ORIGINAL ARTICLE

Reaction behavior of cellulose in various pyridinium-based ionic liquids

Ayako Miyata · Hisashi Miyafuji

Abstract We investigated the reaction behavior of cellulose in the pyridinium-based ionic liquids 1-ethylpyridinium chloride ([EtPy][Cl]), 1-ethylpyridinium bromide ([EtPy][Br]), and 1-ethylpyridinium iodide ([EtPy][I]). The cellulose was treated with the ionic liquids at 120 °C, and was found to exhibit quite a different reaction behavior in each of the different ionic liquids. Cellulose is completely dissolved and depolymerized in [EtPy][Cl]. In contrast, [EtPy][Br] only partially reacts with cellulose, while [EtPy][I] does not dissolve and react with cellulose at all. At the beginning of the treatment, cellulose was depolymerized with [EtPy][Cl] and [EtPy][Br] into various low molecular weight compounds such as cellobiose, cellobiosan, glucose, levoglucosan, and 5-hydroxymethylfurfural. As the treatment continued, some of the low molecular weight compounds reacted to form polymers. These ionic liquids are therefore not only a solvent for cellulose, but also a reagent for both its depolymerization into various low molecular weight compounds and subsequent polymerization of those compounds.

Keywords Cellulose · Ionic liquid · Pyridinium · Reaction behavior

Introduction

In recent times, several energy and environmental problems such as fossil resource exhaustion and global warming have become more serious. To overcome such problems, biomass has been focused as an alternative resource because of its reproductivity and carbon neutrality. Among the various biomass types, lignocellulosics are a promising resource because of the huge feedstock available and because they are unrelated to the food supply. The development of new conversion technologies is indispensable to ensure the effective exploitation of lignocellulosics. Much research has been conducted on various conversions of lignocellulosics such as acid hydrolysis [1], enzymatic saccharification [2], pyrolysis [3, 4], and supercritical fluid treatment [5]. However, efficient methods have not been established yet.

Recently, much attention has been paid to ionic liquid treatment as an attractive and novel technology for the conversion of lignocellulosics. Ionic liquids are organic salts having low melting points around ambient temperature. They can be easily modified by changing the structure of the cation and/or anion, which broadens their applications. Because of their negligible vapor pressure, non-flammability, and recyclability, ionic liquids are regarded as "green solvents". Since Swatloski et al. [6] revealed that some imidazolium-based ionic liquids can dissolve cellulose, there have been many fundamental and applicable studies on various ionic liquid treatments for the chemical conversion of lignocellulosics. Miyafuji et al. [7] reported that 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) penetrated into wood and liquefied the components of the wood by depolymerizing them. It has also been revealed that the reaction atmosphere affects the reaction behavior of wood during [C2mim][Cl] treatment [8]. The detailed mechanisms of wood liquefaction in various ionic liquids have also been clarified [9–12].

Comparative investigations of various ionic liquids have been conducted on cellulose, which is a main component of

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wood. Up to 5–7 wt % fibrous cellulose can be dissolved in 1-butyl-3-methylimidazolium bromide ([C4mim][Br]) and 1-butyl-3-methylimidazolium thiocyanate ([C4mim][SCN]) by microwave heating for 3–5 s, but cannot be dissolved at all in 1-butyl-3-methylimidazolium tetrafluoroborate ([C4mim][BF$_4$]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([C4mim][PF$_6$]) [6]. Sun et al. [11] revealed that acetate-based ionic liquids are superior to chloride-based ones for dissolving cellulose. The solubilization of cellulose in ionic liquids is mainly caused by the hydrogen bonding of cellulose hydroxyl groups to chloride or acetate anions and imidazolium cations [13–15]. Ohno et al. [16] reported that an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]), not only dissolved and decomposed cellulose, but also reacted with the compounds produced by the decomposition to form new polymers.

In addition to these uses, ionic liquids have also been applied as preconditioning agents for enzymatic hydrolysis [17] or saccharification [18] using cellulose, and as solvents for cellulose derivatization reactions such as acetylation [19, 20], carboxymethylation [21], and succination [22].

Ionic liquids consist of various kinds of cations. Piperidinium-, pyrrolidinium-, pyridinium-, and imidazolium-based structures are known representatively (Fig. 1). Although many studies have been conducted on the reaction of cellulose with imidazolium-based ionic liquids, there is little information concerning the reaction with ionic liquids having the other cation. In this study, therefore, we investigated the reaction behavior of cellulose in the pyridinium-based ionic liquids 1-ethylpyridinium chloride ([EtPy][Cl]), 1-ethylpyridinium bromide ([EtPy][Br]), and 1-ethylpyridinium iodide ([EtPy][I]). The fundamental information gained is crucial to understand and apply ionic liquid treatments of cellulose.
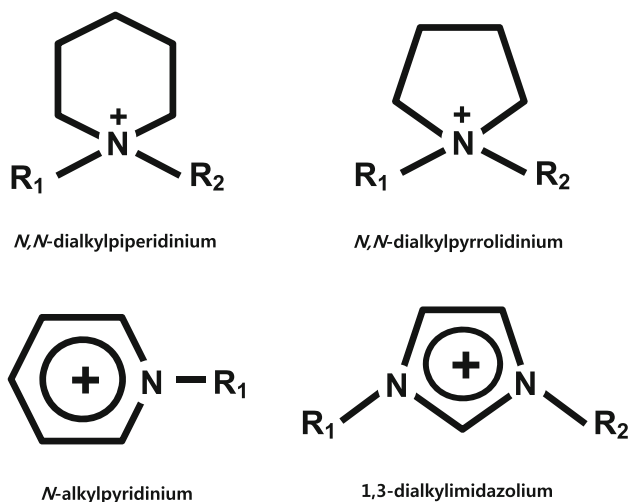
Fig. 1 The representative structures of cations for ionic liquids

Materials and methods

Samples and chemicals

Cellulose samples (Whatman CF11) were dried in an oven at 105 °C for 24 h before use. The ionic liquids 1-ethylpyridinium chloride ([EtPy][Cl]) (m.p. no data) and 1-ethylpyridinium bromide ([EtPy][Br]) (m.p. 117–119 °C) were purchased from Tokyo Kasei Kogyo. 1-Ethylpyridinium iodide ([EtPy][I]) (m.p. 97 °C) was purchased from Kanto Kagaku. Dehydrated dimethyl sulfoxide (DMSO) and potassium bromide (KBr) were purchased from Wako Chemicals.

Ionic liquid treatments

1.5 g ionic liquid was heated at 120 °C in a 50 mL glass flask. Although the melting point of [EtPy][Cl] is unknown, all ionic liquids used in this study were liquid at 120 °C. After the ionic liquid had melted, 0.045 g cellulose was added to the flask to start the reaction. The reaction medium was gently stirred throughout the reaction. 0 h of treatment time was defined as that when media became transparent without any cellulose particles in the flask under treatment with [EtPy][Cl]. It took 1 min. In the case of any other ionic liquid treatments, we used the same definition of 0 h.

Evaluation methods

50 mL distilled water was poured into the flask at the specified reaction time to quench the reaction. After stirring overnight at room temperature, the ionic liquid–water insoluble portions were filtered, washed several times with distilled water, oven-dried at 105 °C for 24 h and weighed to calculate the yields. Fourier transform infrared (FT-IR) spectra of the ionic liquid–water insoluble portions were recorded using a Shimadzu 8200PC spectrophotometer by KBr pellet method, over a spectral range of 4000–400 cm^{-1} with 20 accumulations. X-ray diffractograms (XRD) of the ionic liquid–water insoluble portions were obtained using an Ultima IV diffractometer (Rigaku) with Cu–K$_\alpha$ radiation ($\lambda = 0.1524$ nm) and a K$_\beta$ filter, operating at 40 kV and 30 mA. Relative crystallinities were calculated from peak areas.

Other experiments were carried out to analyze the molecular weight distribution of the compounds solubilized in the ionic liquids. After starting treatment of the cellulose with the ionic liquids as described above, 60 μL of the reaction medium was added to 60 μL of DMSO and mixed until homogeneous. DMSO dissolved completely in ionic liquids used in this study without any precipitates. The mixture was filtered through a 0.45 μm filter and gel

permeation chromatography (GPC) was carried out on the filtrate. The GPC conditions used were: column, Shodex SB-803 HQ; flow rate, 0.3 mL min^{-1}; eluent, DMSO; detectors, refractive index detector (RID) and ultraviolet–visible (UV) detector set at 280 nm; column temperature, 60 °C. Pullulan (Shodex standard P-82) was used as the standard for measurement of the molecular weight distribution. The compounds solubilized in the ionic liquids were also analyzed by high-performance liquid chromatography (HPLC). The samples for this analysis were prepared as follows: at a specified reaction time, 60 μL of the reaction medium was homogeneously mixed with 60 μL of distilled water and then filtered through a 0.45 μm filter. The filtrates were analyzed under the following conditions: column, Shodex Sugar KS-801; flow rate, 1 mL min^{-1}; eluent, distilled water; detector RID; column temperature, 80 °C.

Results and discussion

Visual change of cellulose in ionic liquids

Prior to the detailed analyses on the reaction of cellulose in the ionic liquids, its visual change in the ionic liquids at 120 °C was studied. Cellulose cannot be seen in [EtPy][Cl] 1 min after putting it into [EtPy][Cl]. In contrast, the color of cellulose changes to brown in [EtPy][Br], although its particles remain even after 24 h. In the case of [EtPy][I], cellulose does not change visually in [EtPy][I] at all.

Ionic liquid–water insoluble portions

Figure 2 shows the changes in yield with the treatment time of the ionic liquid–water insoluble portions obtained after treatment of cellulose with different ionic liquids. For [EtPy][Cl], the yield rapidly decreased to 1 % after 10 min treatment. After 10 min, the yield gradually increased again to 35 %. For [EtPy][Br] treatment, the yield decreased rapidly at the beginning of the treatment, but then decreased more gradually to 82 % as the treatment time was extended. In the case of [EtPy][I], in contrast, the yield was constant at around 100 %.

As shown in Fig. 3, the [EtPy][I]–water insoluble portion obtained after 24 h of treatment (a) was white like untreated cellulose, while [EtPy][Br]–water insoluble portion (b) and [EtPy][Cl]–water insoluble portion (d) obtained after 24 h of treatment were brown and black unlike untreated cellulose. The [EtPy][Cl]–water insoluble portion obtained after 2 min of treatment (c), however, was white. This dependence of the color of the ionic liquid–water insoluble portion on the ionic liquid used and
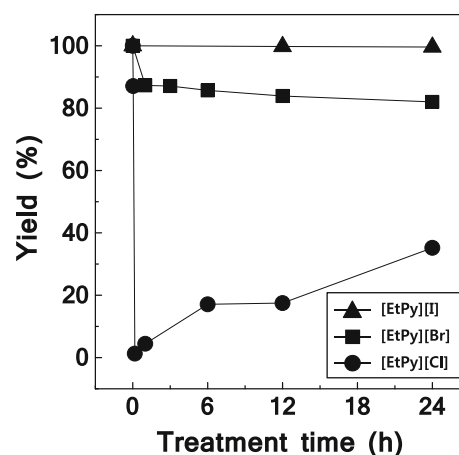
Fig. 2 Changes in yield of ionic liquid–water insoluble portions obtained after treatment of cellulose with different ionic liquids

treatment time indicates different reaction behaviors of cellulose in each of the ionic liquids used in this study.
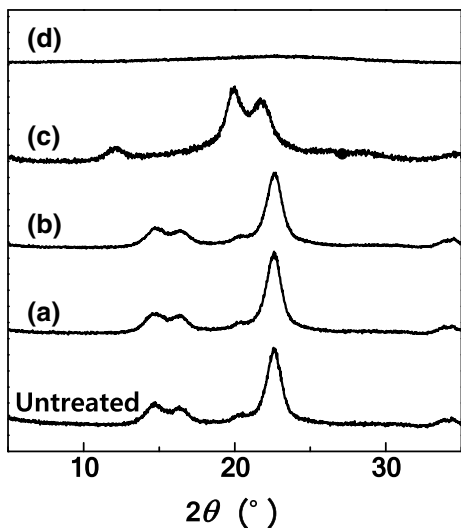
X-ray diffraction

To study their crystalline structure, XRD of the ionic liquid–water insoluble portions obtained from cellulose after treatment with [EtPy][I] for 24 h (a), [EtPy][Br] for 24 h (b), [EtPy][Cl] for 2 min (c), and [EtPy][Cl] for 24 h (d) were measured and are shown in Fig. 4. The XRD pattern of untreated cellulose is also shown for comparison. The XRD pattern of untreated cellulose has peaks at around 14.8°, 16.8°, and 22.6° typical peaks of cellulose I crystals. Similar XRD patterns displaying these three typical peaks of cellulose I were obtained for the [EtPy][I]–water insoluble portion after 24 h of treatment (a) and the [EtPy][Br]–water insoluble portion after 24 h of treatment (b). In contrast, the XRD patterns of the [EtPy][Cl]–water insoluble portion after 2 min of treatment (c) and [EtPy][Cl]–water insoluble portion after 24 h of treatment (d) were completely different from that of untreated cellulose. The former had peaks at around 12.1°, 19.8°, and 22.0°, attributed to the typical peaks of cellulose II. Cellulose dissolved in [EtPy][Cl] was regenerated by adding water and formed this crystalline structure. The latter had no peaks, indicating an amorphous structure. These results revealed that the crystal structure of cellulose treated with [EtPy][Cl] varies with treatment time, but that the original crystal structure of cellulose is retained in the case of [EtPy][I] or [EtPy][Br] treatment.

Figure 5 shows the change in relative crystallinity of the [EtPy][Br]–water insoluble portion. As treatment time progressed, the relative crystallinity was found to increase. The weight of [EtPy][Br]–water insoluble portion obtained decreased with prolonged treatment time as described in
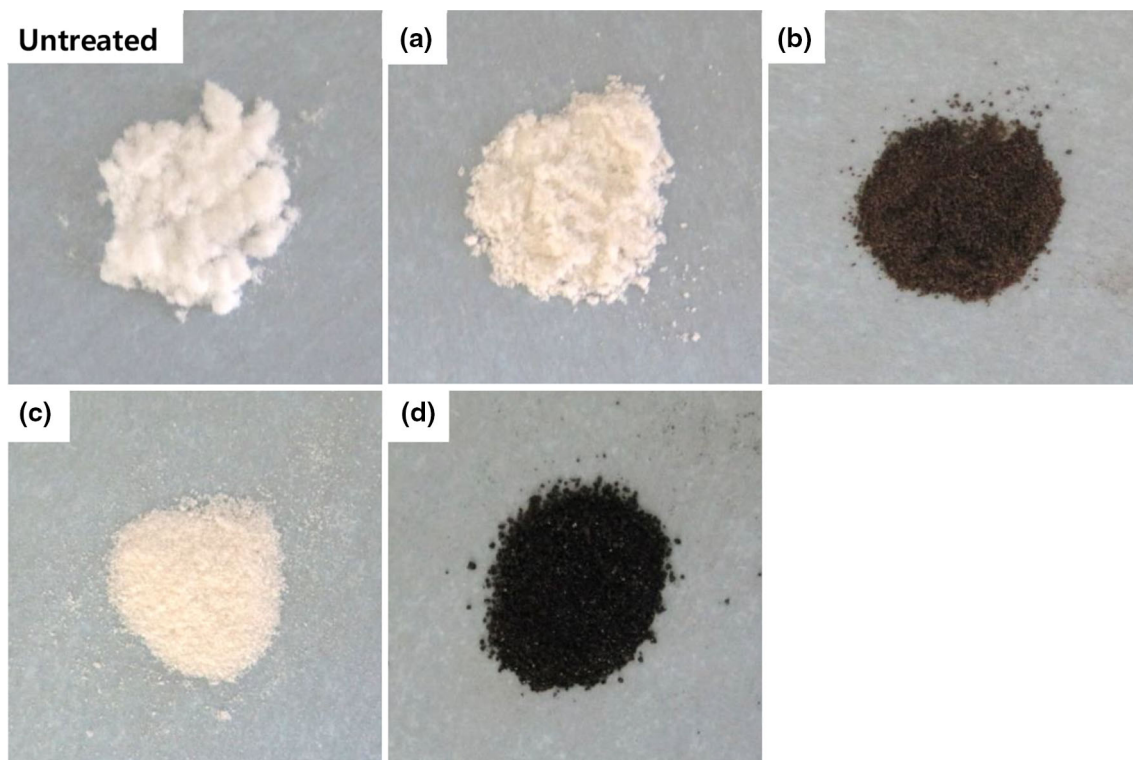
Fig. 3 Photographic images of ionic liquid–water insoluble portions obtained after treatment of cellulose with [EtPy][I] for 24 h (**a**), [EtPy][Br] for 24 h (**b**), [EtPy][Cl] for 2 min (**c**), and [EtPy][Cl] for 24 h (**d**), compared with *untreated* cellulose

Fig. 4 X-ray diffractograms of ionic liquid–water insoluble portions obtained after treatment of cellulose with [EtPy][I] for 24 h (**a**), [EtPy][Br] for 24 h (**b**), [EtPy][Cl] for 2 min (**c**), and [EtPy][Cl] for 24 h (**d**), compared with *untreated* cellulose
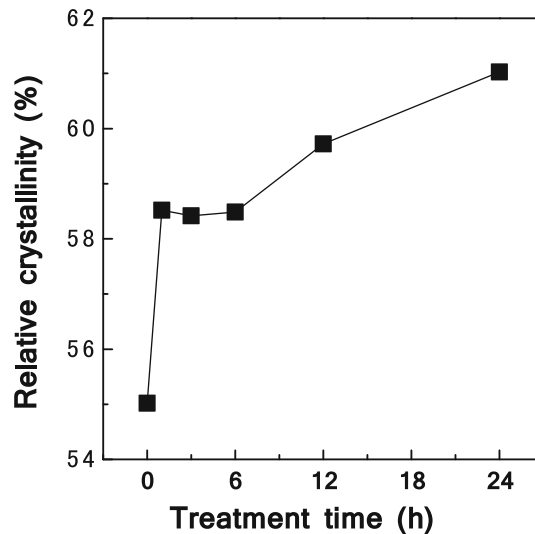

Fig. 5 Change of relative crystallinity for ionic liquid–water insoluble portion from cellulose after treatment with [EtPy][Br]

Fig. 2. Thus, these results suggest that the amorphous parts of cellulose are selectively removed by [EtPy][Br] treatment.

**FT-IR analysis of ionic liquid–water insoluble portions**

Figure 6 shows the FT-IR spectra of ionic liquid–water insoluble portions obtained after treatment of cellulose with [EtPy][I] for 24 h (a), [EtPy][Br] for 24 h (b),
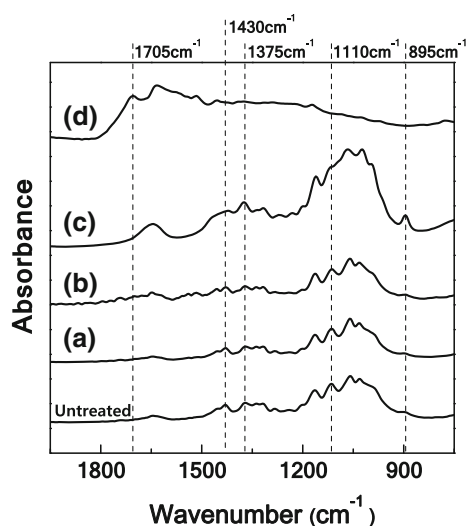
Fig. 6 FT-IR spectra of ionic liquid–water insoluble portions obtained after treatment of cellulose with [EtPy][I] for 24 h (**a**), [EtPy][Br] for 24 h (**b**), [EtPy][Cl] for 2 min (**c**), and [EtPy][Cl] for 24 h (**d**), compared with *untreated* cellulose

[EtPy][Cl] for 2 min (c), and [EtPy][Cl] for 24 h (d), compared with that for untreated cellulose. Peaks at 1110, 1375, and 1430 cm^{-1}, derived from cellulose I [23], were observed in the spectra of the [EtPy][I]–water insoluble portion (a) and [EtPy][Br]–water insoluble portion (b). In the case of the [EtPy][Cl]–water insoluble portion obtained after 2 min of treatment (c), the peaks at 1110 and 1430 cm^{-1} were weakened and the peak at 895 cm^{-1}, derived from the non-crystalline part of cellulose, was more intense, indicating that some parts of the cellulose changed during [EtPy][Cl] treatment. However, this spectrum was generally similar to that of untreated cellulose. In the spectrum of the [EtPy][Cl]–water insoluble portion after 24 h of treatment (d), however, the peaks at 1110, 1375, and 1430 cm^{-1} disappeared, while a new peak was observed at 1705 cm^{-1}. This peak is assigned to C=O, which is not contained in cellulose. This spectrum is quite different from that of untreated cellulose, indicating that the [EtPy][Cl]–water insoluble portion obtained after 24 h of treatment had a quite different chemical structure. These

Fig. 7 GPC chromatograms of compounds solubilized in [EtPy][Cl] (**a**) and [EtPy][Br] (**b**) for various treatment times. *Top*, refractive index detector (RID); *bottom*, UV detector ($\lambda = 280$ nm)
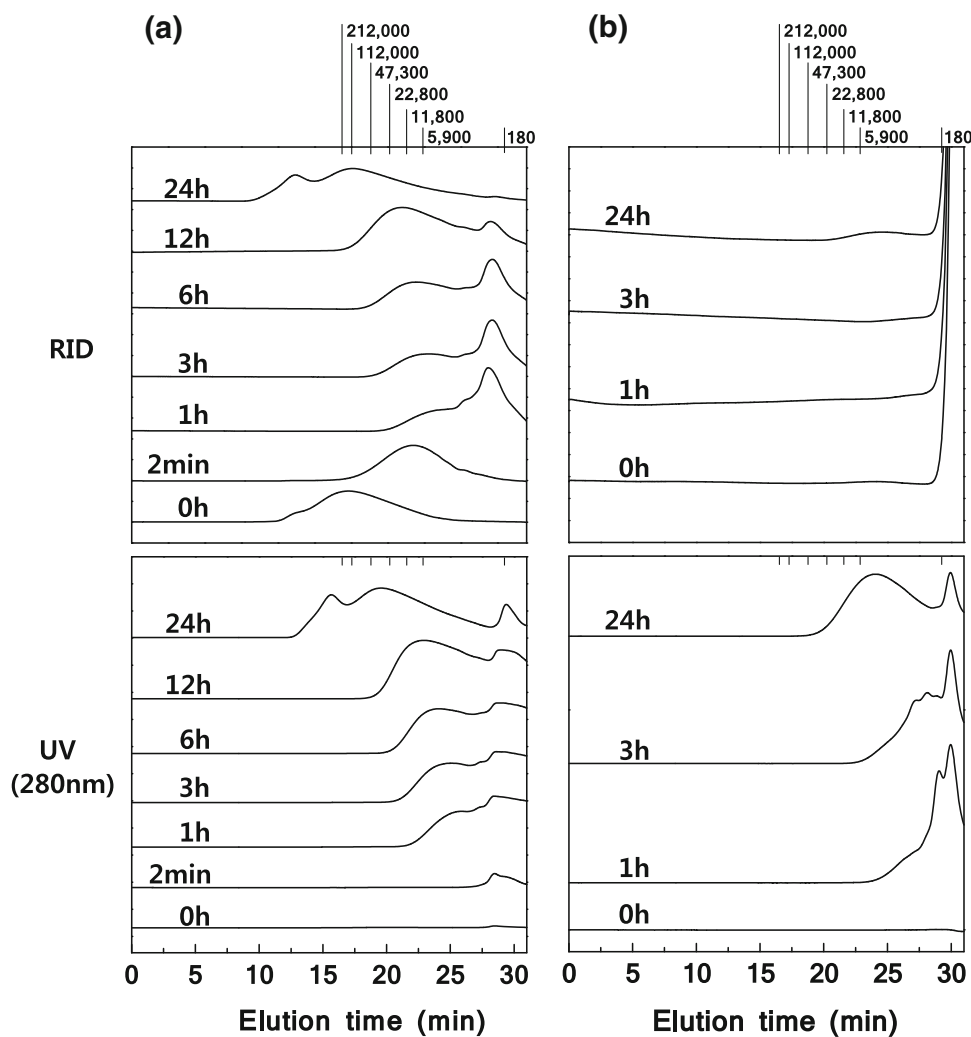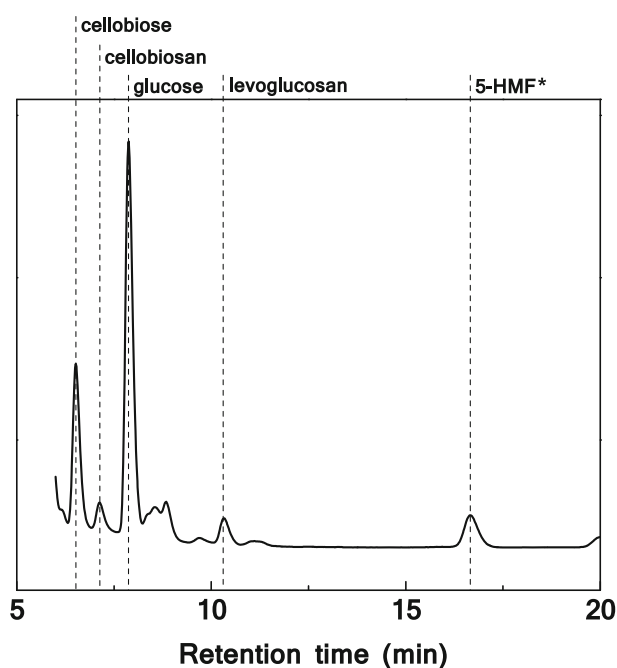
Fig. 8 HPLC chromatogram of compounds solubilized in [EtPy][Cl] after treatment of cellulose at 120 °C for 20 min. *5-HMF 5-hydroxymethylfurfural

results therefore reveal that the [EtPy][I]–water and [EtPy][Br]–water insoluble portions had similar chemical structure to that of untreated cellulose, while the chemical structure of the [EtPy][Cl]–water insoluble portion changed with increasing treatment time.

GPC analysis of compounds solubilized in ionic liquids

The molecular weight distributions of the compounds that were solubilized in the ionic liquids were studied by GPC as shown in Fig. 7. No peaks could be observed at GPC chromatograms for [EtPy][I] treatment, because no compounds solubilized in [EtPy][I] as mentioned above. Thus, the results for [EtPy][Cl] and [EtPy][Br] are shown in this figure. Peaks from [EtPy][Cl] are not visible in Fig. 7a due to their long elution time of around 70 min. Therefore, Fig. 7a essentially displays the molecular weight distribution of cellulose solubilized in [EtPy][Cl]. On the other hand, peaks from [EtPy][Br] are observed in the RID around 70 and 30 min of elution time. Because prominent peaks in the RID around 30 min in Fig. 7b are due to [EtPy][Br], low molecular weight compounds of around 180 MW solubilized in [EtPy][Br] could not be analyzed in the RID, although no peak from [EtPy][Br] could be seen in UV. In the case of treatment with [EtPy][Cl] (Fig. 7a), at 0 h a broad peak is observed below about 212,000 molecular weight (MW) [elution time (ET): around 15 min] in the chromatogram obtained with the RID, while no peaks were seen in the chromatogram obtained using the
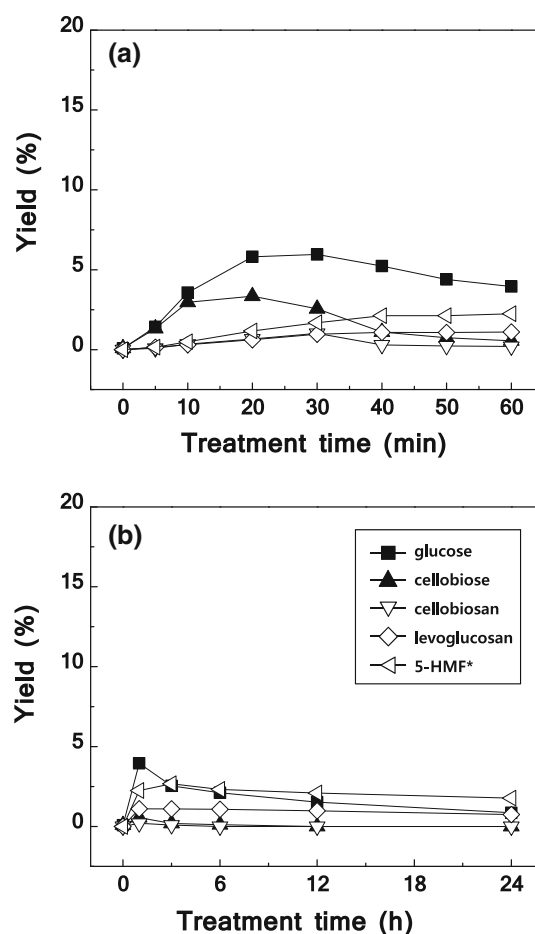
Fig. 9 Changes in yields of various compounds obtained after treatment of cellulose with [EtPy][Cl] for 0–60 min (a) and 0–24 h (b). *5-HMF 5-hydroxymethylfurfural

UV detector. Thus, the RID peak was from cellulose, because cellulose cannot be detected by UV. The cellulose peak shifted to lower molecular weight as treatment time increased. After 1 h of treatment, a peak was observed around 180 MW (ET: around 30 min). Cellulose solubilized in [EtPy][Cl] is thought to be depolymerized to its monomer level. Not only this peak, but also some peaks of over a few thousand MW can be seen in both the RID and UV chromatograms after 1 h of treatment. These peaks decreased with prolonged treatment time, and eventually only one prominent peak at over 212,000 MW (ET: around 15 min) was observed after 24 h of treatment. These results indicate that the cellulose was decomposed into low molecular weight compounds (MW <180) during the initial stage of [EtPy][Cl] treatment. These low molecular weight compounds were then polymerized, forming UV-absorbing products of over a few thousand MW (ET: around 25 min).

In the case of treatment with [EtPy][Br] (Fig. 7b), no peaks from cellulose were observed in the RID

chromatogram at 0 h. This may be because the concentration of cellulose solubilized in [EtPy][Br] is too low to be analyzed by the RID. Other reason is that [EtPy][Br] cannot dissolve cellulose. However, it remains unknown which is correct. In the chromatograms with the UV detector, some peaks were observed at around 180 MW (ET: around 30 min), indicating that some UV-absorbing compounds were produced after 1 h of treatment. After 24 h of treatment, a broad peak was seen at around 5,900 MW (ET: around 23 min) in the RID and UV chromatograms. The peaks around 180 MW (ET: around 30 min) observed with the UV detector decreased, indicating that the peaks around 5,900 (ET: around 23 min) was due to the polymer produced by polymerization of the low molecular weight compounds.

In the case of [EtPy][Cl] treatment, cellulose dissolved completely, meaning that the GPC chromatograms in Fig. 7a shows the reaction of whole cellulose. Cellulose dissolved in [EtPy][Cl] was degraded during the initial stage of reaction to form some low molecular weight compounds. As the treatment time was extended, these compounds reacted to form polymer having UV absorption.

The polymers produced after 24 h of treatment were recoverable by adding water to the reaction medium. These polymers were black as shown in Fig. 3d, and had a different XRD pattern and FT-IR spectrum from those of cellulose.

In the case of [EtPy][Br], on the other hand, the cellulose partially reacted. Although the polymers produced after 24 h of treatment were thought to be recoverable like those in the case of [EtPy][Cl], not only these polymers but also the unreacted cellulose were recovered together as the ionic liquid–water insoluble portion. Thus, the insoluble portion shown in Fig. 3b was presumed to be a mixture. However, no significant differences from cellulose were found in the XRD pattern and FT-IR spectrum, indicating that the unreacted cellulose made up the greatest proportion of the ionic liquid–water insoluble portion. The difference between the molecular weights of the polymers produced in [EtPy][Cl] and [EtPy][Br], as shown in Fig. 7, is due to the difference in the amounts of cellulose reacting in [EtPy][Cl] and [EtPy][Br].

HPLC analysis of compounds solubilized in ionic liquids

HPLC analyses were performed to further study the low molecular weight compounds produced. Figure 8 shows an HPLC chromatogram of compounds solubilized in [EtPy][Cl] after treatment of cellulose at 120 °C for 20 min. Cellobiose, cellobiosan, glucose, levoglucosan, and 5-hydroxymethylfurfural (5-HMF) were identified in

[EtPy][Cl]. Although these compounds were also identified in [EtPy][Br], no products could be detected in [EtPy][I]. Figures 9 and 10 show the changes in the yields of the compounds obtained from cellulose after treatment with [EtPy][Cl] and [EtPy][Br] for (a) 0–60 min and (b) 0–24 h. In the case of [EtPy][Br] treatment, the yields were calculated based on the amount of [EtPy][Br] soluble portion because the cellulose reacted only partially in [EtPy][Br]. The yields of all of the compounds exhibited maxima, although the treatment time required to reach the maximal value differed. In the case of [EtPy][Cl] treatment, as shown in Fig. 9, the maximal yield of cellobiose was 3 % at 20 min, while those of cellobiosan and glucose were 3 and 6 %, respectively, at 30 min. In the case of [EtPy][Br] treatment as shown in Fig. 10, the maximal yield for cellobiose was 7 % at 20 min, while those of cellobiosan and glucose were 4 and 13 %, respectively, at 30 min. The yield of levoglucosan was 16 % at 1 h, the highest yield among the various products obtained. The differences in the yields obtained from [EtPy][Cl] and [EtPy][Br]
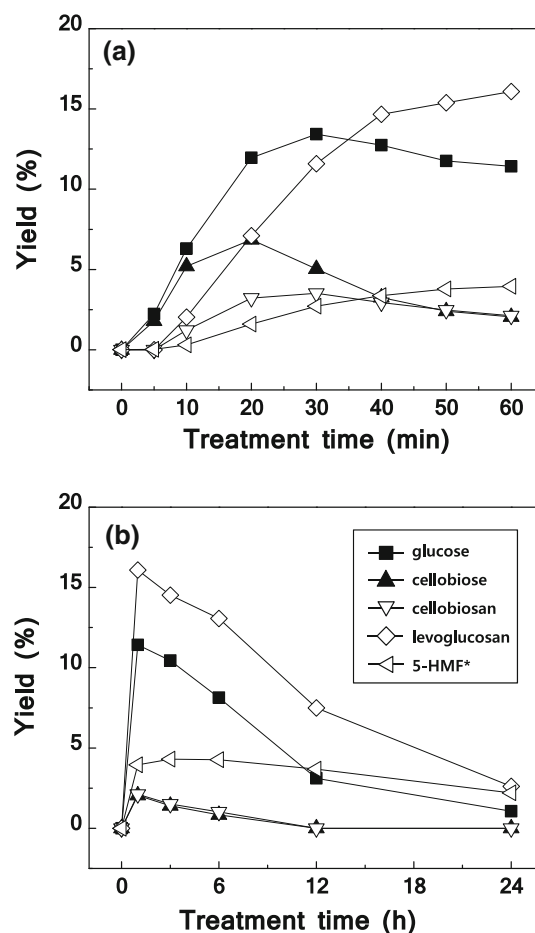
Fig. 10 Changes in yields of various compounds obtained after treatment of cellulose with [EtPy][Br] for 0–60 min (**a**) and 0–24 h (**b**). *5-HMF* 5-hydroxymethylfurfural

treatment are thought to be due to the various compounds produced from cellulose being further converted into other compounds sooner in [EtPy][Cl] than in [EtPy][Br].

Conclusion

We studied the reaction behavior of cellulose in various pyridinium-based ionic liquids. Cellulose is dissolved completely and depolymerized in [EtPy][Cl]. The low molecular weight compounds produced then polymerize to produce polymers exhibiting UV absorption. In contrast, [EtPy][Br] only reacted with the amorphous parts of cellulose selectively. The reaction behavior of ionic liquid soluble portion in [EtPy][Br] is similar to that observed in [EtPy][Cl]. In the case of [EtPy][I], however, cellulose cannot be dissolved and no reactions take place.

Although their cations are the same, the solubility and reactivity of the used ionic liquids toward cellulose are quite different depending on the anion. Consequently, it is important to select an appropriate ionic liquid to effectively exploit cellulose as a resource via chemical conversion with ionic liquids.

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