Size exclusion chromatography and viscometry in paper degradation studies. New Mark-Houwink coefficients for cellulose in cupri-ethylenediamine

Tomasz Łojewski*, Katarzyna Zięba, Joanna Łojewska

Department of Chemistry, Jagiellonian University, 30-060 Kraków, Ingardena 3, Poland

ARTICLE INFO

ABSTRACT

The paper deals with the application of size exclusion chromatography (SEC) for the studies of paper degradation phenomena. The goal is to solve some of the technical problems connected with the calibration of multi-detector SEC system and to find the correlation between SEC and viscometric results of degree of polymerization of cellulose. The results gathered for the paper samples degraded by acidic air pollutant (NO_2) are used as an example of SEC–MALLS application. From the correlation between intrinsic viscosities and absolute value of molecular masses obtained with SEC/MALLS (Multi Angle Laser Light Scattering) technique, Mark-Houwink coefficients for cellulose in cupri-ethylenediamine solution were determined. Thus obtained coefficients were used for the determination of viscometric degree of polymerization (molecular mass) of the aged samples. An excellent correlation was found between the chromatographic values of molecular masses obtained with SEC–UV/VIS detection and the viscometric ones utilizing the improved values of Mark-Houwink coefficients.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The technical revolution in the paper making industry that took place around the year 1850, brought about the popularization of prints. But at the same time, both the use of groundwood and the addition of alum in a new technological process gave rise to dramatic chemical destabilization of cellulose polymer. This is claimed to be caused mostly by the acidic hydrolysis of glucopyranose rings but also by oxidation. The degradation problem that now concerns the vast majority of libraries and archives collections is manifested by brittling and yellowing of paper. Even though the deacidification of paper could be performed using mass-scale processes, still more investigation is needed into its mechanism mostly to improve the existing methods of conservation. There is also high demand for the nondestructive or micro-destructive analytical methods which would be able to assess the current condition of the collections and their expected durability. The most popular and accessible of them involving measurements of paper acidity, mechanical strength and color, important from the point of view of end-users, not necessarily secure the above requirements.

In the studies of polymer degradation Size Exclusion Chromatography (SEC) becomes an analytical method of choice when diminutive effects are to be followed and only small amounts of samples are available. This is exactly the case of paper-based artifacts of historic or artistic value. Since SEC provides a comprehensive information on both the direct values and the distribution of molecular mass, it becomes especially effective in resolving paper degradation kinetics. Together with viscometric measurements of the degree of polymerization SEC is especially effective in tracing the hydrolysis progress during paper degradation, However, for the lignin containing papers for which viscometry fails, thus in fact for the majority of the real archival objects, it becomes the only method available.

Depending on the method of detection the application of SEC for the analyses of paper requires several important technical problems to solve. When equipped with refractive (RI) or UV/VIS detector, the SEC system must be calibrated on standards with known molecular weight distribution (broad or narrow), and since no standards are commercially available for cellulose, other polymers must be used. Alternatively, a fraction of the cellulose with a molecular mass distribution measured in a certain laboratory could serve as a standard but in such a case results would always bear a systematic error connected with the uncertainty of its determination which would finally lead to a logical loop in data proceeding. The calibration with standards having different hydrodynamic volume than cellulose leads also to systematic errors and thus obtained values of molecular masses (M) can only be regarded as a relative measures. In order to evade or reduce the discussed inaccuracy the universal calibration method [1] can be used for the thorough quantitative analysis of the data obtained with SEC–UV/VIS.

The MALLS detector belongs to the family of the so-called absolute detectors for the direct assessment of molar mass of poly-

---

* Corresponding author. Tel.: +48 126632087; fax: +48 126340515.
E-mail address: lojewski@chemia.uj.edu.pl (T. Łojewski).

Table 1
Mark-Houwink coefficients for Eq. (1) for cellulose in CED at 25 °C.

K [cm^3/g]	α	Source
1.87 ± 0.22	0.771 ± 0.016	Present work
0.42	1	Marx-Figini (for $DP < 950$) [11]
2.28	0.76	Gruber and Gruber (for $DP > 950$) [12]
1.37	0.905	Immergut et al. [13]
0.91	0.85	Evans [14]

mers in solutions. The interpretation of the data obtained from SEC–MALLS systems is based on the Rayleigh equation described in the next section. The application of the equation requires the information on the solute concentration which can be collected by concentration detectors (RI or UV/VIS), and on the refractive index increment (dn/dc) obtained from calibration of RI detector [1]. A number of authors rely on the dn/dc values reported in the literature, which again may lead to high systematic errors of the calculated cellulose molecular weights when different temperatures or/and wavelengths are employed in the studies.

As opposed to SEC, the classical capillary viscometric method has been the most popular technique for the determination of cellulose degree of polymerization (DP) and viscosity-average molar weight (M_v) for long decades. This is mainly because it does not need an advanced equipment, the procedure is relatively simple and fast and, last but not the least, the method is specified by the industry standards which employ the solution of cellulose in cupri-ethylenediamine solution (CED) [2]. The main drawback of this method is that its use is limited to lignin-free paper materials which are in minority in archives and libraries collections. A practical obstacle for a user in the interpretation of the results collected for cellulose in CED obtained with this method is that the Mark-Houwink (MH) coefficients used to recalculate intrinsic viscosity values to M_v or DP values much differ from each other and were collected long time ago (Table 1).

Due to widespread use of viscometry in many laboratories dealing with paper conservation and increasing interest in SEC method by the researchers dealing with paper conservation and degradation the question arises to which extent the results obtained with viscometry coincide with SEC results obtained for lignin-free papers. In a very comprehensive study Dupont and Mortha [3] compared two different SEC techniques and viscometry in cadoxen as a tool for the characterization of aged cellulose samples. The results obtained with the two techniques differed considerably between each other: for viscometry in cadoxen – due to the solvent-induced degradation, for SEC in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) – due to complexation occurring between cellulose and solvent constituents. Strlič et al. [4] described the application of SEC in LiCl/DMAc with RI detection and viscosity technique in cupri-ethylenediamine (CED) for the determination of molecular masses of degraded cellulose. The authors have shown that for the series of artificially oxidized paper samples viscometric measurements carried out in an aggressive media (i.e. highly alkaline CED) give a significant underestimation of M_v. The proposed method of cellulose stabilization (reduction with NaBH$_4$) reduced the error observed by authors. In the article [5] the mechanism of paper degradation induced during exposure to light is studied using several techniques, including SEC in LiCl/DMAc and viscosity in CED solution. As in previous publication, the authors underline the fact that viscometry may yield an underestimation values of DP of heavily oxidized cellulose. They emphasize that information obtained by SEC technique is more complex, however the systematic errors were higher for SEC measurements than for viscometric ones.

Taking into account the above mentioned motivations the goal of this paper is threefold: (i) to indicate and discuss some technical aspects of the application of the SEC with Multi Angle Laser Light Scattering (MALLS) and UV/VIS detection, (ii) to verify the values of Mark-Houwink coefficients by independent methods and (iii) to check the correlation of the degree of polymerization (or average molecular mass) obtained with SEC and viscometric methods.

2. Materials and procedures

2.1. Samples

Two types of model paper (PAPER-1 and PAPER-2, TNO, Delft [6]) were used for the study. PAPER-1 is bleached sulphite softwood paper containing hemicelluloses and traces of lignin and PAPER-2 is cotton paper containing pure cellulose [6].

The paper samples were aged in a closed glass vessels for 5 days at the temperature of 100 °C [7] at various concentrations of NO$_2$. The doses of NO$_2$ (0, 0.5, 1, 2, 3, 5, 7 cm^3) were injected into the vessels of a volume of 150 cm^3 filled with approximately 4 g of paper. After 5 day ageing the samples were subjected to the analyses by viscometry and SEC.

2.2. Viscosity measurements

Viscosity measurements were carried out with a capillary viscometer in 0.5 M cupri-ethylenediamine (CED) solution according to the standard [2] in the following way: samples were cut into the little pieces and defibrillated by shaking with few pieces of a copper wire in a plastic bottle with 10 cm^3 of distilled water, paper suspension was than dissolved in 10 cm^3 of 1 M cupri-ethylenediamine solution (CED) and shaken for additional 0.5 h. For each sample two CED solutions were prepared and for each solution the measurement was repeated three times. As the solution of cellulose in CED is non-Newtonian liquid and its viscosity decreases as shear rate increases, the concentration of each sample was set as to obtain the product $[\eta] \cdot c$ dropping into the range of 2.6–3.4 which is the range observed during measurements of paper viscosity in order to maximize the precision of measurements [2].

2.3. SEC measurements

2.3.1. Sample preparation
The original samples were derivatized using phenyl isocyanate to obtain cellulose tricarbanilate (CTC) which were dissolved in tetrahydrofuran (THF) prior to each SEC analysis. The derivative was prepared according to procedure described by Stol et al. [8] in the following way:

- 5 mg of the sample cut into the little pieces (the area of few mm^2) was placed in a glass vial and dried at the temperature of 105 °C for 0.5 h,
- the pre-dried sample was treated with 1 cm^3 of water-free pyridine and 0.1 cm^3 of phenyl isocyanate, flushed with nitrogen, sealed and maintained at 80 °C for 48 h,
- to terminate the substitution reaction 0.1 ml of methanol was added and reaction mixture was then cooled to room temperature.

To minimize a rough random error 4 repetitions of each analyses were performed: two CTC solutions were prepared for each paper sample and each solution was analyzed twice. Prior to SEC/UV/MALLS analyses the CTC solutions were diluted 1:10 with THF and filtered using 0.45 μl PTFE syringe filters.

2.3.2. Analyses
The average molar mass and molar mass distribution were determined using Waters chromatographic system which consist of: isocratic pump, autosampler, column oven, UV/VIS detector (set
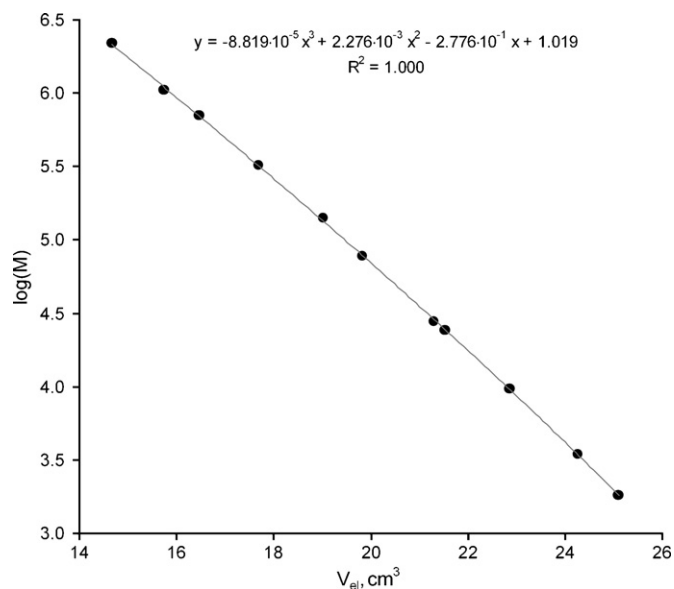
Fig. 1. Calibration curve for columns as a function of logarithm of molecular mass of polystyrene standard versus elution volume; fitted with 3rd order polynomial.

at the wavelength of 254 nm) and MALLS detector (Dawn Heleos, Wyatt Technology, working at 658 nm). For the separation of the CTC samples, a set of two 25 cm × 1 cm mixed-bed polydivinylbenzene columns was used (Jordi). They were thermostated at 35 °C and proceeded by a guard column (Waters). THF (HPLC grade) was used as eluent with a flow rate of 1.0 cm^3/min.

In this study two configurations of the analytic systems were used: the indirect SEC–UV/VIS with universal calibration and the absolute SEC–MALLS.

3. Calibration and data processing

3.1. Viscometric results

The output of the viscometric results is the physical parameter describing intrinsic viscosity [η]. In order to obtain a chemical gauges of paper degradation the viscosity should be transformed to degree of polymerization (*DP*) or viscometric molecular mass (*M$_v$*) according to Eq. (1) or Eq. (2), respectively.

$$[\eta] = K \cdot DP^\alpha \tag{1}$$

$$[\eta] = Q \cdot M^a \tag{2}$$

The two equations have two sets of MH coefficients *K*, α and *Q*, *a* which sometimes are mismatched in the literature, as for example in [1,2].

3.2. SEC results

The interpretation of SEC results is dependent on the configuration used for analyses as it has been mentioned above and the chemical compositions of standards used for calibration. However, a common step is the calibration of columns which involves determining the retention volume or elution time.

In our system the columns were calibrated using polystyrene standards (11 samples with polydispersion 1.06 on average, *Fluka*). Standards were dissolved in THF and mixed into three separately analyzed solutions which were then injected into the columns. The calibration curve obtained in this way as a function of log(*M*) and elution volume was fitted with 3rd order polynomial according to [1] and presented in Fig. 1.

3.2.1. SEC–UV/VIS configuration

Since the use of the UV/VIS detector provides the information on the relative values of molecular mass of a polymer, the hydrodynamic volume of a polymer used as a standard is a key parameter in the calibration of the results from size exclusion chromatography. Since there are no commercially available standards for the cellulose, polystyrene [8] and pullulan standards [3] are used. Certainly, the application of polymer standards which have different chemical structures from an analyzed sample gives the relative values of the obtained molecular masses. The question thus arises to which extent the differences in chemical structure of the standard and analyzed polymer influence the values of molecular masses. The hydrodynamic volume (related to the molecular size) of different types of polymers in a solution cannot be simply related to molar mass [1,8]. The solution to this problem can be the universal calibration [1] which takes into account the viscosity of the polymer solutions. The calibration function is the dependence of the product log[η]·*M* on the retention volume. Thus at any retention volume, the hydrodynamic volumes of two different polymers (*A*, *B*) can be estimated from the following formula:

$$[\eta]_A M_A = [\eta]_B M_B \tag{3}$$

Substituting [η] in Eq. (3) by the relation (2) we obtain the universal calibration function for UV/VIS detector:

$$Q_A M_A^{a_A+1} = Q_B M_B^{a_B+1} \tag{4}$$

3.2.2. SEC–MALLS configuration

The determination of absolute values of molecular masses using size exclusion chromatography with MALLS detection requires the use of Rayleigh's equation:

$$\frac{k \cdot c}{R(\alpha)} = \frac{1}{M \cdot P(\alpha)} + 2A_2 c \tag{5}$$

where *k* is a combined constant including the refractive index increment *dn/dc*:

$$k = \left(2\pi^2 n_0^2 \left(\frac{dn}{dc}\right)^2\right) \frac{1 + \cos^2 \alpha}{N_A \lambda_0^4} \tag{6}$$

To apply Rayleigh equation three parameters should be determined: CTC concentration in THF, *c*, its refractive index increment, *dn/dc* and the second virial coefficient, *A$_2$*. The solute concentration *c* in Eq. (5) was obtained from the UV/VIS detector. The extinction coefficient for the UV/VIS detector was determined according to the Lambert–Beer's law. Its average value amounts to 7669 cm^3/(g cm) (11.2% std. deviation) derived from 23 measurements performed for two paper samples (PAPER-1 and PAPER-2) derivatized to CTC and dissolved in THF according to the procedure described above. In further calculations the literature value of *dn/dc* was used: 0.168 cm^3/g [9], the value obtained for the wavelength 633 nm. As the concentration of CTC in THF is very low, the second virial coefficient (*A$_2$*) in Eq. (5) can be neglected. Weight average molecular mass from Rayleigh equation was calculated with the use of the linear Zimm's model according to recommendation of Wyatt Technology.

Further calibration of MALLS involved the determination of the detector calibration constant which is a proportionality factor between the detector signal and the Rayleigh coefficient *R*(α) for one photodiode and further normalization of the rest of 17 photodiodes in the detector. The calibration constant was found from the measurements using toluene (HPLC purity) as a standard and amounted to 1.2822×10^{-4} ($\pm 0.0006 \times 10^{-4}$). The normalization of photodiodes was done with use of polystyrene standard dissolved in THF. Finally, using polystyrene standards the inter-detector delay (0.029 cm^3) and the calibration constant between UV/VIS and MALLS detectors were found to amount to 0.698.
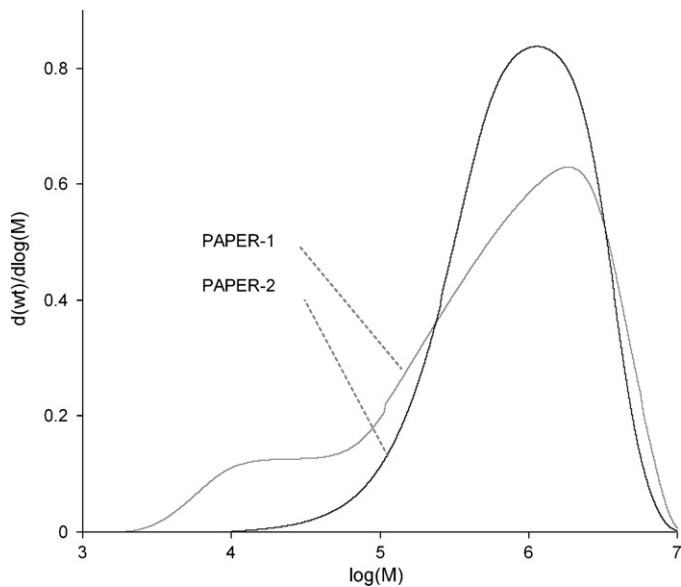
Fig. 2. Molecular weight distribution (SEC–UV/VIS) of an exemplary samples of PAPER-1 and PAPER-2 presented as a density function of log(M).

4. Results and discussion

4.1. Determination of Mark-Houwink coefficients

For the calculations of the molecular masses the cotton paper (PAPER-2) samples were used, since it does not contain hemicelluloses and distribution plot for such a sample is monomodal (see example in Fig. 2). The weight average molecular mass was transformed into the degree of polymerization according to Eq. (7):

$$DP = \frac{M}{M_{\text{mono}}} \tag{7}$$

with the assumption that the degree of substitution of the cellulose samples is 2.925 [10].

The values of MH coefficients K and α, were found from Eq. (1). To build the experimental dependence, the [η] values were found from viscometric results and the DP values – from SEC–MALLS measurements. Each data point represents the DP value calculated from average efflux time from at least 3 measurements with the standard deviation in most cases not higher than 0.5%. The parameters were found fitting the experimental data using nonlinear regression of the power-type function expressed by Eq. (1). The results are shown in Fig. 3. The optimized values amounts to $K = 1.87 \pm 0.22$ cm^3/g, $\alpha = 0.771 \pm 0.016$ for the DP values dropping in the 180–1900. According to [1], the value of α found by us refers to flexible polymer chains ($\alpha = 0$ refers to spherical conformation, $\alpha < 0.5$ – to branched polymer structure, $\alpha > 0.8$ – to more extended molecular conformation and $\alpha = 2$ – rigid rod conformation) which is the case of cellulose in CED. This supports the MH coefficients values determined in this study.

Fig. 4 shows the discrepancies between DP values derived from viscometric measurements with the new optimized values of the MH coefficients and the literature MH values for the cellulose solutions in CED (Table 1). Let us note that the MH coefficients obtained by us cover broader range of DP values than the values found in the literature. For the sake of discussion the DP vales calculated from the literature MH coefficients values cover also the range used by us.

Let us note, that despite substantial differences in the values of MH coefficients, the results by Gruber and Marx-Figini give similar DP values to those determined experimentally in this study.
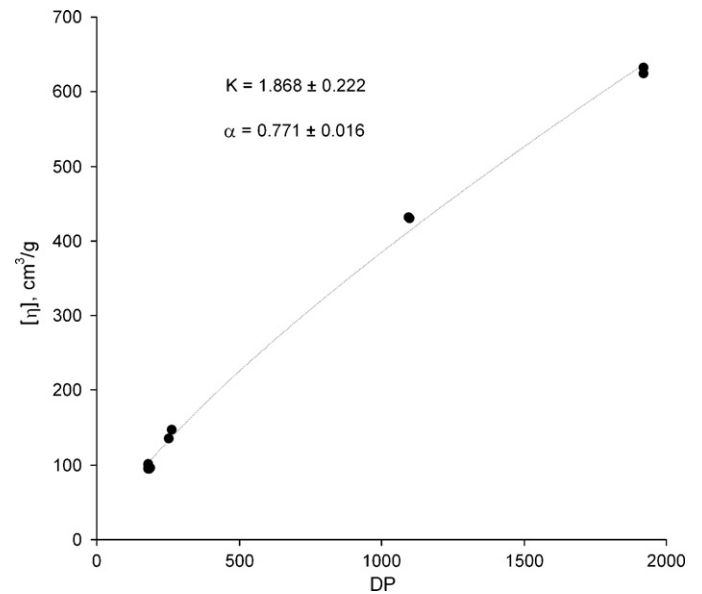

Fig. 3. Dependence of intrinsic viscosity [η] of cellulose in CED solution derived from viscometric measurements on degree of polymerization (DP) derived from SEC–MALLS measurements; both obtained for unaged and aged PAPER-2 samples varying in ageing conditions (NO$_2$ concentration).

The α coefficient responsible for the function concavity is similar for Gruber and our results. In contrast, the Marx-Figini parameters refer in fact to linear [η] dependence of DP, which is not the case of our results even in the range below 950 DP (Fig. 3). An interesting observation is that contrary to the validity ranges given by these authors (Table 1) the trend in the discrepancies is opposite: higher for lower values of DP for Marx-Figini and higher for higher values of DP for Gruber. The calculation of DP with Immergut parameters for the analyzed set of the samples leads to the values which are about 2 times lower, and Evans MH parameters – higher than those obtained by us.
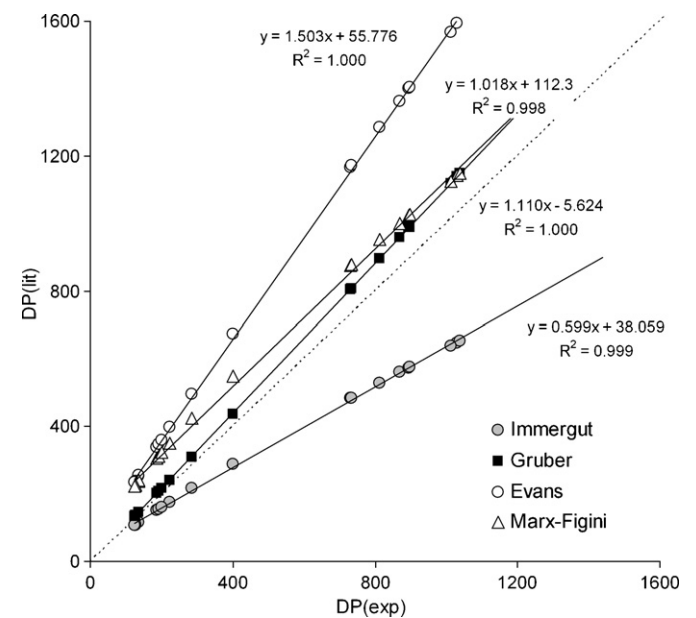
Fig. 4. Comparison of the DP values determined viscometricly in CED solution with use of various sets of MH coefficients: literature (lit) and experimental (exp) for PAPER-1 and PAPER-2 samples aged at various NO$_2$ concentrations (DP of unaged samples also included).
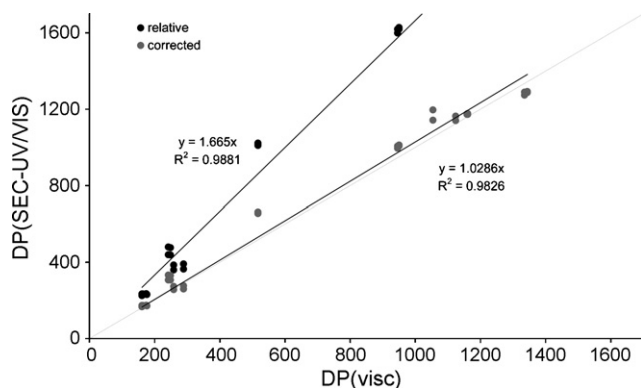
Fig. 5. Correlation between *DP* derived from SEC–UV/VIS and viscometric measurements for PAPER-1 and PAPER-2 samples aged at various NO$_2$ concentrations; *relative* – refers to SEC–UV/VIS calibrated with polystyrene standards without universal calibration, *corrected* – including universal calibration.

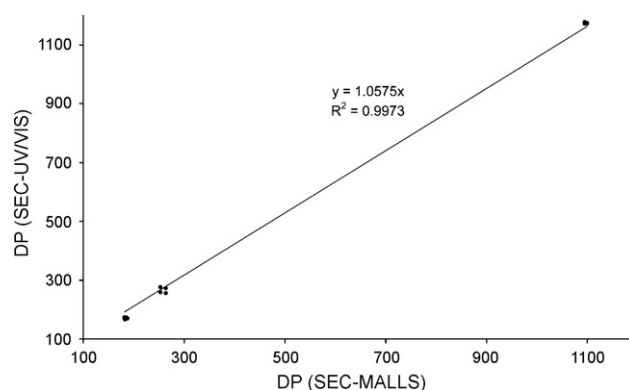### 4.2. Correlation between SEC–UV/VIS and viscometric measurements

The correlation is based on the comparison between the viscometric results of *DP* calculated with the new optimized values of MH coefficients for cellulose in CED found in this study and the *DP* values obtained from MWD from SEC–UV/VIS analyses. Two correlation curves are considered for the SEC results with (corrected *DP* values) and without (relative *DP* values) the universal calibration collected for the PAPER-1 and PAPER-2 samples at various degradation stages. The correlation presented in Fig. 5 represents one viscometric result (average from 3 measurements of the efflux time) plotted against a single chromatographic injection.

The universal calibration can approach the real values of masses of an analyzed polymer provided that the MH coefficients both for an analyzed sample and a standard used for calibration have been determined properly. In our study the literature values of MH coefficients for both the CTC in THF ($Q = 0.00343$ cm^3/g and $a = 0.869$) and the polystyrene in THF ($Q = 0.01258$ cm^3/g and $a = 0.715$) were used. For various sets of the MH coefficients found in the literature and listed in Table 2 the weight average molecular masses were calculated from Eq. (4) and recalculated to *DP* by Eq. (7). No matter which set of the coefficients was used the resulted values did not differ significantly from one another, which may be due to the low impact of the exponent values only slightly differing between each other (Table 2) on the resulting values of molecular masses.

The correlation curves in Fig. 5, represent the *DP* values derived from weight average molecular masses M_w from SEC–UV/VIS experiments viscosity-average molecular masses M_v from viscometric measurements. Since, according to our calculations, the difference between the values of M_w and M_v derived from MWD curves from SEC analyses is very small and does not exceed 5% as related to the M_w (Eq. (8)), the difference between the values lies in the α coefficient in CTC in THF (0.869) used in the formula for M_v (Eq. (9)). Thus, we decided to use consequently M_w for the

Fig. 6. Correlation between *DP* derived from SEC–UV/VIS with universal calibration and SEC–MALLS for PAPER-2 samples aged at various NO$_2$ concentrations (50 measurements).

calculations of *DP* in the whole paper.

$$M_w = \frac{\sum H_i M_i}{\sum H_i} \tag{8}$$

$$M_v = \left[\frac{\sum H_i M_i^\alpha}{\sum H_i} \right]^{1/\alpha} \tag{9}$$

Unlike relative values the corrected values of *DP* obtained from the SEC–UV/VIS measurements with the universal calibration are in a very good agreement with the *DP* obtained from the viscometric measurements with the newly determined MH coefficients (Table 1). Contrary to the works referred in Section 1 [3–5], in our research even for the most degraded paper samples the viscometry technique give results being in general agreement with those obtained by SEC. In our opinion the key factor is the value of the product $[\eta] \cdot c$, which in particular for the samples with low *DP* should be kept within the limits prescribed in the standard [2].

The validation of the universal calibration performed on SEC–UV/VIS results using MH coefficients for cellulose derivative in THF will be compared with the results of the absolute mass determination by SEC–MALLS. The correlation curve for the DP values calculated from M_w (50 measured points) presented in Fig. 6 shows an excellent agreement between two methods of molecular mass determination. However, it has to be taken into account that although the weight average molecular masses coincide the two methods produce the results differing in dispersion as shown in Fig. 7 for the exemplary initial PAPER-2 sample.

The most important conclusion is that to be able to compare the results of viscometric measurements with the results obtained with SEC–UV/VIS universal calibration is the obligatory step in the SEC data processing. It gives the DP values which agree well with the absolute DP derived from SEC–MALLS measurements. A good agreement between viscometric and SEC–UV/VIS results is the validation of both the determination of MH coefficients for cellulose in CED and the universal calibration.

4.3. SEC–MALLS in studies of NO$_2$ induced paper degradation

Despite its complexity, SEC–MALLS seems to be the most sensitive, direct and universal tool to follow the depolimerization of cellulosic materials. In order to demonstrate this a series of degraded cellulose samples used in the present study was obtained in a non-standard method of accelerated aging with use of acidic air pollutant NO$_2$. The influence of NO$_2$ on paper degradation was discussed in details elsewhere [18].

The samples were thermally aged in a sealed glass vessels with different amounts of NO$_2$ injected at the start of a given experi-

Table 2
Mark-Houwink coefficients for Eq. (2) for polystyrene and cellulose derivative CTC in THF.

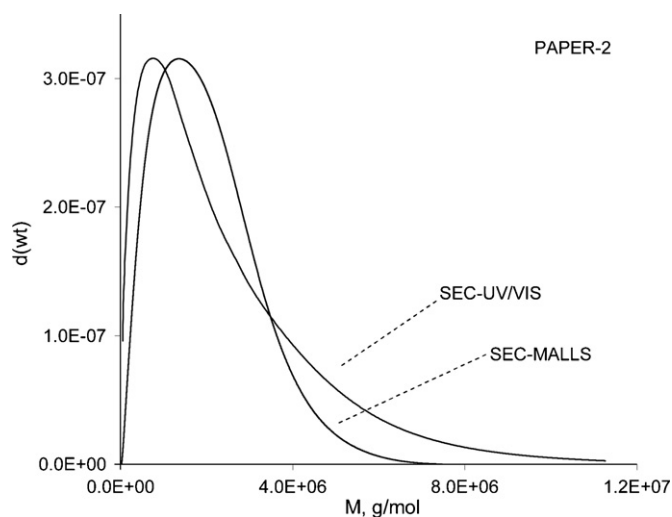| Polymer	Q [ml/g]	a	Source
Polystyrene	0.01258	0.715	Perkins and Haehn [15]
	0.016	0.703	Mahabadi [16]
Cellulose tricarbanilate	0.00343	0.869	Barkalow et al. [17]

Fig. 7. Exemplary molecular mass distribution obtained for the unaged initial PAPER-2 sample with SEC–MALLS and SEC–UV/VIS with universal calibration.

ment. The changes of molecular weight distribution (SEC–MALLS) as a function of the initial concentration of the pollutant are presented in Fig. 8. The profiles are shown here to illustrate the ability of the SEC–MALLS method to trace the extent of degradation. A real advantage of the SEC–MALLS method over SEC–UV/VIS and viscometry is that it provides:

(i) the information on the molecular mass distribution at a certain degradation stage which is important to study the mechanism of cellulose degradation. Looking at the molecular mass distributions presented in Fig. 8 for the PAPER-1 it becomes clear
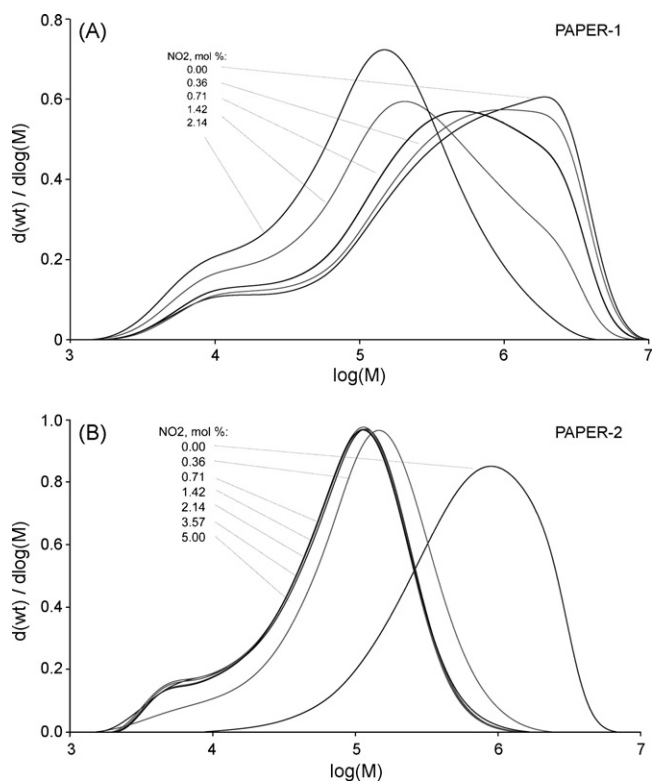

Fig. 8. Molecular mass distributions obtained SEC–MALLS for the series of PAPER-1 (A) and PAPER-2 (B) samples aged in closed vessels at various concentrations of NO$_2$ at 100 °C for 5 days.

that the average values are not fully representative for the whole degradation process especially at low concentrations of the pollutant where we observe broad distributions of the molecular masses.

(ii) the direct values of molecular masses of cellulose. Since cellulose does not have the standards of known average molecular masses and low polydispersion any other than SEC–MALLS configuration requires universal calibration for any kinetic studies of cellulose degradation.

(iii) it can be used for any type of paper including the most popular lignin containing papers for which viscometric methods fails.

5. Conclusions

Classical capillary viscometry and SEC are the most frequently used analytical methods for monitoring degradation of cellulose at a molecular level. Several attempts of the comparative evaluation of both techniques have been made for a number of different solvent systems (cadoxen or CED for viscometry, LiCl/DMAc or CTC/THF for SEC) and large discrepancies were observed. The results obtained in the present work over a wide range of molecular masses for two tested types of paper show a very good correlation between *DP* values from viscometric method and SEC analyses with UV/VIS detection. The viscometric technique could be regarded as a primary method of molecular mass determination for polymers (meaning: requiring no standards) if only Mark-Houwink coefficients are known for a given system (sample/solvent/temperature). The SEC–MALLS results collected here provide new data for determining these values for cellulose.

The efforts of the researchers towards the adjustment of the SEC technique for the analyses of cellulosic materials will bring about its wider implementation in the area of conservation science and in the analytical laboratories of the pulp and paper industry in order to replace the labor-intensive traditional viscometric method limited to pure cellulose samples to easy-to-automate modern instrumental technique giving information-rich highly repeatable results.

In the studies of paper degradation mechanism and kinetics the SEC–MALLS seems to be the most appropriate method as it can provide the information on the whole molecular mass distribution during the processes leading to cellulose depolymerization and gives the direct values of the molecular masses without the necessity of using additional calibrations as in SEC–UV/VIS method.

Nomenclature

A_2	second virial coefficient in Rayleigh equation – solvent–solute interactions
α	Mark-Houwink (MH) coefficient and angle of scattered light in MALLS detector in Rayleigh equation
c	concentration of a polymer, mg/cm^3
DP	degree of polymerization
$[\eta]$	intrinsic viscosity, cm^3/g
K, α	Mark-Houwink (MH) coefficients for a polymer for the $[\eta]$ dependence on DP
Q, a	Mark-Houwink (MH) coefficients for a polymer for the $[\eta]$ dependence on M
λ	vacuum wavelength of incident beam, nm
M	average molecular mass of a polymer, g/mol
M_{mon}	molecular mass of a monomer, g/mol
M_v	viscosity-average molecular mass, g/mol
M_w	weight average molecular mass (obtained by SEC–MALLS), g/mol
n_0	refractive index of a solvent
N_A	Avogadro's number

dn/dc	refractive index increment
$P(\alpha)$	form factor in Rayleigh equation – scattered light dependence on angle
$R(\alpha)$	excess Rayleigh ratio – the difference between Rayleigh ratio for a solution and a pure solvent
V_{el}	elution volume, cm^3
w	fraction of molecular mass M of a polymer

Acknowledgements

References

[1] S. Mori, H.G. Barth, Size Exclusion Chromatography, Springer, Heidelberg, 1999.
[2] SCAN-CM 15:88 Viscosity in cupri-ethylenediamine solution, Scandinavian Pulp, Paper and Board Testing Committee, 1988.
[3] A.L. Dupont, G. Mortha, J. Chromatogr. A 1026 (2001) 129.
[4] M. Strlič, J. Kolar, M. Zigon, B. Pihlar, J. Chromatogr. A 805 (1998) 93.
[5] J. Malešič, J. Kolar, M. Strlič, D. Kočar, D. Fromageot, J. Lemaire, O. Haillant, Polym. Degrad. Stab. 89 (2005) 64.
[6] Step project CT 90-0100, The effects of air pollutants on the accelerated ageing of cellulose containing materials – paper. TNO, Delft, 1994.
[7] T. Sawoszczuk, A. Barański, J.M. Łagan, T. Łojewski, K. Zięba, J. Cult. Heritage 9 (2008) 401.
[8] R. Stol, J.L. Pedersoli Jr., H. Poppe, W.T. Kok, Anal. Chem. 74 (2002) 2314.
[9] J.M. Lauriol, J. Comtat, P. Froment, F. Pla, A. Robert, Holzforschung 41 (1987) 165.
[10] J. Daňhelka, I. Kössler, J. Polym. Sci. 14 (1976) 287.
[11] M. Marx-Figini, Angew. Makromol. Chemie 72 (1978) 161.
[12] M. Gruber, R. Gruber, Das Papier 35 (1981) 133.
[13] E.H. Immergut, J. Schurz, H. Mark, Monatsh. Chem. 84 (1953) 219.
[14] R. Evans, A.F.A. Wallis, Fourth Int. Symp. Wood Chem., Paris, 1987, p. 201.
[15] G. Perkins, J. Haehn, J. Vinyl Technol. 12 (1990) 12.
[16] H.Kh. Mahabadi, J. Appl. Polym. Sci. 30 (1990) 1535.
[17] D.G. Barkalow, R.M. Rowell, R.A. Young, J. Appl. Polym. Sci. 37 (1989) 1009.
[18] A. Johansson, Air Pollution and Paper Deterioration. Causes and Remedies, Doctorate Thesis, Göteborg University, 2000.