Carbohydrate Polymers 50 (2002) 349–353

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Hydrocelluloses with low degree of polymerisation from liquid ammonia treated cellulose

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Received 6 December 2001; revised 25 February 2002; accepted 25 February 2002

Abstract

The heterogeneous hydrolytic degradation of cellulose after treatment with liquid ammonia has been studied. The level off degree of polymerisation (LODP) of liquid ammonia treated (LAT) linters is reached after 3 h when hydrolysed in hydrochloric acid (6.5 mol/l) at 60 °C. The hydrocelluloses were characterized as trimethylsilyl derivatives and as tricarbanilates. LODPs of non-activated celluloses were in the range from 55 to 77, while LAT celluloses had LODPs between 27 and 39. Trimethylsilyl derivatives and tricarbanilates gave almost identical elution curves in size exclusion chromatography indicating comparable hydrodynamic volumes. Glass transition temperatures of trimethylsilyl celluloses with DPs from 27 to 39 were found to be lower than those of the derivatives of the parent celluloses (Avicel, cotton linters) and showed a dependence on molar mass indicating that oligomeric celluloses are obtained by the method reported. Treatment of cellulose in aqueous ammonia was less efficient than liquid ammonia treatment. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ammonia; Cellulose; Hydrocellulose; Cellulose tricarbanilate; Trimethylsilyl cellulose; Hydrolytic degradation

1. Introduction

Naturally occurring cellulose has high molar mass and a supramolecular structure, which allows chemical reactions only after activation mostly with aqueous sodium hydroxide. Celluloses with lower molar mass are of interest for studies of physical properties as function of molar mass and in particular for studies of the solution behaviour.

The degree of polymerisation of cellulose can be lowered by acid hydrolysis under heterogeneous conditions. In the initial stage of the reaction a strong decrease of DP is observed as degradation takes place in the amorphous region. The remaining crystallites of cellulose can be hydrolysed only at the surface. This is the reason why a limiting degree of polymerisation is reached (Battista, Coppick, Howsmon, Morehead, & Sisson, 1956).

The LODP depends on the origin and pre-treatment of cellulose (Krässig, 1993). It is known from a number of reactions that pre-treatment with ammonia enhances reactivity (Koura & Schleicher, 1973; Schleicher, Daniels, & Philipp, 1974). Treatment of cellulose with ammonia prior to acid hydrolysis has been reported by Schleicher (Koura & Schleicher, 1973) but no information on the influence on molar mass distribution and kinetics of the reaction was found in the literature.

In this communication, we report on a simple method for the synthesis of hydrocellulose from liquid ammonia treated cellulose with lower degrees of polymerisation in shorter reaction times than from untreated cellulose.

2. Experimental part

2.1. Methods of characterization

IR spectra were obtained from films using a Bruker Equinox 55 spectrometer. The degree of silylation (DS) was calculated from the IR spectra as published earlier (Mormann, Demeter, & Wagner, 1999). SEC was performed using Polymer Standards Service (PSS GmbH) evaluating system 2000, a constaMetric 3200 pump (Thermo Separation Products) a RI-71 differential refractometer detector (Shodex) and a PSS SDV-gel linear column or four PSS-SDV/5 columns (7.8 × 300 mm; 5 μm particle size; 10^2, 10^3, 10^5 and 10^6 Å pore size) with tetrahydrofuran as mobile phase (flow rate 1.0 ml/min, internal standard 2,6-di-*tert*-butyl-4-methylphenol). Thermal properties were investigated with a Mettler TC 11/15 system with DSC 30 and TG 50 under nitrogen. Heating rates for differential scanning calorimetry (DSC) measurements were 20 K/min, for thermogravimetry (TG) measurements 5 K/min.

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PII: S0144-8617(02)00041-3

Table 1
Acid hydrolysis and silylation of cellulose

No.	Cellulose (pre-treatment)	t[a] (d)	Yield[b] (%)	$n_{AGU}/n_{SiMe_3}/n_{NH_3}$ (m/g of educts)	Yield[c] (%)	DS_{IR}	T_g (°C)	SEC vs. PS-standard		
								DP_n	DP_w	DP_w/DP_n
1	**Avicel PH 101**	0	–	1.00:2.21:34 (1.00:1.10:3.6)	81	2.1	185	98	408	4.2
2	no	3	74	1.00:2.33:30 (1.00:1.16:3.1)	79	2.2	183	62	247	4.0
3	no	5	78	1.00:2.42:29 (0.77:0.92:2.3)	77	2.3	188	55	217	3.9
4	LAT	3	65	1.00:2.37:31 (0.87:1.02:2.8)	85	2.0	178	33	89	2.7
5	LAT	5	60	1.00:2.30:30 (1.00:1.14:3.1)	80	2.3	169	31	83	2.7
6	Activated (16% NH_3)	3	69	1.00:2.25:29 (1.00:1.12:3.0)	80	2.1	169	50	198	3.9
7	**Avicel PH 102**	0	–	1.00:2.97[d]:31 (1:3.70:3.2)	77	2.3	193	74	362	4.9
8	no	5	81	1.00:2.29:30 (1.00:1.14:30)	77	2.1	189	77	272	3.6
9	LAT	5	58	1.00:2.27:30 (1.00:1.13:3.1)	75	2.3	167	27	71	2.7
10	**Linters**	0	–	1.00:2.26:57 (1.00:1.12:6.0)	85	2.2	187	596	1806	3.0
11	no	5	82	1.00:2.25:25 (1.00:1.12:2.6)	82	2.3	184	58	208	3.5
12	LAT	5	68	1.00:2.25:27 (1.00:1.12:2.8)	79	2.2	173	39	109	2.8

[a] Time of degradation.

[b] Of degraded cellulose.

[c] Of silylated cellulose.

[d] Silylated with *N*,*N*-Dibutylaminotrimethylsilane at 100 °C.

2.2. Materials

Cotton linters (Cuoxam-DP 565 from Buckeye) and microcrystalline cellulose (Avicel PH-101 from Fluka and Avicel PH-102 from Lehmann and Voss and Co.) were dried to constant weight at 80 °C, 0.05 mbar. Hexamethyldisilazane (HMDS) was purified by distillation prior to use. Ammonia (grade 2.8, Messer Griesheim) for activation and silylation with HMDS was used without further purification. Tetrahydrofuran was distilled over potassium.

Activation of cellulose. A stainless steel autoclave with internal volume of 28 ml was filled with 5 g cellulose. The autoclave was closed and the same weight of ammonia was introduced from a pressure vessel. The mixture was allowed to stand for 1 h. Then the vessel was opened, ammonia allowed to evaporate and residual ammonia was removed by washing with water until the water showed no alkaline reaction.

Activation of cellulose with less ammonia. A 100 ml flask equipped with a bubble gauge was filled with 5 g of cellulose. 0.96 g of ammonia was condensed to the flask and the mixture allowed to warm to room temperature. Residual ammonia was removed as mentioned earlier.

Activation with aqueous ammonia. A 1 l flask with a magnetic bar was filled with 20 g of cellulose. Six hundred grams of aqueous ammonia (26%) was added and the suspension stirred for 1 h. Residual ammonia was removed as above.

Hydrolytic degradation of cellulose. A 100 ml flask was filled with 5 g of cellulose and 60 ml of hydrochloric acid (6.5 mol/l). The mixture was heated to 60 °C and stirred for the times given in Table 1. After reaction the residual cellulose was washed neutral with water and freeze dried.

Silylation of cellulose. A stainless steel autoclave with internal volume of 55 ml equipped with a magnetic stirrer and an inlet/outlet valve was filled with 1 g of cellulose and

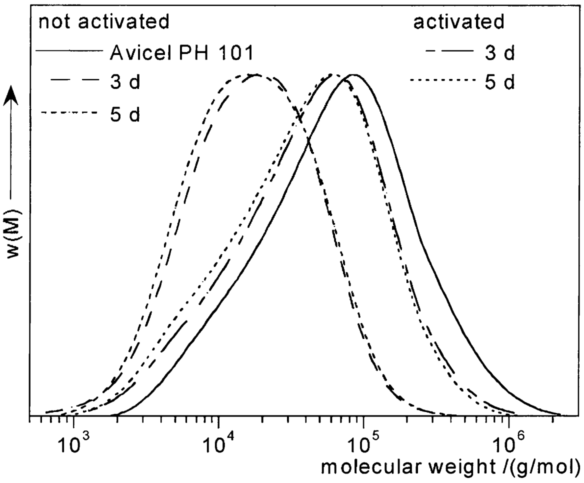


Fig. 1. Effect of activation on mass distribution curves of trimethylsilylated Avicel PH 101 and hydrocelluloses.

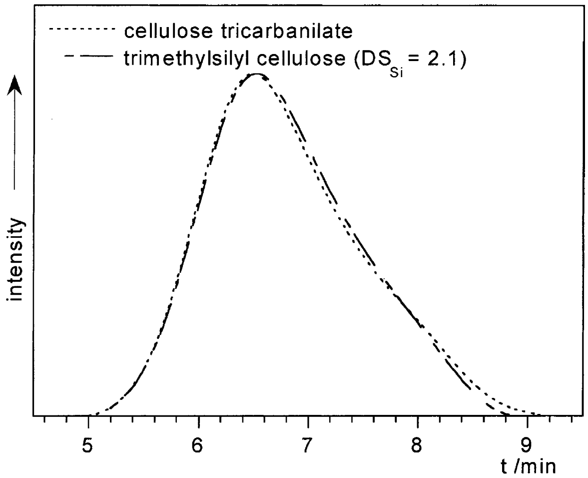


Fig. 2. Comparison of trimethylsilyl cellulose and cellulose tricarbanilate (elution curves).

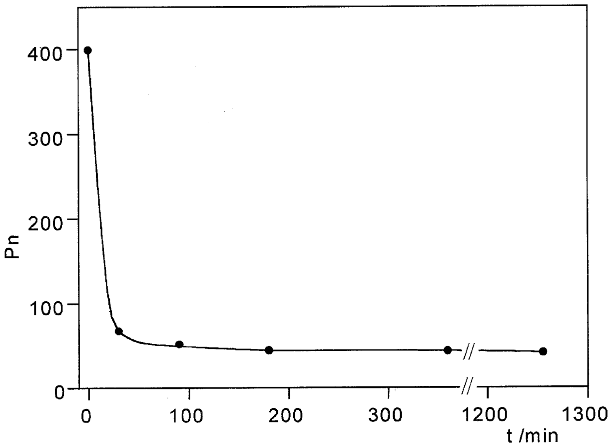


Fig. 3. Kinetics of hydrolytic degradation of LAT linters.

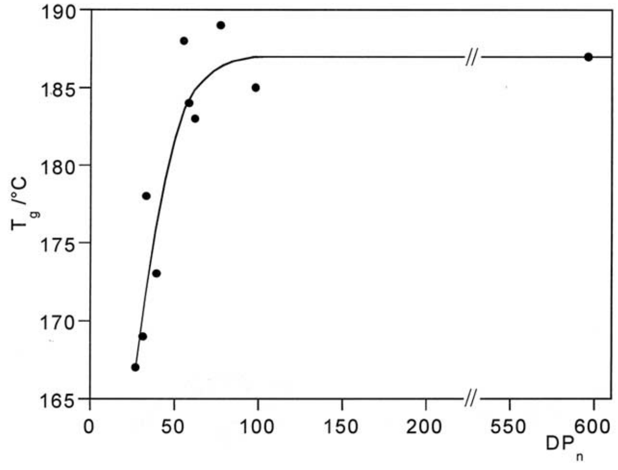


Fig. 4. Glass transition temperatures of trimethylsilyl celluloses.

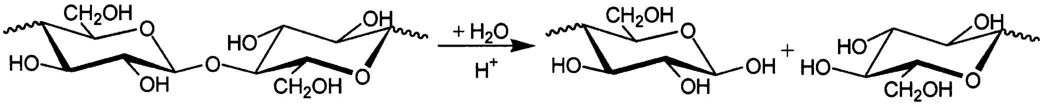
hexamethyldisilazane according to Table 1. The autoclave was closed, liquid ammonia introduced from a pressure vessel and the mixture was heated to 80 °C with a heating jacket for 24 h. After cooling to room temperature, the valve was opened and ammonia was removed first at atmospheric pressure then in vacuo. The crude product was dissolved in tetrahydrofuran and precipitated in methanol/water (*v*/*v* = 5/1).

3. Results and discussion

Cotton linters and Avicel were used as starting materials for the investigation. Linters have a high degree of polymerisation (565), Avicel (DP approximately 100) which is a microcrystalline cellulose itself, is already the product of hydrolytic degradation and therefore particularly suited to demonstrate the activating effect of ammonia. Activation was carried out at room temperature in an autoclave making a dispersion of cellulose in the same amount of liquid ammonia. Cellulose is swollen by intercalation forming a complex with one molecule of ammonia per anhydroglucose unit (AGU; Hess & Gundermann, 1937). As a mass fraction of 10% should be sufficient to form the complex cellulose was also activated with a smaller amount of ammonia and with aqueous ammonia.

After treatment of LAT cellulose with water the cellulose-I-modification is recovered. From X-ray studies was found that the degree of crystallinity of cellulose is lowered by liquid ammonia treatment (Rousselle & Nelson, 1976; Rousselle, Nelson, Hassenboehler, & Legendre, 1976).

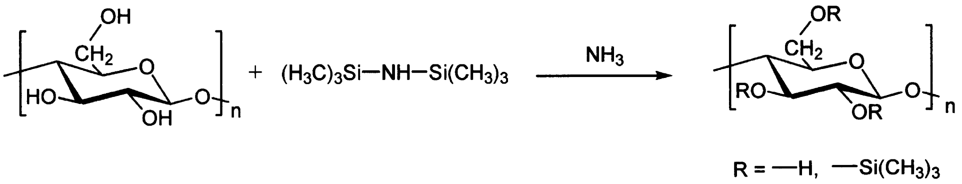
Acid catalysed hydrolysis of cellulose is a cleavage of the 1,4 glycosidic bond through addition of water to the carbon 1 of a AGU as shown in Eq. (1).



(1)

Hydrolysis of non-treated and of LAT celluloses was made in 6.5 M hydrochloric acid at 60 °C. Reaction times, yields and analytical data of the derivatives are included in Table 1. The yields of hydrocelluloses from LAT cellulose were lower than those from non-treated cellulose. Because of the preferential degradation of the amorphous parts of cellulose, the amorphous fraction must have been increased by liquid ammonia treatment, which is in accordance with the results from X-ray diffraction.

The hydrocelluloses were trimethylsilylated (Eq. (2)) to obtain organo-soluble derivatives for SEC. Silylation with hexamethyldisilazane in liquid ammonia is a polymer analogous reaction (Mormann, Demeter, & Wagner, 1998; Mormann & Wagner, 2000) which allows to adjust the DS using appropriate amounts of HMDS (Mormann et al., 1999). Therefore, tetrahydrofuran-soluble trimethylsilyl celluloses were synthesized with a DS between 2.0 and 2.3. In addition, a comparison was made with tricarbanilates synthesized by an improved method (Mormann & Michel, 2002). Molar mass and polydispersity of silylated celluloses are included in Table 1.



(2)

The extent of hydrolytic degradation strongly depends on the type of cellulose and on activation. Without activation for Avicel PH 102 practically no decrease of DP was found after 5 days, for Avicel PH 101 molecular weight went down to 50% of the starting value, while for linters a decrease to 10% from the original value was found. The minor decrease of DP for Avicel as compared to linters is to be expected because Avicel itself is already a partially hydrolysed cellulose. From 3 to 5 days reaction time the DP practically does not change which indicates that the LODP is reached after 3 days. Due to the higher amorphous fraction the DP of linters is decreased more significantly and reaches values, which are comparable with non-activated Avicel.

Activation with liquid ammonia leads to a pronounced decrease of the LODP. The DP ranges from 27 to 39 for the activated and from 55 to 77 for not activated cellulose (Table 1). With Avicel degrees of polymerisation of 31 and 27 are reached after 5 days, 39 from activated linters, which is only slightly higher compared to Avicel.

Fig. 1 shows that the molecular weight distributions of activated and degraded Avicel PH 101 are shifted to lower molecular weight. The polydispersity is also decreased from 4.0 for untreated Avicel to 2.7 for LAT Avicel. Similar results were obtained with Avicel PH 102 and linters. Treatment of Avicel PH 101 with a mass fraction of 16% ammonia at the boiling point (−33.4 °C) resulted in incomplete activation. Treatment in aqueous ammonia (26%) resulted in a higher LODP compared to treatment in liquid ammonia.

Tricarbanilates synthesized for comparison had almost identical properties in SEC, which can be seen from a comparison of the elution curves (Fig. 2). Due to the higher molar mass of the tricarbanilated anhydroglucose unit the calculated degrees of polymerisation are lower compared to the trimethylsilyl derivatives.

Kinetics. The rate of decrease of molar mass by hydrolytic degradation was investigated with LAT linters. Aliquots were taken from the stirred suspension during degradation and carbanilated for characterization by SEC. In Fig. 3 the number average of the degree of polymerisation is plotted against time. In the initial stage of the reaction the DP decreases fast due to degradation of amorphous parts. Cleavage occurs statistically along the polymer chain, which explains the strong decrease. After 3 h the level-off DP is reached. Longer reaction time lowers the DP very slightly because hydrolytic attack can only take place at the surface or ends of the cellulose crystallites.

Thermal properties. Silylation increases thermal stability, organophilicity and thermoplastic character of cellulose. The thermal properties of silylated celluloses were determined with DSC and TG. From Table 1 it can be seen that the glass transition temperature of high molecular weight samples is independent of the molar mass since linters and Avicel PH-101 have comparable glass transition temperatures of 187 and 185 °C, respectively. The temperatures range from 183 to 193 °C.

The glass transition temperatures of trimethylsilyl celluloses with degrees of polymerisation from 27 to 39 are in a range of 167–178 °C which is significantly lower. Glass transition temperature depends on the molar mass for oligomeric materials which is shown for the trimethylsilyl celluloses in Fig. 4. Hence hydrocelluloses obtained from LAT celluloses are oligomers where properties are still depending on molar mass. Deviations from the expected curve are probably due to differences in the degree of substitution. Larger DS values seem to increase the glass transition temperatures.

4. Conclusions

Liquid ammonia treatment of cellulose has been shown to activate cellulose for hydrolytic degradation which not only results in a fast decrease of molar mass to the level-off DP but also in a strong increase of reaction rate. The LODP of LAT cellulose is reached after 3 h. Since amorphous parts of cellulose react preferentially the amorphous part must have been increased by treatment with liquid ammonia. This activation remains even after removal of ammonia by washing with water. The glass transition temperatures of trimethylsilyl celluloses with low molecular weight depend on molecular mass because the chain ends generate additional free volume. Hydrocelluloses obtained by the method described have lower polydispersity and lower molecular weight than those from non-activated cellulose thus allowing to extent the study of structure property relations to the oligomeric regime.

Acknowledgements

We are indebted to the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm ‘Cellulose und Cellulosederivate—molekulares und supramolekulares Strukturdesign’) for financial support.

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