

# Effect of the polymer type and experimental parameters on chemiluminescence curves of selected materials

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Received 4 November 2002; accepted 6 December 2002

## Abstract

Oxidation of a series of common polymers and some low-molecular mass compounds has been examined by chemiluminescence. An oxidation test involving temperature ramp experiments in oxygen in the temperature range 40–220 °C has been used, enabling us to compare the oxidizability of different materials over a large temperature interval from the viewpoint of their chemiluminescence intensity and to discuss the observed discrepancies. According to this approach polymers can be divided into three groups. In the first, there are strongly luminescent polymers like polyolefins, polyamides, etc., in the second, medium luminescent polymers like cellulose, poly(2,6-dimethyl-1,4-phenylene oxide), etc., and in the third, weakly luminescent polymers like polystyrene, poly(methyl methacrylate), poly(ethylene terephthalate), etc. Different mechanisms of initiation may be seen in different temperature regions of polymer oxidation from the chemiluminescence intensity–temperature run depending on the polymer quality and on the physical state of the polymer matrix. The temperature coefficient of the chemiluminescence increase, as derived from the corresponding Arrhenius' graphs is usually rather low below the  $T_g$  of the polymer (around 40–60 kJ/mol) while at high temperatures it reflects the oxidation of the polymer matrix (around 100–150 kJ/mol or more). Any previous oxidation of the polymer may affect the chemiluminescence intensity–temperature run significantly.

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*Keywords:* Chemiluminescence; Thermal oxidation; Degradation; Polyolefins; Polyamides; Polysaccharides

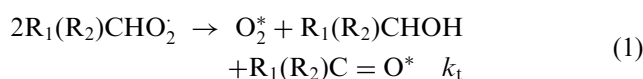
## 1. Introduction

As early as 1964 Schard et al. [1] declared that chemiluminescence measurements should provide us with fundamental knowledge on thermal oxidation of polymers provided that the phenomenon of the light emission is well understood.

However, it was very soon recognized that the problem is much more complex and that chemiluminescence oxidation experiments also often involve changes of the properties of the polymer matrix from glass transition temperature, via melting temperatures to actual oxidation which may differ, moreover, in the mechanism of the initiation.

The problem, which was currently raised by different authors [2], concerns the elementary processes from the oxidation mechanism which might be responsible for

the light emission. Only a little doubt has existed over the last 20 years that it is the recombination (disproportionation) reaction of secondary peroxy radicals  $R_1(R_2)CHOO\cdot$ , which occurs in the sense of Russel's scheme



where the asterisks denote the excited singlet state of oxygen and excited triplet state of carbonyl groups in the polymer chain, respectively. Transfer of these excited species to their ground states provides a very weak light emission. At the same time together with this emissive route of deactivation of excited states there occurs the quenching process taking place in a non-radiative way, the former process being only a small fraction of the latter. The emission from exciplexes of singlet oxygen gives a relatively broad peak situated above 700 nm while that for triplet carbonyls lies somewhere around 460 nm. It seemed therefore quite

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obvious to assume that if chemiluminescence intensity reflects the rate of peroxy radical termination, it should be at the same time proportional to the rate of initiation of polymer oxidation.

In recent years a reservation against the above mechanism has been put forward by Blakey et al. [3] who found direct proportionality between the intensity of the light emission and the increase of concentration of carbonyl groups in oxidized polypropylene. They argue that if the mechanism represented by Eq. (1) is valid then the intensity of the light emission should be proportional to the rate of carbonyl formation. They have recalled an interesting possibility of the so-called chemically induced electron exchange luminescence (CIEEL) mechanism according to which initially formed excited species interact with hydroperoxides providing for them energy for their decomposition.

The oxidation of polypropylene from the viewpoint of chemiluminescence–time or chemiluminescence–temperature patterns has been examined in many papers [4–8], because of the relatively strong luminescence of polypropylene oxidation and because of the apparent potential of the method for the testing efficiency of polymer stabilizers. One should be, however, aware of the fact that the similarity of patterns between sigmoidal increase of chemiluminescence–time runs under isothermal conditions with oxidation runs performed by other methods such as e.g. absorption of oxygen, may be mere coincidence. Recently, Gijsman has shown that the relation between oxygen uptake and chemiluminescence from polymers in oxygen is limited and is temperature and geometry dependent [9]. Chemiluminescence imaging, moreover, revealed that the sigmoidal shape of the chemiluminescence intensity–time patterns might be due to the oxidation spreading around some initially formed nucleation sites of oxidation.

The chemiluminescence from polymers that have much more complex intensity–time patterns, such as, e.g. polyethylene, which shows superposition of two autocatalytic chemiluminescence curves during its oxidation under isothermal conditions, were not interpreted properly at all. There are, moreover, polymers which do not give the autocatalytic shape under isothermal conditions, instead showing a steady decay of the light emission from the very beginning of the oxidation. This may be exemplified by the case of e.g. cellulose, or poly[2,6-dimethyl 1,4-phenylene oxide] [10, 11]. In fact, the mobility of the reactive sites in the polymer matrix, affects the resulting chemiluminescence pattern considerably.

The present paper gives an overview of the chemiluminescence emission from different polymers and of some low molar mass compounds during their oxidation examined under non-isothermal conditions in oxygen in the range 40–220 °C. Here, the chemiluminescence

temperature pattern is considerably more uniform than the isothermal one, measuring the increase of the intensity with temperature until the sample is fully oxidized and the decay may be observed. Such experiments have been already reported by Wendlandt [12–19]; unfortunately his papers did not attract appropriate attention. Non-isothermal runs will bring the most descriptive kinetic information. From one experiment one can directly approximate the oxidizability at ambient conditions regardless at which level of the chemiluminescence intensity we are. In this simplified approach, however, any temperature dependence of the proportionality coefficient between chemiluminescence intensity and the rate of oxidation must be neglected.

## 2. Experimental

The polymers under study were free of stabilizers and were used as indicated in Table 1. Chemiluminescence experiments were performed on the photon counting instrument Lumipol 2 manufactured by the Polymer Institute of Slovak Academy of Sciences, Bratislava, Slovakia. The measurements were done in a gas flow through the sample of 3 l/h with circular discs cut from polymer films or with powder samples placed in aluminium pans. The instrument dark count rate was 2–4 counts/s at 40 °C.

## 3. Results and discussion

### 3.1. Chemiluminescence–temperature runs for the series of different polymers

These runs are illustrated in Figs. 1–3 where 11 different polymers were examined in oxygen under non-isothermal conditions of linear increase of temperature from 40 to 220 °C at a rate of 2.5 °C/min. Intensities of the light emission were normalized to 1 mg of sample. Oxidation of poly(methyl methacrylate), poly(ethylene terephthalate) and polystyrene gives only very weak light intensity (Fig. 1), medium values were obtained from cellulose, poly(2,6-dimethyl-1,4-phenylene oxide) and poly(trimethylsilyl propyne (PTMSP) containing silicon and C=C double bonds in the monomer units (Fig. 2) while the most intense chemiluminescence was found for polymers like polypropylene, polyethylene, polyamide 6, polyamide 6,6 and poly(vinyl pyrrolidone) (Fig. 3). Re-plotting the non-isothermal runs in Arrhenius coordinates reveals several different temperature zones in the evolution of chemiluminescence with temperature (Fig. 4, lines 1 and 2). In the example of polypropylene we may distinguish the zone at high temperature region, which is above the melting temperature of polymer and has a temperature coefficient

Table 1  
Summary of temperature coefficients determined from Arrhenius plots of chemiluminescence intensity–temperature runs

Polymer <sup>a</sup>	Geometry	Zone I	Zone II	Zone III	Ref. [15]
		kJ/mol			
Cellulose	Sheet	115	72	48	
PTMSP	Powder	87	60	87	
PS	Powder	235	71	51	51
PP	Film	205	193	98	44–251
PE	Powder	150	372	50	
PA66	Film	98	48	97	63–97
PA6	Film	133	96	79	64
PVP	Powder	177	49	87	
PPO	Powder	206	58	–	
PMMA	Powder	124	41	–	27–86
PETP	Powder	63	68	–	
Irganox1010	Powder	76	65	57	
Dicaproyl-diamide	Powder	307	110	38	

<sup>a</sup> Cellulose (Whatman); PTMSP—poly(trimethylsilyl propyne); PS—polystyrene; PP—polypropylene; PE—polyethylene; PA 66—polyamide 66; PA 6—polyamide 6; PVP—poly(vinyl pyrrolidone); PPO—poly(2,6-dimethyl-1,4-phenylene oxide); PMMA—poly(methyl methacrylate); PETP—poly(ethylene terephthalate).

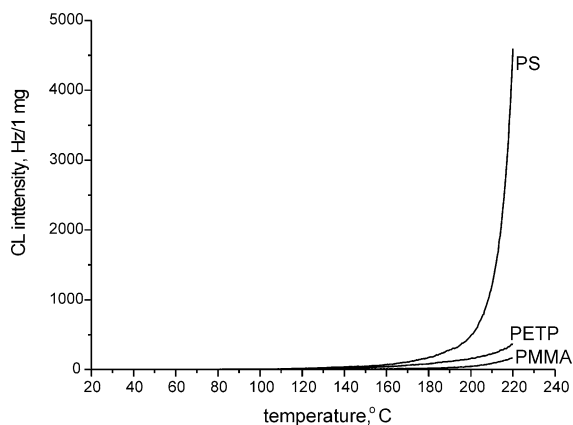


Fig. 1. Non-isothermal chemiluminescence runs for oxidation of polystyrene (PS), poly(ethylene terephthalate) (PETP) and poly(methyl methacrylate) (PMMA), oxygen, heating rate 2.5 °C/min.

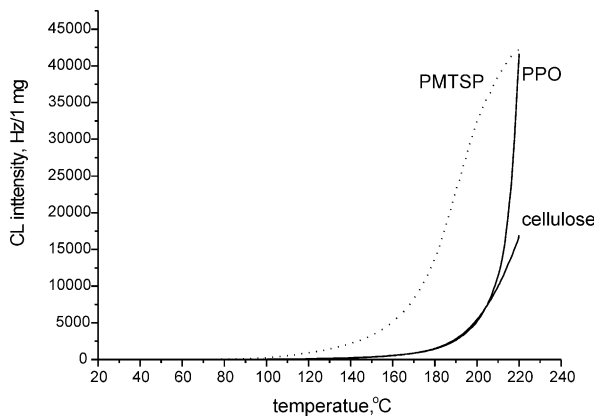


Fig. 2. Non-isothermal chemiluminescence runs for oxidation of poly(trimethylsilyl propyne) (PTMSP), poly(2,6-dimethyl 1,4-phenylene oxide) (PPO) and cellulose, oxygen, heating rate 2.5 °C/min.

around 205 kJ/mol (zone I), below the melting range, which occurs at 150–155 °C, the temperature coefficient is slightly lower (193 kJ/mol) (zone II) while at 85–125 °C there is a zone III which has a temperature coefficient of 98 kJ/mol. Temperatures below 80 °C involve zone IV, where the effect of pre-oxidation of the polymer and annealing of defect structures and hydroperoxides on initiation of oxidation takes place and dominates the increase of chemiluminescence due to increase of temperature. It is easy to realize that zones I and II at the highest temperatures may be attributed to the initiation of oxidation via the combined effects of scission of the weakest C–C bonds and unimolecular decomposition of hydroperoxides (zone II) while in zone III initiation probably occurs via bimolecular decomposition of hydroperoxides. One may also notice that any physical change of the polymer matrix (melting)

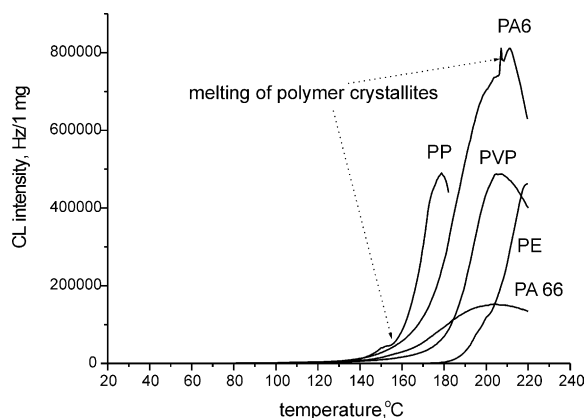


Fig. 3. Non-isothermal chemiluminescence runs for oxidation of polypropylene (PP), polyamide 6 (PA 6), poly(vinyl pyrrolidone) (PVP), polyethylene (PE) and polyamide 66 (PA 66), oxygen, heating rate 2.5 °C/min.

as well as its oxidation history has an impact on the resulting representation of the chemiluminescence intensity–temperature run plotted in Arrhenius coordinates. The temperature coefficients given by Wendlandt [16] are from 44 kJ/mol for the low temperature region to 251 kJ/mol for the high temperature region.

Data for temperature coefficients (activation energies) given in Table 1 show one common phenomenon when plotting chemiluminescence intensity–temperature runs in Arrhenius coordinates, namely that in the higher temperature range the activation energy is usually higher than at lower temperatures, which is in accordance with Wendlandt's results [16]. However there are polymers which show some peculiarities.

### 3.1.1. Polyethylene

Pre-oxidation of polyethylene similarly to polypropylene may be also revealed from non-isothermal experiments (zone IV) (Fig. 4, line 2). Pre-oxidized structures in a polymer bring about an initial fast decay of chemiluminescence intensity which dominates the increase of chemiluminescence intensity due to temperature increase, similarly as in the case of polypropylene, but the extent of preoxidation is considerably larger in the case of our samples of polyethylene (30 vs. 200 mmol of hydroperoxides per kg of polymer). The decay of chemiluminescence intensity is interrupted by melting of the polymer. The increase of chemiluminescence intensity with temperature starts to prevail at temperatures above 140 °C. Increase of chemiluminescence intensity in zone II has an unrealistically high temperature coefficient (372 kJ/mol). One has to bear in mind that during the oxidation in oxygen the superficial layer of the polymer melt assumes a black colour and carbonization takes place temporarily. This layer prevents escape of the volatiles from the polymer until it is disrupted. The rather abrupt release of volatiles is then accompanied by an increase of luminosity and typically shows abnormal values of temperature

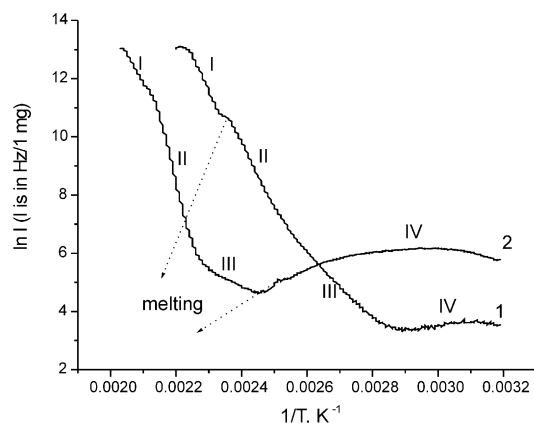


Fig. 4. Arrhenius plots for non-isothermal chemiluminescence runs of oxidized polymers, (1) polypropylene, (2) polyethylene, oxygen, heating rate 2.5 °C/min.

coefficient. One should be aware of the fact that non-isothermal thermogravimetry of polyethylene in oxygen is difficult to perform for the above reasons and due to unstability of the thermobalance caused by sudden releases of volatiles through the carbonized superficial layer. Above 200 °C the temperature coefficient attains a normal value around 150 kJ/mol. Of interest is the behavior of naturally aged polyethylene powder after repeated irradiation by daylight under isothermal conditions. When we put the original sample of polyethylene powder into the chamber of the chemiluminescence instrument we can observe an initial burst of luminosity to rather high levels followed by the fast decay. This decay lasts 20 min at room temperature, at maximum. When the sample is exposed to the daylight for a certain time and chemiluminescence measured again, we see that the chemiluminescence burst repeats, while the intensity depends on the time of the exposure of the polymer powder to light and steadily tends to the initial value (Fig. 5). This phenomenon was observed for polypropylene, polyamides, cellulose and many other polymers; the level of the chemiluminescence intensity bursts was found to be dependent on the extent of preoxidation [20]. The phenomenon recalls the charge recombination luminescence referred to by Mendenhall et al. [21] and Sewell et al. [22]. The latter authors used the phenomenon for measurement of the degree of curing of epoxy resins.

### 3.1.2. Polyamide 66 and polyamide 6

These polymers have  $T_g$  around 60 and 50 °C, respectively. Polyamide 66 shows two regions of the same or very similar temperature coefficient (98 kJ/mol), namely that at low temperature region and high temperature (Fig. 6, line 1) determined by the temperature intervals 40–64 °C and above 135 °C. Within these two intervals the temperature coefficient is rather low (48 kJ/mol). One may identify the value 64 °C with  $T_g$  of polyamide 66. Above  $T_g$  there thus exist two mechanisms of nylon 66 oxidation, the one which has rather low activation energy at lower temperature and is rather fast, while the second of activation energy 98 kJ/mol governs the process at higher temperatures. The value 98 kJ/mol below  $T_g$  is probably related to the phenomenon reported for pre-oxidized polyethylene and polypropylene initiated by daylight. If this process is monitored by non-isothermal chemiluminescence below  $T_g$ , and extent of pre-oxidation is low, it has higher activation energy than the similar process measured above  $T_g$ . Polyamide 6, similarly to polyamide 66 displays two zones of oxidation above  $T_g$  (Fig. 6, line 2) and one zone around and below  $T_g$  which has a lower activation energy than the corresponding zone of polyamide 66 (Table 1).

Fig. 7 is a demonstration of the fact that the chemiluminescence process occurs predominantly in the amorphous phase of the polyamide. Model dicaproyl

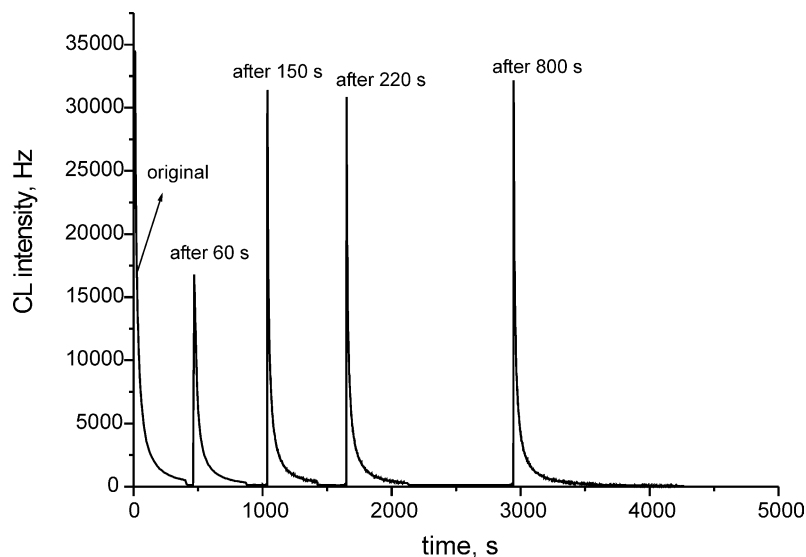


Fig. 5. Chemiluminescence response of PE powder when illuminated by the daylight at 40 °C, measured in oxygen.

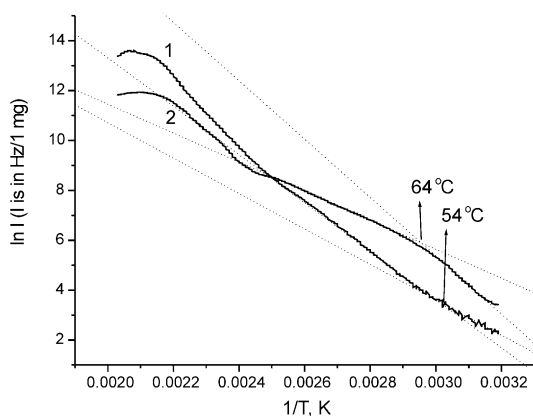


Fig. 6. Arrhenius plots for non-isothermal chemiluminescence of oxidized polymers, (1) polyamide 6, (2) polyamide 66, oxygen, heating rate 2.5 °C/min.

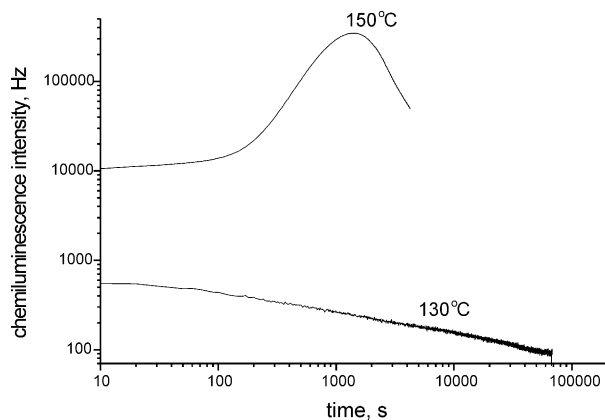


Fig. 7. CL from oxidation of polyamide model dicaproyl hexamethylene diamide  $\text{CH}_3-(\text{CH}_2)_4\text{CONH}-(\text{CH}_2)_6-\text{NHCO}-(\text{CH}_2)_4-\text{CH}_3$  in oxygen.

hexamethylene diamide is a crystalline compound; below the melting point (136 °C), the chemiluminescence signal under isothermal conditions at 130 °C is very low but it becomes rather strong after the crystallites of the diamide melt, which is the case of isothermal experiment at 150 °C. This may be also seen on the Arrhenius graph corresponding to the non-isothermal run of the same compound (Fig. 8, line 1). When the diamide melts, the chemiluminescence intensity increases by several orders of magnitude, however, two zones, as in the case of polyamides, may be observed. One may notice that the melting of fully crystalline material is accompanied by a sharp change of the slope of chemiluminescence intensity–temperature plot in Arrhenius coordinates. In the case of phenolic antioxidant, Irganox 1010 (Fig. 8, line 2), the melting at 117 °C is

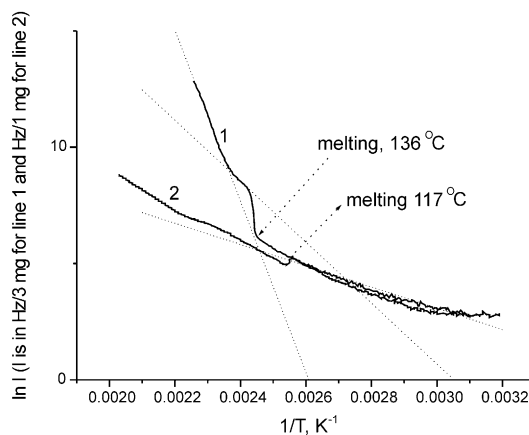


Fig. 8. Non-isothermal runs of chemiluminescence in Arrhenius coordinates, (1) dicaproyl hexamethylene diamide, (2) Irganox 1010, oxygen, heating rate 2.5 °C/min.

accompanied by a rather sharp decrease in the chemiluminescence intensity, which is obviously due to the change of the sample geometry on melting and reduction of the surface area from which light comes out.

### 3.1.3. Other polymers

Cellulose is an example of a polymer whose chemiluminescence pattern changes after extraction by distilled water (Fig. 9). In Arrhenius coordinates we may see three regions (Fig. 10), the second, beginning at 122 °C, is already above  $T_g$  of the polymer. We consider this value as the  $T_g$  of cellulose since at this temperature in samples extracted by water there appears the most distinct break on the Arrhenius plot. The conflicting data on  $T_g$  of cellulose in the literature from 243 to 433 K (–30 to 160 °C) indicate that this property depends very much on the amount of water bound in the cellulose.

Non-isothermal chemiluminescence intensity–temperature runs of other polymers which were plotted in Arrhenius coordinates show features similar to polyolefins or polyamides. Regardless of whether the poly-

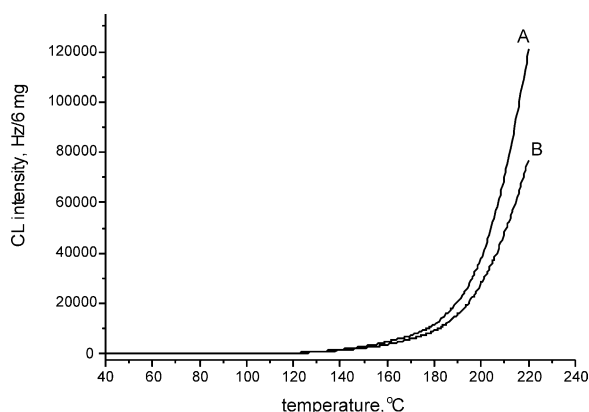


Fig. 9. Chemiluminescence from oxidation of Whatman cellulose, oxygen, heating rate 2.5°C/min. (a) Without any treatment; (b) after extraction with distilled water.

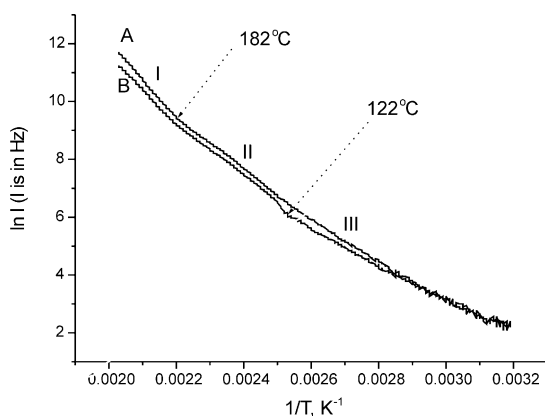
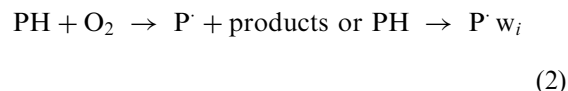


Fig. 10. Arrhenius plot of chemiluminescence intensity–temperature runs for Whatman cellulose in oxygen, heating rate 2.5 °C/min. (a) Cellulose without any treatment; (b) cellulose extracted by distilled water.

mer is strongly or weakly luminescent on oxidation, they show lower slope of the corresponding Arrhenius plot at lower temperatures which increases in the higher temperature region. The changes of the physical state of the matrix are reflected on a given plot quite unambiguously which may be seen in the case of oxidation of poly(2,6-dimethyl-1,4-phenylene oxide) and polyethylene terephthalate (Fig. 11, lines 1 and 2).  $T_g$  of the former polymer may be estimated from the extrapolated break on the corresponding Arrhenius plot while the latter gives a peak (Fig. 11, line 2). The temperature coefficients from Arrhenius' plots in respective zones of oxidation are given in Table 1.

### 3.2. Some remarks on the conditions affecting the shape of chemiluminescence–temperature patterns

- (a) The rate of peroxy radical formation which is the key factor of the polymer oxidizability appears to be very important, however, the contribution from different routes of such a process may modify the resulting chemiluminescence pattern enormously. In Bolland-Gee and other kinetic schemes of hydrocarbon oxidation the reactions are schematically depicted as:



where  $w_i$  is the rate of the process and PH represents the most vulnerable sites on the polymer chains undergoing the oxidative attack.

Eq. (2) usually stands for the unknown mechanism of the first appearance of alkyl free radicals in the system which are subsequently converted to peroxy radicals by fast addition reaction with oxygen molecules.

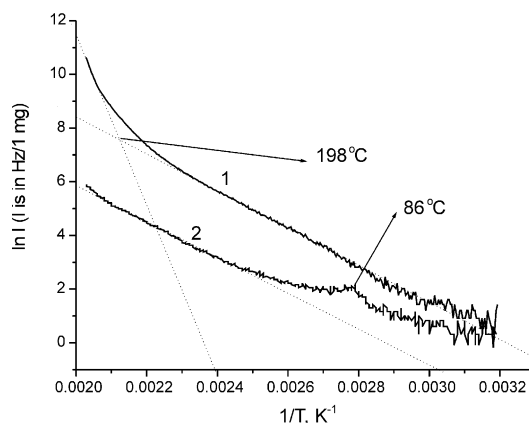
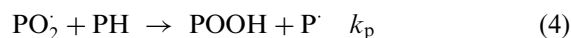


Fig. 11. Arrhenius plots for non-isothermal chemiluminescence runs of oxidized polymers (1) poly(2,6-dimethyl-1,4-phenylene oxide), (2) poly(ethylene terephthalate) oxygen, heating rate 2.5 °C/min.

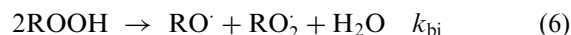
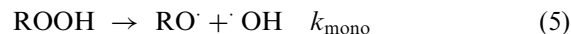


One can only speculate on the possible alternatives of the reactions (1) because they are related in most cases to the defect structures and to the terminal groups in the polymer, to impurities from residual polymerization catalysts, to charge transfer complexes between PH and oxygen which may be formed by the direct effect of the light as well as to the extent of pre-oxidation of stabilizing systems, respectively.

From the above facts one may conclude that if the length of kinetic chains corresponding to the propagation step of the oxidation



is short and thus the resulting level of hydroperoxides is low we face a system where initiation represented by scheme (2) may be dominating the decomposition of hydroperoxides. If the kinetic chain length is large then after some time of oxidation the level of polymer hydroperoxides increases in an autocatalytic manner so that the decisive role in initiation is played by the either unimolecular or bimolecular decomposition of hydroperoxides



Within the terminology of homogeneous kinetics of oxidation, the intensity of chemiluminescence  $I_{CL}$ , which corresponds to the rate of peroxy radicals termination  $k_6[RO_2^\cdot]^2$ , where  $k_6$  is the rate constant of peroxy radicals termination, is proportional to the sum of initiation events which involve reactions (2), (5) and (6) so that under conditions of steady state for concentrations of free radicals we have:

$$w_i + k_{mono}[POOH] + k_{bi}[POOH]^2 = k_6[PO_2^\cdot]^2 \approx I_{CL}$$

The intensity of light emission thus depends on which of the initiation routes prevails. For example for  $k_{mono}[POOH] + k_{bi}[POOH]^2 \ll w_i$  the polymers are weakly luminescent when compared to  $k_{mono}[POOH] + k_{bi}[POOH]^2 \gg w_i$  in a given temperature zone of oxidation, which stands for strongly luminescent polymers.

That the peroxy radical termination is the source of chemiluminescence in polymer oxidation may well be documented by parallel DSC and chemiluminescence measurements. If we compare

the simultaneous DSC and CL measurements from the thesis by Blakey [3], we see that DSC signal is proportional to the square root of chemiluminescence intensity [Fig. 12] which is in perfect agreement with the assumption of the quadratic term of peroxy radicals termination responsible for CL and propagation reaction of peroxy radicals responsible for the heat accumulation.

$$I \approx k_6[RO_2^\cdot]^2 \quad \text{and } \sqrt{I} \approx \text{DSC}$$

$$\text{DSC} \approx k_p[RO_2^\cdot][RH]$$

- (b) The presence of appropriate groups which are able to accept the excess of chemical energy converting it via excited states to the light emission. In polymers, the ideal acceptors appear to be carbonyl groups or  $\alpha,\beta$ -unsaturated carbonyls which require lower amount of energy to transfer them into an excited state. The polymers in which carbonyls are largely formed on oxidation, therefore, belong to the strongly luminescent category.
- (c) The concentration of oxygen in the surrounding atmosphere. The chemiluminescence signal of the polymers examined so far in nitrogen is negligibly low when compared with those in air or in oxygen so that the suspicion may be expressed that traces of oxygen remaining absorbed in the polymer may be responsible for it even in the case of nitrogen atmosphere. For the case of oxidation of Whatman cellulose, for example, we have found a linear relation between the chemiluminescence intensity and the square root of oxygen concentration in surrounding atmosphere [20].
- (d) As was shown in the case of the model diamide, the chemiluminescence signal originates only from the oxidation of the amorphous domains in the polymer.

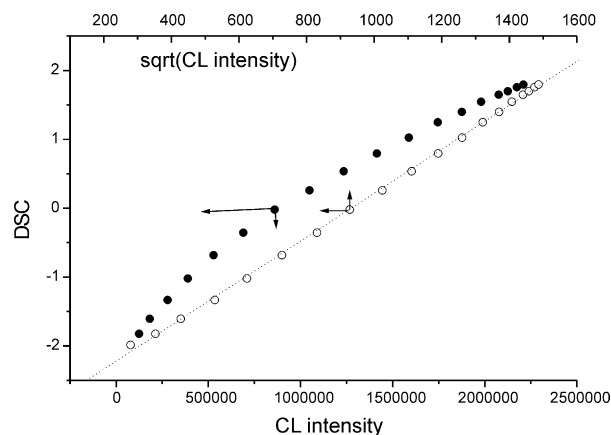


Fig. 12. The comparison of CL and DSC signal recorded from one oven for PP at 145 °C. The data are taken from the thesis by Blakey [3].

#### 4. Conclusions

1. Chemiluminescence intensity–temperature runs are more uniform fingerprints of the oxidizing polymers unifying the oxidizability of strongly and weakly luminescent polymers and indicating any change in the physical state of the polymer matrix when going from low to high temperatures.
2. From Arrhenius plots an easy extrapolation to ambient conditions can be done showing at the same time the impossibility of extrapolations over a large temperature interval from isothermal experiments.
3. The level of preoxidation of the polymer being used for the oxidation test may change the resulting pattern of chemiluminescence intensity considerably. The oxidized polymer is significantly more sensitive to illumination by daylight which manifests itself in the observation of a sudden burst of the light emission decaying over a relatively short time.
4. As it may be demonstrated on cellulose, the chemiluminescence intensity–temperature pattern is changed even by a simple operation such as its extraction by distilled water.

#### Acknowledgements

The authors gratefully acknowledge the support of the European Community, 5th Framework Programme, contract No. EVK4-CT-2000-00038, project PAPYLUM. The work is the sole responsibility of the authors and does not represent the opinion of the Community. The Community is not responsible for any use that might be made of the data appearing herein.

The paper was prepared with partial financial support from Grant Agency VEGA, Slovak Academy of Sciences No.2/7130/20.

The authors express their gratitude to P. Eriksson from the Department of Polymer Technology, KTH University, Stockholm, who supplied the PTMSP samples.

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