Improved Methods for Evaluating the Molar Mass Distributions of Cellulose in Kraft Pulp

Rickard Berggren, Fredrik Berthold, Elisabeth Sjöholm, Mikael Lindström

Swedish Pulp and Paper Research Institute, Box 5604, SE-114 86 Stockholm, Sweden

Received 3 January 2002; accepted 16 April 2002
Published online 18 February 2003 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/app.11767

ABSTRACT: Multi-angle laser light scattering (MALLS) was used to characterize birch kraft pulps with respect to their absolute molecular mass distributions (MMDs). The pulps were dissolved in lithium chloride/*N*,*N*-dimethylacetamide and separated by size exclusion chromatography (SEC). The weight-average and number-average molecular masses of the cellulose fractions of the pulps obtained from the absolute MALLS measurements were compared with the molar masses obtained by direct-standard-calibration relative pullulan standards. Discrepancies between the two detection methods were found, and two ways of correlating the relative pullulan molar masses to the absolute molar masses were examined. In the first method, the correlation was made over a large range of molecular masses. The second method correlated the molecular masses of the standards to the molecular masses of samples by the calculation of fictitious, cellulose-equivalent molar masses of the standards. With the preferred second method, a more correct MMD of kraft pulp samples could, therefore, be obtained from an SEC system calibrated with narrow standards. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1170–1179, 2003

Key words: polysaccharides; light scattering; molecular weight distribution/molar mass distribution; gel permeation chromatography (GPC)

INTRODUCTION

The main purpose of the kraft pulping and bleaching of wood is to release the fibers and remove the lignin. Cellulose, which is the main load-bearing molecule in pulp fibers, is, however, degraded during processing, and this leads to a decrease in the strength properties of the pulp.[1] The degradation of cellulose on a molecular level is usually monitored by the measurement of the intrinsic viscosity of the pulp dissolved in cuprietylenediamine.[2] The intrinsic viscosity provides only an average estimation of the degree of polymerization of the cellulose and the other wood polymers present. More detailed information about the degree of degradation can be obtained if the molecular mass distribution (MMD) of the pulp is characterized with size exclusion chromatography (SEC).

The main complication in the characterization of the MMD of wood polymers by SEC is the limited solubility of the polymers in solvents suitable for chromatography. Several ways to circumvent this have been suggested. Tetrahydrofuran may be used to dissolve tricarbanilated samples, but high-lignin-content samples require delignification before derivatization.[3] The carbanilation may be performed in either pyridine or dimethyl sulfoxide. Losses of low molecular mass materials can, however, occur during carbanilation,[4] and more seriously, the degradation of high molecular mass material can take place.[5]

One of the most commonly used solvents for cellulosic materials is lithium chloride (LiCl) dissolved in dimethylacetamide (DMAc).[6] This solvent–sample system is stable,[7–9] and no derivatization of the sample is needed to dissolve cotton and birch kraft pulp samples.[10,11] However, solubility problems of underivatized softwood pulps due to the hemicellulose content have been reported.[12,13]

The separation system used in SEC needs calibration. The calibration may be performed with broad standards,[14] with a set of narrow standards, or by universal calibration.[14–16] A common method of calibrating the chromatographic system used for the characterization of pulps is using a series of well-characterized pullulan standards. Pullulan is a polymer consisting of α-(1,4)-D-glucopyranose units, with every third 1,4-linkage replaced by a 1,6-linkage, whereas cellulose consists solely of β-(1,4)-glucopyranose units.[17] This difference between standards and samples has been found to cause an overestimation of the molecular mass and its distribution in water-soluble cellulose derivatives[18] and chitosans.[19]

Recent studies have illustrated the ability to characterize dissolving pulps in LiCl/DMAc with light scattering detection,[20,21] which eliminates the need for calibration with standards.[22]

The purpose of this article is to present results obtained by the characterization of birch kraft pulps with SEC and light scattering detection [SEC/multi-angle

Correspondence to: R. Berggren (rickard.berggren@stfi.se).

laser light scattering (MALLS)/refractive index (RI)]. Discrepancies between absolute molar mass determinations and determinations of the molar masses determined relative to pullulan standards (SEC/RI) are pointed out, along with two methods used to correct these discrepancies.

LIGHT SCATTERING THEORY

Static light scattering is an absolute detection technique providing the weight-average molecular mass (M_w) of a sample according to the following equation:

$$\frac{K^*c}{R(\theta)} = \frac{1}{M_w P(\theta)} + 2A_2c \quad (1)$$

where the constant K^* is defined as

$$K^* = \frac{4\pi^2\left(\frac{dn}{dc}\right)^2 n_0^2}{N_A\lambda_0^4} \quad (2)$$

c is the polymer concentration, $R(\theta)$ describes the excess of scattered light from the polymer at angle θ, $P(\theta)$ is a form factor, A_2 is the second virial coefficient, dn/dc is the specific RI increment of the polymer in solution, n_0 is the RI of the solvent, λ_0 is the wavelength of the incident light *in vacuo*, and N_A is Avogadro's number.[22] The measurements can be performed in batch mode, that is, the direct measurement of the scattered light at a number of specified concentrations, or by the attachment of the detector to a SEC column followed by a concentration-sensitive detector. The batch mode provides M_w, A_2, and the radius (root-mean-square radius) of the sample in solution, whereas the online mode provides the mass and radius distributions along with mass averages [number-average molecular mass (M_n), M_w, and z-average molecular mass (M_z)]. As the concentration of the sample and, therefore, the second term of eq. (1) becomes very low, A_2 is normally neglected during online measurements. The molecular mass of the eluting sample is obtained from eq. (1) in every slice of the chromatogram, and this makes the use of standards unnecessary.

EXPERIMENTAL

Materials

The samples used in this study were a selection of unbleached, oxygen-delignified and fully bleached birch kraft pulps, both laboratory- and industrially produced. In total, five unbleached pulps, two oxygen-delignified pulps and one fully bleached pulp were used. The pulp samples had intrinsic viscosities of 1300–970 mL/g.[2]

Wood polymer beads (WPBs) were produced as described by Lindström et al.[23] from a fully chlorine dioxide-bleached industrial kraft pulp with an intrinsic viscosity of 1150 mL/g and from an unbleached birch kraft pulp with an intrinsic viscosity of 1300 mL/g.[2]

All chemicals used were analytical-grade, except for toluene, which was UV-spectroscopy grade. DMAc was obtained from Sigma Aldrich (Steinheim, Germany), and LiCl, toluene, hydrochloric acid, sodium chloride, and methanol were obtained from Merck (Darmstadt, Germany). Polystyrene and pullulan standards were obtained from Pressure Chemicals Co. (Pittsburgh, Pennsylvania) and Polymer Laboratories (Shropshire, UK), respectively.

Degradation of WPBs

WPBs from the fully bleached pulp were degraded under soda–anthraquinone (AQ) pulping conditions. For full details, see Östlund.[24] The temperature was varied between 130 and 170°, the alkali levels were varied between 0.1 and 0.7*M*, and the AQ levels were varied between 0.1 and 9%. The liquid/wood ratio was kept constant at 200/1.

WPBs made from the unbleached pulp were degraded by acid hydrolysis. A sample of 15 mg (o.d.w.) was degraded with 5 mL of 2*M* hydrochloric acid at ambient temperature. The degradation times were 1, 3, and 23 h, respectively. Degraded WPBs were washed repeatedly with deionized water to neutral pH before dissolution.

Dissolution of the samples

The solvent exchange and dissolution of the samples were performed as previously described.[25] Washed samples were swelled with 50 mL of deionized water at 4°C for 1 h. The water was removed by vacuum filtration, and 50 mL of methanol was added. The methanol was removed by vacuum filtration after 30 min, and the procedure was repeated twice with methanol and three times with degassed DMAc. A solution of 8% (w/v) LiCl in DMAc, prepared from dried LiCl and degassed DMAc, was added to 15 mg of each sample and gently stirred under nitrogen at 4°C for 5 days. The dissolution time was shortened from 5 days to 1 day for the WPB samples. The samples were then equilibrated at room temperature for 30 min and diluted with degassed DMAc to a sample concentration of 0.05% and a LiCl concentration of 0.5%, respectively. After 2 h, the samples were deaggregated[25] in a poly(tetrafluoroethylene) (PTFE) ball mill for 30 min, filtered on a 0.45-μm PTFE filter

(Advantec, MFS, Pleasanton, CA), and injected into the chromatographic system.

SEC and MALLS

The chromatographic system consisted of a Waters Corp. (Milford, MA) 2690 separation module that included a guard column (mixed-A, 20 μm, 7.5 $\times$ 50 mm) and four mixed-A columns (20 μm, 7.5 $\times$ 300 mm) connected in series. Two separate column sets were used, one for calibration and one for verification of the calibration. All columns were obtained from Polymer Laboratories and thermostated at 80°C. The mobile phase was 0.5% degassed LiCl/DMAc, the flow rate was 1 mL/min, and the injected sample volume was 200 μL. The mobile phase was filtered with a 0.2-μm PTFE inline filter (Millipore).

SEC characterization was performed relative to pullulan standards with one detector setup (SEC/RI, system I) and by light scattering (SEC/MALLS/RI, system II) with another detector setup. Relative and absolute detection was also performed simultaneously in series. The detectors for system I were a Waters 2487 UV detector operating at a wavelength of 295 nm and a Waters 410 RI detector thermostated at 40°C. For the light scattering detection in system II, the setup was a MALLS detector (Dawn DSP) and an Optilab DSP RI detector (both from Wyatt Technology Corp., Santa Barbara, CA). Both instruments were operated at 488 nm. The order of the detectors was as follows: MALLS, UV, Optilab RI, and Waters RI.

Four mixtures of narrow pullulan standards with nominal masses of 738 Da, 5.8 kDa, 12.2 kDa, 23.7 kDa, 48 kDa, 100 kDa, 186 kDa, 380 kDa, 853 kDa, and 1660 kDa were used for the calibration of system I, the SEC/RI system.

The chromatographic system and data from system I were controlled and evaluated with Millennium 3.05.01 software (Waters).

The Optilab RI used in system II was thermostated at 40°C. The output voltage from the detector was calibrated to a known concentration of the sample by the injection of six known concentrations of sodium chloride dissolved in deionized water; this resulted in an instrument-specific RI calibration constant. The delay volume between the MALLS detector and the Optilab RI detector was 0.267 mL. The light scattering detector was calibrated with toluene and normalized by the injection of 200 μL of a 30-kDa narrow polystyrene standard solution with a concentration of 1 mg/mL in 0.5% LiCl/DMAc.

The detectors used in the Dawn instrument were numbered 4, 5, 6, 7, 8, 10, 12, 14, and 16. Narrow interference filters reducing the fluorescence from any lignin present in the samples were put in front of all the detectors. Detectors at higher and lower angles were omitted because of low signal-to-noise (S/N) ratios.

Light scattering data were evaluated with Astra 4.73.04 software (Wyatt Technology).

RESULTS AND DISCUSSION

dn/dc

dn/dc is a critical constant for light scattering detection because it strongly influences the recorded molecular mass (eq. 2). The constant depends on sample, solvent, temperature and wavelength.[26] dn/dc should be determined by injecting a number of known concentrations of the sample in a calibrated RI detector. Unfortunately, the dn/dc value of LiCl dissolved in DMAc is approximately three times larger (0.324 mL/g)[27] than the reported dn/dc values of cellulose dissolved in LiCl/DMAc.[20,21] In addition, the concentration of LiCl is a magnitude of order larger than the commonly used concentration of cellulosic samples. Consequently, a small variation in the LiCl concentration will strongly affect the estimation of the dn/dc value of cellulose in solution, and therefore introduce an error in the dn/dc value.

For that reason, an alternative method based on the RI response was used. In this method, the area under a chromatogram from a carefully determined amount of the sample is used to calculate the dn/dc value. On the basis of the RI calibration constant and the injected mass, an estimation of dn/dc of the samples is obtained. This procedure assumes a complete recovery of the injected sample. In our case, it was further assumed that the dn/dc value of the constituting wood polymers was the same for the entire sample distribution. This was necessary as the hemicellulose and cellulose distributions in the MMD of a birch kraft pulp overlap.[11] The chromatographic overlap becomes larger the more degraded the pulps are, decreasing the resolution between the MMDs of the hemicellulose and cellulose. The assumption is, however, reasonable, as hemicellulose and cellulose agree chemically to a large extent and no significant differences in the dn/dc values of the substances are expected.

WPBs made from a fully bleached pulp were used for the estimation of dn/dc. It is normally easier to estimate the dry weight of WPBs than that of pulps, and the MMD of the WPBs remains similar to the MMD of the original pulp.[28] Four injections were made at two concentrations (0.499 and 0.698 mg/mL) each. The achieved dn/dc value based on these eight injections was 0.108 $\pm$ 0.006 mL/g.

The dn/dc value determined in this study differs slightly from other reported values for cellulosic samples dissolved in similar solvent mixtures. A dn/dc value of 0.104 in 0.5% LiCl/DMAc analyzed at 633 nm has been reported for dissolving grade pulps[21] con-

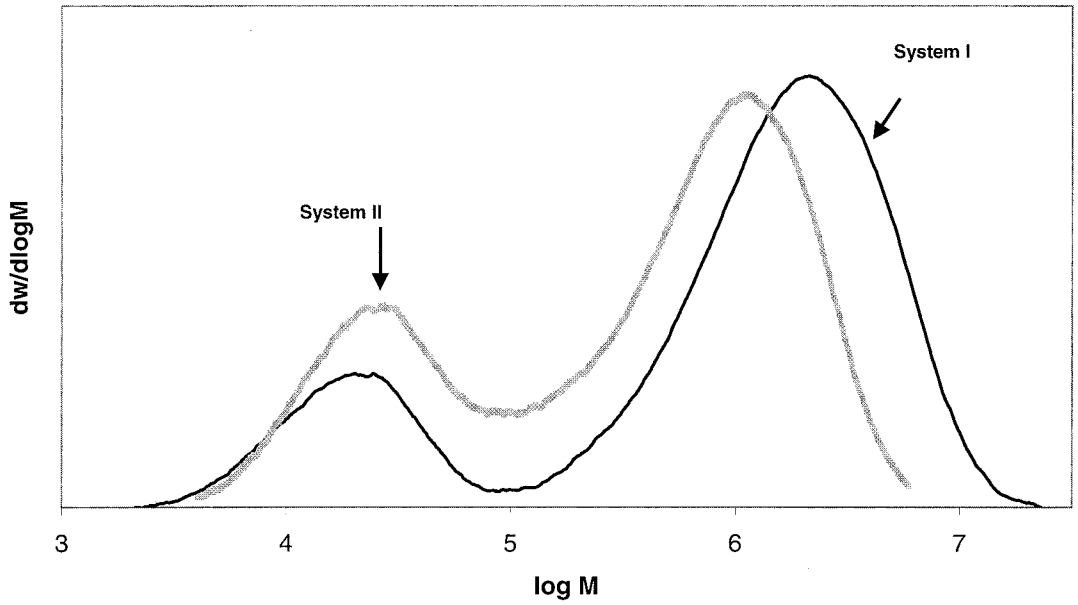

Figure 1 Comparison of MMDs obtained by SEC/RI relative nominal molar masses of pullulan standards (system I) and MMDs obtained by SEC/MALLS/RI (system II) of a bleached birch kraft pulp. The samples were dissolved in 0.5% LiCl/DMAc.

taining only minor amounts of hemicellulose in comparison with kraft pulps. A higher concentration of LiCl (0.9%) in DMAc has also been reported to give higher dn/dc values of cellulose (0.136 mL/g) at 488 nm.[20] As the conditions and samples in the literature differed from those used in this study, the measured value (0.108 mL/g) represents the dn/dc value of cellulose dissolved in 0.5% LiCl/DMAc analyzed at 488 nm.

MMDs of the cellulosic samples

In Figure 1, the MMDs of an unbleached birch kraft pulp measured by SEC/RI (system I) and SEC/MALLS/RI (system II) are shown. The MMD of a hardwood kraft pulp gives a bimodal distribution, with two fairly separated peaks. The distribution in the lower molecular mass range corresponds to the hemicellulose and lignin in the pulp. The part in the high molecular mass range corresponds to the cellulose.[11]

In Figure 2, log M and the RI response, obtained by SEC/MALLS/RI detection, are plotted versus the elution time of the sample. The linear elution curve in the time range 20–27 min indicates no aggregation of cellulose. After 28 min, the linearity of the relationship was disturbed as a result of the lowered S/N because of the low molar mass and low concentration of the hemicellulose and lignin fractions of the sample. The injected amount of the sample was small (0.1 mg), and the hemicellulose fraction was approximately 30% of the injected material in the birch kraft pulp.[11] Because of the low S/N ratio, the low molecular mass range was omitted in this study, and only the cellulose fractions eluting before 28 min were evaluated.

The MMD from system I in Figure 1 resulted in a distribution over a wider molar mass range as well as a larger apparent molar mass of the cellulose fraction than recorded by the SEC/MALLS/RI technique used in system II. The explanation for the wider distribution is not band broadening occurring between the detectors, as no significant band broadening of pullulan peaks was detected between the two RI detectors (data not shown).

The reason for the deviation is probably the structural differences between standards and samples. The standards used for the calibration of system I were pullulans. The 1,6-linkages in pullulan led to conformational freedom of the pullulan.[29] At a given hydrodynamic radius, or elution time, the calculated molecular mass of the cellulose was smaller than the molecular mass of the pullulan, and this led to an overestimation of the molecular mass of the cellulose. This is shown in Figure 3, in which log M of each slice in the chromatogram for three samples of birch kraft pulp obtained by SEC/MALLS/RI and the calibration curve of the pullulan standards with log M according to the supplier are plotted versus the elution time. The difference in the molar masses between the cellulose fraction eluting between 20–28 min and the narrow standard curve increased with increasing molar mass.

Figure 4 shows the logarithm of the molecular masses M_w and M_n of the cellulose fractions estimated by the two detection techniques for two injections of each of 21 samples of various molar masses. The molecular masses from system II (log M_x MALLS) are

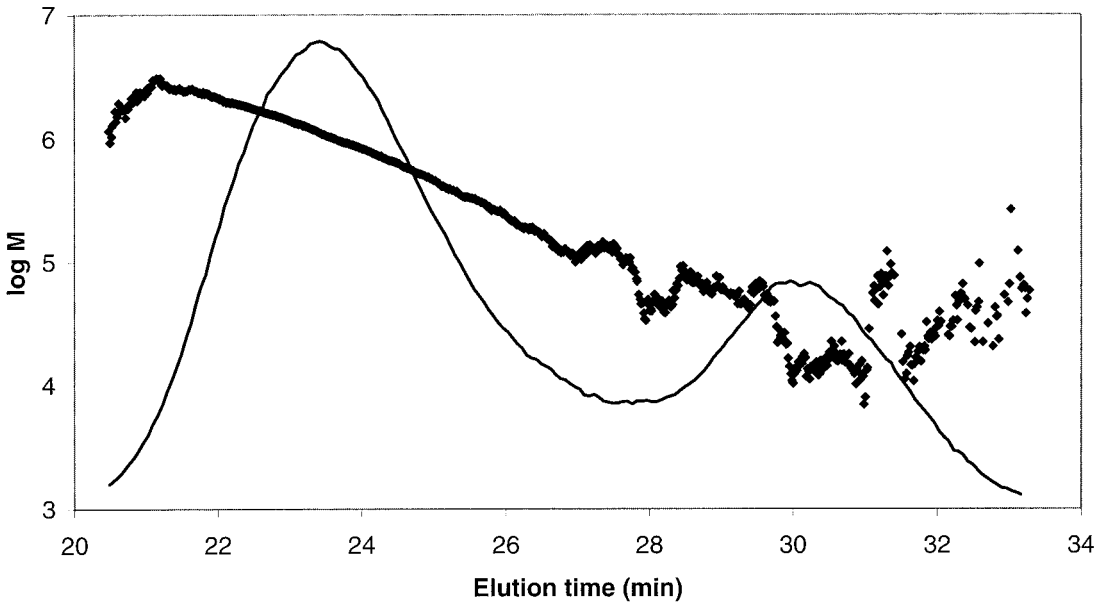

Figure 2 Chromatogram of an unbleached birch kraft pulp, as detected by SEC/MALLS/RI, and the corresponding calibration curve from MALLS.

plotted versus the same average molecular masses (log M_x relative pullulan) obtained by system I. The samples were injected repeatedly over a long period of time (6 months) to include any long-time variation of the chromatographic system. The molar masses of the cellulose were calculated from the distribution plots shown in Figure 1. The lower limit of the cellulose distribution was chosen at the minimum in the MMD around log $M = 5$, at which point a clear distinction between the cellulose and hemicellulose was observed. The deviation between the molar masses obtained by the two detection techniques increased with increasing molar mass. Comparisons between the M_w values of cotton linters obtained by light scattering performed in the batch mode and the M_w values from SEC relative pullulan standards have shown similar

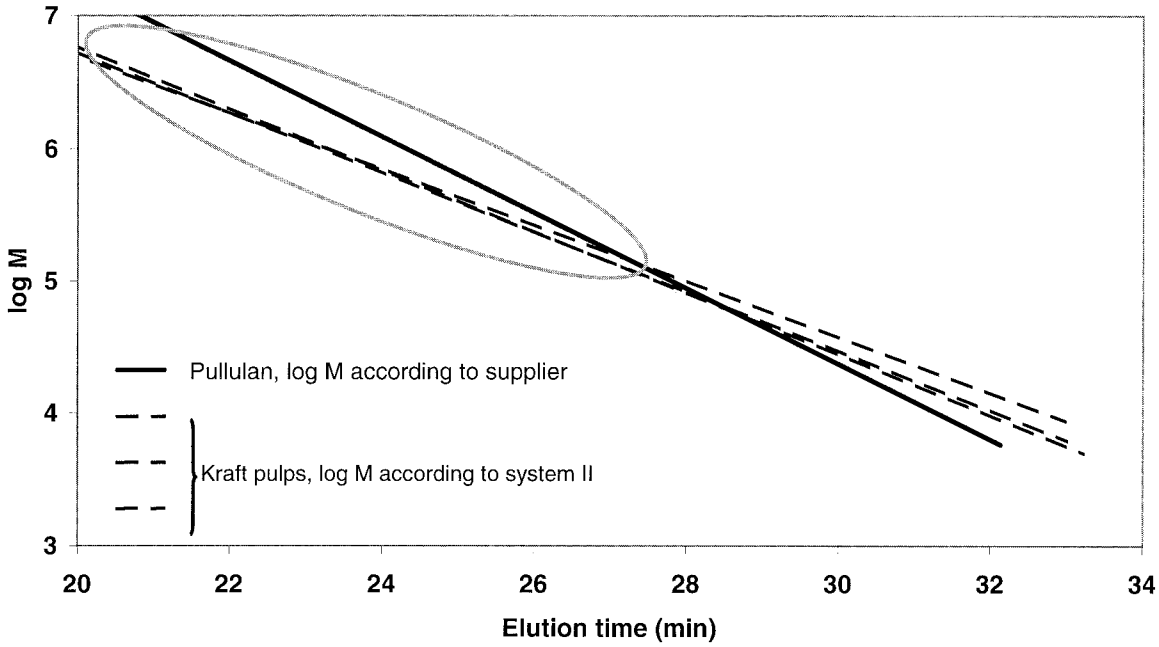

Figure 3 Column calibration curves: log M versus the elution time for pullulan standards and the cellulose fractions of three birch kraft pulps obtained by SEC/MALLS/RI (system II). The circled region corresponds to the molecular mass range of cellulose.

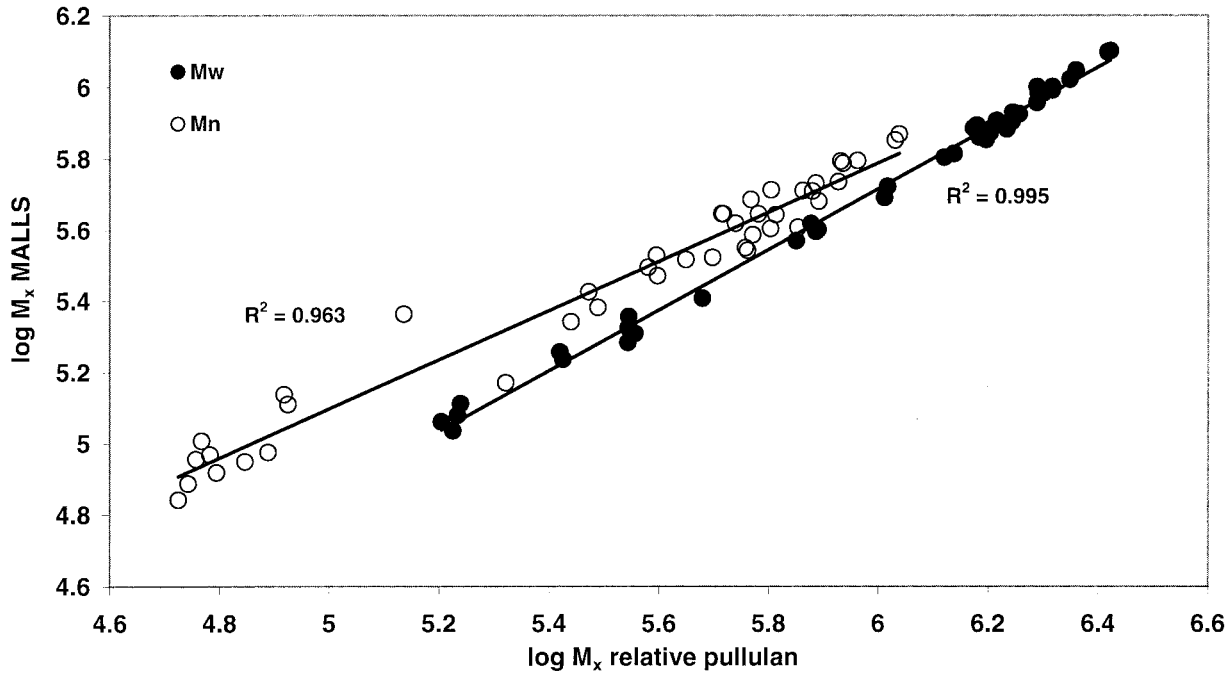

Figure 4 Correlation curve between the molar masses of the cellulose fractions of kraft pulps and WPBs estimated by SEC/MALLS/RI: log M_x MALLS, as the absolute M_w and M_n values, versus log M_x relative pullulan, as the same molar masses estimated by SEC/RI relative nominal molecular masses of standards.

deviations.[25] The deviations in this work were, however, more pronounced than those previously reported.

Improving the evaluation of the MMD of cellulose

The differences in the molar masses calculated by the two detection techniques pointed out in the previous section could be used to improve the accuracy of the molecular masses of cellulose fractions obtained from SEC/RI calibrated with pullulan standards. The corrections could be made in two ways, as proposed by Poché et al.,[18] and the choice depends on the purpose of the correction. If the goal is only to obtain the molar mass of a distribution, the mass determined by SEC/MALLS/RI is correlated to that obtained by SEC/RI, that is, the molar mass of the relative pullulan standards. To obtain a description of the entire MMD that more closely relates to the true molar mass of cellulose, we can use the differences in the slopes and intercepts of the calibration plots in Figure 3 to obtain the cellulose-equivalent molar masses of the pullulan standards dissolved in 0.5% LiCl/DMAc.

Method I: correction of the M_w values of cellulose

This method serves to correlate the incorrect values of M_w and M_n of the cellulose distribution of kraft pulps evaluated with SEC/RI relative standards to more correct values obtained by SEC/MALLS/RI.

The data in Figure 4 can be used to provide correction equations by linear-least-square regression, and the resulting lines from this regression are shown in the figure. The expressions correcting the data from system I to data from system II are described by eqs. (3) and (4), for which the included deviation ranges are calculated according to a t test with a 95% confidence level: [30]

$$M_{w,\text{correlated}} = (4.00 \pm 1.08) \times M_{w,\text{pull}}^{(0.85\pm0.02)} \quad (3)$$

$$M_{n,\text{correlated}} = (43.8 \pm 25.3) \times M_{n,\text{pull}}^{(0.69\pm0.04)} \quad (4)$$

The use of WPBs enabled us to study cellulosic samples with very low molecular masses normally not observed for kraft pulps. The excellent correlations (R^2 = 0.995 and 0.963) are, therefore, also valid in the lower molar mass ranges, indicating the applicability for heavily degraded cellulose samples. A correlation performed in a fashion similar to that for water-soluble cellulose derivatives[18] is, therefore, also valid for underivatized cellulose samples dissolved in LiCl/DMAc and is a convenient method for estimating correct average molar masses by SEC/RI.

Method II: cellulose-equivalent molar masses of pullulan standards

By the recalculation of the molecular masses of the pullulan standards to cellulose-equivalent molar

masses, the entire distribution of cellulose is taken into account. In general, the entire distribution is of interest for the study of the cellulose degradation occurring during kraft pulping and bleaching, not only an average value.[31]

The same procedure was also applied by Poché et al.,[18] and the following serves to show the applicability of the procedure in our solvent–sample system. The slopes and intercepts of the linear calibration curves based on log M of pullulan according to the supplier and those obtained with SEC/MALLS/RI differ (Fig. 3).

The data may be described by two equations:

$$\log M_{\text{pull}} = b_{\text{pull}} + a_{\text{pull}}t \tag{5}$$

$$\log M_{\text{MALLS}} = b_{\text{MALLS}} + a_{\text{MALLS}}t \tag{6}$$

where a is the slope and b is the intercept of the pullulan calibration line and the calibration line from the MALLS measurement, respectively. M_{pull} is the nominal value of the standards, and M_{MALLS} is the molecular mass determined by the MALLS detector at each point of the chromatogram of the pulp sample.

The equations can be used to express cellulose-equivalent molar masses of the pullulan standards, resulting in a better agreement between the data evaluated from SEC/RI and SEC/MALLS/RI. Assuming time t at which the calibration curve of the pullulan and the elution curve of the pulp samples intersect yields

$$M_{\text{MALLS}} = 10^{\left(b_{\text{MALLS}} - \frac{a_{\text{MALLS}} b_{\text{pull}}}{a_{\text{pull}}}\right)} M_{\text{pull}}^{\frac{a_{\text{MALLS}}}{a_{\text{pull}}}} \tag{7}$$

which also may be expressed as

$$M_{\text{MALLS}} = qM_{\text{pull}}^{p} \tag{8}$$

where q and p are functions of the calibration constants a and b in eqs. (5) and (6).

The narrow standards have a nominal molecular mass M_{pull} determined by ultracentrifugal sedimentation equilibrium according to the supplier. This value of an arbitrary pullulan standard may by inserted into eq. (8), and this results in the equivalent molar mass of the cellulose eluting at any time t from the MALLS detection. Knowing that the standards differ from cellulose in structure and, therefore, in the elution time at a given molar mass, we can calculate a cellulose-equivalent molar mass of the narrow standards, $M_{\text{cell.eq.}}$, by eq. (8):

$$M_{\text{cell.eq.}} = M_{\text{MALLS}} = qM_{\text{pull}}^{p} \tag{9}$$

The constants b_{MALLS} and a_{MALLS} differ slightly from sample to sample and also from injection to injection according to Figure 3. To estimate the constants q and p in eq. (8) while minimizing errors, we performed 30 injections with high molecular mass birch kraft pulps and WPBs covering a broad molecular mass range. Only the cellulose fraction was taken into account while we estimated the constants q and p, as the low S/N ratio of the hemicellulose fraction would have increased the error of the constants. The resulting cellulose-equivalent molar masses of the pullulan standards are shown in Table I, with standard deviations.

TABLE I
Nominal and Cellulose-Equivalent Molar Masses of Pullulan Standards Based on Method II Along with Standard Deviations of the Cellulose-Equivalent Molar Masses (n = 30)

Nominal molecular mass	Cellulose-equivalent molecular mass	Standard deviation
738	2,300	980
5,800	11,200	3,600
12,200	19,800	5,500
23,700	33,100	8,400
48,000	57,300	12,700
100,000	101,000	19,100
186,000	164,000	26,800
380,000	287,000	39,300
853,000	540,000	62,300
1,660,000	912,000	98,000

The fictitious calibration curve agrees well with the elution curve of cellulose fractions from system II, as can be seen in Figure 5, especially in the elution range of the cellulose (20–28 min). The two calibration curves deviate only slightly in the low molecular mass range, and the standard deviations also increase in the low molecular range. These larger deviations are, however, located well outside the elution range of cellulose in the studied separation system.

Applicability of the improved evaluation methods

The applicability of the two methods was tested with WPBs from an unbleached birch kraft pulp degraded by acid hydrolysis. The samples were degraded differently than the samples used for calibration, and a brand new column set was used. In Figure 6, the MMDs of the undegraded WPBs, as obtained by three different methods, are shown by SEC/RI relative to the nominal molar masses of pullulan standards ($\text{MMD}_{\text{rel.pull.}}$), by SEC/MALLS/RI ($\text{MMD}_{\text{MALLS}}$), and by SEC/RI relative to cellulose-equivalent molar masses of standards according to method II ($\text{MMD}_{\text{rel.cell.eq.}}$).

The SEC/RI method calibrated with nominal molar masses of pullulan provided a broader distribution of cellulose of the WPBs than the SEC/MALLS/RI tech-

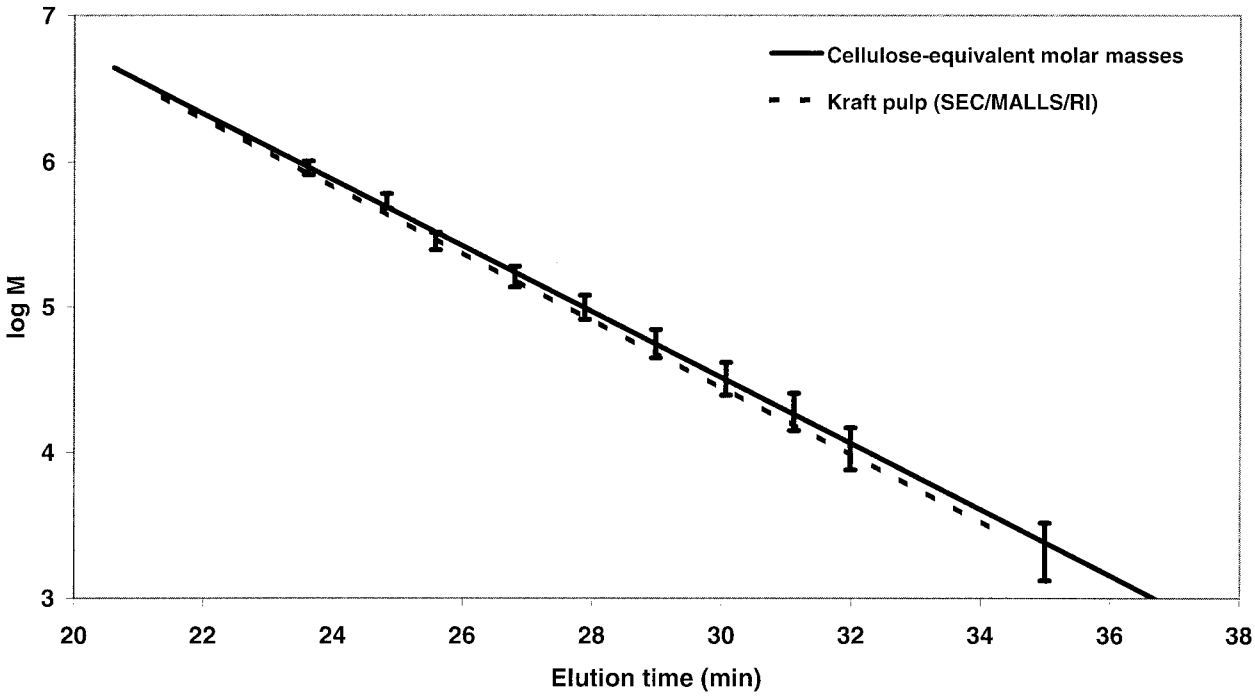

Figure 5 Column calibration curves: log M versus the elution time for cellulose-equivalent molar masses of pullulan standards with standard deviation bars and the calibration curve obtained by SEC/MALLS/RI of the cellulose fraction of a birch kraft pulp.

nique, as previously shown. $MMD_{rel.cell.eq.}$ agrees much better with MMD_{MALLS} than $MMD_{rel.pull.}$. Method II is, therefore, a more correct way of achieving MMDs of cellulosic samples than direct standard calibration.

Figure 7 shows the M_w values of undegraded and acid-degraded WPBs determined in four different ways. M_w was obtained by SEC/RI relative nominal and cellulose-equivalent masses of standards, by SEC/MALLS/RI, and by the application of method I to M_w-values obtained from SEC/RI relative to nominal masses of standards. The calibration with nominal masses widely overestimated the M_w-values in comparison with the M_w-values from SEC/MALLS/RI. These overestimations decreased by using either method I or II.

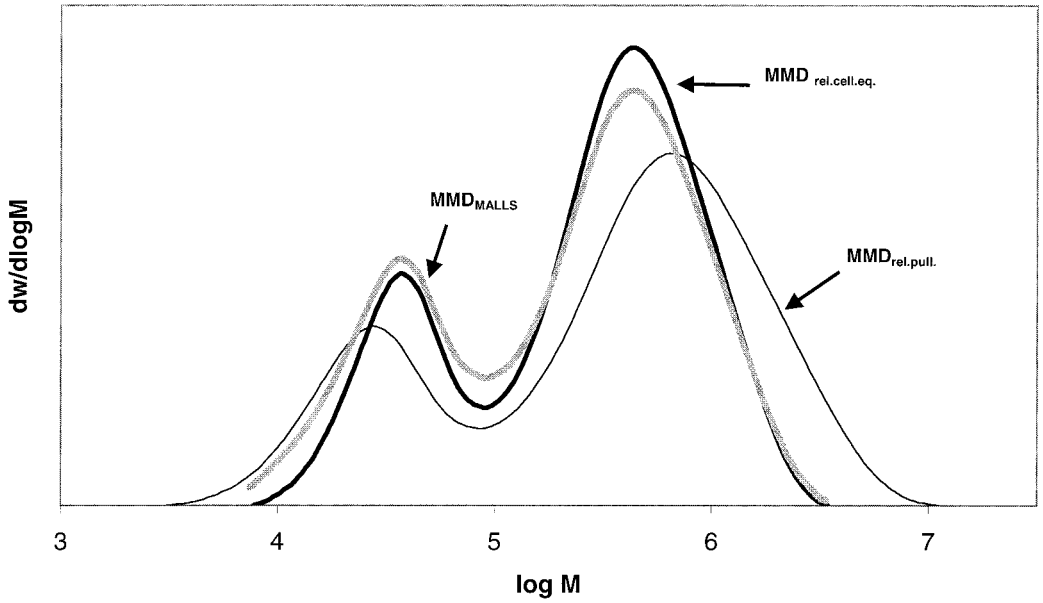

Figure 6 Comparison of MMDs of a bleached birch kraft pulp: $MMD_{rel.pull.}$, $MMD_{rel.cell.eq.}$ (method II), and MMD_{MALLS}.

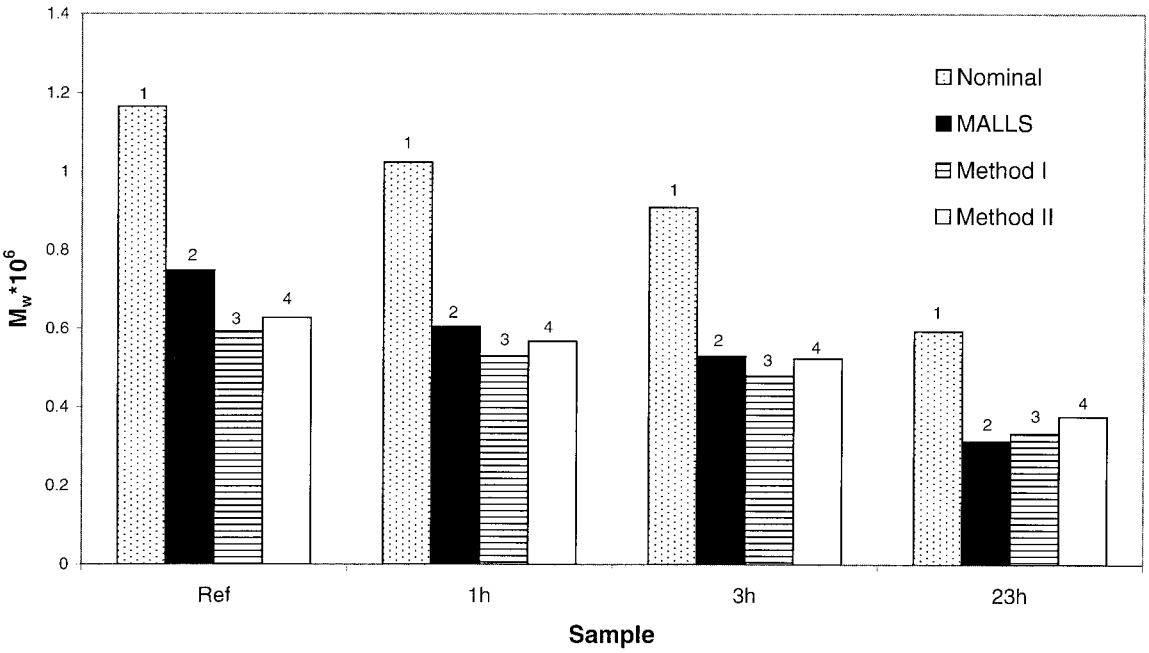

Figure 7 M_w values of the cellulose fractions of undegraded and acid-degraded WPBs (the degradation was performed for 1, 3, and 23h) : (1) relative nominal molar masses of pullulan standards, (2) molar masses determined by SEC/MALLS/RI, (3) molar masses determined with method I (i.e., corrected M_w values estimated from relative nominal molar masses of standards), and (4) molar masses determined with method II (i.e., relative cellulose-equivalent molar masses of pullulan standards).

Under the assumption that SEC/MALLS/RI gives the true value, the errors from the other methods are presented in Table II. The errors decreased significantly, regardless of the method used for correcting the overestimated values obtained by SEC/RI relative nominal molar masses of standards. The accuracy would probably have been even better if the same column set had been used for both calibration and testing, as the chromatographic behavior may vary slightly from column to column.

Therefore, we suggest that method II should be used to characterize cellulose in birch kraft pulps with respect to M_w and MMD by SEC/RI when a MALLS detector is not available, as the error of the estimation is lower in comparison with M_w values estimated from direct pullulan standard calibration.

TABLE II
Relative Error of the Estimated M_w Values of Acid-Hydrolyzed WPBs Shown in Figure 7

Hydrolysis time (h)	a: Nominal (%)	b: Correcting equation	c: Cellulose equivalent (%)
0	+55	−20	−16
1	+70	−12	−6
3	+70	−9	−1
23	+90	+6	+20

M_w estimated: a = relative nominal molar masses of standards, b = by method I, and c = by method II. All values were compared to values from SEC/MALLS/RI. The signs denote overestimation (+) and underestimation (−).

CONCLUSIONS

Two methods of correcting the molar masses of cellulose in birch kraft pulps obtained by performing SEC/RI in LiCl/DMAc by direct-standard-calibration have been presented and discussed. Method I corrects only the M_w and M_n values of the cellulose and can be used to obtain reliable average molecular masses. Method II gives fictitious cellulose-equivalent molar masses of pullulan standards and is the method of choice for studying the changes in the MMD of cellulose during kraft pulping and bleaching. This work shows the importance of conformity between samples and standards, as deviations in the molar masses of cellulose fractions of pulp samples depend on the applied detection technique.

Ida Östlund is gratefully acknowledged for performing AQ degradations on WPBs.

References

1. Rydholm, S. A. Pulping Processes; Interscience: New York, 1967.
2. SCAN standard method No. CM 15:99, Pulps—Viscosity in cupriethylenediamine solution, Scandinavian Paper and Board Testing Committee, 1999.
3. Schroeder, L. R.; Haigh, F. C. Tappi 1979, 62, 103.
4. Wood, B. F.; Conner, A. H.; Hill, C. G., Jr. J Appl Polym Sci 1986, 32, 3703.
5. Evans, R.; Wearne, R. H.; Wallis, A. F. A. J Appl Polym Sci 1989, 37, 3291.
6. Kennedy, J. F.; Rivera, Z. S.; White, C. A.; Lloyd, L. L.; Warner, F. P. Cellul Chem Technol 1990, 24, 319.

7. Turbak, A. F.; El-Kafrawy, A.; Snyder, F. W.; Auerbauch, A. B. U.S. Pat. 4,302,252 (1981).
8. Turbak, A. F. In Wood and Agricultural Residues; Soltes, E. J., Ed.; Academic: New York, 1983.
9. Strlic, M.; Kolar, J.; Zigon, M.; Pihlar, B. J Chromatogr 1998, 805, 93.
10. Westermark, U.; Gustafsson, K. Holzforschung 1994, 48, 146.
11. Sjöholm, E.; Gustafsson, K.; Berthold, F.; Colmsjö, A. Carbohydr Polym 2000, 41, 1.
12. Sjöholm, E.; Gustafsson, K.; Pettersson, B.; Colmsjö, A. Carbohydr Polym 1997, 32, 57.
13. Hortling, B.; Färm, P.; Sundquist, J. In Third European Workshop on Lignocellulosics and Pulp; KTH: Stockholm, Sweden, 1994; p 256.
14. Yau, W. W.; Kirkland, J. J.; Bly, D. D. Modern Size-Exclusion Liquid Chromatography: Practice of Gel Permeation and Gel Filtration Chromatography; Wiley: New York, 1979.
15. Grubisic, A.; Rempp, P.; Benoit, H. A. Polym Lett 1967, 5, 753.
16. Striegel, A. M.; Timpa, J. D. Int J Polym Anal Char 1996, 2, 213.
17. Sjöström, E. Wood Chemistry: Fundamentals and Applications; Academic: London, 1993.
18. Poché, D. S.; Ribes, A. J.; Tipton, D. L. J Appl Polym Sci 1998, 70, 2197.
19. Ottöy, M. H.; Vårum, K. M.; Christensen, B. E.; Anthonson, M. W.; Smidsröd, O. Carbohydr Polym 1996, 31, 253.
20. Schelosky, N.; Röder, T.; Baldinger, T. Papier 1999, 53, 728.
21. Schult, T. Ph.D. Thesis, Norwegian Univ. of Science and Technology, Trondheim, Norway, 2000.
22. Wyatt, P. J. Anal Chim Acta 1993, 272, 1.
23. Lindström, M.; Berthold, F.; Pettersson, B. In 10th International Symposium on Wood and Pulping Chemistry; Japan TAPPI: Yokohama, Japan, 1999; p 102.
24. Östlund, I. M.Sc. Thesis, Chalmers University, 2001.
25. Sjöholm, E.; Gustafsson, K.; Eriksson, B.; Brown, W.; Colmsjö, A. Carbohydr Polym 2000, 41, 153.
26. Michielsen, S. In Polymer Handbook, 4th ed.; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; Wiley: New York, 1999; p VII.547.
27. Fellman, E. Ph.D. Thesis, Technischen Universität Dresden, 1991.
28. Svanberg, S. M.Sc. Thesis, Royal Institute of Technology, 1999.
29. Brant, D. A.; Burton, B. A. In Solution Properties of Polysaccharides; Brant, D. A., Ed.; ACS Symposium Series 150; American Chemical Society: Washington, DC, 1981.
30. Miller, J. C.; Miller, J. N. Statistics for Analytical Chemistry, 3rd ed.; Ellis Horwood: West Sussex, England, 1993; p 110.
31. Berggren, R.; Berthold, F.; Sjöholm, E.; Lindström, M. Nord Pulp Pap Res J 2001, 16, 333.