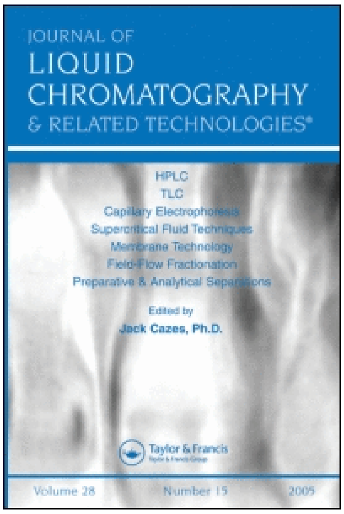

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MOLECULAR MASS CHARACTERIZATION OF POLY(4-VINYLPYRIDINE)

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ABSTRACT

Poly(4-vinylpyridine) samples, synthesized by anionic and radical initiators, have been characterized by Size Exclusion Chromatography, Light Scattering and Intrinsic Viscosity. The mobile phase used in SEC characterization was 50% methanol and 50% 0.1M $LiNO_3$. Broad molecular weight distribution samples of P4-VP, characterized via Low Angle Laser Light Scattering, have been used in the calibration of the SEC system. The polymers show different molecular weight distribution and high polydispersity. Mark-Houwink constants for P4-VP in the SEC mobile phase have also been obtained.

INTRODUCTION

In this paper we present a molecular mass characterization of Poly(4-vinylpyridine) (P4-VP) polymers synthesized in our laboratories. Several papers present a characterization of P4-VP, by way of intrinsic viscosity (1,3-6), light scattering (3-5), osmometry (3,7), sedimentation (7) and pyrolysis (8). To our knowledge nobody presents the whole molecular weight distribution (MWD) of P4-VP polymers by Size Exclusion Chromatography (SEC or GPC) means.

SEC characterization of P4-VP presents various difficulties with respect to the choice of the mobile phase and the calibration of the system. In order to obtain both the sample's solubility and the columns packing compatibility we used 50% methanol and 50% 0.1M $LiNO_3$ as the mobile phase. To test how good this new solvent was we performed the off-line intrinsic viscosity measure of P4-VP samples which was carried out using both methanol and the SEC mobile phase.

An SEC calibration curve was constructed using three P4-VP broad MWD samples characterized by means of static Low Angle Laser Light Scattering (LALLS). Substantially absolute values of the weight-average molecular weight, M_w, and intrinsic viscosity, $[\eta]$, have furnished a reference for checking the SEC method.

EXPERIMENTAL

Materials

Three P4-VP samples were synthesized using anionic initiators, Butyl Lithium (BuLi), under various conditions. The synthesis procedure is described in reference (1). A further two P4-VP samples were synthesized using radical initiators, Cupric Acetate (CuAc) and Azobisisobutyronitrile (AIBN). The last procedures are described in reference (2).

SEC narrow standards, seven Poly(ethylene oxide) (PEO) and four Poly(ethylene glycol) (PEG) with molecular weights ranging from $4.4 \cdot 10^2$ to $8.5 \cdot 10^5$ g/mole, were obtained from Waters (Milford, MA)

Methods

SEC: The SEC system, Waters, consisted of a 600E pump, a U6K injector, 410 differential refractometer and 490 UV detectors (of 254 nm wavelength). Data reduction was carried out by the Waters 840 Data and Chromatography Control Station. The columns set was composed of two Waters Ultrahydrogel (1000 and 250 Å pore size). The experimental conditions consisted of: a mobile phase of 50% methanol and 50% of 0.1M $LiNO_3$ degassed with helium, room temperature, a 0.6 ml/min flow rate, a sample's concentration of 2 mg/ml and a 50 μl injection volume.

Intrinsic viscosity: The intrinsic viscosity, [η], value was determined using an Ubbelohde capillary viscometer (Schott Gerate) with methanol and the SEC mobile phase as solvents at a temperature of 25 °C. Each solution was filtered through a 0.45 μm filter. Sample concentrations ranging approximately from 0.1 to 0.5 g/dl. [η] value were calculated in the usual manner as reduced viscosity, η_{sp}/c, extrapolated to zero concentration according to Huggins equation. Intrinsic viscosity has been correlated with molecular weight by means of the Mark-Houwink equation.

Light scattering: The theory and the experimental protocol of LALLS Chromatix KMX-6 (LDC/Milton Roy) have been described previously (9,10). LALLS measures were performed at a wavelength of 632.8 nm, room temperature and an angle of scattered light collection θ=4°-5°. The solvent used was methanol, filtered through a 0.2 μm filter. Specific refractive index increment dn/dc=0.205 was calculated as follows. At wavelength λ=436 nm dn/dc=0.267 (5); at λ=546.1 dn/dc=0.224 (4), at λ=632.8 the value was calculated by extrapolation with the inverse of λ^2 (Cauchy Equation). The intensity of scattered light was measured at five concentrations ranging from 1 to 6 mg/ml. Each solution was filtered several times through 0.45 μm filters to obtain dust-free solutions. The weight-average molecular weight, M_w, and the second virial coefficient, A_2, were obtained according to the usual Debye equation

$$\frac{k \cdot c}{R_\theta} = \frac{1}{M_w} + 2 \cdot A_2 \cdot c \qquad (1)$$

where R_θ is the excess Rayleigh factor, k the polymer optical constant, and c the concentration.

Mark-Houwink constants: The value of k and a for the narrow standards, PEO/PEG, in the SEC mobile phase at room temperature was obtained by way of a least-squares linear fit of $\mathrm{Log}([\eta]_i)$ vs. Log(Mi), where $[\eta]_i$ is the value obtained from off-line measurement and Mi is the vendor value of molecular weight. The value of the constants for P4-VP in methanol was obtained from reference (1), in the SEC mobile phase solvent was calculated by using the calibration method based on broad MWD samples.

RESULTS AND DISCUSSION

Five P4-VP samples, as received from the synthesis without additional fractionation or cleaning, were characterized. Results and conditions of the synthesis are summarized in Table I.

SEC Mobile Phase

There are only a few solvents suitable for use in SEC of P4-VP polymers. The mobile phase is chosen primarily for sample solubility and secondarily for compatibility with the stationary phase of the columns, finally leading unwanted non-size-exclusion secondary effects. The choice of SEC mobile phase for P4-VP polymers presents two alternatives:

- N-N Dimethyl Formamide (DMF).
- Mixture of water and organic solvent (methanol).

DMF is a commonly used solvent in SEC runs. It is compatible with many packing gels and many polar and apolar polymers. However DMF is of little practical use and the results are occasionally difficult to interpret. We chose the second alternative as. Methanol is a good solvent of P4-VP polymers. Unfortunately a 100% of methanol is not compatible with the packing of Ultrahydrogel columns or other columns used on aqueous SEC. We have used 50% of methanol and 50% 0.1M $LiNO_3$ as the mobile phase. $LiNO_3$ salt was added to prevent the aggregation of macromolecules. P4-VP is completely soluble in the mobile phase. Furthermore Ultrahydrogel aqueous columns allow the use of up to 50% of organic solvent by gradual introduction via the gradient method.

The values of intrinsic viscosity, $[\eta]$, and Huggins coefficient, K_H, of P4-VP samples both in methanol and in SEC mobile phase are reported in Table II. Intrinsic viscosity values in SEC mobile phase significantly decrease respect to the value in methanol. The values of K_H for the five samples of P4-VP in methanol range from 0.32 to 0.43. The values are typically of a random-coil polymer in a good solvent. In the SEC mobile phase the values of K_H range from 0.51 to 0.60. Both $[\eta]$ decrease and K_H increase, going from the methanol to the SEC mobile phase solvent, state decreasing in solvent polymer affinity. Of course this fact is the price to pay for the presence of water, a poor solvent of P4-VP polymers, in the SEC mobile phase.

Table I: Polymerization of Poly(4-Vinylpyridine).

Sample		**BuLi1**	**BuLi2**	**BuLi3**	**AIBN**	**CuAc**
Solvent		Toluene	Toluene	Toluene	Methanol	Methanol
Monomer	mmol	95	190	470	260	270
Initiator	mmol	0.32	0.32	1.92	1.90	0.55
Init/Monom	$\cdot 10^3$	3.37	1.68	4.08	7.31	2.03
Solvent	ml	50	100	200	153	28
Temperature	°C	35	35	35	60	60
Time	h	16	16	16	4	6
Yield	%	95	82	40	25	20

Table II: Characterization of Poly(4-Vinylpyridine)

	SEC		LALLS		INTRINSIC VISCOSITY					
					SEC mobile phase			Methanol		
	$M_w \cdot 10^{-5}$ g/mole	**D**	**$M_w \cdot 10^{-5}$** g/mole	**$A_2 \cdot 10^4$** $ml \cdot mole \cdot g^{-2}$	**[η]** dl/g	**K_H**	**$M_v \cdot 10^{-5}$** g/mole	**[η]** dl/g	**K_H**	**$M_v \cdot 10^{-5}$** g/mole
BuLi1	1.81	9.7	1.88	7.07	0.65	0.51	1.57	0.88	0.43	1.47
BuLi2	1.69	6.8	1.66	7.25	0.59	0.59	1.37	0.84	0.38	1.37
BuLi3	0.67	8.4	0.68	7.91	0.31	0.60	0.58	0.45	0.32	0.55
AIBN	1.32	6.4			0.51	0.57	1.12	0.73	0.38	1.12
CuAc	0.75	11.6			0.35	0.55	0.69	0.52	0.36	0.68

SEC calibration curve

The calculation of molecular weight averages by SEC for any polymer species other than the narrow standards available requires the transformation of molecular weight into that of the specified polymer. The universal calibration (11) has wide applicability. However it requires accurate values of the Mark-Houwink constants for both samples and standards, as well as requiring the absence of non-size-exclusion secondary effects between the sample and gel. In our case suitable narrow standards were lacking, the Mark-Houwink constants were not known and there where conceivable non-size-exclusion secondary effects. Therefore we preferred a calibration with P4-VP broad MWD samples.

The method used to obtain the true calibration curve was suggested by Chiantore and Hamielec (12). Such method requires the universal calibration curve and two chromatograms of broad MWD samples of known M_w. It starts from a primary narrow standards, PEO/PEG, calibration curve. The primary calibration function is denoted

$$M_s(v) = \phi(v) \qquad (2)$$

given k_s and a_s, values reported in Table III, the universal calibration may be expressed as

$$([\eta]\cdot M)(v) = k_s \phi(v)^{1+a_s} \qquad (3)$$

the true calibration curve for P4-VP polymers can be written as

$$M_p(v) = \alpha\phi^{\beta}(v) \qquad (4)$$

where α and β are constants

$$\alpha = \left(\frac{k_s}{k_p}\right)^{\frac{1}{1+a_p}} \qquad \beta = \frac{(1+a_s)}{(1+a_p)} \qquad (5)$$

Combining the definition of the weight-average molecular weight and the eq.(4) the value M_w of every sample can be expressed as

$$M_{w_i} = \alpha\int_0^{\infty} F_i(v)\phi^{\beta}(v)dv \qquad (6)$$

where $F_i(v)$ is the normalized chromatogram of the sample.

Dividing the two eq.(6) we obtain a new equation where only β is unknown. Using an iterative method we can calculate β. Once β has been obtained α may be calculated using eq.(6). Thus the calibration curve, eq.(4), for P4-VP was defined. Finally from the calculated values α and β using eq.(5) we also obtain Mark-Houwink constants, k_p and a_p, of P4-VP in the SEC mobile-phase at room temperature.

In the calibration we used three BuLi samples. From three samples, in three pairs, we calculated the values α and β that minimize the difference between SEC and LALLS M_w values.

The weight-average molecular weight, M_w, of three BuLi samples was obtained from LALLS measure. Both the M_w value and the second

Table III: Mark-Houwink constants at room temperature

Polymer	Solvent	$k \cdot 10^4$ dl/g	a
P4-VP	Methanol	2.4	0.69
P4-VP	SEC mobile phase	0.935	0.74
PEO, PEG	SEC mobile phase	1.74	0.76

virial coefficient A_2 of P4-VP samples are reported in Table II. The M_w values of the samples range from 0.68 to $1.88 \cdot 10^{-5}$ g/mole and the related MWD are adequately far apart to overlap.

SEC results

Table II summarized the characterization results. Examples of P4-VP MWD are also shown. Figure 1 shows the MWD of P4-VP initiated by Butyl Lithium, BuLi3 sample. Figure 2 shows the MWD of P4-VP initiated by Cupric Acetate, CuAc sample. In divergence with the results of Parravano (1) the molecular weight distributions of each sample are unimodal. Only the MWD of the CuAc sample shows a little bimodal form. As seen from Table II the polydispersity index, $D=M_w/M_n$, ranges from 6.4 to 11.6. However these high values are not extraordinary for anionic and radical polymerization.

The agreement between the molecular weight averages obtained from SEC, LALLS and Intrinsic Viscosity is very good. Of course the agreement between SEC and LALLS M_w values depend principally on the fact that the SEC calibration curve was obtained from LALLS M_w data. Elsewhere we point out the good agreement between M_w values obtained from SEC, M_v values obtained from intrinsic viscosity via the Mark-Houwink equation and k and a value reported in Table III, both in methanol and in the SEC mobile phase. This fact we think confirms the consistency of the SEC characterization method.

Finally the Mark-Houwink constants for P4-VP in the SEC mobile-phase at room temperature, a=0.74 (±0.04) k=0.935 (±0.06)$\cdot 10^{-4}$ dl/g,

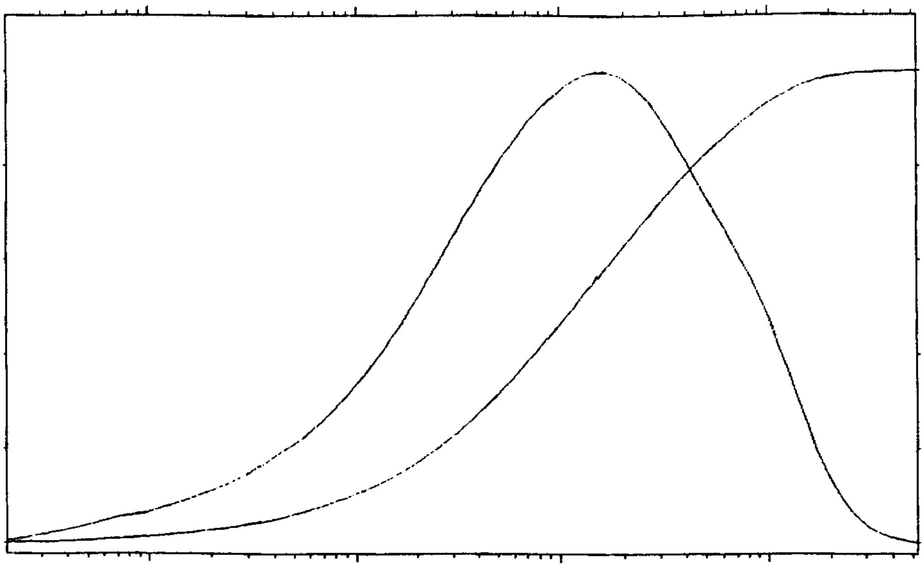

Figure 1: Molecular weight distribution of BuLi3 sample.

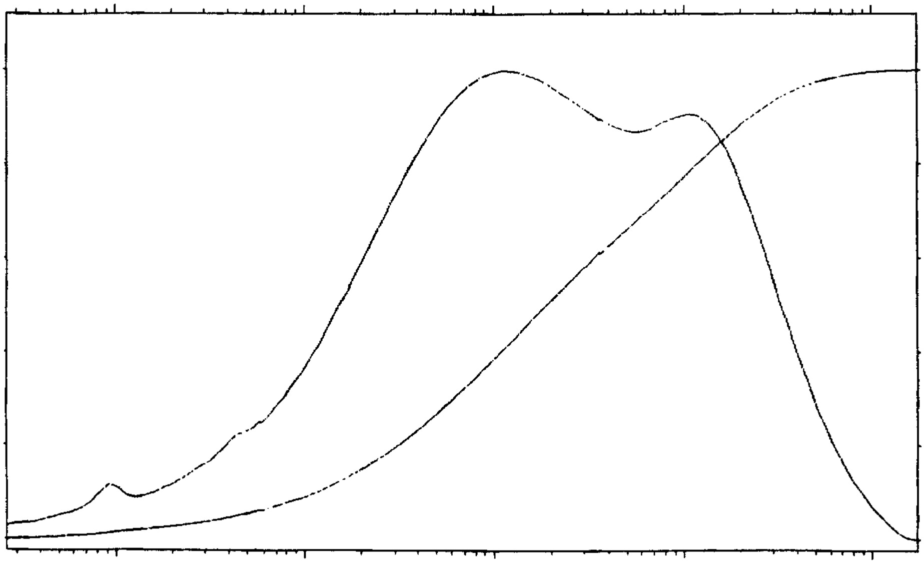

Figure 2: Molecular weight distribution of CuAc sample.

were calculated according to eq.(5). Values precision of k and a is quite low. This low precision depends on the calculation method based on broad MWD samples in opposition to the classical method based on some narrow standards.

CONCLUSION

We have described a SEC method for the characterization of molecular weight distribution of P4-VP polymers. The method uses as a mobile phase a mixture of Methanol and 0.1M $LiNO_3$.

Three dilute solution characterization methods have been utilized to create a coherent and consistent picture of P4-VP molecular mass properties. The agreement between SEC and both off-line viscometry and LALLS data is very good. Thus the intrinsic viscosity and LALLS data confirm the SEC method of characterization of whole MWD of P4-VP. The agreement between the data also confirms the validity of the broad MWD samples calibration method of the SEC system.

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