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Radiation effects on microcrystalline cellulose in 1-butyl-3-methylimidazolium chloride ionic liquid

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ABSTRACT

The radiation processing of cellulose in ionic liquids (ILs) demands a comprehensive knowledge of radiation effects on cellulose in ILs. Herein, gamma radiation-induced degradation kinetics of microcrystalline cellulose (MCC) in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was studied by viscometry. The intrinsic viscosity of MCC in [Bmim]Cl decreased slightly with increasing dose; while chemical structure and crystalline state of cellulose has no obvious change up to 300 kGy. The radiation degradation rate constant (k) of MCC in [Bmim]Cl was 2.60×10^{-7}/kGy, lower than that of solid cellulose, but higher than that in *N*-methylmorpholine-*N*-oxide (NMMO) solvent. Furthermore, k value decreased to 1.12×10^{-7}/kGy in dimethyl sulfoxide (DMSO)/[Bmim]Cl system due to the free radicals scavenging of DMSO. The radicals generated during irradiation play main role in the radiation degradation of MCC in [Bmim]Cl. This work provides a new way to control the average molecular weight of cellulose by radiation-induced degradation of cellulose in ILs.

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1. Introduction

As an abundant biopolymer on the earth, cellulose is renewable, biodegradable and can be derivatized to produce various useful products (Schurz, 1999). However, it is difficult for cellulose to be dissolved in water and most common organic liquids due to the formation of hydrogen-bonded supramolecular structures in cellulose (Finkenstadt & Millane, 1998). During the past decades, some methods have been developed to reduce the processing steps as well as to minimize the amounts of hazardous byproducts in cellulose processing. One of the main alternatives is the Lyocell process, a simple and environmentally friendly process for cellulose fiber production, in which *N*-methylmorpholine-*N*-oxide (NMMO) is generally used as non-toxic direct solvent for cellulose (Fink, Weigel, Purz, & Ganster, 2001; Rosenau, Potthast, Sixta, & Kosma, 2001). However, the NMMO process could not replaced the viscose process due to the nature of fibrillating fiber, side reactions and byproduct, and thermal instability of cellulose/NMMO solutions (Hermanutz, Gaehr, Uerdingen, Meister, & Kosan, 2008). In contrast, room temperature ionic liquids (RTILs) are new, green and direct solvent for cellulose without pretreatment.

RTILs have been used in dissolution, homogeneous derivation and modification of cellulose (Feng & Chen, 2008; Pinkert, Marsh, Pang, & Staiger, 2009; Swatloski, Spear, Holbrey, & Rogers, 2002; Xu, Kennedy, & Liu, 2008; Zhang et al., 2010). The direct dissolution of cellulose in RTILs has many advantages over the NMMO. For example, the processing is more easily controlled, and cellulose can be easily regenerated by adding water or alcohol; the cellulose–RTILs solutions can be used in a dry-jet wet spinning method to produce cellulose fibers, which are already displaying similar properties in terms of tenacity and elasticity (Hermanutz et al., 2008; Laus et al., 2005).

The conventional viscose process uses high concentration of caustic reagents, such as acid, alkali and carbon disulfide (CS_2), which result in some environmental pollution (Sokira & Belasheva, 1992). Compared with these traditional methods, γ-ray radiation is an environmentally friendly process; it can easily penetrate the crystalline regions in cellulose and increase the accessibility of these regions to solvents. Thus lower concentrations of hazardous chemicals can be used, reducing their harm upon the environment. γ-Radiation effects on the physical and chemical properties of natural lignocelluloses polymer have been investigated. It was reported that the predominant reaction of solid cellulose is degradation under the radiation (Khan, Ahmad, & Kronfli, 2006). Up to our best knowledge, few papers on radiation effects of cellulose solution have been published in the literature, including using RTILs or NMMO as cellulose solvent. Due to the feasibility of RTILs in cellulose functionalization combining with radiation method (Hao, Peng, Li, Zhai, & Wei, 2009), it demands a comprehensive knowledge of γ-radiation effects on cellulose in RTILs.

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In this work, the radiation effect on MCC in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) ionic liquid was investigated by determining the changes in the viscosity average molecular weight (M_η) of MCC after irradiation. The radiation degradation rate constant (k) in [Bmim]Cl was obtained and compared with that in NMMO solvent. The effects of co-solvent DMSO were also studied. In addition, the chemical structure and crystalline state of cellulose before and after irradiation was analyzed using micro-Fourier transform infrared spectroscopy (micro-FTIR) and wide angle X-ray diffraction (WAXD), respectively. Finally the radiation degradation mechanism of cellulose in [Bmim]Cl was discussed.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC) was obtained from Sinopharm Chemical Reagent Co. Ltd. [Bmim]Cl (>99%) was purchased from Lanzhou Institute of Chemical Physics (Lanzhou, China) and the water content in the [Bmim]Cl was less than 0.9%, measured by Karl-Fischer titration. NMMO aqueous solutions (50 wt%) was obtained from Alfa Aesar. Prior to use, the water content of NMMO monohydrate was reduced to below 13% by vacuum distillation. Dimethyl sulfoxide (DMSO, analytical grade reagent) was procured from Beijing Chemical Plant and used without further purification. All other chemicals were of analytical grade reagent, and used as received.

2.2. Preparation of samples

Dry MCC was dispersed into [Bmim]Cl and dissolved under stirring at 80 °C for 24 h, yielding a clear solution with different mass concentrations. MCC–[Bmim]Cl solutions were irradiated at room temperature in the air using ^{60}Co source (Peking University, China) with a dose rate of 50 Gy min^{-1}. The dose was determined by Fricke dosimeter. After irradiation, the solution was immediately coagulated in ethanol to obtain the regenerated cellulose. Then, the regenerated cellulose was wholly transferred to a Soxhlet extractor and extracted with ethanol for 48 h to remove [Bmim]Cl. The removal of [Bmim]Cl was confirmed by the elemental analysis using Elementar Analysensysteme GmbH (model: vario EL). Afterward, the regenerated cellulose was dried at about 40 °C in a vacuum oven to a constant weight, and used for the further determination of molecular weight and characterization. For comparison, MCC in NMMO was irradiated, regenerated and analyzed under the same conditions.

To clarify the influence of organic co-solvent on γ-radiation effects of cellulose in [Bmim]Cl, DMSO (DMSO:MCC = 10:1 by weight) was added after dissolution of cellulose in [Bmim]Cl (5 wt%), the mixture was ultrasonic treated at 60 °C to yield homogeneous transparent solution. Then, the solution was irradiated and treated under same conditions.

2.3. Determination of the degree of polymerization (DP)

Dry regenerated cellulose was grinded to fine powder using the agate mortar and dissolved in cupriethylenediamine hydroxide solution (CUEN). The viscosity of the solution was measured using an Ubbel-ohde capillary viscometer at 25 °C according to the table in national standard GB 5888-86. The efflux times that solutions passed the capillary were recorded in triplicate. The relative viscosity (η_r) was calculated as following:

$$\eta_r = \frac{t}{t_o} \tag{1}$$

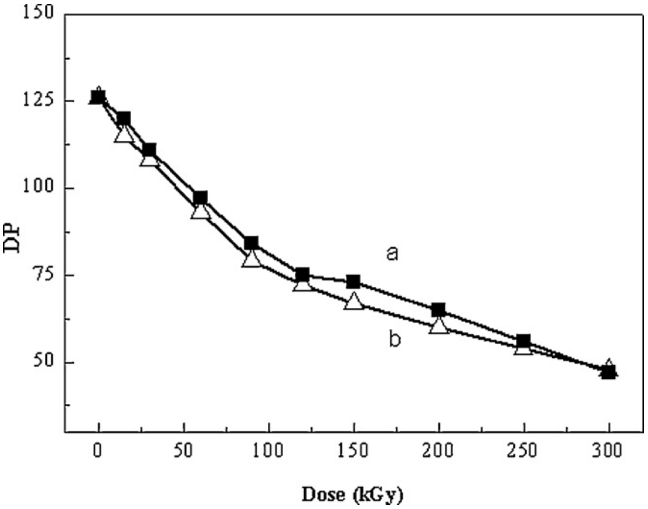


Fig. 1. Influence of absorbed dose on the DP of cellulose–[Bmim]Cl solution with different concentrations: 1 wt% (a); 5 wt% (b).

where t and t_o were the efflux times of the regenerated cellulose–CUEN solution and original CUEN passing through the capillary of viscometer, respectively. Afterward, η' was determined on the basis of GB 5888-86.

The specific viscosity (η_{sp}) and DP were calculated according to Eqs. (2) and (3), respectively:

$$\eta_{\mathrm{sp}} = \frac{\eta'}{C} \tag{2}$$

$$\mathrm{DP} = 156 \times \eta_{\mathrm{sp}} \tag{3}$$

where C was the weight concentration of regenerated cellulose–CUEN solution. Since the molecular weight of the repeat unit of cellulose is 162, the viscosity average molecular weight (M_η) of cellulose can be calculated as following:

$$M_\eta = 162 \times \mathrm{DP} \tag{4}$$

2.4. Characterization

Micro-FTIR analysis of regenerated cellulose, original MCC was performed on a Nicolet (Magna-IR 750) spectrometer. The spectra were measured in absorbance mode in the wave number range of 4000–600 cm^{-1}.

Wide angle X-ray diffraction (WAXD) was used to study the crystallinity of samples. WAXD was performed by XRD-Multiflex (Rigaku Corporation, Japan) using Ni-filtered Cu Kα with 4° min^{-1} from 10° to 60°.

3. Results and discussion

3.1. Radiation-induced effects on MCC in [Bmim]Cl

The viscosity of irradiated MCC–[Bmim]Cl solutions (5 wt%) at different doses was measured by CUEN method (GB 5888-86) to determine the influence of absorbed dose on M_η and k value of MCC in [Bmim]Cl. The effects of absorbed dose on the DP of MCC–[Bmim]Cl solutions with different concentrations was shown in Fig. 1. For the regenerated cellulose in [Bmim]Cl, DP decreased obviously at low absorbed doses, and gradually decreased at dose above 120 kGy. To study the effects of MCC content on degradation, an identical experiment was also conducted in 1 wt% MCC–[Bmim]Cl solutions. As shown in Fig. 1, the content of cellulose in [Bmim]Cl had slight effects on the variation of DP with dose in the studied dose range. Under irradiation, several active

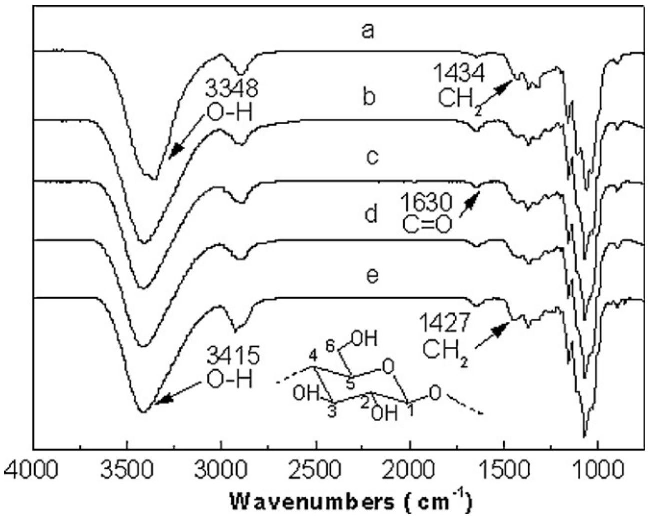


Fig. 2. Micro-FTIR spectra of the original MCC (a), unirradiated regenerated cellulose in [Bmim]Cl (b), irradiated cellulose in [Bmim]Cl with different absorbed doses, 90 kGy (c); 150 kGy (d), irradiated cellulose in [Bmim]Cl/DMSO system at dose of 150 kGy (e).

species, such as solvated electrons (Wishart & Neta, 2003) and radicals maybe formed in RTILs (Marcinek, Zielonka, Gebicki, Gordon, & Dunkin, 2001), and these species may accelerate the degradation of cellulose in [Bmim]Cl. For cellulose–[Bmim]Cl solutions, even at the content of cellulose in [Bmim]Cl of 1 wt%, the solution with high viscosity could be obtained, which may inhibit the diffusion of active species to prevent their recombination. When the cellulose content increased to 5 wt%, the viscosity changed slightly, thus the change of DP with dose was similar.

To fully investigate the radiation effects on the structure of cellulose in [Bmim]Cl, FTIR and WAXD were used to characterize the regenerated cellulose obtained from [Bmim]Cl before and after irradiation. As shown in Fig. 2a, the following characteristic bands in the IR spectrum of original MCC were observed: a large absorption band at 3300–3500 cm^{-1} corresponding to OH groups; a band at 2700–2900 cm^{-1} attributed to CH$_2$ groups; characteristic bands at 1161 and 1109 cm^{-1} for C—O—C from the glucosidic units (Suflet, Chitanu, & Popa, 2006). It was clear that the FTIR spectra of unirradiated regenerated cellulose (Fig. 2b) and the regenerated cellulose obtained from irradiated cellulose/[Bmim]Cl solution with different absorbed doses (Fig. 2c and d) were quite similar to that of original MCC. Compare to the absorption band at 1434 cm^{-1} of original MCC, the peak of the regenerated cellulose before and after irradiation weakened and shifted to a lower wavenumber (1427 cm^{-1}), which assigned to the CH$_2$ scissoring motion. It demonstrated the destruction of intramolecular hydrogen bond involving O at C$_6$ (Higgins, Stewart, & Harrington, 1961). Compared with the broad absorption band at 3348 cm^{-1} of original MCC corresponding to OH groups, the band of unirradiated regenerated cellulose (Fig. 2b) and irradiated cellulose with different absorbed doses (Fig. 2c and d) shifted to a higher wavenumber (3415 cm^{-1}), which suggested the weakening of hydrogen bonds to some extent (Zhang, Wu, Zhang, & He, 2005; Zhou et al., 2001). It is well known that the band at 1630 cm^{-1} is assigned to the absorbance of ketose groups in cellulose sugar ring (Muller, Ratzsch, Schwanninger, Steiner, & Zobl, 2003). Compared to the original MCC (Fig. 2a), the intensity of absorption peak at 1630 cm^{-1} increased after irradiation in [Bmim]Cl (Fig. 2c and d), which denoted that radiation degradation of cellulose lead to the formation of ketose groups in cellulose during irradiation.

The XRD patterns of original MCC and regenerated cellulose from [Bmim]Cl before and after irradiation were shown in Fig. 3.

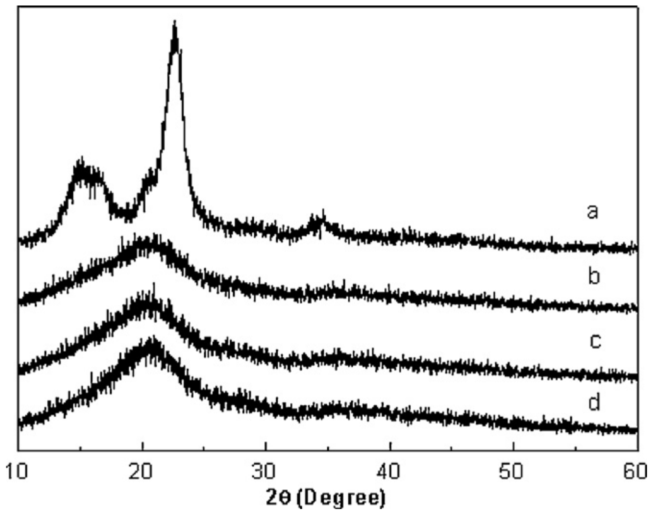


Fig. 3. WAXD spectra of the original MCC (a), regenerated cellulose from cellulose/[Bmim]Cl solutions without irradiation (b), regenerated cellulose from cellulose/[Bmim]Cl solutions after irradiation with different absorbed doses, 90 kGy (c); 150 kGy (d).

Original MCC contained typical cellulose I structure, with a sharp peak at 22.5°, and a wide peak between 14° and 17.5° (Fig. 3a). After dissolution and subsequent coagulation with ethanol, regenerated cellulose exhibited a typical diffraction peak between 20.3° and 21.2° (Fig. 3b). It suggested that the transformation from cellulose I to cellulose II occurred after the dissolution and regeneration in [Bmim]Cl (Raymond, Kvick, & Chanzy, 1995). This is probably attributed to breakage of the intermolecular and intramolecular hydrogen bonds in original MCC by ionic liquid. As can be seen, the regenerated cellulose that irradiated at a total absorbed dose ranging from 90 to 150 kGy (Fig. 3c and d), displayed similar X-ray diffraction spectra to regenerated cellulose without irradiation (Fig. 3b) (Hao et al., 2009; Zhang et al., 2010).

3.2. The radiation degradation kinetics of MCC solution

Radiation-induced degradation kinetics of MCC in [Bmim]Cl was investigated using the equation as follows:

$$\frac{1}{M_\eta} = kD + A \tag{5}$$

where k is the radiation degradation rate constant and A is a constant. D is the dose (kGy). As shown in Fig. 4, M_η of MCC in [Bmim]Cl (5 wt%) decreased continuously with the increasing absorbed dose

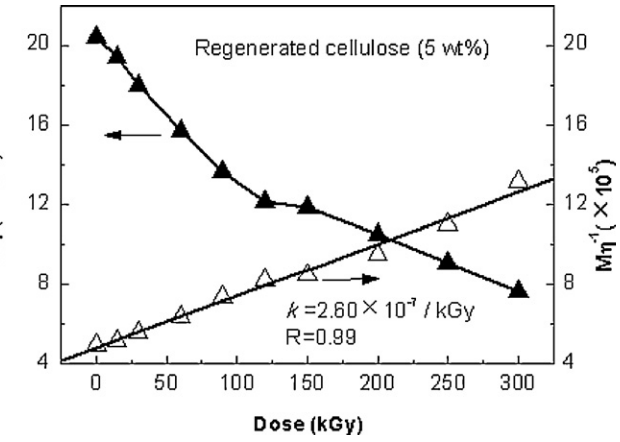
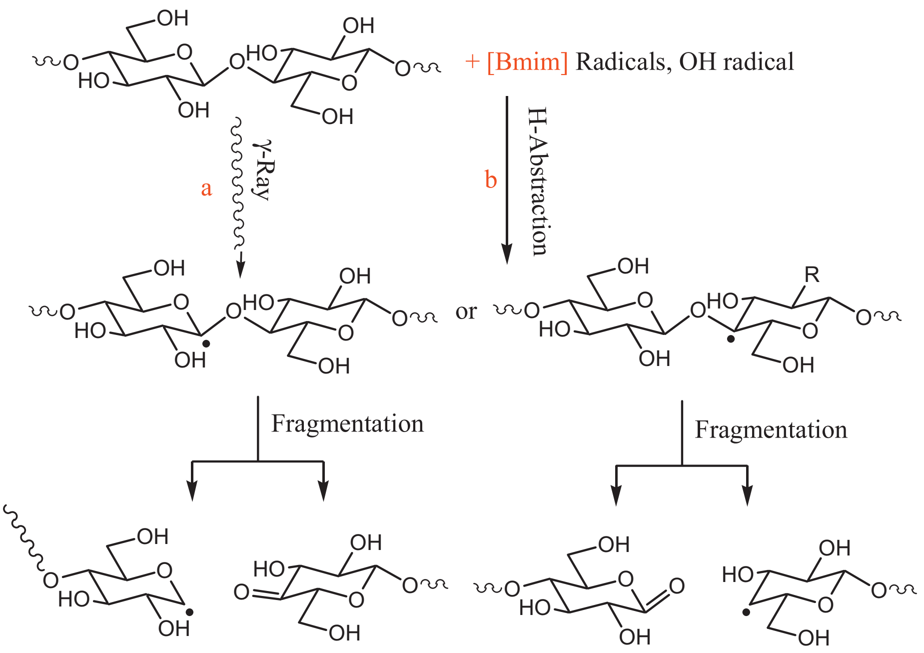


Fig. 4. Influence of absorbed dose on the M_η and $1/M_\eta$ of 5 wt% cellulose in [Bmim]Cl.



Scheme 1. Radiation degradation mechanism of cellulose in [Bmim]Cl.

and k of this solution calculated by Eq. (5) was ca. 2.60×10^{-7}/kGy. Moreover, the linear correlation coefficient (R) is higher than 0.99, indicating that radiation-induced degradation of MCC in [Bmim]Cl belongs to random chain scission.

Due to the high viscosity of cellulose–[Bmim]Cl solutions, sometimes organic diluents are required to efficiently reduce the viscosity and make it easy to handle solution. Taking into account the miscibility with [Bmim]Cl and negligible effect on cellulose precipitation and regeneration in [Bmim]Cl, we chose DMSO as the co-solvent and evaluated the radiation-induced effects on cellulose in DMSO/[Bmim]Cl solvent. According to the relationship between M_η and absorbed doses shown in Fig. 5, k of cellulose in [Bmim]Cl after addition of DMSO was calculated by Eq. (5) to be 1.12×10^{-7}/kGy, which was obviously lower than that of cellulose in [Bmim]Cl.

We speculated the possible radiation degradation mechanism of cellulose in [Bmim]Cl based on the k value of different solvent systems. The active species generated during irradiation in RTILs, such as solvated electrons and some radicals as shown in Eqs. (6)–(10), may initiate the degradation of cellulose. As shown in Table 1, in the presence of DMSO, k value decreased significantly; since the •OH radicals could be scavenged by DMSO (Kennedy & Symons, 1987). Likewise, radicals of ILs which are predominant species produced in ILs could also be scavenged by DMSO as well. Furthermore, the mobility of radical species and following recombination may be responsible for the lower degradation rate of MCC in the presence of ionic liquid and co-solvent. Therefore, the scissions of cellulose molecular chain during irradiation in [Bmim]Cl/DMSO were suppressed significantly (Choi et al., 2008). Besides, as shown in Fig. 2e, DMSO as a co-solvent has no effect on the structure of regenerated cellulose during irradiation.

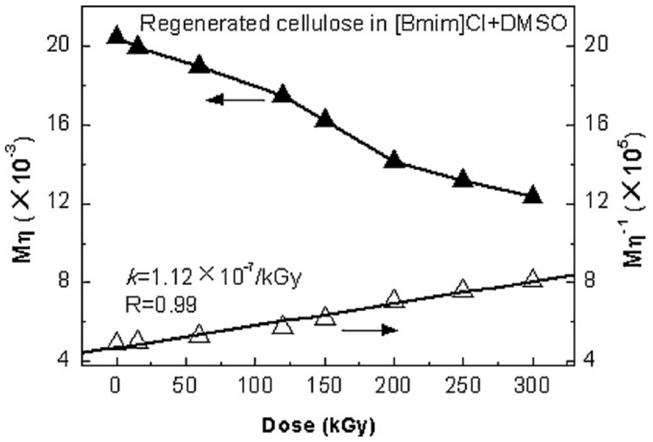


Fig. 5. Influence of absorbed dose on the M_η and $1/M_\eta$ of 5 wt% cellulose–[Bmim]Cl solution with DMSO as co-solvent.

$$[\mathrm{Bmim}]^{+} \overset{\gamma}{\rightsquigarrow} [\mathrm{Bmim}]^{2+\cdot} + e_{\mathrm{solv}}^{-} \tag{6}$$

$$\mathrm{Cl}^{-} \overset{\gamma}{\rightsquigarrow} \mathrm{Cl}^{\cdot} + e_{\mathrm{solv}}^{-} \tag{7}$$

$$\mathrm{Cl}^{\bullet} + \mathrm{Cl}^{-} \rightarrow \mathrm{Cl}_2^{-\bullet} \tag{8}$$

$$[\mathrm{Bmim}]^{+} + e_{\mathrm{solv}}^{-} \rightarrow [\mathrm{Bmim}]^{\bullet} \tag{9}$$

$$[\mathrm{Bmim}]^{+} + [\mathrm{Bmim}]^{\bullet} \rightarrow [\mathrm{Bmim}]_2^{+\bullet} \tag{10}$$

For comparison, radiation effects on cellulose in solid state and cellulose solution with solvent NMMO were studied. As can be seen in Table 1, the degradation rate order of MCC is as follows: solid > [Bmim]Cl > NMMO > DMSO/[Bmim]Cl. k of cellulose in solid state was the highest; it is possibly attributed to that the energy of γ-ray acted on cellulose chain directly in solid state, and in the presence of air, oxygen could accelerate the degradation of cellulose (Ershov & Klimentov, 1984). However, k of cellulose solution with NMMO was slightly lower than that of cellulose in [Bmim]Cl. Since NMMO solvent contains ca. 13 wt% water, the radiolysis of water could produce reactive species such as hydroxyl radicals (•OH), hydrogen atoms radicals (•H) as shown in Eq. (11). These radicals could react with cellulose via hydrogen abstraction to give cellulose radicals and lead to the scission of cellulose chain in NMMO.

Table 1
The radiation degradation rate constant (k) and the linear correlation coefficient (R) of cellulose in solid state and different cellulose solutions at room temperature.

Solutions	Cellulose–[Bmim]Cl (5 wt% without DMSO)	Cellulose–[Bmim]Cl (5 wt% with DMSO)	Cellulose–NMMO (5 wt%)	Cellulose in solid state
k value/kGy	2.60×10^{-7}	1.12×10^{-7}	2.18×10^{-7}	3.15×10^{-7}
R	0.99	0.99	0.99	0.99

Moreover, its viscosity is lower than that in [Bmim]Cl, which lead to the recombination of radicals more easily.

$$H_2O \overset{\gamma}{\rightsquigarrow} \cdot OH, \cdot H, H_2O_2, e^-_{aq}, H_2, H_3O^+, \cdot HO_2 \qquad (11)$$

According to the above experimental results, possible radiation-induced scission of cellulose in [Bmim]Cl are proposed in Scheme 1. Besides the direct action between the gamma ray with cellulose to give cellulose radicals (route a), the radicals generated during the irradiation in [Bmim]Cl, such as [Bmim] radicals and •OH radicals from trace water, could initiate the H-abstraction reaction in cellulose to produce cellulose radicals which are predominant reaction in this system. And then the fragmentation of cellulose macroradicals resulted in the scission of main chain of cellulose (route b). In addition, ketose groups were formed as terminal groups of cellulose chain in the process of radiation-induced degradation.

4. Conclusion

In summary, we reported the first investigation of the γ-ray radiation effects on cellulose in [Bmim]Cl ionic liquid. The radiation-induced degradation of MCC is dominant in [Bmim]Cl which involves a random chain scission. The content of cellulose (1–5 wt%) in [Bmim]Cl has slight effects on the degradation of cellulose. FTIR and WAXD suggested that the chemical structure and crystalline state of regenerated cellulose from [Bmim]Cl changed slightly during the γ-ray irradiation at a total absorbed dose ranging from 10 to 300 kGy. The k value of cellulose in [Bmim]Cl was slightly higher than that of NMMO and lower than that of cellulose in solid state. In addition, the DMSO co-solvent can efficiently inhibit the radiation-induced degradation of cellulose in [Bmim]Cl due to its scavenging for •OH radicals and [Bmim] radicals. This work provided a convenient and simple way to control the DP of cellulose by radiation-induced degradation of cellulose in RTILs system.

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References

Choi, J. I., Lee, H. S., Kim, J. H., Lee, K. W., Lee, J. W., Seo, S. J., et al. (2008). Controlling the radiation degradation of carboxymethylcellulose solution. *Polymer Degradation and Stability*, *93*(1), 310–315.

Ershov, B. G., & Klimentov, A. S. (1984). The radiation chemistry of cellulose. *Russian Chemical Reviews*, *53*, 1195.

Feng, L., & Chen, Z. I. (2008). Research progress on dissolution and functional modification of cellulose in ionic liquids. *Journal of Molecular Liquids*, *142*(1–3), 1–5.

Fink, H. P., Weigel, P., Purz, H. J., & Ganster, J. (2001). Structure formation of regenerated cellulose materials from NMMO-solutions. *Progress in Polymer Science*, *26*(9), 1473–1524.

Finkenstadt, V. L., & Millane, R. P. (1998). Crystal structure of Valonia cellulose I beta. *Macromolecules*, *31*(22), 7776–7783.

Hao, Y., Peng, J., Li, J. Q., Zhai, M. L., & Wei, G. S. (2009). An ionic liquid as reaction media for radiation-induced grafting of thermosensitive poly(N-isopropylacrylamide) onto microcrystalline cellulose. *Carbohydrate Polymers*, *77*(4), 779–784.

Hermanutz, F., Gaehr, F., Uerdingen, E., Meister, F., & Kosan, B. (2008). New developments in dissolving and processing of cellulose in ionic liquids. *Macromolecular Symposia*, *262*, 23–27.

Higgins, H. G., Stewart, C. M., & Harrington, K. J. (1961). Infrared spectra of cellulose and related polysaccharides. *Journal of Polymer Science*, *51*(155), 59–84.

Kennedy, A. R., & Symons, M. C. R. (1987). Water-structure versus radical scavenger theories as explanations for the suppressive effects of DMSO and related-compounds on radiation-induced transformation in vitro. *Carcinogenesis*, *8*(5), 683–688.

Khan, F., Ahmad, S. R., & Kronfli, E. (2006). γ-Radiation induced changes in the physical and chemical properties of lignocellulose. *Biomacromolecules*, *7*(8), 2303–2309.

Laus, G., Bentivoglio, G., Schottenberger, H., Kahlenberg, V., Kopacka, H., Kopacka, H., et al. (2005). Ionic liquids: Current developments, potential and drawbacks for industrial applications. *Lenzinger Berichte*, *84*, 71–85.

Marcinek, A., Zielonka, J., Gebicki, J., Gordon, C. M., & Dunkin, I. R. (2001). Ionic liquids: Novel media for characterization of radical ions. *Journal of Physical Chemistry A*, *105*(40), 9305–9309.

Muller, U., Ratzsch, M., Schwanninger, M., Steiner, M., & Zobl, H. (2003). Yellowing and IR-changes of spruce wood as result of UV-irradiation. *Journal of Photochemistry and Photobiology B: Biology*, *69*(2), 97–105.

Pinkert, A., Marsh, K. N., Pang, S., & Staiger, M. P. (2009). Ionic liquids and their interaction with cellulose. *Chemical Reviews*, *109*(12), 6712–6728.

Raymond, S., Kvick, A., & Chanzy, H. (1995). The structure of cellulose-II – A revisit. *Macromolecules*, *28*(24), 8422–8425.

Rosenau, T., Potthast, A., Sixta, H., & Kosma, P. (2001). The chemistry of side reactions and byproduct formation in the system NMMO/cellulose (Lyocell process). *Progress in Polymer Science*, *26*(9), 1763–1837.

Schurz, J. (1999). Trends in polymer science – A bright future for cellulose. *Progress in Polymer Science*, *24*(4), 481–483.

Sokira, A. N., & Belasheva, T. P. (1992). Effect of gamma-radiation on the physicochemical and technological properties of viscose celluloses. *Fibre Chemistry*, *24*(1), 63–66.

Suflet, D. M., Chitanu, G. C., & Popa, V. I. (2006). Phosphorylation of polysaccharides: New results on synthesis and characterisation of phosphorylated cellulose. *Reactive & Functional Polymers*, *66*(11), 1240–1249.

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellulose with ionic liquids. *Journal of the American Chemical Society*, *124*(18), 4974–4975.

Wishart, J. F., & Neta, P. (2003). Spectrum and reactivity of the solvated electron in the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide. *Journal of Physical Chemistry B*, *107*(30), 7261–7267.

Xu, Q., Kennedy, J. F., & Liu, L. J. (2008). An ionic liquid as reaction media in the ring opening graft polymerization of epsilon-caprolactone onto starch granules. *Carbohydrate Polymers*, *72*(1), 113–121.

Zhang, H., Wu, J., Zhang, J., & He, J. S. (2005). 1-Allyl-3-methylimidazolium chloride room temperature ionic liquid: A new and powerful nonderivatizing solvent for cellulose. *Macromolecules*, *38*(20), 8272–8277.

Zhang, J., Luo, J., Tong, D., Zhu, L., Dong, L., & Hu, C. (2010). The dependence of pyrolysis behavior on the crystal state of cellulose. *Carbohydrate Polymers*, *79*(1), 164–169.

Zhou, S., Tashiro, K., Hongo, T., Shirataki, H., Yamane, C., & Ii, T. (2001). Influence of water on structure and mechanical properties of regenerated cellulose studied by an organized combination of infrared spectra, X-ray diffraction, and dynamic viscoelastic data measured as functions of temperature and humidity. *Macromolecules*, *34*(5), 1274–1280.