



ELSEVIER

Contents lists available at ScienceDirect

## Radiation Physics and Chemistry

journal homepage: [www.elsevier.com/locate/radphyschem](http://www.elsevier.com/locate/radphyschem)

# Crosslinking of polysaccharides in room temperature ionic liquids by ionizing radiation

Atsushi Kimura\*, Naotsugu Nagasawa, Akihiko Shimada, Mitsumasa Taguchi

Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

## HIGHLIGHTS

- Water is a key material for radiation-crosslinked chemical gels.
- RTILs are involved in the crosslinked cellulose gels.
- Chitin gel was first produced in RTILs by ionizing radiation.

## ARTICLE INFO

### Article history:

Received 7 September 2015  
 Received in revised form  
 22 October 2015  
 Accepted 23 October 2015  
 Available online 24 October 2015

### Keywords:

Cellulose  
 Chitin  
 Gel  
 Room temperature ionic liquid  
 Ionizing radiation

## ABSTRACT

Crosslinking of polysaccharides in room temperature ionic liquids (RTILs) by ionizing radiation were investigated by the scavenging method, fluorescent and X-ray photoelectron spectroscopy (XPS) analysis. Radiation chemical yields of hydroxyl radicals inducing the crosslinking of cellulose were estimated with phenol as a scavenger, and increased with water content in 1-ethyl-3-methylimidazolium acetate (EMI-acetate). Cellulose gel was also produced in fluorescent carboxylate-based RTILs, 1,3-dibutylimidazolium acetate (DBI-acetate). Light emission from DBI-acetate in cellulose gel was observed and 20-nm red shifted at a maximum wavelength of 415 nm when excited at 323 nm. Expected elements of carbon and oxygen were detected in neat cellulose by XPS, while additional nitrogen was detected in radiation-crosslinked cellulose gel produced in EMI-acetate. These results indicate that RTILs is incorporated in the cellulose gel. Chitin gel was first obtained in 1-butyl-3-methylimidazolium chloride by  $\gamma$ -ray irradiations, and its gel fraction increased with the dose and reached 86% at 60 kGy.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Natural polysaccharides have been recognized to be the most promising materials in recent years because of outstanding properties such as high biocompatibility and biodegradability, and procurability from animals and plants on the Earth. So functional materials have only been produced by using radiation crosslinking technique either from polysaccharide derivatives or using crosslinking reagents (Fei et al., 2000; Wach et al., 2001; Zhao et al., 2008; Nagasawa et al., 2004). Some polysaccharides are, however, radiation degradation type polymers and have poor solubility in water and organic solvents as well as low chemical reactivity (Kumar, 2000). These limitations could be circumvented by use of specific solvents such as room temperature ionic liquids (RTILs).

\* Corresponding author. Fax: +81 27 346 9422.

E-mail addresses: [kimura.atsushi81@jaea.go.jp](mailto:kimura.atsushi81@jaea.go.jp) (A. Kimura), [nagasawa.naotsugu@jaea.go.jp](mailto:nagasawa.naotsugu@jaea.go.jp) (N. Nagasawa), [shimada.akihiko@jaea.go.jp](mailto:shimada.akihiko@jaea.go.jp) (A. Shimada), [taguchi.mitsumasa@jaea.go.jp](mailto:taguchi.mitsumasa@jaea.go.jp) (M. Taguchi).

Carboxylate-based RTILs, in particular, have high proton-accepting ability and can cleave the hydrogen bonds of polysaccharide main chains to form solution in the concentration range of 0.1–20 wt% (Swatloski et al., 2002; Heinze et al., 2005; Fukaya et al., 2008).

In the previous study, we have produced the chemical gels without any crosslinking reagent by  $\gamma$ -ray irradiation from neat cellulose in the carboxylate-based RTILs under humid conditions for the first time (Kimura et al., 2014). The paste-like solution obtained by mixing 20 wt% cellulose in EMI-acetate under dehydrated conditions was irradiated with  $\gamma$ -rays at a dose of 10 kGy but no insoluble product was obtained under this condition. In this case, radiation-induced reactive species are considered to be mainly hydrogen atom and solvated electron. Their formation yields may not sufficient to cause the crosslinking of cellulose. Therefore, water was added to sample solution to enhance the radiation-induced crosslinking of cellulose. A chemical gel was obtained by the  $\gamma$ -ray irradiation of cellulose in EMI-acetate under humid condition at a dose of 10 kGy. The yield of the cellulose chemical gel increased with a water content in EMI-acetate. Thereby water would play a crucial role to be the source of the

reactive species for the crosslinking of cellulose and control the crystallinity of cellulose in EMI-acetate. Water is decomposed by the ionizing radiation, resulting in the formation of a hydroxyl (OH) radical, hydrated electron, hydrogen atom, proton and hydroxide ion (Getoff, 1996). The OH radical especially is produced at high yield upon water radiolysis and has the high reactivity toward saturated hydrocarbons (Buxton et al., 1988). The radiation-induced crosslinking of cellulose is considered to be initiated by the OH radical. On the other hand, the OH radical is also scavenged by the alkylimidazolium-based RTILs to form their radicals (Behar et al., 2001; Wishart et al., 2005).

Reaction of cellulose with the OH radical in RTILs is not made clear, and it is important to clarify its reaction mechanisms under humid condition. The yields of the radiation-induced OH radicals changing with water contents in carboxylate-based RTILs, EMI-acetate, were investigated by use of the scavenging method in the present study. Cellulose gel was also produced using fluorescent carboxylate-based RTILs to confirm the involvement of RTILs to the crosslinking of cellulose. XPS analysis of the cellulose gel was carried out to investigate chemical structures and components in detail. Moreover, chitin gels were also produced in RTILs by ionizing radiation. Chitin is the second large quantity polysaccharide next to cellulose and widely distributed over nature as cell wall components of fungi, seaweeds and crustaceans. On the other hand, no radiation-crosslinking material has been produced without chemical modification as well as cellulose. The outcomes of these studies are expected to provide insights on new ways of functionalizing materials including cellulose, chitin and other natural polysaccharides.

## 2. Experimental

### 2.1. Sample preparation and $\gamma$ -ray irradiation

Cellulose (Microcrystalline grade, Merck) and chitin (Funakoshi Co., Ltd.) were used as received and dissolved in the solution of 9 wt% LiCl (Wako, 98%) in *N,N*-dimethylacetamide (DMAc, Wako, 97%). Their viscosity-average molecular weights were measured using an Ostwald viscometer to be  $1.2 \times 10^5$  and  $9.3 \times 10^4$  g mol<sup>-1</sup>, respectively. These polysaccharides at initial concentrations in the range 10–30 wt% were mixed with each RTILs to obtain paste-like solutions. 1-Ethyl-3-methylimidazolium acetate (EMI-acetate, Aldrich, 90%) and 1-butyl-3-methylimidazolium chloride (BMI-chloride, TCI, 98%) were purchased and used without further purification. 1, 3-Dibutylimidazolium acetate (DBI-acetate) was synthesized by anion exchange with DBI-chloride (Fukaya et al., 2008), which has been reported as a highly fluorescent hydrophilic ionic liquid (Chen et al., 2011). All the sample solutions were prepared in a glove box (Sanplatec) under dry or wet air saturated conditions, and the water contents were controlled by changing the humidity of the surrounding air. Phenol (Wako, > 99.0%) was used as a scavenger to estimate the yield of the OH radical in RTILs.

The cellulose and chitin solutions were irradiated using a <sup>60</sup>Co  $\gamma$ -ray source at the Japan Atomic Energy Agency, Takasaki, in the dose range of 5–100 kGy (Gy = J kg<sup>-1</sup>) with the dose rates ranging from 5 to 10 kGy h<sup>-1</sup>. Dosimetric experiments were carried out with an ethanol-chlorobenzene dosimeter and an alanine-based dosimeter (Kojima et al., 1993; Kimura et al., 2014).

### 2.2. Analysis of polysaccharide gels

The irradiated sample solutions were washed with a solution of 5 wt% LiCl/DMAc on a stainless steel mesh (SUS316, 200 mesh) for 2 days. Residual matters were washed with water and ethanol repeatedly for 2 days, and then vacuum-dried in oven at 353 K for

2 days. The yield of the gel was estimated by the following equation:

$$\text{Gel fraction (\%)} = (W/W_0) \times 100 \quad (1)$$

where  $W_0$  and  $W$  are the initial mass of the dried sample before irradiation and the final mass of the insoluble product obtained after irradiation, washing, and drying, respectively. Infrared spectra of the sample solutions before and after  $\gamma$ -ray irradiation were recorded by use of FTIR spectrophotometer (Shimadzu, FTIR-8900). The XPS measurements were performed with ULVAC-PHI, PHI 5000 Versa Probe II spectrometer using Al K $\alpha$  ( $h\nu = 1486.6$  eV) X-ray radiation. Spot size of X-rays for measuring was 100  $\mu$ m. Survey scans over 0–1100 eV binding energy range with 1.0 eV step were taken at an analyzer pass energy of 117.4 eV. Absorption, emission, and excitation spectra of the polysaccharide gels before and after irradiation were measured with an absorbance (HITACHI, U-3300) and fluorescent spectrophotometer (HITACHI, F-4500). An HPLC (Agilent, 1100 series) with a reversed phase column (Shodex, RSpak DE-613 and GL Sciences, Inertsil C8-3) at 313 K was used for analyses of phenol in RTILs before and after  $\gamma$ -ray irradiation. Flow rate of 30 vol% acetonitrile in  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> phosphoric acid aqueous solution as an eluent was  $1.0 \times 10^{-3}$  dm<sup>3</sup> min<sup>-1</sup>, and the sample solutions were injected at  $2.5 \times 10^{-4}$  dm<sup>3</sup> in the HPLC. Absorbance of phenol and its irradiation products were monitored at 280 nm using a UV/VIS detector (Waters, 2487 Dual  $\lambda$  Absorbance Detector).

## 3. Results and discussion

### 3.1. Estimation of the yields of hydroxyl radicals in RTILs under humid condition

Phenol was selected as a scavenger because the OH radical rapidly attack phenol with the rate constant of  $k_{\text{OH}} = 6.6 \times 10^9$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> (Field et al., 1982), while the hydrated electrons ( $e^-$ ) and hydrogen atoms (H) react slowly with phenol ( $k_{e^-} = 2 \times 10^7$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>,  $k_{\text{H}} = 1.7 \times 10^9$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>) (Buxton et al., 1988). *G*-values of the primary yields of OH radicals,  $e^-$  and H are 2.7, 2.6 and 0.6 in water by  $\gamma$ -ray irradiation (Buxton et al., 1988), and more than 94% of phenol molecules were degraded by OH radicals in the presence of oxygen (Field et al., 1982; Elliot et al., 1990; Kimura et al., 2012). Scavenging capacity of phenol with OH radicals in EMI-acetate is estimated by following equation (Eq. (2)).

$$\text{Scavenging capacity} = k_{\text{OH}} \times [\text{Scavenger}] \quad (2)$$

20 wt% cellulose is calculated to be 1.2 mol dm<sup>-3</sup> in a monomer unit and the rate constant of cellulose monomer unit with the OH radical is assumed to be about  $5 \times 10^7$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> by that of saturated hydrocarbons (Buxton et al. 1988). The scavenging capacity can be calculated to be  $6 \times 10^7$  s<sup>-1</sup>. Thereby the initial concentration of phenol was set at  $10 \times 10^{-3}$  mol dm<sup>-3</sup> because the rate constant is  $6.6 \times 10^9$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>. The yield of the OH radicals estimated using phenol/EMI-acetate solution can be applied to cellulose/EMI-acetate solution. Phenol in water reacts with the radiation-induced OH radical to produce catechol and hydroquinone mainly (Hashimoto et al., 1979), and the yield of the OH radical could be evaluated as the sum of *G*-values of catechol and hydroquinone formations. Schuler and many researchers have been already reported that dimerization of phenol is occurred by ionizing radiation of phenol aqueous solution under deoxygenated condition such as N<sub>2</sub>O and N<sub>2</sub> saturated (Ye and Schuler, 1989; Taguchi et al., 2006). However, production yields of phenol dimers in this experiment are considered to be low from the following two points: (1) production of OH-adducts from phenol by OH

Download English Version:

<https://daneshyari.com/en/article/1891030>

Download Persian Version:

<https://daneshyari.com/article/1891030>

[Daneshyari.com](https://daneshyari.com)