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Carbohydrate Polymers 43 (2000) 257–262

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Silylation of cellulose with hexamethyldisilazane in liquid ammonia

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Accepted 3 February 2000

Abstract

Silylation of cellulose with hexamethyldisilazane (HMDS) in liquid ammonia at elevated temperature in an autoclave is reported. The influence of temperature, time, concentration of reagents and type of cellulose used for the silylation has been studied. The maximum degree of silylation achievable depends on the starting material. The new method gives higher degrees of silylation than other methods reported in the literature. As indicated by SEC the silylation of cellulose with HMDS/NH_3 proceeds without degradation of the polymer chain. Silylation seems to change the mechanism of thermal degradation in thermogravimetric analysis with respect to that of cellulose. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cellulose; Silylation; Hexamethyldisilazane; Liquid ammonia; Activation; Properties

1. Introduction

Silylation of cellulose as a route to reactive soluble derivatives has been investigated by different groups with a number of silylating agents and solvents (Harmon, De & Gupta, 1973; Keilich, Tihlarik & Husemann, 1968; Klebe & Finkbeiner, 1969; Klemm, Schnabelrauch, Stein, Heinze, Erler & Vogt, 1991; Schempp, Krause, Seifried & Koura, 1984). The big difference in polarity requires special solvents for the reaction, e.g. pyridine (Keilich et al., 1968; Schuyten, Weaver, Reid & Jurgens, 1948), dimethylacetamide/LiCl (Schempp et al., 1984), or formamide (Harmon et al., 1973). Reactive silylating agents like *N*,*O*-bis(trimethylsilyl)acetamide (Klebe & Finkbeiner, 1969), chlorotrimethylsilane (Greber & Paschinger, 1981; Keilich et al., 1968; Schuyten et al., 1948) are mostly used. Chlorotrimethylsilane in addition requires a base to neutralize the hydrogen chloride formed. Tedious purification of the polymer is necessary to remove residual silylating agent, solvents, and salts. Hexamethyldisilazane (HMDS) has also been used for this reaction though an additional catalyst is required in this case.

Greber et al. reported the silylation of polysaccharides in liquid ammonia with chlorotrimethylsilane and stated that this reaction was not feasible with HMDS (Greber & Paschinger, 1981). Klemm and co-workers used ammonia in organic solvents to activate cellulose and chlorotrimethylsilane as silylating agent (Klemm et al., 1991). In a previous paper we reported the successful silylation of poly(vinyl alcohol) with HMDS in liquid ammonia at elevated temperature (Mormann & Wagner, 1995). This method of silylation was extended to polyglucanes since ammonia is known to activate cellulose by intercalation into the lattice and breaking up inter- and intra-molecular hydrogen bonds (Bikales & Segal, 1971; Blackwell, Kolpak & Gardner, 1977) and we reported first results of the successful silylation of cellulose (Mormann & Wagner, 1997).

Silylation of cellulose under clean and easily reproducible conditions which avoid high boiling solvents and tedious purification from salts as by-products could be a way to synthesize other derivatives of cellulose by subsequent reactions, e.g. esterification with acid chlorides or anhydrides. Further, trimethylsilyl cellulose is of interest as an intermediate for the manufacture of regenerated cellulose avoiding ecological problems encountered in the presently used xanthogenate process.

In this paper we describe the silylation of cellulose with HMDS in ammonia as reaction medium and discuss the influence of the cellulose type and of different reaction parameters on the maximum degree of silylation (DS) which can be obtained with this new method.

2. Experimental part

2.1. Methods of characterization

IR spectra were obtained from films or KBr pellets using

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0144-8617/00/$ - see front matter
PII: S0144-8617(00)00173-9

Table 1
Reaction conditions and results of the silylation of celluloses with HMDS/NH_3

No.	Cellulose material (dp)	NH_3:$SiMe_3$:OH[a] (mass)[b]	V_A (ml)[c]	T (°C)	t (h)	DS	Yield (%)
1	Linters (1100)	4.8:3:1 (15:45:10)	150	100	5	2.02	91
2	Linters (1100)	4:2:1 (25:59.7:20)	150	100	8	2.33	95
3	Linters (1100)	4:2:1 (25:59.7:20)	150	100	5	2.20	93
4	Linters (1100)	16:6:1 (7.5:13.44:1.5)	55	160	8	2.52	88
5	Linters (1100)	2.37:4.08:1 (1.49:12.2:2)	55	90	55	2.51	92
6	Linters (1100)	1:1.05:1 (3.15:15.68:10)	150	95	4	2.42	92
7[d]	Linters (1100)	2.8:2:1 (8.9:30:10)	150	95	4	1.86	93
8	Linters from cuoxam	30:12.7:1 (10:19:1)	55	100	50	2.80	82
9	Avicel (290)	4.5:2:1 (28:59.7:20)	150	100	5	2.47	92
10	Avicel (290)	154:50:1 (9.7:15.3:0.2)	55	80	12	2.62	81
11	Avicel (290)	45.5:4.1:1 (14.3:6.12:1)	55	100	45	2.81	83
12[e]	Hydro cellulose from linters (340)	64:10.2:1 (10:7.65:0.5)	55	100	44	2.69	91
13	Hydro cellulose from linters (340)	32:10.2:1 (5:7.65:0.5)	55	100	20	2.80	90
14	Hydro cellulose from avicel (230)	128:10.2:1 (20:7.65:0.5)	55	120	21	2.71	83
15	Hydro cellulose from avicel (230)	64:10.2:1 10:7.65:0.5)	55	120	21	2.73	82
16	Hydro cellulose from avicel (230)	64:10.2:1 (10:7.65:0.5)	55	160	28	2.72	89
17	Hydro cellulose from avicel (40)	32:1.00:1 (40:7.47:5)	150	90	4	2.95	91

[a] Molar ratio of ammonia to silyl groups to hydroxy groups.
[b] Mass of ammonia, hexamethyldisilazane, and cellulose in grams.
[c] Internal volume of the autoclave used.
[d] Without mechanical stirring.
[e] Without saccharin.

a Bruker IFS48 FTIR spectrometer. The DS was calculated from the content of silicon determined gravimetrically (SiO_2) according to McHard, Servais and Clark (1948). 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 (Burchard & Husemann, 1961). Crystallinity of the cellulose samples was estimated from the infrared crystallinity ratio a_{1372}/a_{2900} as proposed by Nelson and O'Connor (1964). Thermal properties were investigated with a Mettler TC 11/15 system with DSC 30 and TG 50. Heating rates for DSC measurements were 20 K/min, for TG measurements 5 K/min. The scans were run under a nitrogen purge to prevent oxidative degradation.

2.2. Materials

Cotton linters (DP 1100) and microcrystalline cellulose (Avicel PH-101, DP 290 from Fluka) were dried to constant weight at 90°C, 0.01 mbar. Various hydro celluloses were obtained by heterogeneous hydrolytic degradation of cotton linters and Avicel with 0.5 m aqueous potassium hydrogen sulphate at 60°C as described by Husemann and Weber (1943). Dissolution of linters in cuprammonium hydroxide (cuam) and regeneration was made as reported by Husemann and Lötterle (1950). Cellulose tricarbanilates were prepared as described by Saake, Patt, Puls and Philipp (1991). 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 A stainless steel autoclave (internal volume as indicated in Table 1) equipped with a magnetic stirring bar ($V_A = 55$ ml) or a mechanical stirrer ($V_A = 150$ ml), a thermocouple, a manometer, and a glass window, inlet/outlet valve was filled with the amounts of cellulose, HMDS and 0.5 mol% of saccharin (relative to the hydroxy groups) given in Table 1. 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. After the reaction time given in Table 1 ammonia was evaporated at atmospheric pressure, residual ammonia was removed in vacuum at 80°C. The crude product was dissolved in tetrahydrofurane and precipitated in methanol. Yields and DS of the trimethylsilylated celluloses are given in Table 1.

3. Results and discussion

3.1. Silylation in hexamethyldisilazane/ammonia

The silylation reaction of cellulose in ammonia is shown in Eq. 1. Two hydroxy groups are transformed into

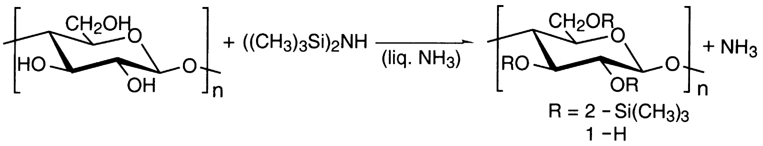
Table 2
Maximum degree of silylation (DS_{max}) for different celluloses

No.	Cellulose material	DP	$Kr_{(IR)}$[a]	DS
1	Linters	1100	0.38	2.52
2	Linters	340	0.40	2.80
3	Linters (cuam)	–	0.35	2.80
4	Avicel	290	0.42	2.81
5	Avicel	230	0.37	2.73
6	Avicel	40	0.39	2.95

[a] IR cristallinity index (Nelson & O'Connor, 1964).

trimethylsiloxy groups by one mol of HMDS, which leaves one mol of ammonia. As ammonia is also the solvent of the reaction only gaseous ammonia has to be removed from the reaction products if HMDS is used in stoichiometric amounts and complete conversion takes place.

The miscibility of ammonia/HMDS has been investigated (Mormann & Wagner, 1997). The components are completely miscible above 24°C.



(1)

Observation of the silylation reactions revealed that during silylation of cellulose the mixture remained heterogeneous unless HMDS was used in excess. HMDS can dissolve silylated cellulose with a DS greater than 2.2. Saccharin in amounts of 0.5 mol% relative to the hydroxy groups was used as catalyst, because it had given good results in the silylation of poly(vinyl alcohol) (Mormann & Wagner, 1995). Silylated cellulose was dissolved in toluene or tetrahydrofurane and precipitated in methanol. Repetition of this procedure did not improve purity. Reaction conditions and amounts of reagents are summarized in Table 1. The silylated polymers were characterized by infrared spectroscopy and DS. The data are also included in Table 1.

3.2. *Influence of reaction conditions*

Different types of cellulose were used for the experiments: cotton linters and microcrystalline avicel, as well as several hydrocellulose materials obtained from acidic hydrolytic degradation of the former. The influence of the main parameters like reaction time, temperature, ratio of cellulose to ammonia and HMDS was studied with these materials (Table 1).

First of all complete conversion of hydroxy to trimethyl siloxy groups could not be achieved in any of the experiments. The maximum DS obtained was different for each type of cellulose. The reaction temperature was varied between 80 and 160°C. Up to 120°C reactions proceed in liquid ammonia, which at 80 and 100°C has a density of 0.5 and 0.45 g/cm^3 and a vapor pressure between 41 and 62 bar. Supercritical conditions i.e. 160°C and 200 bar were applied in runs 4 and 16 (Table 1). The DS obtained under these conditions is not higher (2,5 for run 4 and 2.7 for run 16) than in comparable experiments in liquid ammonia (runs 5 and 15). For runs 15 and 16 all parameters except temperature have been kept constant. These results show that supercritical conditions do not have an advantage over liquid ammonia.

Runs 5 and 6 (Table 1) demonstrate that a reaction temperature of 90 or 95°C gives the same result as supercritical conditions.

The reaction time cannot be directly related to conversion. Long reaction times have a minor effect only (runs 5 and 6 or runs 10 and 11). A DS of 2.51 (run 5) is obtained after 55 h, while 2.42 results after 4 h only (run 6). The highest DS of all experiments, 2.95, was obtained at 90°C after 4 h reaction time (run 17). Stirring seems to be very important, though the reaction is heterogeneous throughout. This is demonstrated with runs 6 and 7. The effect of saccharin as catalyst on the silylation with HMDS is demonstrated with runs 12 and 13. Despite of a more than double reaction time the DS of 12 (2.69) is lower than that of 13 (2.80).

The ratio of trimethylsilyl groups (HMDS) to hydroxy groups has no significant influence on the DS. A sixfold excess of silyl groups with respect to hydroxy groups (run 5) gave almost the same DS as a run where HMDS was reduced to the stoichiometric amount with respect to hydroxy groups (run 6). Even a 50 fold excess gives no higher DS than a ratio of 2:1 (runs 9 and 10). The amount of ammonia can be varied from more than 100 mol per mol hydroxy groups to 1 mol per mol without effecting the DS (run 14 vs. run 15 or run 5 vs. run 6).

Pretreatment of cellulose by dissolution as cuam complex and regeneration (run 7) gave a DS of 2.80. Whether this is due to a reduced crystallinity or to oxidative degradation cannot be decided.

3.3. *Maximum degree of silylation*

The experiments in Table 1 showed that complete conversion of hydroxy to trimethylsiloxy groups could not be achieved with any of the cellulose materials used. The maximum DS, however, was different for the different cellulose types. In Table 2 the maximum DS, the degree of

Table 3
Silylation of cellulose (cotton linters) with different literature procedures

Reference	Reaction conditions	Cellulose used in the reference	DS[a]	DS[b]
Keilich et al., 1968	Chlorotrimethylsilane/ pyridine; 3 h, 15°C	Cotton regenerated from Cuam; DP 3700	3	2.31
Harmon et al., 1973	HMDS/formamide; 2 h, 70°C	Cellulose; Sigma Company, St. Louis, Missouri	3.0	1.92
Klebe and Finkbeiner, 1969	*N,O*-bis(trimethylsilyl)acetamide/ pyridine; DMF; 7 h, 150°C	Wood pulp V-90, Buckeye Corporation	2.7	1.98
Schempp et al., 1984	HMDS/DMAc/lithium chloride; 1 h, 80°C	Wood pulp (beech); DP 1200	2.9	2.02

[a] DS from reference.

[b] DS found with cotton linters (DP 1100).

polymerisation and the crystallinity index is listed for each cellulose used for silylation.

The crystallinity has been determined by infrared spectroscopy as reported by Nelson and O'Connor (1964). The ratio of the absorbance of the C–H bending at 1372 cm^{-1} to that of the C–H streching vibration at 2900 cm^{-1} is the crystallinity index. It has been related to X-ray crystallinity and to crystallinity from density measurements. Small changes of the IR-index correspond to large differences in crystallinity as determined by other methods.

The results in Table 2 show that the maximum DS is not related to the crystallinity of the cellulose used. At first glance it is more likely related to the molecular weight (DP) of the different cellulose materials. This, however, does not make sense because the reaction is heterogeneous. The morphology of the cellulose, e.g. the length of the crystallites can have an influence, though it is not clear why reaction times of more than 50 h have almost no effect on the DS.

On the contrary silylation of low molar mass carbohydrates and of soluble poly(vinylalcohol) proceeds to completion. This rules out an equilibrium between the siloxy compounds, ammonia and HMDS as a reason for the non complete silylation of cellulose. The key seems to be the state of activation and the heterogeneous character of the reaction. This will have to be studied in more detail.

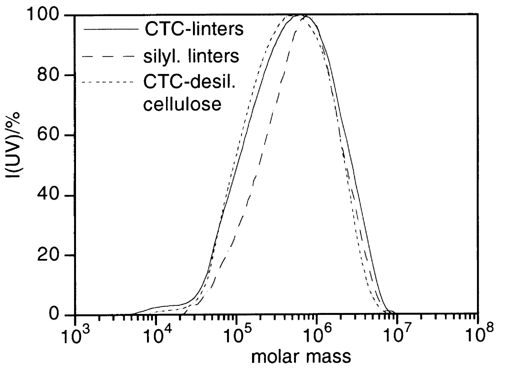


Fig. 1. SEC diagrams of cellulose tricarbanilate (CTC), trimethylsilyl cellulose and tricarbanilate from desilylated trimethylsilyl cellulose.

3.4. Comparison with other silylation procedures

Silylations reported in the literature describe degrees of silylation from 1.5 up to almost 3 (complete silylation) for celluloses of different provenience (Harmon et al., 1973; Keilich et al., 1968; Klebe & Finkbeiner, 1969; Schempp et al., 1984). In order to compare our method to those procedures we repeated some of them with cotton linters used in our silylation experiments. These were silylation with chlorotrimethylsilane in pyridine, silylation with HMDS in formamide, silylation with *N,O*-bis(trimethylsilyl)acetamide in DMF/pyridine, and silylation with HMDS in dimethylacetamide/LiCl. The results in Table 3 show that the degrees of silylation obtained with the literature procedures are lower than that from silylation with HMDS in ammonia, the closest being silylation with chlorotrimethylsilane in pyridine. This suggests that the new silylation method is superior to those reported in the literature.

3.5. Polymer analogous character of the silylation

A further important question is whether the silylation under the conditions reported has polymer analogous character or degradation occurs during silylation. This was checked by the reaction sequence of Eq. (2). A cellulose tricarbanilate (CTC) was prepared from cotton linters (Saake et al., 1991) while another portion was silylated. This was desilylated in methanol under slightly basic conditions (Keilich et al., 1968), isolated and the regenerated cellulose was transformed into the carbanilate by reaction with excess phenyl isocyanate in pyridine. The two carbanilates and the trimethylsilyl cellulose (DS 2.21, run 3) were investigated with size exclusion chromatography (SEC). The results are shown in Fig. 1. The chromatograms prove the polymer analogous character of the silylation reaction. It is noteworthy that the trimethylsilyl cellulose seems to have a lower polydispersity than the

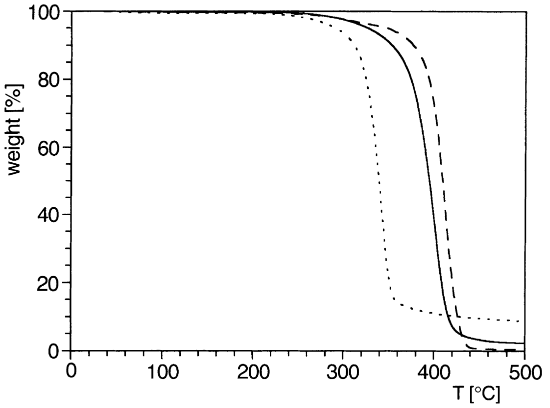
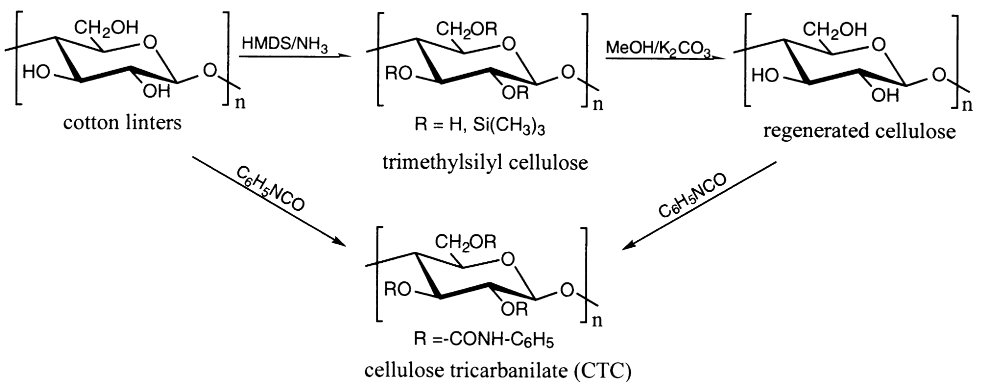


Fig. 2. TGA curves of trimethylsilylated cellulose with DS 2.95 (– – –) and DS 1.86 (—) and of cellulose (···).

two carbanilates. This must be due to some intramolecular interactions because the curves of the two carbanilates are almost identical.



(2)

3.6. Thermal properties of trimethylsilylated celluloses

The trimethylsilylated cellulose with different degrees of silylation were investigated by DSC and thermogravimetry (TGA) to learn about the influence of silylation on thermal properties. TGA curves of a highly silylated cellulose (DS 2.95 from run 17), of a cellulose with DS 1.86 (run 7) and of previously dried linters are shown in Fig. 2. Thermal stability seems to increase with increasing DS; the onset of weight loss is 320°C for cellulose, 373 for cellulose with DS 1.86 and 400°C for cellulose with DS 2.95. 10% of char is left after pyrolysis of cellulose, less than 2% from silyl cellulose with DS 1.86 while no residue is left from the highly silylated sample.

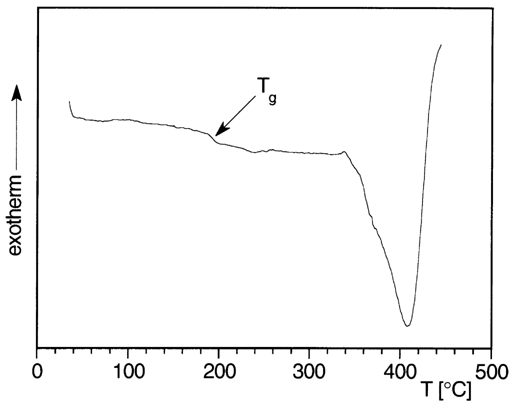


Fig. 3. DSC trace of silylated linters (DS 1.86).

The DSC-trace of the silyl cellulose from run 7 is shown in Fig. 3. It has a glass transition at 190°C and a strong endotherm around 400°C which is due to decomposition and evaporation of volatiles.

4. Conclusions

Silylation of cellulose (cotton linters, microcrystalline avicel and hydro celluloses) with HMDS in liquid ammonia has been investigated. Parameters of the reaction i.e. temperature, reaction time, ratio of reagents and solvents, catalyst have been studied. Temperatures between 80 and 100°C gave best results, supercritical conditions showed no improvement. Reaction times of 4 to 20 h were sufficient. Complete silylation could not be achieved even with high excess of silylating agent, catalyst and long reaction time. Depending on the starting material (crystallinity, degree of polymerisation) different degrees of silylation were obtained. The DS could not be related to any of these properties. The maximum DS obtained with this new variation is higher than with other procedures reported in the literature. The polymer analogous character of the reaction could be proven. The reason of the limitation of the maximum DS achievable, controlled partial silylation, and distribution of silyl groups in the anhydro glucose units are currently under investigation.

Acknowledgements

We are indebted to the Deutsche Forschungsgemeinschaft, to the German Ministry of Agriculture and to the Fonds der Chemischen Industrie for financial support, to Bayer AG for a generous gift of chemicals.

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