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Carbohydrate Polymers 42 (2000) 411–420

Carbohydrate Polymers

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Starch derivatives of high degree of functionalization. 1. Effective, homogeneous synthesis of *p*-toluenesulfonyl (tosyl) starch with a new functionalization pattern

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Accepted 8 November 1999

Abstract

Pure *p*-toluenesulfonyl (tosyl) starch with an insignificant formation of chlorodeoxy groups was prepared by reacting starch dissolved in the solvent system *N*,*N*-dimethyl acetamide in combination with LiCl. Interestingly, the viscosity of the starch dissolved in the solvent system increases with the increasing amount of LiCl. The tosyl starch samples obtained were characterized by means of elemental analysis, FITR and ^{13}C NMR spectroscopy. The degree of substitution (DS_{Tos}) of the products can be controlled in range from 0.4 to 2.0 by adjusting the molar ratio of tosyl chloride per anhydroglucose unit up to 6.0 mol/mol. The tosyl starch samples are readily soluble in various organic solvents. As revealed by means of ^{13}C NMR analysis as well as by analysis of the corresponding 6-iodo-6-deoxy derivatives, a faster tosylation at position 2 than at positions 6 and 3 takes place. The thermal stability of tosyl starch increases with increasing DS_{Tos} and degradation starts at 166°C for the sample of DS_{Tos} of 0.61. The remaining OH groups of tosyl starch are reactive and can be additionally modified by acetylation reactions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: *p*-Toluenesulfonyl starch; Homogeneous synthesis; *N*,*N*-Dimethyl acetamide/LiCl; High degree of tosylation; Distribution of functional groups; Organo-soluble starch derivatives

1. Introduction

Although used for centuries, starch continues to be attractive as a raw material because of its abundant supply, low cost, renewability, biodegradability and ease of chemical modification. Moreover, it is important that starch molecules are multifunctional, i.e. there are three reactive hydroxyl groups per repeating unit, which are, in general, accessible to the typical conversions of primary and secondary alcoholic OH groups. However, most of the starch derivatives which are available commercially have low degree of substitution (DS = 0.01–0.20). Examples are the preparation of starch acetate or succinate, the reaction with ethylene or propylene oxide to form hydroxyalkyl starch, with sodium tripolyphosphate to form starch phosphate, and with sodium monochloroacetate to form carboxymethyl starch (e.g. Wurzburg, 1986). Many other types of starch derivatives have been prepared, including products with high DS values ($DS > 0.5$), but most of these compounds have not been commercialized. Chemical modification continues to provide a dominant route towards starch utilization in polymer-based materials.

In contrast to the recent progress in cellulose chemistry, which is in particular stimulated by the use of non-aqueous cellulose solvents and regioselectively protected or activated derivatives (Heinze & Glasser, 1998), a fully satisfying solution to design high-performance materials based on starch is still missing. Specifically designed starch materials, which can be easily prepared and used for subsequent reactions via different synthesis paths, are a challenge of the recently developed polysaccharide chemistry and of great importance for future applications of the renewable and unique polymer starch.

In this context our interest was focused on sulfonic acid esters of starch, derived from the reaction of organic sulfonyl chloride (e.g. benzene, methane, or toluene sulfonyl chloride). These derivatives can be employed as partially protected and reactive intermediates. Up to now, especially the reaction of starch with *p*-toluenesulfonyl chloride in pyridine was studied, i.e. under heterogeneous

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PII: S0144-8617(99)00182-4

reaction conditions, which may be accompanied by several side reactions (Clode & Horton, 1971; Horton & Meshreki, 1975; Teshirogi, Yamamoto, Sakamoto & Tonami, 1978, 1979). On the contrary, a homogeneous procedure was published using dimethyl sulfoxide as solvent for starch. However, the sulfur contents of the products were very low and an extensive degradation of the polymer occurred (Weill, Kaminsky & Hardenbergh, 1980). The extent of *p*-toluenesulfonylation of primary and secondary groups was determined by the iodination method (Mahoney & Purves, 1942). It was revealed that the reaction proceeds faster at O-6 than at O-2 and O-3 (Horton, Luetzow & Theander, 1973).

In this paper we wish to report about an effective homogeneous synthesis of pure tosyl starch samples having a wide range of DS using the solvent system *N*,*N*-dimethyl acetamide (DMA) in combination with LiCl. The products are characterized by the elemental analysis and the FTIR spectroscopy. The distribution of functional groups were studied by means of ^{13}C NMR spectroscopy and by the characterization of subsequently iodinated products. Further, some relevant properties like solubility and thermal stability dependent on the DS were investigated. The reactivity of the remaining OH groups of the tosyl starch samples was preliminarily determined by acetylation reactions.

2. Experimental

2.1. Materials

The starch material used was HYLON VII (**1**; 70% amylose, *National Starch & Chemical GmbH*, Neustadt, Germany) after drying at 100°C for 24 h under vacuum. The solvents were dried and distilled prior to use according to conventional methods. Anhydrous LiCl was used after drying at 130°C for 2 h under vacuum. Other reagent grade chemicals were used without further purification.

2.2. Measurements

Elemental analysis was carried out by means of a LECO CHNS/932 ultimate analyzer. The FTIR spectra were recorded on a Nicolet Impact 400 spectrometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker AMX 400 spectrometer in DMSO-d_6 or $CDCl_3$ with an accumulation number between 10 000 and 75 000 scans. The solubility of tosyl starch samples were determined at a concentration of 1 g/100 ml in various organic solvents (Table 4). The thermogravimetric analyses were performed by means of a thermogravimetric analyzing system (home made) using 10 mg samples. The curves were run in air at a heating rate of 10 K/min from ambient temperature up to 600°C. The viscosity of the samples was measured by means of a rotational rheometer RS 150 (Haake, Germany) at 25.0 ± 0.1°C using the DG 41Ti measuring container.

2.3. Methods

2.3.1. Dissolution of starch in N,N-dimethyl acetamide (DMA)/LiCl

Dried starch **1** (2.5 g, 15.4 mmol, actual weight of water-free polymer) was suspended in 60 ml of DMA and kept at 160°C for 1 h under continuous stirring. After the slurry had been allowed to cool to 100°C, 5.0 g of anhydrous LiCl was added. During cooling to room temperature under stirring the starch dissolves completely.

2.3.2. Synthesis of p-toluenesulfonyl starch (**4**)

For a typical preparation, to the 4.3% (w/v) solution of 2.5 g starch (**1**, 15.4 mmol) in DMA/LiCl a mixture of 7.4 ml (53.4 mmol) triethylamine and 5.0 ml of DMA was added under stirring. After cooling down to about 8°C, a solution of 5.9 g (30.8 mmol) *p*-toluenesulfonyl chloride in 7.4 ml DMA (see Table 1) was added dropwise under stirring within 30 min. The homogeneous reaction mixture was additionally stirred for 24 h at 8°C and then slowly poured into 700 ml of ice water. The precipitate was filtered off, carefully washed with about 2.3 l of distilled water and 250 ml of ethanol, dissolved in 120 ml of acetone and reprecipitated into 370 ml of distilled water. After filtration and washing with ethanol, the product **4** was dried at 60°C for 8 h under vacuum.

Yield: 3.7 g (70%), degree of substitution (DS_{Tos}) = 1.35 (based on sulfur analysis, 11.64% S, see Table 1).

The DS_{Tos} was calculated from the sulfur content of the product according to the equation:

$$DS_{Tos} = 162 \times S\,(\%)/[3200\,(\%) - 155 \times S\,(\%)],$$

where S is the sulfur determined by elemental analysis.The tosyl starch **4** obtained is soluble in acetone, dimethyl sulfoxide, *N*,*N*-dimethyl acetamide, *N*,*N*-dimethyl formamide, tetrahydrofuran and dioxane (see Table 4).

FTIR (KBr): 3488 (ν OH), 3064 (ν C–H_{arom}), 2943 (νCH), 1599, 1495, 1453 (ν C–C_{arom}), 1362 (ν_{as} SO_2), 1176 (ν_s SO_2), 811 (δ C–H_{arom}) cm^{-1}.
^{13}C NMR: 21.1 (CH_3), 59.8–93.7 (starch backbone), 128.0–144.8 (C–H_{arom}) ppm in DMSO-d_6.
^{1}H NMR: 2.4 (CH_3); 3.4–5.6 (starch backbone); 7.4–7.8 (C–H_{arom}) ppm in DMSO-d_6.

2.3.3. Iodination of p-toluenesulfonyl starch (**32**)

One gram of tosyl starch **4** (DS_{Tos} = 1.35) was dissolved in 50 ml of acetylacetone. Then 1.7 g of anhydrous NaI was added and the reaction mixture was kept for 2 h at 130°C. After cooling down to room temperature, the product was isolated by precipitation into 200 ml of ethanol, filtrated off and carefully washed with 3.2 l of distilled water. The sample was soaked overnight in 170 ml ethanol and then in 170 ml of 0.1 M $Na_2S_2O_3$ solution for 1 h. After filtration and washing with water and ethanol, the product **32** was dried at 50°C for 6 h under vacuum.

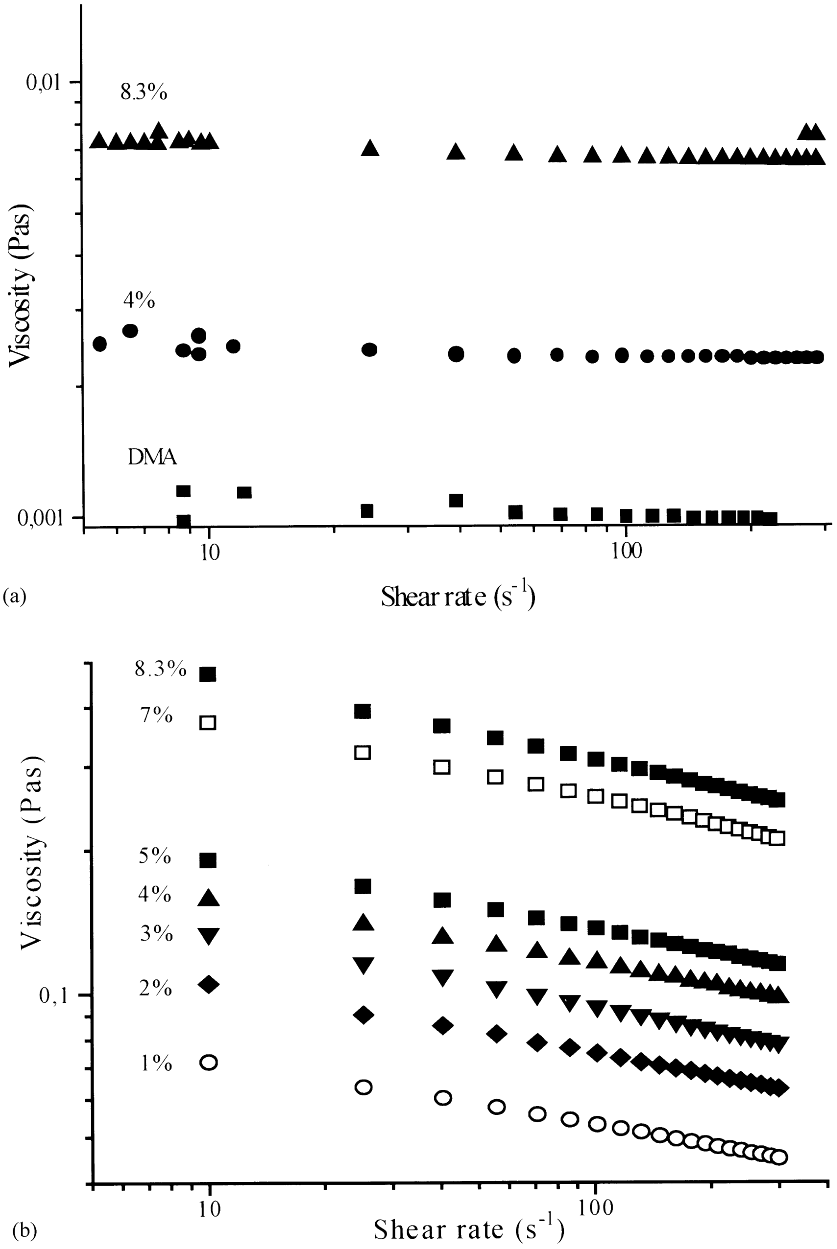


Fig. 1. Viscosity values of *N*,*N*-dimethyl acetamide (DMA)/LiCl (a) and solutions of starch/DMA/LiCl (b) in dependence on the LiCl content at different shear rates.

Degree of substitution (DS_I) = 0.18 (determined on the basis of iodine and sulfur content, 7.38% I and 8.58% S, DS_{Tos} = 0.83, see Table 6).

2.3.4. Acetylation of p-toluenesulfonyl starch (37)

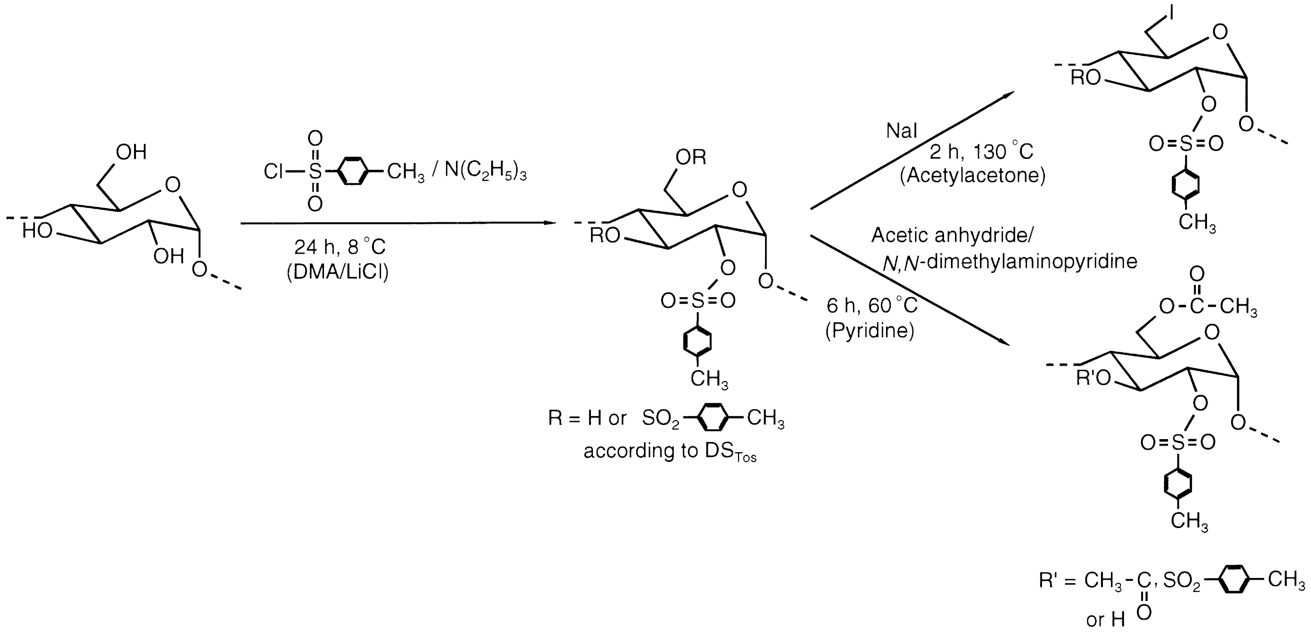
For a typical preparation, to a stirred solution of tosyl starch **6** (1.0 g, 2.6 mmol, DS_{Tos} = 1.43) in 20 ml pyridine 0.3 g *N*,*N*-dimethylaminopyridine and 10 ml (106.0 mmol) acetic anhydride were added. The mixture was kept at 60°C for 6 h. After cooling down to room temperature, the product was isolated by precipitation in 150 ml ethanol, filtered off, washed with ethanol and dried at 60°C for 6 h under vacuum.

Degree of substitution DS_{Acyl} = 1.00 and DS_{Tosyl} = 1.43 (calculated on the basis of elemental analysis, see Table 7). The tosyl starch acetate **37** obtained is soluble in acetone, dimethyl sulfoxide, *N*,*N*-dimethyl acetamide, *N*,*N*-dimethyl formamide and $CHCl_3$.

FTIR (KBr): 3452 (ν OH), 2929 (ν CH), 1 745 (ν C=O), 1631, 1494, 1449 (ν $C–C_{arom}$), 1364 (ν_{as} SO_2), 1177 (ν_s SO_2), 818 cm^{-1} (δ $C–H_{arom}$).

^{13}C NMR: 20.5–21.4 (CH_3, tosylate and acetate), 62.5–96.3 (starch backbone), 127.9–145.2 (C H_{arom}), 170.1 (C=O, acetate residue) ppm in $CDCl_3$.

^1H NMR: 1.56–2.05 (CH_3C=O), 2.38 (CH_3), 3.50–5.30 (starch backbone), 7.23–7.72 ($C–H_{arom}$) ppm in $CDCl_3$.



Scheme 1.

3. Results and discussion

In order to guarantee an even distribution of the functional groups within the polymer chain, a homogeneous procedure for the tosylation reaction was preferred. It was already shown that the homogeneous tosylation using the well-known starch solvent dimethyl sulfoxide does not yield products of sufficient degree of substitution (Weill et al., 1980). Therefore, we carried out the reaction in the solvent system DMA/LiCl that is usually applied for homogeneous functionalization of cellulose. Using this solvent tosyl cellulose samples in a range of DS_{Tos} from 0.4 to 2.3 with an insignificant formation of chlorodeoxy groups were synthesized (McCormick & Callais, 1987; Rahn, Diamantoglou, Klemm, Berghmans & Heinze, 1996), which were subject of a broad variety of subsequent reactions (Heinze, 1996, 1997, 1999; Heinze, Rahn, Jaspers & Berghmans, 1996a,b; Tiller, Berlin & Klemm, 1999).

3.1. Dissolution of the polymer

To dissolve the polymer an activation was carried out which consists in a treatment of starch (HYLON VII, **1**) in a DMA slurry at 130°C or 160°C for 1 h. After the slurry had been allowed to cool to 100°C water-free LiCl was added. We have found that a concentration of LiCl starting from 1.0% (w/v) is appropriate to dissolve the starch completely while at a concentration of 0.5% (w/v) a highly swollen gel was obtained only. As expected the starch solutions possess a distinct viscosity. Interestingly, the viscosity is dependent on the LiCl content of the system. At the same ratio of starch to solvent the dynamic viscosity $[\eta]$ of the solutions increases with an increasing amount of LiCl (Fig. 1b). A solution of 2.5 g starch in 60 ml DMA containing 1.0% (w/v) LiCl possesses a viscosity of $\eta = 0.072$ Pas while the solution containing 8.3% (w/v) LiCl shows a value of $\eta = 0.412$ Pas at a shear rate of 10 s^{-1}. Obviously, the formation of rather well defined “supramolecular” structures of starch in the dissolved state occurs which is driven by the intensive interactions of starch/DMA/LiCl.

For cellulose dissolved in DMA/LiCl various structures were described (Bianchi, Ciferri, Conio & Terbojevich, 1985; Terbojevich, Cosani, Conio, Ciferri & Bianchi, 1985) which include the formation of a so-called macrocation of $Li^+(DMA)_x$ (McCormick, Callais & Hutchinson, 1983). It was revealed that even without starch a significant increase of viscosity of DMA by addition of LiCl appears (Fig. 1a) which may help to explain the behavior found. The same behavior, i.e. an increase of viscosity was measured by addition of LiCl to the solvent dimethyl sulfoxide. This interesting possibility to control the viscosity of a solution of starch in dipolar aprotic solvents simply by an addition of low-molecular inorganic salts as well as investigations about the supramolecular interaction using light-scattering and ^{7}Li NMR will be a topic of further studies.

3.2. Homogeneous synthesis and characterization of tosyl starch

In order to start from solutions with an equal viscosity, in a first series of experiments the starch (**1**) was dissolved in 4.3% (w/v) DMA/LiCl solution. The tosylation was carried out with *p*-toluenesulfonyl chloride (Tos-Cl) and triethylamine as a base within 24 h at 8°C (Scheme 1). To evaluate the accessible range of the degree of substitution (DS_{Tos})

Table 1
Conditions and results of homogeneous tosylation of starch (**1**) with *p*-toluene-sulfonyl chloride in *N*,*N*-dimethyl acetamide/LiCl using triethylamine as a base in dependence on the molar ratio and reaction temperature for 24 h

Molar ratio Tos-Cl/AGU[a]	Reaction temperature (°C)	Tosyl starch				
		No.	DS_{Tos}[b]	S (%)	Cl (%)	Yield (%)[c]
1.0	8	**2**	0.61	7.61	0.19	97
1.5	8	**3**	1.02	10.18	0.20	76
2.0	8	**4**	1.35	11.64	0.30	70
2.0[d]	8	**5**	0.11[e]	1.93	0.10	54
3.0	8	**6**	1.43	11.93	0.42	65
6.0	8	**7**	2.02	13.61	0.32	62
1.0	rt[e]	**8**	0.61	7.63	0.11	96
1.5	rt	**9**	0.87	9.40	0.43	82
2.0	rt	**10**	0.71	8.38	0.45	90
3.0	rt	**11**	1.27	11.34	1.33	74
4.0	rt	**12**	1.26	11.30	1.55	78
6.0	rt	**13**	1.76	12.96	1.48	60

[a] 0.12 mol anhydroglucose units (AGU), 4.3% (w/v) solution, 2 mol triethylamine/mol Tos-Cl.
[b] Degree of substitution (DS_{Tos}), calculated on the basis of sulfur analysis.
[c] Yield: quotient (×100) of amount of polymer isolated to the theoretical weight of tosyl starch according to DS_{Tos}.
[d] Tosylation reaction under heterogeneous condition (in a slurry without addition of LiCl).
[e] Room temperature.

the molar ratio Tos-Cl/ anhydroglucose unit (AGU) was varied from 1.0 to 6.0 mol/mol (Table 1). After an usual work-up procedure by precipitation and subsequent reprecipitation from an appropriate solvent the tosyl starch samples **2**–**7** were obtained as white powders in high yields. The DS_{Tos} was calculated from the sulfur content (see Section 2).

Regarding the results of tosylation (Table 1) it has to be underlined that the DS_{Tos} increases with increasing amount of tosyl chloride per AGU (**2**, 1.0 mol Tos-Cl, $DS_{Tos} = 0.61$ in comparison to sample **7**, 6.0 mol Tos-Cl, $DS_{Tos} = 2.02$). That means that the DS_{Tos} can be simply controlled by adjusting the molar ratio. In comparison to the reaction at 8°C, the tosylation of starch at ambient temperature leads to products **8**–**13** with lower DS_{Tos} values by using the same molar ratio Tos-Cl/AGU.

The elemental analysis of the samples indicates that a minimal amount of chlorine is incorporated into the polymer under the reaction conditions used (Table 1). However, the chlorine content increases from 0.11 to 1.55% according to a DS_{Cl} from 0.01 to 0.08 by increasing the reaction temperature from 8 to 20°C. This indicates that a nucleophilic displacement reaction of the tosylate groups by chloride especially at higher temperature can occur as a

Table 2
Degree of substitution of *p*-toluenesulfonyl (tosyl) starch samples in dependence on the reaction time and the molar ratio Tos-Cl/AGU at 8°C (0.12 mol anhydroglucose units (AGU), 4.3% (w/v) solution, 2 mol triethylamine/mol *p*-toluenesulfonyl chloride (Tos-Cl))

Reaction time (h)	Molar ratio Tos-Cl/AGU	Tosyl starch				
		No.	DS_{Tos}[a]	S (%)	Cl (%)	Yield (%)[b]
1	1.5	**14**	0.81	9.01	0.00	95
3	1.5	**15**	0.98	9.97	0.22	83
5	1.5	**16**	1.02	10.17	0.27	81
24	1.5	**3**	1.02	10.18	0.20	76
1	2.0	**17**	1.09	10.52	0.14	82
3	2.0	**18**	1.08	10.48	0.25	80
5	2.0	**19**	1.15	10.81	0.36	72
16	2.0	**20**	1.29	11.40	0.23	72
24	2.0	**4**	1.35	11.64	0.30	70
48	2.0	**21**	1.35	11.64	0.32	71
1	3.0	**22**	1.14	10.77	0.00	85
3	3.0	**23**	1.25	11.25	0.29	59
5	3.0	**24**	1.33	11.55	0.24	79
24	3.0	**6**	1.43	11.93	0.42	65

[a] Degree of substitution (DS_{Tos}), calculated on the basis of sulfur analysis.
[b] Yield: quotient (×100) of amount of polymer isolated to the theoretical weight of tosyl starch according to DS_{Tos}.

Table 3
DS_{Tos} of tosyl starch samples in dependence on the activation temperature (AT) and different LiCl/starch-molar ratios at 8°C for 5 h (Tos-Cl/AGU = 2 mol/1 mol)

AT (°C)[a]	Molar ratio LiCl/starch	Starch (g)	Tosyl starch				
			No.	DS_{Tos}[b]	S (%)	Cl (%)	Yield (%)[c]
160	2.00	2.5	**19**	1.15	10.81	0.36	72
160	0.50	10.0	**25**	1.46	12.04	0.20	74
160	0.12	10.0	**26**	1.32	11.53	0.45	73
130	2.00	2.5	**27**	1.21	11.07	0.33	76
130	0.12	10.0	**28**	1.28	11.38	0.50	69

[a] Activation for 1 h.
[b] Degree of substitution (DS_{Tos}), calculated on the basis of sulfur analysis.
[c] Yield: quotient (×100) of amount of polymer isolated to the theoretical weight of tosyl starch according to DS_{Tos}.

side reaction. In any case, the tosylation reaction proceeds under totally homogeneous conditions. Samples with a complete tosylation of all OH groups ($DS_{Tos} = 3$) could not be obtained. This was found by tosylation of cellulose as well (Rahn et al., 1996).

In contrast to the results of the homogeneous reaction, the tosylation of starch **1** in a slurry of pure DMA (without LiCl) leads to an insoluble product **5** with a comparatively low DS_{Tos} of 0.11, obviously due to the heterogeneous course of reaction.

The dependence of the DS_{Tos} on the reaction time by using different molar ratios is shown in Table 2. At constant molar ratio it is evident, that the DS_{Tos} increases with increasing reaction time up to 5 h (compare, e.g. sample **14** versus **16**). A further prolongation of the reaction time of up to 48 h leads to a slightly increased DS_{Tos} value only.

As already mentioned, for dissolution of starch an activation at 160°C was carried out which may control the reactivity of starch as well. Moreover, the ratio starch to LiCl also may influence the reactivity. Consequently, the influence of this parameter was studied. Even an activation at 130°C is appropriate to dissolve the starch. The subsequent tosylation yields products with nearly the same DS_{Tos} values under comparable reaction conditions (Table 3). As indicated by these results an activation of starch at 160°C is as effective as at 130°C considering the DS_{Tos} values obtained.

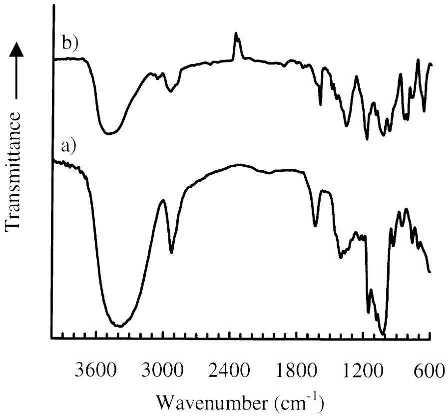


Fig. 2. FTIR spectra of tosyl starch samples (b, **4**, $DS_{Tos} = 1.35$) along with the spectrum of the starting starch (a, **1**).

3.3. Spectroscopic characterization of tosyl starch

3.3.1. FTIR spectroscopy

The structure of the tosyl starch was confirmed by means of FTIR spectroscopy. The spectra show the characteristic absorptions of the starch backbone as well as signals at 3064, 1597, 1495 and 816 cm^{-1} of the aromatics. Further, two bands with a high intensity at 1360 and 1176 cm^{-1} (ν SO_2) confirm the presence of the tosyl groups. A representative FTIR spectrum of sample **4** (b, $DS_{Tos} = 1.35$) is shown in Fig. 2 along with the spectra of the starting polymer (spectrum a).

3.3.2. ^{13}C NMR spectroscopy

Standard ^{13}C NMR spectra of the tosyl starch derivatives were measured in DMSO-d_6. Fig. 3 shows a representative ^{13}C NMR spectrum of tosyl starch **17** ($DS_{Tos} = 1.09$) and the assignment of the signals. The peak for C-6 influenced by tosylation in O-6 appears at $\delta = 69.0$ ppm (C-6_S), i.e. it exhibits a down field-shift at about 8.5 ppm compared with the corresponding carbon of unmodified starch. The carbon atoms of unsubstituted secondary hydroxyl groups give a resonance at $\delta \approx 71.0$ ppm. The signals for the C-5 and the C-4$'$ atoms (index $'$ indicates the influence of a O-3 substitution) appear at $\delta \approx 73.1$ ppm and can not be resolved. The secondary hydroxyl groups substituted by tosyl groups give a new signal at $\delta \approx 80.2$ ppm, and the signal at $\delta = 94.3$ ppm is assigned to C-1$'$ (C-1 atom influenced by a O-2 tosylation). It may be concluded that at $DS_{Tos} = 1.09$ the 6 position is only slightly modified since a signal at about 60 ppm appears which refer to unmodified primary hydroxyl groups. Moreover, at this DS_{Tos} value the positions 2 are fully substituted. On the contrary, for the samples **2** and **8** ($DS_{Tos} = 0.61$) a splitting of the signal for C-1 is detectable (for C-1 at 100.4 ppm and for C-1$'$ at 94.4 ppm) as expected.

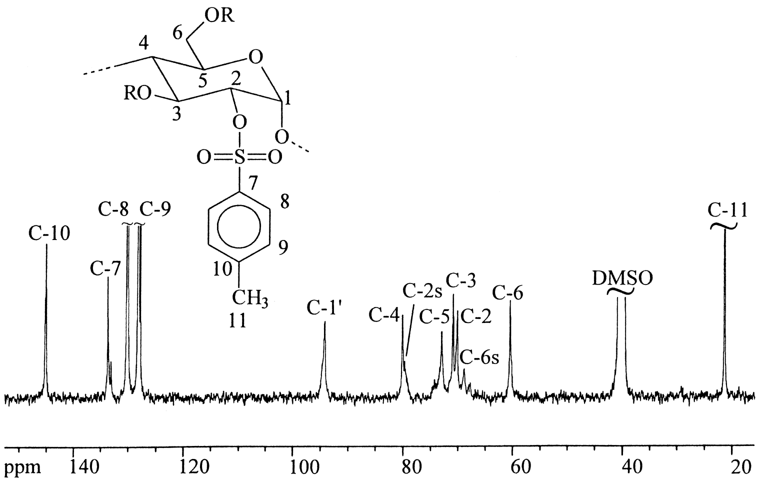


Fig. 3. ^{13}C NMR spectra of tosyl starch samples **17** ($DS_{Tos} = 1.09$) measured in DMSO-d_6 at 60°C (R = H or tosyl according to DS_{Tos}).

The comparison of the signal intensities of each spectrum with one another enables the estimation of the substituent distribution within the AGU. This estimation indicates a more effective esterification at O-2 than at O-6 and O-3.

3.4. Some selected properties

3.4.1. Solubility

An important property of the tosyl starch synthesized is their solubility in common organic solvents. The derivatives with a $DS_{Tos} \geq 0.61$ are soluble in dimethyl sulfoxide (DMSO), DMA and *N*,*N*-dimethyl formamide (DMF) as summarized in Table 4. Samples with a slightly higher DS_{Tos} are soluble in dioxane (≥0.98), tetrahydrofuran and acetone (≥1.15), i.e. in weak polar solvents as well as in a dipolar aprotic solvent with a relatively low dielectric constant. At a DS_{Tos} of 2.02 (**7**) the tosyl starch samples dissolve even in the non-polar solvents dichloromethane and chloroform.

Table 4
Solubility of selected tosyl starch samples in dependence on the degree of substitution (DS_{Tos}) (solubilities were determined at a concentration of 1 g / 100 ml, +, soluble at room temperature, ⊕, swellable, —, insoluble. DMSO, dimethyl sulfoxide; DMA, *N*,*N*-dimethyl acetamide; DMF, *N*,*N*-dimethyl formamide; THF, tetrahydrofuran)

DS_{Tos}	No.[a]	Acetone	DMSO	DMA	DMF	Dioxane	THF	$CHCl_3$
0.61	**2**	—	+	+	+	⊕	⊕	—
0.61	**8**	—	+	+	+	⊕	⊕	—
0.71	**10**	—	+	+	+	⊕	⊕	—
0.87	**9**	—	+	+	+	⊕	⊕	—
0.98	**15**	⊕	+	+	+	+	⊕	—
1.02	**3**	⊕	+	+	+	+	⊕	—
1.02	**16**	⊕	+	+	+	+	⊕	—
1.08	**18**	+	+	+	+	+	⊕	—
1.14	**22**	+	+	+	+	+	⊕	—
1.15	**19**	+	+	+	+	+	+	—
1.25	**23**	+	+	+	+	+	+	—
1.26	**12**	+	+	+	+	+	+	⊕
1.27	**11**	+	+	+	+	+	+	⊕
1.29	**20**	+	+	+	+	+	+	⊕
1.33	**24**	+	+	+	+	+	+	⊕
1.35	**4**	+	+	+	+	+	+	⊕
1.35	**21**	+	+	+	+	+	+	⊕
1.43	**6**	+	+	+	+	+	+	⊕
1.76	**13**	+	+	+	+	+	+	⊕
2.02	**7**	+	+	+	+	+	+	+

[a] See Tables 1 and 2.

It is well known that the solubility of cellulose derivatives may alter with DS. A typical example for such a behavior is trimethylsilyl cellulose. Samples of low DS are soluble in DMSO and DMA, those of medium DS in tetrahydrofuran, while samples of high DS can be dissolved in hexane or CCl_4 only (Klemm, Schnabelrauch, Stein, Philipp, Wagenknecht & Nehls, 1990). Thus, there is no solvent for the whole DS range in case of trimethylsilyl cellulose. From this point of view, it is interesting that the tosyl starch synthesized show a solubility in DMSO independent of DS_{Tos} similar to tosyl cellulose (Rahn et al., 1996).

3.4.2. Thermal behavior

The thermal behavior of tosyl starch was studied by means of thermogravimetry (TG). Thermal analysis of starch **1** and homogeneously synthesized tosyl starch were carried out under air at a heating rate of 10 K/min.

Representative TG curves of the unmodified starch **1** (Fig. 4, curve a) and of the tosyl starch **17** ($DS_{Tos} = 1.09$, Fig. 4, curve b) show that the thermal degradation of the tosyl starch sample was initiated at a lower temperature (196°C) than in the case of the starch (303°C). In contrast to the well investigated tosyl cellulose (e.g. Heinze, 1996b) the main degradation step for tosyl starch can not be clearly subdivided into two parts. Therefore, a temperature range for the main degradation step is given in Table 5. For sample **17** ($DS_{Tos} = 1.09$) the degradation starts at 196.1°C and ends at 307.7°C with a weight loss of 57.3%. The further heating of the sample up to 600°C leads to carbonization of the product to ash. At 460°C a residue of about 32% was evaluated which is further reduced to 6.6% in the case of

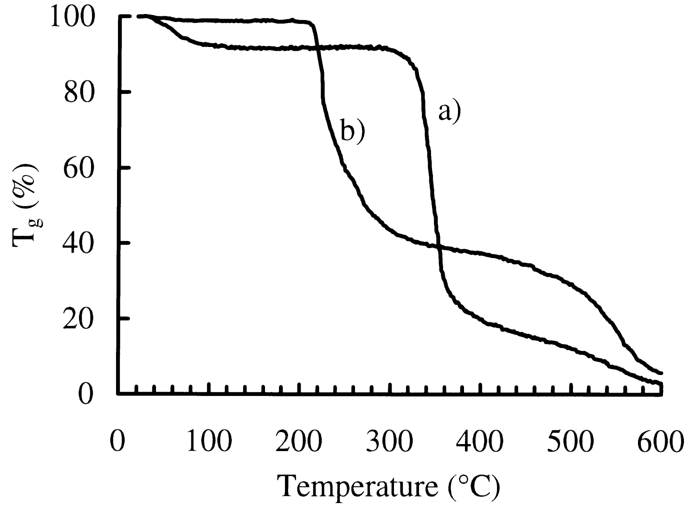


Fig. 4. Thermal analysis of starch **1** (curve a) and tosyl starch **17** ($DS_{Tos} = 1.09$, curve b) under air.

tosyl starch **17**. In comparison to starch there is almost no weight loss for the tosylated samples below 100°C associated with the evaporation of moisture. This is reasonable as the moisture-absorbing capacity of the tosyl starch decreases when the moisture-holding hydroxyl groups are functionalized. With increasing content of tosyl groups ($DS_{Tos} = 0.61$–2.02) an increase in stability from 166 to 213°C occurs.

The thermal stability of tosyl starch is sufficiently high for processing and subsequent chemical modifications. However, in order to prevent thermally induced side reactions the different processes should be carried out below 160°C.

3.5. Subsequent modifications of tosyl starch

3.5.1. Iodination

It has been shown that tosyl groups at the primary positions of sugar units can be substituted by iodide on treatment with an excess of anhydrous NaI in a suitable medium like acetone or acetylacetone whereas esters of secondary alcohol groups are uneffected. This method was also successfully applied to determine the degree of tosylation at the sixth position of various polysaccharide derivatives like tosyl chitin (Kurita & Inoue, 1989), tosyl chitosan (Zhang, Hisamori, Yamada & Hirano, 1994), and tosyl cellulose (Rahn et al., 1996).

To determine the partial DS_{Tos} at C-6 of tosyl starch, selected samples with different DS_{Tos} were treated with NaI in acetylacetone at about 120°C for 2 h, i.e. under typical conditions for a reaction at the six tosylate groups only (see Scheme 1). The obtained iododeoxy tosyl starch samples **29**–**32** show the same solubility in common organic solvents like the starting tosyl starch samples.

The degree of iodine substitution (DS_I) was calculated according to both the iodine and sulfur analysis and is listed

Table 5
Thermogravimetric analysis data of tosyl starch samples

DS_{Tos}	No.	IDT (°C)[a]	FDT (°C)[b]	Weight loss (%)	Residue at 460°C (%)
0.00	**1**[c]	303.4	406.9	48.2	15.8
0.61	**2**	165.9	305.8	60.0	29.1
0.98	**15**	187.9	304.1	57.7	31.7
1.02	**3**	198.3	307.7	57.5	29.3
1.08	**18**	202.7	314.0	60.3	30.8
1.09	**17**	196.1	307.7	57.3	31.7
1.14	**22**	200.9	307.1	57.8	30.0
1.15	**19**	201.9	311.3	61.0	29.5
1.29	**20**	217.0	327.5	62.6	29.1
1.35	**4**	192.6	313.2	62.6	27.9
1.35	**21**	212.4	314.6	59.2	32.9
2.02	**7**	214.0	322.0	63.8	29.2

[a] Initial decomposition temperature.

[b] Final decomposition temperature.

Table 6
Iodination of tosyl starch with NaI in acetylacetone for 2 h at 130°C

Tosyl starch[a]		6-Iodo-6-deoxy tosyl starch					
No.	DS_{Tos}	No.	DS_I[b]	DS_{Tos}[b]	Δ[c]	I (%)	S (%)
18	1.08	**29**	0.20	0.73	0.15	8.65	7.85
19	1.15	**30**	0.23	0.82	0.10	9.35	8.46
4	1.35	**31**	0.18	0.83	0.34	7.38	8.58
7	2.02	**32**	0.73	1.15	0.14	22.19	8.77

[a] See Tables 1 and 2.

[b] Degree of substitution (DS_I and DS_{Tos}) calculated on the basis of iodine and sulfur analysis.

[c] The difference between the DS_{Tos} from the starting tosyl starch and the total degree ($DS_I + DS_{Tos}$) of the product.

in Table 6. The DS_I values obtained confirm that the number of tosyl groups replaceable by iodine reached a maximum DS_I of 0.7 even at a DS_{Tos} of 2.02 of the starting tosyl starch. Subtraction of the groups replaced by iodine from DS_{Tos} left differences which corresponded to the progressive esterification of secondary alcoholic groups (tosylation in O-2 and O-3 position) within the AGU. Already at the lowest DS_{Tos} (1.08) investigated, a remarkably high tosylation of the secondary OH groups ($DS_{Tos} = 0.73$) was confirmed. On the contrary, even at a $DS_{Tos} = 2.02$ (**32**, $DS_I = 0.73$) no complete tosylation of the CH_2OH functions was reached.

The results of substituent distribution obtained by analysis of the corresponding iododeoxy derivatives of tosyl starch are in agreement with those of ^{13}C NMR investigations. From both methods it may be concluded that the tosyl chloride reacts under the reaction conditions used mainly with the secondary hydroxyl group at C-2.

3.5.2. Acetylation

Acetylation of cellulose derivatives has found considerable interest in connection with the determination of the distribution of substituents using NMR spectroscopy (Tezuka, Imai, Oshima & Chiba, 1987). For this purpose a complete acetylation of all free OH groups of the polymer is necessary. The esterification reactions investigated were carried out with the acetic acid anhydride in order to exclude side reactions by a substitution of tosyl groups (see Scheme 1). Reaction conditions and results are listed in Table 7.

In the case of tosyl starch, a complete acetylation could be achieved by reacting the polymer with an approximately 25 molar excess of acetic anhydride per mole free OH groups in pyridine for 6 h at 60°C using *N*,*N*-dimethylaminopyridine (DMAP) as a catalyst (sample **34** and **35**, Table 7). A quantitative acetylation is evident in the FTIR spectra from the disappearance of the hydroxyl absorption at $3300\ cm^{-1}$ (ν OH) along with the appearance of the ester carbonyl absorption at $1750\ cm^{-1}$ (ν C=O). Furthermore, the signals of the tosyl groups at 1362 (ν_{as} SO_2), and $1176\ cm^{-1}$ (ν_s SO_2) are clearly found indicating the stability of the tosyl ester under the applied reaction conditions. The ^{13}C NMR spectra of the tosyl starch acetate (**34**) measured in $CDCl_3$ show the resonance of the starch backbone between $\delta = 62.1$–96.7, signals for the tosyl residue between $\delta = 127.9$–145.5 and at $\delta = 20.5$–21.5 (CH_3, tosylate and acetate), and for the acetyl groups at $\delta = 169, 4$–$169, 9$ (*C*=O) ppm.

By using sodium acetate as a catalyst the acetylation was incomplete under the same reaction conditions (sample **37**). The DS_{Acyl} values of the starch derivatives were determined from the data of elemental analysis (by the use of a computer program which computes analytical data for a range of DS of polyglucan derivatives containing two substituents and matches the percentages calculated to those obtained) and from the data of ^1H NMR spectroscopy. The tosyl starch acetates **34**–**38** are soluble in acetone, dimethyl sulfoxide, DMA, *N*,*N*-dimethyl formamide and $CHCl_3$.

The fully acetylated samples were included in investigations of the determination of the tosyl group distribution by means of ^1H NMR spectroscopy. The results will be published elsewhere.

4. Conclusions

The homogeneous tosylation of starch with tosyl chloride and triethylamine as a base dissolved in DMA/LiCl

Table 7
Conditions and results of the acetylation of tosyl starch in pyridine with *N*,*N*-dimethylaminopyridine (DMAP) as a catalyst for 6 h at 60°C

Tosyl starch[a]		Tosyl starch ester					
No	DS_{Tos}	No.	S (%)	DS_{Acyl}[b]	DS_{Acyl}[c]	ν C=O (cm^{-1})	δ C=O (ppm)
16	1.02	**34**	8.23	1.86	1.88	1749	169.4–169.9
22	1.14	**35**	8.82	1.82	1.84	1750	169.7–169.8
20	1.29	**36**	8.62	1.69	–	1752	169.4–169.9
6	1.43	**37**[d]	10.97	1.00	1.05	1745	169.9–170.1
7	2.02	**38**[e]	11.97	1.49	1.09	1754	169.4–169.5

[a] See Tables 1 and 2.

[b] Degree of substitution (DS_{Acyl}) calculated on the basis of sulfur analysis.

[c] Degree of substitution (DS_{Acyl}) calculated on the basis of ^1H NMR spectroscopy.

[d] Sodium acetate (CH_3COONa) as a catalyst.

[e] Reaction for 24 h with sodium acetate (CH_3COONa) as a catalyst.

represents a suitable and effective method for the preparation of organo-soluble tosyl starch samples. Up to now, this solvent system was not applied for functionalization reactions of starch. It is worth mentioning that the dissolved polymer forms a special supramolecular order dependent on the LiCl added. The amount of LiCl has a distinct influence on the viscosity of the corresponding solutions. At present, ^{7}Li NMR studies of the system starch/DMA/LiCl are carried out to gain detailed information about the state of dissolution, i.e. the interaction between the three components. Tosyl starch samples with DS_{Tos} ranging from 0.61–2.02 were obtained. In contrast to heterogeneously synthesized samples they are soluble in various organic solvents, such as DMSO, DMA, *N*,*N*-dimethyl formamide, acetone, pyridine, tetrahydrofuran, dioxane and chloroform and they contain minimal amounts of chlorodeoxy functions ($DS_{Cl} \leq 0.08$). The tosylation of starch is more effective at position 2 than at the positions 6 and 3 as revealed by means of ^{13}C NMR spectroscopy as well as by analysis of the corresponding iododeoxy tosyl starch samples. In contrast, the tosylation of cellulose dissolved in DMA/LiCl under comparable conditions yields products with a preferred functionalization of the O-6 position. The special influence of the solvent DMA/LiCl on the distribution of the functional groups (O-2 tosylation) is additionally demonstrated by the finding of Horton et al. (1973) that the tosylation in DMSO (i.e. also under homogeneous conditions) leads to polymers with a preferred functionalization at O-6 although the overall DS values are reached in DMSO are rather small.

The remaining OH groups of tosyl starch are reactive and can be modified by acetylation. The quantitative determination of the partial DS values at positions 2, 3, and 6 is under investigation using ^{1}H NMR spectroscopy of the completely functionalized tosyl starch propionates and will be published elsewhere.

Acknowledgements

The general financial support of the Bundesministerium für Ernährung, Landwirtschaft und Forsten and the Fachagentur Nachwachsende Rohstoffe (Agency of Renewable resources) is gratefully acknowledged. Th. Heinze would like to thank the “Fonds der Chemischen Industrie” for the financial support of this investigations. A special thank goes to Dr K. Rahn for her assistance in preparing the manuscript.

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