

Oxidation of wood cellulose using 2-azaadamantane *N*-oxyl (AZADO) or 1-methyl-AZADO catalyst in NaBr/NaClO system

Satoshi Takaichi · Akira Isogai

Received: 28 January 2013 / Accepted: 20 April 2013 / Published online: 27 April 2013
© Springer Science+Business Media Dordrecht 2013

Abstract A wood cellulose was oxidized with catalytic amounts of 2-azaadamantane *N*-oxyl (AZADO) or 1-methyl-AZADO, in an NaBr/NaClO system, in water at pH 10. The oxidation efficiency, carboxylate/aldehyde contents, and degree of polymerization (DP_v) of the oxidized celluloses thus obtained were evaluated in terms of the amount of AZADO or 1-methyl-AZADO catalyst added, in comparison with those prepared using the TEMPO/NaBr/NaClO system. When the AZADO/NaBr/NaClO and 1-methyl-AZADO/NaBr/NaClO oxidation systems were applied to wood cellulose using the same molar amount of TEMPO, the oxidation time needed for the preparation of oxidized celluloses with carboxylate contents of 1.2–1.3 mmol/g was reduced from ≈ 80 to 10–15 min. Moreover, the molar amounts of AZADO and 1-methyl-AZADO that had to be added for the preparation of oxidized celluloses with carboxylate contents of 1.2–1.3 mmol/g were reduced to 1/32 and 1/16 of the amount of TEMPO added, respectively. The DP_v values for the AZADO- and 1-methyl-AZADO-oxidized celluloses after NaBH_4 treatment were in the range of 600–800. This indicated that not only C6-carboxylate groups but also C2/C3 ketones were formed to some extent on the crystalline cellulose

microfibril surfaces during the AZADO- and 1-methyl-AZADO-mediated oxidation. When the AZADO-oxidized wood cellulose, which had a carboxylate content of 1.2 mmol/g, was mechanically disintegrated in water, an almost transparent dispersion consisting of individually nano-dispersed oxidized cellulose nanofibrils was obtained, with a nanofibrillation yield of 89 %.

Keywords Azaadamantane *N*-oxyl · AZADO · Catalytic oxidation · Nanofibrillation · 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)

Introduction

Various chemical reactions have been studied for celluloses, to add some new functionalities or properties to native materials. 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation—which was first applied to water-soluble starch, amylopectin, and pullulan to selectively oxidize their C6-primary hydroxyls to C6-carboxylate groups (de Nooy et al. 1995; Bragd et al. 2004)—is regarded as one of the most promising and efficient chemical reactions for polysaccharides. The major advantage of this TEMPO-mediated oxidation is that it takes place selectively at primary hydroxyls under aqueous and mild conditions. Hence, the TEMPO/NaBr/NaClO oxidation process in water at pH 10, which was first

S. Takaichi · A. Isogai (✉)
Graduate School of Agricultural and Life Sciences,
The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku,
Tokyo 113-8657, Japan
e-mail: aisogai@mail.ecc.u-tokyo.ac.jp

used by de Nooy et al. (1995), has been applied to convert various polysaccharides to new water-soluble polyuronates, the C6-primary hydroxyls of which were mostly or completely oxidized to C6-carboxylate groups (Isogai and Kato 1998; da Silva Perez et al. 2003; Kato et al. 2003, 2004; Tamura et al. 2009).

When TEMPO-mediated oxidation is applied to crystalline native celluloses such as cotton linters, wood pulps, bacterial cellulose, and hemp bast holo-cellulose under suitable conditions, the C6-primary hydroxyl groups exposed on the crystalline cellulose microfibril surfaces are selectively oxidized to C6-carboxylate groups (Saito and Isogai 2004; Saito et al. 2006, 2007; Isogai et al. 2011; Puangsin et al. 2013). In particular, when the TEMPO-oxidized higher plant celluloses contain C6-carboxylate groups of more than ≈ 1 mmol/g, they can be converted to TEMPO-oxidized cellulose nanofibrils 3–4 nm in width, which can be dispersed in water using mild mechanical disintegration treatment, mostly at the individual nanofibril level. Electrostatic repulsions and/or osmotic effects work efficiently in the water between the TEMPO-oxidized cellulose nanofibrils, which have large amounts of anionic charges on their fibril surfaces (Okita et al. 2010; Isogai et al. 2011). The TEMPO-oxidized wood cellulose nanofibrils thus obtained have been extensively studied as new bio-based nanofibers, with the aim of applying them as environmentally friendly gas barrier films, light-weight composites with high strength and ductility, spider-like nano-network fabrics for air filters, optically antireflective layer-by-layer coating films, stiff hydrogels/aerogels, supports for catalytic nano-metal particles, health supplements, among other applications (e.g. Fukuzumi et al. 2009; Koga et al. 2010; Shimotoyodome et al. 2011; Saito et al. 2011; Nemoto et al. 2012; Qi et al. 2012; Wu et al. 2012; Fujisawa et al. 2012).

TEMPO-mediated oxidation therefore allows the effective, selective and sense formation of C6-carboxylate groups on the cellulose microfibril surfaces. However, when the TEMPO/NaBr/NaClO oxidation system was used to prepare TEMPO-oxidized cellulose nanofibrils in water at pH 10, it took more than 1 h to introduce sufficient amounts of C6-carboxylates to the wood cellulose. In this oxidation system, the remarkable depolymerization of the cellulose molecules was inevitable during the oxidation (Shinoda et al. 2012). When the TEMPO/NaClO/NaClO₂ or 4-acetamido-TEMPO/NaClO/NaClO₂

oxidation systems were used in water at pH 5–7 and 40 °C, the oxidized wood celluloses thus obtained had higher molecular weights (Saito et al. 2009). However, in these cases, it took more than 2 days to prepare oxidized celluloses that could be converted to mostly individualized cellulose nanofibrils (Tanaka et al. 2012). Thus, there is a need for a more efficient catalytic oxidation system for the preparation of oxidized wood cellulose nanofibrils with properties similar to those of nanofibrils prepared using conventional procedures. In this new oxidation system, it is desirable for the amount of nitroxyl radical catalyst added to be further reduced, and for the oxidation time required for introduction of sufficient amounts of C6-carboxylate groups to be reduced. None of the TEMPO-analogous compounds or other nitroxyl systems examined so far have had higher wood cellulose oxidation efficiency than TEMPO, when applied under the same conditions (Iwamoto et al. 2010; Biliuta et al. 2010, 2013; Coseri and Biliuta 2012; Coseri et al. 2013).

Recently, 2-azaadamantane *N*-oxyl (AZADO) and its derivatives have been developed as novel nitroxyl radical catalysts to position-selectively oxidize hydroxyl groups to carboxyls or ketones (Shibuya et al. 2006; Iwabuchi 2008). AZADO-mediated oxidation can be used under conditions similar to those in the TEMPO/NaBr/NaClO oxidation system, although AZADO has much higher oxidation efficiency and oxidation rate than TEMPO, at least for low-molecular-weight compounds (Shibuya et al. 2006; Iwabuchi 2008).

In this study, therefore, the AZADO/NaBr/NaClO and 1-methyl-AZADO/NaBr/NaClO oxidation systems were applied to a wood cellulose with different amounts of catalyst, and the oxidized celluloses thus obtained were compared with a TEMPO-oxidized wood cellulose in terms of the reaction time, weight recovery ratio, carboxylate/aldehyde contents, crystallinity and crystal size of cellulose I, degree of polymerization, and nano-fibrillation behavior.

Experimental

Materials

A never-dried softwood bleached kraft pulp was supplied by Nippon Paper Industries Co., Ltd. (Japan)

which had $\approx 90\%$ α -cellulose content. To achieve demineralization, the pulp was soaked in dilute HCl at room temperature for 0.5 h, and then washed repeatedly with water using filtration. This pulp was used as the starting wood cellulose sample. AZADO, 1-methyl-AZADO (1-Me-AZADO), sodium bromide, 1.93 M sodium hypochlorite solution, and other chemicals and solvents were of laboratory grade (Wako Pure Chemicals, Tokyo, Japan) and were used without further purification.

Catalytic oxidation of wood cellulose

The wood cellulose (2 g) was suspended in deionized water (200 mL) containing sodium bromide (0.2 g, 2 mmol) and a chosen amount of AZADO or 1-Me-AZADO (0.000625–0.02 mmol/g-cellulose) in a beaker (300 mL). The AZADO- or 1-Me-AZADO-mediated oxidation was started by adding the NaClO solution (5.2 mL, 5.018 mmol) to the cellulose slurry at room temperature under continuous stirring. The pH of the slurry was maintained at 10 by adding a 0.5 M NaOH solution with a pH stat until no consumption of the NaOH solution was observed. A small amount of ethanol was added to the slurry to quench the oxidation, and the time between the starting of oxidation and the ethanol addition was defined as “reaction or oxidation time” in this study. The AZADO- and 1-Me-AZADO-oxidized celluloses were washed thoroughly with water using filtration, and were stored at 4 °C without drying. An aliquot of the oxidized cellulose (0.35 g) was further oxidized at room temperature for 2 days in an Erlenmeyer flask, using NaClO₂ (0.57 g, 5 mmol) in a 0.05 M acetate buffer (50 mL); this process converted any C6-aldehyde groups (if present) to C6-carboxylate groups (Saito and Isogai 2004). Another aliquot of the oxidized cellulose (0.25 g) was reduced at room temperature for 2 days in an Erlenmeyer flask, using NaBH₄ (0.5 g, 13 mmol) in a 0.5 M NaHCO₃ solution; this process converted any C6-aldehyde groups and C2/C3-carbonyl groups (if present) to hydroxyl groups (Shinoda et al., 2012). After the reduction, the resulting sample was washed thoroughly with water using filtration. The carboxylate contents of the oxidized celluloses before and after the post-NaClO₂ oxidation were determined using the electric conductivity titration method (Saito and Isogai 2004).

Nanofibrillation of oxidized celluloses

The cellulose samples were oxidized using TEMPO of 0.1 mmol/g-cellulose and AZADO of 0.00625 (0.1/16) mmol/g-cellulose, and were suspended in water (25 mL) at a solid content of 0.1 w/v%. The suspensions were homogenized for 2 min at 7,500 rpm, using a double-cylinder-type homogenizer (Phycotron NS-56, Microtec), and were then sonicated using an ultrasonic homogenizer equipped with a 7 mm probe tip (US-300T, Nihon Seiki), at 300 W output power, for 10 min. The partly fibrillated or unfibrillated fraction present in the dispersion was removed using centrifugation at 12,000×g for 10 min.

Analyses

Freeze-dried oxidized celluloses (0.1 g each) were converted to pellets by pressing at 600 MPa for 1 min. These pellets were subjected to X-ray diffraction measurements in reflection mode, using a Rigaku RINT 2000 with monochromator-filtered Cu K α radiation at 40 kV and 40 mA. The crystallinity and crystal size of the cellulose I were calculated from the X-ray diffraction patterns, using a previously reported method (Tanaka et al. 2012). The oxidized celluloses from before and after the NaBH₄ treatment (0.04 g each) were dissolved in 0.5 M copper ethylene diamine (20 mL). The intrinsic viscosity numbers of the oxidized celluloses were determined using a capillary viscometer, and were converted to viscosity-average degrees of polymerization (DP_v) using the Mark–Houwink–Sakurada equation (Shinoda et al. 2012).

Results and discussion

AZADO- and 1-Me-AZADO-mediated oxidation of wood cellulose

The representative AZADO- or 1-Me-AZADO-mediated oxidation of alcohol groups is shown in Fig. 1. The mechanism for the oxidation of alcohol groups by the AZADO/NaBr/NaClO system in water at pH 10 is close to that associated with conventional TEMPO/NaBr/NaClO oxidation. However, the catalytic activity of AZADO is higher than that of TEMPO for the oxidation of low-molecular-weight compounds

(Shibuya et al. 2006; Iwabuchi 2008), because AZADO has a lower steric barrier around the nitroxyl unit in each molecule. Thus, AZADO is expected to oxidize the C6-primary hydroxyl groups that are exposed on the crystalline cellulose microfibril surfaces in wood cellulose more efficiently than TEMPO. However, it is plausible that not only C6-primary hydroxyls, but also some C2 or C3 hydroxyls exposed on crystalline cellulose microfibril surfaces might be oxidized to ketones by the AZADO-mediated oxidation, which is undesirable for the selective oxidation of the C6-primary hydroxyls of cellulose. Thus, 1-Me-AZADO was also used as an intermediate catalyst between TEMPO and AZADO.

The amounts of AZADO and 1-Me-AZADO added were varied from 0.1 to 0.003125 (0.1/32) and 0.00625 (0.1/16) mmol/g-cellulose, respectively; 0.1 mmol/g-cellulose was the minimum amount of TEMPO required for the maximum oxidation of wood cellulose, when the TEMPO/NaBr/NaClO system was used in water at pH 10. Hence, in this study, the molar amounts of AZADO and 1-Me-AZADO added were reduced to 1/32 and 1/16 of that of TEMPO added, respectively. Figure 2 shows the relationships between the amount of AZADO and 1-Me-AZADO added and the reaction time required for the oxidation of the wood cellulose. As a reference, the reaction time for TEMPO (≈ 80 min) was also plotted in this figure. When AZADO or 1-Me-AZADO with the amount of 0.1 mmol/g-cellulose was used, the

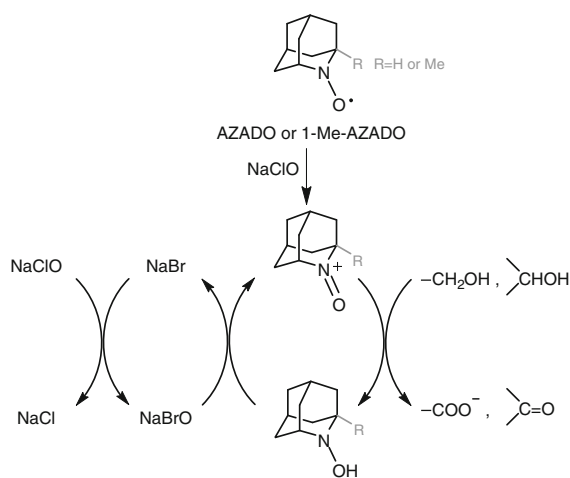


Fig. 1 Oxidation of alcohol groups to carboxyls or ketones by the NaBr/NaClO system with AZADO or 1-methyl-AZADO catalyst in water at pH 10

reaction time was shortened to 10–15 min; the oxidation rate was improved remarkably when AZADO or 1-Me-AZADO was used as a catalyst in place of TEMPO. Even when the molar amount of AZADO or 1-Me-AZADO added was reduced to 1/16 or 1/32 of that of TEMPO added, the reaction time was similar to that observed when TEMPO was used. Thus, at least in terms of the oxidation time, both AZADO and 1-Me-AZADO clearly improved the oxidation efficiency of the wood cellulose compared with TEMPO.

Carboxylate and aldehyde contents of the oxidized wood celluloses

The weight recovery ratios of the oxidized celluloses prepared under the conditions shown in Fig. 2 ranged from 91 to 97 %. The weight recovery losses mostly resulted from the handling of the samples during the isolation and purification processes; the oxidized celluloses were obtained almost quantitatively, irrespective of the amount of catalyst added. The carboxylate and aldehyde contents of the AZADO- and 1-Me-AZADO-oxidized wood celluloses are shown in Fig. 3. Even when the added amounts of AZADO or 1-Me-AZADO were reduced to 0.00625–0.003125 (0.1/16–0.1/32) mmol/g-cellulose, the oxidized celluloses had high carboxylate contents of more than 1.2 mmol/g, which was generally sufficient for the TEMPO-oxidized celluloses to be converted into cellulose nanofibrils dispersed in water by a gentle mechanical disintegration treatment in water. The oxidized celluloses prepared

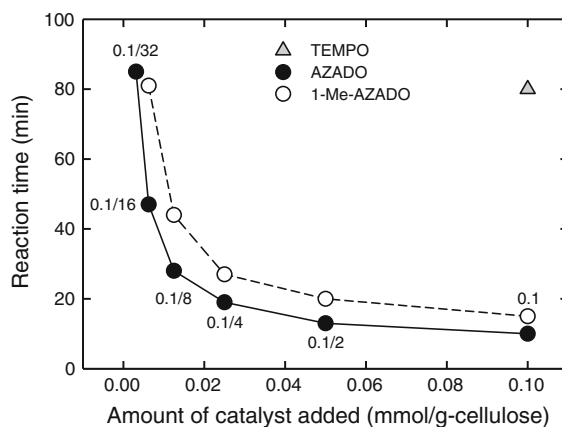


Fig. 2 Relationships between the added amount of TEMPO, AZADO, or 1-methyl-AZADO and the reaction time required for the oxidation of wood cellulose

with 1-Me-AZADO had slightly higher carboxylate contents than those prepared with AZADO, when oxidized using the same molar amount of catalyst. These carboxylate contents were slightly lower than that of the oxidized cellulose prepared using 0.1 mmol/g-cellulose of TEMPO (Fig. 3). It is possible that the NaClO added was consumed not only in the oxidation of C6-primary hydroxyls, but also in the oxidation of C2/C3 hydroxyls to ketones; this is discussed later. It is noteworthy that the aldehyde contents of the oxidized celluloses prepared with both AZADO and 1-Me-AZADO were quite low and 0–0.03 mmol/g, whereas the TEMPO-oxidized cellulose had an aldehyde content of 0.08 mmol/g.

The results given in Figs. 2 and 3 showed that AZADO and 1-Me-AZADO reduced the time needed for the oxidation of wood cellulose, using the same molar amount of catalyst as that used for TEMPO. Alternatively, the molar amount of AZADO or

1-Me-AZADO added could be reduced to 1/16 or 1/32 of that of TEMPO added, although in this case, a reaction time similar to that used with TEMPO was required for the oxidation of wood cellulose to produce carboxylate contents similar to that in the TEMPO-oxidized cellulose. It is well known that AZADO-mediated oxidation can also convert secondary alcohols to ketones to some extent (Iwabuchi 2008). However, in the AZADO/NaBr/NaClO system, when reactants have both primary and secondary alcohols, the primary alcohols are preferentially oxidized to carboxylate groups via aldehyde groups (Nicolaou et al. 2009; Celindro et al. 2012). When AZADO/NaBr/NaClO oxidation is applied to wood cellulose suspended in water at pH 10, three oxidations could feasibly take place: (A) from C6-primary hydroxyls to C6-aldehydes: (B) from C6-aldehyde groups to C6-carboxylates: and (C) from C2/C3 secondary hydroxyls to ketones. The results in Fig. 3 showed that the reactions A and B proceeded preferentially for the wood cellulose in the AZADO- and 1-Me-AZADO-mediated oxidations.

Degree of polymerization of the oxidized wood celluloses

In the TEMPO/NaBr/NaClO oxidation in water at pH 10, some depolymerization of the wood cellulose molecules was inevitable, primarily owing to the β -elimination of the C6-aldehydes formed as intermediates under alkaline conditions, and/or hydroxyl radicals formed in situ as a side reaction (Shinoda et al. 2012). Moreover, when an alkaline 0.5 M copper ethylene diamine solution was used as the solvent to determine DP_v values, additional depolymerization took place artificially, owing to β -elimination on the TEMPO-oxidized celluloses that contained small amounts of C6-aldehydes (Shinoda et al. 2012). Thus, in the case of TEMPO-oxidized celluloses, for DP_v values to be determined accurately, a post-oxidation treatment with NaClO₂ is required to convert residual C6-aldehydes to C6-carboxyls. Alternatively, post-reduction with NaBH₄—to convert C6-aldehydes and C2/C3 ketones to C6-hydroxyls and C2/C3 hydroxyls, respectively,—can also be applied (Shinoda et al. 2012) for the accurate determination of DP_v values for the oxidized celluloses; this also helps to avoid the depolymerization of the oxidized celluloses during DP_v measurements.

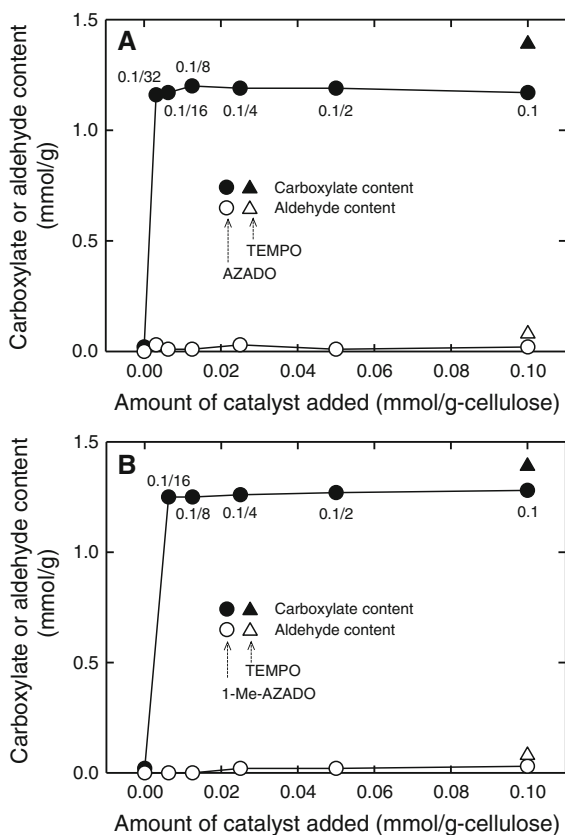


Fig. 3 Relationships between the added amount of TEMPO, AZADO (A) or 1-methyl-AZADO (B) and either carboxyl or aldehyde content of the oxidized wood celluloses

In the case of AZADO-mediated oxidation, the formation of C2/C3 ketones can take place on the wood cellulose to some extent, and can cause depolymerization of the oxidized celluloses via β -elimination during DP_v measurements under alkaline conditions. Thus, in this study, post-reduction with $NaBH_4$ was applied to the AZADO- and 1-Me-AZADO-oxidized wood celluloses before the DP_v measurements. Figure 4 shows the relationships between the amount of AZADO or 1-Me-AZADO added and the DP_v values for the oxidized and then $NaBH_4$ -treated wood celluloses. The DP_v values of AZADO-oxidized celluloses before the $NaBH_4$ treatment are also shown in this figure.

The DP_v value for the original wood cellulose decreased from 1,090 to 600–800 after the AZADO- or 1-Me-AZADO-mediated oxidation, even though the post $NaBH_4$ reduction was applied to the oxidized celluloses; some depolymerization of the cellulose molecules was unavoidable during the AZADO- and 1-Me-AZADO-mediated oxidation in water at pH 10, similar to TEMPO-mediated oxidation (Shinoda et al. 2012). Although the C6-carboxylate and C6-aldehyde contents in the oxidized celluloses were similar for the products prepared using AZADO and 1-Me-AZADO catalysts with the amounts of 0.003125–0.1 (0.1/32–0.1) and 0.00625–0.1 (0.1/16–0.1) mmol/g-cellulose, respectively, the DP_v values for the oxidized cellulose increased with increases in the amount of

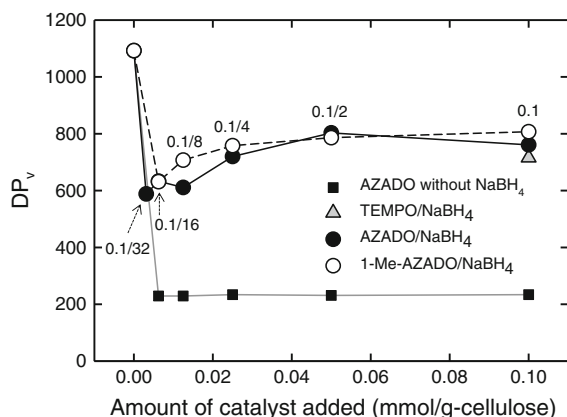


Fig. 4 Relationships between the added amount of TEMPO, AZADO, or 1-methyl-AZADO and the viscosity-average degree of polymerization (DP_v) of the oxidized and then $NaBH_4$ -treated wood celluloses. The effects of the $NaBH_4$ treatment on DP_v are also shown for the AZADO-oxidized celluloses

catalyst added. Thus, as shown in Fig. 2, the longer oxidation time may have been the primary factor influencing the decrease in the DP_v values for the oxidized celluloses.

The DP_v values for the AZADO-oxidized celluloses to which no post- $NaBH_4$ treatment was applied were approximately 200, much lower than those of the $NaBH_4$ -treated samples. Because the C6-aldehyde contents of the oxidized celluloses were sufficiently low (Fig. 3), this depolymerization likely occurred via β -elimination at the C2/C3 ketones during the DP_v measurements, which were performed using 0.5 M copper ethylene diamine, under alkaline conditions. Thus, the results in Fig. 4 indirectly indicated the presence of some C2/C3 ketones in the oxidized celluloses formed during the AZADO- and 1-Me-AZADO-mediated oxidation of wood cellulose in water at pH 10. A reliable method to accurately determine the C2/C3 ketone content in the oxidized celluloses using non-toxic reagents is currently under investigation.

X-ray diffraction patterns for the oxidized celluloses

Figure 5 shows X-ray diffraction patterns for the original wood cellulose, and the AZADO-oxidized wood celluloses prepared using different amounts of

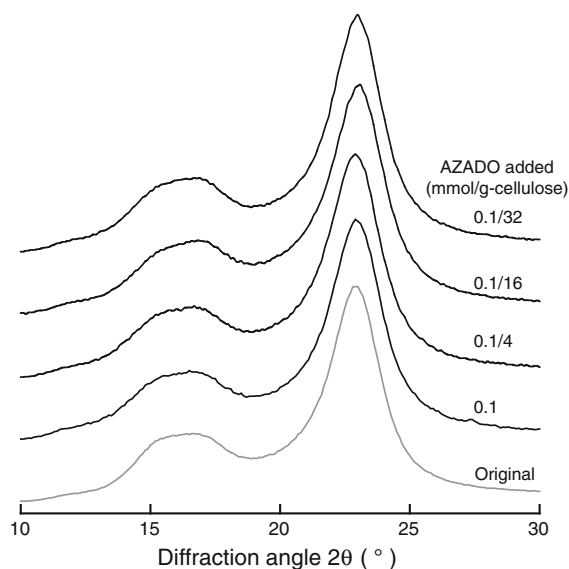


Fig. 5 X-ray diffraction patterns for the original and oxidized wood celluloses prepared with different amounts of AZADO

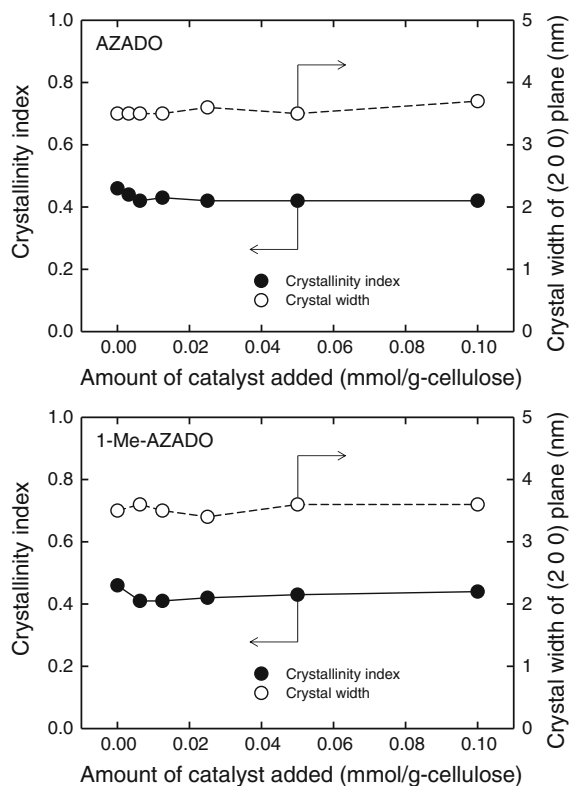


Fig. 6 Crystallinity index or (2 0 0) crystal width of cellulose I for the oxidized wood celluloses prepared using different amounts of AZADO or 1-methyl-AZADO

AZADO. Even though significant amounts of carboxylate groups were present in the oxidized celluloses (Fig. 3), all of the products maintained the original cellulose I crystal structure, indicating that the oxidation of C6-primary hydroxyls (and also C2/C3 hydroxyls, to some extent) took place selectively on the crystalline cellulose microfibril surfaces. Very similar X-ray diffraction patterns were obtained for the 1-Me-AZADO-oxidized celluloses. Figure 6 shows plots of the crystallinity and the (2 0 0) crystal width of cellulose I in the oxidized celluloses. As expected, both the crystallinity and the crystal size were almost unchanged by the oxidation, revealing that the oxidation mostly took place on the crystalline cellulose microfibril surfaces. This position-selective oxidation of wood cellulose was also observed in TEMPO/NaBr/NaClO oxidation in water at pH 10 (Saito and Isogai 2004; Okita et al. 2010; Isogai et al. 2011), TEMPO/NaClO/NaClO₂ oxidation in water at pH 5–7 (Saito et al. 2009), and TEMPO electro-mediated oxidation in water at pH 7–10 (Isogai et al. 2011).

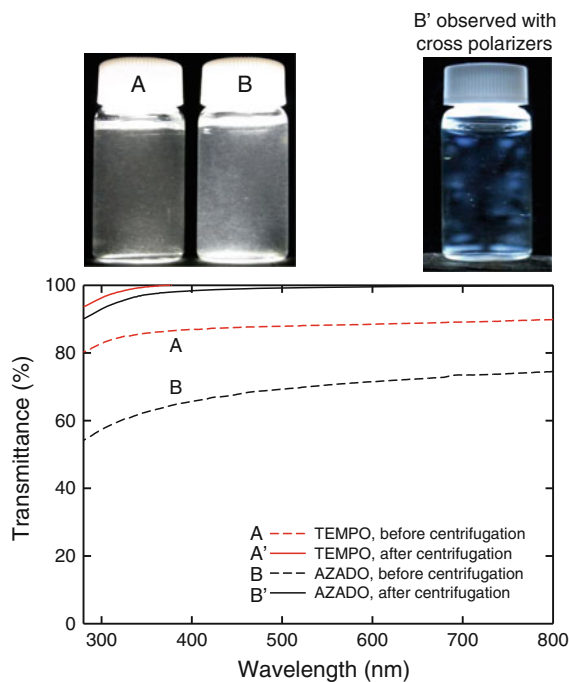


Fig. 7 Wavelength-dependent light transmittance of 0.1 % dispersions of TEMPO- and AZADO-oxidized celluloses before and after centrifugation to remove unfibrillated fractions. Photos of some of the dispersions taken with and without cross polarizers are also shown

Nanofibrillation of the AZADO-oxidized wood cellulose in water

One of the primary purposes of this study was to determine whether AZADO-oxidized wood celluloses with a sufficient number of C6-carboxylate groups could be converted to mostly individualized cellulose nanofibrils dispersed in water under gentle mechanical treatment of the oxidized cellulose/water slurries, as is true in the case of TEMPO-oxidized wood celluloses (Saito et al. 2006, 2007; Isogai et al. 2011). Hence, the oxidized celluloses prepared in the TEMPO/NaBr/NaClO system using TEMPO of 0.1 mmol/g-cellulose, and those prepared in the AZADO/NaBr/NaClO system using AZADO of 0.00625 (0.1/16) mmol/g-cellulose were mechanically disintegrated in water at 0.1 w/v% solid content. Neither post-oxidation with NaClO₂ nor post-reduction with NaBH₄ was applied to these oxidized celluloses. The carboxylate and aldehyde contents of these oxidized celluloses are shown in Fig. 3.

As shown in Fig. 7, the 0.1 % dispersion of AZADO-oxidized cellulose nanofibrils showed a

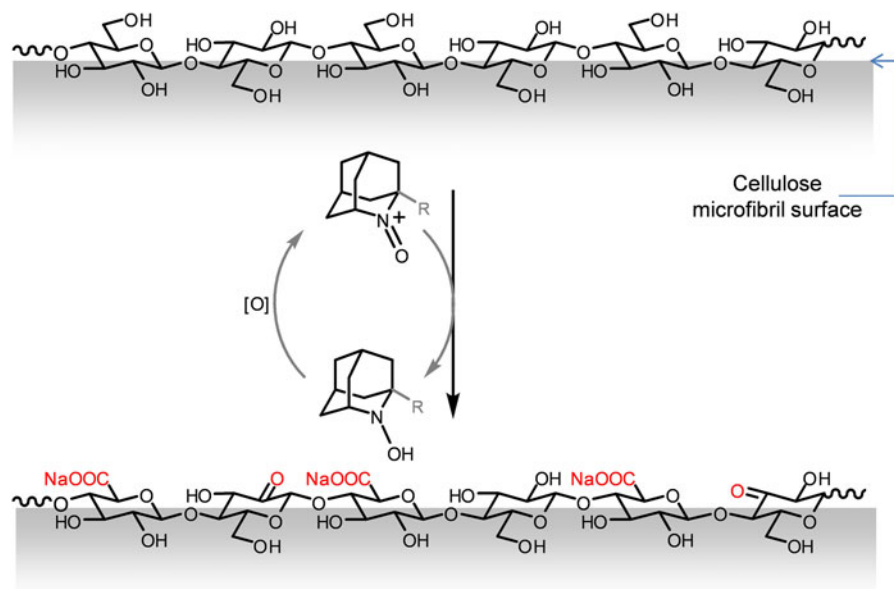


Fig. 8 Oxidation of crystalline wood cellulose microfibrils by the AZADO/NaBr/NaClO or 1-methyl-AZADO/NaBr/NaClO system in water at pH 10

lower light transmittance than the TEMPO-oxidized cellulose nanofibril dispersion, probably because the former had a lower carboxylate content (1.2 mmol/g) than the latter (1.4 mmol/g). The carboxylate contents of the TEMPO-oxidized celluloses sensitively influenced the nano-dispersibility after they were mechanically disintegrated in water under the same conditions (Saito et al. 2007). Photos A and B in Fig. 7 show the visibly different transparency or turbidity in the two dispersions.

Both of the dispersions became highly transparent after the application of centrifugation, because partly fibrillated or unfibrillated fractions were removed by this treatment. The nanofibrillation yields calculated from the dry weight of the removed fractions were 93 and 89 % for the TEMPO-oxidized and AZADO-oxidized celluloses, respectively; both dispersions had sufficiently high nanofibrillation yields. Because the centrifugation-treated dispersion of AZADO-oxidized cellulose showed clear birefringence when observed between cross-polarizers, it was concluded that this dispersion consisted of mostly individualized cellulose nanofibrils (De Souza Lima and Borsali 2004).

Based on the results obtained in this study, Fig. 8 illustrates the AZADO- and 1-Me-AZADO-mediated oxidations of crystalline wood cellulose microfibrils in water at pH 10 in the presence of NaBr and NaClO. The

oxidation of C6-primary hydroxyls to C6-carboxylate took place preferentially on the cellulose microfibril surfaces, maintaining the original crystallinity and crystal size of cellulose I. However, some of the C2/C3 hydroxyls present on the microfibrils surfaces likely oxidized to ketones. There was no intrinsic difference in the oxidation behavior of wood cellulose when AZADO and 1-Me-AZADO catalysts were used.

Conclusion

When the AZADO/NaBr/NaClO and 1-Me-AZADO/NaBr/NaClO oxidation systems were applied to wood cellulose suspended in water at pH 10 and room temperature, the oxidation of C6-primary hydroxyl groups exposed on the crystalline cellulose microfibril surfaces to C6-carboxylates proceeded quite efficiently compared with the conventional TEMPO/NaBr/NaClO oxidation. Specifically, when AZADO or 1-Me-AZADO was used for oxidation, the reaction times were reduced from ≈ 80 min to 10–15 min. Even when the molar amounts of AZADO and 1-Me-AZADO added were reduced to 1/32 and 1/16 of that of TEMPO added, respectively, the carboxylate contents in the oxidized celluloses were as high as 1.2 and 1.3 mmol/g. In these cases, longer reaction times

(≈ 80 min)—similar to that observed in the case of TEMPO-mediated oxidation—were required. When the DP_v values of the AZADO-oxidized celluloses were measured directly using 0.5 M copper ethylene diamine, the obtained DP_v values were as low as ≈ 200 . When the DP_v values of the AZADO- and 1-Me-AZADO-oxidized celluloses were measured after an $NaBH_4$ treatment, the DP_v values were in the range of 600–800, which was still lower than that of the original DP_v of wood cellulose (1,090). Thus, some depolymerization of the cellulose and the oxidized cellulose molecules was inevitable during the AZADO- and 1-Me-AZADO-mediated oxidation. These results also indicated that not only C6-carboxylate groups, but also C2/C3 ketones were formed to some extent on the crystalline cellulose microfibril surfaces during the oxidation. When the AZADO-oxidized wood cellulose with a carboxylate content of 1.2 mmol/g was mechanically disintegrated in water, an almost transparent dispersion consisting of individually nano-dispersed oxidized cellulose nanofibrils was obtained, with the nanofibrillation yield of 89 %.

Acknowledgments This study was supported by the Japan Society for the Promotion of Science (JSPS): Grant-in-Aid for Scientific Research S (21228007).

References

- Biliuta G, Frasc L, Strnad S, Harabagiu V, Coseri S (2010) Oxidation of cellulose fibers mediated by non-persistent nitroxyl radicals. *J Polym Sci A Polym Chem* 48:4790–4799
- Biliuta G, Frasc L, Drobot M, Persin Z, Kreze T, Stana-Kleinschek K, Ribitsch V, Harabagiu V, Coseri S (2013) Comparison study of TEMPO and phthalimide-*N*-oxyl (PINO) radicals on oxidation efficiency toward cellulose. *Carbohydr Polym* 91:502–507
- Bragd PL, van Bekkum H, Besemer AC (2004) TEMPO-mediated oxidation of polysaccharides: survey of methods and applications. *Top Catal* 27:49–66. doi:10.1023/B:TOCA.0000013540.69309.46
- Celindro NC, Kim TW, Kang SH (2012) Total synthesis of (–)-dysiherbaine. *Chem Commun* 48:6295–6297. doi:10.1039/C2CC32736H
- Coseri S, Biliuta G (2012) Bromide-free oxidizing system for carboxylic moiety formation in cellulose chain. *Carbohydr Polym* 90:1415–1419
- Coseri S, Biliuta G, Simionescu BC, Stana-Kleinschek K, Ribitsch V, Harabagiu V (2013) Oxidized cellulose—survey of the most recent achievements. *Carbohydr Polym* 93:207–215
- Da Silva Perez D, Montanari S, Vignon MR (2003) TEMPO-mediated oxidation of cellulose III. *Biomacromolecules* 4:1417–1425. doi:10.1021/bm034144s
- de Nooy AE, Besemer AC, van Bekkum H (1995) Highly selective nitroxyl radical-mediated oxidation of primary alcohol groups in water-soluble glucans. *Carbohydr Res* 269:89–98. doi:10.1016/0008-6215(94)00343-E
- De Souza Lima MM, Borsali R (2004) Rodlike cellulose microcrystals: structure, properties, and applications. *Macromol Rapid Commun* 25:771–787. doi:10.1002/marc.200300268
- Fujisawa S, Ikeuchi T, Takeuchi M, Saito T, Isogai A (2012) Superior reinforcement effect of TEMPO-oxidized cellulose nanofibrils in polystyrene matrix: optical, thermal, and mechanical studies. *Biomacromolecules* 13:21882194. doi:10.1021/bm300609c
- Fukuzumi H, Saito T, Iwata T, Kumamoto Y, Isogai A (2009) Transparent and high gas barrier films of cellulose nanofibers prepared by TEMPO-mediated oxidation. *Biomacromolecules* 10:162–165. doi:10.1021/bm801065u
- Isogai A, Kato Y (1998) Preparation of polyuronic acid from cellulose by TEMPO-mediated oxidation. *Cellulose* 5: 153–164. doi:10.1023/A:1009208603673
- Isogai A, Saito T, Fukuzumi H (2011) TEMPO-oxidized cellulose nanofibers. *Nanoscale* 3:71–85. doi:10.1039/C0NR00583E
- Iwabuchi Y (2008) Exploration and exploitation of synthetic use of oxoammonium ions in alcohol oxidation. *J Syn Org Chem Jpn* 66:1076–1084. doi:10.5059/yukigoseikyokaiishi.66.1076
- Iwamoto S, Kai W, Isogai T, Saito T, Isogai A, Iwata T (2010) Comparison study of TEMPO-analogous compounds on oxidation efficiency of wood cellulose for preparation of cellulose nanofibrils. *Polym Degrad Stab* 95:13941398. doi:10.1016/j.polyimdegradstab.2010.01.017
- Kato Y, Matsuo R, Isogai A (2003) Oxidation process of water-soluble starch in TEMPO-mediated system. *Carbohydr Polym* 51:69–75. doi:10.1016/S0144-8617(02)00159-5
- Kato Y, Kaminaga J, Matsuo R, Isogai A (2004) TEMPO-mediated oxidation of chitin, regenerated chitin and *N*-acetylated chitosan. *Carbohydr Polym* 58:421–426. doi:10.1016/j.carbpol.2004.08.011
- Koga H, Tokunaga E, Hidaka M, Umemura Y, Saito T, Isogai A, Kitaoka T (2010) Topochemical synthesis and catalysis of metal nanoparticles exposed on crystalline cellulose nanofibers. *Chem Commun* 46:8567–8569. doi:10.1039/C0CC02754E
- Nemoto J, Soyama T, Saito T, Isogai A (2012) Nanoporous networks prepared by simple air drying of aqueous TEMPO-oxidized cellulose nanofibril dispersions. *Biomacromolecules* 13:943–946. doi:10.1021/bm300041k
- Nicolaou KC, Zhang H, Ortiz A (2009) The true structures of the vannusals, Part I: initial forays into suspected structures and intelligence gathering. *Angew Chem Int Educ* 48: 5642–5647. doi:10.1002/ange.200902028
- Okita Y, Saito T, Isogai A (2010) Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules* 11:1696–1700. doi:10.1021/bm0703970
- Puangsin B, Fujisawa S, Kuramae R, Saito T, Isogai A (2013) TEMPO-mediated oxidation of hemp bast holocellulose to prepare cellulose nanofibrils dispersed in water. *J Polym Environ* 21:555–563. doi:10.1007/s10924-012-0548-9
- Qi ZD, Saito T, Fan Y, Isogai A (2012) Multifunctional coating films by layer-by-layer deposition of cellulose and chitin

- nanofibrils. *Biomacromolecules* 13:553–558. doi:[10.1021/bm201659b](https://doi.org/10.1021/bm201659b)
- Saito T, Isogai A (2004) TEMPO-mediated oxidation of native cellulose. The effect of oxidation conditions on chemical and crystal structures of the water-insoluble fractions. *Biomacromolecules* 5:1983–1989. doi:[10.1021/bm0497769](https://doi.org/10.1021/bm0497769)
- Saito T, Nishiyama Y, Putaux JL, Vignon M, Isogai A (2006) Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules* 7:1687–1691. doi:[10.1021/bm060154s](https://doi.org/10.1021/bm060154s)
- Saito T, Kimura S, Nishiyama Y, Isogai A (2007) Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules* 8:2485–2491. doi:[10.1021/bm0703970](https://doi.org/10.1021/bm0703970)
- Saito T, Hirota M, Tamura N, Kimura S, Fukuzumi H, Heux L, Isogai A (2009) Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions. *Biomacromolecules* 10:1992–1996. doi:[10.1021/bm900414t](https://doi.org/10.1021/bm900414t)
- Saito T, Uematsu T, Kimura S, Enomae T, Isogai A (2011) Self-aligned integration of native cellulose nanofibrils towards producing diverse bulk materials. *Soft Matter* 7:8804–8809. doi:[10.1039/C1SM06050C](https://doi.org/10.1039/C1SM06050C)
- Shibuya M, Tomizawa M, Suzuki I, Iwabuchi Y (2006) 2-Azaadamantane N-oxyl (AZADO) and 1-Me-AZADO: highly efficient organocatalysts for oxidation of alcohols. *J Am Chem Soc* 128:8412–8413. doi:[10.1021/ja0620336](https://doi.org/10.1021/ja0620336)
- Shimotoyodome A, Suzuki J, Kumamoto Y, Hase T, Isogai A (2011) Regulation of postprandial blood metabolic variables by TEMPO-oxidized cellulose nanofibers. *Biomacromolecules* 12:3812–3818. doi:[10.1021/bm2010609](https://doi.org/10.1021/bm2010609)
- Shinoda R, Saito T, Okita Y, Isogai A (2012) Relationship between length and degree of polymerization of TEMPO-oxidized cellulose nanofibrils. *Biomacromolecules* 13:842–849. doi:[10.1021/bm2017542](https://doi.org/10.1021/bm2017542)
- Tamura N, Wada M, Isogai A (2009) TEMPO-mediated oxidation of (1 → 3)-β-D-glucans. *Carbohydr Polym* 77:300–305. doi:[10.1016/j.carbpol.2008.12.040](https://doi.org/10.1016/j.carbpol.2008.12.040)
- Tanaka R, Saito T, Isogai A (2012) Cellulose nanofibrils prepared from softwood cellulose by TEMPO/NaClO/NaClO₂ systems in water at pH 4.8 or 6.8. *Int J Biol Macromol* 51:228–234. doi:[10.1016/j.ijbiomac.2012.05.016](https://doi.org/10.1016/j.ijbiomac.2012.05.016)
- Wu CN, Saito T, Fujisawa S, Fukuzumi H, Isogai A (2012) Ultrastrong and high gas-barrier nanocellulose/clay-layered composites. *Biomacromolecules* 13:1927–1932. doi:[10.1021/bm300465d](https://doi.org/10.1021/bm300465d)