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# Design of a Capillary Viscometer System for the Determination of Polymer Solution Viscosity

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The viscometer consists of two capillaries and differential pressure transducer assemblies, an HPLC pump, a dampner, a six-port loop valve, and a differential pressure amplifier. Two capillaries are connected in series, solvent is fed with the pump through the dampner to the capillaries continuously, and a polymer solution is fed between the two capillaries. The increase of the differential pressure drop between the two capillaries, one for solvent and the other for polymer solution, is amplified and recorded. The solvent was tetrahydrofuran and the flow rate was 2 mL/min. Intrinsic viscosities of several polystyrenes were measured and the values were in good agreement with those in the literature. Intrinsic viscosity of a polystyrene measured by using a Ubbelohde viscometer agreed with the value obtained with the capillary viscometer. The coefficients of Mark-Houwink equation for polystyrene were  $K = 8.45 \times 10^{-5}$  and  $a = 0.741$  using polystyrene standards of narrow molecular weight distributions.

**KEY WORDS** Capillary viscometer, polymer solution viscosity, intrinsic viscosity, polystyrene, Mark-Houwink equation, viscosity-average molecular weight.

## INTRODUCTION

Several types of capillary viscometers are now commercially available and are used as a molecular weight-sensitive detector for size exclusion chromatography (SEC). These viscometers utilize one, two, or four capillaries: namely, a single-capillary design [1], a two-capillary design [2], and a four-capillary bridge design [3,4]. The single-capillary design is based on the work reported by Lesec and co-workers [5] and by Provder and co-workers [6,7]. The increase in viscosity of the sample solution eluted from SEC columns was less than 1% of the viscosity of the mobile phase (background pressure drop), and therefore, the increase in the output signal of the single-capillary design viscometer had to be amplified, resulting in a noisy signal. Smoothing procedures were required to obtain a noiseless pressure signal increment. Besides this problem, the pressure drop signal of the single-capillary viscometer was highly sensitive to the flowrate pulsation.

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The two-capillary design measures the increase in the viscosity of the sample solution by subtracting the pressure drop across the reference capillary from that across the analytical capillary. The amplification of the small signal increment is also required in this system even though the flowrate pulsation is canceled. The four-capillary bridge design measures the differential pressure across two capillaries, one for the sample solution and the other for the mobile phase and the small increase in the viscosity of the sample solution can be measured directly by using the appropriate differential pressure transducer. Another type of the four-capillary design detector was also reported [8].

When the viscometer is used for the measurement of solution viscosity of polymers, not as an SEC detector, the concentration of polymer in the sample solution can be made high enough to detect the small viscosity increase of the sample solution and the problems associated with the amplification of the pressure transducer can be minimized. This means that a viscometer of a simpler configuration can be used instead of using the viscometer exclusively designed as an SEC detector. In this paper, a modified viscometer (configuration 1 in ref. [2]), which was designed and constructed for the measurement of solution viscosity of polymers, is described and the performance of the viscometer is evaluated in detail. The signal-to-noise performance of the present viscometer was greatly improved as compared to the single-capillary viscometer, and the time required for one analysis was shortened as compared to the other commercially available viscometer [9] because of the absence of an accumulator, which was used as a delay volume. The use of the accumulator requires additional time to flush out with mobile phase.

## EXPERIMENTAL

### Viscometer

A schematic diagram of the viscometer system is shown in Figure 1. The system utilizes two sets of capillary and differential pressure transducer (DPT) (Validyne P305D-28, purchased from Waters, Milford, Mass. USA) assemblies. The capillaries were  $400 \times 0.5$  mm i.d. stainless-steel tubes and the pressure range of the DPT was between 0 and 5.0 kPa. The capillaries were connected in series as shown in Figure 1. Solvent was fed with a pump through a dampener to the capillaries continuously. At the same time, the sample solution in a loop of the six-port loop valve passed through capillary 2 intermittently. The volume of the sample loop was 3.0 mL. The pressure drop of the solvent and the sample solution across capillary 2 ( $\Delta P_{2,0}$  and  $\Delta P_2$ ) was measured with DPT 2 and that of the solvent across capillary 1 ( $\Delta P_{1,0}$ ) was measured with DPT 1. The signals from DPT 2 were recorded on a strip-chart recorder (chart 1).

Signals of the pressure drop from the two capillary-transducer assemblies were fed to the differential pressure amplifier circuit where the difference between the pressure drop of the sample solution  $\Delta P_2$  and that of the solvent  $\Delta P_{1,0}$ , namely  $\Delta\Delta P (= \Delta P_2 - \Delta P_{1,0})$ , was measured and amplified. The signals from the circuit were monitored on a strip-chart recorder (chart 2). Amplification of the differential pressure drop (attenuation) was  $\times 1$ ,  $\times 2$ ,  $\times 4$ ,  $\times 8$ ,  $\times 16$ , and  $\times 32$ . Response sensitivity was adjusted to 1, 5, 10, or 40 where the time constants were 1, 5, 10 and 40 s, respectively.

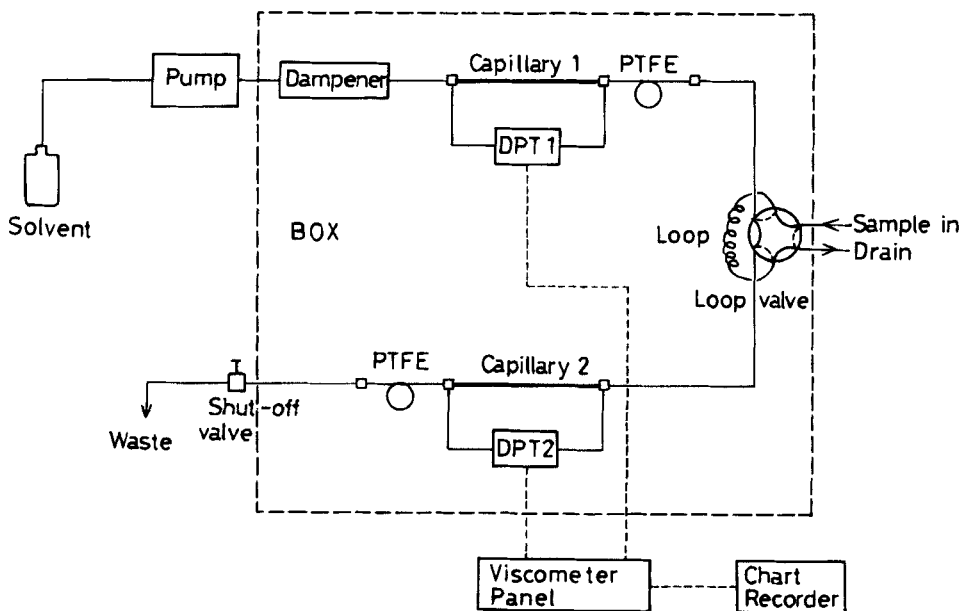


FIGURE 1 Schematic diagram of the viscometer system.

A dampener Model Shodex DP-1 (Showa Denko, Tokyo, Japan) was used to reduce flow pulsations. PTFE (1000 × 2 mm i.d.) tubes were connected after the capillaries to reduce the effects from pressure fluctuation associated with the sample solution injection and from other sources. A stainless-steel tube of 500 × 0.5 mm i.d. was connected between the loop valve and capillary 2 for the same purpose. The dampener, two capillary—DPT assemblies, PTFE tubes, and the loop valve were housed in a box to provide additional thermal stability. The pump was a Hitachi Model L-6000 solvent delivery pump (Hitachi, Tokyo, Japan). A shut-off valve was used to remove air in the closed loops between capillary 2 and DPT 2.

## Measurement

Samples used for the evaluation of this viscometer system were several types of polystyrenes (PS): a series of PS standards of narrow-molecular weight distributions (MWD) obtained from Pressure Chemical Co. (Pittsburgh, PA, USA), NBS 705 and NBS 706 PS from NIST (Washington, DC, USA), Dow 1683 PS from Dow Chemical Co. (Midland, MI, USA) and ESBRITE #1 and #2 from Sumitomo Chemical Co. (Tokyo, Japan).

Tetrahydrofuran (THF) was used as the solvent of which flow rate was 2 mL/min. All measurements were performed at around 25 °C. Degassing the closed loops between a capillary and DPT was made at the beginning of the experiment. Polymers were dissolved in THF at concentrations between 0.01 and 0.5 g/dL and 3.0 mL of the solutions were injected into the viscometer system.

The viscosity measurement using a Ubbelohde capillary viscometer was made at 25.0 °C in a water bath for comparison purpose. The certifications of the viscometer were as follows: viscometer number, 0; a range of kinematic viscosity, 0.3 – 1 cSt; approximate

constant 0.001 cSt/s. Eight different concentrations of ESBRITE #2 PS between 0.02 and 0.5 g/dL were prepared. The average efflux time for a specified volume of solvent THF to flow through the capillary tube was 554 s.

### Data reduction

Specific viscosity  $\eta_{sp}$  of a polymer solution is expressed as

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{\Delta P_2 - \Delta P_{2,0}}{\Delta P_{2,0}} = \frac{\Delta P_2 - \Delta P_{1,0}}{\Delta P_{2,0}} = \frac{\Delta \Delta P}{\Delta P_{2,0}} \quad (1)$$

where  $\eta$  and  $\eta_0$  are the viscosity of the polymer solution and the solvent, and  $\Delta P_2$ ,  $\Delta P_{2,0}$ ,  $\Delta P_{1,0}$  and  $\Delta \Delta P$  are defined in the previous section. Here, it is assumed that dimensions of capillary 1 and 2 are equal, resulting in  $\Delta P_{1,0} = \Delta P_{2,0}$ . Values of  $\Delta \Delta P$  of sample solutions were measured on chart 2 as the height from the baseline. Attenuation correction must be applied to the height. The value of  $\Delta P_{2,0}$  was measured on chart 1 as the distance between the baseline when the solvent was fed under the specified flowrate and the signal when the flowrate was zero.

A plot of reduced viscosity  $\eta_{sp}/c$  vs. concentration of the polymer solution  $c$  and the extrapolation to  $c = 0$  gives the intrinsic viscosity  $[\eta]$  of the polymer sample as

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c \quad (2)$$

## RESULTS AND DISCUSSION

The basic design of our viscometer is essentially the same to that previously reported [2,10] and a dual-capillary viscometer related to the basic design for the determination of fluid viscosities is commercially available as the Y-501 viscometer (Viscotek Corp., Houston, TX) [11]. The viscometer reported by Abbott and Yau [10] has three long tubes of small internal diameter as flow resistors: the first flow resistor was located between a dampener and the reference capillary (similar to capillary 1 in Figure 1), the second between the analytical capillary (similar to capillary 2 in Figure 1) and a concentration detector, and the third near the sample injection valve to provide a solvent flow by-pass. Our viscometer is not installed with these flow resistors. Instead, two PTFE tubes were connected after two capillaries to reduce the effects from pressure fluctuation in the signals generated by the transducers. A stainless-steel tube was connected between the loop valve and capillary 2 to reduce flowrate upsets caused by the valve switching during sample injection. These configurations offer better signal-to-noise performance.

Other improvements and differences of our viscometer compared with Yau's design are as follows: A shut-off valve was connected at the outlet of the system to completely remove air in the closed loop of the transducers. The  $\Delta P$  signals from two pressure transducers can be monitored directly on a strip-chart recorder. The difference of two  $\Delta P$  signals  $\Delta \Delta P$  were fed to a differential pressure amplifier and was monitored on a strip-chart recorder. The volume of the sample loop was 3.0 mL to ensure a flat peak signal. A con-

centration detector was not connected and the calculation of specific viscosity of a polymer solution was based on the peak height of the  $\Delta\Delta P$  signal and the concentration of the polymer solution injected.

When the length of capillary 2 ( $L_2$ ) is not equal to the length of capillary 1 ( $L_1$ ), Equation (1) is not valid, because  $(\Delta P_2 - \Delta P_{2,0})$  is not equal to  $(\Delta P_2 - \Delta P_{1,0})$ . If  $L_2$  is longer or shorter as much as  $L'$  than  $L_1$  ( $L_2 = L_1 + L'$ ), then

$$\begin{aligned}\Delta P_{2,0} &= 8(L_1 + L') \eta_0 Q / (\pi r^4) = f \eta_0 L_1 + f \eta_0 L' \\ &= \Delta P_{1,0} + f \eta_0 L'\end{aligned}\quad (3)$$

where  $f = 8Q/(\pi r^4)$ ,  $\Delta P_{1,0} = f \eta_0 L_1$ ,  $Q$  the flowrate, and  $r$  the radius of the capillary. When only the solvent passes through the capillaries,

$$\begin{aligned}\Delta\Delta P &= \Delta P_{2,0} - \Delta P_{1,0} = \Delta P_{2,0} - (\Delta P_{2,0} - f \eta_0 L') \\ &= f \eta_0 L' = \text{baseline response on chart 2}\end{aligned}\quad (4)$$

When the polymer solution passes through capillary 2,

$$\Delta\Delta P = \Delta P_2 - \Delta P_{1,0} = \Delta P_2 - \Delta P_{2,0} + f \eta_0 L' \quad (5)$$

The electronic matching of the capillary performances can be accomplished by nulling the differential amplifier circuit output when the solvent passes through both capillaries. Alternatively, the baseline on chart 2 represents the values of  $\Delta P_{2,0} - \Delta P_{1,0}$  and the difference of signals of the peak top  $(\Delta P_2 - \Delta P_{1,0})$  and the baseline is expressed as

$$(\Delta P_2 - \Delta P_{1,0}) - (\Delta P_{2,0} - \Delta P_{1,0}) = \Delta P_2 - \Delta P_{2,0} = \Delta\Delta P \quad (6)$$

Therefore, the intrinsic viscosity of a polymer can be calculated using Equation (1).

Examples for the measurement of  $\Delta P_{2,0}$  and  $\Delta\Delta P$  of PS standards are explained in Figures 2 and 3. Figure 2 (A) is the signal and the position when the solvent flow was stopped, and Figure 2 (B) shows the responses of DPT 2 when the solvent or the sample solutions passed through capillary 2. The baseline of the peak represents the value of  $\Delta P_{2,0}$ . The distance from the position of Figure 2 (A) to the position of  $\Delta P_{2,0}$  was 175–178 mm which corresponds to 3.50–3.56 kPa. The pump noise affecting  $\Delta P_{2,0}$  was about 1.5% (0.075 kPa). The signal from  $\Delta\Delta P$  increases with increasing sample concentration and molecular weight (MW) of the PS standards.

The difference of the signals when the polymer solutions were fed ( $\Delta P_2$ ) and that when the solvent passed through capillary 2 ( $\Delta P_{2,0}$ ) can also be measured as the height from the baseline on chart 1 (Figure 2(B)) and specific viscosities can be calculated using these two responses. However, when a 0.1% solution of PS MW 20400 was injected into the system, the response increase was only 1.7% (Figure 2 (B), a) and the signal-to-noise (S/N) ratio required improvement. Therefore, the specific viscosity using DPT 2 was not measured in this study.

The examples of signals from the differential pressure amplifier output are shown in Figure 3. Response sensitivity was set to 5 for all experiments. The noise caused by pump pulsations was completely eliminated and a smoothed baseline was obtained. The noise level at attenuation  $\times 8$  (Figure 3 (c), (d)) was less than 0.4% of full scale (0.0025 kPa) and negligible noise was observed when the attenuation was  $\times 2$  (Figure 3 (a), (b)).

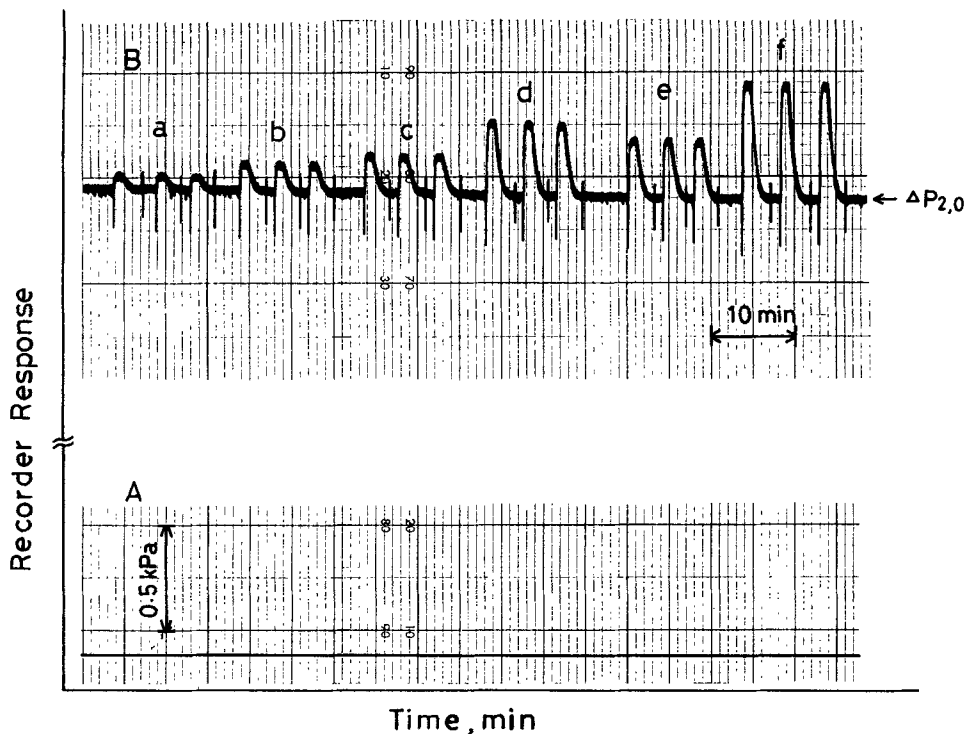


FIGURE 2 Response of DPT 2 for polystyrene standards on chart 1. A: Signal when the solvent flow was stopped; B: responses when the solvent and the sample solutions passed through; samples: PS standards, (a) PS MW 20,400, 0.100%; (b) 0.200%; (c) PS MW 97,200, 0.101%; (d) 0.199%; (e) PS MW 180,000, 0.102%; (f) 0.201%; chart speed: 2mm/min.

Specific viscosity can be calculated as

$$\eta_{sp} = \{\text{Peak height (mm) in Figure 3}\} / \text{Distance (mm) between the position of (A) and } \Delta P_{2,0} \text{ in Figure 2} \times \text{Attenuation} \quad (7)$$

Intrinsic viscosities of several PS standards were determined by plotting reduced viscosity vs. concentration followed by extrapolation to concentration zero and the results are shown in Table I. A logarithmic plot of  $[\eta]$  vs. molecular weight of these data gives the Mark-Houwink equation for PS in THF at 25 °C as

$$[\eta] = 8.45 \times 10^{-5} M^{0.741} \quad (8)$$

The range of parameters  $K$  and  $a$  of Mark-Houwink equation  $[\eta] = KM^a$  in THF at 25 °C in the literature are  $1.10\text{--}1.60 \times 10^{-4}$  dL/g for  $K$  and  $0.70\text{--}0.725$  for  $a$ . The exception is  $6.09 \times 10^{-5}$  for  $K$  and  $0.768$  for  $a$  [12]. The parameters for PS standards of narrow MWD measured using the SEC-viscometer system in THF at 30 °C were  $1.42 \times 10^{-4}$  for  $K$  and  $0.706$  for  $a$  [13]. Similarly, the parameters for PS standards of narrow MWD above 10,000 molecular weight were  $1.28 \times 10^{-4}$  for  $K$  and  $0.712$  for  $a$  [14]. For PS of broad MWD, NBS 706 and Dow 1683, the parameters in THF at 30 °C before correcting concentration effects

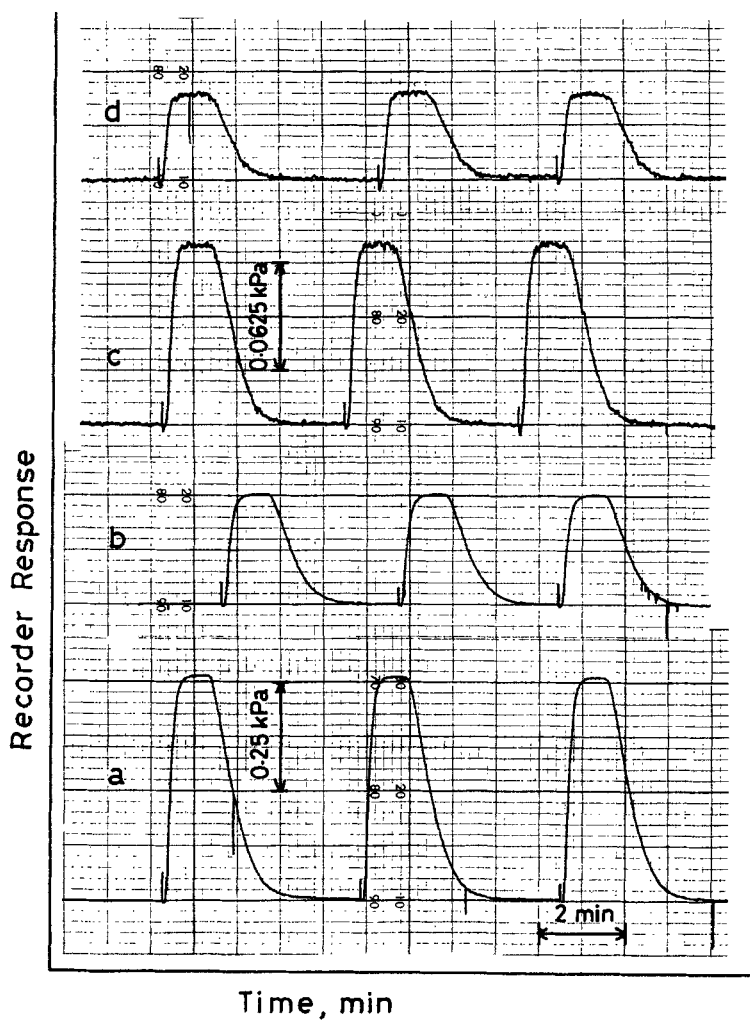


FIGURE 3 Response of the differential pressure amplifier output for polystyrene standard on chart 2. MW, concentration, and attenuation: (a) 180,000, 0.2%,  $\times 2$ ; (b) 180,000, 0.1%,  $\times 2$ ; (c) 20,400, 0.2%,  $\times 8$ ; (d) 20,400, 0.1%,  $\times 8$ ; chart speed: 10 mm/min.

TABLE I

Intrinsic viscosity of polystyrene standards	
Molecular weight	$[\eta]$ , dL/g
20,400	0.132
97,200	0.409
180,000	0.684
670,000	1.72
1,800,000	3.66



were  $1.44 \times 10^{-4}$  and  $1.36 \times 10^{-4}$  for  $K$  and 0.693 and 0.703 for  $a$  and, values after correcting concentration effects were  $9.33 \times 10^{-5}$  and  $9.23 \times 10^{-5}$  for  $K$  and 0.736 and 0.740 for  $a$ , respectively [14]. Our results are similar to those for PS of broad MWD determined by Haney and co-workers. A combination of smaller  $K$  and larger  $a$  values are found in general in the literature.

Plots of reduced viscosity vs. concentration of several polystyrene solutions are shown in Figure 4. From these plots the values of intrinsic viscosities of the polystyrenes were estimated. Viscosity-average molecular weights  $M_v$  of these polymers were also calculated using Equation (8). The results are listed in Table II. Intrinsic viscosities for PS NBS 706 and Dow 1683 in THF reported in the literature are as follows: for NBS 706, 0.93 dL/g at 40 °C [7], 0.931 dL/g [13], 0.869 dL/g [14], and 0.88 dL/g [15] at 30 °C, and for Dow 1683, 0.86 dL/g at 40 °C [7], 0.865 dL/g [13] and 0.841 dL/g [14] at 30 °C. Our results are similar to the value determined by Haney and co-workers for NBS 706, but are still 5% lower for Dow 1683. The intrinsic viscosity of PS ESBRITE #2 measured independently using a Ubbelohde viscometer were 0.983, 0.987, and 0.981 dL/g (average 0.987 dL/g) which coincide with those obtained with our viscometer system.

## CONCLUSION

A capillary viscometer designed in our laboratory was applied for the rapid determination of polymer intrinsic viscosity by measuring polymer reduced viscosity. Determination of reduced viscosities of low-concentration polymer solutions was demonstrated. Intrinsic

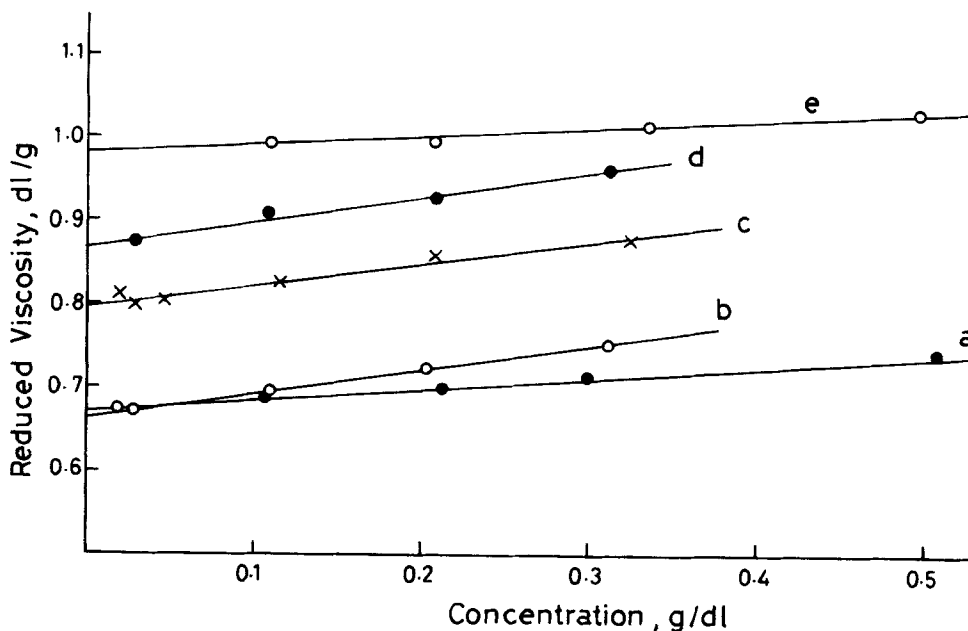


FIGURE 4 Reduced viscosity—concentration plots for polystyrenes in THF at 25 °C. a: ESBRITE #1; b: NBS 705; c: Dow 1683; d: NBS 706; e: ESBRITE #2.

TABLE II

Intrinsic viscosity and viscosity-average molecular weight for polystyrenes measured using the viscometer

Sample	$[\eta]$ , dL/g	$M_v \times 10^{-5}$	$M \times 10^{-5}$
NBS 706	0.868	2.59	$M_w = 2.81^b$ , $M_n = 1.29^b$ $M_v = 2.56^c$ $M_w = 2.58$ (2.88) <sup>d</sup> , $M_n = 1.37^d$
NBS 705	0.664	1.81	$M_w = 1.79^d$ , $M_n = 1.67^d$
Dow 1683	0.798	2.31	$M_w = 2.50^d$ , $M_n = 1.00^d$
ESBRITE #1	0.668	1.82	$M_w = 2.25^b$ , $M_n = 0.834^b$
	0.672	1.84	$M_v = 1.96^c$
	0.662	1.80	
	(0.667) <sup>a</sup>	(1.82) <sup>a</sup>	
ESBRITE #2	0.980	3.05	$M_w = 4.39^b$ , $M_n = 0.614^b$
	0.986	3.07	$M_v = 3.19^c$
	0.986	3.07	
	(0.984) <sup>a</sup>	(3.06) <sup>a</sup>	

<sup>a</sup> mean value;

<sup>b</sup> measured by SEC;

<sup>c</sup> measured by SEC using the exponent of Equation (8);

<sup>d</sup> vendor values.

viscosities and the Mark-Houwink coefficient  $K$  were somewhat smaller. The coefficient  $a$  was larger than for most literature values, although there was good agreement with some values. Intrinsic viscosity of a polystyrene sample measured by the viscometer was comparable to that measured by a Ubbelohde capillary viscometer.

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