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Studies on Non-natural Deoxyammonium Cellulose

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Summary: Ammonium group containing cellulose derivatives are prepared from homogeneously synthesized cellulose *p*-toluenesulfonic acid esters (tosyl cellulose) by conversion with sodium azide and subsequent reduction of the azido moiety applying $NaBH_4/CoBr_2$/2,2′-bipyridine as reagent. Regarding the tosylation, cellulose samples of different degree of polymerization and hemicellulose content possess a different reactivity. The deoxyamino cellulose is water soluble in the protonated state. Elemental analysis, FTIR- and NMR spectroscopy were carried out to analyze the degree of substitution and functionalization pattern. It was also studied to synthesize deoxyazido celluloses without isolation of the tosyl cellulose. However, a predominant formation of deoxychloro moieties occurs.

Keywords: Biopolymers; cellulose; deoxyammonium cellulose; deoxyazido cellulose; NMR

Introduction

Cationic cellulose derivatives are rather scarcely studied. Introduction of cationic moieties in cellulose (pulp) is applied in order to improve its paper-making properties.[1,2] The cellulose is allowed to react with pre-built cationic reagents such as glycidyltrimethylammonium chloride, diallyldimethylammonium chloride, and derivatives of acrylic acid by etherification and grafting reactions yielding products of low degree of substitution (DS).[1,3,4] At higher DS ammonium groups may impart water solubility and bioactivity to polysaccharides.[5]

Amino groups can be attached to the anhydroglucose unit by nucleophilic displacement (S_N) reactions of cellulose *p*-toluenesulfonic acid esters (tosyl cellulose). Tosyl cellulose is simply accessible and a valuable starting material for S_N reactions.[6] The conversion of tosyl cellulose with triethylamine, *N*,*N*-dimethyl-1,3-diaminopropane, and 2,4,6-tris(*N*,*N*-dimethylaminomethyl)phenol leads to cationic cellulose derivatives that are water soluble already at low DS of 0.2 to 0.5, independent on the pH of the solution.[7] The regioselectivity of the S_N reaction can be controlled by the conditions, in particular temperature and solvent, as demonstrated for the conversion of tosyl cellulose with butylamine and pyridine.[8] The S_N reaction of tosyl cellulose with ammonia has also been described yielding insoluble products. The amino group of the deoxyamino cellulose formed may act as nucleophile as well and hence cross-linking occurs.[9–11]

An approach for the preparation of non cross-linked deoxyamino celluloses is the introduction of deoxyazido moieties via S_N reaction of tosyl cellulose and subsequent reduction. The reduction of azido moieties with $LiAlH_4$ leads to 6-deoxy-6-azido cellulose of low degree of polymerization

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(DP).[11] It was found that remaining tosyl groups were completely removed by the reduction as well.

The aim of the work is to synthesize deoxyammonium celluloses with high DP. Different types of cellulose (chemical pulps) were evaluated as starting material for tosyl cellulose and subsequently converted to deoxyammonium celluloses. For reduction, a method described for azido moieties in steroids using $NaBH_4$ activated with a cobalt-2,2′-bipyridine complex was applied.[12] In addition, an *in situ* synthesis, i.e., tosylation and S_N reaction without isolation of the tosyl cellulose was studied.

Experimental Part

Materials and Methods

Avicel® **1** and spruce sulfite pulp **4** were purchased from Fluka. Wood pulps **2**, **3**, and **5** were kindly provided by Wolff Cellulosics. The chemicals were purchased from Fluka and Acros. The cellulose samples were dried for 12 h in vacuum over KOH at 105 °C and LiCl at 150 °C. *N*,*N*-Dimethylacetamide (DMA) and *N*,*N*-dimethylformamide (DMF) were distilled over CaH_2 prior to use.

Cellulose *p*-toluenesulfonic acid esters (tosyl cellulose) were synthesized according to [6] and are listed in Table 2.

Deoxyazido Cellulose

To a solution of 85.0 g tosyl cellulose **6e** (0.299 mol, DS_{Tos} 0.79) in 1.8 l DMF 97.3 g (1.50 mol, 5 mol/mol anhydroglucose unit, AGU) NaN_3 and 200 ml DMF are added. The highly viscous mixture is heated to 100 °C and stirred for 24 h. After cooling down to room temperature, the mixture is poured into 7 l ice water. The precipitate is filtered off, washed 5 times with 2 l water and dried in vacuum at 60 °C.

Yield: 46.0 g (81%, sample **7e**).

DS_{Az} 0.87, DS_{Tos} 0.03.

Elemental analysis: 39.58% C, 5.19% H, 19.16% N, 0.59% S.

The polymer is soluble in dimethyl sulfoxide, DMF and DMA.

Synthesis of Deoxyazido Cellulose without Isolation of the Cellulose *p*-toluenesulfonic Acid Ester

25.0 g (0.1543 mol) Cellulose **4** and 1 l DMA are stirred for 2 h at 120 °C under exclusion of moisture. After addition of 55.0 g LiCl, the mixture is stirred without further heating overnight until dissolution of the polymer occurs. A solution of 73.1 ml (0.525 mol, 3.40 mol/mol AGU) triethylamine in 73.0 ml DMA is added dropwise within 50 min followed by a solution of 50.0 g (0.262 mol, 1.70 mol/mol AGU) tosyl chloride in 100 ml DMA within 45 min. The mixture is stirred for 6 h at room temperature. After addition of 50.2 g (0.772 mol) NaN_3, the temperature is raised to 100 °C and stirring is continued for 16 h. After cooling down to room temperature, the reaction mixture is poured into 5 l ice water. The precipitate is filtered off, washed 5 times with 1.5 l water, 6 times with 0.5 l ethanol and dried in vacuum at 60 °C.

Yield: 24.4 g (sample **8d**).

Elemental analysis: 40.28% C, 5.64% H, 6.63% N, 0.64% S, 7.66% Cl.

DS_{Az} 0.29, DS_{Tos} 0.04, DS_{Cl} 0.39.

FTIR (KBr): 3439 (νOH), 2890 (νCH_3), 2114 (νN_3), 1433, 1298 (δCH), 1067 cm^{-1} (νC-O-C_{AGU}).

The polymer is soluble in DMA and DMF.

Deoxyammonium Cellulose

40.0 g Deoxyazido cellulose **7e** (0.211 mol, DS_{Az} 0.87, DS_{Tos} 0.03) is dissolved in 500 ml dry DMF under argon. A solution of 8.03 g (0.0367 mol, 0.2 mol/mol N_3 group) $CoBr_2$ and 17.2 g (0.110 mol, 0.6 mol/mol N_3 group) 2,2′-bipyridine in 50 ml dry DMF is added to the solution of **7e**. 13.9 g (0.367 mol, 2 mol/mol N_3 group) $NaBH_4$ are added under vigorous stirring and cooling with ice. The reaction mixture forms a hard foam that was crushed with a spatula, subsequently diluted with 150 ml dry DMF and

stirred for 1 h. Again, 13.9 g $NaBH_4$ are added and stirring is continued for 1.5 h until a sample becomes soluble in diluted HCl. 200 ml HCl (20%, v/v) are added dropwise under cooling with ice until the gas formation stopped and the colour turned from blue to pink. The mixture is diluted with 100 ml water and stirred for 1 h. About 1 l DMF/water mixture is distilled off under vacuum and the viscous solution is poured into 1 l acetone. After filtration and drying, the polymer is purified by reprecipitation from water into acetone. The product is finally washed with acetone and dried in vacuum at 60 °C.

Yield: 29.7 g (73%, sample **9b**)

Elemental analysis: 36.63% C, 6.66% H, 5.47% N, 0.52% S, 13.97% Cl.

DS_N 0.76, DS_{Tos} 0.03.

FTIR (KBr): 3422 (νOH), 2930 (νCH), 1372 (δCH), 1054 cm^{-1} (νC-O-C_{AGU}).

The polymer dissolves in water.

Results and Discussion

Different cellulose types are included in the studies in order to investigate the influence of both the degree of polymerization (DP) and hemicellulose content on the degree of substitution (DS) of the cellulose derivatives prepared and to vary the DP of the products (Table 1). Deoxyammonium cellulose products are accessible via tosylation of the biopolymer, nucleophilic displacement (S_N) of the *p*-toluenesulfonic acid ester (tosylate) moiety by azide and subsequent reduction as summarized in Figure 1.

p-Toluenesulfonic acid Esters of Cellulose

Although it is well known that the homogeneous conversion of cellulose with tosyl chloride in *N*,*N*-dimethylacetamide (DMA)/LiCl leads to tosyl cellulose with varying DS depending on the molar ratio reagent to cellulose[6], an influence of the cellulose starting material on the DS may appear. Avicel **1** can be converted to a tosyl cellulose with a DS of tosyl groups (DS_{Tos}) of 0.65 (sample **6a**) applying 1 mol tosyl chloride (TosCl) and 2 mol triethylamine (TEA) per mol AGU within 5 h at 8 °C (Table 2). In case of wood pulp **2** a molar ratio of 1.4 mol TosCl and 2.8 mol TEA per mol anhydroglucose unit (AGU) and a reaction time of 24 h at 8 °C are needed to get a DS_{Tos} 0.62 (**6b**). Further increase of the molar ratio leads to products with DS_{Tos} 0.98 (1.7 mol TosCl per mol AGU, sample **6c**) and 1.47 (4 mol TosCl per mol AGU, sample **6d**). The chlorine content is in the range from 0.55 to 0.70% corresponding to a DS of deoxychloro groups (DS_{Cl}) of 0.05, thus the S_N reaction with chloride ions is negligible. Cellulose **3** is less reactive than **2**. Applying 1.7 mol TosCl per mol repeating unit, a sample with DS_{Tos} 0.79 (**6e**) is obtained.

The FTIR spectra of the samples **6a–6e** show the typical signals of the tosyl moiety at 3068 (νCH_{aromat}), 1598 (νC=C), 1360 ($\nu_{as}SO_2$), 1176 (ν_sSO_2), and 815 cm^{-1} (δ=CH).

Synthesis of Deoxyazido Celluloses

The introduction of deoxyazido moieties in cellulose is achieved by conversion of tosyl cellulose dissolved in *N*,*N*-dimethyl-

Table 1.
Cellulose Samples Used.

Cellulose	No.	Degree of polymerization[a]	Hemicellulose content (%)[b]
Avicel	**1**	280	0
Wood pulp	**2**	600	9.0
Wood pulp	**3**	1377	6.9
Spruce sulfite pulp	**4**	590	4.6
Wood pulp	**5**	2054	12.3

[a] Determined by capillary viscometry in cupriethylenediamine solution.[13]
[b] Determined by means of HPLC after complete depolymerization with $HClO_4$.[14]

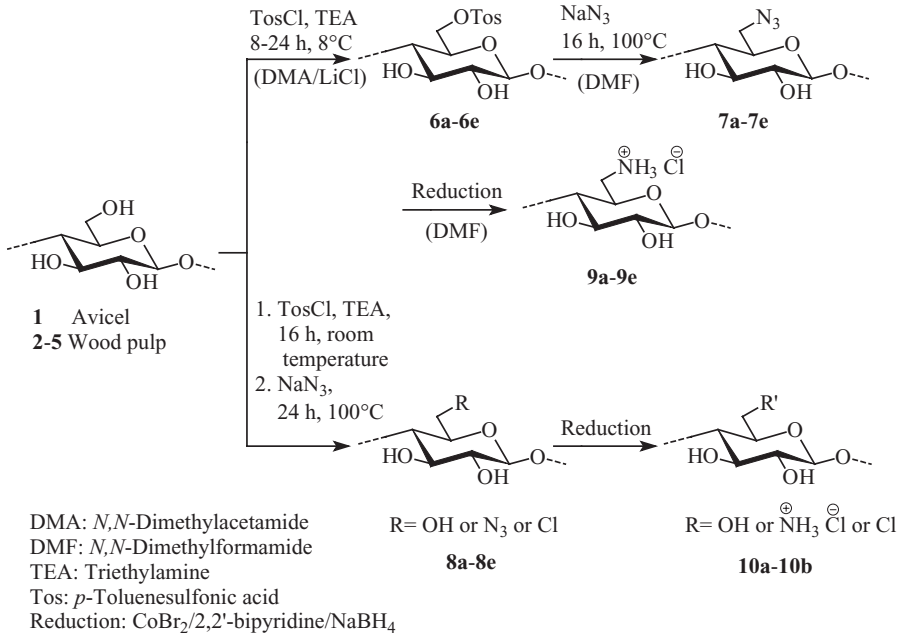

Figure 1.
Synthesis of deoxyammonium celluloses via *p*-toluenesulfonic acid ester formation, nucleophilic displacement with azide ions, and reduction.

formamide (DMF) with 5 mol sodium azide per mol repeating unit under exclusion of moisture. Depending on the DP, up to 150 g tosyl cellulose were used under lab-scale conditions in one batch. Starting from tosyl cellulose with DS_{Tos} ranging from 0.65 to 0.98 an almost complete S_N reaction occurred. The DS of deoxyazido groups (DS_{Az}) of sample **7a** (DS_{Az} 0.64) is comparable with the initial DS_{Tos} of 0.65 (sample **6a**, Table 3). For sample **6b** and **6c** DS_{Az} values of 0.55 (**7b**) and 0.88 (**7c**) were achieved. The tosyl cellulose **6e** gives a product with a DS_{Az} of 0.87 (**7e**). Tosylate groups at positions 2 and 3 can be substituted as well. Tosyl cellulose **6d** (DS_{Tos} 1.47) yields a DS_{Az} of 1.25 (**7d**).

The FTIR spectra of deoxyazido celluloses **7a**–**7d** show the characteristic absorption band of the azide moiety at 2102 cm^{-1}. Moreover, further signals are found in the spectrum of sample **7d** (DS_{Az} 1.25,

Table 2.
Conditions and Results for the Homogeneous Preparation of Cellulose *p*-Toluenesulfonic Acid Esters in *N,N*-Dimethylacetamide/LiCl.

Sample	Conditions			No.	Product			
	Molar ratio[a]	Time (h)	Temperature (°C)		Content (%)		DS_{Tos}[b]	DS_{Cl}[b]
					S	Cl		
Avicel **1**	1:1:2	5	8	**6a**	7.91	0.57	0.65	n.d.
Wood pulp **2**	1:1.4:2.8	24	8	**6b**	7.72	0.70	0.62	0.05
Wood pulp **2**	1:1.7:3.4	24	8	**6c**	9.98	0.55	0.98	0.05
Wood pulp **2**	1:4:8	24	8	**6d**	12.10	0.57	1.47	0.06
Wood pulp **3**	1:1.7:3.4	24	8	**6e**	8.98	n.d.	0.79	n.d.

[a] Molar ratio anhydroglucose unit: *p*-toluenesulfonic acid chloride:triethylamine.
[b] Degree of substitution of *p*-toluenesulfonic acid ester groups (DS_{Tos}) and deoxychloro groups (DS_{Cl}).

Table 3.
Results of the Conversion of Cellulose *p*-Toluenesulfonic Acid Esters with Sodium Azide in *N,N*-dimethylformamide (5 mol/mol Anhydroglucose unit) for 24 h at 100 °C.

Cellulose *p*-toluenesulfonic acid ester			Product						
			No.	Content (%)			DS_{Az}[a]	DS_{Tos}[a]	DS_{Cl}[a]
No.	DS_{Tos}[a]	DS_{Cl}[a]		N	S	Cl			
6a	0.65	0.04	**7a**	14.52	0.86	–	0.64	0.05	–
6b	0.62	0.05	**7b**	12.47	0.85	0.27	0.55	0.05	0.01
6c	0.98	0.05	**7c**	19.40	0.62	0.09	0.88	0.04	–
6d	1.47	0.06	**7d**	23.09	3.05	0.22	1.25	0.22	0.01
6e	0.79	n.d.	**7e**	19.16	0.59	–	0.87	0.03	–

[a] Degree of substitution of *p*-toluenesulfonic acid ester groups (DS_{Tos}), of deoxyazido groups (DS_{Az}), of deoxychloro groups (DS_{Cl}).

DS_{Tos} 0.22) at 1598 cm^{-1} ($\nu C{=}C_{Aromat}$), 1359 cm^{-1} (δCH_3, $\nu_{as}SO_2$), 1175 cm^{-1} ($\nu_s SO_2$), and 829 cm^{-1} ($\delta{=}CH_{Aromat}$), which are caused by the tosyl moiety.

The HSQC-DEPT NMR spectrum of **7d** (DS_{Az} 1.25, DS_{Tos} 0.22, DS_{Cl} 0.01, Figure 2) reveals the signals of the polymer backbone between 51.3 and 104.5 ppm. At 51.3 ppm the peak of the CH_2N_3 moiety appears.

A comparable weak signal at 60.6 ppm is characteristic for the non-functionalized position 6 of the AGU. The peaks at 63.9 and 66.5 ppm may be assigned to a deoxyazido group located at the secondary positions.

However, the methylene group, which should appear at about 69 ppm, can not be clearly assigned in the HSQC-DEPT NMR

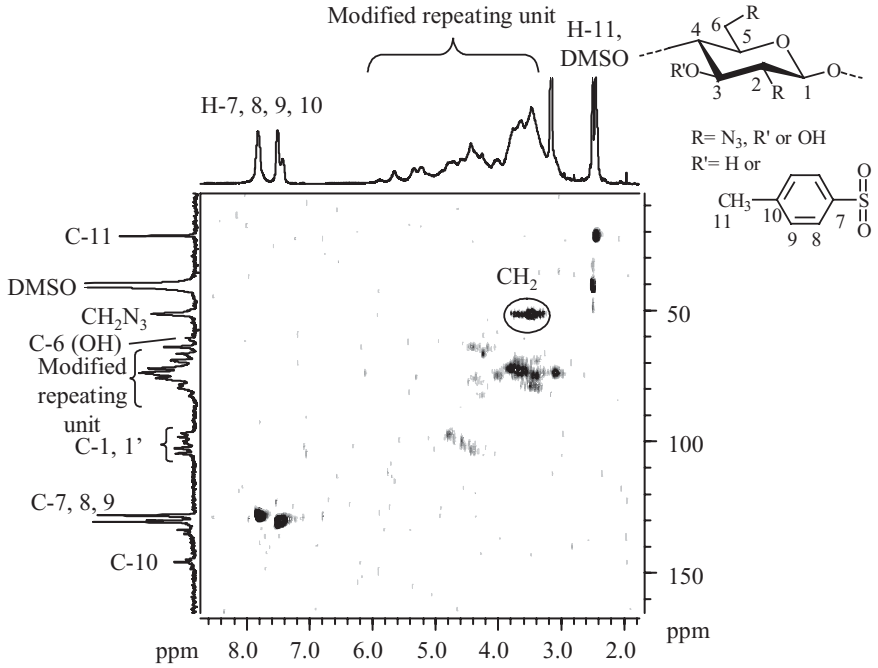

Figure 2.
HSQC-DEPT NMR spectrum of deoxyazido cellulose **7d** (degree of substitution, DS, of deoxyazido groups 1.25, DS of *p*-toluenesulfonic acid ester, tosyl, groups 0.22, DS of deoxychloro groups 0.01) recorded in dimethyl sulfoxide-d_6 (DMSO-d_6).

spectrum. The resonances of positions 2–5 can be seen between 72.1 and 79.6 ppm. C-1 signals are found between 96.7 and 104.5 ppm indicating a different functionalization of position 2. The signals between 128.0 and 145.9 ppm are attributed to the aromatic carbon atoms of the tosyl moiety. The methyl group is detected at 21.5 ppm. The ^{1}H NMR spectrum shows many overlapped signals of the modified AGU between 3 and 6 ppm. Peaks between 5 and 6 ppm are caused by OH groups and do not lead to cross-peaks. In addition, the resonances of the tosyl moiety appear at 2.45 ppm (H-11) and 7.3–8.0 ppm (H-8, 9, 10).

In situ Conversion of Cellulose Tosylate to Deoxyazido Celluloses

The solution of the cellulose in DMA/LiCl is allowed to react with TosCl and TEA for 6 h at room temperature followed by the conversion with sodium azide for 16 h at 100 °C. The conversion of cellulose **3** with 1 mol TosCl/TEA per mol repeating unit and subsequently with 2 mol NaN_3 is not sufficient (Table 4, sample **8b**, DS_{Az} 0.02). Increasing the molar ratio AGU:TosCl:TEA:NaN_3 to 1:1.7:3.4:5 yields sample **8c** with DS_{Az} 0.23. However, a incorporation of deoxychloro moieties occurs (DS_{Cl} 0.43). Avicel **1** and spruce sulfite pulp **4** lead to products with DS_{Az} 0.28 and 0.29 (samples **8a** and **8d**). The high content of Cl^- in the reaction mixture causes a predominant formation of deoxychloro moieties.

Cellulose **5** shows a lower tendency to form deoxyazido groups (DS_{Az} 0.11, sample **8e**) but yields the highest DS_{Cl} of 0.44.

The ^{13}C NMR spectrum of sample **8a** shows the expected signals (Figure 3). The signals of the AGU appear in the range between 60 and 79 ppm (C-2 to C-6) as well as at 99.3–104.1 ppm (C-1, C-1′). The resonance of the 6-deoxy-6-azido group is detected at 50.6 ppm, while the 6-deoxy-6-chloro group leads to a signal at 44.1 ppm. In addition, weak peaks corresponding to the tosyl substituents are detected at 20.8 ppm (C-11) and at 127.4–129.2 ppm (C-7 to C-10). The signal splitting of position 1 indicates a different functionalization of position 2, i.e., a tosyl-, a deoxyazido-, a deoxychloro moiety, and a hydroxyl group may be present. A weak signal at 68.3 ppm corresponds to the tosylated position 6 of the repeating unit.

Reduction of the Deoxyazido Celluloses

The reduction of the azido group is the crucial step in the synthesis of deoxyamino celluloses. It requires powerful reducing agents like hydrogen in combination with catalysts or $LiAlH_4$. An interesting reducing agent known from steroid chemistry is $NaBH_4$ activated with cobalt(II)tris(2,2′-dipyridyl) bromide in dry DMF.[12] The catalyst is freshly prepared by dissolving

Table 4.
In situ Synthesis of Deoxyazido Celluloses Reacting Cellulose in *N,N*-dimethylacetamide/LiCl with *p*-toluenesulfonic Acid Chloride and Triethylamine for 6 h at room Temperature and with Sodium azide for 16 h at 100 °C.

Sample	Molar ratio[a]	Product						
		No.	Content (%)			DS_{Az}[b]	DS_{Tos}[b]	DS_{Cl}[b]
			N	S	Cl			
Avicel **1**	1:1.7:3.4:5	**8a**	6.44	0.61	7.83	0.28	0.04	0.40
Wood pulp **3**	1:1:1:2	**8b**	0.50	0.07	2.18	0.02	0.07	0.10
Wood pulp **3**	1:1.7:3.4:5	**8c**	5.45	0.51	8.44	0.23	0.03	0.43
Wood pulp **4**	1:1.7:3.4:5	**8d**	6.63	0.64	7.66	0.29	0.04	0.39
Wood pulp **5**	1:1.7:3.4:5	**8e**	2.60	0.90	8.65	0.11	0.05	0.44

[a] Anhydroglucose unit:*p*-toluenesulfonic acid chloride:triethylamine:sodium azide.
[b] Degree of substitution of deoxyazido groups (DS_{Az}), of *p*-toluenesulfonic acid ester groups (DS_{Tos}), of deoxychloro groups (DS_{Cl}).

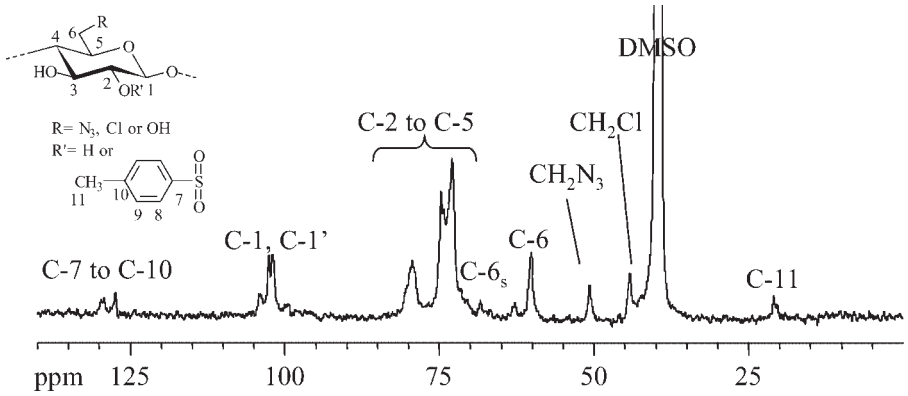

Figure 3.
^{13}C NMR spectrum of deoxyazido cellulose **8a** (degree of substitution of deoxyazido groups 0.28, of *p*-toluenesulfonic acid ester, tosyl, groups 0.04, deoxychloro groups 0.40) recorded in dimethyl sulfoxide-d_6. The index s means substituted by tosyl groups.

$CoBr_2$ in dry DMF, admixture of 2,2′-bipyridine and adding this mixture to the dissolved deoxyazido cellulose followed by $NaBH_4$. The reduction is accompanied with the formation of nitrogen that forms a hard foam with the polymer.

Hydrochloric acid is used to destroy the excess of $NaHB_4$ and to convert the amine into the water soluble ammonium salt. This reduction method could be applied for deoxyazido celluloses with a wide variety of DS_{Az} values (DS_{Az} 0.11–1.25, Table 5). The DS_N corresponds with the DS_{Az} of the samples **9c**–**9d**. A slight deviation of 0.12 to 0.16 DS units is observed for samples **9a**, **9b**, and **9e**. The reduction of the CH_2N_3 moieties is not influenced by other functional groups in the molecule, e.g., deoxychloro moieties of the samples **8d** and **8e** with DS_{Cl} of 0.39 and 0.44. Reduction afforded deoxyammonium celluloses **10a** and **10b** with DS_N 0.31 and 0.23 and DS_{Cl} 0.36 and 0.28. Deviations, e.g., DS_N of **10b** is higher than the DS_{Az} of **8e**, may be caused by the DS calculation from the elemental analysis. Chlorine is present in two substituents, which may cause significant errors in the DS calculation.

NMR spectroscopy proves the generation of the deoxyammonium groups. The ^{13}C NMR spectrum of sample **9a** (DS_N 0.49) shows the typical signals of the cellulose backbone of C–1 at 102.9 ppm and of C-6 bearing the hydroxyl group at 60.6 ppm (Figure 4a). The carbon atoms of position 2 to 5 are detected in the range

Table 5.
Reduction of Deoxyazido Celluloses with $CoBr_2$/2,2′-Bipyridine/$NaBH_4$ in *N*,*N*-dimethylformamide.

Deoxyazido cellulose				Deoxyammonium cellulose			
No.	DS_{Az}[a]	DS_{Tos}[a]	DS_{Cl}[a]	No.	DS_N[a]	DS_{Tos}[a]	DS_{Cl}[a]
7a	0.64	0.05	–	**9a**	0.49	–	–
7b	0.55	0.05	0.01	**9c**	0.51	0.03	–
7c	0.88	0.04	–	**9d**	0.79	0.02	–
7d	1.25	0.22	0.01	**9e**	0.99	0.14	–
7e	0.87	0.03	–	**9b**	0.76	–	–
8d	0.29	0.04	0.39	**10a**	0.31	0.02	0.36
8e	0.11	0.05	0.44	**10b**	0.23	0.06	0.28

[a] Degree of substitution of deoxyazido groups (DS_{Az}), of *p*-toluenesulfonic acid ester groups (DS_{Tos}), of deoxychloro groups (DS_{Cl}), of deoxyammonium groups (DS_N).

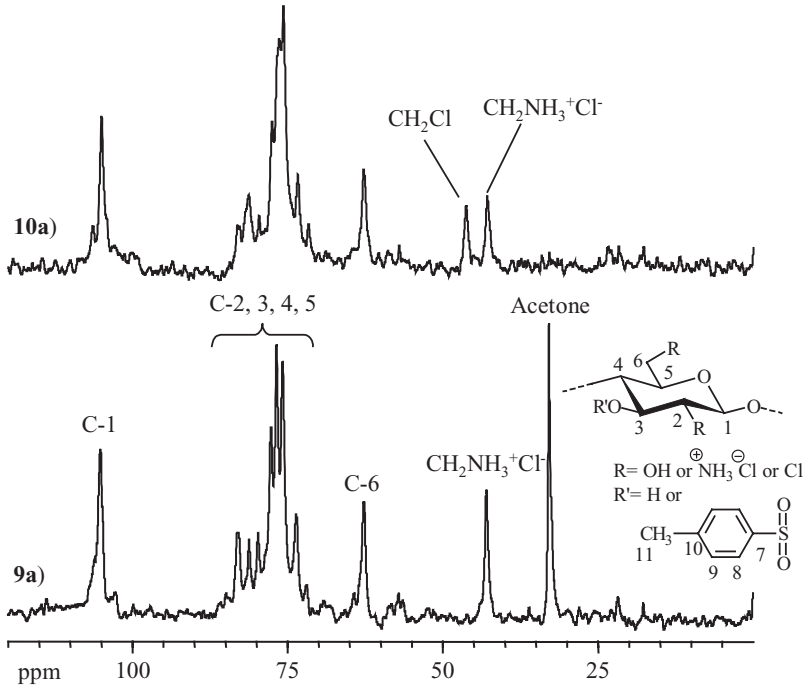

Figure 4.
^{13}C NMR spectra of deoxyammonium cellulose samples **9a** (degree of substitution of deoxyammonium groups, DS_N 0.49) and **10a** (DS_N 0.31, DS of deoxychloro groups 0.36).

between 69.8 to 80.7 ppm. In addition, the peak of the 6-deoxy-6-ammonium moiety appears at 40.8 ppm. However, some acetone remained in the polymer leading to the signal at 30.8 ppm.

The peak assignment of the ^{13}C NMR spectrum of sample **10a** (DS_N 0.31, DS_{Tos} 0.02, DS_{Cl} 0.36) is comparable: 105 ppm (C-1), 71.6–81.2 ppm (C-2-5), 62.7 ppm (C-6, Figure 4b).

The peak of the 6-deoxy-6-ammonium moiety is found at 42.8 ppm. In addition, the deoxychloro group is clearly detected at 46.2 ppm.

Conclusion

The deoxyamino cellulose derivatives are interesting non-natural biopolymer-based polyelectrolytes. To obtain products with a defined structure, a stepwise procedure should be carried out (i.e., the nucleophilic displacement reaction should be carried out with an isolated cellulose *p*–toluenesulfonic acid ester). The *in situ* synthesis yields products with undesired high chlorine content and the amount of deoxyamino moieties that can be introduced is comparable low. The samples are non-natural chitosan-like polyelectrolytes and are included in studies of the biological activity, flocculation behavior, polyelectrolyte complex formation, and rheology. It is of interest to compare the properties with naturally occurring chitin/chitosan.

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