

Synthesis of soluble cellulose tosylates in an eco-friendly medium†

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The tosylation of cellulose in the eco-friendly solvent NaOH–urea in the presence of the nonionic surfactant polyethylene glycol alkyl-(C₁₁–C₁₅) ether (Ibmbentin) yields well soluble *p*-toluenesulfonic acid esters of cellulose (tosyl cellulose). The influence of reaction time, temperature, and molar ratio on the degree of substitution (DS) was studied. The products were characterized by means of NMR- and FTIR-spectroscopy, elemental analysis and size exclusion chromatography. Moreover, 6-deoxy-6-azido-, 6-deoxy-6-(ω -aminoethyl)amino-, and 6-deoxy-6-thiosulfate cellulose could be prepared by nucleophilic displacement (S_N) of the tosyl groups.

Introduction

One of the major limitations for new strategies towards applying the most abundant natural resource cellulose in sustainable technologies is the lack of environmentally friendly and efficient paths towards processing of this natural material. Due to its insolubility in water and most of the common organic liquids, special solvents were developed to dissolve cellulose both for shaping and homogeneous chemical modification of the biopolymer.¹ The most important solvents NaOH–CS₂ (viscose process) and *N*-methylmorpholine *N*-oxide monohydrate (Lyocel process) have serious drawbacks concerning the chemical stability, environmental impact and difficult recycling. Non-aqueous solvents like *N,N*-dimethylacetamide–lithium chloride (DMA–LiCl) and ionic liquids show the potential of homogeneous cellulose modification in lab scale but these compounds seem improper for large scale processing. Thus, new aqueous solvents were studied to combine sustainability with a low environmental impact. But in the case of homogeneous cellulose chemistry problems arise if reagents or the reaction products are highly hydrophobic, for example if silylation, esterification or tosylation reactions are carried out. Insufficient reactivity is observed due to phase separation. Thus, new approaches need to be studied to overcome this problem. As a proof of concept the tosylation of cellulose in an aqueous solvent was investigated to demonstrate that such a concept is reasonable and can lead to the desired combination

of exploiting a renewable material with an environmentally friendly technique.

The *p*-toluenesulfonic acid ester of cellulose (tosyl cellulose) is one of the most promising derivatives for the creation of new polymeric materials by nucleophilic displacement (S_N) reactions and thereby it can open up new paths for the utilization of cellulose. Tosyl cellulose can be transformed by S_N reactions into a broad variety of tailored 6-deoxy-cellulose derivatives with new properties not accessible yet, especially 6-deoxy-aminocelluloses^{2–5} and 6-deoxy-6-azidocelluloses, a precursor for Click chemistry with the polysaccharide.⁶ Nevertheless, it is known that only structurally uniform tosyl celluloses with a proper solubility can be exploited for a subsequent conversion.^{7,8} To achieve a uniform structure, tosylation of highly activated cellulose is essential. Therefore, state of the art is the homogeneous tosylation of cellulose dissolved in *N,N*-dimethylacetamide (DMA)–LiCl with *p*-toluenesulfonyl chloride in the presence of triethyl amine as a base, resulting in products soluble in a broad variety of solvents depending on the total degree of substitution, DS.^{7,9} Applying well soluble tosyl cellulose, the introduction of a multitude of amines, halides, heterocycles, and azide is feasible. Despite its usefulness, tosylation of cellulose has not yet gained importance in technical cellulose chemistry. The major obstacle is the synthesis path described, which involves time- and energy-consuming dissolution steps, the use of expensive chemicals and the application of an amine as a base, which might tend to side reactions and yield hardly removable by-products. Thus, there is a strong need for a new, efficient, and easy synthesis path preferably in an aqueous solvent. A useful medium for the synthesis may be the conversion of cellulose in NaOH containing solvents. Applying aqueous sodium hydroxide as a medium for the tosylation was the first attempt to get this cellulose derivative.¹⁰ Very recently, this synthesis path was reinvestigated in

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the media NaOH-H₂O and NaCl-H₂O;¹¹ however, the tosyl cellulose obtained does not possess the required product quality obviously due to insufficient activation of the polymer prior to the reaction and limited solubility of the tosyl chloride in the aqueous system. In the frame of our studies on the homogeneous chemistry with cellulose, the aqueous solvent NaOH-urea was included.¹² In this paper the synthesis of tosyl cellulose applying this solvent was studied. Although it is an aqueous solvent as well, it turned out that tosyl cellulose can be prepared efficiently in good yield and high purity. Moreover, the tosyl cellulose samples obtained are well soluble. Due to the fact that aqueous NaOH-urea is considered to be an environmentally friendly medium, this synthesis path may open a broader use of this important cellulose derivative and can thereby significantly broaden the commercial application of the most important renewable resource cellulose.

Experimental

Materials

Cellulose (Avicel®, degree of polymerization, DP_w = 330) was dried at 100 °C for 3 h under vacuum before use. All other reagents were of analytical grade and used without pretreatment.

Measurements

NMR spectra were acquired at 25 °C in deuterated dimethyl-sulfoxide (DMSO-d₆) or D₂O using Bruker Avance 250 MHz and 400 MHz spectrometers. ¹³C NMR spectra were recorded with at least 10 000 scans and a sample concentration of 50 mg mL⁻¹. FTIR spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer using the KBr pellet technique. A CHNS 932 Analyzer (Leco) was used for elemental analyses. The halogen content was determined by titration after combustion.¹³ Size exclusion chromatography (SEC) was measured in DMSO + 0.5% LiBr with a JASCO SEC system (degasser DG 980-50, pump PU 980, refractive index detector 930, columns PSS NOVEMA 3000 Å and PSS NOVEMA 300 Å) at 65 °C with an eluent flow rate of 0.5 mL min⁻¹. Pullulan standards (*M* < 104 g mol⁻¹) were used for calibration.

Synthesis

Dissolution of cellulose in an NaOH-urea aqueous system. 1.75 g (43.8 mmol) NaOH, 3 g (50 mmol) urea and 20 mL distilled water (7:12:81 by weight) were mixed in a 250 mL beaker and stirred to get a clear solution. 1 g (6.2 mmol) of cellulose was added with stirring. The mixture was stored in the refrigerator for one hour. After being pre-cooled to -12 °C, the mixture was stirred vigorously at ambient temperature to obtain the transparent cellulose solution.

Tosylation of cellulose. 7.2 g (37.8 mmol) *p*-toluenesulfonyl chloride (3 mol per mol AGU) and 4 mL polyethylene glycol alkyl-(C₁₁-C₁₅) ether were added to the cellulose solution (2 g, 12.3 mmol cellulose). After 15 min a modification of the texture of the reaction mixture occurred. The mixture was

stirred vigorously at 25 °C for 5 h and precipitated into 500 mL 80% (v/v) ethanol. The product was separated by filtration, washed three times with 300 mL ethanol, and dried under vacuum at 60 °C.

Yield (4): 2.73 g (95.5%).

DS_{tos} = 0.43.

Elemental analysis: C 47.06%, H 5.47%, N 0%, S 6.00%, Cl 0%.

FT-IR (KBr, cm⁻¹): 1600 (νC=C_{aromatic}), 1360 (ν_{as}SO₂), 1180 (ν_sSO₂), 816 (νS-O-C).

¹³C NMR (250 MHz, DMSO-d₆, ppm): 145.6, 132.5, 130.7, 128.1 (C_{aromatic}), 103.3 (C-1), 80.7–73.5 (C-4, C-2, C-3, C-5), 68.8 (C-6_{tosylated}), 60.7 (C-6_{non-substituted}), 21.6 (CH₃).

Synthesis of 6-deoxy-6-(ω-aminoethyl)amino cellulose.¹⁴ To 0.5 g (1.6 mmol, DS_{tos} = 0.95) tosyl cellulose 7 dissolved in 10 mL DMSO, 2.7 mL (40.5 mmol, 25 mol per mol modified AGU) ethylene diamine were added at 100 °C. The mixture was allowed to react for 6 h at 100 °C under stirring. After cooling to room temperature, the product was precipitated in 300 mL acetone, washed three times with 150 mL acetone and two times with 150 mL ethanol and dried at 60 °C under vacuum.

Yield: 0.21 g (67.8%).

DS_{amine} = 0.63, DS_{tos} = 0.07.

Elemental analysis: C 41.49%, H 7.00%, N 8.86%, S 1.11%, Cl 0%.

¹³C NMR (400 MHz, D₂O, ppm): 147.7, 130.9, 128.2 (C_{aromatic}), 102.6 (C-1), 99.5 (C-1'), 81.4–73.3 (C-4, C-2, C-3, C-5), 68.5 (C-6_{tosylated}), 60.4 (C-6_{non-substituted}), 49.6 (C-6_{amine}), 39.9 (CH₂(amine)), 21.3 (CH₃(tosyl)).

Synthesis of 6-deoxy-6-azido cellulose. To 0.5 g (1.6 mmol, DS_{tos} = 0.95) tosyl cellulose 7 dissolved in 10 mL DMF, 0.26 g (4.0 mmol) sodium azide was added and the mixture was allowed to react at 100 °C for 24 h under stirring. The product was precipitated in 300 mL ice-water, washed four times with 100 mL water, three times with 100 mL ethanol and dried at 60 °C under vacuum.

Yield: 0.23 g (79%).

DS_{azide} = 0.82, DS_{tos} = 0.05.

Elemental analysis: C 33.26%, H 4.00%, N 18.06%, S 0.88%, Cl 0%.

¹³C NMR (400 MHz, DMSO-d₆, ppm): 145.9, 130.7, 128.3 (C_{aromatic}), 103.3 (C-1), 99.9 (C-1') 80.7–72.1 (C-4, C-2, C-3, C-5), 69.0 (C-6_{tosylated}), 60.8 (C-6_{non-substituted}), 51.2 (C-6_{azide}) 21.6 (CH₃(tosyl)).

Synthesis of 6-deoxy-6-thiosulfate cellulose. To 0.5 g (1.6 mmol, DS_{tos} = 0.95) tosyl cellulose 7 dissolved in 5 mL DMSO, 1 g (6.5 mmol) Na₂S₂O₃ and 1 mL water were added. The mixture was heated to 80 °C for 20 h. After cooling to room temperature, the product was precipitated in 200 mL ethanol, washed five times with 150 mL ethanol and dried at 60 °C under vacuum.

Yield: 0.33 g (81.3%).

DS_{thiosulfate} = 0.75, DS_{tos} = 0.05.

Elemental analysis: C 6.00%, H 0.82%, N 0%, S 35.98%, Cl 0%.

^{13}C NMR (400 MHz, D_2O , ppm): 146.6, 130.4, 128.1 ($\text{C}_{\text{aromatic}}$), 102.4 (C-1), 98.4 (C-1'), 78.36–70.3 (C-4, C-2, C-3, C-5), 60.1 (C-6_{non-substituted}), 54.1 (C-2_{thiosulfate}), 36.4 (C-6_{thiosulfate}) 21.2 ($\text{CH}_3(\text{tosyl})$).

Results and discussion

Dissolution of cellulose in aqueous NaOH–urea could be carried out according to the literature.^{15,16} Thus, cellulose (4 wt%) was treated in aqueous NaOH–urea (81 wt% water, 7 wt% NaOH, 12 wt% urea) and cooled to $-12\text{ }^\circ\text{C}$ for one hour and stirred at room temperature. The cellulose solution obtained was allowed to react with tosyl chloride at $25\text{ }^\circ\text{C}$ (Fig. 1). Due to the basicity of the solvent, it is not necessary to use triethylamine or any other additional base. It is found that the tosyl celluloses obtained are completely insoluble in common solvents like dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA). The insolubility can be caused by the hydrophobic character of the tosyl chloride, the immiscibility with the NaOH–urea aqueous system and the resulting inaccessibility of the reactive hydroxyl moieties of the cellulose. However, soluble products are an important prerequisite not only for further reactions but also for a detailed analysis of the products with advanced methods like liquid state NMR spectroscopy and size exclusion chromatography (SEC). To get soluble products, surfactants were added to the reaction mixture (Table 1).

Table 1 Degree of substitution (DS) and solubility of tosyl cellulose obtained by reaction of the biopolymer dissolved in aqueous NaOH–urea in the presence of a surfactant (reaction time 5 h at $25\text{ }^\circ\text{C}$, molar ratio of anhydroglucose unit (AGU)/*p*-toluenesulfonyl chloride (TosCl) 1/5)

No.	Tenside ^a	Product			Solubility in DMSO ^b
		S (%)	C (%)	DS _s	
1	SDS	3.79	0.28	0.24	–
2	SDS/I	9.45	0.54	0.89	+
3	I	9.60	0.00	0.90	+

^a SDS: sodium dodecyl sulfate, I: polyethylene glycol alkyl-(C11–C15) ether. ^b DMSO: dimethylsulfoxide, +: soluble, –: insoluble.

It has been found that anionic surfactants, *e.g.*, sodium dodecyl sulfate (SDS), cannot improve the solubility of the products obtained by tosylation. However, the presence of non-ionic surfactants especially polyethylene glycol alkyl-(C₁₁–C₁₅) ether (Imbentin) applying comparable conditions leads to tosyl celluloses soluble in DMSO (see Fig. S1†) and a comparatively higher degree of substitution of tosyl groups (DS_{tos}). Moreover, the use of Imbentin prevents the occurrence of undesired S_N substitutions of the tosyl moieties by chloride ions. In Table 2 the reaction conditions and the DS values of the tosyl celluloses synthesized in the NaOH–urea aqueous system with tosylchloride in the presence of Imbentin are

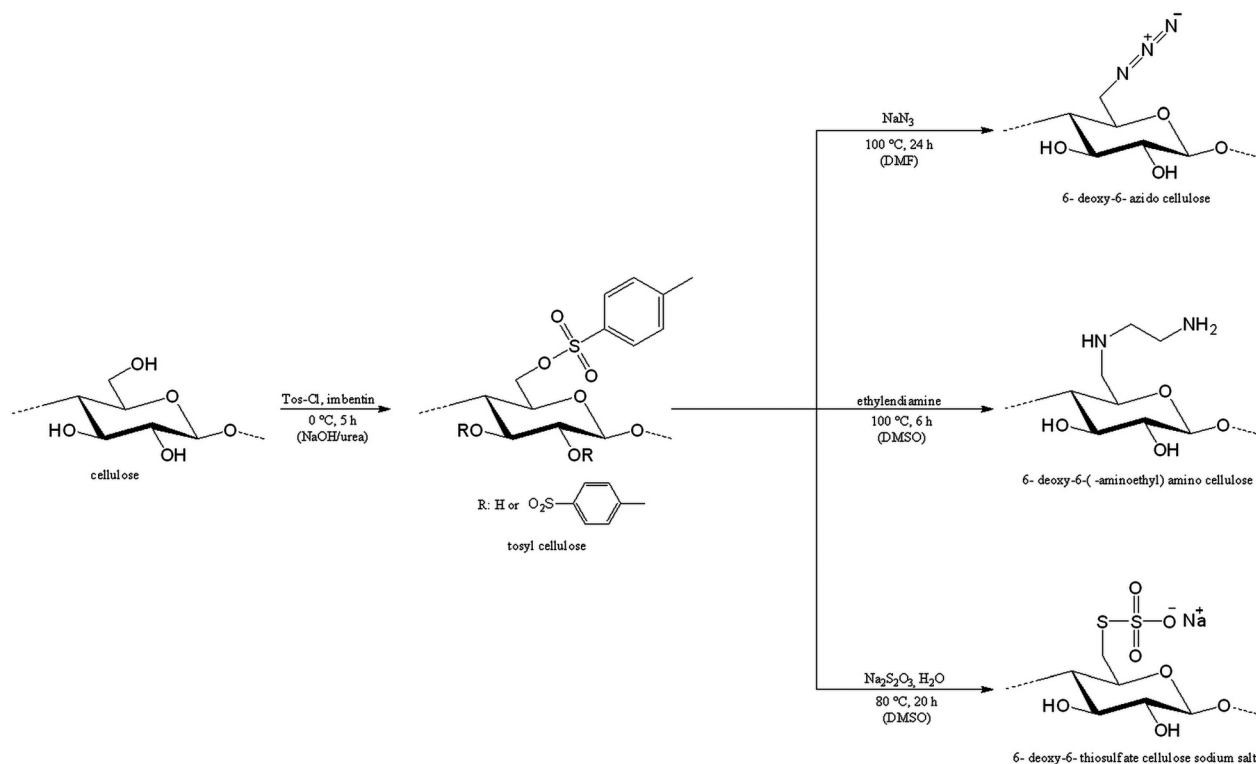


Fig. 1 Synthesis of *p*-toluenesulfonyl cellulose, 6-deoxy-6-(ω -aminoethyl)amino cellulose, 6-deoxy-6-azido cellulose, and 6-deoxy-6-thiosulfate cellulose.

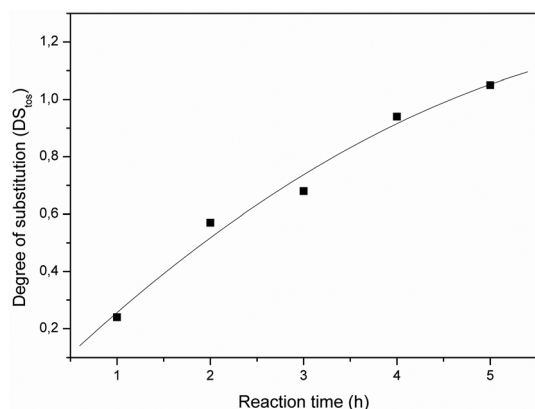
Table 2 Conditions for and results of the tosylation of cellulose dissolved in aqueous NaOH–urea (reaction time 5 h at 25 °C, surfactant: Imbentin)

No.	Reaction conditions		Product		Solubility ^c		
	Temp. (°C)	Ratio TosCl/AGU ^a	DS _{tos} ^b	Yield (%)	DMSO	DMF	DMA
4	25	3	0.43	95	+	–	–
5	25	4	0.81	82	+	–	–
3	25	5	0.90	88	+	–	–
6	25	6	0.95	68	+	+	+
7	25	7	0.95	93	+	+	+
8	40	5	0.54	95	+	–	–
9	0	1	0.02	90	–	–	–
10	0	2	0.24	97	–	–	–
11	0	3	0.72	92	+	–	–
12	0	5	1.68	79	+	+	+

^a Mol tosyl chloride per mol anhydroglucose unit (AGU). ^b Degree of substitution (DS_{tos}) calculated from elemental analysis data. ^c DMSO: dimethylsulfoxide, DMF: *N,N*-dimethylformamide, DMA: *N,N*-dimethylacetamide, +: soluble, –: insoluble.

summarized. Tosyl celluloses with DS_{tos} values between 0.43 and 1.68 could be obtained. The increase of the molar ratio from 1:3 to 1:5 (AGU to tosyl chloride) results in a strong increase of the DS_{tos} from 0.43 (4) to 0.90 (3). However, the further increase of the molar ratio to 1:7 yields products of comparable DS_{tos} of 0.95 (7). The increase of the reaction time from 1 to 5 h leads to an increase of the DS_{tos} from 0.24 to 1.05 (Fig. 2). Products soluble in DMSO are accessible after a reaction time of at least 2 h at 25 °C and a molar ratio of 5 mol tosyl chloride per mol AGU.

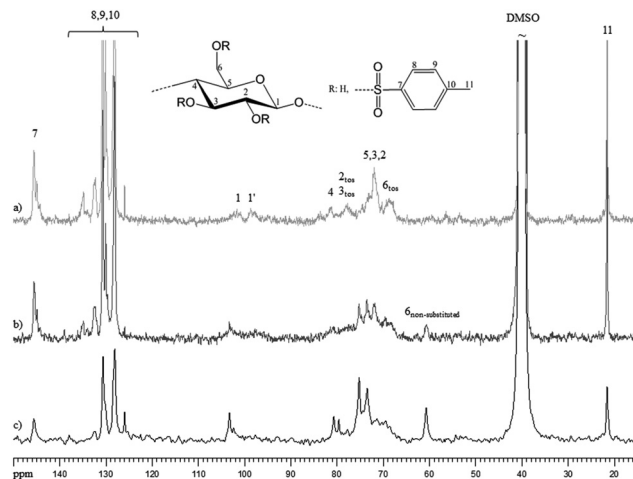
Surprisingly, even higher DS_{tos} values could be obtained by decreasing the reaction temperature; thus, at a reaction temperature of 25 °C a product with DS_{tos} of 0.90 (3) was obtained while the reaction at 0 °C yields a product with a significantly higher DS_{tos} of 1.68 (12). In contrast, an increase of the temperature to 40 °C results in products of lower DS_{tos} (8).

**Fig. 2** Degree of substitution (DS_{tos}) of cellulose tosylate as a function of reaction time (molar ratio of tosyl chloride per anhydroglucose unit of 5, reaction temperature 25 °C).

Elemental analysis data prove that the polymer contains no chlorine. It is assumed that the S_N reaction of the tosyl moieties is inhibited due to the insolubility of tosyl cellulose in aqueous NaOH–urea and the following precipitation. Furthermore, no polymer degradation could be observed as a result of the reaction. The DP_w values determined are in a comparable range (DP_w = 250–330) as found for the starting cellulose (DP_w = 330). The yield of the reaction was at least 80%. As already mentioned, tosyl celluloses soluble in DMSO could be obtained. Tosyl cellulose samples with a DS_{tos} value starting at 0.43 are soluble in DMSO. Samples with a DS_{tos} of 0.95 are additionally soluble in further dipolar aprotic solvents like DMA and DMF. Tosyl celluloses prepared homogeneously applying DMA–LiCl as a cellulose solvent are soluble in DMSO, DMA and DMF starting with a DS_{tos} of 0.46.⁷ Thus, the solubility is comparable applying the different solvents.

The FTIR spectra of cellulose and tosyl cellulose samples with different DS_{tos} values in a range of 500 to 4000 cm^{–1} are shown in Fig. S2.† The introduction of tosyl groups into the polysaccharide is indicated by different bands that can be assigned to the sulfonic acid ester group (1360, 1180 and 816 cm^{–1}) and the aromatic ring (3070 and 1600 cm^{–1}) as known from the literature.^{7,17,18}

In Fig. 3, ¹³C NMR spectra of tosyl celluloses with different DS_{tos} values recorded in DMSO-d₆ at 25 °C are presented. Signals can be found for the *p*-substituted toluene ring (128 and 146 ppm). The signal of the methyl group of the tosyl moiety is observed at 22 ppm.¹⁹ The intensity of the signal at 69 ppm increases with increasing DS_{tos} indicating a tosylation of the primary hydroxyl group. In contrast, the intensity of the signal belonging to an unmodified C-6 atom (61 ppm) decreases. The tosylation of cellulose in the aqueous NaOH–urea occurs mainly at the primary hydroxyl group. There is no signal at about 45 ppm that would indicate the chlorination at position 6. The signals for the C atoms of the secondary hydroxyl groups appear at ~73 ppm. In the spectra of tosyl

**Fig. 3** ¹³C NMR spectra of tosyl celluloses (a) with degree of substitution (DS_{tos}) = 0.43, sample 4, (b) DS_{tos} = 0.95, sample 7, and (c) DS_{tos} = 1.68, sample 9 recorded in DMSO-d₆ at 25 °C.

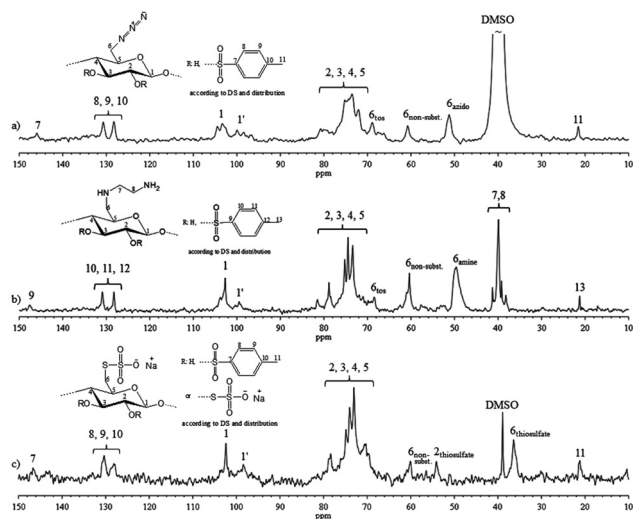


Fig. 4 ^{13}C NMR spectra of (a) 6-deoxy-6-azido cellulose ($\text{DS}_{\text{azide}} = 0.82$, $\text{DS}_{\text{tos}} = 0.05$, recorded in $\text{DMSO}-d_6$ at 25°C), (b) 6-deoxy-6-(ω -aminoethyl)amino cellulose ($\text{DS}_{\text{amine}} = 0.63$, $\text{DS}_{\text{tos}} = 0.07$, recorded in D_2O at 25°C) and (c) 6-deoxy-6-thiosulfate cellulose ($\text{DS}_{\text{thiosulfate}} = 0.75$, $\text{DS}_{\text{tos}} = 0.05$, recorded in D_2O at 25°C).

celluloses 7 and 9, a new signal occurs at 78 ppm indicating secondary positions modified with tosyl moieties. The tosylation on position 2 leads to a splitting of the signal C-1 (C-1').

It has been shown that tosyl cellulose is a key intermediate for the preparation of 6-deoxy-6-substituted cellulose derivatives. Tosyl groups at position 6 can be substituted by a S_{N} reaction. In the present work, the conversions of tosyl cellulose with azide ions, ethylenediamine, and thiosulfate were studied. Fig. 4 shows the ^{13}C NMR spectra of 6-deoxy-6-azido-, 6-deoxy-6-(ω -aminoethyl)amino-, and 6-deoxy-6-thiosulfate cellulose synthesized from tosyl cellulose 7.

The spectra show the presence of residual tosyl groups at the polymer backbone. The signals detected at 22 ppm and between 128 and 146 ppm can be assigned to the tosyl methyl and aromatic ring carbons of modified AGU. The signals of the C-2, 3, 4 and 5 atoms were detected in the range from 70 to 80 ppm. The peaks for C-1 and C-1' appear around 102 ppm and 99 ppm. The signals for tosylated position 6 are detectable at 68 ppm. Additionally, a signal belonging to an unmodified C-6 atom could be determined at 61 ppm. The characteristic peaks of the position C-6 substituted with azide (51 ppm, a), ethylenediamine (49 ppm, b) and thiosulfate (36 ppm, c) are clearly visible.

To demonstrate the potential application of the new synthesis path towards tosyl celluloses in larger scale a multi-gram experiment was performed. Thus a synthesis starting with 20 g cellulose was studied. The reaction was carried out at 25°C for 5 h with a molar ratio of 1 : 5 (AGU to tosyl chloride). A tosyl cellulose well soluble in DMSO with a DS_{tos} of 0.88 could be obtained. These first results of a prospective up-scaling underline the usefulness of this synthesis pathway for commercial application.

Conclusions

The synthesis of tosyl cellulose in the solvent NaOH-urea with polyethylene glycol alkyl-(C_{11} – C_{15}) ether (Imbetin) yields tosyl celluloses well soluble in common solvents like dimethylsulfoxide (DMSO), N,N -dimethylformamide (DMF), and N,N -dimethylacetamide (DMA). The characterization by means of NMR- and FTIR-spectroscopy, elemental analysis, and size exclusion chromatography indicates a uniform structure of the tosyl cellulose. The nucleophilic displacement (S_{N}) reaction of the tosyl groups could be efficiently carried out leading to soluble 6-deoxy-6-substituted cellulose derivatives. The tosylation of cellulose in the aqueous solvent NaOH-urea-Imbetin is a first proof of concept for the combination of exploiting a renewable material with an environmentally friendly technique. The subsequent modification was meant to demonstrate the high quality and the broad scope of the tosyl celluloses prepared in the aqueous medium. Further research is needed to develop a green strategy for the subsequent reactions as well.

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