

Imidazolium Chloride-LiCl Melts as Efficient Solvents for Cellulose

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Received August 23, 2013, Accepted September 25, 2013

1-Alkyl-3-methylimidazolium chloride-LiCl melts were prepared from the reaction of 1-alkyl-3-methylimidazolium chloride ([RMIm]Cl; R=allyl or *n*-butyl) and lithium chloride, and their ability to dissolve cellulose was evaluated. The solubility of cellulose was greatly increased to 320% when [RMIm]Cl was replaced by [RMIm][LiCl₂]. Dissolved cellulose in LiCl/[RMIm]Cl melts was successfully regenerated by adding water and LiCl/[RMIm]Cl melts were easily recovered by removing water. As supported by the computational results, the higher solubility of cellulose in [RMIm][LiCl₂] can be ascribed to the increased bond distance between anion and C(2)-H of the imidazolium ring compared with that in [RMIm]Cl, thereby resulting in the increased interaction between [LiCl₂]⁻ and the hydroxyl groups of cellulose.

Key Words : Cellulose, Dissolution, Ionic liquid, Lithium chloride, Dihedral angle

Introduction

Cellulose is the most abundant bio-resource and possesses a large portion of biomass. However, the low solubility of cellulose in most common solvents truncates its applicability. Although the viscous process is the most well-known cellulose dissolving process, this process has some drawbacks such as using toxic CS₂, complicated, time consuming, and pollutant generating nature.¹ After the development of several solvents prior to the 1950s, such as cuprammonium hydroxide (Cuam),² aqueous solutions of tetraalkylammonium hydroxides,³ and cupriethylenediamine (Cuene),^{2,4} various non-derivative solvent systems have also been found, including LiCl/*N,N*-dimethylacetamide (DMAc),^{5,6} paraformaldehyde/DMSO,⁷ LiCl/*N*-methyl-2-pyrrolidone (NMP),⁸ molten salt hydrates,^{9,10} aqueous solutions of metal complexes,^{11,12} and *N*-methylmorpholine-*N*-oxide (NMMO, the Lyocell process).¹³ LiCl/DMAc (10 wt % LiCl) is one of the most extensively studied solvent systems and it can dissolve up to 16 wt % of cellulose at 150 °C, through the disruption of hydrogen bonds between cellulose threads by an electron donor-acceptor interaction of cellulosic hydroxyl group and solvent molecule. However, LiCl/DMAc requires relatively high temperature and long time to dissolve cellulose.¹⁴

Ionic liquids (ILs) have been interested as a replacement for the common organic solvents in various fields due to their excellent properties, such as the wide range of liquid temperature, high thermal stability, negligible vapor pressure, and high dissolution ability.¹⁵ Several ILs including 1-butyl-3-methylimidazolium chloride ([BMIm]Cl), 1-allyl-3-methylimidazolium chloride ([AMIm]Cl), and 1-ethyl-3-methylimidazolium acetate ([EMIm][OAc]), have been demonstrated as promising solvents for cellulose at over 100 °C.¹⁶⁻²⁰

Recently, Xu et al. reported that the addition of lithium salt affected the solubility of cellulose in ILs through the interaction of Li⁺ with the hydroxyl oxygen of the cellulose.²¹ However, the effect of lithium salt was not so profound because the solubility of cellulose was predominantly governed by the basicity of the AcO⁻ anion of IL.

We have previously prepared LiCl/[BMIm]Cl melts and reported the presence of superhalogenated anions (e.g. [LiCl₂]⁻ and [Li₃Cl₄]⁻) in the melt by increasing the molar ratio of LiCl/[BMIm]Cl. The increased nucleophilicity of Cl⁻ in [LiCl₂]⁻ compare to LiCl was supported by the theoretical calculation which shows that there is an increase in the negative charge character at the chlorine atoms and the lengthening of Li-Cl bond distance.²² Although the theoretical calculations for the superhalogenated species have been reported,²³⁻²⁵ the applications of superhalogenated species were very rare. Herein, we report the solubility of cellulose in LiCl/[RMIm]Cl (R=allyl or *n*-butyl) melt systems as well as the effect of the superhalogenated anion in the dissolution of cellulose. Keys to the success of our approach lie in the increased nucleophilicity of the anion and the decreased association of cation and anion.

Experimental

Chemicals and Methods. Microcrystalline cellulose, 1-methylimidazole, butyl chloride, allyl chloride, and LiCl were purchased from Sigma-Aldrich Chemical Co. [BMIm]Cl, [AMIm]Cl, and their LiCl melts were prepared according to the literature procedures.^{18,22,26} The dissolution of cellulose was monitored by the optical microscope (Eclipse MA100, Nikon Co.) equipped with CCD camera (ARTCAM-150P III, Artray Co.). Fourier Transform Infrared (FT-IR) spectra were recorded on a Nicolet 380 spectrophotometer (Thermo Electron Co.). Thermogravimetric analysis (TGA) was per-

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formed using a thermogravimetric analyzer (Shimadzu) under an oxygen atmosphere between 25 and 800 °C at a ramp rate of 10 °C min⁻¹. The melting temperatures of imidazolium chloride-LiCl melts were determined using a TA Instruments Q10 differential scanning calorimeter (DSC) in the range from -70 to 200 °C at a ramp rate of 5 °C min⁻¹ under nitrogen atmosphere. The morphologies of the resulted materials were studied *via* FE-SEM (Field Emission Scanning Electron Microscope, HITACHI S-4300) at an accelerating voltage of 5 kV. Gold was deposited on the surface of cellulose prior to the observation.

Dissolution and Regeneration of Cellulose. All dissolution experiments were performed in a 20 mL vial with magnetic stirring bar over magnetic stirrer. The dissolution temperature was controlled by an oil bath. Cellulose was added in a vial containing solvent system after the temperature was stabilized at desired temperature. The mixture was stirred until cellulose sample was completely dissolved and transparent solution was obtained. To regenerate the dissolved cellulose, the transparent cellulose solution was poured into 10 mL of distilled water. The solvent systems were recovered by filtration of regenerated cellulose followed by removing water by evaporation. The regenerated cellulose was transferred to 30 mL of water in a 100 mL round bottomed flask equipped with condenser followed by refluxing for 3 h to obtain transparent regenerated cellulose. The regenerated cellulose was washed with running distilled water and dried at 80 °C under vacuum. The degree of polymerization (DP) of microcrystalline and regenerated celluloses was determined by the measurement of intrinsic viscosity (η) according to the SCAN-CM 15:88 method.²⁷ Dried microcrystalline or regenerated cellulose was dissolved in cupriethylenediamine hydroxide (Cuene) solution. The intrinsic viscosity of cellulose in Cuene solution was measured using an Ubbelohde viscometer, and then DP was calculated using the Mark-Houwink-Sakurada equation: $DP^{0.85} = 1.1[\eta]$.²⁸

Quantum Mechanical Calculations. The dissolution of cellulose in [EMIm]Cl and [EMIm][LiCl₂] melt was theoretically investigated using a Gaussian 03 program.²⁹ The geometry optimizations and thermodynamic corrections were performed with hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation functional with the 6-31+G* basis sets for C, H, N, O, Li, and Cl. In order to obtain the most stable geometries, all kinds of possible interaction patterns were optimized. No restrictions on symmetries were imposed on the initial structures. All stationary points were verified as minima by full calculation of the Hessian and a harmonic frequency analysis.

Results and Discussion

Dissolution of Cellulose. The ionic liquids (ILs), 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) and 1-allyl-3-methylimidazolium chloride ([AMIm]Cl), were prepared by modified literature method.²⁶ LiCl/[RMIm]Cl (R=allyl or *n*-butyl) melts were prepared by literature method.²² The

thermal behaviors of LiCl/[RMIm]Cl melts with the molar ratio of 1 were studied by DSC in the range of -70 to 200 °C (see Figure S1 in Supporting Information, SI). Similar to [BMIm]Cl, of which melting temperature was reported as 41 °C, LiCl/[BMIm]Cl melt shows melting temperature at 49 °C and glass transition temperature at -24 °C. Interestingly, LiCl/[AMIm]Cl exhibits melting temperature at -15 °C and glass transition temperature at -45 °C, but the melting temperature of [AMIm]Cl was reported as 55 °C.

The results of cellulose dissolution in [RMIm]Cl or LiCl/[RMIm]Cl melts were summarized in Table 1. To make the cellulose solution, 3 g of [RMIm]Cl or LiCl/[RMIm]Cl melt was put into a vessel followed by the addition of the proper amount of cellulose until transparent solution was obtained. The dissolution process of cellulose was monitored by the optical microscope (see Figure S2 in SI). The dissolution mechanism of cellulose involves the formation of electron donor-acceptor complexes between oxygen and hydrogen atoms of the cellulose with the charged species of the solvents, leading to the disruption and breaking of the intermolecular hydrogen-bonding network of cellulose.^{14,18,30} As shown in Table 1, the concentration of dissolved cellulose in [BMIm]Cl was similar to that in the LiCl/DMAc solvent system at 80 °C during the same dissolving time. [AMIm]Cl, on the other hand, could dissolve cellulose faster and more than [BMIm]Cl and LiCl/DMAc at the same temperature. This may be due to the lower viscosity of [AMIm]Cl and the weak ion association of [AMIm]⁺ cation and Cl⁻ anion, because the free Cl⁻ anion in [AMIm]Cl can disrupt the intermolecular hydrogen bonds between the cellulose strands more efficient than [BMIm]Cl and LiCl/DMAc. The addition of equimolar LiCl into [RMIm]Cl increased the solubility of cellulose dramatically at the same temperature. As shown in Table 1, the solubility of cellulose in LiCl/[AMIm]Cl melt at a molar ratio of 1 was increased by 70% compared to [AMIm]Cl itself under the same experimental condition. More interestingly, the solubility of cellulose in LiCl/[BMIm]Cl melt at a molar ratio of 1 was boosted up to 320% compared to [BMIm]Cl at the same dissolution condition. However, the elongated dissolution time over 2 h did not so

Table 1. Dissolution of cellulose in various solvents^a

Solvent	Dissolution time (h)	Amount of dissolved cellulose (wt %)
LiCl/DMAc ^b	2	< 1
	12	6
[BMIm]Cl	2	1
	12	5
LiCl/[BMIm]Cl ^c	2	3
	12	16
[AMIm]Cl	2	10
	12	13
LiCl/[AMIm]Cl ^c	2	17
	12	19

^aDissolution condition: amount of solvent = 3 g, temperature = 80 °C. ^b10 wt % of LiCl was dissolved in DMAc. ^cMolar ratio of LiCl/[RMIm]Cl = 1.

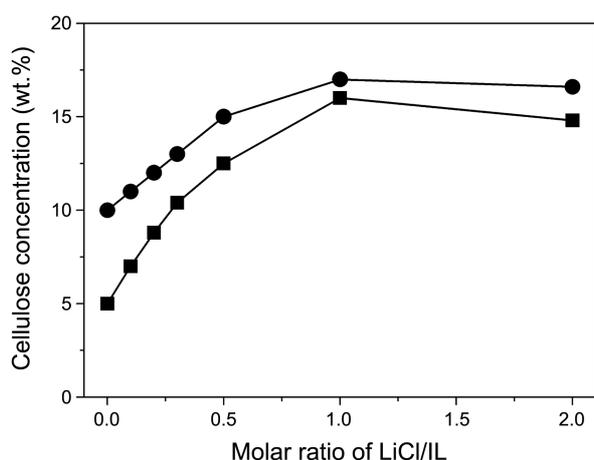


Figure 1. Effect of LiCl on the solubility of cellulose in LiCl/IL melts at 80 °C: (-■-) [BMIm]Cl and (-●-) [AMIm]Cl (dissolution time: [BMIm]Cl and [BMIm][LiCl₂] = 12 h, [AMIm]Cl and [AMIm][LiCl₂] = 2 h).

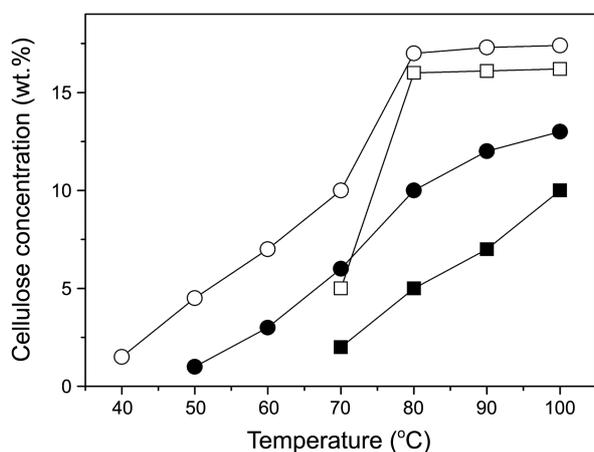


Figure 2. Temperature dependence on the solubility of cellulose: (-■-) [BMIm]Cl, (-□-) [BMIm][LiCl₂] for 12 h and (-●-) [AMIm]Cl, (-○-) [AMIm][LiCl₂] for 2 h.

greatly affect the solubility of cellulose in LiCl/[AMIm]Cl melt. This may be due to the increased viscosity at high concentration of cellulose.

In the previous work, we had proved that the existence of superhalogenated anions such as the mononuclear [LiCl₂]⁻ anion and multinuclear [Li₃Cl₄]⁻ anion in LiCl/[BMIm]Cl melts on the basis of electrospray ionization mass spectrometry (ESI-MS) experiments and theoretical calculations.²² Similarly, in the LiCl/[AMIm]Cl melt system at the molar ratio of 1, [AMIm][LiCl₂] species would exist as a major species. Therefore, the increased solubility of cellulose by the incorporation of LiCl could be ascribed to the stronger intermolecular hydrogen bonding interactions exerted by more nucleophilic [LiCl₂]⁻ than Cl⁻.

Effect of LiCl on the Solubility of Cellulose. To investigate the effect of the incorporation of LiCl on the cellulose dissolution, in the molar ratio of LiCl/[RMIm]Cl was varied from 0 to 2. As shown in Figure 1, the solubility of cellulose increased with increasing molar ratio up to 1, but decreased

thereafter for both [BMIm]Cl and [AMIm]Cl. From this result, it can be suggested that LiCl forms [BMIm][LiCl₂] species by the coordination of the Cl⁻ anion to LiCl at a lower concentration of LiCl, and the ionic interaction between the [BMIm]⁺ cation and [LiCl₂]⁻ anion is much weaker than between the [BMIm]⁺ cation and Cl⁻ anion, as we have shown previously using FT-IR experiments (see also computational result).²² For this reason, the [LiCl₂]⁻ anion interacts with cellulose more efficiently than Cl⁻ anion in spite of the larger size of [LiCl₂]⁻. Therefore, as the amount of LiCl increases up to the equimolar amount of [BMIm]Cl, the solubility of cellulose also increases as shown in Figure 1. However, when the amount of LiCl is more than equimolar amount of [BMIm]Cl, the excess LiCl starts to form the multinuclear anions such as [Li₂Cl₃]⁻, [Li₃Cl₄]⁻, and [Li₄Cl₅]⁻. These multinuclear anions cannot interact with cellulose efficiently because these anions are too large to interact with cellulose. As a result, the solubility of cellulose in melt again starts decreasing.

Temperature Dependence on the Solubility of Cellulose.

The influence of temperature on the dissolution of cellulose in [RMIm]Cl and LiCl/[RMIm]Cl melts at a molar ratio of 1 has also been investigated. Figure 2 shows the result of cellulose dissolution at different temperature in [BMIm][LiCl₂] and [AMIm][LiCl₂] for 12 and 2 h, respectively. The solubility of cellulose in [BMIm]Cl and [BMIm][LiCl₂] melt was measured at 70 and 80 °C because those solvent systems melted at over 41 and 49 °C, respectively, and too viscous at lower than 70 °C. With increasing the temperature, the ionic association of cation and anion becomes lower³¹ and the dissociated anion can interact with hydroxyl groups of cellulose more efficiently. Moreover, the ion association in [BMIm][LiCl₂] and [AMIm][LiCl₂] are weaker than that of [BMIm]Cl and [AMIm]Cl (see computational result). In [AMIm][LiCl₂], only around 1 wt % of cellulose was dissolved at 40 °C. By increasing the temperature from 40 to 80 °C, however, the solubility of cellulose is increased rapidly up to 17 wt %. In the case of [BMIm][LiCl₂], only 6 wt % of cellulose was dissolved at 70 °C. However, the solubility of cellulose increased dramatically to 16 wt % at 80 °C. At over 80 °C, nonetheless, the solubilities of cellulose did not so much increased in both melts. This may be due to the increased viscosity at high concentration of cellulose.

Computational Studies on the Dissolution of Cellulose.

In order to have a deeper insight into the dissolution of cellulose in [RMIm]Cl or LiCl/[RMIm]Cl melts, the theoretical investigation was conducted at the B3LYP level of the theory (6-31+G* basis sets for C, H, N, O, Li, and Cl) using a Gaussian 03 program.²⁹ All possible structures were considered to obtain the most stable geometries. To simplify the calculations, 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) was used as IL instead of [BMIm]Cl or [AMIm]Cl and 1,4-methylated cellobiose was used instead of cellulose. The optimized structures of [EMIm]Cl and [EMIm][LiCl₂] are depicted in Figure 3. Although the structure of [LiCl₂]⁻ itself in gas phase have been calculated as a linear structure,^{24,25} [LiCl₂]⁻ in melt have a bent structure through the interaction

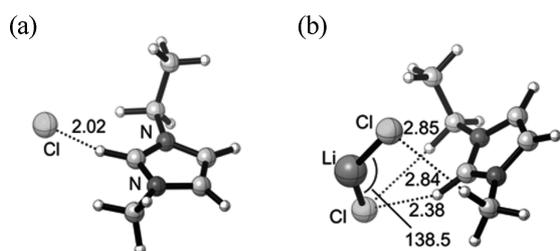


Figure 3. Optimized structures of (a) [EMIm]Cl and (b) [EMIm][LiCl₂] (bond lengths are in 10⁻¹⁰ m).

between the Cl atom in [LiCl₂]⁻ and the C(2)-hydrogen and alkyl hydrogens attached to nitrogen of [EMIm]⁺. The distance between cation and anion is longer in [EMIm][LiCl₂] than in [EMIm]Cl, implying the decreased ionic interaction between cation and anion of the [EMIm][LiCl₂], and this result agrees very well with the results of FT-IR experiments.²² As a result of lower ionic interaction between cation and anion, the anion may get closer to the cellulose and interact more effectively.

The interactions between cation or anion and cellulose were also investigated theoretically. The most important hydrogen bonds in cellulose are the intermolecular hydrogen bonds between C(6)-OH and C(3)-OH of each cellulose strand. As shown in Figure 4a, the bond distances of these intermolecular hydrogen bonds were calculated as 1.91 and 1.92 Å, respectively. We ruled out the cation effect on the dissolution of cellulose because cations themselves do not contribute to the rupturing of intermolecular hydrogen bonds in cellulose (see Figure S3 in SI). As shown in Figure 4(c), the Cl⁻ anion forms a hydrogen bond between the C(6)-OH and C(2)-OH of each strand and the hydrogen bond between C(6)-OH and C(3)-OH is lengthened to 4.47 Å. Interestingly,

the [LiCl₂]⁻ anion forms bonds with C(2)-OH in one strand and C(3)-OH in another strand, through the Li atom and C(3)-OH in one strand and C(2)-OH in other strand by each Cl atom (Figure 4(e)). These local interactions make the dihedral angle between the two cellulose planes larger from -22.6 to -40.8 °C (Figure 4(f)). This motion as a result of interaction between cellulose strand and [LiCl₂]⁻ anion makes the whole cellulose twist, even though the lengthening of the hydrogen bond is smaller than Cl⁻ anion, and the hydrogen bond networks in cellulose break down effectively.

Regeneration of Cellulose. Dissolved cellulose in LiCl/[RMIm]Cl melts was successfully regenerated by the addition of water into the cellulose solution. LiCl/[RMIm]Cl melts were easily recovered by removing water and could be reused over 5 times without loss of dissolving capacity (Figure 5). Regenerated cellulose was refluxed in the pre-

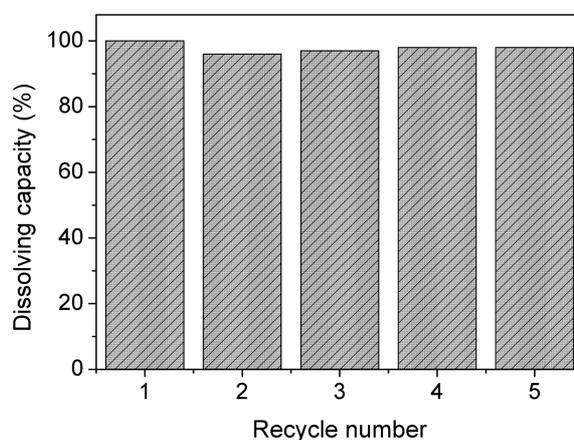


Figure 5. Recycling of [AMIm][LiCl₂] in the dissolution of cellulose.

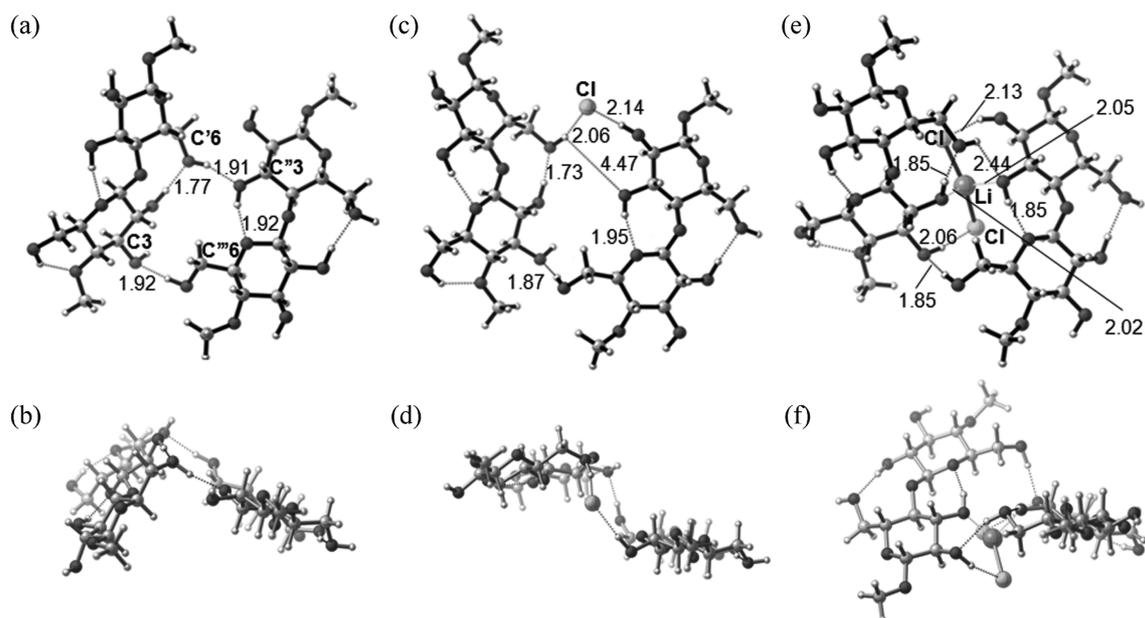


Figure 4. Optimized structures: (a) and (b) 1,4-methylated cellobiose; (c) and (d) 1,4-methylated cellobiose interacting with Cl⁻; (e) and (f) 1,4-methylated cellobiose interacting with [LiCl₂]⁻ (bond lengths are in 10⁻¹⁰ m). Dihedral angles between the two cellulose planes are defined by four methoxy oxygen atoms and are (b) -22.6°, (d) -6.7°, and (f) -40.8°.

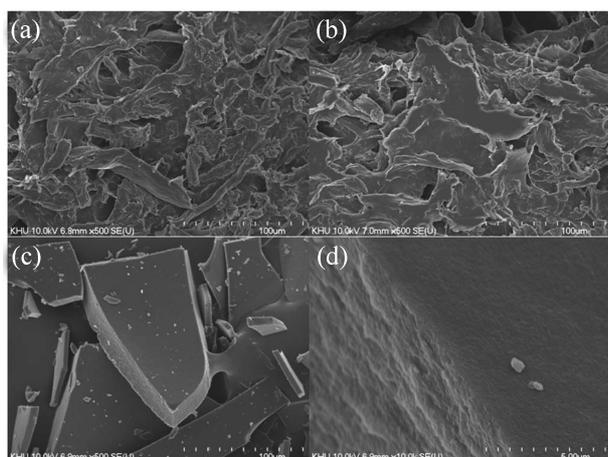


Figure 6. SEM images of regenerated cellulose from [AMIm]-[LiCl₂] after (a) 30 min, (b) 60 min, (c) 120 min, and (d) magnified (c) 20 times.

sence of water for 3 h to remove the remained LiCl/[RMIm]Cl melt in cellulose. The results of FT-IR, thermogravimetric analysis (TGA), and energy dispersive X-ray spectroscopy (EDX) experiments indicate that the removal of the solvent system was successful (see Figures S4-S6 in SI). The images of scanning electron microscopy (SEM) of regenerated cellulose at different dissolution time were shown in Figure 6. The morphologies of regenerated cellulose were significantly changed from the microcrystalline cellulose, indicating that the cellulose was completely dissolved in [AMIm]-[LiCl₂] at 80 °C. It could be seen that at the beginning of dissolution, there were plenty of cellulose fibrils. As time went on, however, the cellulose fibrils disappeared and uniformity from the interior to the exterior was observed, which indicated that the regenerated cellulose had dense texture similar to the previous report.¹⁸

The effect of temperature on the DP of cellulose was also studied by measuring the intrinsic viscosity of cellulose in cupriethylenediamine hydroxide solution (see Figure S7 in SI).^{27,28} In general, the DP value of regenerated cellulose is affected by the dissolution time and temperature. In this study, the regenerated cellulose dissolved in [RMIm][LiCl₂] melts at 70 and 80 °C had similar DP values (DP = 321-341) to the microcrystalline cellulose (DP = 345), indicating that the degradation of cellulose could be ignorable at this temperature. When [AMIm][LiCl₂] was used as the solvent, the DP did not change appreciably in the temperature range from 70 to 100 °C. When [BMIm][LiCl₂] was used as the solvent, however, the DP of regenerated cellulose exhibited an apparent decreasing trend by increasing the dissolution temperature because [BMIm][LiCl₂] needed longer time than [AMIm][LiCl₂] to dissolve the cellulose.

Conclusion

We have investigated the effect of LiCl in the dissolution of cellulose in 1-allyl-3-methylimidazolium chloride ([AMIm]Cl) and 1-butyl-3-methylimidazolium chloride ([BMIm]Cl). The

dissolution process can be considerably enhanced by the addition of LiCl in the dissolution system without chemical changes in the polymeric structure of the cellulose. The theoretical investigation was also conducted to gain a deeper insight into the dissolution of cellulose in [RMIm]Cl (R = allyl or *n*-butyl) or LiCl/[RMIm]Cl melts, and the results agree well with the experimental results. The solubility of cellulose were increased to 170 and 320% in [AMIm][LiCl₂] and [BMIm][LiCl₂] compared to [AMIm]Cl and [BMIm]Cl, respectively. Dissolved cellulose in LiCl/[RMIm]Cl melts was successfully regenerated by adding water and LiCl/[RMIm]Cl melts were easily recovered by removing water. The local interaction between [LiCl₂]⁻ anion of IL and cellulose provides a unique and efficient means for dissolving cellulose at lower temperature than conventional solvent systems by increasing the dihedral angle between the two cellulose planes.

Acknowledgments. This work was financially supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (2011-0013429) and the Fundamental R&D Program for Core Technology of Materials of the Ministry of Trade, Industry and Energy, Republic of Korea.

Supporting Information. Figures S1-S7 are available upon request from the corresponding author.

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