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Dissolution and depolymerization of barley starch in selected ionic liquids

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ABSTRACT

Polysaccharides like starch are poorly soluble in common solvents. However, certain ionic liquids (ILs) have been found to dissolve them, although some depolymerization happens during the dissolution. Dissolution and depolymerization of barley starch in ten ionic liquids have been studied with *p*-TsOH as a catalyst under controlled microwave heating. Dissolution time and the extent of the depolymerization of starch, determined by using HPLC-ELSD, were specific to each IL. Dialkylimidazolium halide ILs dissolved starch fast and depolymerized it substantially producing 79–100% water-soluble starch oligomers with the average molecular weight of 1000–2000 Da. 1-Ethyl-3-methylimidazolium phosphate ([EMIM][Me_2PO_4]) and 2-hydroxyethylammonium formate ([$NH_3CH_2CH_2OH$][HCOO]) dissolved starch slowly and depolymerized it least among the tested ILs. For the slow depolymerization of starch these ILs can be considered as suitable solvents for starch modifications where its depolymerization should be avoided.

1. Introduction

Starch is a highly abundant, non-toxic and renewable biopolymer that is produced in assimilating plants. It is extensively utilized in various fields of industry e.g. in food, paper, wood or pharmaceutical industry (Copeland, Blazek, Salman, & Tang, 2009).

Starch has a semicrystalline, granular structure which affects that it is highly insoluble in most solvents and usually needs physical or chemical modification prior to use (Huber & BeMiller, 2010). Recently it has been discovered that some common ionic liquids (ILs) like 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) dissolve and depolymerize various carbohydrates like cellulose and starch (Kärkkäinen, Lappalainen, Joensuu, & Lajunen, 2010; Stevenson, Biswas, Jane, & Inglett, 2007; Vitz, Erdmenger, Haensch, & Schubert, 2009; Zakrzewska, Bogel-Łukasik, & Bogel-Łukasik, 2010). The chloride counter ion of these ILs has a strong tendency to break inter- and intramolecular hydrogen bonds in starch, hence resulting in starch dissolution and depolymerization (Anderson, Ding, Welton, & Armstrong, 2002; Bentivoglio et al., 2006; Novoselov, Sashina, Kuz'mina, & Troshenkova, 2007; Remsing, Swatloski, Rogers, & Moyna, 2006).

In our previous paper we showed that various starch species can be depolymerized into water-soluble 1500–2000 Da-sized starch oligomers by heating them in [AMIM]Cl. *p*-Toluenesulfonic acid as a catalyst hastens the reaction (Lappalainen, Kärkkäinen, Panula-Perälä, & Lajunen, 2012). In the present work we have compared the dissolution and depolymerization of starch in ten ILs in the presence of the catalyst. Microwave activation was utilized as a heating method in this study since in our previous study it was found to be substantially faster method than conventional heating (Lappalainen et al., 2012).

1.1. Materials

Native barley starch was obtained from Ciba Specialty Chemicals Inc. (Raisio, Finland). Before use starch was dried in an oven at 105 °C for 24 h and stored in a desiccator. Polymer standards (BioChemika Dextran 5, 25, 50, and 150 kDa), maltohexaose, D-(+)-glucose and *p*-TsOH (TM Fluka) were purchased from Sigma Aldrich (Schnelldorf, Germany). 1-Propanol (A.R. 99.5%) and ethanol (99.5%) were purchased from Labscan (Gliwice, Poland) and Altia (Rajamäki, Finland), respectively.

Ionic liquids were prepared by applying the known methods (Bicak, 2005; Huddleston et al., 2001; Kuhlmann, Himmler, Giebelhaus, & Wasserscheid, 2007; Parnham & Morris, 2006; Zhang, Wu, Zhang, & He, 2005), dried before use overnight in high vacuum at 50 °C and stored in a desiccator. Water contents of the ILs determined by the Mettler Toledo DL36 Karl Fischer coulometer were less than 0.1% (w/w). Starting materials for the preparation of ILs i.e. allyl chloride (Reagent Plus®, 99%), 1-chlorobutane (TM Fluka, 99%), 1-bromobutane (TM Fluka, 96%), 1-chlorohexane (99%), 1-bromohexane (98%), trimethyl phosphate (99 + %), 1-methylimidazole (≥99%) and 1-ethylimidazole (99%) 1-butylimidazole, imidazole, 2-hydroxy ethylamine, formic acid and anolyte and catolyte chemicals, Hydranal-Coulomat AG and CG,

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respectively, for Karl Fischer measurements were purchased from Sigma Aldrich (Schnelldorf, Germany).

1.2. Dissolution and depolymerization of barley starch in different ILs and water

In a typical experiment the starch dispersion (10%(w/w)) was prepared in a microwave reactor tube (2–5 ml) by adding native barley starch and the catalyst *p*-TsOH (3%(w(catalyst)/w(starch)) into IL. At room temperature solid IL (e.g. [BMIM]Cl, [BMIM]Br and [EMIM][Me_2PO_4]) was melted before the addition of starch and the catalyst. If IL crystallized during the addition of starch ([BMIM]Cl and [BMIM]Br), the vial was gently warmed in an oil bath until IL melted and the dispersion formed. The dispersion was then carefully stirred and heated in a microwave reactor (Biotage Initiator) at 80 °C until a clear mixture was obtained. The lowest effective power of the microwave reactor (20–30 W) was used for heating.

The progress of the dissolution and depolymerization was monitored at different time intervals by taking 0.1 ml samples into Eppendorf tubes (1.7 ml). The product was precipitated with 1-propanol by filling the sample tube into its maximum volume. The mixture was centrifuged at 13 400 g for 5 min. The supernatant was removed and the product pellet was washed with ethanol by filling the tube to its maximum volume. After centrifuging at 13 400 g for 5 min the supernatant was removed. The pellet was dried in oven at 35 °C for 20 h. Dry pellet was dissolved into 1.7 ml of distilled water, centrifuged as before, filtered through a 1.2 μm nylon membrane filter and analysed with high-performance liquid chromatography equipped with an evaporative light scattering detector (HPLC-ELSD).

1.3. Analytical methods

Depolymerized barley starch samples were analysed with a Shimadzu HPLC-ELSD. The instrument consisted of three isocratic pumps (LC-10AD), a degasser (DGU-14A) and an automatic sampler (SIL-10AD). The analysis was performed using a guard column (Phenomenex PolySep-GFC-P 35 mm × 7.80 mm) and an analytical column (Phenomenex Poly Sep-GFC-Linear 300 mm × 7.80 mm). The temperature of the column oven (Shimadzu, CTO-10AS) was maintained at 40 °C. The ELS detector (Polymer Laboratories PL-ELS 2100) was optimized for the analytes and the following parameters were used: 80 °C for an evaporative temperature, 50 °C for a nebulizer and 0.90 ml/min for a nitrogen gas flow. Distilled–deionized water passed through in-line membrane filters (0.45 μm Millipore, Bedford, MA) was used as the mobile phase with the flow rate of 0.4 ml/min. The system was controlled and data was handled by using LC Solution program (LabSolutions 1.03 SP5 Shimadzu).

2. Results and discussion

The starting point for the selection of the studied ionic liquids was to provide various ILs that are liquids at or near the room temperature and hence practical to use. The ability of IL to form hydrogen bonds with starch guided the selection of the anion. Bromide based ILs were selected since bromide is more nucleophilic than chloride and can therefore form hydrogen bonds more readily and enhance the dissolution of starch. On the other hand halogen-free ILs are more ecological than those containing halogens. Therefore ILs containing anions such as formate and dimethylphosphate were synthesized. The selected ILs are presented in Table 1.

Our study concerning the dissolution and depolymerization of starch in [BMIM]Cl without a catalyst indicated that the molecular weight of starch after dissolution was smaller than that of native starch (Kärkkäinen et al., 2010). This indicates that some depolymerization happened during the dissolution. However, the molecular weight was still substantially high. The aim of our other study was to produce water-soluble starch fragments for bacterial cultivation experiments. The most suitable 1000–2000 Da-sized fragments were produced with *p*-TsOH as catalyst in [AMIM]Cl (Lappalainen et al., 2012). The *p*-TsOH speeded up the dissolution via depolymerization. In this work we have studied the production of corresponding fragments also in other ILs than [AMIM]Cl. Therefore [AMIM]Cl was used as a reference in the experiments.

Barley starch was mixed with each IL and the dispersion was heated in the microwave reactor until a clear solution was obtained (Table 1.) HPLC-ELSD analysis of earlier studies had showed that when the dispersion cleared the starch species had depolymerized mainly into 1000–2000 Da-sized water-soluble starch oligomers. Subsequently, the depolymerization products were precipitated with 1-propanol, dried and their water-solubility was tested. Table 1 shows the dissolution time of starch, the yields of the precipitated products and their water-solubility. The dissolution time and the amount of depolymerization occurring during dissolution were specific to each IL.

The average molecular weight distributions of the products from the depolymerization reactions were analysed with HPLC-ELSD. The graph of the molecular weights of the standards as a function of the retention time is presented in Fig. 1 (the HPLC-ELSD chromatograms of the used standards and native barley starch are provided as a Supplementary material). The average molecular weights of the depolymerization products were calculated based on the retention times (t_r) from the linear prediction equation $\log M_w = -0.5298 \times t_r + 17.072$ (Fig. 1).

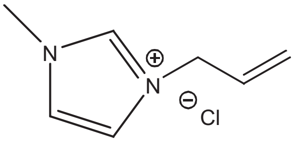
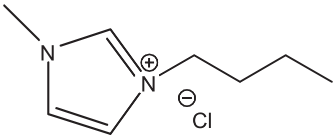
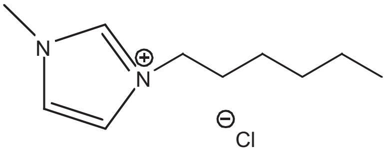
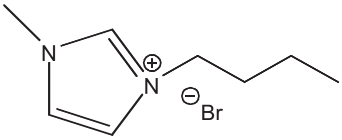
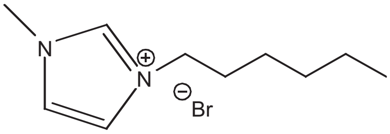
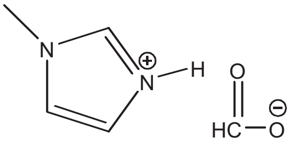
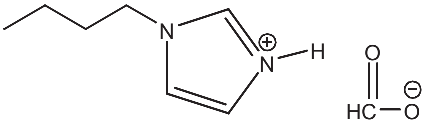
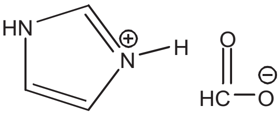
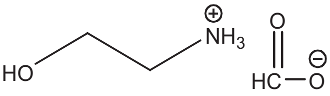
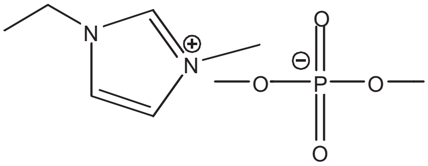
2.1. Dissolution and depolymerization of barley starch in [AMIM]Cl, [BMIM]Cl, [BMIM]Br, [HMIM]Cl and [BMIM]Br

The heating of barley starch in [AMIM]Cl at 80 °C with *p*-TsOH dissolved starch and depolymerized it into 98% water-soluble products in 1.5 h (Table 1). Yield of the precipitated products was high, 84%. The HPLC-ELSD chromatogram of the product contained two peaks (Fig. 2A, Table 2). The peak at the lower retention time was substantially smaller than the peak at higher retention time. According to the HPLC-ELSD chromatograms the majority of the products were on average 1500 Da sized starch oligomers (Fig. 2, Table 2). Thus, products with narrow average molecular weight distribution were produced. However, short-chained or monomeric sugars formed during the reaction started to decompose even before all starch had dissolved, which was detected as a slightly brownish colour of the reaction mixture.

In [BMIM]Cl barley starch dissolved and depolymerized into starch oligomers almost as fast as in [AMIM]Cl, in 2 h. The average molecular weights of the products, that were according to HPLC-ELSD chromatograms of the same order of magnitude in both ILs (Fig. 2A and B, Table 2), started to decompose further before the complete dissolution of the starch. The decomposition of the products was less susceptible in [BMIM]Cl than in [AMIM]Cl as indicated by the higher yield of the products (90%) in [BMIM]Cl. A disadvantage of [BMIM]Cl was its high melting point, ca. 70 °C, and therefore it tended to crystallize during the preparation of reaction mixture. ILs that are liquids at room temperature are therefore more practical in use.

In 1-hexyl-3-methylimidazolium chloride ([HexMIM]Cl) the reaction took twice as much time as in [AMIM]Cl, i.e. 3 h and the yield was 77% (Table 1). The length of the alkyl substituent in the imidazolium ring affected the dissolution of starch. This may be due to the steric hindrance caused by the larger cation which reduces the penetration of IL into the starch granules or the hydrophobicity of the IL, which increases with the increasing alkyl chain length. Additionally the chloride content of [HexMIM]Cl (17.3%) was lower

Table 1
Dissolution time of barley starch, yields and water-solubility of the products from its depolymerization reactions in selected ionic liquids at 80 °C with p-TsOH as catalyst.

Ionic liquid	Structure	Dissolution time/h	Yield[b]/%	Water-solubility of the product/%
1-Allyl-3-methylimidazolium chloride, [AMIM]Cl		1.5	84	98
1-Butyl-3-methylimidazolium chloride, [BMIM]Cl		2	90	99
1-Hexyl-3-methylimidazolium chloride, [HexMIM]Cl		3	77	95
1-Butyl-3-methylimidazolium bromide, [BMIM]Br[c]		0.33	58	79
		3.5[a]	>100	90
1-Hexyl-3-methylimidazolium bromide, [HexMIM]Br		0.05	57	8
		2.5[a]	58	100
1-Methylimidazolium formate, [HMIM][HCOO]		5	>100	95
1-Butylimidazolium formate, [HBIM][HCOO]		5		
Imidazolium formate, [HIM][HCOO]		4	>100	70
2-Hydroxy ethylammonium formate, [$NH_3CH_2CH_2OH$][HCOO]		5	>100	39
1-Ethyl-3-methylimidazolium dimethylphosphate, [EMIM]Me_2PO_4		16 6 5[a]	100 >100 >100	45 40 30

[a] Performed without a catalyst.
[b] Yield of the product precipitated with 1-propanol.
[c] Reactions were performed at 90 °C.

Table 2
Retention times and average molecular weights of the products of barley starch dissolution and depolymerization experiments.

Ionic liquid	Catalyst	Retention time (min)	Average M_w (Da)
[AMIM]Cl	TsOH	22 ± 0.1	$300\,000 \pm 40\,000$
		26.3 ± 0.1	1500 ± 300
[BMIM]Cl	TsOH	19.2 ± 0.1	$8000\,000 \pm 1000\,000$
		20 ± 0.1	$3\,000\,000 \pm 400\,000$
		26 ± 0.1	2000 ± 300
[HexMIM]Cl	TsOH	22 ± 0.1	$300\,000 \pm 40\,000$
		27 ± 0.1	1000 ± 100
[BMIM]Br	–	24 ± 0.1	$25\,000 \pm 3000$
		26.5 ± 0.1	1000 ± 200
[HexMIM]Br	–	21.2 ± 0.1	$700\,000 \pm 100\,000$
		27 ± 0.1	1000 ± 100
[HMIM][HCOO]	TsOH	13.8 ± 0.1	>10 000 000
		24.2 ± 0.1	$20\,000 \pm 3000$
[HIM][HCOO]	TsOH	14.2 ± 0.1	>10 000 000
		24.2 ± 0.1	$20\,000 \pm 3000$
$[NH_3CH_2CH_2OH][HCOO]$	TsOH	25.8 ± 0.1	2500 ± 300
$[EMIM]Me_2PO_4$	TsOH	12.3 ± 0.1	>10 000 000
		23.5 ± 0.1	$40\,000 \pm 7000$
	–	24 ± 0.1	$25\,000 \pm 3000$

compared to [AMIM]Cl or [BMIM]Cl where the chloride contents were 22.2% or 20.1%, respectively (Swatloski, Spear, Holbrey, & Rogers, 2002). [HexMIM]Cl is a viscous liquid like [AMIM]Cl at room temperature, which makes it easier to use than [BMIM]Cl (Swatloski et al., 2002).

Ionic liquids with bromide as a counter anion, [HexMIM]Br or [BMIM]Br, decomposed starch rapidly in 3 or 20 min, respectively, catalyzed by *p*-TsOH. Resulting mixtures were dark brown and yields low (below 60%) (Table 1). The water-solubilities of the products prepared in [HexMIM]Br and [BMIM]Br were 8% and 79%, respectively. This indicated that [HexMIM]Br with longer alkyl chain depolymerized starch slower than [BMIM]Br. Hence starch in [HexMIM]Br preserved its long-chained structure and therefore was less water-soluble. However, due to the bromide anion and the catalyst the small-sized products that formed in both ILs decomposed readily, which decreased the yield. Therefore the reactions in these ILs were performed without the catalyst. Also, the reasonably high melting point of [BMIM]Br (ca. 80 °C) affected that the IL tended to crystallize in the microwave reactor if the reaction temperature was below 90 °C. Therefore that higher temperature was used for the reactions performed in [BMIM]Br and not 80 °C which was used for the reactions performed in other ILs. The absence of the catalyst increased the reaction time significantly demonstrating the power of *p*-TsOH as the catalyst. The reaction times in [HexMIM]Br or [BMIM]Br were 2.5 h or 3.5 h, respectively, which were as long as the reaction time in [HexMIM]Cl with the catalyst (Table 1). Bromide is more nucleophilic than chloride and can therefore form hydrogen bonds more readily. Hence bromide anion breaks inter- and intramolecular hydrogen bonds of starch more effectively than chloride. Bromide content of [BMIM]Br or [HexMIM]Br is 36.5% or 32.4%, respectively. The contents are higher compared to chloride contents in corresponding ILs. Bromide and chloride are both strong hydrogen bond acceptors and coordinate with hydroxyl groups of starch molecules.

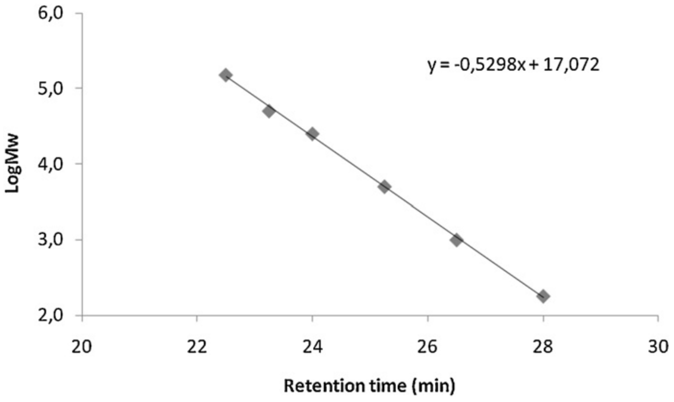


Fig. 1. Graph of log M_w versus retention time of the used standards (Dextran 150, 50, 25 and 5 kDa, maltohexaose 1 kDa and D-(+)-glucose).

Despite the presence or lack of the catalyst, all studied imidazolium-based halide ILs depolymerized starch during dissolution into water-soluble products (Fig. 2A–E, Table 2). The length of the alkyl chain substituting the imidazolium ring affected to the reaction time especially with dialkylimidazolium chlorides. The reaction time increased with increasing alkyl chain length. The main fractions of the products from different reactions, i.e. the fractions with higher retention times, were of same order of magnitude. Discoloration of the reaction mixture from yellow or orange to slightly brownish occurred in all ILs due to the caramelization of short-chained or monomeric sugars.

2.2. *Dissolution and depolymerization of barley starch in $[EMIM][Me_2PO_4]$, [HBIM][HCOO], [HMIM][HCOO], [HIM][HCOO] and $[NH_3CH_2CH_2OH][HCOO]$*

Imidazolium-based formates, imidazolium formate ([HIM][HCOO]) and 1-methylimidazolium formate ([HMIM][HCOO]), dissolved and depolymerized starch easily. 1-Butylimidazolium chloride ([HBIM][HCOO]), however did not dissolve starch at all. During 6 h of heating starch only settled on the bottom of the reactor tube. Reactions in [HMIM][HCOO] and [HIM][HCOO] did not proceed as fast as in imidazolium halide ILs and heating was continued for several hours (Table 1). Formates were easy to use compared to rather viscous halides, as they were very fluid at room temperature. Yields and amounts of the water-soluble products were also good (Table 1). However, according to HPLC-ELSD chromatograms (Fig. 2F and G) the products formed during heating were larger than the products formed in halide ILs (Fig. 2 A–E, Table 2) being ca. 20 000 Da-sized. Their chromatograms contained two peaks indicating that products also included a fraction of substantially longer starch chains (Table 2). The colour of the reaction mixture remained yellow during the reaction indicating that no caramelization of short-chained or monomeric sugars occurred.

The yields of the products, in formate ILs, were higher than 100%. This was related to the precipitation of IL with the products. It

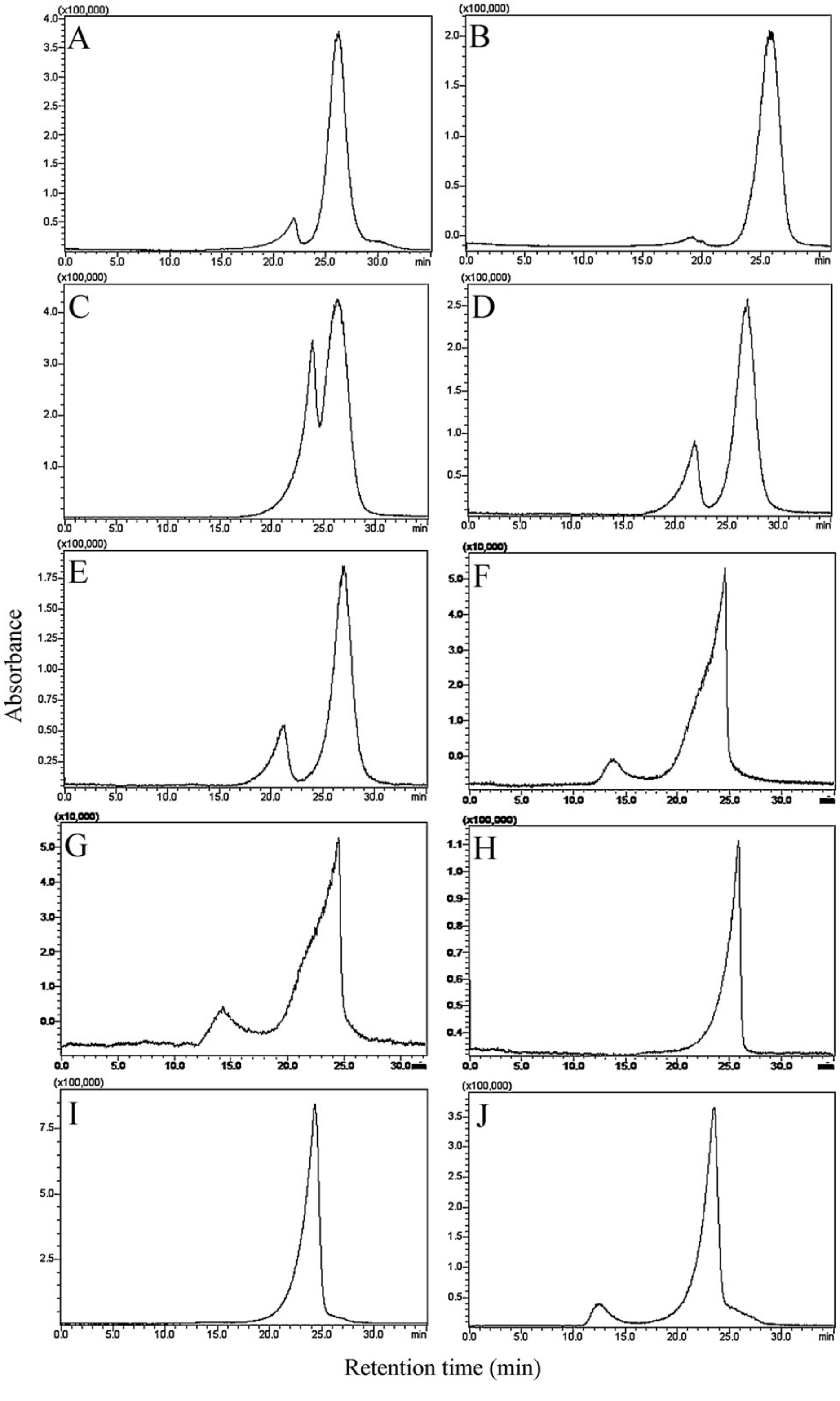


Fig. 2. HPLC-ELSD chromatogram of a sample from the dissolution and depolymerization reaction of barley starch in microwave reactor in (a) [AMIM]Cl for 1,5 h with *p*-TsOH, (b) [BMIM]Cl with *p*-TsOH for 2 h, (c) [BMIM]Br at 90 °C for 3,5 h, (d) [HexMIM]Cl with TsOH for 3 h, (e) [HexMIM]Br for 2,5 h, (f) [HMIM][HCOO] with *p*-TsOH for 5 h, (g) [HIM][HCOO] with *p*-TsOH for 4 h, (h) [$NH_3CH_2CH_2OH$][HCOO] with *p*-TsOH for 5 h, (i) [EMIM][Me_2PO_4] for 5 h, (j) [EMIM][Me_2PO_4] with *p*-TsOH for 16 h.

seemed that in reactions where starch did not depolymerize into oligomeric products, it precipitated as white flakes IL adhered to them. Careful washing with ethanol did not remove IL from the precipitate.

The effect of the structure of the cation on the starch dissolution was clearly seen with imidazolium formates. [HBIM][HCOO] with a four carbon alkyl chain in the cation did not dissolve starch due to the steric hindrance caused by the alkyl chain. [HIM][HCOO] with the symmetric cation without side chains and [HMIM][HCOO] with a methyl substituent in the cation dissolved starch well and depolymerized it extensively.

[EMIM][Me_2PO_4] and [$NH_3CH_2CH_2OH$][HCOO] depolymerized starch least of all ILs. A clear starch solution formed in both of them in a reasonable time, 6 or 5 h, respectively. Both ILs have a good hydrogen bonding ability and low melting points, ca. 21 °C and −82 °C, respectively (Bicak, 2005; Fukaya, Hayashi, Wada, & Ohno, 2008). In the molten state they were very fluid resulting in the easier use than with viscous or solid imidazolium halide ILs. During heating water-soluble products were produced only 39% in [$NH_3CH_2CH_2OH$][HCOO] (Table 1, Fig. 2H) and 40% in [EMIM][Me_2PO_4] (Table 1). Even if [EMIM][Me_2PO_4] was heated for16 h with *p*-TsOH only 45% of water-soluble products were yielded (Table 1, Fig. 2K). For comparison the dissolution of barley starch in [EMIM][Me_2PO_4] was also tested without the catalyst. The dissolution of starch occurred then within 5 h during which 30% of water-soluble products were formed (Table 1, Fig. 2J). Therefore [EMIM][Me_2PO_4] and [$NH_3CH_2CH_2OH$][HCOO] can be considered as suitable solvents for starch modifications in where the depolymerization of starch is not desired. After all the purification of precipitation products is essential, since yields were in these as well as in previous reactions in formate ILs, higher than 100%. It seemed that, the larger the precipitated product was the more IL adhered to it. A search for a more effective purification method for the product is going on. A problem with [$NH_3CH_2CH_2OH$][HCOO] was that when starch was dissolved in it, a heavy gel was formed. Obviously lower starch concentrations than 10%(w/w) must be used if starch is processed in [$NH_3CH_2CH_2OH$][HCOO].

3. Conclusions

The suitability of ten ILs for the barley starch dissolution and depolymerization was tested. Reactions were performed at 80 °C using controlled microwave activation as the heating method. Common dialkylimidazolium halides dissolved and depolymerized starch rapidly into 1000–2000 Da-sized, water-soluble starch oligomers. The reaction time depended on both the cation and the anion part of the IL. Larger cation in [HexMIM]Cl compared to the cation of [AMIM]Cl or [BMIM]Cl led to a slightly longer reaction time, which can be related to the steric hindrance caused by the longer alkyl chain. However more nucleophilic anion in [BMIM]Br and [HexMIM]Br compared to [BMIM]Cl and [HMIM]Cl, respectively, resulted in faster reactions, since the bromide anion broke more effectively than the chloride inter- and intramolecular hydrogen bonds of starch.

ILs with $[HCOO]^-$ or $[Me_2PO_4]^-$ as an anion dissolved starch slower than ILs with halide anion. Also less discoloration of the reaction mixture, due to the decomposition of short-chained or monomeric sugars, occurred in these ILs compared to imidazolium-based halides. The effect of the structure of the cation on the starch dissolving properties of the IL was clearly seen with imidazolium-based formate ILs. [BIM][HCOO] with four carbon alkyl chain in the cation did not dissolve starch at all when heated by using microwave activation. [HIM][HCOO] with the symmetrical cation and [MIM][HCOO] with a methyl substituent in the cation dissolved starch and depolymerized it extensively.

[$NH_3CH_2CH_2OH$][HCOO] and [EMIM][Me_2PO_4] proved to be the best ILs for the starch dissolution purposes. They dissolved starch in 5 or 6 h, respectively, [EMIM][Me_2PO_4] even without a catalyst, but depolymerized it substantially less than other tested ILs.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.04.011.

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