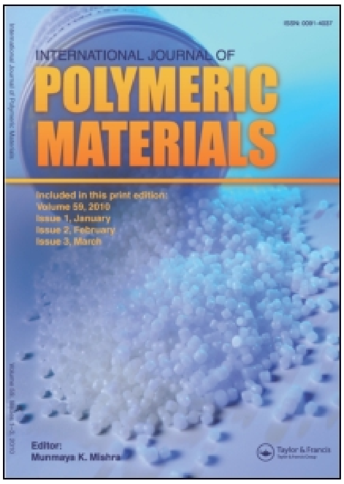

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Yu. A. Mikheyev[a]; L. N. Guseva[a]; G. E. Zaikov[a]
[a] Institute of Biochemical Physics, Russion Academy of Sciences, Moscow, Russia

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Heterophase Features of Chain Reactions of Macromolecules in Noncrystalline Polymer Matrix with Participation of Antioxidants

YU. A. MIKHEYEV, L. N. GUSEVA and G. E. ZAIKOV

Institute of Biochemical Physics, Russion Academy of Sciences, Moscow, Russia

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Principles of kinetic model composition of initiated free radical transformations in an amorphous polymer matrix are discussed. Micellar-sponge model of supermolecular structure which takes into account character of inhomogeneous zone functioning different by sizes and fluctuation dynamics of micropores composing them are put to the base of the chemical modelling. Features of antioxidant effects on chain processes are connected with the existence of conjugated reaction chains localized in separate zones of polymer chain-sponge micelles. Special attention is paid to the mechanism of the process proceeding during the induction period of polyolefine autoxidation which contain sterically hindered alkylated phenols. The induction period precedent to the stage of direct polymer oxidation is characterized as a stage of chain co-oxidation of an antioxidant and a polymer. This chain stage is the steady state order zero or one reaction by alkylphenol in dependence on its molecular structure.

Keywords: Noncrystalline polymers; antioxidants; chain reactions; heterophase structure; micellar-sponge model; chemical kinetics

1. INTRODUCTION

Recently morphological model of noncrystalline polymer has been formulated [1–9] based on a broad complex of physico-chemical properties. Polymer is discussed as a body of tightly contacting globules, whose interior consists of a large number of polymer chains forming to a sponge. Considering the intraglobular chain-sponge micelle as a chemical reactor, the model distinguishes two types of structural zones. In these zones chain units are subjected to different mechanical tensions. They enclose micropores of different sizes and fluctuation dynamics, they present real traps for reaction particles. They also provide unequivalent conditions for excitation of initiation, propagation and termination acts of chain reactions.

Inside the globules the polymer chains do not reach the limit of packing density. They remain more loose by packed as compared with the chain packing in a θ-solvent. The case is that globules in block polymers bind to each other by their coverings forming a continuous spatial *p*-carcass [1, 2, 6, 8]. Paracrystalline domains of this *p*-carcass consist of a small part of chain units and serve as mechanical clips, which do not allow the main parts of polymer chains to reach the conformation of the original density of statistic coils inside the globules.

The combination of three-dimensional extension, fixed by *p*-carcass, with polymer chain flexibility leads to many properties which are different for amorphous polymers from those of homogeneous liquids. Many of initiators and inhibitors of chain processes are capable to be absorbed, but in very small amounts, if they can access to internal structural surfaces of glassy-like polymers [7].

It is the common knowledge that solvent molecules may exchange their places with chain units more or less easy providing high entropy of mixing and transforming intraglobular sponge micelle to a liquid drop of cooperative solution [9]. A molecule of alien nonsolvent has to push apart polymer chain units, preventing their dense packing and placing them in a definite way when the place becomes free from a solvent molecule. This is the way a nonsolvent molecule introduced into a sponge forms a micropore of larger size around as compared to the case without an admixture. The sponge, suppressed by an admixture, shrinks by surface forces from micropore walls which encapsulate the additive molecule, supported by globular paracrystalline covering. Under balanced conditions between sponge elastic tensions and dispersion forces of micropore walls and additive molecule, the latter is localized in a pore volume with a relatively high freedom of rotation.

Polymers lack the ability for dense packing in the sponge micelle structure, but they still strive for reaching higher cohesive density. This is the reason that they form zones possessing micropores of different sizes. In absence of an additive a granule is formed in a carcas-linked globule, filled with narrow micropores possessing sizes of polymer chain thickness order, 0.5 nm.

Such a granule (v-zone) is separated from p-carcass cell walls (i.e. from the globule covering) by a spheric layer of stretched chain segments oriented radially in the globule. These segments play the role of a mechanical brace and fix the layer of stationary super-(s)-micropores possessing sizes of about thermodynamic segment length order ($1.5 \div 3.0$ nm).

The existence of distinct microporous zones in p-carcass cells is the reason for inhomogeneous additive molecule distribution (initiator, inhibitors, oxygen, *et al.*, for example). The additives are accumulated primarily in pithy v-granules, because narrow v-micropores in these granules possess higher sorption energy compared with the big-size s-micropores. As it was mentioned above, the narrow v-micropores have to increase their sizes on entraping an additive to provide significantly high rotation frequency to additive particles. The frequency of additive particle translation acts in the micropore system increases simultaneously. The reason is that thermal fluctuational pulses of sponge v-granules suspended to p-carcass walls stimulate cooperated oscillations of sponge chain units. These thermofluctuational oscillation measure the probability of narrow v-micropores to increase up to s-micropore sizes, although for a short time. As a result, the low molecular additive particles obtain significantly high freedom for translations in the sponge and exchange between v-and s-zones.

The behavior of stationary s-micropores and fluctuationally dynamic v-micropores in sponge micelles influence the mechanism of initiated transformations. The reason is that initiator molecules exist in different steric and energetic states on transfer between s- and v-zones and have to display inequivalent initiating effectiveness in these zones. The overlapping fields of forces from opposite walls is characteristic for narrow v-micropores. In such case the initiator is pushed on to the pore volume where it is subjected to short-time acts of fluctuationally activated jumps. Because the duration of these acts is short, it does not allow radicals to escape from initial radical pair, even if it occurs at occasional decomposition of initiator molecule in v-zone.

Contrary to narrow v-micropores, initiator molecules obtain significantly more favorable conditions for dissociation in s-micropores. The reason of this is in the existence of free space as well as in the absence of fields of overlapping force of opposite walls. Owing to this fact the additive particle spends general time absorbed on the pore surface, and not in the volume. Under these conditions the radicals of spontaneously formed radical pair are not subjected to compression, but attack polymer molecules with increased probability under the influence of adsorption forces.

The existence of inhomogeneous zones also affects polymer radicals capable to decompose with chain scission. It is clear that probability of such act on the surface of *v*-micropore, subjected to compression, is low because this requires a simultaneous shift of a number of chains which fix *v*-micropore walls. This is possible at very high fluctuation dynamics of chain-sponge granules only.

At the same time polymer radicals on *s*-micropore surfaces obtain definite probability for decomposition with chain scission, which is induced by the existence of free space and mechanical stretching of *s*-segments of polymer chains.

The above considered features of heterogeneous chain-sponge micelle arrangement, which compose a matrix of noncrystalline polymer, make kinetic description of the chain process more complex in comparison with homogeneous reaction. In case of a polymer the task of composing an adequate transformation mechanism is bound to calculation of heterogeneity. A simple consideration of the reaction medium as nonstructurized liquid-phase system is no longer applicable [10].

The stage of corresponding modelling of chain polymer transformations has begun with the application of model chain dibenzoyl peroxide reactions with polymers of different structures (such as cellulose triacetate, polycarbonate, polystyrene, polyethylene oxide, polyamide PA-548 [3, 9, 11–13]) and was continued on reactions of polymer hydroperoxide chain decomposition [5, 6].

Concept of the heterophase reaction, summed up on this stage, is that complete transformation picture should consist of:

1. The scheme of initial reaction chains, spreading in super micropores of *s*-zones in sponge micelles;
2. The scheme of secondary reaction chains in narrow *v*-zone micropores;
3. The scheme of interzone transfer of free radicals.

Taking into account the above mentioned facts, we should expect that features of supermolecular organization of polymer chains are also active in transformation of antioxidants applied to polymer material stabilization during processing and exploitation. Wide application of polymer antioxidants has started simultaneously with polymers, however development of scientific ideas about mechanism of their protective action did not progress from the homogeneous reaction theory until now [14–16]. The study of the model chain reaction of dibenzoyl peroxide with polymers displayed important phenolic antioxidant effects, connected with microheterogeneity of a polymer matrix [17, 18]. The present review presents the results of works [17, 18] in brief and analyzes some important but not yet explained data from literature on the mechanism of antioxidant action. Structural kinetic reaction model used for this purpose discloses physical meaning of antioxidant functioning in real heterophase process of polymer ageing.

2. THE MECHANISM OF 4-METHYL-2, 6-DI-TERTBUTYL-PHENOL EFFECT ON CHAIN ANAEROBIC DIBENZOYL PEROXIDE (BP) REACTION WITH GLASSY-LIKE CELLULOSE TRIACETATE AND POLYCARBONATE

Model Reaction Regularities

The investigations of BP reaction with cellulose triacetate (CTA) and polycarbonate (PC) were described in works [2, 11]. This includes studies of BP expenditure ($T \leq 371$ K), accumulation of benzoic acid and phenylbenzoate, formation of broken polymer bonds and grafting of fragments of decomposed BP to polymer chains.

The obtained results allowed us to determine that spontaneous BP decomposition proceeds in such structural zones of polymer matrix, in which macroradicals do not induce BP decomposition and peroxide fragment binding to a polymer in conjugated acts. Effective value of spontaneous decomposition rate constant k_0 is 4.8×10^{-3}min^{-1} (371 K) for both CTA and PC and the activation energy $E_0 = 117$ kJ/mol. The expression describing this constant is:

$$k_0 = k_{0s} K_e m_s m_v^{-1}.$$

Here m_s and m_r are masses of s- and r-zones, respectively; k_{0s} is the rate constant of BP decomposition in s-micropores; K_e is the equilibrium constant for interzone distribution process

$$BP_s \leftrightarrow BP_r.$$

The equilibrium condition of BP exchange between zones is given by

$$c_s = K_e c_r \approx (K_e/\alpha)c. \qquad (2.1)$$

Here c_s, c_r and c are BP concentrations in s-and r-zones and in the whole sample, respectively; α is the mass fraction of sponge consisting of both types of zones. This condition describes the heterogeneous process of radical initiation from the very beginning of the process, and it holds also during BP decomposition, whose rate is significantly lower than that of interzone exchange.

Spontaneously decomposing BP yield phenylbenzoate for CTA, phenylbenzoate and products of BP radical attachment to phenyl PC cycles for PC. Benzoic acid and macroradicals possessing free valences on the side substituents ($R_s^\bullet$) and the main chain ($P_s^\bullet$) possess lower yield ($0.2\ k_0$); macroradicals carrying free valences on the main chain degrade with chain break and decrease of polymer molecular mass.

Terminal radicals occurring at decompositions as well as $R_s^\bullet$ are subjected to transformations which induce destruction of free valence with no formation of cross bonds between polymer chains.

The rate of accumulation of broken polymer chains and the change of breaks concentration (n) with time are similarly expressed for both CTA and PC:

$$\frac{dn}{dt} = k_n c_0 \exp(-kt); \quad n = n_\infty[1 - \exp(-kt)]. \qquad (2.2)$$

Here c_0 is initial BP concentration in a sample; n_∞ is the limit concentration of broken chains; k_n constant possesses $0.062\,k_0$ and $0.14\ k_0$ values at 371 K for CTA and PC, respectively (in presence of oxygen, dissolved in the polymer, k_n value decreases by a factor of two because of $R_s^\bullet$ radical oxidation and new radical formation, which react with primary benzoyloxyls); k is effective rate constant of BP decomposition.

Contrary to polymer chains, located in radical formation zones, polymer chains in *v*-zones transform by another pathway. Since they are not subjected to decomposition acts, they participate in the chain reaction with BP according with BP according to

$$\mathrm{BP} + \mathrm{RH} \rightarrow \mathrm{rH} + \mathrm{Rr}.$$

Here symbol r marks benzoyloxyl radical.

Total process of BP decomposition in sponge micelle zones is characterized by the following exponential law:

$$c = c_0 \exp(-kt) \tag{2.3}$$

In this case the effective rate constant consists of nonchain and chain components

$$k = k_0 + k_c k_0 c_0.$$

Chain constant coefficients k_c are similar for CTA and PC which is contrary to the liquid-phase situation: BP decomposition rate is lower in aromatic liquids than in nonaromatic.

According to results of works [2,11] the same reagents (BP molecules, polymer chain units, free benzoyloxyls and macroradicals) display different chemical properties in different structural zones. In this case three block-schemes are used for description of general picture of transformations proceeding in absence of oxygen dissolved in polymers.

S-scheme displays radical formation process and their further transformations in *s*-micropore zones. It starts with primary radical pair formaiton:

$$\mathrm{BP}_s \xrightarrow{k_{0s}} \left\{\dot{\mathrm{r}}_s \ldots \dot{\mathrm{r}}_s\right\}, \qquad \left\{\dot{\mathrm{r}}_s \ldots \dot{\mathrm{r}}_s\right\} \xrightarrow{k_0'} 2\dot{\mathrm{r}}_s,$$

$$\left\{\dot{\mathrm{r}}_s \ldots \dot{\mathrm{r}}_s\right\} \xrightarrow{k_0''} \mathrm{rph} + \mathrm{CO}_2, \qquad \left\{\dot{\mathrm{r}}_s \ldots \dot{\mathrm{r}}_s\right\} \xrightarrow{k_0'''} \mathrm{rPCr}.$$

Released benzoyloxyls participate in further transformations:

$$\overset{\bullet}{r}_s \xrightarrow{k_{1s}(PH_s)} rH + P_s^\bullet, \quad \overset{\bullet}{r}_s \xrightarrow{k_{2s}(RH_s)} rH + P_s^\bullet,$$

$$\overset{\bullet}{P}_s \xrightarrow{k_{3s}} R_s^\bullet + \text{polymer chain break},$$

$$\overset{\bullet}{R}_s \xrightarrow{k_{4s}} R_{1s}^\bullet \text{ (isomerization)}, \quad R_s^\bullet + R_{1s}^\bullet \rightarrow \text{products}.$$

Here $P_s^\bullet$ and $R_s^\bullet$ designate radicals possessing free valence on the main chain and side substituents, respectively.

The radical transfer from *s*-zone to *v*-zone, occurring in absence of oxygen in samples, is described by *tr*-scheme:

$$r_s^\bullet + PhH_s \xrightarrow{k_1} rPhH_s^\bullet, \quad rPhH_s^\bullet + BP_s \xrightarrow{k_1} rPh + rH + r^\bullet.$$

(Here PhH symbol marks phenyl attached to initial BP, formed benzoic acid and phenylbenzoate). This transfer characterizes sequence of acts performed under favorable disposition of particles-participants of the present chain reaction in the surrounding of rigidly fixed chain segments which bound *s*-micropores.

Secondary benzoyloxyls r•, responsible for chain arylation of macromolecules, occur in *v*-zones as a result of such *s*, *v*-transfer, which proceeds with low probability and has no influence on steady state concentrations of *s*-radicals. The corresponding scheme is:

$$r^\bullet + RH \xrightarrow{k_2} rH + R^\bullet, \quad R^\bullet + BP_v \xrightarrow{k_3} RC_6H_4COOH$$

$$+ r^\bullet; \ RPh + CO_2 + r^\bullet.$$

(here reagent indexes are not shown, except BP_v, and R• which indicates the radical on side $-CH_2^\bullet$ group), *v*-chain terminations broken by movable benzoyloxyls leaving to *s*-zones are given by:

$$r^{\bullet} \xrightarrow{k_4} r_s^{\bullet}.$$

The presented scheme distinguishes between nonaromatic CTA and aromatic PC chemical structure in accordance with experimental results. It shows no interaction of aromatic cycles with light radicals and decomposition acts:

$$r^{\bullet} \longrightarrow ph^{\bullet} + CO_2.$$

Whereas *s*-zones provide the possibility for $r_s^{\bullet}$ radicals to attach PC cycles, *v*-zones possess no such possibility, apparently, because *v*-carcass cycles could not be subjected to conformational changes, required for intermediate stages of attachment.

Absence of *v*-benzoyloxyl decarboxylation characteristic for both polymers, conforms to formation of a single benzoic acid molecule in each unit of BP chain decomposition. This fact does not correlate with the situation in liquids, where the probability of benzoyloxyl decarboxylation is about 100%. Such deviation may be connected with large sizes of rigid monomeric units of CTA and PC and with relatively large volumes of *v*-micropores, in which $r^{\bullet}$ radicals spend a lot of time on rigid *v*-carcass walls. This favors the possibility to detach hydrogen atoms from alkyl macromolecule substituents.

It should be mentioned that chain arylation of polymers decreases the total amount of free phenyl groups, but *s*, *v*-transfer effectiveness is not changed by their participation. The reason is that loss of binuclear BP molecule is combined with formation of single-nuclear benzoic acid, which migrates two times faster along the micropore system. Owing to this fact, the probability of interzone free valence transfer is preserved [2, 9, 11].

The existence of reaction unequivalence of the same particles in *s*- and *v*-zones, described in the above block-schemes, is presented by corresponding kinetic equations. Therefore, the local rate of BP decomposition in *s*-zones equals

$$-\frac{dc_s}{dt} = k_{0s} c_s = \alpha^{-1} k_{0s} K_e c, \tag{2.4}$$

and in *v*-zones it is

$$-\frac{dc_v}{dt} = k_3[\mathrm{R}^\bullet]c_v = k_2[\mathrm{r}^\bullet][\mathrm{RH}],$$

the concentration of benzoyloxyls $\mathrm{r}^\bullet$ participating in this expression being obtained from the condition of reaction *v*-chain initiation and break rate equations is given by:

$$V_{tr} = k_4[\mathrm{r}^\bullet].$$

Here $V_{tr} = k_1[\mathrm{r}_s^\bullet][\mathrm{PhH}_s] = \dfrac{2\varphi k_1[\mathrm{PhH}_s]k_{0s}c_s}{k_{1s}[\mathrm{PH}_s]}$, $\varphi = \dfrac{k_0'}{(k_0' + k_0'' + k_0''')}$,

$[\mathrm{PhH}_s] = 2K_e\alpha^{-1}c_0$ [9].

After corresponding transpositions we obtain

$$-\frac{dc_v}{dt} = k_2[\mathrm{r}^\bullet][\mathrm{RH}] = \frac{k_2[\mathrm{RH}]V_{tr}}{k_4} = \frac{4\varphi k_2[\mathrm{RH}]k_1k_e\alpha^{-1}c_0(k_{0s}K_e\alpha^{-1})c}{k_4k_{1s}[\mathrm{PH}_s]}. \tag{2.5}$$

Transferring from the local specific reaction rates in *s*- and *v*-zones to the rate calculated for the whole sample according to the formula

$$-\frac{dc}{dt} = -\frac{\left(\frac{m_s}{m}\right)dc_s}{dt} - \frac{\left(\frac{m_v}{m}\right)dc_v}{dt},$$

where m_s, m_v, m are masses of *s*-zones, *v*-zones and the whole sample, respectively, and taking into account the expression $\alpha = ((m_s + m_v)/m) \approx (m_v)/m)$ in combination with equations (2.4) and (2.5), we obtain the following expression for the total rate of BP decomposition

$$-\frac{dc}{dt} = k_0c + k_ck_0c_0c = (k_0 + k_ck_0c_0)c. \tag{2.6}$$

The rate of decomposition process proceeding in *s*-zones only according to the *s*-scheme is

$$\frac{dn}{dt}=k_{3s}[P_s^\bullet]=k_{1s}[r_s^\bullet][PH_s]=2\varphi k_{0s}c_s=2\varphi\alpha^{-1}K_e k_{0s}c$$

$$=2\left(\varphi\frac{m}{m_s}\right)k_0c=k_nc. \tag{2.7}$$

The theoretical expressions, (2.6) and (2.7), are in accord with empyrical equations (2.2) and (2.3) and disclose the particular physical essence of heterophase transformations of polymer-chain sponge units in inhomogeneous structural zones.

This particular heterophase scheme readily explains the kinetic regularities for such products as phenylbenzoate, benzoic acid and arylated macromolecules.

Specific Features of Anaerobic Model Reaction in the Presence of Ionol

The unequivalence of transformations of previously considered reagents in different structural zones of sponge micelles is also preserved in the presence of additive ionol (4-methyl-2, 6-ditertbutylphenol), the effect of which on the model BP reaction with polymers has been studied in works [17, 18].

Moreover ionol itself differently influences processes proceeding in *s*- and *v*-zones. For example, while the polymer arylation practically stops at low ionol concentration $c_i \approx 0.05$ mol/kg already, the process of initiated decomposition is retarded just a little bit even at very high concentration c_i. It is characteristic that in the case of PC degradation constant k_n decreases only by a factor of two and remains constant in $c_i = 0.023 \div 0.64$ mol/kg range.

The theoretical model of heterophase reaction explains this fact by two-fold concentration decrease of initial benzoyloxyls $r_s^\bullet$ caused by their interactions with phenoxyls occurred in ionol reactions with side and end macro radicals $R_s^\bullet$:

$$R_s^\bullet + IH_s \xrightarrow{k_{5s}} RH + I_s^\bullet;\quad I_s^\bullet + r_s^\bullet \rightarrow Ir.$$

As a result the decomposition rate expression becomes different from (2.7):

$$\frac{dn}{dt} = 0.5\,k_n c. \tag{2.8}$$

The fact that the decomposition constant k_n decreases least by a factor of two in presence of ionol, indicates a very low effectiveness of direct ionol interaction with initial benzoyloxyls in PC matrix. Apparently, both these reagents do not obtain favorable disposition for reaction in adsorbed state on *s*-micropore walls.

The results obtained by the analysis of the process in PC using heterophase scheme are shown in Figure 1 as calculated curves (2–4) of accumulation of broken polymer bond concentration. These curves prove that limiting concentrations of broken bonds decrease as c_i

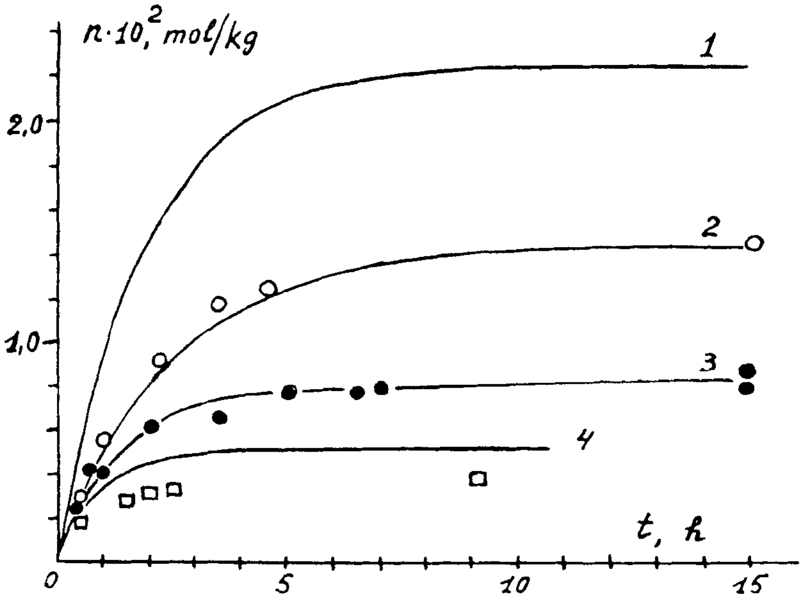


FIGURE 1 Polymer chain scission vs time plots ($T = 371$ K) for the evacuated PC-films containing 0.29 mol kg BP at ionol concentrations: 1 – 0 (calculated curve); 2 – 0,023; 3 – 0,32; 4 – 0.64 mol kg.

increases. This is caused by expenditure of BP in a new reaction, whose mechanism will be considered below. Here we should point out that according to the equation (2.8) the initial decomposition rate, determined by initial parts of curves (2–4), decreases by a factor of two at least comparing with the initial PC degradation rate in the absence of ionol (Fig. 1, curve 1). Some deviation of calculated curve (4) from experimental points is connected with the fact that contribution of direct reaction of ionol with primary benzoyloxyls, neglected in calculations, becomes significant in PC if c_i is very high:

$$r_s^\bullet + IH_s \xrightarrow{k_{6s}} rH + I_s^\bullet; \quad I_s^\bullet + r_s^\bullet \rightarrow Ir.$$

Contribution of this direct reaction to the decomposition rate decrease is more significant for CTA samples, however even in this polymer the decomposition does not stop completely even at high $c_i = 0.32$ mol/kg concentration.

Ionol interaction with benzoyloxyls completely changes in v-zones of chain-sponge micelles, where BP decomposition induced by macroradicals is inhibited already at low c_i values. This is proved by a decrease of the effective constant k_i of BP decay rate as well as by the termination of arylated macromolecule synthesis.

Total process of BP decomposition in presence of ionol is regulated by the kinetic exponential law:

$$c = c_0 \exp(-k_i t), \tag{2.9}$$

in which constant k_i depends on initial BP (c_0) and ionol (c_{i0}) concentrations, characterizing the reaction. Figure 2 shows as an example several curves $c(t)$ obtained for CTA at 371 K and presented in semilogarithmic coordinates.

In accordance with the data of the Figure 2 the lowest k_i value is obtained in samples, heated in air (curve 1), where it equals to the constant k_0 of spontaneous BP decomposition. Constant k_i change is complex in the same range of c_0 and c_{i0}, but in absence of oxygen: at low $c_0 = 0.02$ mol/kg it increases linearly depending on c_i values (Fig. 3, curve 1), and at high c_0 it decreases abruptly reaching its minimum at $c_i = 0.05$ mol/kg, and then increases back again in the range of high c_i values (Fig. 3, curves 2, 3, 5).

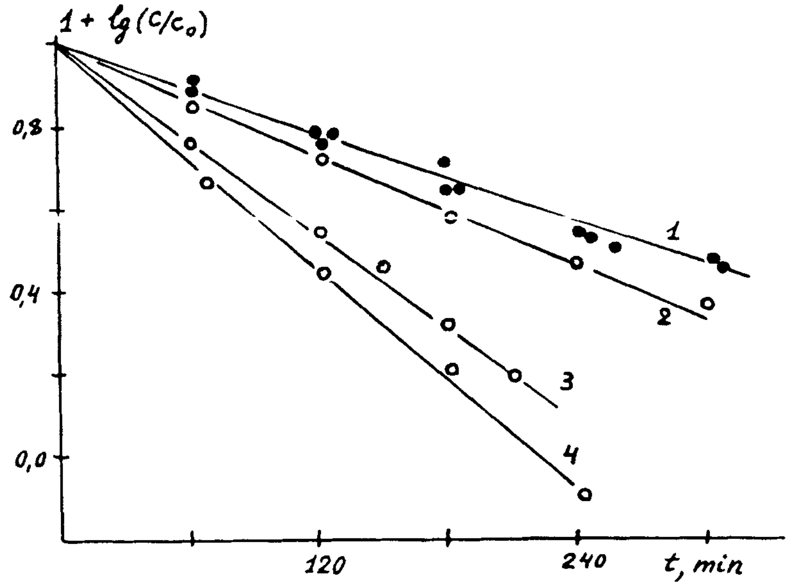


FIGURE 2 BP-decomposition plots ($T = 371$ K) for the aerated (1) and evacuated (2 – 4) CTA-films at BP and ionol concentrations: 1 – $C_0 = 0.02$; 0.25; 0.63 and $C_i = 0.08$; 0.10; 0.11 mol kg, respectively; 2 – $C_0 = 0.02$; $C_i = 0.027$; 3 – $C_0 = 0.66$; $C_i = 0.042$; 4 – $C_0 = 0.02$; $C_i = 0.27$ mol kg.

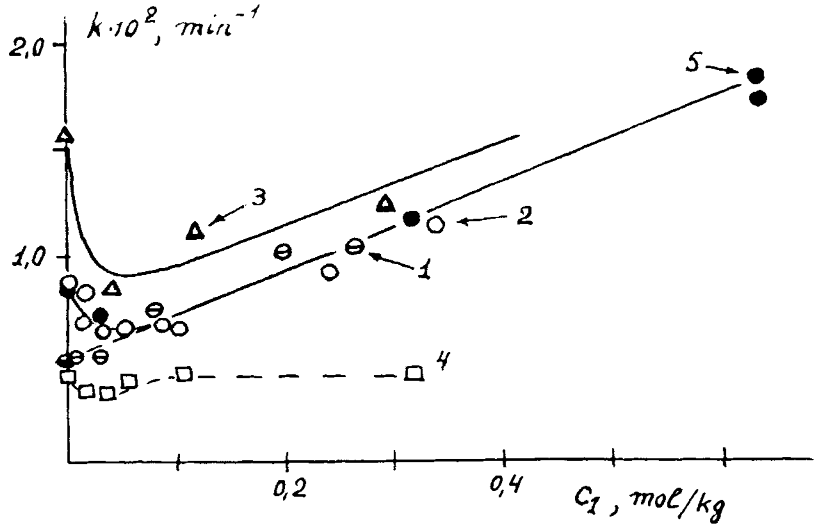


FIGURE 3 Effective rate constant of BP decay vs ionol concentration plots ($T = 371$ K) for evacuated (1 – 3,5) and aerated (4) CTA-films (1 – 4) and PC-films (5) at C_0 values: 1 – 0.02; 2,4,5 – 0.27; 3 – 0.64 mol kg.

The occurrence of catalytic branch of BP decomposition in presence of ionol (Fig. 3) takes place when the chain decomposition rate induced by macroradicals is negligibly low. This is proved first by the curve 1 in the Figure 3, for which contribution of chain arylation is negligibly small even in absence of ionol because of significantly low c_0 value. Second, this is proved by the complete stop of arylation product accumulation, recorded by UV-spectra of CTA after complete BP decay (in $c_0 = 0.15 \div 0.7$ mol/kg range) and full extraction of decomposition products by methanol (Fig. 4). Curve 1, shown in the Figure 4, displays the process of attachment of BP fragments of CTA in absence of ionol. Curve 2 describes the same process in presence of IH ($c_{i0} = 0.22$ mol/kg). Curve 3 was composed according to optical density at UV wave length of 333 nm, which is out of the absorption spectrum of attached BP fragments. Curves 1 and 2 were composed according to optical density at the maximum of absorption spectrum of these fragments ($\lambda = 284$ nm). Curves 2 and 3 completely transform

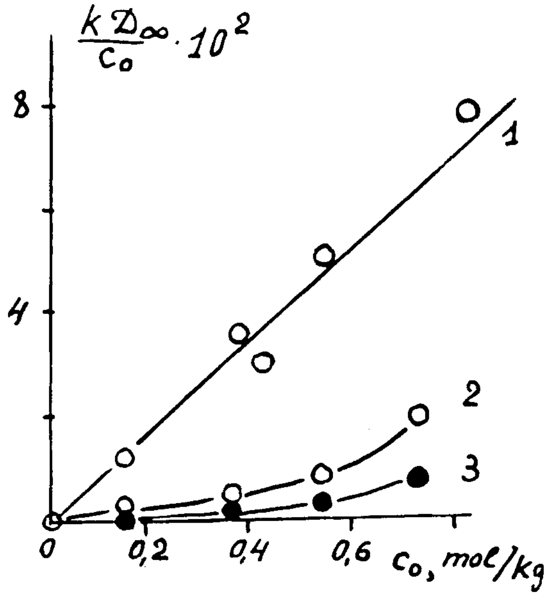


FIGURE 4 Normalized optical density D_∞ of arylated CTA vs BP concentration plots for the polymer films which possesed initialy no ionol (1) and 0,22 mol/kg ionol (2, 3). Analysis of polymer solutions prepared in methylene chloride after the BP decomposition ($T = 371$ K) and extraction of low molecular weight compounds with methanol, analytical UV wave length – 284 (1, 2) and 333 nm (3).

into each other. This fact testifies that in this case the insufficient amounts of products, which absorb UV-light, is connected with the attachment of small amounts of ionol groups, and not BP fragments.

With regard to the occurrence of catalytic branches on curves in the Figure 3 we should outline that they characterize BP decomposition process induced by free ionol radicals, and not by ionol molecules. This is the reason that catalytic effect completely disappears in presence of air dissolved in films: BP decomposition rate in aerated films equals to spontaneous decomposition rate (Fig. 2, curve 1 and Fig. 3, curve 4).

Free phenoxyl could not serve as radical-carrier of new BP decomposition chains, because it provides linear law of macromolecule arylation chain termination. Furthermore, it is the common knowledge that phenoxyl of sterically-hindered phenols (including ionol) are not oxidized by oxygen and dibenzoyl peroxide at 371 K [19–21].

Ionol σ-complex is a new inductor of the chain BP decomposition. It is formed as a result of benzoyloxyl attachment to ionol phenolic circle. We may neglect formation of σ-complexes in ionol reaction with alkyl macroradicals taking into account the data of the Figure 4, which indicates an insufficient rate of such attachment even though at high $c_i = 0.22$ mol/kg.

Ionol and other sterically-hindered phenols do not attach alkyl radicals [16] in liquid solutions, and their σ-complexes with benzoyloxyls are very unstable and dissociate to initial reagents IH and $r^\bullet$ rapidly, inducing no influence on BP decomposition rate [9, 19]. Contrary to liquids, as it was mentioned above, additive particles are subjected to the influence of overlapping surface forces of closely coupled walls of v-micropores in v-zones of chain-sponge micelles. This promotes the mutual contacts of two adjacent particles and complicates their dissociation. Let's remind that similar structural effect of the chain sponge is responsible for BP decomposition rate decrease in narrow micropores of v-zones. The reason of ionol σ-complex stability increase and the increase of probability of their interactions with BP molecules migrating in v-zones is similar.

The above mentioned ionol transformations may be presented by the scheme:

$$r^\bullet + IH_v \xrightarrow{k_6} rIH^\bullet, \quad rIH^\bullet + BP_v \longrightarrow rI + rH + r^\bullet.$$

The termination of new reaction chains is performed by benzoyloxyl passing from v-zones to s-zones (in acts possessing constant k_4) as well as with participation of formed phenoxyls:

$$r^{\bullet} + IH_v \xrightarrow{k_7} rH + I^{\bullet}, \quad r^{\bullet} + I^{\bullet} \longrightarrow rI.$$

The analysis of the above reactions in the composition of previously considered scheme of BP decomposition makes clear that it is not sufficient for explaining the increase of k_i constant in the range of high c_{i0} values, because both the rate of chain reaction with k_6 constant and the rate of reaction chain termination with k_7 constant depend similarly on c_i.

The existence of the linear dependence $k_i(c_i)$, indicated by the data of the Figure 3, reflects the existence of the additional pathway of radical injection from s-zones to v-zones: with participation of ionol

$$r_s^{\bullet} + IH_s \xrightarrow{k_5} rIH_s^{\bullet}, \quad rIH_s^{\bullet} + BP_s \longrightarrow rI + rH + r^{\bullet}.$$

Now taking into account both types of s, v-transfer of free valence (with participation of PhH compounds and ionol) and using the equation of initiation and termination of the reaction v-chain rates, we obtain the following expression for v-benzoyloxyl concentration:

$$[r^{\bullet}] = \frac{(k_1[PhH_s] + k_5 c_{is})[r_s^{\bullet}]}{(k_4 + 2k_7 c_{iv})}. \tag{2.10}$$

Concentration $r^{\bullet}$ significantly decreases at sufficiently high ionol concentration (c_{i0}, c_{is}, c_{iv}). The equation (2.10) transforms simultaneously as follows:

$$[r^{\bullet}] = \frac{k_5 c_{is}[r_s^{\bullet}]}{2k_7 c_{iv}}.$$

This form of the equation states the independence on ionol concentration because at equilibrium the process of interzone exchange of ionol

$$c_{is} = K_{ei} c_{iv} \approx \alpha^{-1} K_{ei} c_{i0}.$$

Here K_{ei} is the constant of corresponding equilibrium. Hence, the equation (2.10) is reduced to:

$$[\mathrm{r}^\bullet] = \mathrm{const} \times k_0 c.$$

In line with broaden heterophase scheme, the rate of BP decomposition in v-zones is composed of two terms:

$$-\frac{dc_v}{dt} = k_3[\mathrm{R}^\bullet]c_v + k_6[\mathrm{r}^\bullet]c_{iv} = k_2[\mathrm{r}^\bullet][\mathrm{RH}] + k_6[\mathrm{r}^\bullet]c_{iv}. \quad (2.11)$$

The first term makes significant contribution only at very high BP concentration c_0, because ionol provides significant decrease of $\mathrm{r}^\bullet$ concentration. Taking into consideration that, total rate of BP decomposition in s- and v-zones may be approximated by the sum:

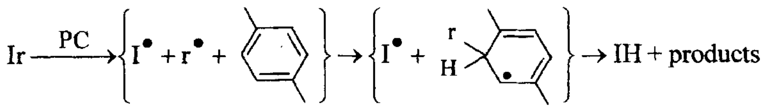
$$-\frac{dc}{dt} = k_0 c + k_i' c_{i0} c = (k_0 + k_i' c_{i0})c = k_i c, \quad (2.12)$$

which characterizes the catalytic branch of BP decomposition, stipulated by ionol effect.

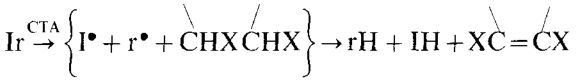
Here we should remind an important fact that initial ionol concentration c_{i0} participates in the expression of the effective constant k_i as the invariable coefficient at every c_{i0} and c_0 ratio (Fig. 2, curves 2–4). Practical invariability of c_{i0} value is confirmed by IR-spectra of CTA and PC films, which display just an insufficient decrease of IR absorption intensity of phenolic OH-groups during the reaction [17, 18]. Such invariability (which is also characteristic for ionol reacting with BP in polystyrene matrix [9]) confirms that polymers possess a mechanism of ionol regeneration from Ir, the main product of its transformation.

Ir compound is unstable in liquid solutions and dissociates rapidly to benzoyloxyls and phenoxyls [19]. Apparently, its molecules also dissociate in the polymer-chain sponge matrix on walls of fluctuationally excited v-micropores, which obtained sizes of big s-micropores for a short time. Then, the radicals formed dehydrate the polymer by one or another mechanism, which depends on macromolecule structure.

The appropriate process for PC may be presented as follows:

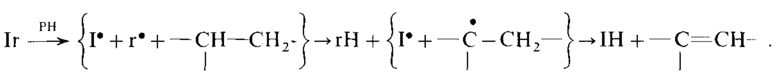


This process for CTA is:



$$\mathrm{Ir}\xrightarrow{\mathrm{CTA}}\left\{\mathrm{I}^\bullet+\mathrm{r}^\bullet+\overset{\diagdown}{\mathrm{C}}\mathrm{HX}\overset{\diagup}{\mathrm{C}}\mathrm{HX}\right\}\to\mathrm{rH}+\mathrm{IH}+\mathrm{X}\overset{\diagdown}{\mathrm{C}}=\overset{\diagup}{\mathrm{C}}\mathrm{X}$$

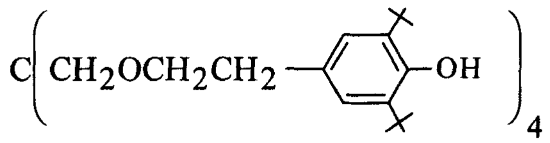
here $X = OCOCH_3$;
The process we obtain for carbo-chain polymer matrix is:



$$\mathrm{Ir}\xrightarrow{\mathrm{PH}}\left\{\mathrm{I}^\bullet+\mathrm{r}^\bullet+-\underset{|}{\mathrm{C}}\mathrm{H}-\mathrm{CH}_2-\right\}\to\mathrm{rH}+\left\{\mathrm{I}^\bullet+-\underset{|}{\overset{\bullet}{\mathrm{C}}}-\mathrm{CH}_2-\right\}\to\mathrm{IH}+-\underset{|}{\mathrm{C}}=\mathrm{CH}-\ .$$

The active particles, dehydrating a polymer, must not leave their reaction n and the process must be completed during the time of excited micropore state existence.

To finish this part let us point out that other sterically-hindered phenols studied, tetraphenol, especially:



as well as 2, 4, 6-tri-tert-butylphenol (at essentially high concentrations) affects BP decomposition. This effect is qualitatively similar to the ionol one (Fig. 5, curves 2–4). However their catalytic effectiveness is much lower (tert-butylphenol does not accelerate BP decomposition at all at low c_0 value, Fig. 5, curve 1), probably, because of lower probability of their participation in acts of interzone s, v-transfer of free valence. This shows that light radicals possessing free valence on oxygen attach aromatic circles of phenols in chain-micellar matrix, and σ-complexes formed in this process participate in further transformations. As a result,

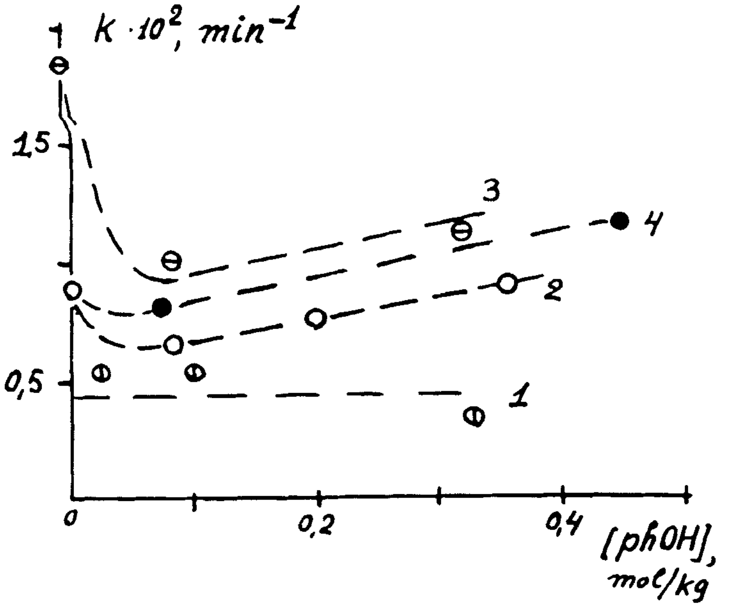


FIGURE 5 Dependence of the effective BP-decay rate constant ($T = 371$ K) on the concentration of tri-t-butyl-phenol (1 – 3) and phenolic groups of Irganox-1010 (4) for evacuated CTA-films at C_0 values: 1 – 0,023; 2,4 – 0,2; 3 – 0,76 mil/kg.

phenolic antioxidants become transport means for free valence between *s*- and *v*-zones as well as intrazone carriers of reaction *v*-chains of BP decomposition.

3. FEATURES OF THE MODEL REACTION IN PRESENCE OF BISPHENOL POSSESSING COMPLIMENTARY PHENOL GROUPS ON ITS MOLECULES

Acceleration of anaerobic BP decomposition in glassy-like CTA seems much more effective in presence of 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol)-bisphenol 2246-HIIH [22]. Plots of BP decay curves, obtained in the presence of that bisphenol and presented in Figure 6 in semilogarithmic coordinates, testify that in this case the process is regulated by the exponential law. However, contary to the reaction with ionol, the effective constant k_m of BP decay with bisphenol increases during the catalytic stage as square concentration of

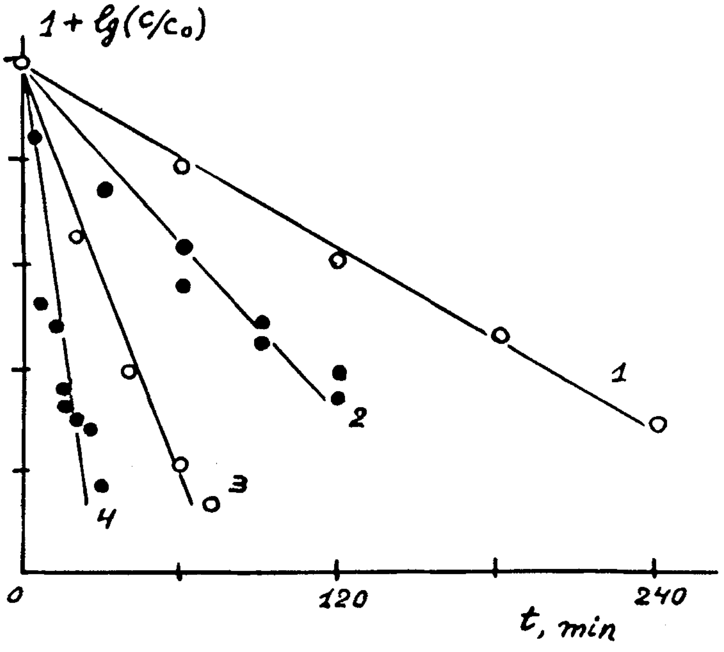


FIGURE 6 BP-decay plots for the evacuated CTA-films (T= 371 K, C_0 = 0,37 mol/kg), obtained at concentration of phenolic groups of methylene-2,2'-bis (4-methyl-6-t-butyl-phenol): 1 – 0,06; 2 – 0,18; 3 – 0,40; 4 – 0,64 mol/kg.

phenolic groups $c_m(c_m = 2[\mathrm{HIIH}])$. Corresponding plot of the dependence $k_m(c_m^2)$ is shown in the Figure 7.

As it is observed, the plot in Figure 7 includes a very short part of k_m decrease in the range of low c_m values and a significantly long catalytic section. Short part existence is connected with inhibition of CTA chain arylation. This was discussed in the previous part. In this part we will consider the mechanism of catalysis by bisphenol, whose effectiveness is significantly higher than that ionol. It reaches values of $((k - k_0)/k_0) = 16 \div 17$ at maximal studied concentration of c_m.

However we can conclude that the existence of a third order reaction for the additive reagents in chain component at its high effectiveness indicates a significantly high mobility of additives in chain-sponge micelles of a glassy-like polymer, even if we do not

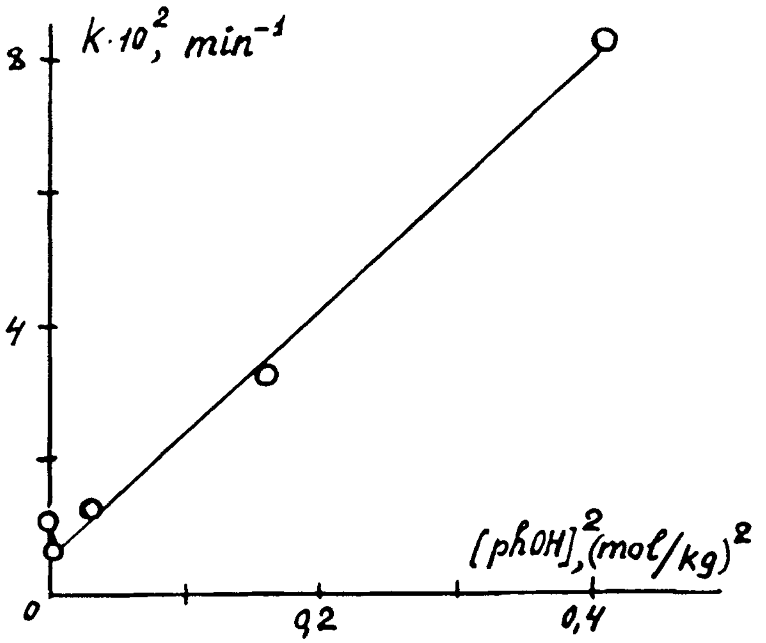
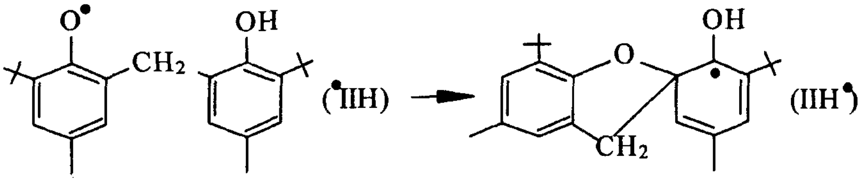


FIGURE 7 Dependence of the effective BP-decay rate constant ($T = 371$ K, $C_0 = 0.37$ mol/kg) on the concentration of phenolic groups of bisphenol 2246.

consider the process mechanism, provided we take into account:

1. The empyric exponential law of BP decomposition $c = c_0 \exp(-k_m t)$;
2. Its effective rate constant $k_m = k_0 + k_c c_m^2$; and
3. The particular expression for the reaction rate $-(dc/dt) = k_0 c + k_c c_m^2 c$.

Turning to the particular mechanism of bisphenol 2246 action it is natural to suppose that bisphenol molecules, representing two interconnected ionol structures, should participate in the same acts of s,v-transfer of radicals, and induced BP decomposition and regeneration as ionol does. At the same time the significant increase of the catalytic effect and change of the chain component order mean some significant difference, which may be connected with specific mutual disposition of phenolic groups in bisphenol molecules. This disposition is favorable for isomerization of phenoxyl, formed from bisphenol, to an intramolecular σ-complex, which, in its turn, is easily oxidized by dibenzoyl peroxide:



$$\text{IIH}^{\bullet} + \text{BP} \rightarrow \text{II} + \text{rH} + \text{r}^{\bullet}.$$

Taking into account this property of bisphenol 2246 its specific effect on the model reaction may be explained by the fact that its phenoxyls and intramolecular σ-complexes do not participate in reaction *v*-chain terminations of BP decomposition, but act as carriers of these chains. Consequently, *v*-benzoyloxyl migrating to *s*-zones, possessing constant k_4, becomes the only pathway for *v*-chain termination.

It should be mentioned that rapid phenoxyl isomerization to a σ-complex •IIH→IIH•, apparently, is also responsible for the fact that in liquid solutions bisphenol 2246 and other bisphenols with similar mutual complimentary phenolic groups display a stoichiometric inhibition coefficient of 2 as ionol, instead of expected 4, based on the additivity condition of phenolic group effect [23].

Taking into account the above mentioned facts we may write the scheme of initiation, propagation and termination of reaction *v*-chains as follows:

$$\text{r}_s^{\bullet} + \text{HIIH}_s \xrightarrow{k_8} (\text{r-IIH}_2^{\bullet})_s \xrightarrow{\text{BP}_s} \text{r}^{\bullet} + \text{products};$$

$$\text{r}_s^{\bullet} + \text{HIIH}_s \xrightarrow{k'_8} \text{rH} + {}^{\bullet}\text{IIH}_s; \quad {}^{\bullet}\text{IIH} \rightarrow \text{IIH}^{\bullet} \xrightarrow{\text{BP}_s} \text{r}^{\bullet} + \text{products}$$

$$\text{r}^{\bullet} + \text{HIIH} \rightarrow \text{rIIH}_2^{\bullet} \xrightarrow{\text{BP}_v} \text{r}^{\bullet} + \text{products};$$

$$\text{r}^{\bullet} + \text{HIIH} \rightarrow \text{rH} + {}^{\bullet}\text{IIH}; \quad {}^{\bullet}\text{IIH} + \text{IIH}^{\bullet} \xrightarrow{\text{BP}_v} \text{r}^{\bullet} + \text{products};$$

$$\text{r}^{\bullet} \xrightarrow{k_4} \text{r}_s^{\bullet} \quad \text{(termination)}.$$

This scheme leads to the following expression of v-benzoyloxyl concentration:

$$[\mathrm{r}^\bullet] = \frac{(k_8 + k_8')c_{ms}}{k_4}.$$

Substituting this expression into the Equation (2.11) and neglecting first term in (2.11), because bisphenol 2246 is stronger radical acceptor than ionol [23], we obtain:

$$-\frac{dc_v}{dt} = k_6[\mathrm{r}^\bullet]c_{mv} = \frac{k_6 c_{mv}(k_8 + k_8')c_{ms}}{k_4}.$$

Taking into account equilibrium conditions for bisphenol molecule ($c_{ms} = K_{em}c_{mv}$) and BP molecule (equation (2.1)) exchange between s- and v-zones we obtain the total rate of BP decay:

$$\frac{dc}{dt} = k_0 c + k_c c_m^2. \tag{2.13}$$

The Equation (2.13) is the theoretical proof of the empyric result reported in [22], and of the qualitative kinetic unequivalence between ionol and bisphenol 2246 in their catalytic actions, characterized by Equations (2.12) and (2.13), respectively.

4. HETEROPHASE MODEL OF THE CHAIN REACTION OF POLYPROPYLENE HYDROPEROXIDE ANAEROBIC DECOMPOSITION

The concept of the heterophase chain reaction is also fruitful for the analysis of processes related to ageing and stabilization of polymers. It allowed us to explain the important features of polyolefine autoxidation and decomposition of polymer hydroperoxides under conditions of high and low fluctuation dynamics of the polymer-chain sponge [4–6]. In this section we consider the mechanism of polypropylene hydroperoxide chain decomposition, proceeding in absence of oxygen dissolved in the polymer.

Polypropylene (PP) differs from glassy-like polymers by its amorphous phase, which already exists in high-elastic state at usual temperatures and consists of separate regions surrounded by crystallites. Solid phase usually forms about 60% of the mass in isotactic PP ($T_{\text{melt}} \approx 439$ K). Its separate crystallites form a continuous rigid carcass, imparting polymer properties of a solid. The oxidation and decomposition of additive reagents proceed in PP samples possessing such structure only in highly elastic regions [14, 15].

The rigid carcass of crystallites influences the structure of noncrystalline PP phase [24], however the specific features of chain-micellar sponge composition of amorphous regions must remain. It is probable that spatial s-micropores in PP will be formed as layers close to the surface of crystallites [24], but the main volume of sponge micelles should be composed by flexible chains as granules possessing more or less narrow v-micropores. If we suppose that chain-micellar sponge retains its microheterogeneous structure even in the case of polyolefines, we should expect existence of a specific unequivalence of radical formation rates in s- and v-zones in this case, too. It is shown in [4, 6, 25] that PP also possesses s-zones in which the hydroperoxide (HP, G) dissociates much faster than in v-zones. Primary reaction chain, initiated in s-zones, induces chain reaction in v-zones due to s, v-injection of radicals. In the case of rigid PP samples the heterophase chemical induction stops at the moment, when HP accumulated in s-zones is completely exhausted.

However HP decay does not stop at this stage because after completion of the heterogeneous-heterophase stage the decay continues by the heterogeneous-homophase which possesses lower rate. This latter stage is connected with v-zones displaying more or less high probability of fluctuational increase of v-micropore sizes up to s-micropores. This stage determines the frequency of HP dissociation reflecting the conditions of polymer sample preparation and residual mechanical tensions, acting in the sample.

Adequate s-scheme of HP transformation, formulated on the base of works [4–6, 25], is the following:

$$\mathrm{G}_s \xrightarrow{k_{0s}} (\mathrm{PO}^{\bullet}_s + \mathrm{HO}^{\bullet}_s) \xrightarrow{\mathrm{PH}_s} \delta \mathrm{P}^{\bullet}_s;$$

$$P^\bullet_s \xrightarrow{k_{1s}} R^\bullet_s \text{ (polymer chain decomposition + products);}$$

$$R^\bullet_s \xrightarrow{k_{2s}} R^\bullet_{1s} \text{ (terminal radical isomerization);}$$

$$R^\bullet_s + R^\bullet_{1s} \xrightarrow{k_{3s}} \text{products.}$$

Here PH symbol marks reaction CH-groups of tertiary and secondary carbon atoms of polymer chains; δ is the coefficient of radical yield in acts of HP dissociation; $P^\bullet_s$ marks the backbone and $R^\bullet_s$, $R^\bullet_{1s}$ mark the terminal macroradicals.

The acts of free valence transfer from *s*- to *v*-zones proceeds with low probability. The corresponding *tr*-scheme reflects the leading role of the most movable reaction end radicals $R^\bullet_s$ in this transfer:

$$R^\bullet_s \xrightarrow{k_m} R^\bullet_m; \quad R^\bullet_m \xrightarrow{k_{-m}} R^\bullet_s; \quad R^\bullet_m + \text{PH} \xrightarrow{k'_{tr}} P^\bullet.$$

These radicals are capable to enter the reaction with CH-bonds in *v*-zones, when exchange their places in the *s*-carcass structure and in micropore volume ($R^\bullet_m$) during their oscillations.

The chain process of HP decomposition yielding water proceeds in *v*-zones owing to this radical transfer. This process is described by the following *v*-scheme:

$$P^\bullet + G \xrightarrow{k1} \text{PH} + \text{POO}^\bullet; \quad \text{POO}^\bullet \longrightarrow {}^\bullet\text{POOH}$$

(β-isomerization of peroxyl to hydroperoxyalkyl);

$${}^\bullet\text{POOH} \longrightarrow \varepsilon + \text{HO}^\bullet$$

(hydroperoxyalkyl decomposition with epoxy compound formation);

$$\text{HO}^\bullet + \text{PH} \longrightarrow H_2O + P^\bullet; \quad 2P^\bullet \xrightarrow{k_2} \text{terminations.}$$

We may obtain an expression for concentration of radicals-translators of valence, applying the stationary radical concentration condition to these block-schemes:

$$[R^\bullet_s] = \frac{\delta k_{0s} g_s}{2k_{2s}}$$

(here g_s is HP concentration in *s*-zones).

We also obtain the expression for s, v-transfer rate:

$$V_{tr} = k'_{tr}[\mathrm{PH}][\mathrm{R}^{\bullet}_{m}] = \frac{k_{tr}k_{m}[\mathrm{R}^{\bullet}_{s}]}{k_{-m}+k_{tr}} = \frac{\delta k_{tr}k_{m}k_{0s}g_{s}}{2k_{2s}(k_{-m}+k_{tr})},$$

it equals the rate of the reaction v-chain death $V_{tr} = 2k_2[\mathrm{P}^{\bullet}]^2$; the concentration of radicals attacking hydroperoxide is:

$$[\mathrm{P}^{\bullet}] = \sqrt{\frac{V_{tr}}{2k_2}};$$

and the rate of chain HP decomposition in v-zones is:

$$-\frac{dg_v}{dt} = k_1[\mathrm{P}^{\bullet}]g_v = k'_e g_v \sqrt{g_s}.$$

Taking into account the current concentration of HP dissociating in s-zones, characterized by exponent equation:

$$g_s = g_{s0}\exp(-k_{0s}t),$$

and considering that the amount of HP in s-zones is small, compared with it in v-zones, and that HP concentration in v-zones is at least equal to that in the amorphous phae ($g_v \approx g$), we obtain a reduced final expression of the HP decomposition rate:

$$-\frac{dg}{dt} = k'_e\sqrt{g_{s0}}\,g\exp(-0.5k_{0s}t) = k_e g\exp(-0.5k_{0s}t). \qquad (4.0)$$

Integrating this expression, we obtain the equation of the HP anaerobic decomposition curve:

$$g = g_0\exp\left\{\left(\frac{k_e}{0.5k_{0s}}\right)[\exp(-0.5k_{0s}t) - 1]\right\}. \qquad (4.1)$$

Formula (4.1) is approximated to the first order equation for significantly small $t \to 0$:

$$g = g_0\exp(-k_e t). \qquad (4.2)$$

For large values, $t \to \infty$, it characterizes the process stop with an unexpensed HP residue:

$$g_\infty = g_0 \exp\left(\frac{-k_e}{0.5k_{0s}}\right).$$

The theoretical Equation (4.1) correlates well with the experiment, which is proved by the data of the Figure 8. Curves 1–4 shown in the Figure 8 were calculated for values $T = 383, 393, 403$ and 413 K, respectively. Corresponding values of the chain decomposition constants, which equal $k_e \times 10^4 \mathrm{s}^{-1} = 0.865$; 2.00; 4.20; 10.00, respectively,

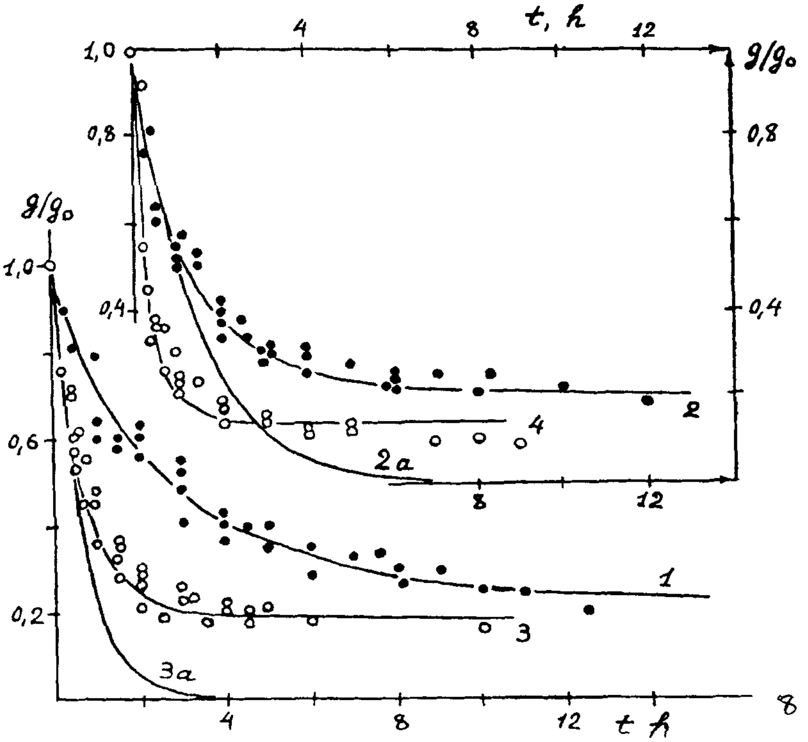


FIGURE 8 PP-hydroperoxide decay curves for evacuated samples at *T*-values: 1 – 383; 2,2*a* – 393; 3,3a – 403; 4 – 413 K. The first order kinetic equation at rate values $2.0.10^{-4}$ and $4.2.10^{-4}\mathrm{s}^{-1}$ were used for the calculation of 2a and 3a curves, respectively.

are generalized by the formula:

$$k_e = 3.9 \times 10^9 \exp\left(-\frac{E_e}{\mathrm{RT}}\right), \quad E_e = (100 \pm 5)\ \mathrm{kJ/mol}, \qquad (4.3)$$

and determined constants of spontaneous decomposition $k_{0s} \times 10^4 \mathrm{s}^{-1} = 1.\ 14;\ 2.48;\ 5.06;\ 10.00$ are generalized as follows:

$$k_{0s} = 6.5 \times 10^8 \exp\left(-\frac{E_{0s}}{\mathrm{RT}}\right), \quad E_{0s} = (93.6 \pm 5)\ \mathrm{kJ/mol}. \qquad (4.4)$$

Curves 2a and 3a, calculated according to the equation (4.2), are shown in the Figure 8 for comparison. It is clear that they deviate from experimental points while the theoretical curves 2 and 3 completely agree with the experimental data.

HP Decomposition Mechanism in the Presence of Dibenzoyl Peroxide

Dependence of the initial rate of HP decomposition (V_0) on dibenzoyl peroxide (BP) concentration was studied in works [15, p.104; 26]. It displayed the existence of a reaction with quadratic termination of the reaction chains:

$$V_0 = k_d g_0 + k_{\mathrm{ind}} g_0 \sqrt{k_b c_0}. \qquad (4.5)$$

Here g_0 and c_0 are initial concentrations of HP and BP, respectively (c_0 was found smaller than 0.05 mol/kg); k_d is the BP decomposition rate constant.

The experimentally determined value $k_d = (1.8 \div 1.9) \times 10^{-5}\mathrm{s}^{-1}$ (365 K) was the same in the absence of BP and in the extrapolation of the dependence (4.5) to $c_0 = 0$. It was supposed that oxidized polymer medium is homogeneous liquid, and the authors [15, 26] suggested the following description of the process rate proceedings in the absence of BP:

$$-\frac{dg}{dt} = k_d g + k'_e g^{1.5}. \qquad (4.6)$$

Here first term ($k_d g$) describes the spontaneous decomposition, and the second the chain degradation. Meanwhile the chain reaction constant $k_e = 1.9 \times 10^{-5} s^{-1}$, calculated at $T = 365$ K by the formula (4.3), equals k_e constant from the equation (4.5). Generally speaking, the suggested equation (4.6) is not in accord with the expression (4.1), which neglects the contribution of the spontaneous HP decomposition.

Let us consider the situation from the point of view of the heterophase mechanism. Note first that BP molecules are rapidly exchanged between zones of chain-sponge micelles:

$$\mathrm{BP} \underset{k_{-s}}{\overset{k_s}{\rightleftarrows}} \mathrm{BP}_s,$$

and dissociate in s-zones:

$$\mathrm{BP}_s \xrightarrow{k_{bs}} 2\mathrm{r}_s^{\bullet}.$$

The equilibrium condition of the interzone BP exchange is the following:

$$c_s = \frac{k_s}{k_{-s}} c_v = K_e c_v = \frac{K_e}{\beta} c. \tag{4.7}$$

Here c_s, c_v and c are BP concentrations calculated for s- and v-zones and for the amorphous PP phase, respectively; β is the amorphous phase part; K_e is the equilibrium constant.

Because of BP dissociation the benzoyloxyradicals occur in s-zones of the polymer-chain sponge. They carry free valence on oxygen atoms. It is the common knowledge that the reactivity of such radicals to hydrogen of OOH—groups is hundred- and thousand-times higher than to CH—groups [27]. That is why the reaction of benzoyloxyl acceptance by hydroperoxide should predominate in s-zones at initial stages of the process:

$$\mathrm{r}_s^{\bullet} + \mathrm{G}_s \longrightarrow \mathrm{rH} + \mathrm{POO}_s^{\bullet}; \quad \mathrm{POO}_s^{\bullet} \rightarrow {}^{\bullet}\mathrm{POOH}_s \rightarrow \varepsilon + \mathrm{HO}_s^{\bullet};$$

$$\mathrm{HO}_s^{\bullet} + \mathrm{PH}_s \rightarrow \mathrm{H_2O} + \mathrm{P}_s^{\bullet}.$$

Taking this into account in the *s*-scheme of HP decomposition considered before, it is easy to obtain an expression for concentration of radicals-predominants in the *s*, *v*-transfer of valence:

$$[\mathrm{R}_s^\bullet] = \frac{\delta k_{0s} g_s + 2k_{bs} c_s}{2k_{2s}},$$

and an expression for *s*, *v*-transfer rate:

$$V_{tr} = \frac{k_{tr} k_m [\mathrm{R}_s^\bullet]}{k_{-m} + k_{tr}} = \frac{k_{tr} k_m (\delta k_{0s} g_s + 2k_{bs} c_s)}{2k_{2s}(k_{-m} + k_{tr})}.$$

Now we obtain the concentration of radicals-inductors of HP decomposition based on the *v*-scheme considered before, and applying the equality condition of the reaction *v*-chain initiation and termination $V_{tr} = 2k_2[\mathrm{P}^\bullet]^2$:

$$[\mathrm{P}^\bullet] = \sqrt{\frac{V_{tr}}{2k_2}}.$$

We also obtain the expression of the chain reaction rate:

$$-\frac{dg}{dt} = k_1 g \sqrt{\frac{k_{tr} k_m}{4k_2 k_{2s}(k_{-m} + k_{tr})}} \sqrt{\delta k_{os} g_s + 2k_{bs} c_s}. \qquad (4.8)$$

Let us mark the number of BP moles in *s*-zones as $p_s = m_s c_s$, when m_s is the mass of *s*-zones, for the purpose of transforming the specific BP decomposition rate

$$-\frac{dc_s}{dt} = 2k_{bs} c_s \qquad (4.9)$$

to the empyric expression (dc/dt). By taking into account that the decrease of BP amount p (in moles) in the sample equals to the decrease of moles in *s*-zones (oxygen completely inhibits BP chain decomposition in polypropylene [28]) we obtain

$$-\frac{dc}{dt} = -m^{-1}\frac{dp}{dt} = -m^{-1}\frac{dp_s}{dt} = -\left(\frac{m_s}{m}\right)\frac{dc_s}{dt}.$$

Substituting the required expressions (4.9) and (4.7) to this equation, we obtain

$$-\frac{dc}{dt} = \frac{2k_{bs}m_sK_ec}{\beta m} = k_bc. \tag{4.10}$$

The effective rate constant of BP decomposition $k_b = (2k_{bs}m_sK_e)/(\beta m)$, which participate in the equation (4.10), equals $1.2 \times 10^{-4}\text{s}^{-1}$ as it follows from the well-known formula [28]

$$k_b = 8.4 \times 10^{13} \times \exp(-124{,}000/\text{RT})\ \text{s}^{-1}.$$

This value goes together with the fact that parameter $2k_{bs} = (k_b\beta m)/(m_sK_e)$ is greater than k_b, because $(m/m_s) \gg 1$ and $K_e < 1$. Consequently, the rate of radical initiation in the equation (4.8) by means of BP dissociation is significantly higher than that caused by HP dissociation, for which $k_{0s} = 2.6 \times 10^{-5}\text{s}^{-1}$ at $T = 365$ K as it follows from the formula (4.4). To express this differently, the Equation (4.8) assumes to the following form in a significant range of initial BP concentrations

$$-\left(\frac{dg}{dt}\right)_0 = k_{\text{ind}}\,g_0\sqrt{k_bc_0}.$$

Only in the range of very low c_0 values it extrapolates to the dependence (4.0), which characterizes HP chain decomposition with quadratic termination of the reaction v-chains.

The heterophase scheme of the HP reaction stimulated by dibenzoyl peroxide explains the kinetic data of works [15, 26]. Moreover, it explains the fact of water formation in the chain process, which was not considered by the homogeneous scheme [15, 26].

5. THE MECHANISM OF THE IONOL EFFECT ON THE RATE OF POLYPROPYLENE HYDROPEROXIDE ANAEROBIC DECOMPOSITION

The interesting results relative to this issue have been obtained in one of the early works [29]. The features of fast and slow kinetic stages in the general process of HP decomposition, discovered in [29], are very specific and require special discussions from the positions of heterogeneous mechanisms.

The work [29] applied low molecular syndiotactic PP($M_n = 13{,}500$), which was oxidized in chlorbenzene solution with an initiator at $T = 373$ K by bubbling oxygen through the solution for the purpose of accumulating hydroperoxide.

Carrying out the experiments on decomposition of HP obtained by the above mentioned technique, in absence of oxygen, the authors [29] discovered two kinetic stages of this process: a fast and a slow one. The second one possessing measurable rate contrary to PP samples oxidized in bulk, which possessed the second stage looking like a kinetic stop (Fig. 8).

In experiments [29] the samples possessed fast stage rate independent on HP and ionol concentrations. For example, at $T = 408$ K and contents of reagents HP/IH (mol/l): 0.0078/0.001; 0.034/0.001; 0.27/0.1; 0.005/0.012, its effective rate constant, $k_{e1} \times 10^4$ s^{-1}, was found: 19.8; 15.1; 19.8; 18.2, respectively; and at $T = 393$ K and HP/IH ratios: 0.034/0.000; 0.011/0.001; 0.0078/0.001; 0.27/ 0.01, $k_{e1} \times 10^4$ s^{-1} was obtained: 5.01; 6.3; 6.41; 6.13, respectively.

At the same time, the formal first order constant k_{e2}, used for characterizing the second stage rate, depended on initial, (g_0) concentration of hydroperoxide, simulating thus the concentration dependence of homogeneous chain reaction. But contrary to this dependence k_{e2} did not change in presence of low and moderate ionol concentrations (up to 0.05 mol/l). The second stage was losing its chain component just at very high ionol concentration, 0.124 mol/l, and k_{e2} constant reached its minimal value, which was also observed in absence of ionol at lowest g_0 concentration.

Discussing the first kinetic stage of HP decomposition the authors of [29] proposed a chain mechanism possessing a specific way of reaction chain spreading along polymer chains. They, however, failed to explain the reason for the discovered decrease of rapidly dissociating HP concentration part from 0.8 ÷ 0.9 to 0.25 at ionol injection of up to 0.124 mol/l concentration.

As to our point of view, the reaction studied in [29] is, indeed a chain mechanism, features of its realization reflecting specific state of the reaction matrix, chain-sponge micelle of the oxidized PP, to be more specific. Here we should mention that local hydroperoxide concentration, g_{s0}, which participates in the equation (4.0), is saturated during PP oxidation. In this case, in accordance with the data of the work [6], constant k_e reaches its maximum (11.0×10^{-4} s^{-1}) at $T = 403$ K. Recalculation of this value for 408 and 393 K (taking into account the effective activation energy $E_e = 100$ kJ/mol, formula (4.3)) gives values 16.0×10^{-4} s^{-1} and 5.15×10^{-5} s^{-1}, respectively. These values fall in the range of values, obtained for k_{e1} in [29]. This coincidence suggests that the investigations performed in [29] have reached the limit of s-zone content of hydroperoxide at the oxidation in solution. Consequently the rate constant k_e of the initial stage of the chain decomposition must not depend on the initial concentration g_0, calculated for the whole sample (Equations (4.0), (4.2)).

Turning to features of the fast stage in the presence of ionol, we should remind that ionol decreased significantly the concentration quota, in which the fast stage is performed, but it did not change k_{e1} value. Such combination may be explained in the ranges of the heterophase model by the fact that ionol decreased the amount of transported radicals by means of additional catalytic pathway of HP decay accumulated in s-zones, but it did not influence the mechanism of radical transfer from s-zones to v-zones.

This situation may be depicted as a s_i-scheme, introduced into the known s-scheme of reactions with ionol participation:

$$G_s \xrightarrow{k_{0s}} 0.5\delta(PO_s^\bullet + HO_s^\bullet); \quad HO_s^\bullet + PH_s \xrightarrow{k_{4s}} P_s^\bullet;$$

$$PO_s^\bullet + IH_s \xrightarrow{k_{5s}} I_s^\bullet; \quad I_s^\bullet + G_s \xrightarrow{k_{6s}} POO_s^\bullet + IH_s;$$

$$POO_s^\bullet + IH_s \xrightarrow{k_{-6s}} I_s^\bullet + G_s; \quad POO_s^\bullet + IH_s \xrightarrow{k_{7s}} POOIH_s^\bullet \rightarrow POH + {}^\bullet OI_s;$$

$$^{\bullet}\mathrm{OI}_s + \mathrm{G}_s \xrightarrow{k_{8s}} \mathrm{IOH} + \mathrm{POO}^{\bullet}_s; \quad \mathrm{POO}^{\bullet}_s \xrightarrow{k_{9s}} \mathrm{HO}^{\bullet}_s + \text{products};$$

$$\mathrm{P}^{\bullet}_s \xrightarrow{k_{1s}} \mathrm{R}^{\bullet}_s; \quad \mathrm{R}^{\bullet}_s \xrightarrow{k_{2s}} \mathrm{R}^{\bullet}_{1s}; \quad \mathrm{R}^{\bullet}_s + \mathrm{R}^{\bullet}_{1s} \xrightarrow{k_{3s}} \text{products}.$$

A number of characteristic features of reagents are displayed in the present scheme. It neglects the reaction of ionol with radicals, $\mathrm{R}^{\bullet}_s$ and $\mathrm{R}^{\bullet}_{1s}$, because all alkylphenols possess significantly low reactivity to polyolefine radicals [14, p.124]. (Even more active bisphenol 2246 does not influence the concentration of PP radicals, eliminating propylene during PP oxidation induction [30].)

The scheme considers phenoxyl reaction with HP [15,16] and both directions of POO$^{\bullet}$ radical attack on phenol molecule, leading to formation of phenoxyl and a σ-complex. Contrary to liquid solutions, as it has been mentioned already, the molecular forces provided by micropores make reversible dissociation of σ-complexes difficult in chain-sponge micelle micropores. This gives the opportunity to these complexes to participate in further transformations. In the present case alkoxyl radical IO$^{\bullet}$ with quinolidic structure results from σ-complex.

It was also taken into account that $\mathrm{HO}^{\bullet}_s$ radicals react faster with a polymer because of their high reactivity. Being adsorbed on *s*-micropore walls, they possess less favorable conditions for reaction with ionol contrary to $\mathrm{PO}^{\bullet}_s$ radicals.

Finally, the reaction of recombination $\mathrm{I}^{\bullet}_s + \mathrm{POO}^{\bullet}_s \longrightarrow \mathrm{POOI}$ is neglected in the *s*-scheme because of high local HP concentration in *s*-zones in samples [29]. The rate of this reaction is supposed to be negligibly low in comparison with the rate of $\mathrm{I}^{\bullet}_s + \mathrm{G}_s \xrightarrow{k_{6s}} \mathrm{POO}^{\bullet}_s + \mathrm{IH}_s$ reaction.

Applying the condition of steady state radical concentration to the s_i-scheme, it is easy to make sure that it does not change the expression of the radical concentration, obtained from the *s*-scheme of the process without ionol (see part 4). Concentration of *s*-phenoxyls relative to the s_i-scheme does not depend on HP_s concentration:

$$[\mathrm{I}^{\bullet}_s] = \frac{\delta k_{0s}}{2k_{6s}} + \frac{\delta k_{0s} k_{-6s}[\mathrm{IH}_s]}{2k_{6s}k_{9s}}, \tag{5.1}$$

concentration of s-peroxyls is $[\mathrm{POO}_s^\bullet] = (\delta k_{0s} g_s)/(2k_{9s})$, and the total rate of s-hydroperoxide decomposition is the sum of several terms:

$$-\frac{dg_s}{dt} = k_{0s}g_s + k_{6s}[\mathrm{I}_s^\bullet]g_s + k_{8s}[\mathrm{IO}_s^\bullet]g_s - k_{-6s}[\mathrm{POO}_s^\bullet][\mathrm{IH}_s]$$
$$= k_{0s}g_s + \frac{\delta k_{0s}g_s}{2} + \frac{\delta k_{0s}g_s k_{7s}[\mathrm{IH}_s]}{2k_{9s}}.$$

We may neglect the second term in this expression comparing it with the first one, which characterizes spontaneous decomposition G_s. Integrating this expression and taking into account the interzone equilibrium condition:

$$c_{is} = \frac{K_{ei}}{\beta} c_i$$

(There $c_{is} = [\mathrm{IH}_s]$ and $c_i = [\mathrm{IH}]$ are ionol concentrations in s-zones and noncrystalline PP phase, respectively; K_{ei} is equilibrium constant; β is amorphous phase amount), we finally obtain the equation of s-hydroperoxide expenditure in the presence of a chain component, catalyzed by ionol:

$$g_s = g_{s0}\exp\{-(k_{0s} + b_i c_i)t\}, \qquad (5.2)$$

here b_i is a complex constant.

Going to the mechanism of HP chain decomposition in v-zones, let us note that according to the work [29] ionol has not influenced k_{e1}value under all studied concentrations c_i, and has influenced k_{e2} value just at very high $c_i = 0.124$ mol/kg. Taking into consideration this feature the authors of the work [29] proposed that the reaction the chain of HP decomposition proceeds by means of the free valency transfer along the polymer chains, and any intermolecular acts of $\mathrm{P}^\bullet$ radical attack on HP with free peroxyl formation are excluded in this case. The present case displays the following image of the above considered v-scheme:

$$\mathrm{P}^\bullet + \mathrm{G} \longrightarrow {}^\bullet\mathrm{POOH} \longrightarrow \mathrm{H_2O} + \mathrm{P}^\bullet + \text{products};$$
$$2\mathrm{P}^\bullet \longrightarrow \text{termination}$$

(here $OH^\bullet$ radical formed reacts with the neighbour CH-group on the same macromolecule), which reflects a significantly porous packing of polymer chains in the structure of chain-sponge micelles.

Structural porosity, i.e. the increased degree of volumetric tension of a chain sponge of PP samples oxidized in solution, is stabilized by fixing of stretched chains on the crystallite carcass. As it is known, syndio- and isotatic PP are easily crystallized, and crystallizing polyolefines form no molecular solutions in hydrocarbons at $T < T_{\mathrm{melt}}$ [31]. But in any case they are able to disperse in liquids in certain amounts as colloid solution, although providing no molecular contacts of the polymer-liquid type [32].

The v-scheme of HP decomposition, modified in accordance with the results of the work [29], does not change acts of initiation and termination of v-chains, considered in the part 4. In this connection the Equation (5.2) may be used in the expression of the chain reaction rate, shown in the part 4:

$$-\frac{dg}{dt} = k_1\,[\mathrm{P}^\bullet]\,g = k'_e\, g\sqrt{g_s} = k_e g \exp\left[-0.5(k_{0s} + b_i c_i)t\right]. \quad (5.3)$$

In (5.3) preexponent k_e coefficient possesses the same structure as in the Equation (4.0), and exponential multiplicand contains additional constant $b_i c_i$, connected to HP chain decomposition inside s-zones.

Integration of (5.3) reduces it to the expression of the HP decay curve:

$$\ln\left(\frac{g}{g_0}\right) = \frac{2k_e}{k_{0s} + b_i c_i}\left\{\exp\left[-0.5(k_{0s} + b_i c_i)t\right] - 1\right\},$$

which transforms to the first order equation for the initial period of the reaction ($t \to 0$):

$$\ln\left(\frac{g}{g_0}\right) = -k_e t; \quad g = g_0 \exp(-k_e t),$$

which coincides with the Equation (4.2) and includes just one constant k_e, independent on ionol concentration.

The same initial formula transforms to the following expression at significant levels of HP decay ($t \to \infty$):

$$\ln\left(\frac{g_{\infty}}{g_0}\right) = \frac{2k_e}{k_{0s} + b_i c_i},$$

or

$$g_{\infty} = g_0 \exp\left[\frac{2k_e}{k_{0s} + b_i c_i}\right].$$

This characterized kinetic stop increases with increasing concentration c_i of ionol in samples and increasing catalytic effect of ionol on HP decomposition in *s*-zones.

Features of the Homophase HP Chain Decomposition

After the end of the fast stage of the reaction in samples of the work [29], the slow stage began instead of the kinetic stop. The rate of this stage did not change at low and moderate concentrations of ionol (up to 0.05 mol/kg). The existence of a relatively low but reliably measurable reaction rate and k_{e2} value for these samples differ from those oxidized in bulk, whose $g(t)$ curves are shown in Figure 8 and which second stage is characterized by extremely low rate of the process.

It should be noted that the rate of the first stage in samples from [29] was also higher (if calculated for equal temperatures) compared with PP oxidized in bulk. It is evident that higher chemical activity of suspension-oxidized polymer should be connected with the existence of incomplete packing of polymer chains in the chain-sponge micelle structure.

Porosity of the micellar material combined with highly elastic flexibility of polymer chains increases the level of *v*-zone ability (which accumulate general amount of hydroperoxide formed during oxidation) for the process of thermofluctuation excitation of *v*-micropores up to *s*-micropore sizes. This causes the increase of excitation act frequency and, consequently, the probability of HP-group dissociation inside intensively fluctuating micropores.

If such thermofluctuation provision exists, the second stage of hydro-peroxide decomposition occurs in the polymer. This stage may be characterized as the heterogeneous-homophase one. The role of it becomes predominant after heterophase s,v-transfer of radicals as a result of HP exhaustion inside s-zones.

The one or another probability of increased fluctuation of v-micropores does always exist in the chain-sponge zones, but it is particularly high for highly elastic or melt polymer state [5, 6]. In this stage the process of free radical initiation may be presented by the following scheme:

$$\mathrm{G}_v \underset{k_{-f}}{\overset{k_f}{\longleftrightarrow}} \mathrm{G}_f \xrightarrow{k_{0f}} (\mathrm{PO}^\bullet_f + \mathrm{HO}^\bullet_f) \rightarrow \delta_f \mathrm{P}^\bullet,$$

in which the heterogeneous acts of excitation, deactivation, dissociation of HP-groups, conjugated with acts of micropores' fluctuation, are marked by constants $k_f, k_{-f}, k_{0_f}, \delta_f$ is yield of radicals from micropore fluctuation.

Combining this heterogeneous scheme with the reaction v-scheme, considered above in the part 4, we obtain the equation of the chain heterogeneous-homophase reaction rate:

$$-\left(\frac{dg}{dt}\right)_c = k_1\,[\mathrm{P}^\bullet]\,g = k_1\sqrt{g^3}\,\sqrt{\frac{\delta k_{0f}k_f}{2k_2(k_{-f}+k_{0f})}}.$$

Taking into consideration that the occurrence of this reaction is connected with a significantly high contribution of fluctuationally-dissociative HP decomposition in v-zones, the total decomposition rate is reduced to

$$-\frac{dg}{dt} = k_d^f g + k_c^f\sqrt{g^3}. \tag{5.4}$$

Here k_d^f and k_c^f are complex rate constants of chain and nonchain v-reactions, respectively.

The true fulfilment of the Equation (5.4) was stated in the work [29] by formal first order rate constant dependence typical for this case on the initial HP concentration:

$$k_{e2} = k_d^f + k_c^f\sqrt{g}$$

Let us mention that the Equation (5.4) is similar in form to the Equation (4.6) of the homogeneous reaction. However, contrary to explanation given in [15, 26], it characterizes the slow stage of polymer hydroperoxide decomposition instead of the fast one.

According to the data [29], the component $k_c^f\sqrt{g}$ of the rate is inhibited by very high ionol concentration only, $c_i = 0.124$ mol/kg. This may be explained by extreme ionol passivity to alkyl polymer radicals $P^\bullet$ and low probability of its interactions with radicals $PO_f^\bullet$ and $HO_f^\bullet$, fixed on walls of thermofluctuationally excited micropore.

6. FEATURES OF THE IONOL EFFECT ON CHAIN PP HYDROPEROXIDE DECOMPOSITION IN THE PRESENCE OF OXYGEN

The presence of dissolved oxygen in oxidized PP samples with ionol fundamentally changes the situation, usual for anaerobic conditions. It puts to the first place the heterogeneous-homophase process. As it was shown in the previous part, this process is limited by low rate of heterogeneous initiation of radicals in the structural zones of chain-sponge micelles, where the main amount of PP hydroperoxide, formed during autoxidation, is accumulated. In this case the chain reaction of HP decomposition, initiated in absence of oxygen, is inhibited by ionol at its very high concentration, because reaction activity of alkyl macroradicals to ionol is negligibly low.

The situation changes in presence of oxygen. It transforms alkyl radicals to peroxyl radicals and sharply increases the rate of their interaction with ionol and simultaneously translates the process to the regime of catalytic HP decomposition.

The example of such change in the reaction catalytic regime is the experimental result of the work [21]. There the kinetics of HP_1 decomposition in films obtained from melt and then oxidized, and HP_2 decomposition in films obtained from colloid PP oxidized in chlorbenzene, were investigated [21]. Ionol injection into these samples induces occurrence of the oxidation induction period at heating in oxygen ($P_{O_2} = 1$atm.). The duration of induction periods are significantly different in dependence on the way of sample preparation as well as on hydroperoxide decomposition rates in the induction periods. The highest activity in this case is displayed by films made from a polymer, oxidized in solution. This should be attributed to increased fluctuation-dynamical properties of chain-sponge micelles (see part 5).

Figure 9 shows the curve (1) of HP_1 expenditure, obtained in [21] on samples possessing low fluctuation dynamics ($T = 403$ K, $g_0 =$ 0,150 mol/l, $c_{i0} = 0.013$ mol/l). It is compared with the curve (2), displaying phenoxyl expenditure, and curves (3) of oxygen absorption and (4, 5) of HP and polymer peroxyl accumulation, observed after the induction period end. The amount of oxygen absorbed during the induction period (350 min) does not exceed the sensitivity threshold of an apparatus, used in the investigation. On this stage kinetic curve of ionol expenditure (it is not shown in the Fig. 9) and curve of phenoxyl

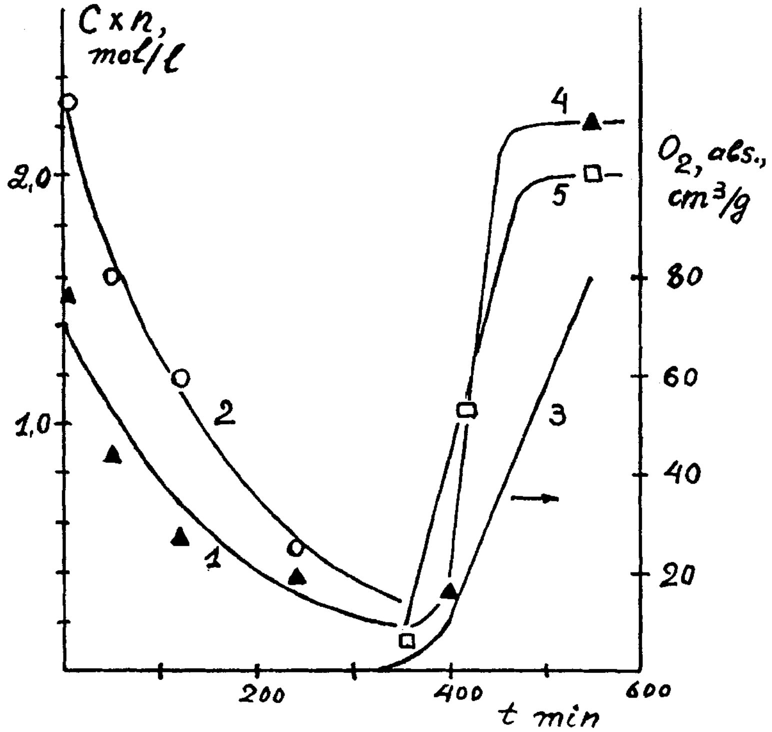


FIGURE 9 The oxidative kinetics at 403 K and $P_{O_2} = 1_{atm}$ both for induction period (1,2) and direct autoxidation of PP (3 – 5): 1-decay of hydroperoxide; 2-ionol phenoxyl disappearence; 3-oxygen absorption; 4,5-accumulation of hydroperoxide and free peroxy-radicals, respectively. Coefficient n values: 1,4 – 10; 2,5 – 1.10^6.

expenditure are described by exponential equations:

$$c_i = c_{i0}\exp(-k_i t), \quad [\mathrm{I}^\bullet] = [\mathrm{I}^\bullet]_0\exp(-k_i t),$$

which possess similar coefficient $k_i = 1 \times 10^{-4}\mathrm{s}^{-1}$. Such combination of kinetic curves means that the condition of steady state concentration is set for ionol phenoxyls at the very beginning of the process. It also means that phenoxyls do not participate in bimolecular termination and do not interact with the oxygen.

Concentration of POO$^\bullet$ radicals is below ESR-spectrometer sensitivity ($\leq 10^{-8}$ mol/l) during the induction period, but it reaches a measurable stationary value $\approx 2 \times 10^{-6}$ mol/l immediately after the end of induction period.

No empiric function has been suggested for $\mathrm{HP_1}$ expenditure curve [21], and yet it is possible to construct a calculated curve (curve 1 in the Fig. 9), taking into account common 10%-mistake of hydroperoxide concentration determination, which fits exponential law with the same constant k_i, displayed in the case of ionol and phenoxyl expenditure:

$$g = g_0\exp(-k_i t).$$

Here the initial concentration is set $g = 0.14$ mol/l. The curve corresponding to this equation, constructed in semilogarithmic coordinates $(1\,g(g/g_0), t)$, is shown in the Figure 10 (straight line 1) with the curves

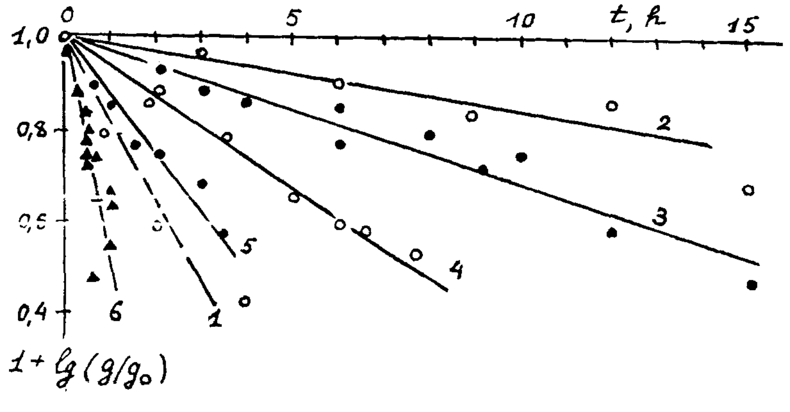


FIGURE 10 PP-hydroperoxide decay plots for PP-samples with ionol(1); tri-t-Bu-phenol (2 – 5) and with no antioxidant (6) in the presence (1 – 5) and in absence (6) of O_2 at *T*-values: 2 – 372; 3 – 383; 4 – 393; 1, 5, 6 – 403.

of HP expenditure, obtained in air in the presence of tri-tert-butylphenol. Our experiments were performed to clear up the picture of experimental value scattering, caused by their small number presented in the work [21].

Specimens (~ 1 mg) of fine-grained PP powder for our experiments were oxidized in air at $T = 413\,\mathrm{K}$ until HP accumulation reached concentration $g_0 = 0.14$ mol/kg. Tri-tert-butylphenol was injected into the oxidized powder from chloroform solution, the solvent was evaporated after 40 min exposure, and its residues were removed by evacuation. HP decomposition was studied by heating samples in air and applying spectrophotometric modification of iodometric analysis of HP [4–6, 25]. The experiments displayed overlapping HP expenditure curves at mass ratio of phenol/PP = 1/1 and 2/1.

The experimental points obtained are shown in the Figure 10 as series characterized by straight respective lines (2–5) for $T = 372$ K (2), 383 K (3), 393 K (4) and 403 K (5). Initial part of the HP decomposition curve at 403 K in absence of oxygen is also shown here for comparison (straight line 6). Comparing the dispersion of these points and points, obtained in [21], it may be concluded that the exponential functions could be applied in all cases. Effective rate constants, calculated according to curves (2–5), equal $k_i \times 10^5\ \mathrm{s}^{-1}$: 0.85; 2.0; 4.26; 8.5, and their generalized expressions is: $k_i = 6.0 \times 10^7 \exp(-E_i/\mathrm{RT})$, $E_i = 91.5$ kJ/mol.

It is characteristic that at similar $T = 403$ K HP decomposition with ionol possesses constant $k_i = 1 \times 10^{-4}\mathrm{s}^{-1}$, insignificantly different from that $0.85 \times 10^{-4}\mathrm{s}^{-1}$ obtained for the process with tri-tert-butylphenol. Both these constants are significantly lower than that ($4.2 \times 10^{-4}\mathrm{s}^{-1}$) characterizing HP decomposition in absence of oxygen and alkylphenol (Fig. 10, straight line 6). However the mentioned rate deceleration could not be connected with partial HP reduction chain PP oxidation or interactions of peroxyls with an inhibitor, because current concentrations g, c_i and [I•] are connected to each other by proportional dependence from the beginning till the end of the induction period. It is also important that the chain absorption of oxygen is completely suppressed in this stage (Fig. 9, curve 3). The simultaneous expenditure of HP and ionol, characterized by the same exponential coefficient $\exp(-k_i t)$, occurs at a ten-fold excess of g_0 over c_{i0}, i.e. when HP formation in the chain termination reaction could by no means compensate a four-fold deceleration of HP decomposition (Fig. 10, straight lines 1 and 6) in the entire volume.

The kinetic law of HP expenditure, applied to the results of the work [21], corresponds to the nonchain homogeneous reaction from a formal point of view. Meanwhile, its effective rate constant occurs in the sequence of anaerobic decomposition constants, known for the heterophase stage [6]. It is much higher than the rate constant of the nonchain component, observed for the heterogeneous-homophase stage. The latter equals, at least, $4 \times 10^{-5}\ s^{-1}$ at 408 K and $1.5 \times 10^{-5}\ s^{-1}$ at 393 K even for fluctuationally active HP_2 samples, whereas HP_1 films possess no measurable value of it at 403 K at all (parts 4 and 5).

The important increase of HP decay rate observed in the presence of oxygen, relative to the rate of the second (homophase) stage of the anaerobic reaction, is connected with alkyl macroradical oxidation to peroxyls. This process does not affect the rate of radical initiation by the mechanism of thermofluctuation excitation of micropores and induces sharp acceleration of polymer radical reactions with alkylphenols and leads to appearance of a new chain reaction of HP decomposition. Let us mention that the introduction of such new reaction was required the characteristics of anaerobic HP decomposition in presence of ionol and was fixed by the s_i-scheme in the part 5. In accordance with the s_i-scheme a new chain reaction of HP decomposition is induced by alkyloxyls formed from ionol, which possess a six-term carbon cyclic structure.

The features of HP decomposition under oxidative conditions, considered in the present part, also require the calculation of the new chain reaction of HP decomposition. This conclusion is supported by the independent fact [29] that oxygen injection significantly accelerates the process in HP_2 samples. For example, according to [29] expenditure of HP_2 and ionol phenoxyls in oxygen at $T = 393$ K ($g_0 = 0.156$ mol/l; $c_{i0} = 0.17$ mol/l) finishes in 20 min, and not in 350 min as it was in the case of HP_1, the half period of transformation being 5–10 min instead of 116 min despite a lower temperature of HP_2 decomposition. The effective rate constant is $\approx 23 \times 10^{-4}\ s^{-1}$ under these conditions, which significantly exceeds the constant of initial stage of the chain anaerobic reaction in the same samples (part 5).

Thus, the phenomenological action of oxygen changes two macroscopic kinetic stages of anaerobic process in the chain mechanism by means of a significant but different acceleration of hydroperoxide degradation for HP_1 and HP_2 catalyzed by ionol.

The initiation of v-chains reaction under the oxidative conditions is performed by the homophase pathway, favored by thermofluctuation excitation of v-micropores, in which hydroperoxide is accumulated. In this case ionol behaves as a good inhibitor of PP autoxidation, intercepting all reaction chains, but it simultaneously participates in HP decomposition reaction chains.

It should be mentioned also that the considered regularities of HP decomposition with oxygen as well as without it (see part 5) exclude any significant alkylphenol molecular reaction with hydroperoxide (and, consequently, of the probability of incresing the degenerated branchings in presence of an inhibitor). Moreover, the preservation of ionol catalytic function during the whole time of the induction period confirms the existence of a definite mechanism of its regenerations.

Taking into account all above mentioned facts, we may write down the following v_i-scheme of transformations in v-zones of polypropylene chain- sponge micelles, which start with the thermofluctuation excitation of v- micropores:

$$G_v \underset{k_{-f}}{\overset{k_f}{\longleftrightarrow}} G_f \xrightarrow{k_{0f}} \delta_f P^\bullet; \quad P^\bullet + O_2 \longrightarrow POO^\bullet;$$

$$POO^\bullet + IH \xrightarrow{k_1} POOIH^\bullet \longrightarrow POH + IO^\bullet;$$

$$IO^\bullet + G \xrightarrow{k_2} IOH + POO^\bullet;$$

$$POO^\bullet + IH \xrightarrow{k_3} G + I^\bullet; \quad POO^\bullet + I^\bullet \xrightarrow{k_4} POOI.$$

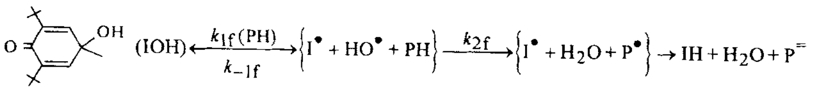
Here propagation of the HP decomposition reaction chains proceeds in the same way as in previously considered s_i-scheme through stages of the intermediate formation of phenol σ-complex with peroxyl and formation of quinoid alcoxyl (possessing constants k_1 and k_2, respectively). However, contrary to the s_i-scheme, the v_i-scheme displays chain termination performed on ionol. Its rate (possessing constant k_3)

is proportional to the rate of HP decomposition chain propagation, which is defined by acts with the constant k_1. The existence of this proportion is responsible for the ionol providing catalytic development of chain HP decomposition, abruptly decreasing peroxyl concentration and reducing the rate of chain PP autoxidation to a negligibly low value. Hence, oxidisation

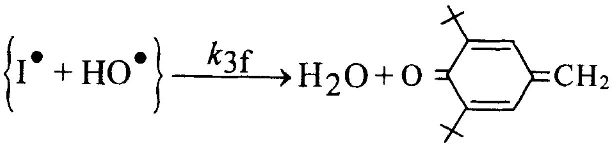
$$POO^\bullet + PH \rightarrow G + P^\bullet; \quad P^\bullet + O_2 \rightarrow POO^\bullet$$

chain reaction is neglected.

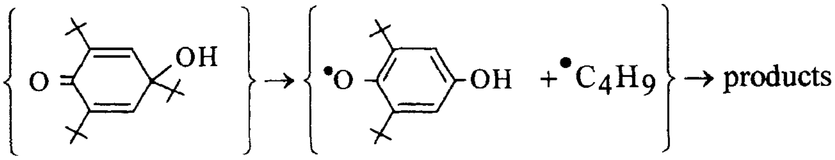
Regeneration of the initial ionol (and tri-tert-butylphenol) in the present process should be performed from the product of its transformation, quinolic alcohol, according to the same way, which provides ionol regeneration from quinolic compound Ir (see parts 2 and 3) in acts of thermofluctuation excitation of *r*-micropores. These acts proceed as 'cryptoradical', or 'intra-cage', ones resulting in dissociation of quinolic alcohol and further reactions of macromolecule dehydrogenation:



Simultaneous partial loss of phenol should be performed in parallel acts of disproportioning, which proceeds in the presence of ionol



with formation of methylene quinone and its further transformation. In the case of tert-butylphenol it is performed by detachment of tert-butyl radicals with final formation of quinone and other products:



Applying the steady state concentration condition to active particles shown in the v_i-scheme (radicals and alcohols IOH), we obtain the equation of initiation and reaction chain termination rates:

$$\delta_f \alpha_f k_{0f} g = 2k_3[\mathrm{POO}^\bullet][\mathrm{IH}].$$

Here δ_f is radical yield in fluctuation HP decomposition in v-zones; $\alpha_f = k_f/(k_{-f} + k_{0f})$. We also obtain the expression for HP decay rate:

$$-\frac{dg}{dt} = \alpha_f k_{of} g + k_1[\mathrm{POO}^\bullet][\mathrm{IH}] - 2k_3[\mathrm{POO}^\bullet][\mathrm{IH}]$$

$$= \alpha_f k_{0f} g + k_1\left(\frac{\delta_f \alpha_f k_{0f} g}{2k_3}\right) - \delta_f \alpha_f k_{0f} g = k_i g,$$

which characterizes the process as the first order reaction by HP and the zero order by alkylphenol:

$$g = g_0 \exp(-k_i t).$$

In accordance with the v_i-scheme phenol expenditure rate is:

$$-\frac{dc_i}{dt} = k_1[\mathrm{POO}^\bullet][\mathrm{IH}] + k_3[\mathrm{POO}^\bullet][\mathrm{IH}] - k_{2f}\left[\left\{\mathrm{I}^\bullet + \mathrm{HO}^\bullet + \mathrm{OH}\right\}\right]$$

$$= \left[k_3 + \frac{k_1 k_{3f}}{k_{2f} + k_{3f}}\right][\mathrm{POO}^\bullet][\mathrm{IH}] =$$

$$= \left[\frac{1}{2} + \frac{k_1 k_{3f}}{2k_3(k_{2f} + k_{3f})}\right]\delta_f \alpha_f k_{0f} g = k_{ii} g.$$

Integrating the obtained expression

$$-\frac{dc_i}{dt} = k_{ii} g,$$

we obtain

$$c_i = \left(\frac{k_{ii} g_0}{k_i}\right)\exp(-k_i t) + \text{const},$$

which is reduced to the following form on taking into account the initial condition $c_i = c_{i0}$ at $t = 0$:

$$c_i = c_{i0} - \left(\frac{k_{ii} g_0}{k_i}\right)\left[1 - \exp(-k_i t)\right].$$

If in this case $c_i = 0$ in the limit $t = \infty$, we obtain

$$c_{i0} = \frac{k_{ii} g_0}{k_i} \quad \text{and} \quad c_i = c_{i0} \exp(-k_i t),$$

which fits the data of the work [21].

As it was mentioned, a quasi equilibrium concentration of phenoxyls in this process is set very fast. The kinetics of their expenditure is described by the theoretical expression:

$$[\text{I}^\bullet] = \frac{k_3}{k_4} c_i = \frac{k_3 c_{i0}}{k_4} \exp(-k_i t),$$

which should be fulfilled from the moment the quasi equilibrium phenoxyl concentration is set till the end of the induction period of PP oxidation. This theoretical expression, as the previous ones, adequately displays experimental results of the work [21], so we may conclude that the model of the heterogeneous-homophase chain reaction correctly reflects the empiric regularities of the oxidative polypropylene HP decomposition in presence of an antioxidant of phenolic type.

Here we should point out that the mechanism of partial phenol regeneration from the product of its chain degradation, quinolic alcohol, expressed similarly to that of phenol regeneration from the product with dibenzoyl peroxide (Ir, parts 2 and 3), are apparently widespread. This is confirmed by the independent experiment with methyl ester of quinolic alcohol prepared from ionol according to methodics [33], carried out by us.

This ester induces qualitatively similar effect on the rate of BP decomposition as alkylphenols did (parts 2 and 3), if injected together with dibenzoyl peroxide into cellulose triacetate films. Figure 11 shows plots of linear anamorphosises of anaerobic BP decomposition

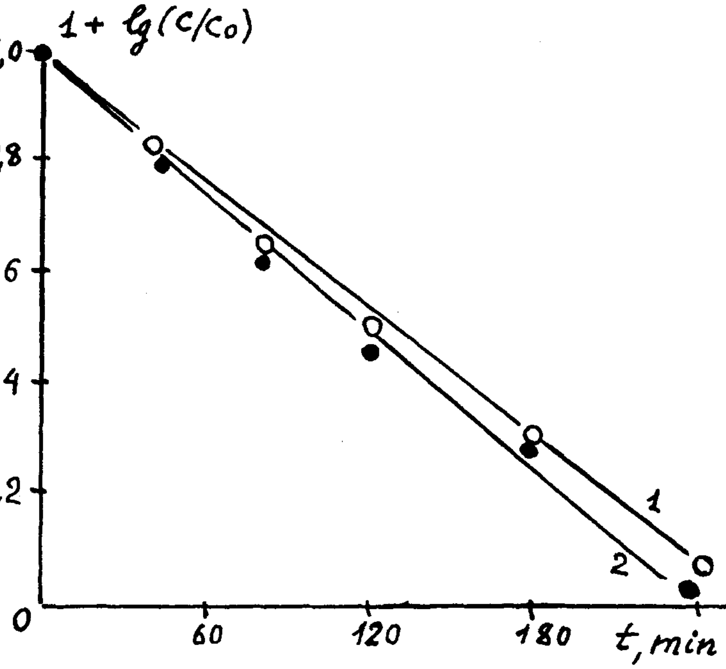


FIGURE 11 BP-decay plots ($T = 371$ K, $C_0 = 0{,}66$ mol/kg) for evacuated CTA-films with 0,08 (1) and 0,32 mol/kg (2) of 1-methyl-1-methoxy-3,5-di-t-Bu-cyclohexadien-4-on.

curves ($c_0 = 0.66$ mol/kg, $T = 371$ K) under initial metoxyquinolic compound concentration of 0.08 mol/kg (straight line 1) and 0.32 mol/kg (straight line 2). It is clearly seen that even at significant difference in initial concentration of reagents, as it is in mixtures with phenols, the reaction proceeds with invariable effective rate constant at any stage of transformations. As it is in systems with phenols, the rate of chain BP reaction induced by polymer radicals reaches its minimum at quinolic ester concentrations ≈ 0.08 mol/kg. The observed values of effective rate constant of BP decay are 2.7×10^{-4}, 1.5×10^{-4} and $1.58 \times 10^{-4} s^{-1}$, at respective quinolic ester concentrations of 0; 0.08 and 0.32 mol/kg. Whereas the BP dissociation constant is 7.5×10^{-5} s^{-1}. The nonphenol quinolic compound performs prolonged inhibiting effect on BP decomposition induced by macroradicals and, in opposite, a catalytic action in the concentration range, where the macroradical effect is deactivated. The concentration of this ester, as well as of phenols, participate as invariables in the expression of effective rate constant of BP reaction. This feature confirms the role of fast thermofluctuation transformation of quinolic compound into corresponding phenol.

7. THE MECHANISM OF THE INITIATED CHAIN REACTION OF IONOL DURING THE INDUCTION PERIOD OF POLYOLEFINE OXIDATION

The material discussed in previous parts allows us to consider one of the fundamental questions of polyolefine stabilization from a new viewpoint. This question concerns the chemistry of the induction period of inhibited oxidation. This field of science contains many experimental data and theoretical methodics, but, as a rule, these methodics are in the range of homogeneous reaction models [14–16].

Two main methodological approaches were developed in this field. One of them is based on application of initiators, tested in liquid-phase reactions [15, 16]. Under conditions of the liquid-phase oxidation this method allows us to determine by means of simple experiments the character and features of the influence of various inhibitors on the rate of oxygen absorption and the duration of the induction period during which inhibitor action is performed and ends.

Another approach studies the process of inhibited polymer oxidation in absence of specially introduced additive initiator [14].

The present part of the review considers oxidation with an additive initiator, with the special attention paid to regularities of oxygen absorption during the induction period. The fact that oxygen absorption is always observed during the induction period of inhibited polyolefin oxidation is known for a long time, but it has not yet obtained suitable explanation. It is sometimes connected with the low rate of oxygen absorption in this stage as compared with the stage of direct polymer oxidation (after the induction period end). In the task of determining the effectiveness of inhibitors or the rate of oxidative chain initiation the investigators used the experimental conditions where the rate of the inhibitor expenditure did not depend on its concentration. It was supposed that provision of such conditions allows one to neglect the process of low rate oxygen absorption during the induction period of the polymer oxidation [15, 16, 28]. We believe that by using the model of polymer clain-sponge system significant improvements of notions about the mechanism of oxidative transformations with participation of inhibitors could be achieved.

Constructing a kinetic model of the oxidation induction period with an initiator we will use the experimental data of the work [28], in which polypropylene, poly-(1-butylene) and polymethylpentene were oxidized (oxygen pressure was 1 atm.) using dibenzoyl peroxide as initiator and ionol as inhibitor. Although the authors of [28], have not considered the origin of significant oxygen absorption during the induction period, they have shown the data and detailed characteristics of absorption rates (V) of oxygen accompanied by ionol expenditure rates (V_i) during induction periods.

The process of oxidation of mentioned partially crystalline polymers proceed only in their amorphous regions, and its extent was limited by the initial stage only, which displayed a 0.6 to 2% of BP conversion.

Values $V_i = c_{i0}/t_{\text{ind}}$ (here c_{i0} is initial ionol concentration; t_{ind} is induction period), measured in T interval of $344 \div 378$ K, are invariable at used BP concentrations as well as value V, which are invariable till abrupt acceleration of the oxidation process, connected with the using up of ionol.

The authors proved clearly the absence of chain BP reaction under oxidative conditions and obtained interesting results on temperature dependence of coefficient

$$A = \frac{c_{i0}}{c_0[1 - \exp(-k_d t_{\text{ind}})]}, \tag{7.1}$$

where k_d is the rate constant of spontaneous BP decomposition. Then they used liquid-phase interpretation of this coefficient and prescribed it the meaning of characteristic of inhibitor effect on radical yield in spontaneous BP reaction.

It is also easy to explain the coefficient A in another way, comparing ionol and oxygen expenditure rates during the induction period. Results of such comparison are shown in Figure 12. Here, the straight lines 1, 3 and 5, constructed in Arrhenius equation coordinates, characterize the change of oxygen absorption rate in the temperature range studied, and the straight lines 2, 4 and 6 characterize that of

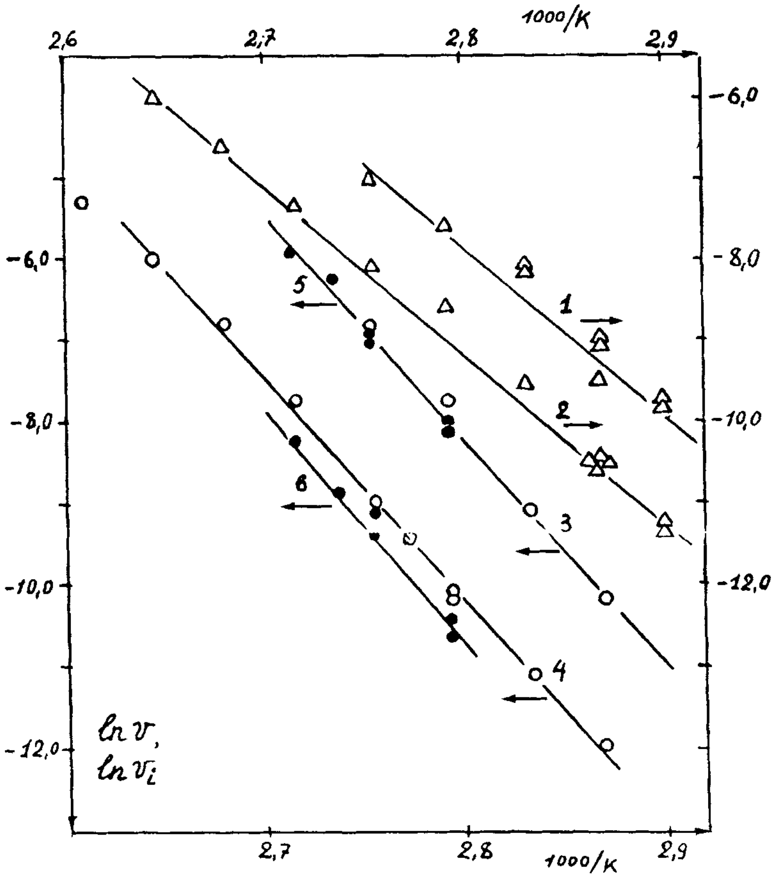


FIGURE 12 Arrhenius plots for O_2-absorption (1, 3, 5) and ionol disappearance (2, 4, 6) in the induction period of BP-initiated oxidation of polyolefins: 1, 2-polypropylene; 3, 4-poly (1-butene); 5, 6-poly (4-methyl-1-pentene).

ionol. Linearity of shown plots, occurred in c_{i0} range of $3.4 \times 10^{-3} \div 72.6 \times 10^{-3}$ mol/l, is the result of independence of the rates mentioned on ionol concentration. The existence of similar slopes of straight lines for each particular polymer, which characterize oxygen absorption and ionol expenditure, indicates the existence of similar effective activation energies of both macroscopic processes $E_i = E_{O_2}$ (172 kJ/mol for PP, straight lines 1 and 2, $c_0 = 0.127$ mol/l; 231.0 kJ/mol for poly-(1-butylene), straight lines 3 and 4, $c_0 = 0.376$ mol/l; 231.0 kJ/mol for polymethylpentene, straight lines 5 and 6, $c_0 = 0.33$ mol/l). In the case that in all temperature ranges studied the number of absorbed oxygen molecules per one expended ionol molecule is constant, it was found that $V/V_i = 3.65$ for PP, 8.0 for poly-(1-butylene) and 13.5 for polymethylpentene.

It is clearly seen that the obtained stoichiometric ratios V/V_i depend on chemical structure of polymers and reach so large values that they could not be ascribed to oxidation of just additive ionol. As a consequence, the process proceeding during the induction period should be interpreted as initiated chain cooxidation of alkylphenol and a polymer, at which the formula (7.1) characterizes the change of ionol amount expended in chains of its cooxidation with polymer calculated for one spontaneously decomposed BP molecule, instead of influence of ionol and temperature on radical yield from a 'cell' of spontaneously dissociating BP.

In accordance with the data [28], the rate constant of spontaneous BP decomposition is $k_d = 8.4 \times 10^{13} \exp(-124{,}650/RT)\,s^{-1}$ in PP and poly-(1-butylene), and $7 \times 10^{13} \exp(-123{,}000/RT)\,s^{-1}$ in polymethylpentene. Such polymers possess activation energy of BP dissociation ($E_d = 123 \div 125$ kJ/mol) significantly lower than that of their cooxidation with ionol ($E_d = 172 \div 231$ kJ/mol). That is why thermal dependence of A set in [28] is natural for very small depth of BP degradation during t_{ind} time ($0.6 \div 2\%$):

$$A = \frac{c_{i0}}{c_0[1 - \exp(-k_d t_{\text{ind}})]} = \frac{c_{i0}}{c_0 k_d t_{\text{ind}}} = \frac{V_i}{V_{d0}},$$

here $V_i = c_{i_0}/t_{\text{ind}}$ and $V_{d0} = k_d c_0$.

Concerning the structural-kinetic cooxidation model, it is easy to construct provided we take into account the above mentioned material and the fact that there is initially no hydroperoxide in the considered systems, capable to decompose in v-zones of the chain-sponge matrix according to the mechanism of fluctuation excitation of v-micropores. In this case it should be taken into account also that BP molecules dissociate to radicals in s-zones:

$$\text{BP}_v \longleftrightarrow \text{BP}_s; \quad \text{BP}_s \xrightarrow{k_{0_s}} 2\delta \text{r}_s^\bullet; \quad \text{r}_s^\bullet \xrightarrow{k_{1s}} \text{P}_s^\bullet \rightarrow \text{R}_s^\bullet;$$

$$R_s^\bullet \xrightarrow{k_{2s}} R_{1s}^\bullet;\quad R_{1s}^\bullet + r_s^\bullet \longrightarrow Rr.$$

The difference between the present *s*-scheme and that considered above lies in the existence of *s*-benzoyloxyl and $R_{1s}^\bullet$ macroradical recombination. The corresponding fact was obtained in the work [34] during the study of material balance of phenyl compounds in BP reaction with PP.

In accordance with the present *s*-scheme steady state concentration of radicals, carrying out interzone *s*, *r*-transfer of free valence, is the following:

$$[R_s^\bullet] = \frac{\delta k_{0s} c_s}{k_{2s}},$$

and *s*, *r*-transfer acts themselves should proceed with low frequency, that induces no influence on $[R_s^\bullet]$ (this is provided by chain-sponge carcass rigidity):

$$R_s^\bullet \underset{k_{-m}}{\overset{k_m}{\longleftrightarrow}} R_m^\bullet;\quad R_m^\bullet + O_{2s} \xrightarrow{k_{tr}} ROO_m^\bullet;$$

$$ROO_m^\bullet + IH \rightarrow ROOIH_m^\bullet \longrightarrow ROH + IO^\bullet.$$

Quinolic alcoxyls, which occur in *r*-zones according to this pathway, initiate chain oxidation of macromolecules, to which ionol is drawn in:

$$IO^\bullet + PH \xrightarrow{k_5} IOH + P^\bullet;\quad P^\bullet + O_2 \longrightarrow POO^\bullet;$$

$$POO^\bullet + IH \xrightarrow{k_1} POOIH^\bullet \longrightarrow POH + IO^\bullet;$$

$$POO^\bullet + IH \xrightarrow{k_3} G + I^\bullet;\quad POO^\bullet + I^\bullet \xrightarrow{k_4} POOI.$$

Here the enumeration of the reaction constants k_1, k_2, k_3 and k_4 prescibed to them in the previous part remains, and the preservation of ionol regeneration and transformation acts is also considered. These acts are characterized by constants k_{1f}, k_{-1f}, k_{2f} and k_{3f} of cryptoradical stages of IOH alcohol transformation.

In accordance with the present heterophase scheme the equation of the reaction v-chain initiation and termination rates is

$$V_{tr} = \frac{k_{tr} k_m \delta k_{0s} c_s [O_{2s}]}{k_{2s}(k_{-m} + k_{tr}[O_{2s}])} = 2k_3[POO^\bullet][IH]. \qquad (7.2)$$

If we suppose that these chains are significantly long, at which the following approximate equation could be used

$$k_5[IO^\bullet][PH] \approx k_1[POO^\bullet][IH],$$

and we obtain condition of stationary quinolic alcohol concentration:

$$k_1[POO^\bullet][IH] = k_{1f}[IOH][PH]\frac{(k_{2f} + k_{3f})}{(k_{-1f} + k_{2f} + k_{3f})}.$$

Expressing [IOH][PH] from this composition and substituting it to the equation of ionol decay rate

$$-\frac{dc_i}{dt} = k_1[POO^\bullet][IH] + k_3[POO^\bullet][IH] - k_{2f}[\{I^\bullet + HO^\bullet + PH\}]$$

$$= (k_1 + k_3)[POO^\bullet][IH] - \frac{k_{2f} k_{1f}[IOH][PH]}{(k_{-1f} + k_{2f} + k_{3f})}$$

$$= (k_1 + k_3)[POO^\bullet][IH] - (1 - \beta)k_1[POO^\bullet][IH],$$

and then neglecting ionol expenditure in chain termination acts (with constant k_3), we obtain [POO$^\bullet$] [IH] for oxygen-saturated system ($k_{-m} \ll k_{tr}$ [O_{2s}]) from (7.2). Taking into account this expression we obtain

$$V_i = -\frac{dc_i}{dt} = \left[\frac{k_{3f}}{k_{2f} + k_{3f}}\right]\left[\frac{k_1 k_m \delta k_{0s} c_s}{2k_3 k_{2s}}\right].$$

And finally by taking into account the interzone BP equilibrium (Equation (2.1)), the following reduced expression is obtained

$$V_i = \beta k_i c,$$

here k_i is complex constant; $\beta = (k_{3f})/(k_{2f} + k_{3f})$.

The same heterophase scheme under above mentioned conditions displays the following expression of oxygen absorption rate

$$V = -\frac{d[O_2]}{dt} = k_5[IO^\bullet][PH] = k_1[POO^\bullet][IH] = \frac{k_1 k_m \delta k_{0s} c_s}{2k_3 k_{2s}} = k_i c.$$

It is clearly seen that the theory of hererophase transformation, in which a polymer obtains significant amounts of oxygen and alkylphenol simultaneously with initiator, leads to expressions of inhibitor (V_i) and oxygen (V) expenditure rates, independent on their concentrations and proportional to each other:

$$\frac{V}{V_i} = \beta^{-1} = \frac{k_{2f} + k_{3f}}{k_{3f}}.$$

The obtained result explains the reason of significant V excess over V_i with alkylphenol regeneration process. In this connection, the increase of V/V_i ratio (from 3.65 to 13.5), observed in the sequence PP, Poly-(1-butylene), polymethylpentene, means growth of regeneration effectiveness (β^{-1}) and, probably, reflects the increase of the number of reactive hydrogen atoms on surfaces of thermofluctuationally excited v-micropores. The higher is the level of hydrogen atoms surrounding $HO^\bullet$ and $I^\bullet$ radicals, the lower is the probability of mutual combination of radicals and the higher is the probability of macromolecule dehydrogenation by 'cryptoradical' mechanism.

We should specially mention in this part that alkylphenol regeneration must be performed particularly by the 'intra-cage' cryptoradical reaction during lifetime of the micropore, increased up to the required size. In this case radical escape from such micropore to the volume of chain sponge v-zones may possess a negligibly low rate which does not affect the steady state v-radical concentrations. We should also mention in this connection that the dependence of parameter

$$A = \frac{c_{i0}}{c_0[1 - \exp(-k_d t_{\text{ind}})]}$$

on temperature, found in [28], does not relate to the process of theoretically active diffusional ionol intrusion into a 'cage' of spontaneously degraded initiator, which was suggested in [28]. In accordance with the fact of chain ionol and polyolefine cooxidation this dependence characterizes the stoichiometry of chain cooxidation. The considered reaction model disclosing the structure of coefficient A is represented by

$$A = \frac{V_i}{V_{d0}} = \frac{\delta\beta k_1 k_m}{2k_3 k_{2s}}.$$

Coefficient β participating in this formula either does not depend on temperature or depends only weakly. This is indicated by similar temperature dependences of V and V_i for each polymer, studied in [28] ($E_{O_2} = E_i$). In this connection the main contribution into temperature dependence of A should be made by acts of the terminal macroradical $R_s^\bullet$ transfer from the carcass wall structures to the volume of s-micropores (acts with constant k_m). The size of correspondent fragment $R_s^\bullet \rightarrow R_m^\bullet$ increases in the sequence PP, poly-(1-butylene), polymethylpentene, so it could be expected that obstacles connected with this motion should become harder. If we take A values, shown in [28], and construct the dependence of $\ln A$ on reciprocal temperature (Fig. 13), we will observe the activation energy increase, E_A, from 50 kJ/mol for PP up to 128 kJ/mol for poly-(1-butylene), and higher increase for polymethylpentene, as it is in accord with the above discussion.

It is characteristic that theoretical bases of the work [28] did not allow the authors to construct plots, shown in the Figure 13. In particular, it follows from these plots that A values becomes 1 at 388 K and exceeds 2 at 405 K (see Fig. 13, axis of ordinates: $\ln 2 = 0.693$). It is evident that not more than two free radicals could occur in the act of BP molecule dissociation, so a true realization of correlation $A > 2$ in the process considered makes senseless the supposition [28] that coefficient A characterizes effectiveness of radical yield in acts of the oxidative chain initiation.

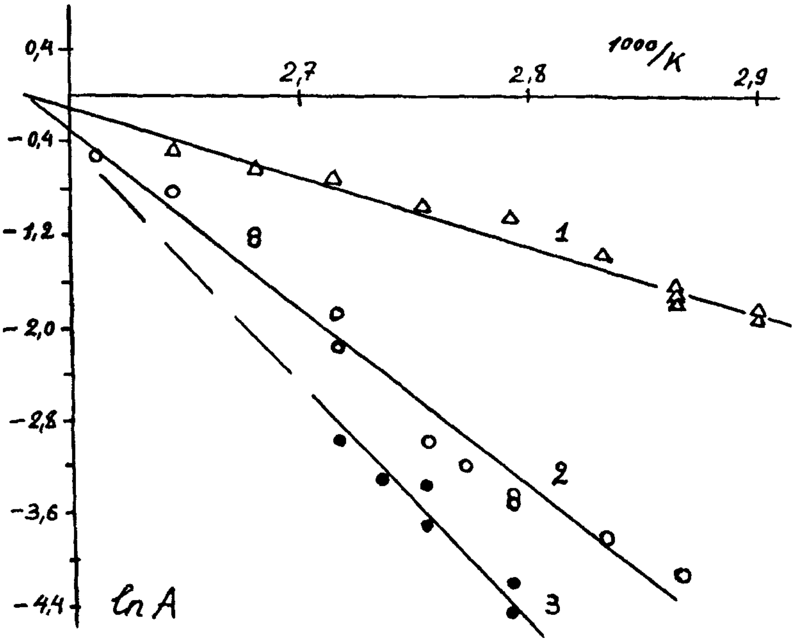


FIGURE 13 Arrhenius plots for the coefficient A: 1-PP; 2-poly(1-butene); 3-poly (4-methyl-1-pentene).

The interpretation of coefficient f determined according to methodics of homogeneous reactions should change simultaneously with interpretation of the coefficient A. In the inhibitor method applied to homogeneous reactions the coefficient f is calculated by the following formula:

$$f = \frac{W_{i0}}{V_i} = \frac{2\delta V_{d0}}{V_i}.$$

Here W_{i0} is the rate of the homogeneous reaction of radical initiation; δ is the coefficient of radical yield in acts of initiator dissociation.

In this method f value characterizes the number of oxidative chains terminated on one inhibitor molecule. At the same time, f depends on the reciprocal value of A according to its definition:

$$f \sim \frac{V_{d0}}{V_i} = A^{-1}$$

The moment of inhibitor exhaustion in a polymer is fixed by a sharp increase of the oxygen absorption rate. This marks the end of cooxidation period and process changes to the stage of polymer oxidation.

Application of the homogeneous reaction model to the induction period of polymer oxidation produces specific contradictions. They are, for example, conclusions of the work [35] in which $f = ((W_{i0})/V_i) = 1$ for PP with ionol and dicumylperoxide as initiator ($P_{O_2} = 1$ atm., $T = 388$ K. Here W_{i0} is the constant rate of radical initiation, obtained by the inhibitor method; V_i is the ionol expenditure rate). Making sure that at constant W_{i0} rate the inhibitor expenditure rate is also constant and stating on this base that all chains terminate on inhibitor and no side reactions of it occur, the authors of [35] stated that the equation $f = 1$ relates to termination of a single oxidative chain on a single ionol molecule (in accordance with the data of [28] coefficient $A = 1$ at $T = 388$ K, too).

The authors of [35] had to point out simultaneously that there was the discrepancy observed with liquid-phase value $f = 2$. They also showed the sequence of their reasonings to prove bimolecular nature of ionol phenoxyl decay for the PP matrix:

$$I^\bullet + I^\bullet \rightarrow \text{products}.$$

However, according to the material considered in the part 6, such reaction is inconsistent with true kinetics of phenoxyls.

8. THE CHAIN ALKYLPHENOL COOXIDATION WITH POLYOLEFINE IN THE ABSENCE OF INITIATOR

In the analysis of cooxidation process proceeding in absence of initiator, we will use the v-scheme considered in the previous part taking into account that the rate of radical initiation in v-zones is negligibly small. Under these circumstances s-zones, which are heterophase sources of radicals, may provide initiation process by either direct oxidation of polymer s-chains or oxidation of inhibitor molecules if the latter possess enough reactivity.

Considering the first stage, we refer to the s-scheme, which allowed us to make kinetic description of initial PP autoxidation stage in absence of initiator and inhibitor [4, 25]. In accordance with this scheme the initiation of radicals is performed in super-micropores of chain-sponge *s*-zones as a result of interactions of polymer chain CH-bonds with oxygen adsorbed on *s*-micropore walls

$$PH_s + O_{2s} \xrightarrow{k^p_{0s}} \delta P^\bullet_s.$$

The following *transformations of s-macroradicals remain the same* as those considered in parts 2 and 5:

$$P^\bullet_s \xrightarrow{k_{1s}} R^\bullet_s; \quad R^\bullet_s \xrightarrow{k_{2s}} R^\bullet_{1s}; \quad R^\bullet_s + R^\bullet_{1s} \xrightarrow{k_{3s}} \text{products}.$$

The expression for the radical-mediator concentration resulting from this scheme, is the following:

$$[R^\bullet_s] = \frac{\delta k^p_{0s}[PH_s][O_{2s}]}{2k_{2s}}.$$

and the process of free valence *s*, *v*-translation, in which they participate, becomes:

$$R_s \underset{k_{-m}}{\overset{k_m}{\longleftrightarrow}} R^\bullet_m; \quad R^\bullet_m + O_2 \xrightarrow{k_{tr}} ROO^\bullet_m;$$

$$ROO^\bullet_m + IH \longrightarrow ROOIH^\bullet \longrightarrow ROH + IO^\bullet.$$

The scheme of *v*-chains reaction of alkylphenol and polymer cooxidation remains with no change as well as the scheme of cryptoradical acts of quinolic alcohol IOH transformation, providing partial regeneration of initial phenol:

$$IO^\bullet + PH \xrightarrow{k_5} IOH + P^\bullet; \quad P^\bullet + O_2 \longrightarrow POO^\bullet;$$

$$POO^\bullet + IH \xrightarrow{k_1} POOIH^\bullet \longrightarrow POH + IO^\bullet;$$

$$POO^\bullet + IH \xrightarrow{k_3} G + I^\bullet; \quad POO^\bullet + I^\bullet \xrightarrow{k_4} POOI$$

The present coincidence of s- and v-schemes fixes the unequivalence of properties of intrazone macroradicals in relation to oxidation and interaction with the inhibitor, namely a low rate in supermicropores, and a high rate in v-zones. As it was already mentioned, such selectivity of reactions is caused by predominant accumulation of low molecular compounds (including oxygen and inhibitor) in sponge micelle granules, filled by narrow micropores [6, 11–13, 25]. An example of such unequivalence was considered in description of ionol transformations in s-steps of initiated macromolecule degradation and in v-chains of CTA and PC arylation (see part 2). We also may point out that there is a number of similar data reported in literature. For example, it is significant that the number of broken polymer chains observed during 26 hours of melt polystyrene oxidation at 473 K ($P = 150$ torr) in presence of bisphenol 2246 inhibitor as well as at its high concentration is practically invariable, when the induction period is not finished yet, and when the oxidation proceeds from the induction period at its low concentration $c_{ii} \to 0$ [36, 37]. The absence of the inhibitor concentration influence on polymer degradation rate during the induction period of oxygen absorption exists also in caoutchouc with ionol [38] and in PP with bisphenol (2246 $T = 473$ K, $P_{O_2} = 300$ torr) [30].

In this way the above constructed heterophase scheme of noninitiated cooxidation of alkylphenol with a polymer fits the general phenomenology of the process during the induction period and allows the calculation of the above considered features of cooxidation in heterophase matrix of chain-sponge micelles.

We can easily find the expression of the free valence s, v-transfer rate, applying the condition of steady state radical concentration to each block of the total system:

$$V_{tr} = k_{tr}[R^{\bullet}_{m}][O_{2s}] = \frac{k_{tr} k_m \delta k_{0s}{}^{p}[PH_s][O_{2s}]^2}{k_{-m} + k_{tr}[O_{2s}]},$$

which transforms in oxygen-saturated polymer ($k_{-m} \ll k_{tr}[O_{2s}]$) to

$$V_{tr} = \frac{\delta k_m k_{0s}{}^{p}[PH_s][O_{2s}]}{2k_{2s}}. \tag{8.1}$$

This equals the termination rate, which is also the rate of the reaction v-chain initiation:

$$V_{tr} = 2k_3[\mathrm{POO}^\bullet][\mathrm{IH}].$$

In described conditions alkylphenol expenditure rate does not depend on its concentration, but depends on oxygen pressure:

$$V_i = -\frac{dc_i}{dt} = (k_1 + k_3)[\mathrm{POO}^\bullet][\mathrm{IH}] - (1-\beta)k_1[\mathrm{POO}^\bullet][\mathrm{IH}] \approx \beta k_1[\mathrm{POO}^\bullet][\mathrm{IH}]$$

$$= \frac{\beta k_1 V_{tr}}{k_3} = \frac{\beta k_1 \delta k_{0s}{}^p k_m[\mathrm{PH}_s][\mathrm{O}_{2s}]}{4k_{2s}k_3} = \beta k_i{}^p \mathrm{P}_{\mathrm{O}_2}. \tag{8.2}$$

Here $[\mathrm{O}_{2s}] = K_{\mathrm{O}_2}[\mathrm{O}_{2v}] = K_{\mathrm{O}_2}\mathrm{P}_{\mathrm{O}_2}\gamma$; K_{O_2} is the equilibrium constant of oxygen exchange between zones; γ is the Henry constant; $\beta = (k_{3f})/(k_{2f} + k_{3f})$ is efficiency of quinolic alcohol expenditure in acts of phenol regeneration (see parts 6 and 7); $k_i{}^p$ is a complex constant.

In accordance with this scheme, the rate of oxygen absorption

$$V = -\frac{d[\mathrm{O}_2]}{dt} \approx k_5[\mathrm{IO}^\bullet][\mathrm{PH}] = k_1[\mathrm{POO}^\bullet][\mathrm{IH}] = k_i{}^p\mathrm{P}_{\mathrm{O}_2}$$

exceeds the rate of inhibitor expenditure and does not depend on its concentration c_i.

These particular regularities have been already obtained in early stages of investigations of antioxidative stabilization mechanism in experiments with phenols marked as weak inhibitors. Such inhibitors are characterized by more or less strict fulfillment of kinetic decay equation of zero order by the inhibitor, order one by oxygen and linear dependence of the induction period duration on inhibitor concentration. The list of such inhibitors includes the following substances: 2,6-di(1,1-dimethylhexyl)-4-methylphenol [39,40] (t_{ind} grows linearily from 9.5 min at $c_i = 0$ to 373 min at $c_i = 0.20$ mol/kg at $T = 473$ K and $\mathrm{P}_{\mathrm{O}_2} = 300$ torr), 2,4,6-tri-tert-butylphenol [41] (effective activation energy of phenol expenditure $E_i = 36$ kcal/mol in temperature interval $453 \div 473$ K), 2,6-di-tert-butylphenol [41] ($E_i = 30$ kcal/mol), bisphenol with spatially separated OH-groups-4,4'-methylene-bis(2,6-di-tert-butylphenol) [41] (t_{ind} grows linearily and significantly: from 9.5 min at $c_i = 0$ to 250 min at $c_i = 0.025$ mol/kg).

The above mentioned phenols possess the feature that their expenditure is not accompanied by water formation, whose occurrence becomes noticeable at the very end of the induction period. This important fact indicates negligibly low rates of decomposition of peroxyl radicals (with $HO^\bullet$ elimination) and polymer hydroperoxide. The conclusion about the absence of HP contribution to the process of radical initiation at the stage of polymer-phenol system cooxidation follows also from the fact that oxygen and inhibitor expenditure rates are invariable from the beginning till the end of the induction period [42].

In accordance with the above said reactions of $POO^\bullet$ radical and HP-group decomposition are absent in the accepted heterophase scheme. The well-known fact that the process is significantly decelerated in presence of dialkylsulfides may serve as an additional and specific proof of the chain mechanism of alkylphenol cooxidation with polyolefine.

About Cooxidation Mechanism Inhibited by Dialkylsulfide

The features of antioxidant transformations in polymer-chain zones of sponge micelles, set forth in the present review, make us turn back again to the question about the mechanism of cooperative functioning of phenolic antioxidants and dialkylsulfides. It is the common knowledge that the latter possess no significant inhibiting effectiveness, but are capable to significantly increase the induction period of polymer cooxidation with 'weak' phenol, changing the kinetic law of phenol expenditure in this case [41,43].

The ideas about the mechanism of nonadditive combination of phenol and dialkylsulfide actions are developed in literature based on the idea of nonradical hydroperoxide decomposition by dialkylsulfide. It is accepted that dialkylsufide degrades hydroperoxide without free radical formation and abruptly decreases the rate of degenerated branching of oxidative chains. However, the role of hydroperoxide as the branching agent in the cooxidation stage is not practically performed because of its low concentration. But even in the samples possessing high content of preliminarily accumulated HP, the branching factor in presence of alkylphenol is zero (see parts 5 and 6), and in this case transformation process is reduced to oxidative chain HP decomposition only.

In this means the mechanism of direct dialkylsulfide and HP interactions, which has not been completely described yet because of its complexity [14], is transformed into an independent problem. It is important for us in this case that dialkylsulfide, which is not the inhibitor of the polymer oxidation itself, inhibits alkylphenol cooxidation. Dialkylsulfide extends the alkylphenol action by sacrifising itself. This is confirmed, for example, by of 2,6-di-(1,1-di-methylhexyl)-4-methylphenol and bisphenol 2246 expenditure kinetic curves, obtained at oxidation temperature $T = 473$ K ($P_{O_2} = 300$ torr) in works [14,43], shown in Figure 14. As it is seen, the expenditure rate of phenols with mixtures of monophenol/sulfide = 0.16 mol/kg/0.08 mol/kg (curve 2) and bisphenol/sulfide = 0.08/0.08 (curve 4) decrease in relation to the rate without sulfide (curves 1 and 3) from the very beginning, when the radical yield in acts of HP decomposition under the influence of phenol as well as sulfide could not be changed . It has been mentioned already that such influence is absent even at high HP concentration (see parts 5 and 6).

Furthermore, we should mention results of the work [30] according to which the rate of propylene yield in the induction period of melt PP oxidation ($T = 473$ K, $P_{O_2} = 300$ torr) is constant during 100 min and is similar in the presence of 0.025 and 0.05 mol/kg of bisphenol 2246, and does not change after injection to the initial mixture of 0.08 mol/kg dodecylsulfide or di-laurylthiopropyonate. Consequently the concentration of depolymerizing terminal macroradicals remains constant under these conditions during 100 min, and the process of degenerated branching with HP and phenol participation may be neglected.

At the same time, the gas chromatographic analysis, performed in [30], showed that dialkylsulfide injection into oxidized PP cause a significant increase of ethylene yield, that indicates a sulfide interaction with polymer peroxyls. Entering into cooxidation with PP, dialkylsulfides induce no significant increase of the induction period. However, in presence of 'weak' phenol they are able to increase the induction period significantly displaying synergism. The mechanism of this phenomenon may be shown if we take into account the fact,

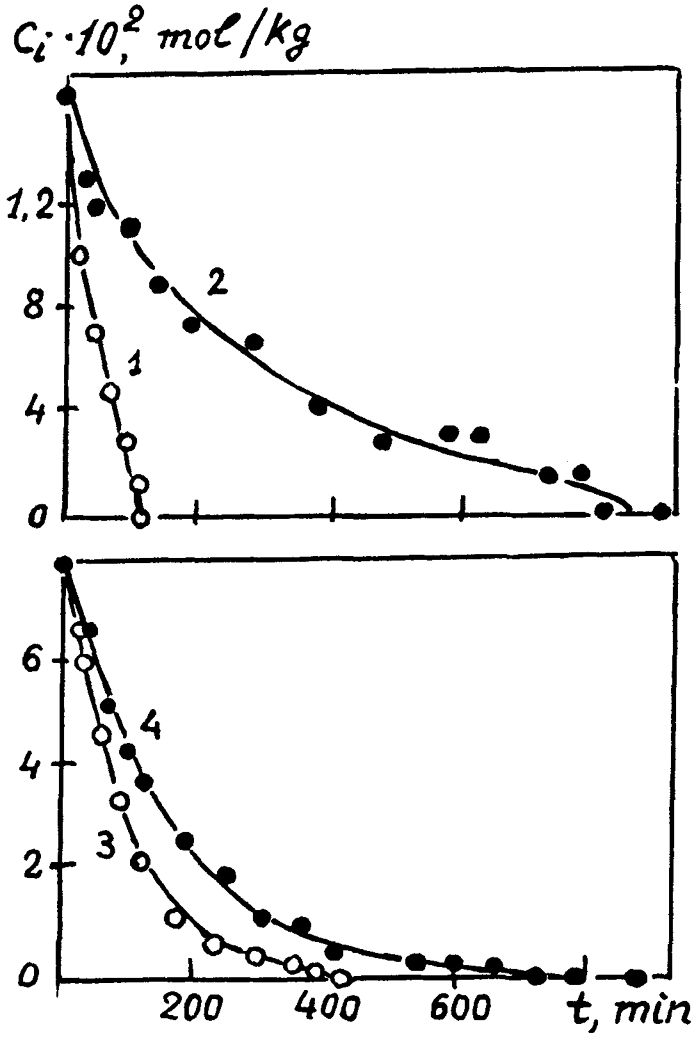
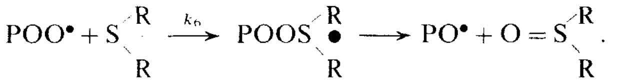


FIGURE 14 Disappearance of 4-methyl-2, 6-di-(1, 1-di-methyl-hexyl)-phenol (1, 2) and methylene-2, 2'-bis (4-methyl-6-t-butyl-phenol) (3, 4) in the induction period of autoxidation ($T = 473$ K, $P_{O_2} = 300$ mm Hg) for PP-samples with no (1, 3) and with (2, 4) 0,08 mol/kg di-decyl-sulphide.

stated in [30], that dialkylsulfides interact with peroxyls. Owing to this interaction the decrease of peroxyl concentration occurs, which induces chain expenditure of alkylphenol.

Dialkylsulfide should provide peroxyl conversion into polymer alkoxyl to carry on such a process. This polymer alkoxyl preferably reacts with the inhibitor



$$\mathrm{POO^{\bullet}} + \mathrm{S}\begin{smallmatrix}\diagup \mathrm{R}\\ \diagdown \mathrm{R}\end{smallmatrix} \xrightarrow{k_6} \mathrm{POOS}\begin{smallmatrix}\diagup \mathrm{R}\\ \bullet\\ \diagdown \mathrm{R}\end{smallmatrix} \longrightarrow \mathrm{PO^{\bullet}} + \mathrm{O{=}S}\begin{smallmatrix}\diagup \mathrm{R}\\ \diagdown \mathrm{R}\end{smallmatrix}.$$

Taking into account the above mentioned, the scheme of reaction v-chains of polymer, phenol and sulfide cooxidation will transform to the following view:

$$\mathrm{IO^{\bullet}} + \mathrm{PH} \xrightarrow{k_5} \mathrm{IOH} + \mathrm{P^{\bullet}};\quad \mathrm{P^{\bullet}} + \mathrm{O_2} \longrightarrow \mathrm{POO^{\bullet}};$$

$$\mathrm{POO^{\bullet}} + \mathrm{IH} \xrightarrow{k_1} \mathrm{POOIH^{\bullet}} \rightarrow \mathrm{POH} + \mathrm{IO^{\bullet}};$$

$$\mathrm{POO^{\bullet}} + \mathrm{IH} \xrightarrow{k_3} \mathrm{G} + \mathrm{I^{\bullet}};\quad \mathrm{POO^{\bullet}} + \mathrm{I^{\bullet}} \xrightarrow{k_4} \mathrm{POOI}.$$

$$\mathrm{POO^{\bullet}} + \mathrm{S} \xrightarrow{k_6} \mathrm{POOS}\bullet \longrightarrow \mathrm{PO^{\bullet}} + \mathrm{O{=}S}.$$

$$\mathrm{PO^{\bullet}} + \mathrm{PH} \xrightarrow{k_7} \mathrm{POH} + \mathrm{P^{\bullet}};\quad \mathrm{PO^{\bullet}} + \mathrm{IH} \xrightarrow{k_8} \mathrm{POH} + \mathrm{I^{\bullet}}.$$

The role of dialkylsulfide in absence of phenol is that it is spent in the act with the constant k_6, transforming peroxyl to alkoxyl, which is transformed to oxidizing alkyl $\mathrm{P^{\bullet}}$ in the act with the constant k_7, reducing finally the $\mathrm{POO^{\bullet}}$ radical. Such sequence of reactions does not change the peroxyl concentration. That is why dialkylsufide expenditure cause no influence on the polymer oxidation rate. The scheme does not show the sulfide transformation will formation of ethylene, which proceeds either by displacement mechanism, mentioned in [30]

$$\mathrm{POO^{\bullet}} + \mathrm{R{-}S{-}R} \longrightarrow \mathrm{POO{-}S{-}R} + \mathrm{R^{\bullet}};\quad \mathrm{R^{\bullet}} \longrightarrow \mathrm{C_2H_4} + \mathrm{R_1^{\bullet}},$$

$$\mathrm{POOS{-}R} \longrightarrow \mathrm{(RO)R_1SO},$$

or as a result of formed alkoxyl reaction with sulfoxide:

$$\mathrm{PO^\bullet + R_2S{=}O \longrightarrow PO(R_2)SO^\bullet \longrightarrow PO(R)SO + R^\bullet;}$$

$$\mathrm{R^\bullet \longrightarrow C_2H_4 + R_1^\bullet}$$

These processes seem less favorable by energetic and steric properties in comparison with the act, marked by constant k_6 in the scheme. This act is followed by the weak peroxide bond-break and formation of a strong thio-oxygen bond. On this base the process of ethylene formation may be considered as the side one. Moreover, if this is taken into calculation, the kinetic picture of cooxidation with phenol will not change as a result of $R_1^\bullet$ radical oxidation to peroxyls, which in turn, participate in further reaction displaying no qualitative difference from polymer peroxyls.

In the above shown cooxidation v-scheme phenol interacts with $PO^\bullet$ radicals terminating oxidative chains, in which dialkylsufide participates. By this means RSR functions as inhibitor, exhibiting a role, which it does not initially possess.

However it could be seen that at significantly high phenol concentration the oxidative function will prevail by means of the reaction rate increase with constants k_1 and k_5, making cooxidation process independent on dialkylsulfide.

It is easy to obtain the expression of inhibitor expenditure rate, by applying the steady state radical concentration condition to the v-scheme and remaining cryptoradical pathway of phenol regeneration

$$V_i = -\frac{dc_i}{dt} \approx \beta k_1[\mathrm{POO^\bullet}]c_i = \frac{\beta k_1 c_i V_{tr}}{2\left(k_3 c_i + \dfrac{k_6 k_8 c_i \mathrm{S}}{k_7[\mathrm{PH}] + k_8 c_i}\right)}$$

This expression is reduced to the same form for opposite concentration ratios, $c_i/\mathrm{S} \ll 1$ and $c_i/\mathrm{S} \gg 1$, showing no dependence on dialkylsulfide concentration S. In the first case inequality $k_7[\mathrm{PH}] > k_8 c_i$ takes place at significantly low concentration c_i. It allows one to neglect the second term in denominator of main V_i expression fraction. In the second case $k_7[\mathrm{PH}] < k_8 c_i$ at significantly high concentration c_i, but inequality $k_3 c_i > k_6$ S takes place simultaneously. Both cases display similar result:

$$V_i = \frac{\beta k_1 V_{tr}}{2k_3},$$

and dialkylsulfide effect on the process rate is absent.

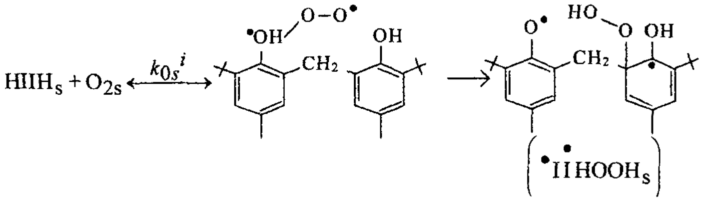
At the same time in intermediate range of concentration ratios $c_i/S \approx 1$, when inequality $k_7[PH] < k_8 c_i$ is combined with $k_3 c_i < k_6 S$ one, the expression of inhibitor expenditure rate becomes

$$V_i = \frac{\beta k_1 V_{tr} c_i}{2k_6 S}.$$

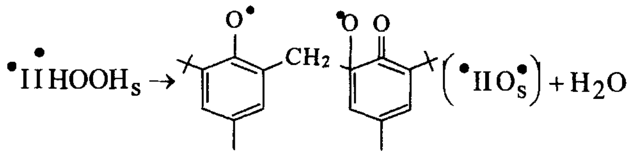
In this situation kinetics is of first order one for phenol at a particular period of time in accordance with the equation (8.1), which discloses the structure of radical translation rate V_{tr} to v-zones of sponge micelles. In this case the rate of 'weak' phenol expenditure will decrease because of complete realization of dialkylsulfide inhibiting activity effect induced by phenol. Curves 1 and 2, shown in the Figure 14, show the real change of inhibitor expenditure kinetic law in accord with the theoretical predictions of the heterophase model of the induction period.

Features of Dialkylsulfide Cooxidation with 2,2'-methylene-bis(4-methyl-6-tertbutylphenol

The influence of dialkylsulfides on the induction period of polyolefine oxidation is weaker in mixtures with bisphenol 2246, which was related to strong inhibitors [14]. Bisphenol expenditure deceleration, observed in this case, is less effective than in the case of weak phenol (Fig. 14, curves 3 and 4). On one hand, bisphenol 2246 molecules differ from the above considered molecules of 'weak' phenols by lower hindrances for OH-groups from the neighbour alkyl substituents (consequently, by better accessibility for attack of radicals and oxygen molecules). On the other hand, they differ by specific mutual disposition of phenolic nuclei (see part 3). Owing to these structural features of molecules the process of direct oxidation with radical formation, proceeding in *s*-zones of polymer-chain sponge, becomes easier for bisphenol



$$^{\bullet}\overset{\bullet}{I}IHOOH_s \rightarrow HIIOOH \text{ (intramolecular disproportionation);}$$



$$^{\bullet}IIO_s^{\bullet} + PH_s \longrightarrow {}^{\bullet}IIOH + P_s^{\bullet};\quad P_s^{\bullet} \xrightarrow{k_{1s}} R_s^{\bullet};$$

$$R_s^{\bullet} \xrightarrow{k_{2s}} R_{1s}^{\bullet};\quad R_s^{\bullet} + R_{1s}^{\bullet} \xrightarrow{k_{3s}} \text{products;}$$

$$R_{1s}^{\bullet} + {}^{\bullet}IIOH_s \longrightarrow R^{=} + HIIOH.$$

As the result of self oxidation, bisphenol 2246 becomes the leading oxidation initiator at a significantly high concentration.

Similar conclusions are reported in the work [30]. It was stated that the evolution rate of propylene (PP depolymerization product) is the same at different concentrations of HIIH (0.025 and 0.05 mol/kg) and increases up to its constant value after 100 min already during the stage of the induction period. The displayed *s*-scheme explains the constancy of the initial propylene evolution rate by the fact that beside initiating and depolymerizing of $R_{1s}^{\bullet}$ alkyl macroradicals, bisphenol also leads to their stationary concentration by their combination with bisphenol phenoxyls •IIOH formed in the acts of radical initiation. In this case the increase of propylene producing rate up to a constant value during the induction period may be connected with dissociation of peroxide initiator with quinolic structure HIOOH, formed from bisphenol, which reaches its stationary concentration.

According to the displayed s-scheme the stationary concentration of radicals-mediators, responsible for interzone, s,v-transfer is

$$[R_s^\bullet] = \frac{\gamma c_{ii} P_{O_2}}{2k_{2s}}.$$

Here γ is complex value, which characterizes effectiveness of bisphenol action as initiator.

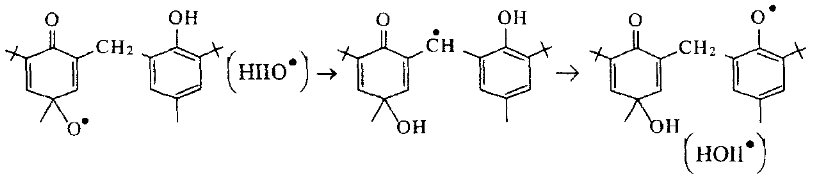
The process of free valence transfer from s-zones to v-zones proceeds through the stage of intermediate active quinolic alcoxyl, as it is in the case of above considered phenols:

$$R_s^\bullet \underset{k\quad m}{\overset{k_m}{\longleftrightarrow}} R_m^\bullet; \quad R_m^\bullet + O_{O_{2,s}} \xrightarrow{k_{tr}} ROO_m^\bullet;$$

$$ROO_m^\bullet + HIIH \longrightarrow ROO\overset{\bullet}{I}HIH_m \rightarrow ROH + HIIO_m^\bullet.$$

This alkoxyl initiates cooxidation process in polymer v-zones, after entering them.

As it is known [14,40,44], bisphenol 2246 provides significantly longer induction periods (cooxidation periods, to say it more correct) comparing with 'weak' monopehnols and less effective response in presence of dialkylsulfide. The reason of both these effects may be connected with specific bisphenol molecule structure, which cause high probability of active alkoxyl isomerization to inactive phenoxyl through an intermediate radical of the benzene type:



The competition between such isomerization acts and s, v-translation acts

$$\mathrm{HIIO}^\bullet_m \xrightarrow{k'_{tr}} \mathrm{HIIO}^\bullet_{m'};\quad \mathrm{HIIO}^\bullet_m \xrightarrow{k_{is}} \mathrm{HOII}^\bullet_{m'};\quad 2\mathrm{HOII}^\bullet_m \longrightarrow \text{products}$$

significantly decreases the rate of the reaction v-chain initiation, which becomes the following in the oxygen-saturated system:

$$V_{tr} = k'_{tr}[\mathrm{HIIO}^\bullet_m] = \frac{\delta_{ii}\gamma c_{ii}\mathrm{P}_{\mathrm{O}_2}}{2k_{2s}}. \qquad (8.3)$$

Here $\delta_{ii} = (k_m k'_{tr})/(k'_{tr} + k_{is}) < k_m$ (contrary to the Equation (8.1)).

Similar isomerization of phenolic alkoxyls (possessing constant k_9) makes its contribution to the cooxidation chain termination in polymer v-zones:

$$\mathrm{HIIO}^\bullet + \mathrm{PH} \xrightarrow{k_5} \mathrm{HIIOH} + \mathrm{P}^\bullet;\quad \mathrm{P}^\bullet + \mathrm{O}_2 \longrightarrow \mathrm{POO}^\bullet;$$

$$\mathrm{POO}^\bullet + \mathrm{HIIH} \xrightarrow{k_1} \mathrm{POOI}^\bullet\mathrm{HIH} \longrightarrow \mathrm{POH} + \mathrm{HIIO}^\bullet;$$

$$\mathrm{POO}^\bullet + \mathrm{HIIH} \xrightarrow{k_3} \mathrm{G} + \mathrm{HII}^\bullet;$$

$\mathrm{HII}^\bullet \rightarrow \mathrm{IIH}^\bullet$(phenoxyl isomerization to σ-complex, see part 3);

$\mathrm{POO}^\bullet + \mathrm{IIH}^\bullet \longrightarrow \mathrm{G} + \mathrm{II}$ (cyclic quinolide);

$$\mathrm{HIIO}^\bullet \xrightarrow{k_9} \mathrm{HOII}^\bullet;\quad \mathrm{POO}^\bullet + \mathrm{HOII}^\bullet \longrightarrow \mathrm{POOIIOH} \longrightarrow \text{products}.$$

Here we suppose that the mechanism of cryptoradical partial regeneration of initial bisphenol from quinolic alcohol HIIOH remains unchanged as we did in the case of monophenols.

Owing to additional pathway of the reaction v-chain termination the process proceeds under the condition of significantly decreased concentration of peroxyls POO•, determined from conditions of the rate equality of v-chain initiation and termination:

$$V_{tr} = 2k_3[\mathrm{POO}^\bullet]c_{ii} + 2k_9[\mathrm{HIIO}^\bullet] = 2k_3[\mathrm{POO}^\bullet]c_{ii} + \frac{2k_1k_9[\mathrm{POO}^\bullet]c_{ii}}{k_5[\mathrm{PH}]}.$$

In this connection and as a result of activity loss during s, v-translation ($\delta_{ii} < k_m$ in the Equation (8.3)) of radicals bisphenol decay rate decreases significantly comparing with the rate of monophenols (equation (8.2)):

$$V_{ii} = -\frac{dc_{ii}}{dt} \approx \beta k_1[\mathrm{POO}^\bullet]c_{ii} = \frac{\beta k_1\delta_{ii}\gamma c_{ii}\mathrm{P}_{\mathrm{O}_2}}{2k_{2s}\left(2k_3 + \dfrac{2k_1k_9}{k_5[\mathrm{PH}]}\right)}.$$

The induction period of the polymer oxidation increases simultaneously, and potential of the realization of synergistic dialkylsulfide cooperation decreases.

Summing up the considered kinetic picture we should point out once again that the heterophase model of the induction period marks it as a macroscopic stage of chain cooxidation of an inhibitor and a polymer. Alkylphenol is active participant of the chain process in this stage and is generally expended in the acts of the cooxidation chain propagation, but not only in acts of chain termination. This period ends when the inhibitor concentration decreases, and the peroxyl concentration increases so that the oxygen absorption rate is already determined by reaction chains of the polymer oxidation [4–6, 25]:

$$\mathrm{POO}^\bullet + \mathrm{PH} \longrightarrow \mathrm{POOH} + \mathrm{P}^\bullet;\quad \mathrm{P}^\bullet + \mathrm{O}_2 \longrightarrow \mathrm{POO}^\bullet;$$

$$\mathrm{POO}^\bullet \rightarrow {}^\bullet\mathrm{POOH} \longrightarrow \mathrm{HO}^\bullet + \text{products};\quad \mathrm{HO}^\bullet + \mathrm{PH} \longrightarrow \mathrm{P}^\bullet + \mathrm{H_2O},$$

and bimolecular acts of chain termination:

$$\mathrm{POO}^\bullet + \mathrm{POO}^\bullet \longrightarrow \text{products}.$$

In this case, the key issue is that the oxidation process with inhibitor, as well as after its full exhaustion, does not fall into the regime with nondegenerated (avalanche-like) branchings of the reaction chains. Transition from the cooxidation stage to the stage of polymer oxidation proceeds under the condition of the peroxyl steady state concentration. Similar conditions remains at the cooxidation regime change from zero order by phenol to an apparent order one on dialkylsulfide injection into polymer.

Here we should mention that the indution period increase, accompanying the change of the regime, is displayed often on curves $t_{\text{ind}}(c_{i0})$ with particular sharpness, and phenol concentration at the breakpoint of the curve is interpreted as the critical concentration of the process transition from the nonstationary regime of the branched chain reaction to the stationary oxidation [14]. The idea of existence of the stage with nonstationary branchings is confirmed by the authors of [14] by the notion that at relatively high temperature of ~ 473 K hydroperoxide the lifetime is counted by seconds. In this case the authors do not take into account the chain heterophase mechanism of anaerobic HP decomposition.

In absence of oxygen, HP decomposition proceeds according to the chain mechanism, and contribution of spontaneous decomposition to total HP expenditure is negligibly small (see part 4) [5, 6]. Although at $T \sim 473$ K HP the lifetime in s-micropores is measured in tens of seconds according to equation (4.4), the dissociative lifetime of main HP amount localized in narrow micropores of chain sponge v-zones is significantly higher. It is important in this case that a half of polystyrene HP is expended in absence of oxygen during 12–15 min at $T = 453$ K. In oxidizing polystyrene melt, (in presence of oxygen HP decomposition mechanism is changed [4]), the hydroperoxide is accumulated together with other oxidation products during 30 and 100 min [45] at $T = 473$ and 453 K, respectively. It does not decompose noticeably until entering the reaction with accumulated products of the polymer oxidation. After that further HP accumulation ends and its concentration decreases.

The material of the present review shows the inadequacy of explanation of 'critical' phenol concentration, presented in [14]. From the point of view of the structural-kinetic reaction model, the breakpoint of $t_{\text{ind}}(c_{i0})$ curve, induced by dialkylsulfide, is stipulated by the phenol expenditure rate decrease during cooxidation stage at transition from the zero order reaction to the first order by inhibitor. This occurs at quasi stationary peroxyl concentration condition and in absence of nonstationary branching of reaction chains.

Inhibitor expenditure rate is constant in the regime of the zero order kinetics

$$-\frac{dc_i}{dt} = V_i = \frac{c_{i0}}{t^i_{\text{ind}}} = \text{const},$$

and respective time of its complete exhaustion (cooxidation) is

$$t^i_{\text{ind}} = \frac{c_{i0}}{V_i}.$$

Adding to this value the reaction development time t_0 after inhibitor exhaustion, we obtain the dependence of the induction period on the initial phenol concentration:

$$t_{\text{ind}} = t_0 + t^i_{\text{ind}} = t_0 + (V_i^{-1})c_{i0}.$$

The linear dependence $t_{\text{ind}}(c_{i0})$ holds for a wide range of monophenol concentrations, studied in [39–41]. In presence of dialkylsulfide the curves $t_{\text{ind}}(c_{i0})$ display a sharp increase of t_{ind} starting from some 'critical' value $c_{i0,cr}$. Similar situation occurs in the case of bisphenol 2246 both in presence and in absence of dialkylsulfide. The cooxidation process in these systems at $c_{i0} > c_{i0,cr}$ (and $c_{ii0} > c_{ii0,cr}$) conforms to first order kinetics characterized by exponential equation

$$c_i = c_{i0}\exp(-k_i t),$$

$$\ln\left(\frac{c_{i0}}{c_i}\right) = -k_i t.$$

This equation holds until $c_{i0,cr}$ value is reached (when the law of the reaction chain termination changes and bimolecular termination $POO^\bullet + POO^\bullet \rightarrow$ products' occurs instead of the linear reaction chain termination on inhibitor molecule).

In this case the total induction period is presented by

$$t_{\text{ind}} = t_0 + (k_i^{-1}) \ln\left(\frac{c_{i0}}{c_{i,cr}}\right).$$

Such dependence is often fulfilled [14].

The presented structural-kinetic model of phenol and polymer cooxidation allows us also to define more exactly the physical nature of monophenol and bisphenol 2246 antagonism at their cooperative injection to polymer, observed in [14, 39, 40]. Despite the increase of the total content of inhibitor, such systems display the induction period decrease in comparison with its value characteristic for single bisphenol 2246.

To account for this phenomenon the authors apply the idea about specific monophenol and bisphenol influence on radical yield from a 'cage' of spontaneously decomposed hydroperoxide. It is assumed that accepting one of radicals from primary radical pair, monophenol impedes the next radical combination, and the radical yield should consequently increase. At the same time, bisphenol 2246 possessing two functional groups, induces no increase of radical yield or increases it less than the monophenol does.

At the same time, despite the above mentioned concept, the material considered in parts 5 and 6 of the present review proves the absence of any significant increase of radical yield from hydroperoxide under ionol effect.

The cause of this effect is that monophenol increases the initiation rate of the cooxidation reaction *v*-chains as a consequence of the increase of free valence transfer rate from *s*-zones to *v*-zones of the polymer-chain sponge. In this case we mean by the reaction 'cage' the general system of supermicropores of structural *s*-zones, and not the homogeneous surrounding formed by polymer chain segments.

Interacting with radical-mediator peroxyl monophenol transforms into quinolic alkoxyl:

$$\mathrm{ROO}_m^{\bullet} + \mathrm{IH} \rightarrow \mathrm{ROOIH}^{\bullet} \longrightarrow \mathrm{ROH} + \mathrm{IO}^{\bullet},$$

which is incapable to isomerize into inactive phenoxyl: it displays $\delta_i = k_m$ contrary to $\delta_{ii} < k_m$ for bisphenol 2246 (equation (8.3)).

Competing with bisphenol for the radical *s*, *v*-transfer, monophenol increases the rate of the cooxidation chain initiation in *v*-zones of the polymer matrix, so it decreases the induction period.

Finishing the present part, we should mention that sterically hindered monophenols from works [41, 43] displayed no transition to the first order reaction in all studied range of their concentrations. However it could not be excluded that such transition will become possible for phenols with lower hindrance for example from alkyl groups and at significantly high concentration c_i. This requires that conditions are favorable for reversibly dissociating phenol complex with oxygen

$$IH_s + O_{2s} \longleftrightarrow (I^{\bullet} \cdots HOO^{\bullet})_s$$

to obtain help, required for it, from another phenol molecule

$$(I^{\bullet} \cdots HOO^{\bullet})_s + IH_s \longrightarrow I^{\bullet}_s + HOOIH^{\bullet}_s;$$

$$HOOIH^{\bullet}_s \longrightarrow H_2O + IO^{\bullet}_s.$$

It should be taken into account that weakening of steric hindrances may induce the occurrence of additional acts of the cooxidation chain termination:

$$IO^{\bullet} + IH \longrightarrow IOH + I^{\bullet}.$$

It is probable that the mentioned properties are responsible for the fact that antioxidant 4,4'-methylene-bis-(2-methyl-6-tert-butylphenol), possessing spatially separated OH-groups in its molecule, displayed the same effectiveness as bisphenol 2246 did [46], and was calssified as weak antioxidant [14]. The occurrence of the above mentioned termination acts may also serve as one of the reasons of synergism in antioxidant mixtures.

9. CONCLUSION

Principles of application of heterogeneous reaction models to description of the chain process proceeding in noncrystalline polymer body matrix were considered in the present review. Basic experimental material required for composing such models was obtained with the help of the model chain reaction of macromolecule arylation by dibenzoyl peroxide. Such study of this reaction on a number of polymers, performed in their glassy-like, highly elastic and melt states allowed us to elucidate its significant kinetic features which differ from dibenzoyl peroxide reactions with liquid analogs of studied polymers.

The concepts, worked out with the help of the model reaction, make possible a detailed consideration of the morphological model of supermolecular organization, disclosing the fine structure of polymer globule interior, which is the main structural unit of the noncristalline polymer spatial carcass.

The existence of a definite interconnection between microheterogeneous composition of noncrystalline polymer matrix and chemistry of polymer transformations has been pointed out in literature during long time on examples of particular processes. However, the separate investigations which displayed just statements of existence of this interconnection have not been yet united into an independent branch of chemical physics of polymers. We could point out that the existence of this interconnection was more or less generally displayed in the model of polychromatic [47] (or polychronic [48]) kinetics. However, the methodology of kinetic polychromatism description is reduced to just one or another variant of mathe- matical formality applying most general physical concepts.

It is evident that construction of adequate chemico-physical models of polymer transformations is undoubtedly connected with the improvement of particular picture of the supermolecular organization of polymer reaction medium. The existence of true microheterogeneous chain-sponge organi- zation of polymer chains significantly increases (if compared with the homogeneous liquid) the number of factors, capable to affect a chemical process in any way, and increases the difficulties connected with formulation of theories. The solution of this problem was possible with the formulation and testing of structural-kinetic reaction models [10].

Models of chain processes, considered in the present review, account in the calculation for the fine structure of polymer chain-sponge micelles contain a more or less dynamic carcass. In present models the dynamics is connected with the property of micropores which change their sizes under the influence of thermofluctions of cooperative units of flexible polymer chains in the structure of microporous sponge. This is different from the abstract idea of a 'molecular-segmental mobility'.

Structural-kinetic modelling method allowed us to find such important regimes of chain reactions as heterogeneous-heterophase and heterogeneous-homophase ones. It also allowed us to improve the concepts of the cryptoradical ('intracage') process, performed inside a micropore which is thermofluctuationally excited up to a supermicropore size.

At least, the construction and analysis of various reaction models make it possible to assume that general conception of chemistry of the microheterogeneous polymer-chain sponge proved its suitability. Broad possibilities remain for further improvement and detailed study of the mechanism of elementary chemical stages proceeding in the fluctuating sponge body medium.

At the present time we have to refuse the idea that the process of polyolefine oxidation, which develops on autoaccelerated stage, may be interpreted in the ranges of nonstationary branched chain reaction mechanism.

It is also assumed [14] that absence of significant deviations from the first order law for inhibitors points out its expenditure preferably in the reaction of direct interaction with oxygen and in acts of oxidative chain termination, initiated in this case. However, it was shown in the present review that the general amount of phenol is expended in chain cooxidation with a polymer in both order one and order zero by inhibitor.

The criterion of the inhibitor method of determination of oxidative chain initiation rate, formulated for homogeneous liquids [15], does also lose its fundamental meaning if applied to polymers. Contrary to homogeneous liquid, the fact of kinetic order zero of inhibitor expenditure does not prove the absence of other acts of inhibitor, except the reaction chain termination, in the microheterogeneous chain-sponge medium. Inhibitor molecules, located in polymer matrix and intercepting all reaction chains, are capable to set free reactive radicals as well as inactive ones and become active participants of cooxidation with polymer.

The present review is the logical continuation of investigations, performed by academician N.M. Emanuel and his school in the branch of science about oxidative processes in the condensed phase [49–53].

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