Journal of Chromatography, 132 (1977) 187–193

CHROM. 9579

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

I. INFLUENCE OF THE COLUMN EFFICIENCY

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(Received July 7th, 1976)

SUMMARY

The causes of some anomalous effects observed while using an automatic capillary viscometer coupled to the separation system of a gel-permeation chromatograph have been investigated. Various systems of separation columns differing in their separation capacity have been used, but the effects have not been completely eliminated, even by means of a system having a very high resolution. The anomalous effects are explained in terms of zone-spreading of the chromatographic bands and of the experimental errors.

INTRODUCTION

The determination of the intrinsic viscosity of a polymer in the eluent leaving a separation system in gel-permeation chromatography (GPC) has been examined by several workers. Meyerhoff[1] described the application of a capillary viscometer coupled with GPC. In his later paper[2] he recommended the function 1 for the calibration of the GPC separation systems

$$[\eta] = f(V_e) \tag{1}$$

where $[\eta]$ is the intrinsic viscosity and V_e is the elution volume. The coupling of a capillary viscometer with GPC for the evaluation of the molecular-weight distribution of polymers, by means of a universal calibration based on the product $[\eta] \cdot M$ (where M is the molecular weight), has several advantages as shown by Benoit[3]. Goedhart and Opschoor[4] demonstrated the agreement between $[\eta]$ values and constants of the Mark–Houwink equation (determined by methods of classical viscometry) with the corresponding values calculated from data obtained by GPC coupled with an automatic capillary viscometer. A similar agreement was obtained by Meunier and Grubisic[5] for linear and branched polystyrene (PS) (however, $[\eta]$ values measured by classical viscometry seemed systematically higher by *ca.* 5%), and by Grubisic-Gallot *et al.*[6]. The same agreement between the $[\eta]$ values was also obtained by

Gallot *et al.*[7], who also pointed out the possible errors in the K and a values of the Mark–Houwink equation calculated from data obtained by use of the automatic capillary viscometer. A somewhat different system for the determination of $[\eta]$ of GPC fractions has been described by Ouano[8,9]. The fractions were not examined by means of a capillary viscometer, but by use of a detector which reacted to the pressure changes due to changes in the viscosity of the solvent in a system having a constant flow of eluent.

Brüssau[10] recently reported some anomalous effects observed with a coupled capillary viscometer. No agreement was obtained between calibration graphs constructed in the standard manner and those obtained from data from an automatic capillary viscometer coupled with a GPC separation system. Part of the present work is an attempt to explain such anomalous results.

EXPERIMENTAL

Gel-permeation chromatography

All of the GPC measurements were carried out with an apparatus constructed at the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences. The separation columns were thermostated to 25 ± 0.1°. Tetrahydrofuran (THF), distilled from cuprous chloride and potassium hydroxide in a nitrogen atmosphere, was used as the solvent. Its flow-rate was 0.375 ml/min. The elution volumes were measured by means of a calibrated siphon having a volume of 1.704 ml (measured at a flow-rate of 0.375 ml/min). The solutions of the samples were injected from a calibrated loop (volume 1.636 ml). The columns were packed with the silica gel Sphérosil (Produits Chimiques, Péchiney-Saint-Gobain, France), Types B, D and E, and connected in series, *i.e.*, two columns E, followed by two of D and two of B. A column packed with porous glass CPG-10-1000 (Electro Nucleonix, Fairfield, N.J., U.S.A.) was used independently.

Automatic capillary viscometer

The capillary viscometer was constructed according to published data[6] on the electronic and recording part of a Sofica automatic viscometer (ARL, Le Mesnil-Saint-Denis, France), and was connected behind the siphon and thermostatted to 25 ± 0.005°. The flow-time of an exactly defined amount of pure THF between two photocells was *ca.* 155 sec.

Polystyrene and poly(vinyl chloride) samples

Polystyrene (PS) standards (Waters Assoc., Milford, Mass., U.S.A.) having a very narrow distribution, several fractions of poly(vinyl chloride) (PVC) and unfractionated PVC samples were used in the investigation. The designations and molecular parameters of the samples are given in Table I. The polydispersity indices, $\bar{M}_w/\bar{M}_n$, of the PS standards were as supplied by the manufacturer; the $[\eta]$ values of the PS standards were measured in ref. 11. The $\bar{M}_w/\bar{M}_n$ and $[\eta]$ values for the PVC samples were measured in ref. 12.

TABLE I

MOLECULAR PARAMETERS ($\bar{M}_w/\bar{M}_n$) AND INTRINSIC VISCOSITIES [η] OF PS STANDARDS AND PVC SAMPLES MEASURED BY CLASSICAL VISCOMETRY AND BY A CAPILLARY VISCOMETER COUPLED WITH A GPC SEPARATION SYSTEM

Sample	$\bar{M}_w/\bar{M}_n$*	[η]* (dl/g)	$\bar{M}_w/\bar{M}_n$**		[η]$_{av}$***	
			A	*B*	*A*	*B*
PS standards						
PS 1	1.21	3.54	1.61	1.18	4.04	4.28
PS 2	1.12	2.07	1.21	1.11	2.33	2.32
PS 3	1.23	1.43	1.15	1.12		
PS 4	1.05	1.25	1.11	1.10	1.27	1.35
PS 5	1.06	0.67	1.07	1.09	0.70	0.69
PS 6	1.02	0.44	1.09	1.09	0.51	
PS 7	1.04	0.28	1.14	1.10	0.28	0.28
PS 8	1.01	0.14	1.24	1.17		
PS 9	1.06	0.09	1.35	1.30		
PS 10	1.09	0.05	1.47			
PVC samples (polymer, fraction)						
5, 2	1.76	1.10	1.41		1.06	
5, 4	1.54	0.81	1.29		0.86	
5, 6	1.37	0.64	1.23		0.70	
5, 8	1.21	0.50	1.21		0.56	
5, 10	1.04	0.35	1.24		0.40	
5, 12	1.29	0.28	1.24		0.27	
1, 0		0.57	2.03		0.57	0.57
3, 0		0.55	2.00		0.51	0.52

* For PS standards: $\bar{M}_w/\bar{M}_n$, manufacturer's data; [η] from ref. 11. For PVC samples $\bar{M}_w/\bar{M}_n$ and [η] from ref. 12.

** Calculated from GPC data.

*** Calculated from coupled capillary-viscometer data.

RESULTS AND DISCUSSION

The intrinsic viscosities, $[\eta]_{av}$, of the individual samples were calculated from data obtained from the capillary viscometer coupled to the GPC separation system according to the equation

$$[\eta]_{av} = \frac{\Sigma [\eta]_i \cdot c_i}{\Sigma c_i} \tag{2}$$

where $[\eta]_i$ and c_i are the intrinsic viscosity and concentration respectively of the individual fractions separated by the siphon. The $[\eta]_i$ values in eqn. 2 were calculated from the data obtained with the automatic capillary viscometer for the respective fractions according to the equation.

$$[\eta]_i = \frac{\eta_{r,i} - 1}{c_i} \tag{3}$$

where $\eta_{r,i}$ is the relative viscosity of the polymer solution of the respective fraction.

The polymer concentration, c_i, can be calculated from the refractometer data by using the equation

$$c_i = \frac{S_i}{S} \cdot \frac{m}{q} \tag{4}$$

where S and S_i are the areas of the whole chromatogram and of the corresponding fraction respectively, m is the weight of the injected polymer and q is the siphon volume. The approximation given by eqn. 3 is possible because the polymer concentrations in the eluent leaving the column are very low.

We first determined the $[\eta]_{av}$ values for all of the samples using a series of six columns denoted by A. The results are summarized in Table I. The averages of the $[\eta]_{av}$ values are within $\pm 7.5\%$ of those measured by classical viscometry. The average reproducibility of the $[\eta]_{av}$ values was $\pm 5\%$ under the given experimental conditions, as verified by several measurements of the PS standards and PVC samples. By plotting $[\eta]_i$ *versus* the respective elution volumes, $V_{e,i}$, we found an anomalous dependence similar to that in ref. 10, although less pronounced. No agreement was obtained between these functions and a calibration graph constructed in the classical manner, *i.e.*, by plotting the $[\eta]$ values obtained by standard viscometry against the elution volume of the maximum of the chromatogram, $V_{e,max}$. This dependence is shown for some PS standards in Fig. 1. Similar behaviour was observed for the PVC fractions.

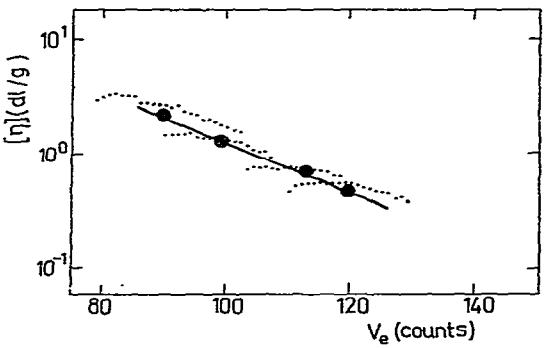

Fig. 1. The function $[\eta] = f(V_e)$ obtained for PS standards with system A. ····, $[\eta]_i = f(V_{e,i})$ measured by use of a capillary viscometer coupled with GPC; ●—●, the function $[\eta] = f(V_{e,max})$, $[\eta]$ being measured in the classical way.

The anomalous behaviour of the $[\eta]_i$ *versus* $V_{e,i}$ functions may be due to spreading of the chromatographic zone. This is suggested by the smaller slope of these graphs compared with the calibration graph of $[\eta]$ against $V_{e,max}$. At high molecular weights the $[\eta]_i$ values are lower owing to spreading, while at low molecular weights they are higher, compared to the respective values from the calibration graph. Such hypothesis is also corroborated by the rather marked disagreement between the functions in the high-molecular-weight region, where the separation efficiency of the A system of columns is lower, as follows from a comparison of the $\bar{M}_w/\bar{M}_n$ values

supplied by the manufacturer for the PS standards with those calculated from the respective GPC chromatograms. The anomalies observed cannot be due to mixing in the siphon, because the moment of elution from the siphon is assumed to correspond to $V_{e,i}$, which means that in an ideal case of an infinitely high resolution all of the experimental points of the function $[\eta]_i$ against $V_{e,i}$ would lie above the calibration graph.

In order to verify the above hypothesis experimentally, we reconstructed the separation system A so that all of the dead volumes, which increase spreading, were minimized. This was achieved by shortening all of the connecting capillaries, especially that between the differential refractometer and the siphon. The separation system thus modified, containing the original six columns and denoted by B, was used for repeated measurements of the PS standards and unfractionated PVC samples. The separation efficiency of system B was somewhat higher than that of system A, as can be seen from a comparison of the $\bar{M}_w/\bar{M}_n$ values calculated from the GPC chromatogram (Table I) which in some cases are even lower than the manufacturer's data[13]. On the other hand, however, the change of the $[\eta]_i$ *versus* $V_{e,i}$ functions of the PS standards for the systems A and B was at the limits of experimental error. Use of the Huggins equation instead of eqn. 3 for calculating $[\eta]_i$ did not result in any important changes in the $[\eta]_i$ *versus* $V_{e,i}$ functions. The Huggins constant, $k_H = 0.362$, was calculated from our earlier experimental data[11]. The $[\eta]_{av}$ values also remained unchanged within the limits of experimental error.

Since a somewhat better agreement between the $[\eta]_i$ *versus* $V_{e,i}$ functions and the classical calibration graph was obtained for the PVC samples having a broader molecular-weight distribution, we prepared a model PS sample having a wide distribution by mixing approximately the same amounts of the PS standards 1, 2 and 4–10. The chromatogram of this sample is shown in Fig. 2, and the $[\eta]_i$ *versus* $V_{e,i}$ function is in Fig. 3. Both figures show that the $[\eta]_i$ values are affected by the precision of the measurements of time with the capillary viscometer ($\pm$ 0.02 sec) and by the precision with which the heights h_i may be read from the GPC chromatogram. For instance, in the region of 100–110 counts, inaccuracies appearing at a large change in the concentration cause undulation of the $[\eta]_i$ *versus* $V_{e,i}$ function. The

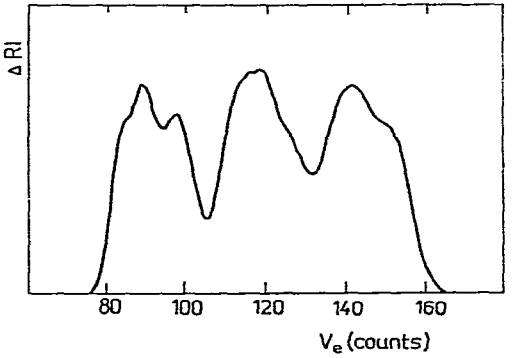

Fig. 2. Chromatogram obtained with system B of the model PS sample having a broad distribution.

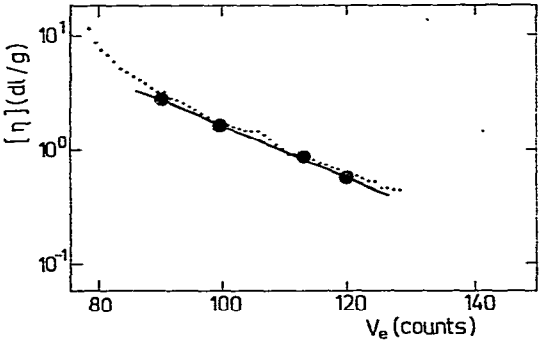

Fig. 3. The function $[\eta] = f(V_e)$ obtained with system B for the model PS sample having a broad distribution. Other details as in Fig. 1.

calculation of the $[\eta]_i$ values at the end of the chromatogram is particularly subject to a large experimental error; we therefore eliminated values which had potentially higher errors than 10%. At the same time, it can be seen from Fig. 3 that a comparatively good agreement was achieved between the $[\eta]_i$ *versus* $V_{e,i}$ function and the original calibration graph for system B.

The results of measurements made with the use of only one column (CPG-10-1000), the separation efficiency of which is considerably lower than the systems A and B, are shown in Fig. 4. One can see clearly the large difference between the $[\eta]_i$ *versus* $V_{e,i}$ function and the original calibration graph compared with the systems A and B. The measurements were carried out at four concentrations of the injected standard PS 3, *i.e.*, at 0.4, 0.2, 0.1 and 0.05% (w/v). In this case too, however, $[\eta]_{av} = 1.57$ corresponds to $[\eta]$ measured by classical viscosimetry, even though a small decrease in $[\eta]_{av}$ was observed with decreasing concentration of the injected PS standard.

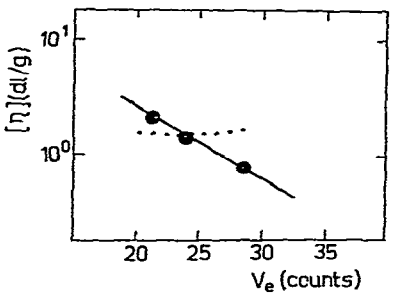

Fig. 4. The function $[\eta] = f(V_e)$ obtained with the CPG-10-1000 column for the PS standards. Other details as in Fig. 1.

Bearing in mind possible experimental errors, the calculation of $[\eta]_i$ from eqn. 3 or by means of the Huggins equation is justified. On the other hand, the determination of the concentration c_i or of the area S_i in eqn. 4 still remains a problem. Since the whole of the chromatogram is divided into constant-count segments, which we regard as equal to unity, the area S_i corresponding to the ith fraction can be calculated from the equation

$$S_i = \frac{h_i + h_{i-1}}{2} \tag{5}$$

where h_i is the height of the chromatogram in arbitrary units starting from the baseline in the ith count. The overall chromatogram area is then a sum of the areas of the individual fractions. In order to determine whether the use of eqn. 5 is justified, we used our earlier results obtained by the preparative GPC fractionation of the copolymer vinyl chloride–vinyl acetate[14]. The actual yield of the fractions obtained was in good agreement with the theoretically assumed yield calculated from the preparative chromatogram. Only the marginal high-molecular- and low-molecular-weight fractions were not in agreement, owing to material losses and the relatively higher errors in the calculation at generally lower yields.

Spreading and experimental errors lead to the observed anomalous behaviour of the $[\eta]_i$ *versus* $V_{e,i}$ functions constructed from the data obtained by GPC coupled with the automatic capillary viscometer compared with the classical calibration graph. On the other hand, the general eqn. 2 for calculations of $[\eta]_{av}$ does not suffer from spreading effects. This is why the $[\eta]_{av}$ values agreed within the limits of experimental error with the $[\eta]$ value measured in the classical way. The "limiting curve", which according to Brüssau[10] can be drawn through the low-molecular-weight ends of the individual $[\eta]_i$ *versus* $V_{e,i}$ functions, has probably no physical meaning. The extra-column contributions to spreading were very low for systems A and B. If columns having an extremely high separation efficiency were available, an even stronger suppression of the anomalous effects would be expected.

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