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One-step preparation of 2,3,6-tricarboxy cellulose

Satoshi Takaichi, Ryoya Hiraoki, Toru Inamochi, Akira Isogai*

Department of Biomaterial Sciences, The University of Tokyo, Tokyo 113-8657, Japan

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ABSTRACT

Water-soluble sodium 2,3,6-tricarboxylate cellulose (NaTCC) or sodium mesotartarate/monohydrated glyoxilate alternating co-polyacetal was prepared from regenerated cellulose in a yield of 82% by one-step oxidation with catalytic amounts of 2-azaadamantane *N*-oxyl (AZADO), NaBr, and excess NaOCl in water at room temperature under alkaline conditions. The AZADO-oxidized product was shown to have an almost homogeneous NaTCC chemical structure by its ^{1}H and ^{13}C NMR spectra. The weight- and number-average molecular masses of the obtained NaTCC were 10,700 and 7000. When AZADO-mediated oxidation was applied to softwood bleached kraft pulp, a water-soluble oxidized product was obtained. However, it had a more heterogeneous chemical structure showing that the complete oxidation of the C2, C3, and C6 hydroxyls to carboxyls is difficult to achieve in native cellulose.

1. Introduction

The preparation of water-soluble polymers from water-insoluble cellulose, which is the most abundant and reproducible natural polymer on earth, is of significance for the applications of bio-based polymers as stable thickeners, emulsion stabilizers, and other additives. Sodium carboxymethyl cellulose, methyl cellulose, and hydroxypropyl and hydroxyethyl celluloses are categorized as typical water-soluble cellulose derivatives, which are prepared by the partial etherification of cellulose hydroxyls under alkaline conditions with or without *i*-propanol, and they are used in various commodity and industrial fields (Heinze, 1998).

The formation of carboxyl groups at the C2, C3, or C6 position of the glucosyl unit of cellulose by oxidation to prepare water-soluble or water-swellable products has been studied at industrial and laboratory levels. Oxycelluloses have been produced from rayon fiber nits by soaking in a N_2O_4-containing chloroform solution. They are used as hemostatic fabrics in medical fields (Martina, Kateřina, Miloslava, Jan, & Ruta, 2009). Some C6-primary hydroxyls are converted to C6-carboxyls during N_2O_4 oxidation although side reactions are inevitable (Nevel, 1951; Yackel & Kenyon, 1942). Water-soluble 2,3-dicarboxy cellulose can be prepared from 2,3-dialdehyde cellulose by oxidation with $NaOCl_2$ in water at pH 4–5 (Heinze, 1998; Kim, Kuga, Wada, Okano, & Kondo, 2000; Maekawa & Koshijima, 1990).

Water-soluble C6-carboxy cellulose, cellouronic acid, or β-(1 → 4)-polyglucuronic acid with an almost homogeneous chemical structure has been prepared from regenerated cellulose by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation in water under weakly acidic or alkaline conditions (Hirota, Tamura, Saito, & Isogai, 2009; Isogai & Kato, 1998; Isogai, Saito, & Fukuzumi, 2011; Tavernier, Delattre, Petit, & Michaud, 2008). Because of the four bulky methyl groups at the C2 and C6 positions of TEMPO, TEMPO-mediated oxidation can be used to convert the C6-primary hydroxyls of cellulose to sodium C6-carboxylates almost position-selectively. Even though extensive depolymerization of cellulose molecules is unavoidable in TEMPO-mediated oxidation under alkaline conditions (Shibata & Isogai, 2003), oxidation using 4-acetamido-TEMPO in water at pH 4.8 can be used to control depolymerization to some extent, thus providing water-soluble cellouronic acids with higher molecular masses.

2,3,6-Tricarboxy cellulose or mesotartaric acid/monohydrated glyoxilic acid alternating co-polyacetal (Fig. 1) was first prepared by the three-step oxidation of cellulose with N_2O_4, $NaIO_4$, and $HClO_2$ (Head, 1948). The two-step oxidation of cellulose with $NaIO_4$ and N_2O_4 to prepare TCC was then reported as a resource for the provision of tartaric acid, a hemostatic agent and a chelator of metallic ions (Bashmakov et al., 2002; Hearon, Cheng, & John, 1975; Sinha & Vasudevan, 1984).

Although the preparation of TCC from cellulose has been already reported, no detailed information concerning the chemical structures of the obtained TCCs using, e.g., NMR, have been reported.

* Corresponding author at: 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan. Tel.: +81 3 5841 5538; fax: +81 3 5841 5269.
E-mail address: aisogai@mail.ecc.u-tokyo.ac.jp (A. Isogai).

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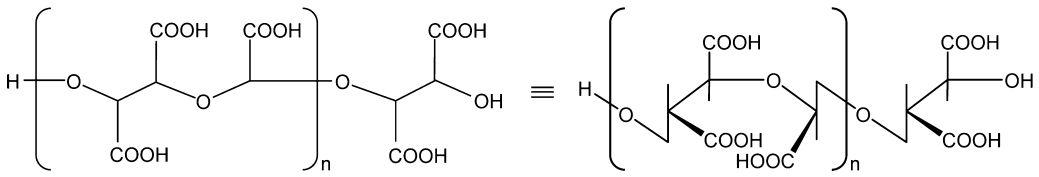


Fig. 1. Chemical structure of 2,3,6-tricarboxy cellulose or mesotartaric acid/monohydrated glyoxilic acid alternating co-polyacetal.

Moreover, two- or three-step reactions using toxic or explosive reagents such as gaseous N_2O_4, $NaIO_4$, and chloroform have been required to prepare TCCs.

In this paper, we report a novel one-step preparation method for the sodium salt of TCC (NaTCC) or sodium mesotartarate/hydrated glyoxilate alternating co-polyacetal (Fig. 1) from regenerated and native celluloses. 2-Azaadamantane *N*-oxyl (AZADO) was used as a catalyst in water under alkaline conditions. AZADO is a stable nitroxyl radical and has the ability to oxidize primary and secondary alcohols to carboxyl and carbonyl groups, respectively, under aqueous conditions (Shibuya, Tomizawa, Suzuki, & Iwabuchi, 2006). In our previous study, an AZADO/NaBr/NaOCl system was applied to native wood cellulose to prepare AZADO-oxidized celluloses with a sufficient amount of sodium C6-carboxylate groups, which were then converted to AZADO-oxidized cellulose nanofibrils individually dispersed in water by gentle mechanical disintegration treatment (Takaichi & Isogai, 2013). We found during the study that almost all the C6-primary hydroxyls and also small amounts of the C2/C3 hydroxyls present on the crystalline cellulose microfibril surfaces of the wood cellulose were converted to C6-carboxyls and ketones, respectively. In this study, therefore, the AZADO/NaBr/NaOCl oxidation system with excess NaOCl was applied to regenerated and native celluloses to prepare NaTCC, and the chemical structures and molecular masses of the oxidized products obtained were studied by NMR, size-exclusion chromatography, and other analysis methods.

2. Materials and methods

2.1. Materials

Bemliese® (Asahi Chemicals Co., Ltd., Tokyo, Japan) produced from cotton linters using a cuprammonium solvent system was used as a regenerated cellulose sample. A never-dried softwood bleached kraft pulp (Nippon Paper Industries, Tokyo, Japan), which had a ~90% α-cellulose content, was used as a native cellulose sample. The pulp was soaked in a dilute aq. HCl solution at room temperature for 0.5 h, and then washed repeatedly with water via filtration. AZADO, sodium bromide, 1.86 M sodium hypochlorite solution, and other chemicals and solvents were of laboratory grade (Wako Pure Chemicals, Tokyo, Japan) and used without further purification.

2.2. Oxidation of regenerated cellulose

Regenerated cellulose (1 g) was suspended in distilled water (100 mL) containing sodium bromide (0.1 g) and AZADO (15.3 mg, 0.1 mmol/g-cellulose) in a beaker (200 mL). The AZADO-mediated oxidation was started by adding the NaOCl solution (22 mL, 40 mmol) to the cellulose slurry at room temperature under continuous stirring. The pH of the slurry was maintained at 10 by the continuous addition of a 1 M NaOH solution using a pH stat for 6 h. Then, the slurry was transferred to an Erlenmeyer flask with an airtight stopper, and the mixture was continuously stirred for 16 h without pH control. Sodium thiosulfate pentahydrate (~2.5 g, ~10 mmol $Na_2S_2O_3$) was added to the transparent solution obtained to quench the oxidation. The crude oxidized product was purified by dialysis against water for 4 days using a dialysis membrane with a cut-off molecular weight of 12,000. Then, 0.05 M NaOH was added to the purified product solution to adjust the pH to 7.8 followed by freeze drying. This process was carried out to convert free carboxyls in the product to sodium carboxylate groups.

2.3. Oxidation of native cellulose

Never-dried softwood bleached kraft pulp (1 g) was suspended in distilled water (100 mL), and oxidized using the AZADO/NaBr/NaOCl system with a slight modification compared with the above-mentioned procedure. The amount of NaOCl solution added during the initial oxidation stage was 13.4 mL (25 mmol) and then a further 8 mL (15 mmol) NaOCl solution was added to the reaction mixture in the Erlenmeyer flask after the initial oxidation period of 6 h and before being tightly sealed with a stopper. Sodium thiosulfate pentahydrate (~2.5 g, ~10 mmol $Na_2S_2O_3$) was added to the translucent reaction mixture to quench the oxidation. The crude oxidized product was purified by dialysis against water for 4 days, and subsequently the solution was filtered through a cellulose ester membrane filter with a 0.05-μm pore size. Then, 0.05 M NaOH was added to the purified and transparent product solution to adjust the pH to 7.8 followed by freeze drying.

2.4. Analyses

The AZADO-oxidized products were dissolved in D_2O and were subjected to ^1H and ^{13}C NMR analysis using an ALPHA-500 (JEOL, Japan) with 3-trimethylsilyl-2,2,3,3-d_4-propionic acid sodium salt (Aldrich, USA) as the internal standard. Quantitative ^{13}C NMR spectra were obtained using a gated decoupling method without a nuclear Overhauser effect (Wei, Furihata, Hu, Miyakawa, & Tanokura, 2010). The acquisition and delay times of the ^{13}C NMR measurement were 0.27 and 2.0 s, respectively. The data accumulation times for the ^1H and ^{13}C NMR spectra were 32 and 25,000, respectively. Heteronuclear single quantum coherence (HSQC) spectrum of the oxidized product was recorded according to a reported method (Kurita & Isogai, 2010). Fourier transform infrared (FT-IR) spectra of the AZADO-oxidized products were recorded on a Jasco FT/IR-6100 spectrometer in transmission mode with 4 cm^{-1} resolution using the KBr disk technique. The carboxylate content of the products was determined using an electric conductivity titration method (Saito & Isogai, 2014). The dried sample (0.04 g) was dissolved in water (55 mL), and 0.01 M NaCl (5 mL) was added to the solutions. Then, 0.1 M HCl was added to the mixture to set the pH 1.8. A 0.15 M NaOH solution was added at the rate of 0.1 mL/min up to pH 11 using a pH stat. The carboxylate content of the sample was determined from the conductivity and pH curves. Molecular mass parameters of the AZADO-oxidized products were measured using a size-exclusion chromatograph (SEC) furnished with a multi-angle laser light-scattering (MALLS) detector (DAWN EOS, k = 690 nm; Wyatt Technologies, USA). The oxidized products (1 mg each) were dissolved in 0.1 M NaCl (1 mL) to prepare 0.1 w/v% solutions. A poly(hydroxymethacrylate) gel (SB-806MHQ, Ø 8 mm × 30 cm, Shodex, Japan) was used as the SEC column. All the sample solutions and eluents were filtered beforehand through 0.45 μm PTFE membranes (Millipore, USA). The MALLS cells and

Table 1
Water-solubility and ^{13}C NMR spectrum simplicity of the oxidized celluloses prepared under various conditions.

Cellulose sample	Reaction conditions	Water solubility	Simplicity of ^{13}C NMR pattern
Regenerated cellulose	Room temp., 22 h, NaOCl: 40 mmol/g-cellulose	–	Unmeasurable
Regenerated cellulose	Room temp., 22 h, AZADO/NaBr/NaOCl, NaOCl: 25 mmol/g-cellulose	+	–
Regenerated cellulose	Room temp., 6 h, AZADO/NaBr/NaOCl, NaOCl: 40 mmol/g-cellulose	–	Unmeasurable
Regenerated cellulose	Room temp., 22 h, AZADO/NaBr/NaOCl, NaOCl: 40 mmol/g-cellulose[a]	+	+
Native cellulose	Room temp., 6 h, AZADO/NaBr/NaOCl, NaOCl: 10 mmol/g-cellulose	–	Unmeasurable
Native cellulose	Room temp., 22 h, AZADO/NaBr/NaOCl, NaOCl: 40 mmol/g-cellulose	±	–
Native cellulose	Room temp., 22 h, AZADO/NaBr/NaOCl, NaOCl: 45 mmol/g-cellulose	±	–
Native cellulose	35 °C, 22 h, AZADO/NaBr/NaOCl at NaOCl: 45 mmol/g-cellulose	±	–
Native cellulose	Room temp., 46 h, AZADO/NaBr/NaOCl for 2 days, NaOCl: 45 mmol/g-cellulose	±	–
Native cellulose	Room temp., 22 h, AZADO/NaBr/NaOCl, NaOCl: 25 + 15 mmol/g-cellulose[b]	±	±

[a] These oxidation conditions were used to prepare NaTCCs from regenerated cellulose, in this study.
[b] These oxidation conditions were used to prepare NaTCCs from native cellulose, in this study.

refractive index detector were kept at room temperature and 40 °C, respectively. Detailed operation and measurement conditions of the SEC-MALLS are described elsewhere (Fujisawa, Isogai, & Isogai, 2010; Hirota et al., 2009; Homma, Isogai, Saito, & Isogai, 2013; Hiraoki, Fukuzumi, Ono, Saito, & Isogai, 2013; Watanabe, Tamura, Fujisawa, Saito, Habu, & Isogai, 2013; Watanabe, Tamura, Saito, Habu, & Isogai, 2014). The specific refractive index increment (dn/dc) of the AZADO-oxidized product prepared from regenerated cellulose, which was dried by freeze drying and the successive vacuum drying, was determined in a 0.1 M NaCl solution using an interferometric refractometer (Wyatt Technologies, USA), and the obtained value was 0.137 mL/g. This value was used for the calculation of molecular masses.

3. Results and discussion

3.1. AZADO-mediated oxidation of regenerated and native celluloses

The regenerated and native celluloses were oxidized using the AZADO/NaBr/NaOCl system with excess NaOCl in water at pH 10 and at room temperature for 6 h. Additional 16-h reaction time was allowed without pH control under alkaline conditions. The regenerated cellulose/water slurry during the initial stage became a transparent solution because of oxidation showing that the water-insoluble regenerated cellulose became water-soluble. For native cellulose, the slurry did not become a completely transparent solution but rather a translucent solution was obtained upon the AZADO-mediated oxidation (Fig. 2). Water solubility and ^{13}C NMR pattern simplicity of the oxidized celluloses prepared from regenerated and native celluloses under various conditions, which were carried out in preliminary experiments, are summarized in Table 1. Because a completely transparent solution could not be obtained for the native cellulose, the water-insoluble fraction present in small quantities in the AZADO-oxidized product was removed via filtration to obtain a water-soluble and transparent fraction. When the same wood cellulose was oxidized using the AZADO-mediated system under milder conditions to prepare AZADO-oxidized cellulose nanofibrils, the original fibrous morphology was found to be maintained during the oxidation (Takaichi & Isogai, 2013). Thus, the addition of more NaOCl and a longer reaction time for the oxidation of wood cellulose provided an oxidized product that is different from those reported previously.

The water-soluble AZADO-oxidized regenerated and native celluloses with sodium counter ions that were obtained after purification had weight recovery ratios of 139 and 111%, respectively, and carboxylate contents of 10.4 and 9.7 mmol/g, respectively (Table 2). Sodium cellouronate or sodium β-(1 → 4)-polyglucuronate with ideal chemical structures that were obtained from regenerated cellulose through TEMPO-mediated oxidation have a carboxylate content of 5.05 mmol/g (Hirota et al., 2009; Isogai & Kato, 1998). Therefore, a higher amount of sodium carboxylate groups was present in the AZADO-oxidized celluloses compared with those of cellouronic acid, indicating that the C6-primary hydroxyls and also some of C2 and C3 hydroxyls were oxidized to carboxyls after the oxidation.

3.2. Chemical structures of the AZADO-oxidized celluloses

The FT-IR spectra of the water-soluble AZADO-oxidized celluloses are shown in Fig. 3. Both the oxidized celluloses prepared from the regenerated and native celluloses had similar patterns; significant amounts of carboxylate groups were present in the products and the C—H groups originally present in the cellulose mostly disappeared.

Fig. 4 shows the ^{1}H NMR spectra of the AZADO-oxidized celluloses. Two major signals were observed at ~4.4 and ~4.9 ppm for the product prepared from regenerated cellulose, and the signal peaks were located at 4.44 and 4.93 ppm. These signals are assigned to the C4/C5 and C1 protons of NaTCC or sodium mesotartarate/monohydrated glyoxilate alternating co-polyacetal on the basis of their chemical shifts and signal areas. The ^{1}H NMR spectrum of the AZADO-oxidized native cellulose consisted of more complicated signals probably because of side reactions that occurred during the formation of NaTCC, and this is discussed later.

The ^{13}C NMR spectra of the AZADO-oxidized regenerated and native celluloses are shown in Fig. 5, and these were obtained

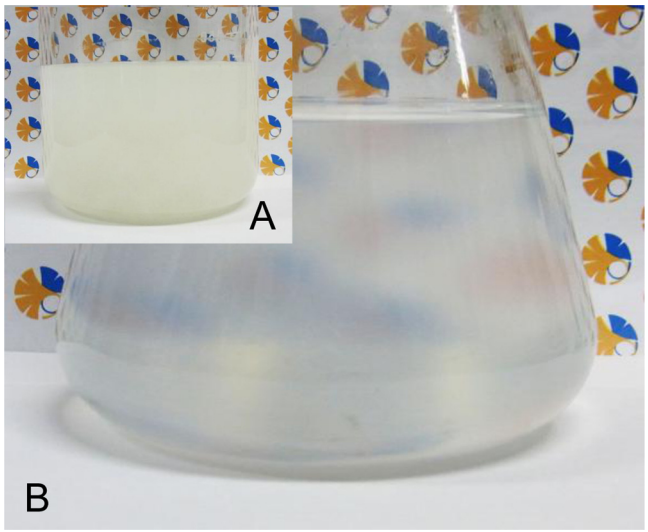


Fig. 2. Photos of the bleached kraft pulp slurries before (A) and after (B) AZADO-mediated oxidation.

Table 2
Weight recovery ratio, carboxylate content, weight- and number-average molecular masses (M_w and M_n, respectively) with the corresponding degrees of polymerizations (DP_w and DP_n, respectively), and polydispersity (M_w/M_n) of the AZADO-oxidized celluloses.

Starting cellulose	M_v[a] (g/mol) [DP_v]	Carboxyl content (mmol/g)[a]	AZADO-oxidized product				
			Weight recovery ratio (%)	Carboxylate content (mmol/g)	M_w (g/mol) [DP_w]	M_n (g/mol) [DP_n]	M_w/M_n
Regenerated cellulose	110,000 [680]	0.00	139	10.4	10,700 [39]	6950 [26]	1.53
Native cellulose	205,000 [1270]	0.01	111	9.7	10,300 [38]	7170 [26]	1.43

[a] These data were reported in previous studies (Hirota et al., 2009; Shinoda et al., 2010).

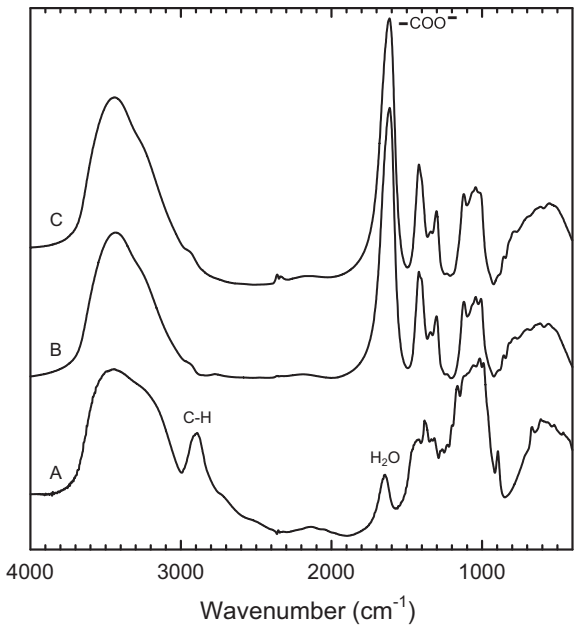


Fig. 3. FT-IR spectra of regenerated cellulose (A), and AZADO-oxidized products prepared from the regenerated (B) and native (C) celluloses.

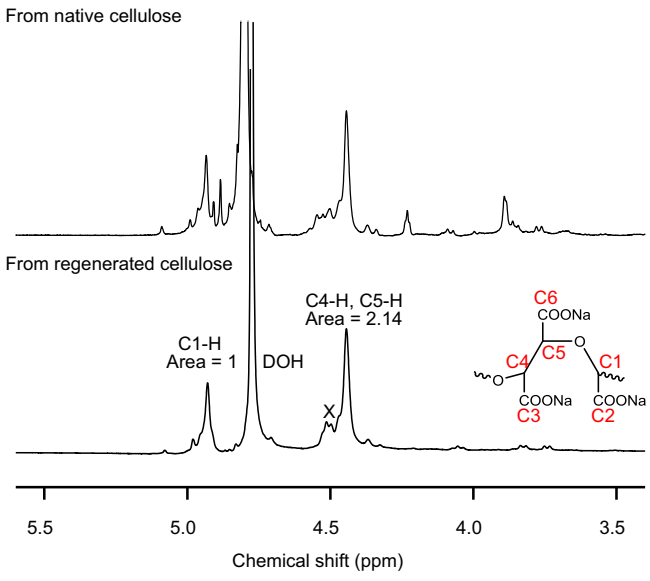


Fig. 4. ^{1}H NMR spectra of the AZADO-oxidized products prepared from the regenerated and native celluloses.

using the quantitative mode. Four major signals were present at 82.5, 103.4, 176.6, and 178.2 ppm for the AZADO-oxidized regenerated cellulose, and these signals are assigned to the C4/C5, C1, C2 and C3/C6 carbons, respectively, of the sodium mesotartarate/glyoxilate alternating acetal dimer repeating units from their chemical shifts and signal areas, and the HSQC spectrum of the AZADO-oxidized regenerated cellulose (Fig. 6). Thus, NaTCC or sodium mesotartarate/monohydrated glyoxilate alternating copolyacetal with an almost homogeneous chemical structure can be obtained from regenerated cellulose by AZADO/NaBr/NaOCl oxi-

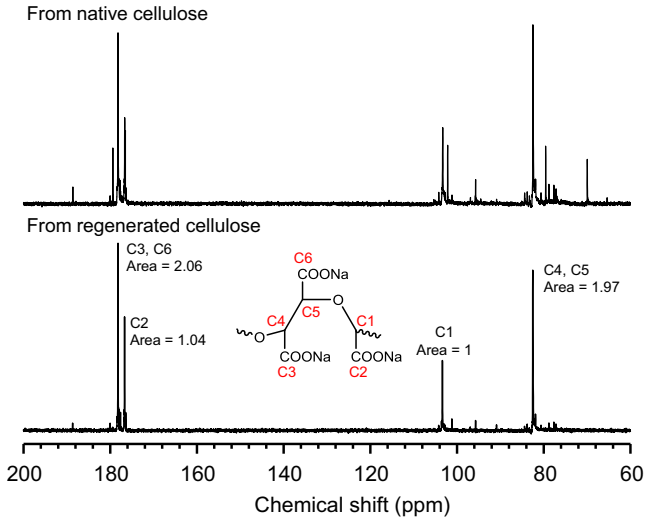


Fig. 5. ^{13}C NMR spectra of the AZADO-oxidized products prepared from the regenerated and native celluloses, and measured using the quantitative mode.

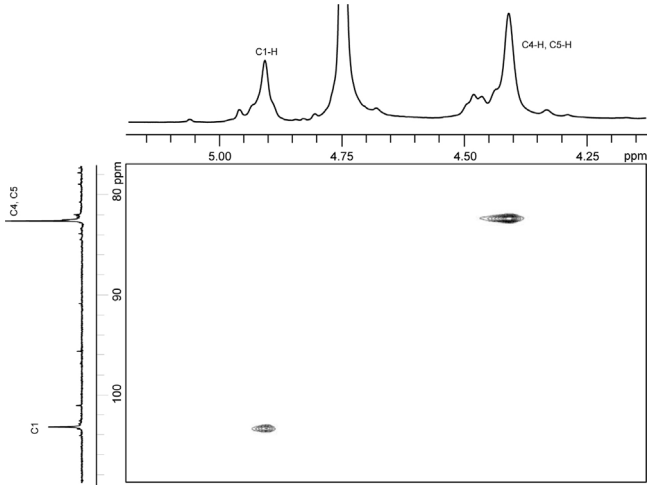
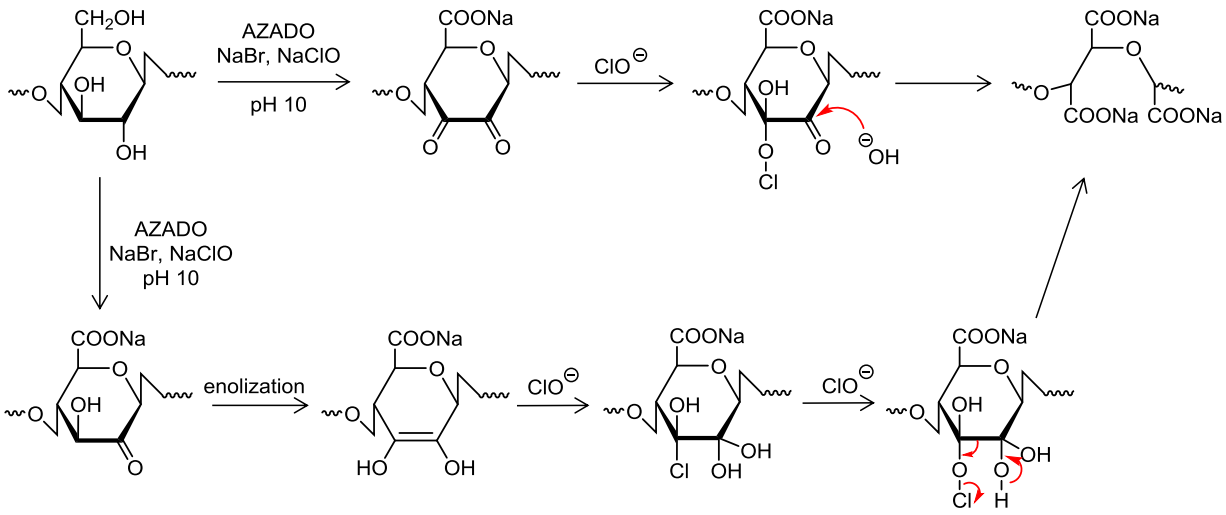


Fig. 6. HSQC spectrum of the AZADO-oxidized product prepared from the regenerated cellulose.



Scheme 1. Possible reaction mechanism to form NaTCC prepared from regenerated cellulose by AZADO/NaBr/NaOCl oxidation.

dation under the relatively harsh conditions used in this study. Because the carboxylate content of NaTCC with a completely homogeneous chemical structure is calculated to be 11.0 mmol/g from the molecular formula of the monomer unit, $C_6H_3O_8Na_3$, the AZADO-oxidized regenerated cellulose with a carboxylate content of 10.4 mmol/g can be regarded as an almost pure NaTCC (Table 2). However, the presence of small signals other than the four major signals observed in Fig. 5 indicates that some minor side reactions took place on the molecules during the oxidation.

When the AZADO-mediated oxidation was applied to the softwood bleached kraft pulp that was used as an example of native cellulose, a water-soluble oxidized product with a carboxylate content of 9.7 mmol/g was obtained after dialysis and subsequent filtration. However, both the ^{1}H and ^{13}C NMR spectra of the oxidized product showed more complicated patterns (Figs. 4 and 5). The ^{13}C NMR spectrum consisted of carbon signals from NaTCC and also from some other by-products at 70.0, 95.7, 102.2, 179.4, and 188.6 ppm. This product had a more heterogeneous chemical structure than that obtained from regenerated cellulose. Because native cellulose containing cellulose I is crystalline and it has molecular mass values much higher than that of the regenerated cellulose containing cellulose II, the latter is likely to have higher accessibility to oxidation than the former resulting in a difference in the chemical structure between the two AZADO-oxidized products.

3.3. Molecular masses of AZADO-oxidized celluloses

The AZADO-oxidized regenerated and native celluloses were dissolved in 0.1 M NaCl, and subjected to SEC-MALLS analysis to determine their molecular masses (Fig. 7 and Table 2). The weight- and number-average degrees of polymerizations (DP_w and DP_n, respectively) were calculated from the corresponding molecular masses, assuming that the oxidized products had homogeneous NaTCC chemical structures. Both AZADO-oxidized celluloses had similar weight-average molecular masses (M_w) of 10,300–10,700 or DP_w values of 38–39 (Table 2), and they had similar molecular mass distribution patterns (Fig. 7). Because the viscosity-average molecular masses (M_v) of the original regenerated and native celluloses were 110,000 and 205,000, respectively, or the corresponding DP_v values were 680 and 1270, respectively (Hirota et al., 2009; Shinoda, Saito, Okita, & Isogai, 2010), extensive depolymerization was unavoidable during the AZADO-mediated oxidation. Some oxidative cleavage of cellulose glycoside bonds owing to hydroxyl radicals and/or β-elimination may have occurred on the oxidized cellulose molecules during the AZADO-mediated oxidation under alkaline conditions in a similar manner to that of TEMPO-mediated oxidation of cellulose (Isogai et al., 2011; Shibata & Isogai, 2003). However, neither ^{13}C NMR signals at 146 and 110 ppm nor UV absorption around 235 nm, which are due to C=C double bonds formed by β-elimination of cellulose (Konno, Habu, Maeda, Azuma, & Isogai, 2006), were detected for the AZADO-oxidized regenerated cellulose, further studies are needed to make clear the detailed depolymerization mechanism of cellulose in the AZADO-mediated oxidation.

When the AZADO-oxidized regenerated cellulose was assumed to have a completely homogeneous NaTCC chemical structure, the yield was calculated to be 82% from the weight recovery ratio of 139%. In a similar manner, the yield of the AZADO-oxidized native cellulose was calculated to be 66% from the weight recovery ratio of 111%. In both cases, some oxidized cellulose molecules with lower molecular masses that were present in the original AZADO-oxidized celluloses may have been lost during dialysis. A dialysis membrane with a cut-off molecular mass of ~12,000 was used. Because both the AZADO-oxidized celluloses had similar M_w or M_n values, the depolymerization mechanism of the AZADO-mediated oxidation is not likely dependent on the original crystal structures, crystallinities, or molecular masses of the regenerated or native celluloses. It is, however, plausible that depolymerization occurs on the water-soluble oxidized cellulose molecules, that formed

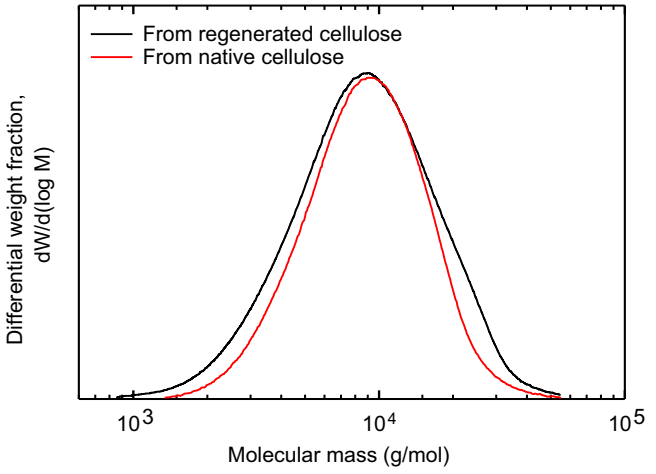


Fig. 7. Molecular mass distribution of the AZADO-oxidized products prepared from the regenerated and native celluloses.

during the AZADO-mediated oxidation under homogeneous oxidation conditions.

3.4. Reaction mechanism for the formation of NaTCC from cellulose during the AZADO-mediated oxidation

In a previous study, the carbon-carbon cleavage reactions of 1,2-diols with the AZADO catalyst were reported and a hypervalent iodine reagent like $PhI(OAc)_2$ or $NaIO_4$ had to be used as a co-oxidant in these reactions (Shibuya, Doi, Shibuta, Uesugi, & Iwabuchi, 2012; Shibuya, Shibuta, Fukuda, & Iwabuchi, 2012). Thus, this is the first report showing that almost all the C2—C3 bonds of cellulose can be cleaved to form dicarboxyls in one step during AZADO/NaBr/NaOCl oxidation with excess NaOCl in water at room temperature under alkaline conditions. The important factors in the formation of NaTCC from celluloses are: (1) the use of AZADO as a catalyst, (2) the addition of excess NaOCl, (3) oxidation over longer periods, and (4) the use of regenerated cellulose as a starting material. Because AZADO can oxidize primary hydroxyls and secondary hydroxyls such as the C2 and C3 hydroxyls of cellulose (Shibuya et al., 2006; Takaichi & Isogai, 2013), two routes toward the formation of the NaTCC structure from cellulose are possible upon AZADO-mediated oxidation in water under alkaline conditions (Scheme 1). As shown in this scheme, NaOCl is a primary oxidant and thus the C2—C3 bond of cellulose is cleaved to form a dicarboxy cellulose structure during the oxidation (Floor, Kieboom, & Bekkum, 1989; Whistler & Schweiger, 1957). However, the oxidation mechanisms in Scheme 1 are hypothetical based on the results obtained in this study and the literature, and thus speculative at present.

4. Conclusion

The preparation of NaTCC or sodium mesotartarate/monohydrated glyoxilate alternating co-polyacetal with an almost homogeneous chemical structure was achieved through a one-step oxidation of regenerated cellulose using the AZADO/NaBr/NaOCl system in water at room temperature under alkaline conditions. The important factors for the preparation of NaTCC are: (1) the use of AZADO and regenerated cellulose as the catalyst and starting material, respectively, and (2) addition of excess NaOCl together with a longer reaction time. Thus, the AZADO-mediated oxidation brings about the cleavage of the C2—C3 bonds of cellulose and the formation of dicarboxyls other than the formation of C6-carboxyls. The yield and carboxylate content of the NaTCC prepared from the regenerated cellulose by AZADO-mediated oxidation were 82% and 10.4 mmol/g, respectively, and its DP_w was 39. Because all primary and secondary hydroxyls of regenerated cellulose can be converted to carboxyls through the one-step oxidation, the AZADO-mediated oxidation would open new fields of polysaccharide chemistry; this oxidation may be applicable to other polysaccharides to prepare new water-soluble tricarboxy polysaccharides and carboxyl-containing monomers in high yields after hydrolysis. Preparation of NaTCCs having more homogeneous chemical structures with higher molecular weights is a challenging issue to use NaTCCs as polysaccharide-based thickeners and builders in household laundry detergents.

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