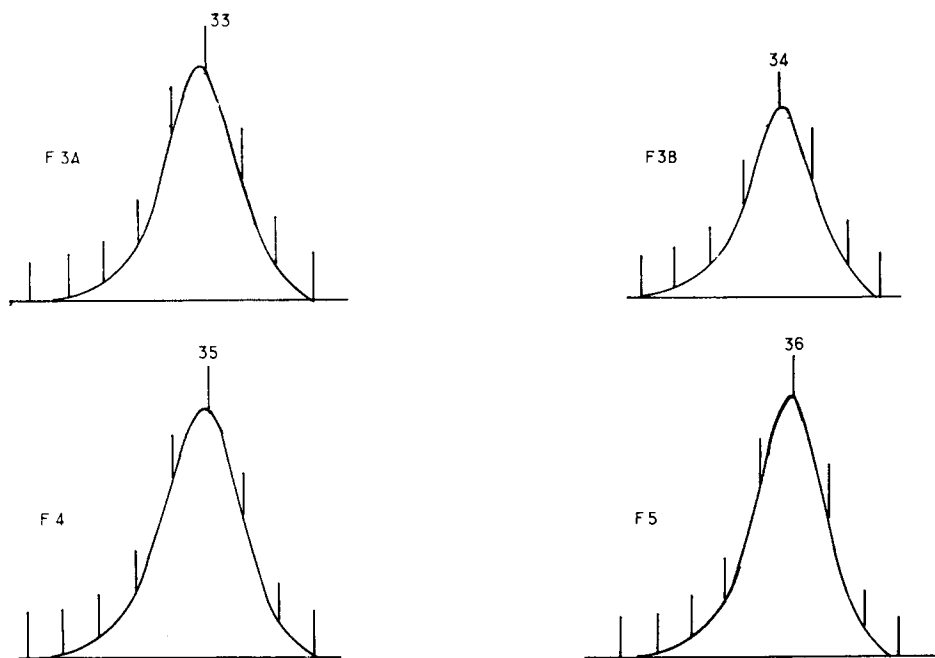


Fig. 4. Chromatograms of fractions of IPSD 3 in THF at 25°C. Fractions were obtained at 50°C with toluene-ethanol as solvent/precipitant system.

methods described have allowed us to obtain ten fractions for IPS 1 and IPS 2 and 15 for IPSD 3.

Tacticity

^{13}C -NMR measurements were used to check that fractionation does not result in selection according to tacticity. These⁷ were carried out on a VARIAN XL 100 apparatus in monochlorobenzene solutions (0.05 g/cm³). The time of spectra accumulation was about $\frac{1}{2}$ hr, and D₂O was used as an external lock. Tacticity was estimated for five fractions (IPS 1, F5; IPS 2, F2, F3, F4, F5) by considering the C₁ peak located at about 150 ppm. The peak obtained (Fig. 5) only revealed the presence of triads *mm* while no *mr* or *rr* triads could be sensitively detected. Considering experimental uncertainties, all fractions have a tacticity higher than 95% attesting that the fractionation method proceeds exclusively by molecular weight selection.

Characterization of IPS Fractions by GPC. Comparison with Other Methods

Principle of Interpretation of GPC Results

The determination of molecular weights was done by taking into account the axial dispersion effect due to the limited efficiency of the columns. To be more precise, the method⁸ of molecular weight correction is based on two hypotheses:

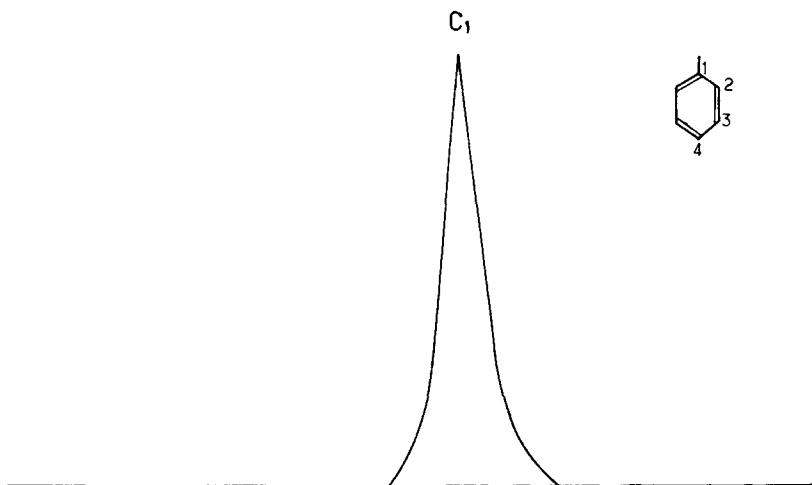


Fig. 5. ^{13}C -NMR spectrum of IPS 2 F5 in chlorobenzene at 50°C ; counting time 30 min; external lock D_2O .

1. The universal calibration curve, valid for any polymer, is linear:

$$V = A \log \phi + B \quad (1)$$

where ϕ is the hydrodynamic volume of the polymer proportional to $[\eta]M$ and V is the retention volume.

2. The axial dispersion is defined by a Gaussian curve. For an ideal monodisperse fraction, the chromatogram would be defined by the relationship

$$y = y_0 \exp\left[-\frac{1}{2\sigma^2} (V - V_0)^2\right] \quad (2)$$

Under these conditions, one is lead to the following expression for the hydrodynamic volume associated with the viscometric molecular weight:

$$\phi_\eta = \phi_e \left[\exp\left\{\frac{\alpha}{2(\alpha + 1)} \tau_\phi^2\right\} \right] \left[1 + \tau_\phi^2 \frac{C'}{C} \right] \quad (3)$$

where ϕ_e is the hydrodynamic volume deduced from the universal calibration curve corresponding to a retention volume V_e ; τ_ϕ is the efficiency parameter of the columns ($\tau_\phi = \sigma/A$) valid for all polymers; C and C' are, respectively, the values of hydrodynamic volume distribution $C(\log \phi_e)$ and of its derivatives; and α is the exponent of the Mark-Houwink viscosity law for the considered polymer.

Another method for obtaining the coefficients of the Mark-Houwink relation is to assume that the distribution of molecular weight gives a Gaussian chromatogram and to use relations already published.⁹ Plotting $\log(\eta)$ versus $\log M$, one obtains experimental values K' and α' which are related to the correct one through the following equations:

$$\alpha' = \frac{\alpha}{1 + \frac{\sigma^2}{a^2} \frac{1}{\gamma^2}} \quad (4)$$

TABLE IV
 Results of GPC–Light Scattering–Osmometry

Sample	M_w^a	M_n^b	M_w/M_n	GPC					
				M_w	M_n	M_w/M_n	$[\eta]$	K	α
IPS 1 F5	440,000			447,000	331,000	1.3	108	3.4×10^{-2}	0.64
IPS 2 F2	660,000	249,000	2.6	681,000	251,000	2.7	151	4.3×10^{-2}	0.61
IPS 2 F3	470,000			440,000	314,000	1.4	106	5×10^{-2}	0.61
IPS 2 F4	234,000			257,000	222,000	1.2	61		
IPS 2 F5	122,000	68,700	1.8	128,000	87,000	1.5	48	6.5×10^{-2}	0.6

^a Measurements in monochlorobenzene solutions at room temperature.

^b Measurements in THF at 25°C.

$$K' = K M_0^{\alpha-\alpha'} \exp \left[\frac{\alpha\alpha' \sigma^2}{2 a^2} \right] \quad (5)$$

where γ^2 is equal to $\ln M_w/M_n$.

Experimental Results (GPC–Light Scattering–Osmometry)

The different fractions were investigated by using a Waters 200 chromatograph coupled with an automatic viscometer.¹⁰ A set of five columns filled with Styragel of porosity 10^7 , 10^6 , 10^5 , 10^4 , and $3 \cdot 10^3$ Å was used with THF as elution solvent with a flow of 1 ml/min. All the experiments were carried out at 25°C.

The results obtained by the different methods are listed in Table IV.

The agreement is quite satisfactory between the molecular weight averages determined by different methods. From the viscosity laws obtained on the different fractions, a mean viscosity law can be deduced:

$$[\eta] = 4.8 \times 10^{-2} M^{0.61} \quad (6)$$

The viscosity law can also be deduced from the light scattering molecular weights and the limiting viscosity index determined by GPC for the fractions. By rejecting the value for IPS-2 F2 of high polydispersity, one obtains

$$[\eta] = 3.15 \times 10^{-2} M^{0.62} \quad (7)$$

which is in satisfactory agreement with eq. (6).

It must be noted at this point that it is possible having the viscosity law to define a relationship between the molecular weights of IPS and APS of identical hydrodynamic volume. This leads to

$$[\eta]_i M_i = [\eta]_a M_a \quad (8)$$

where subscripts i and a refer, respectively, to isotactic and atactic species.

Knowing that $[\eta]_a = 1.41 \times 10^{-2} M^{0.7}$ in THF,² one obtains

$$\log M_i = -0.33 + 1.056 \log M_a \quad (9)$$

The validity of the viscosity law established for IPS in THF can be checked indirectly from the evolution of the geometric dimensions of the isotactic polymer. As IPS D3 fractions of very narrow polydispersity (Fig. 4) were available,

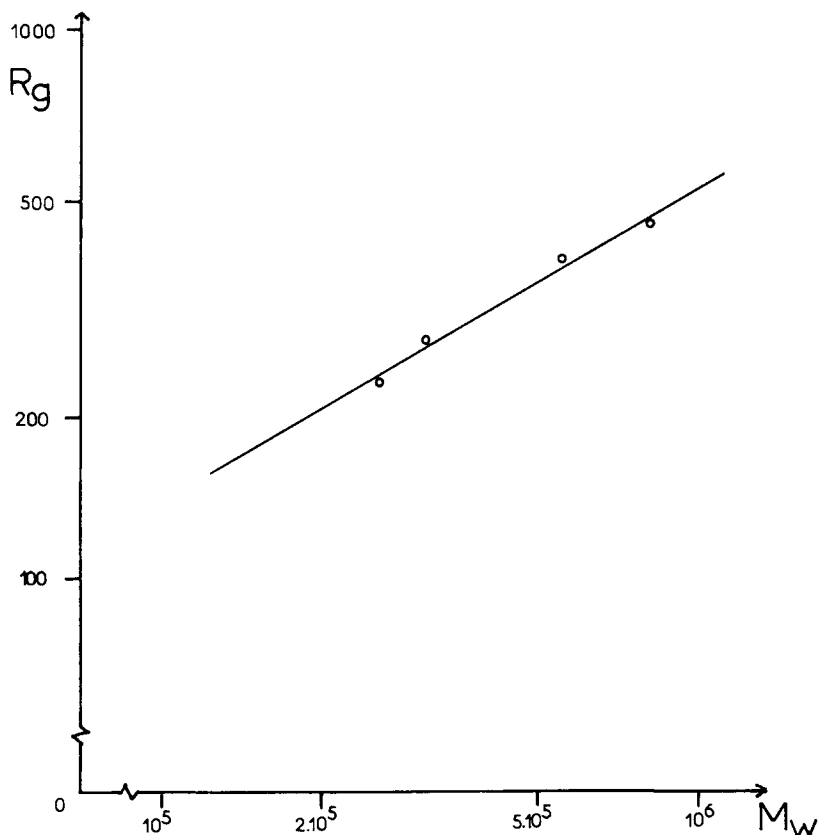


Fig. 6. Determination of the dependence of the radius of gyration R_g on the weight-average molecular weight M_w in THF at 25°C.

the behavior of the radius of gyration in relation to the molecular weight M_w was studied in THF at 25°C by light scattering. The refractive index increment of IPSD 3 in THF at room temperature is $0.182 \text{ cm}^3/\text{g}$ for $\lambda = 5460 \text{ \AA}$.

By plotting (Fig. 6) $\log R_g$ versus $\log M_w$, one finds

$$(R_g)_D = 0.136 M^{0.6} \quad (10)$$

The molecular weight radius of gyration for hydrogenated isotactic polystyrene can be calculated by assuming two hypotheses:

(i) Inasmuch as it is known that the ratio between the unperturbed dimensions of an hydrogenated APS and deuterated APS is approximately 1%,¹¹ it seems reasonable to extrapolate this result to the polymers in good solvents.

(ii) To a first approximation, it can be supposed that the exponent in relationship (10) is not very different for a deuterated or an hydrogenated polymer.

Thus, the constant of relation (10) will change taking into account that

$$M_H/M_D \sim 0.93$$

where M_H and M_D are, respectively, the molecular weights of hydrogenated and deuterated polymers having the same number of monomer units. Then, we have

$$(R_g)_H = C^{te} M_H^{0.6} \text{ and } (R_g)_D = 0.136 M_D^{0.6}$$

This leads to

$$(R_g)_H = 0.141 M^{0.6} \quad (11)$$

Using the Flory law,¹²

$$[\eta]M = \varphi \langle R^2 \rangle^{3/2} \quad (12)$$

the ratio between the hydrodynamic volume of APS and IPS leads to

$$\frac{[\eta]_a M_a}{[\eta]_i M_i} = \left(\frac{\langle R_a^2 \rangle}{\langle R_i^2 \rangle} \right)^{3/2} \quad (13)$$

By using the relationships already established,¹³

$$R_a = 9.45 \times 10^{-2} M^{0.635}$$

$$[\eta]_a = 1.41 \times 10^{-2} M^{0.7}$$

one obtains for $[\eta]_i$

$$[\eta]_i = 4.7 \times 10^{-2} M^{0.6} \quad (14)$$

which is in very good agreement with laws (6) and (7) determined by GPC, underlining the consistency of our measurements.

CONCLUSIONS

In this work, we were able to show that the universal calibration method of GPC can be applied to the case of IPS.

From coupled measurements of GPC and viscosity, the Mark-Houwink law was established for isotactic polystyrene, and the results show significant differences from the values generally given in the literature.¹⁴

From our results, the relationship giving the correspondence between the GPC molecular weight calibration curves of APS and IPS was established, showing the importance of the correction in the range of low and high molecular weights.

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