Carbohydrate Polymers 91 (2013) 502–507

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Comparison study of TEMPO and phthalimide-*N*-oxyl (PINO) radicals on oxidation efficiency toward cellulose

Gabriela Biliuta[a,1], Lidija Fras[b,1], Mioara Drobota[a,1], Zdenka Persin[b,c,1], Tatjana Kreze[b,1], Karin Stana-Kleinschek[b,c,1], Volker Ribitsch[d,1], Valeria Harabagiu[a,1], Sergiu Coseri[a,*,1]

[a] *"Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, 700487 Iasi, Romania*
[b] *University of Maribor, Institute for Engineering Materials and Design, Faculty of Mechanical Engineering, Laboratory for Characterization and Processing of Polymers, Smetanova ulica 17, SI-2000 Maribor, Slovenia*
[c] *Centre of Excellence for Polymer Materials and Technologies, Tehnoloski Park 24, SI-1000 Ljubljana, Slovenia*
[d] *Institute of Chemistry, Rheology & Colloid Science, Karl Franzens University, Heinrichstraβe 28, 8010 Graz, Austria*

ARTICLE INFO

Article history:
Received 4 June 2012
Received in revised form 10 August 2012
Accepted 14 August 2012
Available online 24 August 2012

Keywords:
Cellulose fibers
Oxidation
Surface modification
Nitroxyl radicals
Viscose fibers
TEMPO
N-hydroxyphthalimide

ABSTRACT

Regenerated cellulose fibers, type viscose, have been oxidized with sodium hypochlorite and catalytic amounts of sodium bromide by using two different protocols: first, involving the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) and second, employing *N*-hydroxyphthalimide (NHPI). The reactions were carried out at room temperature and pH = 10.5 for 2.5 h. Viscose oxidized samples were analyzed and compared in terms of the negative charged groups content, as determined by potentiometric titration and methylene blue adsorption, morphologies and crystallinities changes, as well as changes in the degree of polymerization. The highest content of the carboxylic groups and the best preservation of the morphology and molecular weight of the original material have been found in the case of using NHPI/anthraquinone as oxidation mediators. TEMPO-mediated oxidation leads to the highest depolymerization and cause significant degradation of the cellulosic material.

1. Introduction

The oxidation of primary hydroxyl groups in polysaccharides is one of the most studied route of their functionalization, which yields valuable oxidized products such as polyuronic acids and aldehydes, to be further used in various fields as drugs, dyes, glues, thickeners, additives to foodstuffs, cosmetics and many other (Dumitriu, 1998). The oxidation of polysaccharides skeleton can be achieved by using different oxidizing agents (Ponedel'kina, Yu Khaibrakhmanova, & Odinokov, 2010), the majority of them are unfortunately non-specific, and therefore the oxidation reaction is strongly affected by side-products formation. For specific applications of cellulose, in medical or high tech devices, is highly required to obtain materials with improved properties controlled by the selectivity of the process and by the degree of oxidation.

Nanofibrillated cellulosic materials have become a hot topic due to their higher reinforcing potential confirmed by the huge enhancement in the tensile modulus (Besbes, Alila, & Boufi, 2011). Cellulosic bionanofibers have also unique biological activities. It was very recently reported (Shimotoyodome, Suzuki, Kumamoto, Hase, & Isogai, 2011), that cellulose nanofibers administered with glucose and glyceryl trioleate to mice reduce the postprandial blood glucose, plasma insulin, glucose-dependent insulinotropic polypeptide, and triglyceride concentrations. The nanofibrillated material consist of interconnected fibrils and microfibrils, 10–100 nm width and lengths ranging from hundreds of nm to several micrometers depending on the source of cellulose. One of the easiest ways toward preparation of individual nanofibrillated cellulose is to use the selective oxidation of primary hydroxyl groups in cellulose, method recently introduced by Isogai et al. (Isogai, Saito, & Fukuzumi, 2011; Saito & Isogai, 2004; Saito, Kimura, Nishymama, & Isogai, 2007; Saito et al., 2009). Currently, there are two major routes to selective convert the primary hydroxyl groups in cellulose to carboxylic ones: (a) first protocol involved cyclic sterically hindered stable nitroxyl radicals, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (1), and derivatives, 2,2,5,5-tetramethylpyrrolidine-1-oxyl (2), its 3-carboxylic (or amide) derivatives and 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrroline-1-oxyl (3), Fig. 1.

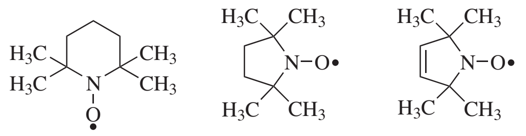
These compounds are uncommonly stable due to the lack of any α-hydrogen atoms, which precludes disproportionation of these

---

* Corresponding author. Tel.: +40 232 217454; fax: +40 232 211299.
E-mail address: coseris@icmpp.ro (S. Coseri).

[1] Members of European Polysaccharides Network of Excellence (EPNOE).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.08.047



1 2 3

Fig. 1. Some stable nitroxyl radicals used for the cellulose selective oxidation.

radicals. The introduction of TEMPO-mediated oxidation, in which sodium hypochlorite and sodium bromide were used as reagents in aqueous media, was first applied to cellulose by Isogai and Kato as early as 1998 (Isogai & Kato, 1998).

(b) The second protocol for the mild and selective oxidation of cellulose was very recently proposed by Coseri et al. (Biliuta, Fras, Strnad, Harabagiu, & Coseri, 2010; Biliuta, Fras, Strnad, Harabagiu, & Coseri, 2011; Coseri et al., 2009). In this case, the non persistent nitroxyl radicals generated in situ from their hydroxyl precursors and an appropriate cocatalyst, are efficient mediators for cellulose oxidation. Some of the most known mediators for this kind of transformation are: *N*-hydroxyphthalimide (NHPI), *N*-hydroxybenzotriazole (HBT), and violuric acid (VA), Fig. 2. The use of these non persistent nitroxyl radicals, especially NHPI, becomes lately one of the most reliable method for the conversion of the OH groups to aldehydes or carboxylic acids for a wide range of organic substrates (Coseri, Mendenhall, & Ingold, 2005; Coseri, 2007, 2008, 2009a, 2009b).

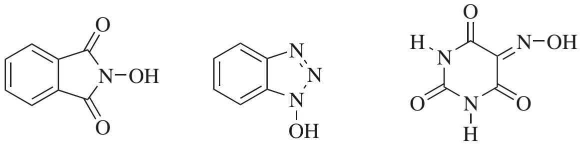
The reaction mechanism for the cellulose selective oxidation is similar for both stable and non persistent nitroxyl radicals, involving the formation of nitrosonium cation, which is the actual oxidant, Fig. 3 (Shibata & Isogai, 2003).

In the present study we applied the above two protocols, i.e. TEMPO and NHPI-mediated oxidation of viscose fibers, and comparatively investigated: the amount of carboxylic groups formed as determined by potentiometric titration and indirectly by methylene blue adsorption method, changes in crystallinity occurred after oxidation by means of X-ray diffraction and iodine sorption value, and analysis of differences in the fibers morphology after oxidation as evidenced by environmental scanning electron microscopy (ESEM) and weight loss experiments. Also, the changes on the degree of polymerization occurred after oxidations were unequivocally determined by viscosimetric measurements. We believe this study can bring a more detailed picture of the experimental procedures used for the surface oxidation of viscose fibers performed via two parallel routes, i.e. stable versus non persistent nitroxyl radicals.

2. Experimental

2.1. Materials

As cellulose source, we have used viscose fibers provided by Lenzing AG Austria, with the following specifications (Kreze, Strnad, Stana-Kleinschek, & Ribitsch, 2001): linear density (dtex) 1.88, average length: 39 mm, average diameter: 14.3 μm, degree of polymerization: 235, molecular mass: 38,500, density: 1.5045 g cm^{-1}.



NHPI HBT VA

Fig. 2. The —OH bearing precursors for the non persistent nitroxyl radicals, used for the cellulose selective oxidation.

NHPI, TEMPO, sodium bromide, 3 mass% sodium hypochlorite solution, cerium (IV) ammonium nitrate (CAN), anthraquinone and other chemicals and solvents, purchased from Sigma Aldrich, were of laboratory grade and used without further purification.

2.2. Fibers preparation

The viscose fibers were added into an aqueous solution containing 200 mL of 0.1 M potassium chloride and 3 mL of 0.1 M hydrochloric acid. The fiber suspension was then stirred with a magnetic stirrer for about a half an hour in order to achieve complete wetting of the fibers and equal charge distribution.

2.3. Nitroxyl-mediated oxidation of viscose fibers

Viscose fibers (10 g) were immersed in deionised water (800 mL) in a 2 L flask. In one set of experiments, TEMPO has been used as stable nitroxyl radical to mediate the oxidation reaction, whereas in another set of experiments, NHPI has been used along with an appropriate cocatalyst, either CAN or anthraquinone to provide in situ, the non persistent phthalimide N-oxyl radical (PINO). In all experiments, sodium bromide (0.25 mmol/g cellulose) and an amount of 3% NaClO solution, corresponding to 5 mmol/g cellulose were added slowly to the cellulose slurry, and the pH of this mixture adjusted to be 10.5, at room temperature by adding a 0.4 mol L^{-1} NaOH solution, using a pH-meter. After stirring for 2.5 h, the oxidation was quenched by adding ethanol (ca. 12 mL). The resulted fibers were washed thoroughly with deionised water and ethanol. The water-insoluble fractions thus obtained were dried by lyophilization followed by vacuum-drying at 40 °C for 48 h, and weight to measure the mass recovery ratios.

3. Methods

3.1. Fourier transform infrared spectroscopy/attenuated total internal reflection spectroscopy (FT-IR/ATR)

FT-IR/ATR experiments were carried out on silicon single-crystal parallelepiped internal reflexion elements (IRE) (55 mm × 5 mm × 2 mm, 45° incident angle), using a Bruker Vertex 70 instrument. All the spectra were the results of 256 co-added scans at a resolution of 4 cm^{-1}.

3.2. Potentiometric titration

The pH potentiometric titration of the fibers suspension was carried out with a two-buret instrument Mettler Toledo T70, in an inert atmosphere (N_2 bubbling). The burettes were filled with 0.1 M HCl and 0.1 M KOH. All solutions were prepared in Mili-Q water with low carbonate content (<10^{-5} M). This was achieved by boiling and cooling under nitrogen atmosphere. The suspension was titrated in a forth and back manner between the initial pH = 2.8 to the preset pH = 11. The titration experiments were carried out at 0.1 M ionic strength, set to its appropriate value with KCl. The titrant was added dynamically within a preset interval of [0.001–0.25] mL. The equilibrium criteria for the timed addition was set to $dE/dt = 0.1/150$ s. Where 150 s was the minimum time to reach equilibrium conditions between two additions of the titrant, and the maximum time was set to 7200 s. The pH value was measured with a Mettler Toledo DG-117 combined glass electrode. A blank HCl–KOH titration was carried out under in the same conditions as stated above. All presented values are the mean values of 3 parallel measurements.