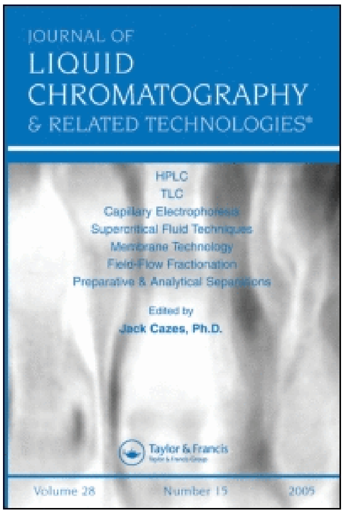

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DETERMINATION OF POLYMER MOLECULAR WEIGHT BY GPC IN THE LOW MOLECULAR WEIGHT REGION

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ABSTRACT

In order to determine the molecular weight of a polymer by GPC in the low MW region, a secondary calibration method can be established when polymer standards of the analysed polymer are not available (1). The efficiency of this method has been checked for the system poly(methyl methacrylate) (PMMA-methyl ethyl ketone (MEK) using polystyrene (PS) standards. When the solvent is poor for one of the polymers, limitations arise due to the secondary separation effects. Furthermore, a GPC method is proposed for the determination of the Dondos-Benoît constants (A_1,A_2) which must be known for the above-mentioned calibration. This method uses either two or at least one polydisperse polymer sample.

INTRODUCTION

Gel permeation chromatography is one of the most popular techniques for the determination of average molecular weights of polymers. When the GPC apparatus is not equipped with a low-angle laser light scattering detector (LALLS), a primary calibration curve must be first established using polymer standards of very narrow molecular weight distribution.

Limitations to this method arise from the lack of such polymer standards, which are available only for few common polymers.

To overcome this difficulty an indirect calibration method has been proposed, based on the universal calibration concept (2) and the Mark-Houwink-Sakurada (MHS) intrinsic viscosity molecular weight relation (3,4).

In the low molecular weight range (M<100.000) the $\log[\eta]$ vs log M plot has been found (5,6) to deviate from linearity, leading to erroneous results in the determination of the molecular weight when the standard values of MHS constants are used (7).

Very recently a new indirect calibration method has been proposed based on the Dondos-Benoit (DB) equation (1,8) which provides a very good linearity in the $[\eta]^{-1}$ vs $M^{-\frac{1}{2}}$ plot (9).

In this communication we check the efficiency of our method by establishing an indirect calibration curve for the GPC analysis of poly(methyl methacrylate) (PMMA) in methyl ethyl ketone (MEK) using polystyrene standards. This system is interesting because the solvent is good for PMMA (MHS exponent α is 0.72) and poor for PS (α=0.63).

As the DB constants are not available for a great number of polymer-solvent systems, a GPC method using one or two polydisperse polymer samples is proposed for the determination of these constants.

CALIBRATION METHOD

According to the universal calibration concept all polymers eluting at a given V_R have the same hydrodynamic volume

$[\eta]M$, provided that all secondary separation effects (e.g. adsorption or partition) are absent. Consequently, we may write

$$[\eta]_p M_p = [\eta]_s M_s \tag{1}$$

where $[\eta]$ is the intrinsic viscosity and M is the molecular weight of the polymer; the subscripts p and s refer to the polymer under analysis and to a standard polymer respectively.

Using the Dondos-Benoît relation which is linear in the low MW region (9)

$$1/[\eta] = -A_2 + A_1/M^{\frac{1}{2}} \tag{2}$$

(where A_1 and A_2 are constants characterizing the polymer-solvent system at a given temperature) and substituting $[\eta]$ from eq.(2) for the polymer (p) and standard (s) into eq.(1), we obtain

$$M_p^{3/2}/A_{1p} - A_{2p}M_p^{1/2} = M_s^{3/2}/A_{1s} - A_{2s}M_s^{1/2} \tag{3}$$

or

$$M_p^{3/2} + (A_{2p}M_s^{3/2}/A_{1s} - A_{2s}M_s^{1/2})M_p^{1/2} - A_{1p}M_s^{3/2}/A_{1s} - A_{2s}M_s^{1/2} = 0 \tag{4}$$

By putting

$$M_s^{3/2}/A_{1s} - A_{2s}M_s^{1/2} = J_s$$

eq.(4) can be rewritten as

$$(M_p^{1/2})^3 + A_{2p}J_sM_p^{1/2} - A_{1p}J_s = 0 \tag{5}$$

which has one real solution

$$M_p = \left[\frac{1}{2} A_{1p}J_s + \left(\frac{1}{27} A_{2p}^3 J_s^3 + \frac{1}{4} A_{1p}^2 J_s^2\right)^{1/2}\right]^{2/3} + \left[\frac{1}{2} A_{1p}J_s - \left(\frac{1}{27} A_{2p}^3 J_s^3 + \frac{1}{4} A_{1p}^2 J_s^2\right)^{1/2}\right]^{2/3} - \frac{2}{3} A_{2p}J_s \tag{6}$$

Eq.(6) can be used to establish a secondary calibration curve for the analysed polymer by converting the experimental calibration curve obtained by standards of another polymer. It is obvious that the DB constants ($A_{1p}, A_{2p}, A_{1s}, A_{2s}$) for both polymers must be known.

DETERMINATION OF A_1 AND A_2

Contrary to the MHS constants, A_1 and A_2 have been determined for a few polymer-solvent systems only (9). A GPC method for the determination of these constants has been already reported by Ito et al. who use the least-squares method in which more than two polydisperse samples must be available (8,10). In the following we shall show that A_1 and A_2 can be found from two or at least one polydisperse polymer sample.

The weight-average and number-average molecular weights and the intrinsic viscosity of a polymer may be written as

$$M_w = \sum_i w_i M_i \tag{7}$$

$$M_n = 1/\sum_i w_i/M_i \tag{8}$$

$$[\eta] = \sum_i w_i J_i/M_i \qquad (w_i = h_i/\sum_i h_i) \tag{9}$$

where w_i, h_i, J_i and M_i are in turn the weight fraction, the chromatogram height, the hydrodynamic volume and the molecular weight of the i-th species.

M_i may be given as a function of J_i, A_1 and A_2 from eq.(6) which can be rewritten as

$$M_i = \left[\frac{1}{2} A_1 J_i + \left(\frac{1}{27} A_2^3 J_i^3 + \frac{1}{4} A_1^2 J_i^2\right)^{1/2}\right]^{2/3} + \left[\frac{1}{2} A_1 J_i - \left(\frac{1}{27} A_2^3 J_i^3 + \frac{1}{4} A_1^2 J_i^2\right)^{1/2}\right]^{2/3} - \frac{2}{3} A_2 J_i \tag{10}$$

Using equations (7), (8) and (9) combined with eq.(10), we can determine A_1 and A_2, since w_i and J_i can be obtained from a GPC chromatogram of a polydisperse sample and the universal calibration curve (Fig.1).

RESULTS AND DISCUSSION

Calibration method for PMMA/MEK system

To avoid a contraction of the packing (μStyragel) in MEK (a poor solvent for PS), silica modified by ether groups (μBondagel) was used as the packing. Figure 2 shows the calibration plot (i.e. log M versus retention volume V_R) for the system PMMA, PS/MEK/μBondagel at 25°C. A primary calibration curve was first obtained using PS standards (dashed line). A secondary calibration curve was then established by converting the PS experimental curve by means of eq.(6) (full line). The values of A_1 and A_2 for the polymer (p) and the standard (s) were respectively (12.2, 8.8×10^{-3}) and (20.4, 14.3×10^{-3})*.

The experimental results obtained by PMMA monodisperse samples are seen to fit approximately the secondary calibration curve in the low molecular weight region. The universal calibration plot (i.e. $\log([\eta]M)$ versus V_R) is presented in Figure 3. It is apparent that the experimental points related to PS samples tend to shift towards higher retention volumes, demonstrating that secondary separation effects are operative. These effects are due to polymer-sorbent interaction which becomes significant in a poor solvent (for PS/MEK system $\alpha=0.63$) (11,12). This poses some limitations on the efficiency of the method, suggesting that the solvent must be good for both polymers ($\alpha>0.65$ approximately). Of course other possible

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* *The values of* $[\eta]$ *are in ml/g.*

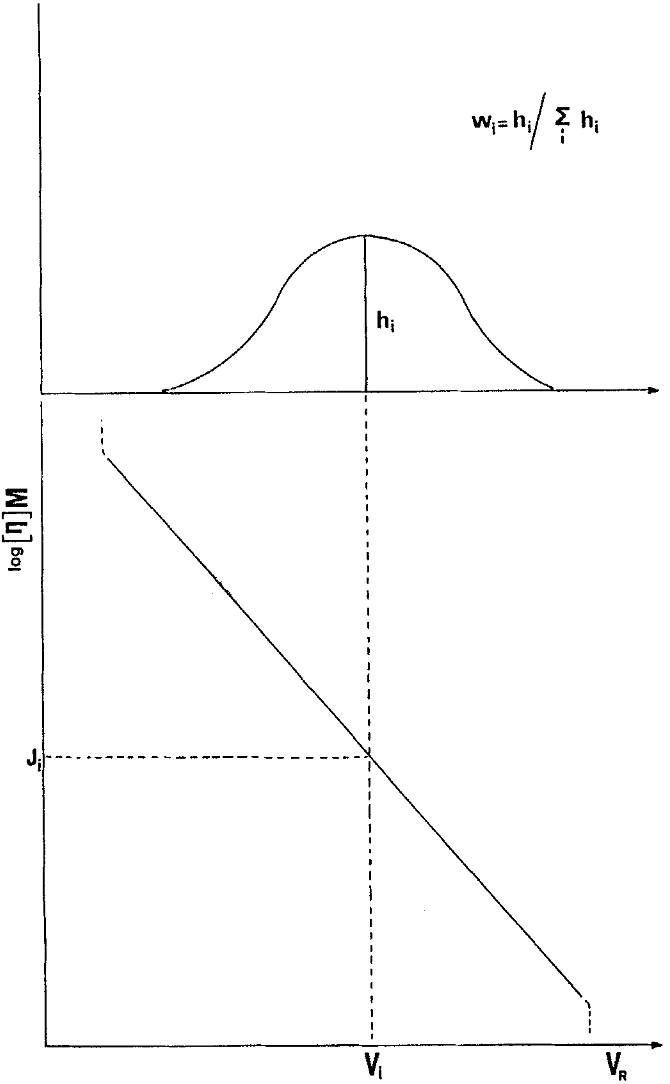

FIGURE 1. Schematic determination of the weight fraction w_i and hydrodynamic volume J_i of the ith species from a GPC chromatogram and the universal calibration plot.

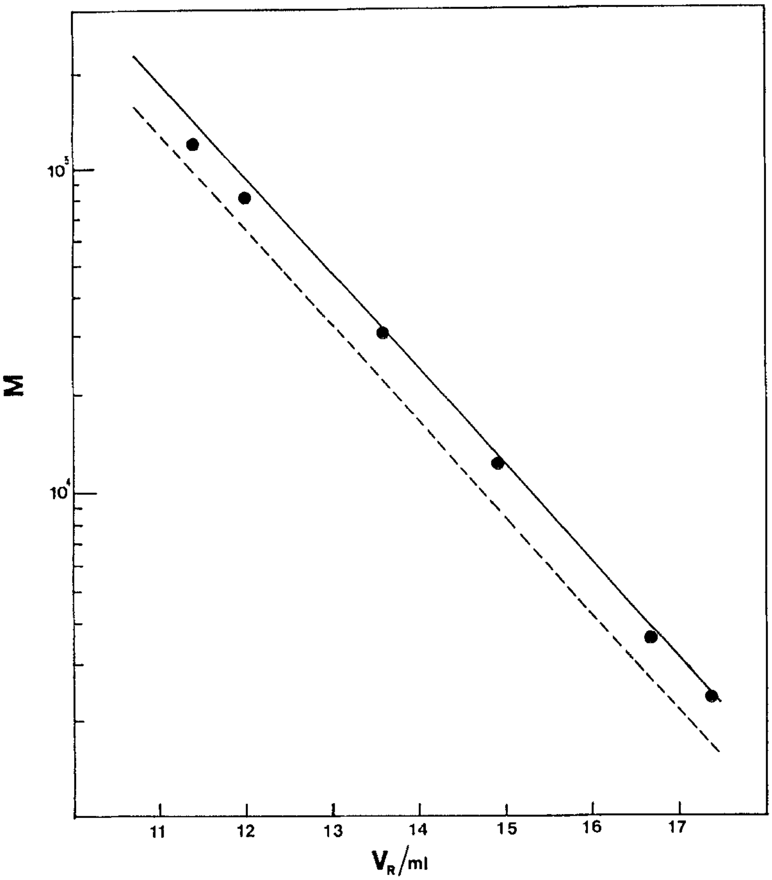

FIGURE 2. Calibration plot for PMMA in MEK at 25°C obtained on μBondagel columns: (---) PS/experimental, (–) PMMA/calculated through eq. (6), (●) PMMA experimental results.

effects which could disturb pure SEC mechanism have to be avoided.

Determination of A_1 and A_2

To examine the efficiency of the GPC method for the determination of the DB constants, we have calculated A_1 and A_2 for PS in THF at 25°C using μStyragel columns.

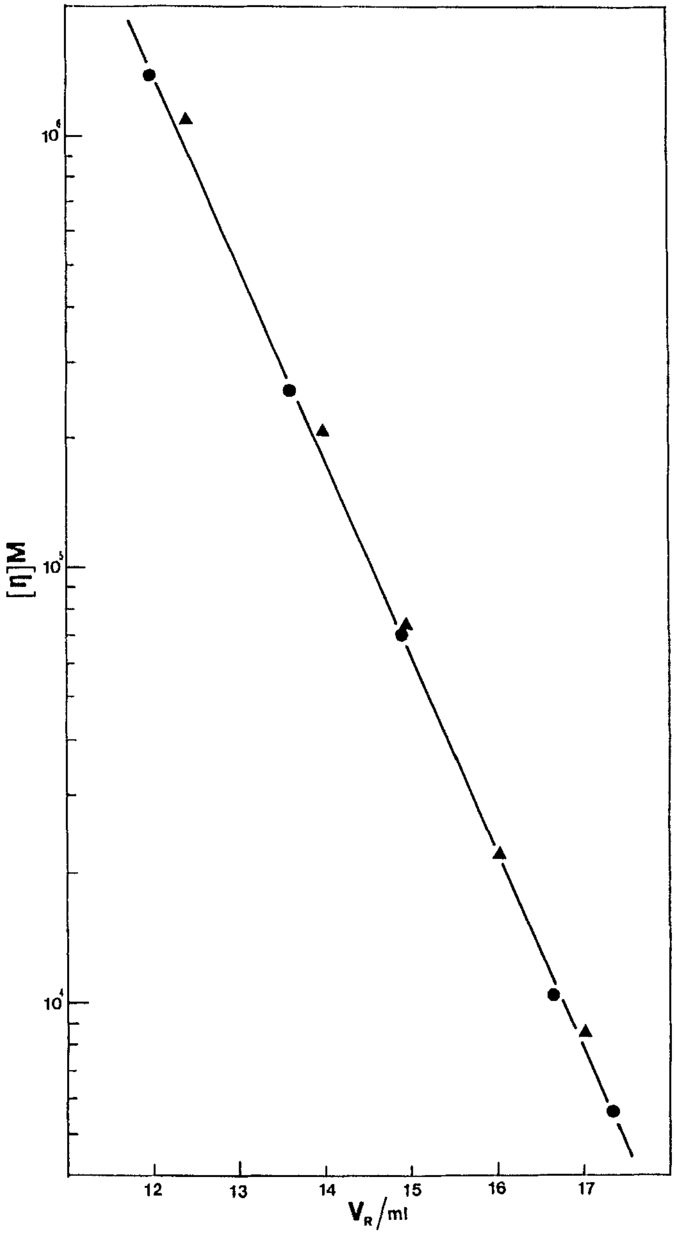

FIGURE 3. Universal calibration plot in MEK at 25°C obtained on μBondagel columns: (●) PMMA, (▲) PS.

TABLE 1. Determination of A_1 and A_2

Samples required	Equations	data	A_1	$A_2 \times 10^3$
1	(8), (9)	$[\eta]=20.8$ Mn=24,500	12.35	19.50
1	(8), (9)	$[\eta]=41.3$ Mn=60,450	12.30	15.05
1	(7), (9)	$[\eta]=41.3$ Mw=81,100	11.96	17.29
1	(7), (8)	Mw=81,100 Mn=60,450	12.30	15.05
From viscometry, ref. (1)			12.30	18.00

TABLE 2. Calculation of MW of PMMA using eq.(6)

PS			PMMA		
Mw	A_1	$A_2 \times 10^3$	A_1	$A_2 \times 10^3$	Mw
2,500	12.30[a]	18.00[a]	12.10[a]	8.77[a]	2540
	12.35[b]	19.50[b]			2540
	12.30[b]	15.05[b]			2520
	11.96[b]	17.29[b]			2580

a. viscometric data (ref.1)

b. data from table 1

The values of A_1 and A_2 have been calculated using one polydisperse sample and a system of two equations which have been solved on a computer. The calculated values are in good agreement with those obtained by viscometry (table 1). However it is worthy to check if the deviations of the calculated A_1 and A_2 from the viscometric values could affect the PMMA calibration established by the proposed procedure. The molecular weight of PMMA having the same hydrodynamic volume of a PS standard with Mw=2,500 has being calculated using eq.(6).

Table 2 shows that the calculated values of the molecular weight of PMMA using various values of A_1 and A_2 for the PS-THF system obtained from table 1 are in excellent agreement with that calculated through direct viscometric data. It is obvious that the uncertainties in A_1 and A_2 resulted from the proposed GPC method have not any remarkable effect on the proposed calibration method. Further work is in progress in which corrections for axial dispersion will be applied.

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