

Dissolution of Softwood Kraft Pulps by Direct Derivatization in Lithium Chloride/*N,N*-Dimethylacetamide

Fredrik Berthold, Kristina Gustafsson, Rickard Berggren, Elisabeth Sjöholm, Mikael Lindström

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

Received 17 March 2003; accepted 18 March 2004

DOI 10.1002/app.20697

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A method for the characterization of the molar mass distributions (MMDs) of softwood kraft pulps dissolved in 0.5% lithium chloride (LiCl)/*N,N*-dimethylacetamide (DMAc) by size exclusion chromatography is presented. The method is based on derivatization with ethyl isocyanate and the dissolution of samples in 8% LiCl/DMAc. In this study, the derivatization of hardwood kraft pulps did not influence the MMD. In the case of softwood pulps, however, the derivatization decreased the proportion of the high-molecular-mass material and increased the proportion of the low-molecular-mass material, which resulted in a distribution similar to the MMD of a hardwood kraft pulp. The results suggest that associations between hemicellulose and cellulose in the softwood kraft pulp were rup-

tured during derivatization. This led to a more correct estimation of the MMD of derivatized softwood kraft pulps than obtained by the dissolution of nonderivatized samples. This new method offers several advantages over derivatization with phenyl isocyanate: a precipitation step is not necessary, it is possible to follow the lignin distribution in the samples, and the method allows very high levels of dissolution of softwood kraft pulps up to a κ number of around 50. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 424–431, 2004

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

INTRODUCTION

The molar mass distribution (MMD) of a polymer is of fundamental importance to its mechanical properties.¹ Size exclusion chromatography (SEC) has proven to be a versatile technique for the characterization of the MMDs of wood polymers, and it makes it possible to study the degradation of wood polymers occurring during the processing of sulfite and kraft pulps.^{2–5} The SEC technique offers several advantages over intrinsic viscosity measurements, the latter being the traditional way of monitoring carbohydrate degradation during pulping and bleaching. The main advantage of the SEC technique is that it permits the estimation of the molar mass averages [number-average molecular weight, weight-average molecular weight (M_w), and *z*-average molecular weight] from the MMD for each of the polymer types in the pulp, that is, not only one average value as is the case with an intrinsic viscosity measurement.

A frequently used solvent system for SEC studies of cellulosic samples is lithium chloride (LiCl)/*N,N*-dimethylacetamide (DMAc), a system first described 2

decades ago.^{6,7} With this solvent system, it is possible to characterize the MMD of hardwood kraft pulps, dissolving pulps, or cotton cellulose without any preceding derivatization step and without the removal of lignin.^{8,9} The sample/solvent system is fairly stable, and little or no degradation of the samples has been observed in LiCl/DMAc.^{10–12} In contrast to many other cellulose solvents, LiCl/DMAc is also suitable for the liquid chromatography¹³ of lignin-containing pulps as it is colorless and has a ultraviolet (UV) cutoff of 270 nm, which makes it possible to study the lignin distribution. The solvent/sample system does, however, have drawbacks. One is the limited solubility of softwood kraft pulps, probably caused by the gelation of the glucomannan fraction,⁹ which leads to poor solubility and adsorption of the samples onto columns used during SEC. Another drawback is the high salt concentration, which both increases the viscosity of the solution and complicates preparative SEC. Although the LiCl/DMAc–cellulose solvent system has been subject to several studies recently,^{14–16} the complex nature of the LiCl/DMAc–cellulose system and the mechanism governing the SEC separations have not yet been fully outlined.

The first reports on the direct dissolution of bleached and unbleached hardwood pulps for MMD determinations with LiCl/DMAc appeared about 10 years ago.^{3,8} It was soon observed that softwood pulps

Correspondence to: F. Berthold (fredrik.berthold@stfi.se).

were more difficult to dissolve than hardwood pulps and that the lignin content had to be very low to achieve acceptable dissolution levels.^{4,9} In addition, LiCl/DMAc has been found to work well as a solvent for a number of cellulose derivatizations.^{6,17}

Hitherto, the MMD of derivatized cellulose has commonly been determined from cellulose carbamates obtained through phenyl isocyanate derivatization.^{18–20} The sample is derivatized in pyridine or dimethyl sulfoxide, precipitated, and redissolved in tetrahydrofuran (THF), which is used as the mobile phase. The precipitation step can lead to a loss of low-molecular-mass (LM) material, and it is necessary to remove the lignin, with, for example, chlorite treatment, before dissolution. Carbohydrate degradation is assumed not to occur during this treatment, but it cannot be excluded. The removal of lignin also leads to a loss of information regarding possible lignin-carbohydrate associations present in the sample.

The aim of this study was to find conditions that would make it possible to characterize lignin-containing softwood kraft pulps by SEC through an increase in the solubility of the samples in 0.5%LiCl/DMAc and thus to avoid non-size-exclusion phenomena and undesired interactions with the column because of adsorption.

EXPERIMENTAL

Materials

Hardwood (birch, *Betula sp.*) kraft pulp with a κ number of 17.4 and an intrinsic viscosity of 1310 mL/g and five softwood (Norway spruce, *Picea abies*) kraft pulps with κ numbers between 20 and 50 from a laboratory flow-through reactor were used.

LiCl and ethyl isocyanate (EIC) were purchased from Fluka; DMAc, propionyl chloride, butionyl chloride, and propyl isocyanate (PIC) were purchased from Aldrich; acetyl chloride and phenyl isocyanate were purchased from Merck; and methyl isocyanate was purchased from Chem Service.

The LiCl was stored in a desiccator, and DMAc was dried with molecular sieves before use.

Derivatization and dissolution

The derivatizations were performed as follows: 15 mg of pulp were preswelled for 1 h in 15 mL of deionized water at 4°C. Thereafter, the fibers were solvent-exchanged three times with 15 mL of dry DMAc at the ambient temperature and placed in a flat-bottomed glass cylinder. Then added were 1.9 mL 8% LiCl/DMAc and 3 mmol of the derivatizing reagent, and the samples were left under argon at the ambient temperature for 5 days with mild magnetic stirring. Finally, the samples were diluted to 0.5% LiCl by the

addition of 27.4 mL of DMAc, and the excess reagent was quenched by the addition of 500 μ L of dry methanol. The dissolved samples were then treated in a Retsch MM-2 vibratory mill for 30 min (intensity = 70)²¹ followed by filtration through a 0.45 μ m PTFE poly(tetrafluorethylene) filter (Advantec, MFS) before chromatographic characterization.

After the dilution with DMAc, samples for the determination of the degree of substitution (DS) were precipitated in methanol and washed twice with water/methanol (7:3) and twice with water. The samples were freeze-dried, and the nitrogen content was determined at Mikrokemi AB (Uppsala, Sweden). The nondissolved residues were determined gravimetrically after ultracentrifugation and washing with water to remove salt and traces of DMAc.

The underivatized pulp samples were dissolved as reported earlier.²¹

SEC

The chromatographic system consisted of a 2690 separation module (Waters Corp.) equipped with a guard column (Mixed-A 20 μ m 7.5 \times 50 mm, Polymer Laboratories) followed by four columns (Mixed-A 20 μ m, 7.5 \times 300 mm, Polymer Laboratories) connected in series. The mobile phase was 0.5% (w/v) LiCl/DMAc, the flow rate was 1 mL/min, and the injection volume was 200 μ L. The mobile phase was filtered through a 0.2- μ m PTFE inline filter. The separations were performed at 80°C. Narrow pullulan standards with molecular masses of 1660, 380, 48, 5.8, and 0.738 kDa (Polymer Laboratories) were used to calibrate the chromatographic system. Detection was performed online with a 2487 dual wavelength absorbance detector (Waters Corp.) at 295 nm, followed by a 410 differential refractometer (Waters Corp.).

Data analysis and control of the hardware were performed with Millenium 3.05.01 software (Waters Corp.).

Additional analysis

The neutral carbohydrate composition of the pulps was determined by gas chromatography after extraction with dichloromethane and acid hydrolysis.²²

Intrinsic viscosity measurements and κ number analyses were performed according to the standard methods SCAN 15:99 and SCAN 1:77, respectively.

RESULTS AND DISCUSSION

MMD of underivatized pulps

It is possible to fully dissolve hardwood kraft pulps with a lignin content below approximately 3% (κ number = 20) with the LiCl/DMAc solvent system. This

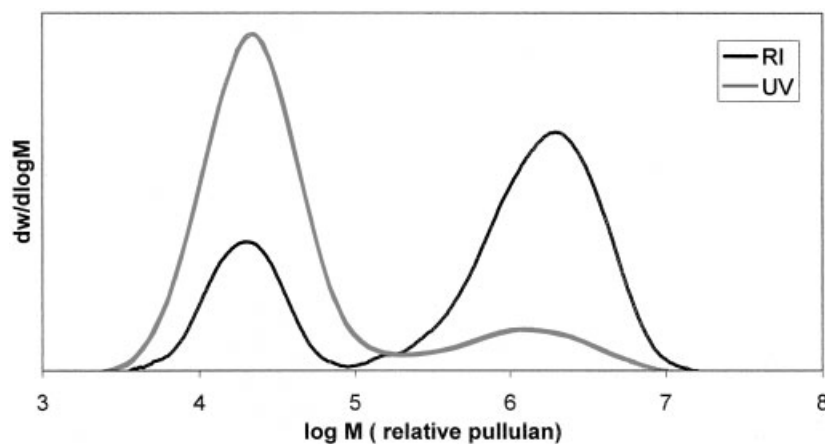


Figure 1 Total (RI) and UV-absorbing (UV) MMDs of underivatized hardwood kraft pulp. Chromatography performed on PL Mixed A columns at 80° with 0.5% LiCl/DMAc as the mobile phase.

makes it possible to determine the MMD with SEC. A typical example of such a MMD is given in Figure 1.

The total mass distribution was recorded by a refractive index (RI) detector, and the UV-absorbing material was recorded at 295 nm by a UV detector. The two fairly separated peaks in the distribution, observed by the RI detector, represent the hemicellulose fraction (LM range) and the cellulose fraction [high-molecular mass (HM) range], respectively.²³ The low lignin content (<3%) of the kraft pulp is assumed to have an insignificant effect on the MMD obtained from the RI detector.

The UV absorption has been shown to be due to the lignin in the pulp.²⁴ Typically, most lignin elutes together with the hemicellulose, whereas a smaller part elutes together with the cellulose, which suggests a very high molar mass for this lignin or, more likely, strong lignin–cellulose associations.⁸

Figure 2 shows the MMD obtained from the evaluation of RI and the UV detection of an underivatized softwood kraft pulp (κ number = 18.4) where 92% of the sample was dissolved. The MMD traces shown in Fig-

ures 1 and 2 differed substantially from each other. From the RI chromatogram, it was evident that only a small amount of the underivatized softwood kraft pulp eluted at the expected molar mass range of hemicellulose, compared to the amount obtained from underivatized hardwood kraft pulp (see also Table I). The MMD of lignin was opposite to that of the hardwood kraft pulp, implying that most of the lignin was associated with the cellulose, whereas only a minor part eluted in the same molecular mass range as the hemicellulose.

In contrast to hardwood kraft pulps, it is not usually possible to fully dissolve softwood kraft pulps in LiCl/DMAc. Problems encountered during the dissolution of softwood pulps have been discussed extensively elsewhere.⁹ Alternative methods for dissolution must be investigated, for example, derivatization of the samples.

Improving the solubility by derivatization

The carbanilation of cellulosic samples with phenyl isocyanate is advantageous because of the high solu-

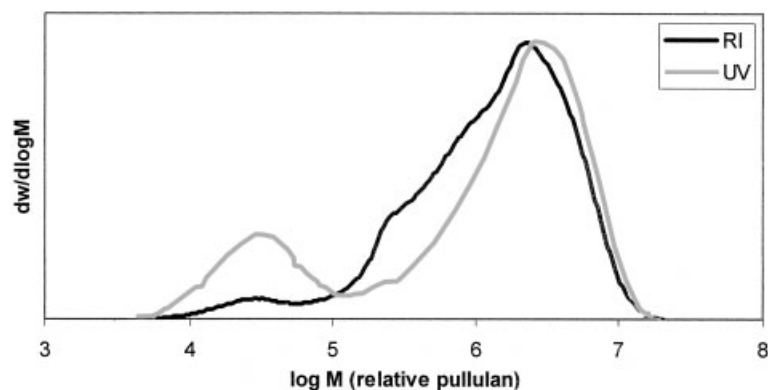


Figure 2 Total (RI) and UV-absorbing (UV) MMDs of underivatized softwood kraft pulp dissolved to 92%. Chromatography performed on PL Mixed A columns at 80° with 0.5% LiCl/DMAc as the mobile phase.

TABLE I
Weight-Average Molar Masses (M_w , Relative Pullulan Standards) and Relative Amounts of LM, and HM Materials as Calculated from the Respective Chromatograms (UV and RI) of EIC-Derivatized and Nonderivatized Softwood and Hardwood Kraft Pulps

Sample	M_w (g/mol)		Area % (RI)		Area % (UV)	
	LM	HM	LM	HM	LM	HM
Softwood ^a	32,000	2,338,000	4	96	19	81
Softwood ^a derivatized	35,400	1,765,000	20	80	75	25
Hardwood ^b	25,000	2,081,000	28	72	84	16
Hardwood ^b derivatized	29,000	2,226,000	28	72	84	16

M_w values were calculated from the RI chromatogram. For the limits of integration, see Figure 5.

^a Nonderivatized sample: intrinsic viscosity = 1075 mL/g and κ number = 18.4.

^b Nonderivatized sample: intrinsic viscosity = 1310 mL/g and κ number = 17.4.

bility attainable, in, for example, THF. It is, therefore, often the preferred method for the characterization of the MMD of cellulose by SEC. However, the drawbacks introduced by the need for precipitation, lignin removal, and the high UV absorbance of the phenyl carbamates make this method difficult to handle. The introduction of a derivatization step into the LiCl/DMAc system would increase its usefulness as a tool for studying the development of pulp fiber properties. Seven reagents were, therefore, screened to determine their ability to enhance the solubility of softwood kraft pulp fiber components in LiCl/DMAc. The reagents tested were acetyl chloride, propionyl chloride, butionyl chloride, methyl isocyanate, EIC, PIC, and phenyl isocyanate.

The reagents were evaluated according to their ability to increase the solubility of a softwood kraft pulp with a κ number of 18.4 and an intrinsic viscosity of 1075 mL/g. The conditions were essentially those used by McCormick and coworkers,^{6,17} except that no pyridine was used in this study. For a compilation of the results, see Table II.

The acylations increased the solubility of the softwood fibers in LiCl/DMAc. An increased degree of

the dissolution of cellulose derivatized with these reagents has previously been reported with triethylamine or pyridine as an acid acceptor.¹⁷ However, we found that treatment with these reagents did not always lead to full dissolution of the softwood kraft pulp when the acceptor was omitted. The reason for the poor reproducibility may have been the lack of the acid acceptor or the fact that the samples in this study had a considerably larger molar mass than those used by McCormick and coworkers,^{6,17} which resulted in a lower accessibility toward the reagents.

All carbanilations increased the solubility of the softwood pulp sample. Phenyl isocyanate worked well, but the strong UV absorption of the phenyl carbamate made the detection of lignin impossible and the use of this reagent was not further studied. Methyl isocyanate was omitted because of its high vapor pressure and handling restrictions because of its toxicity. EIC and PIC worked equally well. EIC is a smaller molecule than PIC and was assumed to affect the hydrodynamic volume of the samples less than PIC, and derivatization with EIC was, therefore, chosen for further studies.

Convincing results indicating that the UV absorption at 295 nm originates from lignin have been presented elsewhere.^{8,24} To determine whether the derivatization introduced UV-absorbing groups into the pulp, a fully bleached pulp, that is, without lignin, was EIC derivatized, and the UV response was measured during SEC. No signal could be detected at 295 nm, so any UV signal present in the derivatized samples was assumed to originate from the lignin in the pulp.

Effect of derivatization on MMD and molar masses

Table I shows the recorded molar masses relative to pullulan standards and the relative amounts of the LM and HM peaks of derivatized and nonderivatized samples of softwood and hardwood kraft pulps. For convenience, calibration with narrow pullulan standards giving the relative MMDs with relative molar

TABLE II
Solubility and UV Distribution of the Various Derivatives

Derivative	Solubility	Effect on UV distribution	Effect on solubility
Acetyl chloride	Increasing	NA	Irreproducible
Propionyl chloride	Increasing	NA	Irreproducible
Butionyl chloride	Increasing	NA	Irreproducible
Methyl isocyanate	Increasing	NA	Reproducible
Ethyl isocyanate	Increasing	None	Reproducible
Propyl isocyanate	Increasing	NA	Reproducible
Phenyl isocyanate	Increasing	Strong	Reproducible

NA = not analyzed. A softwood kraft pulp with a κ number of 18.4 and an intrinsic viscosity of 1075 ml/g was used as the substrate. The effect on UV distribution was studied by SEC characterization.

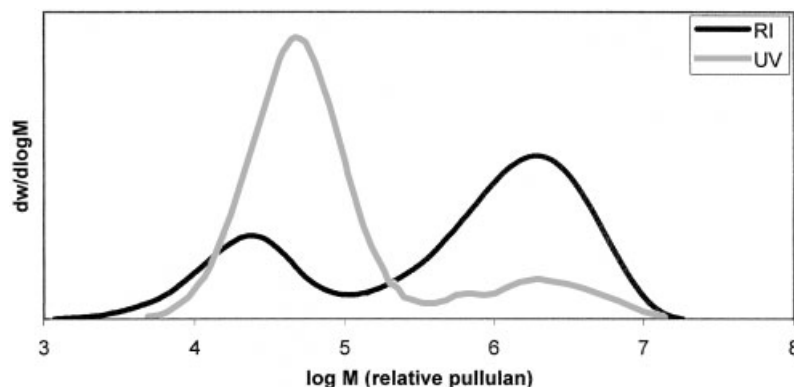


Figure 3 Total (RI) and UV-absorbing (UV) MMDs of EIC-derivatized hardwood kraft pulp. Chromatography performed on PL Mixed A columns at 80° with 0.5% LiCl/DMAc as the mobile phase.

mass averages was chosen, as the scope was not to report the absolute molar masses of the wood polymers, a topic recently debated.¹⁶ The M_w of both the HM and LM distributions in a hardwood kraft pulp was only slightly affected by the derivatization. Both values changed only marginally from the values of the underivatized sample (increase in M_w due to derivatization: HM distribution = 7% and LM distribution = 16%). It was remarkable that the molar masses of the derivatized samples did not change more, when one considers that the molar mass of the monomer almost doubled as a result of the derivatization (see later for results concerning DS). Similar results were obtained from derivatized pullulan standards used for calibration, where no changes in retention times, compared to those of underivatized standards, were observed during SEC calibration (data not shown). This indicated that the change in the hydrodynamic size of the dissolved derivatized samples was, if at all, small compared to the hydrodynamic size of dissolved underivatized samples. An explanation of this small change in size might be the structural similarities of DMAc and EIC. Replacing a DMAc molecule with an EIC molecule in the proposed DMAc/OH/LiCl complex²⁵ probably, therefore, only has a small effect on the hydrodynamic size of the samples in LiCl/DMAc. The proper reason for this ambiguity and the mechanism behind the dissolution of EIC-derivatized cellulose is presently not known and deserves to be studied further.

Derivatization of the hardwood kraft pulp did not change the shape of the MMD (Fig. 3), nor were the relative areas of the LM and the HM distributions changed by the derivatization (Table I). This meant that cellulose and hemicellulose probably reacted to the same extent with EIC, and no redistribution of the pulp components in the MMD of hardwood kraft pulps occurred.

Separating nonderivatized softwood kraft pulps on a similar chromatographic system led to an increased

pressure in the chromatographic system, indicating that adsorption took place onto the columns. Adsorption reduces the lifetime of the columns, but it could be avoided with EIC as the reagent. Furthermore, the recovery of the injected sample was greater than that of the nonderivatized softwood pulps because adsorption was avoided and the composition of the original pulp was described more accurately.

The derivatization of the softwood kraft pulp introduced major changes in the MMD (Fig. 4) compared with that of the underivatized softwood kraft pulp (Fig. 2). The typical bimodal MMD of hardwood pulps was also observed for the derivatized softwood pulp, although the resolution between the LM distribution and the HM distribution was somewhat lower than in the case of the hardwood kraft pulp. The M_w values of the HM distribution in underivatized softwood kraft pulp samples were surprisingly high, especially considering the low intrinsic viscosity of the unbleached pulp (Table I). Derivatization lowered the average molar mass to a more expected value. The relative areas of the LM and HM distribution in the RI chromatograms of derivatized softwood kraft pulps were also different from those of their underivatized counterparts (Table I). The relative areas of the LM and HM distribution of the derivatized softwood pulps (20:80) reflected the ratio between cellulose and hemicellulose in the sample, as the relative carbohydrate composition of the studied softwood kraft pulp was 0.3% arabinose, 7.5% xylose, 5.8% mannose, 0.4% galactose, and 86.0% glucose. The MMD obtained by the UV detector was also different from that of the underivatized sample, indicating association of the major part of the lignin to the LM distribution, that is, a situation similar to that of the hardwood kraft pulp.

It has been proposed, on the basis of dynamic mechanical analyses on a mechanical pulp,²⁶ that glucomannan is associated with cellulose in spruce fibers. High adsorption of glucomannan was observed when cotton linters were treated with softwood glucoman-

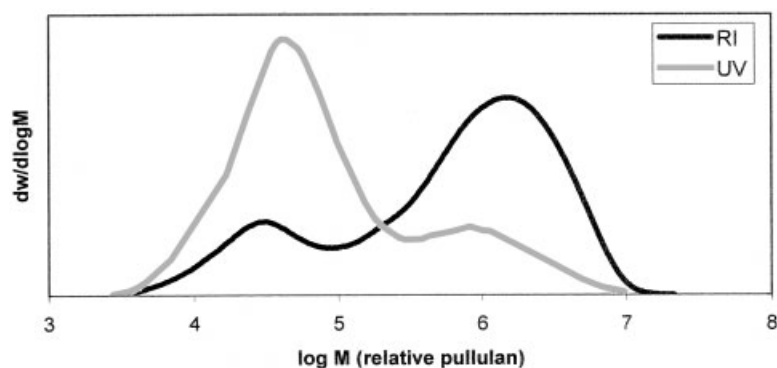


Figure 4 Total (RI) and UV-absorbing (UV) MMDs of EIC-derivatized softwood kraft pulp. Chromatography performed on PL Mixed A columns at 80° with 0.5% LiCl/DMAc as the mobile phase.

nan fractions isolated from holocellulose.²⁷ MMD measurements later showed that HM material was formed when hardwood pulp was treated with softwood glucomannan,²⁸ and this was explained as being due to the formation of strong interactions between cellulose and glucomannan. The carbohydrate composition of the HM distribution isolated from nonderivatized softwood pulp has been reported to contain hemicellulose.²³ All of these observations strongly suggest that there are associations between cellulose and hemicellulose in softwood kraft pulps. The redistribution of material from the HM range to the LM range of the distribution due to the EIC derivatization of softwood kraft pulps, as revealed by the RI and UV detection, clearly indicated that strong associations, mainly those between glucomannan and cellulose, were ruptured by the derivatization of the hydroxyl groups of the carbohydrates. The rupturing of these associations led to a more correct MMD, and this meant that more correct molar masses of the pulp constituents were observed when SEC was performed on EIC-derivatized softwood pulp samples than on underivatized softwood samples.

The concomitant shift of the lignin from the HM to the LM part of the distribution suggests that most lignin was associated with the glucomannan rather than directly with the cellulose. However, the presence of UV absorbance in the high molar mass fraction after derivatization indicates that considerable amounts of lignin remain associated with the HM distribution, in both hard and softwood kraft pulps (Table I). The great similarity between the MMD of hardwood pulp and EIC-derivatized softwood suggests that there were no major differences between these pulp types with regard to the MMDs of cellulose and hemicelluloses.

Reproducibility, DS, and levels of dissolution

The reproducibilities of the derivatization and of the subsequent SEC characterization were evaluated in five separate MMD determinations of the same softwood kraft pulp (Fig. 5). The level of reproducibility of the determination of the molar mass of the HM distribution was high, with a relative standard deviation

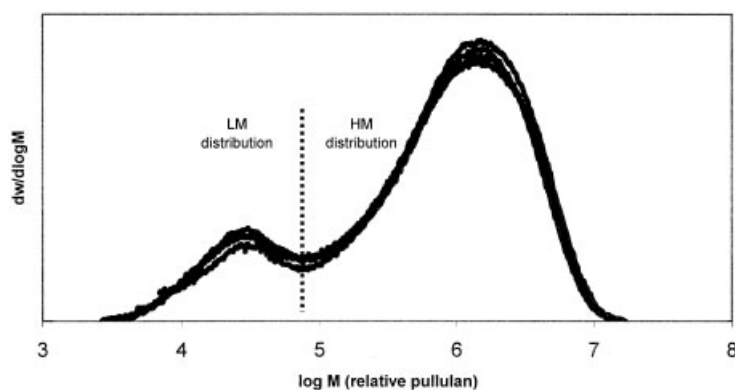


Figure 5 Reproducibility of the method exemplified by the MMDs (RI detection) of five separate derivatizations and dissolutions of the same softwood kraft pulp. Chromatography performed on PL Mixed A columns at 80° with 0.5% LiCl/DMAc as the mobile phase. The vertical line in the figure signifies the limit of integration used in the estimation of the molar masses of the two peaks.

TABLE III
DS of Five Dissolutions of the Same Derivatized Softwood Kraft Pulp and Their Weight-Average Molar Mass Values (M_w , Relative to Pullulan) from the RI Distribution of LM and HM Materials

Sample	DS	Low M_w (1000 g/mol)	High M_w (1000 g/mol)
1	1.9	35.6	1800
2	1.9	34.2	1770
3	2.0	36.1	1770
4	1.7	35.6	1690
5	NA	35.6	1810
Average	1.9	35.4	1770
Standard deviation	0.13	0.72	47.1
RSD	0.067	0.020	0.027

NA = not analyzed. For limits of integration, see Figure 5. Standard deviation.

(RSD) of 2.7% ($n = 5$; see Table III). These numbers were about the same as the reproducibility for hardwood pulps where a RSD of 2.2% ($n = 3$) has been reported for the HM distribution.²¹

Three hydroxyl groups in the glucosidic monomer of the cellulose fraction of the pulp were available for derivatization. The nitrogen content was determined in derivatized softwood kraft pulp samples, and the DS was calculated assuming that the samples contained pure cellulose (see Table III). The DS was found to be 1.9. This value was somewhat lower than the value of 2.1 previously reported with EIC as a derivative and pyridine as a catalyst.¹⁷ It was also slightly lower than the value obtained with phenyl isocyanate as a derivatizing reagent.¹⁹ The value was nevertheless high enough to provide a sufficient degree of dissolution of the samples.

The dissolution of softwood samples providing information on the earlier stages of a kraft cook is de-

sirable, but unfortunately, the solubility of kraft pulps in LiCl/DMAc is decreased by a high lignin content. To study the effect of lignin, five different kraft pulps with κ numbers ranging from 12.8 to 53.3 (corresponding to lignin contents of 2–8%) were dissolved with this EIC/LiCl/DMAc method. On the basis of gravimetric determination of the nondissolved residue, 90% dissolution was possible for kraft pulps with κ numbers of 50 (Fig. 6). Thus, a high degree of dissolution could be obtained even for kraft pulps containing fairly high amounts of lignin.

CONCLUSIONS

It was possible to obtain high levels of dissolution of softwood kraft pulps by derivatization with EIC in LiCl/DMAc, which made it possible to characterize the MMD by SEC with the same solvent system. The method offers several advantages over previous methods with other derivatives, catalysts, and solvents:

- The procedure is a one-pot reaction and is not complicated to perform. No precipitation step is necessary.
- Full dissolution is obtained without the removal of the lignin in the samples by chlorite delignification, and this makes it possible to study the UV-absorbing lignin distribution. A variety of softwood kraft pulps within a large range of lignin contents may thus be studied.
- Adequate resolution between the HM and LM distributions makes it possible to study hemicellulose and cellulose distributions separately. This is not possible when nonderivatized softwood kraft pulps are separated in LiCl/DMAc with SEC.

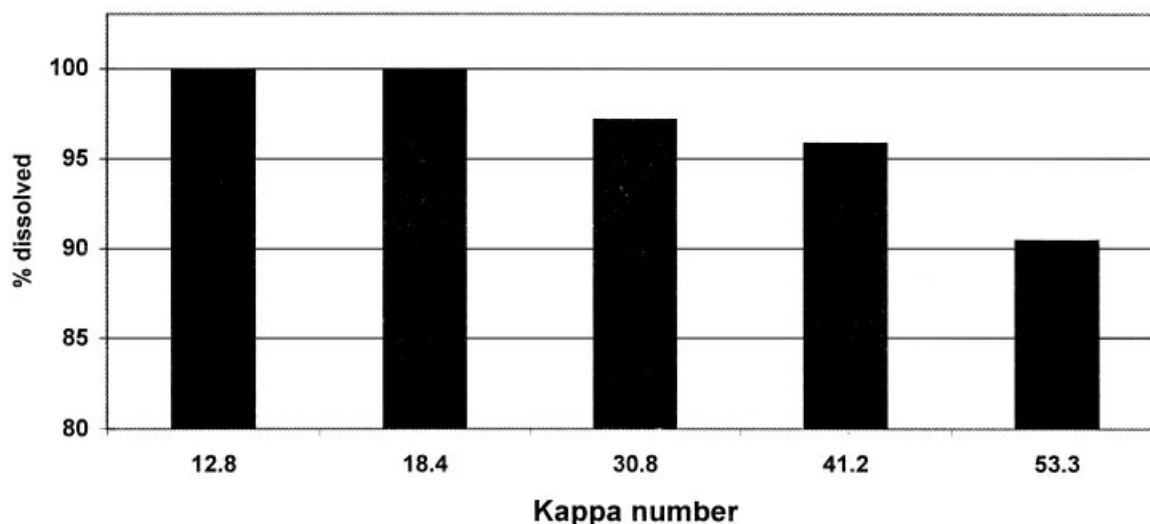


Figure 6 Solubility of derivatized softwood kraft pulps with different lignin contents (measured as the κ number).

Part of this work (by R.B.) was carried out within the framework of the Wood Ultrastructure Research Centre, a VINNOVA (Swedish Agency for Innovative Systems) competence center based at the Swedish University of Agricultural Sciences, Uppsala, Sweden. The authors thank Anthony Bristow for the linguistic revision.

References

1. Seymour, R. B.; Carraher, C. E. *Polymer Chemistry: An Introduction*; New York: Marcel Dekker, 1992; p 39.
2. Silva, A. A.; Laver, M. L. *Tappi J* 1997, 80(6), 173.
3. Kennedy, J. F.; Rivera, Z. S.; White, C. A.; Lloyd, L. L.; Warner, F. P. *Cell Chem Technol* 1990, 24, 319.
4. Hortling, B.; Färm, P., Sundquist, J. In *Third European Workshop on Lignocellulosics and Pulp*; Sverige: Stockholm, Sweden, 1994; p 256.
5. Schelosky, N.; Röder, T.; Baldinger, T. *Papier* 1999, 53, 728.
6. McCormick, C. L.; Lichatowich, D. K. *J Polym Sci Polym Lett Ed* 1979, 17, 479.
7. Turbak, A. F.; El-Kafrawy, A.; Snyder, F. W.; Auerbauch, A. B. U.S. Pat. 4,302,252 (1981).
8. Westermark, U.; Gustafsson, K. *Holzforschung* 1994, 48, 146.
9. Sjöholm, E.; Gustafsson, K.; Pettersson, B.; Colmsjö, A. *Carbohydr Polym* 1997, 32, 57.
10. Turbak, A. F. In *Wood and Agricultural Residues*; Soltes, E. J., Ed.; New York: Academic, 1983; p 87.
11. Strlic, M.; Kolar, J.; Zigon, M.; Pihlar, B. *J Chromatogr A* 1998, 805, 93.
12. Jerosch, H.; Lavédrine B.; Cherton, J. C. *J Chromatogr A* 2001, 927, 31.
13. Ekmanis, J. L.; Turbak, A. F. *GPC Analysis of Cellulose*, Polymer Notes, Waters Chromatography Division; Waters Chromatography Division: Milford, MA, 1986; p 1.
14. Morgenstern, B.; Kammer, H. W. *Trends Polym Sci* 1996, 4, 87.
15. Strlic, M.; Kolenc, J.; Kolar, J.; Pihlar, B. *J Chromatogr A* 2002, 964, 47.
16. Bikova, T.; Treimanis, A. *Carbohydr Polym* 2002, 48, 23.
17. McCormick, C. L.; Callais, P. A. *Polymer* 1987, 28, 2317.
18. Schroeder, R. L.; Haigh, F. C. *Tappi J* 1979, 62(10), 103.
19. Sundquist, J.; Rantanen, T. *Pap Puu* 1983, 65(11), 733.
20. Evans, R.; Wearne, R. H.; Wallis, A. F. A. *J Appl Polym Sci* 1989, 37, 3291.
21. Sjöholm, E.; Gustafsson, K.; Eriksson, B.; Brown, W.; Colmsjö, A. *Carbohydr Polym* 2000, 41, 153.
22. Theander, O.; Westerlund, E. A. *J Agr Food Chem* 1986, 34(2), 330.
23. Sjöholm, E.; Gustafsson, K.; Berthold, F.; Colmsjö, A. *Carbohydr Polym* 2000, 41, 1.
24. Karlsson, O.; Westermark, U. *J Pulp Pap Sci* 1996, 22, J397.
25. Morgenstern, B.; Kammer, H. W.; Berger, W.; Skrabal, P. *Acta Polym* 1992, 43, 356.
26. Salmén, L.; Olsson, A. M. *J Pulp Pap Sci* 1998, 24, 99.
27. Hansson, J. Å. *Holzforschung* 1970, 24, 77.
28. Karlsson, O.; Westermark, U. *Nordic Pulp Paper Res J* 1997, 12, 203.