Novel Bulky Esters of Biopolymers: Dendritic Cellulose

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Summary: Dendronized cellulose derivatives are discussed. Regarding our own studies, novel bulky esters of cellulose were synthesized homogeneously in *N*,*N*-dimethyl acetamide/LiCl or dimethyl sulfoxide in combination with fluoride ions by conversion of the biopolymer with 3,5-dihydroxybenzoic acid based aryl polyester dendrons. The carboxylic acid moieties were efficiently activated *in situ* with *N*,*N*′-carbonyldiimidazole or the acid chloride was applied. Cellulose esters with values of the degree of substitution of up to 0.7 were obtained. The functionalization analyzed by NMR spectroscopy occurs not only at position 6 (primary hydroxyl group) but also the secondary one at position 2.

Keywords: biopolymer; cellulose, dendrimer; esterification; NMR

Introduction

Cellulose is an important raw material and both the unmodified polymer and semi-synthetic derivatives are used in a wide range of industrial applications today worldwide.[1] The high structural uniformity of cellulose being a β-1$\rightarrow$4 linked polyglucan and the high number of functional groups (three reactive OH moieties per repeating unit) makes the polymer an excellent starting material for high valuable products.[2] There is still an increasing research interest due to the improvement of existing synthesis paths and products regarding efficiency of synthesis, control of the structures (the degree of substitution, DS, functionalization pattern etc.), on one hand.[3] On the other, in order to design new ''high tech'' products with unusual properties, new syntheses paths and special functional groups must be studied. Thus, various novel functional moieties were introduced in the polymeric backbone like crown ether or cyclodextrin containing compounds.[4] New reaction media including solvents are increasingly studied. For instance, ionic liquids were applied affording possibilities for an efficient homogeneous derivatization of cellulose.[5,6] Another promising approach in this context is the functionalization of cellulose with dendritic structures. Recently, various attempts are made to synthesize cellulose derivatives that combine the valuable properties of the biopolymer and of dendrons which is discussed in detail in the next section, including the corresponding references.

Dendronized Cellulose – State of the Art

It should be pointed out that not only cellulose was considered as starting material for dendronized biopolymer but also other polysaccharides like chitosan that will not be discussed herein.[7–9] First studies described the transformation of hydroxyethyl cellulose with 2,2-bis(hydroxymethyl)propionic acid anhydride generating

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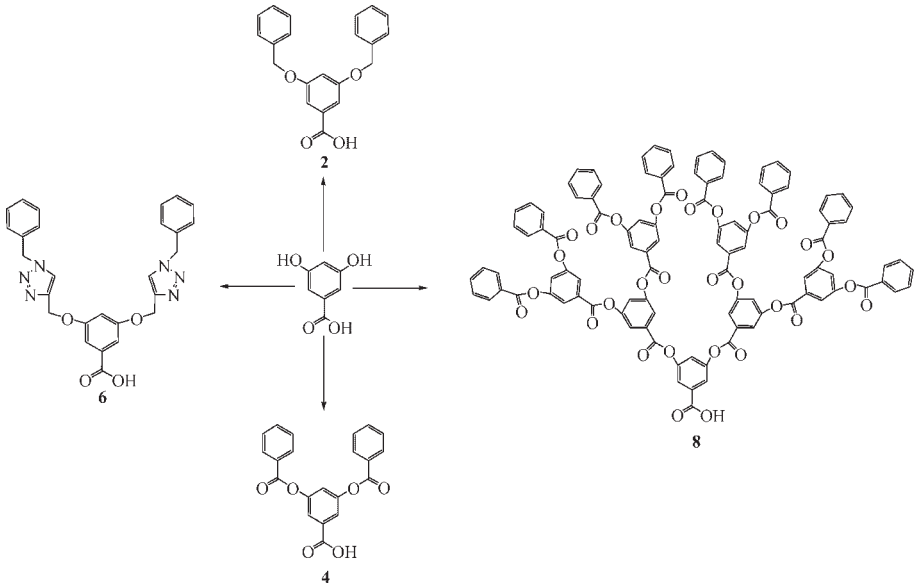
a first generation dendritic cellulose derivative characterized by ATR-FTIR spectroscopy.[10] Deprotection of the peripheric acetal groups and the conversion of the hydroxyl groups formed with 2,2-bis(hydroxymethyl)propionic acid anhydride resulted in higher generations of dendronized cellulose derivatives. It was assumed that the polymers formed nanoscaled, rod shaped objects. Newkome and co-workers studied the modification of cellulose with aminotriester based dendrons of different generations possessing an isocyanate focal group under homogeneous reaction conditions applying *N,N*-dimethyl acetamide (DMA)/LiCl as solvent.[11] Values of the degree of substitution (DS) of up to 1 could be realized. The aminotriester based dendrons were modified with different functions in the periphery and thus, various dendritic cellulose derivatives were prepared using a combinatorial type synthesis.[12] The authors discuss a regioselective reaction at position 6 of the anhydroglucose unit (AGU). However, the NMR spectra published clearly indicate that also a reaction at position 2 and 6 occurred with the isocyanate functionalized dendrons. The third generation of the aminotriester dendritic cellulose was used as a template to form and stabilize CdS quantum dots exhibiting luminescence properties.[13] Further studies illustrated the preparation of a poly(propylene imine) and poly(amido amine) cellulose derivative based on cyanoethyl cellulose with a DS of 2.9.[14] Only the first generation could be obtained without a high degree of imperfection in the structure of the introduced hyperbranched moieties. Zhang et al. synthesized two different types of dendronized cellulose applying a stepwise attachment of Behera's amine (aminotriester based dendrons) to carboxymethyl cellulose (DS 0.7). Subsequent conversion of the *tert*-butyl ester peripheric groups with *N,N*-dimethyl-1,3-propanediamine forms the water soluble derivative with second generation polyamide dendrons as the interior and aminoamide substitutes as hydrophilic tips.[15,16] Thermogravimetric analysis was used to determine the DS of Behera's amine that was found to be 0.37. The dendronized cellulose derivatives showed a much lower intrinsic viscosity compared to carboxymethyl cellulose used as starting material. Additional studies were carried out under varying reaction conditions in order to increase the DS; the highest value was 0.78. The peripheric groups were modified either with 3-chloro-2-hydroxypropyl trimethylammonium chloride or with alkyl halides of different chain length. The resulting polymers are claimed to possess antibacterial property due to the quaternization.[17]

Own Studies about Dendronized Cellulose

The aim of our studies was to synthesize dendritic cellulose derivatives by a polymer analogous reaction without using any spacer like carboxymethyl, hydroxyethyl etc., and to learn about the reactivity of cellulose with the bulky carboxylic acids and the substituent distribution of the dendritic cellulose derivatives.

The synthetic approach of the *in situ* activation of carboxylic acids applying *N,N′*-carbonyldiimidazole (CDI), characterized by the formation of the reactive carboxylic acid imidazolide as an intermediate, affords a broad variety of new and unconventional polysaccharide esters. The by-products formed are CO_2 and imidazole only and thus, they are non toxic.[18] Furthermore, the reaction of cellulose with the acid chloride is a versatile synthesis method as well. In this context various bulky compounds based on 3,5-dihydroxybenzoic acid (Scheme 1) were synthesized and used as starting materials for a homogeneous acylation of cellulose.

The esterification of cellulose with bulky carboxylic acids was studied applying *in situ* activation with CDI homogeneously under various reaction conditions. To dissolve cellulose, *N,N*-dimethyl acetamide (DMA)/LiCl and dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF) were applied.



Scheme 1.
Dendritic compounds based on 3,5-dihydroxybenzoic acid used for the homogeneous functionalization of cellulose.

Conversion of Cellulose with 3,5-Bis(benzyloxy)benzoic Acid Imidazolide or -Chloride

Prior to the esterification of cellulose with the bulky dendritic carboxylic acids, it was of interest to study optimal reaction conditions. 3,5-Bis(benzyloxy)benzoic acid was used for the esterification studies under variation of solvent, molar ratio, temperature and time of reaction as well as esterification agent.

Thus, 3,5-bis(benzyloxy)benzoic acid was allowed to react with CDI for 24 h at 70 °C in DMA yielding the corresponding imidazolide. Subsequently, the dissolved cellulose was added and allowed to react for 8–48 h at 80 °C. The activation of the carboxylic acid should be carried out at 70 °C; activation at room temperature leads to cellulose esters with significantly lower DS (compare samples **3c**, DS 0.29 and **3d**, DS 0.52 in Table 1). The DS values depend on the molar ratio of cellulose to reagent, as expected. The DS values increase from 0.12 (**3a**) to 0.72 (**3h**) with increasing molar ratio from 1:2 to 1:5 applying the well-known cellulose solvent DMA/LiCl, The conversion is complete after 24 h; a further prolongation of reaction time yields products of even lower DS (samples **3f** versus **3g**).

The influence of the cellulose solvent on the DS is quite interesting. At a rather low molar ratio, the reaction carried out in the novel solvent DMSO/TBAF is more efficient compared to DMA/LiCl (see samples **3a** and **3b**). However, comparable DS values are obtained at a molar ration of 1:3 (**3d**, **3f**).

Alternatively, homogeneous syntheses of cellulose[3,5-bis(benzyloxy)benzoate]s was carried out with the corresponding acid chloride in DMA/LiCl at 60 °C. DS values up to 0.68 (sample **3i**) were accessible indicating that the acid chloride is slightly more reactive compared to the carboxylic acid activated with CDI. However, the formation of the acid chloride is rather difficult and also HCl formed during the reaction may be a problem regarding a depolymerization of the cellulose backbone. Again a prolongation of the reaction time from 24 to 48 h results in a product of lower DS (**3k**). Consequently, the most

Table 1.
Reaction conditions and degree of substitution (DS) of the conversion of cellulose with dendritic 3,5-bis(benzyloxy)benzoic acid imidazolide (**3a–h**), with 3,5-bis-(benzyloxy)benzoyl chloride (**3i-k**) and with 3,5-bis(benzoyloxy)benzoic acid imidazolide (**5a–b**).

Molar ratio of anhydroglucose unit: reagent	Solvent[c)]	Temperature (°C)	Time (h)	No.	Product C-content (%)	DS
1:2	DMA/LiCl	80	24	**3a**	51.19	0.12
1:2	DMSO/TBAF	80	24	**3b**	56.01	0.25
1:3[a)]	DMSO/TBAF	80	24	**3c**	57.22	0.29
1:3	DMSO/TBAF	80	24	**3d**	62.11	0.52
1:3	DMA/LiCl	80	8	**3e**	54.11	0.19
1:3	DMA/LiCl	80	24	**3f**	62.79	0.56
1:3	DMA/LiCl	80	48	**3g**	59.67	0.39
1:5	DMA/LiCl	80	24	**3h**	64.86	0.72
1:3:5[b)]	DMA/LiCl	60	24	**3i**	64.51	0.68
1:3:5[b)]	DMA/LiCl	60	48	**3k**	59.53	0.39
1:3	DMA/LiCl	80	24	**5a**	57.32	0.39
1:3	DMA/LiCl	80	36	**5b**	59.02	0.49

[a)]Activation of the carboxylic acid with CDI at room temperature;
[b)]5 mole pyridine;
[c)]*N,N*-Dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), tetrabutylammonium fluoride trihydrate (TBAF).

suitable reaction parameters for the homogeneous conversion of cellulose with the bulky aryl polyester acid are reactions applying the acid imidazolide (formed *in situ* with CDI) at a molar ratio of 1:3 (anhydroglucose unit:carboxylic acid) at 80 °C for 24 h.

The structure of the cellulose[3,5-bis(benzyloxy)benzoate] derivatives was confirmed by FTIR- and NMR spectroscopy. The typical signal for the carbonyl function in the FTIR spectrum is visible at 1724 cm^{-1}. Moreover, signals for the aromatic moieties introduced can be observed in the range from 3089 to 3062 and from 1596 to 1440 cm^{-1}. Cellulose[3,5-bis(benzyloxy)benzoate]s are well soluble in organic solvents including DMSO, DMA, *N,N*-dimethyl formamide (DMF) and yielded well-resolved NMR spectra. Besides the signals for the carbon atoms of the anhydroglucose unit (AGU) at $\delta = 102.8$ to 60.9 ppm in the ^{13}C NMR spectrum (Figure 1), resonances assigned to

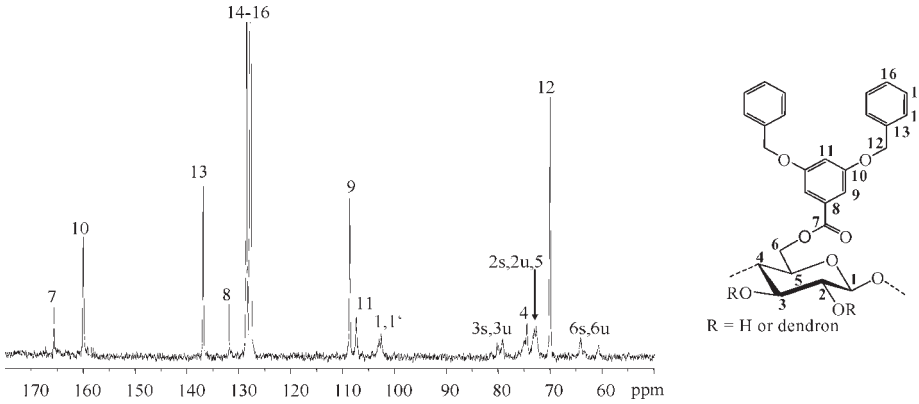


Figure 1.
^{13}C NMR spectrum of cellulose[3,5-bis(benzyloxy)benzoate] (**3i**, DS 0.68) recorded in DMSO-d_6 at 70 °C.

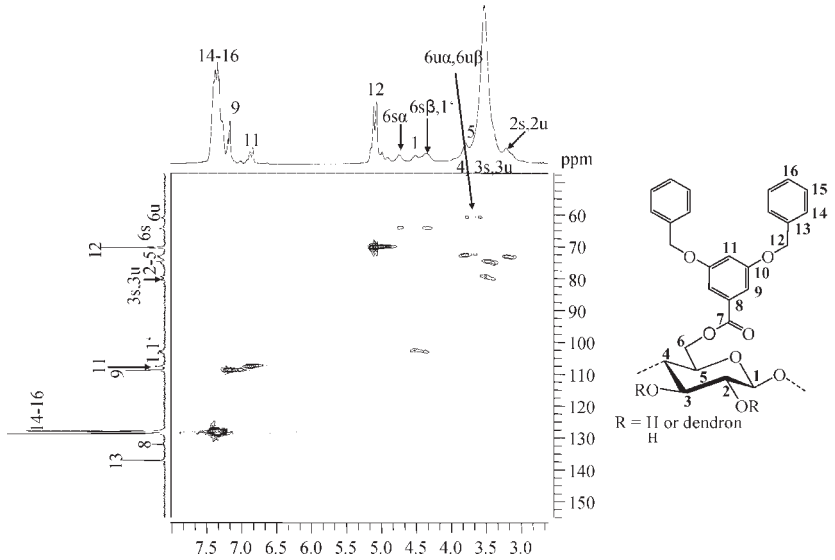


Figure 2.
HSQC-DEPT NMR spectrum of cellulose[3,5-bis(benzyloxy)benzoate] (**3i**, DS 0.68) recorded in DMSO-d_6 at 70 °C.

the aromatic carbon atoms of the 3,5-bis(benzyloxy)benzoate moieties are visible between $\delta = 159.9$ (C-7) and 107.8 (C-11) ppm. Other characteristic signals were found at $\delta = 165.6$ ppm for the carbonyl groups of the ester moiety and at $\delta = 70.2$ ppm for the CH_2 moiety (C-12) of the peripheric phenyl groups. The peak for the acylated position 6 (C-6s) appears at $\delta = 64.3$ ppm. In addition, the spectrum shows a signal at $\delta = 102.8$ ppm, corresponding to C-1 adjacent to a position 2 bearing a 3,5-bis(benzyloxy)benzoate moiety. These results indicate that a functionalization of position 2 and 6 appeared.

In addition, HSQC-DEPT spectrum of sample **3i** was measured in order to get more detailed information about the functionalization pattern (Figure 2). The reaction of the bulky 3,5-bis(benzyloxy)benzoate moiety occurred at all reactive sites. To assign the signals of the HSQC-DEPT spectrum, ^{1}H, ^{1}H-COSY NMR was used (not shown). Protons of the aromatic moieties are visible in the range $\delta = 7.41$ to 7.19 ppm for the peripheric phenyl groups and $\delta = 7.16$ to 6.83 ppm for the inner aryl moiety. The signals of the protons of C-12 appear at $\delta = 5.07$ ppm. Signals of the AGU are observed between $\delta = 3.12$ to 4.71 ppm. Thus, the bulky groups possess no pronounced regioselectivity. It becomes obvious that the carboxylic acids of Fréchet-type dendrons studied show an external bulk of the focal moiety while an internal bulk is missing that would lead to a regioselective reaction.

Conversion of Cellulose with 3,5-Bis(benzoyloxy)benzoic Acid Imidazolide

For the preparation of cellulose[3,5-bis(benzoyloxy)benzoate], 3,5-bis(benzoyloxy)-benzoic acid imidazolide was allowed to react with cellulose dissolved in DMA/LiCl for 24 or 36 h at 80 °C. Pure cellulose[3,5-bis(benzoyloxy)benzoate]s (**5a–b**) could be obtained by precipitation of the product in ethanol and reprecipitation from DMSO in methylene chloride. Samples with a DS value of 0.39 (**5a**, 24 h) and 0.49 (**5b**, 36 h) were obtained.

The structure of the cellulose[3,5-bis(benzoyloxy)benzoate]s could be confirmed by signals characteristic for the aromatic moieties introduced at 3066,

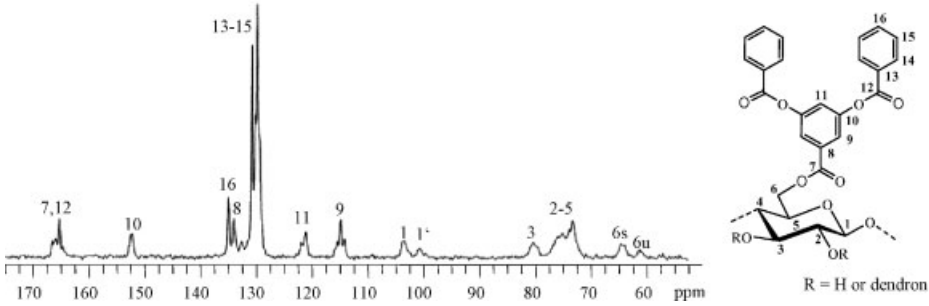


Figure 3.
^{13}C NMR spectrum of cellulose[3,5-bis(benzoyloxy)benzoate] (**5b**, DS 0.49) recorded in DMSO-d_6 at 70 °C.

1599 and 1450 cm^{-1} as well as for the carbonyl functions at 1731 cm^{-1} in the FTIR spectrum. Figure 3 shows the ^{13}C NMR spectrum of polymer **5b** recorded in DMSO-d_6 at 70 °C. The characteristic signals of the AGU carbon atoms (C-1 to C-6) are visible between $\delta = 60.1$ and 103.2 ppm.

Resonances at $\delta = 134.6$ and 129.0 to 130.0 ppm are assigned to the carbons C-13 to C-16 of the peripheric aromatic moieties. The signal at $\delta = 151$ ppm is attributed to the carbon atoms of the 3,5-branching unit. The peaks for the carbonyl functions at C-7 and C-12 are found between $\delta = 163$ and 165 ppm. The cellulose[3,5-bis(benzoyloxy)benzoate] derivatives are well soluble in addition in DMA and DMF.

Conversion of Cellulose with 3,5-Bis((1-benzyl-triazolo)-4-methoxy)Benzoic Acid

According to the conditions of the homogeneous conversion of cellulose with 3,5-bis(benzyloxy)benzoic acid, the reaction of the even more bulky 3,5-bis((1-benzyl-triazolo)-4-methoxy)benzoic acid imidazolide with cellulose was studied. The bulky acid was allowed to react with CDI for 24 h at 80 °C and subsequently the cellulose dissolved in DMA/LiCl was added. After a reaction time of 24 h at 80 °C, the product was isolated by a typical work-up procedure resulting in a cellulose ester with a low DS value of 0.28. Structural elucidation was possible by FTIR- and NMR spectroscopy. New signals appear due to the introduced 3,5-bis((1-benzyl-triazolo)-4-methoxy)benzoic acid moiety at 3063, 1599, and 1450 cm^{-1} for the aromatic moieties and at 1716 cm^{-1} for the carbonyl function of the new ester linkage. The cellulose ester is soluble in DMSO, DMA and DMF and well resolved NMR spectra were obtained. In the ^{13}C NMR spectrum (not shown) characteristic signals for the carbon atoms of the outer aromatic moieties can be observed at $\delta = 136.3$ (C-16) and between $\delta = 129.2$ to 128.4 (C-17-19) ppm. The peaks for the inner aromatic group are assigned to $\delta = 132.2$ (C-8), 109.2 (C-9) and 107.6 ppm for C-11. Besides the signals for the carbon atoms of the modified AGU ($\delta = 103.2$ to 60.9 ppm), characteristic resonances assigned to the 3,5-branching unit at C-10 at $\delta = 159.7$ ppm and at 143.3 and 125.0 ppm attributed to the carbon atoms of the triazole moiety can be observed.

In order to get information of the functionalization pattern, HSQC-DEPT NMR spectroscopy was applied (Figure 4). It is interesting to note that the conversion of cellulose with the very bulky 3,5-bis((1-benzyl-triazolo)-4-methoxy)benzoic acid imidazolide leads to a cellulose ester only substituted at position C-6. This may be attributed due to increase of the sterical demand and the rather small DS. Furthermore, assignment of the protons of the introduced bulky carboxylic acid moiety was possible. The signals for the protons of the peripheric aromatic groups are attributed to $\delta = 7.30$ to 7.33 ppm. The protons of the inner aromatic moieties appear at $\delta = 7.25$ (H-9) and 7.01 (H-11) ppm and

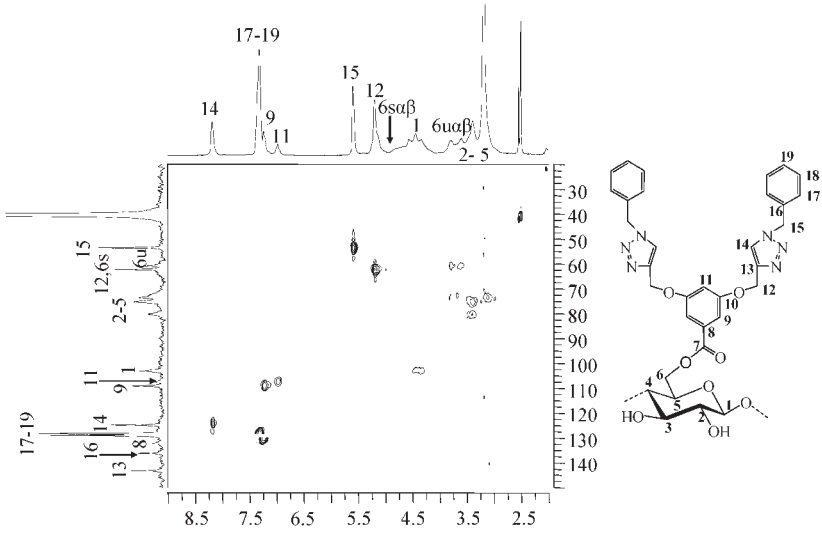
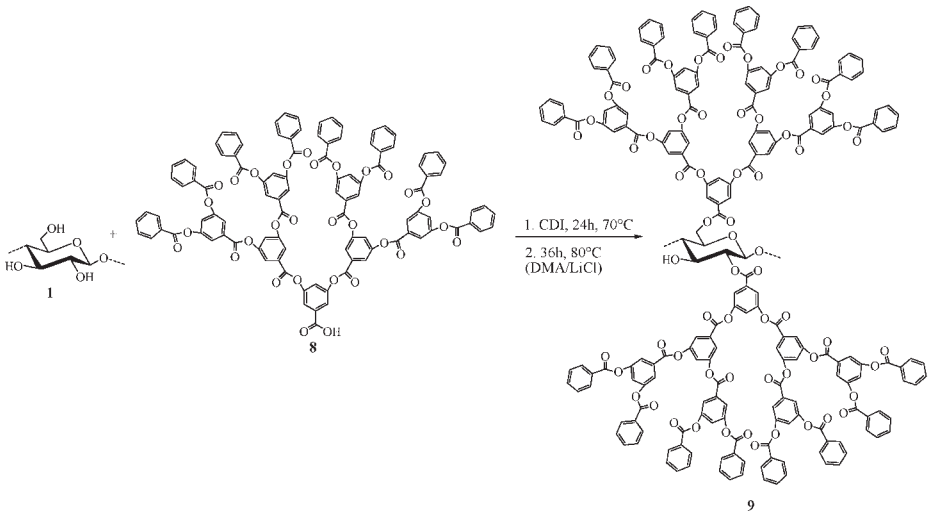


Figure 4.
HSQC-DEPT NMR spectrum of cellulose[3,5-bis((1-benzyl-triazolo)-4-methoxy)benzoate] (**7**, DS 0.28, recorded in DMSO-d_6 at 60 °C).

the proton of C-14 of the triazole linker is visible at $\delta = 8.19$ ppm. Signals for the AGU protons could be observed at $\delta = 3.12$–3.42 ppm (H-2-5). Due to incomplete substitution of position 6, signals appear at $\delta = 4.60$ to 4.31 ppm according to substituted position 6 and at $\delta = 3.58$-3.85 ppm attributed to the unmodified position 6.

Conversion of Cellulose with Third Generation of Aryl Polyester Dendritic Acid Applying Activation with CDI

The introduction of the bulky third generation 3,5-bis(3,5-bis(3,5-bis(benzoyloxy)-benzoyloxy)benzoyloxy)benzoic acid (**8**) into the cellulose backbone was also possible by the homogeneous conversion



Scheme 2.
Acylation of cellulose with 3,5-bis(3,5-bis(3,5-bis(benzoyloxy)benzoyloxy) benzoyloxy)benzoic acid (**8**).

of the polymer dissolved in DMA/LiCl after the *in situ* activation of the carboxylic acid with CDI (Scheme 2). The pure cellulose[3,5-bis(3,5-bis(3,5-bis (benzoyloxy)-benzoyloxy)benzoyloxy)benzoate] (**9**) could be obtained simply by precipitation of the product in ethanol and purification by reprecipitation from DMSO in methylene chloride. The DS value determined by elemental analysis is 0.21 after a reaction time of 36 h.

The polymer **9** is soluble in polar aprotic solvents including DMSO, DMF, DMA and *N*-methylpyrrolidone and yields a well-resolved ^{13}C NMR spectrum as shown in Figure 5. Besides the signals for the carbon atoms of the modified AGU ($\delta = 103.9$ to 61.0 ppm), resonances assigned to the carbon atoms of the carbonyl groups of the ester functions at $\delta = 163.2$ to 165.1 ppm (C-7, 12, 17 and 22) as well as resonances of the 3,5-branching units at $\delta = 151.3$ ppm (C-10, 15 and 20) could be determined. The peaks at 134.3 ppm and between $\delta = 129.3$ to 130.5 ppm appear from the carbon atoms of the exterior aromatic moieties. Due to esterification of position 6, the spectrum shows a peak at $\delta = 63.5$ ppm (C-6s). In addition, the signal at $\delta = 100.2$ ppm corresponds to C-1′ adjacent to position 2 influenced by esterification. Thus, esterification of cellulose with the bulky 3,5-bis(3,5-bis(3,5-bis-(benzoyloxy)benzoyloxy)benzoyloxy)benzoic acid takes place at positions 2 and 6 of the AGU that is remarkable considering the rather low total DS of 0.21.

Conclusion

The homogenous conversion of cellulose dissolved either in DMA/LiCl or in the novel solvent DMSO/TBAF with carboxylic acid-containing dendrons leads to novel polysaccharide esters with bulky functional groups. The carboxylic acid moieties were efficiently activated *in situ* applying CDI or as acid chloride. Novel bulky cellulose esters could be obtained with DS values ranging from 0.12 to 0.72. NMR spectroscopy has proved to be a suitable tool to gain detail information about the structure of the cellulose derivatives synthesized for the first time. It is important to note that although the dendrons are bulky, the reaction occurred not only at position 6 (primary hydroxyl group) but also at the secondary position 2. The biopolymer derivatives obtained are soluble in aprotic polar solvents and can be shaped to films of particles.

The investigations about dendronized cellulose will be continued with regards to

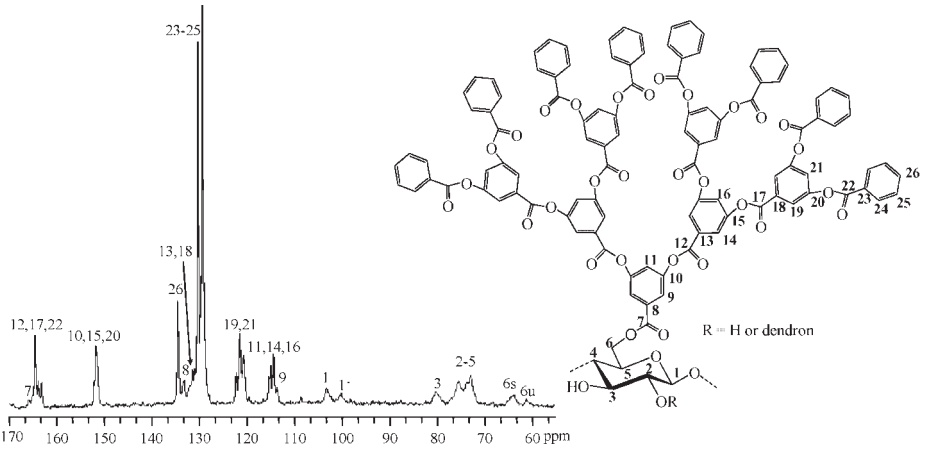


Figure 5.
^{13}C NMR spectrum of cellulose[3,5-bis(3,5-bis(3,5-bis(benzoyloxy)benzoyloxy) benzoyloxy)benzoate] (**9**, DS 0.21) recorded in DMSO-d_6 at 70 °C.

the structure-property-relationships of the new products, the use of different dendritic systems including the variation of the peripheric groups and the synthesis of regioselectively dendronized cellulose derivatives. One approach in this regard is the conversion of 6-azido-6-deoxy cellulose with polyamidoamine (PAMAM) dendrons possessing an ethynyl focal moiety via the copper catalyzed Huisgen reaction (click reaction).[19]

Experimental Part

Materials

Avicel®-PH 101 (DP 280) was purchased from FMC and was dried for 4 h at 110 °C before use. *N*,*N*′-carbonyldiimidazole (CDI) and pyridine were obtained from Fluka. LiCl is a Merck product. All reagents were used without further purification. Acetone, dimethyl sulfoxide (DMSO), *N*,*N*-dimethyl acetamide (DMA) and ethanol were reagent grade chemicals.

Measurements

FTIR spectra were recorded on a Nicolet Avatar 370 spectrometer using the KBr-technique. The one- (^{1}H- and ^{13}C-NMR) and two-dimensional (^{1}H,^{1}H-COSY and HSQC) spectra were acquired on a Bruker AVANCE 400 spectrometer in DMSO-d_6 at 70 °C. For ^{1}H NMR spectra 16 scans and for ^{13}C NMR spectra 12,000–16,000 scans were accumulated.

Methods

The cellulose was dissolved in DMA/LiCl as described in reference[20] and in DMSO/tetrabutylammonium fluoride trihydrate (TBAF) following the procedure described in reference.[21] The aryl polyester dendrons were prepared according to reference[22] and the conversion of the aryl polyester dendritic carboxylic acids with cellulose was carried out as described in reference.[23] 3,5-Bis((1-benzyl-triazolo)-4-methoxy)benzoic acid was obtained by a combinatorial synthesis according to references.[24,25]

Preparation of Cellulose[3,5-Bis((1-benzyl-triazolo)-4-methoxy)benzoate] (7) Applying CDI

3,5-Bis((1-benzyl-triazolo)-4-methoxy)benzoic acid (**6**, 6.5 g, 13.1 mmol) was activated with (2.1 g; 13.1 mmol) CDI in 50 ml DMA for 24 h at 70 °C. Subsequently, 0.7 g (4.36 mmol) cellulose dissolved in 25.6 ml DMA/LiCl was added and the mixture was stirred for further 24 h at 80 °C. Isolation of the product was carried out by precipitation in 400 ml of a 1:1 mixture of methanol/water, washing once with methanol/water (1:1; 350 ml) and afterwards with methanol (400 ml). The product was purified by reprecipitation from DMSO into 250 ml acetone and washing twice with 250 ml of acetone. After filtration the polymer was dried in vacuum at 60 °C (**7**).

DS: 0.28 (calculated from N-content determined by EA).

EA: Found N 7.94%, C 52.86% and H 5.54%; Calculated (for DS 0.28) C 53.73% and H 5.64.

IR (KBr): ν (cm^{-1}) = 3 440 (OH), 3 063 (C–H_{arom}), 2 890 (C–H and CH_2), 1 716 (C=O), 1 599, 1 450 (C–C_{arom}), 1 264, 1 063 cm^{-1} (C–O–C).

^{1}H NMR (DMSO-d_6): δ = 3.12–3.42 (H-2-5, AGU), 3.58-3.85 (H-6u$\alpha\beta$, AGU), 4.42 (H-1, AGU), 4.60–4.31 (H-6s$\alpha\beta$, AGU), 5.20 (H-12), 5.60 (H-15), 7.01 (H-11), 7.25 (H-9), 7.32 (H-17-19), 8.19 (H-14).

^{13}C NMR (DMSO-d_6): δ = 165.64 (C-7), 159.72 (C-10), 143.29 (C-13), 136.31 (C-16), 132.22 (C-8), 129.18-128.38 (C-17-19), 124.97 (C-14), 109.18 (C-9), 107.58 (C-11), 103.25 (C-1), 80.46-75.65 (C-2-5), 63.15 (C-6s), 62.31 (C-12), 60.92 (C-6u), 53.50 (C-15).

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