Photochain destruction of excited peroxide polystyrene macroradicals

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Abstract

Photo-oxidation of the polystyrene (PS) includes two mechanisms—a hydroperoxide one and a photochain one (caused by the photosensitivity of peroxide macroradicals). A hypothetical scheme of the photochain dissociation of excited peroxide radicals has been proposed. The latter are destroyed during photo-oxidation of polystyrene to H_2O and CO_2. More then 90% of the oxygen absorbed is consumed according to the photochain mechanism.
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1. Introduction

Investigation of the processes occurring on photo-oxidation of polystyrene (PS) is of considerable interest both for elucidating the general patterns of photo-conversions in polymers and for seeking ways of stabilizing them on ageing in natural conditions. The mechanism of PS photo-oxidation is often considered to resemble that of thermo-oxidation, supposing that only the initiation stages differ [1,2]. However, mechanism of photo-induced oxidation can differ from that for the thermal process not only in the initiation stage but also in the propagation processes, as well as in the nature and yield of intermediate and final products.

On the basis of the quantitative studies of the reactions taking place during UV irradiation of polystyrene it has been established that PS photo-oxidation has a dual character and occurs by two competing mechanisms—a photochain mechanism and a classical hydroperoxide mechanism [3]. The estimation of the absorbed O_2 consumption for each mechanism has shown that more than 90% of oxygen is used in the photochain process and about of 1% of O_2 in the hydroperoxide channel.

The peculiarities of the hydroperoxide mechanism were considered in our previous work [3] and they lie in the fact that light participates in this case just in the initiation stage and in the degenerated branching of the chains. According to the photochain mechanism which includes the decay of the excited peroxide radicals the light acts during all the process in both the initiation and in the chain propagation, as well as in the chain termination. The photochain mechanism was revealed for the first time in [4] during an investigation of the photo-conversion reactions of peroxide radicals ($ROO^\bullet$) in PS.

In the present work using experimental data previously obtained [3,5–7] we tried to compose a hypothetical scheme for the photochain reaction of the dissociation of excited peroxide radicals. This reaction takes place during the polystyrene photo-oxidation simultaneously with the conversion of a small part of $ROO^\bullet$ ($\sim$10% [3]) by a hydroperoxide mechanism.

2. Experimental technique

The experimental techniques were given in detail elsewhere [3,5–7]. It should be noted that commercial polystyrene with molecular weight $M_w \cong 7.4 \times 10^5$ has been used in all experiments. The polymer was produced by thermal spontaneous polymerization and did not contain any special additives. The samples were prepared as films of thickness from $25\,\mu$ to $2\,mm$. Some samples were prepared as a powder (dia. $\approx 0.2\,mm$). UV-irradiation of the samples was carried out at 77–340 K in air or in atmosphere of oxygen ($P \cong 150\,Torr$). All quantitative measurements for the determination of quantum yields of photoreactions (with the exception of a total quantum yield of initiation, φ_R) were carried out on film samples exposed to the light with $\lambda = 253.7\,nm$. The value of the quantum yield of initiation was obtained for the irradiation of polystyrene powder with light at $\lambda \geq 236\,nm$ in the air at room temperature.

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Light sources intensity was 10^{16}–10^{17} quantum/(cm^2 s). Polystyrene photo-oxidation was explored in a micromanometric set up (volume 5–10 cm^3) with analysis of frozen-out gaseous products of destruction. This allowed the evaluation both of the oxygen consumption and the amount of evolved products of photo-oxidation (H$_2$O and CO$_2$) with an accuracy of 10^{16} molecules [7].

ESR spectra were recorded using X-range ESR radiospectrometer at 77 K and at u.h.f. power of about 10^{-4} W.

3. Results and discussion

3.1. Initiation

The initial radical obtained during the irradiation of polystyrene with the light in the intrinsic absorption band of polystyrene is radical

–CH$_2$–C$^\bullet$–CH$_2$– (I).
    | |
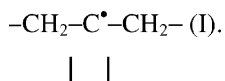
Its spectrum consists of five main components ($\Delta H = 2$ mT) arising as a result of interaction of an unpaired electron with four β-H-atoms of the main chain and in additional subsplitting of 0.5 mT on a quadruplet due to an interaction with the three equivalent hydrogen atoms of the benzene ring (Fig. 1, spectrum 1). This spectrum is detected in the earlier stages of low temperature (77 K) photolysis. For prolonged irradiation, double bonds appear in the sample. In this case,
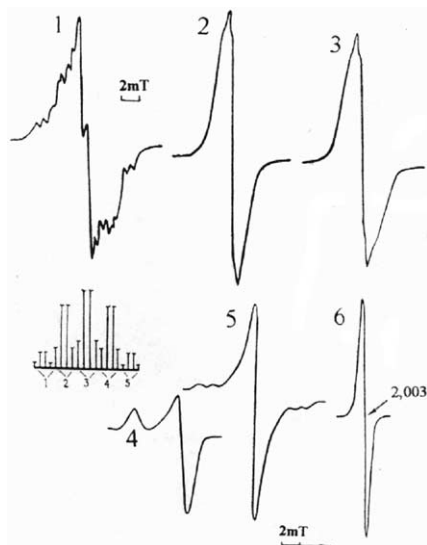

Fig. 1. ESR spectra of free radicals in UV-irradiated polystyrene: (1) spectrum of benzyl radical (I); (2) and (5) spectra of allyl radicals (II) and (V), respectively; (3) spectrum received by computer simulation with 25% of spectrum (1) and 75% of spectrum (2); (4) spectrum of radicals formed during irradiation ($\lambda \geq 236$ nm) of PS in air at 315 K for several seconds and (6) for several hours (spectrum of the radical R$_{pol}^\bullet$). Spectra recorded at 77 K.

or during photolysis of PS at room temperature, more stable radicals of allyl type –CH$_2$–C$^\bullet$(Ph)–CH=C(Ph)–CH$_2$– (II) are formed from radical (I). The stability of the radical (II) is due to the conjugation of an unpaired electron with π-electrons of the double bonds of the polymer chain and of the aromatic rings. This is the reason why its spectrum assumes the form of the isotropic singlet with $\Delta H = 2$ mT. This screens HFS by superimposing it on five component spectrum of radical (I), the general spectrum assumes the form as on Fig. 1, spectrum 2. During prolonged irradiation of PS there is a balance between allyl and benzyl radicals. To obtain a quantitative relationship between R$^\bullet$ (I) and R$^\bullet$ (II) we used a computer analysis. The simulated (3) spectrum comes to a good agreement with experimental (2) spectrum when the superposition of signals of radicals (I) and (II) at the ratio of their concentrations 1:4 was used. Thus, for prolonged photolysis of PS at 77 K, both radicals (allyl and benzyl) are stabilized; at the same time allyl radicals (II) dominate (∼75%).

During the photo-oxidation (at 300 K in the presence of oxygen) both radicals R$^\bullet$ (I) and R$^\bullet$ (II) convert into corresponding peroxide radicals –CH$_2$–C(OO$^\bullet$)(Ph)–CH$_2$– (III) and CH$_2$–C(OO$^\bullet$)(Ph)–CH=C(Ph)–CH$_2$– (IV). The quantum yield of accumulation of ROO$^\bullet$ and R$^\bullet$ at 300 K is $\varphi_R \approx 10^{-3}$ and it corresponds to the total quantum yield of the initiation of PS photo-oxidation in both channels—the hydroperoxide and photochain ones. The ESR spectrum consists of superposing of R$^\bullet$ and ROO$^\bullet$ signals (Fig. 1, spectrum 4). At the same time the amount of peroxide radicals (determined from the general ESR spectrum using the shape factor) reaches ∼80% after a few seconds irradiation of the sample.
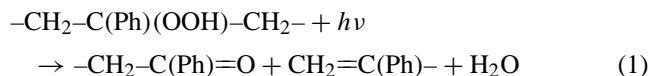
3.2. Chain propagation

One can assume that the middle peroxide radicals (III) and (IV) located in the polymer chain of macromolecules start the kinetic chain of photo-oxidation. Two reactions of chain propagation are available for them:

(1) An ordinary reaction (for the chain oxidation of hydrocarbons) of ROO$^\bullet$ with the macromolecule leading to the formation of a hydroperoxide and to its further decomposition.
(2) Destruction of excited ROO$^\bullet$ accompanied by the polymer chain rupture to form a terminal peroxide radical which initiates the photochain process.
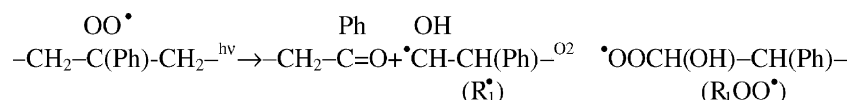
The first way of ROO$^\bullet$ conversion is a classical hydroperoxide mechanism which we have considered earlier in [3]. We determined the initiation quantum yield φ_i and kinetic chain length (l) of the photo-oxidation process reacting in the hydroperoxide mechanism ($\varphi_i \approx 10^{-4}$, $l = 7$–10 units). Taking in to consideration the entire quantum yield of initiation by both mechanisms ($\varphi_R \approx 10^{-3}$) one can conclude that only 10% of radicals obtained in the initiation stage convert according to an ordinary hydroperoxide mech-

anism. In this case, ROOH results from the bimolecular reaction of ROO$^\bullet$ with macromolecule ($\varphi_{ROOH} \approx 10^{-3}$). Further decomposition of ROOH leads to the macromolecule break off ($\varphi_{SC} \approx 10^{-3}$), the formation of terminal carbonyl groups ($\varphi_{C=O} \approx 10^{-3}$), double bonds and water [8]:

$$-CH_2-C(Ph)(OOH)-CH_2- + h\nu$$
$$\rightarrow -CH_2-C(Ph)=O + CH_2=C(Ph)- + H_2O \quad (1)$$

Only ~1% of absorbed O_2 is used in the hydroperoxide channel.

Most (90%) of the peroxide radicals of PS formed in the initiation stage takes part in another reaction—the photochain reaction of chain propagation. This reaction is connected with an excitation and complete decomposition of ROO$^\bullet$ macroradicals with the formation of H_2O and CO_2. Being photosensitive intermediates, ROO$^\bullet$ either

$$\overset{OO^\bullet}{-CH_2-C(Ph)-CH_2-} \overset{h\nu}{\rightarrow} -CH_2-\overset{Ph}{C}=O + \overset{}{^\bullet}CH-CH(Ph)- \overset{O_2}{\rightarrow} \overset{OH}{^\bullet}OOCH(OH)-CH(Ph)-$$
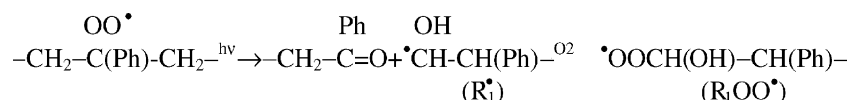$$(R_1^\bullet) \qquad\qquad (R_1OO^\bullet)$$

absorb the light or accept the excitation energy from other chromophores. In excited pπ^*- or πp-states, ROO$^\bullet$ dissociates with rupture C–C, O–O and C–H bonds [6]. As a result of the bonds breaking, new radicals R$^\bullet$ form. The latter are capable of being oxidized and propagating the kinetic chain. Thus, a photochain reaction takes place—the sequence of alternate reactions of the R$^\bullet$ oxidation and ROO$^\bullet$ destruction. The process goes on until free valency disappears. The length of such a kinetic photochain may reach $l = 10^2–10^3$ units and if the pressure of the oxygen exceeds 400 Torr the length turns out to be $l = 10^4$ units. The consumption of the oxygen in photochain channel exceeds 90%.

In order to compose a hypothetical scheme (the scheme which includes destruction of excited peroxide radicals) of the reaction of the chain propagation in the photochain channel, it is necessary to consider the following experimental data.
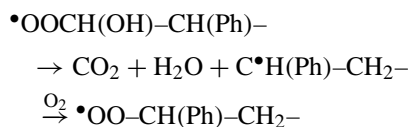
1. CO_2 is evolved with a quantum yield close to 10^{-1} [3]. Its formation unambiguously indicates the destruction of the C–C bonds of the macromolecule. This is because neither the decomposition of the hydroperoxide or of the carbonyl groups, nor the ruptures of polymer chains (quantum yields 10^{-3}) can provide the formation of CO_2 when the quantum yield is two orders of magnitude more. Therefore, it is necessary to suppose that the rupture of the C–C bonds start from the terminal of the macromolecule which is destroyed from one of its ends like a "candle burning", and peroxide radicals become the active particles promoting photochain.
2. The RO$_2$$^\bullet$ terminals are formed in the course of destruction (with the rupture of polymer chain) of an excited "middle" ROO$^\bullet$ of benzyl or allyl type (that is the radicals III and IV).

3. During the alternation of the ruptures of C–C, O–O and C–H bonds, free valency transfers in series and within the molecule. If this were not the case, at the transfer of the chain the low-molecular fragments of the polymer molecule would appear leading to a sharp decreasing of molecular mass. In fact, according to the viscosimetric data [3] the molar mass of photo-oxidated PS decreases not more than a factor of two.
4. Benzene, phenol and their low-molecular derivatives are absent among the products of photo-oxidation. It is possible to conclude from this that in the process of photochain destruction of ROO$^\bullet$ the aromatic rings are destroyed completely. It should be noted that information about the rings destruction is in the literature [1]. Considering the above, the scheme of photochain destruction of excited peroxide macroradicals of PS may be drafted as follows.

The formation of terminal radicals $R_1$$^\bullet$ and $R_1OO$$^\bullet$:
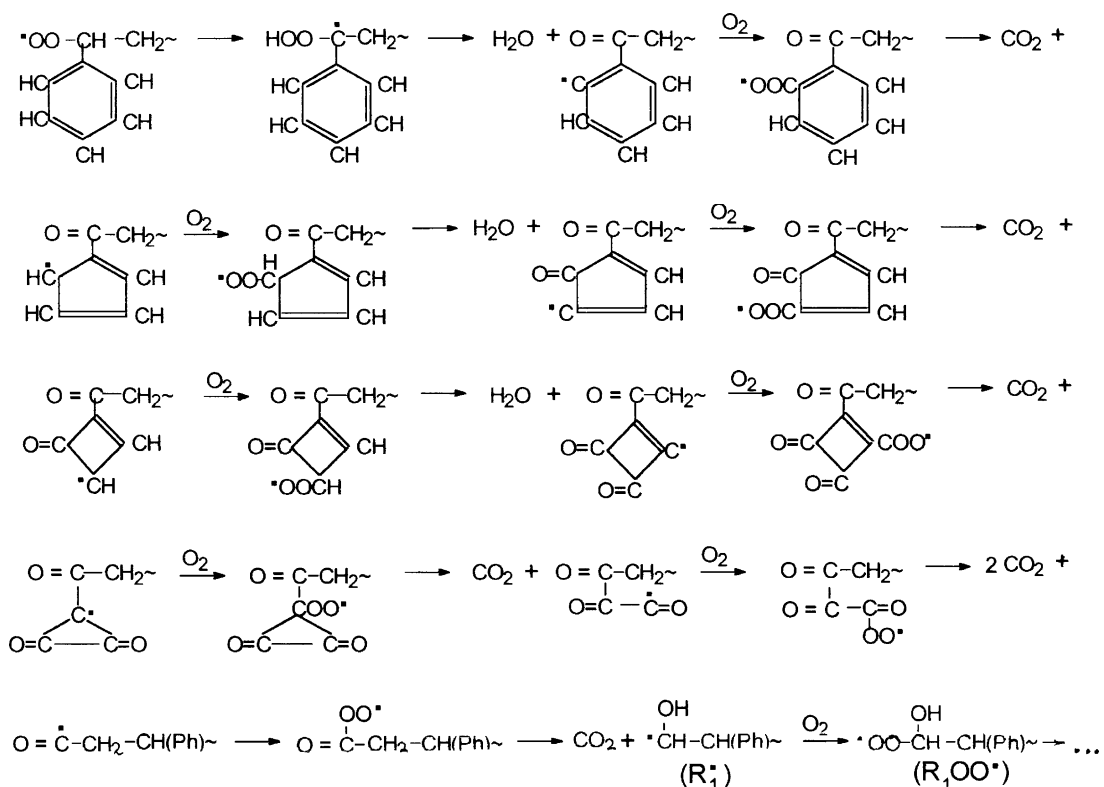
The photodestruction of $R_1OO^\bullet$ with the evolution of H_2O and CO_2 accompanied by the formation of new radicals:

$$^\bullet OOCH(OH)-CH(Ph)-$$
$$\rightarrow CO_2 + H_2O + C^\bullet H(Ph)-CH_2-$$
$$\overset{O_2}{\rightarrow} {}^\bullet OO-CH(Ph)-CH_2-$$

Two repetitive processes taking place during photodestruction of the ring in which the free valency located on the fragments $(>C^\bullet-H)$ and $(-C^\bullet=)$. In the first case the oxidation of the radical leads to the formation of the hydroperoxide group. The latter dissociates along the O–O bond to form H_2O. An electronic rearrangement of the oxide radical is ended by the formation of intermediate carbonyl $>C=O$. When the free valency transfers to the fragment $-C^\bullet=$ during the oxidation process, the radical $\equiv C-OO^\bullet$ forms. The photodestruction of this radical includes the splitting of the C–C bonds with the release of CO_2 gas. At that time, the amount of the carbonic atoms in the ring decreases but the cycle structure remains. The conjugation of the radical with the carbonyl groups also remains. Such species are good chromophores.

It is difficult to present in the frame work of the classical model of one-center transitions the series of hydrogen abstraction reactions, C–C and O–O bonds rupturing reactions, and the formation of the radical and molecular products. It is necessary to propose a series of multi-center synchronous transitions. Then, in one act (after the electronic excitation of ROO$^\bullet$) the rearrangements of the bonds may occur with the breaking of the old bonds and the formation of the new ones, including the formation of the radical intermediates [9]. At that time, the endothermic effect of the bonds
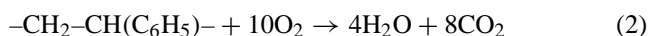
The cycle is repeated.

rupturing will be compensated by the exothermic effect of the formation of new bonds, and also by the energy of the excitation of $ROO^\bullet$.

Now let's consider the quantitative fit between experimental data and the products received according to the given scheme.

The ratio between the amount of the absorbed O_2 and the amount of the evolved gaseous products (a sum of $[H_2O] + [CO_2]$) is seen from kinetic data given on Fig. 2(a). It remains close to 1:1 for a prolonged time during irradiation. The same ratio between the absorbed O_2 and the evolved gaseous products ($H_2O + CO_2$) has been obtained by Geuskens, et al. [8]. The quantum yields at the oxygen pressure 150 Torr turned out to be $\varphi_{O_2} \approx 0.33$; $\varphi_{GAS} \approx 0.29$. At that time, $\varphi_{H_2O} \approx 0.20$; $\varphi_{CO_2} \approx 0.09$ [3,7]. After 10 h of irradiation these decrease almost two orders of magnitude to $\varphi_{O_2} \approx \varphi_{GAS} = (4.6-5.0) \times 10^{-3}$. It should be noted, that this is at the pressure 400 Torr $\varphi_{O_2} \approx \varphi_{GAS} \approx 1.1$.

The ratio between the amount of evolved H_2O and CO_2 is seen on kinetic data of Fig. 2(b). It does not correspond to the ratio between H_2O and CO_2 obtained according to the equations of the proposed scheme. The scheme was drafted taking as an analogue the complete burning of one link of the polymer. At that time the amount of water must be two times less than the amount of CO_2:

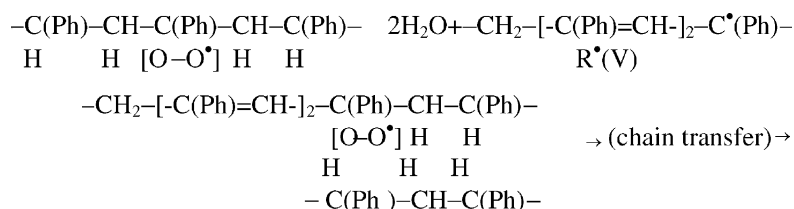$$-CH_2-CH(C_6H_5)- + 10O_2 \rightarrow 4H_2O + 8CO_2 \qquad (2)$$

The opposite situation is observed during PS photo-oxidation. As can be seen from Fig. 2(b), at the initial stages the amount of water exceeds the amount of CO_2 by approximately three times and only after 8 h irradiation (in these conditions) the ratio $H_2O:CO_2$ approaches to 1:1, what also comes to an agreement with the results [8]. But even this amount of H_2O exceeds the value, which would correspond to the stechiometric Eq. (2). The contribution of the hydroperoxide channel in the water production does not exceed 10^{-3}. In order to explain the evolution of H_2O with the quantum yield $\varphi_{H_2O} \approx 0.2$ it is necessary to consider other factors, in particular, the formation of the polyconjugated systems. This process is connected with the abstraction of the hydrogen from C–H groups, which converts into H_2O in the conditions of photo-oxidation, and with the formation of the unsaturation of the macromolecules. The proof of the appearance of the polyconjugated fragments during photo-oxidation of polystyrene is the appearance of the wide band of the luminescence of the polyenes at the range 400–550 nm [8].

The formation of nonsaturated bonds with H_2 evolution is observed already during the photolysis of PS in vacuum [10]. At the same time in the ESR spectra the singlets (with widths 2.0 and 1.4 mT, respectively) of the allyl radicals $-CH_2-C^\bullet(Ph)-CH=C(Ph)-$ (II) and $-CH_2-C^\bullet(Ph)-CH=C(Ph)-CH=C(Ph)-$ (V) (Fig. 1, spectra 2 and 5) are registered. In the presence of oxygen the

radicals II and V are oxidized to ROO$^\bullet$. The oxidation of the radical (II) is possible to observe from the ESR spectra during irradiation of polystyrene in the air at 315 K for several seconds (Fig. 1, spectrum 4). For prolonged irradiation (during several hours) in the atmosphere of oxygen, the spectrum 4 is transformed into a narrow single line ($\Delta H = 0.5$ mT, $g = 2.003$) from the polyene radicals $R_{pol}^\bullet$ (spectrum 6). The polyene radicals, in contrast to the allyl radicals, do not oxidize, and they possess the high thermostability and keep well in irradiated PS for months.
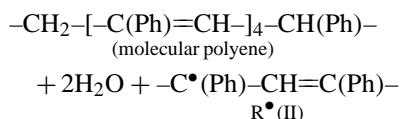
chain participate in conjugation. In other words, the conjugated system of polyene radicals consists of four monomeric links: $\sim CH_2–C^\bullet(Ph)–CH=C(Ph)–CH=C(Ph)–CH=C(Ph)–$ ($R_{pol}^\bullet$). This is the maximum length of conjugation, which may be characteristic also for the molecular polyene structures, because as Grassie and Weir suggested [10], the further growth of the nonsaturation is hampered because of the coplanarity of conjugated chains.

The formation of the polyene systems with participation of the peroxide radicals (III) may be presented as follows:

$$-C(Ph)–CH–C(Ph)–CH–C(Ph)–\quad 2H_2O+–CH_2–[-C(Ph)=CH-]_2–C^\bullet(Ph)–$$
$$HH[O–O^\bullet]\ HHR^\bullet(V)$$

$$-CH_2–[-C(Ph)=CH-]_2–C(Ph)–CH–C(Ph)–$$
$$[O–O^\bullet]\ HH\rightarrow (\text{chain transfer})\rightarrow$$
$$HHH$$
$$- C(Ph)–CH–C(Ph)–$$

Apparently, the formation of $R_{pol}^\bullet$ is connected with the reactions of the conversion of ROO$^\bullet$. They may include the elimination of H$_2$O, that increases the length of conjugation in the polymer chain. As the result in addition to the polyene radicals, the molecular polyenes appear.

According to ESR data, the conjugated system of polyene radicals includes up to 15 double bonds [3,5]. That means beside those of four benzene rings, three double bonds of the

$$-CH_2–[–C(Ph)=CH–]_4–CH(Ph)–$$
$$\text{(molecular polyene)}$$
$$+ 2H_2O + –C^\bullet(Ph)–CH=C(Ph)–$$
$$R^\bullet(II)$$

A small contribution to the process of water formation (at the earlier stages) might come from atomic oxygen which is formed during excited peroxide radicals ROO$^\bullet$ dissociation along O–O bond:

$$RO–O^\bullet + h\nu \rightarrow RO^\bullet + O : \tag{3}$$

The main reaction of atomic oxygen with hydrocarbons is the rupture of C–H bonds associated with the formation of HO$^\bullet$ and R$^\bullet$ radicals. The main reaction of HO$^\bullet$ is the abstraction of hydrogen atom from the macromolecule to form water [11]. Consequently, the appearance of two new valences of oxygen atoms leads to the formation of the additional amount of the radicals. In this connection, the reactions of atomic oxygen can be considered as the reactions of kinetic chain branching in the photochain mechanism:

$$R–H + O : \rightarrow R^\bullet + HO^\bullet \tag{4}$$

$$HO^\bullet + R–H \rightarrow H_2O + R^\bullet \tag{5}$$

It should be noted, that in the atmosphere of oxygen the reaction of O: with O$_2$ to form ozone is also possible. According to data [12] ozone can react at room temperature with solid PS breaking C–H bonds at tertiary carbon atoms to form HO$^\bullet$ and RO$_2^\bullet$ radicals. However, the reactions of the ozone with PS are less effective than the reactions of atomic oxygen.

The formation of the additional radicals [in the reactions (4) and (5)] has to be reflected on the curves of total concentration of radicals at ROO$^\bullet$ photolysis. It has been observed experimentally, confirming the mechanism of dissociation of ROO$^\bullet$ along O–O bond. The curves of the change of the total concentration of radicals [R$^\bullet$ + ROO$^\bullet$] under UV-irradiation (in different conditions) of PS films,
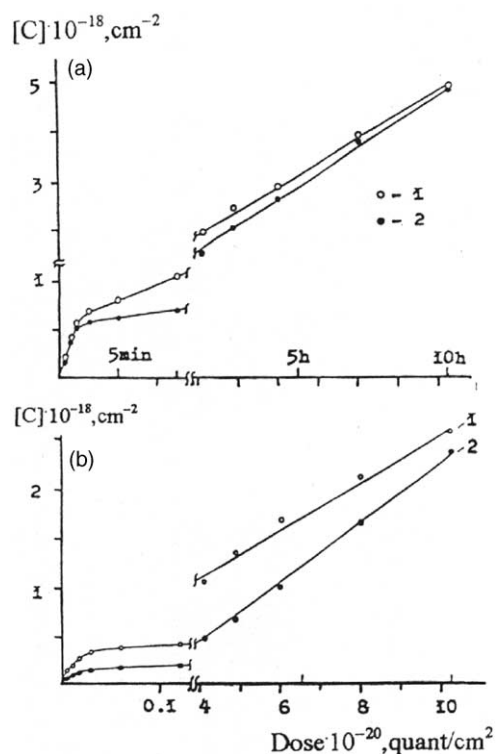

Fig. 2. (a) Comparison of kinetic curves of oxygen absorption (1) and evolution of oxidation products (H$_2$O + CO$_2$) (2); (b) comparison of curves of water liberation (1) and evolution of carbon dioxide (2) during photo-oxidation of polystyrene (λ=253.7 nm; 2×10^{16} quantum/cm^2 s; 150 Torr O$_2$; 300 K); (where (1) Torr $\cong$ (1) mm Hg $\cong$ (133) Pa).
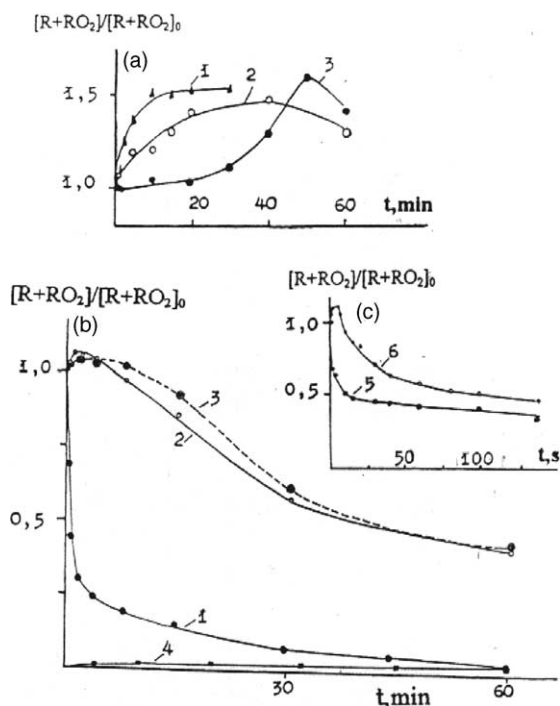
Fig. 3. Kinetics of change of total concentration of radicals $[R^\bullet + ROO^\bullet]$ in PS samples irradiated with light with: (a) $\lambda \geq 236$ (1), $\lambda \geq 300$ (2) and $\lambda \geq 440$ nm (3) at 77 K; (b) $\lambda = 253.7$ (2) and $\lambda \geq 300$ nm (3) in oxygen atmosphere (600 Torr) at 273 K; (c) $\lambda \geq 440$ nm (6) in the air at 315 K. The curves b-1 and c-5 describe free radical decay in the dark at 273 and 315 K (in oxygen atmosphere and in the air), respectively; 4-a standard experiment on the accumulation of radicals during photolysis of initial PS with light with $\lambda = 253.7$ nm at 77 K.

containing peroxide radicals, are given on Fig. 3. A small increase (1.5 times) of $[R^\bullet + ROO^\bullet]$ total concentration can be noticed at earlier stages of photolysis (when the concentration of $ROO^\bullet$ corresponds to its maximum). This may be caused by kinetic chain branching on atomic oxygen. This effect can be observed under light with $\lambda \geq 440$ nm, which is ineffective for the initial polymer, but effective for $ROO^\bullet$ photoconversion (Fig. 3(a)). A small increase of $[R^\bullet + ROO^\bullet]$ concentration may be detected on the curves of $ROO^\bullet$ photolysis at 273 and 315 K, when the radicals are thermally unstable (Fig. 3(b) and (c); curves 2, 3, 6). Their further decay (that is kinetic chain termination) when they are exposed to light slows considerably in comparison with the conventional dark reaction of decay (curves 1 and 5). The slowing down effect may also be connected with the generation of the additional amount of radicals due to the reactions of atomic oxygen in parallel with the decay process.

In analyzing the products of photo-oxidation of polystyrene, it is possible to conclude that the main part of oxygen absorbed (>90%) is transformed into the products of the deep oxidation (H_2O and CO_2) in the photochain channel. The elimination of them from the polymer is accompanied by the formation of the polyene structures in the macromolecules, by the lowering of weight and thickness of the film samples.

The amount of O_2 fitted into the polymer chain coincides with that consumed in the hydroperoxide channel (that is $\sim 1\%$).

The scheme outlined for photochain reaction of destruction of the peroxide radicals in polystyrene is apparently simplified and it demands the previous modifications. Nevertheless, in the sum total with the peroxide channel it satisfactorily balances the oxygen and much better reflects the experimental data of the photo-oxidation of polystyrene, then the hydroperoxide mechanism alone, (which has attracted the most attention in the literature to date). In addition, in the case of polystyrene it is possible to see, that the process of photo-oxidation may be in principle different from the thermal one if the radical intermediates have the photosensitivity and become the additional chromophores. Their photochemical reactions essentially change the general direction of the process and influence on the yield of the final products. In polystyrene light is absorbed not by only proper chromophores, but by the peroxide radicals too. The latter are the additional chromophores (and acceptors of excitation energy), that appear in the process of photo-oxidation. The participation of the light, in both initiation and propagation of photochain, provides long kinetic chains (10^2–10^4 links). Because of that, the quantum yields of photo-oxidation (the absorption of O_2 and the evolution of H_2O and CO_2) reach values exceeding 1. It allows us to assume the polystyrene is a system in which high levels of transformation of the light energy takes place.

Acknowledgements

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