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Synthesis of water-soluble cellulose esters applying carboxylic acid imidazolides

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Abstract Water-soluble, non-ionic cellulose esters with a degree of substitution in the range from 0.11 to 3.0 were synthesized homogeneously using ionic liquids (1-butyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium chloride, and 1-allyl-3-methylimidazolium chloride) as reaction medium. Highly substituted 3,6,9-trioxadecanoic acid esters and 3,6-dioxaheptanoic acid esters of cellulose were obtained via the activation of the carboxylic acids with *N*,*N*'-carbonyldiimidazole. The products were characterized by the means of FTIR-, ^{1}H- and ^{13}C NMR spectroscopy.

Introduction

Various ionic liquids (ILs) have proved to be excellent solvents for cellulose and useful reaction media for homogeneous phase chemistry [1, 2]. In the pioneering studies of Wu et al. and Heinze et al., it was shown that cellulose esters of high degree of substitution can be prepared [3–5]. Moreover, for the first time bacterial cellulose of high molecular mass (degree of polymerization, DP of 6500) could be dissolved and esterified homogeneously [6]. Meanwhile, a broad variety of reactions of cellulose starting with the dissolved biopolymer in different ILs was studied

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indicating their usefulness in the field of cellulose chemistry [7–11]. In this context, it must be pointed out that IL may also be reactive, e.g., 1-ethyl-3-methylimidazolium acetate ($[C_2mim]^+Ac^-$) acts not exclusively as solvent. The esterification or etherification of cellulose dissolved in $[C_2mim]^+Ac^-$ with reagents such as 2-furoyl chloride or triphenylmethyl chloride yielded a mixed anhydride or tritylacetate, which does not react to the expected derivatives but formed cellulose acetate [12, 13]. In the course of our studies on ILs, 1-butyl-3-methylimidazolium chloride ($C_4mim]^+Cl^-$), 1-ethyl-3-methylimidazolium chloride ($[C_2mim]^+Cl^-$) and 1-allyl-3-methylimidazolium chloride ($[Amim]^+Cl^-$) were investigated as reaction media for the esterification of cellulose with oxacarboxylic acids, namely 3,6,9-trioxadecanoic- and 3,6-dioxaheptanoic acids. The cellulose esters that could be obtained are non-ionic, and may show water solubility and a high salt tolerance. Such properties are of interest for stabilization of aqueous systems.

Experimental part

Materials

The ILs, 1-butyl-3-methylimidazolium chloride ($[C_4mim]^+Cl^-$), melting point (mp) 73 °C, 1-ethyl-3-methylimidazolium chloride ($[C_2mim]^+Cl^-$), mp 80 °C, and 1-allyl-3-methylimidazolium chloride ($[Amim]^+Cl^-$), mp 52 °C, were used as received from FLUKA.

3,6-Dioxaheptanoic acid (DOHA), 3,6,9-trioxadecanoic acid (TODA) and *N*,*N*′-carbonyldiimidazole (CDI) were commercial products and purchased from FLUKA and MERCK. All other chemicals were used without further purification.

The cellulose materials used were microcrystalline cellulose, Avicel, with a degree of polymerization (DP) of 280 and bacterial cellulose (BC) with a DP of 6500. BC was synthesized according to a known pathway; the bacteria *Gluconacetobacter xylinus* (from the stock collection of the Research Centre of Medical Technology and Biotechnology, Bad Langensalza, Germany) were cultivated in glass vessels containing 3.5 L of Schramm-Hestrin medium in static culture at 30 °C for about 30 days [14]. As inoculation medium, a bacterial suspension of 10 ml (turbidity by McFarland 3–4) was used [15]. The cellulose layer with a thickness of 3–4 cm was separated from the culture medium, cut into small pieces and washed twice by boiling in aqueous sodium hydroxide (NaOH) solution for 30 min. In order to neutralize the NaOH, the BC was washed with distilled water. Afterwards, the BC was freeze-dried, milled and dried again at 60 °C in vacuum. The Avicel was dried in vacuum for 1 h at 100 °C before use.

Measurements

NMR spectra were acquired on a Bruker Advance 250 MHz or a 400 MHz spectrometer with 16 scans for ^1H NMR and up to 200,000 scans for ^{13}C NMR spectra by using a standard 5-mm probe at room temperature in D_2O, the spectra of the peracetylated samples were acquired in $CDCl_3$ to determine the DS.

The FTIR spectra were recorded on a Nicolet AVATAR 370 DTGS spectrometer with the KBr technique.

The DP of the BC was determined by capillary viscosimetry according to DIN 54270 applying copper(II)ethylenediamine as solvent.

Dissolution of cellulose

The cellulose and the molten ionic liquid were mixed at mp, and the temperature was increased to 10 °C above the mp, and kept for 12 h to complete the dissolution.

Esterification of cellulose with TODA (**A4**), typical example

A solution of 1.5 g CDI (3 mol per mol anhydroglucose unit, AGU) and 1.65 g TODA (3 mol per mol AGU) in 2.5 g $[C_4mim]^+Cl^-$ were stirred for 30 min at 80 °C and subsequently added to a solution of 0.5 g Avicel and 4.5 g $[C_4mim]^+Cl^-$. The mixture was allowed to react for 5 h at 80 °C. In order to isolate the product, the homogeneous reaction mixture was cooled to room temperature and the product was precipitated into 150 mL isopropanol. After filtration, and washing with 100 ml isopropanol (four times), the product was dried at room temperature in vacuum.

DS: 1.60 (determined by the means of ^1H NMR spectroscopy), see Table 1.

FTIR (KBr): 3440 ν (OH), 2950, 2878 ν (CH), 1763 ν (CO) cm^{-1}.

^{13}C NMR (D_2O): $\delta = 102.7$ (C-1), 99.9 (C-1′), 79.5 (C-3_s, 2_s), 75.6 (C-4), 74.9 (C-4′), 73.7-72.2 (C-2, 3, 5), 71.1-69.5 (C-10-14), 67.9 (C-8), 63.1 (C-6_s), 59,6 (C-6), 58.2 (C-16) ppm.

Peracetylation of **A4**

To the sample **A4** (0.3 g) dissolved in 5 mL pyridine, 5 mL acetic anhydride and 0.1 g *N*,*N*-dimethylaminopyridine as catalyst were added and allowed to react overnight at 80 °C under stirring. The peracetylated cellulose derivative was isolated by precipitating into ethanol. The solid was filtered off, washed three times with 100 ml ethanol and dried in vacuum at 60 °C. The product is soluble in chloroform-d_1.

FTIR (KBr): no ν (OH), 1762 ν (CO) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 5.0$ (H-3), 4.7-3.3 (cellulose backbone, H_{Ester}), 2.2-1.9 ($H_{acetate}$) ppm.

Results and discussion

Ionic liquids (ILs) were found to be efficient reaction medium for cellulose acylation with carboxylic acid chlorides or carboxylic acid anhydrides [3–5]. The reaction of cellulose dissolved in IL with carboxylic acid does not yield cellulose esters. An acidic catalyst, which is useful for esterification of low-molecular alcohols or for the acetylation of cellulose is not appropriate, because a degradation of the polymer chain during the reaction occurs, and the long-chain acids are not

Table 1 Conditions for and results of the esterification of cellulose (Avicel and bacterial cellulose, BC) in ionic liquids with 3,6,9-trioxadecanoic acid imidazolide, TODA

Conditions					Product				
Type of cellulose	Ionic liquid	Molar ratio[a]	Reaction time in h	Reaction temperature in °C	No.	DS[b]	Yield in %	Solubility[c]	
								DMSO	H_2O
Avicel	$[C_4mim]^+Cl^-$	1/1/1	5	80	**A1**	0.37	94	+	+
Avicel	$[C_4mim]^+Cl^-$	1/1/1	3	80	**A2**	0.36	92	+	+
Avicel	$[C_4mim]^+Cl^-$	1/1/1	3	80	**A3**	0.11	94	−	−
Avicel	$[C_4mim]^+Cl^-$	1/3/3	3	80	**A4**	1.60	71	+	+
Avicel	$[C_4mim]^+Cl^-$	1/3/3	3	80	**A5**	0.55	72	+	+
Avicel	$[C_4mim]^+Cl^-$	1/6/6	5	80	**A6**	3.00	64	S	S
Avicel	$[C_4mim]^+Cl^-$	1/6/6	3	80	**A7**	3.00	53	+	+
Avicel	$[Amim]^+Cl^-$	1/1/1	3	80	**A8**	0.99	92	+	−
Avicel	$[Amim]^+Cl^-$	1/3/3	3	80	**A9**	2.43	67	+	−
Avicel	$[C_2mim]^+Cl^-$	1/1/1	3	80	**A10**	0.47	91	−	−
Avicel	$[C_2mim]^+Cl^-$	1/3/3	3	80	**A11**	1.99	95	+	+
BC	$[C_4mim]^+Cl^-$	1/3/3	3	90	**B1**[d]	1.78	84	+	−
BC	$[C_4mim]^+Cl^-$	1/6/6	3	90	**B2**[d]	2.17	47	+	+

TODA was allowed to react with *N,N′*-carbonyldiimidazole in the ionic liquid separately from cellulose within 30 min to form the imidazolide. In the case of products **A3** and **A5**, the formation of the imidazolide runs through 17 h

[a] Anhydroglucose unit/*N,N′*-carbonyldiimidazole/3,6,9-trioxadecanoic acid

[b] Degree of substitution

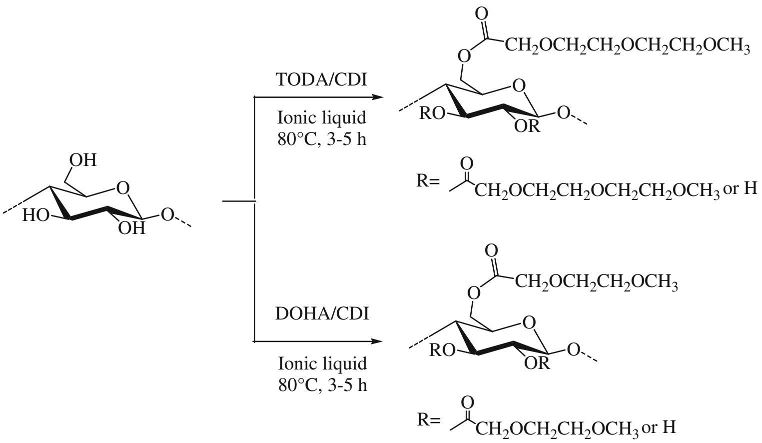
[c] Dimethyl sulfoxide (DMSO), + soluble; − insoluble; S swollen

[d] The formation of the activated imidazolide took place in dimethyl sulfoxide

reactive at all. A known path for cellulose modification with carboxylic acid is the activation of the acid with *N,N′*-carbonyldiimidazole (CDI) [16]. The reactive carboxylic acid imidazolide is soluble in IL; thus, a complete homogeneous reaction could be realized. For activation, CDI instead of p-toloulsulfonic chloride (TosCl) was used. The application of TosCl leads in combination with DMA/LiCl to degradated products, while the use of CDI yielded to samples with the same DP as the starting material.

In the course of our studies, 3,6,9-tioxadecanoic acid (TODA) and 3,6-dioxaheptanoic acid (DOHA) were applied for the acylation of cellulose. Scheme 1 demonstrates the synthesis pathway. The ILs applied were 1-butyl-3-methylimidazolium chloride ($[C_4mim]^+Cl^-$), 1-ethyl-3-methylimidazolium chloride ($[C_2mim]^+ Cl^-$) and 1-ally-3-methylimidazoilum chloride ($[Amim]^+Cl^-$).

In the first series of experiments, cellulose dissolved in $[C_4mim]^+Cl^-$ was allowed to react with TODA forming the corresponding cellulose esters (Table 1). Using Avicel, cellulose derivatives with a degree of substitution (DS) in ranging from 0.11 (**A3**) to 3.00 (**A6**, **A7**) were obtained, depending on the molar ratio ranging from 1/1/1 (**A1, A3**) (anhydroglucose unit (AGU)/TODA/CDI) to 1/6/6



Scheme 1 Reaction path for the acylation of cellulose. TODA = 3,6,9-trioxadecanoic acid; DOHA = 3,6-dioxaheptanoic acid; CDI = *N,N′*-carbonyldiimidazole

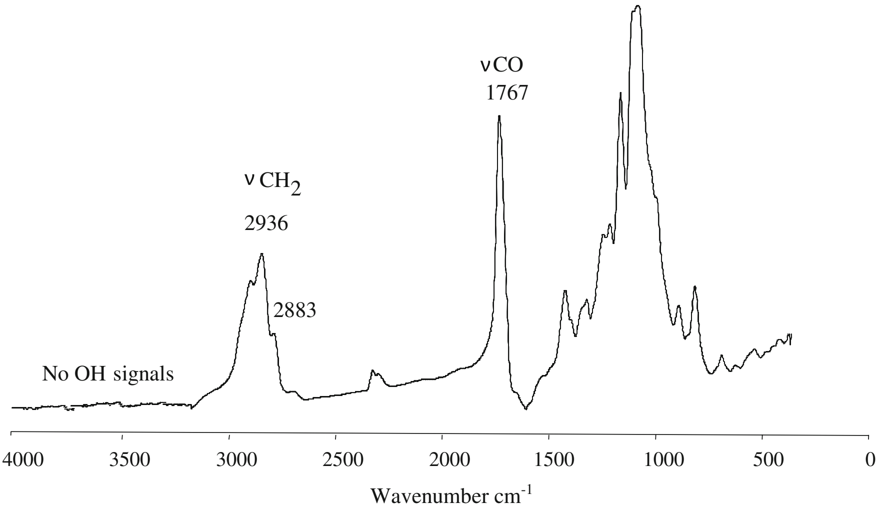


Fig. 1 FTIR spectrum of a completely substituted cellulose ester synthesized with 6 mol 3,6,9-trioxadecanoic acid and 6 mol *N,N′*-carbonyldiimidazole per mol anhydroglucose unit within 3 h at 80 °C (**A7**)

(**A7**). Within 3 h and 80 °C and an amount of 6 mol TODA and 6 mol CDI per mol AGU, a completely substituted cellulose ester (**A7**) could be obtained. The FTIR spectrum (Fig. 1) shows the typical signals for the carbonyl group at 1767 cm^{-1}, the CH_2 signal at 2936 and 2883 cm^{-1}. No OH signal appears that would be expected at 3,400 cm^{-1}.

TODA and CDI were allowed to react for 30 min to form the carboxylic acid imidazolide. The prolongation of the time to form it shows an unexpected effect;

after 17 h of activation, and the DS of the product obtained by subsequent acylation was 0.55 (**A5**) in contrast to **A4** with a DS of 1.6 (30-min activation). Obviously, a decomposition of the imidazolide during the long time occurred. In $[\text{Amim}]^+\text{Cl}^-$, a cellulose ester with a DS of 0.99 (**A8**) can be obtained by applying a molar ratio of 1/1/1 (AGU/TODA/CDI), i. e. nearly 100% conversion of the reagent was obtained. An increase of the amount of reagent to 3 mol per mol AGU leads to the product **A9** with DS of 2.43. $[\text{C}_2\text{mim}]^+\text{Cl}^-$ was successfully used as reaction medium for homogeneous acylation as well. The cellulose dissolved in $[\text{C}_2\text{mim}]^+\text{Cl}^-$ is less reactive than that dissolved in $[\text{Amim}]^+\text{Cl}^-$. Applying a molar ratio of 1/1/1 (AGU/TODA/CDI), a cellulose ester with a DS of 0.47 (**A10**) was prepared. The DS could be increased up to 1.99 by increasing the molar ratio to 1/3/3 (**A11**) using $[\text{C}_2\text{mim}]^+\text{Cl}^-$. The results showed that the DS and the solubility of the cellulose esters depend on the IL used. The reactivity of the dissolved cellulose is $[\text{Amim}]^+\text{Cl}^- > [\text{C}_2\text{mim}]^+\text{Cl}^- > [\text{C}_4\text{mim}]^+\text{Cl}^-$. Cellulose esters synthesized in $[\text{Amim}]^+\text{Cl}^-$ are soluble in dimethyl sulfoxide (DMSO) and insoluble in water. Using $[\text{C}_2\text{mim}]^+\text{Cl}^-$, the products are soluble in water and DMSO at DS > 1.99. The cellulose esters prepared in $[\text{C}_4\text{mim}]^+\text{Cl}^-$ are both water- and DMSO-soluble starting at a DS of 0.36. Moreover, the fully substituted product is additionally soluble in ethanol and acetone. It may be expected that the state of dissolution of cellulose in different ILs is different as shown for $[\text{C}_4\text{mim}]^+\text{Cl}^-$ and 1-ethyl-3-methylimidazolium acetate [17]. As a consequence, cellulose esters with different functionalization patterns may be formed. It is well known that the functionalization pattern influences the solubility as studied in detail for cellulose acetate, e.g., [18]. Obviously, it is the case of oxacarboxylic acid esters of cellulose. Detailed studies on the functionalization pattern are under investigation.

For the comparison of the reactivity of the two oxacarboxylic acids, depending on the IL, the results are not appropriate. More studies including the knowledge of the solubility of the acids in IL are needed.

Bacterial cellulose (BC) was dissolved in $[\text{C}_4\text{mim}]^+\text{Cl}^-$ and allowed to react with TODA imidazolide, yielding an insoluble cellulose ester. The application of DMSO as solvent for the imidazolide formation leads to highly substituted BC esters (**B1**, **B2**) with DS values of 1.78 and 2.17 due to the dilution of the reaction medium (DMSO acts as co-solvent). The products are soluble in DMSO and additionally in water at DS 2.17. Well resolved ^{13}C NMR spectra (in D_2O) were acquired from the samples **B1** and **B2**. Figure 2 shows a typical ^{13}C NMR spectrum of the 3,6,9- trioxadecanoic acid ester of BC **B2**. Resonances assigned to the carbon atoms of the TODA moieties are visible at $\delta = 58.2$ ppm (C-16) and $\delta = 67.9$-71.1 ppm (C-8, C-10-14). The signals of the carbon atoms of the modified AGU are detected in the range from $\delta = 102.7$ to 63.5 ppm. The signals at $\delta = 72.2$, 73.5 and 73.7 ppm result from the carbon atoms 2 and 3 of the non-esterified secondary hydroxyl groups and from C-5. The signals of the modified secondary hydroxyl groups (C-2s, C-3s) are detected at $\delta = 79.4$ ppm. The signals C-1 are found at $\delta = 102.7$ ppm and at $\delta = 100.0$ ppm, the C-1′ (C-1 atom influenced by an esterification at O-2). The C-4 and C-4′ signals appear at $\delta = 75.8$ and 74.7 ppm indicating an influence of a functionalization at O-3.

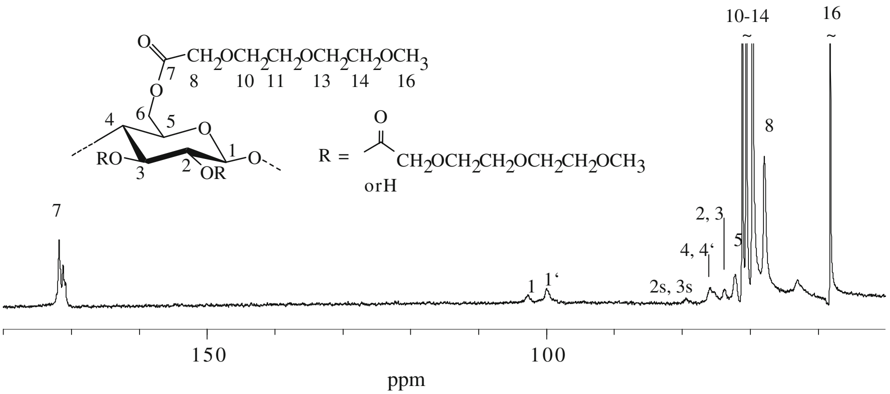


Fig. 2 ^{13}C NMR spectrum of 3,6,9-trioxadecanoic acid ester of bacterial cellulose (**B2**, degree of substitution 2.17) recorded in D_2O. Index s means substituted, ' means influenced by a functionalization of the adjacent position

In order to determine the DS of the cellulose esters, the samples were treated with acetic anhydride in pyridine to generate the peracetylated products. The peracetylated samples were well soluble in chloroform and could be acquired highly resolved ^1H NMR spectra. Figure 3 shows a typical spectrum of peracetylated 3,6,9-trioxadecanoic acid ester of cellulose (**A4**). The signal of the H-3 atom of the AGU is observed at about 5 ppm. The two resonances of the H-2 and H-1 of the AGU are

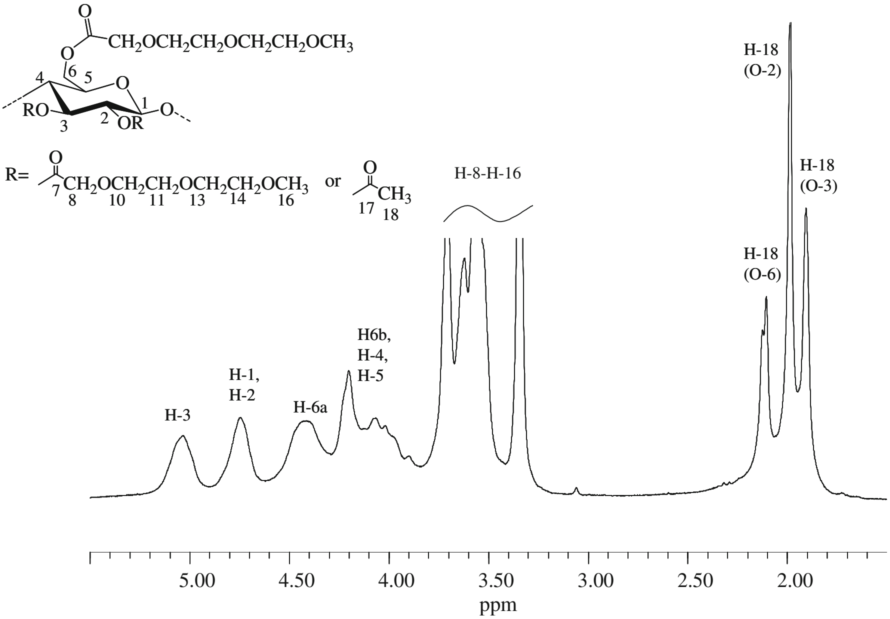


Fig. 3 ^1H NMR spectrum of peracetylated 3,6,9-trioxadecanoic acid ester (**A4**, degree of substitution 1.6) recorded in chloroform-d_6

at 4.6 and 4.5 ppm, respectively. These signals can be related to the resonances of the protons of the acetate moieties (1.9-2.1 ppm) to calculate the DS of the products.

The reaction of Avicel with 1 mol DOHA and 1 mol CDI per mol AGU leads to a product with a DS of 0.27 (**A12**) within 3 h at 80 °C (Table 2). An increase of the molar ratio to 1/3/3 (AGU/DOHA/CDI) yields cellulose esters with DS 2.64 (**A13**) and to 1/6/6 (AGU/DOHA/CDI) leads to a fully substituted product (**A14**). The application of $[Amim]^+Cl^-$ as reaction medium yields highly substituted products with DS in the range from 0.91 (**A15**) to 2.24 (**A16**). The application of $[C_2mim]^+Cl^-$ is less efficient; at comparable molar ratio, products with lower DS (**A17**; DS 0.16, **A18**; DS 1.5) were obtained. The products are soluble in DMSO and water at DS > 0.27.

By using $[C_4mim]^+Cl^-$ and DMSO, the synthesis of DOHA cellulose esters from BC is possible. The DS values are 1.63 (**B3**) and 2.09 (**B4**). The products are soluble in DMSO and water. On comparison of the efficiency of the ILs used, a different result was found; here, $[C_4mim]^+Cl^-$ is the most efficient reaction medium, followed by $[Amim]^+Cl^-$ and $[C_2mim]^+Cl^-$ depending on the reagent used.

By means of GPC, it was found that during the reaction, Avicel is not degradated. The starting material and the product show the same DP. In the case of BC, a degradation by 40%—from DP 6500 to DP 2600—occurs during the esterification.

Table 2 Conditions for and results of the esterification of cellulose (Avicel and bacterial cellulose, BC) in ionic liquids with 3,6-dioxaheptanoic acid imidazolide, DOHA

Conditions					Product				
Type of cellulose	Ionic liquid	Molar ratio[a]	Reaction time in h	Reaction temperature in °C	No.	DS[b]	Yield in %	Solubility[c]	
								DMSO	H_2O
Avicel	$[C_4mim]^+Cl^-$	1/1/1	5	80	**A12**	0.27	98	+	+
Avicel	$[C_4mim]+Cl^-$	1/3/3	3	80	**A13**	2.64	64	+	+
Avicel	$[C_4mim]^+Cl^-$	1/6/6	5	80	**A14**	3.00	83	S	S
Avicel	$[Amim]^+Cl^-$	1/1/1	3	80	**A15**	0.91	84	+	+
Avicel	$[Amim]^+Cl^-$	1/3/3	3	80	**A16**	2.24	72	+	+
Avicel	$[C_2mim]^+Cl^-$	1/1/1	3	80	**A17**	0.16	90	−	−
Avicel	$[C_2mim]^+Cl^-$	1/3/3	3	80	**A18**	1.52	86	+	+
BC	$[C_4mim]^+Cl^-$	1/3/3	3	90	**B3**[d]	1.63	95	+	−
BC	$[C_4mim]^+Cl^-$	1/6/6	3	90	**B4**[d]	2.09	47	+	+

The DOHA was allowed to react with *N,N′*-carbonyldiimidazole in ionic liquid for 30 min previously to the addition to the cellulose solution

[a] Anhydroglucose unit/*N,N′*-carbonyldiimidazole/3,6-dioxaheptanoic acid

[b] Degree of substitution

[c] Dimethyl sulfoxide, + soluble; − insoluble; S swollen

[d] The formation of the activated imidazolide took place in dimethyl sulfoxide

Conclusion

Applying $[C_4mim]^+Cl^-$, $[Amim]^+Cl^-$ and $[C_2mim]^+Cl^-$ as reaction media, non-ionic cellulose esters were prepared by activation of TODA or DOHA with CDI. Within short reaction time and comparably low amount of reagent, highly substituted cellulose derivatives were obtained. TODA- and DOHA esters of cellulose were prepared in DMA/LiCl, possessing significantly lower DS values applying tosyl chloride for activation of the acids [19]. The products are soluble in DMSO, water, ethanol, and acetone depending on DS. Not only microcrystalline cellulose, but also BC of high molecular weight could be modified under mild conditions, applying IL and DMSO as co-solvent homogeneously.

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