

DELAYED LUMINESCENCE OF SOLID POLYMERS

L. Kubera-Nowakowska, K.Lichszteid and I. Kruk

Institute of Physics, Szczecin University of Technology, 70-310 Szczecin, Al.Piastów 48/49, Poland

Received: December 30, 2006

Abstract. Delayed luminescence after UV-B irradiation of polyamide 12 (PA12), poly(ethylene terephthalate) (PET) and poly(buthylene terephthalate) (PBT), before and after ageing was investigated. Polymers were ageing at various pH of the water environment. Molecular oxygen, hydrogen peroxide and hydroxyl radicals, generated in a Fenton reaction, were used as ageing species. Light sums and kinetic curves of luminescence from PA12, PET and PBT were measured. The decay of luminescence was described as $I(t) = (A_1 + k_1 t)^{-1/2}$ in both time periods (from 0 to 180 s) and (from 180 to 600 s) respectively. Changes of all kinetics parameters during ageing were observed. Luminescence spectra of the investigated polymers were also measured using cut-off filters. The spectra show three bands with maxima at 460 nm, 500 nm, and 590 nm. These findings suggest that excited carbonyl containing compounds and molecular oxygen in its singlet state formed during termination reactions involved in the polymers oxidation are the main emitters of delayed luminescence.

1. INTRODUCTION

Polymeric materials are used on a large scale for commercial purpose. Many processes change the physical and chemical properties of a polymer, leading to the deterioration of its quality. Two kinds of processes responsible for polymer degradation may be distinguished: oxidation of polymers in air occurring under mild chemical conditions and photooxidation with participation of ultraviolet and visible light [1]. Usually both types of the processes occur simultaneously. In addition, many industrial pollutants present in an atmosphere changes pH of the rain water which contacts the polymer surface. Also metallic impurities arising from manufacturing processes could play the role of a catalyst. Degradation of polymers by reactive oxygen species present in wet and polluted atmosphere, like superoxide radical anion (O_2^-), hydroxyl radi-

cal (HO^\bullet), hydrogen peroxide (H_2O_2) and singlet oxygen (1O_2), is yet another important chemical factor in polymer's oxidation reactions. The oxidation of polymers changes their physical and mechanical properties and is a radical chain reaction which propagates in the presence of molecular oxygen [2,3]. Early studies showed that products of the termination reactions are compounds containing carbonyl group and singlet oxygen [4,5]. Several studies of polymer luminescence have reported that both natural and synthetic polymers show delayed light emission after ultraviolet and visible irradiation. Kinetics of these emissions depends on degree of a polymer ageing [6-8].

The luminescent technique often provides important information unobtainable by other means. Although there is an agreement that luminescence comes from a triplet carbonyl group and singlet

Corresponding author: I. Kruk, e-mail: kruk@ps.pl

oxygen ($^1\text{O}_2$), there is an argument about mechanisms of the emitters production [9].

Recently, we presented a very simple, non-destructive and sensitive luminescent method useful to analyse the oxidative degradation of polymers in different form at room temperature. The aim of the present work is to investigate in detail the luminescence accompanying oxidative degradation of three commercially important polymers: polyamide 12, poly(ethylene terephthalate) and poly(buthylene terephthalate).

2. EXPERIMENTAL

Materials and preparation

Polymer samples: polyamide 12 (PA12), poly(ethylene terephthalate) (PET) and poly(buthylene terephthalate) (PBT) were in a form of pellets. They were obtained from Polymer Institute, Szczecin University of Technology, Poland (PA12), BORYSZEWSKA, division "ELANA", Toruń, Poland (PET), and "JELCHEM-POLIMERY Ltd.", Jelenia Góra, Poland (PBT). Other reagents were purchased from POCh (Gliwice, Poland). Polymers were used as obtained. Degradation of polymers was carried out at room temperature in water at different pH, in the presence of air, sunlight or its absence using different concentrations of H_2O_2 , as well as in the presence of hydroxyl radicals. A Fenton-like reaction ($\text{Co(II)} + \text{H}_2\text{O}_2$) was used as a source of these radicals. 0.1M citrate and 0.05M boraxate buffers were used during the polymer ageing.

Methods of research

Luminescence was induced by irradiation of examined polymers with UV Famed-1 170W (type L6/58) mercury lamp with a Wood's filter. The optimum time found for the UV irradiation was 30 min. The decay of luminescence was measured by the photomultiplier M12FQC51 (Germany) with S20 cathode, sensitive from 180 nm to 800 nm, operating with a K-200 recorder (Karl Zeiss Jena, Germany), interfaced with a PC for data acquisition and computing. Instrumentation set-up was described in detail in previous paper [1]. Luminescence spectra were registered with a set of cut-off filters (GOST 9411-66, Russia) and an EMI 9203QB photomultiplier. The light emission detection was started 6 seconds after the ending of polymer irradiation. Parameters of the decay of the luminescence signal ($I = f(t)$) as well as the integral area under the luminescence curves, i.e. the light

sum defined as $\Sigma I = \int_0^{600} I(t)dt$ were calculated. All experiments were done at room temperature at least three times. Data are presented as mean \pm standard deviation. *P*-value less than 0.05 were considered statistically significant.

3. RESULTS AND DISCUSSION

All investigated polymers shows delayed luminescence after UV irradiation. Fig. 1A presents the representative luminescence decay of polyamide PA12 before and after degradation in darkness and in daily light in the presence of hydrogen peroxide dissolved in boraxate buffer, pH=8.0. The kinetics showed an initial fast decay over the first 180 s followed by a slower decay. The luminescence decay can be fitted by two subsequent second order reactions given by $I_j(t) = (A_j + k_j t)^{-2}$, where $j=1$ for $t < 180$ s, and $j=2$ for $t > 180$ s (Fig. 1B). The param-

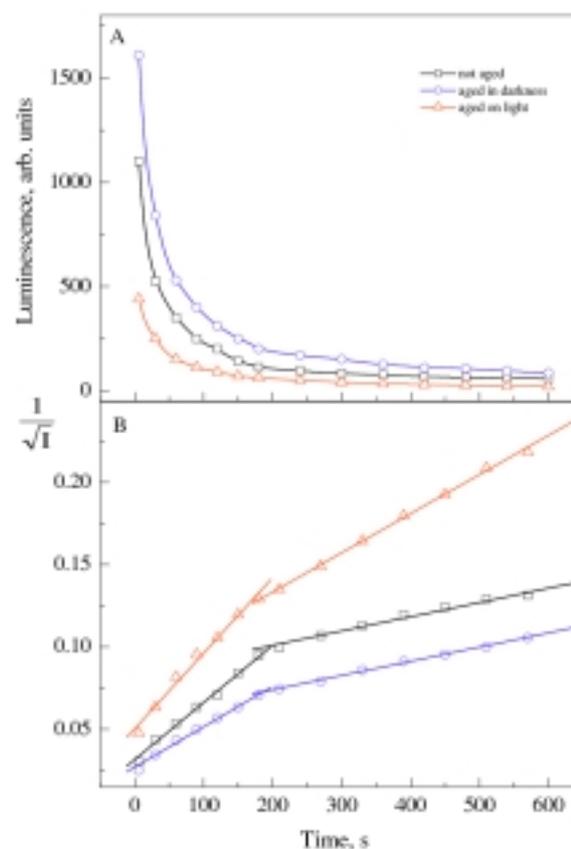


Fig. 1. Typical curves of the decay of luminescence ($I = f(t)$) after UV-B irradiation of PA12 before and after ageing in darkness and on daily light (part A). Ageing conditions: boraxate buffer, pH 8.0, 0.1mM H_2O_2 . Part B – Analysis of the decay curves shown in part A.

Table 1. Kinetic parameters of delayed luminescence of polymers before and after ageing in the absence and presence of daily light.

pH	<i>Darkness</i>					<i>Daily light</i>				
	k_1 [10^{-4}s^{-1}]	k_2 [10^{-4}s^{-1}]	A_1	A_2	ΣI	k_1 [10^{-4}s^{-1}]	k_2 [10^{-4}s^{-1}]	A_1	A_2	ΣI
PA 12										
	3.38*	0.86*	0.033*	0.084*	81 477*					
3.0	3.03	1.41	0.033	0.061	86 760	4.94	2.72	0.068	0.103	25 240
4.8	2.85	1.38	0.030	0.058	100 900	5.13	2.46	0.058	0.100	29 800
7.4	2.97	1.26	0.033	0.063	90 920	4.44	2.02	0.055	0.098	35 500
8.0	3.08	1.35	0.032	0.060	113 414	4.43	2.23	0.056	0.096	34 150
9.0	2.60	0.86	0.027	0.061	127 670	4.14	1.88	0.051	0.091	41 250
10.0	2.60	0.92	0.026	0.059	129 450	4.00	1.68	0.046	0.089	46 930
11.0	2.67	0.86	0.026	0.062	129 270	3.55	1.92	0.045	0.072	53 450
PET										
	8.14*	2.76*	0.170*	0.284*	5 805*					
3.0	5.54	2.59	0.141	0.197	9 671	13.2	5.96	0.250	0.438	2 710
4.8	7.32	1.36	0.151	0.251	8 376	13.6	5.23	0.240	0.385	2 635
7.4	5.17	1.96	0.138	0.202	10 647	10.5	5.07	0.238	0.341	3 099
8.0	5.13	2.04	0.125	0.186	12 101	12.4	5.05	0.216	0.352	3 143
9.0	4.65	2.03	0.112	0.163	14 782	9.5	3.93	0.208	0.331	3 902
10.0	4.81	1.78	0.119	0.176	13 755	7.7	3.38	0.193	0.263	5 321
11.0	4.34	1.03	0.107	0.177	17 241	7.7	3.06	0.183	0.256	5 841
PBT										
	7.6*	5.3*	0.219*	0.439*	3 153*					
3.0	13.8	6.7	0.259	0.364	2 356	18.8	4.1	0.355	0.618	1 364
4.8	13.2	7.5	0.254	0.338	2 414	19.0	3.8	0.350	0.618	1 390
7.4	13.4	3.9	0.254	0.446	2 475	18.8	3.4	0.318	0.609	1 535
8.0	13.6	3.5	0.258	0.453	2 468	14.1	2.5	0.348	0.566	1 738
9.0	13.0	4.1	0.255	0.401	2 664	15.6	2.7	0.360	0.582	1 599
10.0	12.5	2.9	0.259	0.421	2 795	17.3	3.3	0.317	0.562	1 695
11.0	11.7	3.1	0.248	0.391	3 067	16.4	2.2	0.318	0.557	1 848

Symbols used: k_1 and k_2 – rate constants of the luminescence decay, A_1 , A_2 – initial intensities of luminescence, ΣI – the light sum. The symbol (*) means data obtained for polymers before the ageing process.

eters of observed luminescence decay of polyamide P12 and both polyesters examined, calculated from the decay curves in the absence of H_2O_2 , and are shown in Table 1.

The luminescence decay rate constants depended on the degradation conditions but the plots were linear that independently on pH, H_2O_2 concentration, presence or absence of daily light and yielded a peroxy radical half-life [9] (data not shown).

For all examined polymers, the rate constants show higher values after degradation in the pres-

ence of daily light as compared to those degraded in darkness as well as for nondegraded, exception PET, pH=10, and 11 (Table 1). Moreover, calculated rate constants k_1 for PA12 and PET aged in the darkness were lower than those of polymers that had not been degraded. Similar results were obtained for polymers degraded in the presence of H_2O_2 . For PA12 degraded in the darkness slight decreases of k_1 and k_2 values with an increase of the environment pH was observed in the presence of H_2O_2 as well as in its absence. For PA12 and PET we observed greater initial intensity of lumi-

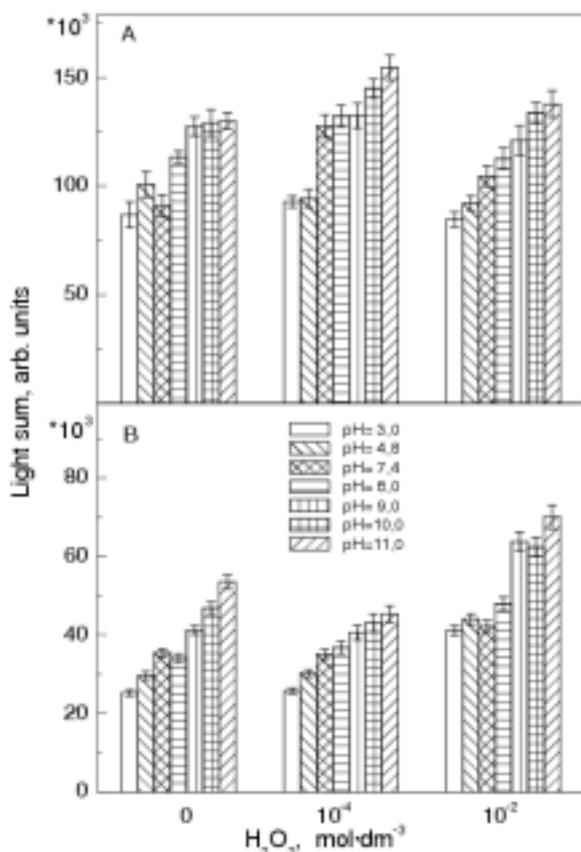


Fig. 2. The light sums of delayed luminescence after ageing of PA12 in different pH and in the presence of different concentrations of H_2O_2 . A, B – ageing in the absence and in the presence of daily light, respectively.

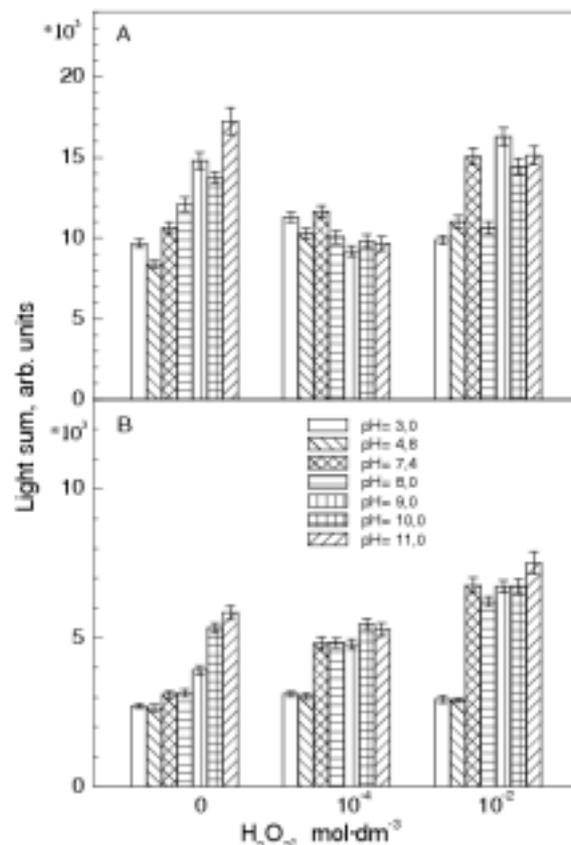


Fig. 3. The light sums of delayed luminescence after ageing of PET. Conditions are identical to those given in Fig. 2.

nescence and its slower decay when the polymers were degraded in basic solution. This indicated a greater concentration of the luminescence centres and their slower disappearance.

Figs. 2-4 represent light sums calculated for the investigated polymers after ageing in different conditions. From the figures we can see a very strong effect of daily light on the light sums; degradation in the presence of light was followed by more than their 2-fold decrease. In addition, significant increases of light sums accompanying an increase of pH values, both in the presence and in the absence of H_2O_2 , as well as after ageing in darkness or on daily light, were observed.

Reactive oxygen species are constantly formed in the atmosphere. Among these species hydroxyl radical is considered as the strongest oxidant [10].

Due to its strong reactivity with molecules we have examined degradation of polymers tested in the reaction generating HO^\bullet . The radical was formed from H_2O_2 in a reaction catalysed by cobalt ions, known as the Fenton-like reaction:



where $\text{Me} = \text{Fe(II)}, \text{Co(II)}, \text{Cu(I)}$ [11].

Ageing of polymers in the Fenton-like reaction significantly influences their degradation followed by a change of the delayed luminescence intensity (Fig. 5). For all investigated polymers we observed statistically significant decrease of the light sum as compared to that measured before the polymer degradation.

In order to identify the luminescence emitters we measured the emission spectra. In spite of low

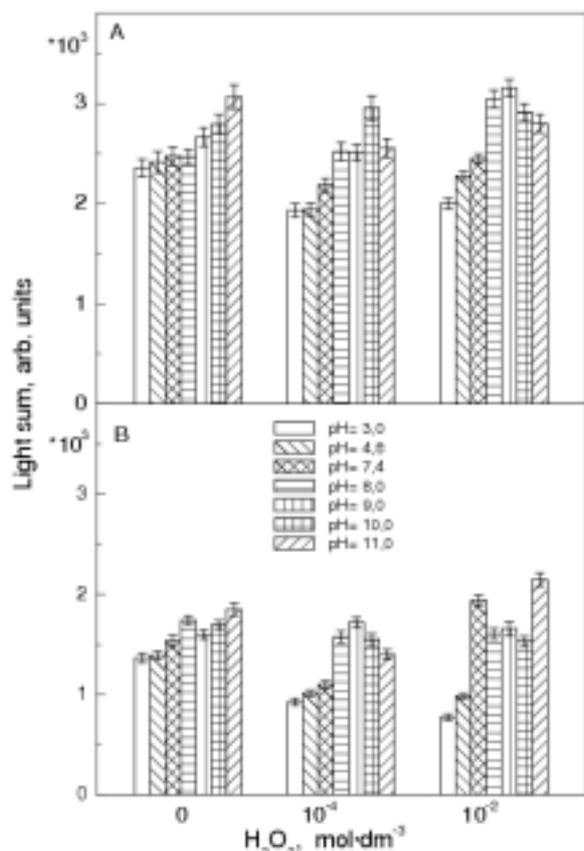
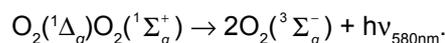


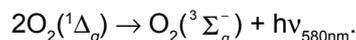
Fig. 4. The light sums of delayed luminescence after ageing of PBT. Conditions are identical to those given in Fig. 2.

quantum efficiency of the light emission the spectral distribution measurements were possible using series of cut-off filters only. Fig. 6 presents the spectra of PA12 registered at various times after ending of UV-B irradiation. The spectra exhibit two major bands in the range 400-650 nm with maxima at about 460 nm and 500 nm. The emission bands may originate mainly from carbonyl groups excited to the triplet state directly or in consecutive reactions.

The emission from 1O_2 dimers of molecules in their singlet states $^1\Delta_g$ and $^1\Sigma_g^+$ with vibrational quantum numbers (0,0) may also participated in the band of 500 nm [12,13]:



A minor band at 590 nm may result from the transition in the 1O_2 dimers of molecules in the $^1\Delta_g$ state with vibrational quantum numbers (1,0):



The positions of the emission bands were not changed during the decay of luminescence. The emission spectra of the remaining polymers examined were weaker; they also exhibited bands at 460 nm and 500 nm. These findings indicate that an emission may have a common origin irrespective of the chemical structure of the examined polymers.

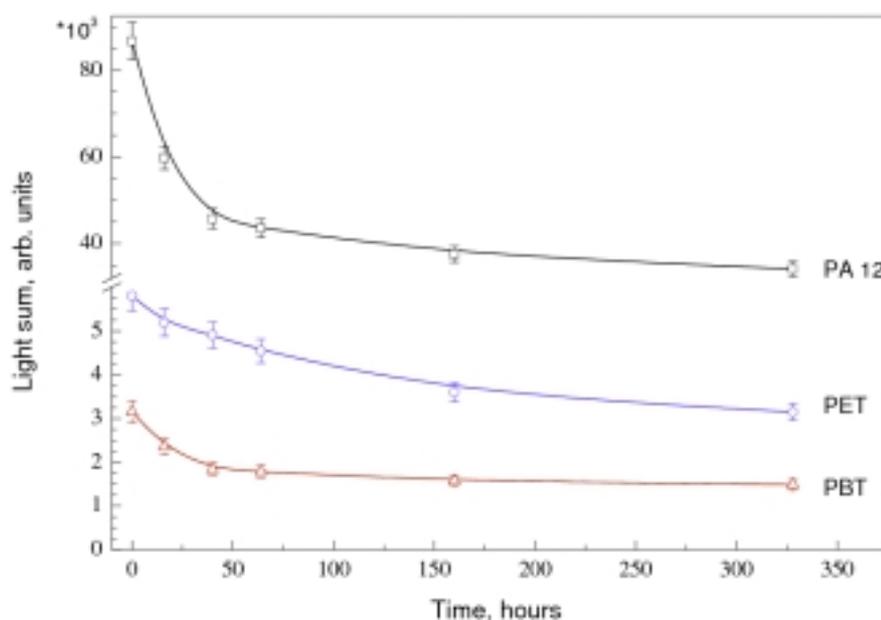


Fig. 5. Changes of light sums of delayed luminescence after ageing of polymers by the Fenton-like reaction. Conditions: 10mM $CoCl_2$, 1M H_2O_2 , boraxate buffer, pH 11.0.

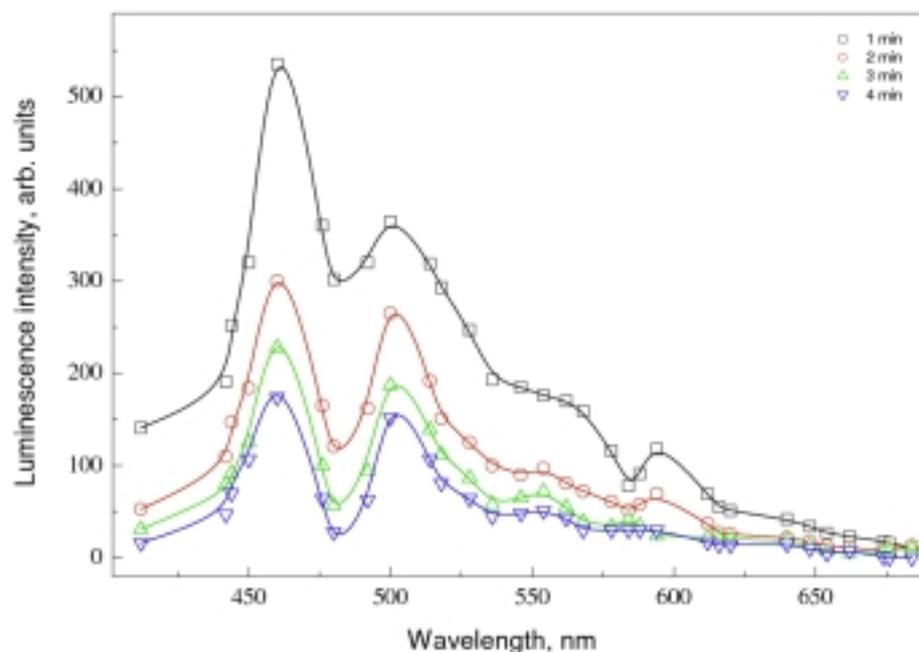
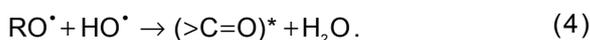
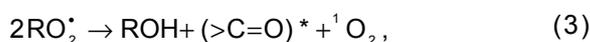
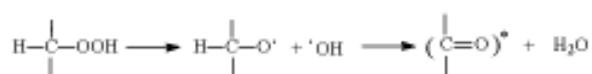


Fig. 6. The luminescence spectra of PA12 measured in various times after ending of UV-B irradiation.

The low energy of the emission as well as its long half-life suggests that a triplet state of a carbonyl oxidation product is populated. Commercial polymers contain a number of UV-B absorbing chromophores, which may be involved in free-radical formation, and the hydroperoxide group is considered as the primary photoinitiation centre [9]. In both peroxidized and non-oxidized polymer samples the bimolecular decomposition of hydroperoxides may be responsible for the observed luminescence:



This suggestion is supported by analysis of the luminescence decay, which showed the second order kinetics. In addition, the obtained rate constants agreed with that found by other authors from analysis of the hydroperoxide decay [14]. Reaction (3) is sufficiently exothermic for the excitation of a carbonyl group to the triplet or singlet states or molecular oxygen to its singlet states ${}^1\Delta_g$ and ${}^1\Sigma_g^+$, and to ensure luminescence above 400 nm. Also the direct decomposition of hydroperoxides gives an excited carbonyl compound:



Both the above mentioned mechanisms for delayed luminescence have been used by other authors to explain the data obtained for different polymers [15].

4. CONCLUSIONS

The luminescence technique used to detect the oxidative degradation of polymers is highly sensitive. Therefore it might be possible to investigate the influence of pH, the visible light and the presence of different oxidants, like O_2 , HO^{\bullet} , and H_2O_2 on polymers. All these degrading factors caused the significant changes in the parameters of long-lived luminescence. Especially great influence was observed when the hydroxyl radicals were used as an oxidant. These radicals are considered to play significant role in initiation of the chain reaction of polymer degradation.

REFERENCES

- [1] B. Ranby and J.F. Rabek, In: *Ultraviolet light induced reactions in polymers*, ed. by S.C. Labona (Series 25 ACS Symposium, 1976) p. 391.

- [2] J.F. Rabek, J. Lucki and B. Ranby // *Eur. Polym. J.* **15** (1979) 1089.
- [3] M.L. Kaplan and M.A. Trozollo, In: *Singlet Oxygen* ed. by H.H. Wasserman and R.W. Murray (Academic Press: New York, 1979) p.575.
- [4] J.F. Rabek and B. Ranby // *Appl. Polym. Sci.* **23** (1979) 2481.
- [5] G. A. Russel // *Chem. & Ind.* **12** (1956) 1483.
- [6] T.V. Veselova, V.A. Veselovsky, A.A. Krasnovsky Jr. and K. Lichsztełd // *Biofizika* **XXX** (1985) 711.
- [7] K. Lichsztełd // *Sci. Rep. Tech. Univ. Szczecin* **356** (1988) 133.
- [8] L. Kubera-Nowakowska, S. Spychaj and I.Kruk // *Rev. Adv. Mater. Sci.* **12** (2006) 172.
- [9] G.A. George, In: *Luminescence techniques in solid-state polymer research*, ed. by L. Zlatkewich (Marcel Dekker Inc., New York and Basel, 1989) p. 93.
- [10] S. Goldstein, D. Meyerstein and G. Czapski // *Free Radic. Biol. Med.* **15** (1993) 435.
- [11] F. Haber and J. Weiss // *Proc. R. Soc. London Ser. A.* **147** (1934) 332.
- [12] V. Dudler and D.J. Lacey, In: *Bioluminescence and Chemiluminescence. Fundamentals and Applied Aspects*, ed. by A.K. Cambell, L.J. Kricka and P.E. Stanley (Willey&Sons: Chichester, 1994) p. 621.
- [13] N.S. Allen and E.D. Owen, In: *Luminescence techniques in solid-state polymer research*, ed. by L. Zlatkevich (Marcel Dekker Inc.: New York and Basel, 1989) p.51.
- [14] G.A. George, G.T. Egglestone and S.Z. Riddell // *Polym. Eng. Sci.* **23** (1983) 412.
- [15] L. Matisova-Rychla, J. Rychly and M. Vavrekova // *Eur. Polym. J.* **14** (1978) 1033.