Carbohydrate Polymers 92 (2013) 651–658

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Dissolution and recovery of cellulose from 1-butyl-3-methylimidazolium chloride in presence of water

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ARTICLE INFO

Article history:
Received 28 July 2012
Received in revised form 30 August 2012
Accepted 9 September 2012
Available online 29 September 2012

Keywords:
Cellulose
Ionic liquid
Water
Degree of polymerization
Cellulose II

ABSTRACT

The dissolution and recovery of microcrystalline cellulose from 1-butyl-3-methylimidazolium chloride, [bmIm][Cl], were studied. At 90 °C and 5 h dissolution time, the regenerated cellulose could be recovered above 80 wt% with a less than 10% decrease in the value of the viscosity-average degree of polymerization, DP_v, regardless of water content. Recovery ratio and DP_v of regenerated cellulose at 120 °C decreased with time regardless of water content. The regenerated cellulose after dissolution at 120 °C for 10 h regardless of water content had cellulose II structure. Regenerated cellulose at short dissolution times or low temperature had high amorphous content. Both [bmIm][Cl] and [bmIm][Cl] with water act as a non-derivatizing solvent for microcrystalline cellulose at 90 °C, and as a derivatizing solvent at 120 °C. The main effect of added water on the dissolution of cellulose at high temperature was the promotion of cello-oligosaccharide and levoglucosan formation.

1. Introduction

Cellulose consists of linear chains of poly[β-1,4-D-anhydroglucopyranose] ($C_{6n}H_{10n+2}O_{5n+1}$ where n = degree of polymerization) and has cellobiose as its repeating unit. The β-1,4 glycosidic bonds makes it easy to form intra-hydrogen bonding between C3 hydroxyl group and O5 which consists of a six-membered ring. The combination of glycosidic bonds and hydrogen bonding among glucose result in chain linearity and rigidity, so that cellulose does not dissolve in water and common organic solvents.

Ionic liquids, which are organic salts that are liquid at mild conditions (<100 °C), were found to be able to dissolve cellulose in an early pioneering study (Swatloski, Spear, Holbrey, & Rogers, 2002). Since then, many studies have reported on the solubilities of cellulose in ionic liquids and their use in preparing materials after being dissolved in ionic liquids (Pinkert, Marsh, Pang, & Staiger, 2009). According to the mechanistic background presented by Pinkert (2012), ionic liquids are generally non-derivatizing solvents for cellulose, which means that cellulose does not undergo chemical modification upon dissolution (Pinkert, 2012). However, it has been noted in a number of studies that regenerated cellulose after dissolution can undergo changes in its degree of polymerization. Barthel and Heinze showed that the viscosity-average degree of polymerization (DP_v) of regenerated cellulose from several ionic liquids decreases (Barthel & Heinze, 2006). Vitz et al. reported that the DP_v and yields of regenerated cellulose from ionic liquids are different (Vitz, Erdmenger, Haensch, & Schubert, 2009). Some of the discrepancies between the ionic liquid acting as a non-derivatizing solvent and reports of chemical structure changes of cellulose upon dissolution in the ionic liquid can be attributed to temperature, water content, kinetics (stirring, viscosity, time), the nature of cellulose and atmosphere (nitrogen, air) as pointed out by Pinkert (2012). In this study, we addressed the question of whether or not an ionic liquid with and without water acts as a derivatizing solvent for cellulose in view of many possible conditions. The ionic liquid [bmIm][Cl] was chosen for study due to the availability of literature results.

Table 1 shows a summary of the available data for DP_v of cellulose after its dissolution into [bmIm][Cl]. In Table 1, most DP_v values of regenerated cellulose from [bmIm][Cl] decreased except for the data of Avicel taken from Barthel and Heinze (2006). Chen et al. and Liu et al. investigated the temperature dependence on DP_v (Chen, Zhang, Cheng, & Wang, 2009; Liu et al., 2011). Chen et al. reported that the DP_v of the dissolved cellulose pulp at 120 °C changed 0.7 times that of the raw cellulose whereas at 90 °C, the DP_v changed changes about 0.95 times (Chen et al., 2009). Liu et al. showed that the DP_v of cotton pulp dissolved at 90 °C for 5 h became a value that was 0.4 times its original value (Liu et al., 2011). The results Chen et al. and Liu et al. are inconsistent for the DP_v change. Su et al. reported that the DP_v of cotton linters decreased greatly when adding water in the presence of catalyst (Su et al., 2009). Rinaldi

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http://dx.doi.org/10.1016/j.carbpol.2012.09.021

Table 1
Available data for viscosity-average degree of polymerization, DP_v, of cellulose before it has dissolved into 1-butyl-3-methylimidazolium chloride, [bmIm][Cl], and after it has been regenerated from [bmIm][Cl] at various conditions.

Substance	DP_v		Temp. (°C)	Time (h)	Conc. (wt%)	Water (eq.)	Ref.
	Before	After					
Avicel	286	307	83	12	18	n.a.	Barthel and Heinze (2006)
Avicel	398	311	100	2	8	0.3	Vitz et al. (2009)
Avicel	398	172	100 (microwave)	0.5	8	0.3	
		255		1			
		230		2			
Sulfite pulp	593	544	83	12	13	n.a.	Barthel and Heinze (2006)
Cellulose pulp	505	487	90	5	n.a. (≥6)	n.a.	Chen et al. (2009)
		437	110				
		337	120				
Cotton pulp	510	390	90	1	10	n.a.	Liu et al. (2011)
		230		5			
		180		7			
Cotton pulp	510	230	90	0.25	13	n.a.	
		180	110		17		
		140	120		20		
Cotton pulp	510	180	90	7	13	n.a.	
		120			15	5 wt% DMSO added	
Cotton linters	1198	812	83	12	10	n.a.	Barthel and Heinze (2006)
Cotton linters	317	286	120	1	10	n.a. + catalyst	Su et al. (2009)
Cotton linters	286	160	120	0.1	10	Catalyst + 2.0 eq. water added	
		2		0.5			
α-Cellulose	1200[a]	900[a]	100	5	5	3.6 eq.	Rinaldi et al. (2008)
		<100[a]				Catalyst + 3.6 eq.	

n.a., not available in the reference.
[a] DP_w is used instead of DP_v.

et al. reported that by addition of water in the presence of catalyst, a large decrease in the DP_v of α-cellulose occurred (Rinaldi, Palkovits, & Schüth, 2008). In these studies, it is clear that the DP_v of cellulose changes upon the dissolution conditions, but it is insufficient to understand whether the derivatization of cellulose is caused by the chemical characteristics of the ionic liquid solvent or whether it is due to the experimental conditions.

Water content in ionic liquid should affect stability of dissolved cellulose in ionic liquid. Cellulose-dissolving ionic liquids are hydroscopic and cellulose has water content in nature. Thus, water content in the ionic liquid should increase as cellulose dissolves in the ionic liquid. At lower water concentrations, water acts as a viscosity reducing agent for cellulose + ionic liquid solutions (Le, Sescousse, & Budtova, 2012), whereas at higher water concentrations (ca. 15 wt%), water acts as an anti-solvent for the cellulose solutions (Mazza, Catana, Vaca-Garcia, & Cecutti, 2009). When water is added to cellulose + ionic liquid solutions, the conformation of cellulose in the ionic liquid changes and the hydrodynamic radius of cellulose increases (Kuzmina, Sashina, Troshenkowa, & Wawro, 2010; Le et al., 2012). In the absence of catalyst, water can promote chemical derivatization reactions at higher temperatures (ca. 120 °C) (Zhang, Du, Qian, & Chen, 2010) and at lower temperatures (ca. 100 °C), water and ionic liquid mixtures are considered to be non-derivatizing solvents (Rinaldi et al., 2008). However, the stability of cellulose in the ionic liquid at higher temperatures in the presence and in the absence of water is not clear. A low water concentration (2.3 wt%) was chosen in this study to investigate the influence of water on the stability of cellulose in the ionic liquid.

Mixtures of dimethyl sulfoxide, DMSO, and cellulose + ionic liquid solution are homogeneous solutions (Gericke, Liebert, Seoud, & Heinze, 2011), and DMSO acts as a viscosity reducing agent for the cellulose solution (Lv et al., 2012; Quan, Kang, & Chin, 2010; Rinaldi, 2011). Liu et al. showed that a decrease in the DP_v of the regenerated cellulose occurred regardless of adding DMSO to cotton pulp + [bmIm][Cl] solutions (Liu et al., 2011). However, the effect of addition of DMSO is not clear from the limited amount of reported data.

In this study, microcrystalline cellulose was chosen as the carbohydrate to study since it is readily characterized. The objective of this study was to understand the recovery and the stability of the dissolved microcrystalline cellulose in [bmIm][Cl] as evaluated from its precipitation products and their viscometric and chemical properties. Cellulose was dissolved into [bmIm][Cl] at different concentrations, temperatures, water contents for various dissolution times and in the presence of DMSO, and a wide range of chemical analyses were used to evaluate the regenerated cellulose and remaining ionic liquid solutions. Conditions were controlled so as to make general conclusions on the derivatizing nature of ionic liquid + water solutions for dissolving cellulose.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (Asahi Kasei Co.) was sieved to have particle sizes less than 75 μm, and was dried at 50 °C in vacuum for overnight before each experiment. Water content of the dried microcrystalline cellulose was estimated to be below 0.5 wt% by measuring weight loss. The degree of polymerization of microcrystalline cellulose was 310 as determined by intrinsic viscosity measurements according to ISO 5351:2010 using parameters of Marx-Figini (1978). The microcrystalline cellulose was confirmed to be cellulose I by X-ray diffraction patterns and the crystallinity index was 80% calculated by Segal method (Segal, Creely, Martin, & Conrad, 1959). Amorphous cellulose was prepared by ball milling from microcrystalline cellulose in a jar with alumina balls (d = 10 mm) for 1 day using a rotor apparatus (Asahi Rika, AV-1; 110 rpm).

Ionic liquid, 1-butyl-3-methylimidazolium chloride, [bmIm][Cl] (>99%, Sigma–Aldrich Co.) was dried in vacuum at 80 °C over 20 h before each experiment. Water content in the dried ionic liquid was measured with Karl-Fisher columetric titration (Kyoto Electronics Manufacturing Co., MKC-501) before adding cellulose samples to the ionic liquid. The [bmIm][Cl] was found to contain 240 ± 50 ppm of 1-methylimidazole from analysis with an HPLC system that had

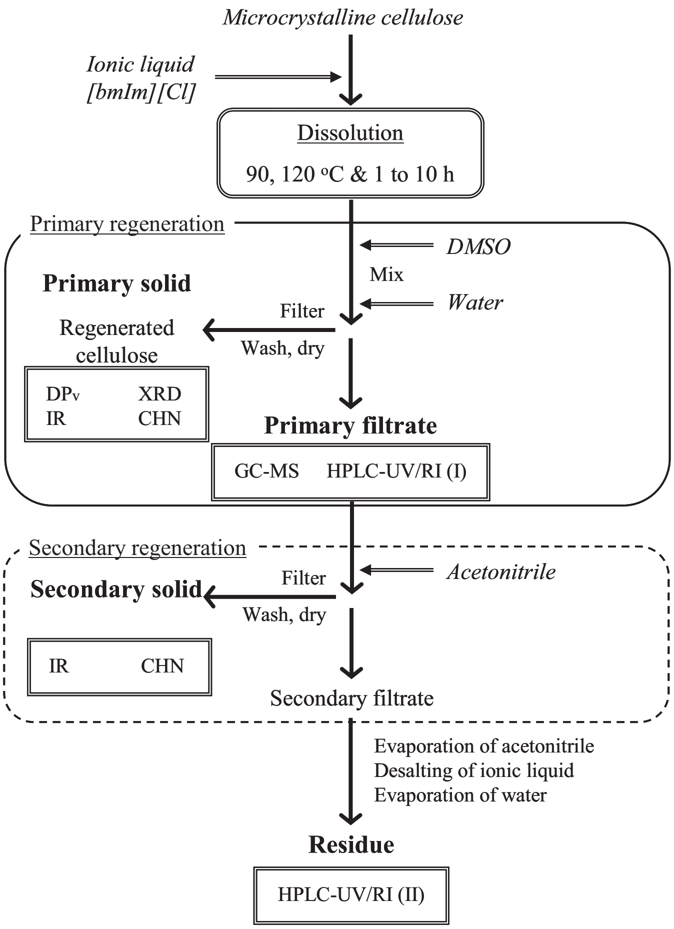

Fig. 1. Flowchart for experiment steps and characterization methods for dissolution of microcrystalline cellulose in 1-butyl-3-methylimidazolium chloride, [bmIm][Cl], and cellulose regeneration.

a 20 μl sample loop on an ODP2 HP-4D column (Showa Denko K.K., 0.8 ml/min of 10 mM $Na_2HPO_4/CH_3CN = 50/50$, v/v, 40 °C) and UV detector (JASCO Co., UV-1570) at 208 nm.

Water (<6 μS/m) was used for the regeneration of cellulose from ionic liquid. Dimethyl sulfoxide, DMSO (99.9%, Wako Pure Chemical Industries, Ltd.) was purified by molecular sieves 4A (Wako Pure Chemical Industries, Ltd.), and was used as a viscosity reducing agent for the cellulose + [bmIm][Cl] solution. Acetonitrile (>99.9%, Sigma–Aldrich Co.) was used as an anti-solvent for the liquid filtrate after cellulose was precipitated from the cellulose + [bmIm][Cl] solution. A solution of 1.0 M cupriethylenediamine, CED (GFS Chemicals, Inc.) was used for intrinsic viscosity measurements. Potassium bromide, KBr (Wako Pure Chemical Industries, Ltd.) was used as a dilution agent for infrared, IR, measurements. Mixtures of [bmIm][Cl] and microcrystalline cellulose were prepared by mixing samples with KBr powder with an agate mortar. A solution of N-trimethylsilylimidazole in pyridine solution, TMSI-C, (GL Sciences, Inc.) was used as a silylation agent for the GC–MS analysis.

2.2. Experimental

Fig. 1 shows the flowchart that gives an overview of the dissolution and regeneration steps used for primary and secondary regeneration of the microcrystalline cellulose. First, microcrystalline cellulose was dissolved into [bmIm][Cl] at the desired temperature for a predetermined time. Then, primary regeneration from cellulose + [bmIm][Cl] solution was performed by adding DMSO, mixing and then water to the cellulose + [bmIm][Cl] solution, which resulted in a precipitate and an ionic liquid-rich solution. These are defined as primary solids and primary filtrates, respectively. Then, secondary regeneration of the filtrate was performed by adding acetonitrile to the filtrate that caused an additional precipitate in some cases. These are denoted as secondary solids and secondary filtrates. Residues were obtained after evaporation and desalting of the secondary filtrates. Details on the procedures are given in the next sections.

2.2.1. Dissolution step

The ionic liquid in flask was put into the oil bath at desired temperature for 1 h in vacuum. A known weight of cellulose was dispersed into the ionic liquid. The cellulose + ionic liquid solution was stirred for a predetermined time under a nitrogen atmosphere. After one hour had passed, a sample of the solution was taken and observed with polarized light microscopy (Olympus Co., SZX12) to check whether the dissolution of cellulose in the ionic liquid was complete or not, and then 2.3 wt% of water (4 equivalents to glucose unit of cellulose) or DMSO was added for the case of adding solvent to the solution. Cellulose solutions were prepared at 1 and 5 wt% concentrations. Dissolution temperature was set to 90 and 120 °C, and dissolution time was set from 1 to 10 h.

2.2.2. Primary regeneration step

After the flask containing cellulose and [bmIm][Cl] was removed from the oil bath, 10 ml of DMSO was added to the cellulose + [bmIm][Cl] solution with stirring. When the solution was clear, 80 ml of water was added to the solution gradually with stirring. Precipitated samples that are commonly called regenerated celluloses were separated from the solution by suction filtration using 0.2 μm PTFE membranes (Millipore). After several times of washing with water, regenerated cellulose was dried in vacuum at 50 °C until a constant mass was obtained. The regenerated cellulose from this step is defined as the primary solid (Fig. 1).

2.2.3. Secondary regeneration step

Acetonitrile 300 ml was added to primary filtrates while stirring (Fig. 1). Secondary solids (Fig. 1) were separated from secondary filtrates by suction filtration using 0.2 μm PTFE membranes (Millipore). Secondary solids were dried in vacuum at 50 °C until a constant mass was obtained. Secondary filtrates (Fig. 1) were evaporated at 25 °C in vacuum for 2 h to remove acetonitrile. Some samples of secondary filtrates were desalted by an electrodialyzer (S1, Astom Co.; 0.25 M $NaNO_3$ aq.) with membrane (AC-210-20), and evaporated at 25 °C in vacuum for several hours.

2.3. Characterization

Characterization methods used for solids and liquids are shown in Fig. 1. Primary solids were analyzed with intrinsic viscosity for DP_v, XRD for crystal structure, IR and chemical elemental analyses for the chemical structure. Primary filtrates were analyzed with both GC–MS and HPLC- RI/UV (HPLC I) for decomposition products of dissolved cellulose in [bmIm][Cl]. Secondary solids were analyzed with IR measurements and chemical elemental analyses for the chemical structure. Residues were analyzed with HPLC-RI/UV (HPLC II) analyses for decomposition products of dissolved cellulose.

2.3.1. Confirmation of water in ionic liquid

Water was controlled in the experiments. Before the experiments, time dependence on water concentration in [bmIm][Cl] at 120 °C was measured with Karl-Fisher titration. The water concentration in [bmIm][Cl] changed from 2.16 ± 0.05 to 2.14 ± 0.04 wt%

after 5 h at 120 °C. This indicates that water added into [bmIm][Cl] remained constant at the conditions of the experiments.

2.3.2. *Calculation of recovery ratio*

The recovery ratios of primary and secondary solids were calculated as follows:

$$\text{Primary recovery [wt\%]} = 100 \times \frac{\text{Mass of primary solids}}{\text{Mass of original cellulose}} \qquad (1)$$

$$\text{Secondary recovery [wt\%]} = 100 \times \frac{\text{Mass of secondary solids}}{\text{Mass of original cellulose}} \qquad (2)$$

Mass of solids was obtained after washing and drying.

2.3.3. *Degree of polymerization for primary solids*

Viscosity-average degree of polymerization, DP_v, was determined by the intrinsic viscosity number of primary solids in CED solution according to ISO 5351:2010. Two types of Ostwald viscometers (d = 0.5 and 0.75 mm, shear rate = 700 and 500 s^{-1}) were used for ensuring reliable results. The primary solid (150 mg) was placed in a 30 ml flask and 15 ml of water was added. The mixture was stirred at room temperature for 20 min to allow swelling of the primary solid. Then, 15 ml of CED was added to the flask, and the flask was put into water bath at 25 °C for 20 min with stirring. Dissolution of the primary solid was confirmed by transferring a small amount of the cellulose + CED solution (ca. 100 μl) onto a brown fibrous surface (Kim Towel, Nippon Paper Crecia Co.) and examining the residue. After confirmation of dissolution, 8 ml of the cellulose + CED solution was transferred to each viscometer, and efflux times of the solution were determined for at least 5 trials. Results were used to calculate a mean value. DP_v values of the cellulose samples were calculated with parameters of Marx-Figini (1978) as follows:

$$[\eta] = 0.42\ DP_v \qquad (3)$$

The ratio of DP_v of the primary regenerated solids from [bmIm][Cl] to that of the original cellulose (DP_v = 310), DP_v ratio, was calculated as follows:

$$DP_v\ \text{ratio} = \frac{DP_v\ \text{of regenerated cellulose}}{DP_v\ \text{of original cellulose (310)}} \qquad (4)$$

2.3.4. *XRD measurements for primary solids*

The crystal structure of primary solids was determined by X-ray diffraction patterns with Cu Kα radiation (λ = 1.5406 Å) at 30 kV and 15 mA in the range of 2θ = 10–40° at 0.02° interval with the fixed time method using an X-ray difftactometer (MiniFlex, Rigaku Co.). Samples were placed horizontally on an aluminum plate. The crystallinity index, CrI, of cellulose II in the sample was calculated from Segal method as follows (Segal et al., 1959):

$$\text{CrI} = 100 \times \left(1 - \frac{I_{am}}{I_{200}}\right) \qquad (5)$$

where I_{am} and I_{200} are the intensity above base line at 2θ = 16° and 2θ = 19.8°, respectively.

2.3.5. *Chemical elemental analyses*

Chemical elemental compositions of primary and secondary solids were measured with a CHNS/O elemental analyzer (2400 series II CHNS/O system, PerkinElmer Inc.) in CHN mode. Cysteine was used as the calibration standard substance. Samples were dried at 50 °C in vacuum for overnight before the analysis. Dried samples, ca. 2 mg, were placed a stannum vessel, and weighed with a micro balance equipped with apparatus.

2.3.6. *IR measurements*

Infrared spectra were measured with diffuse reflectance (FT-IR 230, JASCO) between 4000 and 800 cm^{-1} with a resolution of 4 cm^{-1}, and several hundred times of scans. Samples were dried at 50 °C in vacuum for overnight before the analysis. Dried samples were mixed with KBr powder using an agate mortar.

2.3.7. *GC–MS analyses for primary filtrates*

Qualitative analysis of primary filtrates was measured with a GC system (Agilent 5975C, Agilent Technologies Ltd.) with 1 μl injection on an InertCap 1MS column (GL Sciences Inc., 1 ml/min of He, from 50 to 250 °C with 10 °C/min) and total ion monitoring with electron impact ionization. Primary filtrates were filtered through a cation exchange resin (Grace, SCX) and were evaporated at 25 °C in vacuum for several hours. A silylation agent was added to the sample before analysis.

2.3.8. *HPLC I analyses for primary filtrates*

Glucose, cellobiose and 5-hydroxymethylfurfral in primary filtrates were determined by HPLC system with 20 μl sample loop on an SH1011 column (Showa Denko K.K., 0.6 ml/min of 10 mM H_2SO_4, 60 °C) and RI (JASCO, RI-2031) and UV detector (JASCO, UV-1570) at 280 nm. Primary filtrates were diluted with water, and filtrated through a cation exchange resin (Grace, SCX) and a 0.2 μm syringe filter (Millipore) before analysis.

2.3.9. *HPLC II analyses for residues*

Mono- and oligosaccharide in residues were measured with HPLC system with 20 μl sample loop on an NH2P 40-3E column (Showa Denko K.K., 0.3 ml/min of acetonitrile/water = 2/1, v/v, 35 °C), and RI (Showa Denko K.K., RI SE-61) and UV detector (JASCO, UV-1570) at 210 and 280 nm. Equal volumes of acetonitrile and water were added to the residue (Fig. 1) before analysis.

3. Results and discussion

3.1. *Regenerated solids*

Table 2 shows recovery ratios of primary and secondary regenerated solids at different dissolution conditions. At all dissolution conditions, primary solids could be recovered, however, recoveries were between 65 and 100 wt%. At 90 °C, there were only small differences in the recovery ratio of primary solids for cases of without added water or with added water. Secondary solids were not formed in runs 1–5 in Table 2. On the other hand, the recovery ratio of primary solids decreased with time at 120 °C in the absence and in the presence of water (runs 5–7, Table 2). At long dissolution times (runs 6 and 7, Table 2), 3 wt% and 1 wt% secondary solids were recovered at 120 °C for 10 h without and with added water, respectively. Some researchers observed a decrease in the recovery of regenerated solid after dissolution in ionic liquid (Duchemin, Mathew, & Oksman, 2009; Li, Sevastyanova, & Ek, in press; Vitz et al., 2009), and the amount of regenerated solid decreased with temperature (Li et al., in press).

The DP_v ratios of the primary solid at different conditions are show in Table 2, and the time variation of DP_v ratio for 1 and 5 wt% cellulose + [bmIm][Cl] solutions at dissolution times from 1 to 10 h are shown in Fig. 2. The DP_v of primary solid decreased after dissolution and regenerated from [bmIm][Cl] in all experiments in this study. High cellulose concentration is discussed first (runs 1–7, Table 2). At 90 °C, the DP_v ratio did not change much with or without added water or for DMSO at dissolution times up to 5 h (runs 1–5, Table 2). The DP_v ratio decreased with time at 120 °C (runs 5–7, Table 2) but did not change with or without added water. For the case of low cellulose concentration (runs 8–10, Table 2), the

Table 2

Experimental conditions for dissolution of cellulose in [bmIm][Cl] with ratio in DP_v of primary solid to that of original cellulose, DP_v ratio, crystallinity index of primary solid, CrI, and recoveries of regenerated solids. Both intrinsic viscosity numbers and viscosity-average degrees of polymerization of the primary solid are given in Supplementary information (Table A.1).

Run no.	Dissolution condition				Primary solid			Secondary solid
	Cellulose (wt%)	Water (eq.)	Temp. (°C)	Time (h)	Recovery (wt%)	DP_v ratio	CrI (%)	Recovery[a] (wt%)
1	5	<0.2	90	2	90 ± 8	0.90 ± 0.06	50	n.s.
2	5	<0.2	90	5	84 ± 8	0.91 ± 0.05	50	n.s.
3	5	4	90	5	83 ± 8	0.86 ± 0.10	50	n.s.
4	5	<0.2 + 2.3 wt% DMSO added	90	5	87 ± 8	0.97 ± 0.10	50	n.s.
5	5	<0.2	120	5	83 ± 8	0.49 ± 0.09	50	n.s.
6	5	<0.2	120	10	69 ± 10	0.21 ± 0.10	70	3 ± 2
7	5	4	120	10	72 ± 7	0.20 ± 0.08	60	<1
8	1	2	90	1	95 ± 8	0.97 ± 0.10	–	–
9	1	2	90	3	100 ± 8	1.01 ± 0.10	–	–
10	1	2	90	5	93 ± 8	0.77 ± 0.10	–	–

[a] n.s., no solid formed when acetonitrile added.

DP_v ratio of primary solid gradually decreased with time. The measured DP_v ratios were plotted as shown in Fig. 2. For the case of the same dissolution time (2 h), DP_v at 90 °C measured in this study (run 1, Table 2) was higher than that at 100 °C measured by Vitz et al. (2009). The DP_v ratio at 83 °C measured by Barthel and Heinze did not change much with increasing time (Barthel & Heinze, 2006). The trend of results in this study agreed with results in the literature (Barthel & Heinze, 2006; Vitz et al., 2009).

The XRD patterns of the primary solid at different dissolution condition (runs 2–7, Table 2) are shown in Fig. 3. In all experiments, the XRD patterns of the primary solid were different from the original microcrystalline cellulose, since most of patterns contained features of amorphous cellulose. Cellulose I, which is the original cellulose used (Fig. 3e), is thermodynamically unstable. Thus, the transformation of regenerated cellulose from cellulose I to amorphous or other forms is evidence that cellulose dissolution occurs in [bmIm][Cl] (Jiang, Huang, Wang, Zhang, & Wang, 2012). At 90 °C, there were small differences in the XRD pattern of the primary solid for cases with added or without water and DMSO. However, the XRD patterns of the primary solid at 120 °C for 10 h dissolution times with and without added water were different from those at 5 h. In this study, two types of XRD patterns were observed: (i) a pattern that had a broad peak around 19–23° (Fig. 3a-1 to a-3 and b), and (ii) a pattern that had three peaks at 12, 20 and 22° that is attributed to cellulose II (Fig. 3c-1 and c-2) (Takahashi & Matsunaga, 1991). As shown in Fig. 3, the large amorphous content causes peak broadening. In Table 2, the crystallinity indexes of cellulose II in runs 1–5 were smaller than those in runs 6 and 7. The patterns that had broad peaks from 19 to 23° of runs 1–5 are probably derived from cellulose II, and might also contain amorphous regions (Li et al., in press). However, some differences in the XRD patterns might also be caused by the DP_v values of the solid samples. Low DP solids could possibly form crystals, however,

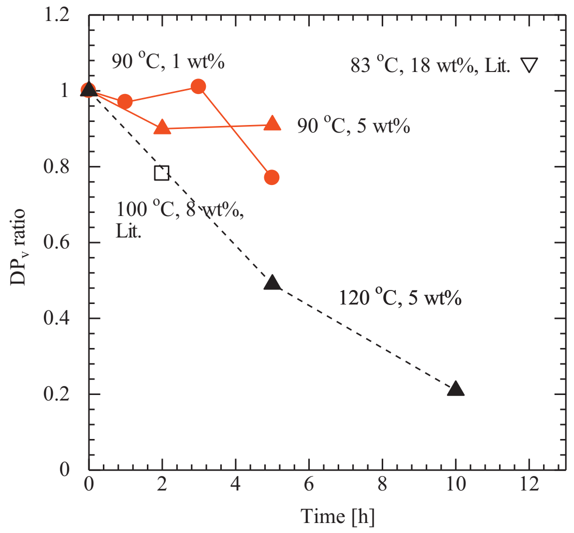

Fig. 2. Comparison of DP_v ratios for microcrystalline cellulose among this work (●: 1 wt% and ▲: 5 wt%; straight line: 90 °C and dotted line: 120 °C) and the literature: (▽) Barthel and Heinze (2006) and (□) Vitz et al. (2009) with different dissolution conditions.

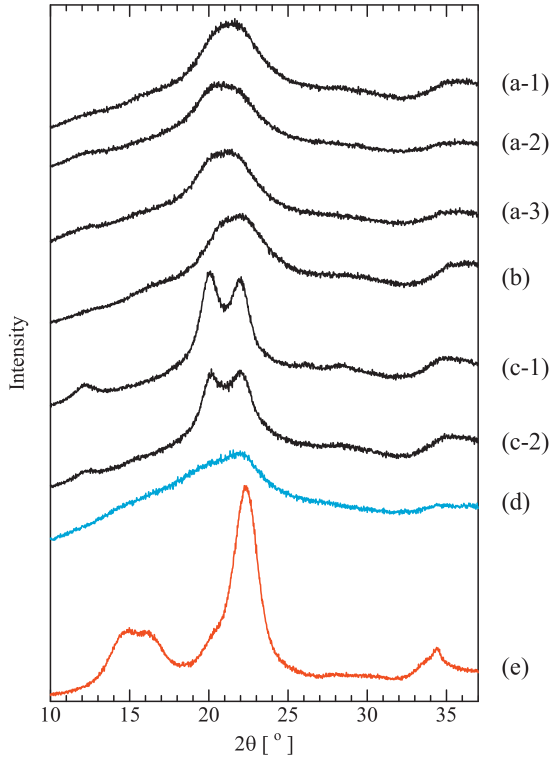

Fig. 3. XRD patterns for primary solid of (a-1) run 2 in Table 2 dissolution at 90 °C for 5 h, (a-2) run 3 dissolution at 90 °C for 5 h with added water, (a-3) run 4 dissolution at 90 °C for 5 h with added DMSO, (b) run 5 dissolution at 120 °C for 5 h, (c-1) run 6 dissolution at 120 °C for 10 h, (c-2) run 7 dissolution at 120 °C for 10 h with added water, (d) amorphous cellulose prepared by ball milling and (e) microcrystalline cellulose.

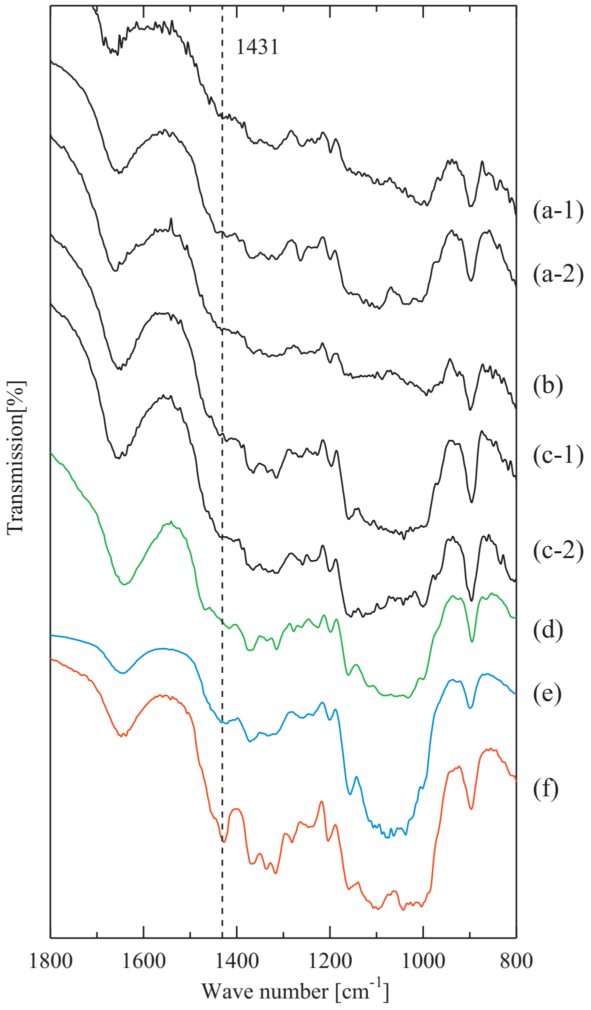

Fig. 4. IR absorption spectra between 1800 and 800 cm^{-1} of primary solid of (a-1) run 2 in Table 2 dissolution at 90 °C for 5 h without added water, (a-2) run 3 dissolution at 90 °C for 5 h with added water, (b) run 5 dissolution at 120 °C for 5 h, (c-1) run 6 dissolution at 120 °C for 10 h and (c-2) run 7 dissolution at 120 °C for 10 h with added water, and (d) secondary solid of run 6 after dissolution at 120 °C for 10 h, (e) amorphous cellulose and (f) microcrystalline cellulose.

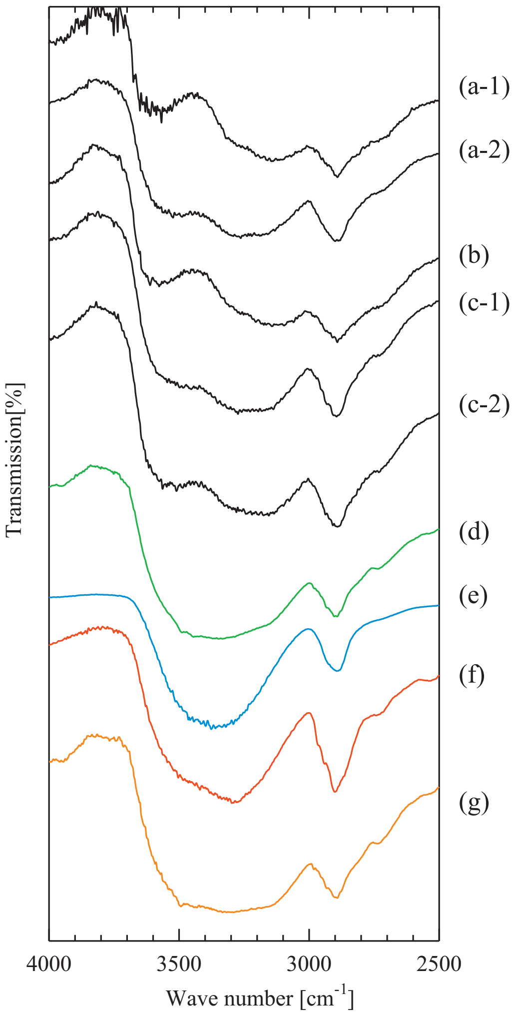

Fig. 5. IR absorption spectra between 4000 and 2500 cm^{-1} of primary solid of (a-1) run 2 in Table 2 dissolution at 90 °C for 5 h without added water, (a-2) run 3 dissolution at 90 °C for 5 h with added water, (b) run 5 dissolution at 120 °C for 5 h, (c-1) run 6 dissolution at 120 °C for 10 h without added water and (c-2) run 7 dissolution at 120 °C for 10 h with added water, (d) secondary solid of run 6 after dissolution at 120 °C for 10 h, (e) amorphous cellulose, (f) microcrystalline cellulose and (g) cellohexaose.

this is difficult for high DP solids. Some researchers have reported on the crystal forms of regenerated cellulose from the ionic liquids as being cellulose II according to their XRD patterns (Cao, Li, Zhang, Zhang, & He, 2010; Ding et al., 2012; Li et al., in press; Quan et al., 2010; Zhang, Wu, Zhang, & He, 2005). The XRD patterns of Fig. 3(c-1 and c-2), which are assigned to cellulose II in this study, were different from those in the literature since peaks around 19–23° were split, whereas in the literature, the peak split is not observed (Kuo & Lee, 2009; Quan et al., 2010). The peak split is attributed to the low DP solids for experiments at high temperatures.

Figs. 4 and 5 show IR absorption spectra at low and at high wave numbers, respectively, for the regenerated solids obtained at different dissolution conditions (runs 2, 3, 5, 6 and 7, Table 2). IR absorption spectra of regenerated solids were similar to those of the original cellulose. Peaks at 1431 cm^{-1}, which is assigned to bonding of CH_2 at C6, disappeared when the crystal structure transformed from cellulose I to cellulose II or amorphous cellulose (Oh et al., 2005; Schwanninger, Rodrigues, Pereira, & Hinterstoisser, 2004). Fig. 4 shows the absence of a peak at 1431 cm^{-1} in all experiments. The transformation of microcrystalline cellulose from cellulose I for all primary regenerated cellulose is consistent with the XRD measurements (Fig. 3). From band 3000 to 3600 cm^{-1} in Fig. 5, IR absorption spectra of primary solid were similar to microcrystalline cellulose rather than amorphous cellulose, however there were some differences in the shape of bands from 3000 to 3600 cm^{-1}, which is probably due to differences in the hydrogen bondings between the primary solids and the original microcrystalline cellulose. These differences imply that the primary solids in all experiments had a different crystalline content from the original cellulose. On the other hand, IR absorption spectra of the secondary solids were similar to that of cellohexaose, which is a linkage of glucose molecules by β1-4 bonds (Fig. 5). In Fig. 4, the absence of the peak at 1570 cm^{-1} in the spectra of regenerated solids indicates that the regenerated solids were not contaminated with the ionic liquid (Supplementary data, Fig. A.1).

IR measurements for primary and secondary solids showed that the primary solids were similar to microcrystalline cellulose whereas that the secondary solid was similar to cello-oligosaccharides. The composition of CHNO of the primary and secondary solids was investigated (Supplementary data, Fig. A.2). From the chemical elemental analyses of primary solids (runs 6 and 7, Table 2), the ratios of H/C and O/C for primary solids agreed with those of cellulose, which means that it is likely that the primary solids have the same chemical structure as that of the original

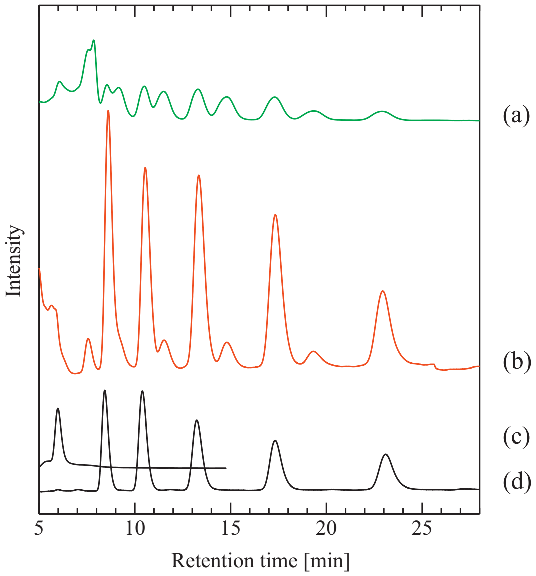

Fig. 6. Chromatograms of HPLC I for (a) residue of run 6 in Table 2 dissolution at 120 °C for 10 h without added water, (b) residue of run 7 dissolution at 120 °C for 10 h with added water, (c) levoglucosan and (d) standard solution of cello-oligosaccharides.

cellulose. However, the ratios of H/C and O/C for the secondary solids were different from those of cellulose and were consistent with that of a hydrolyzed primary solid as interpreted from van Krevelen diagram (Supplementary data, Fig. A.2).

3.2. Residues

Recoveries of the primary solid at 120 °C for 10 h (runs 6 and 7, Table 2) were relatively lower than those obtained at other conditions, which indicates some products remained in the primary filtrate. The primary filtrate of each runs was analyzed by both GC and HPLC I systems. GC–MS analysis of the primary filtrate of run 6 (Table 2) allowed the products as levoglucosan and glucose to be indentified (Supplementary data, Fig. A.3). The HPLC I analysis of the primary filtrate of run 6 (Table 2) showed major products have larger molecular sizes larger than glucose.

Fig. 6 shows chromatograms of HPLC II with RI detector for residues of runs 6 and 7 in Table 2. Retention times of standard substances revealed the formation of cello-oligosaccharide and levoglucosan in the residues. From the intensities of the RI detector, more sugars were formed with added water than without added water. This indicates that the role of the added water seemed to be the promotion of hydrolysis of dissolved cellulose in the ionic liquid to form cello-oligosaccharides. The UV absorption at 210 and 280 nm was not observed in Fig. 6, which means that sugar links to the [bmIm] cation or those that contained furans were not formed at the conditions of the experiment.

3.3. General characteristic of [bmIm][Cl] with water as a solvent for cellulose

At 90 °C, the DP_v value of regenerated cellulose did not change much with water content, dissolution time or cellulose concentrations. Thus, both [bmIm][Cl] and [bmIm][Cl] with water can be thought of as a non-derivatizing solvent for microcrystalline cellulose at 90 °C. Mixtures of [bmIm][Cl] and DMSO can also be considered to be non-derivatizing for microcrystalline cellulose since the DP_v value of regenerated cellulose did not change much by the addition of DMSO. This result is in accordance with the literature in that the addition of DMSO does not seem to change the conformation of cellulose in the ionic liquid (Lv et al., 2012). At somewhat higher temperatures (100 °C, Table 1), both [bmIm][Cl] and its mixtures with water might also act as a non-derivatizing solvent for microcrystalline cellulose. However it is clear from Table 1 that this generalization only seems to hold for convective heating since microwave heating causes large changes in the DP_v value of regenerated cellulose for relatively short dissolution times.

At 120 °C, the DP_v value of cellulose changes greatly for the case of dissolution with or without water. Thus both [bmIm][Cl] and [bmIm][Cl] with water acts as a derivatizing solvent for microcrystalline cellulose. However, according to results in this study (Table 2), the DP_v ratio of microcrystalline cellulose decreased by about the same (ca. 0.2) for the case of dissolutions with or without water (runs 6 and 7, Table 2) and the recovery ratios were about the same (ca. 70 wt%). For these cases, the main effect of water on the dissolution products would seem to promote hydrolysis of the cello-oligosaccharides. The residues at 120 °C without water had a relatively low amount of hydrolytic products compared with the case of dissolution with water as shown in Fig. 6.

4. Conclusions

Temperature is an important factor for recovery of cellulose after dissolution in [bmIm][Cl], whereas water content had a little influence on recovery of cellulose after dissolution in [bmIm][Cl]. At low temperature (ca. 90 °C), recovery ratio and degree of polymerization ratio of cellulose after dissolution and regeneration did not change much. At 90 °C, both [bmIm][Cl] and [bmIm][Cl] with water behave as a non-derivatizing solvent for microcrystalline cellulose. At 120 °C, recovery ratio and degree of polymerization decreased with dissolution time, thus, both [bmIm][Cl] and its mixtures with water behave as a derivatizing solvent for microcrystalline cellulose. The effect of water on the product distribution in the dissolution experiments at 120 °C seems to be one of mainly hydrolyzing cello-oligosaccharides. Chemical structures of the regenerated cellulose in all experiments were similar to that of the original microcrystalline cellulose, whereas, crystal structure of regenerated cellulose was different for the conditions. At high temperatures and long dissolution times (120 °C, 10 h), regardless of water content, the crystal structure of the regenerated cellulose changed from cellulose I to cellulose II. Conditions of short dissolution times (≤5 h) or low temperatures (90 °C) gave solids that had a high amorphous content.

Acknowledgments

The authors wish to acknowledge the Global Educational Center of Excellence (GCOE) and the partial financial support of the Ministry of Education, Science, Sports and Culture for support of this research.

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.2012.09.021.

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