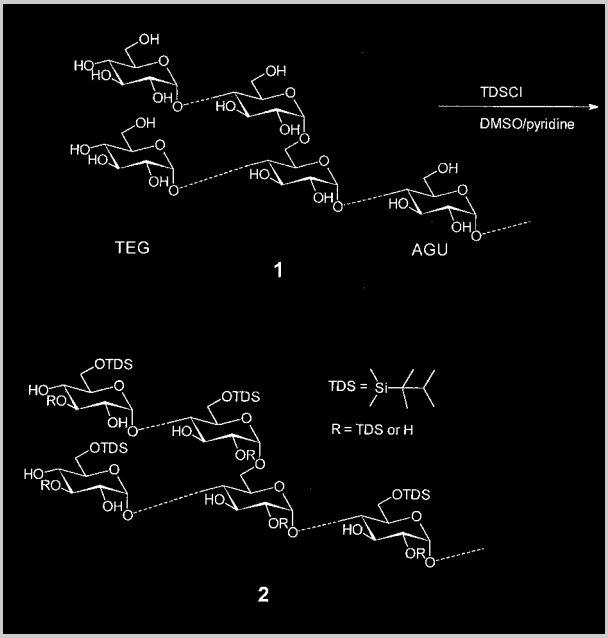
Full Paper: Reaction of starch **1** dissolved in dimethyl sulfoxide (DMSO) with bulky thexyldimethylchlorosilane (TDSCl) in the presence of pyridine leads to regioselectively functionalized silyl ethers with a degree of substitution (DS) up to 1.8. The control of the DS_{Si}, of the regioselectivity, and of the reaction pathway is described in detail. The reaction proceeds homogeneously up to DS_{Si} of 0.6. With ongoing silylation the polymers form a separate phase incorporating the silylating agent to form TDS-starches with DS_{Si} values higher than 1.0. After peracetylation of the silyl starches, the substitution pattern has been characterized not only in the anhydroglucose repeating units (AGU) but also in the non-reducing terminal end groups (TEG) by means of two-dimensional ^{1}H NMR techniques. Up to DS_{Si} 1.0, a very high regioselective functionalization of the primary 6-OH groups in the AGU as well as in the TEG is detectable. With increasing silylation ($DS_{Si} > 1.0$), the subsequent silylation takes place at the 2-OH groups of the AGU and at the 3-OH groups of the TEG. These results are compared with our own investigations on the silylation of starch in the reaction system *N*-methylpyrrolidone (NMP)/ammonia and on the silylation of cellulose in *N,N*-dimethylacetamide (DMA)/LiCl/pyridine solution.



Silylation of starch **1** dissolved in DMSO with bulky thexyldimethylchlorosilane (TDSCI) in the presence of pyridine. For reaction conditions and DS_{Si} values see Table 1. AGU: anhydroglucose units, TEG: non-reducing terminal end

Preparative and ^{1}H NMR Investigation on Regioselective Silylation of Starch Dissolved in Dimethyl Sulfoxide

Lars Einfeldt,[a] *Katrin Petzold, Wolfgang Günther, Armin Stein,*[b] *Manfred Kussler, Dieter Klemm**

Institute of Organic and Macromolecular Chemistry, Friedrich Schiller University of Jena, Humboldtstraße 10, D-07743 Jena, Germany

Introduction

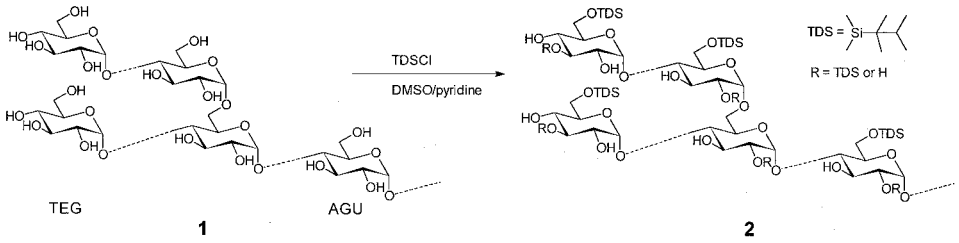
The properties of chemically functionalized polysaccharides can be substantially influenced by the substitution pattern. Therefore, it is a very important question in polysaccharide chemistry to develop synthetic pathways for regioselectively functionalized polysaccharides and to improve the structural characterization of such polysaccharide derivatives directly at the macromolecule. During recent years, progress has been made in the field of cellulose chemistry.[1–6] In comparison, analogous investigations on the industrially important biopolymer starch have been relatively rare.

In previous papers on cellulose functionalization, the polymer-analogous silylation has been proved to be a very useful reaction on a laboratory scale. It proceeds easily under mild conditions and with high regioselectivity by use of bulky alkyl residues in the silylating agents.[7–9] Moreover, various subsequent reactions can be carried out at the free hydroxyl groups. With respect to the protecting-group technique, silylated hydroxyl groups can also be regenerated with tetrabutylammonium fluoride under mild conditions.

From the silylation of low molecular weight and oligomeric carbohydrate chemistry, especially by using silylating agents with bulky alkyl residues, the preferred silylation of primary hydroxyl groups is well-known, too.[10, 11] But, also, the choice of the reaction medium and the reac-

[a] Present address: Frommanstr. 3, D-07743 Jena, Germany
[b] Present address: Klostermattenstr. 6a, D-79341 Kenzingen, Germany

  1616-5187/2001/0811–0341$17.50+.50/0



Scheme 1. Silylation of starch **1** dissolved in DMSO with bulky thexyldimethylchlorosilane (TDSCl) in the presence of pyridine. For reaction conditions and DS_{Si} values see Table 1. AGU: anhydroglucose units, TEG: non-reducing terminal end groups.

tion conditions can differentiate the preferred silylation.[11, 12] In the case of polymer-analogous reactions on polysaccharides, the polymer solubility, the accessibility of functional groups, and phase and conformation state of the polysaccharide play a more critical role during reaction. Additionally, the characteristic features of native starches containing the polymers amylose and amylopectin (Scheme 1) are very important. Whereas amylopectin is high molecular weight and branched, the amylose shows essentially lower molecular weights and nearly no branching.[13] Depending on the plant origin, the amylose content is between 20 and 25% for most native starches.

The present study is directed to the silylation of native starch with the bulky silylating agent thexyldimethylchlorosilane (TDSCl) in the classic starch solvent dimethyl sulfoxide (DMSO).[14, 15] Under variation of the reaction conditions, the TDS ethers of starch could be synthesized with high regioselectivity and characterized by means of ^{1}H NMR spectrometry. Not only the substitution pattern in the anhydroglucose units (AGU), but also the significant amounts of non-reducing terminal end groups (TEG), show regioselective distributions of the silyl groups.

Experimental Part

Materials

Different maize starches (Hylon VII, Amioca Powder, and Normal Maize Starch) from *National Starch & Chem.* were used as starting polymers. All starch materials were dried under vacuum over potassium hydroxide at 100 °C and 0.1 torr for 1 h. TDSCl from ABCR (Karlsruhe, Germany) was used as supplied. All syntheses were carried out under anhydrous conditions.

Measurements

The one- and two-dimensional NMR spectra were measured on a 400-MHz spectrometer (DRX 400, Bruker) with Bruker standard pulse programs and processed with Bruker software package XWINNMR in $CDCl_3$ at 50 °C. The COSY experiment (^{1}H/^{1}H correlated spectrum) was performed with a double quantum filter for an effective suppression of singlets. The DS_{Si} (EA, elemental analysis) values were calculated from silicon-contents estimated gravimetrically,[16] the DS_{Si} (NMR) values from ^{1}H NMR spectra of the peracetylated TDS-starches.

Silylation of Starch (**1**) *in DMSO/Pyridine*

Starch **1** was dissolved in DMSO (4–12%, w/v) by heating for 2 h at 80 °C. Then, pyridine (2.0 mol · (mol TDSCl)$^{-1}$) was added. Different amounts of silylating agent (0.6–6.0 mol · (mol AGU)$^{-1}$, Table 1) were slowly dropped to the stirred solution. The reaction mixture was kept for 20–40 h at room temperature. In the case of **2e** and **2f**, the mixture was heated additionally at 100 °C (see Table 1). After cooling, all solvents were poured off, the crude polymer product was suspended in water or alcohol, washed, and air-dried. After dissolution in tetrahydrofuran (THF), the silylated starches **2** were reprecipitated in alcohol, washed and dried under vacuum up to 100 °C. For characterization of the polymers see Table 1.

Acetylation of Silylated Starches (**2**) *in THF/Pyridine*

The starch silylethers **2** were dissolved in THF (7%, w/v). Then, pyridine (5.0 mol · (mol acetic anhydride)$^{-1}$), catalytic amounts of 4-*N,N*-dimethylaminopyridine and acetic anhydride (4.0 mol · (mol AGU)$^{-1}$) were added while the mixture cooled slightly. The mixture was heated at 50 °C for 7 h. After cooling to room temperature, the product was precipitated in methanol, washed, and dried under vacuum up to 100 °C. ^{1}H NMR characterization of the polymers is presented in Table 2 and Figure 2 and 3.

Results and Discussion

Starch **1**, dissolved in DMSO, was silylated in the presence of pyridine with different amounts of TDSCl at room temperature (Scheme 1 and Table 1). The reaction proceeds homogeneously up to a DS_{Si} of 0.6. During further silylation, the silylated starches precipitate viscously without further dissolution in the reaction medium, also by increasing temperature. A similar behavior was observed by the silylation of starch with *tert*-butyldimethylsilyl chloride (TBDMSCl).[12] But the silylation using TDSCl shows higher regioselectivity. Therefore, only it will be discussed in this section.

Table 1. Degree of silyation (DS_{Si}) of TDS-starches **2** as function of reaction conditions.

Starch silylether	TDSCI / mol · (mol AGU)$^{-1}$	Reaction conditions	DS_{Si}	
			EA[a]	NMR[b]
2a	0.6	20 °C, 24 h	0.6	0.5
2b	0.9	20 °C, 24 h	0.9	0.9
2c	1.2	20 °C, 40 h	1.1	1.0
2d	1.4	20 °C, 20 h	1.3	1.2
2e	2.5	20 °C, 20 h; 100 °C, 16 h	1.7	1.6
2f	6.0	20 °C, 20 h; 100 °C, 14 h	1.8	1.7

[a] DS_{Si} calculated from elemental analysis (EA) using Si content.
[b] S_{Si} calculated from ^{1}H NMR spectra after peracetylation.

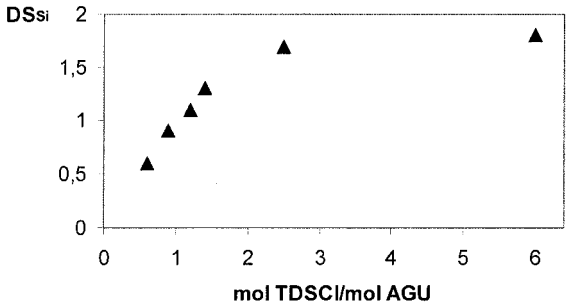


Figure 1. Degree of silylation (DS_{Si}) of TDS-starches and its dependence on the amount of TDSCl during silylation in DMSO/pyridine.

Table 1 summarizes the DS_{Si} values of TDS-starches **2**. Well-defined DS_{Si} are attained by adjusting the amount of silylating agent as well as the reaction temperature. For example, silylation at room temperature using 0.6 to 1.4 (mol TDSCl) · (mol AGU)$^{-1}$ the silylated starches **2a**–**2d** with DS_{Si} values in the range of 0.6 to 1.3 were obtained. With respect to these silylation conditions, the reaction proceeds in this range of TDSCl equivalents nearly quantitatively. On the other side, the silylated starch **2e**, DS_{Si} 1.7, shows, in spite of 2.5 (mol TDSCl) · (mol AGU)$^{-1}$ and continuous high reaction temperatures (100 °C), a much lower degree of silylation with respect to the used equivalents of TDSCl. A further increase of functionalization could not obtained using an excess of even 6.0 (mol TDSCl) · (mol AGU)$^{-1}$ (**2f**, DS_{Si} 1.8) (Figure 1). The synthesized TDS-starches **2a**–**2f** are soluble in aprotic solvents. For instance, TDS-starch **2a**, DS_{Si} 0.6, is soluble in polar solvents such as DMSO, *N*-methylpyrrolidone (NMP) or *N,N*-dimethylformamide (DMF). With increasing DS values the TDS-starches dissolve in non-polar solvents; e. g., TDS-starch **2f**, DS_{Si} 1.7, is soluble in THF, chloroform, toluene, and hexane.

To elucidate the substitution pattern of the TDS-starches **2**, ^{1}H NMR spectroscopy was used after peracetylation of the OH groups in the glucan chains. The peracetylation of **2** was carried out in THF with acetic anhydride/pyridine using catalytic amounts of 4-*N,N*-dimethylaminopyridine. The DS_{Si} values of the peracetylated silylated starches **2**, calculated by ^{1}H NMR spectroscopy, are in good agreement with the results using elemental analysis (Table 1). The peracetylation is of great importance for the NMR analysis. First of all, the lack of free OH groups prevent an aggregation of the glucan chains by hydrogen bonding and the mobility of the single-chain segments of amylose and amylopectin in solution is increased. 2-wt.-% solutions of peracetylated TDS-starches **2** in chloroform show almost no increase in viscosity. Therefore, a remarkable low linewidth of proton signals has been observed (Figure 2, part a). Furthermore, the acetyl substituents induced a significant down-field shifting of the methine and methylene protons (H-2, H-3, H-6a and H-6b) of the AGU.[7, 17] For this reason, the proton signals expand along the ppm scale. In summary, the spectral resolution is improved, and by using two-dimensional NMR techniques unambiguous evidence of the substitution pattern in the AGU can be obtained.

Figure 2b and Figure 3 show a typical two dimensional NMR-COSYDQF spectrum of the peracetylated TDS-starch **2d**, DS_{Si} 1.3. The crosspeaks assign the couplings between methine and methylene protons of the AGU (Figure 2). Further crosspeaks with relatively high intensity are detectable (Figure 3). These signals have to be assigned to structures of the TEG of the branched amylopectin (compare Scheme 1). With 4–5% branching, starch contains a high amount on TEG.[13] From our own investigations on peracetylated starches by means of ^{1}H NMR spectroscopy, it is known that these TEG are more flexible than the rigid AGU in the glucan chain.[18] Caused by the higher mobility of the TEG, the transversal magnetization of these methine and methylene protons decreases much more slowly. The linewidths (1–2 Hz) of the signals are only slightly larger than those known for other low molecular weight carbohydrates. Therefore, the crosspeaks of the TEG appears with sufficiently high intensity in the NMR-COSYDQF spectrum. In summary, the TDS-starches **2** prepared in DMSO/pyridine can be analyzed not only in view of the regioselectivity of silylation in the AGU, but also with regard to the TEG of amylopectin.

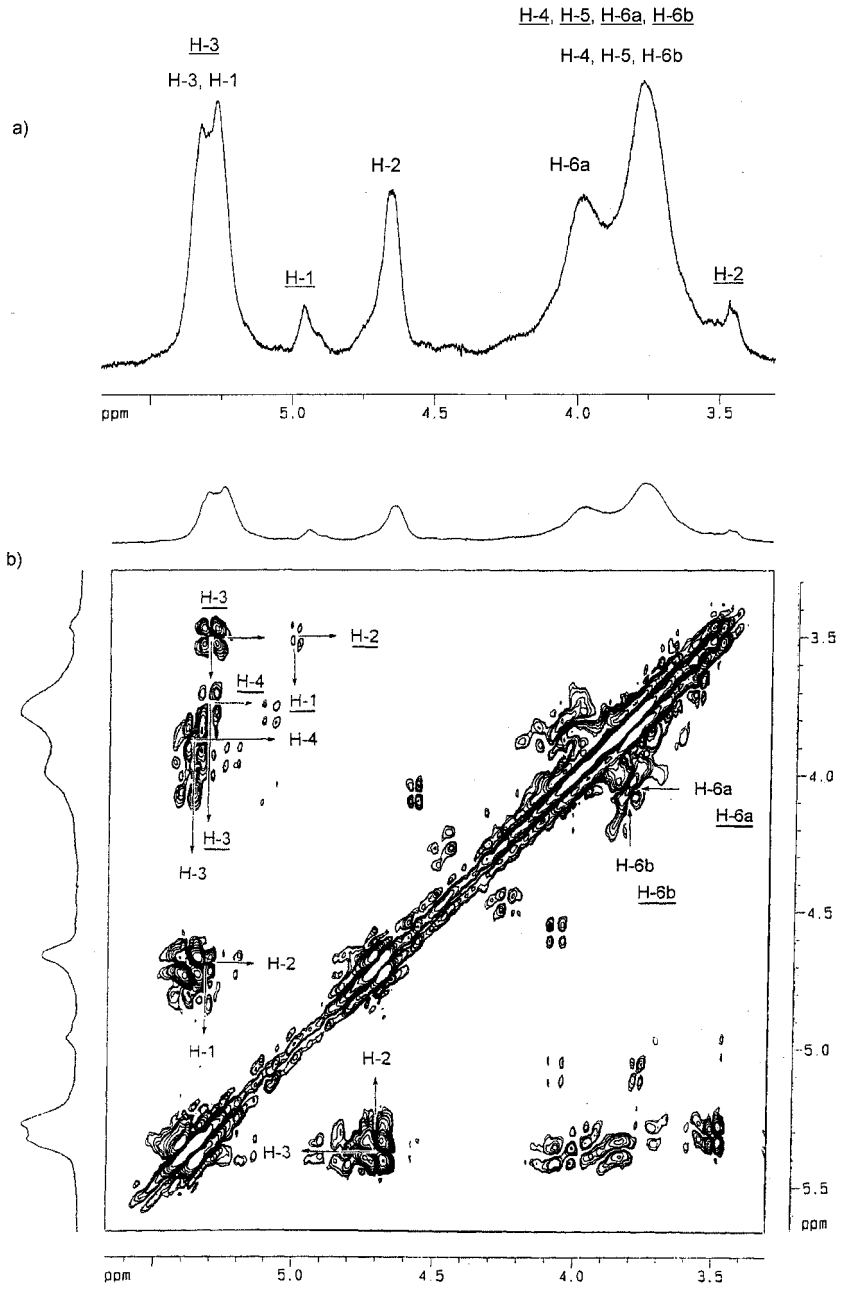


Figure 2. ^{1}H NMR spectrum (a) and [^{1}H,^{1}H]-COSYDQF-NMR spectrum (b) of peracetylated TDS-starch **2d**: assigned crosspeaks of the AGU [2,3-*O*Ac-6-*O*TDS] and the AGU [3-*O*Ac-2,6-*O*TDS] (methine and methylene protons are underlined).

The chemical shifts of H-1, H-2, and H-3 methine protons in the AGU [2,3-*O*Ac-6-*O*TDS] of the peracetylated TDS-starch **2c**, DS_{Si} 1.1, are in agreement with the signals of peracetylated amylose at 5.27 (H-1), 4.67 (H-2), and 5.34 ppm (H-3) (Table 2).[19, 20] The TDS-starch **2c** is almost completely functionalized with TDS groups at the 6-O position. A lack of silylation on the primary hydroxyl groups of the AGU would be induce a significant downfield shifting of the methylene protons to 4.45 ppm (H-6a) and 4.27 ppm (H-6b) due to the corresponding peracetylation. In this frequency area, no significant signals could be detected (spectra not shown). That means, the silylation of starch in DMSO/pyridine with bulky TDSCl at low temperatures takes place firstly at the primary OH groups. Using equimolar amounts of silylating agents, an almost complete regioselectively substituted 6-*O*-TDS-starch (**2b** and **2c**), DS_{Si} 0.9–1.1, can be obtained (Table 1 and 2).

With increasing amount of TDSCl, the 2-OH groups are silylated in the described reaction system. The significant high-field shifts of the proton signals at 4.99 ppm (H-1) and 3.48 ppm (H-2) are typically for this AGU [3-

Table 2. [1]H NMR data of TDS-starches **2** after peracetylation.

Structural units of peracetylated TDS-starches **2a**–**2f**	$\delta^{a)}$ / ppm						
	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b
AGU [2,3-*O*Ac-6-*O*TDS]	5.27	4.66	5.37	3.82	3.72	4.01	3.77
AGU [3-*O*Ac-2,6-*O*TDS]	4.99	3.48	5.32	3.74		4.02–3.70	
TEG [2,3,4-*O*Ac-6-*O*TDS]	5.30	4.77	5.31	5.19	3.88	3.72	3.64
TEG [2,4-*O*Ac-3,6-*O*TDS]	5.29	4.56	4.05	5.07	3.74	3.65	3.54

a) All spectra were recorded in $CDCl_3$ at 50 °C.

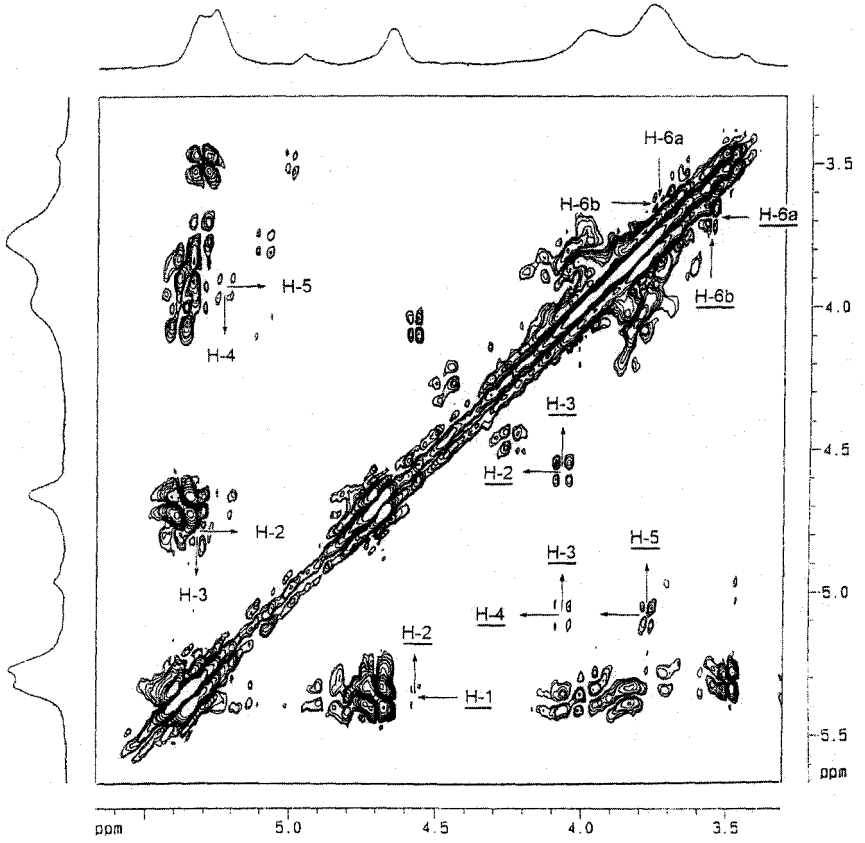


Figure 3. [1H,1H]-COSYDQF-NMR spectrum of peracetylated TDS-starch **2d**: assigned crosspeaks of the TEG [2,3,4-*O*Ac-6-*O*TDS] and the TEG [2,4-*O*Ac-3,6-*O*TDS] (methine and methylene protons are underlined).

*O*Ac-2,6-*O*TDS]. The peracetylated silyl starch **2d**, DS_{Si} 1.3, represents a copolymer of [2,3-*O*Ac-6-*O*TDS] and [3-*O*Ac-2,6-*O*TDS]. Both structures are clearly detected in the two-dimensional NMR-COSYDQF-spectrum of peracetylated TDS-starch **2d** (Figure 2, Table 2).

The TDS-starch **2c** – prepared using 1.2 (mol TDSCl) · (mol AGU)$^{-1}$ – yields the complete silylation of the 6-OH groups and additional 10% of silylated secondary groups. In the case of TDS-starch **2d** – silylation with 1.4 (mol TDSCl) · (mol AGU)$^{-1}$ – this amount is further increased up to 25%. These partial DS_{Si} values at the 2-O position were estimated from [1]H NMR spectroscopy. The results are in agreement with the total DS_{Si} of the peracetylated silyl starches **2c** and **2d** calculated by elemental analysis, if a total silylation of the 6-OH group had been predicted.

But with increased silylation of the 2-OH groups, the linewidths of the signals of the methine and methylene protons are increased clearly in the NMR spectra of the silyl starches **2e** and **2f**. Due to the fast decay of the transversal magnetization, two-dimensional NMR techniques are not useful for peracetylated TDS-starches with $DS_{Si} > 1.3$. But, a comparison of the [1]H NMR spectra of the peracetylated TDS-starches **2e**, DS_{Si} 1.7, and **2f**, DS_{Si} 1.8, with the peracetylated TDS-starches **2c**, DS_{Si} 1.1, and **2d**, DS_{Si} 1.3, allows an explicit statement on the

regioselectivity of silylation. Especially, the difference of the chemical shift of the peaks of the H-1 and H-2 between the [2,3-*O*Ac-6-*O*TDS] and [3-*O*Ac-2,6-*O*TDS] AGU indicates an increase of functionalization on the 2-OH groups with increased DS_{Si} (Table 2). Furthermore, the ^{13}C NMR spectrum of peracetylated TDS-starch **2f** in $CDCl_3$ (data not shown) gives only a single carbonyl signal (169.6 ppm) typically assigned for the 3-*O* bounded carbonyl groups of amylose triacetate.[19] Generally, no proof for silylation of the 3-OH groups of the AGU was detected in the ^1H NMR spectra of the peracetylated TDS-starches **2a**–**2f**. Unfortunately, a complete silylation of the 2-OH groups in the AGU could not be realized under these conditions. The maximal degree of functionalization amounts DS_{Si} 1.8 (Figure 1); in other words, TDS-starch **2f** contains 20% free 2-OH groups in the AGU.

Comparing with the regioselective silylation of the AGU, the silylation of the TEG of starch with TDSCl in the solvent system DMSO/pyridine proceeds in a different way. Both in the AGU and in the TEG, the silylations starts with high regioselectivity at the 6-O position. If the primary OH group of the TEG is functionalized completely, the silylation takes place exclusively at the 3-OH groups (Figure 3). In the COSYDQF-NMR spectrum of the peracetylated TDS-starch **2c**, DS_{Si} 1.1, mainly the TEG [2,3,4-*O*Ac-6-*O*TDS] was identified (spectrum not shown). With increased silylation, the amount of the TEG [2,4-*O*Ac-3,6-*O*TDS] is also increased, as could be proved with the peracetylated TDS-starch **2d**, DS_{Si} 1.3, (Figure 3). Any further substitution pattern of the TEG was not detectable.

The significant down-field shifts of the methine proton H-4 at 5.19 ppm as well as 5.07 ppm are typical for the described structures of the TEG (Figure 3, Table 2). Furthermore, the methylene protons H-6a (3.72 ppm) and H-6b (3.64 ppm) of the TEG [2,3,4-*O*Ac-6-*O*TDS] as well as H-6a (3.65 ppm) und H-6b (3.54 ppm) of the TEG [2,4-*O*Ac-3, 6-*O*TDS] showed a higher high-field shift than the methylene H-6a (4.01 ppm) and H-6b (3.70 ppm) of the AGU [2, 3-*O*Ac-6-*O*TDS]. A further consideration of the signals H-6a and H-6b of the silylated 6-OH group of the TEG and of the AGU show that the chemical shifts of these diastereomeric protons varies in significant differences between H-6a und H-6b: 0.1 ppm at the TEG and 0.3 ppm at the AGU. In Figure 3, the crosspeaks of both substitution patterns in the TEG of peracetylated TDS-starch **2d**, DS_{Si} 1.3, are characterized. By selective excitation of the methine proton H-4 at 5.19 ppm and 5.07 ppm, respectively, a 1D-TOCSY-NMR spectrum of the TEG [2,3,4-*O*Ac-6-*O*TDS] as well as of the TEG [2,4-*O*Ac-3,6-*O*TDS] are available (Figure 4).[9]

In contrast, the silylation of starch with TDSCl in the reaction system NMP/ammonia proceeds both within the glucan chain (AGU) as well as at the chain ends (TEG) exclusively at the 6-OH groups, also with an excess of the silylating agent.[21]

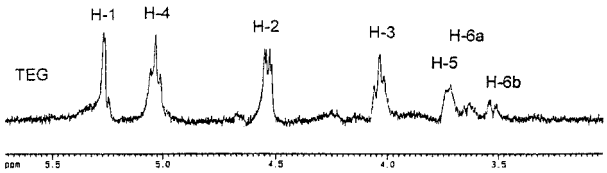


Figure 4. 1D-TOCSY-NMR spectrum of peracetylated TDS-starch **2d**. Selective excitation at 4.56 ppm shows the TEG structure [2,4-*O*Ac-3,6-*O*TDS].

A comparison of the results of the silylation of starch with the results of the homogeneous silylation of cellulose with TDSCl in DMA/LiCl/pyridine shows remarkable differences in the regioselectivity of functionalization at comparable DS values of 1.0. Whereas, the TDS-starch **2c**, DS_{Si} 1.1, has nearly no non-substituted AGU, TDS-cellulose, DS_{Si} 1.05, has about 10% non-substituted AGU and about 15% 2-O silylation.[8]

Conclusion

In the solvent system DMSO/pyridine, native starches were functionalized with bulky silylating agents such as TDSCl up to a maximum of DS_{Si} 1.8, independent of the amylose/amylopectin content. The DS_{Si} of silylated starches could be regulated by the choice of reaction conditions. The regioselectivity of the silylation with TDSCl was analyzed using ^1H NMR spectroscopy after peracetylation of the TDS-starches. Up to DS_{Si} 1.0, a very high regioselective functionalization of the primary 6-OH groups in the AGU as well as in the TEG is detectable. With increasing silylation with TDSCl in DMSO/pyridine ($DS_{Si} > 1.0$), the 2-OH groups in the AGU and the 3-OH groups in the TEG are further silylated.

The different substitution pattern of silylation of the secondary OH groups of the AGU and the TEG of the TDS-starches **2d**–**2f** was surprising. In carbohydrates generally the 2-OH group has a higher reactivity than the 3-OH group as a result of its nearness to the glycosidic linkage. Furthermore, to explain the incomplete silylation of the 2-OH group in the reaction medium DMSO/pyridine is not simple. In our opinion, the phase separation during the functionalization has a significant influence on this polymeranalogous reaction. During the aggregation of the silylated starch, the direct local concentration of reagent at the polymer backbone increases. The changed solvation in that phase could be responsible for an increased accessibility and acidity of the 3-OH group in the TEG. Further influencing factors on the regioselectivity of silylation both in the AGU and the TEG are the conformational effects determining by the α-glycosidic linkages. In DMSO, starch develops its typical helical

structure again.[13] The (1,4)-α-glycosidic linkage in the glucan chains and the hydrogen bonding between 2-OH and 3-OH groups of neighboured AGU by inclusion of the dipolar-aprotic DMSO solvent molecules are responsible for that conformation in solution.

Received: May 15, 2001
Revised: September 10, 2001

[1] D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. Wagenknecht, in: *Comprehensive Cellulose Chemistry*, 1st edition, Wiley-VCH, Weinheim 1998, Volume 2.
[2] D. Klemm, T. Heinze, B. Philipp, W. Wagenknecht, *Acta Polym.* **1997**, *48*, 277.
[3] B. Philipp, W. Wagenknecht, I. Nehls, D. Klemm, A. Stein, T. Heinze, *Polym. News* **1996**, *21*, 155.
[4] T. Kondo, D. G. Gray, *Carbohydr. Res.* **1991**, *220*, 173.
[5] T. Kondo, *J. Polym. Sci., Polym. Phys.* **1997**, *35*, 717.
[6] T. Kondo, *Carbohydr. Res.* **1993**, *238*, 231.
[7] D. Klemm, A. Stein, *J. Macromol. Sci. – Pure Appl. Chem*. **1995**, *A 32*, 899.
[8] A. Koschella, D. Klemm, *Macromol. Symp*. **1997**, *120*, 115.
[9] D. Klemm, L. Einfeldt, *Macromol. Symp*. **2001**, *163*, 35.
[10] K. Takeo, H. Mitoh, K. Uemura, *Carbohydr. Res.* **1989**, *187*, 203.
[11] P. Fügedi, *Carbohydr. Res.* **1989**, *192*, 366.
[12] P. Mischnik, M. Lange, M. Gohdes, A. Stein, K. Petzold, *Carbohydr. Res.* **1995**, *277*, 179.
[13] R. L. Whistler, J. E. BeMiller, E. F. Paschall, in: *Starch: Chemistry and Technology*, 2nd edition, Academic Press, New York 1984.
[14] G. Tegge, in: *Ullmanns Encyklopädie der technischen Chemie*, 4th edition, E. Bartholome', E. Biellert, H. Hellmann, H. Ley, M. Weigert, E. Weise, Eds., Verlag Chemie, Weinheim 1982, Volume 22, pp. 165.
[15] W. Vorwerg, W. Burchard, *Makromol. Chem., Makromol. Symp.* **1992**, *61*, 342.
[16] A. Stein, *Dissertation*, **1991**, University of Jena, Germany.
[17] A. Stein, D. Klemm, *Das Papier* **1995**, *49*, 732.
[18] L. Einfeldt, W. Günther, unpublished results.
[19] Y. Tezuka, *Biopolymers* **1994**, *34*, 1477.
[20] B. Laignel, C. Bliard, G. Massiot, J. M. Nuzzieard, *Carbohydr. Res.* **1997**, *298*, 251.
[21] K. Petzold, L. Einfeldt, W. Günther, A. Stein, D. Klemm, *Biomacromolecules* **2001**, *2*, 965.