

Determination of Absolute Molar Mass Distribution of Paraloid B72

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Abstract *Determination of Absolute Molar Mass Distribution of Paraloid B72.* In this molar mass distribution of Paraloid B-72 was determined by size exclusion chromatography using polystyrene and poly(methyl methacrylate) standards. The results were verified by determining intrinsic viscosity of Paraloid in tetrahydrofuran. Smaller deviation of the results was found in the case of using the calibration based on polystyrene. The calibration curve was successfully modified by numeric methods to obtain full consistence of chromatography and viscometry results.

Keywords: Paraloid B72, molar mass distribution, size exclusion chromatography, universal calibration, viscometry

INTRODUCTION

Wood is one of the most valuable materials used by man for thousands of years. Its main drawback is the relatively low stability, resulting from the processes of destruction by biological, chemical and physical agents. One way to improve the stability of wood, especially partially destroyed, is the use of polymers consolidation (Ciabach 2001). There are a lot of polymers fulfilling this role, but Paraloid B-72 is the wood consolidant the most often used, due to its resistance and elasticity (glass transition temperature is 40°C) (Chapman & Mason 2003). Paraloid B-72 is copolymer of ethyl methacrylate (EMA) and methyl acrylate (MA). Ciabach (1998) stated its composition to be 30% of MA and 70% of EMA, while Lazari and Chiantore (2000) stated different composition of MA (32.0%), EMA (65.8%) and addition of butyl methacrylate (BMA, 2.2 %). Polymerisation degree is about 900, although individual samples have a bit different values (Melo *et al.* 1999, Chiantore *et al.* 2000, Lazari & Chiantore 2000).

Molar mass is an important parameter characterizing polymers, which can be determined conveniently by size exclusion chromatography (SEC). The method gives complete information on molar mass distribution. Unfortunately, the result of determination is not absolute but dependent on the molar mass standards used. While direct standards for Paraloid are non-available, standards of poly(methyl methacrylate) (PMMA) are commonly used (Melo *et al.* 1999 Lazari & Chiantore 2000). Paraloid as a copolymer with a considerable fraction of acrylic esters may, however, show different hydrodynamic properties, which may result in falsifying the analysis results. Neither Mark-Houwink universal calibration can be applied to Paraloid because there are no Mark-Houwink coefficients available in the literature.

In this paper, direct calibrations with PMMA and polystyrene (PS) standards were applied, while viscometry was used in order to verify the results of the SEC.

MATERIALS AND METHODS

A sample of Paraloid B-72 from Rohm & Haas was used for investigations, which was designated as “unaged” one. Another sample, named “aged”, was investigated in parallel, which was previously oven-heated at 110°C for 170 hours.

Molar mass distribution was analysed by Shimadzu LC-20AD chromatograph equipped with degasser DGU-20A₃, CTO-20A oven, LC-20AD pump and RID-10A refractometer. The samples were injected by Rheodyne 7725i manual valve with the loop 20 µl. Sample separation was conducted on Nucleogel M-10 column from Macherey-Nagel at 30°C. Tetrahydrofuran (THF, analytical grade, from ChemPur) was used as eluent at a flow 2 cm³/min. Shimadzu LC Solution software was applied for data collection and apparatus controlling. Chromatogram processing for molar mass analysis was performed using Polymer Standard Service (PSS) software, PSS Calibrationprogram V2.99 and PSS WinGPC scientific V2.74. Two sets of standards were used – polystyrene (Polymer Laboratories) of molar mass range $6.85 \times 10^6 \div 1.70 \times 10^3$ and PMMA (PSS) of molar mass range $9.81 \times 10^5 \div 1.02 \times 10^2$. Concentrations of standards solutions were 1.0 g/dm³, except for samples with the highest masses ($M > 10^6$), for which the concentration was 0.5 g/dm³.

Viscosity analyses were carried out on Ubelhode viscometer No. I, with ViscoClock automatic measuring head (Schott Instruments GmbH). The measuring system was placed in thermostat at 30°C. Polymers solutions in THF was made of concentrations $c \approx 5 \text{ g/dm}^3$ and next series of solutions diluted at 1:1, 1:4, 1:8 and 1:12 ratio, respectively. Hagenbach correction for kinetic energy (ϑ) was calculated according to equation $\vartheta = 9903 \cdot t^{-2}$, where t is the time of flow through the capillary. On the basis of the results obtained, values of relative viscosity (η_{rel}) were calculated.

RESULTS AND DISCUSSION

The results of viscosity measurements obtained for both samples are presented in the Figure 1. Intrinsic viscosity values $[\eta]$ were determined from extrapolation of the expression $\ln(\eta_{\text{rel}})/c$ to zero concentration limit. Calculations were made using the spreadsheet MS Excel and LINEST function (REGLINP in Polish language version) as points of intersection of trend line with Y axis Y. In the case of Paraloid unaged, the result was $[\eta] = (49.33 \pm 0.19) \text{ cm}^3/\text{g}$, while for the sample aged $[\eta]^* = (53.70 \pm 0.18) \text{ cm}^3/\text{g}$. The calculated uncertainties of measurement show good accuracy of the intrinsic viscosity determination.

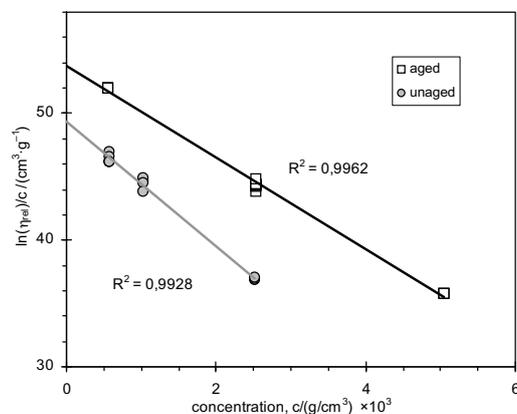


Fig. 1 Determination of intrinsic viscosity for Paraloid B-72 in THF at 30°C

As a result of the aging of Paraloid sample increase of its solution viscosity is observed, hence the molar mass also increases. This phenomenon proves the ongoing process of combining molecules of Paraloid B-72 during thermal aging. Methacrylate polymers undergoes usually depolymerisation on aging, while in the case of acrylic polymers an increase in molar mass is common, especially during photolytic aging. Since Paraloid B-72 is a copolymer of acrylate and methacrylate, dominance of one of these processes is difficult to predict. Lazzari and Chiantore (1993) obtained at a higher temperature (150°C) results indicating depolymerisation of Paraloid B-72. Parallel studies by the same authors on Paraloid B-44, which is a copolymer of ethyl acrylate (30%) and methyl methacrylate (70%), carried out at 135°C showed, in turn, increase in molar mass during aging, as in the studies presented in this paper.

Next the values of the intrinsic viscosity of Paraloid B-72 were determined by size exclusion chromatography. The calibration curves obtained from PS and PMMA standards are presented in the Figure 2. Despite the apparently minor differences between the curves, the results obtained differ very clearly (Table 1), largely because of different Mark-Houwink coefficients. The values of the coefficients (K and α) for PS were taken from the software database (PSS), and for PMMA were assumed after Chen *et al.* (1993).

Table 1 The results of intrinsic viscosity determination by SEC

standards	$K/(cm^3 \cdot g^{-1})$	α	$[\eta]$ (unaged)	$[\eta]^*$ (aged)
PS	0.01363	0.714	46.51	50.03
PMMA	0.00756	0.731	27.90	29.76

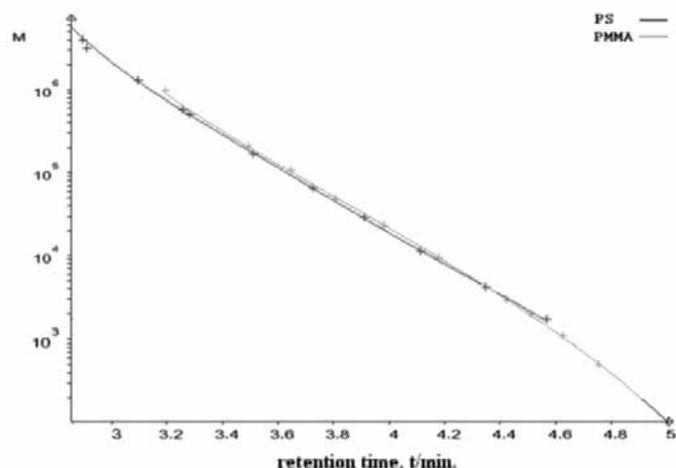


Fig. 1 Calibration curves for PS and PMMA on applied column

Determined intrinsic viscosities of Paraloid B-72 show that the values obtained by polystyrene calibration are closer to the absolute results than those from poly(methyl methacrylate) calibration. This means that the polystyrene molecule is more similar to Paraloid B-72 than PMMA, from the viewpoint of chain shape in solution. It is likely, that α coefficient, which refers to the chain rigidity, is closer to the values for PS. Polyacrylates have a single substituent with every second carbon in the chain, in contrast to polymethacrylates, which rigidity is increased by the presence of additional methyl group at the same carbon atoms. Because of Paraloid B-72 is formed by copolymerisation, its chain segments of greater rigidity (ethyl methacrylate) are separated by more elastic (methyl acrylate). As the result, the whole chain is less stiff than PMMA, like a chain of polystyrene.

With actual values of the intrinsic viscosity for Paraloid B-72 an attempt to modify SEC calibration curve was made in order to obtain agreement of chromatographic and viscometric results. On the base of PS calibration, new K and α coefficients were sought using Solver function of MS Excell in a way that the following relationships were retained:

$$[\eta]_{PS} M_{PS} = [\eta]_{B72} M_{B72} \quad \text{and} \quad K_{PS} M_{PS}^{\alpha_{PS}+1} = K_{B72} M_{B72}^{\alpha_{B72}+1}.$$

While seeking the solution that meeting above requirements a series of matching values were obtained, presented in Table 2. A detailed numerical analysis has shown that further optimisation is not possible, as the solution is not a pair of values, but a set of points forming a curve in coordinate system K and α .

Table 2 Selected K and α coefficients of optimised range.

α	0,653	0,685	0,704	0,726	0,738	0,751
K	0,03063	0,02114	0,01714	0,01328	0,01156	0,01005

For further calculations, a pair of parameters was chosen, bold-assigned in Table 2, guided by additional criteria. Mark-Houwink coefficients for acrylic homopolymers show diversity. Buback *et al.* (1998) stated that for poly(methyl acrylate) $K = 0.00195\text{cm}^3/\text{g}$ and $\alpha = 0.660$, while Beuermann *et al.* (1998), estimated $K = 0.00122\text{cm}^3/\text{g}$ and $\alpha = 0.700$ for the

poly(butyl acrylate). Comparing these parameters with those for PMMA (Table 1) The presence of methyl substituent in the chain as well as greater length of the alcohol in ester group may be supposed to increase the value of α coefficient. Since Paraloid B-72 is a copolymer of methyl acrylate and ethyl methacrylate, α may be assumed about 0.7. Considering the Table 2, the following parameters were taken for Mark-Houwink calibration: $\alpha_{B72} = 0.704$ and $K_{B72} = 0.01714\text{cm}^3/\text{g}$. These values cannot be regarded as actual Mark-Houwink parameters for Paraloid B-72, but as certain computational factors only, which can be used to modify the calibration curve.

Application of the new calibration gave SEC results of $[\eta] = 49.66$, and $[\eta]^* = 53.38\text{ cm}^3/\text{g}$, which are consistent with viscometry with a deviation less than 0.7%. The full molar mass distribution curves for Paraloid B-72, depending on the calibration applied, are shown in Figure 3 and 4. There is a noticeable discrepancy between the curve obtained from PMMA calibration and this calculated on the base of assumed K_{B72} and α_{B72} . On the other hand, molar mass distribution based on polystyrene calibration is closer to the actual. This proves better suitability of polystyrene standards of molar mass for Paraloid B-72 analysis than PMMA standards, commonly used today.

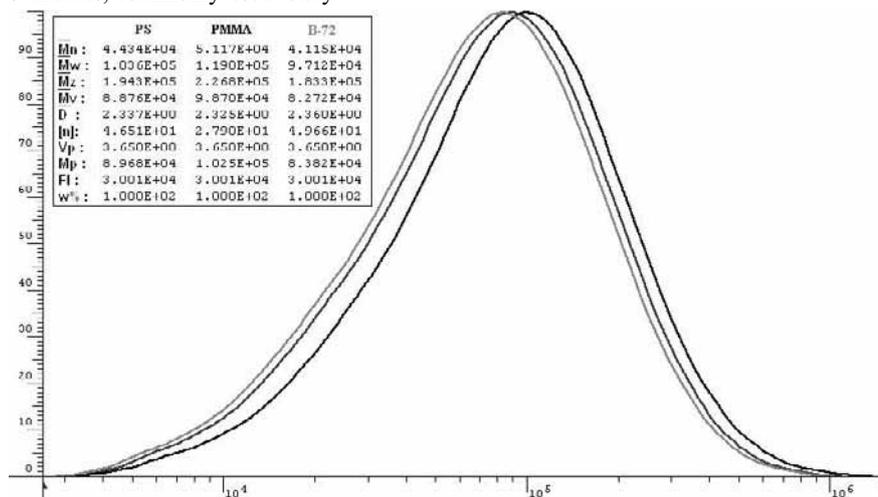


Fig. 3 Molar mass distribution of unaged Paraloid B-72 depending on calibration applied

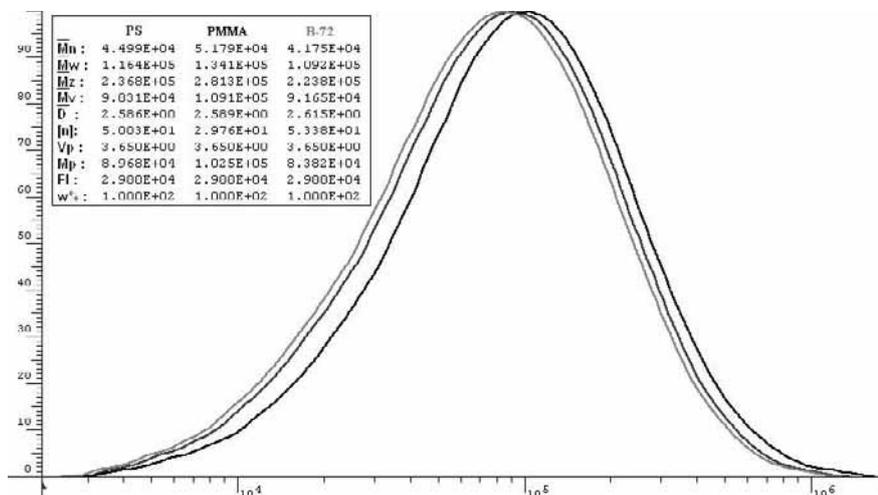


Fig. 4 Molar mass distribution of aged Paraloid B-72 depending on calibration applied

Earlier studies of other authors on Paraloid B-72, based on PMMA calibration, showed that $M_n = 41$, $M_w = 88$, and polydispersity, $D = 2.15$ (Lazzari and Chiantore 1999) or $M_n = 44.8$, $M_w = 104.9$ and $D = 2.34$ (Melo *et al.* 1999). In this paper, the results obtained by calibration of PMMA are $M_n = 51.17$, $M_w = 119.0$ and $D = 2.32$. Lack of the results repeatability is clearly visible, what maybe corresponds with product properties rather than measurement inaccuracy. Thus, further studies seem to be valuable, especially on the polystyrene standards application, which proves to be more useful than previously used poly(methyl methacrylate).

CONCLUSIONS

The results of our investigations study allow the following conclusions:

- It is relatively easy to verify the results of the chromatographic determination of the molar mass of polymers, including copolymers, like Paraloid B-72, using viscometry as a second analytical method. The same measurement conditions, i.e. solvent and temperature have to be ensured.
- SEC column calibration with polystyrene standards allows getting results of intrinsic viscosity of Paraloid B-72 more consistent with viscometric measurements than the commonly used calibration with poly(methyl methacrylate) standards.
- It is possible to modify numerically the calibration curve according to the results of viscometry and thus obtain the actual molar mass distribution of Paraloid B-72.
- Thermal degradation of Paraloid B-72 at 110°C for 170 hours leads to its molar mass increase, as macromolecules bonding processes predominate depolymerisation.

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Streszczenie: *Oznaczanie bezwzględnego rozkładu mas molowych Paraloidu B-72.* W pracy przeprowadzono oznaczenie rozkładu mas molowych Paraloidu B-72 metodą chromatografii wykluczania przestrzennego z zastosowaniem wzorców z polistyrenu i poli(metakrylanu metylu). Zweryfikowano wyniki poprzez wyznaczenie wartości granicznej liczby lepkościowej Paraloidu w tetrahydrofuranie. Stwierdzono mniejsze odchylenia wyników w przypadku zastosowania kalibracji na bazie polistyrenu. Z sukcesem numerycznie zmodyfikowano krzywą kalibracyjną, by uzyskać pełną zgodność wyników chromatografii i wiskozymetrii.

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