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An alternative approach for deprotection of triphenylmethyl cellulose

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Summary

The triphenylmethyl (trityl) moiety is often used to protect primary hydroxy groups of polysaccharides. In this work a new procedure of the deprotection of trityl cellulose is described. Molten salt hydrates like $LiClO_4{}^*3H_2O$ and $ZnCl_2{}^*4H_2O$ were firstly used as media for this reaction. The complete deprotection of trityl cellulose occurs in comparatively short reaction time (3-5 hours). The completeness of the detritylation reaction was demonstrated by means of FT-IR and ^{13}C CP/MAS NMR spectroscopy.

Introduction

At present, there is an increasing interest in highly engineered cellulose derivatives, with carefully selected sites of functionalization within the repeating anhydroglucose units (AGU) as well as along the polymer chains (1-3). To synthesize such cellulose products, protecting group techniques were extensively studied as a tool for a selective subsequent functionalization. Thus, the triphenylmethyl (trityl) group is a widely used protective group for the primary OH-function in polysaccharides which allows selective subsequent functionalization of the remaining secondary OH-groups (4,5). The preparation of 2,3-di-O-carboxymethyl cellulose was first carried out via homogeneously synthesized trityl cellulose (6). On the other hand, the synthesis of model cellulose esters for spectroscopy like 6-mono-O-2,3-di-O-propanoyl- and 2,3-di-O-acetyl-6-mono-O-propanoyl-cellulose was possible (7). Even 6-O-methyl and 6-O-benzyl cellulose were obtained starting from trityl cellulose via allylation, detritylation, isomerization and methylation respectively benzylation and removal of 1-propylene groups (8,9). Furthermore, 6-deoxy-6-fluorocellulose was prepared via trityl cellulose (10). It is obvious that in any synthesis path mentioned a detritylation step is necessarily included. The most common and effective methods are treatments of the polymers with gaseous hydrogen chloride in tetrahydrofuran, chloroform or methanol or with hydrogen bromide in acetic acid within a few minutes up to 16 hours (6,7,11,12). However, in some cases it is difficult to reach a complete removal of the trityl functions.

Recently, Fischer et al. (13,14) have found that various molten inorganic salt hydrates dissolve cellulose, e.g. $LiClO_4{}^*3H_2O$, LiI^*2H_2O and $ZnCl_2{}^*4H_2O$. They can be applied to transform cellulose to fibers and sheets as well as to carry out chemical functionalization reaction under homogeneous conditions. The etherification of cellulose dissolved in $LiClO_4{}^*3H_2O$ was preliminarily studied (15). It was found that carboxymethyl cellulose with a degree of substitution of up to 0.7 with a statistic functionaliztion pattern is accessible.

In this ongoing research, we studied the behavior and solubility of various cellulose derivatives in molten inorganic salt hydrates including trityl cellulose. In the present paper we report about the behavior of trityl cellulose in melts of $LiClO_4{}^*3H_2O$ and $ZnCl_2{}^*4H_2O$ and the development of a new effective detritylation procedure.

Experimental

Materials

For melt preparation $LiClO_4{}^*3H_2O$ and anhydrous $ZnCl_2$ (Merck, for analysis) were used. To get the melt composition ($ZnCl_2{}^*4H_2O$) a stoichiometric amount of water was added to $ZnCl_2$. The removal of the protecting triphenylmethyl (trityl) group was studied on trityl celluloses with a degree of substitution (DS) of 0.65 and 0.80.

Deprotection of trityl cellulose

$LiClO_4{}^*3H_2O$ was melted in a closed flask at 110 °C. Reactions in $ZnCl_2{}^*4H_2O$ were carried out at 65 °C. Trityl cellulose was added (1-3 % w/w) to the molten salt hydrates under permanent stirring at constant temperature for 3 to 5 h yielding suspensions. After an adequate time the salts were removed by washing with water which results in a solid mixture of cellulose and triphenyl carbinol. The polymer was isolated by extraction with acetone.

Measurements

^{13}C CP/MAS NMR spectra were aquired on a Bruker MSL 300 at a resonance frequency of 75.47 MHz. The samples were inserted in a 7 mm zirconia rotor at a spinning frequency of 5 kHz. All spectra were obtained with a contact time of 1 ms and a repetition time of 5 s.

The FT-IR measurements were performed with a Nicolet 510 spectrometer using the KBr technique.

Results and discussion

During our work on the solubility and reactivity of different cellulose derivatives in molten salts we studied the behavior of triphenylmethyl (trityl) cellulose in the cellulose solvents $LiClO_4{}^*3H_2O$ and $ZnCl_2{}^*4H_2O$. It was observed that in the course of dissolution of the cellulose derivative in these salt melts a yellow color appears which might indicate a cleavage of the triphenylmethyl (trityl) ether groups. It was found that solutions with 1 to 3 % (w/w) trityl cellulose represent highly efficient systems to achieve even a complete detritylation during reasonable reaction times. Complete deprotection in molten $LiClO_4{}^*3H_2O$ was possible after 3 to 5 hours depending on the polymer concentration and in $ZnCl_2{}^*4H_2O$ after 3 hours. The deprotection was not significantly influenced by the total DS_{Trityl} of the starting derivative. Reaction conditions are summarized in Tab. 1.

Tab. 1: Conditions and results of detritylation of triphenylmethyl cellulose with different degree of substitution (DS) in molten salt hydrates

Trityl cellulose DS	Melt composition	Temperature (°C)	Reaction time (h)
0.65	$LiClO_4*3H_2O$	110	5
0.65	$ZnCl_2*4H_2O$	65	3
0.80	$LiClO_4*3H_2O$	110	5
0.80	$ZnCl_2*4H_2O$	65	3

FT-IR and ^{13}C CP/MAS NMR analysis were applied to elucidate the course of reaction. In Fig. 1a the FT-IR spectrum of the trityl cellulose with the typical band of an aromatic system (marked with *) is shown. These bands disappear entirely after a treatment with the respective molten salts at the mentioned conditions (Fig. 1b). Moreover, the spectrum obtained is characteristic for an unmodified cellulose indicating a complete deprotection.

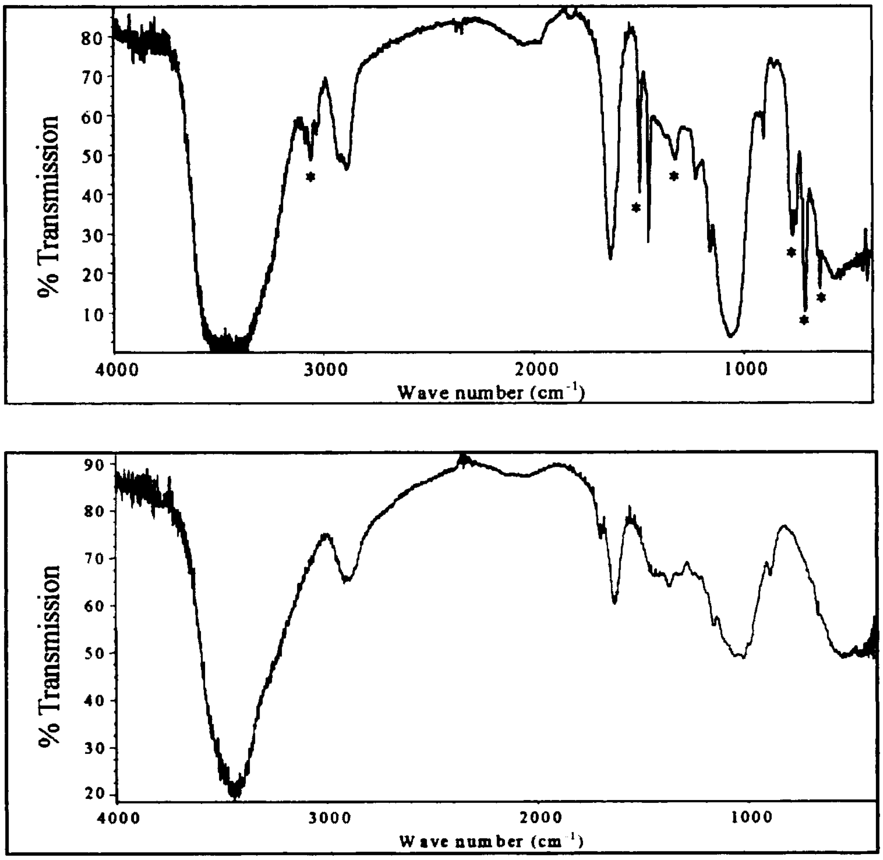

Fig. 1: FT-IR spectra of a) tritylphenylmethyl cellulose and b) the detritylation product

Further evidence for the completeness of the detritylation reaction was gained from ^{13}C CP/MAS NMR measurements. In Fig. 2 the spectra of the starting material and the detritylated product are compared.

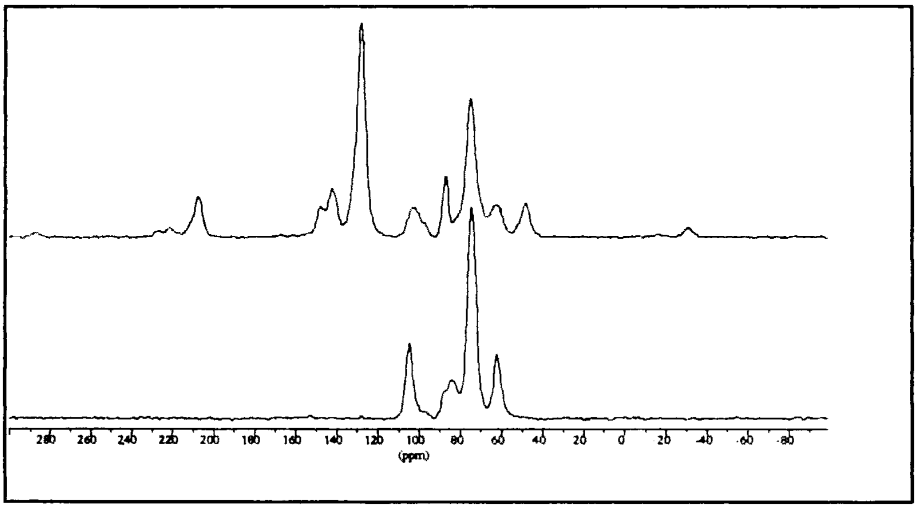

Fig. 2: ^{13}C CP/MAS NMR spectra of a) tritylphenylmethyl cellulose and b) the detritylation product

The corresponding chemical shifts are summarized in Tab. 2. It can be seen that after a treatment of the trityl cellulose with the salt melts all signals in the aromatic region (between 120 and 150 ppm) have disappeared. The obtained spectrum shows the chemical shift pattern of a cellulose of the crystal modification II (16). The ^{13}C-NMR data (see Tab. 2) are comparable with those of the regenerated celluloses from molten salts relating to signal position and half width.

Tab. 2: ^{13}C chemical shifts of triphenylmethyl (trityl) cellulose and the detritylation product in comparison to cellulose regenerated from molten $LiClO_4*3H_2O$

Sample	^{13}C chemical shifts in ppm				
	C 1	C 2,3,5	C 4	C 6	aromatic moiety
trityl cellulose	102.8	75.0	87.1	62.2	147.9, 142.2, 128.0
detritylation product	104.9	74.8	84.3	62.5	<0.5% detectable
regenerated cellulose	104.5	74.5	82.4	62.0	-

By determining the intensity ratio of the different signals of the C-4 carbon an estimation of the crystallinity of the samples is possible, because the intensity distribution of these signals can be explained by the occurrence of crystalline and noncrystalline regions in the cellulose samples [16)]. The crystalline component can be observed between 87.5 and 88.5 ppm, the noncrystalline at approximately 84 ppm. The cellulose regenerated from molten $LiClO_4^*3H_2O$ is highly disordered, the spectra of this sample shows almost no signal for crystalline components. The detritylation product regenerated from molten $LiClO_4^*3H_2O$ has similar properties (17).

Because of the fact that the detritylation product is cellulose II the cellulose formed during the reaction was rapidly dissolved in the melts as schematically shown in Fig. 3.

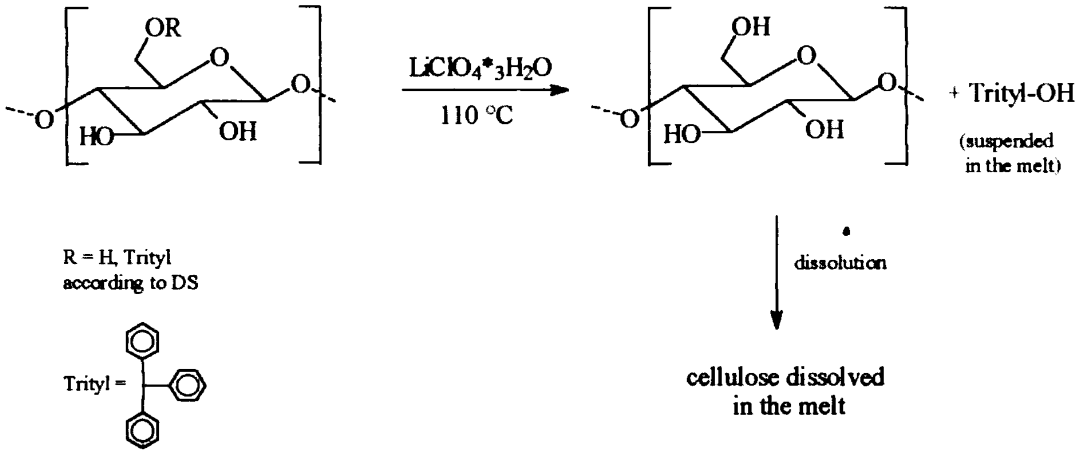

Fig. 3: **Reaction scheme of detritylation in molten salt hydrates**

The immediately dissolved cellulose is continuously removed from the suspended trityl cellulose. Thereby the equilibrium of the reaction is shifted towards the formation of the regenerated cellulose. Besides the high acidity of the molten hydrates this could be another reason for the rapid and complete detritylation under these conditions.

The cellulose formed by the detritylation process should be degradated to a less degree like shown in an earlier work relating the dissolution of cellulose in molten salts (17).

The used molten salt hydrates could be recrystallized and used for further detritylation reactions.

Conclusions

It was shown that the molten salt hydrates are effective and convenient reagents for the deprotection of trityl cellulose. Within 3 to 5 hours the reaction leads to pure cellulose of the crystal modification of type II as revealed by FT-IR and ^{13}C-NMR spectroscopy. The fast detritylation is combined only with a very low degradation of the polymer. Both the detritylation of subsequently functionalized trityl celluloses and the reactions of different cellulose derivates, e. g. acetates, in salt melts are under investigation. The detritylation reaction is just one example of a wide variaty of reactions possible in molten salt hydrates.

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