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# Distribution of Substituents along the Cellulose Chain on Cellulose Xanthate and Carboxymethyl Cellulose

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**Summary:** The distribution of substituents of cellulose xanthogenate and carboxymethyl cellulose along the cellulose chains and therefore in relation to the molecular mass can be measured using size exclusion chromatography including a multi angle laser light scattering and mass detection for determining the molecular mass of the derivative assisted by an UV- detection for determining the xanthate groups and carboxymethyl groups after derivatisation, respectively. The results investigating cellulose xanthogenate show that the temperature used in dissolving xanthogenate and in ripening viscose influences the distribution of xanthate groups in a different way; but all steps processing viscose are connected with a loss in the degree of substitution in ripening the distribution of substitution additionally becomes more even.
The investigated carboxymethyl cellulose revealed different distribution of carboxylic groups in dependence on the viscosity of the CMC.

**Keywords:** carboxymethyl cellulose; cellulose xanthogenate; heterogeneous polymers; molecular weight distribution

## Introduction

The distribution of substituents along the cellulose chain is an important issue for partial substituted cellulose derivatives. In order to obtain this information, the following approach has been pursued i.e. size exclusion chromatography including a multi angle laser light scattering (MALLS) and mass (RI) detection for determining the molecular mass (Mw) of the derivative, assisted by an UV- detection for determining the introduced groups. [1,2] Xanthate groups, being UV- active themselves, can be measured directly whereas carboxymethyl groups of a carboxymethyl cellulose (CMC) have to be transformed into UV- active groups on conditions keeping retrained the polymer.

This paper is divided into two main sections. One part deals with parameters which influence the distribution of introduced xanthate groups in viscose and another part with the characterisation of carboxymethyl cellulose.

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## Cellulosexanthogenate

The viscose production process is approximately 100 years old, but the distribution patterns of the substituents along the cellulose chains are only partly known. However, the distribution of xanthate groups on the macromolecules influences a lot of properties of viscose such as state of dissolution, filterability, behaviour during spinning.

The aim of this part was to investigate the influence of α-cellulose content, temperature during the dissolving process and ripening of viscose on the distribution of the introduced xanthate groups in dependence on the molecular weight of the cellulose xanthogenate.

## General Comments on Viscose

The reaction of anionised cellulosic hydroxyl groups with carbon disulphide leads to moderately stable cellulosic – dithiocarbonic acid half ester anions.

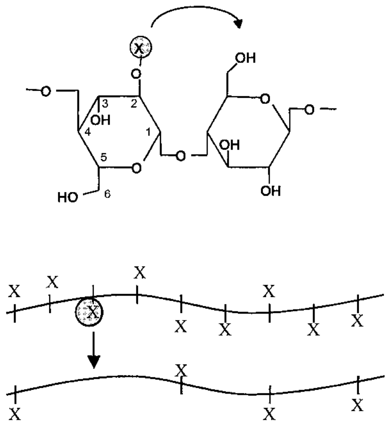
$$\text{Cell O}^-\text{Na}^+ + \text{CS}_2 \longrightarrow \text{Cell O CSS}^-\text{Na}^+$$

The sodium salt of the half ester makes the cellulose polymer water or alkali soluble by transforming it into a polyelectrolyte.

The formation of xanthate is connected with both a xanthation of alkali cellulose and a hydrolysis of carbon disulphide. Due to the difference in the activation energy for xanthation ($E_A$ ~ 13 kcal/mol) and hydrolysis ($E_A$ ~21 kcal/mol), free $CS_2$ and by-products especially trithiocarbonate and sulphide are formed with increasing xanthation temperature[3].

All three hydroxyl groups of an AGU can participate in these reactions, however, xanthation of fibrous alkali cellulose is usually characterised by an average degree of substitution (DS) of about 0.5, preferentially substituted at the $C_2$ position. On the other hand, when a homogeneous xanthation is applied, at which all hydroxyl groups are freely available, the $C_6$ position is favoured[3].

Therefore, the cellulose xanthogenate solution that means a solution which is in a nearly homogeneous dissolution state undergoes complex chemical and colloidal changes during its storage at room temperature, the so- called viscose ripening, which is of high relevance for the spinning process.



a) transxanthation from $C_2$ / $C_3$ to $C_6$ according to Philipp and Liu [5] and a preferred decrease of $C_2$- substituted xanthate (König[4])

b) transxanthation between the chains[7]

Figure 1. Reactions occurring during viscose ripening (x: xanthate group).

Most of the research associate the ripening process with a process of dexanthation and re-xanthation in an aqueous alkaline solution of cellulose xanthogenate, which leads to a re-distribution of xanthate groups by transxanthation. As a consequence of the transxanthation process xanthate groups are transferred from the $C_2$ to the $C_6$ position,[4;5] resulting also in a more even distribution along and between the cellulose chains[7] (Figure 1).

During ripening, transxanthation can also lead to an improved xanthation of the highly ordered cellulose[7] (Figure 1). A side reaction during the ripening process increases the concentration of low molecular weight by-products, i.e. sodium trithiocarbonate at the expense of free hydroxyl ions and sodium sulphide, which enhance the tendency of the system to coagulate after addition of an electrolyte (e.g. $NH_4Cl$; NaCl).

Through the size exclusion chromatography (SEC) using a multi- detection system (Figure 2) it is possible to determine introduced xanthate groups situated along the cellulose chain, whereas the light scattering detector (MALLS) and RI- detector are used for calculation of the molecular mass per slight, and an UV- detector for determining the introduced xanthate groups in relation on the molecular weight. In this way a solution of cellulose xanthate can be better characterised [1].

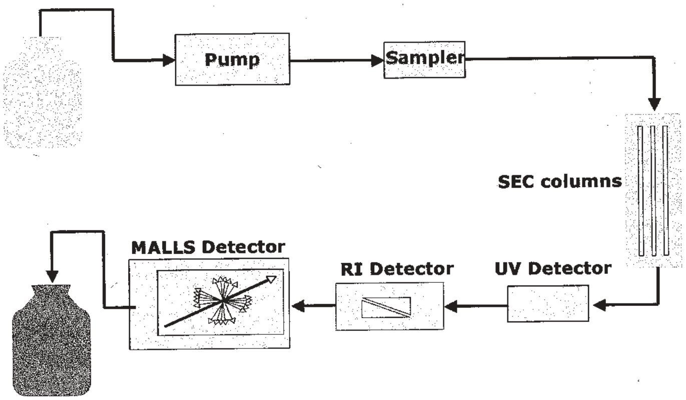


Figure 2. Scheme for determining molecular weight distribution of cellulose xanthogenate including the introduced xanthate groups.

## Experimental

Viscose was prepared from commercial Eucalyptus sulphite pulp according to a Treiber[6] standard method using a charge of 30 % $CS_2$ (24% $CS_2$ for irradiated pulp). For measuring the molecular weight distributions viscose samples were prepared as published earlier[1].

## Results and Discussion

Figure 3 shows the typical pattern for the molecular weight distribution of cellulose xanthogenate, including the introduced xanthate groups characterised by a degree of substitution (DS) from 0.3 up to 0.5 in the low weight molecular region, and from 0.2 to 0.1 in the region of high molecular masses. Furthermore, the pattern in Figure 3 show the reproducibility both for making viscose and for measuring the molecular weight distribution of cellulose xanthogenate including the distribution of xanthate groups.

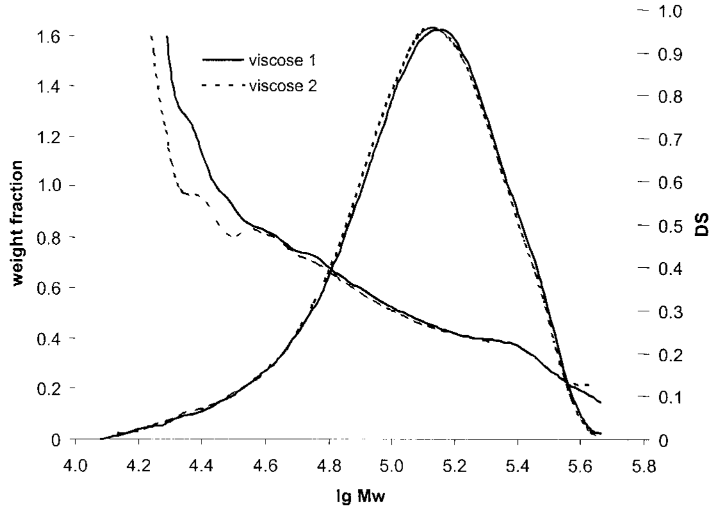
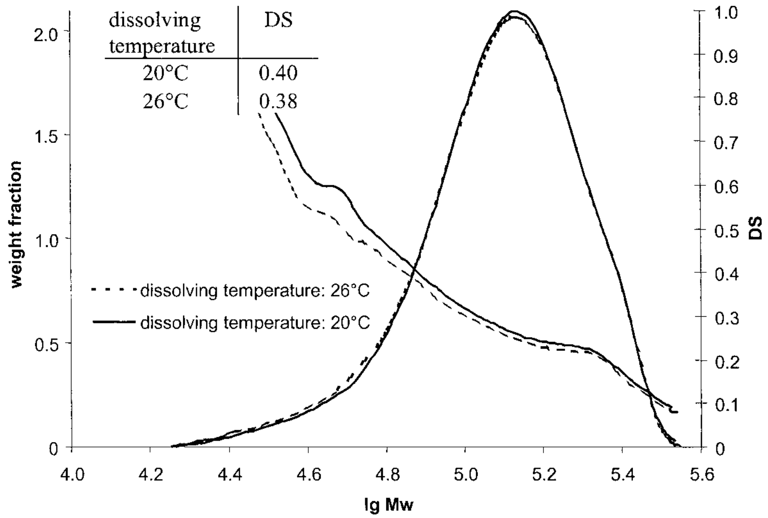


Figure 3. Reproducibility of viscose preparation, measurement of the molecular weight and the degree of substitution.



| dissolving temperature | DS |
|---|---|
| 20°C | 0.40 |
| 26°C | 0.38 |

Figure 4. Influence of the dissolving temperature on the DS and the distribution of the xanthate groups produced from a 92 α- pulp.

Viscose was produced from two pulps characterised by different α- cellulose contents under a variation of the temperature for dissolving between 20 and 26°.

Figure 4 shows the results obtained for a 92 α- pulp. The main part of cellulose xanthogenate shows a degree of substitution between 0.2 to 0.35.

An increase in temperature during dissolution from 20 to 26°C resulted in a loss of substitution through the whole range of molecular masses.

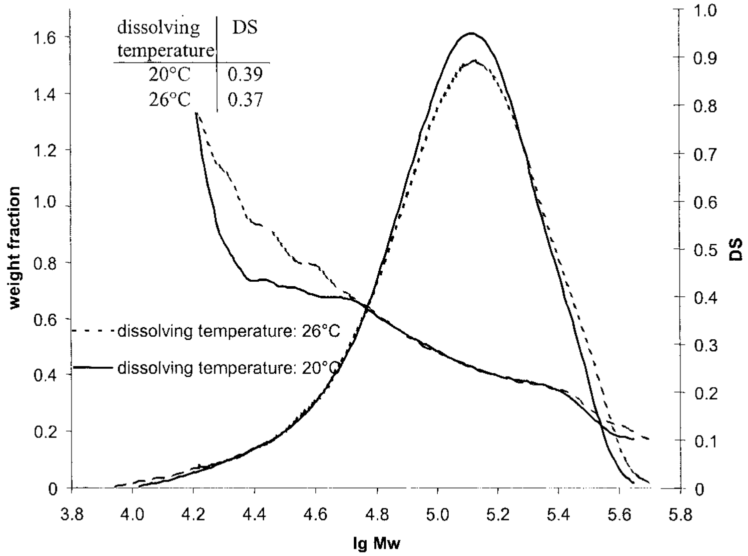


Figure 5. Influence of the dissolving temperature on the DS and the distribution of the xanthate groups produced from a 94 α- pulp.

Such a strong influence of the dissolving temperature on the degree of substitution cannot be observed considering the viscose produced from a 94 α- pulp as can be seen in Figure 5.

The results show that the rate of decomposition of the xanthate is primarily governed by the chemical constitution of the pulp; in this case it depends decisively on the α - cellulose content of the pulp.

Comparing the distribution curves for the degree of xanthation using a 92 and a 94 α - pulp, provided that the temperature for dissolving was comparable, the degree of substitution of the viscose prepared from a 94 α - pulp is more even through the whole range of molecular weights (comparing Figure 4 and Figure 5).

The higher content of hemicelluloses and short- chain cellulose in a 92 α - pulp in comparison to a 94 α - pulp is the cause for a stronger dependence of the decomposition of the cellulose xanthogenate on an increase in temperature during the dissolving process.

Ripening of viscose e.g. a storage of viscose at 20°C for 16 hours results in a loss of substitution over the whole range of molecular weight (Figure 6). Therefore, the hypothesis of Samuelson[7] in respect to a transxanthation of the high molecular weight part of the xanthate could not be estimated.

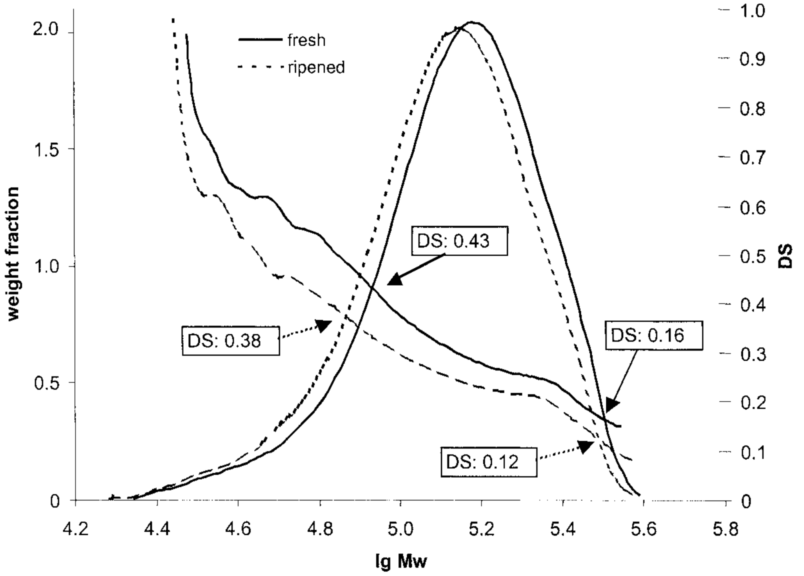


Figure 6. Influence of the ripening process on a viscose prepared from a 92 α- pulp.

The results of these investigations show clearly that ripening of viscose is strongly connected with decomposition of xanthate groups especially in the range of the low and middle molecular weight cellulose xanthogenate. The loss in substitution during the ripening process is smaller using a 94 α- pulp in comparison to a 92 α- pulp (compare Figure 6 and Figure 7).

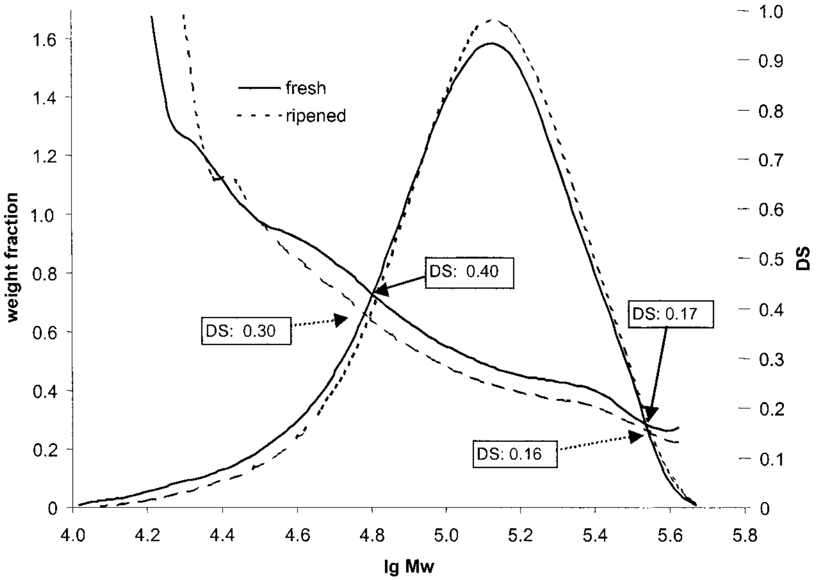


Figure 7. Influence of the ripening process on a viscose prepared from a 94 α- pulp.

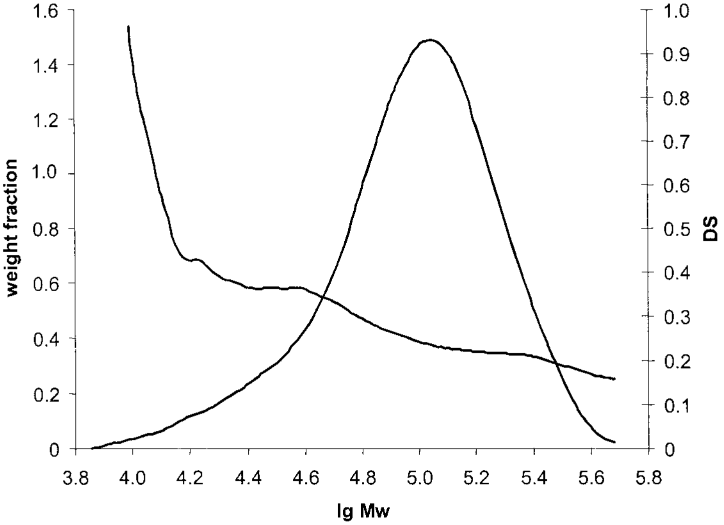


Figure 8. Molecular weight distribution including distribution on a viscose prepared from irradiated pulp.

These results are in agreement with results of past investigations carried out with irradiated pulps[8] (Figure 8). The distribution of xanthate groups in viscose made from irradiated pulp which had a better accessibility for the reactants NaOH and $CS_2$ is also very even over the whole molecular weight region of the cellulose xanthogenate.

Summarising these results much potential for optimising the old viscose process can be seen.

## Carboxymethyl Cellulose

### General Comments on Carboxymethyl Cellulose

Considerable effort has been spent on assessing the distribution of carboxymethyl groups along the polymer chain using a combination of several techniques of degradation, separation, and fragment characterisation. A random degradation by enzymes or strong acids, and the characterisation of the resulting fragments by HPLC or GC, and comparing the real substituents distribution through a mathematical model was the approach up to now.[9-12]

In these investigations it was tried to characterise the carboxymethyl groups on the polymer chain via a direct route. In order to obtain this information a two step derivatisation has been employed at first in which sodium carboxymethyl groups are converted into its methyl ester by a reaction with dimethyl sulphate in DMF. The subsequent amidation with an araliphatic amine allows the measurement of the UV- active amido carboxymethyl cellulose using a multi detection SEC system.

### Experimental

1.1 g of the sodium salt of carboxymethyl cellulose is suspended in 60 ml DMF. 20 ml of dimethyl sulphate was added drop by drop. The mixture was stirred at 45 °C for 48 hours, precipitated into 400 ml of methanol, filtered, washed several times with methanol and dried. The yield was nearly quantitative.

The CMC methyl ester is re-suspended in 20 ml DMF and 15 ml benzyl amine with a catalytic amount of ammonium chloride. The mixture was heated for 5 hours to 70 °C and then precipitated with ethanol : acetone (50:50 v/v). The workup is similar to the first step. All used solvents were analytical grade delivered from Merck.

## Results and Discussion

Several ways are known for modifying carboxylic groups forming ester or amide structures. One possibility is the reaction of sodium carboxylate with thionyl chloride, followed by an amidation with benzyl amine in pyridine according to a method developed by Rahn and co-worker using 6-carboxycellulose[13]. The conversion rate of the carboxylic acid groups was 84% causing a side reaction by chlorinating some AGU units.

The direct reaction of a carboxylic acid group with an amine activated by e.g.. dicyclohexyl carbodiimide, which is known from the protein chemistry, did not work as only a partial conversion of the carboxylic acid groups was observed.

The main path followed for obtaining the methyl ester was the WURTZ- reaction of the sodium salt of the carboxymethyl cellulose, which was carried out in dimethyl sulphoxide according to Tezuka[14]. This ester can be easily converted into an amide by reacting it with an aliphatic or araliphatic amine (Figure 9).

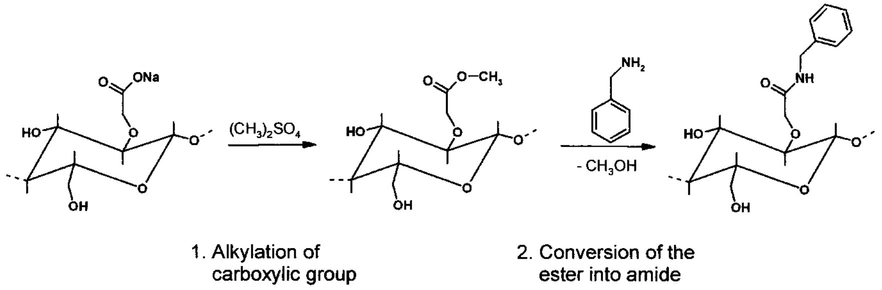


Figure 9. Method used to make CMC UV-active.

Dimethyl formamide was used as solvent in order to prevent the macromolecule against degradation[15] instead of dimethyl sulphoxide. For some carboxymethyl cellulose samples, a pre-activation by re- precipitation CMC from water followed by a drying procedure in vacuum was necessary. The reaction progress was followed by IR- spectroscopy using the shift of the signals at 1610$cm^{-1}$ and 1420$cm^{-1}$ ($COO^-$) to 1752$cm^{-1}$ for the new ester band which was replaced by the amide I and amide II band at 1655$cm^{-1}$ and 1555$cm^{-1}$ in the second step.

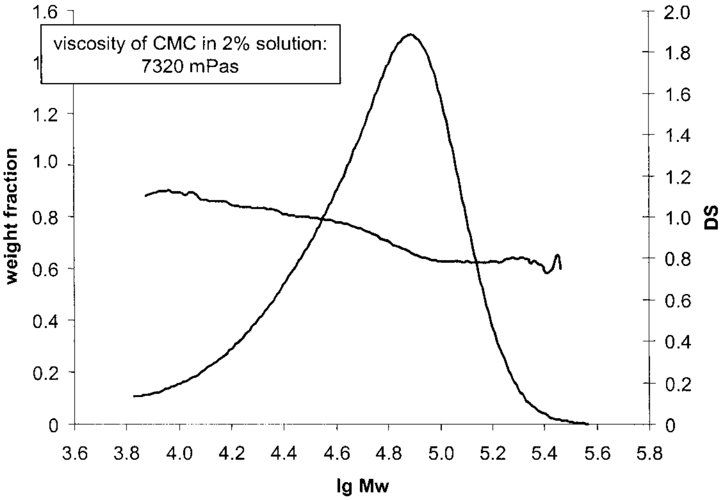


Figure 10. Molecular weight distribution of an amido carboxymethyl cellulose including the distribution of the substituents.

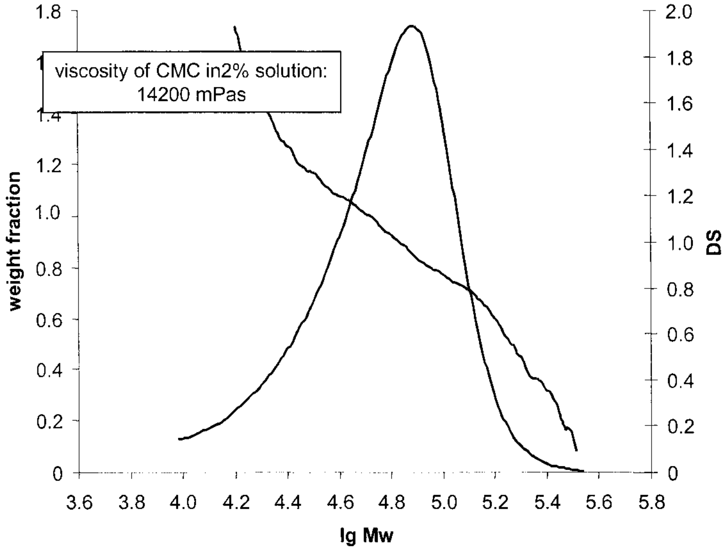


Figure 11. Molecular weight distribution of an amido carboxymethyl cellulose including the distribution of the substituents.

The first samples of modified CMC were examined by the multi detection SEC system distributing the polymer with a diluted sodium hydroxide solution. The sample in Figure 10 is an amido derivative of a low viscosity CMC. The amido carboxymethyl substituents are distributed nearly even above the whole range of the molecular masses.

The next sample shows the molecular weight distribution of an amido carboxymethyl cellulose, including the distribution of the substituents, prepared from a CMC which had a higher viscosity in its origin (Figure 11).

The first results showed that the distribution of the carboxyl groups along the polymer chain can differ significant from one sample to another.

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