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Unconventional Cellulose Products Through Nucleophilic Displacement Reactions

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Summary: The paper highlights the synthesis of unconventionally functionalized cellulose derivatives obtained by nucleophilic displacement (S_N) reactions. The key intermediates, cellulose sulphonates, are discussed due to the fact that sulphonate groups play the major role as leaving group in S_N reactions with the biopolymer. A short overview about "classical" S_N reactions will be given. The main part of the review is focused on novel cellulose products in particular aminodeoxy cellulose derivatives showing monolayer formation, click chemistry with cellulose starting from deoxyazido (copper-catalyzed Huisgen reaction) yielding products with methylcarboxylate-, 2-aniline-, 3-thiophene moieties, e.g., and new selectively dendronized cellulose based materials. Structure characterization and typical applications are briefly reviewed as well.

Keywords: cellulose; cellulose sulphonates; dendronized cellulose; Huisgen reaction; nucleophilic displacement

Introduction

The chemical modification of polysaccharides is still underestimated regarding the structure and hence property design of biopolymer-based materials. Chemical modifications of cellulose have been mainly directed to the hydroxyl groups of the polymer chains. At present, the cellulose derivatives commercially produced in large scale are limited to some ester with C_2 to C_4 carboxylic acid and ethers with methyl-, hydroxyalkyl-, and carboxymethyl functions and oxidative products.[1–3] It is well known from the chemistry of low-molecular alcohols that hydroxyl functions are converted to a good leaving group for nucleophilic displacement reactions by the formation of the corresponding halides or sulphonic acid esters.[4] Therefore, novel products may be obtained by unconventional chemistry like "click reactions" and new selectively dendronized celluloses via nucleophilic displacement (S_N) reactions. The aim of this review is to highlight recent advances in chemical modification of cellulose for the alternative synthesis of new products by using S_N reactions considering own research results adequately. Some applications of the products will be discussed as well.

Halodeoxy Celluloses

Conventional procedures for preparation of halodeoxy celluloses include the S_N reaction of a good leaving group, e. g. tosylate or mesylate with metal halide salts. In contrast, one-step paths were developed recently. To get pure and well-defined halodeoxy cellulose, cellulose dissolved in non-aqueous solvents e. g. chloral/*N,N*-dimethyl formamide (DMF) is most efficient. Thionyl chloride[5] and mesyl chloride[6,7] were employed as chlorination

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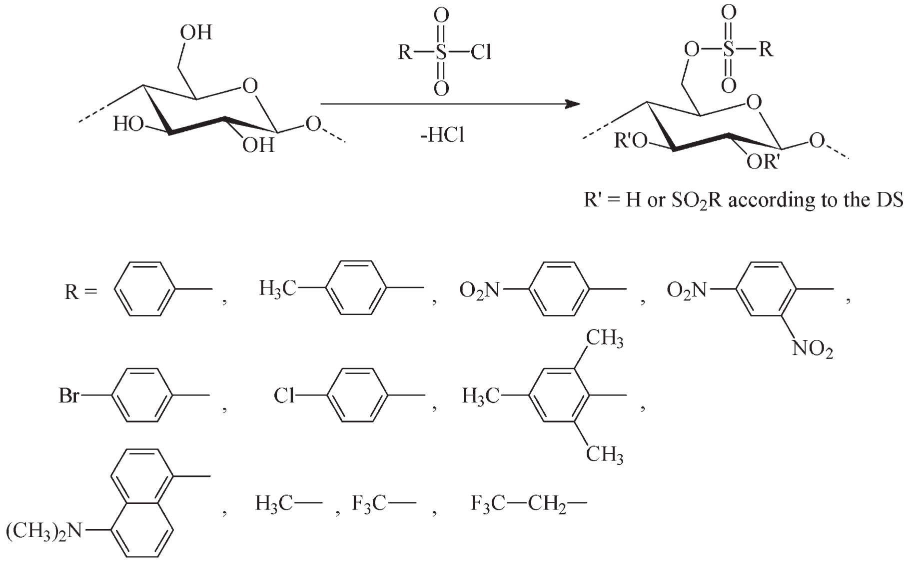
agents. Degree of substitution (DS) values of up to 2.8 were obtained, but the reactions were distinguished by significant chain degradation. A mild and selective conversion is the chlorination of cellulose with *N*-chlorosuccinimide-triphenylphosphine in *N,N*-dimethyl acetamide (DMA)/LiCl, which succeeds in early state only in position 6 following by an inversion at position 3 to a maximum DS of 1.86.[8,9] Recently, chlorination was described with thionyl chloride in DMF which is assumed to form 6-chloro-6-deoxy cellulose.[10] Bromodeoxy cellulose selectively modified at C-6 (DS up to 0.98) was synthesized homogeneously in different media (DMF, DMA, and *N*-methylpyrrolidone, NMP) with *N*-bromosuccinimide-triphenylphosphine and LiBr.[11,12] A drastic reduction of the reaction time was found by the conversion with *N*-bromosuccinimide-triphenylphosphine in DMA/LiBr by application of microwave under preservation of the selectivity of the functionalization in position 6.[13] A mixture of tribromoimidazole, triphenylphosphine, and imidazole proves to be an alternative bromination reagent for cellulose dissolved in DMA/LiBr that yields DS values up to 1.6, i.e. with a conversion of position 3 and 6 combined with inversion of position 3.[14] Selectively functionalized 6-deoxy-6-iodo cellulose was obtained by nucleophilic displacement reaction of cellulose tosylate[15,16] or chlorodeoxy functions[17] with NaI. An elegant way to 6-deoxy-6-fluoro cellulose is a conversion applying diethylaminosulphur trifluoride (DAST) starting from trityl cellulose.[18]

Cellulose Sulphonates

Typical structures of sulphonic acid esters applied in polysaccharide chemistry are shown in Scheme 1 and Table 1. The synthesis of sulphonic acid esters is realized heterogeneously by reaction with sulphonic acid chlorides in aqueous alkaline media (NaOH, Schotten-Baumann reaction), or completely homogeneous in a solvent like DMA/LiCl. A major drawback of heterogeneous procedures is the combination with a variety of side reactions including undesired nucleophilic displacement reactions caused especially by long reaction times and high temperatures required. In contrast, the homogeneous conversion of



Scheme 1.
Typical sulfonic acid esters of cellulose.

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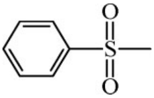
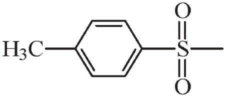
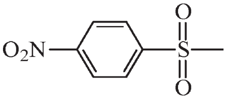
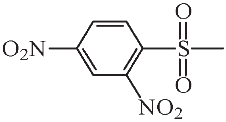
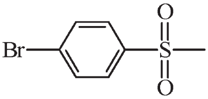
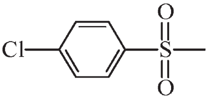
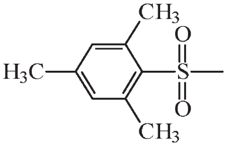
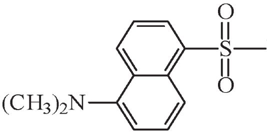
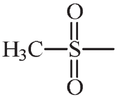
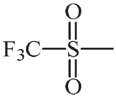
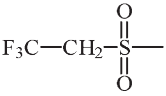
Table 1.
Examples for typical sulfonic acid esters used in cellulose chemistry.

Structure	Ester derived from	Abbreviation	References
	Benzenesulphonic acid		[22]
	*p*-Toluenesulphonic acid	Tosyl, tosylate	[15,19,26,72–76]
	4-Nitrobenzenesulphonic acid		[77]
	2,4-Dinitrobenzenesulphonic acid		[24]
	4-Bromobenzenesulphonic acid	Brosyl	[78–80]
	4-Chlorobenzenesulphonic acid		[24]
	2,4,6-Trimethylbenzenesulphonic acid		[24]
	5-*N,N*-Dimethylaminonaphthalene-sulfonic acid	Dansyl	[23]
	Methanesulphonic acid	Mesyl, mesylate	[22,25,77,81–83]
	Triflouromethanesulphonic acid	Triflate	[20]
	Triflouroethanesulphonic acid	Tresyl, tresylate	[84]

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cellulose dissolved in DMA/LiCl yields soluble sulphonic acid esters.[19]

One of the most reactive leaving groups in nucleophilic displacement reactions is the trifluoromethanesulphonate (triflate) moiety. Up to now, the isolation of the highly reactive cellulose triflates was not feasible because of their sensitivity to even mild nucleophils.[3] Investigations about the introduction of triflate moieties were carried out by conversion of cellulose acetate (DS 2.5) and methyl cellulose (DS 1.7) with trifluoromethanesulphonic acid anhydride in pyridine in inert atmosphere at 5 °C forming a stiff gel. The highly reactive cellulose triflate forms methylene ether cross-links by reaction with unmodified cellulose segments, which could by identified by IR spectroscopy.[20,21] Interestingly, soluble trimethylsilyl cellulose (TMSC) can yield partial desilylation with tetrabutylammonium fluoride (TBAF) and simultaneous treatment with trifluoromethanesulphonic anhydride in tetrahydrofuran (THF).[22] Soluble 5-dimethylamino-1-naphthalenesulphonyl (dansyl) esters of cellulose with DS from 0.7 to 1.6 were prepared by conversion of the polymer dissolved in DMA/LiCl. The remaining OH groups can be completely acetylated. The polymers show typical fluorescence and adsorptions spectra, which are in good agreement with quantum chemical calculations.[23] Soluble sulphonic acid esters with benzene or substituted benzene moieties like 4-chlorobenzene-, 2,4-dinitrobenzene-, and 2,4,6-trimethylbenzene were synthesized by reaction of cellulose with the corresponding sulphonic acid chloride in DMA/LiCl in the presence of triethylamine (TEA).[24]

The *p*-toluenesulphonic (tosyl) and the methanesulphonic (mesyl) acid esters are most widely used sulphonic acid esters, due to their availability and hydrolytic stability.[4] The conversion of cellulose with methanesulphonic acid chloride in the presence of TEA in DMA/LiCl leads to products with a DS of 1.3 at a reaction temperature of 7 °C for 24 h.[22] Subsequent mesylation of mesyl celluloses (DS up to 1.3) yields DS values of 2.1.[25] The cellulose mesylates are soluble in dimethyl sulfoxide (DMSO) starting at DS of 1.3 and in addition in DMF and NMP at a DS of 2.1. Products with lower DS values swell only.

The homogeneous conversion of cellulose in DMA/LiCl with p-toluenesulphonyl chloride permits the preparation of cellulose tosylate with defined DS values controlled by the molar ratio reagent to AGU at short reaction times, with almost no side reactions.[15,19,21,26] The product structure may depend on both the reaction conditions and the workup procedure used.[27] The tosyl chloride reacts with DMA in a Vilsmeier-Haak type reaction forming the *O*-(*p*-toluenesulphonyl)-*N,N*-dimethylacetiminium salt, which react with the OH groups of the cellulose depending on the reaction conditions used. For an effective tosylation of cellulose, stronger bases such as triethylamine (pK_a 10.65) or 4-(dimethylamino)-pyridin (pK_a 9.70) are necessary, which react with the *O*-(*p*-toluenesulphonyl)-*N,N*-dimethylacetiminium salt building a quaternary ammonium salt and hence lead to the formation of tosyl cellulose without undesired side reactions (Scheme 2).[27] Using weak organic base like pyridine (pK_a 5.25) or *N,N*-dimethylaniline (pK_a 5.15), the reaction with cellulose leads a reactive *N,N*-dimethylacetiminium salt, which can form chlorodeoxy celluloses at high temperatures or yields cellulose acetate after aqueous workup.[4]

Various cellulose materials with DP values from 280 to 1020 could be transformed to the corresponding tosyl esters.[15] DS values in the range of 0.4 to 2.3 with negligible incorporation of chlorodeoxy groups were obtained at reaction temperatures at 8–10 °C with 5–24 h (Table 2).

Cellulose tosylate are soluble in various organic solvents; beginning at DS of 0.4, solubility in aprotic dipolar solvents like DMA, DMF, and DMSO appears. The cellulose tosylates become soluble in acetone and dioxane at a DS value of 1.4 and solubility in chloroform and methylene chloride appears at DS of 1.8. Structure characterization by means of FTIR- and

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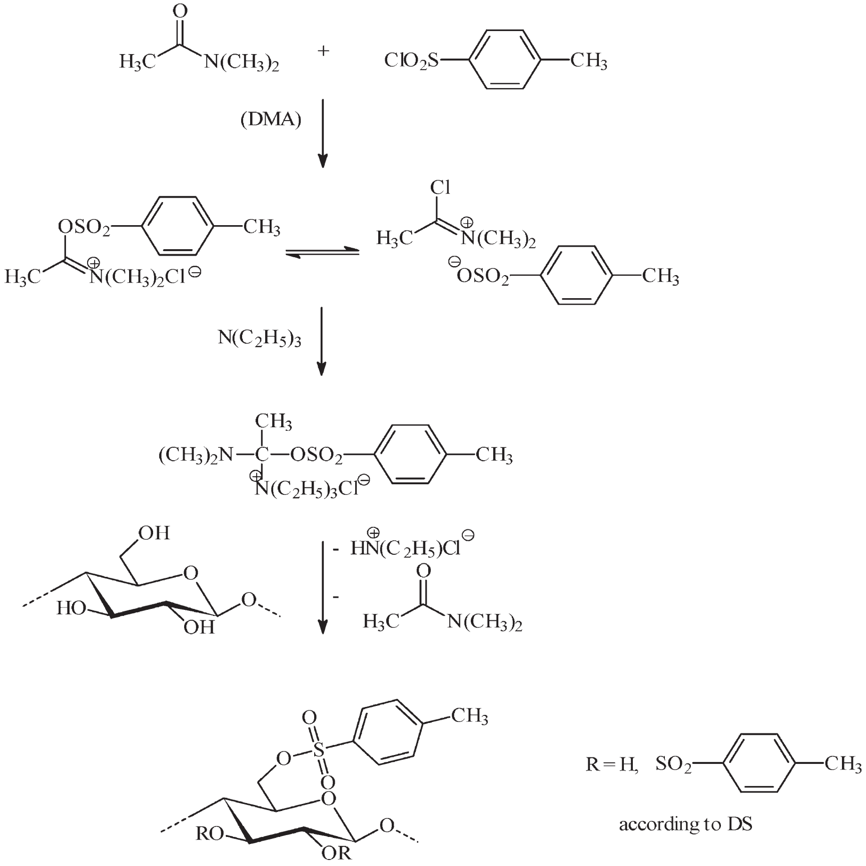

Scheme 2.
Mechanism of the reaction of cellulose with *p*-toluenesulphonyl chloride in DMA/LiCl in the presence of triethylamine (adopted from[27]).

NMR spectroscopy of cellulose tosylates shows that position 6 reacts faster compared to the secondary OH groups at C-2 and 3.[15]

Nucleophilic Displacement Reactions (S_N)

A broad diversity of deoxy cellulose derivatives were prepared by nucleophilic displacement (S_N) reactions starting from halodeoxy cellulose derivatives with thiourea and with iminodiacetic acid[28], or with thiols[29,30] are known yielding unusual cellulose based polymers. The most versatile starting material is bromodeoxy cellulose due to i) selective synthesis, ii) bromide is a better leaving group than chloride (1000 times higher reaction rate of bromodeoxy cellulose with halogenated methylgycoside than chlorodeoxy cellulose[31]), and iii) bromodeoxy cellulose shows a higher thermal stability than iododeoxy cellulose.[7] Bromodeoxy cellulose was utilized for the synthesis of 6-deoxy-6-sulfonato cellulose[32], and 6-deoxy-6-mercapto cellulose[33], which can be applied for metal ion adsorption due to the affinity of sulfur to various metal ions.

Cellulose sulphonates are studied for a broad variety of S_N reactions as discussed in various review papers by Belyakova[34], Hon[1], and Siegmund[21]. The mechanism (S_N1 vs. S_N2) of nucleophilic substitution reaction of cellulose derivatives is still a subject of discussion. A remarkable finding

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Table 2.
Results and conditions of the reaction of cellulose with *p*-toluenesulphonyl chloride (TosCl) in DMA/LiCl applying triethylamine as base (2 mol/mol TosCl) for 24 h at 8 °C (adopted from[15]).

Cellulose	Degree of polymerization	Molar ratio TosCl/AGU[a)]	Cellulose tosylate		
			DS[b)]	S	Cl
Microcrystalline	280	1.8	1.36	11.69	0.47
		4.5	2.30	14.20	0.43
Spruce sulphite pulp	650	1.8	1.34	11.68	0.44
		9.0	1.84	13.25	0.49
Cotton linters	850	0.6	0.38	5.51	0.35
		1.2	0.89	9.50	0.50
		2.1	1.74	12.90	0.40
		3.0	2.04	13.74	0.50
Beech sulphite pulp		1.8	1.52	12.25	0.43

[a)] AGU anhydroglucose unit;
[b)] degree of substitution, calculated on the basis of sulphur content.

is that a treatment of partially substituted cellulose tosylates (DS 1.2–1.5) with strong nucleophils like azide- or fluoride ions leads to a substitution of both primary and secondary tosylates.[25,35] By the treatment of cellulose tosylate (DS 1.5) with azide ions, it is assumed that an epoxide-type intermediate is formed during the conversion. If a perpropionated cellulose tosylate is used as starting material, i.e., a product without remaining OH groups, the reaction does not exceed DS values of 1 and the substitution occurs exclusively at the primary C atoms.[25] Studies about S_N reactions of cellulose tosylate (DS 2.02, $DS_{C\text{-}6}$ 1.0) with butylamine shows a dependence of the regioselectivity at C-6 on the reaction temperature: the highest regioselectivity regarding C-6 was reached at 25 °C and 50 °C; substitution at C-2 occurred at 75 °C and 100 °C.[36]

The water-soluble 6-deoxy-6-*S*-thiosulphato celluloses[37,38] synthesized via S_N reaction of cellulose tosylate with sodium thiosulphate can be oxidized by H_2O_2 – in analogy to nonpolymeric compounds of this type[39] – under formation of S-S bridges leading to new water-born coatings. The water-soluble 6-*O*-(2,3-*bis*(thiosulphato) propyl-oxy-2-hydroxypropyl) cellulose was synthesized by addition of tetrathionate to 6-*O*-(allyl-oxy-2-hydroxypropyl) cellulose. The polymers form monolayers on gold surface by chemisorption.[40] Water-soluble 6-deoxy-6-thiomethyl-2,3-carboxymethyl cellulose formed by S_N reactions of cellulose tosylate with $NaSCH_3$ followed by carboxymethylation of the remaining OH groups forms self-assembled monolayers at a gold surface.[41] The S_N reaction of cellulose tosylate with aqueous Na_2SO_3 solution leads to water-soluble sodium deoxy cellulose sulphonate-co-tosylate.[42,43]

S_N reactions of cellulose tosylate with iminoacetic acid yield water-soluble cellulosics with high swelling ability depending on the DS values between 0.39 and 0.53. The insoluble products show high water retention values of up to 11,000%.[44] A number of aminodeoxy celluloses were accessible. The S_N reaction with various amines yields water-soluble 6-deoxy-6-trialkylammonium cellulose.[45]

Conversion of cellulose tosylate with diamines or oligoamines results in polymers of the type $P{-}CH_2{-}NH{-}(X){-}NH_2$ (P = cellulose, (X) = alkylene, aryl, aralkylene or oligoamine) at C6 and solubilizing groups in C2/C3, which forms transparent films that may be applied for the immobilization of enzymes like glucose oxidase, peroxidase, lactate oxidase. The products are used as biosensors.[46–51] New water-soluble and film-forming amino cellulose tosylates from alkylenediamines can be used as enzyme support matrices with Cu^{2+}-chelating properties.[52] The S_N reaction of cellulose tosylate with R(+)-, S(−)-

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and racemic 1-phenylethylamine leads to new 6-deoxy-6-amino cellulose derivatives with a DS in the range from 0.4 to 0.6. The initial chirality of the cellulose does not have any significant influence on its reactivity with either of the two enantiomeric amines.[53] Methylamino celluloses synthesized by S_N reaction of cellulose tosylate with methylamine are suitable as hydrophilic polymer matrices for immobilization of appropriate ligands for extracorporeal blood purification, e.g. quaternary ammonium groups.[54] The synthesis of 6-deoxy-6-amino-cellulose via azido derivative was reinvestigated in detail. The reaction conditions for a complete functionalization at C-6 were optimized, as well as various subsequent reactions of the product were studied (e.g. *N*-carboxymethylation, *N*-sulfonation).[55,56]

Further details on the preparation of deoxy celluloses with carbon-nitrogen, carbon-sulphur, carbon-phosphorus, and carbon-carbon bonds as well as related structures like cellulosenes and anhydrocellulose are reviewed and critically discussed.[57] Applications for the deoxy celluloses are numerous and characterized by biological, chemical, and physical uses (Table 3).

Recently, Sharpless introduced click chemistry, i.e., a modular approach that uses only the most practical and reliable transformation, which are experimental simple needing no protection from oxygen, requiring only stoichiometric amounts of starting materials, and generating no by-products.[58] The 1,3-dipolar cycloaddition of an azide moiety and a triple bond (Huisgen reaction) is the most popular click reaction to date.[59,60] The path of tosylation, nucleophilic substitution with sodium azide in combination with the copper-catalyzed Huisgen reaction can significantly broaden the structural diversity of polysaccharides because the method yields compounds, which are not accessible via etherification and esterification, the most commonly applied reactions.[61] Scheme 3 shows the reaction path for the preparation of 6-deoxy-6-azido cellulose and subsequent copper(I)-catalyzed Huisgen reaction of 1,4-disubstituted 1,2,3-triazols formed as linker for the modifica-

Table 3.
Selected applications of deoxy cellulose (adopted from[57]).

Application field	Functionalization	Reference
Biological		
Bacteriostatic	Different cellulosics including deoxy cellulose treated with 5-nitrofuroyl chloride	[85,86]
Immobilization of enzymes	Aminodeoxy cellulose	[46,47]
Anticoagulants	Sulphated aminodeoxy cellulose	[87,88]
Enzyme purification	Aminodeoxy cellulose	[89]
Chemical		
Removal of heavy metals e.g.		
Hg	Chlorodeoxy cellulose + ethylenediamine, thiourea, thiosemicarbazide, thioacetamide	[90]
Hg^{2+}, Cu^{2+}	6-Deoxy-6-hydrazino cellulose	[91]
Cu, Mn, Co, Ni	6-Chlorodeoxy cellulose + diamines	[92]
Hg, Ag	S-substituted 6-deoxy-6-mercapto cellulose	[33]
Flocculent	Cellulose tosylate + amines	[45,93]
Preconcentration of trace elements	Tosyl cellulose treated with piperazine and CS_2 (cellulose piperazinedithiocarboxylate)	[94]
Sorption of uranium	Cellulose piperazinedithiocarboxylate	[95]
Chelating and complexing agents	Chlorodeoxy cellulose + iminodiacetic acid Schiff base formation from aminodeoxy cellulose	[96,97]
Physical		
Flame retardants	Chlorodeoxy cellulose	[98]
Propellants	Azidodeoxy cellulose	[99]
Electrostatic printing	Different cellulosics including aminodeoxy derivatives	[100]
Electron transfer catalysts	Viologens from ethyl cellulose derivatives	[101]

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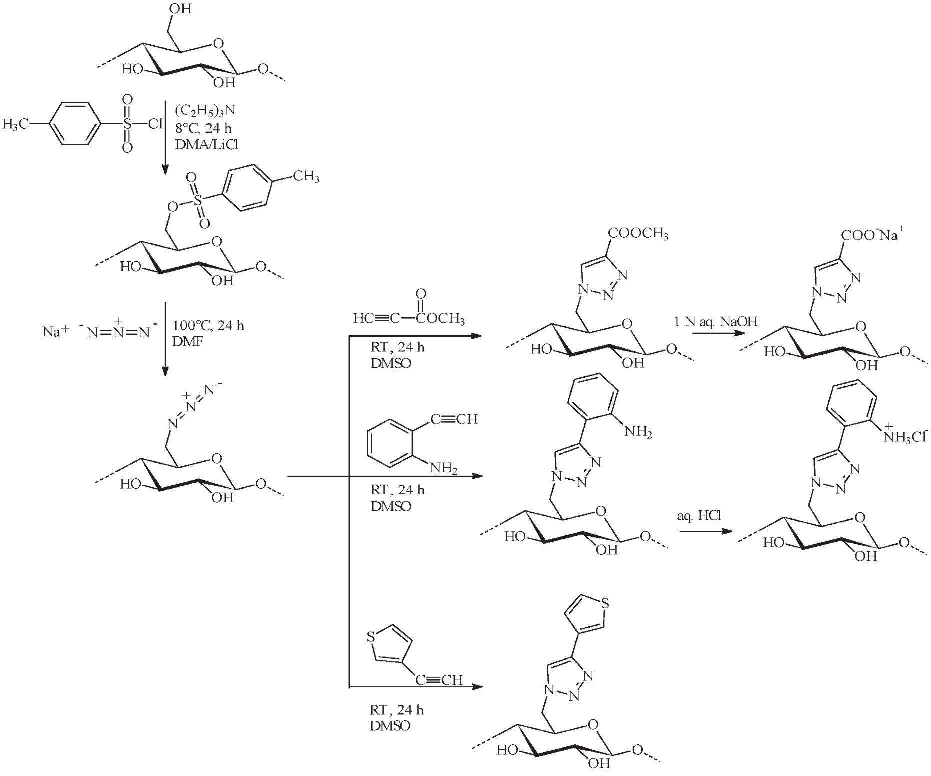

Scheme 3.
Reaction path for the preparation of 6-deoxy-6-azido cellulose and subsequent copper(I)-catalyzed Huisgen reaction of 1,4-disubstituted 1,2,3-triazols used as linker for the modification of cellulose with methylcarboxylate, 2-aniline and 3-thiophene moieties.

tion of cellulose with methylcarboxylate, 2-aniline and 3-thiophene moieties. The conversions succeed without side reactions yielding pure and well-soluble products with conversion efficiency of the azido moiety of 75–98% depending on the reaction temperature and the molar ratio (Table 4).

Even at elevated temperatures (70 °C), no hints for structural impurities are

Table 4.
Conditions of the copper-catalyzed Huisgen reaction of 6-deoxy-6-azido cellulose (azido cellulose) and degree of substitution (DS) of the products (adopted from[61]).

Azido cellulose	Reagent		Temperature [°C]	Product	
DS	Type	Molar ratio[a]		DS	Conversion [%]
0.88	Methyl propiolate	1	25	0.86	98
0.88	Methyl propiolate	1	70	0.67	76
0.88	Methyl propiolate	3	70	0.81	92
0.88	2-Ethynylaniline	1	25	0.67	76
0.99	2-Ethynylaniline	3	25	0.80	81
0.99	2-Ethynylaniline	3	70	0.77	78
0.60	3-Ethynylthiophene	1	70	0.45	75
0.99	3-Ethynylthiophene	3	25	0.91	92
0.99	3-Ethynylthiophene	3	70	0.93	94

[a] Mole reagent per mole repeating unit of 6-deoxy6-azido cellulose, reaction time 24 h.

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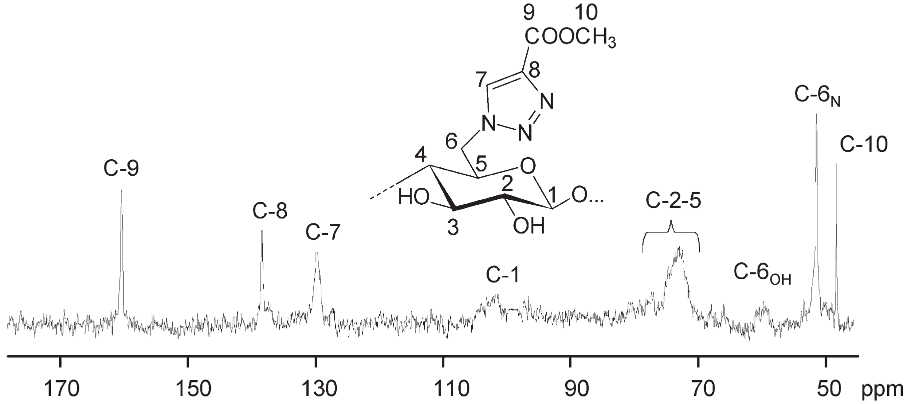
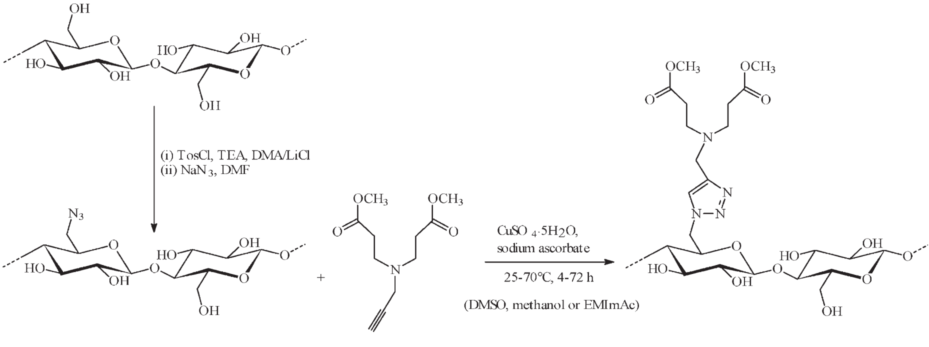


Figure 1.
^{13}C NMR spectrum of methylcarboxytriazolo cellulose (DS 0.81) in DMSO (with permission from Wiley-VCH, T. Liebert, C. Hänsch, Th. Heinze, Click chemistry with polysaccharides, *Macromol. Rapid Commun.* **2006**, *27*, 208–213).[61]

observed. The structure characterization of the products succeeds by FTIR and NMR spectroscopy. An example is the ^{13}C NMR spectrum of 6-deoxy-6-methylcarboxytriazolo cellulose (DS 0.81) in DMSO (Figure 1). The peaks at 48.5 ppm for the methyl ester and at 160.6 ppm are typically for the carbonyl moiety. The C-atoms of the triazole moieties give peaks at 138.6 and 129.9 ppm, and signals in the range from 51.6 to 110 ppm are related to the carbons of the repeating unit. A weak signal at about 60 ppm discloses the existence of remaining OH groups in position 6.

Huisgen reaction has been used for a variety of selective conversions, e.g., the synthesis of dendrimers[62] or the modification of proteins.[63] A promising approach for the synthesis of new cellulose derivatives with unconventional properties is the introduction of dendrons in the cellulose backbone, which are easily accessible thought the convergent synthesis of dendrimers.[64] Beside the first described amino-triester-based dendrons (Behera's amine) with an isocyanate moiety,[65,66] carboxylic acid-containing dendrons[67,68] are studied, which were allowed to react with cellulose homogenously, e. g. in DMA/LiCl or DMSO/TBAF. Moreover, regioselective introduction of dendrons in cellulose was realized via S_N reaction starting



Scheme 4.
Reaction path for conversion of cellulose with propargyl-PAMAM dendron of first generation via tosylation, nucleophilic displacement by azide, and conversion with the dendron.

from cellulose tosylate by sodium azide. For the synthesis of the first generation of dendronized polyamidoamino (PAMAM) cellulose bound via 1,4-disubstituted 1,2,3-triazole linker, 6-deoxy-6-azido cellulose were allowed to react with propargyl-PAMAM-dendron in DMSO homogeneously or in methanol heterogeneously in the presence of $CuSO_4 5H_2O$/sodium ascorbate (Scheme 4, Table 5).[69] An interesting novel reaction medium for the introduction of the propargyl-PAMAM-dendron to cellulose are ionic liquids like 1-ethyl-3-methylimidazolium acetate (EMImAc) cause of the solubility of 6-deoxy-6-azido cellulose (Scheme 4, Table 5).[70]

Under homogeneous conditions 6-deoxy-6-azido cellulose reacts also with propargyl-PAMAM dendrons of second and third generation. The structure characterization of the dendric PAMAM-triazolo celluloses succeeds by FTIR and NMR spectroscopy including two-dimensional techniques. As an example, Figure 2 shows the HSQC-DEPT NMR spectrum of second generation PAMAM-triazolo cellulose (**2c**), which allows the complete assignment

Table 5.
Degree of substitution (DS) of dendric PAMAM-triazolo cellulose derivatives of first (**1**), second (**2**), and third (**3**) generation synthesized homogeneously in dimethylsulfoxide (DMSO) or 1-ethyl-3-methylimidazolium acetate (EMImAc) as well as heterogeneously in methanol by reacting 6-deoxy-6-azido cellulose (DS 0.75) with propargyl polyamidoamine dendrone of first, second, and third generation via copper-catalyzed ($CuSO_4 5H_2O$/sodium ascorbate) Huisgen reaction.

Conditions				Product	
Molar ratio	Solvent	Temperature [°C]	Time [h]	No.	DS
1:1	DMSO	25 °C	24	**1a**	0.57
1:1	DMSO	25	48	**1b**	0.68
1:3	DMSO	25	24	**1c**	0.65
1:3	DMSO	25	48	**1d**	0.67
1:3	DMSO	60	24	**1e**	0.69
1:3	DMSO	70	24	**1f**	0.62
1:3	DMSO	25	24	**2a**	0.56
1:3	DMSO	25	48	**2c**	0.59
1:3	DMSO	25	72	**2d**	0.58
1:3	DMSO	25	72	**3a**	0.31
1:1	EMImAc	25	24	**1g**	0.52
1:2	EMImAc	25	24	**1h**	0.55
1:2	EMImAc	25	48	**1i**	0.60
1:3	EMImAc	25	24	**2e**	0.48
1:1	EMImAc	25	72	**3b**	0.28
1:1	Methanol	25	72	**1j**	0.63
1:3	Methanol	25	24	**1k**	0.63
1:3	Methanol	25	72	**1l**	0.63

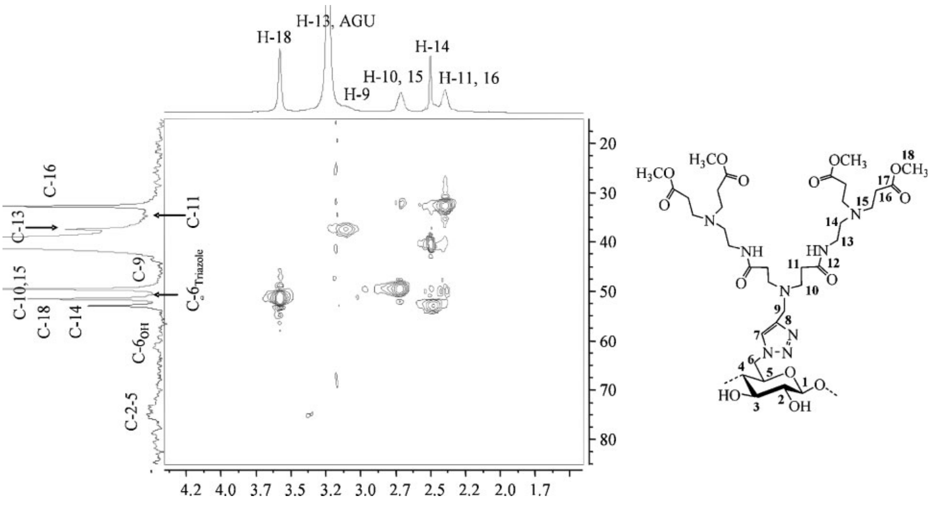


Figure 2.
HSQC-DEPT NMR spectrum of second generation PAMAM-triazolo cellulose (**2c**, DS 0.59) (with permission from Wiley-VCH, M. Pohl, J. Schaller, F. Meister, Th. Heinze, Selectively Dendronized Cellulose: Synthesis and Characterization, *Macromol. Rapid Commun.* **2008**, *29*, 142–148.).[69]

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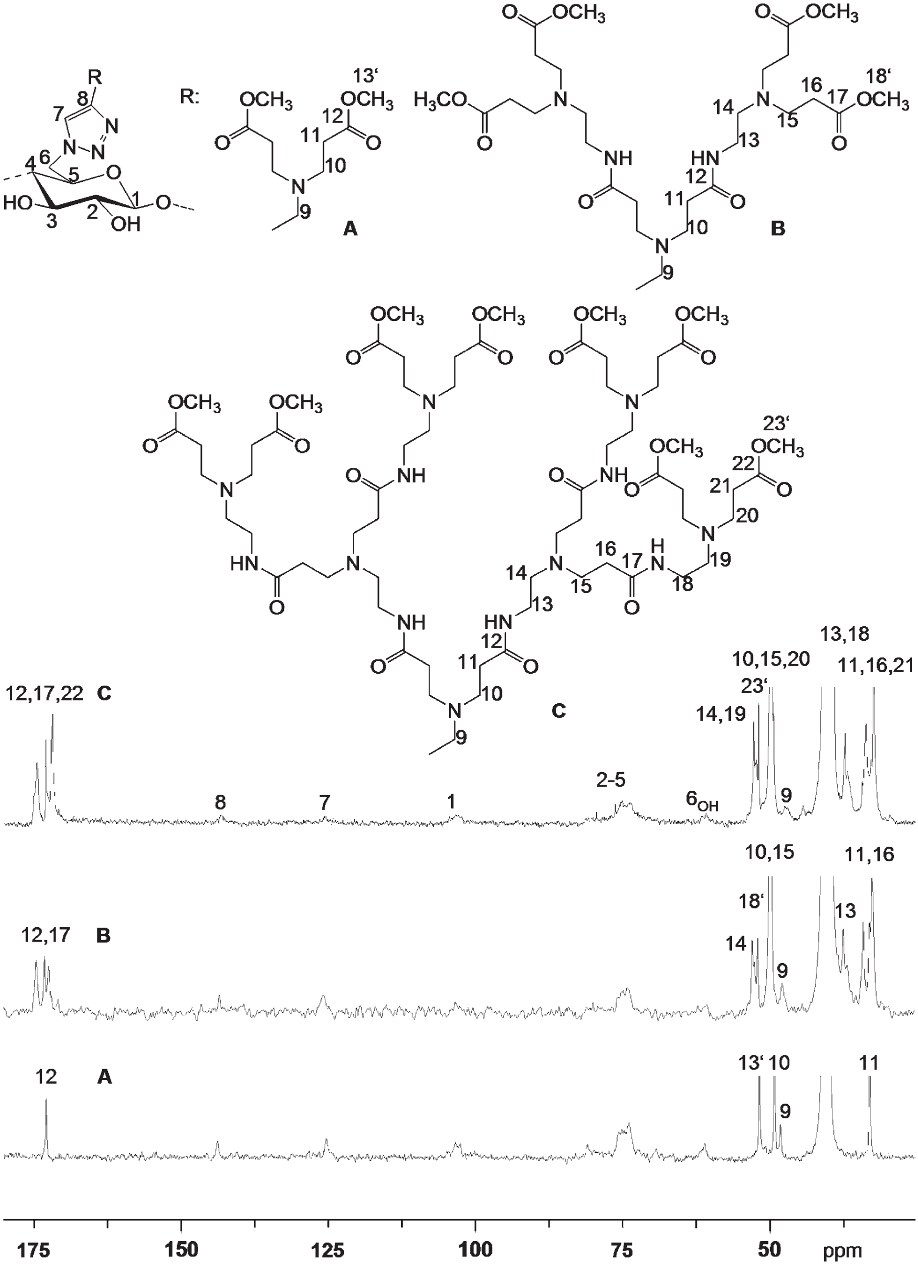

Figure 3.

^{13}C NMR spectra of **A** first (**1i**, DS 0.60), **B** second (**2e**, DS 0.48), and **C** third (**3b**, DS 0.28) generation PAMAM-triazolo cellulose in DMSO-d_6 at 60 °C (with permission from Wiley, T. Heinze, M. Schöbitz, M. Pohl, F. Meister, Interactions of Ionic Liquids with Polysaccharides: IV. Dendronization of 6-Azido-6-Deoxy Cellulose, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* , 3853–3859.).[70]

of the signals of the protons of the substituent in ^{1}H NMR spectra.

In Figure 3, ^{13}C NMR spectra of first, second and third generation PAMAM-triazolo cellulose synthesized in EMImAc demonstrate the possibility to assign the signals of the dendrons and the AGU. However, the intensity of the peaks of the carbon atoms of the AGU decreases due to the large number of branches and corresponding carbon atoms.

Conclusion

The examples discussed illustrate the enormous structural diversity accessible by these new and efficient methods based on S_N reactions. Based on the examples given, it is clearly obvious that S_N reactions undoubtedly will lead to a variety of sophisticated products. Moreover, Huisgen reaction with cellulose was already successfully realized and new dendronized cellulose derivatives will appear. For instance, biofunctionalized surfaces based on dendronized cellulose were prepared either by embedding of dendritic 6-deoxy-6-[1,2,3-triazolo]-4-polyamido amine (PAMAM) cellulose (degree of substitution, DS 0.25), obtained by homogeneous conversion of 6-deoxy-6-azido cellulose with propargyl-PAMAM dendron via the copper-catalyzed Huisgen reaction, in a cellulose acetate (DS 2.50) matrix or by the heterogeneous functionalization of deoxy-azido cellulose film with the dendron.[71]

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