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Oxidized cellulose—Survey of the most recent achievements

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ABSTRACT

The functionalization and particularly the oxidation of cellulose is an intriguing and challenging topic due to the presence of multiple reactive sites, which can undergo specific reactions. The variety of the oxidizing agents used to improve the selectivity and yields of these transformations is illustrated by the steadily growing of the number of publications and patents reported. This paper is focused on the most selective agents for cellulose oxidations, i.e., sodium periodate and stable or non persistent nitroxyl radicals, emphasizing on the most recent developments reported so far.

1. Introduction

The oxidation of cellulosic materials is a pivotal reaction in cellulose chemistry, used to impart special properties on the different cellulosic sorts. The cellulose's chemical modification through oxidation leads to added value products, being a prime factor to determine macroscopic properties and chemical behavior of cellulosic materials.

Moreover, the preparation of oxidized cellulose containing carboxyl groups is of special interest because it has several useful medical applications. Oxidized cellulose is completely bioresorbable and easily degradable under physiological conditions, being widely used as absorbable hemostatic scaffolding material (Dias, Peplow, & Teixeira, 2003; Galgut, 1990), and as a postsurgical adhesion prevention layer (Wiseman, Saferstein, & Wolf, 2002). Other applications of oxidized cellulose as carrier material for agricultural, cosmetic and pharmaceutical applications are reported (Banker & Kumar, 1995; Jin & Wu, 2005). Oxidized cellulose is also used for the treatment of moderate tubal hemorrhage during laparoscopic sterilization of women and for small uterine perforations (Sharma & Malhotra, 2003; Sharma, Malhotra, & Pundir, 2003). As blood clotting agents, oxidized cellulose fibers are superior to oxidized regenerated cellulose (Pameijer & Jensen, 2007). Remarkable application on using oxidized cellulose in osseous regeneration have been reported (Dias et al., 2003), making oxidized cellulose an excellent scaffolding material, able to replace the most widely used material today, i.e., collagen. In the field of separation techniques, the oxidized cellulose exerts a powerful activity to purify and fractionate proteins, including enzymes, hemoglobins, hormones and seed proteins. Oxidized cellulose is extensively used as well in the chromatography of peptides, amino acids, alkaloids, nucleic acids, nucleotides and metallic ions (Guthrie, 1971). In the paper industry, it is well known that carbonyl and carboxyl functionalities play a decisive role in the pulping process and therefore in the final paper properties. For example, sheets made from the partially oxidized fibers (below 8% conversion) experienced higher wet and dry tensile index, presumably due to an increased opportunity of electrostatic interactions between anionic pulp and cationic polyamideamine-epichlorohydrin, which was added as a wet-strength agent (Kitaoka, Isogai, & Onabe, 1999). In the last five years the preparation of individualized, surface-carboxylated cellulose nanofibers from abundant and renewable plant celluloses (Saito, Nishiyama, Putaux, Vignon, & Isogai 2006), lead to new patented applications of the cellulose nanofibers, namely oxygen barrier (Mukai et al., 2010), gel (Isogai, Kado, & Goi, 2010a), thickener (Isogai, Kado, & Goi 2010b), papermaking (Suzuki et al., 2009), composite (Kato, Isogai, Saito, Oaki, & Nishimura, 2010), cosmetic

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(Isogai, Kado, & Goi, 2010c) and flexible display panels, electrical devices (Isogai, Saito, & Fukuzumi, 2011). The main object of the present work is focused on reviewing the most recent papers on cellulose selective oxidation using 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) and *N*-hydroxyphthalimide (NHPI).

2. Cellulose oxidation

Cellulose, because of its polyhydric alcohol structure, is very sensitive to various oxidizing reagents. The extensive modifications which occur during oxidation, give rise to products whose physico-chemical properties strongly depend upon the factors such as: the nature of the oxidizing reagent used, the acidity or basicity of the oxidation medium, and so on. The chemical structure of cellulose is changed in a way that hydroxyl groups are oxidized into the corresponding carbonyl structure, i.e., an aldehyde at C-6 and a ketone at C-2 and C-3, or carboxyl moiety, at C-6. The wide range of potential oxidizing reagents for cellulose can be divided into non-selective (nitrogen oxides (Butrim, Bil'dyukevich, Butrim, & Yurkshtovich, 2007), alkali metal nitrites and nitrates (Painter, 1977), ozone (Johansson & Lind, 2005), permanganates (Manhas, Mohammed, & Khan, 2007), peroxides (Borisov et al., 2004) and selective, such as periodates (Calvini, Gorassini, Luciano, & Franceschi, 2006; Fras et al., 2005; Zimnitski, Yurkshtovich, & Bychkovsky, 2004) and nitroxyl radicals (Biliuta, Fras, Strnad, Harabagiu, & Coseri, 2010; Cato, Kaminaga, Matsuo, & Isogai, 2004; Chang & Robyt, 1996; Coseri et al., 2009; Davis & Flitsch, 1993; De Nooy, Besemer, & Van Beckum, 1995; Gomez-Bujedo, Fleury, & Vignon, 2004; Isogai & Kato, 1998; Tahiri & Vignon, 2000).

The cellulose oxidation in the presence of nitrogen (IV) oxide require high temperature (343 K) and high pressure (70 atm) (Zimnitski et al., 2004). The process is rather slow and yields a material with considerable amount of side products containing nitrogen. Many efforts to limits the non-selective character of the oxidation reaction in presence of the nitrogen oxide has been made. Recently, the cellulose oxidation by nitrogen dioxide dissolved in pressurized carbon dioxide was reported (Camy, Montanari, Rattaz, Vignon, & Condoret, 2009). The global reaction is illustrated in Scheme 1.

However, despite of the "*green*" character of the supercritical CO_2, in the case of cellulose oxidation, its role is not as neutral as expected. The authors (Camy et al., 2009), suspected that CO_2 interacts with NO_2, inhibiting the reactivity of this latter towards cellulose. Moreover, the degree of the cellulose oxidation depends on the amount of the introduced CO_2.

2.1. Periodates as selective agents for cellulose oxidation

Periodates are specific oxidants able to oxidize the vicinal hydroxyl groups at carbon atoms 2 and 3 in an anhydroglucose unit (AGU) of cellulose, forming thus two aldehyde groups. Concomitantly, the carbon—carbon bond between the carbon atoms 2 and 3 is broken, Scheme 2.

In this reaction, as depicted in Scheme 2, when one AGU is oxidized, one mole of iodate is liberated as waste. Therefore, there is an increasing demand to find more efficient oxidation protocols. The efficiency of the periodate oxidation can be improved by using metal chlorides as chemicals able to disrupt the intermolecular hydrogen bond between the oxygen atom O(3) in the cellulose molecule and a hydroxyl hydrogen atom (O(6)H) at the carbon atom 6 in another cellulose molecule (Dumitriu, 2005). For example LiCl, $ZnCl_2$, and $CaCl_2$ improves the periodate oxidation efficiency of cellulose at elevated temperatures, when a molar ratio of 7 between metal chlorides and the anhydroglucose unit (AGU) was used (Sirvio, Hyvakko, Liimatainen, Niinimaki, & Hormi, 2011) due to a better solubility of the cellulose.

The reaction time has a crucial role in the efficiency of this reaction, as the aldehyde content is more than double when the oxidation time is raised from half an hour to one hour, namely, from 0.114 to 0.264 mmol/g in the case of the birch cellulose periodate oxidation (Sirvio et al., 2011).

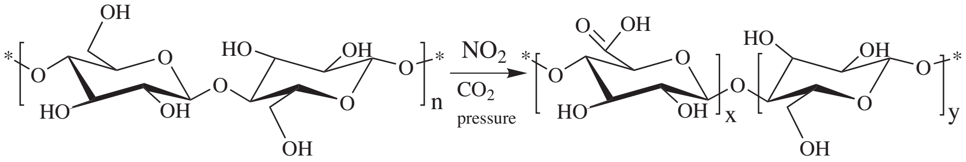
The carbonyl groups in oxidized cellulose can indirectly assessed by using of the so called *copper number*. However this method is not very accurate since the copper number is not directly linked with the quantity of a specific oxidized function. Group-selective fluorescence labeling in combination with multi-detector gel permeation chromatography (multi-angle laser light scattering, refractive index, fluorescence) are valuable and powerful techniques developed in the last years for cellulose analytics (Kostic, Potthast, Rosenau, Kosma, & Sixta, 2006; Potthast et al., 2003).

2.2. Stable nitroxyl radicals as selective agents for cellulose oxidation

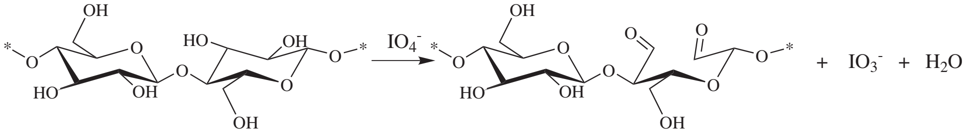
Since 1994, when De Nooy, Besemer, and Van Bekkum (1994), reported for the first time the use of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) for the transformation of primary alcohol groups in polysaccharides to the corresponding polyuronic analogues, this process has become one of the most studied topics in the field of selective oxidation of various polysaccharides in general, cellulose particularly. TEMPO-oxidation process is highly effective in the conversion of high molecular weight polysaccharides and ensures high reaction rates and yields, high selectivity, just modest degradation of polysaccharide through-out process.

Concerning this new approach, Vignon et al. (Gomez-Bujedo et al., 2004), recently reported: "it appeared that this method was very selective, primary hydroxyl groups being exclusively oxidized, whereas secondary hydroxyl groups remained unaffected." The actual oxidizing species is the nitrosonium ion (structure C, Scheme 3), the oxidized form of TEMPO (structure B, Scheme 3). The generation of nitrosonium ion takes place in situ through the reaction of TEMPO with oxidants, such as hypobromide ions, which in turn is being generated from bromide salts and sodium hypochlorite (Scheme 3). Upon acting as oxidant species, C is converted into N-hydroxy-2,2,6,6-tetramethylpiperidine (structure A, Scheme 3), the reduced form of TEMPO. The formation of 1 mole of carboxylic acid requires consumption of 2 mole of oxoammonium cation (C), thus consuming 2 mole of hypohalite for its regeneration from A. To maintain pH of the reaction mixture at optimum value (around 10.5) it is necessary to neutralize the formed carboxylic acid by adding an alkali, Scheme 3. The consumption of NaOH can serve as a measure of the degree of conversion of the primary OH groups to carboxylic ones (Bordenave, Grelier & Coma, 2008). However, it was observed that the consumption of NaOH is higher than the amount of detected COOH groups. That can be explained (Kato, Matsuo, & Isogai, 2003), by the formation of sodium salt of aldehyde hydrate (structure D, Scheme 3). Aldehydes are formed at very early stages of oxidation reactions. Hemiacetals structures could also be formed by intra- or intermolecular reactions of the alcohol and aldehyde groups (Kato et al., 2003). Oxoammonium cation subsequent oxidizes the aldehyde hydrate and/or hemiacetals affords the sodium salt of the acid and the reduced form of TEMPO (structure A). The oxidation cycle is restarted by the regeneration of oxoammonium cation from oxidation of A with a hypohalite.

When native celluloses were subjected to the TEMPO/NaBr/NaClO oxidation at pH 10, the C6 primary hydroxyl groups of cellulose microfibril surfaces were effectively converted to sodium carboxylate groups, maintaining the original fibrous morphologies, crystallinities, and crystal sizes (Araki, Wada, & Kuga, 2001; Saito & Isogai, 2004). The high selectivity of the TEMPO oxidation is substantiated by theoretical calculations (Bailey, Bobbitt, & Wiberg, 2007). According with these calculations,



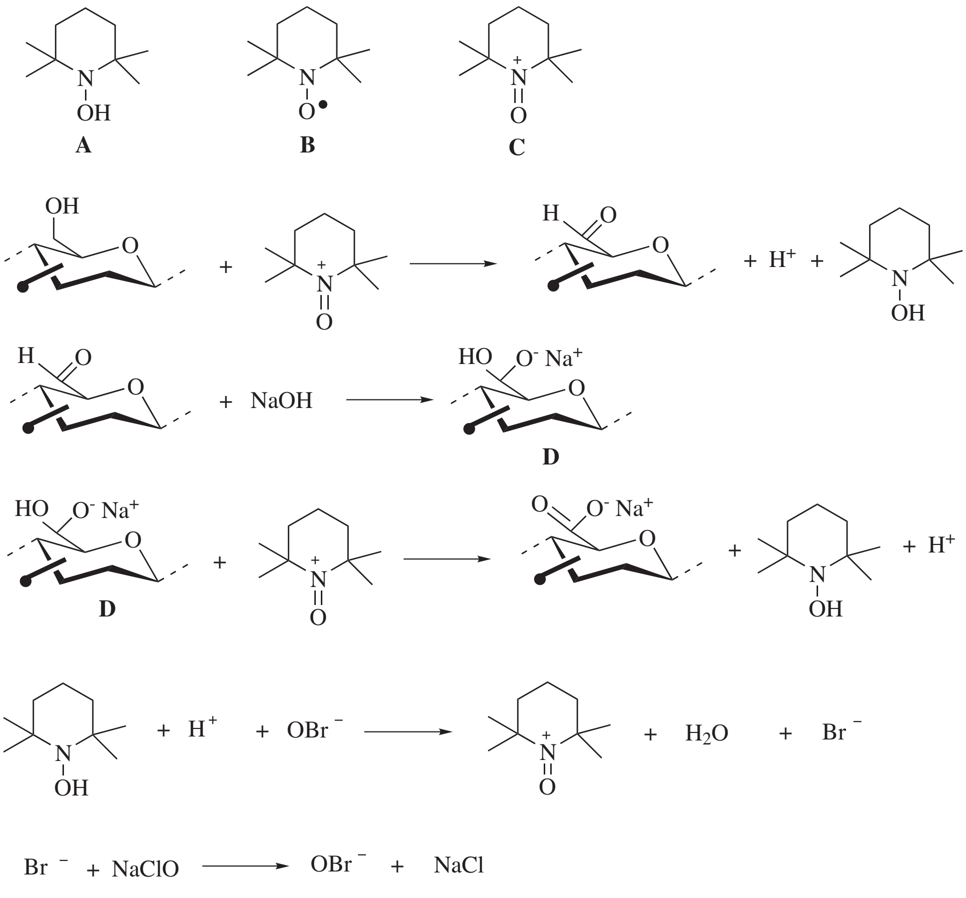
Scheme 1. Cellulose oxidation by nitrogen dioxide in pressurized carbon dioxide.



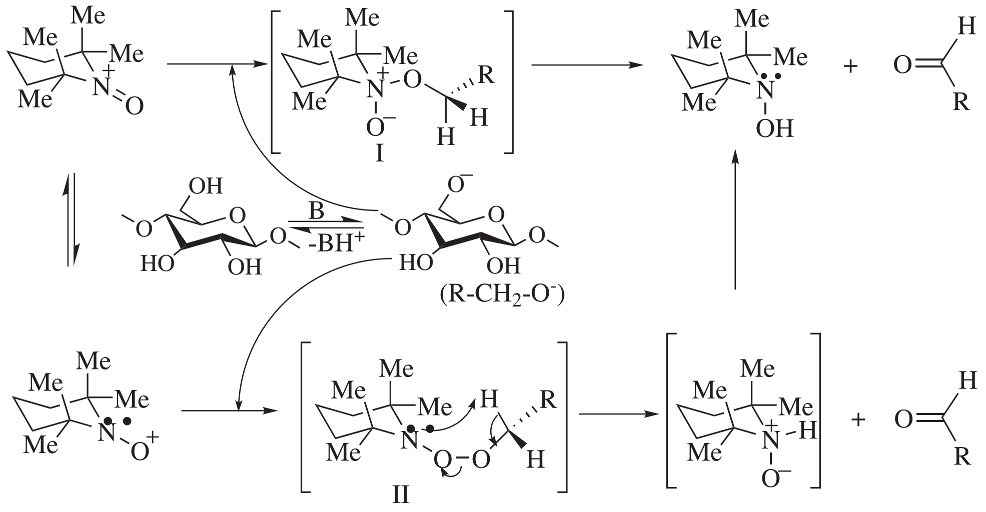
Scheme 2. Periodate oxidation of cellulose.

the cellulose oxidation in alkaline medium could begin with a nucleophilic attack of an alkoxide on the nitrogen or oxygen atom of the strongly polarized N═O bond of nitrosonium cation, which results in the formation of either complex I or II (Scheme 4). The oxidation via peroxide complex is less probable according to calculations, hence the reaction path via complex I is much more possible.

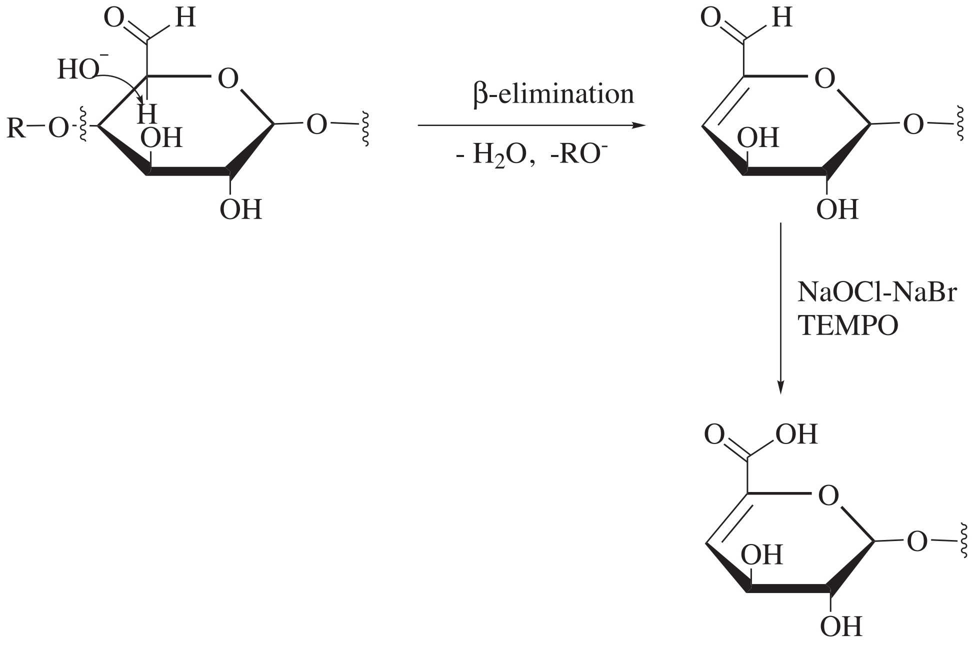
The oxidation of cellulose under the action of NaOCl was usually carried out in alkaline aqueous media in the presence of TEMPO (0.5–4 mol% with respect the substrate) and NaBr (5–30 mol%) as the catalysts (Saito & Isogai, 2004). Tahiri and Vignon (2000), investigated the TEMPO-oxidation of cellulose, and their results showed the lowest depolymerization of the amorphous cellulose when worked at pH 10 and 4 °C. The oxidation at room temperature using TEMPO–NaBr–NaClO system has been used to increase the carboxyl content of several different cellulosic samples by other authors (Isogai & Kato, 1998). They have been found that the key factors controlling the depolymerization of regenerated or mercerized cellulose are the charge of TEMPO, reaction time, and temperature. The depolymerization of cellulose during TEMPO-mediated oxidation has been attributed to sodium hypochlorite present in the system, which cause 2,3-scissions of glucose unit, forming dialdehyde and dicarboxylic groups (De Nooy et al., 1994). The formation of carbonyl groups at C-2, C-3 in glucose unit facilitates depolymerization of celluloses via β-alkoxy fragmentation in alkaline medium (Calvini, Conio, Lorenzoni, & Pedemonte, 2004). Depolymerization during TEMPO-oxidation can occur also via β-elimination reaction, Scheme 5 (Calvini et al., 2004).



Scheme 3. Oxidation scheme of primary hydroxyl groups of cellulose to carboxyl groups by the TEMPO-mediated oxidation.



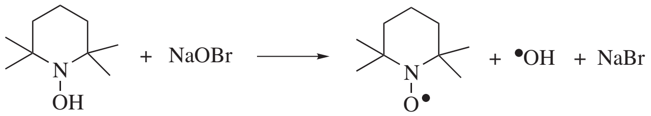
Scheme 4. TEMPO-oxidation reaction mechanism of cellulose under alkaline conditions. B is a base.



Scheme 5. Depolymerization during TEMPO-oxidation via β-elimination reaction. R is a polysaccharide residue.

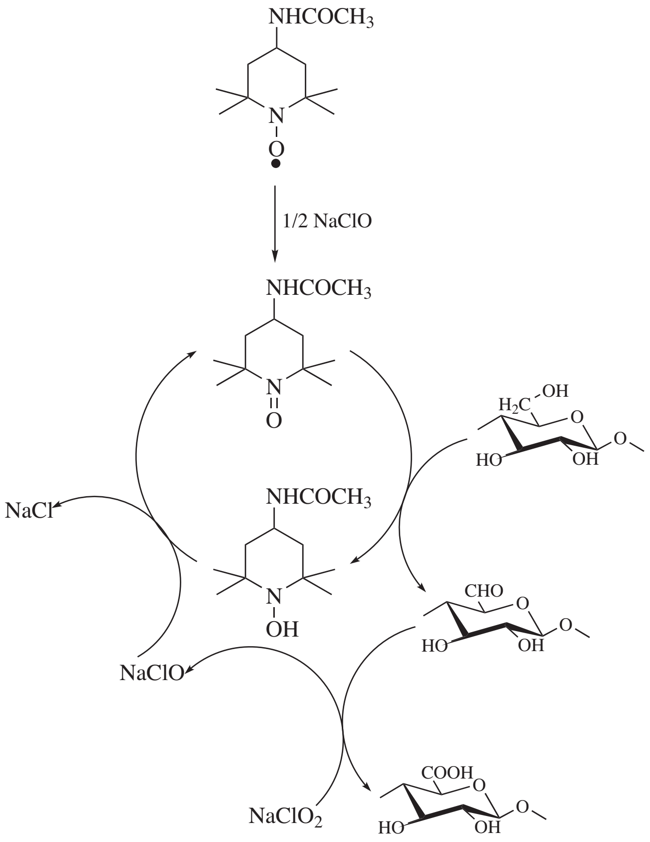
Significant depolymerization of cellouronic acid prepared by TEMPO–NaBr–NaClO system at pH 11 can occur due to the presence of hydroxyl radicals resulted upon reaction between 2,2,6,6-tetramethylpiperidine and sodium hypobromide, Scheme 6 capable of anhydroglucose unit cleavage (Shibata & Isogai, 2003).

Several attempts to overcome the depolymerization issues during TEMPO–NaBr–NaClO oxidation of cellulose have been reported. Thus, working with TEMPO-derivates, such as 4-acetamide-TEMPO/NaClO/NaClO$_2$ system, at 60 °C and pH 4.8–6.8 for 1–5 days (Hirota, Tamura, Saito, & Isogai, 2009a; Hirota, Tamura, Saito, & Isogai, 2009b), high yields of water-soluble cellouronic acids with higher degree of polymerization have been obtained by oxidation of regenerated celluloses. In this case, the NaClO$_2$ acts as a primary oxidant, whereas the NaClO added in catalytic amounts starts the oxidation cycle, Scheme 7. NaClO oxidizes 4-acetamide-TEMPO to the corresponding *N*-oxoammonium ion, which then rapidly oxidizes the primary hydroxyl to aldehyde under acidic conditions, forming the hydroxylamine. The aldehyde is oxidized to carboxyl by the primary oxidant NaClO$_2$, forming NaClO, and the hydroxylamine is oxidized to the *N*-oxoammonium ion again by the NaClO thus generated, Scheme 7.



Scheme 6. Hydroxyl radical generation during TEMPO/NaBr/NaClO oxidation of cellulose.

However, it can be noted, that relatively higher oxidation temperatures, around 40–60 °C and longer oxidation times of 1–5 days are needed. From environmental point of view, it may be better not to use chlorine-containing chemicals such as NaClO or NaClO$_2$. Moreover, side reactions caused by NaClO or NaClO$_2$ cannot be avoided as long as the above TEMPO-mediated oxidation systems are adopted. In the last years, development of suitable



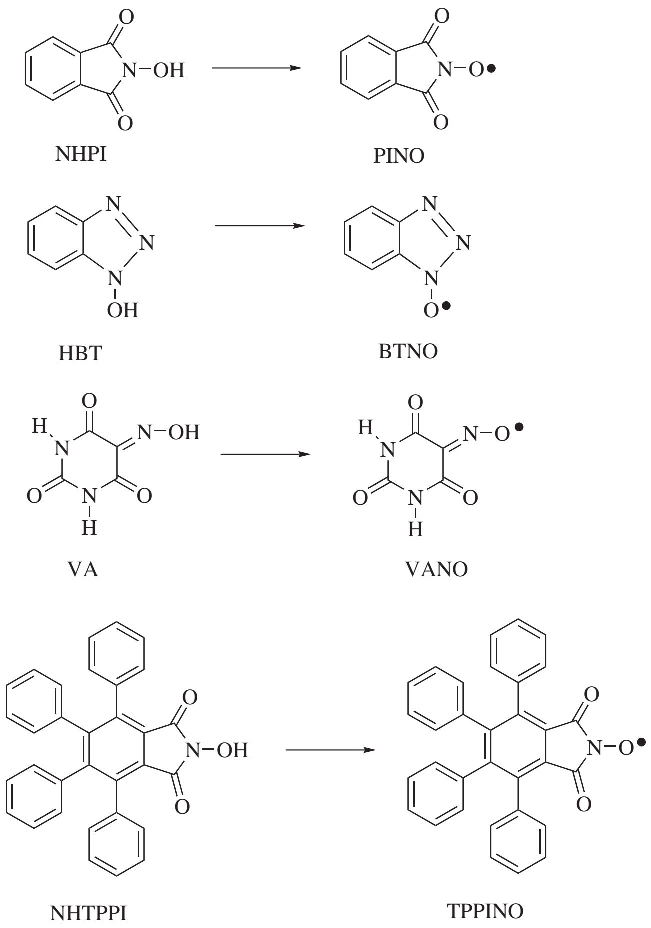
Scheme 7. Catalytic cycle of the 4-acetamide-TEMPO/NaClO/NaClO$_2$ system for oxidation of cellulose.

electrochemical methods for oxidation of organic compounds, that is, electro-organic oxidation, has attracted worldwide attention as *green* chemistry (Danaee, Jafarian, Mirzapoor, Gobal, & Mahjani, 2010; Zhang et al., 2010). The main feature of the electro-organic oxidation of cellulose in the presence of TEMPO is the absence of depolymerization. Recently, the TEMPO-electromediated oxidation of some polysaccharides including regenerated cellulose fiber has been reported (Isogai, Saito, & Isogai, 2010). The reaction takes place in the 0.1 M phosphate buffer at pH 6.8 and room temperature for 45 h. 4-Acetamide-TEMPO catalyst was found to be quite specific, differing from other TEMPO-mediated oxidations. Significant amounts of C6-carboxylate and C6-aldehyde groups (1.1 and 0.6 mmol/g, respectively) were formed. Interestingly, the original fibrous morphology as well as the fine surface structures was maintained.

2.3. Non persistent nitroxyl radicals as selective agents for cellulose oxidation

Among the different kinds of catalysts reported in the literature, *N*-hydroxyphthalimide (NHPI), Scheme 8, is another catalyst having excellent performance in oxidation reactions (Coseri, 2007, 2008, 2009a, 2009b; Coseri, Mendenhall, & Ingold, 2005). These oxidative reactions occur via the intermediary phthalimide *N*-oxyl (PINO) radical.

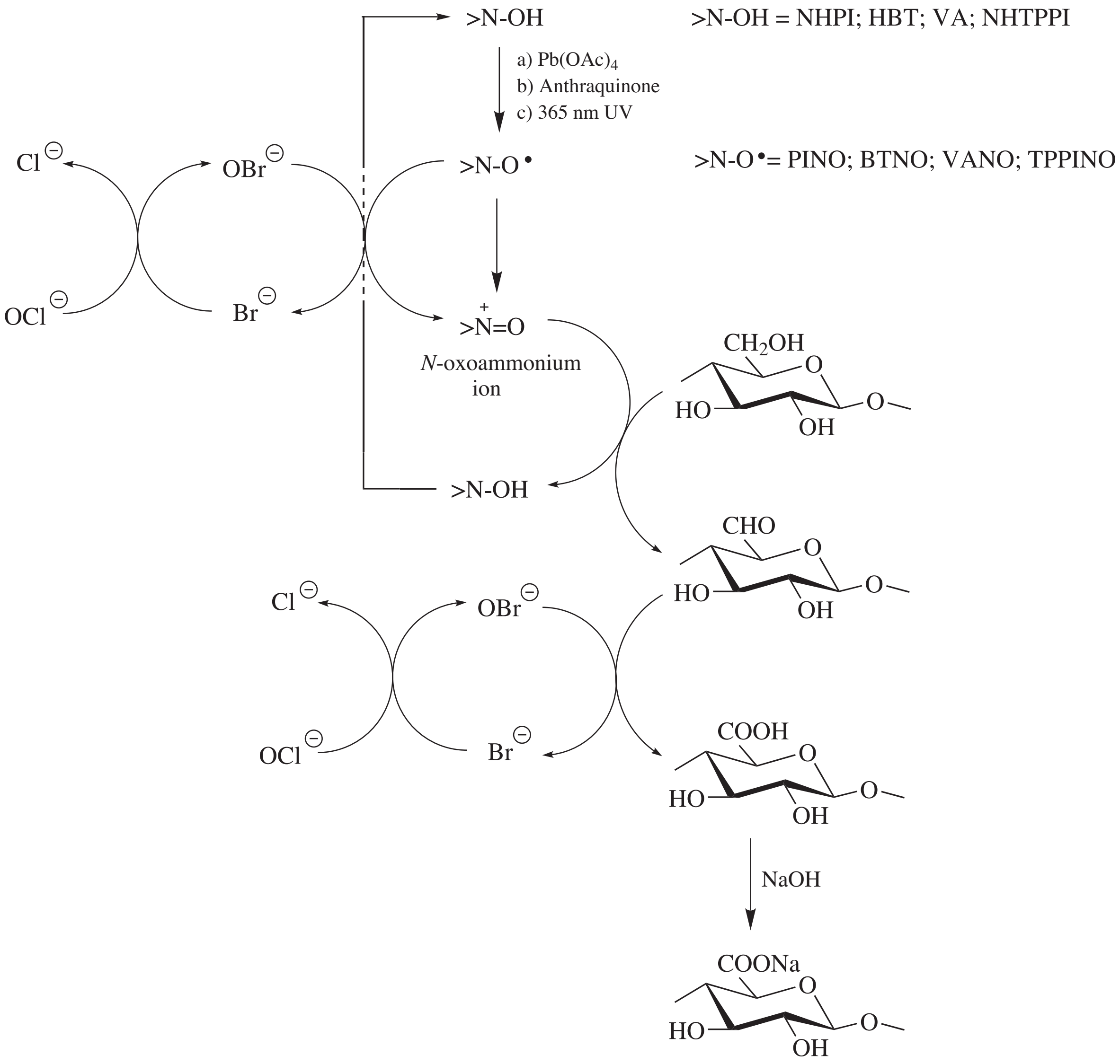
The mild and selective oxidation of viscose fibers in the presence of PINO radical (in situ generated from NHPI and various cocatalysts, i.e., lead tetraacetate, cerium (IV) ammonium nitrate, anthraquinone) with very low amount of sodium hypochlorite and sodium bromide was very recently reported (Coseri et al., 2009). Soon after, several other nonpersistent free radicals, generated in situ from their OH correspondents: *N*-hydroxybenzotriazole (HBT), violuric acid (VA), and *N*-hydroxy-3,4,5,6-tetraphenylphthalimide (NHTPPI), Scheme 8, had shown their efficiency for the cellulose fibers oxidation at pH 10 and room temperature in the presence of dilute solution of NaClO and NaBr (Coseri et al., 2009). The reaction mechanism involves in the first step the activation of the parent hydroxyl precursors through their transformation into corresponding free radical compounds. In the presence of hypobromide ions, these nitroxyl radicals are oxidized to *N*-oxoammonium ions, which are actually the oxidizing species. At this point, the primary —OH groups of cellulose are converted into carboxylic groups, process which proceeds via aldehyde stage. However, the aldehyde groups are undetectable in the final products, being rapidly oxidized to carboxylic groups, in the presence of hypobromide ions. Due to the presence of NaOH, the carboxylic groups are obtained in their sodium salt form, Scheme 9.



Scheme 8. The —OH bearing precursors for the nonpersistent free radicals generation.

This process appears to be very selective and the morphology of the resulted oxidized fibers seems to be unchanged, Fig. 1.

Both stable and non persistent nitroxyl radicals used as mediators require the presence of quite large amount of sodium bromide (between 10 and 30%) in order to restart the catalytic cycle. However, from both, industrial and environmental points of view, a process without sodium bromide would be a better alternative to those existing today. Few reports on bromide-free oxidizing systems are published, only on different polysaccharides than cellulose (Bragd, Besemer, & Van Bekkum, 2000). To overcome this drawback, a new oxidizing protocol for viscose fibers has been proposed (Simionescu, Biliuta, & Coseri, Unpublished results). This new protocol mimic the natural oxidative processes, involving the presence of Cu(II) ions which are constituents of many enzymes able to



Scheme 9. Oxidation scheme of cellulose fibers performed by NHPI, HBT, VA and NHTPPI.

catalyze the aerobic oxidation of hydroxyl groups (Fabbrini, Galli, & Gentili, 2002; Sheldon, Arends, Dijksman, 2000; Whittaker et al., 2000). The presence of the Cu(II) ions has a double role, first to convert NHPI to PINO radical, and then to oxidize the PINO to oxoammonium PINO$^+$, the actual oxidizing species, Scheme 10. Moreover, the formation of reduced Cu(I) allow further reoxidation of NHPI, thus minimizing the catalyst loading (Nechab, Einhorn, & Einhorn, 2004). The oxoammonium ions will convert the primary

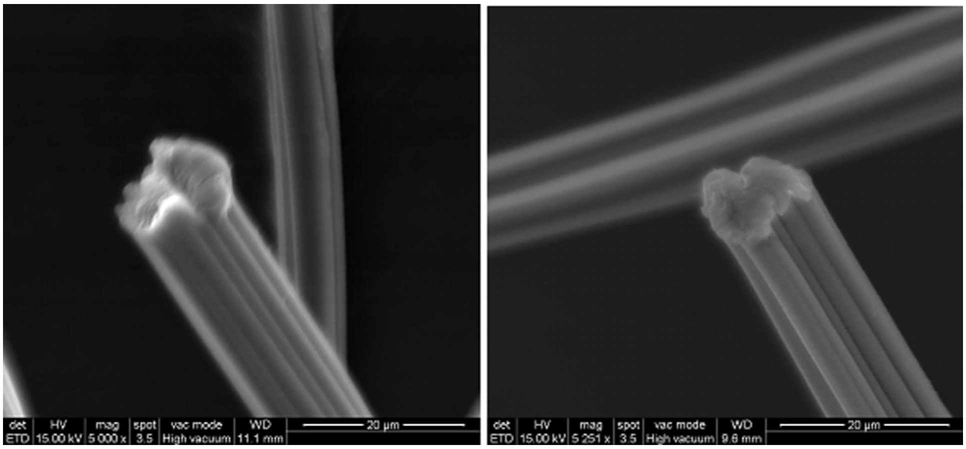
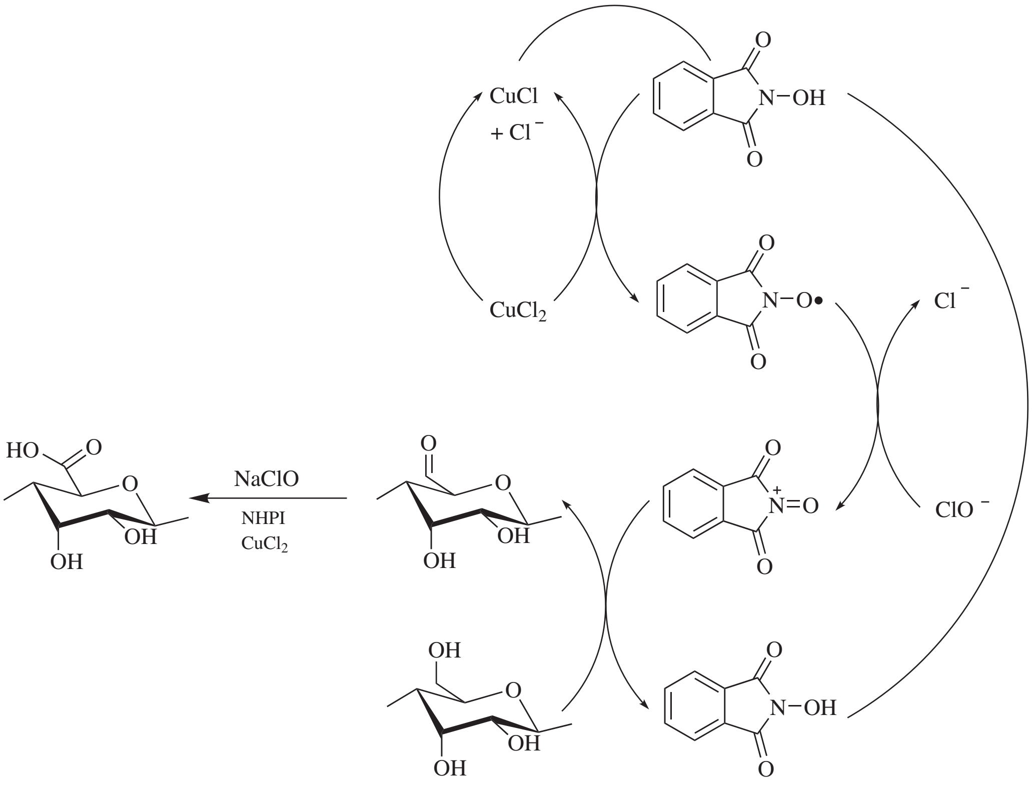


Fig. 1. ESEM images of viscose fibers before (left) and after oxidation with NHPI/anthraquinone/NaClO/NaBr for 2 h (right).

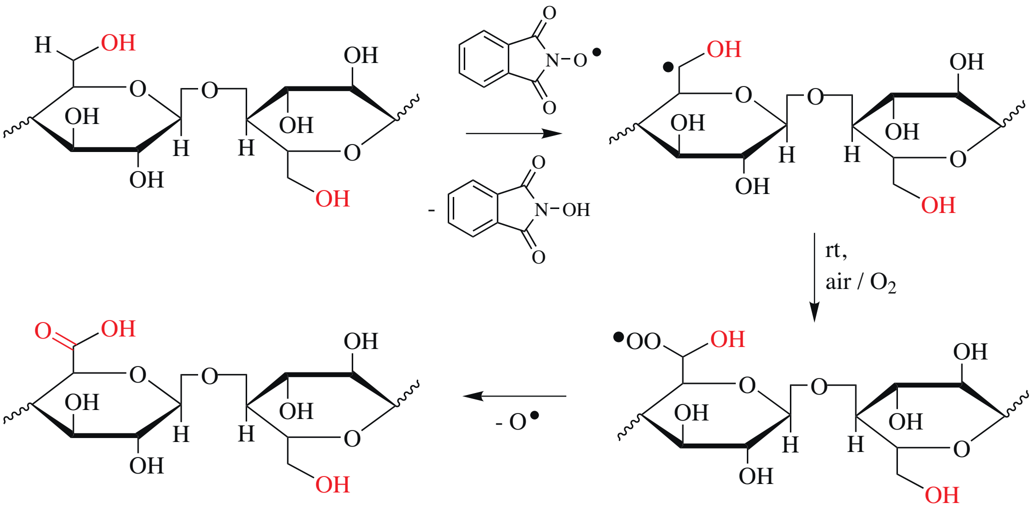


Scheme 10. NHPI–$CuCl_2$–NaClO oxidation cycle of viscose fibers.

OH groups from cellulose to aldehyde groups, the catalytic cycle allowing the further oxidation to carboxylic groups. The amount of negatively charged groups as determined by potentiometric titration have been found to be 80 mmol/kg for the viscose fibers oxidized for 2 h.

Another approach of using NHPI as catalyst and molecular oxygen as ultimate oxidizing agent for the oxidation of viscose and modal fibers has been recently reported (Biliuta, Fras, Harabagiu, & Coseri, 2011). In this case, the oxidation reaction takes place at room temperature, at neutral pH, and converts moderately the primary OH groups from cellulose to carboxylic ones. The key species of this process is PINO radical generated in situ. The potency of PINO to abstract a hydrogen atom from the CH_2 group is related with the bond dissociation enthalpy value (BDE) of NHPI, i.e., 88 kcal mol^{-1}. This value is much higher than the BDE value of the N-OH precursor of TEMPO, which is only 69 kcal mol^{-1} (Astolfi et al., 2005), TEMPO thus being inactive by radical mechanism with cellulosic substrates. After PINO abstract hydrogen, the carbon centered radical is trapped by dioxygen and form the oxygenated products, Scheme 11.

Notably, the degree of polymerization and molecular mass of original materials are preserved during the oxidation reaction, only modest decreases of these parameters being observed.



Scheme 11. Cellulose oxidation in the presence of NHPI and oxygen.

3. Conclusions and future work

There is still much effort to carry in the direction of using oxidizing agents like nitrogen oxides, permanganates, peroxides for cellulose, to find the proper reaction conditions (temperature, pressure, appropriate solvents) in order to diminish the non-selective character of those. The introduction of supercritical carbon dioxide as reaction solvent could be a step forward, especially for biomedical applications where the product purity must be strictly ensured. Sodium periodate is one of the most selective reagents for the cellulose oxidation to 2,3-dialdehyde products, which are subsequently convert to 2,3-dicarboxycellulose. The efficiency of this reaction can be increased by improving the solubility of the substrate either by using metal salts able to disrupt the intermolecular hydrogen bond, or by using imidazole-based solvents. Stable and non persistent nitroxyl radicals are the most effective mediators to convert primary OH groups in cellulose to carboxylic moieties in the presence of sodium bromide and sodium hypochlorite. The reaction mechanism implies the presence of the corresponding oxoammonium ion which is the actual oxidizing agent. The oxidation efficiency depends thus on redox potential of the monoelectronic oxidation to the oxoammonium form ($>\mathrm{N}{=}\mathrm{O}^+$). PINO has an redox potential of 1.09 V/NHE, since TEMPO's redox potential is only 0.69 V/NHE (Astolfi et al., 2005), suggesting that PINO could be more efficient than TEMPO in ionic mechanisms of cellulose oxidation. A radical mechanism for the cellulose oxidation is also possible when NHPI is used in the presence of molecular oxygen, in the absence of both sodium bromide and sodium hypochlorite. According with the BDE's values, TEMPO is unable to react by radical mechanism due to the lower BDE value of the parent hydroxyl amine. Some drawbacks should also be considered: TEMPO is rather an expensive reagent also needs larger amounts of sodium bromide to mediate the oxidation reaction; NHPI is poorly soluble in water and requires an additional reagent to form the active PINO. To better understand the action mechanism of TEMPO and NHPI on cellulose oxidation, a comparative study will definitely solve more questioning points which are unsolved. Therefore we envisage an oxidation protocol performed under the same reaction conditions on various sorts of cellulosic materials in the presence of either TEMPO or NHPI. Fully analyses of the resulted oxidized products in terms of negatively charged group formation, changes in crystallinity and morphology, degree of depolymerization, will bring valuable information on the efficiency, selectivity and mildness of the used mediator.

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References

Araki, J., Wada, M., & Kuga, S. (2001). Steric stabilization of a cellulose microcrystal suspension by poly(ethylene glycol) grafting. *Langmuir*, *17*, 21–27.

Astolfi, P., Brandi, P., Galli, C., Gentili, P., Gerini, M. F., Greci, L., et al. (2005). New mediators for the enzyme laccase: Mechanistic features and selectivity in the oxidation of non-phenolic substrates. *New Journal of Chemistry*, *29*, 1308–1317.

Bailey, W. F., Bobbitt, J. M., & Wiberg, K. B. (2007). Mechanism of the oxidation of alcohols by oxoammonium cations. *The Journal of Organic Chemistry*, *72*, 4504–4509.

Banker, G. S., & Kumar, V. (1995). Microfibrillated oxycellulose. US Patent 5,405,953.

Biliuta, G., Fras, L., Harabagiu, V., & Coseri, S. (2011). Mild oxidation of cellulose fibers using dioxygen as ultimate oxidizing agent. *Digest Journal of Nanomaterials and Biostructures*, *6*, 291–297.

Biliuta, G., Fras, L., Strnad, S., Harabagiu, V., & Coseri, S. (2010). Oxidation of cellulose fibers mediated by nonpersistent nitroxyl radicals. *Journal of Polymer Science Part A: Polymer Chemistry*, *48*, 4790–4799.

Bordenave, N., Grelier, S., & Coma, V. (2008). Advances on selective C-6 oxidation of chitosan by TEMPO. *Biomacromolecules*, *9*, 2377–2382.

Borisov, I. M., Shirokova, E. N., Mudarisova, R. Kh., Muslukhov, R. R., Zimin Yu, S., Medvedeva, S. A., et al. (2004). Kinetics of oxidation of an arabinogalactan from larch (*Larix sibirica* L.) in an aqueous medium in the presence of hydrogen peroxide. *Russian Chemical Bulletin*, *53*, 318–324.

Bragd, P. L., Besemer, A. C., & Van Bekkum, H. (2000). Bromide-free TEMPO-mediated oxidation of primary alcohol groups in starch and methyl α-D-glucopyranoside. *Carbohydrate Research*, *328*, 355.

Butrim, S. M., Bil'dyukevich, T. D., Butrim, N. S., & Yurkshtovich, T. L. (2007). Structural modification of potato starch by solutions of nitrogen (IV) oxide in CCl_4. *Chemistry of Natural Compounds*, *43*, 302–305.

Calvini, P., Conio, G., Lorenzoni, M., & Pedemonte, E. (2004). Viscometric determination of dialdehyde content in periodate oxycellulose. Part I: Methodology. *Cellulose*, *11*, 99–107.

Calvini, P., Gorassini, A., Luciano, G., & Franceschi, E. (2006). FTIR and WAXS analysis of periodate oxycellulose: Evidence for a cluster mechanism of oxidation. *Vibrational Spectroscopy*, *40*, 177–183.

Camy, S., Montanari, S., Rattaz, A., Vignon, M., & Condoret, J. S. (2009). Oxidation of cellulose in pressurized carbon dioxide. *Journal of Supercritical Fluids*, *51*, 188–196.

Cato, Y., Kaminaga, J., Matsuo, R., & Isogai, A. (2004). TEMPO-mediated oxidation of chitin, regenerated chitin and *N*-acetylated chitosan. *Carbohydrate Polymers*, *58*, 421–426.

Chang, P. S., & Robyt, J. F. (1996). Oxidation of primary alcohol groups of naturally occurring polysaccharides with 2,2,6,6-tetramethyl-1-piperidine oxoammonium ion. *Journal of Carbohydrate Chemistry*, *15*, 819–830.

Coseri, S. (2007). A new and efficient heterogeneous system for the phthalimide-*N*-oxyl radical (PINO) generation. *European Journal of Organic Chemistry*, *2007*, 1725–1729.

Coseri, S. (2008). N-hydroxyphthalimide (NHPI)/lead tetraacetate, a peculiar system for the phthalimide-*N*-oxyl (PINO) radical generation. *Mini-Reviews in Organic Chemistry*, *5*, 222–227.

Coseri, S. (2009a). Phthalimide-*N*-oxyl (PINO) radical, a powerful catalytic agent; its generation and versatility towards various organic substrates. *Catalysis Reviews: Science and Engineering*, *51*, 218–292.

Coseri, S. (2009b). N-hydroxyphthalimide (NHPI)/lead tetraacetate reactions with cyclic and acyclic alkenes. *Journal of Physical Organic Chemistry*, *22*, 397–402.

Coseri, S., Mendenhall, G. D., & Ingold, K. U. (2005). Mechanisms of reactions of aminoxyl (nitroxide), iminoxyl, and imidoxyl radicals with alkenes and evidence that in the presence of lead tetraacetate, N-hydroxyphthalimide reacts with alkenes by both radical and nonradical mechanisms. *The Journal of Organic Chemistry*, *70*, 4629–4636.

Coseri, S., Nistor, G., Fras, L., Strnad, S., Harabagiu, V., & Simionescu, B. C. (2009). Mild and selective oxidation of cellulose fibers in the presence of *N*-hydroxyphthalimide. *Biomacromolecules*, *10*, 2294–2299.

Danaee, I., Jafarian, M., Mirzapoor, A., Gobal, F., & Mahjani, M. G. (2010). Electrooxidation of methanol on NiMn alloy modified graphite electrode. *Electrochimica Acta*, *55*, 2093–2100.

Davis, N. J., & Flitsch, S. L. (1993). Selective oxidation of monosaccharide derivatives to uronic acids. *Tetrahedron Letters*, *34*, 1181–1184.

De Nooy, A. E., Besemer, A. C., & Van Beckum, H. (1995). Highly selective nitroxyl radical-mediated oxidation of primary alcohol groups in water-soluble glucans. *Carbohydrate Research*, *269*, 89–98.

De Nooy, A. E. J., Besemer, A. C., & Van Bekkum, H. (1994). Highly selective TEMPO mediated oxidation of primary alcohol groups in polysaccharides. *Recueil des Travaux Chimiques des Pays-Bas*, *113*, 165–166.

Dias, G. J., Peplow, P. V., & Teixeira, F. (2003). Osseous regeneration in the presence of oxidized cellulose and collagen. *Journal of Materials Science: Materials in Medicine*, *14*, 739–745.

Dumitriu, S. (2005). *Polysaccharides: Structural diversity and functional versatility*. New York: Marcel Dekker.

Fabbrini, M., Galli, C., & Gentili, P. (2002). Comparing the catalytic efficiency of some mediators of laccase. *Journal of Molecular Catalysis B: Enzymatic*, *16*, 231–240.

Fras, L., Johansson, L.-S., Stenius, P., Laine, J., Stana-Kleinschek, K., & Ribitsch, V. (2005). Analysis of the oxidation of cellulose fibers by titration and XPS. *Colloids and Surfaces A: Physicochemial and Engineering Aspects*, *260*, 101–108.

Galgut, P. N. (1990). Oxidized cellulose mesh. I: Biodegradable membrane in periodontal surgery. *Biomaterials*, *11*, 561–564.

Gomez-Bujedo, S., Fleury, E., & Vignon, M. R. (2004). Preparation of cellouronic acids and partially acetylated cellouronic acids by TEMPO/NaClO oxidation of water-soluble cellulose acetate. *Biomacromolecules*, *5*, 565–571.

Guthrie, J. D. (1971). Ion-exchange celluloses. In N. M. Bikales, & L. Segal (Eds.), *Cellulose and cellulose derivatives*. New York: Wiley-Interscience.

Hirota, M., Tamura, N., Saito, T., & Isogai, A. (2009a). Oxidation of regenerated cellulose with $NaClO_2$ catalyzed by TEMPO and NaClO under acid-neutral conditions. *Carbohydrate Polymers*, *78*, 330–335.

Hirota, M., Tamura, N., Saito, T., & Isogai, A. (2009b). Preparation of polyuronic acid from cellulose by TEMPO-mediated oxidation. *Cellulose*, *16*, 841–851.

Isogai, A., Kado, H., & Goi, Y. (2010a). *Gel composition containing oxidized cellulose fibers with good resistance to salts and ionic surfactants*. Japan: Daiichi Kogyo Seiyaku Co., Ltd. Application: JP, 43 pp.

Isogai, A., Kado, H., & Goi, Y. (2010b). *Spray compositions containing oxidized cellulose fibers as thickener, and sprayers therefore*. Japan: Daiichi Kogyo Seiyaku Co., Ltd. Application: JP, 25 pp.

Isogai, A., Kado, H., & Goi, Y. (2010c). *Cosmetics compositions containing oxidized cellulose fibers and functional components*. Japan: Daiichi Kogyo Seiyaku Co., Ltd. Application: JP, 19 pp.

Isogai, A., & Kato, Y. (1998). Preparation of polyuronic acid from cellulose by TEMPO-mediated oxidation. *Cellulose*, *5*, 153–164.

Isogai, A., Saito, T., & Fukuzumi, H. (2011). *Nanoscale*, *3*, 71–85.

Isogai, T., Saito, T., & Isogai, A. (2010). TEMPO electromediated of some polysaccharides including regenerated cellulose fiber. *Biomacromolecules*, *11*, 1593–1599.

Jin, B., & Wu, W.-T. (2005). Compositions for veterinary and medical applications. PCT WO/2005/020997.

Johansson, E. E., & Lind, J. (2005). Free radical mediated cellulose degradation during high consistency ozonation. *Journal of Wood Chemistry and Technology*, *25*, 171–186.

Kato, T., Isogai, A., Saito, T., Oaki, Y., & Nishimura, T. (2010). *Composite material, functional material, process for producing composite material, and process for producing composite-material thin film. Chemical Indexing Equivalent to 152:264550 (WO) pp*. Japan: Tokyo University. Application: JP, 38 pp.

Kato, Y., Matsuo, R., & Isogai, A. (2003). Oxidation process of water-soluble starch in TEMPO-mediated system. *Carbohydrate Polymers*, *51*, 69–75.

Kitaoka, T., Isogai, A., & Onabe, F. (1999). Chemical modification of pulp fibers by TEMPO-mediated oxidation. *Nordic Pulp and Paper Research Journal*, *14*, 279–284.

Kostic, M., Potthast, A., Rosenau, T., Kosma, P., & Sixta, H. (2006). A novel approach to determination of carbonyl groups in DMAc/LiCl-insoluble pulps by fluorescence labeling. *Cellulose*, *13*, 429–435.

Manhas, M. S., Mohammed, F., & Khan, Z. (2007). A kinetic study of oxidation of β-cyclodextrin by permanganate in aqueous media. *Colloids and Surfaces A: Physicochemial and Engineering Aspects*, *295*, 165–171.

Mukai, K., Kumamoto, Y., Isogai, A., Meiwa, Z., Maezawa, T., & Ugajin, T. (2010). *Gas-barrier material, gas-barrier molded article, and method for producing the gas-barrier molded article*. Japan: Kao Corporation. Application: WO, 108 pp.

Nechab, M., Einhorn, C., & Einhorn, J. (2004). New aerobic oxidation of benzylic compounds: Efficient catalysis by N-hydroxy-3,4,5,6-tetraphenyl phthalimide (NHTPPI)/CuCl under mild conditions and low catalyst loading. *Chemical Communications*, 1500–1501.

Painter, T. J. (1977). Preparation and periodate oxidation of C-6-oxycellulose: Conformational interpretation of hemiacetal stability. *Carbohydrate Research*, *55*, 95–103.

Pameijer, C. H., & Jensen, S. (2007). Agents and devices for providing blood clotting functions to wounds. US Patent Appl. 20,070,190,110.

Potthast, A., Rohrling, J., Rosenau, T., Borgards, A., Sixta, H., & Kosma, P. (2003). A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 3: Monitoring oxidative processes. *Biomacromolecules*, *4*, 743–749.

Saito, A., Nishiyama, Y., Putaux, J. L., Vignon, M., & Isogai, A. (2006). Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules*, *7*, 1687–1691.

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.

Sharma, J. B., & Malhotra, M. (2003). Topical oxidized cellulose for tubal hemorrhage hemostasis during laparoscopic sterilization. *International Journal of Gynecology and Obstetrics*, *82*, 221–222.

Sharma, J. B., Malhotra, M., & Pundir, P. (2003). Laparoscopic oxidized cellulose (Surgicel) application for small uterine perforations. *International Journal of Gynecology and Obstetrics*, *83*, 271–275.

Sheldon, R. A., Arends, I. W. C. E., & Dijksman, A. (2000). New developments in catalytic alcohol oxidations for fine chemical synthesis. *Catalysis Today*, *57*, 157–166.

Shibata, I., & Isogai, A. (2003). Depolymerization of cellouronic acid during TEMPO-mediated oxidation. *Cellulose*, *10*, 151–158.

Simionescu, C. B., Biliuta, G., & Coseri, S. Bromide-free oxidizing system for cellulose fibers functionalization, Unpublished results.

Sirvio, J., Hyvakko, U., Liimatainen, H., Niinimaki, J., & Hormi, O. (2011). Periodate oxidation of cellulose at elevated temperatures using metal salts as cellulose activators. *Carbohydrate Polymers*, *83*, 1293–1297.

Suzuki, A., Madawaska, S., Katsukawa, S., Abe, H., Iijima, Y., & Isogai, A. (2009). *Cellulose nanofiber-containing base paper for processing paper*. Japan: Nippon Paper Industries Co., Ltd. Application: JP, 10 pp.

Tahiri, C., & Vignon, M. R. (2000). TEMPO-oxidation of cellulose: Synthesis and characterisation of polyglucuronans. *Cellulose*, *7*, 177–188.

Whittaker, M. M., Ekberg, C. A., Peterson, J., Sendova, M. S., Day, E. P., & Whittaker, J. W. (2000). Spectroscopic and magnetochemical studies on the active site copper complex in galactose oxidase. *Journal of Molecular Catalysis B: Enzymatic*, *8*, 3–15.

Wiseman, D. M., Saferstein, L., & Wolf, S. (2002). Bioresorbable oxidized cellulose composite material for prevention of postsurgical adhesions. US Patent 6,500,777.

Zhang, Y., Zhang, L., Shuang, S., Feng, F., Qiao, J., Guo, Y., et al. (2010). Electro-oxidation of methane on roughened palladium electrode in acidic electrolytes at ambient temperatures. *Analytical Letters*, *43*, 1055–1065.

Zimnitski, D. S., Yurkshtovich, T. L., & Bychkovsky, P. M. (2004). Synthesis and characterization of oxidized cellulose. *Journal of Polymer Science Part A: Polymer Chemistry*, *42*, 4785–4791.