Available online at www.sciencedirect.com

ScienceDirect

Carbohydrate Polymers 69 (2007) 50–64

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Chemiluminescence related to degradation of thermally oxidized pullulans. Comparison with cellulose and dextran

Martina Pleteníková, Lyda Matisová-Rychlá, Jozef Rychlý *, Igor Lacík

Polymer Institute, Centre of Excellence for Degradation of Biopolymers (CEDEBIPO), Slovak Academy of Sciences,
Dúbravská Cesta 9, 842 36 Bratislava, Slovak Republic

Received 20 July 2006; received in revised form 31 August 2006; accepted 31 August 2006
Available online 12 October 2006

Abstract

The degradation of pullulan, cellulose and dextran in the presence of oxygen was examined by chemiluminescence and by size-exclusion chromatography (SEC) methods. While 1,4-α glycosidic bonds in pullulan are split thermally only with a slight effect of oxygen, thermolysis of 1,4-β bonds in cellulose and 1,6-α bonds in dextran is preceded by free radical oxidation of carbon 6 of glucopyranose unit with formation of carboxyl groups and water contributing to the subsequent induced degradation of polysaccharide. MgO which remains in polysaccharide after its impregnation by methoxy magnesium methyl carbonate (MMMC) promotes the reaction of terminal semiacetal groups and/or hydroperoxides which has considerably higher quantum yield of light emission.

Keywords: Thermal oxidation; Degradation; Chemiluminescence; Pullulan; Cellulose; Dextran

1. Introduction

The mechanism of thermal degradation of solid polysaccharides in the presence of oxygen is much more complex when compared e.g., with polyolefins. Oxygen heteroatoms in polysaccharide macromolecule linking glucopyranosyl structural units undergo to hydrolytic reactions initiated thermally and by hydrogen cations, if they are present. Such degradation leads to terminal aldehydes (semiacetals) which are oxidized by the free radical process initiated by oxygen giving carboxylic acids which promote the course of an ionic process. In any case, if terminal aldehydic groups are present, the free radical mechanism of oxidation of polysaccharide appears to be important in its degradation mechanism. The possible alternatives of the free radical course of polysaccharide degradation involve, particularly tertiary carbon atoms which are in the positions 1 and 4 of glucopyranosyl ring and may be easily attacked by free radicals (Shafizadeh & Bradbury, 1979). The reactivity of carbon atoms in position 6 with respect to oxidation and its comparison with other carbons of glucopyranosyl units still awaits for its quantification. The facility of the oxidation process, which ultimately leads to degradation of polysaccharide macromolecule and to the reduction of its molar mass depends on temperature and concentration of oxygen and on intervention of other factors such as water being formed in oxidation, initial pH and the presence of ionic admixtures, modifying not only the chemical resistance but also having the impact on physical properties of polysaccharide, such as T_g, the extent of crystallinity, etc.

Until now the main experience on the thermal degradation of polysaccharides in the presence of oxygen was obtained from the study of cellulose degradation as e.g., in papers by Mc Burney (1954), Baranski, Lagan, and Lajewski (2005), and Shafizadeh and Bradbury (1979).

For quantification of the polysaccharides degradation, the methods involving the determination of the degree of polymerization, determination of functional groups (such as carbonyls, carboxyls, etc.), together with other tests,

---

* Corresponding author. Tel.: +421 2 5477 1626; fax: +421 2 5477 5923.
E-mail address: upoljory@savba.sk (J. Rychlý).

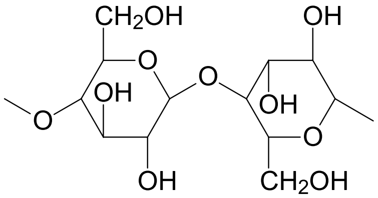
0144-8617/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2006.08.022

which are usually rather laborious may be used similarly as for cellulose. In paper by Rychlý et al. (2004) on degradation of cellulose we have attempted to complement the above methods by chemiluminescence method which is based on the measurement of extremely weak light emitted from the oxidized material. In the case of cellulose oxidation, the resulting light intensity is the sum of contributions from several oxidation mechanisms, involving different reaction sites. The light emission may, moreover, originate from several elementary reaction steps like disproportionation of secondary peroxyl radicals, decomposition of hydroperoxides, etc., all producing excited triplet carbonyl groups and/or singlet oxygen (Rychlý et al., 2004).

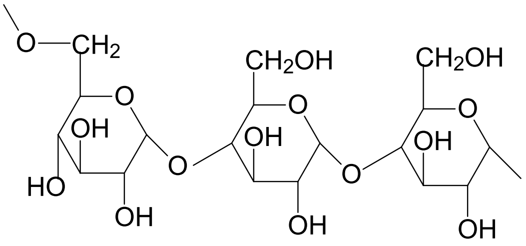
The crucial problem, however, is to discriminate between ionic and free radical mechanism of degradation of polysaccharides in its first stages, which determine the ultimate mechanism of the process. The chemiluminescence method belongs to one of the possible approaches having the potential to overcome this problem.

In predominating number of studies such as e.g., Matisová-Rychlá and Rychlý (1993), Billingham and George (1990), George (1981), Zlatkevich (1989, chap. 4), Hosoda et al. (1993), Audouin-Jirackova and Verdu (1987), Setnescu, Jipa, and Osawa (1996), Tiemblo, Gomez-Elvira, Teyssendre, Massines, and Laurent (1998), Matisová-Rychlá, Rychlý, and George (1999), and Matisová-Rychlá et al. (2002) on chemiluminescence from polymers, the attention was paid to the thermo-oxidation of synthetic polymers. The light emission from oxidized cellulose and other polysaccharides was investigated to a lesser extent [see e.g., the papers by Kelly, Williams, Mendenhall, and Ogle (1979), Konoma, Cai, and Osawa (2000), Strlič, Kolar, Pihlar, Rychlý, and Matisová-Rychlá (2001), Rychlý, Matisová-Rychlá, and Strlič (2000), Rychlý, Strlič, Matisová-Rychlá, and Kolar (2002), Strlič, Rychlý, Haillant, Kočar, and Kolar (2005, chap. 8), and Strlič et al. (2003)]. Rychlý et al. (2002) have shown that the average rate constant determined from the kinetics of non-isothermal chemiluminescence runs for oxidation of cellulose in oxygen is well comparable with the rate constant determined from the decrease of the polymerization degree. Non-isothermal chemiluminescence runs were approximated by the sum of two parallel reactions being initiated from two kinds of reaction sites, statistically formed on the cellulose backbone. The faster and slower reaction which were thus noticed may well correspond to the initiation of degradation via ionic and free radical sites, respectively. Rychlý, Matisová-Rychlá, Bukovský, Pleteníková, and Vrška (2006a) presented an interesting observation, namely that magnesium ions significantly promote the chemiluminescence emission if the initial pH of cellulose sample is around 9. It is generally agreed that the free radical mechanism of polysaccharide degradation predominates if initial pH of the sample is above 7.

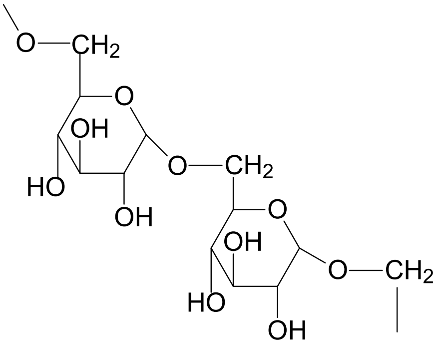
In the present paper, we complement the chemiluminescence measurements on cellulose (1,4-β glycosidic bonds) with those done with polysaccharide pullulan (1,6-α and 1,4-α glycosidic bonds) and dextran (1,6-α glycosidic bonds) of different initial molar mass.



Structure of cellulose



Structure of pullulan



Structure of dextran

When compared with cellulose and dextran the discrepancy between the values of average rate constants determined from non-isothermal chemiluminescence measurements and from kinetics of the decay of polymerization degree was found for pullulan, which is worthy of detailed study. This may be consistent with a different mechanism of the oxidation process being due to different structure of oxygen linkages between glucopyranosyl units.

The effect of magnesium ions on intensity of chemiluminescence from pullulan, dextran and cellulose has been established and the mechanism of the process leading to the light emission was proposed.

2. Experimental

2.1. Measurements

2.1.1. Chemiluminescence (CL) measurements

Chemiluminescence (CL) measurements were carried out with the luminometer Lumipol 2, produced at the

Polymer Institute of SAS, Bratislava. The intensity of emitted light (in counts/s) was recorded under non-isothermal conditions as the records of intensity on temperature (the rate of heating was usually 2.5 °C/min) or in isothermal mode in oxygen or nitrogen atmosphere. The instrument dark count rate was 2–3 counts/s.

Under non-isothermal conditions the measurement was interrupted at a certain temperature and the sample was analyzed by the size-exclusion chromatography (SEC).

Samples of the initial weight (around 6.5 mg) were placed on aluminum pans of the diameter 9 mm and put into the oven of the CL apparatus; the gas flow through the sample was 3 l/h.

2.1.2. Thermogravimetry

Thermogravimetry was carried out using Mettler–Toledo TGA/SDTA 851^e thermobalance in nitrogen and oxygen atmosphere (30 ml/min) in the temperature range 25–500 °C and at the heating rate 5°/min.

2.1.3. Size-exclusion chromatography

The aqueous phase size-exclusion chromatography was used to analyze molecular weight and molecular weight distributions of pullulan samples. The setup consisted of a Waters In-line degasser, a Waters pump 515 equipped with a plunger washing kit, a Rheodyne 7725i injector, a 8 × 50 mm guard and three 8 × 300 mm Suprema columns (Polymer Standards Service, Mainz, Germany) with 10 μm particles and pore sizes 100, 1000 and 3000 Å (positioned in a Waters column heater module) and a differential refractometer Waters M2410. The analysis was performed at 60 °C using distilled water as an eluent containing 200 ppm, Na_2HPO_4. Ethylene glycol was used as the flow marker to control the eluent flow rate at 1.0 ml/min. Pullulan samples were dissolved in the eluent at concentrations around 2 mg/ml and filtered via a 0.45 μm filter prior to analysis. The loop volume was 200 μL. The molecular weights were obtained via calibration using narrow-distributed pullulan standards (Gearing Scientific, UK) of molecular weight between 738 and 788,000 g/mol. Data acquisition and analysis were performed with WinGPC® 7 software (Polymer Standards Service, Mainz, Germany).

2.2. Materials

Cellulose (Whatman filter paper No. 1, Maidstone, UK, molar mass 486 kg/mol) is a (1 → 4)-β-D glucan containing (1 → 4)-β linked glucopyranose structural units.

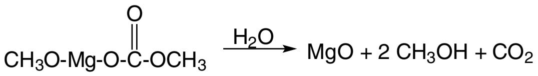
Pullulan is a (1 → 4, 1 → 6)-α-D glucan containing (1 → 6)-α linked maltotriose structural units.

Pullulan of different molar mass (set of SEC standards) with molar mass peaks at 5.9, 11.8, 22.8, 47.3, 112, 212, 404 and 788 kg/mol, respectively, were purchased from Gearing Scientific (UK) and used as received.

Dextran is a (1 → 6)-α-D glucan containing (1 → 6)-α linked glucopyranosyl units.

The samples were purchased from American Polymer Standards Corp. Ohio, USA; their molar mass was 20.5, 50.2, 110, 212.5, 401.6, 845 and 2200 kg/mol, respectively.

Impregnation of respective polysaccharides has been performed by 4 mg of 2% methanol solution of methoxy magnesium methyl carbonate (MMMC), directly in the pan used for chemiluminescence measurement. The samples were dried at room temperature until the constant weight. In the presence of water, MMMC is converted into MgO which is the ultimate compound remaining in the polysaccharide sample after its thermal treatment.



$$CH_3O\text{-}Mg\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}OCH_3 \xrightarrow{H_2O} MgO + 2\,CH_3OH + CO_2$$

2.3. Determination of kinetic parameters from non-isothermal chemiluminescence run

Kinetic parameters from experimental runs in oxygen of chemiluminescence intensity vs. temperature, which occur as a monotonous increase of light emission until 220 °C, may be found if a suitable model relating chemiluminescence intensity with the rate of oxidation reaction is used.

The kinetic model of the cellulose degradation, which has been the subject of numerous papers, was first used by Ekenstam (1936) and developed by Emsley, Heywood, Ali, and Eley (1997). Degree of polymerization (DP) is defined here as the ratio of concentration of monomer units (N) and polymer molecules (i) as follows:

$$\mathrm{DP} = \frac{N}{i}. \tag{1}$$

The concentration of polymer molecules increases in time with increasing extent of degradation reaction. The process of chain scissions is assumed to be of zero order ($\frac{di}{dt} = k$) and the concentration i of macromolecules changes in time as a linear function of time.

$$i = i_0 + kt, \tag{2}$$

where k is the rate constant of main chain scissions and i_0 is initial concentration of macromolecules in the system, respectively. For DP we thus have

$$\mathrm{DP} = \frac{N}{i_0 + kt} \tag{3}$$

or $\mathrm{DP} = \frac{\mathrm{DP}_0}{1+\frac{k}{i_0}t}$, where $\mathrm{DP}_0 = \frac{N}{i_0}$. After transformation we receive

$$\frac{1}{\mathrm{DP}} - \frac{1}{\mathrm{DP}_0} = \frac{k}{i_0 \mathrm{DP}_0} t \tag{4}$$

$$\text{or } \frac{\mathrm{DP}_0}{\mathrm{DP}} = 1 + \frac{k}{i_0} t. \tag{5}$$

The Eq. (4) is the Ekenstam equation known from the literature. However, it is better to work with Eq. (5), which gives the rate constant $\frac{k}{i_0}$ of the magnitude s^{-1}. This allows for a direct comparison between samples of different initial DP.

The chemiluminescence intensity I is proportional to the rate of change of hydroperoxides concentration [POOH] in a solid polymer (Billingham & George, 1990; George, 1981; Matisová-Rychlá & Rychlý, 1993). Provided that these hydroperoxides are formed statistically along the macromolecular chain, the rate of the change of their concentration should be at the same time proportional to the rate of change of degree of polymerization DP in time as follows:

$$I = \Phi_1\left[-\frac{\mathrm{d[POOH]}}{\mathrm{d}t}\right] = \Phi\left[-\frac{\mathrm{dDP}}{\mathrm{d}t}\right] \tag{6}$$

Φ_1 and Φ are proportionality constants, involving quantum yield of chemiluminescence reaction.

The above case corresponds to the randomly distributed hydroperoxide sites on polysaccharide backbone which decompose subsequently via alkyloxy radicals and reduction of molar mass.

According to Eq. (5) $-\frac{\mathrm{dDP}}{\mathrm{d}t} = \frac{k}{i_0\mathrm{DP}_0}\mathrm{DP}^2$ and for non-isothermal conditions we obtain

$$-\frac{\mathrm{dDP}}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{A\exp(-E/\mathrm{R}T)}{i_0\mathrm{DP}_0}\mathrm{DP}^2. \tag{7}$$

Here, T is temperature, A and E are pre-exponential factor and activation energy, respectively, and $\frac{\mathrm{d}T}{\mathrm{d}t} = \beta$ is the linear rate of sample heating.

After integration of Eq. (7) and back substitution into Eq. (6), for non-isothermal conditions we receive

$$I = \Phi\frac{A\exp(-E/\mathrm{R}T)}{i_0} \times \frac{\mathrm{DP}_0}{[1 + \frac{A}{\beta i_0}\int_{T_{\mathrm{room}}}^{T}\exp(-E/\mathrm{R}T)\,\mathrm{d}T]^2}. \tag{8}$$

We used the above approach to fit the experimental curves of chemiluminescence intensity vs. temperature. It was assumed that the light emission comes from several component runs corresponding to several independent initiating events. Provided that the process of light emission corresponds to two such events ($i = 2$) we have

$$I = \sum_{i=1}^{2}\frac{P_i}{[1 + \frac{A_i}{\beta i_0}\int_{T_{\mathrm{room}}}^{T}\exp(-E_i/\mathrm{R}T)\,\mathrm{d}T]^2}. \tag{9}$$

Here, P_i is the proportionality constant, including the corresponding terms from Eq. (8), A_i and E_i are pre-exponential factor and activation energy of respective component of the initiation reaction.

Averaged rate constant k_{av} for two components of initiation ($i = 2$), leading to the light emission is defined as

$$k_{\mathrm{av}} = \frac{P_1}{P_1 + P_2}\frac{k_1}{i_0} + \frac{P_2}{P_1 + P_2}\frac{k_2}{i_0} \tag{10}$$

k_1/i_0 and k_2/i_0 are rate constants at a given temperature of the respective initiating process. They have the magnitude of the first order reaction (s^{-1}). The first constant corresponding to the faster process may be tentatively assigned to the heterolytic reaction initiated by ionic species while the second corresponding to slower process may be attributed to free radical degradation.

In practical computation procedure we determine the corresponding parameters for any of the two initiating events by non-linear regression analysis taking into account the experimental runs normalized to one at the maximum temperature of the experiment 220 °C.

3. Results and discussion

Fig. 1 shows dependence of chemiluminescence intensity on temperature for runs of pullulans of different initial molar mass in the temperature interval from 40 to 220 °C (oxygen atmosphere, rate of heating 2.5 °C/min). The signal intensity depends significantly on the initial molar mass; the lowest being for the highest initial molar mass. This is particularly seen for the intensity of the light emission at the highest temperature of oxidation. The time evolution of chemiluminescence signal for isothermal runs at 190 °C in Fig. 2 shows that the sample of higher molar mass has lower signal intensity at time $t = 0$. However, it increases gradually and finally exceeds that for lower initial molar mass. Obviously, this is an confirmation of the role of terminal groups in the mechanism of chemiluminescence from pullulan. Low molar mass samples have the higher initial concentration of terminal groups. This seems to be the reason that the initial uptake of light emission for the sample of low molar mass is higher than that for the higher molar mass (Fig. 2). In the latter case the concentration of terminal groups will increase due to degradation process.

The area under the chemiluminescence curves between 40 and 220 °C for different initial molar mass of pullulan from Fig. 1 is plotted against the reciprocal value of initial molar mass and gives a straight line shown in Fig. 3. The reciprocal value of the molar mass is proportional to the initial chain ends concentration. The fact that low molar mass fragments are formed from larger molecules of pullulan in a stepwise degradation reaction is supported by SEC experiments. Fig. 4 depicts that higher molar mass (212 kg/mol) samples shift the maximum of molar mass to lower values in dependence on temperature of sampling. The temperatures of pullulan sampling in non-isothermal chemiluminescence runs were 98, 150, 180, 206 and 220 °C, respectively. The experiments were performed so that the measurement has been stopped at a respective temperature and the sample was analyzed by SEC. With the progress of degradation of high initial molar mass of pullulan, the molar mass distribution of degraded samples becomes broader and its maximum is shifted towards lower molar mass. On the other hand Fig. 5 shows that the sample of pullulan with lower molar mass such as 11.8 kg/mol the maximum of molar mass distribution shifts to higher values slightly for sampling at 220 °C.

Oxygen has not very significant effect on reduction of molar mass of pullulan when compared with

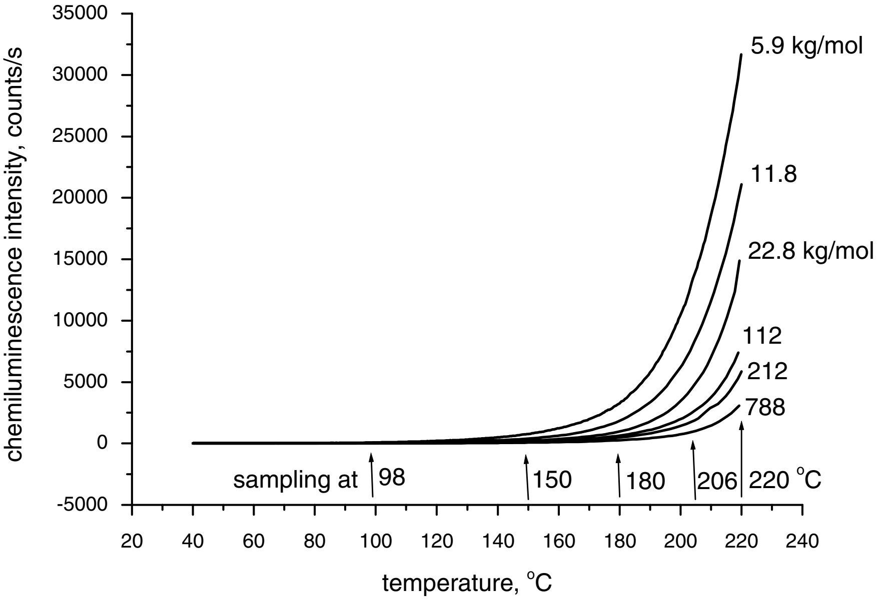


Fig. 1. Non-isothermal chemiluminescence runs for pullulan of different initial molar mass in kg/mol (see the numbers) (oxygen, the rate of heating 2.5 °C/min, the temperature changed from 40 to 220 °C). The arrow indicates the temperature when measurement was interrupted and the sample analyzed by SEC.

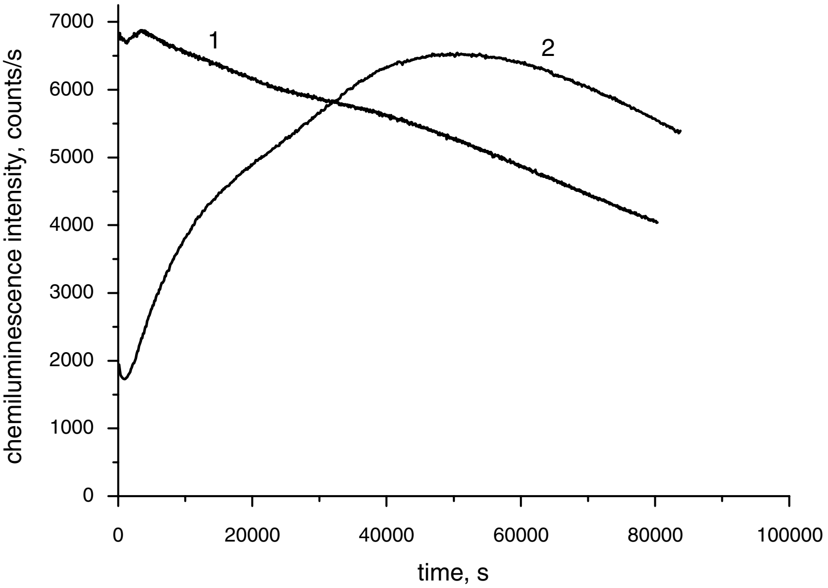


Fig. 2. Isothermal chemiluminescence runs in oxygen at 190 °C for pullulan of initial molar mass 11.8 (1) and 212 kg/mol (2). The mass of sample was 6.5 mg.

nitrogen. Fig. 6 shows non-isothermal thermogravimetry experiments on pullulan and cellulose where the temperature of the maximum rate of release of volatiles is almost identical for both oxygen ant nitrogen atmosphere. On the other hand, the formation of volatile products from heated cellulose is quite distinctly dependent on the atmosphere of degradation; in oxygen the temperature of maximum rate of decomposition into volatiles is significantly lower than that for nitrogen. The amount of charred residue being formed in oxygen and observed at temperatures above 300 °C is, however, higher for pullulan. This is probably brought about by secondary cross-linking process initiated by oxygen which apparently starts on lower molar mass fragments. Fig. 5 showing SEC experiments with lower molar mass pullulan (11.8 kg/mol) and the slight shift of the distribution curve to higher molar mass, confirms such an assumption. In the case of cellulose, the role of hydroperoxides decomposition which are formed statistically along a macromolecular chain thus appears to be more important than that for the case of pullulan. Hydroperoxides cleave thermally to oxyl radicals which in β-scission give fragments of lower molar mass. Fig. 7 showing a

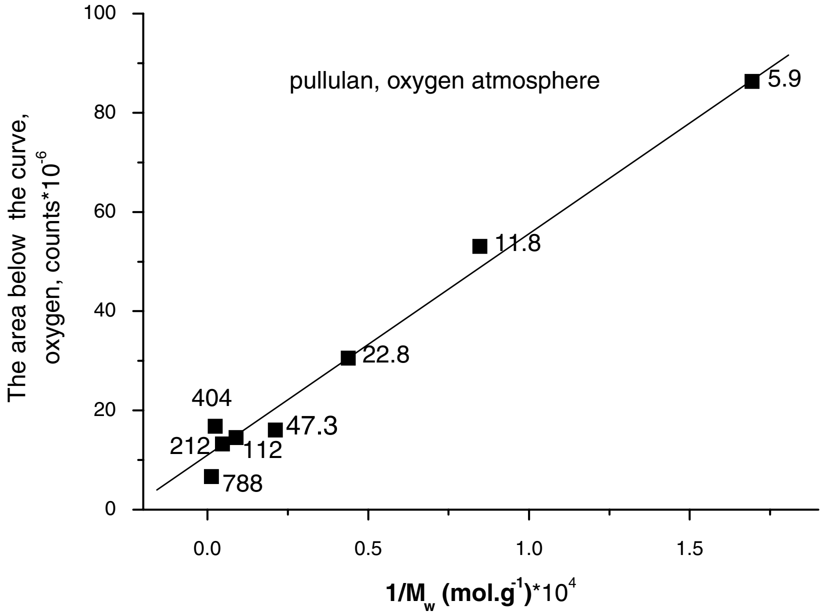


Fig. 3. Plot of the area below non-isothermal chemiluminescence run vs. reciprocal value of molar mass of pullulan samples in oxygen (see Fig. 1). Numbers denote the molar mass of pullulans in kg/mol.

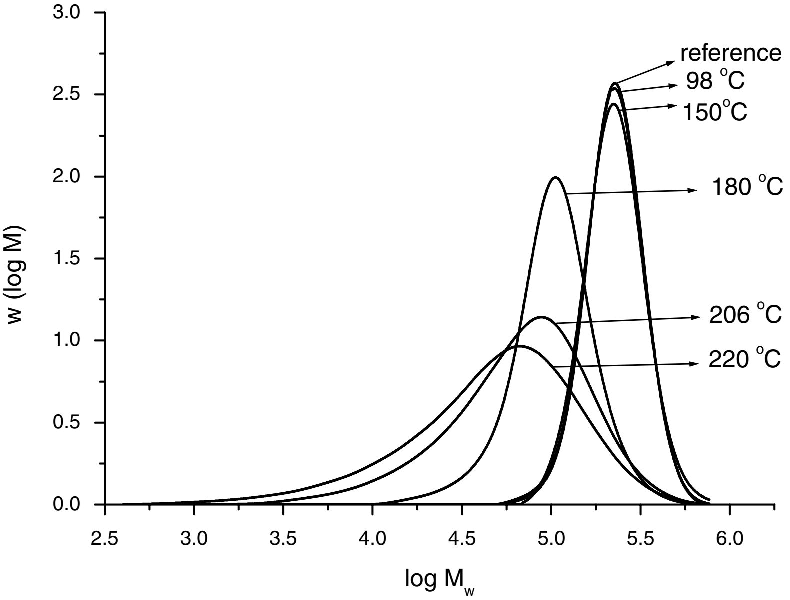


Fig. 4. The molar mass distribution curves of pullulan of initial molar mass 212 kg/mol after the sampling from chemiluminescence measurements in Fig. 1.

gradual increase of chemiluminescence intensity with reduction of initial molar mass of pullulan due to its previous thermal degradation in nitrogen at 190 °C for 0–5 h indicates again that the oxidation of pullulan predominantly occurs at chain ends which are formed at the preceding heterolytic scissions of glycosidic bonds.

Of interest is also comparison of temperature cycling experiments in oxygen for cellulose and pullulan. In Figs. 8 and 9 the samples were periodically heated and cooled down within an interval 50 (minimum of signal) and 220 °C (maximum of signal) by the rate of heating/cooling 2.5 °C/min. The pattern of cellulose (11 cycles) seen in Fig. 8 shows the continuous decay of maximum chemiluminescence intensity at 220 °C with increasing number of heating/cooling cycle. For pullulan (Fig. 9) 9 cycles were made showing an increase from lower value of maximum chemiluminescence intensity with the decay observed after the 5th cycle.

In Table 1 the values of activation energy determined according to Eqs. (9) and (10) for faster and slower process

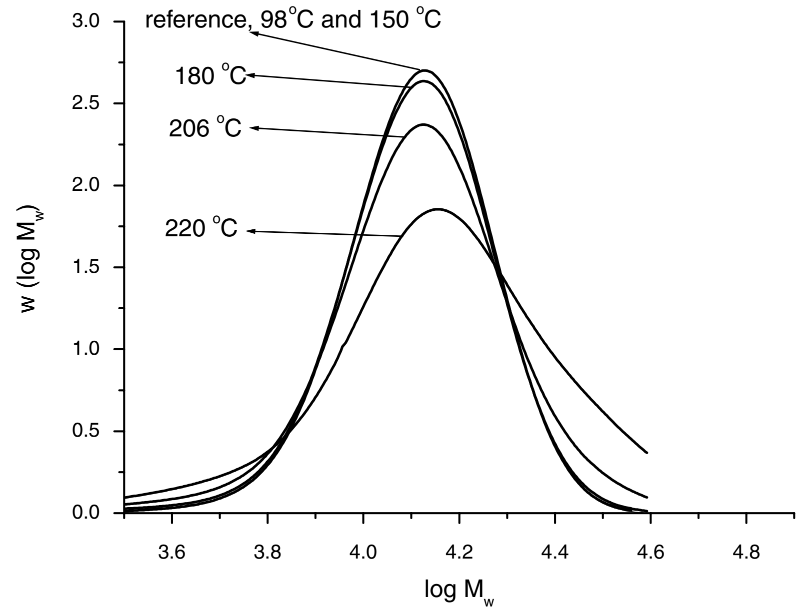


Fig. 5. The molar mass distribution curves of pullulan of initial molar mass 11.8 kg/mol after the sampling from chemiluminescence measurements in Fig. 1.

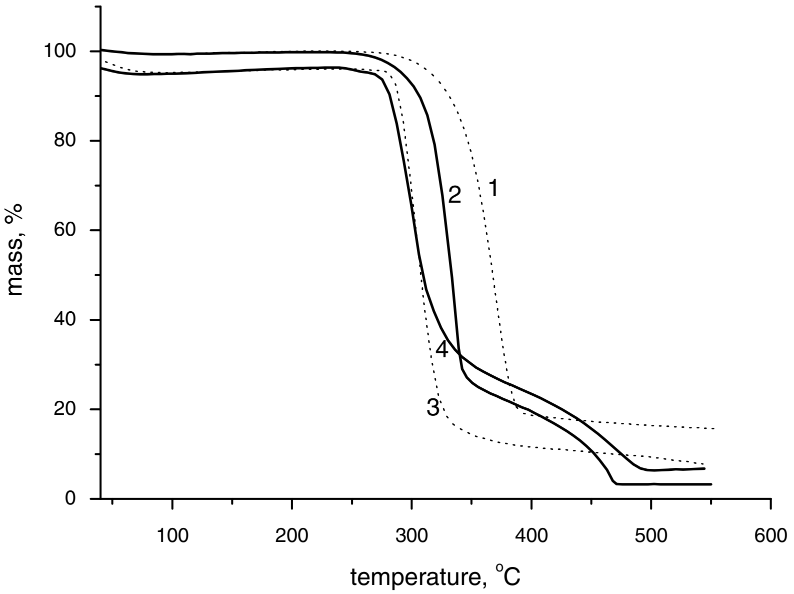


Fig. 6. Effect of atmosphere on mass changes in thermogravimetry experiment with Whatman cellulose (1 – nitrogen and 2 – oxygen) and pullulan of initial molar mass 788 kg/mol (3 – nitrogen and 4 – oxygen). The rate of heating was 10 °C/min for Whatman cellulose and 5 °C/min for pullulan sample (3 and 4).

of cellulose and pullulan degradation are between 50–65 and 60–85 kJ/mol for faster process and between 120–155 and 175–245 kJ/mol for slower process, respectively. The former values appear to correspond with ionic process while the latter with a free radical process. The values between 120 and 155 kJ/mol for the free radical process may be ascribed to hydroperoxide decomposition while those between 175 and 245 kJ/mol correspond more to thermolytic process of direct C–O–C bonds scissions which thus become the rate determining process in a respective case.

In Fig. 10 and Table 1 the discrepancy between average rate constant for oxidation of pullulan at 180 °C and that from degree of polymerization (DP) changes is evident.

The reduction of molar mass of pullulan is considerably faster than that of cellulose (Fig. 10). The ratio of the corresponding rate constants of pullulan and cellulose reduction of molar mass determined for 180 °C in oxygen (Eq. (5) and data from papers by Strlič et al. (2003) & Strlič et al. (2005, chap. 8)) is almost 200 for initial stages of degradation and 20 for the latest stages of degradation.

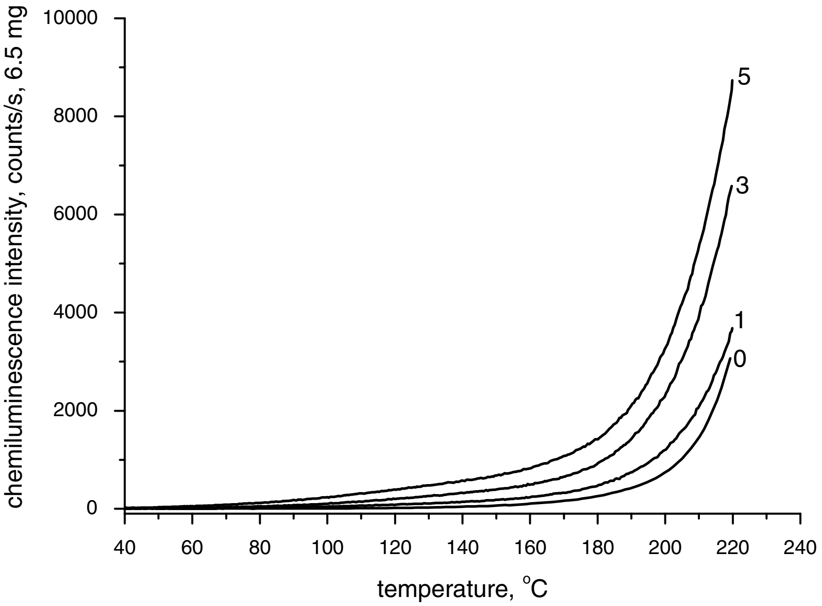


Fig. 7. Pullulan of initial molar mass 788 kg/mol degraded in nitrogen for 0, 1, 3 and 5 h (numbers in the graph) at 190 °C and chemiluminescence run measured subsequently in oxygen from 40 to 220 °C by the rate of heating 2.5 °C/min.

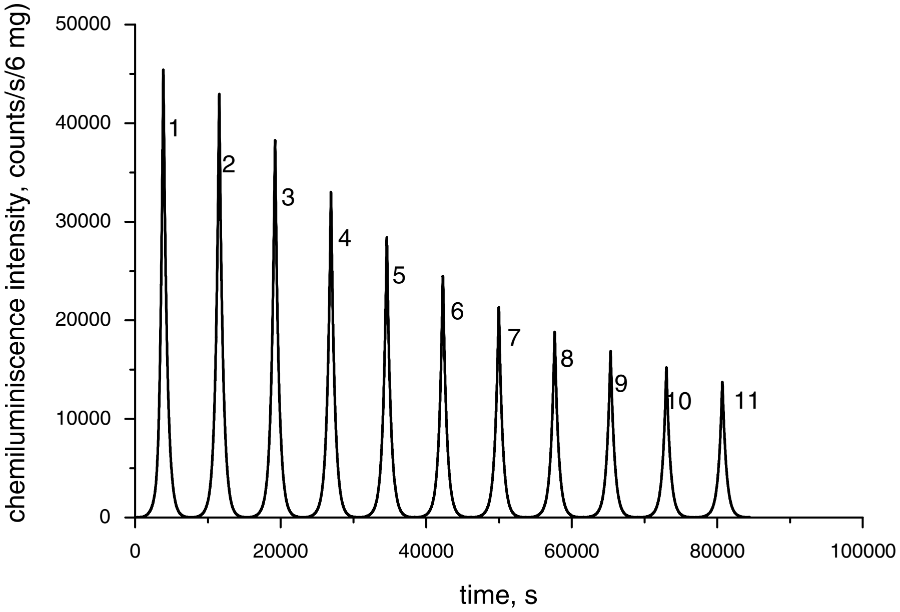


Fig. 8. Periodical changes of temperature within 40–220 °C by the rate 2.5 °C/min and corresponding response of chemiluminescence intensity. Whatman cellulose, molar mass 486 kg/mol, oxygen atmosphere.

On the other hand cellulose gives coincidence for both the non-isothermal chemiluminescence and degree of polymerization methods. The average rate constant of pullulan oxidation at 180 °C decreases with an increase of initial molar mass which is most likely related to a reduced concentration of terminal semiacetal groups at the beginning of the oxidation process. Pullulan pre-degraded in nitrogen gives higher rate constant of oxidation which may be again brought about by an increasing amount of terminal semiacetal groups which are formed during the pre-degradation (see Fig. 7). At the same time, activation energy of faster process falls down almost to 30 kJ/mol while that for slower process to 140 kJ/mol (Table 1).

3.1. On the origin of chemiluminescence at the oxidation of polysaccharides

The oxidation of polysaccharide on carbon 6 is obviously rather slow process at low temperatures and starts to be important at temperatures above 100 °C. The stoichiometry of the reaction for cellulose is depicted in Scheme 1.

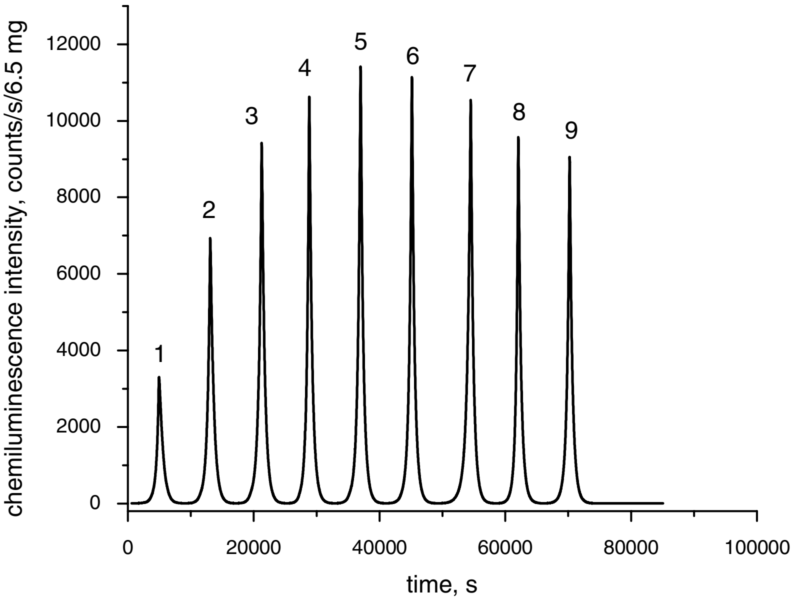


Fig. 9. Periodical changes of temperature within 40–220 °C by the rate 2.5 °C/min and corresponding response of chemiluminescence intensity. Pullulan, molar mass 788 kg/mol, oxygen atmosphere.

Table 1
Kinetic parameters of oxidation of polysaccharides determined from non-isothermal chemiluminescence measurements in oxygen (the rate of heating 2.5 °C/min)

Sample	No. of cycle in temperature cycling experiment	E_1 (kJ/mol)	E_2 (kJ/mol)	k_{av} at 180 °C $s^{-1} \times 10^5$	Comment
Cellulose	1	55	152	5.6	
	2	64	132	4.4	
	3	60	124	4.2	
	4	64	133	5.1	
	5	63	132	5.5	
	6	65	139	6.2	
	7	60	126	4.5	
	8	61	131	5.1	
	9	60	131	5.1	
	10	58	123	3.2	
	11	59	129	4.6	
Pullulan 788	1	78	214	4.4	
	2	64	168	3.5	
	3	63	168	4.0	
	4	65	174	4.2	
	5	65	171	3.5	
	6	68	179	3.8	
	7	67	175	3.6	
	8	82	198	–	
	9	70	178	3.0	
Pullulan 5.9	1	62	153	4.8	
Pullulan 11.8	1	78	177	5.1	
Pullulan 22.8	1	94	232	3.9	
Pullulan 112	1	89	249	3.5	
Pullulan 212	1	83	232	3.0	
Pullulan 404	1	96	282	2.6	
Pullulan 788	1	74	237	1.5	
Pullulan 788	1	38	145	2.5	After 1 h at 190 °C in N_2
Pullulan 788	1	36	149	6.0	After 3 h at 190 °C in N_2
Pullulan 788	1	31	141	6.9	After 5 h at 190 °C in N_2
Dextran 401.6	1	87	236	5.8	

The numbers at a respective polysaccharide denote initial molar mass in kg/mol.

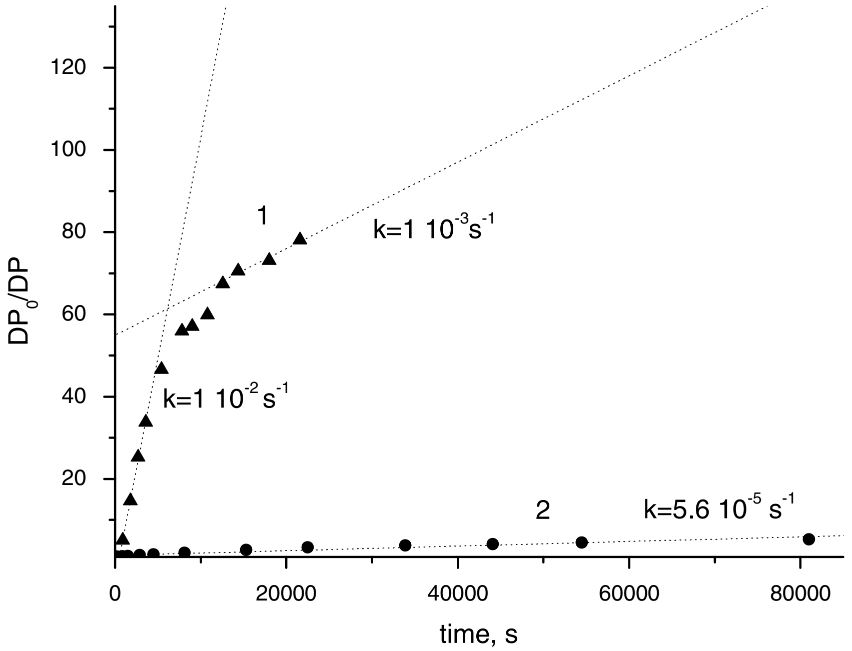
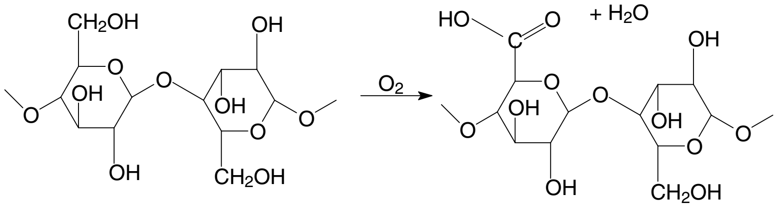


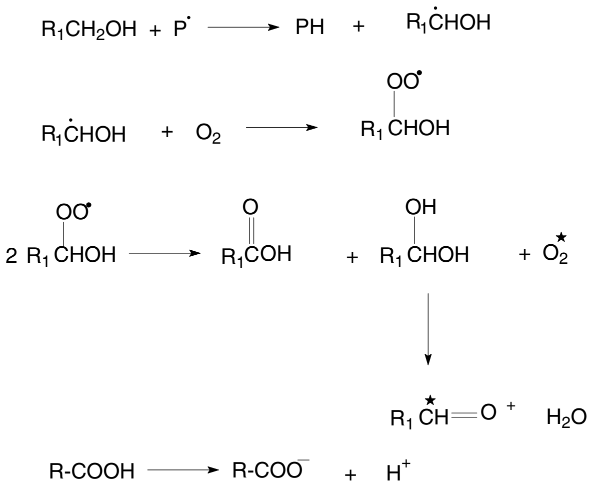
Fig. 10. The plot of time changes of relative peak molar mass for pullulan (1) and Whatman cellulose (2) expressed as the ratio of degrees of polymerization DP$_0$/DP in oxygen atmosphere at 180 °C. The constants *k* correspond to the slope in Eq. (5). The curves were reconstructed from data in papers by Strlič et al. (2003) and Strlič et al. (2005, chap. 8).



Scheme 1.

The process has free radical mechanism. It is initiated by free radicals P$^\bullet$ which appear there due to e.g., hydroperoxide decomposition induced thermally or by trace amounts of metal ions present in any polysaccharide. One cannot exclude even direct interaction of polysaccharide with oxygen in its ground triplet state which has the biradical character. Hydroperoxidic and/or peracids moieties are easily formed by oxidation of semiacetal chain end groups. The sequence of reactions on carbon 6 of polysaccharide structural unit which ultimately may lead to chemiluminescence is shown in Scheme 2.

The most probable elementary step from which chemiluminescence is emitted is disproportionation of secondary peroxyl radicals which may be formed only on carbon 6 of glucopyranosyl unit. According to various authors who accept the Russel scheme of disproportionation of secondary peroxyl radicals (Billingham & George, 1990) it may be deduced that carboxylic acid, excited triplet aldehyde, singlet oxygen and water are formed when this scheme is applied to polysaccharides. The simultaneous formation of carboxylic acid and water may lead to a subsequent heterolytic cleavage of C–O–C bonds linking glucopyranosyl units.



Scheme 2.

Notice that peroxyl radicals which are potentially formed on carbons 1, 2, 3, 4 and 5 are tertiary peroxyl radicals which in their recombination give oxygen and two

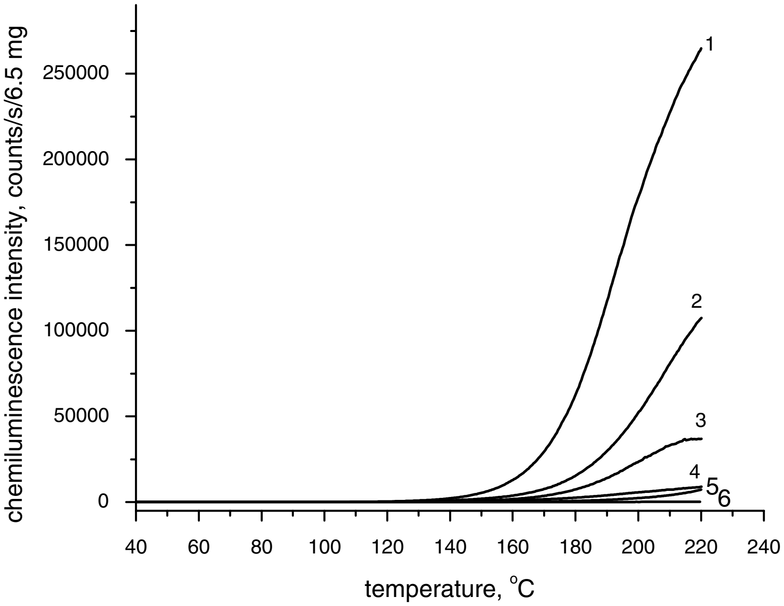


Fig. 11. Chemiluminescence intensity – temperature runs for pullulans of molar mass 112 (2 and 4) and 404 kg/mol (1 and 3) heated in oxygen (1 and 2) and nitrogen (3 and 4) from 40 to 220 °C by the rate of heating 2.5 °C/min. The samples of pullulan were impregnated by methoxy magnesium methyl carbonate (MMMC). The lines 5 and 6 stand for original pullulan 112 measured in oxygen (5) and nitrogen (6).

oxyl radicals or dialkyl peroxide, respectively, in a radiationless route.

Which is the reason of a significant increase of chemiluminescence when MMMC is added to pullulan and cellulose as seen in Figs. 11 and 12. We know that MgO remains in the sample after thermal treatment of the sample. Only slight effect of MMMC on chemiluminescence was observed for dextran both in oxygen and nitrogen (Fig. 13). Initial pH of the system at the presence of MMMC is about 9. The significant increase of the light emission was also observed when cellulose was treated with magnesium carbonate (Rychlý et al., 2006a). Provided that calcium carbonate giving initial pH also around 9 is used instead of magnesium carbonate no increase of chemiluminescence above the reference level was observed (Rychlý et al., 2006b). Cellulose impregnated by magnesium carbonate and subsequently treated with hydrochloric acid to have pH around 7 did not give an increase as well (Rychlý et al., 2006b) The difference between atomic volumes of Mg and Ca which are 13.97 and 29.9 cm^3/mol,

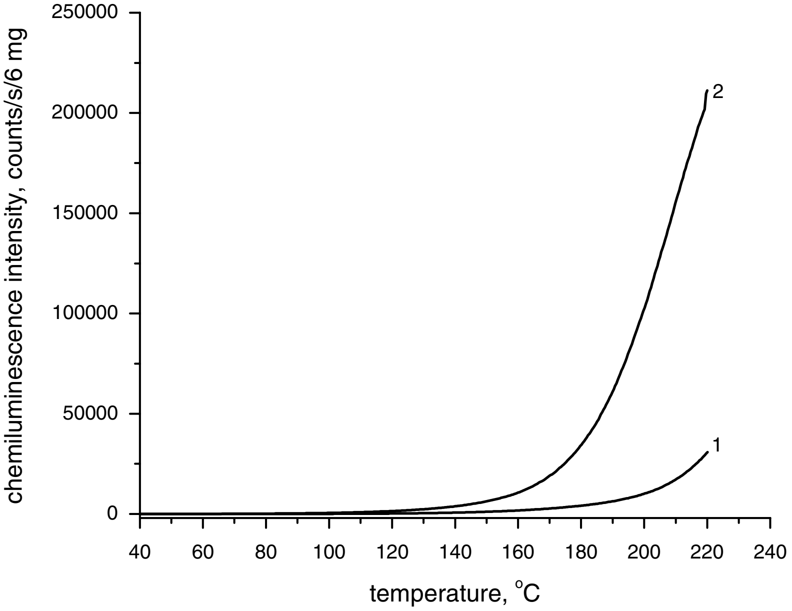


Fig. 12. Chemiluminescence runs from 40 to 220 °C of Whatman cellulose (initial peak molar mass 486 kg/mol), reference sample (1) and cellulose impregnated by MMMC (2), oxygen, the rate of heating 2.5 °C.

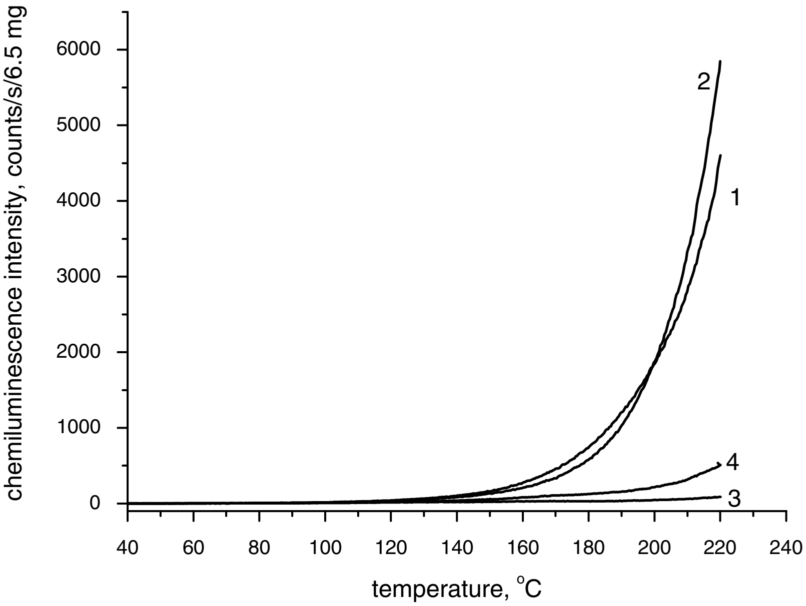
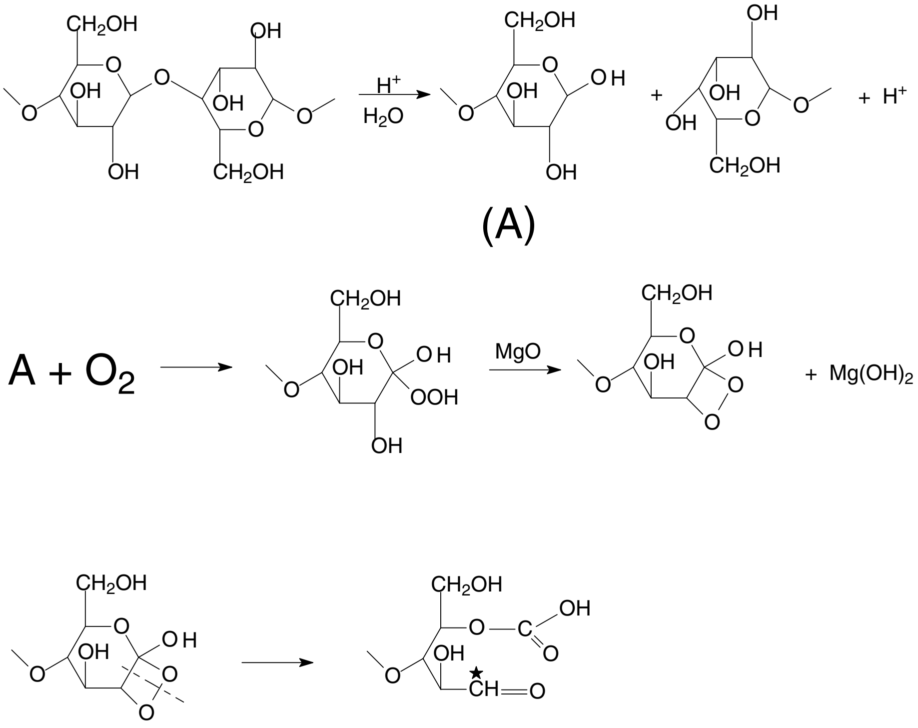


Fig. 13. Non-isothermal chemiluminescence runs from 40 to 220 °C (the rate of heating 2.5 °C/min) for dextran of initial molar mass 401 kg/mol, oxygen (1,2), nitrogen (3,4). Samples impregnated by MMMC correspond to lines 2 and 4.

respectively, and between Pauling's electronegativities which are 1.00 for Ca, and 1.31 for Mg together with alkaline medium are obviously responsible for the observed chemiluminescence uptake due to Mg ions.

An easy peroxidation of terminal aldehydic groups A in Scheme 3 in polysaccharides tend us to consider chemiluminescence reaction which has a considerably higher quantum yield of light emission than disproportionation of secondary peroxyl radicals. This may the decomposition of dioxetanes which chemiluminescence was examined on relatively stable samples of e.g., tetramethyl dioxetane. Such dioxetanes may be prepared from corresponding β-bromohydroperoxide in the presence of alkaline Ag_2O suspension (Broska, 1996). Provided that terminal end groups A are peroxidized we receive β-hydroxy hydroperoxide. In the presence of alkaline MgO a similar reaction may occur for which the



Scheme 3.

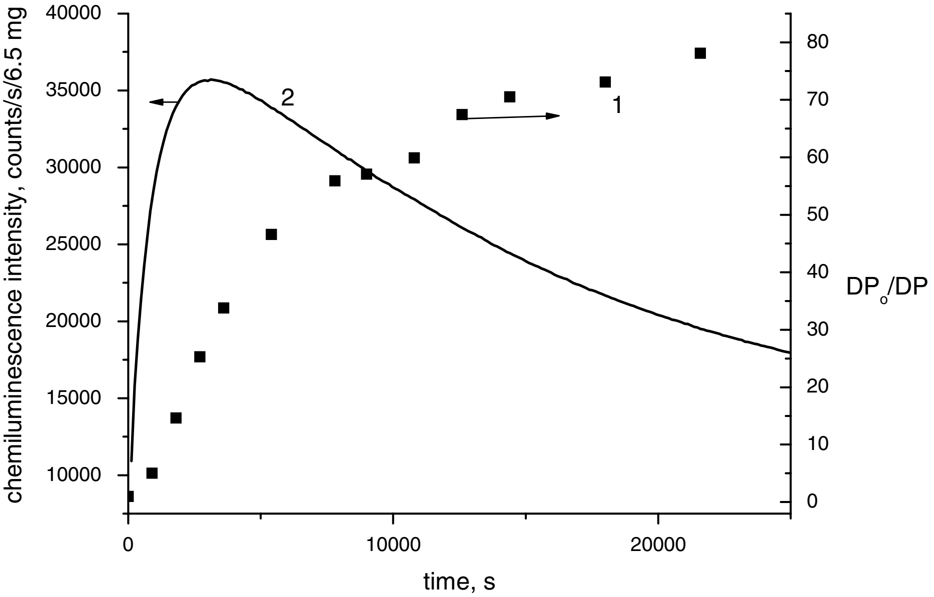


Fig. 14. A comparison of change of degree of polymerization (1) for pullulan of initial molar mass 380 kg/mol (paper by Strlič et al. (2003) and isothermal chemiluminescence intensity (2) for pullulan of initial molar mass 404 kg/mol (2) impregnated by MMMC in oxygen at 180 °C.

magnitude of magnesium ions seems to be favourable for the mechanism shown in Scheme 3.

When compared with pure pullulan samples isothermal chemiluminescence run for pullulan impregnated by MMMC in oxygen at 180 °C corresponds approximately to that of changes of degree of polymerization (DP). In the Fig. 14 we see that DP_0/DP (DP_0 is the degree of polymerization at time $t = 0$) increases linearly up to the maximum chemiluminescence intensity and then declines to a lower slope. Maximum chemiluminescence intensity for pure pullulan sample is attained almost after 9 h while pullulan impregnated with MMMC gives 1300 s. This may be seen in Fig. 15, where comparison of pure pullulan and pullulan impregnated by MMMC is shown for 190 °C. The reciprocal values corresponding to these times are 3×10^{-5} and $7.7 \times 10^{-4}\ s^{-1}$, respectively. One can see that for pullulan impregnated by MMMC the latter value approaches to the rate constants obtained from DP changes.

In Fig. 16 one may see that dextran heated in nitrogen to 220 °C by the rate of heating 2.5 °C/min practically does not shift a maximum of the molar mass to lower values

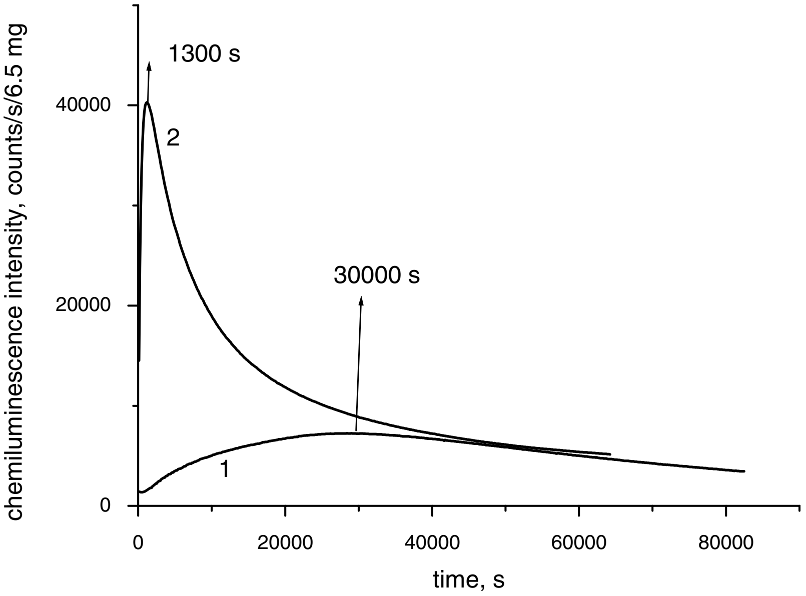


Fig. 15. A comparison of chemiluminescence isothermal runs for pullulan of initial molar mass 404 kg/mol impregnated by MMMC (2) and reference sample (1) at 190 °C in oxygen atmosphere.

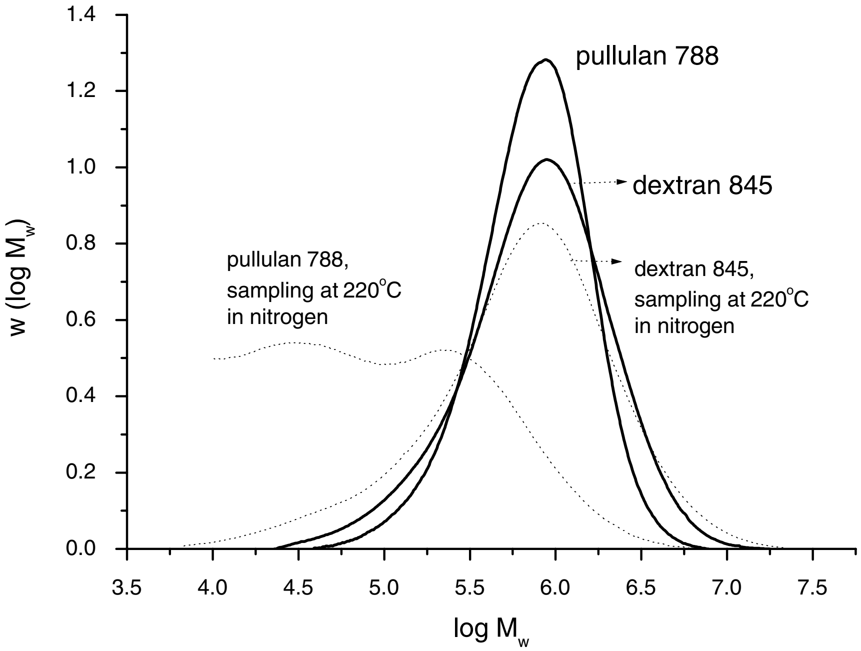


Fig. 16. Molar mass distribution of pullulan and dextran of initial molar mass 788 and 845 kg/mol after heating the sample from 40 to 220 °C by the rate 2.5 °C/min in nitrogen.

as it is in the case of pullulan, where a significant portion of low molar mass fragments can be found under comparable conditions. It seems that this may be the confirmation of the fact that the 1,4-α linkages are thermolytically the least stable structure in the examined polysaccharides.

4. Conclusions

The combined experiments of chemiluminescence, molar mass decrease and thermogravimetry may contribute to further understanding of the extent of both the hydrolytic and thermo-oxidation degradation during thermal treatment of various polysaccharides. It seems that chemiluminescence reflects total oxidation process focused on several oxidizable groups or atoms in macromolecule while molar mass decrease indicates only main chain scissions. It may be shown that thermogravimetry may decide how the degradation of respective polysaccharide is sensitive towards oxygen and discriminate between the importance of free radical and ionic mechanism degradation of polysaccharide.

Table 2 shows that 1,4-α glycosidic linkage is more sensitive towards thermolytic scission when compared with 1,6-α and 1,4-β linkages.

The promotion of chemiluminescence signal due to MMMC should be understood as being due to peroxidation of terminal semiacetal (aldehydic) groups which in the presence of MgO leads to the formation of reactive intermediates, presumably dioxetanes, having significantly higher quantum yield of light emission on the decomposition. The comparison of chemiluminescence and polymerisation degree runs for cellulose and pullulan has shown that the degradation of cellulose at elevetad temperatures is likely to occur via slow free radical oxidation of carbon in position 6 of glucopyranosyl unit with formation of carboxylic groups and subsequent acid initiated cleavage of C–O–C bonds. The similarity of rate constants of cellulose oxidation determined from non-isothermal chemiluminescence runs with those from polymerization degree measurements is also an evidence that the oxidation of carbon in position 6 is a decisive process leading to chemiluminescence in the absence of MMMC.

Table 2
Summary of oxygen linkages and promoting effect of MMMC on chemiluminescence intensity from polysaccharides

Polysaccharide	Linkages on macromolecular backbone	Promotion of chemiluminescence intensity by MMMC
Pullulan	1,4-α and 1,6-α	Yes
Cellulose	1,4-β	Yes
Dextran	1,6-α	No

Averaged rate constants of the first order determined from the sum of two independent first order processes which are responsible for the initiation of the polysaccharide thermo-oxidative degradation may serve as a quantitative way of oxidative stability of different polysaccharides.

Acknowledgments

The paper was supported by CEDEBIPO project, by VEGA Grant Agency, Projects No. 2/5109/25 and 2/6115/26 and by KNIHA-SK 2005 project.

References

Audouin-Jirackova, L., & Verdu, J. (1987). Chemiluminescence of hydrocarbon polymers. *Journal of Polymer Science, Part A, Polymer Chemistry, 25*, 1205–1217.

Baranski, A., Lagan, J. M., & Lajewski, T. (2005). Acid catalyzed degradation. In M. Strlic & J. Kolar (Eds.), *Ageing and stabilization of paper* (pp. 93–109). Ljubljana, Slovenia: National and University Library.

Billingham, N. C., & George, G. A. (1990). Chemiluminescence from oxidation of polypropylene. Some comments on a kinetic approach. *Journal of Polymer Science, Part B: Polymer Physics, 28*, 257–265.

Broska, R. (1996). *Study of chemiluminescence reactions of low molar mass precursors in polymer matrices*, Thesis, Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovakia and references therein, p. 22.

Ekenstam, A. (1936). Behaviour of cellulose in solution of mineral acids. II. Kinetic study of cellulose degradation in acid solutions. *Berrichte der Deutschen Chemischen Gesselschaft, 69*, 553–559.

Emsley, A. M., Heywood, R. J., Ali, C. M. M., & Eley, C. M. (1997). On the kinetics of degradation of cellulose. *Cellulose, 4*, 1–5.

George, G. A. (1981). Use of chemiluminescence to study the kinetics of solid polymers oxidation. In N. Grassie (Ed.). *Developments in polymer degradation* (Vol. 3, pp. 173–206). Barking: Applied Science Publishers.

Hosoda, S., Kihara, H., & Seki, Y. (1993). Chemiluminescence of polymer materials during thermal oxidation and stress. In R. L. Clough, N. C. Billingham, & K. T. Gillen (Eds.), Advances in chemistry, series 249: *Polymer durability, degradation, stabilization and life-time predictions* (pp. 195–212). Washington DC: ACS.

Kelly, G. B., Williams, J. C., Mendenhall, G. D., & Ogle, C. A. (1979). The use of chemiluminescence in the study of paper permanence. In G. B. Kelly & R. K. Eby (Eds.). *Advances in chemistry series* (Vol. 95, pp. 117). Washington: American Chemical Society.

Konoma, F., Cai, X., & Osawa, Z. (2000). Chemiluminescence from the thermal and photo-oxidation of several wood pulps. *Polymer Degradation and Stability, 65*, 105–111.

Lacey, D. J., & Dudler, V. (1996). Chemiluminescence from polypropylene. Part 1. Imaging thermal oxidation of unstabilized films. *Polymer Degradation and Stability, 51*, 101–108.

Matisová-Rychlá, L. & Rychlý, J. (1993). Inherent relations of chemiluminescence and thermooxidation of polymers. In R. L. Clough, N. C. Billingham, & K. T. Gillen (Eds.), Advances in chemistry, series 249: *Polymer durability, degradation, stabilization and life-time predictions* (pp. 175–193). Washington DC: ACS.

Matisová-Rychlá, L., Rychlý, J., & George, G. A. (2002). Chemiluminescence from thermal oxidation of poly(2,6-dimethyl 1,4-phenylene oxide). *Polymer Degradation and Stability, 75*, 385–396.

Mc Burney, L. F. (1954). Degradation of cellulose. I. Kinetics of degradation reactions. In E. Ott, H. M. Spurlin, & M. W. Grafflin (Eds.), *Cellulose and cellulose degradation I* (pp. 99–130). Intersience, New York.

Rychlý, J., Matisová-Rychlá, L., Bukovský, V., Pleteníková, M., & Vrška, M. (2006a). The progress of ageing of lignin containing paper and its relation to chemiluminescence – temperature runs. *Macromolecular Symposia, 231*, 178–192.

Rychlý, J., Matisová-Rychlá, L., Lazár, M., Janigová, I., Strlič, M., Kočar, D., Hanus, J., Mináriková, J., & Katuščák, S. (2006b). *Comptes Rendus, Chimie*, accepted for publication.

Rychlý, J., Matisová-Rychlá, L., & Strlič, M. (2000). Kinetic aspects of chemiluminescence response to periodic changes of temperature during thermal treatment of cellulose. *Polymer International, 49*, 981–986.

Rychlý, J., Rychlá, L., Slovák, K., Strlič, M., Kočar, D., Kolar, J., et al. (2004). Thermal oxidation of cellulose investigated by chemiluminescence. The effect of water at temperatures above 100 °C Carbohydrate. *Polymers, 58*, 301–309.

Rychlý, J., Strlič, M., Matisová-Rychlá, L., & Kolar, J. (2002). Chemiluminescence from paper. I. Kinetic analysis of thermal oxidation of cellulose. *Polymer Degradation and Stability, 78*, 357–367.

Setnescu, R., Jipa, S., & Osawa, Z. (1998). Chemiluminescence study on the oxidation of several polyolefins. I. Thermally induced degradation of additive-free polyolefins. *Polymer Degradation and Stability, 60*, 377–383.

Shafizadeh, F., & Bradbury, A. G. W. (1979). Degradation of cellulose in air and nitrogen at low temperatures. *Journal of Applied Polymer Science, 23*, 1431–1442.

Strlič, M., Rychlý, J., Haillant, O., Kočar, D., & Kolar, J. (2005). Chemiluminiscence of cellulose and paper. In M. Strlič, & J. Kolar (Eds.), *Ageing and stabilisation of paper* (pp. 133–148), ISBN 961-6551-03-5.

Strlič, M., Kočar, D., Kolar, J., Rychlý, J., & Pihlar, B. (2003). Degradation of pullulans of narrow molecular weight distribution – the role of aldehydes in the oxidation of polysaccharides. *Carbohydrate Polymers, 54*, 221–228.

Strlič, M., Kolar, J., Pihlar, B., Rychlý, J., & Matisová-Rychlá, L. (2001). Initial degradation processes of cellulose at elevated temperature revisited – chemiluminescence evidence. *Polymer Degradation and Stability, 72*, 157–162.

Tiemblo, P., Gomez-Elvira, J. M., Teyssendre, G., Massines, F., & Laurent, Ch. (1999). Chemiluminescence spectral evolution along the thermal oxidation of isotactic polypropylene. *Polymer Degradation and Stability, 65*, 113–121.

Zlatkevich, L. (1989). Chemiluminescence in evaluation of thermal oxidation stability. In L. Zlatkevich (Ed.). *Luminescence techniques in solid state polymer research* (pp. 135–194). New York and Basel: Marcel Dekker, Inc.