Silylcellulose from Silylation / Desilylation of Cellullose in Ammonia

Werner Mormann*, Jürgen Demeter+, Thomas Wagner#

Universität-GH Siegen, Fachbereich 8, Laboratorium für Makromolekulare Chemie, Adolf-Reichwein-Str. 2, 57068 Siegen, Germany
+present address BASF AG, 67056 Ludwigshafen
#present address Wolff-Walsrode GmbH, 29655 Walsrode

Summary

Silylation of cellulose with hexamethyldisilazane (HMDS) in liquid ammonia is described emphasizing mechanistic features. Conditions for complete as well as for stoichiometric partial silylation have been established which proved that the ratio of silylating agent and hydrogen bonding capability of the solvent are crucial for complete silylation. The heterogeneous reaction follows first order kinetics in the presence of saccharine as catalyst indicating that the accessability of hydroxy groups is not the rate determining factor. Stoichiometric desilylation of trimethylsilyl cellulose is also possible in tetrahydrofurane containing ammonia as hydrogen bond donor. Trimethylsilyl celluloses have a solubility window in THF with a DS from 1.6 to 2.6 which is narrower for higher molecular weight of the cellulose. Trimethylsilyl celluloses with DS above 2.7 show thermotropic behaviour.

Introduction

Conversion of hydroxy to trimethylsiloxy groups is extensively used in organic chemistry as well as in carbohydrate chemistry to impart volatility and to improve solubility in non polar solvents[1]. Silylation of Cellulose has been studied by several research groups using different silylating agents and reaction media. Reactive silylating agents like chlorotrimethylsilane[2-4], N,O-bis(trimethylsilyl)acetamide[5, 6] or hexamethyldisilazane (HMDS)[7] were commonly used.

The lack of solubility and the need of activation of cellulose prior to reaction on one side, the non polar character of trimethylsilyl cellulose on the other require special solvents for the silylation. Normally these reactions are heterogeneous at least in a certain range of conversion. Pyridine[2, 3], dimethylacetamide/LiCl[8], formamide[7], dimethylsulfoxide/paraformaldehyde[6] or hexamethylphosphoric acid triamide[5, 9] have been used.

Greber and Paschinger were the first to report silylation of cellulose with chlorotrimethyl-

CCC 1022-1360/00/$ 17.50+.50/0

silane in liquid ammonia. They also reported that silylation with HMDS does not occur under these conditions[4]. Klemm and coworkers used ammonia to activate cellulose in organic solvents like tetrahydrofurane, DMF oder Dimethylsulfoxide and chlorotrimethylsilane[10] .

We studied silylation in ammonia in order to combine activation of cellulose and the use of HMDS as silylating agent. HMDS gives ammonia as the only by-product. High boiling solvents or salts as formed in the case of chlorotrimethylsilane decrease stability of silyl cellulose or require tedious purification. Complete silylation of cellulose could be achieved by this procedure for the first time[11].

The present paper describes the synthesis of trimethylsilyl cellulose with predictable and reproducible degrees of silylation from silylation and desilylation with emphasis on mechanistic and reactivity aspects of the reactions involved and deal with some properties of the celluloses obtained.

Results and discussion

Activation

Activation of cellulose with ammonia has been used for a number of reactions. Ammonia replaces the OH---O-hydrogen bonds of cellulose by OH---N-bonds, forming an ammonia-cellulose-complex with one ammonia per anhydroglucose unit (AGU) being intercalated [12]. Liquid ammonia treated (LAT) cellulose has increased reactivity as reported by Schleicher et al. in a study of heterogeneous reactions of LAT cellulose [13].

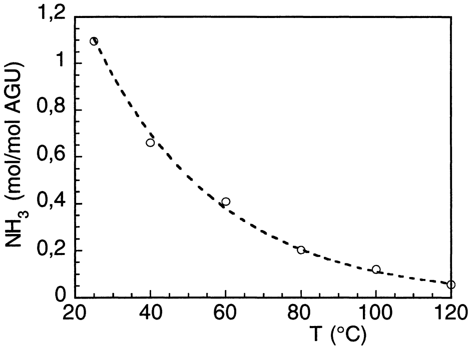


Fig. 1: NH_3-uptake of linters with temperature

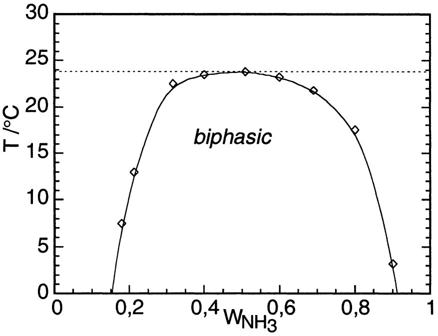


Fig.2: Phase diagramme of $HMDS/NH_3$

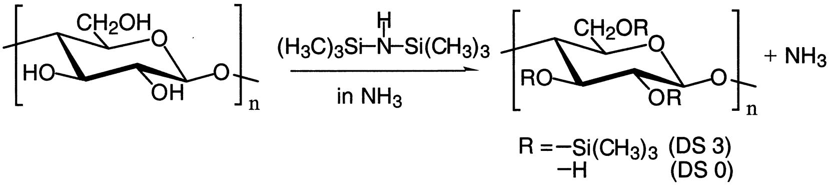
Saturation of dried cellulose (Linters, Avicel) with gaseous ammonia or with liquid ammonia in an argon atmosphere results in an ammonia/AGU ratio of approximately 1 : 1. With increasing temperature the ammonia content continuously decreases to a ratio of only 1 : 10 at 120 °C as shown in Fig. 1. Obviously the cellulose-ammonia-complex is a temperature dependend equilibrium rather than a stoichiometric compound.

Miscibility studies of ammonia and HMDS revealed complete miscibility above 24 °C and two phase behaviour below this temperature (Fig. 2)[14]. This also explains why Greber [4] was not able to achieve silylation with HMDS in liquid ammonia.

Silylation with HMDS/ammonia

Details of the silylation of cellulose as shown in equation 1 and of other hydroxy group containing polymers and low molar mass compounds have been reported previously [11, 14].

Eq. 1:



Complete silylation could not be achieved with high excess of HMDS, long reaction times or high temperature. The maximum degree of silylation proved to be independent also on the crystallinity of the cellulose used[15]. Use of saccharin (2-sulfo-benzoic acid imide) as catalyst[16] also had no effect. Surprisingly, use of saccharin and variation of the ammonia / HMDS ratio led to conditions for complete silylation (Tab. 1). Decrease of the amount of ammonia from 20 to 2 mol per mol OH (to 0.4 in the case of Avicel) with constant amount of HMDS (1.1 mol per mol OH) gave complete silylation. A higher excess of HMDS on the other hand leads to a decrease of the degree of silylation which rules out that an equilibrium is responsible for incomplete silylation with higher excess of ammonia.

Trimethylsilyl cellulose with a DS of 2.5 is soluble in HMDS. Attempts were made therefore to obtain fully silylated cellulose by further silylation of such a cellulose. The results are presented in Fig. 3. After 4 days at 80 °C the DS has increased from 2.6 to 2.75 without further reaction after 15 days. Addition of triethylamine as hydrogen bond acceptor enabled silylation up to a DS of 2.95 after additional 20 days with no change after 50 more days. It is worth mentioning that as the DS increased beyond 2.75 the reaction mixture became opalescent and turned into a suspension of trimethylsilyl cellulose in HMDS / triethylamine at even higher conversion.

Tab. 1: Complete silylation of cellulose with HMDS/ammonia

No.	Cellulose	n_{OH} : n_{Si} : n_{NH_3}	DS
1	Avicel PH 101	1 : 3.4 : 30	2.72
2	"	1 : 3.4 : 17	2.87
3	"	1 : 3.4 : 9	2.94
4	"	1 : 3.4 : 2	3.0
5	"	1 : 3.4 : 0.4	3.0
6	"	1 : 13.5 : 2	2.96
7	Avicel PH 102	1 : 3.4 : 2	3.0
8	Linters	1 : 3.4 : 2	3.0
9	Linters DS 2.57	1 : 78 : 24.3	2.95
10	Linters DS 2.95	1 : 78 : 60	3.0

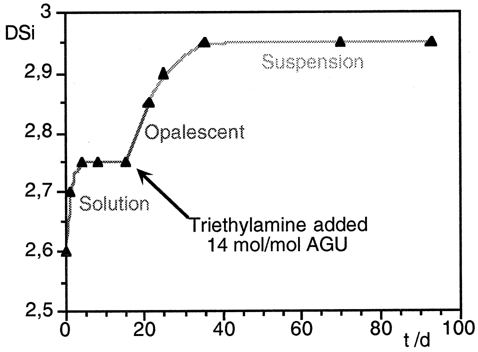


Fig. 3: Effect of hydrogen bonds on silylation of cellulose

"Post-silylation" of silyl celluloses was performed with HMDS in ammonia (Tab. 1, entries 9 and 10). It resulted in complete silylation when the ratio of HMDS to ammonia was 2.6 : 1 while the DS was 2.95 for a ratio of 6.4 : 1. Obviously it is the ratio of HMDS / ammonia which is important and not the absolute amounts of them as long as there is enough silylation agent present.

Once reaction conditions for complete silylation were established, the kinetics of this heterogeneous reaction at 80 °C was studied using saccharine as catalyst, HMDS sufficient for a DS of 1.68, and 60 mol ammonia per anhydroglucose unit (AGU). The results are given in Tab. 2 and in Fig. 4. For each data point a silylation was made. A THF soluble and an insoluble fraction was obtained in all cases. The insoluble fractions had a DS of 0.7 and less while those of the soluble fractions increased from 1.7 to 2.3.

Tab. 2: Kinetics of silylation of Avicel with HMDS/ammonia

t / min	THF-sol. / w.-%	DS THF-sol.	DS insol.	DS total
30	41.6	1.70	0.19	0.65
60	66.8	1.73	0.71	1.32
120	74.0	2.22	0.41	1.54
180	69.0	2.31	0.57	1.57
360	72.4	2.33	0.42	1.58

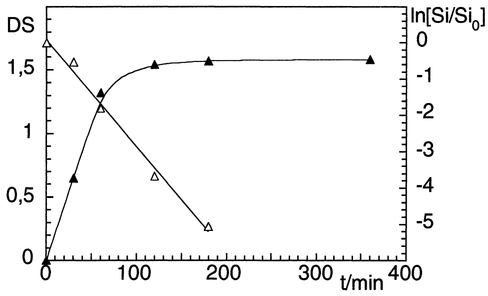


Fig. 4: Kinetics of silylation of Avicel

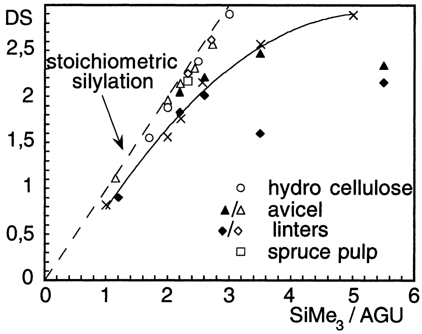


Fig. 5: Partial silylation of cellulose (open HMDS, black chlorotrimethylsilane)

Kinetic analysis showed that silylation of cellulose in ammonia under these conditions is of first order for the formation of trimethylsiloxy groups in cellulose. First order kinetics have been found also for the silylation of poly(vinyl alcohol) under similar conditions[17] which, however is a homogeneous reaction. Obviously the active silylating agent is trimethylsilylated saccharin (cf. scheme 1) which is formed in a fast reaction to ensure constant concentration. First order behaviour for the hydroxy groups of cellulose requires that accessability of hydroxy groups is high enough to have no influence on the rate of reaction up to a DS of 1.6. Furthermore 3 hours are a sufficiently long reaction time for complete reaction of all HMDS present in the mixture.

As HMDS reacted completely in the silylation, partial silylation of cellulose was attempted (cf. Fig. 5). In the range between 1.1 and 2.9 degrees of substitution can predictibly obtained with stoichiometric amounts of HMDS[18]. Use of chlorotrimethylsilane under conditions reported in the literature requires excess silylation agent[19] .

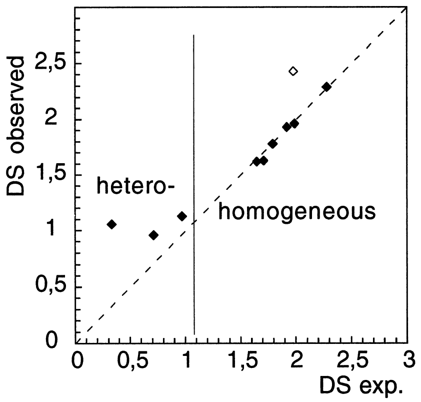
Desilylation of trimethylsilyl cellulose

Desilylation is an important process for regeneration of cellulose. It is normally done with alcohols in the presence of acidic or basic catalysts. Attempts to achieve partial desilylation to a lower DS in THF-solutions were not successful. Again ammonia as hydrogen bond acceptor and donor enabled stoichiometric desilylation in 10 % solutions of silyl cellulose in THF containing 10 % ammonia and saccharin as catalyst. DS below 1 cannot be obtained by this method probably because trimethylsilyl cellulose with a DS of 1 becomes insoluble in the reaction mixture.

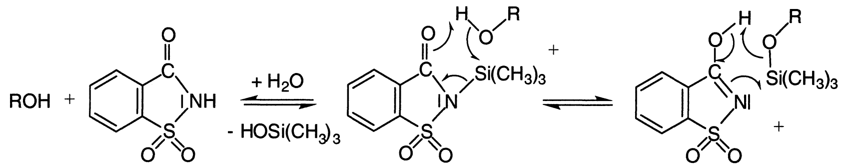
Tab. 4: Stoichiometric desilylation of trimethylsilyl cellulose (Avicel)

Run	DS start	DS calc.	DS observed
1	2.96	2.3	2.29
2	2.79	2.0	1.96
3	2.79	1.9	1.93
4	2.96	1.7	1.63
5*	2.96	2.0	2.43
6	2.92	1.0	1.13
7	2.92	0.7	0.96
8	2.96	0.3	1.06

*: without ammonia



Saccharin which has been used first by Bruynes and Jurriens as catalyst for the silylation with HMDS is also a very effective catalyst in desilylation[16]. The active species most likely is silylated saccharin. We think the combined action as silyl group donor and proton acceptor is essential in silylation while it is silyl group acceptor and proton donor in the desilylation. The rather long reaction times are caused by the slow combination of trimethylsilanol to hexamethyldisiloxane and water.



$$2\ HOSi(CH_3)_3 \longrightarrow H_2O + Me_3Si\text{-}O\text{-}SiMe_3$$

Properties of trimethylsilyl celluloses

Silylation as well as desilylation are polymer analogous reactions which has been shown by SEC analysis of suitable derivatives. Thus cotton linters has been converted into the tricarbanilate by reaction with phenyl isocyanate while another sample was silylated, desilylated and then also transformed into the tricarbanilate [14].

Trimethylsilyl celluloses from the silylation reaction described have some peculiarities in the solubility (Fig. 6). They become partly insoluble in THF with a DS below 1,8 and also with high degrees of substitution. The window of solubility becomes smaller with increasing molar mass of the cellulose. Avicel with a DS of 3.0 is soluble only to about 4 % in THF.

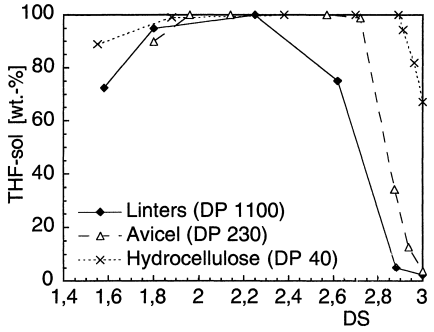


Fig. 6: Solubility vs DS of different silyl celluloses

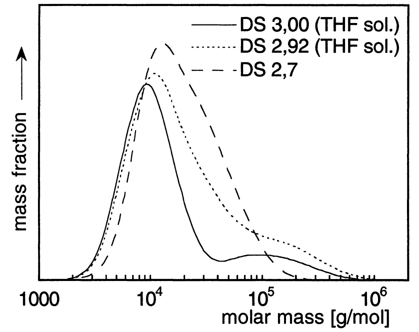


Fig.7: Molar mass distribution of Avicel with different degrees of silylation

SEC proved that only the low molar mass fraction is soluble in THF (Fig. 7). The THF-soluble fraction of Avicel (DS 3.0) has a much lower molar mass than a completely soluble non fractionated sample of silylated Avicel. The poor solubility of highly substituted trimethylsilyl cellulose is due to aggregation via interaction of the silyl groups.

Aggregation shows from the bimodal mass distribution curves of highly silylated cellulose. Branching of cellulose molecules via covalent bonds can be excluded as carbanilates obtained after complete desilylation and subsequent reaction with phenyl isocyanate have a monomodal distribution. Cellulosetricarbanilates are known to be molecularly dispersed in dilute solution[20].

Thermal properties of trimethylsilyl celluloses also depend from the degree of substitution. Soluble silyl celluloses behave like normal thermoplastic materials in dynamic mechanic thermal analysis (Fig. 8). They show a glass transition between 190 und 210 °C and a rubber plateau for linters which has five times the molar mass of Avicel. Linters and other highly silylated celluloses show only a slight decrease in modulus above the glass transition. This is in agreement with the results from differential scanning calorimetry.

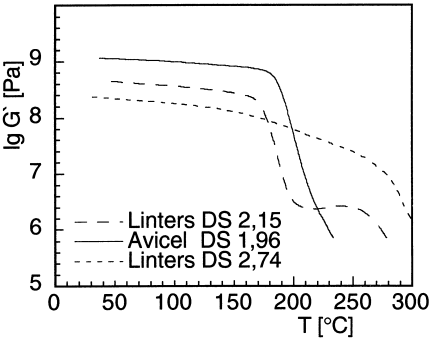


Fig. 8: DMTA of silyl celluloses with different DS

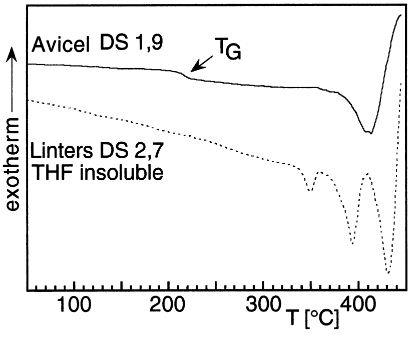


Fig. 9: DSC of silyl celluloses with different DS

The DSC-traces (Fig. 9) have a glass transition at about 200 °C and decomposition at about 400 °C for trimethylsilyl cellulose with a DS below 2.5. The insoluble trimethylsilyl cellulose does not show a glass transition but an endotherm which can still be seen after multiple heating/cooling. Up to 360 °C no significant weight loss can be detected from thermogravimetric analysis. Enthalpies of 1-6 kJ/mol as well as the high viscosity above TG suggest that the endotherm is caused by a liquid crystalline transition.

Conclusions

Silylation of cellulose with HMDS / ammonia is a new variation which allowed the synthesis of completely silylated trimethylsilyl cellulose. Partially silylated cellulose could be obtained in a reproducible manner by stoichiometric silylation as well as by stoichiometric desilylation.

Acknowledgement

Financial support of this work by the DFG (Forschungsschwerpunkt Cellulose) and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

1) E. W. Colvin, "Silicon Reagents in Organic Synthesis", in: Best Synthetic Methods, 1st edition, A.R. Katritzky, O. Cohn, C. W. Rees, Eds., Academic Press, New York 1988

2) H.A. Schuyten, J.W. Weaver, J.D. Reid, J.F. Jurgen,. *J. Am. Chem. Soc.* **70**, 1919 (1948)

3) G. Keilich, K. Tihlarik, E. Husemann, *Makromol. Chem.* **120**, 87 (1968)

4) G. Greber, O. Paschinger, *Das Papier* **35**, 547 (1981)

5) J.F. Klebe, H.L. Finkbeiner, *J. Polym. Sci., Part A1* **7**, 1947 (1969)

6) N. Shiraishi, Y. Miyagi, S. Yamashita, T. Yokota, Y. Hayashi, *Sen'i Gakkaishi* **35**, 466 (1979)

7) R.E. Harmon, K.K. De, S.K. Gupta, *Staerke* **25**, 429 (1973)

8) W. Schempp, T. Krause, U. Seifried, A. Koura, *Das Papier* **38**, 607 (1984)

9) J.F. Klebe, H. Finkbeiner, D.M. White, *J. Am. Chem. Soc.* **88**, 3390 (1966)

10) D. Klemm, M. Schnabelrauch, A. Stein, T. Heinze, U. Erler, S. Vogt., *Das Papier* **45**, 773 (1991)

11) W. Mormann, J. Demeter, *Macromolecules* **32**, 1706 -1710 (1999)

12) K. Hess, J. Gundermann, *Ber. Dt. Chem. Ges.* **70**, 1788 (1937)

13) H. Schleicher, C. Daniels, B. Philipp.,. *J. Polym. Sci. Symp.* **47**, 251-260 (1974)

14) W. Mormann, T. Wagner., *Makromol. Chem., Rapid Commun.* **18**, 515 (1997)

15) W. Mormann, T. Wagner., *Carbohydrate polymers* **42**, in press

16) C.A. Bruynes, T.K. Jurriens, *J. Org. Chem.* **47**, 3966 (1982)

17) W. Mormann, T. Wagner, *J. Polym. Sci., Part A: Polym. Chem.* **33**, 1119 (1995)

18) W. Mormann, J. Demeter, T. Wagner, *Macromol. Chem. and Phys.* **200**, 693 (1999)

19) Ger(East)DD 298,644 (1989), invs.: A. Stein, W. Wagenknecht, D. Klemm, B. Philipp, *Chem. Abstr.* **107**, P 92503 b

20) L. Schulz, W. Burchard, *Das Papier* **47**, 1 (1993)