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## COUPLING OF A GEL PERMEATION CHROMATOGRAPH AND AN AUTOMATIC CAPILLARY VISCOMETER

### II. METHOD FOR THE DETERMINATION OF THE MOLECULAR WEIGHT DISTRIBUTION AND OF THE RESOLUTION FACTOR

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#### SUMMARY

The elucidation of some anomalous phenomena described in the literature for gel permeation chromatography coupled with an automatic capillary viscometer and investigated in Part I led to a suggestion for a method for the determination of correct polydispersity indices,  $\bar{M}_w/\bar{M}_n$ . The method also enables one to determine the resolution factor of the column system used. Experimental results indicated that the polystyrene standards commonly in use probably had a narrower distribution than that stated by the manufacturer.

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#### INTRODUCTION

In Part I (ref. 1) we tried to elucidate some anomalous phenomena observed by Brüssau<sup>2</sup> when using an automatic capillary viscometer coupled with the separation system in gel permeation chromatography (GPC). No agreement could be reached between the calibration graphs constructed by plotting the intrinsic viscosities,  $[\eta]$ , against the elution volumes of the maxima on the gel permeation chromatograms,  $V_{e \max}$ , of polystyrene (PS) standards in semi-logarithmic coordinates and those obtained from data from the automatic capillary viscometer coupled with the GPC separation system.

Our study has shown that it is predominantly the spreading of the chromatographic zone that causes the anomalous phenomena observed. The experimental errors at very low polymer concentrations in the eluent are also operative to some extent.

Fig. 1 shows the two extreme hypothetical cases of results obtained from the GPC data and from the coupled automatic capillary viscometer. In the first instance the thick straight line in Fig. 1a represents the calibration function in the coordinates  $\log [\eta]$  versus  $V_e$ ; the GPC separation system has an infinitely high resolution. Fig. 1b shows the envelope curve of the chromatogram of a polydisperse polymer obtained

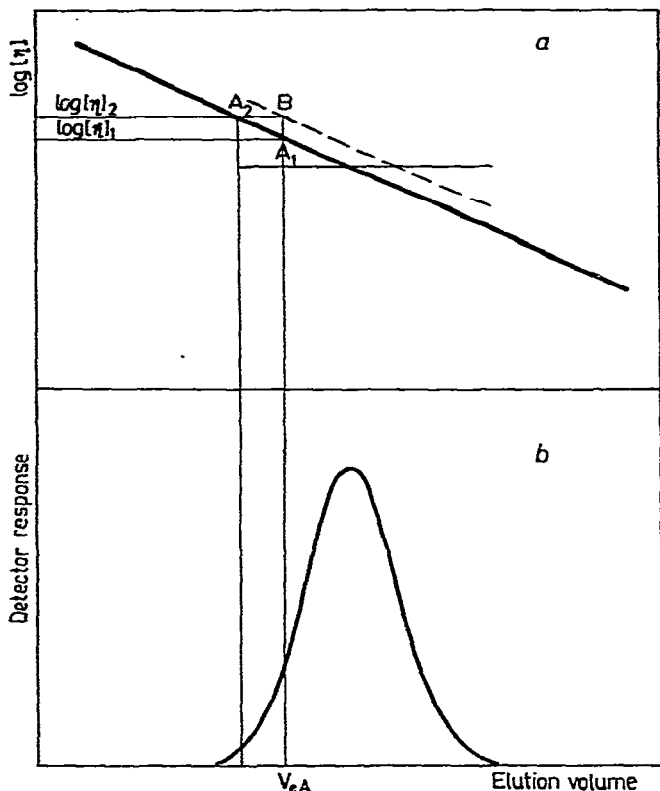


Fig. 1. (a) Calibration function and (b) chromatogram of the GPC separation system and coupled automatic capillary viscometer.

in this instance, or a non-normalized differential distribution curve of the polymer in the given coordinates. The vertical lines in Fig. 1b denote the moments of outflow from the siphon; the distance between them indicates the difference in elution volume equal to the siphon volume. At the moment of outflow from the siphon at the elution volume  $V_{eA}$ , the solution in the siphon contains macromolecules whose  $[\eta]_p$  values lie between the points  $A_1$  and  $A_2$  of the calibration function in Fig. 1a, *i.e.*, between the  $[\eta]_1$  and  $[\eta]_2$  values. The resulting  $[\eta]_i$  of the solution in the *i*th siphon will be the weight average of  $[\eta]_p$  of all macromolecules present in solution; the experimental point of the calibration function constructed from data obtained by means of the coupled automatic capillary viscometer lie on the intercept between  $A_1$  and B in Fig. 1a. The whole calibration line (dashedline in Fig. 1a) constructed in this way is approximately parallel with the original calibration straight line. It is evident that the smaller the siphon volume or the denser the relative segmentation of the chromatogram, the better is the agreement between the original calibration straight line and the calibration line calculated from data obtained with the coupled automatic capillary viscometer.

In the second instance the curve in Fig. 1b shows the chromatogram of a monodisperse polymer obtained by using the separation system having the above calibra-

tion curve and a finite resolution. The  $[\eta]_i$  values in each siphon volume must be constant, and the calibration line (thin straight line in Fig. 1a) constructed from data from the coupled automatic viscometer is parallel with the  $V_e$  axis. The density of experimental points on this line is given by the siphon volume.

The hypothetical example outlined above shows that in real cases the calibration curves constructed from data from the automatic capillary viscometer coupled with the GPC separation system lie between both extreme cases. The calibration curve for a polydisperse polymer on the separation system with a finite resolution is then the sum of the contributions of the individual monodisperse fractions. Indeed, in Part I<sup>1</sup> for a model sample of the PS standard with a wide distribution we obtained this type of calibration curve constructed from data from the coupled capillary viscometer.

By treating the data from the coupled capillary viscometer and using the fractionation theory, we can obtain the correct molecular weight distribution of the polymer sample under investigation. The resolution of the separation system under particular experimental conditions must be sufficiently high and the siphon volume sufficiently low so that, within the limits of experimental error, the equation  $\bar{M}_w \approx \bar{M}_n$  (where  $\bar{M}_w$  is the weight-average molecular weight and  $\bar{M}_n$  being the number-average molecular weight) would hold for a polymer dissolved in the volume of one siphon after the GPC separation. Calculation using an uncorrected gel-permeation chromatogram gives a distribution that will be wider by the dispersion contribution. The resolution factor for the given separation system can then be obtained by correlating the above values.

If the function  $F(V)$  represents the chromatogram of a polydisperse sample and the function  $M_0(V)$  represents the original calibration curve constructed by plotting molecular weights against the elution volumes of the maximum of the chromatogram, then for the uncorrected  $\bar{M}'_w/\bar{M}'_n$  value calculated from the gel-permeation chromatogram we have

$$\bar{M}'_w/\bar{M}'_n = \frac{\int_{V_A}^{V_B} F(V)M_0(V)dV \cdot \int_{V_A}^{V_B} F(V)M_0^{-1}(V)dV}{\left[ \int_{V_A}^{V_B} F(V)dV \right]^2} \quad (1)$$

The correct  $\bar{M}_w/\bar{M}_n$  value calculated from the data of the coupled capillary viscometer is

$$\bar{M}_w/\bar{M}_n = \frac{\int_{V_A}^{V_B} F(V)M(V)dV \cdot \int_{V_A}^{V_B} F(V)M^{-1}(V)dV}{\left[ \int_{V_A}^{V_B} F(V)dV \right]^2} \quad (2)$$

where  $M(V)$  is the calibration curve calculated from the function  $[\eta]_i = f(V_{ei})$  by means of the Mark-Houwink equation. In the case of linear dependences of  $M_0(V)$  and  $M(V)$ , which can be expressed, e.g., by the functions  $M_0 = C_1 e^{C_2 V}$  and  $M = D_1 e^{D_2 V}$ , where  $C_1, C_2, D_1, D_2$  are constants, on substituting into eqns. 1 and 2 one can see in what way the different slopes of the calibration lines  $C_2$  and  $D_2$  become operative if  $\bar{M}'_w/\bar{M}'_n$  and  $\bar{M}_w/\bar{M}_n$  are compared with each other.

## EXPERIMENTAL

PS standards (Waters Assoc., Milford, Mass., U.S.A.) with very narrow distributions and several fractions of poly(vinyl chloride) (PVC) were used in the investigation.

The molecular parameters of all samples investigated in this work were given in Part I<sup>1</sup>. Three different column systems were used in the GPC separations. The first two, designated as A and B, consisted of a series of six columns and had slightly different separation efficiencies. The third system, C, contained only a single column, and its separation efficiency was therefore comparatively low.

The experimental conditions used in the GPC separations, a description of the coupled automatic capillary viscometer and the method of evaluation of the experimental data were presented in detail in Part I<sup>1</sup>.

## RESULTS AND DISCUSSION

Experimental points of the functions  $[\eta]_i = f(V_{ei})$  constructed from data from the coupled automatic capillary viscometer for the PS standards depart from a linear dependence (*cf.*, Fig. 1 in Part I<sup>1</sup>). To calculate  $\bar{M}_w/\bar{M}_n$  values using eqn. 2, one would have to determine the analytical calibration function  $M(V)$  and the function  $F(V)$  describing the chromatogram. In this instance, a numerical solution using discrete values seemed more appropriate and simpler. The calculation was performed using the equation

$$\bar{M}_w/\bar{M}_n = \frac{\sum ([\eta]_i^{1/\alpha} \cdot c_i) \cdot \sum ([\eta]_i^{-1/\alpha} \cdot c_i)}{(\sum c_i)^2} \quad (3)$$

which can be obtained from the definitions of  $\bar{M}_w$  and  $\bar{M}_n$  and from the Mark-Houwink equation. The corresponding concentrations  $c_i$  were calculated using relationships given in Part I<sup>1</sup>. The  $\bar{M}'_w/\bar{M}'_n$  values were calculated in the standard way from the gel-permeation chromatograms without correction for the spreading of the chromatographic zone.

The experimental results are presented in Table I. Comparison of the  $\bar{M}_w/\bar{M}_n$  values given by the manufacturer for the PS standards or measured by light scattering and osmometry for the PVC fractions with those calculated from the gel-permeation chromatograms without correction for the spreading of the chromatographic zone shows that most of the results obtained by GPC are higher. The effect of the separation efficiency of the column system used is obvious. The lowest  $\bar{M}'_w/\bar{M}'_n$  values were obtained with a system having the highest separation efficiency (B), while the highest  $\bar{M}'_w/\bar{M}'_n$  values were obtained with the single separation column (C). With a few exceptions (PVC 5/2 and 5/4), the  $\bar{M}_w/\bar{M}_n$  values calculated from data from the coupled automatic capillary viscometer were lower than those calculated from the gel-permeation chromatograms. In a number of instances they were even lower than those given by the manufacturer of the PS standards or the values for the PVC fractions measured by independent methods. It should be noted that the separation efficiency of the column system used had only a slight influence on the  $\bar{M}_w/\bar{M}_n$  values calculated from data from the coupled automatic capillary viscometer.

TABLE I

POLYDISPERSITY INDICES  $\bar{M}_w/\bar{M}_n$ 

The data were supplied by the manufacturer of PS standards, measured by light scattering or osmometrically for PVC samples, calculated from gel-permeation chromatograms or calculated from data from the coupled automatic capillary viscometer for systems A, B and C.

Sample	Sample No.	Manufacturer's data	GPC			Viscometry		
			A	B	C	A	B	C
Polystyrene standards*	PS 1	1.21	1.61	1.18		1.18	1.08	
	PS 2	1.12	1.21	1.11		1.07	1.07	
	PS 3	1.23	1.15	1.12	1.25			1.09
	PS 4	1.05	1.11	1.10		1.07	1.05	
	PS 5	1.06	1.07	1.09		1.03	1.09	
	PS 6	1.02	1.09	1.09		1.06		
	PS 7	1.04	1.14	1.10			1.05	
PVC**	5/2	1.76	1.41			1.55		
	5/4	1.54	1.29			1.30		
	5/6	1.37	1.23			1.15		
	5/8	1.27	1.21			1.12		
	5/10	1.04	1.24			1.12		
	5/12	1.29	1.24			1.07		

\* For further manufacturer's data, see Part I<sup>1</sup>.

\*\* Polymer/fraction, for data see Part I<sup>1</sup>.

These results show that the method of determination of correct  $\bar{M}_w/\bar{M}_n$  values suggested in this paper was successful.

The  $\bar{M}_w/\bar{M}_n$  values calculated from data from the coupled automatic capillary viscometer correspond better to the correct  $\bar{M}_w/\bar{M}_n$  values which can be determined by independent methods, such as light scattering and osmometry. For polymers with very narrow distributions the method described here for the determination of the  $\bar{M}_w/\bar{M}_n$  polydispersities is probably more reliable than the combination of the classical light scattering and osmometry, which are restricted to certain ranges of molecular weights and can also lead to incorrect  $\bar{M}_w/\bar{M}_n$  values owing to the experimental precisions of both methods.

The correct  $\bar{M}_w/\bar{M}_n$  values determined by the method described here can be used in the determination of the resolution factor of the given GPC separation system. The once-through method<sup>3</sup>, in which the correct  $\bar{M}_w/\bar{M}_n$  values are compared with the  $\bar{M}'_w/\bar{M}'_n$  values calculated from the gel-permeation chromatogram without correction for spreading, can be employed for this purpose. According to Balke and Hamielec<sup>3</sup>

$$\frac{\bar{M}_w/\bar{M}_n}{\bar{M}'_w/\bar{M}'_n} = e^{2D_2^2/h} \quad (4)$$

where  $h$  is the resolution factor and  $D_2$  is the constant of the calibration function  $M = D_1 e^{D_2 V}$ . The once-through method is used more advantageously than the reverse-flow method in the determination of the resolution factor<sup>3</sup>.

The assumption that  $\bar{M}_w \approx \bar{M}_n$  for a polymer dissolved in one siphon volume after the GPC separation was verified by injecting a sample of the PS 4 standard using

separation system B, taking a one-count volume of solution in the region of the maximum of the chromatogram, and re-injecting this volume. An uncorrected value of  $\bar{M}'_w/\bar{M}'_n = 1.05$  was calculated from the chromatogram of the re-injected fraction, and comparison with the corrected value of  $\bar{M}_w/\bar{M}_n = 1.01$  for this fraction justifies the above assumption. The resolution factor determined for the PS 4 standard under the given conditions by means of eqn. 4 and using the comparison of polydispersities calculated from the gel-permeation chromatogram and from data from the coupled automatic capillary viscometer was used for the correction.

## CONCLUSION

Experimental results have confirmed within acceptable limits our assumption regarding the way in which the coupling of an automatic capillary viscometer and the GPC separation system could be used in calculating correct polydispersity values, especially for polymers with very narrow distributions. The method also makes possible a direct and simple determination of the resolution factor of the separation system employed. The resulting  $\bar{M}_w/\bar{M}_n$  values of the PS standards used in the experiments indicate that in some instances the polydispersity values given by the manufacturer are incorrect, and that the real values are somewhat lower. This problem will be investigated in detail later.

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