# Cellulose conversion into alkylglycosides in the ionic liquid 1-butyl-3-methylimidazolium chloride

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The conversion of cellulose into alkylglycosides is carried out in the ionic liquid 1-butyl-3-methylimidazolium chloride in the presence of an acidic catalyst. Primary alcohols like *n*-butanol and *n*-octanol were used as alkylating reagents. The acidic resin Amberlyst 15DRY proved to be the optimum heterogeneous catalyst: it catalyzes the hydrolysis of the β(1→4) links in the cellulose polymeric chain as well as the alkylation of the hydroxyl groups at the C1 position of the glucose intermediate. The cellulose was fully converted under mild conditions; in a reaction with *n*-butanol, the obtained yield of butylglucopyranoside isomers was 86%.

## Introduction

Alkylglycosides are a class of biodegradable nonionic surfactants with a broad application scope, *e.g.* in the cosmetic, detergent, food and pharmaceutical industries.[1] One of their interesting features is their ability to form liquid crystals.[2] The conventional alkylglycoside synthesis was first described by E. Fischer as the formation of a glycoside by the reaction of an aldose or ketose with an alcohol in the presence of acid species,[3a] and since then numerous homogeneous and heterogeneous catalysts have been proposed and applied for their synthesis.[3–6] Typical drawbacks of this reaction, such as the necessity for functional group protection and deprotection,[6] or the formation of oligomeric species, can be avoided by using specific heterogeneous acidic catalysts like sulfonated resins,[7] acid clays [8] and zeolites.[9–10]

Ionic liquids (ILs), and in particular chloride-containing ones, can be suitable solvents for cellulose. They disrupt the hydrogen bonds and dissolve the cellulose chains at the molecular level.[11] For instance, 1-butyl-3-methylimidazolium chloride (BMImCl) can dissolve up to 25 wt% of cellulose.[12] There are already multiple examples of successful cellulose transformations in ILs, such as derivatization of the cellulose chains,[13] or production of composite materials that besides cellulose also contain carbon nanotubes or inorganic materials.[14] Cellulose hydrolysis was successfully conducted in the IL BMImCl with glucose as the major product in the presence of homogeneous acids, or of the heterogeneous acidic catalyst Amberlyst 15DRY.[15] However, prolongation of the reaction time can cause pyrolysis of glucose, and when homogeneous acids are used, a ceiling yield of 50% is reached at which hexose degradation starts to decrease the overall process yield.[15b]

It is worthwhile to investigate whether glucose, formed through acid hydrolysis of cellulose, can be further transformed in a one-pot process into more stable compounds such as alkylglycosides. We have recently reported that addition of hydrogen and hydrogenation catalysts allows the conversion in one pot of the intermediately formed glucose into polyols, but the poor solubility of hydrogen in BMimCl is a serious handicap for efficient hydrogenation.[16] This urged us to consider hexose acetalization as an alternative reaction. Not only does this allow us to use the most abundant carbohydrate source available for alkylglycoside production; the alkylation may in addition suppress the undesired pyrolysis of glucose. There is an apparent compatibility between hydrolysis and alkylation reactions as they both require acid catalysis. In this work, we demonstrate an effective one-pot transformation of cellulose in the presence of Amberlyst 15DRY to butylglucopyranosides and octylglucopyranosides in 1-butyl-3-methylimidazolium chloride as the solvent under relatively mild conditions. Similar work on BMimCl, cellulose and alcohols appeared when our paper was ready for submission.[17]

## Experimental

1-Butyl-3-methylimidazolium chloride (99%), ethyltributylphosphonium diethyl phosphate (>95%) and tetrabutylphosphonium chloride (>95%) were obtained from IoLiTec Ionic Liquids Technologies GmbH. 1-Ethyl-3-methylimidazolium diethyl phosphate (≥98.0% (HPLC/T)) and 1-ethyl-3-methylimidazolium acetate (97%) were obtained from Sigma-Aldrich. The cellulose used was Avicel PH 101 (DP 215–240). α-D-glucopyranoside (min 98%), butyl α-D-gluco-pyranoside and butyl β-D-glucopyranoside (min 98%) were obtained from Carbosynth Limited. Amberlyst 15DRY was purchased from Sigma-Aldrich. The H-β zeolite was a commercial sample from the PQ corporation (CP 811 BL-25). The H-MCM-22 was prepared in-house based on a literature recipe.[18] Reactions were conducted in sealed glass vials (10 mL) with continuous stirring.

Other chemicals were obtainedfrom commercial suppliers and were used as received. For reactions with methanol and ethanol, 10 ml stainless steel batch pressure reactors were employed under 0.8 MPa of argon. After reaction, samples were derivatized using

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**Table 1** Initial experiments on glucose alkylation in ionic liquids

| Entry | Solvent | *n*-Butanol (mL) | Catalyst | Yield of α-BGP (%) | Yield of β-BGP (%) |
|---|---|---|---|---|---|
| 1 | — | 1 | 0.01 g Hβ zeolite | 45 | 30 |
| 2 | 1 g BMImCl | 0.3 | 0.005 g PTSA | 31 | 26 |
| 3 | — | 1 | 0.01 g Amberlyst 15DRY | 48 | 32 |
| 4 | 1 g BMImCl | 0.3 | 0.01 g Amberlyst 15DRY | 17 | 10 |

Reaction conditions: 0.01 g glucose, 90 °C, 4 h.

**Table 2** Initial experiments with cellulose

| Entry | Catalyst | Yield of α-BGP (%) | Yield of β-BGP (%) | Yield of BGF (%) | Yield of glucose (%) | Yield of levoglucosan (%) | Total conversion of cellulose (%) |
|---|---|---|---|---|---|---|---|
| 1 | 0.01 g H-β | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 0.01 g H-MCM-22 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 | 0.01 g Amberlyst 15DRY | 29 | 16 | 5 | 10 | 7 | 67 |

Reaction conditions: 0.05 g cellulose, 1 g of BMImCl, 20 µl of water, 0.3 mL *n*-butanol, 110 °C, 24 h.

MSTFA (*N*-(trimethylsilyl)-*N*-methyltrifluoroacetamide) and injected onto a 30 m HP-1 column in a GC (HP 5890) or a GC-MS (Agilent 6890 GC and 5973 MS) instrument. Typically, a *ca.* four-fold excess of MSTFA with respect to the –OH groups was added to 0.3 mL of sample mixed with 0.3 mL of pyridine, and the mixture was stirred for 3 h at 80 °C. Derivatized compounds were then extracted into 0.5 mL of dibutylether and analyzed. The procedure was verified and made quantitative using known amounts of reference compounds such as glucose, butyl-α-D-glucopyranoside, butyl-β-D-glucopyranoside, and others. The water content of the ILs was determined with a coulometric Karl–Fischer titrator (Mettler Toledo DL39).

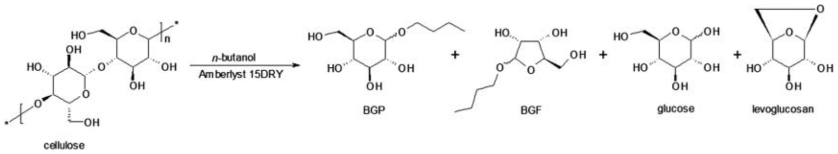
## Results and discussion

In a first phase, glucose was used as a substrate for the alkylation in ILs. Multiple interesting procedures for glucose alkylation have been reported.[7–10] In order to investigate the effect of the IL solvent on the alkylation, we performed alkylation reactions with or without BMImCl in *n*-butanol, without adding any other solvent. All catalysts tested, including Amberlyst 15DRY, showed significant activity for butylation of glucose at 90 °C (Table 1, entries 1–4). Amberlyst 15DRY is a macroporous Brønsted acid resin.

The main products were butyl-α-D-glucopyranoside (α-BGP) and butyl-β-D-glucopyranoside (β-BGP). Yields in the presence of BMimCl are considerably lower than in pure BuOH. This is simply a thermodynamic and kinetic consequence of the three-fold lower *n*-BuOH concentration when the reaction was carried out in the presence of the IL. Nevertheless, the result in the presence of *para*-toluene-sulfonic acid shows that a >50% yield of butylglucosides can be achieved easily, even in an IL (Table 1, entry 2).

As a step-up towards cellulose, cellobiose was investigated as a reaction substrate, in view of its molecular structure being an intermediate between those of glucose and cellulose. This compound consists of two glucose units linked by a β(1→4) bond, and thus represents a dimeric model for the cellulose polymer. Just like glucose, cellobiose is readily soluble in BMImCl. In the reaction with this dimeric substrate, the acid catalyst should not only be capable of alkylation but also of hydrolysis of the β(1→4) bond. This also implies that some water should be available in the reaction medium. Minor contamination of the hydrophilic BMImCl by water is hard to avoid; Karl–Fischer titration showed that the level of contamination was *ca.* 0.1 wt% of water. To ensure that at least a stoichiometric amount of water is available, 20 µl of water was added per g of IL. We applied Amberlyst 15DRY, a catalyst previously reported to hydrolyze cellulose in BMImCl.[15a] Cellobiose (0.05 g) was successfully hydrolyzed and butylated by using 0.01 g of Amberlyst 15DRY and 0.3 mL of *n*-butanol in 1 g of water-enriched BMImCl at 110 °C for 24 h. α-BGP and β-BGP were obtained with yields of 43% and 24%, respectively. By-products were glucose (31%) and levoglucosan (2%). The detection of the latter product indicates that under certain conditions alkylation in the presence of an acidic catalyst can lead to degradation reactions, as will be demonstrated below. 110 °C has previously been reported as an optimal temperature for glucose butylation.[9–10]

Next, cellulose was employed in the form of the microcrystalline commercial product Avicel. The cellulose reagent may contain some additional water which can be consumed in the hydrolysis (typically 4–7 wt% based on cellulose).[19] In our first attempt, H-β zeolite (Si/Al = 13) and H-MCM-22 zeolite (Si/Al = 30) were applied besides Amberlyst 15DRY[7c] for reactions with *n*-butanol. The zeolite materials that were chosen are both strong heterogeneous acids with ample access to the acid sites, due to the small crystal size, in the case of H-β, or due to the flaky morphology, in the case of H-MCM-22. Moreover, zeolites like H-β[9] have been reported to be suitable catalysts for alkylation of monomeric carbohydrates. However, when the zeolites were tested, no products of cellulose depolymerization were detected at all, not even after a 24 h reaction time (Table 2, entries 1 and 2). Significantly better results were obtained with Amberlyst 15DRY (Table 2, entry 3). This suggests that the



**Scheme 1** Splitting of cellulose with formation of α-BGP, β-BGP, glucose and levoglucosan.

dissolved polymer chains can only interact with well-accessible acid sites in macropores.

Detailed product identification by comparison with reference compounds, by comparison with results of reported reactions and by GC-MS identification showed that the major product was BGP in its α- and β-forms, with the α-anomer as the dominant product. A smaller amount of butylglucofuranosides (BGF) was also detected, as well as of glucose (Table 2, entry 3; Scheme 1). Levoglucosan, a pyrolysis product, has also been identified. It is worth noting that the pyrolysis of glucose and similar compounds can also lead to dehydrated compounds such as furans;[15] however, these were not detected here by means of GC or GC-MS.

Fig. 1 shows that glucose is the major primary product of the reaction. At 110 °C and under the conditions specified, its concentration passes through a maximum at 1 h and then decreases with time. The total yield of alkylated carbohydrates is more or less constant in the 2–4 h time interval. The BGPs are the major products, and in this fraction, α-BGP is dominant. However, the selectivity slowly changes. The α-BGP to β-BGP ratio increases from 1.5 at the first sampling point, to 1.7 at maximal product yield, and eventually evolves towards 2 at long reaction times. Between reaction times of 2 h and 4 h, the furanosides are gradually isomerized into pyranosides. α-BGP is indeed thermodynamically more stable than β-BGP and the BGFs.[10] This variation of the α-BGP to β-BGP ratio early in the reaction has also been reported by Moreau for the alkylation of D-glucose with *n*-butanol. Remarkably, in a zeolite-catalyzed, solventless reaction of glucose, β-BGP is the kinetically favored product, and the initial α-BGP to β-BGP ratio is as low as 0.5. Only at over 90% conversion does the α/β ratio stabilize at ~2, which is close to the value observed in the IL mediated reaction. This suggests that the IL facilitates the β-BGP to α-BGP conversion in the alkylglycoside fraction.

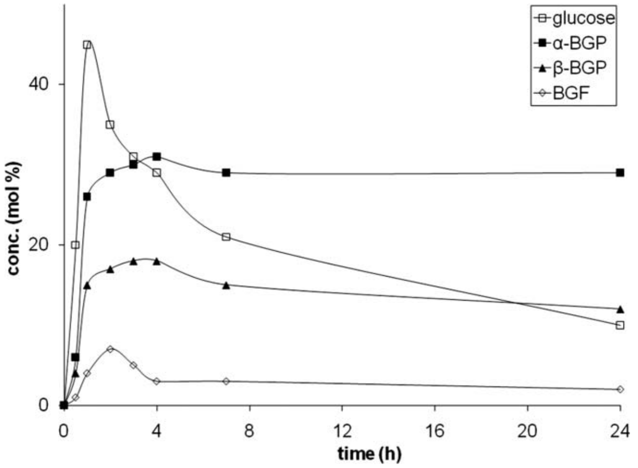


**Fig. 1** Run profile of reaction between cellulose (0.05 g) and *n*-butanol (0.3 mL) in BMImCl (1 g) in the presence of Amberlyst 15DRY (0.01 g) at 110 °C.

While attempting to reach the equilibrium by extending the reaction time up to 24 h, it was observed that the product yield starts to decrease slowly. In order to understand this phenomenon, pure α-BGP and glucose were dissolved in BMImCl in the presence of the acid resin, and the mixture composition was monitored *versus* time. This clearly showed that at 110 °C, α-BGP is more resistant to acidic hydrolysis caused by Amberlyst 15DRY than glucose, as is shown in Fig. 2. Especially initially, the concentration of glucose falls faster than that of α-BGP. We observed that under the same conditions but without the acidic catalyst, concentrations of glucose and α-BGP remained virtually unchanged during the same periods of time. The fact that even the α-BGP concentration decreases is likely due to the dynamic nature of the equilibrium between glucose and α-BGP: as glucose starts to disappear, the equilibrium shifts to glucose and α-BGP is transformed back into glucose, even in the presence of *n*-butanol.

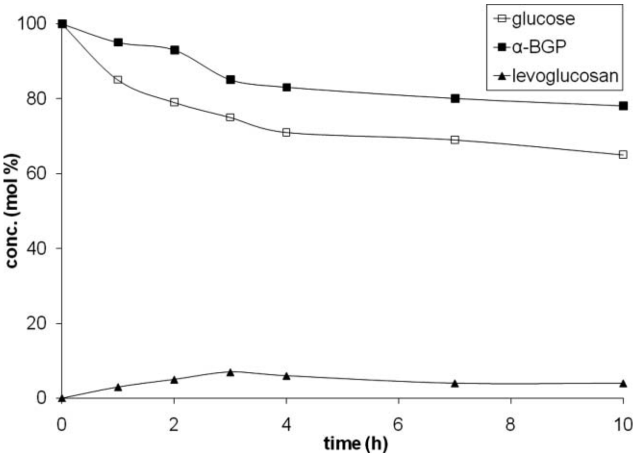


**Fig. 2** Stability of a mixture of glucose and α-BGP in BMImCl (1 g) in the presence of Amberlyst 15DRY (0.01 g) at 110 °C.

In order to maximize the yield of butylated products two approaches were used. First, it was attempted to shift the equilibrium *via* the law of mass action. This was achieved by adding an additional volume of *n*-butanol after some time of cellulose hydrolysis, when the extra solvent no longer causes precipitation of the polymeric material (Table 3, entries 2–3). Indeed, addition of a large excess of *n*-butanol right from the start could impede smooth cellulose dissolution. In a second approach, part of the Amberlyst 15DRY particles were removed after some reaction time. It was speculated that the amount of acid catalyst required for the hydrolysis may be higher than the amount needed for the alkylation (Table 3, entries 4–7).

**Table 3** Conversion of cellulose to butylglycosides over Amberlyst 15DRY in various conditions[a]

| Entry | Solvent | Co-reagent | Yield of α-BGP (%) | Yield of β-BGP (%) | Yield of BGF (%) | Yield of glucose (%) | Yield of levoglucosan (%) | Total yield of butylated products (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 g BMImCl | — | 29 | 16 | 5 | 10 | 7 | 50 |
| 2[b] | 1 g BMImCl | — | 53 | 30 | 3 | 9 | 6 | 85 |
| 3[b] | 1 g BMImCl | 3 μL $H_2O$ | 61 | 25 | 0 | 11 | 4 | 86 |
| 4[c] | 1 g BMImCl | — | 37 | 20 | 13 | 18 | 12 | 70 |
| 5[d] | 1 g BMImCl | — | 33 | 16 | 12 | 27 | 12 | 61 |
| 6[e] | 1 g BMImCl | — | 28 | 12 | 11 | 15 | 8 | 51 |
| 7[f] | 1 g BMImCl | — | 24 | 10 | 9 | 18 | 9 | 43 |
| 8 | 1 g [EMIm][$Et_2PO_4$] | — | 0 | 0 | 0 | 0 | 0 | 0 |
| 9 | 1 g [EMIm][AcO] | — | 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | 1 g [EMIm][AcO] | 4 μL $H_2O$ | 0 | 0 | 0 | 0 | 0 | 0 |
| 11 | 1 g [$Bu_3PEt$][$Et_2PO_4$] | — | 12 | 12 | 0 | 19 | 5 | 24 |
| 12 | 1 g [$Bu_3PEt$][$Et_2PO_4$] | 4 μL $H_2O$ | 14 | 14 | 0 | 22 | 0 | 28 |
| 13 | 1 g [$Bu_4P$][Cl] | — | 0 | 0 | 0 | 0 | 0 | 0 |
| 14 | 1 g [$Bu_4P$][Cl] | 4 μL $H_2O$ | 0 | 0 | 0 | 0 | 0 | 0 |

[a] General reaction conditions: 0.05 g cellulose, 0.3 mL *n*-butanol, 0.01 g Amberlyst 15DRY, 110 °C, 24 h. [b] After 4 h 1.2 mL of *n*-butanol was added to the reaction mixture. [c] 95% of the Amberlyst 15DRY particles were removed after 4 h. [d] 70% of the Amberlyst 15DRY particles were removed after 4 h. [e] 95% of the Amberlyst 15DRY particles were removed after 2 h. [f] 70% of the Amberlyst 15DRY particles were removed after 2 h.

Particularly the first approach was successful in raising the alkylglycoside yield, and using an overall *n*-BuOH to glucose monomer ratio of 50, the yield climbed up to 86%. Note that this is much higher than the ~50% maximal yield of glucose from cellulose that is obtained when no secondary reaction is performed in the same pot.[15b] The same experiment was also performed on a five-fold increased scale, with otherwise identical ratios of reactants and ionic liquid solvent. A summed 84% maximal yield of alkylated compounds was retrieved, using the same overall 50 : 1 ratio of butanol to carbohydrate monomeric units. Regarding the partial removal of the acid catalyst, the best effect was noted when 95% of the particles were removed after 4 h (Table 3, entries 4–5), with finally a yield of 70% butylated products at the relatively low molar *n*-BuOH to glucose monomer ratio of 10. Such a procedure constitutes a compromise between a sufficient catalyst contact to allow smooth hydrolysis and alkylation, and on the other hand, prevention of acid-catalyzed degradation late in the reaction.

We also tried to use alternative ILs that dissolve cellulose, such as 1-ethyl-3-methylimidazolium diethylphosphate, 1-ethyl-3-methylimidazolium acetate, ethyltributyl-phosphonium diethylphosphate or tetrabutylphosphonium chloride (Table 3, entries 8–14). Note that some of these ILs are considerably more hydrophobic than BMImCl. Therefore, these IL solvents were also tested with the addition of an amount of water that is stoichiometric with respect to the cellulose. Only ethyltributylphosphonium diethylphosphate showed some suitability for the reaction (Table 3, entries 11–12). Using other anions than chloride may be problematic, since some anions that have been reported as suitable for cellulose dissolution, *e.g.* acetate, may actually act as a buffer and consequently quench the acidity of the resin. This could account for the lack of product formation in the presence of 1-ethyl-3-methylimidazolium acetate. One of the factors contributing to the suitability of ethyltributylphosphonium diethylphosphate could be the asymmetric nature of its cation, which decreases the viscosity of the IL medium and thus increases diffusivities and reaction rates.[20] While the addition of a minute amount of water (0.25 or 0.33 wt%) did not hinder the dissolution of the cellulose, it had no significant effect in this type of reaction (Table 3, entries 2, 10, 12, 14). None of the assessed alternative ILs matched the performance of BMImCl.

Besides *n*-butanol, *n*-octanol was also used as an alkylating agent. Using the same 10 to 1 molar ratio of alcohol with respect to the glucose monomer, a similar kinetic profile was observed. Fig. 3 shows that α-OGP (octylglucopyranoside) is the major product of the reaction after 30 min. Its concentration passes through a maximum at 4 h and then decreases with time. Again, the β-isomer and the furanosides are the prevalent by-products. By analogy with the alkylation with butanol, the predominance of α-OGP can be explained by its higher thermodynamic stability in comparison with β-OGP and OGF (octylglucofuranoside).[21] Control experiments showed that α-OGP is again more resistant to acidic degradation caused by Amberlyst 15DRY than the intermediate glucose. Reaction between 0.05 g of cellulose and 0.5 mL of *n*-octanol in 1 g of ethyltributylphosphonium diethyl phosphate, in the presence of 0.01 g of Amberlyst 15DRY at 110 °C during 24 h gave the following product yields: 20% of α-OGP, 5% of β-OGP, 22% of glucose and 5% of levoglucosan. This confirms that

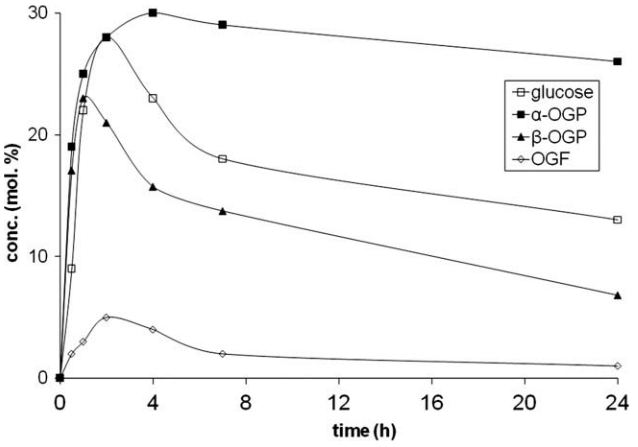


**Fig. 3** Run profile of reaction between cellulose (0.05 g) and *n*-octanol (0.5 mL) in BMImCl (1 g) in the presence of Amberlyst 15DRY (0.01 g) at 110 °C.

**Table 4** Transalkylation of α-BGP with *n*-octanol

| Entry | Amberlyst 15DRY mass (g) | Yield of α-OGP (%) | Yield of β-OGP (%) | Yield of OGF (%) | Yield of glucose (%) | Yield of BGF (%) | Yield of BGP (%) | Yield of levoglucosan (%) | Total yield of octylated compounds (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.020 | 38 | 21 | 5 | 15 | 6 | 5 | 10 | 64 |
| 2 | 0.010 | 30 | 10 | 4 | 12 | 4 | 10 | 8 | 44 |
| 3 | 0.001 | 6 | 4 | 8 | 0 | 0 | 80 | 0 | 18 |
| 4 | 0 | 0 | 0 | 3 | 0 | 0 | 90 | 0 | 10 |

Reaction conditions: 0.05 g α-BGP, 1 g BMImCl, 0.5 mL *n*-octanol, 110 °C, 24 h.

other ILs than BmimCl are also potential solvents in these reactions.

In solvent-free systems, the rate of glucose alkylation decreases with increasing length of alcohol alkyl chain.[22] This is due to the decreasing solubility of glucose in more apolar alcohols. We have observed a different situation when cellulose dissolved in BMimCl is the carbohydrate source: octylation is initially faster than butylation. On the other hand, using shorter alcohols negatively affected the reaction. Thus, when methanol or ethanol were applied in the same molar ratio with respect to the glucose monomers, the cellulose was not visibly dissolved, and no products of etherification or hydrolysis could be detected. It seems that the short alcohols compete more successfully than the cellulose for the hydrogen bond formation with the chloride anions. As the chain length of the alcohol reagent increases, its hydrogen bond donor capacity decreases, and this allows a better solvation of the cellulose by the IL and a faster reaction.

However, an alkyl chain that is too long, as in 1-dodecanol, again decreases the product yields. Thus, no products were obtained from a 24 h reaction of cellulose and *n*-dodecanol in BMImCl at 110 °C, even if a visually homogeneous reaction mixture was formed. Apparently, BMimCl is not a suitable solvent to effect the reaction between dissolved glucose and *n*-dodecanol, which have widely different polarities.

In an alternative approach to prepare the long-chain alkylglycosides, it was attempted to perform a transalkylation, starting from a short-chain alkylglycoside. The data in Table 4 prove that this transalkylation can easily be performed in an IL: reaction of α-BGP and *n*-octanol gave up to 64% yield of octylated compounds within 24 h. The acidic catalyst concentration required for this transalkylation is similar to the amount of catalyst typically used in the cellulose depolymerization, *i.e.* at least 10 mg of catalyst per g of IL (Table 4, entries 1–4). In order to synthesize dodecylglucosides, a reaction was performed using 0.05 g of cellulose (0.31 mmol monomers), 0.3 mL of *n*-butanol, 10 mg of Amberlyst 15DRY and 20 μL of water in 1 g of BMImCl. After 1 h of stirring at 110 °C, 0.611 g of *n*-dodecanol (3.2 mmol) was added. After another 3 h at 110 °C, *n*-butanol was evaporated from the reaction mixture in a rotary evaporator, and an extra portion of 0.611 g of *n*-dodecanol was added. As is shown in Fig. 4, equilibrium was apparently reached after 10 h. At this point, the yield of DGP is 45% (29% α-DGP and 16% β-DGP), with the α-glucopyranoside isomers dominating over the β-isomers during the whole course of the reaction (DGP = dodecylglucopyranoside). This proves that hydrolysis followed by alkylation and transalkylation is a viable route in forming the long-chain alkylglycosides from cellulose.

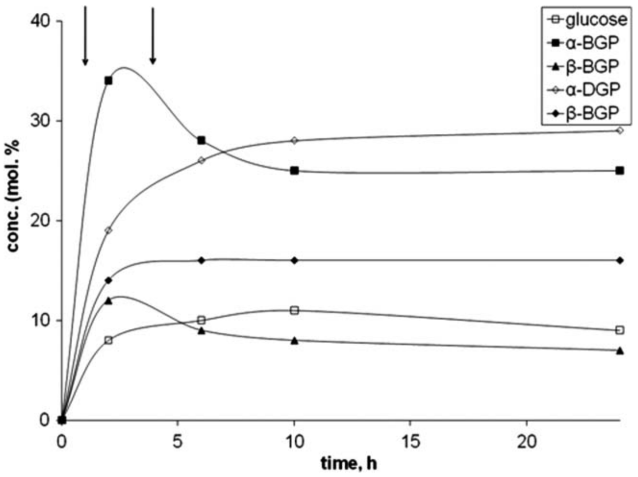


**Fig. 4** Run profile of reaction between cellulose (0.05 g), *n*-butanol (0.3 mL) and subsequently *n*-dodecanol (two loads of 0.611 g, indicated by arrows) in BMImCl (1 g) in the presence of Amberlyst 15DRY (0.01 g) at 110 °C.

## Conclusions

The results prove that when the cellulose structure is unfolded in an ionic liquid, the depolymerization becomes rather easy, and can be carried out under moderate conditions. Two ionic liquids were identified that allow to dissolve the cellulose and to perform the acid-catalyzed hydrolysis and alkylation. While the use of an acid catalyst could cause degradation of the formed hexoses, it was demonstrated here that this problem can be alleviated by *in situ* conversion of the glucose to alkylglycosides. When an excess of the alcohol was offered, or when part of the acid catalyst was removed during the alkylation phase, the yield of alkylglycoside could be maximized. The direct synthesis of alkyl glycosides with longer chains, such as dodecylglycopyranosides, is less easy, but can be achieved *via* transalkylation. To separate the reaction products from the ionic liquid, supercritical antisolvent precipitation with carbon dioxide could be a promising technique.[23]

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