

# Molar mass distribution of polyvinylalcohol as determined by size exclusion chromatography in DMSO

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(Received 6 January 1997)

The molar mass distributions of various polyvinylalcohol (PVA) samples having molar masses ranging from 14 to 610 kg mol<sup>-1</sup> have been determined by size exclusion chromatography (s.e.c.) using dimethylsulfoxide (DMSO) as the eluent. Four sets of columns were tested. The best results were obtained with two Ultrahydrogel columns (Waters). Calibration was performed using seven polyethyleneoxide (PEO) samples having known molar masses and narrow molar mass distributions. The PEO calibration curve was transformed to a PVA calibration curve by application of a broad standard calibration procedure. The validity and reliability of the new method was verified by a comparison of the  $M_w$  and  $[\eta]$  calculated from the molar mass distribution and the values determined by independent off-line light-scattering and Ubbelohde viscometry. The data are in very good agreement even up to very high molar masses of 610 kg mol<sup>-1</sup>. © 1997 Elsevier Science Ltd.

(Keywords: molecular characterization; s.e.c.)

## INTRODUCTION

Polyvinylalcohol is a polymer with a wide variety of applications<sup>1-3</sup>. Revelation of the molar mass (distribution) (MMD) is important since the MMD not only supplies information about the process kinetics of the polymerization but may also contribute to a better understanding of relations between structure and properties. In order to determine molecular parameters by light-scattering, viscometry and s.e.c. it is a prerequisite to obtain molecularly dispersed and stable solutions.

Unfortunately, it is a well-known phenomenon that PVA solutions age, for instance in water<sup>4-12</sup>. Hence the solution properties change as a function of time. These changes are attributed to the formation of aggregates, a process depending on the thermal history of the polymer and the (dis)solution temperature<sup>4,5</sup>. Aggregation leads to strongly curved angular dependencies<sup>4,5</sup>, to extreme high molar masses as compared to the equivalent polyvinylacetate (PVAc)<sup>6</sup>, to low or even negative second virial coefficients in light-scattering and high values<sup>7</sup> for the Huggins constant (0.7 or even higher) in viscometry. The existence of the aggregates was also shown by Nagy<sup>8</sup> in the chromatograms of the s.e.c. coupled with Low Angle Laser Light Scattering (s.e.c.-LALLS). An extensive review on the characterization of PVA using aqueous s.e.c. was recently published by Nagy<sup>9</sup>. The formation of aggregates may also influence the viscosity of more concentrated solutions of PVA in water<sup>10</sup>. Hence molecular characterization of PVA in solvents which exhibit aging may strongly be hampered leading to unreliable results. The aging process can be suppressed by addition of propanol<sup>11</sup> but not stopped<sup>6,12</sup>. In order to cope with these difficulties, it was proposed to modify PVA to

PVAc<sup>6</sup>. Subsequent characterization of the PVAc should give the molecular structure of the PVA. However, the chemical modification<sup>13</sup> is not always as complete as desired and the procedure is time consuming. Finally, the modification with working-up procedure might lead to partial fractionation and consequently to an overestimation of the  $M_n$ .

Fortunately, Tacx and Schoffeleers<sup>14</sup> showed that PVA could successfully be dissolved in DMSO. The solutions remained stable for at least 2 days. Zimm-plots of PVA in DMSO showed approximately straight angular dependencies and high values for the second virial coefficients ranging from 8 to 15 × 10<sup>-4</sup> ml g<sup>-2</sup> mol<sup>-1</sup>. The molar masses were in good agreement with the molar masses expected on the molar masses of the equivalent reactylated PVA (r-PVA). The Huggins constant was 0.3 and the exponent of the Mark-Houwink equation 0.80 indicating that DMSO is a very good solvent for PVA. Based on these findings, we started an investigation aimed at the determination of the molar mass distribution of PVA by s.e.c. in DMSO.

## EXPERIMENTAL

### S.e.c.

S.e.c. was performed on a Hewlett-Packard chromatograph (HP 1090) equipped with a refractive index (RI) detector. Various sets of s.e.c. columns (Table 1) were applied. The eluent (DMSO, spectrophotometric grade, Aldrich) was degassed using an Erma ERC 3522 degasser. The solvent flowrate was 0.5 ml min<sup>-1</sup> and the system pressure approximately 65 bar. The column compartment temperature was 65°C. The tube connecting the aperture of the columns and the RI detector was carefully isolated to minimize the thermal noise. The detector

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**Table 1** Column sets applied for the separation of PVA using SEC

Column	Type	Pore size	Material
Microstyrigel (TSK)	5000, 4000 and 3000	10 $\mu$	Polystyrene
Microbondagel (DuPont)	E-500, E-300	10 $\mu$	Ether coated silica
Plaquagel (Polymer Lab)	P-3	8 $\mu$	Hydroxy surface
Ultrahydrogel (Waters)	1000 and 2000 Å	10 $\mu$	Hydroxymethacrylate

**Table 2** Characteristics of the PVA used in this investigation

PVA	$M_w$ (kg mol <sup>-1</sup> )	$[\eta]_{\text{DMSO}}^{65^\circ\text{C}}$ (dl g <sup>-1</sup> )
PVA1	14	0.59
PVA2	86	1.59
PVA3	145	1.97
PVA4	230	2.98
PVA5	285	4.24
PVA6	610	6.65

temperature was 45°C. Calibration was performed using seven polyethyleneoxide (PEO) standards (TSK) having narrow molar mass distributions and known molar masses ranging from 25 to 860 kg mol<sup>-1</sup>. The polymers (PVA and PEO) were dissolved in DMSO at 65°C for 4 h. The concentration was chosen in such a way that the product of intrinsic viscosity and concentration ( $[\eta]^*c$ ) was less than 0.2. DBPC (0.05 wt%) was added as an internal standard. The solutions were filtered using Millex filters (0.5  $\mu$ m).

All data were processed using a Hewlett-Packard (HP) 300 computer equipped with standard software package.

#### Preparation of PVA

The synthesis of the PVA samples was reported previously<sup>14</sup>. The characteristics are mentioned in Table 2. From the results reported in this work it appeared also that PVA exhibits a linear structure.

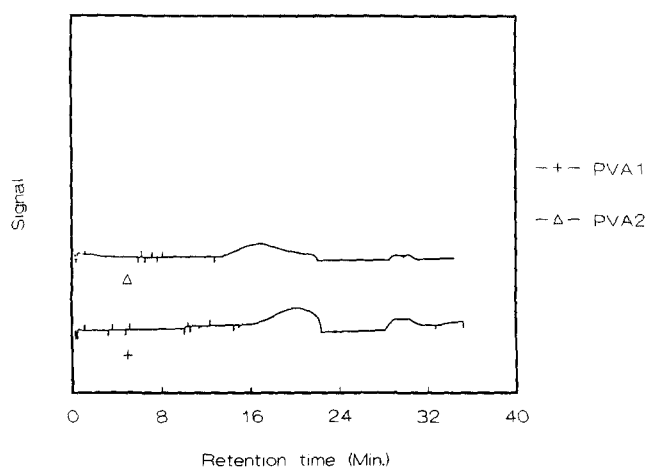
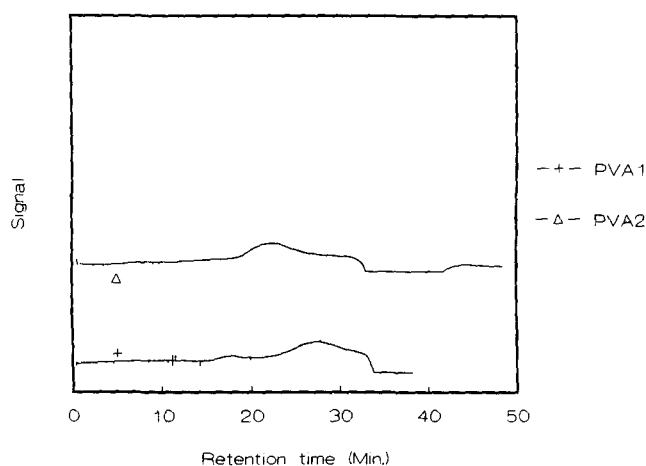
## RESULTS

#### Choice of columns

In order to determine the MMD of PVA a s.e.c. system must be developed using DMSO as the eluent. The eluent-column combination has to fulfil certain requirements:

- (1) Good and stable solvent for the polymer.
- (2) The polarity of the eluent must be higher than that of the packing material in order to prevent adsorption of the polymer. The packing on the other hand must be somewhat polar in order to be compatible with the solvent.
- (3) The packing material must swell in the solvent DMSO.
- (4) The viscosity of the eluent must be as low as possible.

Clearly columns applied in s.e.c. using water as the eluent fulfil these requirements as well as is possible. However it was unknown whether DMSO can be used without causing damage to the columns. Hence we investigated the performance of three types of columns used in

**Figure 1** Chromatogram of PVA1 and PVA2 using Microstyrigel columns**Figure 2** Chromatograms of PVA1 and PVA2 using two Microbondagel columns

water applications, namely microbondagel, plaquagel and ultrahydrogel and one classical set, microstyrigel. Details about the sets are mentioned in Table 1.

In Figure 1 the results are presented of the separation of two PVAs having molar masses of 14 and 86 kg mol<sup>-1</sup> respectively using micro-styrigel columns. The separation is poor with a relatively broad peak of the internal standard. An unknown negative peak hampers determination of  $M_n$ . Consequently, this set was excluded. The results of the separation of the same PVA and internal standard using microbondagel are presented in Figure 2. It is readily seen that this set also cannot be applied. In Figure 3 results are presented of the separation of the PVA using Plaquagel columns. Both the PVA and the internal standard DBPC are (reproducibly) separated. The platenumber of 3600, adequate for such a viscous system, remained stable for a period of at least 3 months. The best results were obtained with Ultrahydrogel columns. The platenumber was again 3700 and the columns remained stable for at least 2 years. The optimum separation conditions are mentioned in the Experimental part.

#### Optimization of the separation performance of the Ultrahydrogel columns

Separation of polymers according to hydrodynamic

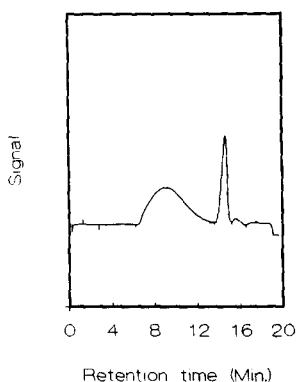


Figure 3 Chromatogram of PVA1 using one Plaquagel column

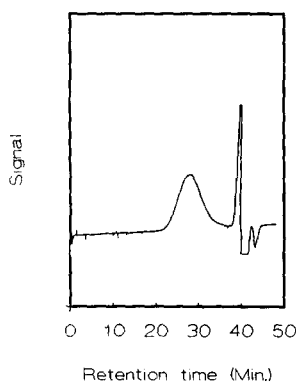


Figure 4 Chromatogram of PVA2 using two Ultrahydrogel columns

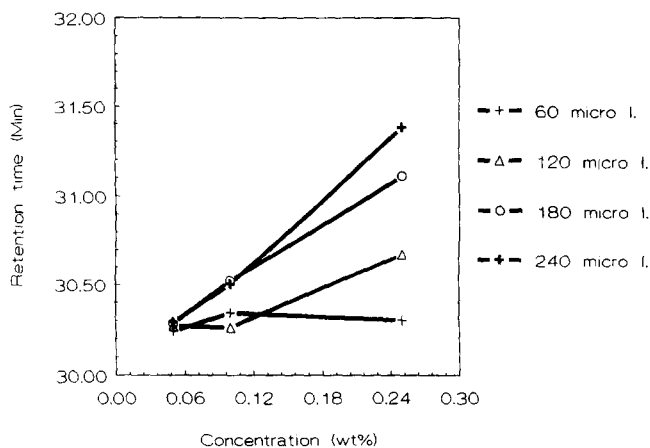


Figure 5 Influence of concentration on the retention time of PVA3 at four different injection volumes

volume can only be performed in a reliable way if the influence of column overload is minimized. Unfortunately no information is available concerning this system. Hence we started an investigation aimed at the determination of the optimum concentration and injection volume combinations. For this purpose PVA with a medium high molar mass ( $145 \text{ kg mol}^{-1}$ ) was applied. At various concentrations ranging from 0.05 to 0.25 wt%, four injection volumes were applied ranging from 60 to 240  $\mu\text{l}$ . The concentration dependence of the retention time is given in Figure 5. From the results it becomes clear that at high concentrations and high injection volumes the retention times are strongly dependent on the concentration. At an injection volume of 240  $\mu\text{l}$  and

concentrations of 0.25 wt% the retention time shifts by as much as 1 min. Fortunately at low injection volumes (60–120  $\mu\text{l}$ ) there is nearly no dependence of the retention times on column load. Based on these results an injection volume of 60  $\mu\text{l}$  was chosen. In the region where the dependence of the retention time on concentration is minimized,  $[\eta]^*c < 0.5$  holds. A value of 0.2 was considered as a safe and practical measure for the calculation of the concentration of the various types of PVA.

#### Calibration

In principle, determination of the MMD by s.e.c. is a relative method. Hence calibration is a prerequisite. Unfortunately, no PVA calibration standards with narrow molar mass distributions (MMD) are available. In order to cope with this difficulty, a broad standard calibration procedure was proposed by Goetz<sup>15</sup>. This simple procedure needs only one well-known calibration standard and a calibration curve without an *a priori* knowledge about the Mark–Houwink constants. However, due to the application of one standard only, calculation of biased molar masses may occur. Application of a standard having a narrow MMD might cause an undesired shift of slope of the calibration curve leading to the calculation of unreliable molar masses. This effect is more pronounced if the molar masses are outside the range of the standard. Application of a standard having a very broad molar mass distribution is also not recommended since the signal to noise ratio decreases as a result of the broadness of the MMD. Hence baseline settings and calculations become inaccurate leading to unreliable results. However, samples having an optimum width of approximately 5–7 and a linear structure are not available for PVA. Consequently, a well-characterized PVA (PVA3) with a medium high molar mass ( $145 \text{ kg mol}^{-1}$ ) was used as the broad standard. The correctness of the calculated PVA calibration curve was checked by calculating the molar masses ( $M_w$ ) and intrinsic viscosity ( $[\eta]$ ) of PVA with a significantly higher average molar mass (PVA6,  $M_w = 610 \text{ kg mol}^{-1}$ ) and MMD outside the range of PVA3. The values for  $M_w$  and  $[\eta]$  calculated from the distribution must be in agreement with the results of off-line light scattering and Ubbelohde viscometry.

First, a calibration curve was set up using seven polyethyleneoxide standards with a narrow MMD and known molar masses ranging from 25 to  $740 \text{ kg mol}^{-1}$ . The PEO calibration curve was transformed to the PVA calibration curve using the above-mentioned procedure available in the software. The results are given in Table 3. From the results it might be inferred that the values determined off-line and on-line are in good agreement even up to very high molar masses of  $610 \text{ kg mol}^{-1}$ , indicating that the proposed procedure is reliable. Consequently application of the proposed method leads to molar mass distributions of PVA and avoids the time-consuming chemical modification of the polymer to polyvinylacetate.

#### Influence of parameter settings in the calibration procedure

The input parameters for the broad standard calibration procedure were obtained from lightscattering and s.e.c. on PVA and reacylated polyvinylalcohol (r-PVA). These data show an upper limit for the experimental error of 10%. In order to investigate the influence

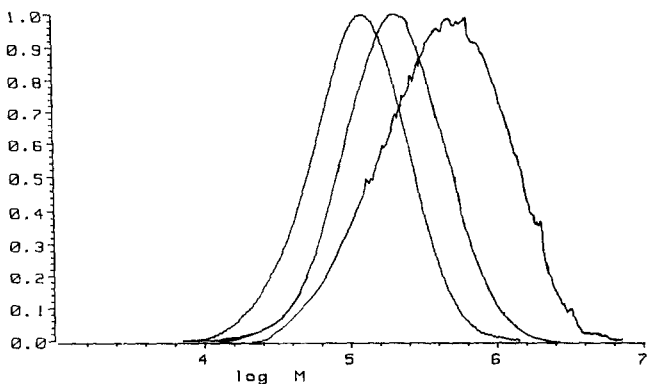
**Table 3** Comparison of the molar masses and intrinsic viscosities determined on-line (s.e.c. with broad standard calibration procedure) and off-line using light scattering and Ubbelohde viscometry

PVA	On-line SEC			Off-line	
	$M_n$	$M_w$	$[\eta]$	$M_w$	$[\eta]$
PVA3	73	145	2.06	145	1.97
PVA4	140	264	3.34	230	2.98
PVA5	171	267	4.33	285	4.24
PVA6	221	619	6.5	610	6.65

$[\eta]$  determined at 65°C in DMSO

**Table 4** Influence of the settings of the input parameters on molecular parameters ( $M_w$  and  $[\eta]$ ) calculated from the molar mass distribution of PVA6. The values determined by independent off-line methods:  $M_w = 610 \text{ kg mol}^{-1}$ ,  $[\eta] = 6.65 \text{ dl}^{-1}$ 

Parameter setting for standard		Calculated molecular parameters for PVA6		
$M_w \text{ (kg mol}^{-1}\text{)}$	$M_w/M_n$	$M_w \text{ (kg mol}^{-1}\text{)}$	$M_w/M_n$	$[\eta]$
145	2.2	686	3.2	7.03
145	2.0	619	2.80	6.51
145	1.8	547	2.40	5.95

**Figure 6** MMD of three different PVA polymers (PVA3, PVA6 and PVA7)

of variations in the data due to the experimental errors, the input parameters were changed by 10%. The results are given in Table 4. From a comparison of the values for  $M_w$  and  $[\eta]$  determined off-line and on-line it appears, not unexpectedly, that the calculation of the molar mass using this method is relatively sensitive for variation in the input parameters. Fortunately, by choosing the correct values and checking the results for PVA6 which MMD is mainly outside the molar mass range of the standard, the method can be applied very successfully.

The values obtained for  $M_w/M_n = 2$  seem to be the most reliable. Also the setting of  $M_w = 145 \text{ kg mol}^{-1}$  seems to be the optimum choice since an increase or a decrease of the value leads to an unreliable setting for the polydispersity as an input parameter. Despite the application of only one standard the proposed method is reliable over a broad range of molar masses.

#### Molar mass distributions of various PVAs

In Figure 6 the chromatograms of various types of PVA (PVA3, 4 and 6) with molar masses of 145, 230 and  $610 \text{ kg mol}^{-1}$  respectively are presented. The distributions are relatively narrow ( $M_w/M_n = 2$ ). This was also

expected on grounds of the polymerization conditions<sup>14</sup>. In case of PVA6 the MMD shows some noise. This is caused by the very low concentration of the polymer.

The method was set up using the broad standard method calibration and PEO calibration samples. For PVA polymers having a linear structure this route is reliable for obtaining a molar mass distribution. However if long chain branching (LCB) is present only the apparent MMD (MMD\*) can be determined. The ratio of  $[\eta]$  and  $[\eta]^*$  contains information about the average LCB. Application of a differential viscometer is recommended to obtain information about the absolute MMD and the LCB ( $g'$  as a function of molar mass). This is the subject of future investigations.

## CONCLUSIONS

A s.e.c. system has been developed using DMSO as the eluent and Ultrahydrogel columns for the determination of the MMD of PVA without chemical modification of the polymer and without the presence of aging of solutions. The optimum temperature for the column compartment was 65°C and for the refractive index detector 45°C. The calibration is performed using PEO standards having known molar masses and narrow MMDs. This calibration curve can be transformed to a PVA calibration curve using a broad standard calibration procedure without *a priori* knowledge of the Mark-Houwink constants. The validity and reliability of the method was checked by a comparison of the  $M_w$  and  $[\eta]$  calculated from the molar mass distribution and the  $M_w$  and  $[\eta]$  determined by independent off-line light scattering and Ubbelohde viscometry. The method could be successfully applied for PVA having average molar masses ranging from 14 to  $610 \text{ kg mol}^{-1}$  and a polydispersity of approximately 2.

## ACKNOWLEDGEMENTS

The authors wish to acknowledge Dr H. C. Booij for very stimulating discussions. Furthermore the authors gratefully acknowledge permission by DSM Research to publish this work.

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