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Silylation of Cellulose with Hexamethyldisilazane in Liquid Ammonia—First Examples of Completely Trimethylsilylated Cellulose

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Introduction. Silylation of cellulose as a route to reactive soluble derivatives has been investigated by several research groups.[1−5] Different combinations of solvents and silylating agents have been used. Chlorotrimethylsilane is the most common silylating agent. It has been used in pyridine by Schuyten and by Keilich,[1,6] in liquid ammonia by Greber and Paschinger,[7] and in THF/ammonia, DMF/ammonia, or DMSO/methylamine by Klemm and Stein.[5,8,9] Schempp used HMDS in dimethylacetamide/LiCl;[4] Harmon used it in formamide.[2] Klebe and Finkbeiner made silylations of cellulose in *N*-methylpyrrolidone with *N*,*O*-bis(trimethylsilyl)acetamide,[3] and Bredereck and co-workers worked with trimethylsilylacetamide as solvent and reagent.[10] The degree of silylation reported varied according to the method and to the type and pretreatment of the cellulose used.

We directed our interest toward silylation in liquid ammonia using HMDS instead of chlorotrimethylsilane as reported by Greber.[7] After the first successful attempts to react poly(vinyl alcohol) with HMDS in liquid ammonia at an elevated temperature,[11] we extended this method to cellulose[12] because ammonia is known to activate cellulose by intercalation into the lattice, thus breaking up the inter- and intramolecular hydrogen bonds.[13,14] Silylation with HMDS gives ammonia as the only byproduct which can be removed together with the ammonia used as the reaction medium.

Trimethylsilylation of different cellulose materials has been studied.[15] Comparison of the ammonia/HMDS procedure with other methods using cotton linters as substrate for all reactions gave highest degrees of silylation with this method. We did not succeed, however, in the preparation of fully silylated cellulose. The highest degree of silylation was 2.95, which was obtained from a hydrocellulose with a rather low degree of polymerization (40).[15]

In this paper we describe the synthesis and some properties of the first completely trimethylsilylated cellulose obtained from silylation with HMDS in liquid ammonia and compare the new method with literature procedures.

Results and Discussion. Silylation in Hexamethyldisilazane/Ammonia. Silylation of cellulose with HMDS in liquid ammonia at an elevated temperature was made in stainless steel autoclaves equipped with an inlet/outlet valve, stirrer, glass window, temperature, and pressure control. The silylation reaction of cellulose is shown in eq 1. Upon conversion of a hydroxy into a trimethylsiloxy group, ammonia is generated from HMDS. Only gaseous ammonia has to be removed from the reaction products if HMDS is used in stoichiometric amounts.

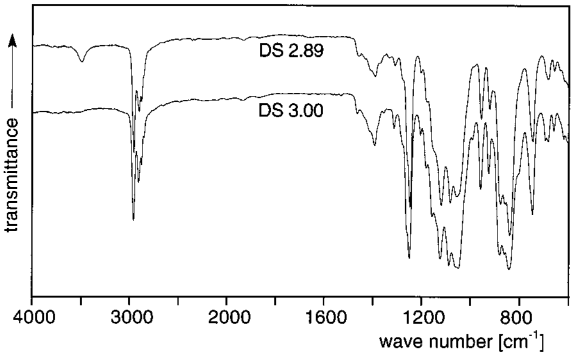
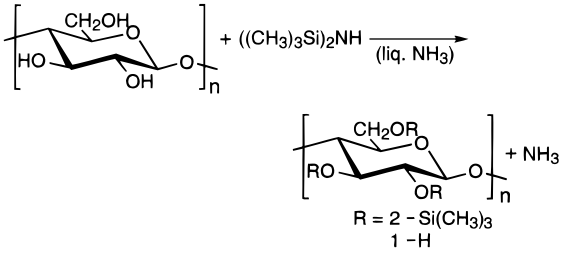


Figure 1. IR spectra of trimethylsilyl cellulose (DS 3.00 and 2.89); film from THF.



(1)

Under the reaction conditions used either ammonia or HMDS were used in excess in order to be able to stirr the heterogeneous mixture.[15] Saccharin as catalyst had an effect but the reaction proceeded also without catalyst though to a smaller DS. A catalyst concentration of 0.5 mol % saccharin/mol of hydroxy groups, a temperature of 80 °C, and a reaction time of 24 h were chosen for the reactions reported in the present paper.

An experiment designed for a different purpose lead us to reaction conditions under which complete silylation is possible.

Avicel PH-101 was reacted with HMDS and ammonia in the presence of saccharin as catalyst (entry 5 in Table 1). The ratio of trimethylsilyl groups to hydroxy groups was 3.4 to 1; the amount of ammonia was 1.2 mol/mol of AGU. This ratio is almost equal to that of the ammonia−cellulose complex.[16] After 24 h the reaction mixture was hardly soluble in THF. It was stirred three times for 1 day in THF; the supernatant liquid was decanted after centrifugation.

Both the soluble and the insoluble fraction had a DS of 3.00 based on the silicon content. The infrared spectrum of the soluble fraction is shown in Figure 1. No band at 3500 cm^{-1} caused by the O−H stretching vibration can be detected in the spectrum. The sensitivity of this method can be seen from the second spectrum in Figure 1. A cellulose with a degree of silylation of 2.89 has a clearly visible O−H stretching absorption.

On the basis of this result, the amount of ammonia was systematically increased keeping all other parameters in particular the ratio of trimethylsilyl to OH groups constant. Work up was made as described for entry 5. The amounts and ratio of reagents and ammonia, the amount and degree of silylation of both the

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Table 1. Silylation of Different Celluloses with HMDS/Ammonia ($T = 80$ °C, $t = 24$ h)

					THF soluble			THF insoluble		
no.	cellulose	NH_3:$SiMe_3$:OH [mol]	NH_3:$SiMe_3$:OH [g]	yield [%]	DS	*m* [g]	%	DS	*m* [g]	DS_{total}
1	Avicel PH-101	29.6:3.39:1	14.1:7.65:1.51	85	2.72	2.85	100			2.72
2	Avicel PH-101	17.4:3.40:1	8.28:7.65:1.51	87	2.90	1.03	34	2.86	1.97	2.87
3	Avicel PH-101	9.26:3.41:1	4.37:7.65:1.50	86	2.90	0.38	13	2.94	2.59	2.94
4	Avicel PH-101	1.99:3.41:1	0.94:7.65:1.50	92	3.00	0.12	4	3.00	3.12	3.00
5	Avicel PH-101	0.40:3.41:1	0.18:7.65:1.51	81	3.00	0.11	4	3.00	3.05	3.00
6	Avicel PH-101	1.92:13.5:1	0.91:30.3:1.50	86	2.95	0.19	6	2.96	2.80	2.96
7	Avicel PH-102	0.40:3.40:1	0.18:7.65:1.51	95	2.65	0.21	6	2.95	3.07	2.93
8	linters	0.40:3.42:1	0.19:7.65:1.50		DS 0.44[a]					0.44
9	linters	1.86:3.43:1	0.93:7.65:1.50	95	DS 3.00					3.00
10	hydrocellulose from Avicel	0.49:3.42:1	0.19:7.65:1.50	81	3.00	1.90	67	3.01	0.93	3.00

[a] DS of sample.

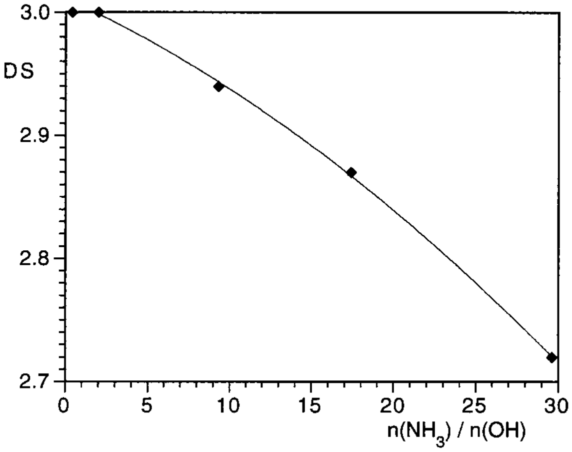

Figure 2. Degree of silylation as a function of the ammonia/hydroxy group ratio.

soluble and insoluble fraction of these experiments are included in Table 1, entries 1 to 5.

The striking result of this series is that the degree of silylation decreases as the amount of ammonia is increased. In Figure 2 the DS is plotted against the molar ratio of ammonia to hydroxy groups. For ratios of 0.4 and 2 a DS of 3 is found. With increasing ratio the DS decreases in an almost linear fashion from 2.94 via 2.87 to 2.72 for a ratio of 30. Water, which can be present to 0.1% in ammonia, cannot be responsible for this decrease as the excess of HMDS is high enough even if all the water has been converted to trimethylsilanol or hexamethyldisiloxane. Another possible reason could be an equilibrium between trimethylsiloxy groups of cellulose and ammonia on one side and HMDS and free hydroxy groups on the other side, i.e., the reverse reaction of eq 1.

In case of an equilibrium, the same state has to be reached from both sides as shown in Scheme 1. To prove this the conditions of entry 1 in Table 1 were taken as reference. A trimethylsilyl cellulose with a DS of 3.00 was suspended in ammonia to give a ratio NH_3/AGU of 92 plus 3.5 mol of HMDS and catalyst. If this mixture were to reach the DS of entry 1, the concentrations of HMDS and ammonia would be identical to those of entry 1 after reaction. No desilylation took place, however, after 40 h at 80 °C, ruling out the possibility of an equilibrium.

A further argument against an equilibrium was obtained from the experiment in entry 6 in Table 1 where the ratio of HMDS to OH was increased by a factor of 4. The DS was 2.96, i.e., a decrease despite of a higher excess of silylating agent.

Influence of the Type of Cellulose. Four celluloses with different provenience and physical properties were silylated under the conditions of entry 5 of Table 1. Apart from Avicel PH-101 these were Avicel PH-102, linters, and a hydrocellulose with a DP of 40. The results are included in Table 1, entries 7–10.

A DS of 3 was obtained only with hydrocellulose, while it was 2.93 for Avicel PH-102 and only 0.44 for

Scheme 1

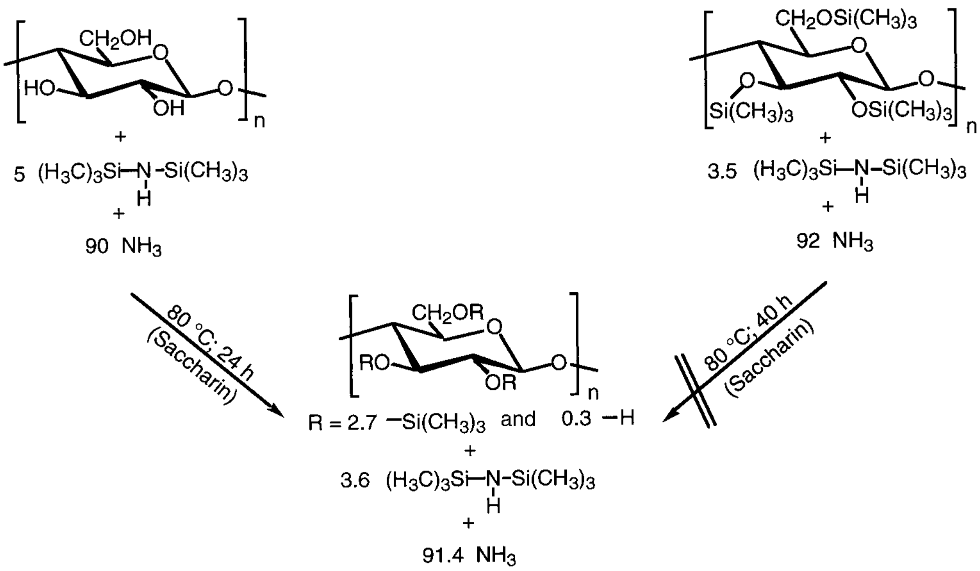

Table 2. Silylation of Preactivated Linters with HMDS/Ammonia (T = 80 °C)

					THF soluble			THF insoluble		
no.	activation time [h]	NH$_3$:SiMe$_3$:OH (m [g])	t [h]	yield [%]	DS	m [g]	%	DS	m [g]	DS$_{total}$
1	24	0.47:3.27:1 (0.22:7.37:1.51)	24	100	2.85	0.124	4	2.88	3.33	2.88
2	48	0.80:3.34:1 (0.38:7.53:1.51)	42	90	2.75	0.49	16	2.92	1.97	2.89

Table 3. Silylation of Cellulose Changing the Amount of Ammonia during the Reaction (T = 80 °C)

		1st silylation		2nd silylation			THF-soluble			THF-insoluble		
no.	cellulose	NH$_3$:SiMe$_3$:OH (m [g])	t [h]	n_{NH3}:n_{AGE}	t [h]	yield [%]	DS	m [g]	%	DS	m [g]	DS$_{total}$
1	linters	15.10:3.40:1 (7.18:7.65:1.51)	7.5	0.5:1	16.5	95	2.70	0.224	6.8	2.89	3.06	2.88
2	linters	15.78:3.40:1 (7.46:7.65:1.50)	4.5	0.5:1[a]	16.5	97	2.85	0.168	5.0	2.88	3.16	2.88
3	linters	7.17:3.42:1 (22.6:51.0:10.0)	48	2.1:1	72	98	2.95	0.535	2.2	3.00	22.31	3.00
4	Avicel PH-102	6.73:3.42:1 (10.6:25.5:5.0)	8	1:1	12	85	2.95	0.770	7.8	2.96	9.11	2.96
5	Avicel PH-102	6.61:3.42:1 (20.8:51.0:10.0)	48	2.1:1	72	92	3.00	0.966	4.5	3.00	20.52	3.00

[a] After evaporation of ammonia 7.65 g of HMDS was added.

linters. Increasing the amount of ammonia to 2 mol/hydroxy group gave complete silylation also in this case.

As the ammonia cellulose I complex is the reactive structure for all celluloses, the kinetics of the activation should depend on the morphology and superstructure of the cellulose material. The crystallinity of these celluloses decreases in the order Avicel > hydrocellulose > linters. Hence, this cannot be responsible of the different reactivity. The particle size (Avicel PH-101 has 50 μm and Avicel PH-102 has 90 μm average particle size) and the size of crystallites most likely are the origin of the differences in reactivity of the celluloses in the experiments described.

The influence of the morphology of cellulose on the time required for complete activiation was taken into account by chosing sufficiently long times for the activation (cf. Table 2). Linters was activated in the autoclave for 24 and 48 h, then the amount of ammonia was reduced to almost that of entry 5, Table 1 and HMDS was added so that a ratio NH$_3$:SiMe$_3$:OH of 0.47:3.27:1 resulted. After 24 h of silylation, a DS of 2.9 was obtained. In a variation of this procedure, silylation was performed in two steps (see Table 3). First silylation was performed in a large excess of ammonia (7−15 mol per mol OH), then ammonia was reduced to approximately 0.5−2 mol per mol AGU.

The result in Table 3 shows that complete silylation of cellulose regardless of provenience and pretreatment is possible, if the time for activation and reaction is sufficiently long and if at least during the final stage of reaction the amount of ammonia is on the order of 0.5−2 mol per mol AGU.

Solubility of Trimethylsilyl Cellulose. Trimethylsilylated cellulloses with DS 3 described in this paper were not completely soluble in THF, toluene, or cyclohexane. Other solvents with different polarity or boiling point (dimethylacetamide, *o*-dichlorobenzene, tetraline) did not work either. Silylated Avicel PH-101 with DS 2.72 is completely soluble in THF, the soluble fraction decreases to 5% as the DS reaches 3. Fully silylated hydrocellulose with a DP of 40 is to 67% soluble in THF, while fully silylated linters (DP 1100) is completely insoluble. SEC diagrams of the soluble fraction of Avicel PH-101 (DS 3) and of soluble Avicel PH-101 with DS 2.57 are shown in Figure 3. The peak areas are normalized to the soluble fraction. From these curves follows that only the low molar mass fraction is extracted with THF, while the DS values of the soluble and insoluble fractions are equal. Hence, extraction of the crude material results in fractionation of molar mass and not of DS.

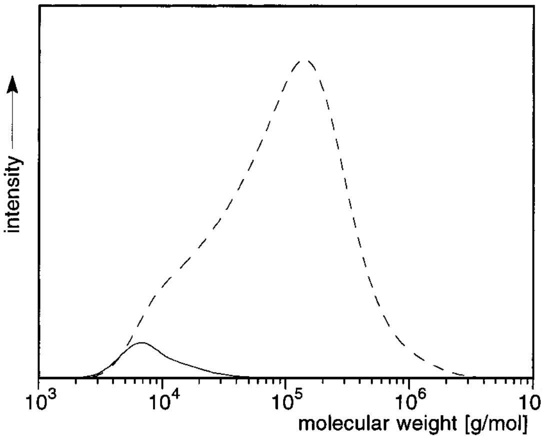

Figure 3. SEC diagrams of the soluble fraction of trimethylsilylated Avicel PH-101, DS 3.00 (—), and of completely soluble Avicel PH-101, DS 2.57 (- - -).

The insolubility of trimethylsilyl cellulose with high DS seems to be due to some kind of aggregation of the hydrophobic trimethylsilylated AGUs. A first indication comes from the thermal behavior. DSC traces of two silyl celluloses are shown in Figure 4 with DS 1.96 and in Figure 5 with DS 3.0. The glass transition at 185 °C present for DS 1.96 cannot be detected for DS 3 (Figure 5). This sample has an endotherm at 370 °C which shows as an exotherm on cooling and is still present on second heating. The viscosity (from shearing in the hotstage under the microscope) is much higher than that of the sample with DS 1.96.

It is possible that the highly silylated cellulose forms a higher ordered mesophase. This mesophase could not be proven by polarized light microscopy on a hotstage. At the high temperature near the assumed clearing transition (370 °C!) decomposition occurred before textures were formed from the rather viscous material. At temperatures around 250 °C the viscosity was too high

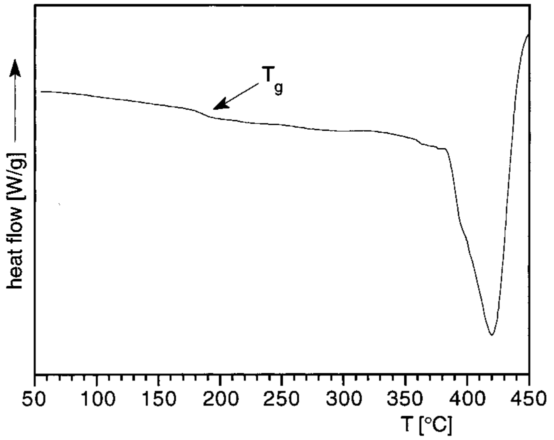

Figure 4. DSC trace of trimethylsilylated Avicel PH-101, DS 1.96.

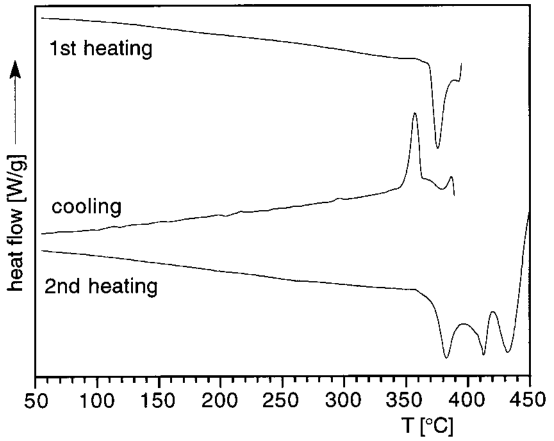

Figure 5. DSC traces of trimethylsilylated Avicel PH-101, DS 3.00.

to observe any textures. The existence of a liquid crystalline phase will have to be proven with other methods.

Fully Silylated (Trimethylsilyl)cellulose in the Literature. The unexpected solubility and thermal behavior of 2,3,6-tris(O-trimethylsilyl)cellulose prompted us to have a closer look into papers reporting a fully silylated (trimethylsilyl)cellulose. Keilich[1] calculated DS 3 from the C, H content, but the IR-spectrum still had an OH absorption (cf. Figure 1).

The patents of Stein et al.[8,9] claim 2,3,6-tris(*O*-trimethylsilyl)cellulose without giving an example. The highest DS reported in an example with linters using chlorotrimethylsilane/DMSO/methylamine was 2.48 from Si content, and DS 2.72 for a pulp from silylation with chlorotrimethylsilane/THF/NH_3.

Klemm et al.[5] used chlorotrimethylsilane/pyridine/(dimethylamino)pyridine/THF without giving an experimental procedure. In another paper the method first described by Schempp was adopted without giving analytical data.[17] Schempp et al.[4] specifically mentioned in their original paper that they did not obtain DS 3.

Bredereck et al.[10] had a DS of 2.95 (from Si analysis) and also an OH absorption in the IR-spectrum.

The solubility properties we found were not mentioned by any of the authors. We do not know wether the heterogeneous nature of the silylation under the conditions applied by us favors this "hydrophobic" aggregation. This too is currently under investigation.

Conclusions. Reaction conditions have been found to obtain fully silylated (trimethylsilyl)cellulose with HMDS in liquid ammonia in the presence of saccharin as catalyst. The ratio of ammonia to AGU has to be between 1.2 and 6; a higher excess lowers the DS even in the presence of excess silylating agent. A ratio of trimethylsilyl groups to OH of 3.4 is suitable for complete silylation, a large excess (e.g. 14:1) also gives a lower DS. This rules out the existence of an equilibrium. Depending on the type of cellulose used (microcrystalline Avicel, cotton linters, hydrocellulose) activation is crucial. Activation can be achieved by separate treatment of cellulose with ammonia prior to silylation or by a two-step reaction first with a large excess of ammonia then with an amount between 1.2 and 6 mol/mol of AGU.

Trimethylsilyl cellulose described in the literature so far, was not completely silylated as careful analysis of the literature data and IR-spectra revealed. Highly silylated trimethylsilyl cellulose becomes more and more insoluble in common organic solvents such as THF or toluene. Soluble and insoluble fractions have similar or identical DS, hence fractionation occurs according to molar mass not according to degree of silylation. Highly silylated cellulose has thermal properties different from those with a DS below 2.5. A reversible endotherm shows in the DSC above 360 °C, which may be due to a clearing transition or to some kind of gel melting. The origin of the lack of solubility which has not been mentioned in the literature before is currently under investigation.

Experimental Part. Methods of Characterization. IR spectra were obtained from films or mulls in poly(chlorotrifluoroethylene) oil between NaCl plates using a Bruker IFS48 FTIR spectrometer. Films were prepared on NaCl plates from the trimethylsilylated celluloses dissolved in THF or toluene. The solvent was removed at 100 °C under vacuum (0.01 mbar). The degree of silylation (DS) was calculated from the content of silicon determined gravimetrically (SiO_2) according to McHard et al.[18] The average degree of polymerization (DP) of the various celluloses used was determined by intrinsic viscosity measurements of the corresponding cellulose tricarbanilates in acetone at 20 °C.[19] Cellulose tricarbanilates were prepared as described by Saake and co-workers.[20] Crystallinity of the cellulose samples were estimated from the infrared crystallinity ratio a_{1372}/a_{2900} proposed by Nelson and O`Conner.[21] SEC was performed with a PSS 2000 evaluating system, a constaMetric 3200 pump (Thermo Separation Products) a RI-71 differential refractometer (Shodex) and three PSS SDV−Gel columns (7.8 × 300 mm; 10^3, 10^5 and 10^6 Å pore size) with THF as mobile phase (flow rate 1.0 mL min^{-1}, internal standard 2,6-di-*tert*-butyl-4-methylphenol). The concentration of the polymer solution was about 0.1% and 100 μL were injected per run. Molecular weights are relative to polystyrene standards. Thermal properties were investigated with a Mettler TC 15 system with DSC 30. Heating rates were 20 K/min. Nitrogen was used as purge gas to prevent oxidative degradation.

Materials. Cotton linters (DP 1100) and microcrystalline cellulose (Avicel PH-101/PH-102, DP 220) from Fluka were dried at 90 °C under vacuum (0.01 mbar) to constant weight. Hydrocellulose was obtained by heterogeneous hydrolytic degradation of Avicel PH-101 with 0.5 m aqueous potassium hydrogen sulfate at 60 °C as described by Husemann and Weber.[22] HMDS was purified by distillation prior to use. Ammonia (2.8, Messer Griesheim) was used without further purification. Saccharin from Janssen was used as received.

Silylation of Cellulose: General Procedure. A stainless steel autoclave with 55 mL internal volume equipped with a magnetic bar was filled with the amounts of cellulose, HMDS and 0.5 mol % of saccharin (relative to the hydroxy groups). The autoclave was sealed and liquid ammonia was pressed into the reactor from a heated pressure vessel. The mixture was heated to reaction temperature using a heating jacket and stirred for the times given in Table 1. Ammonia was evaporated off at room temperature and atmospheric pressure, and residual ammonia, in a vacuum at 80 °C. The crude product was extracted three times for 1 day by stirring in the 50-fold amount of THF. The insoluble part was separated from the solution by centrifugation. The soluble part was concentrated to a solution of 4% and precipitated in methanol. The soluble and insoluble fractions were dried to constant weight at 90 °C under vacuum (0.01 mbar). Amounts of starting materials, yields, and properties of the trimethylsilylated celluloses are given in Table 1.

Preactivation of Linters and Silylation. A stainless steel autoclave with 55 mL internal volume equipped with a magnetic bar was charged with 1.51 g (9.3 mmol AGU) linters and 26 mg (0.14 mmol) saccharin. The autoclave was sealed and 20.5 g (1.20 mol) liquid ammonia was pressed into the reactor from a heated pressure vessel. After the mixture was stirred at room temperature, ammonia was evaporated at atmospheric pressure and HMDS was added by a manually operated spindle press. The silylation of the cellulose and workup was done as described above. Time for preactivation, amounts of starting materials, reaction times, yields, and properties of the reaction products are included in Table 2.

Silylation of Cellulose with Various Amounts of Ammonia during the Reaction. The silylation and workup was done as described in the general procedure. After the first silylation step, ammonia was released at room temperature and atmospheric pressure to the amount given in Table 3 (second silylating step). Amounts of starting materials, yields, and properties of the trimethylsilylated celluloses are given in Table 3.

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