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Photochemical Oxidation of Polyolefins and Prediction of Their Useful Lifetime

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By analysing the experimental data for individual elementary steps in the photochemical oxidation of pure polyolefins and by considering the kinetics of the process as a whole, it is shown that the latter is a chain reaction with degenerate photobranching by hydroperoxides and carbonyl compounds and quadratic chain termination. The available data are sufficient to describe the process at a quantitative level under any conditions. The use of this reaction as a model made it possible to elucidate the characteristic features of the photochemical oxidation of thermally stabilised and oriented polyolefins.
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I. INTRODUCTION

Polyolefins have been used traditionally to study the ageing of polymeric materials. Tens of original studies devoted to the degradation, oxidation, thermal, and photo- and radiation-induced ageing of polyolefins (PO) and several reviews are published annually. The interest in polyolefins as objects of study is due to a number of causes. On the one hand, polyolefins are some of the simplest polymeric molecules with thoroughly investigated low-molecular weight analogues—aliphatic hydrocarbons. On the other hand, polyolefins, particularly polypropylene (PP) are comparatively readily oxidised, which makes the problem of the stabilisation of these polymeric materials particularly urgent and at the same time facilitates the study of this process. Furthermore polyolefins are produced industrially on a wide scale and are used in practice in a comparatively pure form—in the presence of added stabilisers only. This permits an easy comparison of laboratory studies with the results of tests on a real polymeric material under natural conditions.

Polyolefins are usually employed at a temperature much higher than their glass point. Therefore, in describing the mechanism of the ageing of polyolefins, there are almost no difficulties characteristic of the description of solid-phase reactions. The formal process kinetics remain the same as in a viscous liquid or in the melt.

Several years ago, the present author published a review[1] in which a general mechanism of the entire polypropylene photooxidation process was "synthesised" on the basis of data for the mechanisms of individual elementary steps of the photochemical oxidation reaction and it was shown that the data available at the time for this process could be described at a quantitative level within the framework of the mechanism proposed. Despite the comparatively short period which has elapsed since the publication of the earlier review[1], a large amount of new experimental data, confirming the earlier hypothesis concerning the mechanism of the photooxidation of polypropylene has now accumulated. They now make it possible to regard the photochemical oxidation of polypropylene as a model reaction whose mechanism has been elucidated at a quantitative level.

The present review deals with the question of how this model reaction can be used to describe the kinetics of the variation of properties of polyolefins of practical importance, to elucidate the fundamental features of the mechanism of the action of various stabilisers, and to investigate the mechanism of the oxidation of polymers in an oriented state. The study of all these problems will permit a close approach to the performance of one of the fundamental tasks in the study of the ageing of polymers—the determination of the useful lifetime of polymeric materials—in the present instance those based on polyolefins.

II. KINETICS OF THE PHOTOCHEMICAL OXIDATION OF POLYPROPYLENE

By analysing the experimental data available at the time, it was shown in the earlier review[1] that the photochemical oxidation of polyolefins is a chain process with quadratic chain termination and degenerate photobranching by the hydroperoxide. The kinetic mechanism of this process can be formulated thus:

$$S \xrightarrow{w_s} PO_2^{\cdot}, \quad (1)$$

$$PO_2^{\cdot} + PH \xrightarrow{k_p} POOH + P^{\cdot}, \quad (2)$$

$$P^{\cdot} + O_2 \xrightarrow{k_2} PO_2^{\cdot},$$

$$PO_2^{\cdot} + PO_2^{\cdot} \xrightarrow{k_t} (C{=}O), \quad (3)$$

$$POOH + h\nu \xrightarrow{\alpha} PO^{\cdot} + OH^{\cdot} \xrightarrow{PH} (C{=}O) + 2PO_2^{\cdot}, \quad (4)$$

$$(C{=}O) + h\nu \xrightarrow{\alpha'} f\,PO_2^{\cdot}. \quad (5)$$

where S is the sensitiser present in the polymer and ensuring the primary initiation, $PO_2^{\cdot}$ are peroxy-radicals derived from the polymer PH, POOH is the hydroperoxide, (C=O) are carbonyl compounds, and f is the probability of the release of the radicals into the bulk phase on photolysis of the carbonyl compound. The rate constants for the corresponding reactions are indicated above the arrows, those for the photochemical reactions (α and α') characterising the probability of the decomposition of the given

substance per unit time under the influence of light having an intensity I subject to the condition that light is absorbed uniformly throughout the thickness of the specimen. The quantity α is related to the quantum yield of the decomposition into radicals ϕ and the extinction coefficient ε:

$$\alpha = \int \varphi I \varepsilon \, d\lambda. \qquad (6)$$

A change in the concentration of carbonyl compounds in the specimen is known to have no appreciable influence on the rate of photochemical oxidation[2,3] and the formation of radicals in the decomposition of C=O can therefore be neglected.

In this case the kinetics of the process are analogous to those of the familiar thermal oxidation of hydrocarbons[4]. If it is assumed that the principle of quasi-stationary concentrations of peroxy-radicals holds throughout the process, then, at a constant light intensity, the kinetics of the accumulation of reaction products are determined[1] solely by the parameter $k_p/\sqrt{k_t}$ and the probabilities of the photochemical decomposition of peroxides and carbonyl compounds—α and α':

$$[\mathrm{POOH}] = [\mathrm{POOH}]_\infty (1 - e^{-\alpha t/2})^2, \qquad (7)$$

$$[\mathrm{C{=}O}] = \frac{2\alpha}{\alpha'}[\mathrm{POOH}]_\infty \left(1 - e^{-\alpha t} - \frac{4\alpha'}{2\alpha' - \alpha}(e^{-\alpha t/2} - e^{-\alpha' t}) + \frac{\alpha'}{\alpha' - \alpha}(e^{-\alpha t} - e^{-\alpha' t})\right). \qquad (8)$$

For $\alpha' = 0$, we obtain

$$[\mathrm{C{=}O}] = 2[\mathrm{POOH}]_\infty (\alpha t - (3 - e^{-\alpha t/2})(1 - e^{-\alpha t/2})),$$

where

$$[\mathrm{POOH}]_\infty = (2k_p^2/\alpha k_t)[\mathrm{PH}]^2.$$

All the parameters in Eqns.(7) and (8) can be determined independently. It is known[5] that aliphatic hydroperoxides decompose into radicals in the step involving the absorption of each light quantum and α can therefore be calculated from spectroscopic data. Apart from spectroscopic data for carbonyl compounds, it is necessary to know the quantum yield ϕ_I of their decomposition via a Norrish type I reaction in order to determine α' †. The yields ϕ_I for different types of (C=O) in polyolefins are available in the literature (see, for example, Carlsson and Wiles[6] and Hartley and Guillet[7]).

The parameter $k_p/\sqrt{k_t}$ is determined from data for the initiated oxidation of the polymer. The calculation[1] yielded a satisfactory agreement with the results of experiments on the oxidation of pure polypropylene[8]; at that time only isolated data were available for the kinetics of the photochemical oxidation of polypropylene in which all the necessary characteristics of the process conditions were indicated: temperature and the intensity and spectral composition of the effective radiation.

Detailed studies have been made on the kinetics of the photochemical oxidation of polypropylene under the influence of light of different intensity and different spectral composition[9], the range of temperatures in which the parameters $k_p/\sqrt{k_t}$ were measured has been significantly extended, and the absolute values of the constants k_p and k_t have been determined (Table 1). All the results obtained concern the validity of the proposed mechanism. As an example, Fig.1 shows how the calculation agrees with data for the accumulation of (C=O) in the photochemical oxidation of different polypropylene specimens under the influence of light at a wavelength of 254 nm.

Table 1. Kinetic parameters of the oxidation of polypropylene* and the extinction coefficients of the branching products.

Parameter	Value	Refs.
$k_p/\sqrt{k_t}$, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$17\ e^{-6630/RT}$	11
$k_p/\sqrt{k_t}$, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$72\ e^{-8500/RT}$	9
k_p, litre mol^{-1} s^{-1}	$68\cdot10^{10}\ e^{-20840/RT}$	11
k_p, litre mol^{-1} s^{-1}	$28.8\cdot10^{11}\ e^{-22700/RT}$	9
k_t, litre mol^{-1} s^{-1}	$1.6\cdot10^{21}\ e^{-28500/RT}$	12
$k_p/\sqrt{k_t}$ at 20 °C, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$2\cdot10^{-4}$	11
$k_p/\sqrt{k_t}$ at 20 °C, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$4\cdot10^{-5}$	9
$k_p/\sqrt{k_t}$ at 20 °C, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$1\cdot10^{-4}$	10
k_p at 20 °C, litre mol^{-1} s^{-1}	$2.4\cdot10^{-4}$	11
k_p at 20 °C, litre mol^{-1} s^{-1}	$9\cdot10^{-5}$	9
k_t at 20 °C, litre mol^{-1} s^{-1}	1.2	12
	0.15	2
ε_{POOH} at 254 nm, litre mol^{-1} cm^{-1}	12.5	5
ε_{POOH} at 313 nm, litre mol^{-1} cm^{-1}	0.252	5
ε_{POOH} at 365 nm, litre mol^{-1} cm^{-1}	0.01	5
$\varepsilon_{C=O}$ at 254 nm, litre mol^{-1} cm^{-1}	8	5
$\varepsilon_{C=O}$ at 313 nm, litre mol^{-1} cm^{-1}	10	5
$\varepsilon_{C=O}$ at 365 nm, litre mol^{-1} cm^{-1}	0.44	5

*All the parameters were calculated taking into account the fact that the oxidation develops only in the amorphous component of the polymer[13].

Thus it has become possible to treat the photochemical oxidation of polypropylene from a single standpoint as a model process whose mechanism has been fully elucidated also at a quantitative level and the rate constants for all the elementary processes have been determined by independent methods. A characteristic feature of this process is a non-linear relation between the rate of reaction and the rate of formation of active centres. As a result of this non-linearity, the kinetics of the given process are qualitatively different from the kinetics of processes described as elementary nth order reactions.

For example, polypropylene does not absorb light at a wavelength greater than 200 nm; nevertheless, it is effectively oxidised under the influence of this light. The explanation is not inadequate purity of the polymer but the fact that the destruction of radicals proceeds via a second-order reaction. At low rates of initiation the oxidation chain length tends to affinity. Because of this, the solution of the differential equation describing the process kinetics is unstable at low rates of initiation and even at low rates of side processes the concentration of the hydroperoxide increases fairly rapidly; the quasi-stationary concentration of peroxy-radicals is also rapidly established.

A rigorous analysis of the kinetic scheme showed[14] that, for the majority of hydrocarbons and polymers, the decrease of the rate of primary initiation cannot alter significantly the induction period of the oxidation reaction, which is defined as the time required to accumulate the hydroperoxide at a concentration of $\sim 10^{-2}$ M.

† Norrish type II decomposition actually leads to the decomposition of the macromolecule and not to the consumption of the carbonyl group.

Another unusual consequence of the quadratic termination of the oxidation chains is a weak dependence of the stationary rate of photochemical oxidation on light intensity. Some time after the onset of oxidation (at $t \gg 1/\alpha$) the accumulation of the hydroperoxide virtually ceases completely and its quasi-stationary concentration is established. According to Eqn.(8), the concentration is inversely proportional to the light intensity. On the other hand, the rate of formation of carbonyl compounds, which under the given conditions is a measure of the rate of oxidation, is proportional to the concentration of the peroxide and the light intensity, i.e. [the hydroperoxide concentration] is independent of the light intensity#.

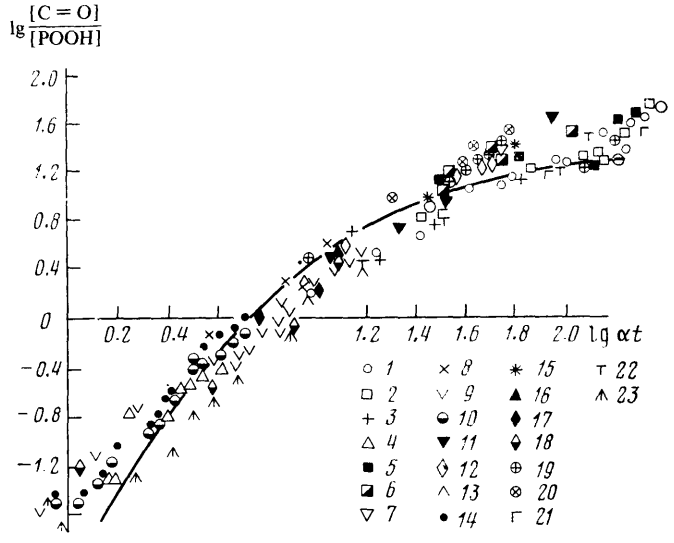


Figure 1. The logarithmic forms of kinetic curves for the accumulation of carbonyl compounds in the photochemical oxidation of different polypropylene specimens. Intensity of incident light $10^{-15} I$ (quanta cm^2 s^{-1}): 1), 5), 11), and 15) 4; 2), 6), 12), and 16) 2; 3), 7), 13), and 17) 0.5; 19) 0.7; 8) 0.44; 4), 9), and 18) 0.16; 10) and 14) 0.04; 20) 0.63; 21) 4; 22) 2; 23) 0.04 [21)–23) specimens consisting of large spherolites]; continuous line—calculation[9].

Within the framework of the mechanism under consideration, the stationary concentrations of the peroxide and carbonyl compounds are defined by the relations

$$[\mathrm{POOH}]_{\mathrm{stat}} = [\mathrm{POOH}]_\infty \frac{2\theta + f}{2\theta - f}, \qquad (9)$$

$$[\mathrm{C=O}]_{\mathrm{stat}} = [\mathrm{POOH}]_\infty \frac{\alpha}{\alpha'} 4 \frac{2\theta + f}{(\theta - f)^2}, \qquad (10)$$

where θ is the probability of the destruction of the carbonyl compound in the cage on decomposition via a Norrish type I reaction. With the aid of Eqns.(9) and (10), the values of θ and f have been determined for polypropylene[15] ($\theta = 0.75$ and $f = 0.15$).

It has been shown[16] that this treatment, which does not take into account the consumption of the substance oxidised, is valid only when one considers photochemical oxidation; in thermal oxidation $[\mathrm{POOH}]_\infty$ is usually comparable to [PH].

Thus the photochemical oxidation of polypropylene is a process which proceeds despite the fact that the initial substance does not absorb light and its stationary rate is independent of the light intensity.

III. CHARACTERISTICS OF THE ELEMENTARY STEPS AND THEIR INFLUENCE ON THE PHOTOCHEMICAL OXIDATION OF POLYOLEFINS

In the course of the study of the elementary reactions in polyolefins, certain features of their occurrence and quantitative characteristics were elucidated. This section deals with the conditions under which these features can influence the photochemical oxidation of polyolefins and the way in which this can be done.

1. Primary Initiation

According to a number of workers, the cause of the low stability of polyolefins with respect to the action of light is the sensitising role of impurities contaminating the polymer in the course of synthesis and processing[17,18]. Charge-transfer complexes between the polymer and oxygen[19–21], singlet oxygen donors[22–25], admixtures of aromatic compounds[26–28,34], residual amounts of catalysts[29–31], and unsaturated carbonyl compounds[18] have been considered as sensitisers of this kind. It has been shown that under certain conditions these compounds can serve as sources of free radicals. However, in estimating the influence of these impurities on the photochemical oxidation of polyolefins, it is necessary to compare the efficiency of their action with the efficiency of other stages of the process—in the first place the branching stage.

In the majority of cases such estimates were not made, which led to an apparent conflict between the available literature data. For example, it has been shown that, in the photolysis of aromatic[34] or carbonyl compounds, free radicals are formed. On the other hand it has also been shown that in many instances the presence of these impurities does not affect the photochemical oxidation[18]. This apparent contradiction is due to the fact that free radicals are formed from aromatic compounds at low temperatures in two-quantum processes, which do not occur in the photochemical oxidation of polyolefins close to room temperature. Carbonyl compounds are indeed sources of free radicals, but, together with these, photochemical oxidation of polyolefins gives rise to a much more effective source of free radicals—the hydroperoxide, and the role of sensitisation by carbonyl compounds is therefore insignificant.

A special analysis of the possible role of singlet oxygen donors in the photochemical oxidation of polyolefins and natural rubbers has been carried out[33]. It was assumed that the initiating function of $^1O_2$ consists in the fact that its interaction with unsaturated compounds can give rise to a hydroperoxide, which serves as an additional source of free radicals. It was shown[33] that the introduction of singlet oxygen donors does not accelerate the photochemical oxidation of the polymers investigated, occurring under the influence of ultraviolet radiation at fairly short wavelengths.

#In fact the increase of the concentration of carbonyl compounds is limited by their photochemical decomposition, which results in the formation of a certain amount of free radicals and this leads to some increase of the quasi-stationary concentration of the hydroperoxide.

On this basis, the authors[33] concluded that $^1O_2$ is not involved in the photochemical oxidation of natural rubbers and polyolefins. They showed[33] that this conclusion is valid only when the polymer is acted upon by ultraviolet radiation of sufficiently short wavelengths, which is effectively absorbed by the hydroperoxide. For a quantitative estimate of the influence of singlet oxygen, it is necessary to compare the rate w_0 at which it forms the hydroperoxide with the rate of its formation in the chain propagation reaction. For the photochemical oxidation of polypropylene, the influence of $^1O_2$ may be neglected if

$$\frac{k_p}{\sqrt{k_t}}\sqrt{2\alpha\,[\mathrm{POOH}]} \gg w_0. \qquad (11)$$

Consequently in the initial stages of the process the influence of singlet oxygen can be manifested throughout; it disappears under the condition

$$(1-e^{-\alpha t/2}) \simeq \frac{\alpha t}{2} \gg \frac{w_0 k_t}{2k_p^2}. \qquad (12)$$

Accordingly, the role of singlet oxygen donors can be neglected when the concentration of reaction products z exceeds a certain limit

$$[\mathrm{POOH}] > \frac{w_0^2 k_t}{2\alpha k_p^2}, \qquad (13)$$

$$z > \frac{w_0^2 k_t^2}{2\alpha k_p^4},$$

where z is the concentration of the products formed in the chain termination reaction.

The sensitising activity of the impurities generating free radicals can be estimated similarly. It has been shown[1] that the role of these impurities becomes insignificant when

$$\alpha t \gg \frac{\sqrt{w_i}}{k_p/\sqrt{k_t}}. \qquad (14)$$

Instead of Eqn.(13), we have in this case

$$[\mathrm{POOH}] > \frac{w_i}{2\alpha}, \qquad (15)$$

$$z > \frac{w_i^{3/2}}{\alpha k_p/\sqrt{k_t}}.$$

There are virtually no data at present based on a quantitative estimate of the role of sensitising impurities in photochemical oxidation. Therefore, as in the study of Karpukhin and Slobodetskaya[1], one can only say that, in the photochemical oxidation under the influence of ultraviolet radiation absorbed by peroxides, the role of sensitisation and $^1O_2$ is insignificant, since the available data can be accounted for without allowance for them and since the kinetic curves for the accumulation of the reaction products clearly reveal an acceleration of the process, which is impossible in the case of a process sensitised by impurities.

Photochemical oxidation cannot become sensitised under the influence of near ultraviolet (>360 nm) and visible light, which is not absorbed by hydroperoxides. This is indicated also by the examination of the criteria defined by Eqns.(12)–(15) which were discussed above.

2. Propagation and Termination of the Kinetic Chain

The kinetics of chain oxidation usually depend little on the absolute rate constants for chain propagation (k_p) and termination (k_t). When the principle of quasi-stationary radical concentrations holds, the kinetics are determined by the parameter $k_p/\sqrt{k_t}$. This parameter can be determined in different ways from the kinetics of the thermal and photochemical oxidation of polyolefins.

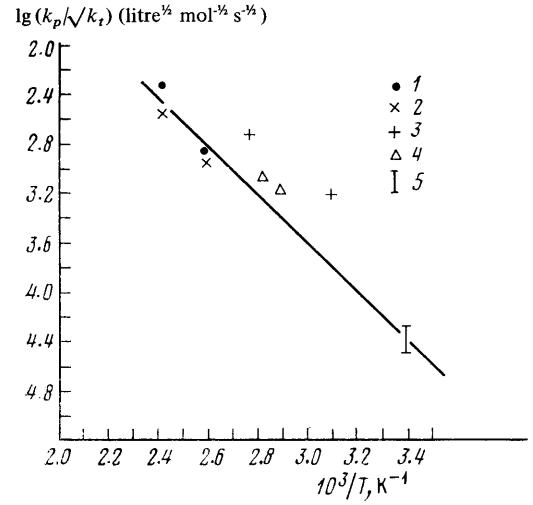


Figure 2. Temperature dependence of the parameter $k_p/\sqrt{k_t}$ for the oxidation of polypropylene according to different data: 1) Chien and Boss[68]; 2) Pudov et al.[16]; 3) Shanina et al.[11]; 4) Rapoport et al.[10]; 5) Karpukhin and Slobodetskaya[9].

The range of temperatures in which this parameter has been measured for polypropylene has been greatly extended recently. Fig.2 presents the data in terms of the variables of the Arrhenius equation. Evidently almost all the available data can be described by a single relation§; only at low temperatures is there some tendency towards an increase of the activation energy.

Table 2. The influence of the plasticiser and the hydroperoxide on the kinetic parameters of the oxidation of polypropylene[36].

Parameter*	Value of the parameter
	in the presence of 1 M *o*-dichlorobenzene
$k_p/(k_p)_0$	5.3
$k_t/(k_t)_0$	11
$(k_p/\sqrt{k_t})/(k_p/\sqrt{k_t})_0$	1.6
	in the presence of POOH**
k_t, litre mol^{-1} s^{-1}	170 (0.25); 12 (2.5); 5.2 (10)

*Subscript 0 refers to polypropylene without a plasticiser.
**The values of 10^2 [POOH] (M) are given in brackets.

§Only the data of Shanina et al.[11] deviate somewhat from the relation.

The absolute chain termination rate constants have been measured by EPR. It was observed that the rate of chain termination depends greatly on temperature[12,35] and is influenced by the molecular mobility of the medium[36] and the concentration of hydroperoxy-groups in the polymer[37]. The simultaneous measurement of the parameter $k_p/\sqrt{k_t}$ in the same systems showed[36] that all these factors have little effect on its value. The cause of this kind of compensation effect has not so far been established. Nevertheless the kinetics of the oxidation of polypropylene can be described under virtually any conditions using a single value of the parameter $k_p/\sqrt{k_t}$.

The parameters $k_p/\sqrt{k_t}$ for other polyolefins are much smaller. It is known that in the case of polyethylene (PE) the parameter has different values for low-pressure polyethylene (LPPE) and high pressure polyethylene (HPPE). This is explained by the fact that HPPE contains a greater number of tertiary hydrogen atoms, which react more effectively with the peroxy-radicals[38]. It is also known that a much smaller amount of hydroperoxides is formed in the photochemical oxidation of polyethylene than for polypropylene. This is associated with the lower value of the parameter $k_p/\sqrt{k_t}$ for polyethylene. In the thermal oxidation the parameter $k_p/\sqrt{k_t}$ for HPPE was measured in the melt[39]; furthermore, data have been published[40] on the accumulation of the HPPE hydroperoxide at 150–170 °C. The above parameter for HPPE was determined[41] from these results:

$$\frac{k_p}{\sqrt{k_t}}[\mathrm{PH}] = 34e^{-7000/RT}.$$

Photochemical oxidation of HPPE and LPPE was studied[41] at room temperature. The quantity $(k_p/\sqrt{k_t})[\mathrm{PH}]$ proved to be 1×10^{-4} (mol litre^{-1} s^{-1})$^{1/2}$, which virtually agrees with the value of this parameter extrapolated to room temperature in the study of Chokraborty and Scott[40].

3. Photobranching

The fundamental photoinitiation reaction in the photochemical oxidation of polyolefins is the photolysis of POOH. This reaction proceeds with a quantum yield of unity and with formation of two free radicals[5]. The presence of carbonyl compounds has no influence on the rate of this reaction. Thus a change in the concentration of carbonyl compounds by an order of magnitude does not affect the photolysis of POOH in polypropylene[42].

The absence of an initiating effect of (C=O) in polypropylene is associated with the low degree of liberation of radicals into space during their photolysis ($f_{200}=0.15$).[2] The situation is somewhat more complex in the case of polyethylene. Since the concentration of the hydroperoxide in polyethylene is very low and frequently cannot be determined analytically, it has been suggested in a number of studies that (C=O) is in fact a branching agent in polyethylene[43].

It is known[44] that, if 1% of C=O groups is introduced into polyethylene, the polymer becomes susceptible to decomposition by light and loses its strength characteristics much faster than pure polyethylene. On the other hand, it has been shown[40,45] that the rate of oxidation of specimens subjected to preliminary thermal oxidation varies in parallel with their hydroperoxide content (the hydroperoxide concentration in them was varied from 1×10^{-2} to 5×10^{-2} M). According to the data of Karpukhin et al.[41], when polyethylene is irradiated by light at a wavelength of 254 nm, the principal branching agents are also hydroperoxides. Analysis of literature data shows that the cause of this is (as for polypropylene) the low yield of radicals in the photolysis of carbonyl compounds (Table 3).

The observed contradictions can be resolved as follows. The photolysis of carbonyl compounds on irradiation of polyethylene by short-wavelength and particularly long-wavelength light proceeds extremely effectively. The photolysis of "central" ketones via a Norrish type II reaction involves the rupture of polymer chain. Thus the decomposition of the polymer takes place in two parallel processes: in the radical photochemical oxidation reaction and in the non-radical decomposition of ketones. Evidently the relative contributions of these processes will be determined by the irradiation conditions and by the concentration of ketones in the polyethylene. For example, calculation¶ for polyethylene used in practice, containing 10^{-2} M ketones, has shown that the role of the second process is small whatever the spectral composition of the incident light. When polyethylene containing ~0.5 M ketones is irradiated with long-wavelength light, the contributions of the two processes are comparable. This in fact explains the rapid decomposition of the ethylene–carbon monoxide copolymer. On the other hand, the degree of liberation of radicals into space during the photolysis of ketones is small; they make a small contribution to the rate of formation of radicals in polyethylene and a particular consequence of this is therefore that they have virtually no influence on the rate of photochemical oxidation of polyethylene.

Table 3. The quantum yields in the photochemical decomposition of aliphatic ketones in polyolefins.

Polymer	Ketone	φ_I	φ_{II}^*	f	$f\varphi_I$	Method of determination of φ	Refs.
PP	central	0.08	0.007	0.15	0.01	analysis of volatile products and weight loss on photolysis	6
PP	terminal	0.008	0.09	—	—	ditto	6
PE	central		0.025	—	0.003	change in molecular weight	46

*Here ϕ_{II} is the quantum yield of the decomposition via a Norrish type II reaction.

Thus the above analysis of data for the mechanisms and the quantitative characteristics of the elementary reactions which may occur in the photochemical oxidation of polyolefins showed that, under the usual conditions, the kinetics of this process are determined solely by the characteristics of the photochemical decomposition of hydroperoxides and carbonyl compounds and by the parameter $k_p/\sqrt{k_t}$.

IV. THE USE OF THE MODEL POLYPROPYLENE PHOTOCHEMICAL OXIDATION REACTION FOR THE STUDY OF THE INFLUENCE OF STABILISERS AND ORIENTING EXTRUSION ON THE PHOTOCHEMICAL OXIDATION OF POLYOLEFINS AND FOR PREDICTING THE USEFUL LIFETIME OF THE POLYMERS

The knowledge of the mechanism of the photochemical oxidation of pure polypropylene at a quantitative level makes it possible to use this reaction as a model whereby one

¶For the calculation, see E.M.Slobodetskaya, T.V.Magomedova, O.N.Karpukhin, and V.G.Protasov, Vysokomol.Soed. (in the Press).

can elucidate the details of more complex processes occurring both in the given polymer matrix and in other matrices with a similar structure.

1. Characteristics of the Oxidation of Oriented Polyolefins

Orienting extrusion is widely used in industry to obtain highly modular or specially strong fibres and films[47], which are used in various branches of technology. In particular, oriented polypropylene (OPP) films are used as packing materials in the food industry, for the packing of hygroscopic reagents and medicines, as insulating and protecting materials, etc.[48] The practical employment of these materials has shown that, compared with isotropic polypropylenes (IPP), they have not only more effective physicomechanical properties but are also more resistant to thermal oxidation[47]. A number of studies have been published recently whose authors attempt to discover the causes of this unusual structural stabilisation[49–51].

It is shown below that the data for the mechanism of the photochemical oxidation of isotropic polyolefins have been used to explain the fundamental stages of the oxidation of oriented polymers (OPO).

Polyolefins are semicrystalline polymers, the degree of crystallinity of which is usually in the range 60–70%. When crystalline polyolefins are extruded, their crystalline and amorphous components are oriented and the orientation of crystallites is virtually completed for low extrusion factors ($\bar{\lambda} = 4-5$), while for high extrusion factors all the changes occur in the amorphous part of the material[52].

The oriented fibres and films have a fibrillar structure, i.e. the polymer consists of microfibrils ~100 Å in diameter and several microns long, in which the amorphous and crystalline components alternate. The average periodicity in the polyolefin fibrils (the so-called long period) is ~100 Å and depends mainly on the extrusion temperature. The fraction of amorphous regions in the long period is inversely proportional to the degree of crystallinity of the polymer and usually amounts to 0.3–0.5 of the latter in industrial polyolefins. The composition of the crystallite usually includes several macromolecules. Consequently a large number of molecules in the amorphous region are "transient", i.e. pass from one crystallite to another through the amorphous layer. Indeed, according to Marikhin[53] 80–90% of the molecules in the amorphous region are transient and only 10–20% form the free ends and loops of the polymeric molecules projecting outside the limits of a single crystallite. Thus various parts of almost every macromolecule are incorporated simultaneously in several crystallites and contain several transient chains. The presence of a large number of transient chains is responsible for the increase in the stength of oriented polymers relative to isotropic polymers; according to Zhurkov et al.[52], the strength of fibres varies in parallel with the degree of orientation of macromolecules in the amorphous part.

Since the crystalline component of the specimens is not oxidised because the oxygen molecule cannot penetrate a crystallite, the oxidation of oriented polyolefins develops in their amorphous region[13]. According to Tochin et al.[54], considerable changes in the diffusion coefficients and in the solubility of gases in the amorphous portion of oriented polyethylene are observed only for $\bar{\lambda} > 12$. This shows, that, for $\bar{\lambda} = 4-5$, the orientation involves only a small fraction of the transient chains, while the rest remain in the same state as before orientation. When the oriented polymer is heated to a high temperature, its amorphous component undergoes partial disorientation, the degree of which depends on the annealing conditions—temperature, duration of annealing, and the strain in the macromolecule. This disorientation is caused by the "tearing out" of the transient chains from the crystallites or their "slip" relative to one another. Isometric annealing also leads to the disorientation of the amorphous part of the polymer, but here the width and the thickness of the specimen contract. The disorientation of the amorphous component of oriented polyolefins is indicated by the decrease of their contraction strain[55], the extent of which can serve as a measure of the orientation of the amorphous component of the polymer.

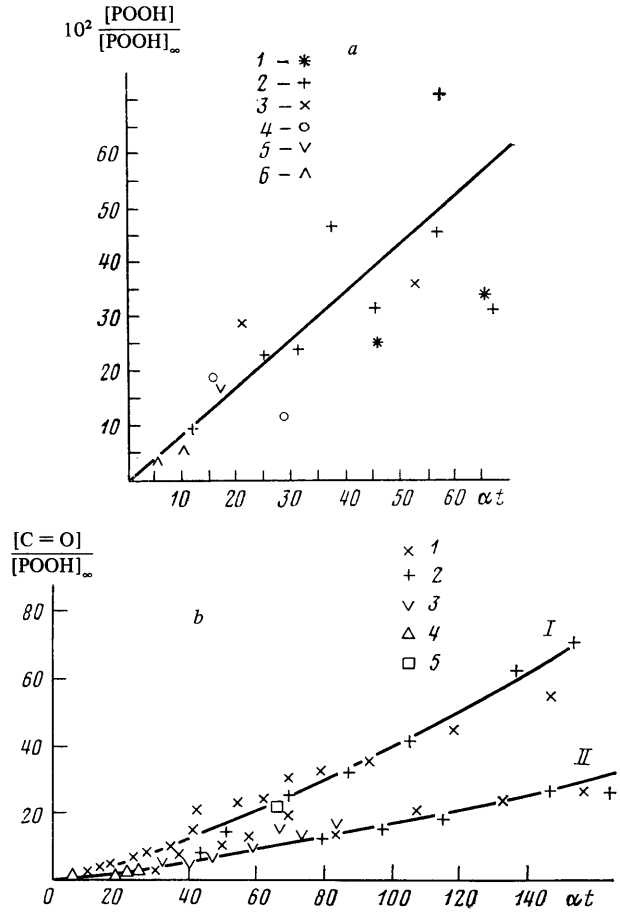


Figure 3. Kinetics of the accumulation of POOH (*a*) and carbonyl compounds (*b*) in the photochemical oxidation of OPP by light at a wavelength of 254 nm.[15] *a*) Intensity of incident light 10^{-15} *I* (quanta cm^2 s^{-1}): 1) 3.3; 2) 1.5; 3) 0.75; 4) 0.6; 5) 0.46; 6) 0.15; extrusion factor $\bar{\lambda} = 4-5$; *b*) intensity of incident light 10^{-15} *I* (quanta cm^2 s^{-1}): 1) 4; 2) 1; 3) 0.74; 4) 0.3; 5) 0.08; extrusion factor $\bar{\lambda}$: I) 4–5; II) 9–10.

A characteristic feature of the oxidation of oriented polypropylene compared with the isotropic material (IPP) is that, other conditions being equal, POOH accumulates in it at a much lower concentration. The decrease of the rate of accumulation of POOH is not related to the overall decrease of the rate of the process, which also occurs in thermal

oxidation, but is due to a qualitative change in the composition of the oxidation products.

In thermal oxidation of oriented polypropylene the yield of hydroperoxide per mole of absorbed oxygen decreases from virtually unity for IPP to 0.13 for OPP with $\bar{\lambda}=4-5$ and to 0.05 for OPP with $\bar{\lambda}=9$.[51] In the photochemical oxidation of OPP with $\bar{\lambda}=4-5$ the rate of accumulation of POOH at the beginning of the process decreases compared with IPP by a factor of hundreds, while the rate of formation of carbonyl compounds hardly changes (Fig.3). Isometric annealing at 165 °C fully eliminates the characteristics of the oxidation of OPP.[50] These results show that the changes in the physical structure of the amorphous component of polypropylene alter radically the mechanism of the oxidation process.

The small change in the rate of accumulation of carbonyl compounds on photochemical oxidation of OPP compared with IPP in the almost complete absence of POOH at the beginning of the process can be explained by assuming that in this case the photochemical decomposition of carbonyl compounds becomes an important source of free radicals or that the carbonyl compounds are formed in the chain propagation reaction on photochemical oxidation of OPP. The increase of the release of radicals into space on photolysis of strained polymers is indicated by the results of studies[57-59], where the increase of the concentration of radicals on photolysis of strained PA and PMMA compared with unstrained polymers was observed by EPR. The degree of liberation of radicals into space in the photolysis of ketones in OPP was determined[15] on the assumption that two kinds of carbonyl compounds are present in the OPP. Some of the carbonyl groups are distributed along the extended polymer chains and in their photochemical decomposition $f=2$, while others are distributed along non-extended chains and have the same properties as in IPP. The effective value of f was found by comparing the rate of accumulation of carbonyl compounds with the current concentration of POOH in the OPP. It was found that f increases compared with IPP almost by an order of magnitude and reaches $f=2$ at the beginning of the process.

As a result of the appearance of a second source of free radicals in the OPP, namely carbonyl compounds, the orientation of polypropylene does not always increase its stability. Thus, under the influence of light with $\lambda=254$ nm, the rates of accumulation of carbonyl compounds in OPP ($\bar{\lambda}=4.5$) and in IPP are virtually the same, while under the influence of light with $\lambda>300$ the photochemical oxidation of OPP is significantly faster than that of IPP.[56] This result can be readily explained by the fact that the extinction coefficients of POOH and carbonyl compounds at a wavelength of 254 nm are almost identical, while at $\lambda>300$ nm carbonyl compounds absorb light almost 20 times more effectively than POOH (Table 1).

In the thermal oxidation of polyolefins orientation always increases their stability, since a new source of free radicals does not appear in this process.

In the course of the oxidation of OPP the oriented macromolecules are ruptured with a consequent gradual disorientation of the amorphous component (chemical relaxation); the rate of accumulation of POOH increases, its yield per mole of absorbed oxygen also increases[50], while the effective liberation of free radicals into space in the photochemical decomposition of carbonyl compounds diminishes[56]. However, despite the fact that extensive and varied data have been obtained for the oxidation of OPP, at the present time the mechanism of this process has not been established at a quantitative level and only its fundamental features are clear.

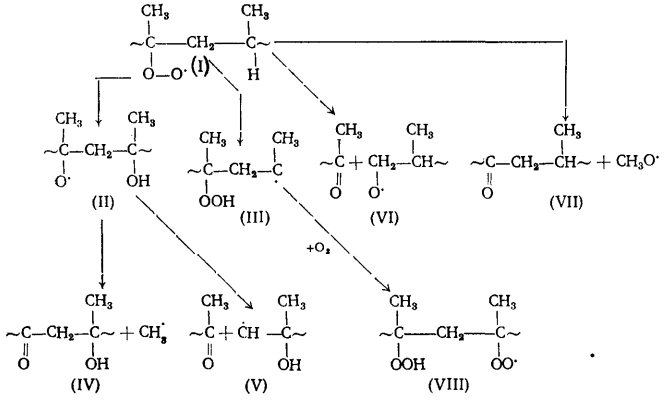
1. OPP is oxidised via a chain mechanism with quadratic chain termination.

2. The formation of free radicals by the photochemical decomposition of carbonyl compounds plays an important role in the photochemical oxidation of OPP, so that, depending on the intensity and spectral composition of the light acting on the polymer, the orientation of polypropylene can lead to both a decrease and an increase of the rate of photochemical oxidation, while thermal oxidation of polypropylene is always inhibited when the latter is oriented.

3. In the course of oxidation there is a gradual disorientation of the amorphous component of the OPP and the qualitative differences in the oxidation of OPP and IPP gradually diminish.

The results could be seemingly accounted for on the hypothesis that the oriented transient chains in OPP play a role akin to inhibitors which terminate the oxidation chains. However, under the conditions of this process mechanism, the kinetics of the photochemical oxidation should be determined by the dose of the light incident on the specimen, since in linear chain termination the rate of formation of any reaction product is linearly related to the rate of initiation. Furthermore, this conclusion is inconsistent with the available experimental data. Thus in the photochemical oxidation of OPP the efficiency of the formation of carbonyl compounds (per quantum of the light incident on the specimen) is higher the lower the irradiation intensity[56]. This result can be explained only by assuming that the branched products (carbonyl compounds) accumulate in the chain propagation reaction with quadratic termination or in accordance with a more complex kinetic mechanism in which the interaction between the reaction products plays an important role. This mechanism of the formation of carbonyl compounds in the chain propagation reaction can be set up by postulating that the peroxy-radical group on the strained chain is unstable and isomerises or decomposes, yielding ultimately a carbonyl compound.

Formally one can postulate the following different pathways leading to such isomerisation:



The consecutive isomerisation of the radicals (I) → (III) → (II), involved in competition with the oxidation of radical (III) leading to the formation of POOH (VIII) has been considered[49-51]. The authors believe that their observation of an increase of the yield of hydroperoxide per mole of absorbed oxygen with increase of O_2 pressure from 150 to 600 mmHg constitutes proof of this mechanism[60]. This conclusion appears to be ambiguous, since oxygen accelerates the oxidation of any alkyl radicals and the increase of the yield of POOH can be accounted for by competition between the oxidation of labile alkyl radicals and their interaction with strained polymer chains. The rate constant for the latter reaction should greatly exceed that for the

chain propagation in IPP, since otherwise the rates of oxidation of OPP and IPP would differ insignificantly, because the majority of chains in OPP are unstrained. Therefore the role of the competition between these reactions should be effective at considerably higher oxygen pressures than in the case of competition between analogous reactions in IPP involving an unstrained chain. This reaction is known[4] to be significant in IPP only at $p_{O_2} < 100$ mmHg. At higher p_{O_2} the influence of oxygen is determined by the competition between the reactions involving the formation of block hydroperoxides and the transfer of valence by the alkyl radical to another macromolecule[60]. In the oxidation of OPP these reactions are apparently less important, since the formation of POOH does not constitute the main pathway to the oxidation of OPP.

2. Prediction of the Kinetics of the Variation of the Practically Important Properties of a Polyolefin on the Basis of the Known Mechanism of Its Ageing

The data described above show that studies of the mechanism of the ageing of polyolefins have usually been directed towards the investigation of the changes in their chemical composition. Studies were made of the interconversion of the active centres propagating the process and of the accumulation of reaction products. However, for practical purposes, the variation of the physicomechanical characteristics of polyolefins is usually of interest and not the variation of their composition.

At the same time it is known that the kinetics of the variation of the physicomechanical properties of polyolefins are frequently not determined by the variation of their composition. Evidently, the variation of the physicomechanical properties of polyolefins and the variation of their composition in the course of ageing are caused by the same elementary processes, so that, in order to predict the kinetics of the variation of the practically important properties of the polymer, it is necessary to discover which elementary process is the primary determinant of its properties. This was achieved in the study of the photochemical oxidation of polypropylene and polyethylene.

A characteristic feature of this process is the fact that the reaction products accumulate more effectively at lower light intensities, where the branching product (the hydroperoxide) is formed in a process with longer chains. The available literature data show[41] that this feature holds qualitatively when one considers the kinetics of the variation of the molecular weight and the mechanical characteristics [the strength σ and the elongation on rupture ε (%)] of polypropylene and polyethylene.

The nature of the relation between the physicomechanical properties of polyolefins and their composition and the causes of the differences in the form of the kinetic curves for the variation of ε(%) in the case of specimens prepared in different ways are unknown, but the available data are in good qualitative agreement with the data for the mechanism of the photochemical oxidation of polyolefins. The lower the light intensity, the greater the chain length in the formation of the branching product (POOH), and consequently the higher the efficiency of all the processes occurring in the polymer.

Fig.4 presents the same relations for polypropylene obtained by plotting along the abscissa axis the amount of radicals formed in the specimen by a given instant and not the amount of light incident on the specimen:

$$\Omega = \int_0^t (2\alpha[\text{POOH}] + f\alpha'[\text{C=O}])\,\mathrm{d}t. \qquad (16)$$

Evidently, in terms of these coordinates, the data obtained at different light intensities fit the same relation. The quantity Ω can be calculated with the aid of a system of equations for any variable operating conditions, while the relation between ε(%), σ and Ω, can be obtained empirically for different polypropylene specimens.

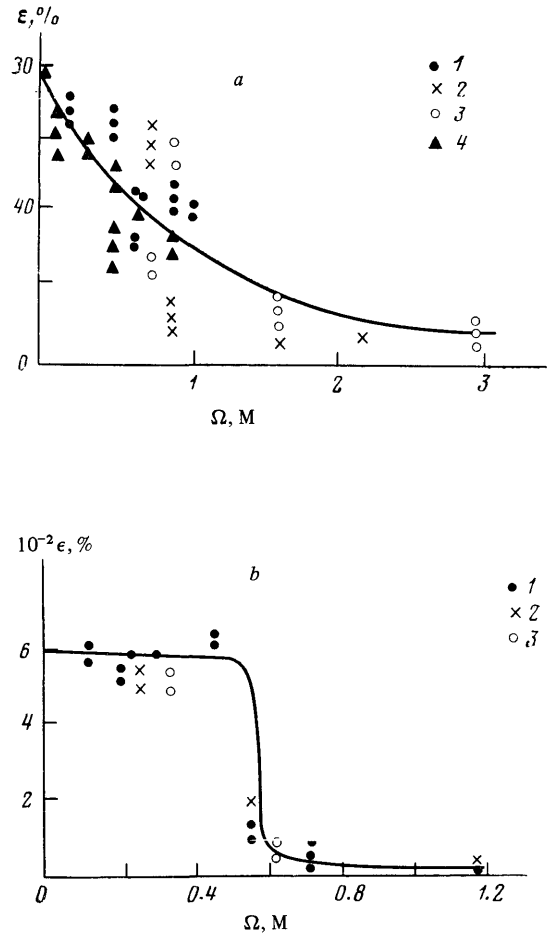


Figure 4. Dependence of the relative elongation on the dose of radicals Ω: *a*) triply oriented and annealed specimen; *b*) IPP. Intensity of incident light 10^{-15} I (quanta cm^2 s^{-1}): 1) 4; 2) 0.7; 3) 0.24; 4) 4 (in the presence of 0.15 M Methylox)[9].

Polyethylene is a much more stable polymer than polypropylene and its photochemical decomposition time is several times longer than the time required to decompose polypropylene. Analysis of Eqn.(16) shows that, for high values of t, the rate of accumulation of Ω is independent of the intensity of the incident light. Fig.5 illustrates the kinetics of the variation of ε(%) and σ for polyethylene at different light intensities. Evidently the results fit a single relation, as in the case of polypropylene. Thus on the basis of the known mechanism of the accumulation of the products of the photochemical oxidation of pure polyolefins,

it was possible to describe the kinetics of the variation of their physicomechanical characteristics.

As stated above, the mechanism of the photochemical oxidation of OPP has not been established at all hitherto. Nevertheless it has been shown[15] that the variation of the physicomechanical characteristics of OPP is correlated with the variation of Ω. The difference relative to the oxidation of IPP discussed above consists in the fact that Ω was calculated from experimental kinetic curves for the accumulation of POOH and carbonyl compounds and not on the basis of a known oxidation mechanism. Thus, even when the mechanism of the photochemical oxidation of the polymer is not known completely, it is possible to describe the kinetics of the variation of its physicomechanical properties in this process.

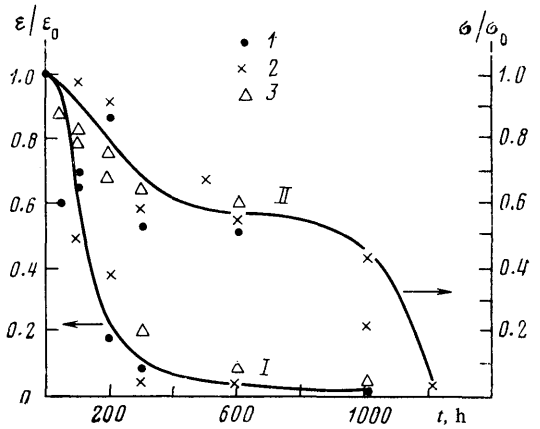


Figure 5. Dependence of the relative elongation (I) and strength (II) on the radical dose in the photochemical oxidation of HPPE.[41] Intensity of incident light 10^{-15} I (quanta cm^2 s^{-1}): 1) 2; 2) 1; 3) 0.3.

3. Photochemical Oxidation of Polypropylene Thermally Stabilised by Sterically Hindered Phenols

The example of the photochemical oxidation of pure polypropylene discussed above is to a large extent of academic interest. Only polypropylenes containing thermal and light stabilisers, which increase their useful lifetime, are used in practice. The widely employed stabilisers of the phenolic type are acceptors of the free radicals which inhibit the dark stages of the oxidation process. At the same time these stabilisers absorb the short-wavelength component of sunlight fairly effectively and function as photosensitisers of the oxidation process. Therefore, in the study of the photochemical oxidation of polymers in the presence of phenols, it is necessary to take into account not only the inhibiting effect of the antioxidant but also its initiating capacity. Furthermore, one must take into account the initiating activity of the inhibitor conversion products. For example, it has been shown[61] that the methylenequinone formed in the oxidation of ionol can dehydrogenate decane, increasing at the same time the rate of initiation. The mechanism of the sensitisation of the photochemical oxidation by phenols is complex and has not so far been ultimately established[62,63].

The photochemical transformation of the thermal stabiliser Methylox [the methyl ester of β-(3,5-di-t-butyl-4-hydroxyphenyl)propionic acid] in polypropylene has been investigated[63]. It was shown that the photochemical oxidation of Methylox results in the formation of two different photochemically active products A and B. Product A absorbs light in the longer-wavelength part of the spectrum than Methylox and many of its characteristics (the form of the absorption spectrum, the quantum yield of the photochemical decomposition) correspond to 2,6-di-t-butyl-4-methylmethylenequinone. Product A sensitises the photochemical decomposition of Methylox. Under the influence of light, products A and B decompose with different quantum yields and in the presence of large radiation doses both products are consumed almost completely and the specimen ceases to absorb light with $\lambda > 220$ nm.

Despite the very complex mechanism of the photochemical transformation of phenols in the polymer, the knowledge of the principal features of the mechanism of the photochemical transformation of pure polypropylene made it possible to discover the fundamental stages of the process which determine the photochemical decomposition of the thermally stabilised polymer.

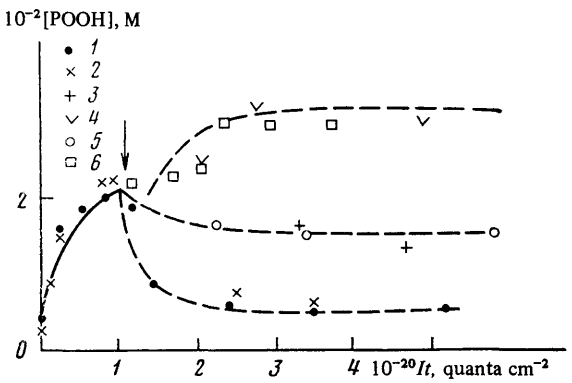


Figure 6. Kinetic curves for the accumulation of POOH in specimens containing 0.15 M Methylox[63]. Intensity of incident light 10^{-15} I (quanta cm^2 s^{-1}): 1) and 2) 4; 3) and 5) 1.4; 4) and 6) 0.7. The calculated curves are shown dashed. In plotting curves 3 and 4 the irradiation dose $It = 1.2 \times 10^{20}$ quanta cm^{-2} was attained at $I = 4 \times 10^{-15}$ quanta cm^2 s^{-1}. The arrow indicates the instant at which Methylox is consumed.

Fig.6 illustrates the kinetics of the variation of the concentration of POOH in the photochemical oxidation of polypropylene thermally stabilised by Methylox. Evidently, at different light intensities the amount of accumulated POOH at the beginning of the process is determined by the amount of light incident on the specimen. By the time of the virtually complete consumption of the phenol, the kinetic curves describing the variation of the POOH concentration begin to diverge. At low light intensities POOH continues to accumulate, while at high light intensities the POOH concentration falls.

The observed features can be readily explained within the framework of the kinetic mechanism of the photochemical oxidation of pure polypropylene with a certain initial concentration of POOH accumulated at the beginning of the process. If the initial POOH concentration is higher than the limiting value for the given intensity, then, after the consumption of the phenol, the POOH concentration will diminish; if it is lower, then POOH will continue to accumulate. The kinetics of the variation of the POOH concentration should then be described by the equation

$$[POOH] = [POOH]_\infty (1-(1-\sqrt{[POOH]/[POOH]_\infty}) \times e^{-\alpha t/2})^2. \quad (17)$$

Fig.6 shows that Eqn.(17) describes satisfactorily the kinetics of the accumulation of POOH after the consumption of Methylox. This shows that the products of the photochemical transformation of Methylox do not function as sensitisers of the photochemical oxidation process.

The variation of the physicomechanical properties of the thermally stabilised polypropylene is described by the same relation as for the pure polymer; the dose of the radicals formed in the photochemical decomposition of POOH is then calculated from the data for the kinetics of the variation of the concentration of POOH. The identity of the two relations (for the pure and thermally stabilised polymers) show that the variation of the physicomechanical properties is determined in both cases by the kinetics of the same radical reactions.

Thus, in order to develop a method for predicting the kinetics of the variation of the properties of thermally stabilised polypropylene, it is only necessary to calculate the kinetics of the consumption of Methylox and to discover at which concentration of the latter the process mechanism begins to be described by the kinetic mechanism for the photochemical oxidation of pure polypropylene. The latter problem is solved relatively simply: it is sufficient to assume that, as long as Methylox is present in the polymer, it is consumed both via its intrinsic photochemical decomposition and in terminating all the oxidation chains initiated as a result of the decomposition of POOH. Presumably, as long as the polymer contains Methylox, POOH is not effectively consumed in the photochemical decomposition steps, since it is constantly regenerated by the interaction of Methylox with peroxy-radicals.

On the basis of the foregoing, it is possible to obtain the following system of differential equations describing the kinetics of the formation of POOH in polypropylene in the presence of Methylox:

$$\frac{d[M]}{dt} = -\alpha_M [M],$$
$$\frac{d[POOH]}{dt} = f_M \alpha_M [M], \quad (18)$$

where [M] is the concentration of Methylox, f_M the yield of hydroperoxide per Methylox destruction step, $\alpha_M = \int_\lambda \phi_M \varepsilon_M I d\lambda$, ε_M the extinction coefficient of Methylox, and ϕ_M the quantum yield in the consumption of Methylox. The quantity ϕ_M has been included in the integral, since the consumption of Methylox is not an elementary photochemical reaction[63] and ϕ_M can therefore depend on the wavelength of the acting radiation. Under the influence of light with $\lambda = 254$ nm, we have $\phi_M = 2.7 \times 10^{-2}$ and $f_M = 0.14$.

After the consumption of the thermal stabiliser, the kinetics of the variation of the POOH concentration are described by Eqn.(17) for an initial non-zero POOH concentration calculated with the aid of Eqn.(18).

Thus, despite the fact that the mechanism of the sensitising effect of phenols in the polyolefin has not been established and the nature of the relation between the composition of the photochemical oxidation products and the kinetics of the variation of the physicomechanical properties of the polymer is unknown, it was possible to put forward, on the basis of ideas concerning the fundamental features of the process mechanism, a method for the prediction of the kinetics of the variation of the properties of a thermally stabilised polymer.

4. Prediction of the Useful Lifetimes of Polyolefins under Natural Conditions

The elucidation of the mechanism of the photochemical oxidation of polypropylene and the determination of the correlation between the kinetics of this process and the kinetics of the variation of the physicomechanical properties led to the formulation of the problem of the calculation of the rate of change of these properties in the course of the natural ageing of polypropylene.

As shown above, the kinetics of the variation of the physicochemical mechanical properties of polypropylene are determined unambiguously by the amount of radicals formed in the polymer throughout the process—the dose of the radicals Ω. Consequently the determination of the useful lifetime of polypropylene reduces to the calculation of Ω under the operating conditions. Two problems arise in the calculation of this quantity.

1. Eqns.(7) and (8), describing the kinetics of the photochemical oxidation of polypropylene, are non-linear and the kinetics of the variation of Ω under conditions varying with time cannot therefore be reduced to the kinetics of the variation of this quantity under equivalent conditions which are constant in time. Indeed, under variable conditions, even when the condition of a quasi-stationary concentration of free radicals holds, the kinetics of the variation of Ω in the photochemical oxidation of IPP are desdribed by the integral equation

$$\Omega = \int_0^t e^{-D} \left(\int_0^t k_p [PH] \sqrt{\alpha/k_t}\, e^{D/2} dt \right)^2 \alpha\, dt, \quad (19)$$

where $D = \int_0^t \alpha dt$. Evidently one cannot replace the variable characteristics of the conditions by average quantities. In this case one can speak of an average temperature, provided that the intensity of the light and the temperature are in no way correlated. The average light intensity can in principle characterise the quantity D; however, the light intensity also enters into the integrand independently of D.

Analogous relations should apparently hold also in thermal oxidation. The activation energies for the thermal decomposition of POOH and for the process described by the integrand may not be the same; this means that the process kinetics cannot be described within the framework of the same activation energy and it is therefore also not always possible to adjust the thermal process to an equivalent temperature.

The above calculation is illustrated in Fig.7, where the kinetic curves for the variation of Ω at different constant light intensities are shown. In the calculation it was assumed† that the light intensity varied periodically; during approximately one tenth of the period, the light intensity

†O.N.Karpukhin and E.M.Slobodetskaya, J.Polymer Sci., Polymer Chem.Ed., **17**, 3687 (1979).

was I_0 (and $\alpha = \alpha_0$), while in the course of the remaining nine tenths of the period it was 100 times lower.

It is seen from the data presented that, under the conditions of a variable intensity the process proceeds in accordance with a qualitatively different law. The limiting rate of increase of Ω, which is independent of light intensity under constant conditions, under variable conditions does depend on the law governing the time variation of I. In the example under consideration it is almost three times smaller than for the average intensity.

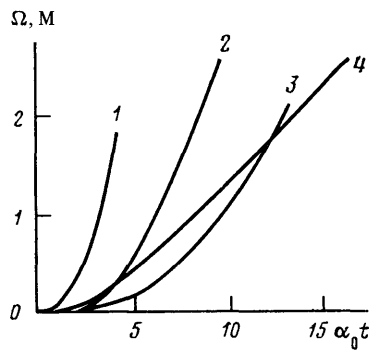


Figure 7. Calculated curves based on the measurement of Ω in the photochemical oxidation of polypropylene for variable (cruve 4) and constant (curves 1–3) light intensities[64]. The law governing the variation of I is described in the text: 1) $0.1I_0$; 2) $0.03I_0$; 3) $0.015I_0$.

Thus the calculation requires data for the dynamics of the variation of the light intensity and temperature in the course of ageing and not simply the average characteristics of the operating conditions of the polyolefin.

2. Modern computer techniques permit the calculation of Ω after substituting in the initial system of equations the primary data for the variation of the temperature and the intensity and spectral composition of the effective radiation. However, it has been found that, apart from Moscow, systematic regular measurements (over a period of many years) of the ultraviolet component of sunlight, which largely determines Ω, have hardly been made anywhere.

It is therefore necessary to resort to the advances in modern meteorology in order to set up a program for the calculation of Ω on the basis of the available meteorological data. This program includes the following initial data[64]: (a) the physicochemical characteristics of the process (the rate constants for the elementary reactions of the Arrhenius form, the absorption spectra, and the quantum yields of the decomposition of POOH and carbonyl compounds); (b) the spectral characteristics of the sun and the Earth's atmosphere (the spectrum of the sun at the outer edge of the atmosphere, the absorption spectrum of the ozone layer of the atmosphere, and the characteristics of the light scattering by the atmosphere); (c) the results of meteorological observations (temperature, thickness of the ozone layer, and the characteristics of the cloud cover); (d) geographical coordinates of the site where the tests are performed and the geometry of the arrangement of the polymer specimens (the angle with respect to the horizon and the direction of inclination).

In the calculation it was assumed that the variation with respect to the spectral composition of the solar radiation occurs only due to the change in the effective thickness of the ozone layer, while clouds play the role of an absolutely grey light filter. Fig.8 presents kinetic curves, calculated from meteorological data (Moscow, 1974)[64], for the variation of Ω and the accumulation of the products of the oxidation of free horizontally arranged polypropylene specimens exposed on the first of each month. Evidently the useful lifetime of the specimens varies with the time of the beginning of the exposure, since during cold months the photochemical oxidation is extremely slow. Fig.8 also shows that the same value of Ω, i.e. the same degree of change in the mechanical properties of polypropylene, is obtained at different concentrations of hydroperoxy- and carbonyl groups.

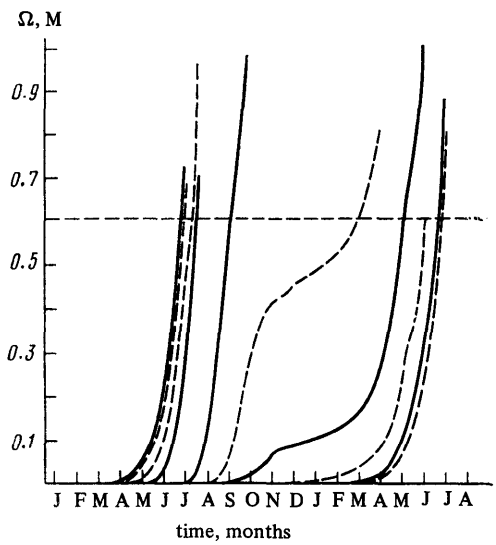


Figure 8. Calculated kinetic curves for the variation of Ω on exposure of polypropylene. Ω = 0.6 M corresponds to the loss of useful operating properties by the polypropylene.

A special computational experiment shows[64] that, in order to determine the useful lifetime of the polymer in the given case, one can employ the average monthly temperatures and average monthly coefficients of the screening of ultraviolet radiation by clouds. The average monthly coefficient of the screening of ultraviolet radiation by clouds K is calculated from the empirical formula proposed by Belinskii et al:[65]

$$K = \frac{n_1 + 0.8n_2 + 0.6n_3 + 0.35n_4}{N},$$

where N, n_1, n_2, n_3, and n_4 are respectively the total number of days, the total number of clear days, the number of days with a variable cloud cover, the number of cloudy days, and the number of days without sunshine. The quantities n_1, n_2, n_3, and n_4 are recorded systematically in the course of meteorological observations.

Comparison of the results of the calculation with the results of tests under natural conditions showed that the experimental useful lifetime is systematically shorter than the calculated lifetime. This arises apparently because the temperature of the exposed polymer specimens is always higher than the temperature of the ambient layer, since they are heated as a result of the absorption of light by the support on which the specimen rests. According to the results of Kurzhenkova and Pashchenko[66], for example, films stretched on agricultural implements age preferentially at the sites of contact with the frame, which is due to the higher temperature at these sites compared with the free film. It has been shown[67] that the film exposed under natural conditions on a black support is heated to 40–50 °C, while on a white support its temperature is 25–27 °C. It is also known that the films used for fencing in seed beds are at a temperature higher by 10–15 °C than that of the surrounding medium[67].

Thus the data presented show that in the given case the exact determination of the useful lifetime of the polymeric material is limited by the lack of exact data concerning its operating conditions.

REFERENCES

1. O.N.Karpukhin and E.M.Slobodetskaya, Uspekhi Khim., **42**, 391 (1973)[Russ.Chem.Rev., No.3 (1973)].
2. V.L.Bodneva, O.N.Karpukhin, and E.M.Slobodetskaya, Vysokomol.Soed., **B19**, 276 (1977).
3. D.J.Harper and J.F.McKellar, Chem.Ind.(London), 848 (1972).
4. N.M.Emanuel', E.T.Denisov, and Z.K.Maizus, "Tsepnye Reaktsii Okisleniya Uglevodorodov v Zhidkoi Faze" (Liquid-Phase Chain Oxidation Reactions of Hydrocarbons), Izd.Nauka, Moscow, 1969.
5. J.G.Calvert and J.N.Pitts, "Photochemistry" (Translated into Russian), Izd.Mir, Moscow, 1968.
6. D.J.Carlsson and D.M.Wiles, Macromolecules, **2**, 587 (1969).
7. G.H.Hartley and J.E.Guillet, Macromolecules, **4**, 232 (1972).
8. J.A.Melchore, Ind.Eng.Chem., **1**, 165 (1968).
9. O.N.Karpukin and E.M.Slobodetskaya, Vysokomol. Soed., **A16**, 1624 (1974).
10. N.Ya.Rapoport, V.B.Miller, A.G.Goniashvili, and M.S.Akutin, Vysokomol.Soed., **A20**, 1432 (1978).
11. E.L.Shanina, V.A.Roginskii, and V.B.Miller, Vysokomol.Soed., **A18**, 1160 (1976).
12. V.A.Roginskii and V.B.Miller, Dokl.Akad.Nauk SSSR, **215**, 1164 (1974).
13. N.E.Korduner, T.A.Bogaevskaya, B.A.Gromov, V.B.Miller, and Yu.A.Shlyapnikov, Vysokomol. Soed., **B12**, 693 (1970).
14. O.N.Karpukhin, Kinetika i Kataliz, **17**, 589 (1976).
15. O.N.Karpukhin, E.M.Slobodetskaya, I.R.Mardaleishvili, and A.N.Neverov, Vysokomol.Soed.(in the Press).
16. V.S.Pudov, B.A.Gromov, E.G.Sklyarova, and M.B.Neiman, Neftekhimiya, **3**, 743 (1963).
17. D.J.Carlsson and D.M.Wiles, J.Macromol.Sci., **C14**, 65 (1976).
18. N.S.Allen and J.F.McKellar, Brit.Polymer J., **9**, 302 (1977).
19. T.Tsubomura and R.S.Mulliken, J.Amer.Chem.Soc., **82**, 5166 (1960).
20. J.C.W.Chien, J.Phys.Chem., **69**, 4317 (1965).
21. T.Tsuji and T.Seihi, J.Polymer Sci., **B8**, 817 (1970).
22. D.J.Carlsson and D.M.Wiles, Rubber Chem.Technol., **47**, 999 (1974).
23. D.J.Carlsson and D.M.Wiles, J.Polymer Sci., Polymer Letters Ed., **11**, 759 (1973).
24. A.M.Trozzolo and F.H.Winslow, Macromolecules, **1**, 98 (1968).
25. M.L.Kaplan and P.G.Kelleher, J.Polymer Sci., **9**, 565 (1971).
26. R.H.Partridge, J.Chem.Phys., **45**, 1679 (1966).
27. J.Boustead and A.Charlesby, Europ.Polymer J., **3**, 459 (1967).
28. A.P.Pivovarov, Yu.G.Gak, and A.F.Lukovnikov, Vysokomol.Soed., **A13**, 2110 (1971).
29. O.Chiccetti and F.Gratani, Europ.Polymer J., **8**, 561 (1972).
30. L.Balaban, J.Majer, D.Resary, and L.Shoma, Kunststoffe, **60**, 341 (1970).
31. O.Chiccetti, Adv.Polymer Sci., **7**, 70 (1970).
32. N.S.Allen, J.Homer, and J.F.McKellar, J.Appl. Polymer Sci., **20**, 2553 (1976).
33. V.B.Ivanov, M.N.Kuznetsova, L.G.Angert, and V.Ya.Shlyapintokh, Dokl.Akad.Nauk SSSR, **228**, 1144 (1976).
34. L.M.Baider, Candidate's Thesis, Moscow State University, Moscow, 1969.
35. L.A.Davis, C.A.Pampillo, and T.C.Chiang, J.Polymer Sci., **A2**, 11, 841 (1973).
36. E.L.Shanina, V.A.Roginskii, and V.B.Miller, Vysokomol.Soed., **B19**, 447 (1977).
37. V.A.Roginskii, E.L.Shanina, and V.B.Miller, Vysokomol.Soed., **A20**, 265 (1978).
38. A.P.Gol'denberg and S.A.Pirozhnaya, "Molekulyarnaya Spektroskopiya" (Molecular Spectroscopy), Izd.Leningrad.Gos.Univ., 1960.
39. F.Tudos, T.Kelen, and M.Iring, Europ.Polymer J., **12**, 35 (1976).
40. K.B.Chokraborty and G.Scott, Europ.Polymer J., **13**, 731 (1976).
41. O.N.Karpukhin, E.M.Slobodetskaya, and T.V.Magomedova, Vysokomol.Soed., **B22**, 595 (1980).
42. D.J.Carlsson and D.M.Wiles, Macromolecules, **2**, 597 (1969).
43. C.H.Chew, L.M.Gan, and G.Scott, Europ.Polymer J., **13**, 361 (1976).
44. V.Pozzi, A.E.Silvers, and L.Giuffre, J.Appl. Polymer Sci., **19**, 923 (1975).
45. M.U.Amin, G.Scott, and M.K.Tillekeratne, Europ. Polymer J., **11**, 85 (1975).
46. G.H.Hartley and J.E.Guillet, Macromolecules, **1**, 413 (1968).
47. I.K.Yartsev and V.I.Pilipovskii (Editors), "Polipropilen" (Polypropylene), Izd.Khimiya, Moscow, 1967.
48. Brit.Plast., **35**, No.1, 32 (1962).
49. N.Ya.Rapoport and V.B.Miller, Dokl.Akad.Nauk SSSR, **227**, 911 (1976).
50. N.Ya.Rapoport, N.M.Livanova, and V.B.Miller, Vysokomol.Soed., **A18**, 2045 (1976).
51. N.Ya.Rapoport and V.B.Miller, Vysokomol.Soed., **A18**, 2343 (1976).
52. S.N.Zhurkov, I.I.Novak, B.Ya.Levin, A.V.Savitskii, and V.I.Vettegren', Vysokomol.Soed., **7**, 1203 (1965).
53. V.A.Marikhin, Fiz.Tverd.Tela, **19**, 1036 (1977).
54. V.A.Tochin, I.N.Musaelyan, D.N.Sapozhnikov, R.A.Shlyakhov, and K.T.Masolimov, "III Vsesoyuznaya Konferentsiya 'Diffuzionnye Yavleniya v Polimerakh'" (The IIIrd All-Union Conference 'Diffusion Phenomena in Polymers'), Riga, 1977, p.73.

55. N.M.Livanova, N.Ya.Rapoport, V.B.Miller, and I.N.Musaelyan, Vysokomol.Soed., **A18**, 2260 (1976).
56. O.N.Karpukhin, E.M.Slobodetskaya, and A.N.Neverov, Dokl.Akad.Nauk SSSR, **236**, 677 (1977).
57. G.G.Samoilov and E.E.Tomashevskii, Fiz.Tverd.Tela, **10**, 3039 (1968).
58. G.G.Samoilov and E.E.Tomashevskii, Fiz.Tverd.Tela, **10**, 1729 (1968).
59. T.B.Boboev, V.R.Regel', T.P.Sanfirova, and N.N.Chernyi, Mekhanika Polimerov, 661 (1968).
60. S.G.Kiryushkin and Yu.A.Shlyapnikov, Dokl.Akad. Nauk SSSR, **220**, 1364 (1975).
61. G.S.Popova, Candidate's Thesis, Leningrad Polytechnic Institute, 1975.
62. E.M.Slobodetskaya and O.N.Karpukhin, Vysokomol. Soed., **B18**, 184 (1976).
63. E.M.Slobodetskaya, M.G.Vorob'ev, and O.N.Karpukhin, Vysokomol.Soed., **A17**, 1533 (1975).
64. O.N.Karpukhin, E.M.Mostovaya, B.V.Novozhilov, and E.M.Slobodetskaya, Plast.Massy (in the Press).
65. V.A.Belinskii, M.P.Garadzha, L.N.Mezhennaya, and E.I.Nezval', "Ul'trafioletovaya Radiatsiya Solntsa i Neba" (Ultraviolet Radiation from the Sun and Sky), Izd.Moskov. Gos.Univ., 1968.
66. M.S.Kurzhenkova and T.E.Pashchenko, "Sbornik Trudov po Agronomicheskoi Fizike" (Collected Reports on Agronomical Physics), Gidrometeoizdat, Leningrad, 1976, No.36, p.121.
67. V.A.Kolyaseva, I.N.Kotovich, T.E.Pashchenko, and V.E.Emel'yanova, "Sbornik Trudov po Agronomicheskoi Fizike" (Collected Reports on Agronomical Physics), Gidrometeoizdat, Leningrad, 1976, No.36, p.130.
68. C.J.W.Chien and C.R.Boss, J.Polymer Sci., **A1**, 5, 3091 (1967).

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