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Rheological properties of poly (vinylpyrrolidone) as a function of molecular weight

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ABSTRACT

Different grades of poly (vinylpyrrolidone) (PVP) were studied as dispersant for gadolinium doped cerium oxide (CGO) in ethanol-based colloidal dispersions. The average molecular weights M_w , M_n , and M_z were determined by gel permeation chromatography (GPC), and then used in a numerical method to evaluate the viscosity molecular weight (M_v) via an empirically modified Mark-Houwink-Sakurada (MHS) equation. The MHS equation parameters (a and K), and the polydispersity correction factor (q_{MHS}) were also evaluated. Molecular weight was found to affect only the amount of PVP required for achieving full stabilized dispersions. Indeed, no influence on the packing properties was observed.

INTRODUCTION

Polyvinylpyrrolidone (PVP) is an extensively used polymer due to its solubility in both aqueous and organic polar solvents^{1,2}, excellent film forming properties³, and ability of acting as dispersant for colloidal particles in suspension⁴. Molecular weight (M_w) and M_w distribution (MWD) are among the most relevant factors affecting the end-use physical properties of polymers.

Generally, polymers exist as blends of chains with a distribution of lengths and the full information about a given polymer's M_w

is given by the distribution profile of its chains' molar masses. However, in a number of cases single number information is easy to handle and therefore preferred. Accordingly, the molecular weight of a polymer is expressed as an average value originating from a statistical analysis. More precisely the k -th average molecular weight is defined as the ratio between the $(k+1)$ -th and the k -th moments of MWD (see Appendix section). For instance, the number average molecular weight (M_n) corresponds to $k = 0$ and is the arithmetic mean of the MWD, accounting for the colligative properties of polymer solutions. The weight average molecular weight (M_w) corresponds to $k = 1$ and accounts for static light scattering of dilute polymer solutions. The next average molecular weight (M_z) corresponds to $k = 2$ and is associated to motion of polymer molecules in solution e.g. under ultracentrifugation. Eventually, a viscosity average molecular weight (M_v) is defined based on viscosity behaviour of polymers in solutions. In contrast to the previously mentioned averages, M_v is not an intrinsic characteristic of a given polymer and in general cannot be expressed by integral MWD moments. Besides being affected by the polymer chain size, M_v also depends on the temperature and specific polymer-solvent interactions (affinity). Such dependence is expressed by the Mark-Houwink-Sakurada (MHS) equation (Eq. 1),

which relates the intrinsic viscosity ($[\eta]$) to the polymer molecular weight⁵:

$$[\eta] = KM_v^a \quad (1)$$

where K and a are constants for given polymer-solvent system and temperature. Specifically, the a constant accounts for the polymer chain shape in solution. $[\eta]$ is the inherent ability of any solute to increase the viscosity of the solvent.

Eq. 1 can be rearranged resulting in a modified MHS equation (Eq. 2)⁶:

$$[\eta] = Kq_{MHS}M_w^a \quad (2)$$

where q_{MHS} is the polydispersity correction factor, a measure of the width of the MWD. It ranges from 0 to 1, the closer to 1, the narrower the MWD, and vice versa. It varies from a sample to another as it depends on a (MHS shape parameter) and average molecular weight. An estimation of q_{MHS} , K and a constants from $[\eta]$ data, can be achieved by a numerical method using Eq. 2. This approach provides also an estimation of M_v , otherwise not experimentally accessible.

The focus of this work is on exploring the influence of molecular weight in affecting the ability of PVP as dispersant for gadolinium doped cerium oxide (CGO) in ethanol-based colloidal dispersions. M_n , M_w , and M_z have been determined by gel permeation chromatography (GPC), whereas M_v has been estimated applying a numerical method to the modified MHS equation. An estimation of polydispersity correction factor (q_{MHS}) and of the two MHS constants (K and a) is also obtained.

EXPERIMENTAL

Materials

Seven different PVP polymers with M_w ranging from 10 to 49 kDa were obtained from different suppliers (namely Sigma Aldrich, Fluka, AppliChem, Alfa Aesar). Polymers were labelled as indicated in Table

1, where the sequential numbering (from 1 to 6) next to PVP acronym refers to M_w in decreasing order.

Commercial Gadolinium doped Ceria powder ($Gd_{0.10}Ce_{0.9}O_2$) with a moderately low specific surface area (SSA) ($6.59 \text{ m}^2/\text{g}$) was used for preparing CGO colloidal suspensions. The powder SSA was determined by BET isotherm measurements.

Polymer solutions and CGO colloidal suspensions were prepared using ethanol as solvent.

All the materials were used as received.

Sample preparation

The polymer solutions were prepared by a dilution method. The appropriate amount of a solution (with a concentration of typically $1 \text{ g}\cdot\text{dl}^{-1}$) was added to a volumetric flask using a micro pipette. Then, the required volume of solvent was added. The solutions were then gently rolled at 21°C overnight prior to measurements.

Suspensions at increasing amount of dispersant ($2\text{-}12 \text{ mg}/\text{m}^2$) and at fixed ceramic loading (28% vol) were prepared. The dispersant was dissolved in the solvent in a PE bottle containing zirconia balls. Then CGO powder, typically 25-30 g, was gradually added and mixed with the dispersant and the solvent. The suspensions were left to roll for at least 72 hours.

Suspensions, at a fixed amount of PVP (the optimal, as defined in Figure 5 below), with increasing ceramic loading (from 10% to 46% in volume) were prepared following the same procedure.

Gel permeation chromatography (GPC)

Gel permeation chromatography was used to determine the molecular weights and their distribution. The measurements were performed with Tetrahydrofuran (THF) as solvent. The flow rate was $0.5 \text{ ml}/\text{min}$ at a temperature of 20°C . 1x Waters HT 6E + 1 x Polymer Laboratories PL gel column-D were used in series. The chromatograph was connected to a Shimadzu RID-10A detector.

In order to relate retention time to molecular weight, a conventional calibration was made using various polystyrene standards.

Rheological Characterization

The rheological properties were measured with a rotational rheometer (Anton Paar MCR302). A constant temperature of 21°C was maintained during the experiments using a temperature control unit.

All the samples (both polymer solutions and CGO dispersions) were characterized by Flow Curve Tests (FCT) (rotational mode) in the shear rate range of 0.1-100 s⁻¹ in up and down ramp. FCTs were conducted in step mode using 45 steps with a waiting time of 10 s. The step mode procedure allows the sample to reach equilibrium thus avoiding possible transient effects. A pre-shear treatment at 0.1 s⁻¹ for 2 minutes followed by 2 minutes at rest (0 s⁻¹ shear rate), was applied to level out any possible effect due to the sampling and loading of suspensions.

The experiments on dilute polymer solutions were performed using a double gap configuration with an inter space of 26.7 mm (DG 26.7). For each polymer a number of 5-6 concentrations were measured. Data were expressed as the means of at least three replications with the corresponding standard deviations.

The experiments on CGO suspensions were performed using a parallel plate of 50 mm in diameter (PP 50) at a gap distance of 0.6 mm. This value was selected based on a study of the effect of gap distance on the viscosity behaviour.

Methods

Determination of $[\eta]$

The intrinsic viscosity $[\eta]$ can be estimated either by the extrapolation method or by single point determination. In this work the extrapolation procedure was adopted and the most commonly used

equations for determining $[\eta]$, Huggins (1)⁷ and Kramer (2)⁸, were used:

$$\eta_{sp}/c = [\eta] + K_H[\eta]^2 c \quad (3)$$

$$(\ln \eta_r)/c = [\eta] - K_K[\eta]^2 c \quad (4)$$

where η_r is the relative viscosity, η_{sp} is the specific viscosity ($\eta_r - 1$), η_{sp}/c is the reduced viscosity, $(\ln \eta_r)/c$ is the inherent viscosity, and K_H , and K_K are Huggins, and Kramer constants, respectively. $[\eta]$ is obtained by extrapolation of the reduced viscosity (η_{sp}/c) or inherent viscosity ($\ln \eta_r/c$) to zero concentration. The extrapolation method requires a linear dependence of the reduced or inherent viscosity as function of concentration. Therefore, limitations on the concentration range must be defined in order to satisfy the linearity requirement. The Huggins and Kramer equation have been found to be strictly applicable for $[\eta]c \ll 1$. For higher concentrations the interaction among single polymer coils is not any longer negligible and it affects the flow properties leading to a deviation from the linear trend.

Polydispersity correction factor (q_{MHS}) and M_v estimation

The numerical method adopted for the estimation of the polydispersity correction factor, q_{MHS} , is a well-established method which requires the knowledge of the M_n , M_w , and M_z according to Eq. 5⁶:

$$q_{MHS} = \left(\frac{M_w}{M_n}\right)^b \left(\frac{M_z}{M_w}\right)^c \quad (5)$$

where b and c are empirical polynomial functions of the MHS shape parameter a ; c depends only on a according to Eq 6:

$$c = 0.113957 - 0.844597 * a + 0.730956 * a^2 \quad (6)$$

b depends on a and (M_z/M_w) (Eq. 7):

$$b = k_1 + k_2 \left[\left(\frac{M_z}{M_w} \right) - 1 \right]^{k_3} \quad (7)$$

where k_1 , k_2 , and k_3 depend on a through the following polynomials:

$$k_1 = 0.048663 - 0.265996*a + 0.364119*a^2 - 0.146682*a^3 \quad (8)$$

$$k_2 = -0.096601 + 0.181030*a - 0.084709*a^2 \quad (9)$$

$$k_3 = -0.252499 + 2.31988*a - 0.889977*a^2 \quad (10)$$

These numerical coefficients were empirically calculated by Guaita *et al.*⁹.

However, the prior knowledge of MHS a constant is required. This limitation was overcome by using an iterative procedure. An initial value of q_{MHS} has been used for each sample according to Eq. 3. M_n , M_w , and M_z obtained by GPC, have been inserted in Eq. 3. The initial value of a was assumed equal to unity. The logarithmic form of Eq. 2 can be rearranged as follows:

$$\text{Log}[\eta] - \text{Log } q_{MHS} = \text{Log } K + a \text{Log } M_w \quad (11)$$

The quantity $(\text{Log}[\eta] - \text{Log } q_{MHS})$ was plotted against $\text{Log } M_w$ yielding a straight line whose slope provided a new value for the constant a . The latter value was then used to calculate a new value for q_{MHS} . The procedure was repeated until two successive values for a differed by less than $1 * 10^{-5}$. The final value for the intercept and slope of the linear $(\text{Log}[\eta] - \text{Log } q_{MHS})$ versus $\text{Log } M_w$ plot provided K and a , respectively.

RESULTS AND DISCUSSION

$[\eta]$ was evaluated by extrapolation method. For clarity, in Fig 2 only Huggins and Kramer plots for PVP-FLK30 are reported as explicative of the extrapolation method. Within the experimental error the equations of Huggins and Kramer provided equal values for $[\eta]$. As expected, $[\eta]$ increases with the molecular weight M_w (see Table 2).

Table 1. Molecular weights obtained from Gel Permeation Chromatography.

Grades	Mw (kDa)	Mn (kDa)	Mz (kDa)	PD (Mw/Mn)
PVP_1	49.60	15.30	205.70	3.24
PVP_2	20.00	3.38	177.10	5.92
PVP_3	17.80	4.73	118.90	3.76
PVP_4	13.40	3.47	100.30	3.86
PVP_5	10.30	2.76	49.90	3.73
PVP_6	10.20	2.60	47.90	3.92

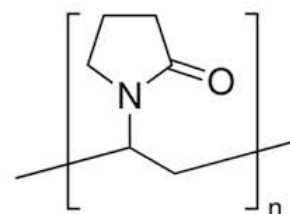


Figure 1. Polyvinylpyrrolidone chemical structure.

For the estimation of the viscosimetric constants (a and K) and of M_v , hereafter $[\eta]_H$ (Huggins intrinsic viscosity) was used in the MHS equation.

In Fig. 3 the plot of $(\text{Log}[\eta] - \text{Log } q_{MHS})$ against $\text{Log } M_w$, resulting upon convergence of the iterative procedure, is shown. The values obtained for the a and K constants are (0.66 ± 0.02) and $(2.99 * 10^{-4} \pm 0.07 * 10^{-6})$ respectively with R^2 equal to 0.99554.

The shape constant a , in addition to providing information about the conformation of the polymer in solution, is a measure of the solvent quality for the polymer. According to the mean-field theory¹⁰, its value ranges from 0 to 0.5 in poor solvents (with polymer exhibiting a compact conformation), and 0.5 is the value at *theta-conditions*. In a good solvent it

varies from 0.5 to 0.76, with the polymer exhibiting a flexible expanded conformation, whereas values in the range of 0.76-1.0 are characteristic for inherently stiff macromolecules such as cellulose derivatives and DNA¹⁰. Eventually, for highly extended chains, such as a polyelectrolyte in solution with very low ionic strength, it varies in the range from 1.0 to 1.8¹⁰.

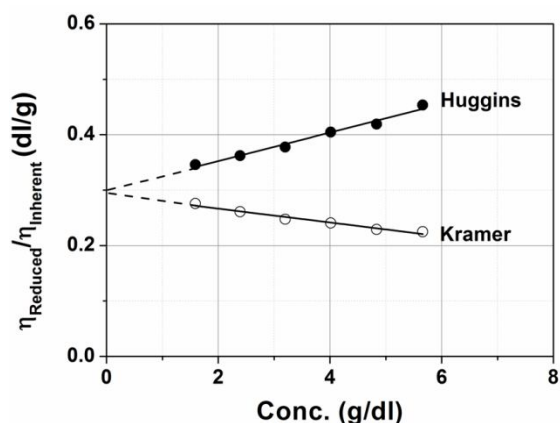


Figure 2. Huggins (H) and Kramer (K) plots for PVP-FLK30.

Table 2. Huggins and Kramer intrinsic viscosity.

Grades	$[\eta]_H$ cl/g	$[\eta]_K$ cl/g
PVP_1	3.01 ± 0.18	2.98 ± 0.16
PVP_2	1.36 ± 0.08	1.39 ± 0.06
PVP_3	1.32 ± 0.06	1.28 ± 0.05
PVP_4	1.12 ± 0.02	1.10 ± 0.02
PVP_5	1.00 ± 0.01	0.99 ± 0.02
PVP_6	0.98 ± 0.01	0.96 ± 0.02

The estimated a value obtained qualifies ethanol as a good solvent for PVP. Furthermore, a flexible conformation in

ethanol is suggested for a linear PVP structure (Fig. 1).

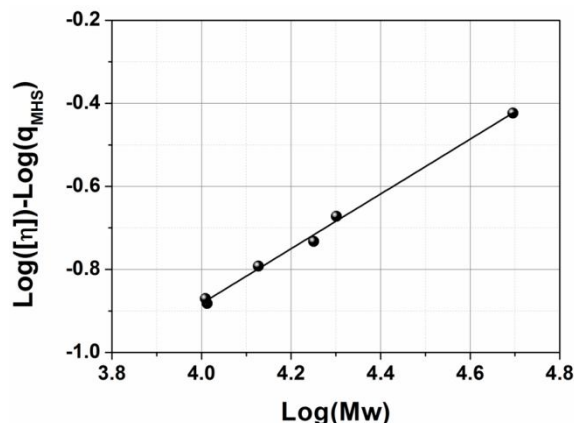


Figure 3. $(\text{Log}[\eta]-\text{Log } q_{MHS})$ as function of $\text{Log } M_w$ for PVP.

The polydispersity correction factor, q_{MHS} , for PVP samples in ethanol were also calculated (see Table 3). The constant a together with the factor q_{MHS} were further used to determine M_v (Table 3) by using Eq. 2. M_v , besides being dependent on chain length, it also accounts for the MWD. Specifically, for a given M_w the wider MWD is, the lower is M_v . Such an influence (expressed by the q_{MHS} in Eq. 2) can be used to explain the difference observed for on one side PVP_2 and on the other side PVP_5 or PVP_6. The ratio between their M_w is close to 2 (see table 1), however the corresponding ratio between their M_v is only 1.6 (see table 3), which is significantly lower. Yet, this can be ascribed to the MWD effect.

The plot of $\text{Log}[\eta]$ against $\text{Log}M_v$ is shown in Fig. 4. The values of slope (0.67 ± 0.02) and intercept ($2.46 \cdot 10^{-4} \pm 0.09 \cdot 10^{-6}$) were obtained for a and K , respectively (with $R^2=0.99442$).

The values for the MHS constants obtained from the conventional (Eq. 1) and modified (Eq. 2) MHS equation are consistent with each other. This indicates that the iterative method adopted is appropriate for determining the critical

parameters related to the MHS equation (a , k , q_{MHS} , and M_v).

Table 3. Polydispersity correction factor (q_{MHS}), and viscosity molecular weight (M_v) for the PVP polymers investigated.

Grades	q_{MHS}	M_v (kDa)
PVP_1	$0.79 \pm 0,01$	39.18
PVP_2	$0.64 \pm 0,01$	12.79
PVP_3	$0.71 \pm 0,01$	12.69
PVP_4	$0.69 \pm 0,01$	9.30
PVP_5	$0.76 \pm 0,01$	7.85
PVP_6	$0.76 \pm 0,01$	7.79

PVP_2, PVP_5, and PVP_6 (having M_v in the range of 13.00-7.80kDa) were further investigated as dispersants for gadolinium doped cerium oxide (CGO) in ethanol. The focus was on the identification of the optimal amount of PVP required to stabilize the system.

The stabilization is achieved when the interparticle repulsive forces exceed the attractive forces. This state corresponds to covering the ceramic surface with a monolayer of the dispersant. At these conditions the resultant ceramic colloidal suspensions exhibit the lowest viscosity. The optimization of the system was achieved by studying the variation of viscosity at increasing amount of dispersant.

In Figure 5 a-c, the shear viscosity at shear rate of 10 s^{-1} for the three different PVP is plotted as function of the increasing amount of dispersants at fixed ceramic loading (28 vol.%). A minimum in the viscosity, corresponding to optimal amount of dispersant, can be observed in the plots. For PVP_5 and PVP_6 the minimum in

viscosity was identified in the range of 4-6 mg/m^2 , whereas the optimal concentration for PVP-2 was found in the range of 2-4 mg/m^2 . These results indicate that the higher is M_v and the lower is the amount of polymer required for a complete coverage of the CGO surface.

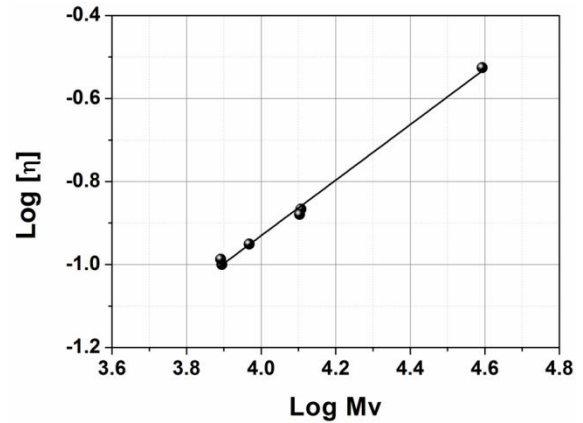


Figure 4. Mark-Houwink-Sakurada equation for PVP.

Furthermore, it is worth noticing that all the stabilized suspensions possess the same value of viscosity (i.e. around 30 mPa s) regardless of the PVP grade. No effect related to the molecular weight on the viscosity was thus observed. This is ascribable to the thickness of the dispersant monolayer, where thicker layer leads to higher viscosities. Moreover, since the dispersant in a dispersion occupies volume, the thickness of the monolayer eventually affects the maximum volume fraction (ϕ_m) and the packing properties of colloids.

This point was further investigated by studying the viscosity at increasing amount η_r - ϕ plot for PVP_2 and PVP_5.

Fig. 6 shows η - ϕ relation for systems containing as dispersant PVP_2 and PVP_5. The influence of solid volume fraction on flow behaviour is clearly illustrated: at low ceramic loadings (lower than around 30% vol) a slight variations in the viscosity can be detected, whereas for higher ceramic

loadings the viscosity significantly increases up to asymptotically reach ϕ_m .

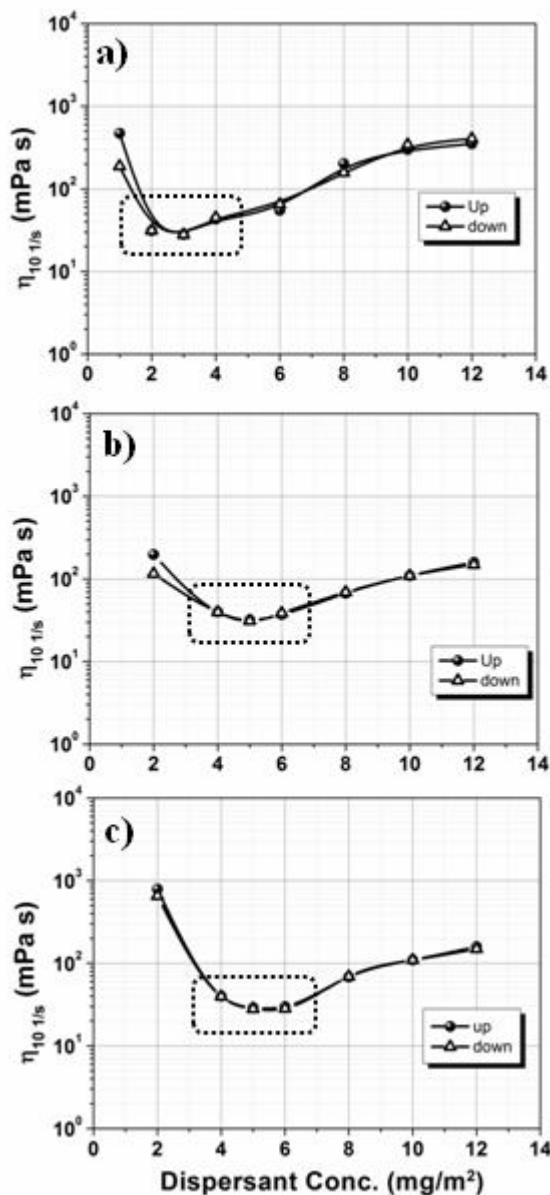


Figure 5. Viscosity (at 10 s^{-1} shear rate) for CGO suspensions ($\phi \sim 28\% \text{ vol}$) as function of increasing concentration of (a) PVP_2, (b) PVP_5, and (c) PVP_6.

The experimental data for the two PVP grades overlap producing same ϕ_m , which has been obtained by fitting the data with Dabak's model,¹¹.

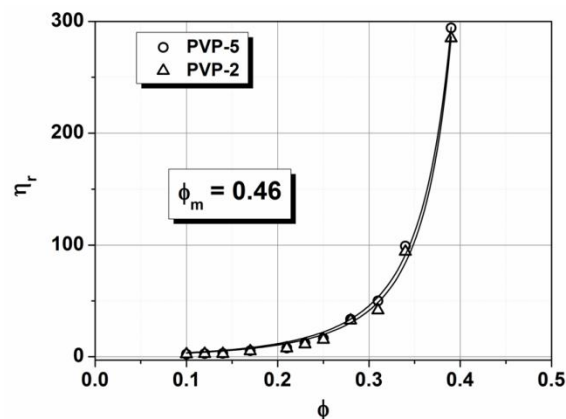


Figure 6. Dependence of relative viscosity on the volume fraction modelled by Dabak's equation at shear rate of 10 s^{-1} .

CONCLUSIONS

Different grades of PVP were compared for their ability of acting as dispersant for CGO in ethanol-based colloidal systems. A characterization of the molecular weight was achieved combining the gel permeation chromatography (M_n , M_w , and M_z) and the viscosimetry approach (M_v). The viscosimetric constants a and K for PVP samples in ethanol were also estimated applying an iterative numerical method in an empirically modified MHS equation. The value obtained for the exponent a (0.66) indicates that ethanol is a good solvent for PVP and suggests for this class of polymers a flexible random coil conformation in agreement with its linear structure. In addition, the polydispersity correction factors (q_{MHS}) was estimated. PVP grades with M_v in the range of 13-8 kDa were further investigated as dispersants for gadolinium doped cerium oxide (CGO) in ethanol. Molecular weight influences only the amount of dispersant required for achieving the stabilization of the system (extent of the dispersant monolayer), without affecting the packing properties and ϕ_m (the monolayer thickness).

APPENDIX

The different average molecular weights discussed in the text are defined as follows:

- a) Molecular weight can be generally expressed by the equation:

$$M = \frac{\sum_i N_i M_i^{k+1}}{\sum_i N_i M_i^k} \quad (12)$$

where $k=0$ gives M_n , $k=1$ gives M_w , and $k=2$ gives M_z .

- b) Viscosity average molecular weight (M_v)

$$M_v = \left[\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right]^{\frac{1}{a}} \quad (14)$$

where a is the exponent in the MHS equation.

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