



# Towards determination of absolute molar mass of cellulose polymer by size exclusion chromatography with multiple angle laser light scattering detection



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## ABSTRACT

The study focuses on determination of a set of crucial parameters for molar mass calculation of cellulose from the results of size exclusion chromatography coupled with multiple angle laser light scattering (MALLS) and differential refractive index (DRI) detectors. In the present work, cellulose has been derivatised to obtain cellulose tricarbanilate (CTC) soluble in tetrahydrofuran (THF). The parameters of Rayleigh scattering in the MALLS detector: refractive index increment ( $dn/dc$ ) and second virial coefficient ( $A_2$ ) of CTC in THF were determined for laser wavelength 658 nm. In order to avoid errors resulting from cellulose derivatisation by-products present in the CTC solution, the so called “on-line” method of measuring  $dn/dc$  and  $A_2$  was applied. Based on the  $A_2$  determination, its influence on cellulose molar mass calculations and cellulose molecular dimensions were critically assessed. The latter includes evaluation of artificially aged cellulose towards conceivable branching by conformation plot analysis.

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## 1. Introduction

In the studies of degradation of polymers and the kinetics of both their formation and degradation, Size Exclusion Chromatography (SEC) with Multiple Angle Laser Light Scattering (MALLS) is the most comprehensive and robust analytical method for determining the distribution of molar masses with no need for synthetic standards of mass usually of different structure.

The most advanced methods in size exclusion chromatography of cellulose have been well established in the literature during recent years [1–7]. Molar mass (sometimes expressed also as a degree of polymerisation (DP)) obtained by SEC is a commonly utilised measure for the evaluation of paper condition and its degradation kinetics [8–10].

Understanding cellulose degradation can be applied practically to historical paper in books and archives, as well as modified cotton textiles and papers for special applications (such as those doped with different fillers or highlighters). The latter especially concerns modern materials based on cellulose fibres with various additives that result in diverse properties such as anti-fading,

highlighting and antimicrobial. These, together with other exogenous and endogenous phenomena may affect the physical and thus mechanical properties of paper or textile made of cellulose [11], thus causing accelerated degradation.

A complete description of cellulose degradation can be obtained by measuring three parameters: degree of polymerisation (DP), degree of oxidation, and crystallinity [10,12–15]. This study focuses on the application of SEC for determining the degree of cellulose polymerisation.

SEC appears as the most direct way of evaluating the polymer chain length reflected as degree of polymerisation. This method is especially valuable when small amounts of a sample are available and subtle effects must be studied [16]. In recent years, several papers have been published about SEC of cellulose with use of two particular methods:

- Indirect dissolution of cellulose in DMAc with LiCl [6,7,17–22].
- Derivatisation procedure with phenyl isocyanate in pyridine to cellulose tricarbanilate (CTC), with further dissolution in THF acting as a mobile phase [2,5,23,24].

Judging by the statistics in the literature, the latter method is less utilised. This may be a reason for the difficulty in finding consistent coefficients values for SEC-MALLS analyses. Lauriol et al. [24]

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elaborated an SEC method for CTC in THF, including determination of  $dn/dc$  and  $A_2$ . However,  $A_2$  was determined in a static experiment (the so called batch-mode), which indicates that carbanilation by-products were not removed from the solution. In fact, the presence of other compounds can lead to an incorrect value being obtained for  $A_2$ . Furthermore, the authors do not indicate which method was utilised for  $dn/dc$  determination. As in the case of  $A_2$ , the batch-mode measurement of  $dn/dc$  gives a value including all species present in the analysed sample. Finally, the specific refractive index increment of CTC has been determined at 20 °C, which means that the importance of this  $dn/dc$  value is low, as most of SEC analyses in THF are conducted in 35 °C.

Cellulose polymeric chain is known to have a linear structure due to  $\beta(1\rightarrow4)$ -glycosidic bonds, in principle disabling branching. However, Yamamoto et al. suggested that some wood components may have a branched structure in the high molecular weight cellulose fraction [22].

The aim of this research is to improve the method of analysis of molar mass of cellulose from SEC-MALLS experiments, using the CTC in THF method. The approach is based on the interpretation of Rayleigh light scattering by polymer molecules, with particular reference to determining the refractive index increment and second virial coefficient.

In this paper, we focus on gathering constants crucial for the determination of molecular weights of cellulose tricarbanilates in THF by SEC-MALLS. The method of preparing cellulose as a CTC, presented previously [5,14], was applied in order to calculate the second virial coefficient  $A_2$  and specific refractive index increment ( $dn/dc$ ) of CTC in tetrahydrofuran. Moreover, conformation plots from light scattering data were analysed in order to establish whether accelerated ageing might cause branching of cellulose. The paper samples used were made of cotton (pure cellulose) [14], which was artificially aged in closed vessels in the presence of volatile organic compounds emitted during cellulose degradation at 90 °C and 59% relative humidity. Molecular weight distributions and degree of polymerisation were also recalculated, based on the new set of coefficients.

### 1.1. The approach to molar mass determination

The determination of absolute values of molecular weights using size exclusion chromatography with MALLS detection is based on the Rayleigh equation:

$$\frac{K_c}{R_\theta} = \frac{1}{M_w P(\theta)} + 2A_2 c \quad (1)$$

where  $K$  is a combined constant including the refractive index increment  $dn/dc$ :

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

There are several parameters that have to be known in order to apply the Rayleigh equation: solute concentration  $c$ , its specific refractive index increment, and the second virial coefficient  $A_2$ . Exact information on the application of the Rayleigh equation for polymer mass calculation can be found in ref. [25,26]

Solute concentration can be determined using concentration sensitive detectors, among them a UV detector, suitable for samples absorbing ultraviolet light, or a differential refractive index detector, more universal and applicable also for those analytes that do not absorb UV.

Another parameter in the Rayleigh equation, the specific refractive index increment ( $dn/dc$ ), describes how much the refractive

index of a solution varies for a given increment in concentration, and its value is expressed in  $g/cm^3$ :

$$\nu = \left. \frac{dn}{dc} \right|_{c=0} = \lim_{c \rightarrow 0} \left( \frac{n - n_0}{c} \right) \quad (3)$$

The  $dn/dc$  appears in the optical constant  $K$ , and is necessary to characterise light scattering from a macromolecule connected with its ability to polarise. It is also required to calculate the absolute concentration of a solute. For linear polymers,  $dn/dc$  does not vary significantly with molar mass, and can be assumed to be constant for each elution volume slice [26].

The third factor that should be taken into account is the second virial coefficient ( $A_2$ ).  $A_2$  is a measure of interaction between the solute and solvent. A negative value indicates repulsive forces between them, while a positive value expresses attracting interactions. The second virial coefficient varies slightly with molecular mass for most polymers, and is commonly neglected in molecular mass calculations as being considered negligible. Sometimes, molar masses are calculated by iteration with the use of  $A_2 = 0 \text{ mol cm}^3/g^2$ , to calculate weight average molar mass ( $M_w$ ), which is then used to calculate  $A_2$  from the following equation:

$$A_2 = kM^{-\vartheta} \quad (4)$$

where  $k$  is a constant and value of  $\vartheta$  is in range 0.15–0.35.

Opinions about ignoring or accepting  $A_2$  in molar mass calculations are rather consistent in the literature. It is considered that differences in obtained  $M_w$  values are negligible for narrow poly-disperse polymers, and abandoning the concentration effect gives an error of 2% [26].

## 2. Materials and methods

### 2.1. Samples and ageing tests

The model paper (denoted P2) obtained from TNO, Delft was used for the study [14]. The paper consists of high quality pure linter cellulose, and is also in old prints.

In order to differentiate the cellulose material in degree of polymerisation, and to study paper degradation effects, the paper samples were aged in closed vials at a temperature of 90 °C, in air at relative humidity of 59% for 12, 24 and 47 days. The conditions were chosen to accelerate ageing by the influence of gaseous products on the sample. The procedures concerning experimentation in closed vials are described in detail in [27].

### 2.2. SEC measurements

#### 2.2.1. Sample preparation

The paper samples were derivatised using phenyl isocyanate (Fluka, GC) to obtain cellulose tricarbanilate (CTC). Further, they were dissolved in tetrahydrofuran (THF HPLC grade, J. T. Baker) prior to each SEC analysis. The derivatives were prepared according to the procedure described in [5,14] in the following way:

- 5 mg of the sample was cut into the little pieces and placed in a glass vial for drying at a temperature of 105 °C for 0.5 h.
- The pre-dried sample was treated with 1 cm<sup>3</sup> of water-free pyridine and 0.1 cm<sup>3</sup> of phenyl isocyanate (PIC), flushed with nitrogen, sealed, and maintained at 80 °C for 48 h.
- To terminate the substitution reaction, 0.1 cm<sup>3</sup> of methanol was added to destroy excess PIC. The reaction mixture was then cooled down to a room temperature. Four repetitions of each analysis were performed in order to minimise the possibility of a rough random error. Two CTC solutions were prepared for each paper sample and each solution was analysed twice. Prior to

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