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Design of a differential pressure detector for use in the size-exclusion chromatography of polymers

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ABSTRACT

A differential pressure (DP) detector (a differential capillary viscometer) with four capillaries and two differential pressure transducers was constructed and its performance was evaluated. The effluent containing polymer fractions passed through one capillary while the mobile phase flowed through the other capillary, and the differential pressure between the two inlets of the capillaries was measured with a differential pressure transducer. The other two capillaries were used for the compensation of the flow fluctuation during the elution of a polymer fraction. The small increase in the pressure drop across a capillary (*i.e.*, less than 1%) for a polymer fraction was measured precisely and accurately. The delay of the response of the DP detector was observed and the size of the response delay was estimated by comparing the measured DP chromatogram with the calculated DP chromatogram. For the point-by-point calculation, the correction of the response delay for the DP chromatogram was applied and the calculated average molecular masses (M_r) were comparable to the reference data. The shear degradation of polystyrenes having $M_r > 10^6$ during passing through the size-exclusion chromatographic columns was observed.

INTRODUCTION

Several types of capillary viscometers which measure the pressure drop across a capillary or the differential pressure across two capillaries are now commercially available [1–4], in addition to laboratory-made instruments [5–7]. These viscometers are used exclusively as a molecular-mass-sensitive detector together with a concentration detector such as a refractive index (RI) detector for size-exclusion chromatography (SEC). When a polymer solution flows through a capillary, the pressure drop across the capillary is proportional to the viscosity of the polymer solution, and the intrinsic viscosity of the polymer can be calculated by knowing the pressure drop across the capillary and the sample concentration of the polymer solution. Therefore, the use of the capillary viscometer in combination with an RI detector as SEC detectors can make possible the determination of the molecular mass (M_r) of an unknown polymer by knowing the hydrodynamic volume of polymer standards by multipling the intrinsic viscosity by the molecular mass of the polymer standards.

The laboratory-made capillary viscometers reported in the literature contained one capillary and the pressure drop across a capillary was detected with two pressure transducers [6] or one differential pressure transducer [7]. However, the increase in viscosity of the sample solution eluted from SEC columns was less than 1% of the viscosity of the mobile phase, and therefore, in these laboratory-made viscometers with one capillary, the increase in the output signal of the pressure transducer for the sample solution had to be amplified, resulting in a noisy signal. Smoothing procedures were required to obtain a smoothed differential pressure signal in these viscometers [8,9].

Commercially available viscosity detectors utilize one to four capillaries, namely, single-capillary design [3], two-capillary design [4] and four-capillary bridge design [1,2]. The two-capillary

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design developed by Yau [4] utilizes two sets of capillary tubing and pressure transducer assemblies connected in series. The analytical capillary–transducer system is connected ahead of the reference capillary–transducer system and a 5–10-ml delay volume is added between them. The increase in the viscosity of the sample solution is measured by the pressure drop across the analytical capillary and the viscosity of the mobile phase by the pressure drop across the reference capillary. The two signals of the pressure drop are fed into a differential logarithmic amplifier to give a direct readout of the natural logarithmic value of the relative viscosity of the sample solution. Haney's four-capillary bridge design [1,2] measures the differential pressure across two capillaries, one for the sample solution and the other for the mobile phase, and can monitor the differential pressure directly on a strip-chart recorder.

The laboratory-made assembly is attractive owing to its relative simplicity in design, ease of data reduction and low cost compared with the commercial viscometers. In this paper, a new design with four capillaries is described. It measures the differential pressure across two capillaries, one for a sample solution and the other for the mobile phase, directly without any computational treatments. The system is simple and easy to construct in any laboratory.

EXPERIMENTAL

Differential pressure detection system

A schematic flow sheet and the assemblies of the differential pressure (DP) detection system for SEC are shown in Fig. 1. The system was composed of four capillaries, two differential pressure transducers, a delay reservoir and two SEC columns. Two of the capillaries (Nos. 1 and 3) were used for the adjustment of flow resistance on the sample and reference sides of the system, respectively. The capillaries were 1 m × 0.13 mm I.D. stainless-steel tubes. The pressure ranges of the two differential pressure transducers (Model M-7D; Tsukasa-Sokken, Tokyo, Japan) were between 0 and 507 kPa for DP0 and between 0 and 10.1 kPa for DP1. The transducers were activated by amplifiers and generated a

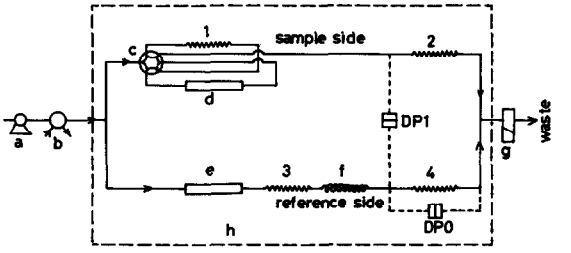

Fig. 1. Schematic flow diagram of a differential pressure detection system for SEC. a = Pump; b = sample loop injector; c = six-port valve; d = SEC column on the sample side; e = SEC column on the reference side; f = delay reservoir; g = RI detector; h = air oven; 1–4 = capillaries; DP0, DP1 = differential pressure transducers.

0–10-V output signal. These assemblies were housed in an air oven to keep them at a constant temperature.

As the mobile phase was delivered with one pump to both the sample and the reference sides at identical flow-rates, the flow resistance between the outlet of the sample loop injector and the inlet of the RI detector in Fig. 1 on both sides was adjusted to the same value by changing the length of capillary No. 1. A sample solution was injected with the sample loop injector b and was divided into two equal portions on both sides. When the sample solution was injected, the six-port valve c was on the broken-line position and the sample solution flowed into the SEC column d without passing through capillary No. 1. When the whole sample solution was introduced into the SEC column, the valve was changed to the full-line position.

The delay reservoir f was a 13 m × 1 mm I.D. stainless-steel tube with a capacity of 10 ml. This volume was approximately the same as the volume of the mobile phase in the SEC column used in this experiment. A polymer sample was fractionated in SEC columns d and e and the fractions from column d on the sample side entered capillary No. 2 and capillary No. 3 from the column e on the reference side. While the polymer fractions on the sample side passed through capillary No. 2, the polymer fractions on the reference side remained in capillary No. 3 and the delay reservoir, and only the mobile phase was flowing through capillary No. 4. The pressure difference, $\Delta\Delta P$, between the pressures

at the inlets of both capillaries Nos. 2 and 4 was measured with the differential pressure transducer DP1. The pressure drop of the mobile phase, ΔP_0, across capillary No. 4 was measured with DP0. The effluents from capillaries Nos. 2 and 4 were combined and entered the RI detector.

Size-exclusion chromatography

A Model LCP-150 syringe-type pump for liquid chromatography (Japan Spectroscopic, Tokyo, Japan) was used to deliver the mobile phase. A Model SE-11 differential refractive index detector (Showa Denko, Tokyo, Japan) was used as a concentration detector. Two Shodex SEC A-80M columns (50 cm × 8 mm I.D.) packed with polystyrene (PS) gels for polymer fractionation were used, one for the sample side and the other for the reference side. These two columns were selected so as to have similar column parameters (*i.e.*, the interstitial volume and the inner volume of the gels). The columns, capillaries Nos. 1–4, the delay reservoir and the pressure transducers were housed in a Model TU-100 air-oven (Japan Spectroscopic) at 35°C.

PS samples were PS standards with narrow M_r distributions (Pressure Chemical, Pittsburgh, PA, USA) and NBS SRM 706 PS. These polymers were dissolved in tetrahydrofuran (THF) at concentrations of 0.02–0.2%, depending on their M_r and M_r distributions. The mobile phase was THF and the flow-rate was 0.5 ml/min on each side. The injection volume of the sample solutions was 0.25 ml, so that half of the volume entered each column. Poly(vinyl chloride) (PVC), poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA) and poly(isobutyl methacrylate) (PIBMA) were purchased from several sources.

Data reduction

When the pressure drop of the mobile phase across the capillary is ΔP_0, the difference between the pressure drop, ΔP, of the polymer solution and ΔP_0 is expressed as [5]

$$\Delta\Delta P = \Delta P - \Delta P_0 = \frac{8lQ}{\pi r^4}(\eta - \eta_0) \quad (1)$$

where r is the capillary radius, l the capillary length, Q the fluid flow-rate and η and η_0 the fluid viscosity of the sample solution and the mobile phase, respectively. The value of $\Delta\Delta P$ corresponds to the differential pressure between the pressures at the inlet of the sample capillary No. 2 (ΔP) and the inlet of the reference capillary No. 4 (ΔP_0) in Fig. 1 and the differential pressure is measured with the differential pressure transducer DP1. Similarly, the value of ΔP_0 is obtained with the differential pressure transducer DP0.

For very dilute polymer concentrations, such as those existing in SEC, the intrinsic viscosity $[\eta]$ of the polymer sample is defined as [8]

$$[\eta] = \lim_{C\to 0}\frac{1}{C}\cdot\frac{\eta-\eta_0}{\eta_0} = \frac{1}{C}\cdot\frac{\eta-\eta_0}{\eta_0}$$
$$= \frac{1}{C}\cdot\frac{\Delta P-\Delta P_0}{\Delta P_0} = \frac{1}{C}\cdot\frac{\Delta\Delta P}{\Delta P_0} \quad (2)$$

where C is the sample concentration and is obtained from the response of the refractive index detector.

The intrinsic viscosity of a polymer fraction eluted at a retention volume i is obtained as [7]

$$[\eta]_i = \frac{1}{C_i}\cdot\frac{\Delta\Delta P_i}{\Delta P_0} \quad (3)$$

When the RI chromatogram of a sample is divided into intervals y, then C_i is calculated as

$$C_i = \frac{Wh_i}{y\sum h_i} \quad (4)$$

where W is the mass of the sample injected into the sample column and h_i is the height of the RI chromatogram at retention volume i. The influence of temperature on the fluctuation of the height of the RI chromatogram [10] can be prevented by the use of this equation. The units of y and W in this experiment were dl and g, respectively.

Similarly, the intrinsic viscosity of the whole polymer can be calculated by using the equation

$$[\eta] = \frac{y}{W \Delta P_0} \sum \Delta\Delta P_i \quad (5)$$

RESULTS AND DISCUSSION

Performance of the system

Examples of the RI and DP chromatograms of a PS standard are shown in Fig. 2. The polymer had average M_r of 411 000. This sample had a bimodal distribution; one was the main peak and the other appeared in the high-molecular-mass region as a small peak. This distribution was observed on both chromatograms.

The single-capillary design is simple and measures the pressure drop across a stainless-steel capillary: the pressure drop ΔP_0 for pure solvent and ΔP for a sample solution. The key components of the system are DP0 and capillary No. 4 in Fig. 1. When the sample elutes from an SEC column, the increase in the viscosity of the effluent is very small because of the low sample concentration. Under typical chromatographic conditions, the increase in the viscosity due to the elution of polymer fractions is less than 1% of the background viscosity (*i.e.*, the viscosity due to the mobile phase itself). When a single-capillary system is applied to measure the pressure drop across the capillary–transducer system, this small change in the overall pressure drop must be amplified about 100-fold to display the viscometer signal properly, resulting in a low signal-to-noise ratio. An example is shown in Fig. 3. Computer smoothing procedures such as a non-linear regression [7] or fast Fourier transform smoothing [11] are required in order to obtain a smoothed viscometer signal.

When two capillaries, one for the sample solution and the other for the mobile phase, are used with two differential pressure transducers, similar assemblies to that in Fig. 1 can be considered except for the sample injection valve, capillaries Nos. 1 and 3 and the delay reservior. The six-port valve in Fig. 1 is used for sample injection in this instance. A sample solution is introduced into the SEC column on the sample side only. However, when a sample polymer passed through capillary No. 2, a difference in the pressure drops across the two capillaries was generated and, as a result, the flow-rate on the reference side was apt to increase, which, in turn, decreased the response on the pressure transducer DP1. The peak response on DP1 obtained in this system was about 15% smaller than that obtained in the system shown in Fig. 1.

A polymer sample enters the RI cell after passing through capillary No. 2 in Fig. 1. The sum of the dead volume of the connecting tubing and half the volumes of capillary No. 2 and of the RI cell was about 0.06 ml. However, the measured difference in the peak tops for a polymer sample between the two detectors was 0.15 ml (see Fig. 2). Lecacheux and Lesec [11]

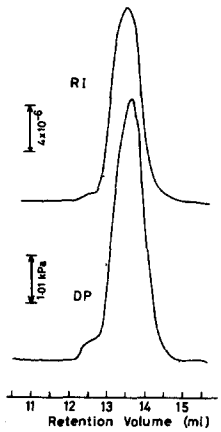

Fig. 2. RI and DP chromatograms for PS standard with M_r 411 000. Sample concentration injected, 0.11%; attenuation, RI × 4 ($\times 10^{-5}$ refractive index units full scale), DP 10 V (full scale).

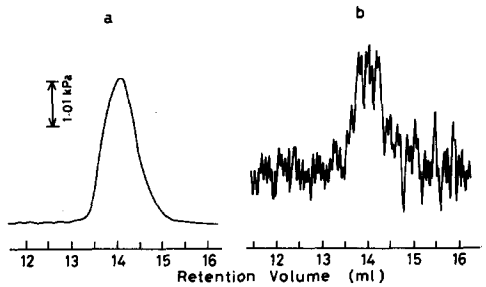

Fig. 3. DP chromatograms of PS of M_r 180 000 obtained (a) with the present system and (b) with a single-capillary design. Sample concentration injected, 0.1%; injection volume, (a) 0.25 ml and (b) 0.125 ml.

pointed out that the geometric estimate of the dead volume was not suitable and that the experimentally obtained value was greater than the geometric value. When a universal calibration graph is constructed with PS standards having narrow M_r distributions, the peak position calibration is not adequate because of not only the inaccurate estimation of the geometric dead volume but also the inconsistency of the peak tops between DP and RI chromatograms. It is easily conceivable that the polymer fraction at the peak top of a DP chromatogram does not correspond to the maximum concentration (the peak top) of the RI chromatogram, but rather has a higher M_r than that of the polymer fraction at the peak top of the RI chromatogram.

The differences between our system and the commercially available four-capillary system are as follows. The commercial system is based on a fluid analogue of a Wheatstone bridge. The polymer effluent from the SEC column enters the bridge and is divided equally into two lines: one enters the capillaries R_1 and R_3 and the other the capillaries R_2 and R_4 (after a hold-up/dilution reservoir). The effluent passed through R_1 enters R_3 and that passed through R_2 enters the hold-up/dilution reservoir. During the passage of the effluent through R_3, the mobile phase enters R_4 and the pressure difference between R_3 and R_4 is monitored. Our system, on the other hand, is not based on a Wheatstone bridge, but one capillary is attached before the SEC column on the sample side. The sample solution injected into the SEC system is divided equally into two parts and enters both the sample side and the reference side. The effluent from the SEC column on the reference side enters capillary 3 and that from the sample side enters capillary 2. The pressure difference between capillaries 2 and 4 which is occupied by the mobile phase is monitored. Our system has advantages over the commercial system: the fluctuation of the flow-rate is kept to a minimum during the measurement because the pressure drop of both sides (lines) is the same; as the pressure difference across capillaries 2 and 4 is measured as soon as the polymer effluent leaves the SEC column on the sample side, the influence of polymer degradation during passage through the capillary before entering the capillary for the measurement of the pressure drop can be neglected.

Evaluation of the measurement of PS molecular mass

The universal calibration graph constructed with PS standards is shown in Fig. 4. The molecular masses of the PS standards used for this purpose were 2100, 6200, $2.04 \cdot 10^4$, $9.72 \cdot 10^4$, $1.8 \cdot 10^5$, $4.11 \cdot 10^5$, $6.7 \cdot 10^5$, $1.8 \cdot 10^6$ and $4.48 \cdot 10^6$. Retention volumes at the peaks on the RI chromatograms were used for the calibration graph. The intrinsic viscosity of these polymers was calculated with eqn. 5.

The plot of log $[\eta]$ *versus* log M_r for the PS standards was linear in the M_r range between 10^4 and 10^6, but it was curved slightly at $M_r > 10^6$ and $<10^4$. The values of the intrinsic viscosity of PS of M_r $1.8 \cdot 10^6$ and $4.48 \cdot 10^6$ were smaller and those of PS of M_r 2100 and 6200 were higher than expected. The shear degradation during the passage of polymers with $M_r > 10^6$ through the SEC columns has been reported [12] and, therefore, the DP responses for the PS standards with $M_r > 10^6$ became smaller than expected. A molecular mass around 10^4 is known as the critical

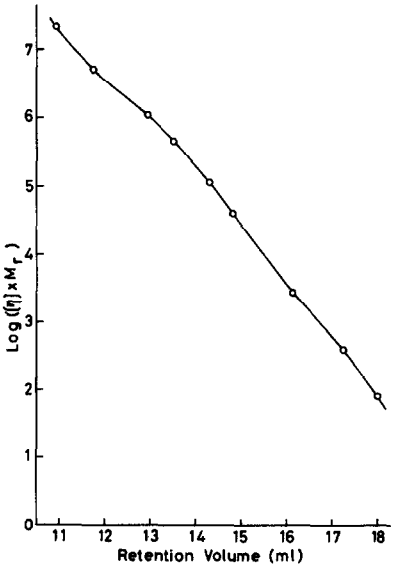

Fig. 4. Universal calibration graph of log $([\eta]M_r)$ *versus* retention volume for PS standards.

point between an oligomer and a polymer and the slope of the linear equation of log $[\eta]$ *vs.* log M_r changes at this point [13]: the slope of the equation for oligomers with $M_r < 10^4$ is smaller than that for $M_r > 10^4$. Therefore, the intrinsic viscosities of oligomers of $M_r < 10^4$ are higher than the expected values.

The RI and the DP chromatograms for NBS SRM 706 are shown in Fig. 5. The baseline of the RI chromatogram has been raised for ease of the comparison of the RI and DP chromatograms. The peak of the measured DP chromatogram [DP(a)] appeared about 0.1 ml ahead of that of the RI chromatogram.

The average molecular masses of NBS SRM 706 calculated by the conventional method using the RI chromatogram and the PS calibration graph were nearly equal to the certified values. However, average molecular masses obtained by the present method using the RI chromatogram, the DP chromatogram, the universal calibration graph in Fig. 4 and eqns. 3 and 4 are far from the NBS data certified values: $\bar{M}_n$ obtained was half the NBS value and $\bar{M}_w$ was 17% higher than the NBS value. Point-by-point calculation using the value of the dead volume of 0.06 ml was employed in this calculation.

The theoretical DP chromatogram of NBS SRM 706 can be calculated with the RI chromatogram in Fig. 5, calibration graphs of retention volume *versus* log M_r and retention volume *versus* log $([\eta]M_r)$ (Fig. 4) and eqn. 3. The result is shown in Fig. 5 [DP(b)]. The measured DP chromatogram (the experimentally obtained chromatogram) was not coincident with the calculated DP chromatogram (the theoretically obtained chromatogram). The response delay of the DP detector was observed and the difference in retention volumes at the peak positions for both DP chromatograms was about 0.175 ml. Inclusion of air in the DP chamber influenced the response delay and the peak broadening, and frequent release of the air from the DP chamber was therefore required in order to obtain reasonable results. The sampling point for the DP chromatogram was changed from $(i - 0.06)$ to $(i + 0.175)$ ml compared with the sampling point i for the RI chromatogram. This correction was effective and the average molecular masses thus calculated were comparable to the NBS certified values.

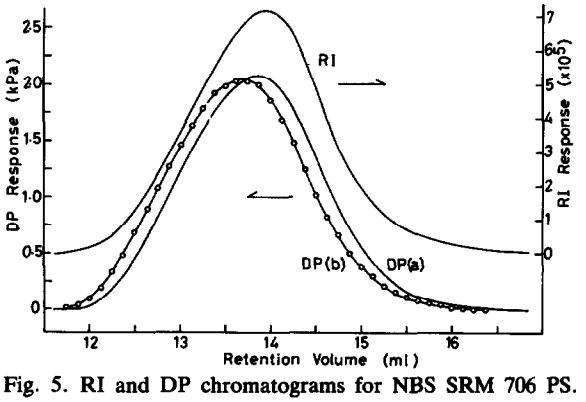

Fig. 5. RI and DP chromatograms for NBS SRM 706 PS. DP(a), measured DP chromatogram; DP(b), calculated DP chromatogram; sample concentration, 0.2%; attenuation, RI × 4, DP 10 V.

Application to polymer samples

Average molecular masses of several polymers were determined using the present system. For the point-by-point calculation, the value at a retention volume i ml for the RI chromatogram was matched against that at retention volume $(i + 0.175)$ ml for the DP chromatogram. The results are given in Table I. Good correlations between the observed values and the manufacturer's data were obtained except PMMA and PVAc.

The intrinsic viscosity of a polymer can be

TABLE I

AVERAGE MOLECULAR MASSES OF POLYMERS DETERMINED BY THE PRESENT METHOD

Polymer	Manufacturer's data		Observed	
	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$
PVC-1	5.4	13.20	8.0	14.35
PVC-2	4.4	11.80	6.64	11.44
PVC-3	3.74	8.35	4.94	9.00
PVC-4	2.55	6.86	3.44	7.02
PVAc	8.3	33	6.7	18.9
PMMA	3.32	6.06	7.5	13.4
PEMA	14.40	39.5	18.55	36.80
PBMA	7.35	32.0	14.11	30.31
PIBMA	14.00	30.0	15.01	27.42

TABLE II

MARK–HOUWINK CONSTANTS FOR DIFFERENT POLYMERS

Polymer	Observed		Literature value		
	a	$K \times 10^4$	a	$K \times 10^4$	Ref.
PS	0.71	1.15	0.717	1.17	14
PVC	0.758	1.33	0.77	1.60	15
PVAc	0.640	2.79	0.698	1.49	16
PMMA	0.677	1.03	0.677	1.48	17
PEMA	0.712	0.783			
PBMA	0.72	0.638			
PIBMA	0.78	0.385			

calculated using an RI chromatogram, a DP chromatogram and eqn. 5. Mark–Houwink constants, a and K, can be obtained from the relationship between $[\eta]$ and M_r. The results are given in Table II.

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