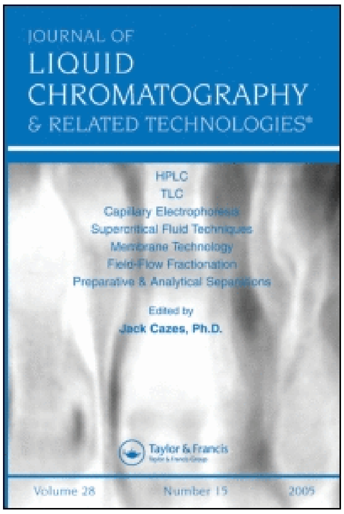

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PERFORMANCE EVALUATION OF A CONTINUOUS VISCOMETER FOR HIGH SPEED GPC.

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ABSTRACT

The performance of a home-made continuous viscometer with pressure transducer, as a GPC detector, is described. This device, which is very sensitive to flow rate variations, can precisely monitor the mobile phase flow rate and general operation of the GPC apparatus. Any trouble in the instrument markedly affects the viscometer baseline, thus allowing its detection. Finally, using concentration data from the refractometer, the viscometer continuously provides the viscosity throughout the chromatographic peak, which, in turn, enables one, after smoothing and correction, to obtain the viscosity law of the injected polymer.

INTRODUCTION

Benoit's universal calibration ([1]) for the precise characterization of polymers usually requires viscosity measurements. In high speed GPC, these determinations are not practical with classical viscometers because of the extremely small volume of the mobile phase. Only the continuous viscometer, originally described by Ouano ([2]) involving measurement of the pressure drop in a capillary tube with a pressure transducer, is capable of determining the viscosity of a polymer, during its elution, with sufficient accuracy. If the sample

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concentration C_i is deduced from refractometric data, intrinsic viscosities can be calculated, assuming that concentrations are low enough to apply the relationship :

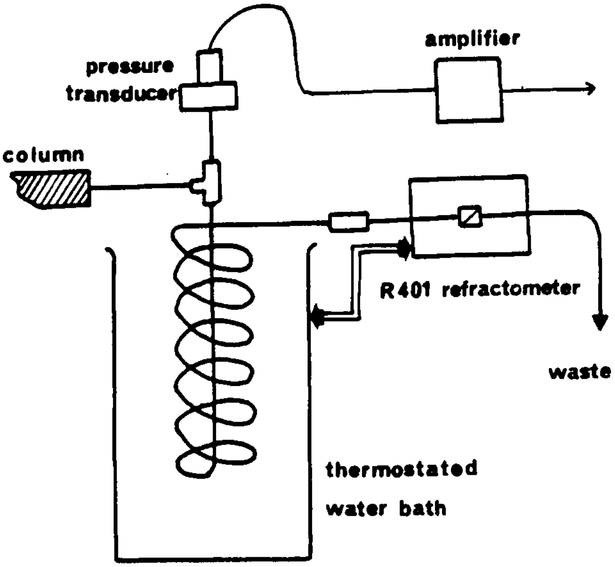
$$[\eta]_i = \frac{1}{C_i} \cdot \mathrm{Ln}\,\frac{\eta}{\eta_0}$$

where η_0 and η are, respectively, the viscosities of pure solvent and solution. Lesec (^{3}) has described an apparatus which includes such a continuous viscometric detector, that allows the rapid and automatic calculation of average molecular weights and upon which our study (^{4}) is based. The main characteristic of this detector is that it is simultaneously a very accurate flowmeter and a viscometer, and, accordingly, we will describe both of these functions.

APPARATUS

The viscometer consists of a stainless steel capillary tube with small internal diameter immersed in a controlled temperature water bath and inserted between the column set and the refractometer with low dead volume fittings (figure 1). A piezo-resistive transducer (Kistler 4041), measures the pressure drop between the viscometer inlet and the refractometer cell which is at the atmospheric pressure. We tried to select the best tubing length and internal diameter in order to obtain the best signal/noise ratio. A classical capillary tube (1/16" O.D., 9/1 000" I.D.) was used with various lengths (1 to 3 meters), but this parameter exhibits only a small influence on the signal/noise ratio. We then fitted the capillary length to the transducer sensitivity and chose a 3 meter length tube, having an internal volume of about 120 μl. This large volume is not a drawback since the very small capillary diameter does not permit solute remixing.

The final viscometer characteristics are : internal diameter : 9/1 000" ; length : 3 meters ; temperature : 30°C ; solvent : THF at a flow rate of 2 ml/mn ; range of the Kistler 4041 transducer : 0 -10 bars. Under these conditions, the pressure drop for



length (meter)	1	2.5	3
noise /signal	2 %	1.6 %	1.4%

Figure 1 : Scheme of the continuous viscometer

pure solvent is about 8 bars and the Reynolds number about 400. Consequently, the flow is laminar for pure solvent and accordingly, for polymer solutions. The Poiseuille law, which gives a linear relationship between viscosity and pressure drop :

$$\eta = \frac{\Delta P.\pi.d^4}{128.l.q}$$

where ΔP is the pressure drop, d the capillary diameter, l its length and q the mobile phase flow rate, can therefore be applied and the ratio η/η_0, used in the intrinsic viscosity equation, can be strictly expressed by the experimental $\Delta P/\Delta P_0$ ratio.

THE FLOWMETER FUNCTION

As described above, the Poiseuille law also leads to a linear relationship between the flow rate and the pressure drop when the viscosity is held constant. This is the flowmeter function shown in figure 2, where viscometric and refractometric signals are recorded on the same chart, for a classical GPC analysis of a polystyrene standard (M : 111,000) (4-5). We varied the flow rate from 2 ml/mn to 2.1 ml/mn and the resultant baseline shift, corresponding to this .1 ml/mn variation, was more than twice the polymer peak height. Consequently, to use this device as a viscometric detector with an acceptable signal/noise ratio, flow rate variations must be kept smaller than 10^{-3} ml/mn, corresponding to 3.5 millibars (.05 PSI), since this noise can just barely be detected under our classical recording conditions. The flow rate measurement accuracy of this device obviously depends upon a precise calibration. In addition, the very high sensitivity of this viscometer permits its use for checking all components of the GPC apparatus that affect flow rate ; this, of course, enables us to operate under favorable signal/noise conditions when the device is used as a viscometric detector.

Checking of the pumping system

The pumping system used was a Waters M 6 000 A reciprocating pump which produces pressure pulses. The noise is represented in fig.3 under different operating conditions. This figure shows that, to obtain a good baseline for valid GPC experiments as shown in figure 2, it is necessary to connect the high sensitivity filter and, in fact, to add a second one. The noise residue is then smoothed by the column set. It is relatively easy to detect pump problems, consequently, since they result in a baseline shift and an increase in noise level. Also, the pump noise is not constant whatever the flow rate. These variations are represented in figure 4 (curve I) and show that pulse magnitude is relatively constant for flow rates greater than 1.5 ml/mn but becomes very important when flow rate decreases to values below this limit.

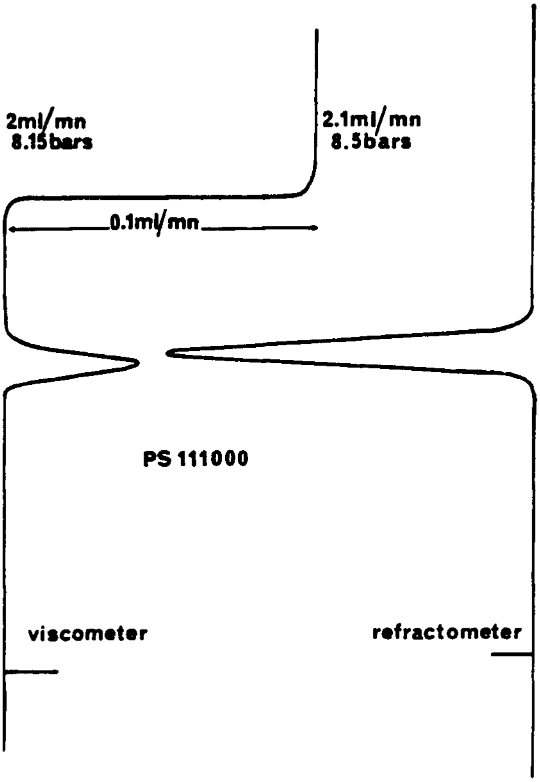


Figure 2 : Description of flowmeter sensitivity - viscometer : 9/1 000" I.D. - length 3m - solvent : THF - θ = 30°C.

Checking of the column set

The main problem that we encountered during visometer adjustement is flow fluctuations in columns. These random variations are of low frequency (compared to pump noise) ; their magnitudes are plotted versus flow rate in figure 4 (curve II). They are negligible for low flow rates and gradually increase as flow rate increases. It appears that they are due to difficulty of solvent passing through the porous metal discs in column end fittings, since this noise dramatically increases as fittings become dirty. This is described below. Pump noise (I) and column noise (II) vary in opposite directions and, in order to determine the optimum flow rate conditions,

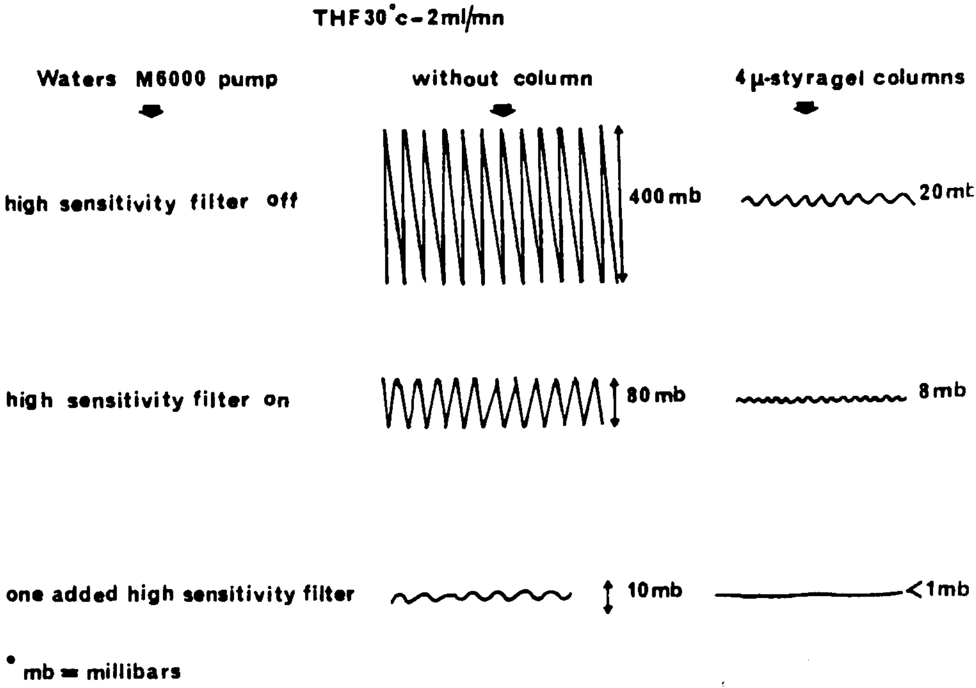


Figure 3 : Noise pulses of Waters M 6 000 A pumping system under various conditions (THF, 2 ml/mn).

we have plotted, in figure 4, the curve (III), which is the summation of curves (I) and (II). This curve has a minimum near 1.7 ml/mn ; which permits us to easily run at 2.0 ml/mn. Fortunately, this value falls within the recommended flow rate range for modern columns such as µ-Styragel. Therefore, we always run at this flow rate.

Checking for microleaks

"Microleaks" are usually difficult to detect when using a volatile solvent, because evaporation is faster than the leak rate. They lead to errors in molecular weight determination because flow rate is overestimated and molecular weight values are accordingly, underestimated. Microleaks can be easily detected with the viscometer, first by a weak baseline shift towards lower pressures, but

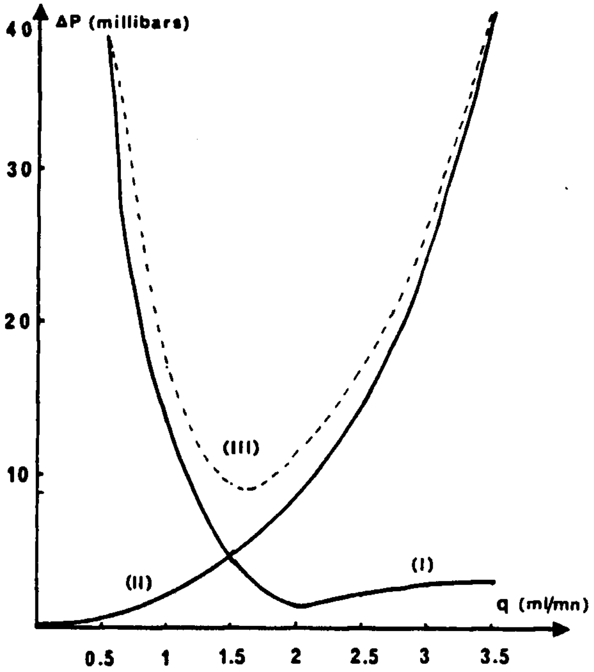


Figure 4 : Variations of viscometer baseline noise as a function of mobile phase flow rate.
(1) pump noise - (II) column set noise - (III) summation of (1) and (II).

particularly because they provide a characteristic baseline as represented in figure 5. These microleaks mainly occur in the injector or in poor tubing connexions.

Checking of end fitting plugging

When an unfiltered sample is injected, plugging of the first filter can occur and cause sudden solvent flow variations that result in a characteristic baseline as represented in figure 5. When injecting a polymer sample, polymer viscosity and solvent compressibility give rise to flow variations as sample passes through each partially plugged column end fitting so that these crossings can easily be detected (figure 5). Filters must then be replaced

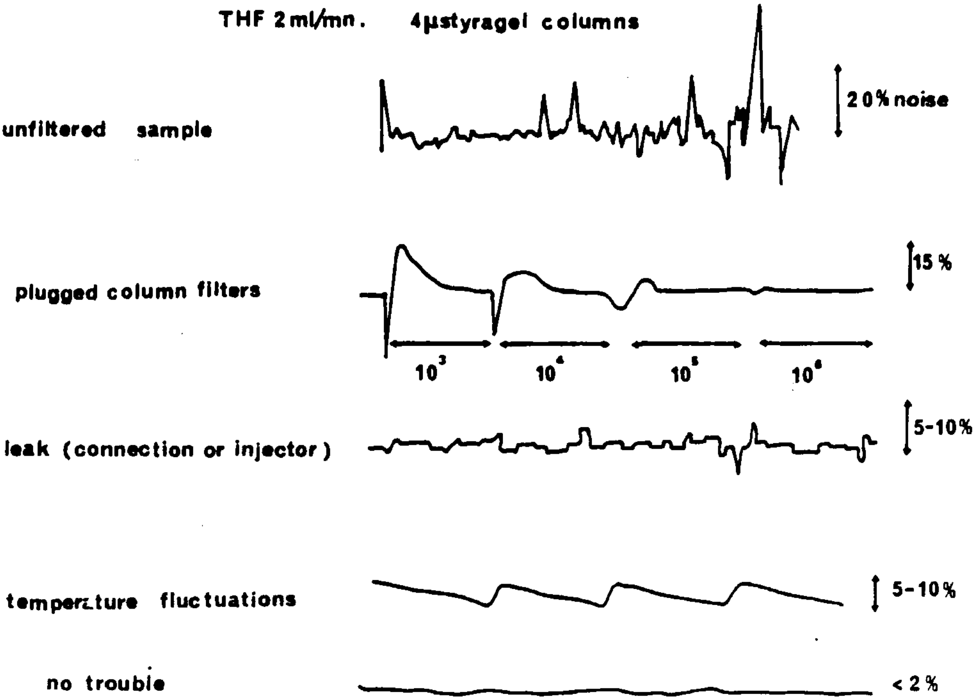


Figure 5 : Typical viscometer baselines when troubles occur.

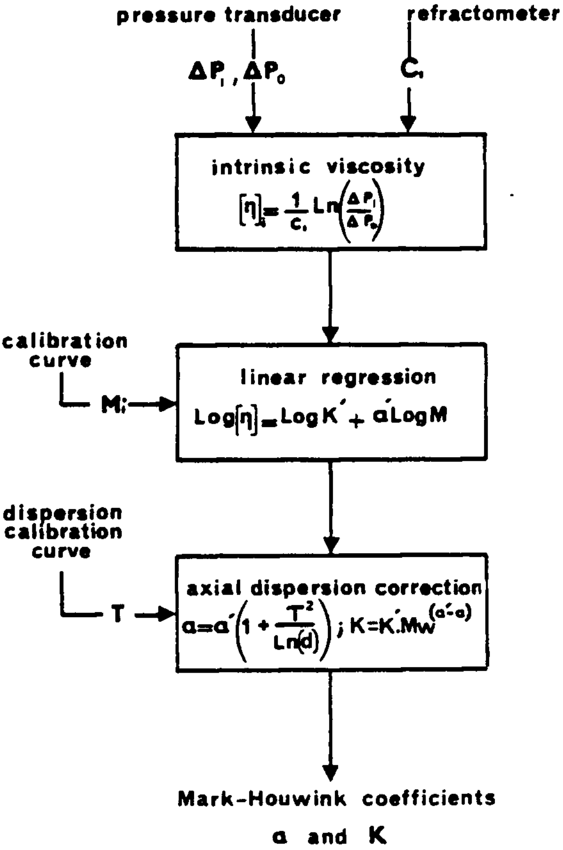
to re-establish a normal baseline. These partial "pluggings" are the main reason of viscometer malfunction.

Checking for temperature stability

Finally, viscosity is, likewise , sensitive to temperature variations ; consequently, the water bath in which viscometer is located must have an extremely constant temperature.Control to a hundredth of a degree is generally sufficient but, if the temperature regulation power is unsettled, a baseline similar to that shown in figure 5 can be obtained.

THE VISCOMETER FUNCTION

When every part of the GPC instrument is in a perfect running status, the mobile phase flow rate is kept constant and the linear



$T^* = \frac{\sigma}{a}$ $\quad d = \frac{Mw}{Mn}$

Figure 6 : Computation scheme of Mark-Houwink coefficients.

relationship between pressure drop and viscosity enables the intrinsic viscosity determination as previously proven. This is the viscometer function. Calculation can be achieved point by point and provides a set of viscometric data that can be computed as outlined in figure 6. If the injected polymer has a linear structure, linear regression leads to a linear relationship between Log M and Log[η]. As this law includes an axial dispersion error, it is necessary to make a correction (^{5}) ; we used the recent Marais'method (^{6})

which, after mathematical treatment, gives the Mark-Houwink coefficients α and K. This correction can only be performed with a sufficient accuracy when the sample polydispersity is not too near to unity. Below 1.2 - 1.3, the coefficients α and K are aberrant since viscosity determinations are achieved in too narrow a molecular weight range. The viscosity straight line rotation, resulting from the axial dispersion correction is the more important and becomes increasingly inaccurate as polydispersity is decreased. Figure 7 shows an example of a GPC analysis obtained with our automatic instrument (^{5}). Points represent the logarithms of experimental viscosity data plotted as a function of the logarithm of molecular weight, and the straight line is the corrected viscosity law. In addition, α and K values are printed near the calculated molecular weight averages. We have given, in Table 1, some examples of Mark-Houwink constants. For the two first samples, sample polydispersity is very small and the α and K values are incorrect. For the other results, comparison with literature is difficult because very few viscosity determinations have been reported in THF at 30°C.

CONCLUSION

The continuous viscometer, measuring pressure drop in a capillary tube, that we have constructed is, simultaneously, a very accurate flowmeter. It enables the measurement of very weak flow rate variations and provides a means of checking every part of the GPC instrument, since each malfunction affects its baseline. The main problem in obtaining a good baseline is to avoid partial plugging of column filters. This can be accomplished by strict clarification of samples and solvent . However, it is still necessary to routinely change column filters. When this device is inserted into a properly functioning automatic GPC instrument, the computation of viscometric and refractometric data leads to the determination of the viscosity law coefficients α and K, with a single injection, if the sample polydispersity is greater than 1.2 - 1.3. Computation details will be published in a later paper (^{5}).

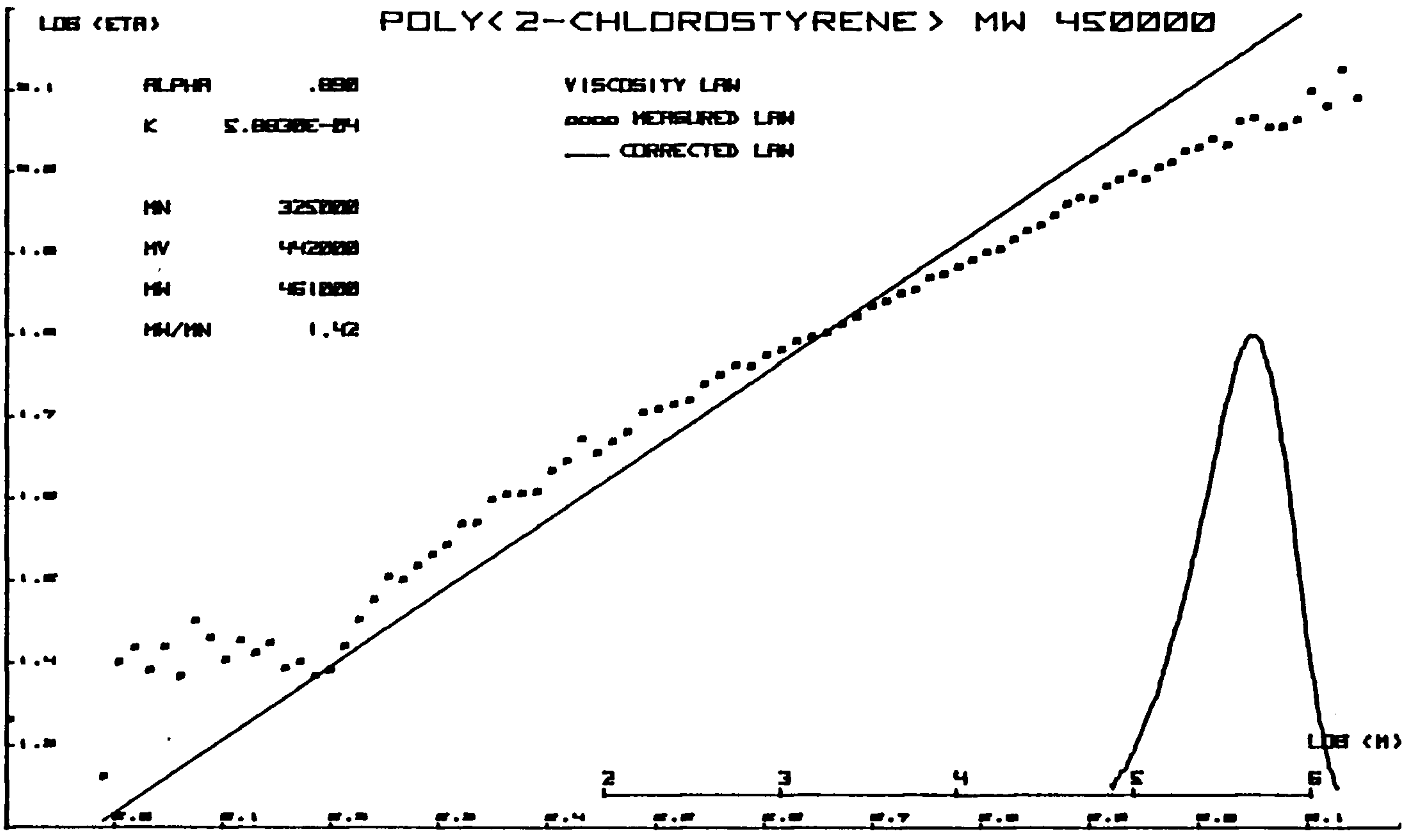


Figure 7 : Example of viscosity law determination

TABLE 1

Polymer - (THF - 30°C)	Polydispersity	α	K
Polystyrene	1.03	.27	3
Polystyrene	1.16	.45	$3.64\ 10^{-1}$
Polystyrene	1.97	.703	$9.79\ 10^{-3}$
Polybutadiene	1.96	.66	$4.64\ 10^{-3}$
Polyisobutene	1.91	.61	$4.55\ 10^{-3}$
Cellulose nitrate	2.50	.80	$1.88\ 10^{-2}$
Polymethylmethacrylate	2.13	.63	$1.58\ 10^{-2}$
Poly-vinylchloride	2.00	.67	$3.09\ 10^{-2}$
Poly-O-chlorostyrene	1.42	.89	$5.88\ 10^{-4}$
Poly-vinylacetate	1.60	.75	$5.68\ 10^{-3}$

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