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1-Allyl-3-methylimidazolium Chloride Room Temperature Ionic Liquid: A New and Powerful Nonderivatizing Solvent for Cellulose

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ABSTRACT: A new and highly efficient direct solvent, 1-allyl-3-methylimidazolium chloride (AMIMCl), has been used for the dissolution and regeneration of cellulose. The cellulose samples without any pretreatment were readily dissolved in AMIMCl. The regenerated cellulose materials prepared by coagulation in water exhibited a good mechanical property. Because of its thermostable and nonvolatile nature, AMIMCl was easily recycled. Therefore, a novel and nonpolluting process for the manufacture of regenerated cellulose materials using AMIMCl has been developed in this work.

Introduction

The synthetic polymer industry has offered great benefits to modern society. However, nonbiodegradable plastics have become a threat to the environment and are exhausting much limited petroleum resource. Therefore, people are increasingly paying attention to the exploitation of natural polymers. As the oldest class of such materials, cellulose materials are the most abundant in nature, and they are renewable, biodegradable, and biocompatible. However, because of their stiff molecules and close chain packing via numerous intermolecular and intramolecular hydrogen bonds, it is extremely difficult to dissolve cellulose in water and most common organic solvents. Therefore, the multistep and polluting viscose process has long occupied the leading position in the regenerated cellulose (RC) industry. With increasing governmental regulations in industries, the need to implement "green" processes for preventing the pollution is becoming increasingly important and acting as a strong driving force to discover effective solvents for cellulose. Since the 1970s, novel solvents for cellulose have been sought to replace the viscose process. To date, only a limited number of solvent systems have been found, for example, LiCl/*N*,*N*-dimethylacetamide (DMAc),[1−5] LiCl/*N*-methyl-2-pyrrolidine (NMP),[6] LiCl/1,3-dimethyl-2-imidazolidinone (DMI),[7] DMSO/paraformaldehyde (PF),[8,9] *N*-methylmorpholine-*N*-oxide (NMMO),[10] some molten salt hydrates,[11,12] such as $LiClO_4 \cdot 3H_2O$, $LiSCN \cdot 2H_2O$, and some aqueous solutions of metal complexes.[13,14] However, these solvents have some limitations such as volatility, toxicity, costly, difficulty for solvent recovery, or instability in application. Among the above cellulose solvents, the $NMMO/H_2O$ system is the solely industrialized for manufacturing regenerated cellulose fibers and films.[15] However, the $NMMO/H_2O$ system has some disadvantages associated with its use, such as the demand for high temperature to dissolve, the degradation of cellulose, the side reactions of the solvent itself without an antioxidant, and its high cost as well.

Room temperature ionic liquids (ILs), which are considered as desirable green solvents, have been used to replace the organic solvent in a wide range due to their advantages such as width of liquid range, excellent dissolution ability, free from the effect of vapor pressure, and ease of recycling.[16,17] Furthermore, ILs may be easily modified through changing the structure of cations or anions, which will broaden their application fields. Recently, ILs have been used to dissolve native cellulose.[18] It has been found that cellulose can be dissolved without derivatization in high concentrations using 1-butyl-3-methylimidazolium (BMIMCl) chloride as the solvent. More recently, a novel IL, 1-allyl-3-methylimidazolium chloride (AMIMCl), was synthesized in our lab and was used to carry out homogeneous esterification of cellulose.[19] In the present article, we present the details of the dissolution process of cellulose in AMIMCl and the formation of the regenerated cellulose materials. The structure and properties of the regenerated cellulose materials are investigated. Moreover, the recovery of AMIMCl is also discussed.

Experimental Section

Materials. The cellulose samples used in this study include microcrystalline cellulose (MCC), dissolved pulp, and cotton linters. The viscosity-average degree of polymerization (DP) of these three cellulose materials measured by using an Ubbelodh viscometer in CUEN (cupriethylenediamine hydroxide solution) was 220, 650, and 1600, respectively.

Synthesis of AMIMCl. The room temperature ionic liquid AMIMCl was synthesized as described in our previous work.[20] 1-Methylimidazole (400 mL) and allyl chloride (800 mL) at a molar ratio 1:1.25 were added to a round-bottomed flask fitted with a reflux condenser for 8 h at 55 °C with stirring. The unreacted chemical reagents and other impurities, such as water, were removed by vacuum distillation, and the obtained product, AMIMCl, is slightly amber. The refractive index of AMIMCl measured with an Abbe's refractometer is 1.5465.

Measurement of the Conductivity of AMIMCl. A Zahner IM6e electrochemical workstation (made in Germany) was used to measure the conductivity of AMIMCl. The cell constant was calibrated with aqueous 0.01 M KCl at 25 °C, and the cell constant was 1.60 cm^{-1}.

Observation of Dissolution of Cellulose in AMIMCl. Because of the high degree of crystallinity, the dissolution process of natural cellulose in the isotropic ILs can be simply observed by polarized light microscopy. Optical microscopic observation was carried out with a Leica DMLP-MP30 microscope fitted with a hot stage and a multicolor digital camera. Polarizing filters improved the contrast of images. Several cellulose microfibers and a drop of AMIMCl solvent were

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Table 1. Sample Codes of Regenerated Cellulose Films and Their Dissolution Conditions

code	original cellulose	dissolution temperature (°C)	dissolution time (min)
RC-P100	pulp	100	40
RC-P110	pulp	110	40
RC-P130	pulp	130	40
RC-C240	cotton	110	240
RC-C150	cotton	110	150
RC-C120	cotton	110	120
ReRC-P	pulp	100	40
ReRC-C	cotton	110	180

sandwiched between two pieces of cover glasses and put on the hot stage at 80 °C. The process of dissolution was monitored by a digital camera until cellulose fibrils in the eyeshot selected completely dissolved. The viscosity of the solvent and of the solution was measured with a parallel plate rheometer (DSR200, Rheometric Scientific) at 80 °C. ^{13}C NMR measurement of the cellulose solution in AMIMCl (8 wt % of MCC) was performed on a Bruker DMX 300 spectrometer at 90 °C.

Preparation of Regenerated Cellulose Film and Solvent Recovery. Cellulose samples were cut into small pieces and dried at 70 °C for 3 h in a vacuum oven before use. A known weight of cellulose sample was dispersed into 20 mL of AMIMCl in a flask, and the mixture was heated and stirred until cellulose samples were completely dissolved. Finally, a transparent cellulose solution with about 4% polymer concentration was obtained. The solution was cast onto a glass plate to give a thickness of about 0.50 mm, took off air bubble in a vacuum oven, and then immediately coagulated in the water to obtain a transparent regenerated cellulose gel. The thickness of the cellulose solution was controlled to within 0.5 mm; otherwise, the dried regenerated cellulose films became curly. The regenerated cellulose gel was washed with running distilled water and dried at 60 °C in a vacuum oven. The recovery of ILs was accomplished by evaporating water from the precipitation liquid. A series of regenerated cellulose films were prepared from cotton and pulp and were coded as RC-P100, RC-P110, RC-P130, RC-C240, RC-C150, and RC-C120 for the regenerated cellulose dissolved with ILs under different dissolution conditions and as ReRC-P and ReRC-C for the regenerated cellulose dissolved with recovered ILs (ReIL). The conditions for dissolving cellulose, codes of regenerated cellulose, and materials of RC films are presented in Table 1.

Structure and Properties of Regenerated Cellulose Film. The regenerated cellulose films were cut into small pieces and dried at 70 °C in a vacuum oven before use. The intrinsic viscosity of the regenerated cellulose in CUEN (cupriethylenediamine hydroxide solution) was measured by using an Ubbelodhe viscometer, and then the DP of regenerated cellulose films was calculated. The dry regenerated cellulose films were frozen in liquid nitrogen, fractured, and vacuum-dried. The free surface (side in direct contact with the coagulant) and the fracture surface of the films were coated with gold and observed and photographed with a Hitachi S-530 scanning electron microscope.

The natural cellulose was ground into powder for infrared (IR) measurement. The IR spectra were recorded with a Fourier transform IR (FT-IR) spectrometer (FT-IR 2000, PE). The regenerated cellulose films were cut into strips of 10 mm long and 15 mm wide for the measurement of X-ray diffraction patterns. The X-ray diffraction patterns with Cu Kα radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA were recorded in the range of $2\theta = 5-40°$ with an X-ray diffraction diffractometer (D/MAX-2500, Rigaku Denki, Japan).

The tensile strength (σ_b) of the regenerated cellulose films was measured by using a universal testing machine (Instron 1122, UK) at a crosshead speed of 5 mm min^{−1}. The size of the samples was 50 mm long and 10 mm wide, and a gauge length of 30 mm was used. All the strength data were collected under the same conditions, such as temperature and air humidity.

Results and Discussion

Synthesis of AMIMCl and Its Capability To Dissolve Cellulose. In comparison with other imidazolium chloride ionic liquids, such as 1-butyl-3-methylimidazolium chloride (BMIMCl) and 1-ethyl-3-methylimidazolium chloride (EMIMCl), the synthesis of AMIMCl was more readily carried out. In a typical synthesis, the conversion ratio of the imidazolium reached up to 80% after a reaction time of 3 h and almost 100% after 6 h. This was a result of the relatively high reactivity of allyl chloride.

AMIMCl exhibited a good thermostability despite its unsaturated chemical structure. It was reported that *N*-allylcarbazole, which had a similar chemical structure to AMIMCl, had not been homopolymerized even after heating at 228 °C for 6 h.[21] The TGA curve of AMIMCl showed that the onset temperature of degradation was about 273 °C, which was slightly higher than BMIMCl (254 °C).[22] More interestingly, AMIMCl showed a lower melting point at ca. 17 °C and a considerably lower viscosity of 685 mPa s at 30 °C, in contrast with BMIMCl, which has a melting point of 65 °C and a viscosity of 11 000 mPa s at 30 °C.[23] The relatively lower melting point and viscosity for AMIMCl were attributed to the suppressed crystallization of the IL effectively by an allyl group on the N-position.[24]

The dissolution of cellulose in AMIMCl at different temperatures was investigated. At room temperature, AMIMCl only swelled cellulose but could not dissolve it. However, cellulose dissolved readily in AMIMCl at 60 °C with stirring. With increasing temperature, cellulose dissolved more rapidly. Dissolving process of cellulose in AMIMCl at 80 °C was real time monitored by PLM and shown in Figure 1. It is interestingly observed that cellulose with a degree of polymerization as high as 650 dissolved in AMIMCl within 30 min. To the best of our knowledge, such rapid dissolution rate of cellulose in a solvent was only reported in the TBAF/DMSO solvent system for cellulose.[25] Different from the NMMO system,[26] remarkable swelling was not observed in the dissolution. It was also observed that, at initial stage, the dissolution occurred very rapidly. Then dissolution rate decreased, which might be the result of more perfect crystalline structure in residual cellulose fibrils and increased viscosity of cellulose solution. Despite this, at 80 °C, a cellulose/AMIMCl solution of 5 wt % concentration was obtained only within 30 min. The viscosity of the solution strongly depended on the concentration of cellulose. The values of viscosity of 4% and 8% cellulose solutions (dissolved pulp) in AMIMCl at 80 °C were 110 and 1480 Pa s, respectively. With increasing dissolution temperature and time, higher concentrations of cellulose solution with higher viscosities were prepared in AMIMCl. In the present work, a solution containing up to 14.5 wt % cellulose (dissolved pulp) in AMIMCl was formed as a clear and viscous solution after a little longer dissolution time at 80 °C. Furthermore, 8.0 wt % cotton linter was also dissolved in AMIMCl at 80 °C, although it was difficult to be dissolved in some other solvents. For solutions containing higher concentrations of cellulose in AMIMCl such as 10%, a strong anisotropy was optically observed between polarizing filters.

From the industrial point of view, it is important that cellulose samples without any pretreatment or activation were dissolved in AMIMCl rapidly above 60 °C. In contrast, in most cases of other solvent systems for cellulose such as DMAC/LiCl and NaOH/H$_2$O, the
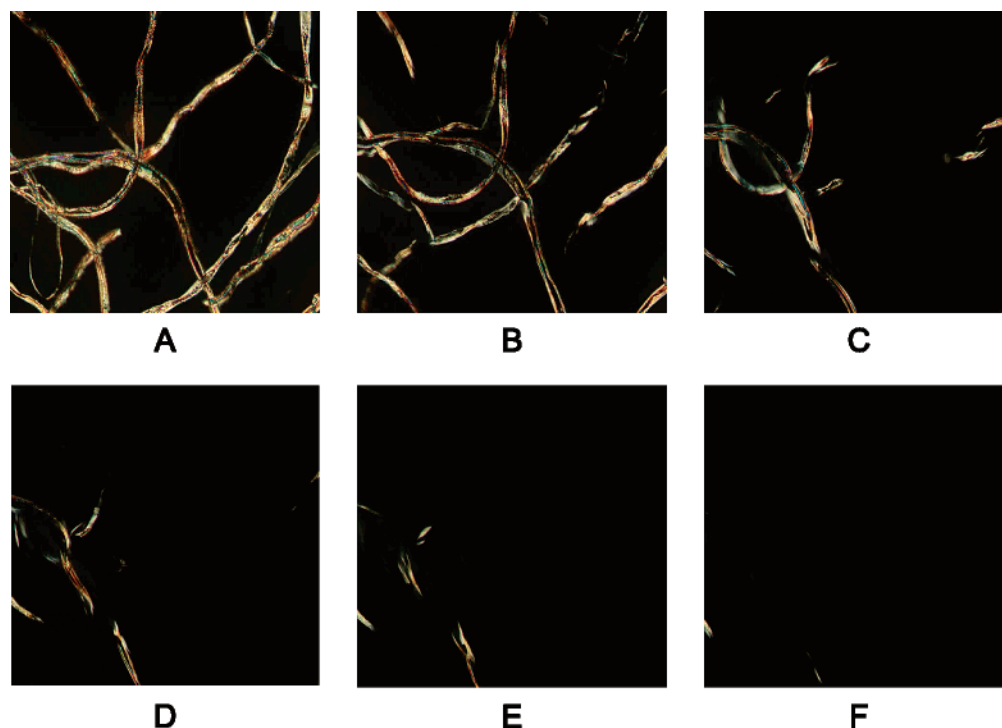
Figure 1. PLM images of cellulose (pulp) dissolution in AMIMCl at different time: (A) 0, (B) 10, (C) 15, (D) 17.5, (E) 25, and (F) 30 min.
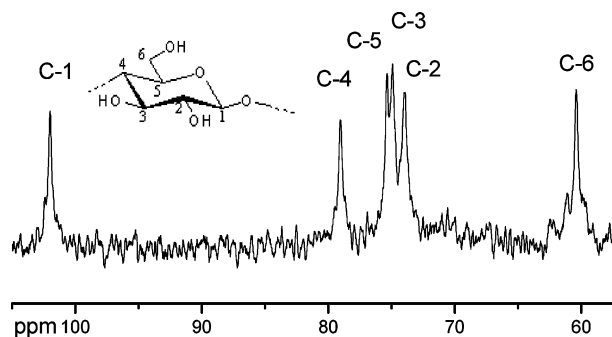

Figure 2. ^{13}C NMR spectrum of cellulose (MCC) in AMIMCl solution at 90 °C.

Figure 3. Temperature dependence of the conductivity for AMIMCl.

pretreatment or activation of original cellulose is often needed.[27,28] Figure 2 shows the ^{13}C NMR spectrum of cellulose (MCC) dissolved in AMIMCl. The six signals of the unmodified anhydroglucose unit appear clearly at 102.7 (C-1), 79.0 (C-4), 75.4 (C-5), 74.9 (C-3), 74.0 (C-2), and 60.4 ppm (C-6). The signals of the carbon atoms C_1-C_6 are well-resolved, and the spectrum is very similar to that of cellulose dissolved in other solvents like sodium hydroxide solution[29] and BMIMCl.[30] Therefore, AMIMCl can be considered as a truly solvent, in which cellulose could be molecularly dispersed.

To study the influence of temperature on the dissolution of cellulose in AMIMCl, the effect of temperature on the conductivity of AMIMICl was measured (Figure 3). It is clear that with increasing temperature the conductivity increases. It should be noted that there is a slope change at about 43 °C, which possibly indicates a critical temperature. Huang et al.[31] used the NMR technique to measure the diffusion coefficient of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF$_4$) room temperature ionic liquid in the temperature range from 300 to 360 K. The phase change in the vicinity of 333 K (60 °C) was observed and ascribed to the transformation of the diffusion particle from "discrete ion pair" to "individual ion" at temperatures above 335 K (62 °C)
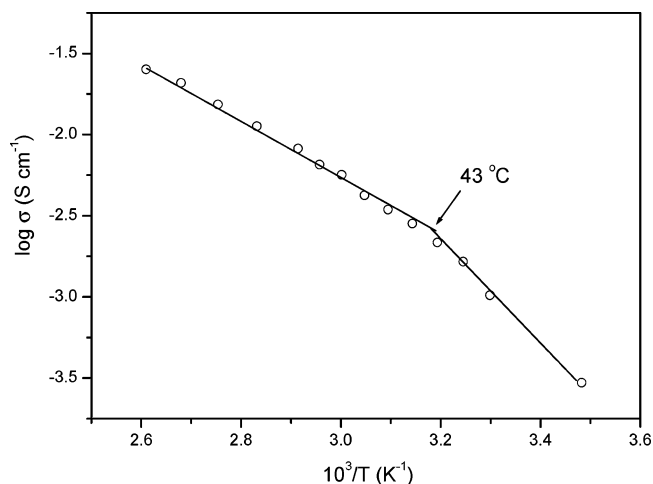
due to the decomposition of the EMI-BF$_4$ ion pair. In the present case of AMIMCl, above 43 °C, ion pair or hydrogen bonding of AMIMCl might have dissociated, and the diffusion rate of ions increased significantly, which lead to the abrupt increase of conductivity.

After the dissolution completed, a clear cellulose solution with light amber color was obtained. When cooled to room temperature, AMIMCl/cellulose solution remained in its liquid state with a little increased viscosity. Interestingly, no recrystallization of the cellulose solution occurred, which was commonly observed in the BMIMCl/Cellulose system. Furthermore, neither crystallization nor precipitation of the cellulose/AMIMCl solution occurred after keeping the solutions at room temperature for more than 3 months.

It is generally recognized that, in order to dissolve cellulose, to disrupt its great number of inter- and intramolecular hydrogen bonds is required. In the case of ionic liquid BMIMCl used as a solvent for cellulose,

Scheme 1. Possible Dissolution Mechanism of Cellulose in AMIMCl
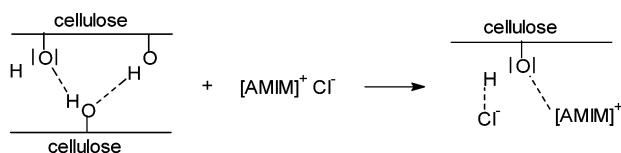
the relatively high chloride concentration and activity in this IL were thought to play the key role in dissolving cellulose.[18,32] However, the fact that the chemical structure of cations of solvents will affect the cellulose dissolution should also to be considered. The effect of cations was found in other solvent systems. For example, mixtures of lithium chloride (LiCl) in *N,N*-dimethylacetamide (DMAC) were good solvents for cellulose, in which chloride ions were suggested to interact with cellulose hydroxyl groups. However, the only alkali metal salt which led to cellulose dissolution was LiCl; other chloride salts, such as soldium, potassium, barium, calcium, and zinc, were found ineffective. Swotloski et al. also found that, in the case of ILs used as solvents, the solubility of cellulose decreased with increasing size of the cations such as lengthy alkyl groups substituted on the imidazolium ring.[18] In comparison with BMIMCl, the cation [AMIM]$^+$ had a smaller ion size due to three carbon atoms and a double bond in N-substituted methimidazonium cation of AMIMCl. It is suggested that in salt solutions with small, strong polarizing cations and large polarizable anions, intensive interactions with cellulose occur.[33] According to this criterion, it can be speculated that the small cation [AMIM]$^+$ favors the attack on oxygen atom of cellulose hydroxyl. Moreover, the less electronic chemical structure caused by alkyl group also enhances the interaction between cations in IL and oxygen atoms of hydroxide group in cellulose. The possible dissolution mechanism of cellulose in AMIMCl is shown in Scheme 1 and described as follows: above the critical temperature, the ion pairs in AMIMCl dissociated to individual Cl$^-$ and AMIM$^+$ ions. Then free Cl$^-$ ions associated with the cellulose hydroxyl proton, and the free cations complex with the cellulose hydroxyl oxygen, which disrupted hydrogen bonding in cellulose and led to the dissolution of cellulose. To clearly understand the mechanism of dissolving cellulose in AMIMCl, further investigation by using some more effective characterization techniques, such as NMR and Raman spectroscopy, is still needed.

Structure and Morphology of Regenerated Cellulose Films from AMIMCl. As AMIMCl was completely miscible with water in any ratio, the regenerated cellulose materials were easily obtained by coagulation in water. The AMIMCl/cellulose solution was cast onto a glass plate and then coagulated in water. After removing AMIMCl and drying completely, a transparent cellulose film was obtained. The cellulose fiber regenerated from AMIMCl was prepared easily either by wet spinning or dry jet-wet spinning process and coagulated with water.

FTIR spectra of cellulose before and after regeneration are shown in Figure 4. It can be seen that the two spectra are quite similar, and no new peaks appear in the regenerated sample, indicating no chemical reaction occurred during the dissolution and coagulation processes of the cellulose. In other words, AMIMCl was a direct solvent for cellulose. For the regenerated cellulose films, the absorption band at 1426 cm^{-1}, assigned to the CH$_2$ scissoring motion, weakened and shifted to a lower
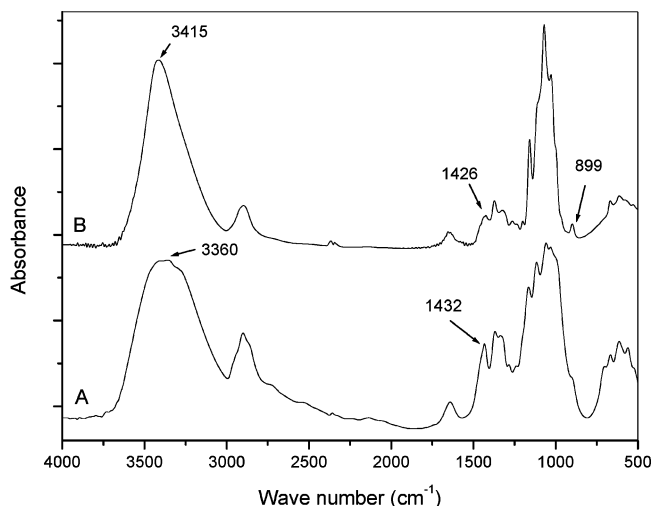

Figure 4. FTIR spectra of original cellulose and regenerated cellulose: (A) original cellulose (pulp); (B) regenerated cellulose from AMIMCl/pulp cellulose solution (RC-P100).
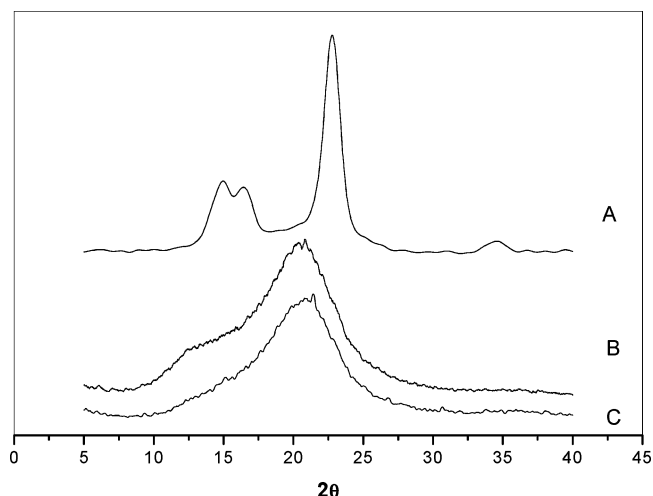

Figure 5. WAXD patterns of original cellulose and regenerated cellulose: (A) original cellulose (pulp); (B) regenerated cellulose from AMIMCl/pulp cellulose solution (RC-P100); (C) regenerated cellulose from recovered AMIMCl/pulp cellulose solution (ReRC-P).

wavenumber, compared to the 1432 cm^{-1} peak for the original cellulose. This indicates the destruction of the intramolecular hydrogen bond involving O at C$_6$.[34] A new shoulder at 899 cm^{-1}, belonging to the C−O stretching vibration in the amorphous region, is observed only in the regenerated cellulose films, but not in the original cellulose. Characteristic for the O−H vibrations of cellulose, a broad vibration band locates in the range of 3000−3500 cm^{-1}. Its shape being broader than that of free hydroxyls is believed to be caused by the association of the cellulose chains through hydrogen bonds. In contrast, the band of the O−H vibration of the regenerated cellulose shifted to a higher frequency (3415 cm^{-1}) and became sharper and narrower. This is a hint for splitting hydrogen bonds to some extent.[35,36]

The X-ray diffraction patterns of the cellulose films are shown in Figure 5. The original cellulose such as cotton and dissolved pulp is cellulose I as indicated by the typical diffraction peaks at $2\theta = 14.8°$, 16.3°, and 22.6°.[37] After dissolution and subsequent coagulation with water, the regenerated cellulose exhibits the typical diffraction patterns of cellulose II at $2\theta = 20.3°$ and 21.2°. These results indicate that the transformation
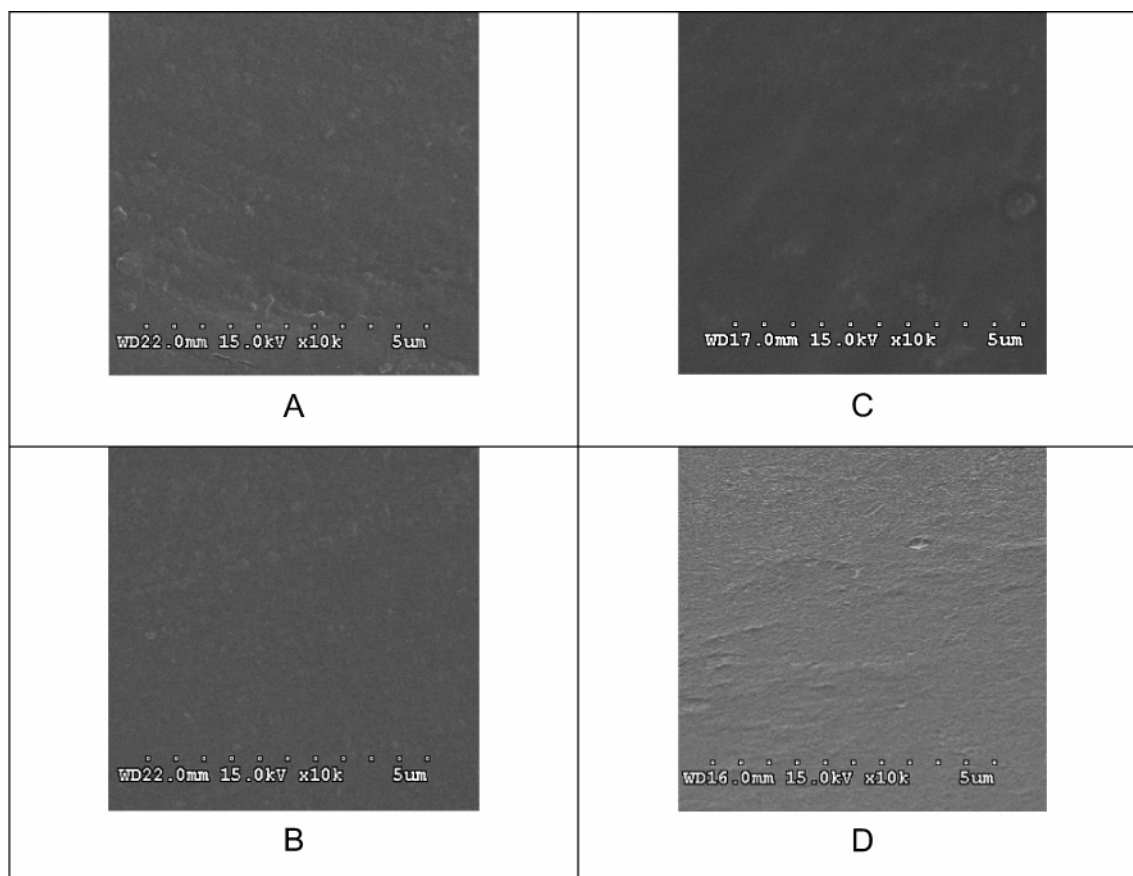
Figure 6. SEM photographs of the free surface and fracture surface of the regenerated cellulose films: (A, C) free surface and fracture of regenerated cellulose from AMIMCl/pulp cellulose solution (RC-P130); (B, D) free surface and fracture of regenerated cellulose from recovered AMIMCl/pulp cellulose solution (ReRC-P).

from cellulose I to cellulose II occurred after the dissolution and regeneration in AMIMCl.[38,39] This phenomenon was also reported in most other known solvent systems for cellulose.[40] Compared to the original cellulose, the intensity of diffraction peaks of these regenerated cellulose films reduced significantly. In other words, the crystallinity of these regenerated cellulose films was lower than the original cellulose. This phenomenon means that, in the dissolution process, IL rapidly broke intermolecular and intramolecular hydrogen bonds and destroyed the original crystalline form. Moreover, the coagulation process was so transitory that unfavorable to the cellulose crystallization.

SEM micrograms of the regenerated cellulose films are shown in Figure 6. It can be seen that the free surface and fracture surface of the regenerated films display a uniformity from the interior to the surface, indicating a dense texture. Different from the structure of the cellulose regenerated from NaOH/H$_2$O, no porous structure was observed.[41,42]

Properties of Regenerated Cellulose Films from AMIMCl. The degree of polymerization (DP) of the regenerated cellulose materials has a crucial effect on its mechanical properties. Generally, the DP of the regenerated cellulose is affected by the dissolution time and temperature. In the present study, the dependence of the DP of the regenerated cellulose on the temperature is shown in Figure 7 and that on the time in Figure 8. In the temperature range from 110 to 130 °C, the DP did not change appreciably in ca. 40 min. In contrast, the DP of a cotton sample with a higher DP reduced with dissolving time at 110 °C. When the recycled AMIMCl was used as the solvent, the DP of the
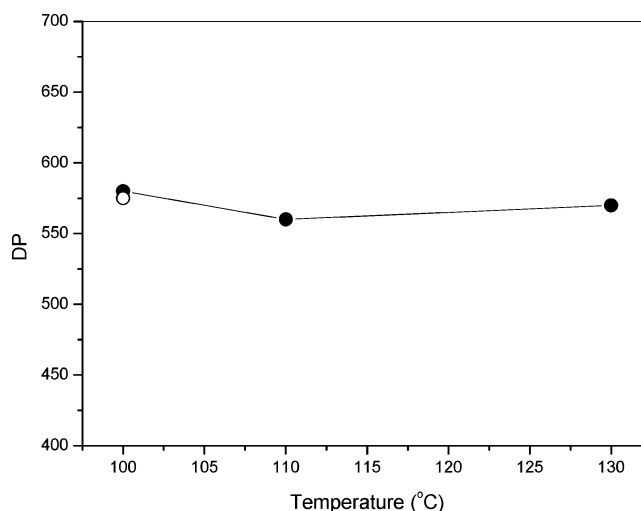

Figure 7. Degree of polymerization of regenerated cellulose from AMIMCl/pulp cellulose solutions prepared at different temperatures. Cellulose: pulp; dissolution time: 40 min. Open symbol: regenerated cellulose from recovered AMIMCl/pulp cellulose solution.

regenerated cellulose also showed a similar decrease trend. The regenerated cellulose film exhibited a good mechanical property. The tensile strength of the regenerated cellulose film with a DP of 480 was as high as 138 MPa.

Recycling of the Ionic Liquid. After the regeneration of cellulose, the residual ILs in the coagulation bath were recovered by simply reducing the pressure and subsequently distilling to remove water, as confirmed
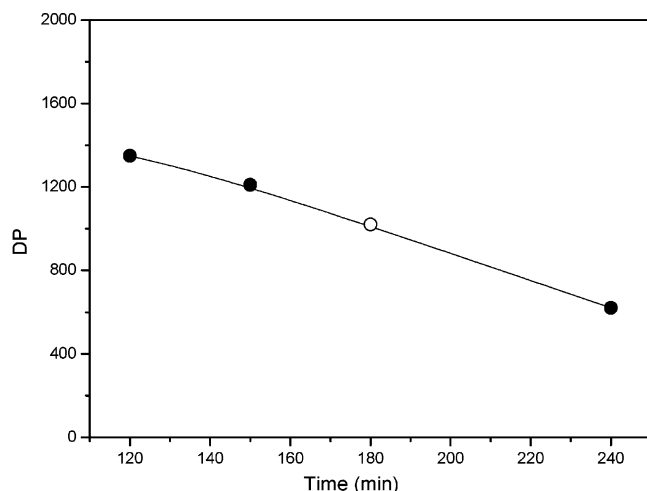
Figure 8. Degree of polymerization of regenerated cellulose from AMIMCl/cotton cellulose solutions prepared at different times. Cellulose: cotton; dissolution temperature: 110 °C. Open symbol: regenerated cellulose from recovered AMIMCl/cotton cellulose solution.

by ^{1}H NMR spectroscopy to show its purity. Recently, Swatloski et al.[43] demonstrated that BMIMCl could be recycled or concentrated from aqueous solution by using aqueous biphasic systems (ABS), in which the BMIMCl solution in water was contacted with concentrated solutions of the water-structuring salts such as K_3PO_4, and then formed two aqueous phases: an upper IL-rich phase and a lower K_3PO_4-rich phase. Using this way, AMIMCl was also effectively concentrated from a dilute aqueous solution and then almost completely recovered. It is apparent that this advantage will promote the industrial application of ILs.

Conclusions

In summary, a novel ionic liquid of AMIMCl was found to be a powerful, nonderivatizing single-component solvent for cellulose. The untreated or unactivated cellulose, such as cotton and dissolved pulp, was dissolved in this IL rapidly. The cellulose materials regenerated by coagulation with water exhibited a good mechanical property. On the basis of the fact that AMIMCl is thermostable and nonvolatile, and can be easily prepared and recycled, this process of dissolution and regeneration of cellulose seems to be a promising "green process" for the preparation of regenerated cellulose materials and can overcome the inherent environmental problems of waste (toxic) gases in the current industrial processes for cellophane and viscose rayon.

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