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Unconventional Reactivity of Cellulose Dissolved in Ionic Liquids

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Summary: Ionic Liquids (IL) were applied as solvent and reaction medium in the field of homogeneous cellulose chemistry. Whereas investigations on tosylation and nucleophilic displacement reactions lead to unexpected products the application of the Huisgen reaction was successful. The standard conditions for tosylation of cellulose using the IL 1-ethyl-3-methylimidazolium acetate (EMImAc) as solvent lead exclusively to cellulose acetate, due to activation of the acetate ion of the IL by forming a mixed anhydride with *p*-toluenesulfonyl chloride. Further investigations showed that the anions of EMImAc and 1-ethyl-3-methylimidazolium chloride (EMImCl) are able to act as nucleophiles, thus substituting tosyl groups of tosylcellulose and forming unexpected products. Using EMImAc as solvent first to third generation propargyl-polyamidoamine (PAMAM) dendrons were attached to 6-azido-6-deoxy cellulose (degree of substitution, DS 0.75) utilising the copper catalysed Huisgen reaction leading to novel dendronized cellulose derivatives with DS values of up to 0.60. Detailed structure characterisation of the products, including elemental analysis, FTIR and NMR spectroscopy, indicates that the synthesis approach leads to products without impurities or remaining IL.

Keywords: 6-azido-6-deoxy cellulose; cellulose; dendrons; Huisgen reaction; ionic liquid; NMR

Introduction

Being the most widely available biopolymer and possessing the uniform structure of a β-1-4-linked polyglucan, increasing attention is paid to cellulose and its derivatives to replace oil-based products and materials. Three hydroxyl groups per anhydroglucose repeating unit allow a versatile structure design due to chemical modification.[1,2] Using advanced organic chemistry under homogeneous reaction conditions new avenues for innovative products are opened. In a pioneering work of Newkome, aminotriester-based dendrons of different generations possessing an isocyanate focal group were allowed to react with cellulose dissolved in *N,N*-dimethyl aceteamide(DMA)/LiCl, resulting in the synthesis and characterisation of dendronized cellulose with DS values of up to one.[3–5] The reaction of cellulose with the carboxylic acid groups of aryl polyester dendrons applying *N,N*′-carbonyldiimidazole as activation agent was proven to be a successful path to modify cellulose dissolved in DMA/LiCl or in the novel solvent system consisting of DMSO and tetrabutylammonium fluoride.[6] Despite the bulkiness of the dendrons no regioselective conversion occurred, in addition the recycling of mixtures of polar aprotic solvent and salt proved to be rather difficult.

Increasing attention is paid to a new type of cellulose solvent, namely ionic liquids. They are exhibiting not only a high chemical and thermal stability,

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nonflammability and a negligible vapour pressure, but also the recycling of these solvents is comparably easy. Therefore homogeneous cellulose functionalization applying IL as solvent and reaction media is promising even under commercial conditions.[7] Typical esterification and etherification reactions of cellulose performed in IL proved to be successful, resulting in cellulose acetates,[8,9] trimethylsilyl-[10] and triphenylmethyl cellulose[11] of different DS values, showing the efficiency of this novel type of solvents for the biopolymer.

In the frame of our studies to prepare novel and unconventional cellulose derivatives in combination with the investigation of IL as solvent, the question appeared if application of these solvents leads to a different regioselective functionalization. Thus, our goal was to transfer the three steps of preparation of dendronized cellulose, namely tosylation of cellulose, nucleophilic displacement leading to azidodeoxycellulose and linking of propargyl polyamidoamine dendrons using the copper catalysed Huisgen reaction, into IL and compare the products with those synthesised using conventional solvents.

Experimental Part

Solvents and Reagents

Cellulose (Modo 500, Modo Paper Domsjö, Sweden, degree of polymerization, DP 500) was dried under vacuum at 110 °C for 3 h before use. *p*-Toluenesulfonyl chloride was purchased from Merck. $CuSO_4 \cdot 5\ H_2O$ and sodium ascorbate were obtained from Acros. DMA was obtained from Riedel de Haën and sodium azide from Alfa Aesar. Imidazole was obtained from Alfa Aesar. 1-Ethyl-3-methylimidazolium acetate and 1-Ethyl-3-methylimidazolium chloride was purchased from BASF. All reagents were used without further purification.

Measurements

FTIR spectra were recorded on a Nicolet Avatar 370 spectrometer using the KBr-technique. The ^1H and ^{13}C NMR spectra were acquired on a Bruker AVANCE 400 spectrometer in DMSO-d_6 at 25 °C. For ^1H NMR spectra 16,000 scans and for ^{13}C NMR spectra 8,000–16,000 scans were accumulated. Elemental analyses (EA) were performed with a Vario El III from Elementar Analysensysteme, Hanau, Germany.

Dissolution of Cellulose in N,N-dimethyl acetamide/LiCl

5 g (30.9 mmol) Cellulose were suspended in 200 ml of DMA and stirred at 130 °C for 2 h. After the slurry had been allowed to cool to 100 °C, 10 g of anhydrous LiCl were added. By cooling to room temperature and stirring the cellulose dissolves completely.

Dissolution of Cellulose in IL

The IL (16 g) was heated to 80 °C. 0.5 g (3.09 mmol) cellulose was mixed with the melted IL and the mixture was stirred at this temperature for 2 h yielding an optically clear solution.

Tosylation of Cellulose

To a solution of 20 g (123.46 mmol) cellulose in DMA/LiCl a mixture of 59.4 ml (427.2 mmol) triethylamine and 40.6 ml DMA was added under stirring. After cooling to about 8 °C and stirring, a solution of 40.7 g (213.6 mmol) *p*-toluenesulfonyl chloride in 60 ml DMA was added dropwise within 0.5 h. The homogeneous reaction mixture was stirred for 24 h at 8 °C, and then slowly poured into 5 l of ice water. The precipitate was filtered off, washed carefully with about 15 l of distilled water and 2 l of ethanol, suspended in 1 l of acetone and reprecipitated into 3 l of distilled water. After filtration and washing with ethanol, the sample was dried at 50 °C under vacuum.

FTIR (KBr, cm^{-1}): 3523 (OH), 3072 (CH_{arom}), 2891 (CH), 1598, 1500, 1453 (CC_{arom}), 1364 (SO_2), 1177 (SO_2), 1177 (SO_2), 814 (CH_{arom}).

^{13}C NMR (400 MHz, DMSO-d_6, ppm): 21.2 (CH_3), 59.0–101.4 (cellulose backbone), 127.8–145.1 (CH_{arom}).

Reaction of Cellulose with p-Toluenesulfonyl Chloride in EMImAc

Imidazole (2.1 g, 30.9 mmol) was added to a solution of 1 g of cellulose dissolved in 32 g EMImAc and stirred for 12 h at 25 °C. The temperature was decreased to 7 °C and 2.3 g (12.3 mmol) *p*-toluenesulfonyl chloride were carefully added. The homogeneous reaction mixture was stirred for 5 h and then precipitated into 300 ml of ethanol and the polymer was collected by filtration. After washing three times with 100 ml of a 4:1 (v/v) mixture of ethanol/water the sample was dried at 60 °C under vacuum.

$DS_{Acetate}$: 0.55 (determined by ^1H NMR spectroscopy after perpropionylation)

FTIR (KBr, cm^{-1}): 3409 (OH), 2889 (CH_2), 1726 (C=O ester), 1232 (COC ester).

^{13}C NMR of the perpropionylated derivative (400 MHz, $CDCl_3$, ppm): $\delta = 170.2–169.2$ (CO), 100.3 (C-1), 75.8–71.7 (C-2_s-5), 62.0 (C-6), 20.7 (CH_3).

^1H NMR of the perproionylated derivative (400 MHz, $CDCl_3$, ppm): $\delta = 5.1–3.5$ (cellulose backbone, H_{ester}), 2.4–2.2 (CH_2 propionate), 2.1–1.9 (CH_3 acetate), 1.2–1.0 (CH_3 propionate).

Preparation of Azidodeoxycellulose from Tosylcellulose

To a solution of 28.0 g (100.6 mmol) tosylcellulose (DS = 0.75) in 200 ml DMF 32.8 g (504.6 mmol) NaN_3 were carefully added and the solution was stirred at 100 °C for 24 h. After cooling to room temperature the polymer was precipitated into 1 l of water, filtered of and subsequently washed five times with 300 ml of water and five times with 250 ml of ethanol. The product was dried at 60 °C under vacuum.

DS_{Azide}: 0.75 (calculated from *N*-content determined by EA).

FTIR (KBr, cm^{-1}): 3404 (OH), 2103 (N_3), 1033 (O–C–O).

Reaction of Tosylcellulose with Sodium Azide in EMImCl

To a solution of 1 g (2.77 mmol) tosylcellulose (DS = 1.33) in 32 g EMImCl 0.88 g (13.6 mmol) NaN_3 were added. After stirring for 2 h the polymer was precipitated into 300 ml ethanol, filtered of and subsequently washed fife times with 50 ml of water and 50 ml of ethanol. The product was dried at 60 °C under vacuum.

DS: Azide 0.42; Cl 0.37; Tosyl 0.25 (calculated from *N*-, *Cl*- and *S*-content determined by EA).

FTIR (KBr, cm^{-1}): 3408 (OH), 2107 (N_3), 1028 (O–C–O).

Elemental Analysis: C 39.75%, H 4.85%, N 8.08%, S 3.61%, Cl 6.1%.

Preparation of PAMAM-Triazolo Cellulose (4–6)

To the solution of 6-azido-6-deoxy cellulose (DS 0.75, 0.5g, 2.78 mmol) in 16 g EMImAc, the propargyl –PAMAM dendron, $CuSO_4$ 5 H_2O (0.1 g, 0.41 mmol, in 0.5 ml of water) and sodium ascorbate (0.2 g, 1.02 mmol, in 1 ml of water) were added. The mixture was stirred at 25 °C for 24 h for the first an second generation and for 72 h for the third generation. Isolation was carried out by precipitation in 200 ml ethanol, washing two times with 100 ml ethanol, dissolution in 10 ml DMSO, reprecipitation in 200 ml ethanol and washing three times with ethanol for the first generation. Second and third generation were diluted with 20 ml of ethanol and dialysed for 5 days against water. All products were dried in vacuum at 60 °C.

First Generation PAMAM-Triazolo Cellulose (4)

DS: 0.60 (calculated from *N*-content determined by EA).

FTIR (KBr, cm^{-1}): 3410 (OH), 2108 (N_3), 1723 (C=O), 1025 (C–O–C).

^{13}C NMR (400 MHz, DMSO-d_6, ppm): 172.8 (C=O), 143.7, 125.2 ($C{=}C_{Triazole}$), 103.2–60.9 (C-1-C-6_{OH}, AGU), 51.4–50.0 (C-$6_{Triazole}$, C-6_{Azide}, AGU), 51.5 (CH_3), 48.8, 32.8 (CH_2).

^1H NMR (400 MHz, DMSO-d_6, ppm): 7.97 ($H_{Triazole}$), 5.4–3.4 (H, AGU), 3.59 (CH_3), 2.8–2.4 (CH_2).

Second generation PAMAM-Triazolo Cellulose (5)

DS: 0.48 (calculated from N-content determined by EA).

^{13}C NMR (400 MHz, DMSO-d_6, ppm): 172.9, 172.2 (C=O), 103.0–61.0 (C-1-C-6_{OH}, AGU), 52.0–51.0 (C-$6_{Triazole}$, C-6_{Azide}, AGU), 51.7 (CH_3), 52.6, 49.7, 49.3, 33.7, 32.7 (CH_2).

^{1}H NMR (400 MHz, DMSO-d_6, ppm): 7.8 ($H_{Triazole}$), 5.4–3.4 (H, AGU), 3.6 (CH_3), 3.3–2.3 (CH_2).

Third generation PAMAM-Triazolo Cellulose (6)

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

^{13}C NMR (250 MHz, DMSO-d_6, ppm): 174.4, 172.9, 171.7 (C=O), 143.1, 125.4 (C=$C_{Triazole}$)103.0–61.6 (C-1-C-6_{OH}, AGU), 52.5–52.1 (C-$6_{Triazole}$, C-6_{Azide}, AGU), 51.7 (CH_3), 49.5–32.1 (CH_2).

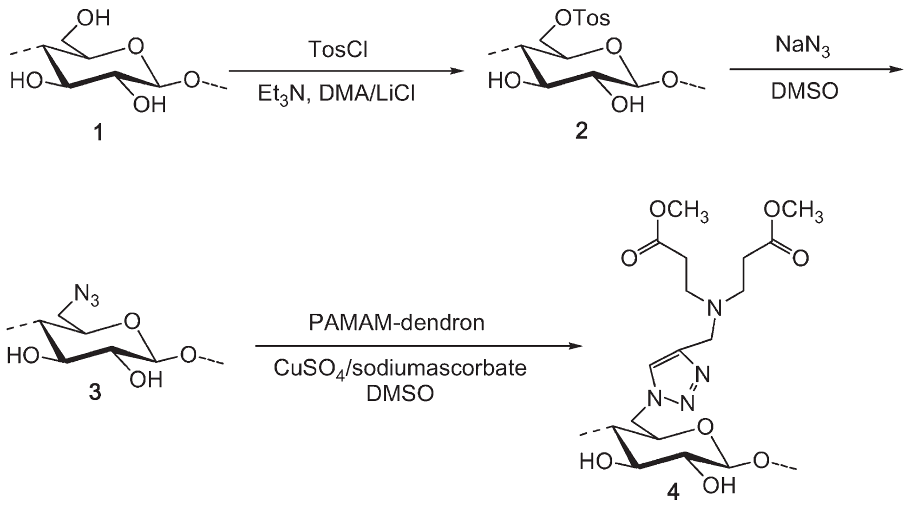
^{1}H NMR (250 MHz, DMSO-d_6, ppm): 7.85 ($NH_{Dendron}$), 3.56 (CH_3), 3.34–2.10 (CH_2), the protons of the AGU are not visible because of a strong line broadening.

Results and Discussion

The aim of our studies was the transfer of the three synthesis steps that are conventional carried out in typical organic solvents into ILs (Scheme 1). We used primarily the IL 1-ethyl-3-methylimidazolium acetate, due to the low melting point, allowing reactions without diluting even at low temperatures.

Studies of the Tosylation in EMImAc

The first step of synthesis contained the preparation of tosylcellulose. Commonly tosylcellulose is prepared in DMA/LiCl solutions of cellulose applying *p*-toluenesulfonyl chloride as reagent and triethylamine as base at low temperatures, to prevent side reactions resulting in chlorodeoxycellulose. Due to the immiscibility of triethylamine in EMImAc, imidazole was used as base whereby a homogeneous solution was obtained. After cooling a solution of cellulose and imidazole in EMImAc to 8 °C, *p*-toluenesulfonyl chloride was added and the mixture was stirred for 5 h. Subsequent workup of the reaction mixture resulted in an organo-soluble product. Though neither elemental analysis nor IR spectroscopy showed any sulphur present in the product. Further NMR analysis showed typical peaks for ester moieties at 170 ppm and for a methyl group at 20.93 ppm (Figure 1). Therefore, the solubility of the product in DMSO was a result of the formation of cellulose acetate.



Scheme 1.
Synthesis route for PAMAM-triazolo cellulose using conventional solvents.

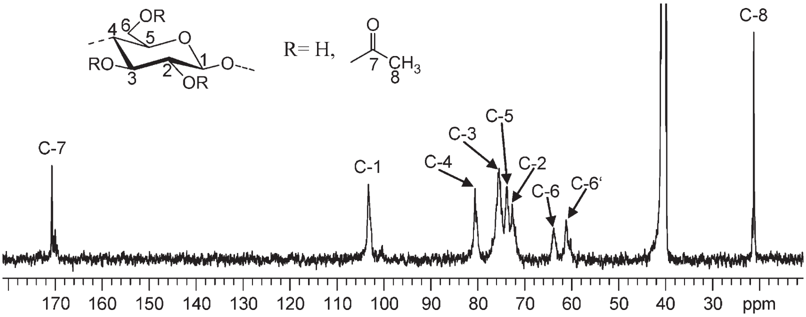


Figure 1.
^{13}C NMR spectrum of cellulose acetate obtained by reaction of cellulose with *p*–toluenesulfonyl chloride in EMImAc, recorded in DMSO-d_6 at 25 °C.

An inspection of the reagents used shows, that the formation of cellulose acetate is only possible by a reaction of the acetate anion of the ionic liquid with the dissolved cellulose.

In order to investigate this unexpected reaction, a model system consisting of EMImAc and *p*-toluenesulfonyl chloride was studied by NMR spectroscopy. It was assumed that the EMImAc reacts with the *p*-toluenesulfonic acid to a mixed anhydride, which acts as acetylating agent and consequently forms cellulose acetate.

From the ^{13}C NMR spectrum (Figure 2) it is obvious that there are two different types of carbonyl moieties. At 172 ppm appears the more deshielded carbon atom C-7 of the acetate anion whereas at 167.4 ppm the atom C-7′ is visible, which is bound in the mixed anhydride.

The methyl moiety splits up into two signals; at 21.4 ppm appears the peak of the acetate anion, whereas at 22.3 ppm the peak of the methyl moiety in the mixed anhydride appears. Using a typical squared sinusoidal window function for transforming the FID data enables the detection of the splitting of the aromatic carbon atom next to the methyl moiety of the *p*-toluenesulfonyl group (C-10, C10′).[12]

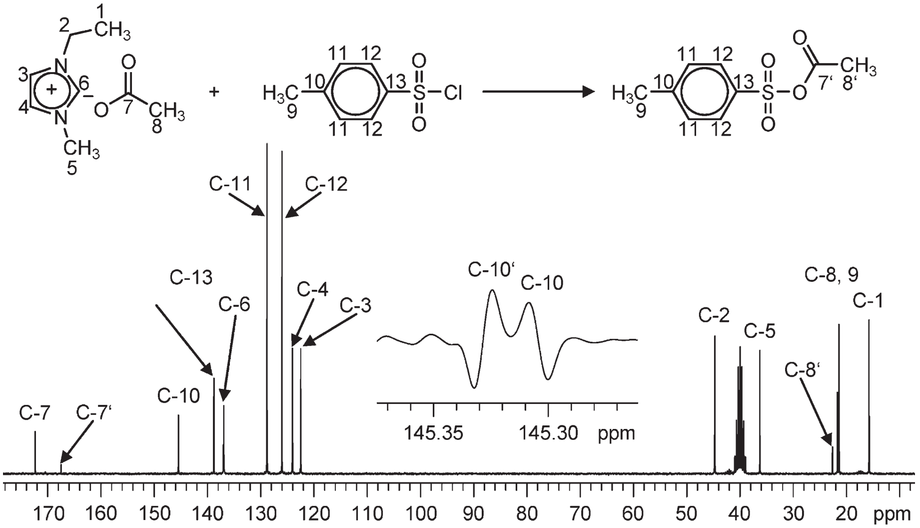


Figure 2.
^{13}C NMR spectrum of a mixture of *p*-toluenesulfonyl chloride and EMImAc in DMSO-d_6 after 24 h at 25 °C.[12]

p-Toluenesulfonyl moieties are also well known leaving groups in nucleophilic displacement reactions. Thus, the formation of cellulose acetate could be the result of a displacement of *p*-toulenesulfonyl groups of intermediary formed tosyl cellulose by the acetate anions sufficiently available in EMImAc. Therefore, the behaviour of cellulose tosylate (DS = 1.33), dissolved in EMImAc at 70 °C, was investigated by FTIR-spectroscopy and elemental analysis of samples taken after different time intervals. A clear decrease in DS of tosyl moieties down to 0.14 after 4 h was observed, on one hand. On the other, the introduction of acetyl moieties could be observed using FTIR spectroscopy. An increase in the signal intensity of the carbonyl moiety of the acetate group at 1734 cm^{-1} and a decrease in the intensity of the tosyl group at 1176 cm^{-1} was observed (Figure 3), indicating the substitution of tosyl moieties by acetate groups. The nitrogen content of the isolated cellulose acetate was amounted to be 0.08%, thus confirming that the acetate peaks do not result from incorporated IL.

Consequently, the acetylation caused by the conversion with tosyl chloride could be a combination of both mechanisms, i.e. acetylation by nucleophilic displacement of the tosyl group and by the reaction with the mixed anhydride formed.

Preparation of Azidodeoxycellulose

Conventionally, the preparation of azidodeoxycellulose originating from tosylcellulose occurs in DMF at a temperature of 100 °C. Therefore, we used apart from EMImAc the IL EMImCl, which has a higher melting point of 85 °C. In both cases the azide anion reacted with the tosyl moiety forming azidodeoxycelluose, as could be observed at the azide peak in the FTIR spectra (not shown) at 2100 cm^{-1} and at the increasing nitrogen content determined by elemental analysis. Nevertheless, besides the azide peak there was also a carbonyl ester peak at 1750 cm^{-1} clearly visible, when using EMImAc as

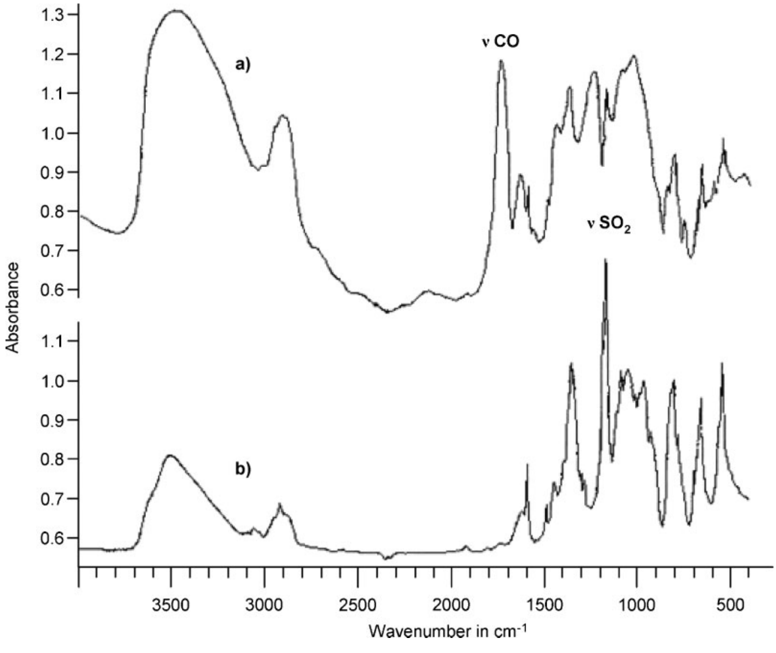


Figure 3.

IR spectra of **a)** cellulose acetate obtained by dissolution of cellulose tosylate (degree of substitution DS = 1.33) in EMImAc for 4h at 70 °C and **b)** cellulose tosylate (DS = 1.33).

solvent and an extraordinary high chlorine content of 7.3% was determined by elemental analysis, when using EMImCl as solvent. Thus, it was apparent, that a nucleophilic displacement reaction with the anion of the respective IL occurred, therefore forming an azidodeoxycellulose acetate or azidochlorodeoxycellulose. In Figure 4, the ^{13}C NMR spectrum of the azidochlorodeoxycellulose obtained is shown, which was recorded in DMSO-d_6 at 25 °C. The peaks in the range of 125–146 ppm and the single peak at 21 ppm are attributed to remaining tosyl groups. The characteristic signals of the AGU can be seen around 100 (C-1), in the range of 70–90 (C-2-5) and from 44–65 ppm (C-6). Due to different substituents at position 2 there are multiple signals for C-1. At 99.8 ppm the signal of C-1_{OH} can be observed, the signals of the more deshielded carbon atoms of the three other substituents appear in the range of 102–106 ppm. The C-6_{Cl} gives a clearly visible peak at 44 ppm, whereas the C-6_{Azide} appears at 51 ppm. Due to the same reason there are four different C-6 signals, at 64 ppm C-6_{OH}, at 60.5 ppm C-6_{Tos}, at 51 ppm C-6_{Azide} and at 45 ppm C-6_{Cl}. It is to be expected that ILs possessing weak nucleophilic anions such as tetrafluoroborate or hexafluorophosphate does not engage nucleophilic displacement reaction, unfortunately these ILs are not able to dissolve cellulose.

Preparation of Dendronized Cellulose

Earlier investigations showed that the conversion of azidodeoxycellulose with propargylpolyamidoamine dendrons via the copper catalyzed Huisgen reaction depends on the temperature.[13] The higher the reaction temperature is, the lower is the yield. An optimal reaction temperature is 25 °C. Due to the high melting point of EMImCl, it was no suitable solvent for the reaction. Therefore, EMImAc was preferred as solvent for the studies on dendronization of cellulose.

The starting material 6-azido-6-deoxy-cellulose dissolves completely in EMImAc at a temperature of 80 °C. The dissolution was observed by optical microscopy using a polarization filter (Figure 5). The major part of the polymer is dissolved after 30 minutes and complete dissolution occurs after 3.5 h. The polymer remains in solution after cooling to room temperature, which is essential for further derivatization.

The first generation PAMAM-triazolo cellulose was prepared by homogeneous synthesis of 6-azido-6-deoxy cellulose with propargyl-PAMAM dendron dissolved in EMImAc in the presence of $CuSO_4 \cdot 5\,H_2O$/sodium ascorbate for 4–48 h at 10–25 °C.

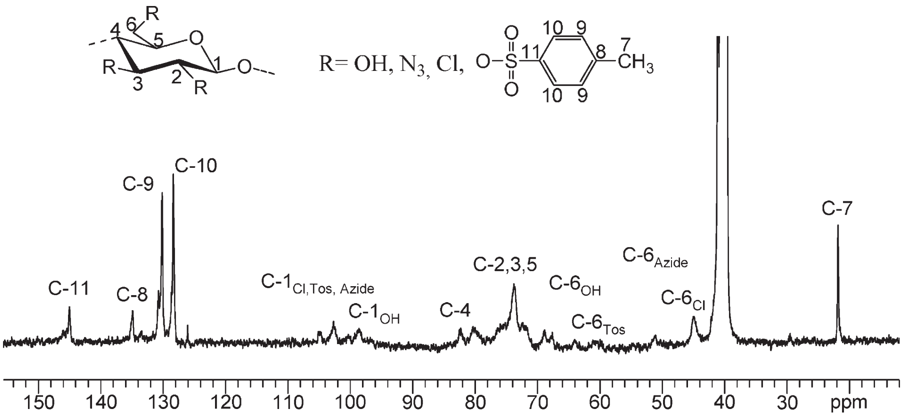


Figure 4.
^{13}C NMR spectrum of azidochlorodeoxycellulose in DMSO-d_6 at 25 °C.

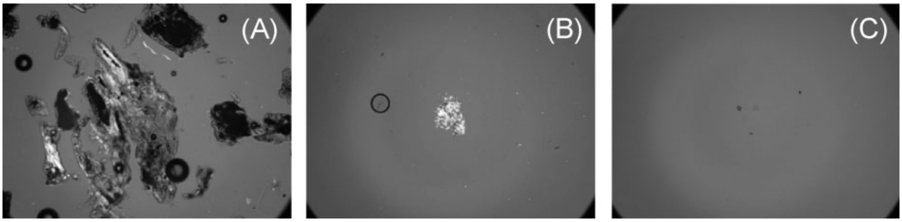


Figure 5.
Course of dissolution of 6-azido-6-deoxy cellulose in EMImAc observed by optical microscopy using a polarization filter, directly after addition (A), after 30 min at 80 °C (B), and after 3.5 h at 80 °C (C).[14]

The DS values of the products obtained after precipitation in ethanol and reprecipitation from dimethyl sulfoxide (DMSO) into ethanol were in the range from 0.18 to 0.60 (Table 1, samples **4a–e**). The lowest DS of 0.18 was obtained at a temperature of 10 °C and a reaction time of 24 h. A remarkable increase of the DS to 0.55 was found at a reaction temperature of 25 °C. Thus, further experiments were carried out at a temperature of 25 °C.

Product **4b** with a DS value of 0.30 was obtained after a reaction time of 4 h while prolongation of time to 48 resulted in an increased DS of 0.60 (**4e**) applying a molar ratio of 6-azido-6-deoxycellulose to propargyl-PAMAM of 1 to 2. The use of an equimolar ratio of 6-azido-6-deoxy cellulose to first generation propargyl-PAMAM dendron gave a sample of slightly decreased DS of 0.52 (**4c**, Table 1). Consequently, up to 80% of the azide moieties can be converted selectively by a polymeranalogous reaction under mild conditions. The samples are soluble in polar aprotic solvents like DMSO, DMF, and DMA.

Table 1.
Degree of substitution (DS) of dendritic PAMAM-triazolo-cellulose derivatives of the first (**4a–e**), second (**5**) and third (**6**) generation synthesised homogeneously in 1-ethyl-3-methylimidazolium acetate by reaction of 6-azido-6-deoxy cellulose (**3**, DS 0.75) with propargyl-polyamidoamine dendron of first, second, and third generation via copper-catalysed Huisgen reaction.

Molar Ratio[a)]	Conditions		Product	
	Temperature (°C)	Time (h)	No.	DS
1:2	10	24	**4a**	0.18
1:2	25	4	**4b**	0.30
1:1	25	24	**4c**	0.52
1:2	25	24	**4d**	0.55
1:2[b)]	25	48	**4e**	0.60
1:3	25	24	**5**	0.48
1:1	25	72	**6**	0.28

[a)] Mol repeating unit (6-azido-6-deoxy cellulose, DS 0.75): mol propargyl-PAMAM dendron;
[b)] Uses 0.05 g $CuSO_4 \cdot 5\ H_2O$ in 0.5 ml of water and 0.11 g sodium ascorbate in 1 ml of water as catalyst.

The structure of the products was confirmed by FTIR and NMR spectroscopy. Remaining azide moieties can be observed at 2137 cm^{-1} as a weak signal in FTIR spectra. The carbonyl signal of introduced methyl ester moiety of the PAMAM dendron was found at 1733 cm^{-1}. Well resolved NMR spectra were yielded after dissolution of the first generation PAMAM-triazolo-cellulose derivatives in DMSO-d_6. A typical ^{13}C NMR spectrum of sample **3e** (DS 0.60) acquired in DMSO-d_6 shows peas at 51.5 ppm for the peripheric methyl ester and at 172.8 ppm for the carbon atom of the corresponding carbonyl moiety (Figure 6). The resonances of the carbon-atoms of the triazole linker can be observed at 143.7 and 125.2 ppm.

The signals of the carbons one to fife of the repeating unit are visible between 103.2 and 69.1 ppm. The peaks at 60.9, 50.6 and 49.8 ppm are attributed to the three different types of C-6 bearing either an OH-, azide- or triazole moiety. The resonances of the CH_2 moieties of the first generation propargyl-PAMAM dendron are assigned to signals at 49.0, 48.0, and 32.8 ppm. In the ^1H NMR spectra signals for all structural

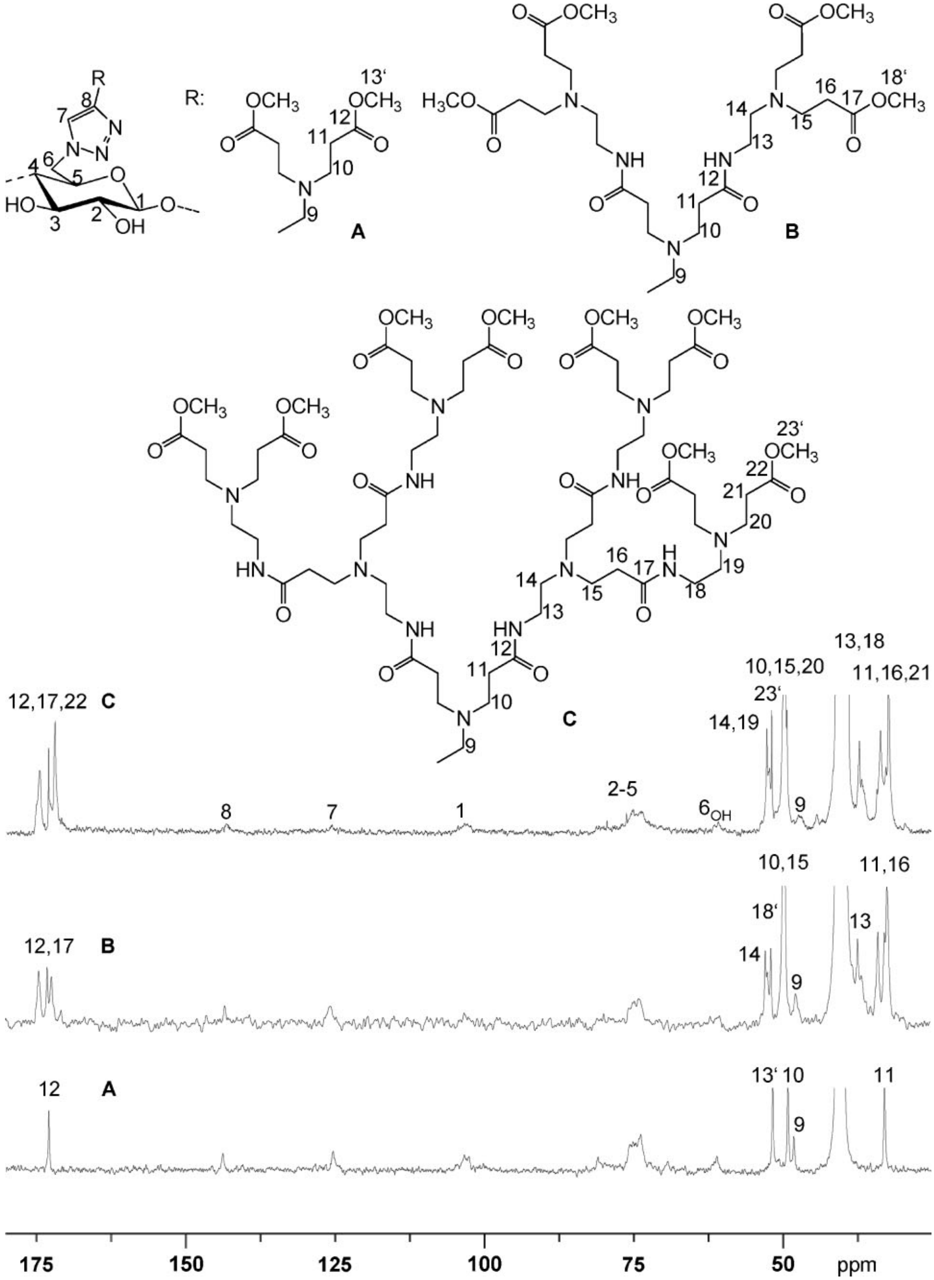


Figure 6.

^{13}C NMR spectra of **A** first (**4e**, degree of substitution, DS 0.60), **B** second (5, DS 0.48) and **C** third (**6**, DS 0.28) generation polyamidoamine-triazolo-cellulose, recorded in DMSO-d_6 at 60 °C.[14]

features are found, that is, at 7.97 ppm for the triazole, at 5.40–3.40 ppm for the repeating unit, and at 3.59 ppm for the methyl group of the ester.

Second and Third Generation PAMAM-Triazolo Cellulose

The preparation of second and third generation PAMAM-triazolo cellulose occurred analogue to the preparation of the first generation. The difference arose during the workup of the product. Neither the second nor the third generation can be precipitated in solvents miscible with EMImAc, such as water, ethanol or methanol. Therefore, the reaction mixture was diluted with ethanol and subsequently dialyzed against water for 5 days and freeze dried. Applying a molar ratio of 6-azido-6-deoxy cellulose to second generation propargyl-PAMAM dendron of 1:3 resulted in a product with a DS of 0.48 (**5**) and a ratio of 1:1 for the third generation and prolongation of the reaction time to 72 h lead to a product with a DS of 0.28 (Table 1). Due to the increasing bulkiness of the dendron the reactivity remarkably decreases even at prolonged reaction time. This is typical for graft-to strategies to attach dendrons onto polymers.[15]

The products are soluble in the polar aprotic solvents like DMSO, DMA, and DMF, and for the third generation even in water. Complete structure characterisation using FTIR and NMR spectroscopy was possible. The ^{13}C NMR spectra of **5** and **6** recorded in DMSO-d_6 at 60 °C are shown in Figure 6. In comparison with the first generation of dendronized cellulose the intensity of the AGU carbon atoms is low, due to the bulkiness of the substituent that dominates the spectrum as well known from NMR studies of cellulose derivatives with other bulky functions.

Conclusion

It was found, that the ILs EMImAc and EMImCl are no suitable solvents for different types of cellulose modification. In point of fact it must be considered, whether the reagents are stable versus nucleophilic displacement reactions with the anion and whether there are reactive species formed with the IL, which leads in both cases to unexpected products.

EMImAc dissolves 6-azido-6-deoxy cellulose with a DS of 0.75 very well and represents a suitable reaction medium for the homogeneous conversion of 6-azido-6-deoxy cellulose with propargyl-PAMAM dendrons via copper catalysed Huisgen reaction. First to third generation PAMAM-triazolo-cellulose derivatives with DS values of up to 0.60 were obtained.

Preliminary investigations show that coatings can be prepared applying these new cellulose derivatives. Due to the high density of functional groups and the biocompatibility of the cellulose backbone, it is expected that these coatings can be used as anchors for enzyme immobilisation. Relevant research work is currently performed.

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