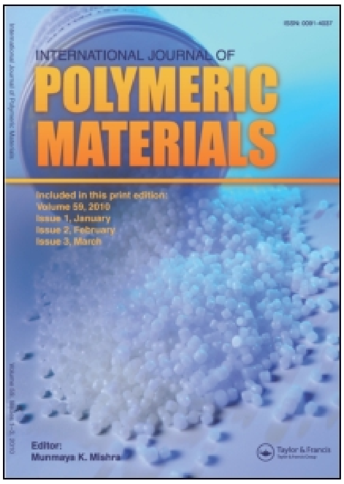

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Chemilumunescence of Isotactic Polypropylene Induced by UV Irradiation

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The kinetics of the weak chemilumunescence (CL) and peroxyl radical decay after UV irradiation of isotactic polypropylene (PP) have been studied. The correlation has been found between CL and the reaction of chain termination under the PP post-oxidation at room temperature in air. Kinetics of CL decay, its compliance with kinetics of peroxyl radical decay, relative quantum yield of CL per one act of radical termination and effects of the plasticizer, accelerating both radical termination and CL decay, have been determined. Kinetic features of CL decay indicates the distributions of peroxyl radicals on both rate constants of termination and quantum yields of CL in the acts of the disproportionation of two peroxyl radicals. In terms of these distributions it is possible to describe quantitatively observed kinetics of CL decay under the post oxidation of PP after the UV irradiation in air.

Keywords: Chemilumunescence; kinetics; isotactic polypropylene UV irradiation; peroxyl radical

1. INTRODUCTION

Chemilumunescence (CL) during the oxidative degradation of polymers have been widely studied in the past 30 years (see the review [1]). The modern technique of measuring the weak CL emission is considered to have great potential due to ultra high sensitivity of light detectors. So many attempts are undertaken to use a CL for an estimation

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*Corresponding author. e-mail: almar@sky1.chph.ras.ru of efficiency of stabilizers and initiators, a control of slow processes of the polymer ageing, a forecasting of polymer lifetime, a study of the oxidation mechanism [1–5].

However till now the mechanism of CL-emission under the oxidation of polymers in solid state remains unknown in some important details. The interpretation of CL, based on homogeneous reaction kinetics, has been suggested by Zlatkevich [5], but his approach has been questioned seriously by Billingham and George [6]. The microphotographs of PP samples during the oxidation show a non-uniform luminescence of PP surface that confirms inhomogeneity of PP oxidation [7]. This conclusion was put under doubt in the subsequent work [8].

Earlier CL was assumed to arise from a cage reaction of alkoxyl radicals, produced by the decomposition of polymer hydroperoxides [9–11]. Subsequently this assumption has not been confirmed, since CL has been shown to be suppressed by inhibitors which can not affect a cage reaction [12]. Upon the hydrocarbon oxidation, CL arises from the disproportionation of peroxyl radicals [13]. Presently this reaction is also considered as the most probable source of CL upon the PP oxidation [12, 14] .

Some unusual features of CL observed must be mentioned. Thus, in inert atmosphere at high temperatures hydroperoxides of PP decomposes *via* first-order reactions, but CL from decomposition of hydroperoxides is shown to decay more rapidly than do the peroxides, following second-order kinetics [12]. In polyethylene after photooxidation the intensity of CL is proportional to t^{-2}, as it should be for CL emission from homogeneous reaction of bimolecular termination of peroxyl radicals [15]. However in aliphatic polyamides the intensity of CL is proportional to $t^{-1/3}$, that differs significantly from the dependence expected for second-order reactions [16].

In solid polymers the kinetics of termination of peroxyl radicals in absence of a mixing can mimic some kinetic properties of simple reactions and depends on initial distribution of free radicals on its reactivity [17]. It has been shown for PP, as the most studied polymer, that such inhomogeneous kinetics does not coincide completely with kinetic laws for simple reactions of the first and second orders [18, 19]. So in the present work we attempted to compare kinetics of CL decay with the kinetics of peroxyl radical decay in PP.

2. EXPERIMENTAL

Transparent undrawn films of isotactic PP ("Kaplen"), supplied by Moscow oil refining factory, of 80 microns thickness has been made by extrusion. The films were purified by repeated extraction by chloroform and ethanol at room temperature. Hexachloro-p-xylene (HCPX) was used as a photoinitiator in a number of experiments. HCPX was purified by repeated recrystallization from ethanol and was introduced in PP film from a saturated ethanol solution at room temperature. PP films with or without HCPX were irradiated in air at 20°C. UV irradiation was carried out using a low-pressure mercury lamp without any filter. The main wavelength in the spectrum of this lamp is 253, 7 nm. PP samples after UV irradiation were put into the dark chamber of chemiluminometer SNK-7 [13]. Measurement of CL intensity from PP film was started after 30 seconds from the stop of UV irradiation at 20°C. Concentration of peroxyl radicals was determined by ESR method using a spectrometer ESR-V of ICP RAS also at 20°C.

3. RESULTS

The weak luminescence is observed after a short-term irradiation of PP films by UV light. This CL proceeds for hours and completely disappears up to the next day. The typical curve of decaying CL intensity I_{CL} is shown in Figure 1 (curve 1). The photochemical post-effect at room temperature is observed because the radicals, formed by UV irradiation, do not vanish instantly, when the light is switched off, but disappear gradually in slow reactions of their termination. Initial CL intensity I_o was varied by increase of intensity of UV irradiation. Varying of irradiation time (from 5 to 240 seconds) was also used to increase CL intensity up to maximum value at the stationary state photooxidation. All the obtained data show that CL decay after PP photooxidation without additives follows the kinetic equation (1)

$$I_{CL}/I_o = 1/(1 + t/\tau)^n, \qquad (1)$$

Where I_{CL} and I_o are the current and initial intensities of CL, respectively, t is time, τ is the initial lifetime of CL, when the CL

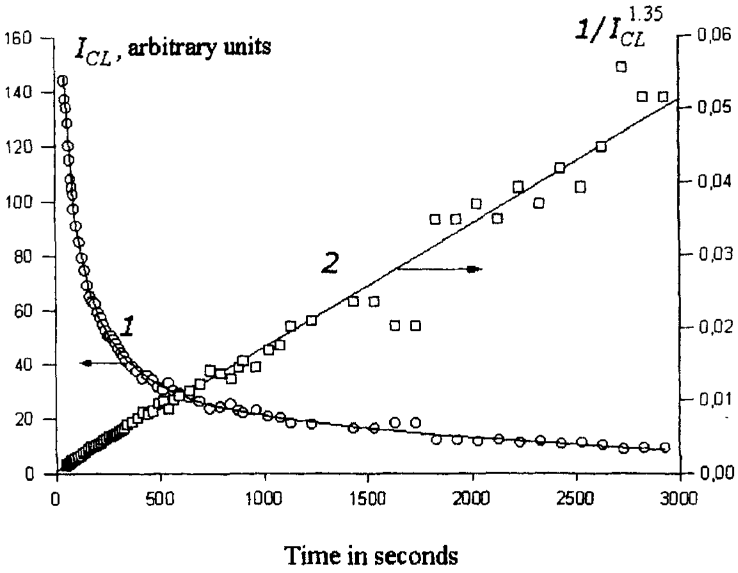


FIGURE 1 A kinetic curve of CL decay in PP (1) and its linear anamorphosis (2) in post-effect of photooxidation during 20 seconds at light with wavelength of 254 nm in air at 20°C.

intensity falls to half of its original value, n is the parameter which equals about 1.

The Eq. (1) can be transformed to Eq. (2) which is convenient to check the linearization of kinetic data

$$I_{\mathrm{CL}}^{-1/n} = I_o^{-1/n} + (I_o^{-1/n}/\tau)t \qquad (2)$$

Typical linearization of kinetic curve of CL decay according to Eq. (2) is shown in Figure 1 (straight line 2). Parameter n is found by method of the least squares provided that the linear correlation coefficient R is the highest. The values of R were determined for different values of n and then the best value of n with the highest R was taken out for the best linearization of the kinetic data. Then the initial lifetime τ of CL decay was calculated from the slope and the intercept of the plot of $I_{\mathrm{CL}}^{-1/n}$ against time t.

It should be noted that the linear correlation coefficient R is not sensitive enough to detect only one value of n. Various values of n, differring on 0.2, give the same value of R (for example, R = 0,995).

The error in determination of parameters may be caused by both properties of general hyperbola according to Eq. (1) and an error of measurements. For exact determination of n the measurements of I_{CL} are required down to very low values. But relative accuracy of measurements decreases with the decrease of absolute value of I_{CL}.

The values of n are found to be 0,7 – 1,0 for all CL decay curves with the initial intensities I_o varied by 10 times. The initial lifetime τ of CL decay is found to be 20 ± 10 seconds with no appreciable dependence of τ on I_o. In addition to the decrease in initial CL intensity by an order of magnitude, the intensity of CL decay in a course of PP post-oxidation was decreased in more than 10 – 30 times. So the empirical Eq. (1) describes data on CL intensities in a range of more than two orders of magnitude.

Equation (1) with $n \approx 1$ for CL in solid PP is quite distinguished from Eq. (1) with $n = 2$ for CL in studies of oxidation of liquid hydrocarbons, where therefore the CL decays faster than concentration of peroxyl radicals decreases. The kinetics of the decay of peroxyl radicals in solid PP is also quite different from that in a liquid phase and follows to the kinetic law (3), which can not been fitted to first-order kinetics, as well as to second-order kinetics [18]:

$$[RO_2]/[RO_2]_o = 1/(1 + t/\tau), \tag{3}$$

where $[RO_2]$ and $[RO_2]_o$ are current and initial concentrations of peroxyl radicals respectively, and τ is the initial half-life of radicals. The value of τ remains constant, τ = const, irrespective of the initial concentration of free radicals, but depends on the way by which this initial concentration of free radicals has been achieved.

By comparison of Eq. (3) and Eq. (1) with $n \approx 1$, it must be concluded that the kinetics of CL decay is similar to the kinetics of termination of peroxyl radicals in solid PP. This is the first correlation feature observed between CL-emission and radical decay.

The second correlation feature is the comparable effect of a degree of PP oxidation on both half-life of CL and half-life of the macroperoxyl radicals. Lifetime of CL has been found to be higher for a preoxidised PP sample ($\tau = 100 - 300$ seconds) than for unoxidised PP ($\tau = 15 - 30$ seconds). To receive appreciable effect, it is enough to carry out photooxidation of PP during 2 hours. If then to anneal radicals by heat at 100°C during 5–10 minutes up to disappearance of CL-emission, the subsequent short-term irradiation leads to long-lived CL-emission (Fig. 2, straight line 2). This effect is similar to known effect of a degree of oxidation on a half-life of peroxyl radicals in solid PP. The significant increase in radicals half-life at a high degree of PP oxidation was attributed to the distribution of radicals on its reactivity [18]. In the case of unoxidised PP the free radicals are formed mainly in the most mobile regions of polymer. So the distribution of radicals is enriched by shortlived mobile radicals at the early stages of the photooxidation. In the case of oxidised PP the hydroperoxides ROOH become the main photoinitiator. Under its photodecomposition they eliminate a light hydroxyl radical OH which is able to diffuse at a large distance and to generate the long-lived macroradicals in hard-to-reach areas with low mobility. So the distribution of radicals is enriched by long-lived slow-moving radicals in oxidised PP.

The third correlation feature is the comparable effect of the photoinitiator HCPX on a half-life of both CL and macroperoxyl

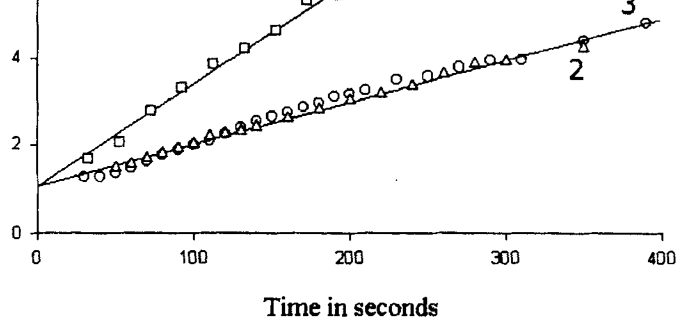


FIGURE 2 Kinetics of decay of intensity I_{CL} of chemilumunescence from unoxidized (1) and preoxidized (2) PP with no additive, and also unoxidized PP with the additive of the photoinitiator (HCPX) (3) after 1 minute of the UV irradiation in air at 20°C.

radicals. CL-emission induced by the HCPX photoinitiation has been found to have an increased half-life of about 120 seconds for unoxidised PP (Fig. 2, straight line 3). The same effect is known for macroperoxyl radicals of PP which have a half-life of about 100–180 seconds if they are formed by the HCPX photoinitiation in unoxidised PP. The photodecomposition of HCPX, as well as the photodecomposition of hydroperoxides, produces light particles (in this case, chlorine atoms), capable to form long-lived macroradicals in rigid areas of polymer [18]. It will increase a half-life of CL in unoxidised PP.

Thus, it is possible to make a conclusion that the lifetimes of both CL and macroperoxyl radicals changes in the same manner over a wide range of CL intensities and at three different ways of photoinitiation. It means CL intensity is proportional to concentration of macroperoxyl radicals, *i.e.*, $I_{\mathrm{CL}} \sim [RO_2]$. This was confirmed by direct measurement of $[RO_2]$ and I_{CL} under the same conditions of post-oxidation (Fig. 3, curves 1 and 2 respectively). As shown in Figure 3, CL intensity, to within the experimental accuracy, is proportional to

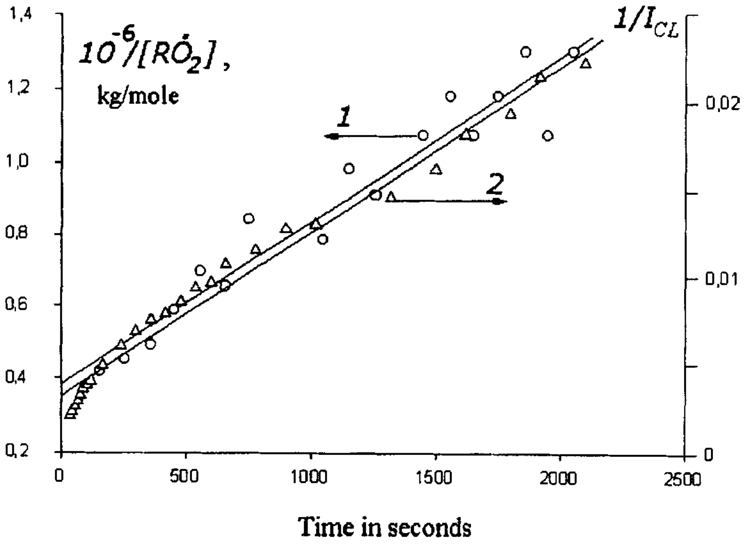


FIGURE 3 Decay of concentration of peroxyl radicals of PP (1) and relative intensity of CL emission from PP (2) after 2 minutes of irradiation of PP films by light with wavelength of 254 nm in air at 20°C.

concentration of peroxyl radicals over the range of measurable concentrations.

4. THEORY

Unusual relationship between CL intensity and radical concentration may be caused by inhomogeneous reaction of peroxyl radicals in solid PP. The Eq. (3) implies that the rate of radical decay is proportional to radical concentration, *i.e.*, the radicals disappear *via* the first order reaction, and the time dependence of average concentration is due to the distribution of macroperoxyl radicals on rate constants k of their termination [20]. If $R(k)dk$ is the amount of radicals with the rate constant k in the interval from k to $k+dk$ at time $t = 0$, the average concentration of radicals is determined by integration of $R(k)$ on all values of k.

$$[RO_2]/[RO_2]_o = \int R(k)\exp(-kt)dt \tag{4}$$

Combining Eqs. (3)–(4), we obtain the function $R(k)$ for distribution of radicals:

$$R(k) = \tau\exp(-k\tau) \tag{5}$$

Intensity of CL-emission is equal to rate of chemiluminescent reaction occurring in the acts of the termination of macroperoxyl radicals:

$$I_{\mathrm{CL}} = [RO_2]_o \int \phi(k)k\tau\exp[-k(\tau+t)]dk, \tag{6}$$

Where $\phi(k)$ is a quantum yield of CL, *i.e.*, the amount of photons emitted per 1 act of radical termination with the rate constant k.

Equation (6) gives empirical Eq. (1) for CL decay at

$$\phi(k) \sim k^{n-2} \tag{7}$$

In our case where $n \approx 1$, Eq. (7) indicates that the quantum yield of CL $\phi(k)$ significantly increases as the rate constant k is decreased. Since the rate constants are controlled by the molecular mobility, it can be concluded that the yield of CL in PP depends on the molecular mobility of area where the radical termination occurs.

The probability of phosphorescence strongly increases with decreasing molecular mobility due to the suppression of non-radiative deactivation of the excited molecules [21]. Various molecules begin to phosphorescence due to the transition from a liquid to a solid state. Therefore, the yield of CL in more ordered areas of PP can be higher at the expense of an increased yield of phosphorescence of excited molecule formed in chemiluminescent reaction.

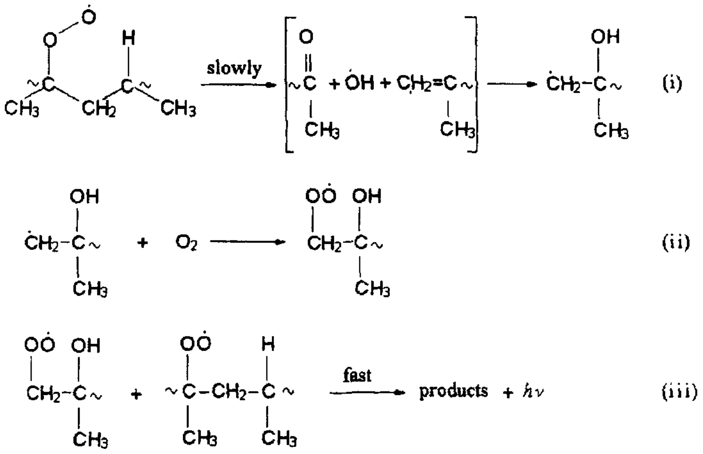
The effect of local mobility on the quantum efficiency for CL emission allows to understand qualitatively the observed kinetics of CL decay in PP. At the start of experiment the macroperoxyl radicals disappear in areas of PP with the highest mobility of chain segments where CL yield is the lowest, next radicals disappear in less mobile areas with higher CL yield *etc*. Thus the short-lived radicals give off less photons per 1 radical than the long-lived radicals. As a result, the fall of CL caused by the decrease of rate of recombination of radicals is partially compensated by increase of CL yield.

We have undertaken an estimation of relative CL yield from the data, shown in Figure 3. The yield of CL at the end of kinetic curve of radical termination was found to be 4 times higher than that at the begining. The additional support was received in direct experiments with plasticizer: immersing of a luminous film after photooxidation in chloroform increases rate of termination of radicals, but simultaneously reduces integrated CL-emission. These experiments show that yield of CL is reduced by increase of molecular mobility of polymer.

5. DISCUSSION

5.1. Mechanism of CL

The data obtained show that CL arises at the stage of termination of tertiary macroperoxyl radicals which are predominant radicals under the oxidation of PP. However, triplet states will not be formed directly in the act of recombination of two tertiary peroxyl radicals. This controversy may be avoided by the known mechanism suggested earlier [20] to explain the linear termination of chains of PP oxidation at low concentrations of radicals. Such linear termination may be the most probable mechanism for CL emission from PP.



SCHEME 1 CL reaction in PP.

According to the scheme, the decomposition of tertiary peroxyl radical *via* six-member complex with elimination of hydroxyl radical, scission of macromolecule and formation of end C═C bond is the limiting reaction (i) of the stage of radical termination. The subsequent fast reaction of hydroxyl radical with end double bond in a cage leads to the formation of an alkyl radical. This alkyl radical will react with oxygen to a secondary peroxyl radical at the end of polymer chain (reaction (ii)). The end macroradicals are more mobile than middle macroradicals because of a greater degree of freedom. So they terminate quickly in bimolecular reaction (iii) with the rate that is limited by slow first-order reaction (i). Bimolecular disproportionation of peroxyl radicals (reaction (iii)) proceeds *via* the Russell mechanism [22] to give an electronically excited carbonyl, an alcohol and oxygen [13, 23], *i.e.*, it may give rise to CL.

The scheme shows that the rate constant *k* for linear termination equals to double rate constant for reaction (i). This radical decomposition should be sensitive to molecular environment because of its concert mechanism of simultaneous scission of O—O, C—H and C—C bonds with the formation of C═O, O—H and C═C bonds.

The distribution of macroperoxyl radicals on rate constants k may be caused by both heterogeneity of molecular structure and difference in local mobility of chain segments.

5.2. Life-time of Reaction

The distribution on reactivity is a nature of any reaction. In liquid or gas phase, as a rule, this distribution remains constant due to thermal motion of both molecules and reactive centers; therefore the reaction occurs always from the highest reactive state. But in solid phase the molecular motion is not fast enough to restore the losses of high reactive species. In this case the distribution is enriched subsequently by low reactive species and the reaction has to occur non-homogeneously from states with different reactivities. So the increase of a reaction lifetime during time-course of the first-order reaction may be a common rule for the non-homogeneous reaction. Thus, in solid PP the half-lives of both the first-order termination of macroperoxyl radicals and CL decay increase with increasing time.

The similar hyperbolic curves have been observed for CL-decay accompanying the polystyrene (PS) oxidation initiated by the first-order decomposition of azobisisobutironitrile at elevated temperatures [24]. These curves have been explained in terms of the physical inhomogeneity of a solid polymer. The half-life of radical reaction has been shown to decrease down to the initial value if reaction at a later stage with long half-life is interrupted, the PS sample is dissolved in benzene, then it is prepared again, and the decomposition of azobisisobutironitrile is continued. Renewal of the reaction distribution has been attributed to the sample dissolution [24].

The inhomogeneity of a reaction is no doubt when a half-life becomes infinite at low degree of conversion. The problem arises when the non-homogeneous reaction reproduces some kinetic features of a simple reaction. In this case the half-life analysis may be useful for interpretation of CL data. For example, one can conclude that the CL decay induced by the decomposition of PP hydroperoxides in nitrogen at 100°C follows second-order kinetics because of the plot of $I_{CL}^{-1/2}$ against time is linear [25]. But it can be seen from the data [25], that the initial half-life of CL decay is independent on the initial CL intensity as it must be for the first-order reaction. Therefore, it is impossible to consider the CL decay in PP at 100°C as a second-order reaction. A constancy of the initial half-life of CL decay may be caused by the first-order decomposition of hydroperoxides. Then the inhomogeneity of reaction may be responsible for hyperbolic curves of CL decay.

The same situation has been reported for CL of solid polyethylene (PE) unduced by UV irradiation at room temperature [15]. The plot of $I_{\mathrm{CL}}^{-1/2}$ against time is linear. But the initial half-life of CL delay increases slightly with increasing initial intensity of CL. It means that the CL reaction in PE does not follow second-order kinetics. No doubt, the radical termination in PE may be complicated by variety of reaction species. Nevertheless, the possibility of deceleration of radical termination due to the inhomogeneity of PE should be important.

Another similar result must be noted for CL emission from γ-irradiated PP at 40°C in air [26]. As one can see from the data presented [26], the initial half-life of CL decay does not decrease with increasing CL intensity.

We can conclude that the above-mentioned data on CL decay are consistent with our conception of CL emission from PP due to non-homogeneous first-order recombination of macroperoxyl radicals.

5.3. Prehistory of Reaction

In addition to a half-life, the second (and it may be the most important) indicator of a non-homogeneous reaction is the effect of its prehistory on reagent distribution under the same average concentrations of reagents and products. Fast thermal motion erases any memory about previous radical locations and distributions, so a homogeneous reaction is determined by concentrations of reagents and products. It is not dependent on the way by which the same concentrations are achieved. A non-homogeneous reaction depends on the radicals distribution which can be changed by various events of prehistory at the same degree of conversion. In the study of PS oxidation a prehistory of a given degree of chemical conversion was changed by dissolution of PS sample and repeated preparation of the sample [24].

A prehistory has been reported to effect on CL emission from polyamides after UV irradiation at room temperature [16]. Unfortunately the data on the effect of a prehistory at the same degree of conversion are not available in order to distinguish non-homogeneous reaction from homogeneous one. However, CL decay follows Eq. (1) with $n = 1/3$. This may indicate a non-homogeneous nature of the reaction.

In our study a different prehistory of CL reaction at a given concentration of macroperoxyl radicals of unoxidised PP was created by two ways of radical production (with or without HCPX). A prehistory of CL reaction in solid PP has been found to be of a great importance. Earlier we have shown that the reactivity of macroperoxyl radicals of PP at a given concentration of radicals and hydroperoxides depends on the way of radical formation (nature of photoinitiator, wavelength of light, duration of irradiation, temperature at which free radicals are formed) [17–19, 27]. This has wider implications for the interpretation of CL data and for the alteration of polymer reactivity.

6. CONCLUSIONS

One important conclusion from this study is that the quantum efficiency for CL emission is dependent on molecular mobility, falling with increasing local mobility. This conclusion is consistent with the data on temperature dependence of the average quantum efficiency of CL, which falls with increasing temperature [12]. The mobility dependence of the quantum efficiency for local emission will be useful for interpretation of CL data.

The inhomogeneous model of PP photooxidation with the distribution of peroxyl radicals on both reactivity and quantum efficiency for CL emission allows to explain quantitatively the observed kinetics of CL decay in solid PP.

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