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Cellulose gels produced in room temperature ionic liquids by ionizing radiation

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HIGHLIGHTS

- Cellulose gels were produced in room temperature ionic liquids (RTILs).
- Water plays a crucial role in the cross-linking reaction.
- Cellulose gels swollen with RTILs show good electronic conductivity (3.0 mS cm^{-1}).

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ABSTRACT

Cellulose-based gels were produced in room temperature ionic liquids (RTILs) by ionizing radiation. Cellulose was dissolved at the initial concentration of 20 wt% in 1-ethyl-3-methylimidazolium (EMI)-acetate or *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium (DEMA)-formate with a water content of 18 wt%, and irradiated with γ -rays under aerated condition to produce new cellulose gels. The gel fractions of the cellulose gels obtained in EMI-acetate and DEMA-formate at a dose of 10 kGy were 13% and 19%, respectively. The formation of gel fractions was found to depend on the initial concentration of cellulose, water content, and irradiation temperature. The obtained gel readily absorbed water, methanol, ethanol, dichloromethane, *N,N*-dimethylacetamide, and RTILs.

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1. Introduction

In recent years, natural polymers have attracted significant attention as alternative green materials because of the exhaustion of petroleum and non-renewable resources, and the increase in environmental pollution. Polysaccharides such as cellulose, chitin/chitosan, starch, and alginic acid are natural polymers. Large quantities of polysaccharide-based biomass are ubiquitous on Earth. They possess unique structures, distinctive properties, and offer the advantages of being non-toxic and biodegradable. They are often modified to produce functional materials, such as viscose rayon, personal care products, and biodegradable plastics. Ionizing radiation is widely used as a convenient tool for the modification of polysaccharides via decomposition, grafting, and cross-linking (Seko et al., 2005). Besides, chemically modified polysaccharides such as carboxymethyl cellulose, hydroxypropylmethyl cellulose, carboxymethyl chitin/chitosan, and carboxymethyl starch, all of

which dissolve in water at high concentrations, have also been irradiated with ionizing radiation to obtain derivative gels that are used as materials for making water absorbents and wound dressings (Fei et al., 2000; Wach et al., 2001; Zhao et al., 2003, 2008; Nagasawa et al., 2004; Pekel et al., 2004; Wang et al., 2007). Until now, radiation cross-linked materials have only been produced either from polysaccharide derivatives or using cross-linking reagents, as certain natural polysaccharides have poor solubility in water and organic solvents as well as low chemical reactivity (Kumar, 2000). These limitations could possibly be circumvented by the use of organic solutions that have high proton-accepting ability, such as chloroform in dimethylsulfoxide, *N*-methylmorpholine-*N*-oxide, lithium chloride (LiCl) in *N,N*-dimethylacetamide, calcium chloride in methanol, and room temperature ionic liquids (RTILs), which can cleave the hydrogen bonds of the polysaccharides to form solutions in the concentration range of 0.1–20 wt% (Swatloski et al., 2002; Heinze et al., 2005; Fukaya et al., 2008).

Among these organic solutions, RTILs have attracted much attention in the diverse fields of chemistry, biology, engineering, and environmental science because of their unique functionalities such as specific solubility, chemical and thermal stabilities, unusual

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dynamical properties linked to high viscosity, and wide potential windows (Rogers and Seddon, 2003). So far, several studies have been reported in the fields of photo- and radiation chemistry to identify more effective reactions between the charged reactive species in RTILs (Wishart and Neta, 2003; Wishart et al., 2005; Kondoh et al., 2009; Katoh and Takahashi, 2009; Kimura et al., 2010). In addition, extensive fundamental and applied research have been conducted on RTILs used in various fields such as radiation-induced polymerization (Qi et al., 2008) and radiation-induced grafting polymerization (Hao et al., 2009). However, to the best of our knowledge, there are no studies reported so far on the use of RTILs in radiation cross-linking reactions.

Therefore, in this study, we focus on the application of RTILs as “specific solvents for the dissolution of polysaccharides,” and their use in establishing a “proper reaction field for radiation cross-linking.” We propose a new method for the radiation modification of polysaccharides using RTILs to produce new functional and sustainable materials. Cellulose was selected as the polysaccharide of choice as it is the most prevalent plant-derived polysaccharide, which comprises the main component of plant plasma membranes and fibrous raw materials such as paper, wood material, and cotton. Recently, it has been reported that the degree of polymerization of 5 wt% cellulose dissolved in 1-butyl-3-methylimidazolium (BMI)-chloride tends to reduce as a function of dose (Hao et al., 2012). Meanwhile, the scission reaction is preferred over the cross-linking reaction when the concentration of polysaccharide in the organic solvent is less than approximately 10 wt% (Tabata et al., 1991; Nagasawa et al., 2004). We assume that cross-linked materials could be produced from cellulose via ionizing radiation in RTILs, which are capable of dissolving more than 10 wt% of cellulose.

We designed and synthesized some RTILs as the reaction medium, in which cellulose could be dissolved to concentrations in excess of 10 wt%, and further investigated the radiation-induced cross-linking of cellulose in each RTIL. The outcome of this study is expected to provide insights on new ways of functionalizing materials, including cellulose and other natural polymers.

2. Experimental

2.1. Sample preparation

Cellulose powder (Microcrystalline grade, Merck) was used as received and its viscosity-average molecular weight was estimated by the following Mark-Kuhn-Houwink-Sakurada equation:

$$[\eta] = K M_v^\alpha \quad (1)$$

where $[\eta]$ and M_v are the viscosity and viscosity-average molecular weight of the sample solution, respectively, and K and α are constants reported as $1.278 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1}$ and 1.19, respectively (McEormick et al., 1985). In the typical process, pre-determined quantity of cellulose was dissolved in the solution of 9 wt% LiCl (Wako, 98%) in *N,N*-dimethylacetamide (DMAc, Wako, 97%). The viscosity of the cellulose solutions in the concentration range $1\text{--}4 \text{ g L}^{-1}$ was measured using Ostwald and oscillatory viscometers (CBC Co., Ltd., Viscomate VM-10A). The weight-average molecular weight of cellulose was analyzed using a high-performance liquid chromatograph (HPLC, Shimadzu, SCL-10A) with gel permeation chromatography (GPC) columns (TSL-GEL ALPHA and 2500, Tosoh) and a refractive index detector (RI 704, GL Science). For HPLC measurement, the flow rate of the 30 mmol L^{-1} LiCl/DMAc eluent was maintained as 0.3 mL min^{-1} , and the column temperature was set at 313 K. Subsequently, $100 \mu\text{L}$ each of the prepared cellulose solutions was injected to the HPLC. The standard for the GPC analysis was prepared by dissolving $1\text{--}4 \text{ g L}^{-1}$ of polymethylmethacrylate (PMMA, Shodex,

molecular mass in the range $1.8 \times 10^3\text{--}2.0 \times 10^5 \text{ g mol}^{-1}$) in a solution of 0.2 wt% LiCl/DMAc.

Cellulose was dissolved in each RTIL using a hybrid mixer (KEYENCE, HM-500) to achieve initial concentrations in the range 1–30 wt% and to obtain various viscous and paste-like solutions. The RTILs used in this study, namely, BMI-bis(trifluoromethylsulfonyl)amide (TFSA), BMI-thiocyanate, BMI-chloride, diallylimidazolium (DAI)-chloride, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium (DEMA)-chloride, and 1-ethyl-3-methylimidazolium (EMI)-bromide, were purchased from Kanto Chemical Co., Inc., Japan. EMI-acetate, at 90% concentration, was also purchased from Aldrich Chemical Co., Inc. The other RTILs used in this study, namely, BMI-acetate, DAI-formate, DAI-acetate, DEMA-formate, and DEMA-acetate were synthesized by the methodology reported in the literature (Fukaya et al., 2008). In the typical process, RTILs having halides, namely, BMI-chloride, DAI-chloride, and DEMA-bromide, were used as precursors, which were converted into their respective hydroxides using a column filled with an anion-exchange resin (Aldrich, Amberlite IRA 400-OH). The obtained aqueous solutions of RTILs with a pH of 12 were neutralized with either formic acid (Wako, 97%) or acetic acid (Wako, 1 mol L^{-1} aqueous solution) to prepare RTILs functionalized with formate or acetate, respectively. These RTILs were then washed with hexane (Wako, 96%) and pure water (TOC: 4 ppb, electrical resistance: $18.2 \text{ M}\Omega \text{ cm}^{-1}$) supplied from a Millipore Milli-Q system, and vacuum dried overnight at 353 K. All the sample solutions were prepared in a glove bag (Glass-Col) or glove box (Sanplatec) under dry or wet air saturated conditions. The water content in the RTIL solutions was controlled by changing the humidity of the surrounding air. This humidity was controlled by using a $0.1\text{--}2 \text{ mol L}^{-1}$ aqueous solution of calcium chloride (Wako, 99%) in both the bag and box (Stokes and Robinson, 1949). The water content in the cellulose solutions was measured with a thermo-balance (Shimadzu AUW120D) and a Karl Fischer titration system (Kyoto Electronics Manufacturing Co., Ltd., MKC-501).

2.2. ^{60}Co γ -ray irradiation

The cellulose solutions were irradiated using a ^{60}Co γ -ray source facility at the Japan Atomic Energy Agency, Takasaki, in the dose range of 5–100 kGy ($\text{Gy} = \text{J kg}^{-1}$) with the dose rates ranging from 5 to 10 kGy h^{-1} . The temperature of the sample solutions was controlled using a thermostatic chamber (DTU-1C, TAITEC) during the irradiation. Dosimetric experiments were carried out with an ethanol (Wako, >99.7%, HPLC grade)-chlorobenzene (Aldrich, 99.9%, HPLC grade) dosimeter and an alanine-based dosimeter (Hitachi Cable, Ltd., AMINOGRAY, alanine 70%, polystyrene 30%, volume: $\varnothing 3 \times 30 \text{ mm}$) in a plastic container ($\varnothing 12 \times 50 \text{ mm}$, 4 mm in thickness) (Kojima et al., 1993).

2.3. Measurements

The irradiated sample solutions were subsequently washed with a solution of 5 wt% LiCl/DMAc to remove any residues of unreacted cellulose, RTILs, and degradation products. The residual matter was rinsed with water on a stainless steel mesh (SUS316, 200 mesh) and then dried overnight at 353 K. The dried sample was weighed in a thermo-balance. Rheological measurement of the sample solutions after γ -ray irradiation was performed on a dynamic viscoelasticity measurement system (TA instruments, ARES RDA-3) at 353 K, in the frequency range of $0.5\text{--}100 \text{ rad s}^{-1}$. Besides, the residual solutions containing unreacted cellulose, RTILs, and degradation products were analyzed in the HPLC system with the GPC column and the refractive index detector. Electrical conductivity of the samples was evaluated using a chemical

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