Pergamon

Eur. Polym. J. Vol. 34, No. 8, pp. 1157–1162, 1998

Printed in Great Britain
0014-3057/98 $—see front matter

PII: S0014-3057(97)00246-2

THE PHOTO-OXIDATION OF POLYMERS—3. THE MAIN REACTION OF CHAIN PROPAGATION IN POLYSTYRENE PHOTO-OXIDATION

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(Received 17 March 1997; accepted in final form 24 June 1997)

Abstract—The photochain dissociation of peroxide macroradicals followed by effective absorption of oxygen and liberation of volatile products of destruction (H_2O and CO_2) in the quantities comparable with the quantity of the absorbed O_2 is shown to be the main reaction of the chain propagation in photo-oxidation of polystyrene. (The reaction chain length is 10^2–10^3 links.) The photochain reaction mechanism is confirmed by the special experiments with the participation of light at the stage of chain propagation when the photo-oxidation of polystyrene having the peroxide macroradicals was carried out under the action of longwave light with $\lambda \geq 440$ nm, that was inactive to the starting polymer.

INTRODUCTION

A great deal of effort has been directed to studying the polystyrene (PS) photo-oxidation during recent years. The earlier works performed mainly on the qualitative level using IR and UV spectroscopy techniques investigated structural changes in a polymer during its irradiation.

In spite of a number of quantitative works that have been appearing, including determination of the quantum yields of a series of main reactions [1–7], the mechanism of polystyrene photo-oxidation has not yet been completely established and demands further study.

A great role in PS photo-oxidation free radicals (especially peroxide ones) play and their photochemical reactions. However, it is the study of free-radical reactions that did not attract sufficient attention.

The first papers on PS photo-oxidation of the present series were devoted to the stage of free-radical initiation and the reaction of photodissociation of peroxide macroradicals in the photo-oxidation of PS [8, 9].

The aim of the current work is quantitative study (on the rate of oxygen absorption and evolution of gaseous products) of the main reaction of chain propagation, that of photodissociation of peroxide macroradicals; its chain character is revealed and the length of kinetic chains of PS photo-oxidation is evaluated.

EXPERIMENTAL

Commercial grade polystyrene (PS) as 25 μm thick films was used in this work. The polymer was obtained by thermal polymerization and did not contain any special additives. PS samples 2 mm thick were prepared from the commercial film (25 μm thick) according to the published technique [8]. Irradiation with UV light at λ = 253.7 nm and by polychromatic light of a high-pressure mercury lamp ($\lambda \geq 236$ nm) was carried out at 300–315 K in the presence of oxygen ($P_{O_2} = 25$–400 Torr). The individual regions of mercury lamp radiation spectrum were separated with a set of glass light filters.

The photo-oxidation was studied against the rate of oxygen absorption and evolution of the destruction volatile products during PS samples irradiation in a closed manometric set-up (the scheme is given in Fig. 1). A quartz cell (1) with plane-parallel walls (where the polymer sample was placed) was connected to a mercury manometer (3) through an adapter with a trap (2). The set-up was switched in to the vacuum pump and connected with the system of oxygen supply through a slide (4). A small volume of the set-up (5–10 cm^3) allowed us to measure the gas amount of 10^{-7} mol for the area of the irradiated samples of 0.5–2 cm^2 with a simultaneous registration (by an ESR technique) of free radicals in a sample. Accumulation and analysis of photo-oxidation gaseous products (H_2O and CO_2) was performed by a cryogenic method, through freezing them out into a trap cooled with liquid nitrogen down to 77–140 K (depending on the oxygen pressure in the system). All the measurements of the amounts of the absorbed oxygen and the evolution of the volatile products of destruction were carried out in post-effect in the dark 1.5–2.0 h after the sample was irradiated. That allowed us to exclude the influence of the sample heating by light flux on the pressure and permitted the oxidation products to leave the polymer and to be condensed in the trap. On slow defreezing of the trap in the temperature range 155–190 K, carbon dioxide evolved and in the range 265–300 K it was water. The amount of these substances was found by the gain in the pressure magnitude in the trap–manometer system. The use of only one working cell (without a cell of comparison) and a cryogenic method of removing the oxidation products, as well as measuring under equilibrium conditions made it possible to increase considerably the sensitivity of the set-up and to reach the earlier regions of the kinetic curves. That

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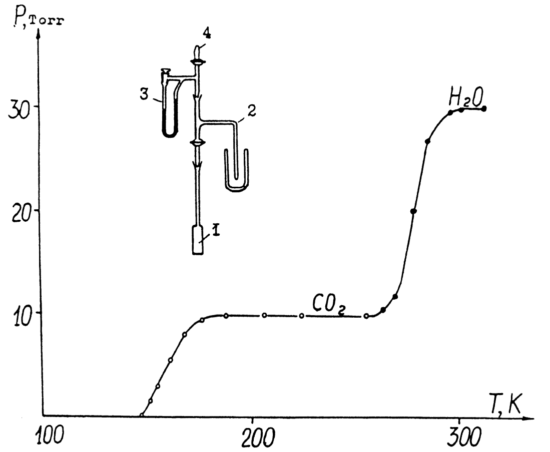


Fig. 1. The set-up scheme (1–4) for the study of PS photo-oxidation and the curve of the liberation of the photo-destruction gaseous products (H_2O and CO_2) during slow defreezing of the trap.

permitted us to reach the higher (by a factor of 50 as compared with the literature data [1–5]) of the measured values of the photo-oxidation quantum yields. The quantum yields of the photoreactions were determined in the approximation of full absorption of active light by the 2 mm thick samples according to the published technique [8]. Free radicals were recorded on 3-cm band radiospectrometers (EPR-2 and EPR-21) at u.h.f. power of about 10^{-4} W and at 77 K.

RESULTS AND DISCUSSION

The kinetic curves of the absorption of oxygen and the evolution of gaseous products during PS irradiation with light at λ = 253.7 nm (I = $2{\cdot}10^{16}$ quanta/cm^2·s) in the presence of oxygen (P_{O_2} = 150 Torr, 300 K) are given in Fig. 2. As seen from Fig. 2, the O_2 absorption and gaseous products evolution begin immediately at the moment of sample irradiation, i.e. the curves do not have any induction period or autocatalytic stage in agreement with Ref. [1, 2]. The initial period of 10–15 min of the irradiation time (which corresponds to doses of $< 2{\cdot}10^{19}$ quanta/cm^2) shows a higher oxidation rate than the subsequent region where it becomes constant for a long period of time. Such a form of the kinetic curves is characteristic of all the PS samples: films, powder, a fibrous and lyophilized polymer with highly developed surface. Besides, the character of the oxidation does not depend on the way it is performed (exposition time, sample heating time in the dark after irradiation) which may probably testify for the absence of any obstacles for the oxygen diffusion. The latter suggestion is confirmed by the fact of practically full oxidation of the initial radicals in the dark after irradiation with light $\lambda \geq 236$ nm at 315 K when, after switching off the light source, within 5–7 s the radicals oxidation degree reaches nearly 100% (Fig. 3).

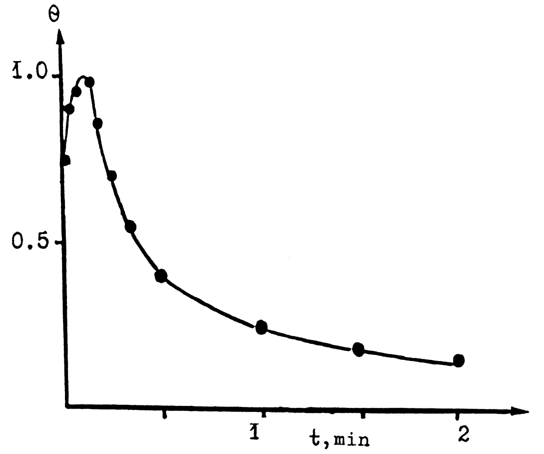


Fig. 3. Kinetics of the radicals oxidation degree variation (θ) in the dark in air at 315 K after UV-irradiation of a PS sample.

The oxygen absorption takes place also on PS irradiation with long-wave light with $\lambda \leq 440$ nm lying outside the polymer absorption band, which was also observed by Grassie and Weir when irradiating PS with light with λ = 365 nm [1, 2]. The active spectrum boundary for the photo-oxidation

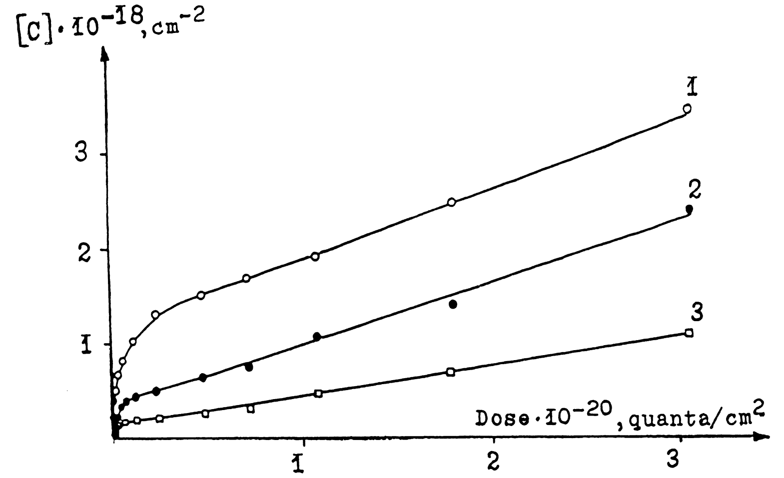


Fig. 2. Kinetics of the oxygen absorption (1), the evolution of H_2O (2) and CO_2 (3) in the polystyrene photo-oxidation (λ = 253.7 nm, P = 150 Torr, 300 K).

reaction (of O_2 absorption and evolution of gaseous products) is at $\lambda \simeq 440$ nm and coincides with the reaction of free radical formation $R^{\bullet}$ in PS [8]. Thus, the unique free-radical mechanism is characteristic of PS photo-oxidation for all ranges of the wavelengths studied (both in the intrinsic polymer absorption band and in the range 280–440 nm where the admixed chromophore groups absorb). The kinetic curves of O_2 absorption during PS irradiation with light at different wavelengths up to 440 nm are given in Fig. 4.

The photo-oxidation quantum yield using the initial rate of O_2 absorption (Fig. 2 for the data) is $\varphi_{O_2} \simeq 0.3$. In PS photo-oxidation, water and carbon dioxide, the only low-molecular products of the polymer photo-oxidative destruction [1, 2], are liberated simultaneously with oxygen absorption, the quantum yield of their formation (φ_{gas}) being close to φ_{O_2}, i.e. $\varphi_{O_2} \simeq \varphi_{gas} \simeq 0.3$. Hence nearly all the oxygen absorbed in the photo-oxidation comes from the polymer in the composition of the deep oxidation products, which is clearly demonstrated in Fig. 5(a)1 and 2.

The quantum yields φ_{O_2} and φ_{gas} depend on the oxygen pressure. Thus, on PS irradiation with light in the intrinsic absorption band (λ = 253.7 nm, $I = 10^{16}$ quanta/cm^2·s) under pressures of less than 200 Torr, φ_{O_2} (and φ_{gas}) increase linearly and at $P_{O_2} > 200$ Torr they reach a value of $\varphi_{O_2} \simeq 1$ [Fig. 5(b)3]. It is therefore concluded that during the irradiation of PS with active light and under O_2 pressures higher than 200 Torr the active light is used at its maximum.

With the decreased light intensity (from 10^{17} to 10^{15} quanta/cm^2·s) the quantum yields of the photo-oxidation increase to $\varphi_{O_2} \simeq \varphi_{gas} \simeq 3.5$. The linear dependence of the photo-oxidation initial rate on oxygen pressure was reported in Ref. [1, 2] also.

The quantum yield of the initiation of PS photo-oxidation (at 315 K in the presence of atmospheric

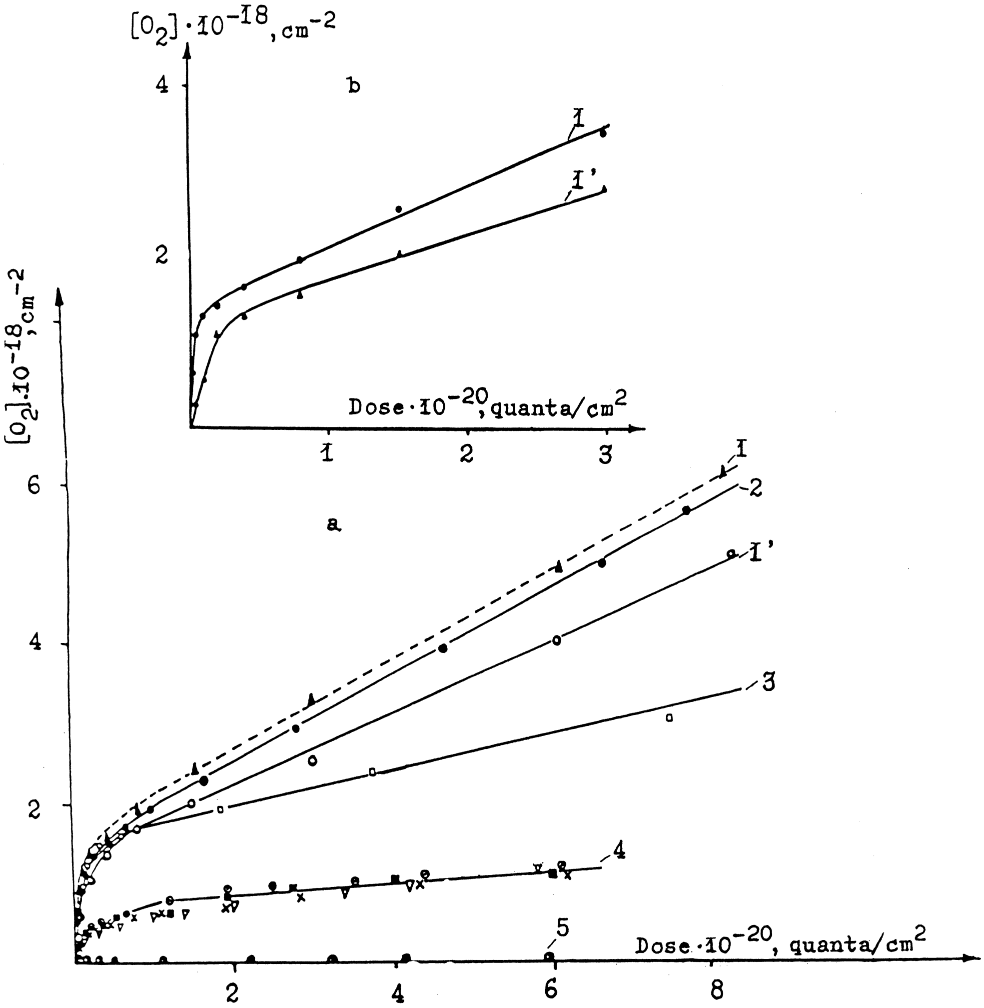


Fig. 4. (a) The kinetic curves of O_2 absorption on the polystyrene photo-oxidation under the action of light with different wavelengths for the determination of the active spectrum boundary: 1, $\lambda \geq 236$ nm; 1′, $\lambda \geq 236$ nm at 350 K; 2, λ = 253.7 nm; 3, $\lambda \geq 290$ nm; 4, $\lambda \geq 340$ nm; $\lambda \geq 360$ nm; $\lambda \geq 400$ nm; $\lambda \geq 420$ nm; 5, $\lambda \geq 440$ nm. (The sample thickness is 2 mm, $P_{O_2} = 150$ Torr, 300 K); (b) The temperature dependence of the PS photo-oxidation rate ($\lambda \geq 236$ nm, P = 150 Torr): 1, O_2 absorption at 290 K; 1′, O_2 absorption at 350 K.

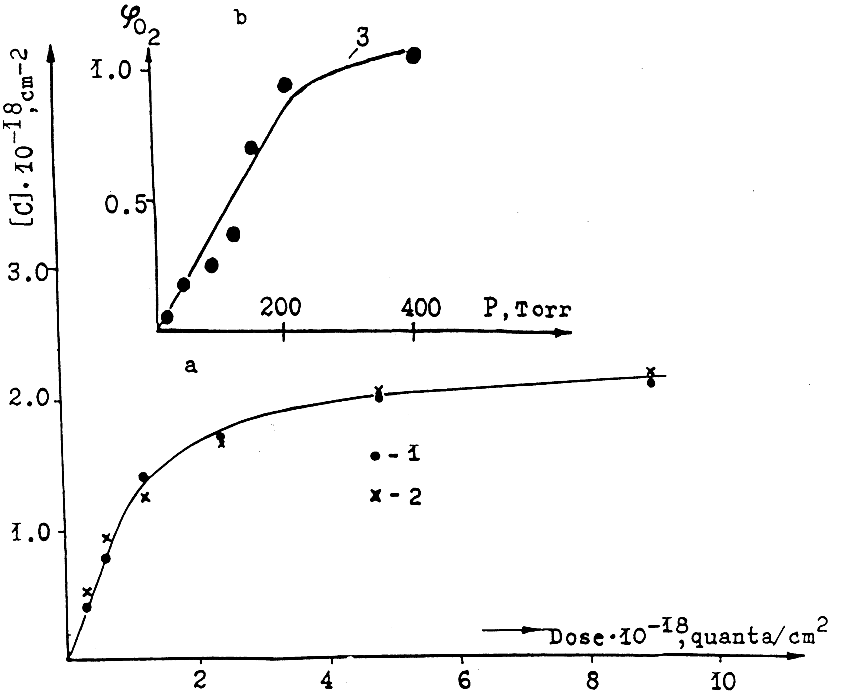


Fig. 5. Kinetics of the O_2 absorption (1) and the liberation of the photo-destruction gaseous products, H_2O and CO_2 (2) in PS photo-oxidation at P = 400 Torr (a) and the dependence of the photo-oxidation quantum yield (φ_{O_2}) on oxygen pressure (b) (λ = 253.7 nm; intensity 10^{16} quanta/cm^2·s; 300 K; the temperature of freezing out of the volatile products is 77–140 K).

oxygen) $\varphi_R \simeq 10^{-3}$ [8]. The consumption of oxygen and the formation of oxidation products (under an O_2 pressure of 150 Torr) occur with quantum yields of $\varphi_{O_2} \simeq \varphi_{gas} \simeq 0.3$ (for the data of Fig. 2), which markedly exceeds φ_R. This fact may be explained in two ways:

(1) In the process of photo-oxidation, the rate of initiation is increased, for example, because of chain photo-branching on hydroperoxide groups. Hence φ_R increases from 10^{-3} to 10^{-2}–10^{-1}.

(2) PS photo-oxidation occurs by the chain mechanism with very long kinetic chains.

To check the first assumption, we determined the quantum yield of the radical formation in a pre-photo-oxidized PS sample, in which the content of hydroperoxide groups was one order increased compared to the background value. However, φ_R at the initial stage of oxidation hardly doubled [8], which could not explain the high values of the quantum yields exceeding φ_R by 2 and at $P_{O_2} > 200$ Torr, by 3 orders of magnitude. Hence, it is admitted that the PS photo-oxidation proceeds by the chain mechanism with very long kinetic chains. Such a mechanism may be associated with the photosensoric properties of peroxide macroradicals. Under the action of light with $\lambda < 500$–550 nm, the PS peroxide radicals enter into photochemical reactions. On irradiation, the long-wave light is absorbed by the peroxide radical itself, on light irradiation in the band of polymer absorption, the excitation energy can be transferred from phenyl (and admixed) chromophores to the peroxide radicals. In the electron-excited state, $RO_2^{\bullet}$ dissociates at the O–O bond to form end oxyradicals. Thermally unstable $RO^{\bullet}$ isomerize to give end alkyl and allyl radicals. The isomerization here is followed by dissociation of C–C and C–H bonds of the macromolecule [9] leading to formation of H_2O and CO_2, the only low-molecular products of polystyrene photo-oxidation [1,2]. In the presence of oxygen, alkyl and allyl radicals are again oxidized and continue the kinetic chain [9,10]. Therefore, PS photo-oxidation provides the conditions for alternating the thermal reactions of $R^{\bullet}$ oxidation and $RO_2^{\bullet}$ photochemical reactions followed by the formation of products of deep polymer oxidation.

It is rather difficult to imagine the scheme of photochain dissociation of peroxide macroradicals since the reaction should involve decomposition down to H_2O and CO_2 of not only the main chain of macromolecule but of benzene rings as well. The reaction is probably initiated by an end macroradical. Its oxidation and a subsequent decomposition transfer free valency through the macromolecule, while the C–C and C–H dissociations give water and carbon dioxide. The free valency repeatedly migrates in chemical ways through out the polymer molecule until the free radical disappears due to recombination. Such a process is called a photochain one, as the light quanta not only initiates the oxidation chain, but also takes part in each act of its propagation inducing the photo-excitation and decay $RO_2^{\bullet}$.

A more detailed discussion of the mechanism of this reaction of PS photo-oxidation will be given in the next paper. Here it may be represented in general as:

$$PS \xrightarrow{h\nu} \dot{R} \xrightarrow{O_2} \dot{R}O_2 \longrightarrow \dot{R}$$
$$+ \text{products}(H_2O,\ CO_2) \xrightarrow{O_2} \dot{R}O_2, \text{ etc.} \quad (1)$$

In this case, in spite of low initiation rates ($\sim 10^{-3}$), the photo-oxidation quantum yield measured using the O_2 absorption rate or the rate of the gaseous products evolution reaches a high value due to the long kinetic photochain (l). It can be evaluated by the ratio of the quantum yields of photo-oxidation and initiating:

$$l = \varphi_{O_2}/\varphi_R = 10^2 - 10^3 \text{ links.}$$

For the chain propagation in the dark:

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \longrightarrow RHR^{\bullet} \quad (2)$$

the chain length found from the ratio of the amount of the absorbed oxygen to the amount of the radicals arising in the sample is $l_{\text{thermo}} = 7–10$ links.

The difference in the kinetic chain lengths as well as in the products that are formed in the thermo- and photo-oxidation of PS is connected with the different states of $RO_2^{\bullet}$ in these two processes and, therefore, with their different reactions. In photo-oxidation, the electron-excited $RO_2^{\bullet}$ dissociate to give destruction of a macromolecule to H_2O and CO_2. In thermo-oxidation, in gaseous destruction products the CO_2 is absent, while the decay of the peroxide radicals in the dark at 300 K proceeds by the mechanism of intramolecular rearrangement with a rupture of the C–C bond, formation of water, terminal carbonyl groups and double bonds [10, 11].

It should be noted that the observed values of the quantum yields $\varphi_{O_2} \geq 1$ are evidently connected with the following fact. After each photochemical act of chain propagation by Equation (1), with a decrease in light intensity and an increase in oxygen pressure, the $RO_2^{\bullet}$ radical can take part also in the thermal oxidation by Equation (2) with a chain length of 7–10 links.

In order to define clearly the chain free-radical mechanism of PS photo-oxidation and to confirm the key role of the reaction of peroxide radicals in this process we have carried out special experiments on PS photo-oxidation under the action of long-wave light with $\lambda \geq 440$ nm. As indicated earlier [8, 9], the light with such a spectral composition does not induce the formation of alkyl radicals and does not initiate the PS photo-oxidation but leads to $RO_2^{\bullet}$ photoconversion. Therefore, a small shift between the active spectra for the reactions of $R^{\bullet}$ formation (λ < 440 nm) and $RO_2^{\bullet}$ photoconversion allows us to separate the initiation stage from the chain propagation stage. The initiation (formation of primary radicals) may be performed in different ways: by photolysis, radiolysis or using chemical initiators, etc.

Figure 6(a) demonstrates the experimental results, where the primary radicals were generated by low-temperature radiolysis (77 K). After slow heating of the radiolyzed samples (as films) under atmospheric oxygen and conversion of the alkyl radicals into peroxide ones, the samples were carefully evacuated at 300 K (to remove the low-molecular radiolysis products and unreacted oxygen). In this case the amount of the peroxide radicals stabilized at room temperature was *ca.* $1.5 \cdot 10^{15}$ spin/sample (or *ca.* 3% of the initial concentration of the radiolysis-stabilized radicals). When irradiating the samples containing peroxide radicals with light with $\lambda \geq 440$ nm under atmospheric oxygen (150 Torr, 300 K) we observed oxygen absorption (curve 1) and liberation of water and carbon dioxide (curves 2 and 3) in the amounts comparable with the amount of the absorbed oxygen. The concentration of the stabilized radicals and their oxidation degree (75%) practically did not change during the light action (curve 4). The kinetic chain length for the photochain oxidation was determined from the ratio of the absorbed O_2 to the amount of the radicals in a sample: $l = 10^3$ links. Neither O_2 absorption nor

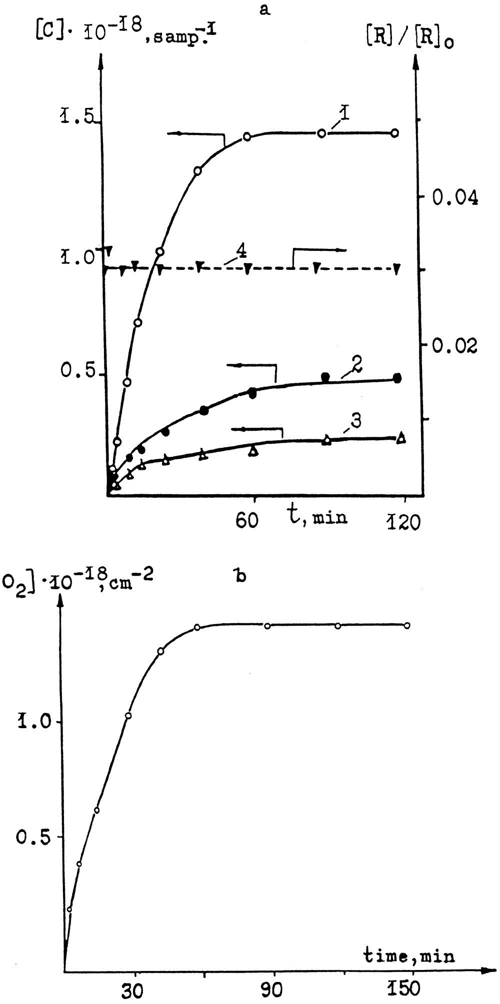
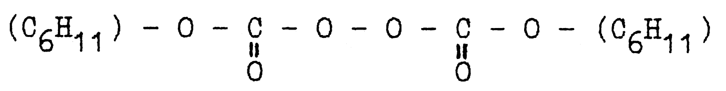


Fig. 6. Kinetics of the oxygen absorption (1), the evolution of H_2O (2), CO_2 (3) and the variation in the peroxide radicals concentration (4) in $RO_2^{\bullet}$, containing polystyrene irradiation with yellow light with $\lambda \geq 440$ nm at 300 K and 150 Torr of O_2 (a) and oxygen absorption by a PS sample containing 5% of the initiator (dicyclohexylperoxidicarbonate) during irradiation with light with $\lambda \geq 440$ nm at room temperature and 400 Torr O_2 (b).

H_2O and CO_2 liberation were observed in the reference experiments on yellow light irradiation of gamma-irradiated PS films held for 1 month at room temperature where free radicals could not be already registered by an ESR technique.

The second series of experiments involved chemical initiation. For this purpose PS films having 5% of a dicyclohexylperoxidicarbonate initiator (CPC) were cast (from toluene solution).

initiator (CPC),



$$(C_6H_{11})-O-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-O-(C_6H_{11})$$

If a PS sample having the initiator is affected by yellow light with $\lambda > 440$ nm, the oxygen absorption is observed [Fig. 6(b)]. It can be connected only with the photochain reaction of the peroxide radicals forming in the polymer as a result of the initiator action, since the photolysis by light with $\lambda > 440$ nm does not induce $R^{\cdot}$ formation in the samples having the initiator (no signals in the ESR spectra were observed). It also points to the fact that an introduction of 5% of the initiator does not shift the boundary of the active spectrum for the $R^{\cdot}$ formation in PS.

Thus, the experiments on PS photo-oxidation under long-wave light with $\lambda \geq 440$ nm may be considered as a confirmation of the existence here of the photochain oxidation mechanism connected with the photochemical activity of the peroxide macroradicals in PS.

An indication to the photochain mechanism may also serve a reciprocal temperature dependence of the photo-oxidation rate. With a temperature increase from 290 to 350 K, the oxidation rates, initial and steady-state, are reduced considerably. The quantum yield of φ_{O_2} is more than three times decreased [Fig. 4(b)]. This dependence is naturally explained in the framework of the radical chain mechanism by reduction of the concentration of free radicals due to an increased rate of their decay at higher temperatures.

Thus, the photochain mechanism of polystyrene oxidation when light takes part both in the stage of chain initiation and propagation, is confirmed by the following facts:

(1) The ESR-recorded photoconversion of spectra of peroxide macroradicals into the spectra of allyl and alkyl radicals at 77 K [9, 10].

(2) The high quantum yield of the photo-oxidation (for the oxygen absorption and the liberation of destruction products $\varphi_{O_2} \simeq \varphi_{\text{gas}} \simeq 0.3–1.0$) with the low quantum yield of initiation (10^{-3}).

(3) A reciprocal temperature dependence of the photo-oxidation rate.

(4) The experimental evidence of the participation of light in the chain propagation when the photo-oxidation in the PS sample having the peroxide radicals occurred under irradiation with visible light with $\lambda \geq 440$ nm inactive to a starting polymer.

Judging by the closeness in the values of the quantum yields of the O_2 absorption and the liberation of gaseous products (H_2O and CO_2), we may conclude that the photochain reaction of the peroxide macroradicals is the main reaction of chain propagation. It changes appreciably the general direction of the PS photo-oxidation (as compared to the conventional hydroperoxide mechanism) affecting the nature and yields of the final products.

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