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Innovative Concepts for the Shaping and Modification of Cellulose

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Summary: The conception and first results for a newly established project at the Center of Excellence for Polysaccharide Research in Jena are described. The work is focused on the investigation of new cellulose solvents and activating agents. Besides the use of a variety of Ionic Liquids it is the interaction of carbohydrates with boric acid and boronic acid, which will be exploited for the regeneration and chemical modification of the biomacromolecule. Two new ILs bearing cellulose activating anions were discovered which can dissolve the polysaccharide. Studies on the dissolution and chemical conversion of cellulose in ILs show the potential for homogeneous reactions but also reveal a number of side reactions especially for acetate containing ILs. In case of boronic acids a covalent binding on the secondary OH functions of glucose and glucose based polymers can be evidenced for the first time at intact molecules.

Keywords: boron derivatives; cellulose; chemical modification; ionic liquids; regeneration

Introduction

In June 2005 the German Agency for Renewable Resources (Fachagentur Nachwachsende Rohstoffe, FNR) launched a call for projects focused on the use of plant ingredients as feedstock for new materials both for use in industries and research. Six projects were granted. Besides the expected scientific progress the goal of the FNR is to strengthen the position of this important subject at universities and research institutions. One of these projects is dealing with the search for new activating and dissolving media for cellulose. These media can be applied for the regeneration of the polymer cellulose leading to new shaping processes which could substitute older methods, e.g. the Viscose process, with the related environmental problems. In addition, such new media could open up commercially relevant paths for the homogeneous chemical functionalization of cellulose leading to new high value products in larger scale. Two strategies will be investigated. On one hand, it is the application of Ionic Liquids which are considered as one of the most promising new cellulose solvents since the first report in 2002.[1] On the other, the use of boron containing compounds as activating agents for cellulose will be studied. Boron containing derivatives of cellulose are scarcely investigated because of the broad variety of interactions possible for the reaction of boric acid, boronic acid or boron containing salts with polyols.[2]

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Discussion

Cellulose Solvents

The search for new cellulose solvents is one of the most important ways to increase the amount of cellulose used as feedstock for the production of various polymeric materials because it may open up new routs for the regeneration and chemical modification of this important polysaccharide. The conventional processes such as the

Viscose process already established in 1892 by Charles Frederick Cross and Edward John Bevan[3] and the Cupro method first applied 1890 by Louis-Henri Despeissis[4] are no longer acceptable because of the sulfur containing by-products and the heavy metal containing waste water. An alternative is the *N*-methylmorpholine-*N*-oxide (NMNO) method for the regeneration.[5] The problems here are the instability of the solvent and the fiber quality of the regenerated cellulose. Moreover, a chemical modification of cellulose in this solvent is almost impossible.[6] Thus, numerous aqueous and non aqueous cellulose solvents were developed over the last three decades. A selection of these solvents is given in Table 1. None of these solvents found broad commercial interest for cellulose regeneration.

DMAc/LiCl is considered as most valuable solvent system for homogeneous chemical modification of cellulose up to now, especially for tailored esterification reactions.[20] It was demonstrated that esterification in this system leads to a broad variety of derivatives not accessible via heterogeneous steps. Nevertheless, the solvent is expensive and a recycling of this two-component medium is rather complicated hindering large scale utilization. The same is true for the fairly new solvents DMSO/TBAF[18] and the isolated organosoluble cellulose intermediates, e.g. cellulose formates[13] which are reasonable only for lab scale experiments. Therefore, alternative media for the dissolution of cellulose are necessary. One exciting development in this context is the utilization of Ionic Liquids (ILs).

Ionic Liquids

Molten organic salts with low melting points now referred to as ILs, attracted remarkable interest in the early 1960ths at the U.S. Air Force Academy as salt electrolytes for thermal batteries.[21] Most of these substances melt below 100 °C. Some of them are liquid at room temperature. These water-free systems consist completely of ions making ILs the solvent of choice for a variety of synthesis. Because of their low vapor pressure and the possible recycling they are considered as green solvents. In 2002 Rodgers et al. published the use of ILs as cellulose solvent both for the regeneration of cellulose and for the chemical modification of the polysaccharide.[1] Although that publication started a whole new development in the field of cellulose research there were earlier attempts to use comparable compounds for the dissolution and modification of cellulose. The first report on salt-like cellulose solvents was published in 1934 by Greanacher.[22] Here the ethylammonium nitrate was applied. Husemann and co-workers in Freiburg/Germany utilized ethylpyridinium chloride as medium for the homogeneous conversion of cellulose.[14] The most fruitful ILs for the modification of cellulose are the 1-alkyl-3-methylimidazolium salts.[23] It

Table 1.
Summary of typical aqueous, derivatizing and non-derivatizing organic solvent systems for cellulose.

Type of solvent	Solvent	Intermediate Formed	Ref.
Aqueous	Nitren	–	[7]
	Molten inorganic salt hydrates	–	[8]
Organic/derivatizing	N_2O_4/DMF	Cellulose nitrite	[9]
	Paraformaldehyde/Dimethyl sulfoxide (DMSO)	Methylol cellulose	[10]
	Chloral/DMF/Py	Cellulose trichloroacetale	[11]
	Trifluoroacetic acid	Cellulose trifluoroacetate	[12]
	Formic acid	Cellulose formate	[13]
Organic/non-derivatizing	*N*-Ethylpyridinium- chloride	–	[14]
	DMAc/LiCl	–	[15,16]
	DMI/LiCl	–	[17]
	DMSO/TBAF	–	[18]
	DMSO/DEA/SO_2	–	[19]

was concluded from NMR spectroscopy in particular from ^{13}C and $^{35/37}Cl$-NMR experiments on solutions of cellulose in BMIMCl that the chloride anion is much more involved in the disruption of the hydrogen bond system and the solubilization of the chains then the cation.[24] The postulated interaction Cl-OH-cellulose is comparable to the mechanism in DMAc/LiCl.[25] Still, this finding can not explain the fact that only ILs with nitrogen containing cations are able to dissolve cellulose. No NMR results are known for ILs with acetates as counter-ion, which dissolve cellulose to a higher extend than the chlorides. Recently, formate and dicyanoamide containing solvents are described as cellulose solvents as well.[25] Thus, the dissolution mechanism is still a matter of ongoing research.

Thus, one intension is the investigation of the interaction IL-cellulose by means of NMR spectroscopy. Because the resolution of the NMR spectra is directly related to the DP of the cellulose, the preparation of suitable cellooligomers or cellodextrines is studied. The preparation method for oligomers which can mimic the behavior of cellulose should yield only β-1 $\rightarrow$ 4 linked glucoses and should not show any side reactions such as partial functionalization. It was found that this can be achieved via degradation of cellulose with phosphoric acid and product isolation by precipitation in THF. The details of this process are described in ref.[26] The cellooligomers thus synthesized were dissolved in D_2O, 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-ethyl-3-methylimidazolium acetate (EMIMAc) and 1-ethyl-3-methylimidazolium chloride (EMIMCl) and the solutions were studied by ^{13}C NMR spectroscopy (Figure 1). All the carbon atoms are clearly assignable in ^{13}C NMR spectra of a cellooligomer with an average DP of 6 in D_2O. In the region between 92 to 96 ppm the C-1 signals of the reducing end groups are clearly visible. If comparable

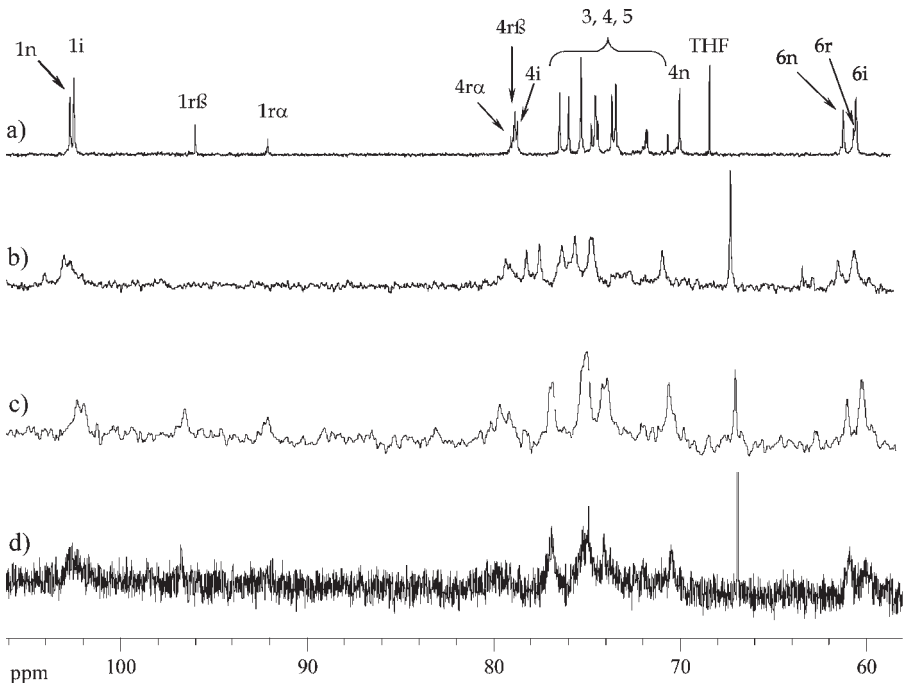

Figure 1.
^{13}C NMR spectra of cellodextrin a) in D_2O, b) in EmimAc, c) in EmimCl and d) in BmimCl.

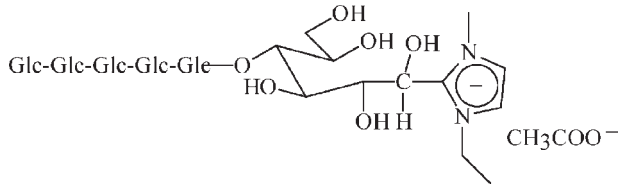

Figure 2.
Structure proposed for a possible covalent binding of EMIMAc to a cellooligomer.

spectra are recorded in BMIMCl a very bad resolution of the AGU region is observed (Figure 1d), in contrast to the signals for the IL, leading to the assumption that there is still some aggregation of the chains left in these solutions. A much better resolution can be found if the oligomers are dissolved in EMIMCl indicating a good solubilization of the chains in this IL (Figure 1c). All the signals for carbon atoms of the AGU may be determined. In particular the C-1 signals of the reducing end group are still determined in the spectrum. Surprisingly, these peaks are not present if the oligomers are dissolved in EMIMAc (Figure 1b) although a good spectral resolution is obtained.

The absence of the C-1 signals is a first hint for the reaction of the reducing end group with EMIMAc. A possible explanation would be the formation of a covalent bond between the IL and the aldehyde function. It is known that aldehydes can be converted with ILs at the reactive proton in position 2[27] according to the formula shown in Figure 2.

It is not known yet if this conversion of the end group leads to additional side reactions during the dissolution and the chemical modification of these oligomers or the cellulose. Further investigation is needed concerning the hydrolytic stability of the intermediate formed and to elucidate if this reaction in EMIMAc can be used for the activation of the aldehyde function of cellulose, or if it may even serves as a protective group.

In addition to the commercially available halogenid containing ILs, new ILs are under investigation with anions of acids known to activate cellulose. Especially, formic acid, trifluoroacetic acid, dichloroacetic acid and their derivatives are considered as activating agents. It should be mentioned that formic acid and trifluoroacetic acid dissolve cellulose at room temperature within days.[12,13] A clear mechanism for this dissolution is not established yet. Among the intermediates discussed are non-covalent complexes of the corresponding anions with the polymer.[12] A selection of new ILs is shown in Table 2.

To synthesize these unconventional ILs the commonly known synthesis pathways

Table 2.
New Ionic liquids with a cellulose activating anions.

	R_1	R_2	A^-
	Me	But	NO_3
	Me	But	HCOO
	Me	But	CH_3COO
	Me	But	CF_3COO
	Me	But	CCl_3COO
	Me	But	C_4F_9COO

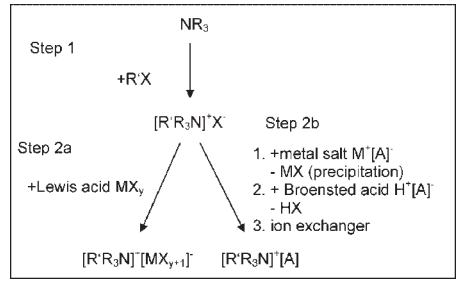

Figure 3.
Synthesis paths for the preparation of nitrogen containing Ionic Liquids.

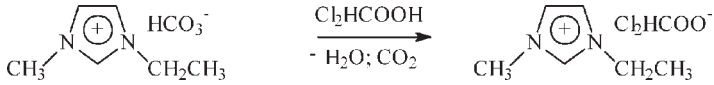

Figure 4.
Preparation of 1-ethyl-3-methylimidazolium dichloroacetate (EMIMdiclac) via 1-ethyl-3-methylimidazolium hydrogencarbonate.

for the preparation of ILs can be applied as displayed in Figure 3.[21] A very useful approach for the introduction of anions of carboxylic acids with rather low pKs value is the conversion of the imidazolium hydrogencarbonates (Figure 4). An example for this very efficient synthesis is the preparation of the 1-ethyl-3-methylimidazolium dichloroacetate (EMIMDiclac, Figure 4). ^{13}C NMR spectra of ILs prepared via this path confirm the purity of these new substances as demonstrated for the new room temperature IL EMIMDiclac in Figure 5.

First results show that trifluoroacetates are not able to dissolve cellulose completely. In contrast the newly synthesized compound BMIM trichloroacetate gives a clear solution with Avicl and the cellulose can be regenerated as a membrane. Dichloroacetates of the EMIM and the BMIM cation are very interesting room temperature liquids of low viscosity. Nevertheless, if cellulose is added black solutions are obtained and the cellulose may only be regenerated as dark particles. In addition to the recently published formate containing ILs[28] we have synthesized a BMIM formate which dissolves cellulose efficiently. Solutions of cellulose in these promising new ILs are now under investigation towards the basic understanding of the interaction with the cellulose molecule (cellooligomer as mimic), the regeneration and the morphology of these regenerates, and the suitability for homogeneous synthesis.

Regeneration of Cellulose form ILs

One of the first applications of ILs in the field of polysaccharide research was the regeneration of cellulose mainly for

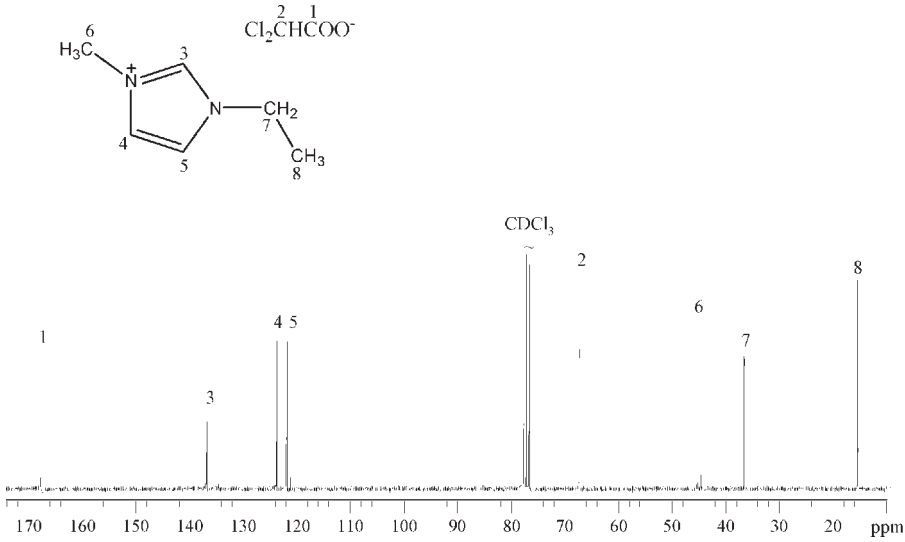

Figure 5.
^{13}C-NMR spectrum of 1-ethyl-3-methylimidazolium dichloroacetate (EMIMdiclac).

the production of fibers[29] in contrast to the membrane formation from ILs which is scarcely studied. Such membranes are valuable materials for medical and biotechnological applications.[30] Thus, separation of fermentation media or the separation of biological fluids, such as blood, is of increasing interest. Cellulose membranes are already well established in the field of dialysis.[31] Most of the membranes used are still produced via the Viscose process or the Cupro process. It is known that the separation and the biocompatibility are strongly influenced by the surface properties.[32] In case of IL these surface properties can be largely affected by the precipitation step because a coagulation of the cellulose in a broad variety of solvents and solvent mixtures is possible.

REM images of a cellulose membrane obtained by a Viscose process (Figure 6a) and a membrane isolated from an EMIMAc solution (Figure 6b) by precipitation in ethanol are shown in Figure 6. A clear difference in the surface topography is visible. The membrane isolated from the IL is a very porous material.

Specific binding of proteins such as Lysozym, Ovalbumin and BSA onto these porous layers was investigated. Interestingly, proteins consisting of large quantities of serine and tyrosine (Lysozym) can bind very efficiently to the material thereas the more hydrophobic proteins do not show adhesion and may be separated by dialysis on these materials according to the cut off.

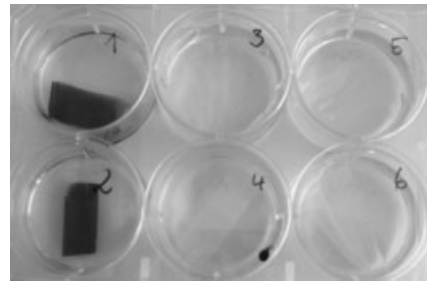

Figure 7.
Cellulose membranes prepared from EMIMAc after treatment with protein solutions, washing and staining of the membranes with Coomassie blue: Sample 1 and 2 Lysozym; sample 3 and 4 Ovalbumin and sample 5 and 6 BSA.

The specific binding of Lysozym is illustrated in Figure 7 showing cellulose membranes prepared from EMIMAc after treatment with protein solutions, washing and staining with Coomassie blue. Only for Lysozym an attachment was determined (Sample 1 and 2 in Figure 7).

This phenomenon of a selective protein binding is now studied for protein isolation from protein mixtures on fermentation media which would allow an easy protein fractionation and could even lead to new analytical methods.

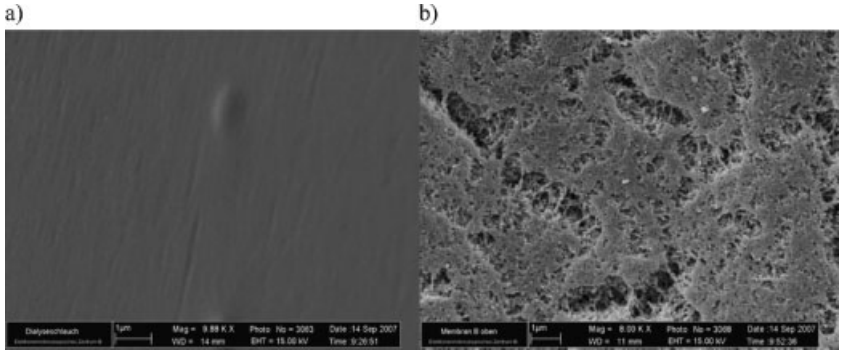

Figure 6.
REM images of cellulose membranes prepared via the Viscose process (a) and a membrane prepared by dissolution of cellulose in EMIMAc and precipitation in ethanol (b).

Chemical Modification of Cellulose in ILs

A broad variety of chemical modification reactions under homogeneous conditions are now carried out.[25] The question here is how efficient are these conversions. Are ILs comparably suitable as DMAc/LiCl and most important do the ILs lead to side reactions or could they be reused quantitatively? The first reaction we studied in detail was the silylation of cellulose with HMDS in BMIMCl. Preliminary results showing a high efficiency are discussed in ref.[33]

Boron-containing Agents for the Dissolution and Activation of Cellulose

A rather new approach for the activation of cellulose is the exploitation of the interaction of cellulose with boric acid or boric acid derivatives that are well suitable for the analysis, activation, protection, and cross-linking of this huge group of biomolecules.[2] Most of the conversions are based on diol-boric acid reactions. In aqueous media one obtains a borate-type complex as shown in Figure 8. This reaction can be exploited for the analysis of carbohydrates.

In earlier attempts simple titration was applied for this purpose.[34] A recent development is the utilization of the selective attachment in sensor applications using fluorescent boronic acids.[35] In case of polysaccharides the complexation may be applied for cross-linking between the chains. For guar gum it was shown that a borate complexation is also possible along a single polymer chain.[36] A large variety of these negatively charged species may be formed during these reactions as shown in Figure 9. Both with monosaccharide and

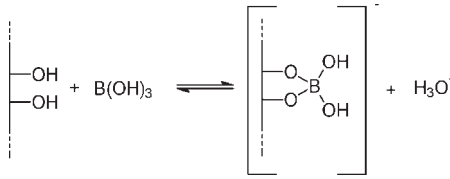

Figure 8.
Basic interaction of boronic acid with diol structures.[2]

with polysaccharides five and six-membered rings are observed.[2]

In organic aprotic media esterification is possible with boric acid and boronic acids. Attempts are known to utilize this modification as protection for diol structures.[37] In both cases, i.e. during the formation of complexes and during the esterification five and six membered rings are discussed. These rings are preferably formed with *cis*-1,2 or *cis*-1,3 diol units. However, the most important carbohydrates glucose and the glucose based polymers cellulose and starch exhibit *trans* diol-structures. For these structures the formation of five or six membered rings is limited because of high ring tension. Nevertheless, interactions are determined. Among the explanation for these interactions are the formation of furanoses with flexible diol-functions, monovalent binding and the expectation of larger ring systems of the boric or boronic acids under inclusion of two molecules of the acids, i.e. rings with two boron nuclei. First hints for such larger rings were obtained by MS measurements.[38] In contrast NMR spectroscopy was not able to confirm the occurrence of such rings at intact molecules.[39]

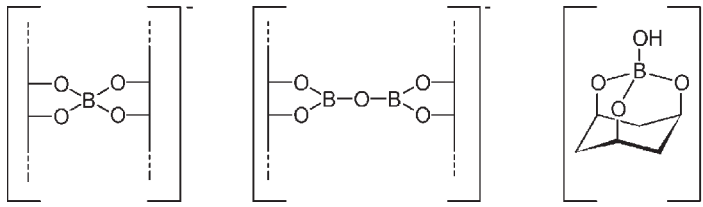

Figure 9.
Different complexes formed during the interaction of boric acid with polysaccharides.[2]

Because of the potential use both for sensor applications of fluorescent boronic acids and as activating agents for glucose based polymers, most important cellulose, the formation of monovalent binding and the formation of large rings had to be investigated. This should lead to a new understanding and a tailoring of such processes. Thus, reactions of boric acid, protected boric acids and boronic acids with glucose, cellobiose, cellodextrins and the methylglycosides of the carbohydrates in organic media are now carried out and the products are analyzed by different NMR methods in correlation with MS.

Esterification of carbohydrates with boric acid in DMF was simply achieved by removing the reaction water from the system via azeotropic distillation with toluene. If the reducing end group is blocked by glycocidation the formation of the known six-membered ring of the trans 1,3 diol structure at position 4 and 6 is observed by ^{13}C NMR spectroscopy (Figure 10).

Even with an excess of boric acid and the use of 2,2-dimethoxy propane as dewatering agent no evidence for an esterification at the secondary OH groups can be obtained. Experiments were carried out to initiate monovalent esterification of carbohydrates with protected boric acids, which would be a second path for an activation of polysaccharides. For this purpose boric acid was converted with catechol and the obtained anhydride (Figure 11) was treated with the methyl-D-glucopyranoside (α and β form) in DMF. In any case the pure boric acid ester of the carbohydrate without the protecting group was obtained (Figure 10) meaning that a very fast transesterification succeeds.

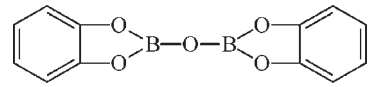

Figure 11.
Anhydride of a catechol protected boric acid.

The occurrence of broad NMR signals leads to the assumption that the transesterification is a dynamic equilibrium, i.e. further transesterification at the carbohydrates and between the carbohydrates has to be considered. This fast transesterification might be the reason why no hints for a

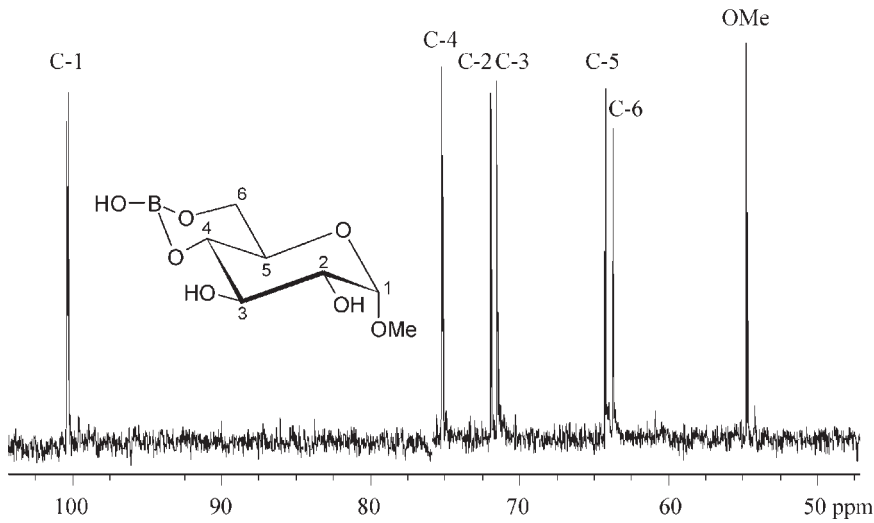

Figure 10.
^{13}C NMR spectrum (DMSO-d_6) of methyl-4,6-O-borato-D-glucopyranoside confirming the formation of a six-membered ring of the trans 1,3 diol structure at position 4 and 6 of a methyl-α-D-glucopyranoside.

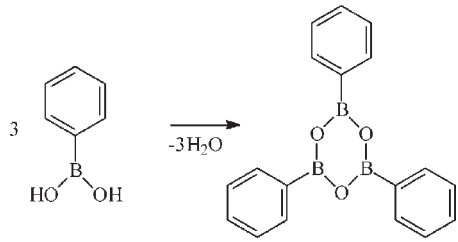

Figure 12.
Synthesis of 2,4,6-triphenyl cyclotriboroxane from phenylboronic acid.

conversion at position 2 and 3 are determined.

Therefore, esterification with boronic acid, especially phenyl boronic acid was conducted. Here one OH function is substituted diminishing the tendency towards transesterification. In addition, the electronic system of the phenyl function could stabilize the formed esters and should slow down or even avoid the transesterification. For the efficient synthesis of the boronic acid esters of carbohydrates the 2,4,6-triphenyl cyclotriboroxane, a cyclic anhydride of phenyl boronic acid, was synthesized.[40] The esterification was again performed by conversion in DMF removing the water formed with 2,2-dimethoxy propane. The product was studied by mass spectroscopy using ''electron impact'' ionization (EI). A signal of m/z 470 is determined which is the molecule ion M^+.

This correlates with the molecular mass of the expected boronated methyl glucoside shown in Figure 13.

Strong signals are found at m/z 160 and m/z 250 which confirms the fragmentation according to the two cyclic boronate fragments **II** and **III** shown in Figure 14. This finding is an evidence for the proposed seven membered ring in position 2 and 3 and is in agreement with earlier work.[39] These results can be supported by ^{1}H NMR studies.

In Figure 15 a comparison of the ^{1}H NMR spectra of the methyl-4,6-O-phenylboronat-α-D-glucopyranoside (obtained by conversion of methyl-α-D-glucopyranoside with 2,4,6-triphenyl cyclotriboroxane applying a molar ration 1:1) and of the phenylboronate obtained with an excess of 2,4,6-triphenyl cyclotriboroxane are shown. It is obvious that in case of the methyl-4,6-O-phenylboronat-α-D-glucopyranoside signals for the protons of the OH functions in position 6 and 4 can not be determined revealing complete conversion with the boronating agent. In comparison with spectra of the methyl-α-D-glucopyranoside the signal of the anomeric proton (H' in Figure 15) is shifted to higher field because of the substitution at 6 and 4.

The two doublets at 5,18 and 4,92 ppm correspond to the remaining protons of the OH functions at position 2 and 3, wich can

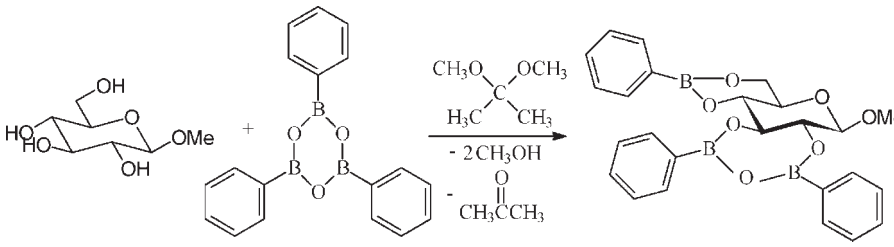

Figure 13.
Schematic plot of a complete conversion of methyl-D-glucopyranoside with 2,4,6-triphenyl cyclotriboroxane.

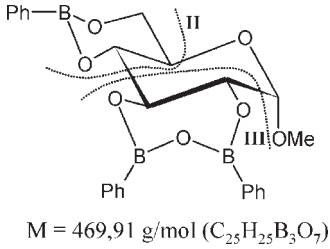

Figure 14.
Fragmentation pattern for a fully phenylboronated methyl glucoside.

additionally be confirmed whith the values of the couling constants. If this compound is again treated with 2,4,6-triphenyl cyclotriboroxane the NMR spectrum shows an almost complete removal of the doublets indicating a conversion at position 2 and 3. Furthermore, the occurrence of a new signal for the anomeric proton (H'' in Figure 15) is a second evidance for a boronation in position 2. These NMR results are a first direct evidence for the occurrence of an interaction of the phenylboronic acid with the OH functions in position 2 and 3. In combination with the MS results these findings confirm the expected formation of a seven membered ring at the secondary HO functions of the carbohydrates. Further research with two dimensional NMR spectroscopy and $^{[11]}$B NMR spectroscopy as well as investigation on cellodextrins and cellulose are necessary to learn more about the formation, stability and transesterification of these functions on the trans diol system of carbohydrates and its possible use as activating agent, analysis tool or protecting function.

Conclusion

It can be shown that commercially available ILs and newly synthesized ILs are suitable materials for the dissolution and defined regeneration of cellulose with a new topography which may lead to new separating materials. Nevertheless, the dissolution of the polysaccharide may be combined with side reactions at the reducing end. Therefore, such interactions need to be studied with cellulose mimics, e.g. cellodextrins accessible by degradation of cellulose. The same careful consideration of homogeneous modification reactions of cellulose in IL is necessary to avoid undesired side reactions.

The investigation of the interaction carbohydrates boric acid or boronic acid could lead to new paths for the activation and analysis of these biomolecules. It was shown that such interactions may occur at the position 2 and 3 of glucose derivatives. Here the formation of a seven membered ring was confirmed leading to the assumption that a comparable structure might be formed in the glucose based macromolecules cellulose and starch. The analysis and defined synthesis of such structure is subject of the ongoing research.

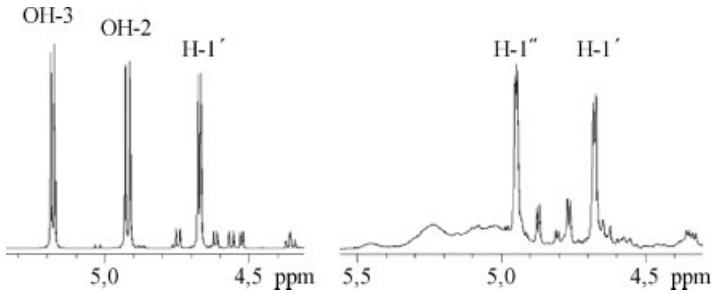

Figure 15.
^{1}H NMR spectra of a phenylboronate of methyl-α-D-glucopyranoside (left) obtained by stoichiometric conversion (molar ration 1:1, middle) and obtained with an excess with 2,4,6-triphenyl cyclotriboroxane (right).

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[1] R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, *J. Am. Chem. Soc.* **2002**, *124*, 4974;J. Moulthrop, R. P. Swatloski, G. Moyna, R. D. Rogers, *Chem. Commun.* **2005**, 1557.
[2] J. Lehmann, in: *Kohlenhydrate, Chemie und Biologie*, Thieme Verlag, Stuttgart, New York **1996**.
[3] British Patent 8700 (1892), C. F. Cross, E. J. Bevan, C. Beadle.
[4] French. Patent 203,741 (1890), L. H. Despeissis.
[5] US Patent 3,447,956 (1969), D. L. Johnson.
[6] Th. Heinze, T. Liebert, *Prog. Polym. Sci.* **2001**, *26*, 1689.
[7] J. Burger, G. Kettenbach, P. Klüfers, *Macromol. Symp.* **1995**, *99*, 113.
[8] S. Fischer, W. Voigt, K. Fischer, *Cellulose* **1999**, *6*, 213.
[9] B. Philipp, I. Nehls, W. Wagenknecht, *Carbohydr. Res.* **1987**, *164*, 107.
[10] D. C. Johnson, M. D. Nicholson, F. G. Haigh, *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1976**, *28*, 931.
[11] L. P. Clermont, N. Manery, *J. Appl. Polym. Sci.* **1974**, *18*, 2773.
[12] M. Cemeris, N. P. Musko, N. Cemeris, *Khim. Drev.* **1986**, *2*, 29.
[13] T. Fujimoto, S. Takahashi, M. Tsuji, M. Miyamoto, H. Inagaki, *J. Polym. Sci., Polym. Lett.* **1986**, *24*, 495.
[14] E. Husemann, E. Siefert, *Makromol. Chem.* **1969**, *128*, 288.
[15] C. L. McCormick, T. R. Dawsey, *Macromolecules* **1990**, *23*, 3606.
[16] C. L. McCormick, D. K. Lichatowich, *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 479.
[17] A. Takaragi, M. Minoda, T. Miyamoto, H. Q. Liu, L. N. Zhang, *Cellulose* **1999**, *6*, 93.
[18] Th. Heinze, R. Dicke, A. Koschella, A. H. Kull, E.-A. Klohr, W. Koch, *Macromol. Chem. Phys.* **2000**, *201*, 627.
[19] A. Isogai, A. Ishizu, J. Nakano, *J. Appl. Polym. Sci.* **1987**, *33*, 1283.
[20] Th. Heinze, T. Liebert, A. Koschella, in: *Esterification of Polysaccharides*, Springer Verlag, Heidelberg **2006**.
[21] P. Wasserscheid, T. Welton, in: *Ionic Liquidsin Synthesis*, Wiley-VCH, Weinheim **2003**.
[22] U.S. Patent1,946,176 (1934), C. Graenacher.
[23] S. Zhu, *Green Chem.* **2006**, *8*, 325.
[24] R. C. Remsing, *Chem. Commun.* **2006**, 1271.
[25] O. A. El Seoud, A. Koschella, L. C. Fidale, S. Dorn, Th. Heinze, *Biomacromol.* **2007**, *8*, 2629.
[26] T. Liebert, M. Seifert, T. Heinze, *Macromol. Symp.* submitted.
[27] V. K. Aggarwal, I. Emme, A. Mereu, *Chem. Commun.* **2002**, 1612.
[28] Y. Fukaya, A. Sugimoto, H. Ohno, *Biomacromol.* **2006**, *7*, 3295.
[29] German Patent DE 031025 B3 (2005), C. Michels, B. Kosan, F. Meister.
[30] E. Staude, in: *Membranenund. Membranprozesse*, Wiley VCH, Weinheim, New York 1992.
[31] German Patent DE 19750527 A1 (1999), W. Ansorge, M. Diamantoglou, J. Rathenow, F. Wiese.
[32] M. Ulbricht, *Polymer* **2006**, *47*, 2217.
[33] Th. Heinze, S. Dorn, M. Schöbitz, T. Liebert, S. Köhler, F. Meister, *Macromol. Symp.* submitted.
[34] N. Wiberg, in: *Lehrbuch der Anorganischen Chemie 101.* Auflage, de-Gruyter, Berlin **1995**, p. 1035.
[35] T. D. James, K. R. A. S. Sandanayake, S. Shinkai, *Angew. Chem.* **1996**, *108*, 2038.
[36] M. Bishop, N. Shahid, J. Yang, A. R. Barron, *J. Chem. Soc., Dalton Trans.* **2004**, *17*, 2621.
[37] R. J. Ferrier, *Adv. Carbohydr. Chem.* **1978**, *35*, 31.
[38] D. S. Robinson, J. Eagles, R. Self, *Carbohydr. Res.* **1973**, *26*, 204.
[39] R. Smoum, A. Rubinstein, M. Srebnik, *Magn. Reson. Chem.* **2003**, *41*, 1015.
[40] J. Morgan, J. T. Pinhey, *J. Chem. Soc., Perkin Trans.* **1990**, *1*, 715.

