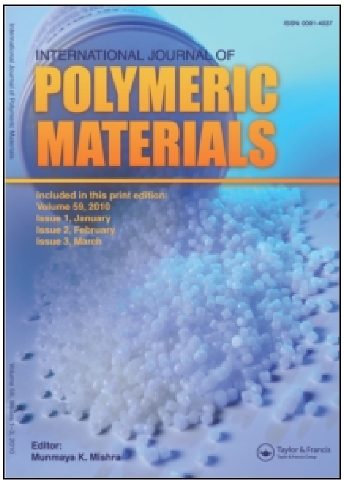

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Fractal Kinetics of the Oxidation of Aliphatic Polyamides

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Analysis of reactions kinetics in solid polymers requires a consideration of structural inhomogeneity of different levels and transport retardation of active particles peculiar to polymers. However, for multi-step reactions this problem may be only posed after sufficiently comprehensive description of their specific mechanism representing the balance of separate steps correlation. The kinetic justification of a new mechanism of aliphatic polyamides photooxidation that was completed recently makes this possible. Sufficient extending of measured rates diapason to the post-effect area of UV-irradiation allows to estimate correlation of homogeneous and inhomogeneous factors of this process in the context of fractal kinetic model.

Keywords: Oxidation; reaction kinetics; aliphatic polyamides; solid state; photooxidation; fractals

1. INTRODUCTION

We have completed in [1, 2] the formal-kinetic substantiation of earlier proposed mechanism of chain photooxidation of aliphatic polyamides (PA). This new mechanism, for which no analogs have been yet discovered in photooxidation of polymers, is different in rather surprising peculiarity: oxidation of the objects of essentially inhomogeneous nature (different PA dissimilar greatly in supermolecular structure, below their vitrification temperature) is quantitatively expressed by known and rather small set of kinetic parameters, and each of them has the physical meaning of a rate constant of an elementary chemical reaction which is treated in terms of Smolukhowskii's homogeneous kinetics.

The possibility of such description presents a rare example among usually observed kinetic behaviours of chemical transformations in polymers, for which the need to use inhomogeneous kinetics concept (unusual reactions order, "kinetic halts" etc.) becomes progressively more evident. As for polyamides, if they didn't contain special additives, we haven't yet met any influence of their structural inhomogeneity on the kinetics of process in all earlier investigated regimes of their photooxidation, though it was every time expected. This influence has been found to occur [3–5] as dependence of photooxidation kinetics on the procedure of incorporation of some additives into PA; these additives provide retardation of this process, i.e. they decrease by some means the concentration of radicals leading the oxidation chain. Such dependence that seems to be a result of inhomogeneous distribution of the additive over specimen, is in clear conflict with the experimentally justified homogeneous PA photooxidation model.

Thus, from the possibility to observe in PA photooxidation both homogeneous and inhomogeneous kinetics effects, we can conclude that in this case the investigated system is in the area of transition between kinetic laws of two types. This situation is of interest because in the transition point all the variety of inhomogeneous kinetics manifestations is only coming into play and then, on moving away from this point, their complex hierarchy grows with inevitable increase of difficulties of quantitative analysis.

Probably Zeldovich was the first who perceived the necessity of the transition area investigations. He showed in [6] that for bimolecular reactions there should be a lower concentration boundary under which Smolukhowskii's homogeneous kinetics ceases to be true. While giving considerable attention to this question, Zeldovich also pointed toward the problem of choosing proper object for investigation of such phenomenon which arises because of limited potentialities of experimental technique. It was precisely the achievements of physical experimental technique that subsequently provided support for Zeldovich's ideas. These have been supported many times in studies on simple recombination processes, especially of physical nature such as exciton recombination [7]. In the field of chemistry these ideas evolved mainly in theoretical works (see, for example, [8]) where the kinetics of complex multi-step reactions was hardly discussed because of the lack of proper experimental base. If considering these reactions, such problem could be posed after sufficiently detailed description of their mechanism with possibility to represent the balance of separate steps correlation in a wide range of the reaction conditions.

In the example of PA photooxidation, we are the first to have available the necessary minimum of such preliminary information to try to extend the diapason of measured oxidation rates kinetic mechanisms changes taking place on transition from homogeneous kinetics to inhomogeneous one. To keep kinetic description of such complex system from becoming too involved we'll not use any chemical additives. Furthermore, let us adopt the fractal kinetics model that fits in Zeldovich's opinion [9], most adequately the nature of transition area.

In accordance with this model, two groups of facts demonstrating homogeneous and inhomogeneous behaviour of the system relate to passing through some critical concentration $[PO_2]_{cr}$ of radicals leading the oxidation chain; the structural inhomogeneity of PA reflects the process kinetics at $[PO_2] < [PO_2]_{cr}$. The model is based upon familiar facts [10], that the rate "constant" of active particles recombination below their certain concentration starts to depend on time (in unsteady-state mode). In experiments on PA photooxidation [2], the steady-state concentration $[PO_2]_{st}$ corresponding to minimal measured rate of process not being retarded by any additives was calculated to be 4×10^{-7} mol/kg. In photochemical experiment, such values can't be measured directly by ESR, but they are quite sufficient to yield quantifiable rate of oxygen consumption in the post-effect of PA irradiation, or to explain the long time intensity decay of chemiluminescence which appears as a result of radicals recombination. The present paper is devoted to analysis of regularities observed in such processes. (The term "post-effect" expresses the whole set of processes occurring after the termination of PA irradiation in consequence of transformations of free radicals and intermediate molecular products that have been accumulated in PA on irradiation).

2. EXPERIMENTAL

For examination of chemiluminescence PA-6 and PA-548 films as well as PA-6 fibers were irradiated in free air by filtered light of DRS-1000 lamp at wavelength equal 313 nm or 360–440 nm. After certain time of irradiating by light of known intensity, the specimens were placed into light-tight chamber of chemiluminescence installation SNK-6 and then kinetics of glow intensity decrease was recorded. (For details of the procedure see [11]). For description of kinetics of oxygen consumption by UV-irradiated PA-548 films the experimental data from [12] were used.

3. RESULTS AND DISCUSSION

To consider rigorously the kinetics of post-effect in PA free from additives, we should use the general scheme of their photooxidation mechanism [1] except the reactions of photoinitiation. After this simplifications the scheme becomes as follows

$$PO_2 + PA \xrightarrow{+O_2} POOH + PO_2 \qquad (1)$$

$$PO_2 \longrightarrow A + r \qquad (2)$$

$$PO_2 \longrightarrow B + r \qquad (2')$$

$$r + PA \xrightarrow{+O_2} rH + PO_2 \qquad (3)$$

$$A \xrightarrow{+2O_2} K \qquad (4)$$

$$A \xrightarrow{+2O_2} K' \qquad (4')$$

$$K + r \longrightarrow PO_2 + S \qquad (5)$$

$$K' + r \longrightarrow PO_2 + S \qquad (5')$$

$$PO_2 + r \xrightarrow{-O_2} S \qquad (6)$$

The numbers of above reactions will be used later as indexes of rate constants (k_n) of these reactions. S denotes the scission of a macromolecule. (Other necessary comments on the scheme are given in [2]).

In the case of homogeneous kinetics there corresponds to this scheme the set of differential equations in macroradicals concentration PO_2, low-molecular radicals r, intermediate molecular products K and K' and absorbed oxygen O_2

$$\frac{d[PO_2]}{dt} = -(k_2 + k'_2)[PO_2] + k_3[r] + [r](k_5[K] + k'_5[K'])$$

$$-k_6[PO_2][r]$$

$$\frac{d[r]}{dt} = (k_2 + k'_2)[PO_2] - k_3[r] - [r](k_5[K] + k'_5[K'])$$

$$-k_6[PO_2][r]$$

$$\frac{d[K]}{dt} = \frac{k_4}{k_4 + k'_4} k_2[PO_2] - k_5[K][r]$$

$$\frac{d[K']}{dt} = \frac{k_4}{k_4 + k'_4} k_2[PO_2] - k'_5[K'][r]$$

$$\frac{d[O_2]}{dt} = (k_1 + 2k_2)[PO_2] + k_3[r] - k_6[PO_2][r] = W.$$

The rate constants of all above-listed reactions have been estimated in [2]. Analysis of the homogeneous model of long-wave PA photooxidation (which goes at minimal free radicals concentration in comparison with other studied regimes of this process) performed in this paper has been started from assumptions of fixed rate constant of recombination of radicals leading the oxidation chain. The magnitude of this constant $k_6 = 2.6 \times 10^6$ kg/mol·s was evaluated from theoretical reasoning [13] and used for estimating of some other kinetic parameters that describe kinetic curves of photooxidation process. The resulting estimates have permitted us to give quite satisfactory description of all experimental data concerning other regimes of PA photooxidation [1].

However, if posing the problem of conditions range when "constant" k_6 keeps its magnitude invariable, this value must be estimated independently as parameter of experimental dependence between the steady-state photooxidation rate W_m and intensity I_m of operating light (where m denotes a certain experimental point). Theoretical expression of this dependence follows from equations for steady-state photooxidation regimes described in [2] and can be given as:

$$\frac{I_1}{I_m}=\frac{2\alpha k_2/a+h_m}{2\alpha k_2/a+h_1}\cdot\frac{h_1^2}{h_m^2},$$

where

$$h_1=1-\sqrt{1+bk_6W_1/a^2},\quad h_m=1-\sqrt{1+bk_6W_m/a^2},$$

$$a=k_1+2k_2+k_2'=9.74\times10^{-2}\text{s}^{-1},\quad b=4k_2'/k_3=2.77\times10^{-3},$$

$$\alpha=k_4/(k_4+k_4').$$

Based on experimental data obtained in [1,2] and solving by nonlinear regression method the set of $m-1$ such equations for unknown k_6 and α (in the case of long-wave photooxidation, $m=9$), we find: $k_6=(2.69\pm0.02)\times10^6$ kg/mol·s and $\alpha=0.69\pm0.02$ instead of previous $k_6=2.6\times10^6$ kg/mol·s and $\alpha=0.5$ which were calculated without error estimate. (The algorithm described in [14] was used for these calculations).

Although these corrections have no practical meaning in description of PA photooxidation kinetics, small magnitude of possible error allows us to conclude that in the steady-state regimes of this process k_6 is to be considered as a true rate "constant", which keeps constancy at O_2 consumption rates varying by a factor of 10^3 (down to concentration $[PO_2]=4\times10^{-7}$mol/kg).

The kinetic curves of all variables were described for various photooxidation regimes in [1,2]. Behaviour of these kinetic curves obviously changes after turning off the photoinitiation and that is the subject of interest in the post-effect theory. For example, if in some photooxidation regimes, the concentrations $[PO_2]$, $[r]$, $[K]$, $[K']$ and constant photooxidation rate $d[O_2]/dt$ have reached the steady-state value, their further changes after termination of irradiation are determined by solution of the equations set cited above. Figure 1 shows the example of such changes. Their character allows us to simplify the given set of equations in the following manner.

First, calculations show that within a very wide range of conditions $[r] \ll [PO_2]$ and $d[r]/dt \ll d[PO_2]/dt$, with a distinction factor of 10^3. Thus, instead of exact equation $d[PO_2]\, dt + d[r]/dt = -2k_6[PO_2][r]$ we can always use approximate equation $d[PO_2]/dt = -2k_6[PO_2]$ $[r]$ and represent $[r]$ by $[PO_2]$

$$[r] = \frac{(k_2 + k_2')[PO_2]}{k_3 + k_5[K] + k_5'[K'] + k_6[PO_2]}.$$

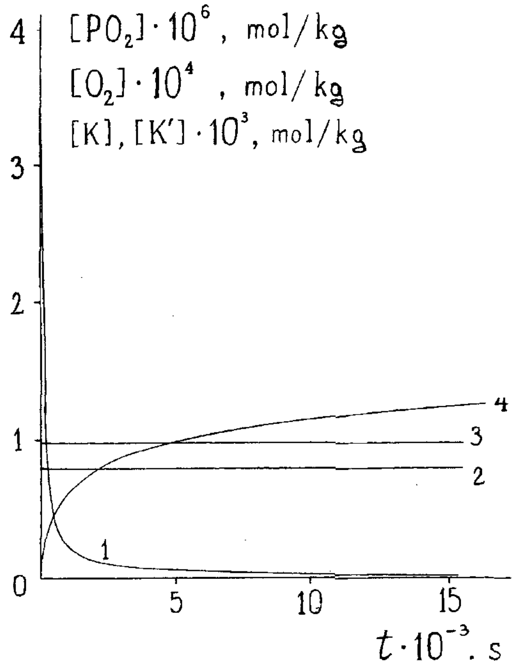

FIGURE 1 The partial solutions of the complete set of differential equations for the post-effect in UV-irradiated polyamides. Kinetic curves: expenditure of PO_2 radicals (1); intermediate products K (2) and K'(3) concentrations; oxygen consumption (4).

Second, Figure 1 shows that at existing extent of $[PO_2]$ and $[O_2]$ change, the values $[K]$ and $[K']$ may be considered as constant, though they are not exactly. This means that the three reactions of extension of chain by radicals r can all be characterized by a single effective rate constant $c = k_3 + k_5[K] + k'_5[K']$, which of course is true only for a specific set of initial conditions.

So, we have an equation for radicals PO_2

$$\frac{d[PO_2]}{dt} = -\frac{2k_6(k_2 + k'_2)[PO_2]^2}{c + k_6[PO_2]} \tag{1}$$

that has following solution

$$\frac{[PO_2]_0}{[PO_2]} = 1 + \frac{k_6[PO_2]_0}{c}\left[2(k_2 + k'_2)t - \ln\frac{[PO_2]_0}{[PO_2]}\right] \tag{2}$$

which differs from that of equation of second order reaction in presence of term $\ln([PO_2]_0/[PO_2])$. Its contribution is negligible within the accuracy limits of experiment [15] measuring the decay of PO_2 radicals, where their concentration decreased from 2×10^{-4} to 1×10^{-5} mol/kg. Note that this contribution is asymptotic to zero at reasonably large t. Therefore, in the case of homogeneous kinetics, for post-effect processes observed for a long time, the simple equation of second order reaction must be valid

$$\frac{d[PO_2]}{dt} = -\frac{2k_6(k_2 + k'_2)}{c}[PO_2]^2 = -2k_h[PO_2]^2 \tag{3}$$

As for inhomogeneous kinetics, we have to take into account that at concentrations $[PO_2]$ below some critical magnitude $[PO_2]_{cr}$ (when $t > t_{cr}$), the "constant" k_6 becomes a function of time [10], that is

$$k_6 = k_6^0\left(\frac{t}{t_{cr}}\right)^{(d/2-1)}, \quad \text{where} \quad k_6^0 = k_6 \quad \text{at} \quad t < t_{cr}$$

and d denotes "spectral" dimensionality of free radicals random-walk space. It was shown that $d < 2$ [10]. Thus, the corresponding equation is as follows

$$\frac{d[\mathrm{PO_2}]}{dt} = -\frac{2k_6^0(k_2 + k_2')}{c}\left(\frac{t}{t_{\mathrm{cr}}}\right)^{(d/2-1)}[\mathrm{PO_2}]^2 = -2k_{ih}[\mathrm{PO_2}]^2$$

$$= -2k_h\left(\frac{t}{t_{\mathrm{cr}}}\right)^{(d/2-1)}[\mathrm{PO_2}]^2 \tag{4}$$

and hence doesn't present an equation of second order reaction.

In the same manner, the solutions of these equations differ. For homogeneous kinetics (at $t < t_{\mathrm{cr}}$)

$$\frac{1}{[\mathrm{PO_2}]} = \frac{1}{[\mathrm{PO_2}]_0} + 2k_h t \tag{5}$$

whereas for inhomogeneous kinetics (at $t > t_{\mathrm{cr}}$)

$$\frac{1}{[\mathrm{PO_2}]} = \frac{1}{[\mathrm{PO_2}]_{\mathrm{cr}}} + \frac{4k_h}{d}t_{\mathrm{cr}}^{(1-d/2)}(t^{d/2} - t_{\mathrm{cr}}^{d/2}) \tag{6}$$

i.e. after achieving t_{cr} (or, $[\mathrm{PO_2}]_{\mathrm{cr}}$), the fall of $[\mathrm{PO_2}]$ concentration slows down substantially. This difference must inevitably reflect on kinetics of chemiluminescence intensity decay as well as on oxygen consumption in the post-effect of PA irradiation.

3.1. Chemiluminescence

In a number of works, for example [16, 17], there have been obtained enough evidences that chemiluminescence observed after UV-irradiating of PA appears as a result of disproportion reactions into which peroxide macroradicals $\mathrm{PO_2}$ enter. In these reactions, energy sufficient for electron excitation of the formed carbonil compounds, is released. Such recombinational chemiluminescence is well known, and in the most simple cases of homogeneous kinetics, when an excited molecule of initial product appears as an emitter of irradiation, its intensity I_{chl}

is described by equation

$$I_{\text{chl}} = -\gamma \frac{d[\text{PO}_2]}{2dt} = \gamma k_h [\text{PO}_2]^2 \tag{7}$$

Here γ is an unknown coefficient which is excluded while considering relative changes of I_{chl}

$$\frac{I^0_{\text{chl}}}{I_{\text{chl}}} = \frac{k_h[\text{PO}_2]^2_0}{k_h[\text{PO}_2]^2} = \frac{[\text{PO}_2]^2_0}{[\text{PO}_2]^2} \tag{8}$$

where “0” index relates to the starting moment. With the time dependence of $[\text{PO}_2]$ (Eq. (5)), we have expression

$$\frac{I^0_{\text{chl}}}{I_{\text{chl}}} = (1 + 2k_h[\text{PO}_2]_0 t)^2 \tag{9}$$

which usually describes recombinational chemiluminescence in gas or liquid media [18]. The emitter of chemiluminescence in PA is not the initial product of disproportioning of PO_2 and r radicals but ketoimide K to which the energy of initial excitation is transferred. Because of this, constant k_h in this equation should be substituted for constant k_{chl} which may be quite small ($k_{\text{chl}} \ll k_h$) depending on the mechanism of energy transfer. As a first approximation, we can designate $k_{\text{chl}} = \beta k_h$ and write the equation (9) as

$$\frac{I^0_{\text{chl}}}{I_{\text{chl}}} = (1 + 2\beta k_h [\text{PO}_2]_0 t)^2 \tag{10}$$

where increasing value $I^0_{\text{chl}}/I_{\text{chl}}$ is also asymptotic to the square-law dependence on observation time t.

However, resulting experimental data show that when observing the post-effect in UV-irradiated PA, dependence of (10) type is never obeyed [16]. Lately much greater complexity of this process has been discovered involving many factors. But among these results one can set apart and consider separately a special feature of chemiluminescence which is easily reproduced, regardless of preceding history of PA specimens. This feature is that after sufficiently long irradiation in open air of all PA-6 and PA-548 specimens (except those which content special additives) by light of 313 nm or 360–440 nm wavelength, the kinetics of chemiluminescence decay is described in a wide time range by the empirical equation

$$\ln\frac{1}{I_{\mathrm{chl}}^{\mathrm{rel}}}=\ln f+\frac{1}{3}\ln t \tag{11}$$

or, what is the same,

$$\frac{1}{(I_{\mathrm{chl}}^{\mathrm{rel}})^{3}}=f^{3}t \tag{12}$$

In the equations above, f denotes a constant, and $I_{\mathrm{chl}}^{\mathrm{rel}}=I_{\mathrm{chl}}/I_{\mathrm{chl}}^{1}$ is current chemiluminescence intensity related to intensity I_{chl}^{1} at an arbitrary chosen but constant time moment t_1, which is sufficiently far from the start of measurements to avoid an error due to a too steep initial decay of chemiluminescence (this error depends, in particular, on the delay from the start of measurements and on the time constant of registration device).

In Figure 2 curve 1 illustrates the expected behaviour of kinetics of $I_{\mathrm{chl}}^{0}/I_{\mathrm{chl}}$ value change in accordance with equation (9), if using all

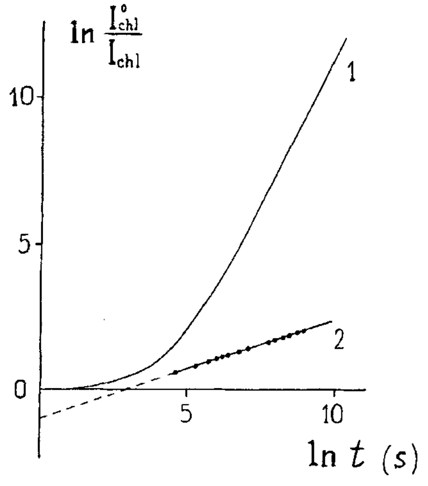

FIGURE 2 Dependence of $\ln(I_{\mathrm{chl}}^{0}/I_{\mathrm{chl}})$ on ln t. Calculation in assumption of homogeneous kinetics (1) and experimental result (2).

preliminary estimated [1, 2] parameters of homogeneous kinetics, and $[PO_2]_0 = 3.4 \times 10^{-6}$ mol/kg is a steady-state radicals concentration reached under irradiation of PA in oxygen atmosphere by light with wavelength 360–440 nm and intensity 6.4×10^{-8} Einstein/cm^2·s. Straight line 2 illustrates the observed chemiluminescence kinetics on the same specimens after their long-term irradiation under similar conditions; by convention, the maximum value from which measurements of I_{chl} decay started in actuality is taken as I_{chl}. (Analogous kinetic data by George [16] represented on the same coordinates, give also a straight line near to line 2 although they do not coincide entirely. His data are different only in that preliminary irradiation has been carried out not in oxygen but in inert atmosphere, and oxygen has been entered after irradiation. In this paper, a sharp departure from the second order reactions kinetics is also noted).

In Figure 3, analogous kinetic data are represented on coordinates of equation (12). Corresponding straight lines are practically the same for different PA specimens after they have been irradiated by light of different wavelength (if light is not absorbed by polymer's own chromophor (amide) groups), and are characterized by the same slope with an accuracy of 5 %.

Thus, correlating the logarithmic representation of equations (9) and (12), we can see that time dependence of chemiluminescence decay is characterized by abruptly distinct asymptotics: instead of the only possible asymptotics in homogeneous kinetics

$$\ln \frac{I^0_{chl}}{I_{chl}} \to 2 \ln t$$

another intermediate dependence is observed

$$\ln \frac{I^1_{chl}}{I_{chl}} \to \frac{1}{3} \ln t.$$

The sharp change of parameter of new asymptotics describing PO_2 radicals recombination (1/3 instead of 2) is the obvious proof that Smolukhowskii's homogeneous kinetics ceases to be true. Absence of any smooth transition between these parameters means in fact that some "critical point" separating homogeneous and inhomogeneous areas exists, as it was supposed by equations (4) and (6).

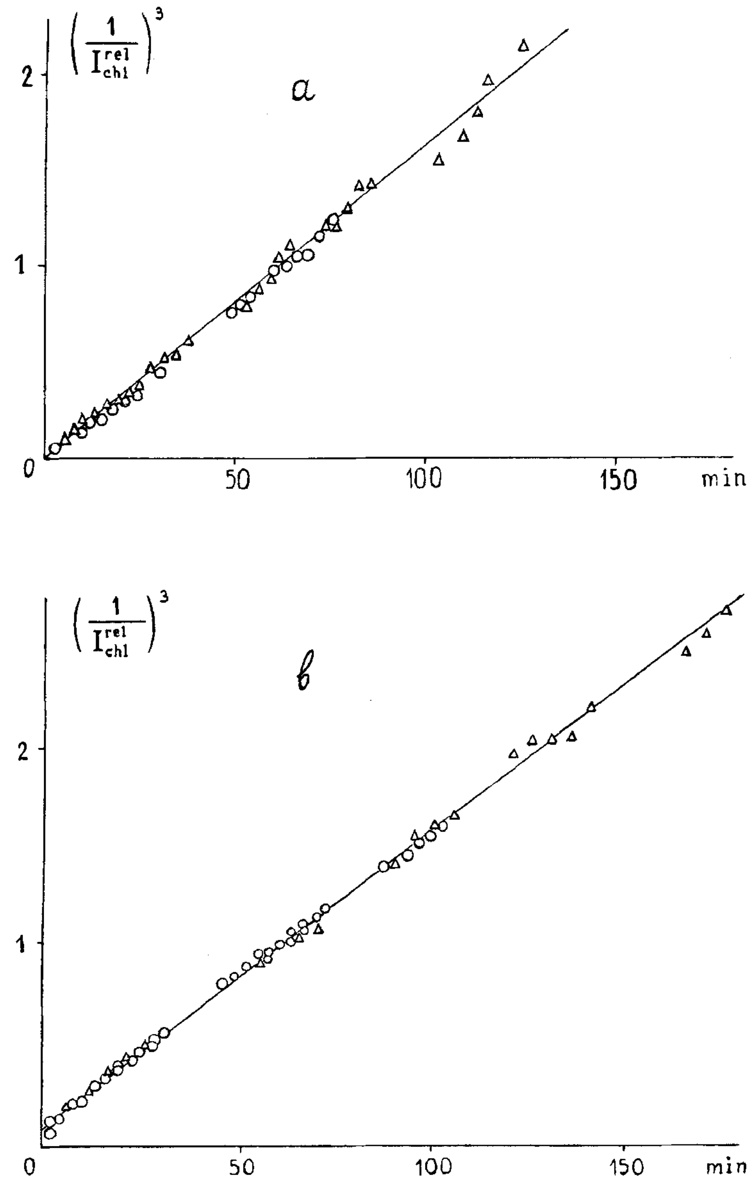

FIGURE 3 Experimental dependence of relative chemiluminescence intensity on time after termination of UV-irradiating. (a) – PA-6 fibers: after irradiating by light of 313 nm (circles) and of 360–440 nm (triangles). (b) – polyamides films after irradiating by light of 360–440 nm: PA-6 films (circles) and PA-548 (triangles).

In the case of inhomogeneous kinetics, i.e. at $[Po_2] < [PO_2]_{cr}$ in accordance with (4) and (6) we obtain

$$\frac{I_{chl}^{cr}}{I_{chl}} = \frac{k_{chl}^{0} t_{cr}^{(d/2-1)}}{k_{chl}^{0} t^{(d/2-1)}} \left(\frac{[PO_2]_{cr}}{[Po_2]}\right)_{chl}^{2}$$

$$= \left(\frac{t_{cr}}{t}\right)^{(d/2-1)} \left[1 + [PO_2]_{cr} \frac{4\beta k_h}{d} t_{cr}^{(1-d/2)} (t^{d/2} - t_{cr}^{d/2})\right]^2 \quad (13)$$

where $t > t_{cr}$, and "chl" index at the expression in parenthesis just implies necessity of β coefficient to be introduced.

When t_{cr} is unknown, this equation can hardly be related to experimental data, but we can transform it in the following manner. Behaviour of experimental kinetic curves allows us to assume that the condition $[PO_2] < [PO_2]_{cr}$ is fulfilled from the very beginning of chemiluminescence measurements. Hence, we can exclude t_{cr} value from consideration and think of it as an initial time point. Then let us denote PO_2 radicals concentration at the moment of termination of irradiating as $[PO_2]_0$, and time required to reach this concentration in post-effect (if starting from $[PO_2]_{cr}$) – as t_0. In doing so, the current concentration $[PO_2]$ corresponds to $t_0 + t$ moment, where t is counted from the moment of termination of irradiation t_0. Because the time t includes a poorly defined time delay of beginning of chemiluminescence measurements, the results in the very first period of measurements are not reliable. So, we keep designations I_1 and t_1 as well as $[PO_2]_1$, that were used in (11) and (12) and relate them to some point arbitrarily chosen in the middle of kinetic curve, with respect to which it is convenient to compare various experimental data. Such scaling transformations allow us to write down:

$$\frac{[PO_2]_1}{[PO_2]} = 1 + \frac{[PO_2]_0 \frac{4k_h}{d} t_0 \left[\left(1 + \frac{t}{t_0}\right)^{d/2} - \left(1 + \frac{t_1}{t_0}\right)^{d/2}\right]}{1 + [PO_2]_0 \frac{4k_h}{d} t_0 \left[\left(1 + \frac{t_1}{t_0}\right)^{d/2} - 1\right]} \quad (14)$$

and represent (13) as follows

$$\frac{I^1_{\mathrm{chl}}}{I_{\mathrm{chl}}}=\left(\frac{t_0+t_1}{t_0+t}\right)^{d/2-1}\left[1+\frac{[\mathrm{PO_2}]_0\frac{4\beta k_h}{d}t_0\left[\left(1+\frac{t}{t_0}\right)^{d/2}-\left(1+\frac{t_1}{t_0}\right)^{d/2}\right]}{1+[\mathrm{PO_2}]_0\frac{4\beta k_h}{d}t_0\left[\left(1+\frac{t_1}{t_0}\right)^{d/2}-1\right]}\right]^2 \tag{15}$$

Obviously, equation (15) can fit the empirical equation (12) only when $t \gg t_0$, $d = 4/3 \pm 5\%$ and the factor in square brackets is close to 1.

The results shown schematically by straight line 2 in Figure 2 that actually represent as many as 23 experimental points of dependence of $I^1_{\mathrm{chl}}/I_{\mathrm{chl}}$ on t (at $t_1 = 3000$ S), can serve as a convenient example for correlating equation (15) with experimental data. These results were obtained immediately after long-term irradiating of transparent PA-6 films by light of 360–440 nm wavelength and 6.4×10^{-8} Einstein/cm$^2\cdot$s intensity. It was reported in [6] that irradiation of such parameters leads to a steady-state concentration $[\mathrm{PO_2}] = 3.4 \times 10^{-6}$ mol/kg. Using the under such conditions known value $k_h = 2300$ kg/mol$\cdot$s, we evaluate by nonlinear regression method the following parameters: $\beta = (1.6 \pm 0.6) \times 10^{-3}$; $t_0 = 29.5 \pm 0.7$ s, $d = 1.36 \pm 0.02$. The substitution of these parameters into equation (15) gives a result practically equal to the empirical dependence expressed by (12).

Now, after determination of all kinetic parameters, we can obtain from Equation (14) relations between $\mathrm{PO_2}$ radicals concentrations at any point on kinetic curve of their expenditure. In particular, $[\mathrm{PO_2}]_{\mathrm{cr}}$ comes to be accessible for determination and can be given by a simple expression

$$[\mathrm{PO_2}]_{\mathrm{cr}}=\frac{[\mathrm{PO_2}]_0}{1-[\mathrm{PO_2}]_0 4k_h t_0/d}. \tag{16}$$

The resulting value $[\mathrm{PO_2}]_{\mathrm{cr}} = 1.05 \times 10^{-5}$ mol/kg, is localized at the lower edge of the area, where direct measurements [15] of $\mathrm{PO_2}$ radicals decay have been carried out, and second order of their expenditure has been observed.

Such result supports the possibility to introduce fractal concept, when the range of measured rates of radical reactions is significantly extended. This is not a new idea, but as for its validation in reactions of active particle recombination, it was confirmed up to now only in rather exotic systems like exciton recombination. In our case the only fractal parameter $d = 4/3$ which allows one to describe all the kinetic curves on Figure 3, appears to have a universal character. This is precisely the value which is known as "universal" (not dependent on euclidean dimensionality) value of "spectral dimensionality" of random percolation cluster [10]. Of course, it would be prematurely to draw conclusions from this analogy. Only further experimental data will permit us to judge the commonness of observations made here. But first of all, it is important to get such information from kinetic measurements not limited to data on chemiluminescence.

3.2. Oxygen Consumption

In comparison with chemiluminescence kinetics which allows us to follow the radical recombination directly, the kinetic curves of oxygen consumption in the post-effect of PA irradiation have an integral pattern. This is why the influence of the passing through radical critical concentration on these curves can not be sharply defined. So, in this case, we must be sure that kinetic data on chemiluminescence and oxygen consumption are not contradictory to each other. It is, therefore, essential for getting more impartial assessment by representing the results obtained on PA by other authors [12].

In order to avoid too cumbersome expressions, it is enough to take into account a single term of differential equation of oxygen consumption

$$\frac{d[O_2]}{dt} = (k_1 + 2k_2)[PO_2]$$

(because the total contribution of other two terms doesn't exceed 10 % and is well within experimental accuracy). Substituting expression of $[PO_2]$ (Eq. (6)) with $d = 4/3$ in equation above, we have

$$\frac{d[O_2]}{dt} = \frac{[PO_2]_{cr}(k_1 + 2k_2)}{1 + 3k_h[PO_2]_{cr}t_{cr}^{1/3}(t^{2/3} - t_{cr}^{2/3})} \tag{17}$$

(at $t > t_{cr}$) or, because $k_h = k_6^0(k_2 + k_2')/c$

$$d[O_2] = \frac{(k_1 + 2k_2)c}{3k_6^0(k_2 + k_2')} t_{cr}^{-1/3} \frac{dt}{g^2 + t^{2/3}} \tag{18}$$

where

$$g^2 = \frac{c t_{cr}^{-1/3}}{3k_6^0(k_2 + k_2')[PO_2]_{cr}} - t_{cr}^{2/3}.$$

Integration at $t > t_{cr}$ gives

$$[O_2] = [O_2]_{cr} + \frac{(k_1 + 2k_2) c t_{cr}^{-1/3}}{k_6^0(k_2 + k_2')} \left(t^{1/3} - t_{cr}^{1/3} + g\left(\operatorname{arctg}\frac{t_{cr}^{1/3}}{g} - \operatorname{arctg}\frac{t^{1/3}}{g} \right) \right) \tag{19}$$

(where $[O_2]_{cr}$ – amount of oxygen absorbed before time reaches t_{cr}).

This equation provides at sufficiently large t asymptotic approach to linear dependence of $[O]_2$ on $t^{1/3}$; it is confirmed in Figure 4 by experimental data from [12] represented on corresponding coordinates. The

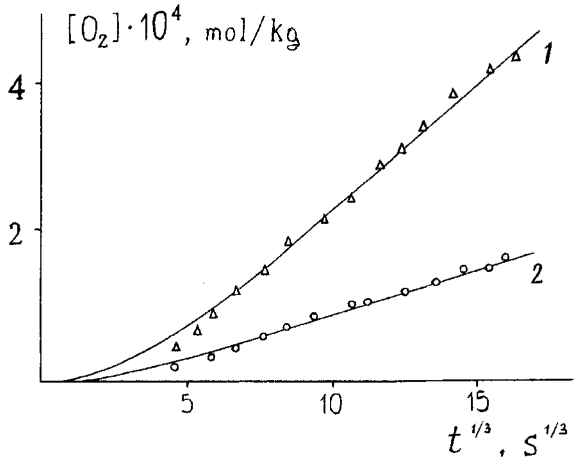

FIGURE 4 Representation on the coordinates of equation (19) of kinetics of O_2 consumption by PA-548 films after irradiating by light of wavelength > 270 nm: oxidized (1) and "unoxidized" (2) specimens.

missing values of kinetic parameters may be defined at once from linear portions of the curves

$$ct_{\mathrm{cr}}^{-1/3}/k_6^0 = 1.267 \times 10^{-5}\,\mathrm{mol \cdot kg^{-1} \cdot s^{-1/3}} \text{ for curve 1}$$

and

$$ct_{\mathrm{cr}}^{-1/3}/k_6^0 = 4.503 \times 10^{-6}\,\mathrm{mol \cdot kg^{-1} \cdot s^{-1/3}} \text{ for curve 2.}$$

For full description of these curves the expression for $[\mathrm{O_2}]_{\mathrm{cr}}$ is to be represented in analytic form. In accordance with equation (5) it is equal to

$$\begin{aligned}[\mathrm{O_2}]_{\mathrm{cr}} &= \frac{c(k_1+2k_2)}{2k_6^0(k_2+k_2')}\int_0^{t_{\mathrm{cr}}} \frac{dt}{\dfrac{c}{2k_6^0(k_2+k_2')[\mathrm{PO_2}]_0}+t} \\ &= \frac{c(k_1+2k_2)}{2k_6^0(k_2+k_2')}\ln\left(1+\frac{2k_6^0(k_2+k_2')[\mathrm{PO_2}]_0}{c}t_{\mathrm{cr}}\right) \\ &= -\frac{c(k_1+2k_2)}{2k_6^0(k_2+k_2')}\ln\left(1-\frac{2k_6^0(k_2+k_2')[\mathrm{PO_2}]_{\mathrm{cr}}}{c}t_{\mathrm{cr}}\right). \qquad (20)\end{aligned}$$

After substituting of (20) into (19) and using all experimental magnitudes $[\mathrm{O_2}]$ and t from [12], we find by nonlinear regression method the likely values of t_{cr} and $[\mathrm{PO_2}]_{\mathrm{cr}}$ parameters

for curve 1: $t_{\mathrm{cr}} = 1.02 \pm 0.03$ s, $[\mathrm{PO_2}]_{\mathrm{cr}} = (1.72 \pm 0.75) \times 10^{-5}$ mol/kg, $g = 2.52\,\mathrm{s}^{1/3}$;

for curve 2: $t_{\mathrm{cr}} = 1.00 \pm 0.04$ s, $[\mathrm{PO_2}]_{\mathrm{cr}} = (9.09 \pm 0.71) \times 10^{-6}$ mol/kg, $g = 1.98\,\mathrm{s}^{1/3}$.

It means that under conditions of experiment described in [12] t_{cr} is negligibly small, i.e. practically the whole observed oxygen consumption proceeds in inhomogeneous kinetics regime ($[\mathrm{Po_2}] < [\mathrm{PO_2}]_{\mathrm{cr}}$). As the light used here is more short-wave than in experiments on chemiluminescence, radical concentrations starting for observation of post-effect are found to be higher. But in the original paper [12] the values of operating light intensity are not given and the degree of approach to steady-state regime during preliminary photooxidation, i.e. c and k_h values are not reported. Now they can be calculated and appear to be equal

for curve 1: $c = 32.9\,\mathrm{s}^{-1}, k_h = 2.73 \times 10^3\,\mathrm{kg/mol \cdot s}$;
for curve 2: $c = 11.7\,\mathrm{s}^{-1}, k_h = 7.68 \times 10^3\,\mathrm{kg/mol \cdot s}$.

Curve 2 in the [12] is obtained on "unoxidized" PA, which has been specially treated to remove unstable oxidation products. In a limiting case with such "cleaning" one might expect a minimal magnitude $c = k_3 = 7.8\,\mathrm{s}^{-1}$, so the result is quite consistent with the whole collection of data presented in papers [1, 2] for justification of the new mechanism of PA photooxidation.

4. CONCLUSIONS

In the present paper a rather good agreement was shown between $[PO_2]_{cr}$ values estimated from three independent arrays of experimental data on chemiluminescence and oxygen consumption. This is, in our opinion, an important evidence for using the fractal concept in studies of chain reaction kinetics in solid polymers. Without this approach, the close agreement between parameters describing the processes of very different duration from nanoseconds in excition recombination to hours in that of radicals is hard to explain. Nevertheless, it is too early for stating that this flexible concept can replace the existing alternative approaches [8] in which parameters having no definite explanation are also used.

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