

CHROM. 6358

GEL PERMEATION CHROMATOGRAPHIC ANALYSIS OF
POLY-(2-VINYLPYRIDINE) SAMPLES

A. GOURDENNE

Centre de Biophysique Moléculaire—C.N.R.S., 45-Orléans-La Source (France)

AND

N. HODUC AND H. DAOUST

Department of Chemistry, Université de Montréal, Montréal (Canada)

(First received April 11th, 1972; revised manuscript received September 12th, 1972)

SUMMARY

Satisfactory gel permeation chromatographic (GPC) analysis of poly-(2-vinylpyridine) (PVP) has been achieved by using Porasil-packed columns and N,N-dimethylformamide (DMF) as eluent at 50°. The polymer samples were prepared by anionic polymerization; well defined polystyrene fractions were used for calibration. The standard $\log \overline{M}_w = f(V_e)$ plot seems to be satisfactory as a calibration curve. Viscosity measurements were made in the same solvent at 50° for the two series of polymer samples in order to test the universality of BENOIT and co-workers' $\log [\eta] \overline{M}_w = f(V_e)$ plot. However, the results for the two polymers do not fall on a single line because the column support is not inert towards PVP. The longer retention time for PVP is believed to be caused by some specific interaction between glass beads and PVP; this interaction was not entirely overcome by using a strongly polar solvent such as DMF. The molecular weight distribution curve from GPC analysis was compared with that obtained from sedimentation analysis; the discrepancy between the two curves may be explained by the creation of some reverse GPC.

INTRODUCTION

Each method that is used to characterize a polymer in dilute solution requires well defined conditions for its application, and the same applies to the gel permeation chromatography (GPC) analysis of poly-(2-vinylpyridine) (PVP). Data on osmotic pressure, light scattering and viscosity measurements have already been reported for PVP¹, but none have been reported on GPC analysis. It is impossible to obtain a chromatogram for PVP when tetrahydrofuran (THF) is used as eluent and when crosslinked polystyrene (Styragel) or silica beads (Porasil) are used as the stationary phase. With Styragel, incompatibility between PVP and the support might be responsible for the polymer retention, *i.e.*, the sample to be eluted is precipitated out of the solution. The case with Porasil, which will be described here, is quite different. PVP, being polar, may be retained by silica beads and it takes a strongly polar solvent

such as N,N-dimethylformamide (DMF) to overcome the assumed electrostatic interactions between the glass beads and PVP. The comparison between the results obtained for PVP and those obtained for the well defined polystyrene standards used for GPC calibration, which do not interact with silica, is of interest because the two polymers have chemical similarities.

EXPERIMENTAL

Synthesis of PVP samples

All the samples were prepared by anionic polymerization. Sodium naphthalene or biphenyl and sodium diphenylmethyl² were used as initiators in THF solutions. The rate of propagation of the polymerization of 2-vinylpyridine (v_p) is very high and the polydispersity of the synthesized samples depends on the value of the rate of initiation (v_i). The initiation by sodium naphthalene or biphenyl, *i.e.* by electron transfer, is very fast and complete, but leads to side reactions². However, the polymers obtained under those conditions have an average molecular weight distribution ($\overline{M}_w/\overline{M}_n \approx 1.3$) that is usually encountered in anionic polymerization. When the initiator is sodium diphenylmethyl, $v_i \ll v_p$. Hence the monomer is completely converted before the end of the initiation step and then the polymers are not monodisperse ($\overline{M}_w/\overline{M}_n \approx 1.5$).

Average molecular weights, \overline{M}_w and \overline{M}_n

The weight average molecular weights (\overline{M}_w) of the PVP samples were determined in dioxan solutions from light-scattering measurements carried out with a SOFICA light-scattering photometer. Measurements were made at 25° with unpolarized light at a wavelength of 546 nm and observations were made at 90° (Debye's method). Solutions were filtered through a Millipore filter directly into the measuring cell in order to obtain dust-free solutions. The average specific refractive index increment has been previously determined³ and is equal to 0.167 ml/g.

Number average molecular weights (\overline{M}_n) were determined by using a Mechrolab Model 501 high-speed membrane osmometer fitted with a Hewlett-Packard variable temperature controller. The solvent was dioxan and the temperature was 37°.

Table I gives the experimental values of \overline{M}_n and \overline{M}_w for PVP samples and

TABLE I

EXPERIMENTAL RESULTS ON POLY-(2-VINYLPYRIDINE) SAMPLES

Sample	\overline{M}_n	\overline{M}_w	$[\eta]^a$ (50°C)	$[\eta] \times \overline{M}_w$ ($\times 10^{-3}$)	S_0° (25°C)	Elution volume counts, 5 ml ^a (50°C)
1	20 000	30 000	0.16	4.79	2.06	20.5
2	58 000	59 000	0.25	14.7		18.7
3	85 000	111 000	0.375	41.2	3.57	17.25
4	110 000	140 000	0.44	61.6		17.15
5	165 000	170 000	0.51	86.7	4.05	16.25
6	—	277 000	0.78	216	4.95	15.8

^a DMF was used as solvent.

TABLE II

EXPERIMENTAL RESULTS ON STANDARD POLYSTYRENE SAMPLES

Sample	\overline{M}_n	\overline{M}_w	$[\eta]^a$ (50°C)	$[\eta] \times \overline{M}_w$ ($\times 10^{-3}$)	Elution volume counts, 5 ml ^a (50°C)
1	9 700	10 300	0.073	0.755	23.0
2	19 650	19 850	0.11	2.18	21.25
3	49 000	51 000	0.19	9.74	18.5
4	96 200	98 200	0.33	32.6	17.1
5	164 000	173 000	0.405	70.0	16.3
6	392 000	411 000	0.635	261	15.6

^a DMF was used as solvent.

Table II those provided by Waters Associates Inc. for standard polystyrene (PS) samples used for the calibration of GPC columns.

Intrinsic viscosity

Viscometry measurements were made in N,N-dimethylformamide (DMF) at 50°, which is the temperature of the GPC columns, with a Hewlett-Packard automatic viscometer. The intrinsic viscosities (dl/g) determined for PVP and PS samples are presented in Tables I and II.

Sedimentation

Sedimentation studies on PVP in DMF were carried out by using a Spinco Model E-HT analytical ultracentrifuge at 25°. The technical details and the treatment of the results in order to obtain the value of the sedimentation coefficient at 1 atm and zero concentration (S^0) have been described elsewhere⁴.

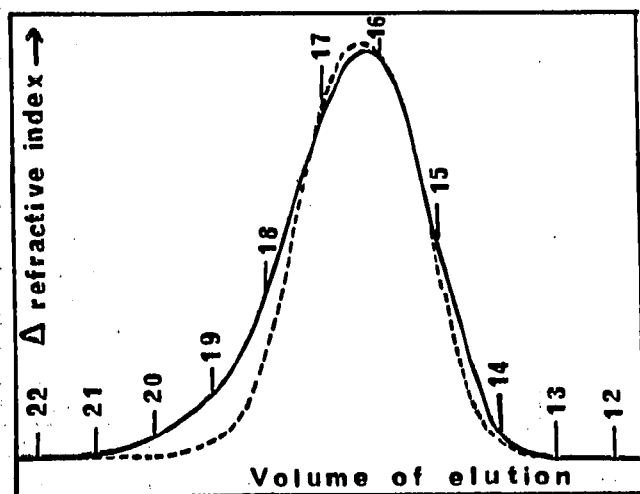


Fig. 1. Gel permeation chromatograms. Broken line: polystyrene, $\overline{M}_w = 173\ 000$; solid line: poly-(2-vinylpyridine), $\overline{M}_w = 170\ 000$.

GPC analysis

The GPC experiments were carried out on a Waters Associates Model 200 instrument equipped with three Porasil-packed columns (3×10^3 – 8×10^3 , 8×10^3 – 2×10^4 and 2×10^4 – 5×10^4 Å) at 50° . The eluent was DMF. The injection time was 2 min and the flow-rate 1 ml/min. The detector was a differential refractometer. All the chromatograms are moderately sharp and symmetrical. Fig. 1 shows chromatograms for PVP and PS samples with similar \overline{M}_w values. The maximum of the peak is taken as the elution volume for each polymer sample. The results for all the polymers are collected in Tables I and II, where the values of the elution volumes, V_e , are given in 5-ml increments (counts).

RESULTS AND DISCUSSION

The analysis of the results on viscosities gives the following intrinsic viscosity–molecular weight relationships for the two polymers at 50° in DMF solutions:

$$\text{poly-(2-vinylpyridine): } [\eta] = 1.23 \times 10^{-4} \overline{M}_w^{0.69}$$

$$\text{polystyrene: } [\eta] = 2.88 \times 10^{-4} \overline{M}_w^{0.60}$$

The slightly higher exponent in the Mark–Houwink equation for PVP indicates that its configuration is more extended than that of PS. Consequently, the elution volume, V_e , should be smaller for PVP than for PS at a constant value of \overline{M}_w , according to GPC theory. However, Fig. 2 seems to indicate that both series of results can be represented by a single curve. Fig. 3 shows the graph of $\log [\eta] = f(V_e)$ for both polymers; for similar values of $[\eta]$, the elution volumes for PVP are always larger than those for PS, contrary to expectations. A combination of Figs. 2 and 3 leads to plots of $\log [\eta] \overline{M}_w$ versus V_e . The product $[\eta] \overline{M}_w$ is proportional to the hydro-

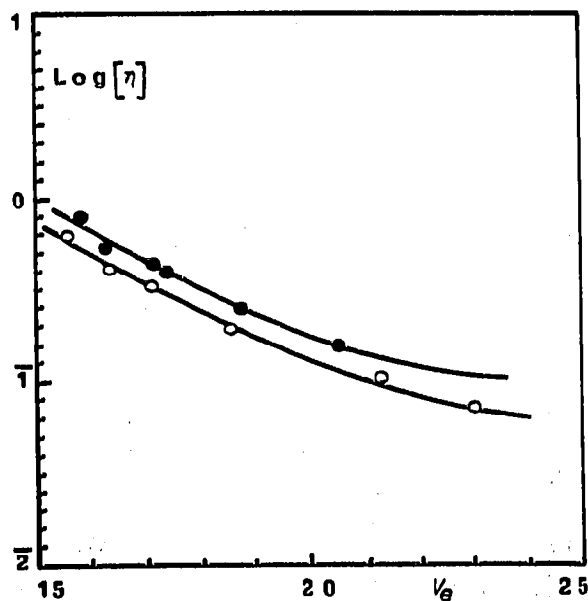
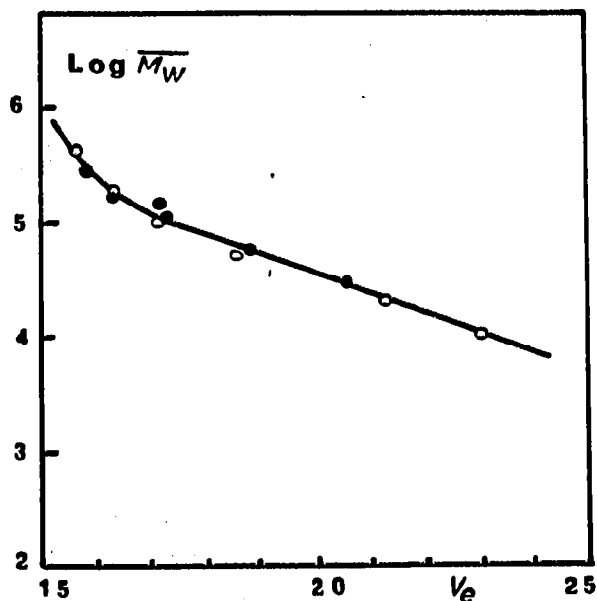


Fig. 2. Standard calibration curves $\log \overline{M}_w$ versus V_e for polystyrene (○—○) and poly-(2-vinylpyridine) (●—●).

Fig. 3. Variation of $\log [\eta]$ with V_e for polystyrene (○—○) and poly-(2-vinylpyridine) (●—●).

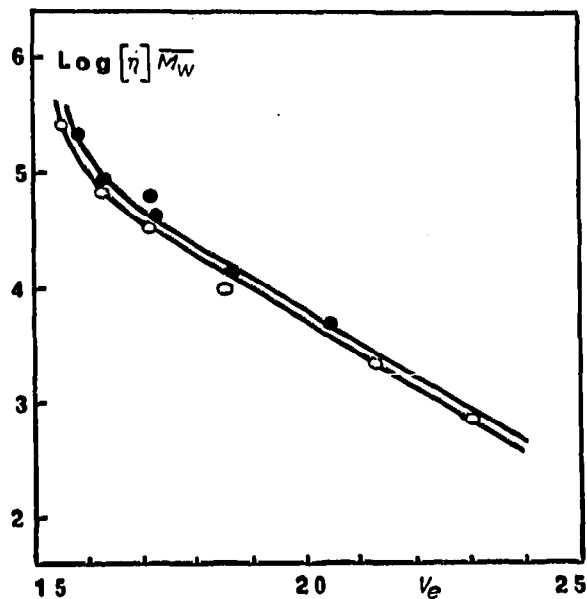


Fig. 4. Universal GPC plots for polystyrene (\circ — \circ) and poly-(2-vinylpyridine) (\bullet — \bullet).

dynamic volume of the solvated polymer chain, as defined by BENOIT and co-workers^{5,6}, and which would be the only parameter responsible for GPC retention. Obviously, these plots give two curves as shown in Fig. 4, one for each polymer, instead of a single one as predicted by BENOIT and co-workers. However, this fact does not contradict the universality of BENOIT and co-worker's plot, as we believe that PVP is retained a little longer than PS in the column at the same value of the hydrodynamic volume on account of the remaining weak interaction between PVP and silica beads, in spite of the use of DMF as the eluent. Indeed, it was suggested in the INTRODUCTION that when THF is used as the eluent the retention of PVP in the columns is due to the strong electrostatic interaction between silica beads and polymer chains. When a solvent with a high dielectric constant, such as DMF, is used, PVP is eluted as the electrostatic bonds are now mostly broken. In order to verify the hypothesis of interaction between PVP and the stationary phase when THF is used as solvent, the following experiment was carried out. A 2-ml volume of a 1% polymer solution was shaken with 100 g of silica beads and, the reaction was followed by UV spectroscopy. The spectra shown in Fig. 5 were recorded successively, and indicate the drastic decrease in the polymer concentration of the solution. The phenomenon is more pronounced inside the Porasil-packed columns, where the solution of the polymer to be eluted remains in contact with the silica stationary phase for a longer period. The experiment was repeated with DMF as solvent and no noticeable decrease in polymer concentration has been found, even after contact of the solution with the beads for 36 h. The interaction between PVP and silica beads is probably a dipole-dipole interaction. For comparison, the values of the dipole moments (in benzene)⁷ of DMF and THF and also for 2-ethylpyridine and ethylbenzene, which are the "free" basic units of PVP and PS chains, respectively, are as follows: N,N-dimethylformamide, 3.82; 2-ethylpyridine, 2.58; tetrahydrofuran, 1.70; and ethylbenzene, 0.35 Debye units.

These values show that DMF should be the strongest solvating agent, thus

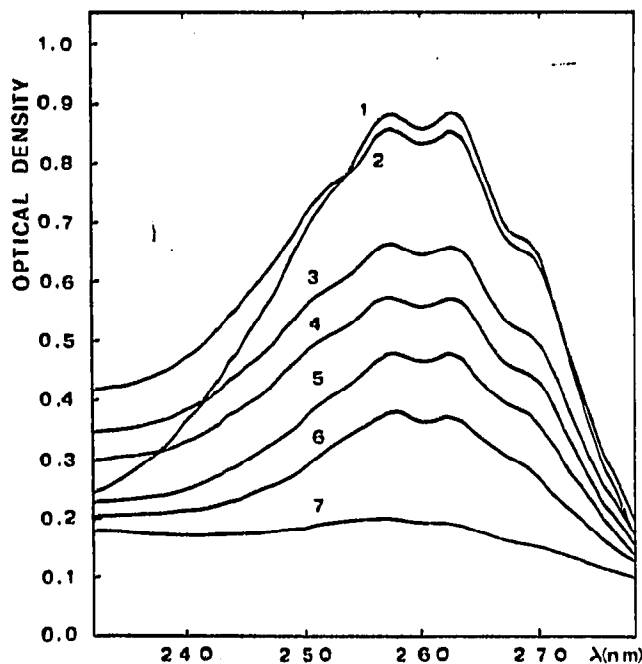


Fig. 5. Action of silica beads on PVP in THF solution. Spectrum 1: solution with PVP only. Spectra 2-7: solution with PVP and silica beads.

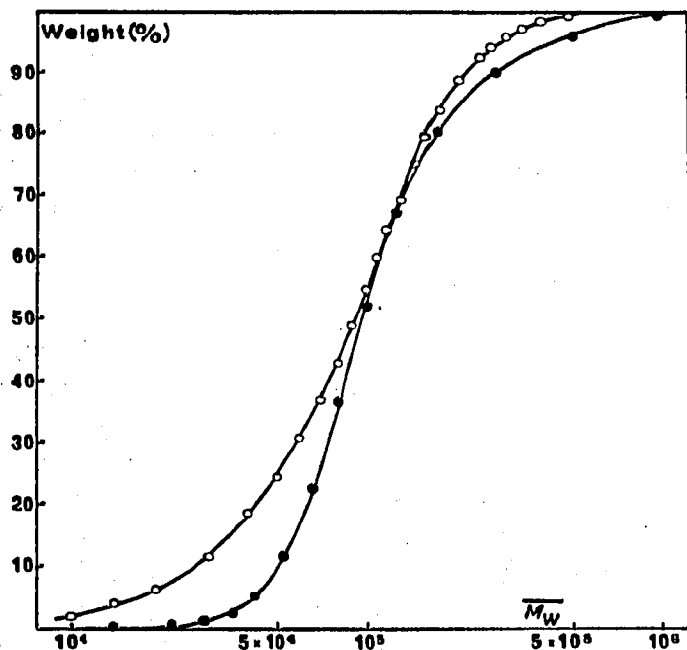


Fig. 6. Integral molecular weight distribution function for PVP sample 3: ●—●, GPC; and ○—○, sedimentation.

reducing to a great extent the interactions between PVP and the silica beads. On the other hand, it can be seen that PS should be quite inert towards silica beads.

The observed deviations from the universal plot of BENOIT and co-workers as shown in Fig. 4 can be explained from the fact that in spite of a larger chain expansion of PVP than PS in DMF, the longer retention of the PVP chains in the columns is

due to some remaining dipole-dipole interactions with the silica beads, which shift the plot of PVP towards higher values of the elution volumes.

Fig. 6 shows the integral molecular weight distribution functions for PVP sample 3, as calculated from GPC and sedimentation data. The curve obtained from the first technique was calculated directly from the chromatogram by using the calibration curve given in Fig. 2 for PS. The integral distribution function obtained from sedimentation analysis was calculated from the differential molecular weight distribution function⁸, which is itself obtained from the differential sedimentation coefficient distribution function⁹ from the relationship

$$S_0^\circ = 3.7 \times 10^{-2} \overline{M_w}^{0.39}$$

where S_0° (expressed in Svedberg units) is given in Table I for four different samples of PVP in DMF at 25°. No attempt was made to correct the chromatogram¹⁰ in order to obtain the "true" molecular weight distribution function, for two reasons: (a) the mechanism of elution of PVP is affected by the remaining interaction forces between the polymer and the stationary phase; (b) as the chains were retained for a longer period as the molecular weight increased, a "temporary" local coating of the beads may lead to the phenomenon of phase distribution chromatography¹¹, in which the polymer fractions of lowest molecular weight are eluted first when glass beads have previously been coated with a high-molecular-weight fraction of the same polymer. Such a phenomenon may seriously modify the shape of a chromatogram and also the values of V_e . The fact that GPC analysis indicates a smaller percentage of low-molecular-weight fractions and a higher percentage of high-molecular-weight fractions may be explained by the creation of some reverse GPC.

REFERENCES

- 1 M. FONTANILLE AND P. SIGWALT, *Bull. Soc. Chim. Fr.*, (1967) 4083.
- 2 A. GOURDENNE, *Polym. Prepr.*, 12, No. 2 (1971) 129.
- 3 G. MULLER, *Ph. D. Thesis*, University of Paris, 1964.
- 4 N. HO-DUC AND H. DAOUST, *Can. J. Chem.*, 47 (1969) 3299.
- 5 H. BENOIT, Z. GRUBISIC, P. REMPP, D. DECKER AND J. G. ZILLION, *J. Chim. Phys.*, 63 (1966) 1507.
- 6 Z. GRUBISIC, P. REMPP AND H. BENOIT, *Polym. Lett.*, 5 (1967) 753.
- 7 A. L. MCCELLAN, *Tables of Experimental Dipole Moments*, W. H. Freeman and Co., San Francisco and London, 1963.
- 8 R. L. BALDWIN, *J. Amer. Chem. Soc.*, 76 (1954) 402; *J. Phys. Chem.*, 63 (1959) 1570.
- 9 J. E. BLAIR, *J. Polym. Sci., C*, 8 (1965) 287.
- 10 L. H. TUNG, *J. Appl. Polym. Sci.*, 10 (1966) 375.
- 11 R. H. CASPER AND G. V. SCHULZ, *J. Polym. Sci., A-2*, 8 (1970) 833.

J. Chromatogr., 74 (1972) 225-231