Radiation-induced degradation of cellulose: From partial depolymerization to complete self-disassembly

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A B S T R A C T

The radiation-induced degradation of cellulose is analyzed taking into account the effect of temperature on the formation and interconversion of macroradicals. Non-chain depolymerization, consisting in the random cleavage of glycosidic bonds, occurs at low and moderate temperatures. As a result, oligomeric polysaccharides are formed in which the C:O:H atomic ratio is only slightly different from the original one. When the hydrogen bonds disappear and the fragmentary radicals are thermally generated, the depolymerization can proceed via the chain mechanism. Another mechanism, which we term self-disassembly, consists in consecutive shortening the polymer chain from its end at pre-pyrolysis temperatures. It is realized via the dehydration of macroradicals and leads to the elimination of monocyclic furans.

1. Introduction

At present, the radiation treatment of cellulosic feedstocks is used for a variety of purposes: to obtain nanocellulose and gels (Fekete et al., 2016a, 2016b; Kimura et al., 2016, 2014; Kuzina et al., 2013), to fabricate packaging materials and dressings (Irimia et al., 2017; Stoica-Guzun et al., 2013), to receive advanced sorbents (Desmet et al., 2011; Dong et al., 2016; Takács et al., 2012; Yu et al., 2016), to modify and preserve the cultural heritage (Bicchieri et al., 2016; Kodama et al., 2016), to create advanced composites and copolymers (Barsbay et al., 2016; Madrid and Abad, 2015), to synthesize biofuels and reagents (Driscoll et al., 2014; Ponomarev et al., 2012; Tissot et al., 2013), to obtain monosaccharides and oligosaccharides (Duarte et al., 2013; Ribeiro et al., 2013; Shin et al., 2012), and so on. These applications are based on radiolytic generation of short-lived ions and radicals in cellulose and their subsequent participation in the cross-linking or fragmentation processes.

Cellulose belongs to radiation-degradable polymers. The degree of its degradation depends significantly on temperature (Ershov, 1998), and there can be two types of radiation-thermal degradation of cellulose (Ponomarev and Ershov, 2014). The first type of degradation consists in the random splitting of glycosidic bonds and, accordingly, leads to a decrease in the polymerization degree of cellulose. The second type of degradation provides a chain transformation of glucopyranose units into furans. In this paper, the mechanism of both types of cellulose degradation is analyzed.

2. Primary low-temperature radiolytic processes

The cellulose macromolecule consists of glucopyranose units having the chair conformation with axially arranged hydrogen atoms. Fibrils of cellulose contain crystalline and amorphous regions, with crystalline regions predominant. The polymer is characterized by high rigidity due to intermolecular and intramolecular hydrogen bonds (shown in dashed lines), formed mainly with the participation of hydroxyl groups:
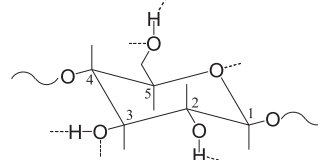
Due to the rigid crystalline structure, the most realizable of primary radiation-chemical processes is the interaction of the thermalized electron with the parent cationic center positioned on one of the monomeric units of cellulose (Ershov, 1998). Due to neutralization this unit becomes excited and then dissociates via cleavage of the weakest C-H bond at the C(1) or C(4) position:

$$(RH)^* \rightarrow \bullet R + \bullet H \qquad (1)$$

H atoms, being highly mobile and chemically active, are also involved in the dehydration of cellulose

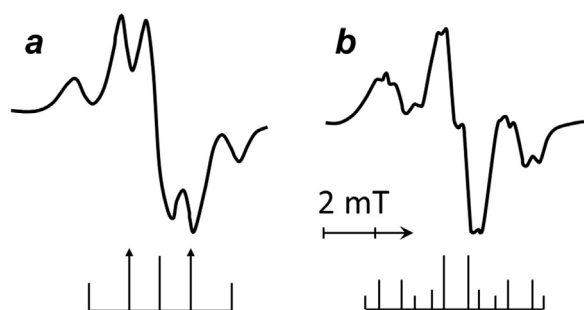$$RH + \bullet H \rightarrow \bullet R + H_2, \qquad (2)$$

Fig. 1. (*a*) overall EPR spectrum in dry microcrystalline cellulose irradiated at 77 K and (*b*) the individual triplet of R(4) with an additional quadruplet structure due to γ-H atoms at 290 K.

Reaction (2) probably leads to H abstraction from any of the C(1) - C(6) positions in the monomer unit.

The EPR spectrum (Fig. 1*a*) of irradiated cellulose is the superposition of triplet, doublet, and singlet signals (Ershov and Isakova, 1984; Kameya et al., 2013; Kuzina and Mikhailov, 2006). The hyperfine structure is due to the interaction of an unpaired electron with protons of neighboring alkyl groups. The singlet corresponds to the stabilized electron e_{st}^-. The doublet signal (the hyperfine splitting constant $a_{\beta-H}$ = 2.6 ± 0.1 mT) corresponds to the R(1) radical whose unpaired electron is positioned at the C(1) atom. The triplet signal (intensity ratio 1: 2: 1, $a_{\beta-H}$ = 3.0 ± 0.2 mT) belongs predominantly to the R(2) - R(4) radicals with the unpaired electron at C(2) - C(4), respectively.

The R(4) individual triplet (Fig. 1*b*) has a hyperfine splitting constant $a_{\beta-H}$ = 2.6 ± 0.2 mT and an additional quadruplet structure with ΔH = 0.6 ± 0.1 mT due to the interaction of an unpaired electron with γ-protons (Kuzina and Mikhailov, 2006). The broadening of the triplet in the overall EPR spectrum (Fig. 1*a*) to $a_{\beta-H}$ = 3.0 ± 0.2 mT is due to the contributions of the R(2) and R(3). At 77 K and 10–20 kGy, the R(1) and R(4) are formed in an equal amount. In turn, the contribution of R(2) and R(3) becomes significant at a dose above 100 kGy. The total yield of paramagnetic centers at 77 K is 0.26–0.36 μmol J^{-1}.

In saturated organic compounds, atom C has four sp^3-hybrid orbitals. When a single C–H bond is cleaved, sp^2-hybridization takes place, and the unpaired electron occupies a $2p_z$ orbital perpendicular to the plane of the three sp^2 orbitals. In this position, it effectively interacts with β-protons. As shown by analysis of the hyperfine splitting constants (Ershov and Isakova, 1984) the sp^2-hybridization is realized only when the adjacent glycosidic bond is cleaved. Otherwise, the hyperfine splitting constants would not correspond to the experiment. Those, the R(1) and R(4) are converted to the terminal radicals - R(1)$_t$ and R(4)$_t$, respectively
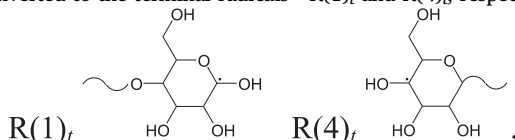
Fragmentation of a radical usually occurs via cleavage of a bond in the β-position relative to the radical center (Woods and Pikaev, 1994). The H abstraction (2) at C(2), C(3), C(5) or C(6) results in the appearance of a radical center in the β-position relative to the glycosidic bond or ether bridge within the pyranose ring. The cleavage of the corresponding C–O bonds leads to the appearance of the same R(1)$_t$ and R(4)$_t$. The resulting terminal radical can be positioned either at the same monomer unit that participated in the reaction (2) or at the adjacent unit, for example:
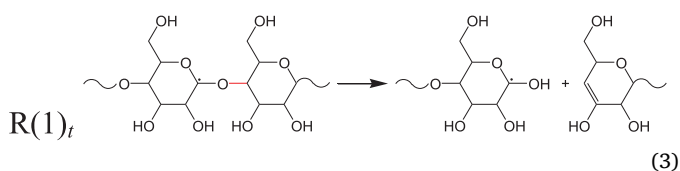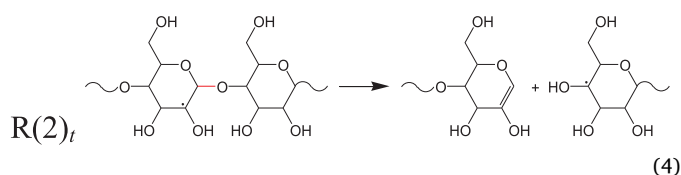

(3)

Table 1
The terminal radicals arising via the H abstraction from the Y pyranose unit in the −X–Y–Z–chain.

The position of the abstracted H atom, unit / C atom	The location of the terminal radical after cleavage of the glycosidic bond, unit / C atom
Y / C(1)	Y / C(1)
Y / C(2)	Z / C(4)
Y / C(3)	X / C(1)
Y / C(4)	Y / C(4)
Y / C(5)	X / C(1)
Y / C(6)	Z / C(4)

(4)

In the sequence of three internal pyranose units –X–Y–Z–, the H abstraction from the Y unit at one of the C(1)-C(6) positions leads to the formation of the R(1)$_t$ or R(4)$_t$ at the same unit or at an adjacent one, as shown in Table 1. Thus, the abstraction of any of the H atoms results in the formation of R(1)$_t$ or R(4)$_t$ radical.

3. Radiolytic processes under moderate heating and low dose rate

At room temperature, the total yield of paramagnetic centers is ≈ 0.62 μmol J^{-1}, which is close to the observed yield of macromolecules fragmentation. The EPR spectra of cellulose irradiated at 77 K and heated to 300 K and cellulose irradiated directly at 300 K are similar in structure and differ only in the contributions of the doublet and triplet signals. In dry cellulose, a less stable R(1)$_t$ (doublet) disappears at 240 K (Ershov and Isakova, 1984; Kuzina and Mikhailov, 2005).

Fig. 2 (curve 1) illustrates the change in the polymerization degree of cotton cellulose as a function of the absorbed dose of γ-radiation (Ponomarev and Ershov, 2012). Cleavage of the polymer chain is accompanied by the accumulation of carbonyl > C=O and carboxyl -COOH groups (Fig. 2). Table 2 demonstrates that each cleavage of the polymer chain results in equimolar elimination of CO$_2$. This fact indicates a high instability of the terminal radicals.

As shown in Fig. 3*a*, the radiation degradation of cellulose can be enhanced via heating (Ponomarev and Ershov, 2012). As the yield of cellulose degradation increases, the yield of the carbonyls and carboxyls also increases. The result of radiolysis of cellulose under moderate heating and low dose rate is depolymerization. The ratio of C: O: H atoms in the initial sample and the resulting oligomers differs
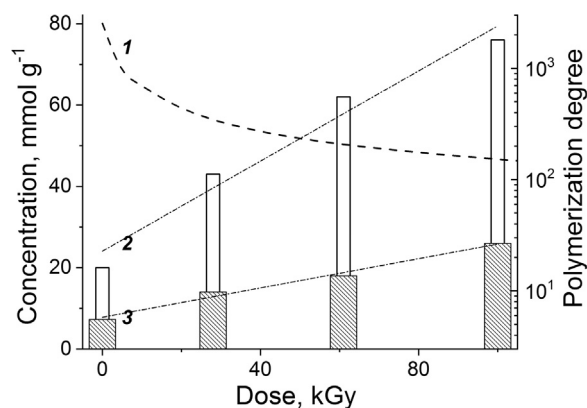

Fig. 2. Dependence of the polymerization degree (*1*) and the concentration of carbonyl (*2*) and carboxyl (*3*) groups on the dose in cotton cellulose at room temperature.