

# Cationization of Cellulose by Using *N*-Oxiranylmethyl-*N*-Methylmorpholinium Chloride and 2-Oxiranylpyridine as Etherification Agents

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Received 4 June 2008; accepted 4 April 2009

DOI 10.1002/app.30548

Published online 23 June 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Cationization of cellulose under aqueous alkaline conditions was studied. Two new epoxy reagents, *N*-oxiranylmethyl-*N*-methylmorpholinium chloride and 2-oxiranylpyridine, were used for preparation of cationic cellulose ethers. Using the first agent, cationic ethers were obtained in one step, whereas the latter one yielded a reactive intermediate used as a precursor for two different cationizations. Etherification with the commonly used 2,3-epoxypropyltrimethylammonium chloride was also performed and used as a reference reaction. By changing water content in the reaction mixture two groups cellulose ethers with different degrees of cationization were prepared. As expected, reducing the water content resulted in a higher degree of etherification and hence a more pronounced cati-

onic character of the obtained ethers. Characterization by FTIR, elemental- and gravimetric analysis confirmed the formation of the desired ethers. Their ability to interact with water and adsorb the acid dye, methyl orange, was also studied, confirming further introduction of the cationic substituents and revealing different reactivities of the used epoxy reagents. From characterization, it could be concluded that *N*-oxiranylmethyl-*N*-methylmorpholinium chloride exhibits higher reactivity toward cellulose than both the reference compounds and 2-oxiranylpyridine. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1449–1456, 2009

**Key words:** cationized cellulose; cationized cotton; cellulose ethers; adsorption of acid dyes

## INTRODUCTION

Cationization of cellulose is of considerable industrial importance involving the preparation of moisturizers and conditioners for cosmetic applications,<sup>1–3</sup> adsorbents and chromatography media, paper additives,<sup>4</sup> pollutant adsorbents, as well as antibacterial agents in various water systems.<sup>3</sup>

Main strategies for this modification comprise attachment of various prebuilt quaternary nitrogen structures to the cellulose backbone or quaternization of previously attached amino groups. Introduction of the prebuilt quaternary structures by means of etherification is nowadays the preferred route. It usually uses epoxypropyl- or 3-chloro-2-hydroxypropyl trialkylammonium salts as etherification agents and alkaline activation of cellulose hydroxyl groups.<sup>4–10</sup>

Etherification of cellulose with epoxypropyl-trialkylammonium salts has been known for a long time and is based on the reactivity of the epoxide functionality. Under alkaline conditions, this ring is read-

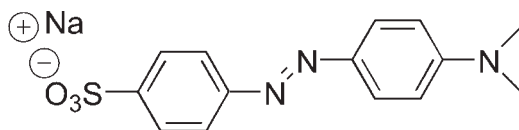
ily opened by nucleophilic attack of cellulose alkoxides creating an ether bond to the cellulose backbone.

In the late 1960s Cuvelier et al.<sup>5</sup> cationized cellulose with epoxypropyl-trialkylammonium salts in aqueous alkaline solutions. Baouab et al.<sup>6</sup> showed that a more effective cationization with the same agent could be obtained in an organic solvent/base system.

One-pot reactions of cellulose with epichlorohydrin and various tertiary amines is another way of using epoxide ring opening chemistry for cationization of cellulose. Ever since Bradley and Rich,<sup>12</sup> and Benedich and Frecso<sup>11</sup> treated cellulose with epichlorohydrin and triethanolamine to produce a cationic derivative in the 1950, this method has been subject to numerous optimization efforts. Different alkali activations and several tertiary amines have been used.<sup>4,7–8</sup>

However, studies on prebuilt epoxy functionalized cationization agents have almost exclusively focused on reagents containing methyl and ethyl groups attached to the quaternary nitrogen.<sup>5,6</sup> In this work, we report on cationization of cellulose by using two structurally different epoxide reagents: *N*-oxiranylmethyl-*N*-methylmorpholinium chloride, (**1**, Fig. 2)

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**Figure 1** Chemical structure of methly orange.

and 2-oxiranylpyridine (2, Fig. 2) that subsequently may be quaternized to afford cationic moieties (3, Fig. 2). This in order to broaden knowledge of structure-properties relationship in synthesis and properties of cellulose ethers.

Etherification with the commonly used 2,3-epoxypropyl-trimethylammonium chloride, EPTMAC was also performed and used as a reference reaction.

By varying water content in etherification reactions, two different groups of cellulose ethers were prepared: in the first group etherifications were conducted in diluted water suspensions, whereas in the second group reactant concentrations were raised by reducing amount of water. The cellulose ethers obtained from etherification with 2-oxiranylpyridine in the second series were further treated with two different alkylating agents to obtain cationic derivatives. Structures of the synthesized cellulose ethers are shown in Table I and Figure 3.

Characterization of the obtained cellulose was performed by FTIR, and elemental, thermogravimetric, and molecular weight distribution analysis. Water retention and adsorption of anionic material were also studied, the latter being based on the fact that cationized cellulose has ability to adsorb anionic dyes through ion exchange. Several previous reports explore adsorption of different anionic dyes to celluloses of varying cation content.<sup>12–14</sup> It has been shown that adsorption capacity reflects the degree of cationization of the cationic cellulose. The anionic dye used in this study is methyl orange, shown in Figure 1.

Adsorption isotherms for aqueous solutions of this dye were constructed for each synthesized cationic

ether to demonstrate and compare their interaction with anions.

## EXPERIMENTAL

### Materials

Cotton linters cellulose was supplied by Munktell Filter AB, Sweden. All other chemicals were obtained from Aldrich and were used without further purification.

### Measurements

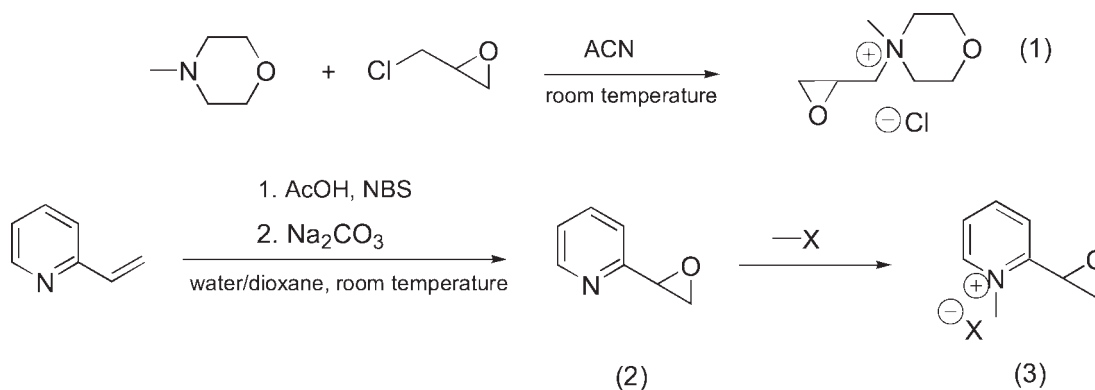
<sup>1</sup>H and <sup>13</sup>C NMR were recorded at room temperature using a Varian UNITY-400 and a Varian UNITY-500 spectrometer, respectively. FTIR spectra were recorded with a Perkin Elmer 16 PC FTIR spectrometer using the KBr technique. Thermogravimetric analysis was carried out using a Perkin Elmer TGA7 and the temperature was increased from 40 to 600°C with a heating rate of 40°C/min. Elemental analysis was performed by Mikroanalytisches Laboratorium, Mülheim an der Ruhr. All adsorption studies were carried out in 25 mM sodium phosphate buffer (pH 7.0), on a Cary 4000 Bio-UV-Vis spectrophotometer (Varian). GPC analysis was performed in DMAc/LiCl as described in Röhrling et al.<sup>15</sup> without labeling.

### Synthesis of the etherification agents

#### *N*-Oxiranylmethyl-*N*-methylmorpholinium chloride (1)

Twenty milliliter (0.18 mmol) *N*-methylmorpholine was mixed with 5 mL acetonitrile and 14.7 mL (0.18 mmol) epichlorohydrin (Fig. 2). During stirring at 38°C the product, a white solid precipitated. After 48 h the solid was isolated by filtration, washed with diethyl ether, and dried. Yield: 65%

<sup>1</sup>H NMR (D<sub>2</sub>O), δ 4.09 – 4.02 (m, 5H, 4 morpholine + 1 glycidyl), 3.70 – 3.53 (m, 5H, 4 morpholine + 1 glycidyl), 3.38 – 3.32 (s, 3H, CH<sub>3</sub>), 3.08 (t, 1H, glycidyl), 2.82 (dd, 1H, glycidyl).



**Figure 2** Synthesis of epoxy functionalized cations for etherification of cellulose. Yield: 65%

**TABLE I**  
Chemical Structure of the Studied Cellulose Ethers

Structure	Name
	HPTMAC-cellulose
	NMM-cellulose
	Py-cellulose
	MPy-cellulose
	TMAPy-cellulose

### 2-Oxiranylpyridine (2)

Twenty gram (0.19 mol) of 2-vinylpyridine was dissolved in 500 mL mixture of dioxane-water (3 : 7) and treated with 10 mL of glacial acetic acid (Fig. 2). Thirty-six gram (0.202 mol) of *N*-bromosuccinimide

was added to the mixture in portions during 30 min. After 1 h, 40 g of Na<sub>2</sub>CO<sub>3</sub> was added over a 15-min period. The reaction mixture was stirred overnight at room temperature.

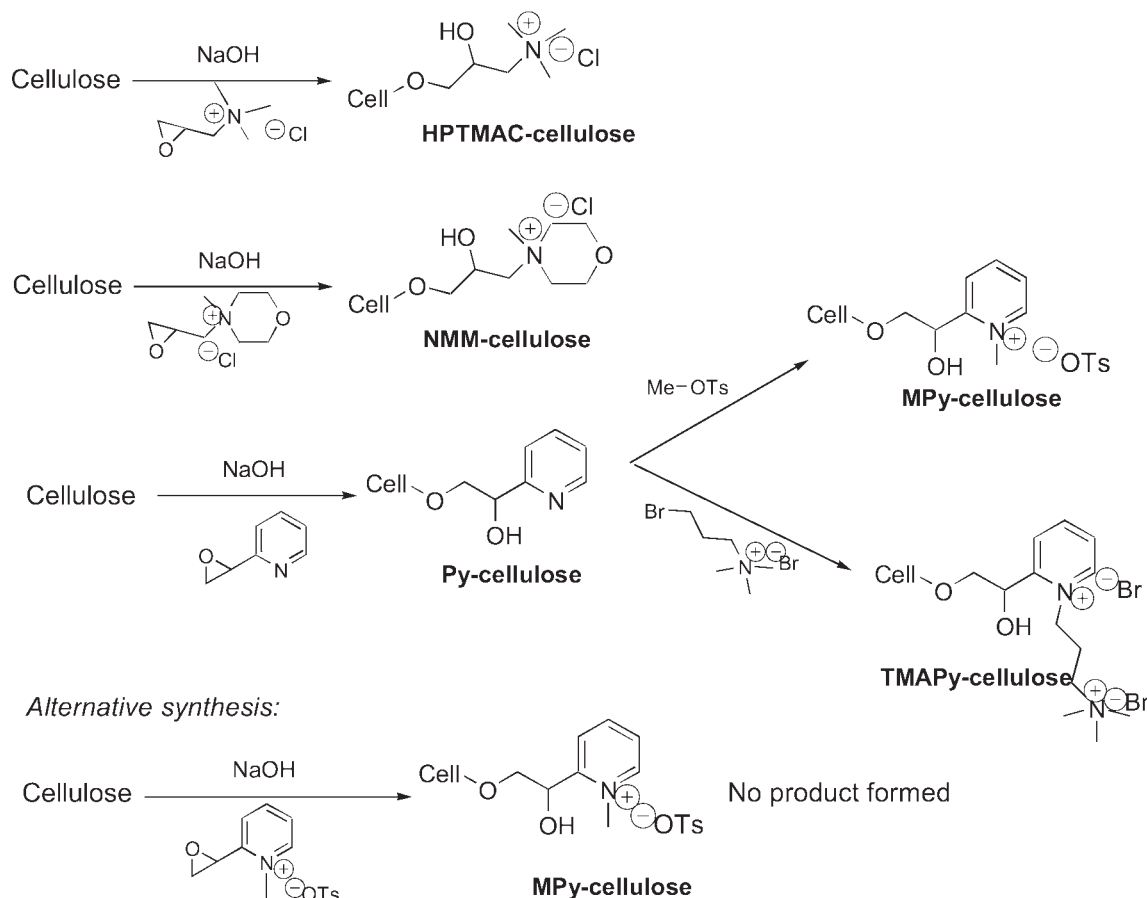
The organic phase was extracted by diethyl ether (6 × 100 mL) a washed with water. 2-Oxiranylpyridine was isolated as colorless oil by vacuum distillation. Yield: ~ 95%

<sup>1</sup>H NMR (CD<sub>3</sub>Cl<sub>3</sub>), δ 8.59 (d, 1H), 7.70 (t, 1H), 7.22-7.29 (m, 2H), 4.05 (dd, 1H), 3.20 (dd, 1H), 2.99(dd, 1H).

### 2-Oxiranyl-*N*-methylpyridinium tosylate (3)

A total of 15.4 g (82.5 mmol) methyl-*p*-toluenesulfonate was added to the solution of 10 g (82.5 mmol) 2-oxiranylpyridine in 20 mL diethyl ether (Fig. 2). During refluxing a very viscous wine-red liquid was formed. After 5 h, the obtained liquid was washed with diethyl ether to yield the pure product as a wine-red ionic liquid. Yield: 83%

<sup>1</sup>H NMR (D<sub>2</sub>O), δ= 9.19 (d, 1H), 8.70 (t, 1H), 8.38 (t, 2H), 8.09 (d, 2H), 7.77 (d, 2H), 5.21 (s, 3H, CH<sub>3</sub>), 4.98 (t, 1H), 3.86 (t, 1H), 3.41 (dd, 1H).



**Figure 3** Reaction scheme for synthesis of cationic cellulose ethers.

### Preparation of cationic cellulose ethers

#### Etherification reactions

Two etherification series were performed. In the first series, cellulose ethers were synthesized starting from 7% suspension of cotton linters in water. In the second series, the concentration of cotton linters in the reaction suspension was raised to 11%. The suspensions were treated with solid NaOH (weight NaOH/weight dry cellulose was 0.54). After 30 min at room temperature, epoxy reagent was added (1 equiv. per cellulose hydroxyl) and the temperature was raised to 65°C. After 2 h, the reaction mixture was neutralized with acetic acid and diluted with water. The product was filtered, washed thoroughly with distilled water, and dried.

#### Quaternization of pyridyl cellulose ether

For preparation of two cationic ethers from the pyridyl cellulose ether, 3 g of the starting material was immersed in 80 mL DMSO. After 30 min stirring, methyl *p*-toluenesulfonate (3.5 g) or bromopropyltrimethylammonium bromide (5 g) was added for the synthesis of MPy-cellulose and TMAPy-cellulose, respectively. Quaternizations were performed at 85°C for 5 h. Finally, reaction mixtures were diluted with distilled water and the solid material was filtered off. After thorough wash with acetone and water including resuspension in DMSO with a subsequent wash step, the products were dried.

An attempt to apply harsher reaction conditions for quaternization with the bromopropyltrimethylammonium bromide by raising temperature to 110°C and prolonging reaction time to 8 h resulted in severe degradation of cellulose yielding no solid product.

### Characterization

#### Adsorption of methyl orange

To construct adsorption isotherms for the studied cellulose ethers, 200 mg of each ether was suspended in aqueous solutions of methyl orange ranging from 0.025 to 3.5 mM. After stirring for 48 h at room temperature, the remaining concentration of methyl orange in water solution was determined measuring absorbance of the solution at the wavelength corresponding to the absorbance maximum ( $\lambda_{\text{max}} = 463 \text{ nm}$ ). Dye concentration adsorbed to the cellulose ether was calculated as difference between the initial and final dye concentration in water. Concentration of the adsorbed methyl orange was then plotted as function of the concentration in water solution (Fig. 5).

#### Water retention value

For determination of water retention values cellulose ethers were immersed with excess of water for 24 h. The wet samples were then centrifuged at  $4000 \times g$  for 10 min and weighted ( $W_w$ ). After drying at 105°C the samples were reweighted ( $W_d$ ) and the amount of retained water per weight dried ether was calculated as:

$$\text{WRV} = (W_w - W_d)/W_d$$

## RESULTS AND DISCUSSION

### Synthesis of etherification agents

Usage of epoxy functionalized structures in cellulose etherifications is usually associated with high cost and limited commercial availability of the reagents. Here, we used two simple syntheses of epoxy cations suitable for large scale preparation. One of them is based on epoxidation of 2-vinylpyridine, whereas the other one is a simple quaternization of tertiary amine with epichlorohydrin. (Fig. 2).

Synthesis of *N*-oxiranylmethyl-*N*-methylmorpholinium chloride was performed at room temperature by simply stirring an equimolar mixture of *N*-methylmorpholine and epichlorohydrin in the presence of small amount of acetonitrile.

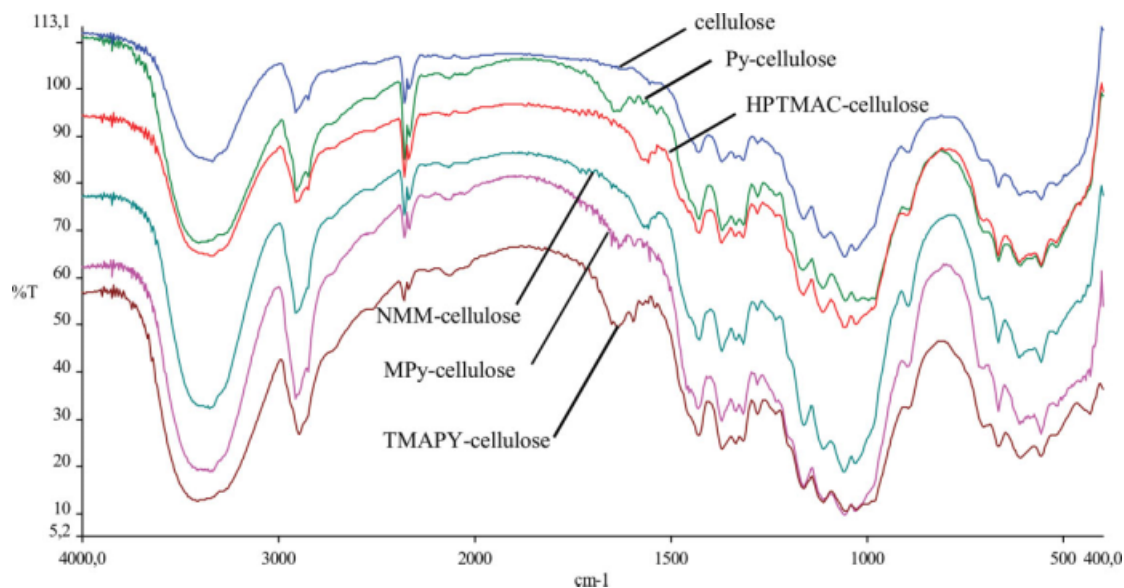
Preparation of 2-oxiranylpyridine is an efficient one-pot reaction, where 2-vinylpyridine is treated with acetic acid and *N*-bromosuccinimide to introduce bromine and a hydroxyl group to the double bond. Addition of  $\text{Na}_2\text{CO}_3$  results in intramolecular displacement of bromine by the deprotonated hydroxyl group and thus formation of the epoxide.

### Etherification of cellulose

Etherification reactions with the above described epoxy structures were performed in alkaline cellulose slurry in water, according to the reaction scheme in Figure 3.

The reaction with 2-oxiranylpyridine yielded a slightly discolored cellulose material, Py-cellulose, whereas *N*-oxiranylmethyl-*N*-methylmorpholinium chloride and the reference compound EPTMAC formed white cellulose derivatives, NMM-cellulose and HPTMAC-cellulose, respectively. During filtration with water, the NMM- and HPTMAC-cellulose showed a tendency to gel, typical of cationized celluloses. As expected, the gelation was more pronounced in the second etherification series, where due to the increased reactant concentrations higher degrees of etherification were expected.





**Figure 4** FTIR spectra of the studied cellulose ethers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Subsequent quaternizations of Py-cellulose with methyl-*p*-toluenesulfonate or bromopropyltrimethylammonium bromide at elevated temperatures in DMSO afforded MPy- and TMAPy-cellulose, respectively. (Fig. 3).

Interestingly, an attempt to raise the reaction temperature to 110°C and prolong the reaction time to 8 h to obtain a more efficient quaternization with the bromopropyltrimethylammonium bromide resulted in severe degradation of the Py-cellulose.

DMSO-mediated degradation of cellulose has been previously reported, mainly as a side reaction during carbanilations in DMSO. Proposed mechanisms include oxidation of cellulose with DMSO with subsequent  $\beta$ -elimination and require presence of carbonyl groups in the starting cellulose material.<sup>16</sup> Here, further investigation of quaternization reactions including separate treatments of Py-cellulose and quaternization agents with DMSO, revealed that DMSO and the quaternization agents generate extremely acidic conditions at high temperatures. Depolymerization of cellulose is thus probably a result of acidic hydrolysis of the glycosidic bonds.

DMSO is well known for its oxidizing abilities and in this case acidification of the reaction mixture might have its origin in the oxidation of the alkylating agent by DMSO, a process generating  $H^+$ .<sup>17,18</sup>

It is also interesting that the attempts to obtain the MPy-cellulose by one step etherification with the quaternized 2-oxiranylpyridine failed. (Fig. 3).

Since a NMR study of the alkaline hydrolysis of the studied epoxy reagents did not indicate any drastic differences in degradation rates, the failed etherification could not be a result of too fast hydrolysis of the reagent. Instead, it might be explained

by sterical hindrances induced by the close proximity of the epoxide to the quaternized nitrogen atom of the pyridine ring bearing a methyl group and a counterion.

### Characterization

Characterization by means of FTIR spectroscopy, elemental, thermogravimetric, and molecular weight distribution analysis, as well as water and methyl orange interactions confirms formation of the desired ethers. FTIR spectra of cotton and synthesized ethers are shown in Figure 4.

FTIR-spectra of Py-, MPy-, and TMAPy-celluloses show characteristic bands at 1630–1650  $cm^{-1}$  assigned to C–N vibrations in the pyridinium groups.

Furthermore, all the spectra also show increased signal from C–H stretching, indicating presence of the substituent structures in the obtained cellulose ethers. Absorption bands at  $\sim 1540\ cm^{-1}$  in the spectrum of NMM and HPTMAC cellulose can be attributed to C–N vibrations in methylmorpholinium and trimethylammonium moieties of these ethers.

The nitrogen content of the studied ethers was determined through elemental analysis and used to estimate degree of substitution. The results are given in Table II.

Despite using one molar equivalent of cationic reagents per cellulose hydroxyl, etherification reactions yielded very modest substitution of cellulose, with DS ranging from 0.027 to 0.077 (Table II). According to the NMR studies performed on the reagents under similar conditions, these low values may be mainly attributed to alkaline hydrolysis of

**TABLE II**  
**Nitrogen Content and DS of Studied Cellulose Ethers**

Cellulose ether	Series I (Etherification on 7% w/w cellulose suspension)		Series II (Etherification on 11% w/w cellulose suspension)	
	Nitrogen content (%)	DS	Nitrogen content (%)	DS
HPTMAC-cellulose	0.33	0.040	0.47	0.057
NMM-cellulose	0.40	0.049	0.61	0.077
Py-cellulose	0.23	0.027	0.32	0.038
MPy-cellulose			0.22	–
TMAPy-cellulose			0.18	–

the reagents during the reactions. Poor accessibility of the cellulose structure in cotton linters combined with dilution and hydrolysis of the reagents renders very low rate of etherification. Under such conditions, the alkaline hydrolysis of the reagent is probably the dominating reaction resulting in very low DS values.

As expected, degrees of etherification were significantly raised by reducing water content of the reaction slurry in the second synthesis series (Table II).

In the case of the ethers prepared in one step, HPTMAC-, NMM- and Py-cellulose, degree of substitution could be estimated from the nitrogen content data. MPy- and TMAPy-cellulose are prepared from Py-cellulose and contain, thus, probably the same quantity of pyridyl moieties. However, estimation of their cation content based on the above data is troublesome. Unreasonable changes in nitrogen content during quaternization reactions (Table II) indicate side reactions of the quaternizing agents with cellulose hydroxyls that might have been activated by alkali during the previous etherification step.

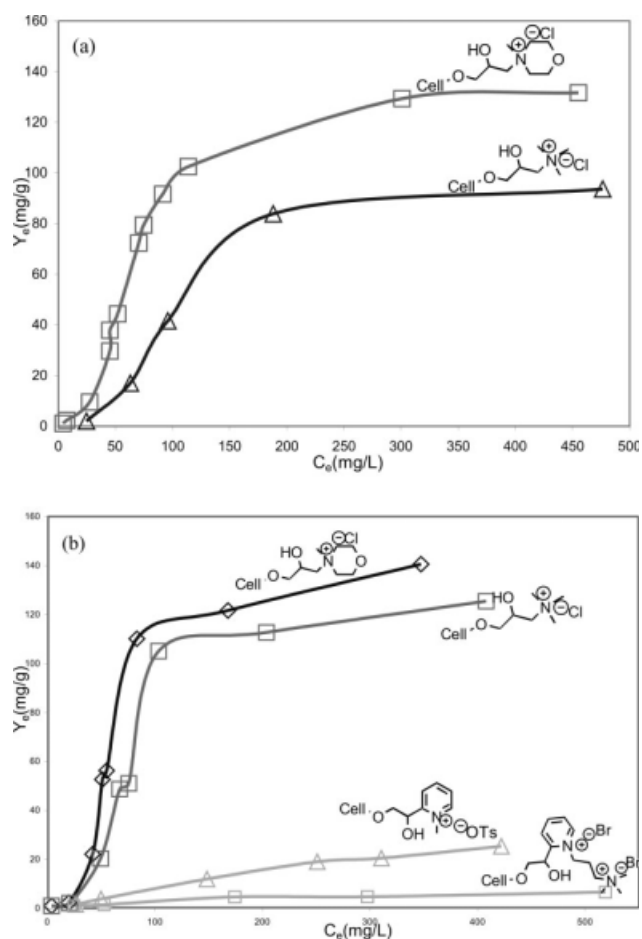
However, based on these results it might be concluded that *N*-oxiranylmethyl-*N*-methylmorpholinium chloride exhibits higher etherification reactivity toward cellulose than both 2-oxiranylpyridine and EPTMAC under aqueous alkaline conditions. As mentioned above, one of the reasons for the significantly lower reactivity of 2-oxiranylpyridine might be sterical hindrance due to the close proximity of the epoxide and the pyridine ring, as well as rather poor solubility of the 2-oxiranylpyridine in water.

These results are further confirmed by the methyl orange adsorption studies, as shown in Figure 5 displaying dye concentration adsorbed to the cellulose ether (mg dye/g cellulose ether,  $Y_e$ ) as a function of dye concentration in the water solution (mg dye/L water,  $C_e$ ).

In Table III, the maximal observed adsorption values are listed along with the number of available

cationic sites calculated from the degrees of substitution as mmol/g cellulose ether.

As shown from the adsorption isotherms, NMM-cellulose prepared with the *N*-oxiranylmethyl-*N*-methylmorpholinium chloride displays highest methyl orange adsorption in both etherification



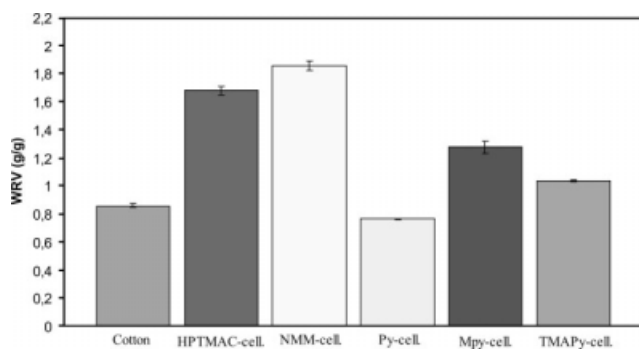
**Figure 5** Adsorption of Methyl Orange on the synthesized cellulose ethers: (a) series I, etherification in 7% w/w cellulose suspension and (b) series II, etherification in 11% w/w cellulose suspension.

**TABLE III**  
Maximum Adsorption of Methyl Orange for the Two Series of Cationic Ethers (mmol/g)

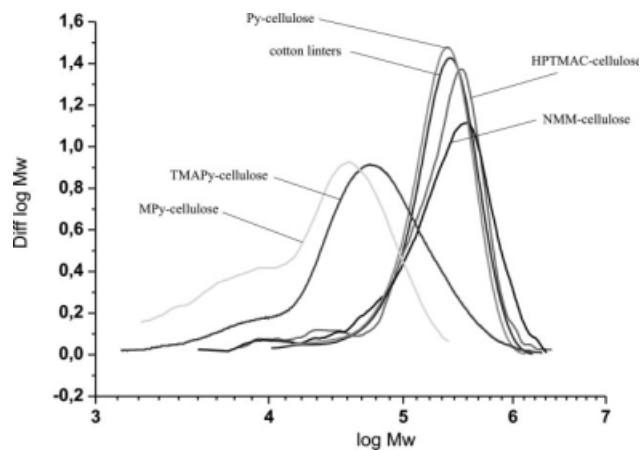
Sample	Equilibrium adsorption of methyl orange (mmol/g)
Series I	
NMM-cellulose	0.40
HPTMAC-cellulose	0.28
Series II	
NMM-cellulose	0.43
HPTMAC-cellulose	0.38
MPy-cellulose	0.06
TMAPy-cellulose	0.02

series. On the other hand, both cationic ethers synthesized from the less reactive 2-oxiranylpyridine show significantly lower dye adsorption. Differences in reactivity of the *N*-oxiranylmethyl-*N*-methylmorpholinium chloride and 2-oxiranylpyridine toward cellulose, as well as incomplete quaternization of pyridine nitrogen account partly for these observations. However, different basicity and thus different ion exchange potential of the quaternary ammonium salts and pyridine salts has to be taken into account as well. As stronger basic ion exchangers, quaternary ammonium substituents of NMM- and HPTMAC-cellulose contribute to higher methyl orange adsorption compared to the pyridinium substituents of TMAPy- and MPy-cellulose.

Further, it is difficult to draw a parallel between the nitrogen content and methyl orange adsorption of the TMAPy- and MPy-cellulose, since their nitrogen percentages contain different types nitrogen (quaternized and nonquaternized pyridine nitrogen, as well as quaternized trimethylammonium nitrogens that are introduced to the pyridinium moieties or reacted with cellulose hydroxyls). In addition, all these cationic sites display different adsorption properties depending on their position and the type of quaternary nitrogen. For these reasons, no estima-



**Figure 6** Water retention values of the cellulose ethers (Series II) and unmodified cotton.



**Figure 7** Molecular weight distribution for the studied cellulose ethers.

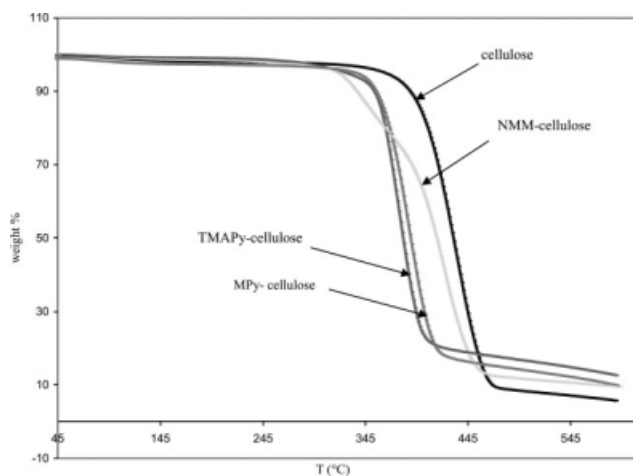
tion of the amount available cationic sites could be done for these two ethers (Table III).

It is interesting that the methyl orange adsorption on NMM-cellulose only to a very limited extent reflects increase in nitrogen content between the two series, whereas HPTMAC-cellulose seems to adsorb an excess of the dye compared to the number available sites. This is probably due to the different ion exchange potentials of the substituents combined with possibilities of dimeric and nonelectrostatic dye adsorption.

As observed during the filtration of the obtained ethers, cationization rendered significantly improved interaction with water. When in water the cationized celluloses displayed a strong tendency to gel, observation confirmed by studying swelling in water, measured as water retention values (WRV). These values reflect the cationic nature of the ethers and follow variations in DS values (Fig. 6).

Apparently, cationization results in a significant improvement of water retention, with NMM- and HPTMAC-cellulose being able to retain about double amount of the water retained by unmodified cotton. A slightly higher water retention value for NMM-cellulose reflects the higher degree of cationization of this ether compared to HPTMAC-cellulose. The less cationized MPy- and TMAPy-celluloses exhibit, as expected, lower increase in WRV, whereas substitution with the rather hydrophobic pyridinium moiety reduces swelling capacity of the fibers.

Molecular weight distributions (Fig. 7) after performed one-step cationizations indicate no significant depolymerization of the starting material. On the other hand, the two-step preparation of MPy- and TMAPy-cellulose involving quaternization of the pyridine nitrogen in DMSO leads evidently to a significant depolymerization of the cellulose backbone. As discussed above, this is most likely a consequence of acidic hydrolysis resulting from a side



**Figure 8** Thermogravimetric analysis of unmodified cellulose and cationic cellulose ethers, series II.

reaction between DMSO and the quaternizing agents.

To investigate the thermal stability and the decomposition pattern of the synthesized ethers, thermogravimetric analysis was performed in the temperature range from 40°C up to 600°C and compared to that of unmodified cotton.

Because of the presence of easily pyrolyzed cationic moieties the three cationic ethers exhibit a decreased thermal stability compared to the unmodified cotton (Fig. 8). Another effect of the introduction of cationic substituents and their counterions is a higher amount of the residual material after pyrolysis.

## CONCLUSIONS

A group of cationic cellulose ethers has been synthesized using *N*-oxiranylmethyl-*N*-methylmorpholinium chloride and 2-oxiranylpyridine under aqueous alkaline conditions.

Dilution of reaction mixture and sterical hindrances at the epoxy moieties proved to considerably reduce etherification efficiency.

Even though the 2-oxiranylpyridine exhibited somewhat lower reactivity in etherification of cellulose, it is a valuable chemical anchor, since it introduces reactive pyridine moieties to the cellulose structure. This pyridine substituted cellulose might be used as a starting material for a plethora of further modifications, where quaternization of pyridine nitrogen with alkyl halides or *p*-toluenesulfonates is one example, shown in this article. Quaternization

conditions need to be adjusted to obtain maximum quaternization with minimized side reactions of quaternizing agents, especially processes leading to depolymerization of cellulose.

Cationized celluloses exhibit major improvement of swelling capacity. Introduction of the cationic *N*-methylmorpholinium chloride at a DS of 0.077, for instance, results in more than a twofold increase of water retention value.

All obtained cationic ethers displayed a significant adsorption of the anionic dye methyl orange. However, methyl orange adsorption isotherms do not trustworthy reflect degree of cationization probably due to troublesome adsorption mechanisms involving sterical factors, variations in ion exchange capacities among the different substituents and uneven cation distribution.

The authors would like to thank Södra Skogsägarnas Stiftelse för Forskning, Utveckling och Utbildning for financial support and everyone involved in "Avancell – Centre for fibre engineering" for good cooperation. Dr. Mats Wallin, Södra Cell AB is especially thanked for establishing the Avancell program.

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