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Characteristic features of heterophase macromolecular chain reactions involving antioxidants in a non-crystalline polymer matrix

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Abstract. The principles of kinetic modelling of free-radical chain processes initiated in an amorphous polymer matrix are presented. The chemical modelling was based on a micellar-sponge model of the supermolecular structure, which takes into account the behaviour of the heterogeneous zones, differing in size and fluctuational dynamics of micropores forming these zones. The influence of antioxidants on chain processes is associated with the existence of conjugated reaction chains localised in various zones of chain-sponge micelles. Considerable attention is paid to the mechanism of autooxidation of polyalkenes, containing sterically hindered alkylphenols, during the induction period. The induction period preceding the oxidation of a polymer is considered as a stage involving chain co-oxidation of the antioxidant and the polymer, which follows zero- or first-order kinetics with respect to the antioxidant (alkylphenol) depending on its molecular structure. The bibliography includes 54 references.

I. Introduction

According to the morphological model of a noncrystalline polymer, developed recently,[1–9] an amorphous polymer consists of globules occurring in close contact with one another and incorporating large numbers of sponge-like polymer chains. An intraglobule chain-sponge micelle is considered as a chemical reactor. Two types of structural zones are distinguished within a micelle. In these zones, chain units experience unequal mechanical tension; they are confined by micropores, the real traps for reactive species, which have different sizes and are characterised by different fluctuation dynamics. Consequently, non-equivalent conditions for the excitation of generation, propagation and termination of reaction chains are developed in different zones .

The closest packing of polymer chains cannot be achieved inside the globules; the degree of their loosening remains higher than that in a θ-solvent. This is due to the fact that globules in a block polymer are joined through their shells, the latter forming a continuous spatial p-framework.[1,2,6,8] Paracrystalline domains of this p-framework, formed from small sections of chain units, act as mechanical clamps preventing the main regions of the polymer chains inside the globules from assuming a conformation of statistical knots characterised by maximum close packing.

The combination of spatial stretching fixed by the p-framework with the flexibility of polymer chains predetermines many features distinguishing amorphous polymers from homogeneous liquids. For example, there exist indirect methods that make glassy polymers compatible with low-molecular-weight compounds, although they are not mixed spontaneously upon direct contact.[7] Many initiators and inhibitors of chain processes, used practically, which are sufficiently volatile and have access to the inner surfaces of structural cavities in a glassy polymer can be absorbed in it but only in minor amounts. However, larger amounts of the same compounds can often be introduced into the polymer from their joint solution in a common solvent at the stage of solvent evaporation.[7]

It is known that solvent molecules can exchange places, more or less easily, with chain segments, which ensures high entropy of mixing, and an intraglobule sponge micelle is thus converted into a liquid drop of a joint solution.[9] A non-solvent molecule of a foreign admixture, which occupies in a chain sponge the site formerly belonging to a solvent molecule, is forced to push the polymer chain units apart, thus preventing them from packing more closely and, to some extent, ordering them with respect to itself. Consequently, a non-solvent molecule introduced into the sponge forms a micropore to 'match' its size, which is larger than the micropore existing without the admixture, and thus creates room for itself. The crowded sponge is compressed and, pressing against the paracrystalline globule shell, it in turn exerts an influence on the admixture through the surface forces of the micropore walls, which encapsulate the admixture molecule. Since the elastic forces of the sponge and the dispersion forces of interaction of the micropore surface with the admixed molecule

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are balanced with one another, the admixed molecule is localised within the pore and thus has more freedom to rotate.

Polymer chains that have no opportunity to form close packing within a sponge micellar structure but tend to reach the highest cohesion density, create zones containing micropores with different sizes. In the absence of admixtures, a grain is formed inside a globule bound in a framework; the grain contains narrow micropores with sizes of up to 0.5 nm, which corresponds in order of magnitude to the thickness of the polymer chain.

Such a grain (called v-zone) is separated from the walls of the p-framework cell (*i.e.* from the shell of the globule) by a spherical layer of stretched chain segments oriented in radial directions in the globule. These segments act as mechanical tension wires and fix a layer of stationary super-s-micropores, the sizes of which are close to the length of a thermodynamic segment (1.5 – 3.0 nm).

The presence of separate microporous zones within the p-framework cells accounts for the heterogeneous distribution of molecules of admixtures (for example, initiators, inhibitors, oxygen, etc.). The greater part of an admixture is accumulated in the internal v-grains, because the energy of sorption in the narrow v-micropores of these grains is larger than that in the ample s-micropores. As has already been noted, upon capturing an admixture, the narrow v-micropores are forced to become larger, which ensures a fairly high frequency of rotation of admixed particles. The frequency of steps of migration of the admixed particles along the micropore system also increases. This is because thermal fluctuation pulsations of the sponge v-grains hanging on the walls of the p-framework stimulate the cooperative vibrations of the chain segments of the sponge. Owing to these fluctuations, a probability appears, although only for a short period, that the size of the narrow v-micropores will increase up to that of the s-micropores. Consequently, relatively small admixture particles become fairly free to move within the sponge, which enhances exchange between the v- and s-zones.

The functioning of stationary s-micropores and fluctuation-labile v-micropores in sponge micelles has an effect on the mechanism of initiated transformations, because molecules of an initiator migrate between the s- and v-zones thus changing their steric and energy states. Consequently, their initiating ability in these two zones would be different. In fact, in narrow v-micropores, the force fields of the opposite walls overlap. Under these conditions, the initiator molecule is pushed to the bulk of the pore and is mostly located there, executing only short-term fluctuation-activated jumps. Owing to the short duration of these jumps, even if a primary radical pair arises upon occasional decomposition of the initiator molecule in the v-zone, the radicals of this pair cannot move far from each other.

To the contrary, in ample s-micropores, conditions for the dissociation of initiator molecules are much more favourable than those in narrow v-micropores. This is due not only to the presence of free space but also to the fact that the force fields of the opposite walls do not overlap and, consequently, an admixed particle spends most of the time on the pore surface as an adsorbed species rather than within the pore bulk. Under these conditions, the radicals of a radical pair formed spontaneously do not experience compression forces any longer; instead, under the action of adsorption forces, they efficiently attack polymeric molecules.

The presence of dissimilar zones also influences the fate of the polymeric radicals, which are able to decompose with rupture of the chains. It is clear that the probability of this event occurring on the surface of a compressed v-micropore is low, since this requires that a series of segments ensuring the fixing of the v-micropore walls would shift synchronously, which is possible only if the fluctuation mobility of the chain-sponge grains is very high.

At the same time, on the surface of s-micropores, the probability for the degradation of polymer radicals accompanied by chain rupture is substantially higher. This is due to the presence of free space and to mechanical stretching of the s-segments of polymer chains.

The above characteristic features of the heterogeneous structure of chain-sponge micelles constituting the matrix of a non-crystalline polymer make the problem of kinetic description of a chain process more complicated than that of a homogeneous reaction. To construct an adequate mechanism for a polymer transformation, one must take into account the heterogeneity of the system and abandon the simplified representation of the reaction medium as a structureless liquid-phase system. This resembles the situation, which arose at one time in the field of heterogeneous catalysis;[10] therefore, the current problem could also be solved by design and selection of structural-kinetic models for reactions.

The modelling of chain transformations of polymers has been started with consideration of a model chain reaction of dibenzoyl peroxide (BP) with polymers of various structures (cellulose triacetate, polycarbonate, polystyrene and polyamide PA-548).[3,9,11–13] Later, chain decomposition of polymeric peroxides has been modelled.[5,6]

According to the views of that time on a heterogeneous reaction, a complete representation of a transformation should include: (1) a scheme for the primary reaction chains, which propagate in the ample micropores of s-zones of sponge micelles; (2) a scheme for the secondary reaction chains, which occur in the narrow micropores of v-zones; and (3) a scheme for the transfer of free radicals between the zones.

It may be expected that peculiar features of the supermolecular organisation of polymer chains will also influence the transformations of antioxidants used to stabilise polymeric materials during their processing and operation. Antioxidants have been widely employed in polymers since the polymers themselves came into universal use; however, up to now, the development of scientific views about the mechanism of their protective effect has remained within the framework of theories of homogeneous reactions.[14–16] At the same time, the study of model chain reactions of dibenzoyl peroxide with polymers made it possible to discover significant specific features of the influence of phenolic antioxidants on this process resulting from microheterogeneity of the polymer matrix.[17,18] In this review, we report briefly these results and analyse some important published data on the mechanism of the action of antioxidants, which have not yet been adequately explained. A structural-kinetic reaction model is developed, which discloses the physical essence of the action of antioxidants in a real heterogeneous process, polymer ageing. This model necessitates complete revision of the attitude towards the postulates, transferred from the theory of homogeneous reactions to the chemistry of polymers.

II. The mechanism of the influence of 2,6-di-*tert*-butyl-4-methylphenol on the anaerobic chain reaction of dibenzoyl peroxide with glassy cellulose triacetate and polycarbonate

1. Regularities of a model reaction

Studies of the reaction of BP with cellulose triacetate (CTA) and polycarbonate (PC)[2,11] included measurements of the kinetics of consumption of BP ($T \leqslant 371$ K) and of accumulation of benzoic acid and phenyl benzoate and determination of the numbers of ruptured polymeric bonds and decomposition fragments of BP grafted to polymer chains.

Spontaneous decomposition of BP was found to occur in those structural zones of the polymer matrix in which macroradicals do not induce decomposition of BP and the related addition of the peroxide fragments to the polymer. The effective rate constant k_0 for the spontaneous decomposition of CTA or PC at 371 K is 4.8×10^{-3} min^{-1} (the activation energy E_0 = 117 kJ mol^{-1}). The rate constant is described by the expression $k_0 = k_{0s} K_e m_s m_v^{-1}$, where m_s and m_v are masses of the s- and v-zones, respectively, k_{0s} is the rate constant for decomposition of

BP in s-micropores, and K_e is the equilibrium constant for the interzone distribution

$$BP_v \rightleftharpoons BP_s .$$

The condition of equilibrium for the BP exchange between the zones has the following form:

$$c_s = K_e c_v \approx \frac{K_e c}{\alpha}, \quad (1)$$

where c_s, c_v and c are the concentrations of BP in s-zones, in v-zones, and in the whole sample, respectively; α is the mass fraction of sponge micelles consisting of both types of zones. This equilibrium, which ensures heterogeneous generation of radicals from the very beginning of the process, is not disturbed during the decomposition of BP, the rate of which is much lower than the rate of the interzone exchange.

Spontaneous decomposition of BP gives molecular products in high yields. These are phenyl benzoate and products resulting from the addition of radicals derived from BP to the benzene rings of PC. Benzoic acid and macroradicals with free valences located either in side groups ($R_s^{\cdot}$) or in the backbone ($P_s^{\cdot}$) are formed in a lower yield (the effective rate constant is $0.2k_0$). Decomposition of the latter is accompanied by chain rupture and by a decrease in the molecular weight of the polymer.

The terminal radicals arising upon destruction of the chain as well as the $R_s^{\cdot}$ radicals undergo transformations, which lead ultimately to the elimination of the free valence without formation of cross-linking bonds between the polymer chains.

The rate of accumulation of ruptured polymer chains and the variation of the concentration of breaks (n) with time during the processes involving CTA and PC are expressed by identical relations:

$$\frac{dn}{dt} = k_n c_0 \exp(-kt);$$

$$n = n_\infty [1 - \exp(-kt)]. \quad (2)$$

Here, c_0 is the initial concentration of BP in the sample; k is the effective rate constant for decomposition of BP; n_∞ is the limiting concentration of the ruptured chains; the k_n constant at 371 K is $0.062\,k_0$ and $0.14\,k_0$ for processes involving CTA and PC, respectively (if the polymer contains dissolved oxygen, k_n halves, due to the oxidation of radicals $R_s^{\cdot}$ yielding new radicals that react with the initial benzoyloxyl radicals);

Transformations of polymer chains in the v-zones differ from those in the zones of radical generation. They do not degrade but instead, they enter into a chain reaction with BP according to a simple stoichiometric ratio

$$BP + RH \longrightarrow rH + Rr$$

(here, the symbol r refers to a benzoyloxyl radical).

The overall process of decomposition of BP in sponge micelle zones is described by an exponential equation

$$c = c_0 \exp(-kt), \quad (3)$$

and the overall effective rate constant consists of the non-chain and chain components:

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

The coefficients k_c in the chain component are similar for the reactions involving CTA and PC, unlike the situation occurring in liquid-phase systems: the rate of decomposition of BP in aromatic liquids is lower than that in non-aromatic liquids.

It has been found[2,11] that the same reagents (BP molecules, polymer chain units, free benzoyloxyl radicals and macroradicals) exhibit different chemical properties in different structural zones. Three block schemes are used to describe the overall picture of transformations occurring in polymers in the absence of dissolved oxygen.

The s-scheme describes generation of radicals and their subsequent transformations in zones of s-micropores. The process starts with the steps of formation of primary radical pairs:

$$BP_s \xrightarrow{k_{0s}} \{ r_s^{\cdot} \ldots r_s^{\cdot} \},$$

$$\{ r_s^{\cdot} \ldots r_s^{\cdot} \} \xrightarrow{k_0'} 2r_s^{\cdot},$$

$$\{ r_s^{\cdot} \ldots r_s^{\cdot} \} \xrightarrow{k_0''} rPh + CO_2,$$

$$\{ r_s^{\cdot} \ldots r_s^{\cdot} \} \xrightarrow{k_0'''} rPCr .$$

The liberated primary benzoyloxyl radicals undergo further transformations:

$$r_s^{\cdot} \xrightarrow{k_{1s}(PH_s)} rH + P_s^{\cdot},$$

$$r_s^{\cdot} \xrightarrow{k_{2s}(RH_s)} rH + R_s^{\cdot},$$

$$P_s^{\cdot} \xrightarrow{k_{3s}} R_s^{\cdot} + \text{rupture of the polymeric chain},$$

$$R_s^{\cdot} \xrightarrow{k_{4s}} R_{1s}^{\cdot} \text{ (isomerisation)},$$

$$R_s^{\cdot} + R_{1s}^{\cdot} \longrightarrow \text{products}$$

(here, the symbols $P_s^{\cdot}$ and $R_s^{\cdot}$ refer to radicals with the free valence in the backbone and in the side groups, respectively).

The transfer of radicals from the s-zone to the v-zone in the absence of oxygen in the samples is described by the tr-scheme:

$$r_s^{\cdot} + AH_s \xrightarrow{k_1} rAH_s^{\cdot},$$

$$rAH_s^{\cdot} + BP_s \longrightarrow rA + rH + r^{\cdot}$$

(here, the symbol A denotes the phenyl group of both the initial BP and the benzoic acid and phenyl benzoate formed). This scheme characterises the sequence of events occurring at a favourable arrangement of the species participating in this reaction bridge and surrounded by rigidly fixed chain segments, which confine s-micropores.

As a result of this s,v-transfer, the probability of which is low and which has no influence on the steady-state concentrations of s-radicals, secondary benzoyloxyl radicals $r^{\cdot}$ responsible for chain arylation of macromolecules appear in v-zones. The corresponding v-scheme has the following form:

$$r^{\cdot} + RH \xrightarrow{k_2} rH + R^{\cdot},$$

$$R^{\cdot} + BP_v \xrightarrow{k_3} RC_6H_4COOH + r^{\cdot},$$

$$R^{\cdot} + BP_v \xrightarrow{k_3} RPh + CO_2 + r^{\cdot}$$

(indices at the reagents are omitted, except for BP_v, the symbol $R^{\cdot}$ corresponds to a radical with the free valence at a side-chain group, $-CH_2^{\cdot}$). These reaction v-chains are terminated *via* the departure of mobile benzoyloxyl radicals to s-zones):

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

This v-scheme does not take into account the differences between the chemical structures of non-aromatic CTA and aromatic PC, which is consistent with experimental results; it does not also include steps of interaction of the aromatic rings of PC with light radicals and steps of decomposition

$$r^{\cdot} \longrightarrow Ph^{\cdot} + CO_2 .$$

Whereas the $r_s^{\cdot}$ radical can add to the rings of PC in s-zones, this is apparently impossible in v-zones, because the rings in the v-framework cannot undergo conformational changes needed for the addition to proceed at intermediate stages.

The fact that decarboxylation of benzoyloxyl radicals in v-zones is absent for both polymers implies that one molecule of benzoic acid is formed in each unit of the chain decomposition of BP. This differs completely from the observations made for the reactions carried out in liquids in which the probability of decarboxylation of benzoyloxyl radicals is close to 100%. This distinction can be explained by the fact that rigid monomeric units in CTA and PC are fairly large and the volume of v-micropores is relatively small; consequently, the $r^{\cdot}$ radicals spend a lot of time on the rigid walls of the v-framework and thus have a good chance of abstracting hydrogen atoms from the alkyl substituents of macromolecules.

It should be noted that chain arylation of polymers decreases the total number of free phenyl groups, but this does not change the efficiency of the s, v-transfer involving them. This is due to the fact that the loss of a binuclear BP molecule is accompanied by the formation of a mononuclear benzoic acid molecule, which migrates along the system of micropores twice as fast as the molecule of BP. Hence, the probability of the interzone transfer of free valence is retained.[2, 9, 11]

The non-equivalent reactivity of the same species in s- and v-zones, reflected in the above schemes, can be expressed in terms of the corresponding kinetic equations.

For example, the local rate of decomposition of BP in s-zones is described by the following equation

$$-\frac{dc_s}{dt} = k_{0s}\, c_s = \frac{k_{0s} K_e c}{\alpha}, \qquad (4)$$

while that in v-zones is described by another equation

$$-\frac{dc_v}{dt} = k_3 [R^{\cdot}] c_v = k_2 [r^{\cdot}][RH].$$

The concentration of benzoyloxyl radicals $[r^{\cdot}]$ can be found from the condition of equal rates of generation and termination of the reaction v-chains [9]

$$V_{tr} = k_4 [r^{\cdot}],$$

where

$$V_{tr} = k_1 [r_s^{\cdot}][PH_s] = 2\varphi k_1 \frac{[PH_s] k_{0s} c_s}{k_{1s} [PH_s]} \quad \text{(Ref. 9)},$$

$$\varphi = \frac{k_0^{'}}{k_0^{'} + k_0^{''} + k_0^{'''}},$$

$$[PH_s] = 2\,\frac{K_e c_0}{\alpha}.$$

After the necessary substitutions, we obtain

$$-\frac{dc_v}{dt} = k_2 [r^{\cdot}][RH] = \frac{k_2 [RH] V_{tr}}{k_4} =$$

$$= 4\varphi \frac{k_2 [RH] k_1 K_e \alpha^{-1} c_0 (k_{0s} K_e \alpha^{-1}) c}{k_4 k_{1s} [PH_s]}. \qquad (5)$$

Now we pass from the local specific reaction rates in s- and v-zones to the overall reaction rate in the sample on the whole. This is calculated from the formula

$$-\frac{dc}{dt} = -\frac{m_s}{m}\frac{dc_s}{dt} - \frac{m_v}{m}\frac{dc_v}{dt}$$

where m_s, m_v and m are masses of s-zones, v-zones, and the whole sample, respectively. Taking into account the relation

$$\alpha = \frac{m_s + m_v}{m} \approx \frac{m_v}{m}$$

and Eqns (4) and (5), we obtain the following expression for the overall rate of the decomposition of BP

$$-\frac{dc}{dt} = k_0 c + k_c k_0 c_0 c = (k_0 + k_c k_0 c_0) c. \qquad (6)$$

The rate of destruction, which occurs only in s-zones according to the s-scheme, is equal to

$$\frac{dn}{dt} = k_{3s} [P_s^{\cdot}] = k_{1s} [r_s^{\cdot}] [PH_s] = 2\varphi k_{0s} c_s =$$

$$= \frac{2\varphi K_e k_{0s} c}{\alpha} = \frac{2\varphi m k_0 c}{m_s} = k_n c. \qquad (7)$$

Both theoretical expressions, (6) and (7), are fully consistent with empirical formulae (2) and (3) and disclose the physical essence of heterophase transformations of units of polymeric-chain sponge in the inhomogeneous structural zones.

The heterophase scheme under consideration can be used equally well to explain the kinetic regularities of the formation of products of non-chain and chain reactions such as phenyl benzoate, benzoic acid and arylated macromolecules.

2. Characteristic features of the model anaerobic reaction in the presence of ionol

The non-equivalence of transformations of reagents in different structural zones of sponge micelles is also retained when ionol (2,6-di-*tert*-butyl-4-methylphenol, IH) is present as an admixture. The influence of this substance on model reactions of BP with polymers has been studied.[17, 18]

Ionol itself influences the processes occurring in s- and v-zones in different ways. For example, ionol present in a relatively low concentration, $c_i \approx 0.05$ mol kg^{-1}, causes virtually complete termination of chain arylation of polymers, whereas the process of initiated destruction is only slightly decelerated even at very high c_i. In the case of PC, as c_i varies from 0.023 to 0.64 mol kg^{-1}, the rate constant for destruction (k_n) decreases only by one half and then remains constant.

In terms of the theoretical model for a heterophase reaction, this is explained by the two-fold decrease in concentration of primary benzoyloxyl radicals $r_s^{\cdot}$ due to their interaction with the phenoxyl radicals arising *via* the reaction of ionol with side-chain and terminal macroradicals $R_s^{\cdot}$.

$$R_s^{\cdot} + IH_s \xrightarrow{k_{5s}} RH + I_s^{\cdot},$$

$$I_s^{\cdot} + r_s^{\cdot} \longrightarrow Ir.$$

Thus, expression (7) for the rate of destruction assumes the form

$$\frac{dn}{dt} = 0.5\, k_n c. \qquad (8)$$

The fact that the rate constant for destruction (k_n) decreases in the presence of ionol by only 50% indicates that the efficiency of direct interaction of ionol with primary benzoyloxyl radicals in a PC matrix is extremely low. Apparently, the spatial arrangement of these reagents adsorbed on the walls of s-micropores is unfavourable for the reaction.

Figure 1 presents the results obtained by analysis of the decomposition of dibenzoyl peroxide in PC in terms of the heterophase scheme. The character of the curves describing the accumulation of ruptured polymer bonds (*2–4*) indicates that the limiting concentrations of the ruptured bonds decrease upon an increase in c_i, because BP is consumed in another reaction, the mechanism of which will be considered below. Here we only

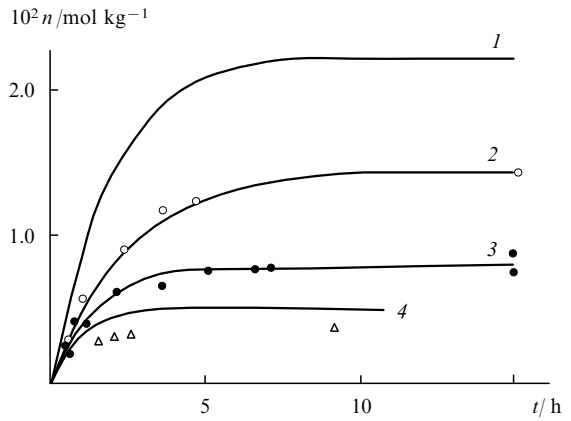


Figure 1. Accumulation of broken polymeric chains during decomposition of 0.29 mol kg^{-1} of dibenzoyl peroxide at 371 K in evacuated polycarbonate films containing ionol in concentrations, c_i / mol kg^{-1}: 0 (*1*); 0.023 (*2*); 0.32 (*3*); 0.64 (*4*).
Curves (*1–4*) were obtained by calculations, and the points show the experimental results.

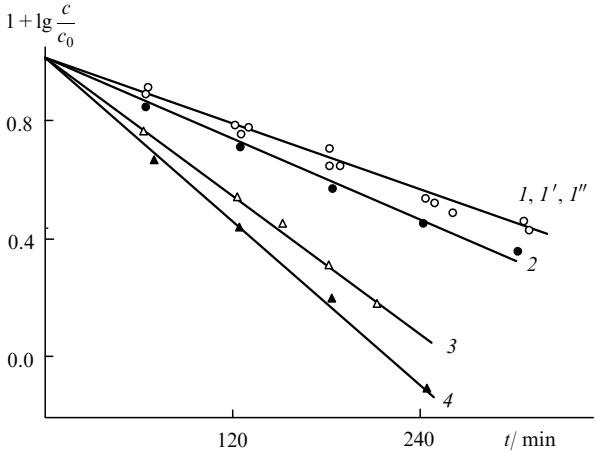


Figure 2. Semilogarithmic plots for the curves for consumption of dibenzoyl peroxide at 371 K in aerated (*1*) and evacuated (*2–4*) cellulose triacetate films containing BP and ionol in concentrations, mol kg^{-1}: for (*1*), (*1′*), and (*1″*) — c_0 = 0.02, 0.25, and 0.63, c_{i0} = 0.08, 0.10, and 0.11, respectively; (*2*) — c_0 = 0.02, c_{i0} = 0.027; (*3*) — c_0 = 0.66, c_{i0} = 0.042; (*4*) — c_0 = 0.02, c_{i0} = 0.27.

mention that according to Eqn (8), the initial rate of the destruction, which can be found from the initial sections of curves *2–4*, decreases by only one half with respect to the initial rate of the destruction of PC in the absence of ionol (Fig. 1, curve *1*).

Some deviation of the calculated curve *4* from the experimental points is due to the fact that for very high c_i values, the contribution of the direct reaction between ionol and primary benzoyloxyl radicals

$$r_s^{\bullet} + IH_s \xrightarrow{k_{6s}} rH + I_s^{\bullet},$$

$$I_s^{\bullet} + r_s^{\bullet} \longrightarrow Ir,$$

which is not taken into account, becomes noticeable. In the reaction involving CTA, this contribution is greater; however, in this case too, destruction is not terminated completely even at a high concentration of ionol, $c_i = 0.32$ mol kg^{-1}.

In the v-zones of chain-sponge micelles, in which decomposition of BP induced by macroradicals is inhibited even at low c_i, ionol reacts with benzoyloxyl radicals in a completely different way. This is manifested both in a decrease in the effective rate constant (k_i) for the consumption of BP and in the fact that the synthesis of arylated macromolecules ceases.

The overall process of BP decomposition in the presence of ionol obeys an exponential kinetic law

$$c = c_0 \exp(-k_i t), \qquad (9)$$

According to this equation, the k_i constant, which characterises this reaction at any degree of conversion, depends on the initial concentrations of BP (c_0) and ionol (c_{i0}). To illustrate this, several $c(t)$ dependences plotted in semilogarithmic coordinates and referring to the decomposition of BP in CTA films, are presented in Fig. 2.

It can be seen from Fig. 2 that the smallest k_i value is achieved in those samples, which have been heated in air (curve *1*); in this case, k_i coincides with the constant k_0 for spontaneous decomposition of BP. For c_0 and c_{i0} ranging over the same limits but in the absence of oxygen, k_i varies in a complex manner: at low c_0 (0.02 mol kg^{-1}), it increases proportionally to c_i (Fig. 3, straight line *1*), whereas at high c_0, it sharply diminishes as c_i increases, reaches a minimum at $c_i = 0.05$ mol kg^{-1}, and then increases again (Fig. 3, curves *2*, *3* and *5*).

In the presence of ionol, a catalytic branch of BP decomposition appears (Fig. 3) in which the rate of chain decomposition under the action of macroradicals is negligibly small. Firstly, this is indicated by straight line *1* in Fig. 3: in this case, chain arylation

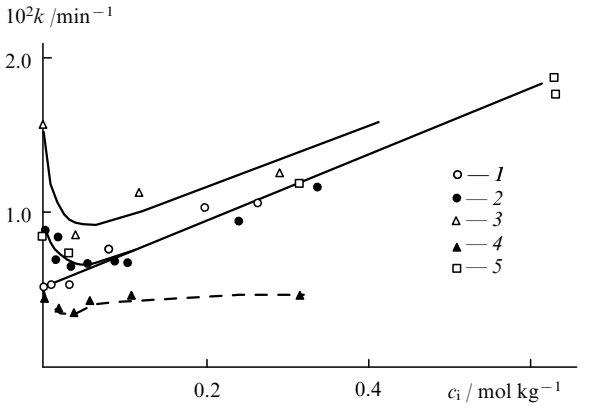


Figure 3. Dependence of the effective rate constant for the decomposition of BP at 371 K on the concentration of ionol in evacuated (*1–3*, *5*) and aerated (*4*) CTA (*1–4*) and PC (*5*) films containing BP in the following initial concentrations /mol kg^{-1}: 0.02 (*1*); 0.27 (*2*, *4*, *5*); 0.64 (*3*).

does not make significant contribution to the decomposition of BP even when no ionol is present, because c_0 is fairly low. Secondly, this is confirmed by the fact that the accumulation of arylation products, which is followed using the UV spectra of CTA, almost ceases after BP has wholly decomposed (in the range of c_0 from 0.15 to 0.7 mol kg^{-1}) and the decomposition products have been extracted with methanol (Fig. 4). The straight line *1* in Fig. 4 corresponds to chain grafting of BP fragments to CTA in the absence of ionol, and curve *2* corresponds to the same process in the presence of ionol ($c_{i0} = 0.22$ mol kg^{-1}). Curve *3* was constructed using measurements of the optical density at $\lambda = 333$ nm, which is beyond the absorption spectrum of grafted BP fragments, while curves *1* and *2* were obtained by measuring the optical density at the maximum of the absorption band of these fragments ($\lambda = 284$ nm). Complete correlation between curves *2* and *3* indicates that the formation of a minor amount of UV-absorbing products in this case is associated with grafting of only a small number of ionol groups and not of BP fragments to the polymer.

Speaking again about the reasons for the appearance of catalytic branches in the curves in Fig. 3, it should be mentioned that they refer to decomposition of BP caused by free radicals derived from ionol rather than by ionol molecules. This is why the

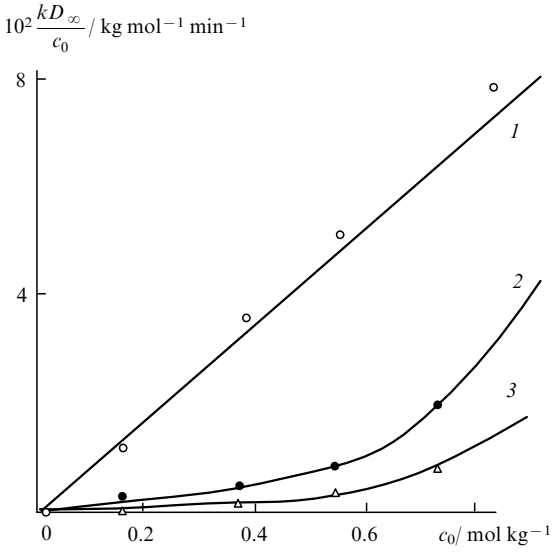


Figure 4. Dependence of the normalised optical density D_∞ of arylated CTA on the concentration of BP without antioxidant (*1*) and in the presence of 0.22 mol kg^{-1} of ionol (*2*, *3*). The D_∞ values were measured at an UV radiation wavelength of 284 (*1*, *2*) and 333 (*3*) nm for solutions of films in dichloromethane, after anaerobic decomposition of BP at 371 K and extraction of low-molecular-weight compounds from the films with methanol.

catalytic effect disappears completely when the polymer films contain dissolved air; the rate of decomposition of BP in aerated films is equal to the rate of its spontaneous decomposition (straight line *1* in Fig. 2 and curve *4* in Fig. 3).

Free phenoxyl cannot act as a radical carrying new chains of BP decomposition, since it ensures linear termination of chains of arylation of macromolecules. In addition, it is known that phenoxyl radicals derived from sterically hindered phenols (including ionol) are not oxidised by oxygen and dibenzoyl peroxide at 371 K.[19–21]

The σ-complex formed upon addition of benzoyloxyl to the benzene ring of ionol acts as a new initiator of the chain decomposition of BP. The formation of σ-complexes in reactions of ionol with alkyl macroradicals can be neglected, because the data presented in Fig. 4 indicate that the rate of this addition is low even at high concentrations of ionol (c_i = 0.22 mol kg^{-1}).

In solutions, ionol and other sterically hindered phenols also do not add alkyl radicals,[16] and their σ-complexes with benzoyloxyl radicals are extremely unstable; they rapidly dissociate into the initial species, r$^\cdot$ and IH, and exert no influence on the rate of decomposition of BP.[9, 19] However, admixture species in v-zones of chain-sponge micelles, unlike those in liquids, experience the effect of the overlapping surface forces from the closely spaced walls of v-micropores; consequently, these species are localised within the bulk of the pores. This favours mutual contacts between the species and hampers their dissociation. Recall that a similar structural effect of the chain sponge accounts for the decrease in the rate of dissociation of BP in narrow micropores of v-zones. For a similar reason, the stability of the ionol σ-complexes and the probability of their interaction with BP molecules migrating in v-zones increase.

These transformations of ionol can be represented by the following scheme:

$$r^\cdot + IH_v \xrightarrow{k_6} rIH^\cdot,$$

$$rIH^\cdot + BP_v \longrightarrow rI + rH + r^\cdot.$$

The termination of new reaction chains occurs both upon the migration of benzoyloxyl radicals from v-zones to s-zones (with rate constant k_4) and in processes involving the phenoxyl radicals formed

$$r^\cdot + IH_v \xrightarrow{k_7} rH + I^\cdot,$$

$$r^\cdot + I^\cdot \longrightarrow rI\,.$$

If we consider these reactions in terms of the above scheme for the decomposition of BP, it is not difficult to find out that they do not suffice to account for the increase in the constant k_i in the region of high c_{i0} values, since both the rate of the chain reaction (k_6) and the rate of chain termination (k_7) depend on c_i in the same manner.

The linear $k_i(c_i)$ dependence in the catalytic branches of the curves (see Fig. 3) indicates that an additional route for the injection of radicals from s-zones to v-zones, which involves ionol, should be considered:

$$r_s^\cdot + IH_s \xrightarrow{k_5} rIH_s^\cdot,$$

$$rIH_s^\cdot + BP_s \longrightarrow rI + rH + r^\cdot.$$

Now, taking into account both routes of the s,v-transfer of free valence (involving PhH and ionol) and the fact that the rates of generation and termination of the reaction v-chains are equal, we obtain an expression for the concentration of benzoyloxyl radicals in the v-zone:

$$[r^\cdot] = \frac{(k_1[PhH_s] + k_5 c_{is})[r_s^\cdot]}{k_4 + 2k_7 c_{iv}}. \qquad (10)$$

When the content of ionol (c_{i0}, c_{is} and c_{iv}) is relatively high, the concentration of r$^\cdot$ markedly decreases, and Eqn (10) is transformed into the following expression

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

which actually implies that [r$^\cdot$] does not depend on the concentration of ionol, because during the interzone exchange of ionol, the following equilibrium is established:

$$c_{is} = K_{ei} c_{iv} \approx \frac{K_{ei} c_{i0}}{\alpha},$$

(here K_{ei} is the constant of the corresponding equilibrium). Thus, Eqn (10) assumes the following form

$$[r^\cdot] = \text{const}\, k_0 c.$$

In conformity with the extended heterophase scheme, the rate of decomposition of BP in v-zones is the sum of two terms

$$-\frac{dc_v}{dt} = k_3[R^\cdot] c_v + k_6[r^\cdot] c_{iv} = k_2[r^\cdot][RH] + k_6[r^\cdot] c_{iv}. \qquad (11)$$

The contribution of the first term is significant only at very high concentrations of dibenzoyl peroxide c_0, because ionol decreases markedly the concentration of r$^\cdot$. Taking this into account, the overall rate of decomposition of BP in s- and v-zones can be approximated by the expression

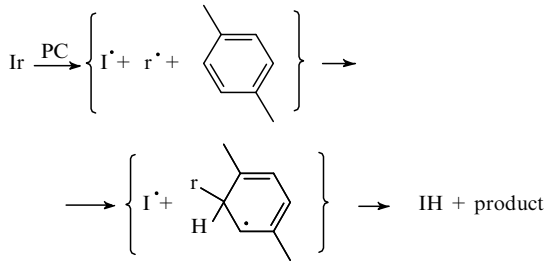
$$-\frac{dc}{dt} = k_0 c + k_i' c_{i0} c = (k_0 + k_i' c_{i0}) c = k_i c\,, \qquad (12)$$

which characterises the catalytic branch of decomposition of BP associated with the influence of ionol.

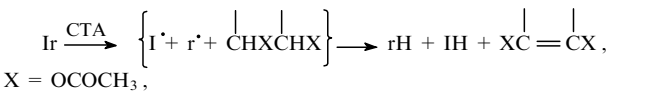
Here the following important circumstance should be recalled: the initial concentration of ionol c_{i0} appears in the expression for the effective rate constant k_i as a constant parameter at any ratios of c_{i0} and c_0 (Fig. 2, straight lines *2–4*). The fact that the c_{i0} is virtually invariant has been confirmed by IR spectroscopic analysis of CTA and PC films, which indicates that the intensity of IR absorbance by phenolic OH groups decreases only slightly

during the reaction.[17,18] This invariance of absorbance (which is also typical of the reaction of ionol with BP in a polystyrene matrix[9]) implies that a mechanism for the regeneration of ionol from the main product of the transformations, Ir, is accomplished in the polymers.

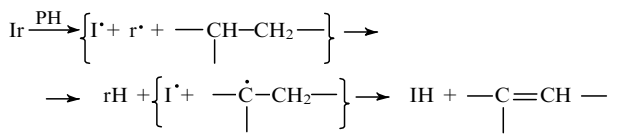
The compound Ir is unstable in solutions and dissociates quickly to give benzoyloxyl and phenoxyl radicals.[19] Apparently, molecules of this compound also dissociate in a polymer-chain sponge matrix on the walls of the fluctuationally excited v-micropores, which have become as large as s-micropores for a short period. The free radicals thus formed cause dehydrogenation of the polymer by one or another mechanism, depending on the structure of macromolecules. In the case of PC, the corresponding process can be represented in the following way:



Dehydrogenation of CTA occurs by the following scheme:

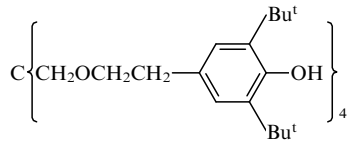


while the transformation in a carbocyclic polymer follows the scheme



The reactive species dehydrogenating the polymer should not leave their reaction cage, and the whole process, which occurs by a sort of 'latent radical' mechanism, should be accomplished over the life span of the excited state of the micropore.

The influence of other sterically hindered phenols studied by us, in particular, of the tetraphenol



and 2,4,6-tri-*tert*-butylphenol (at a relatively high concentration) on the decomposition of BP is qualitatively similar to that of ionol (Fig. 5, curves *2–4*). However, their catalytic efficiency is much lower (when the concentration of BP is small, tri-*tert*-butylphenol does not accelerate its decomposition at all, curve *1*), which is apparently due to the fact that the participation of these phenols in the steps in the interzone s, v-transfer of free valence is less probable. However, the results considered above clearly indicate that in the chain-micellar matrix of a polymer, the radicals with free valence on oxygen atoms add to the aromatic rings of the phenols, and the σ-complexes thus formed participate in subsequent transformations. Consequently, phenolic antioxidants act as carriers of the free valence between s- and v-zones and intrazone carriers of the reaction v-chains of the BP decomposition.

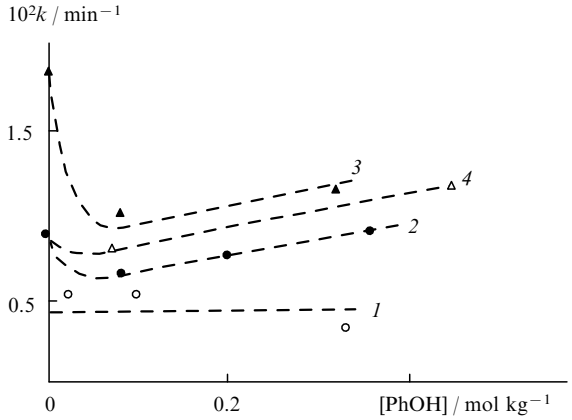


Figure 5. Dependence of the effective rate constant for the decomposition of BP at 371 K in evacuated CTA films on the concentration of 2,4,6-tri-*tert*-butylphenol (*1–3*) and on the concentration of phenolic groups of the tetraphenol 'Irganox-1010' (*4*) at c_0 / mol kg^{-1}: 0.023 (*1*) ; 0.2 (*2*, *4*); 0.76 (*3*).

III. Specific features of the model reaction in the presence of bisphenol

In the presence of 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) or bisphenol 2246 (HIIH), the rate of anaerobic decomposition of BP in glassy CTA increases to even a greater degree.[22] The curves describing the decomposition of BP in the presence of HIIH, plotted on semilogarithmic coordinates (Fig. 6), indicate that in this case, too, the process obeys an exponential law. However, unlike the situation with ionol, the apparent rate constant k_m for decomposition of BP in the presence of bisphenol increases in the catalytic stage proportionally to the squared concentration of the phenolic groups c_m (c_m = 2[HIIH]). The corresponding dependence of k_m on c_m^2 is shown in Fig. 7.

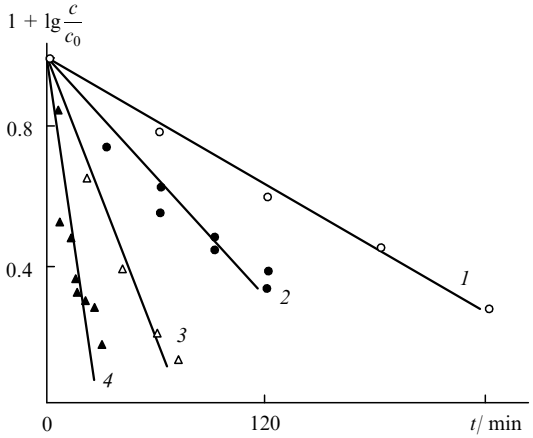


Figure 6. Influence of the concentration of phenol groups of 2,2′-bis-(6-*tert*-butyl-4-methylphenol) on the transforms of the curves for decomposition of BP (c_0 = 0.37 mol kg^{-1}) at 371 K in evacuated CTA films. 2[HIIH] / mol kg^{-1}: 0.06 (*1*), 0.18 (*2*), 0.40 (*3*), 0.64 (*4*).

It can be seen that in the region of low c_m, this plot contains a very short section in which k_m decreases and a fairly extended catalytic branch. The first portion is due to the inhibition of the chain arylation of CTA; it was briefly considered in the previous Section. Here we shall discuss the mechanism of catalysis by bisphenol, the efficiency of which is much higher than that of catalysis by ionol and reaches a maximum value of

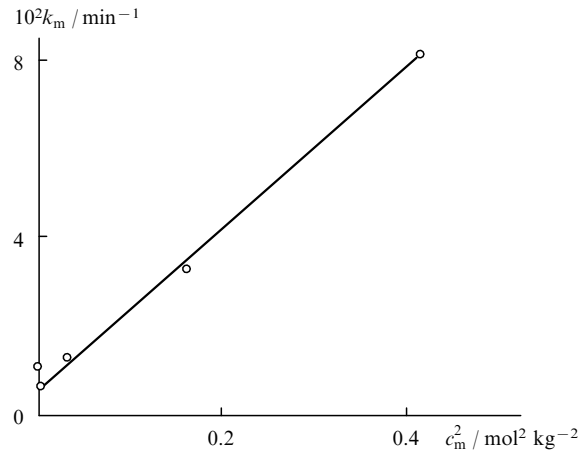


Figure 7. Influence of the concentration of the phenol groups of 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) on the effective rate constant for decomposition of BP at 371 K in evacuated CTA films at $c_0 = 0.37$ mol kg^{-1}.

$$\frac{k - k_0}{k_0} = 16 - 17$$

at the highest concentration c_m studied. To begin with, we note that the empirical exponential law for the consumption of BP

$$c = c_0 \exp(-k_m t),$$

and the expressions for the effective rate constant

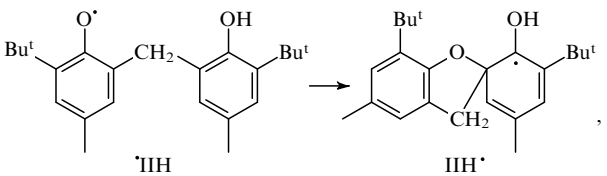
$$k_m = k_0 + k_c c_m^2$$

and for the reaction rate

$$-\frac{dc}{dt} = k_0 c + k_c c_m^2 c$$

make it possible to conclude that the chain constituent of the process obeys formally third order kinetics with respect to admixed reagents. At a high rate of the chain reaction, this alone indicates, irrespective of the mechanism of the process, that admixtures in the chain-sponge micelles of a glassy polymer are fairly mobile.

As regards the particular mechanism of the action of bisphenol 2246, it is natural to assume that its molecules, which actually consist of two ionol structures linked together, should enter into the same steps of s,v-transfer of radicals, induced decomposition of BP, and regeneration as does ionol. At the same time, the substantial enhancement of the catalytic effect and the change in the apparent order of the chain constituent of the reaction attest to an essentially different mechanism for the decomposition of BP in the presence of HIIH, which can be attributed to the specific mutual arrangement of the phenolic groups in the bisphenol molecule. This arrangement is quite favourable for the phenoxyl radical formed from bisphenol to isomerise into an intramolecular σ-complex, which, in its turn, is readily oxidised by dibenzoyl peroxide:



$$IIH^{\bullet} + BP \longrightarrow II + rH + r^{\bullet}$$

In view of this feature of bisphenol 2246, its specific influence on the model reaction can be explained by the fact that phenoxyl radicals and intramolecular σ-complexes derived from bisphenol do not participate in the termination of the reaction v-chains of decomposition of BP, and act as chain propagating species. Therefore, the transfer of v-benzoyloxyl radicals to s-zones occurring with the rate constant k_4 becomes the only route for the termination of the reaction v-chains.

Apparently, fast isomerisation of the phenoxyl radical into the σ-complex ($^{\bullet}IIH \rightarrow IIH^{\bullet}$) also accounts for the fact that in solutions, the stoichiometric coefficient of inhibition by bisphenol 2246 and by other bisphenols containing analogous complementary phenolic groups is 2, as in the case of ionol, rather than 4, which might be expected with the assumption that the influences exerted by each phenolic group are additive.[23]

With allowance for the above considerations, the following scheme can be proposed for generation, propagation, and termination of reaction v-chains:

$$r_s^{\bullet} + HIIH_s \xrightarrow{k_8} (r-IIH_2^{\bullet})_s \xrightarrow{BP_s} r^{\bullet} + \text{products},$$

$$r_s^{\bullet} + HIIH_s \xrightarrow{k_8'} rH + {}^{\bullet}IIH_s,$$

$${}^{\bullet}IIH_s \longrightarrow IIH_s^{\bullet} \xrightarrow{BP_s} r^{\bullet} + \text{products},$$

$$r^{\bullet} + HIIH \longrightarrow rIIH_2^{\bullet} \xrightarrow{BP_v} r^{\bullet} + \text{products},$$

$$r^{\bullet} + HIIH \longrightarrow rH + {}^{\bullet}IIH,$$

$${}^{\bullet}IIH \longrightarrow IIH^{\bullet} \xrightarrow{BP_v} r^{\bullet} + \text{products},$$

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

According to this scheme, the concentration of v-benzoyloxyl radicals should be described by the expression

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

If we substitute this relation in Eqn (11) and neglect the first term in this equation, which can be done because bisphenol 2246 is even a stronger acceptor of radicals than ionol,[23] we obtain the relation

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

Taking into account the conditions for equilibrium in the exchange of bisphenol molecules ($c_{ms} = K_{em} c_{mv}$) and BP (Eqn 1) between s- and v-zones, we obtain an expression for the overall rate of the decomposition of BP:

$$-\frac{dc}{dt} = k_0 c + k_c c_m^2. \qquad (13)$$

Eqn (13) can serve as a theoretical justification for the experimental data reported earlier.[22] It confirms the kinetic non-equivalence of the catalytic effects of ionol and bisphenol 2246.

IV. Heterophase model for anaerobic chain decomposition of polypropylene hydroperoxide

The concept of heterophase chain reaction also proved to be fruitful in the analysis of ageing and stabilisation processes in polymers. Important characteristic features of autooxidation of polyalkenes and of decomposition of polymeric hydroperoxides under conditions of high and low fluctuation dynamics in a polymer-chain sponge have been rationalised in terms of this concept.[4–6] Here, we consider the mechanism of chain decom-

position of polypropylene hydroperoxide in the absence of oxygen dissolved in the polymer.

Polypropylene (PP) differs from glassy polymers in that its amorphous phase exists in a highly elastic state even at ambient temperature. The amorphous phase consists of separate areas surrounded by crystallites. The crystalline phase ($T_{melt} \approx 438$ K) usually accounts for 60 mass % of isotactic PP. Separate crystallites are joined in a continuous rigid framework, which imparts properties of a solid to the polymer. In samples of PP with this structure, the processes of oxidation and decomposition of admixtures occur mostly in highly elastic areas.[14,15]

The rigid framework of crystallites influences in some way the structure of the non-crystalline phase of PP;[24] however, characteristic features of the chain-micellar sponge structure of the amorphous areas are retained. It cannot be ruled out that wide s-micropores in PP are also formed as layers near the surface of crystallites;[24] however, the greater part of the sponge micelles must consist of flexible chains as grains with more or less narrow v-micropores. Assuming that the chain-micellar sponge in polyalkenes retains its microheterogeneous structure, one should expect that the characteristic non-equivalence of the rates of radical generation in v- and s-zones will be manifested. In fact, it has been shown[4–6,25] that PP contains s-zones in which hydroperoxide dissociates much more rapidly than in v-zones. A primary reaction chain generated in v-zones induces chain reaction in v-zones due to the s,v-injection of radicals, the probability of which is relatively low. In rigid PP specimens, the heterophase chemical induction stops at the instant when the hydroperoxide accumulated in s-zones is entirely exhausted.

However, in the general case, decomposition of polypropylene hydroperoxide is not terminated at this point; its heterogeneous-heterophase stage, which has come to an end, is replaced by a slower heterogeneous-homophase stage. The occurrence of the latter stage is due to the fact that in v-zones a possibility exists that v-micropores will grow up to the size of s-micropores, due to fluctuations. At this stage, the frequency of the acts of hydroperoxide dissociation is largely determined by the conditions under which the polymeric specimens were prepared and by the residual mechanical tension in them.

An adequate s-scheme for the transformation of hydroperoxide (G) based on the results reported in a number of studies[4–6,25] has the following form:

$$G_s \xrightarrow{k_{0s}} (PO_s^{\bullet} + HO_s^{\bullet}) \xrightarrow{PH_s} \delta P_s^{\bullet},$$

$$P_s^{\bullet} \xrightarrow{k_{1s}} R_s^{\bullet} \text{ (destruction of polymeric chains + products)},$$

$$R_s^{\bullet} \xrightarrow{k_{2s}} R_{1s}^{\bullet} \text{ (isomerisation of a terminal radical)},$$

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

Here, the designation PH_s corresponds to the reactive CH groups at tertiary and secondary carbon atoms in the polymeric chains; δ is a coefficient of the yield of radicals upon dissociation of hydroperoxide; $P_s^{\bullet}$ are internal macroradicals; and $R_s^{\bullet}$ and $R_{1s}^{\bullet}$ are terminal macroradicals.

The probability for the transfer of a free valence from s-zones to v-zones is low, and, according to the tr-scheme, this transfer is largely accomplished by the most mobile and most reactive terminal radicals $R_s^{\bullet}$.

$$R_s^{\bullet} \xrightarrow{k_m} R_m^{\bullet},$$

$$R_m^{\bullet} \xrightarrow{k_{-m}} R_s^{\bullet},$$

$$R_m^{\bullet} + PH \xrightarrow{k'_{tr}} P^{\bullet}.$$

The $R_s^{\bullet}$ radicals, which exchange their positions within the s-framework and in the micropore bulk during vibrations ($R_m^{\bullet}$), are capable of reacting with CH bonds in v-zones.

Owing to this transfer of radicals, chain decomposition of hydroperoxide yielding water occurs in v-zones; this process can be described by the following v-scheme

$$P^{\bullet} + G \xrightarrow{k_1} PH + POO^{\bullet},$$

$$POO^{\bullet} \longrightarrow {}^{\bullet}POOH \text{ (β-isomerisation of peroxyl radical to hydroperoxyalkyl radical)}$$

$${}^{\bullet}POOH \longrightarrow \varepsilon + HO^{\bullet} \text{ (decomposition of hydroperoxyalkyl to give an epoxide)},$$

$$HO^{\bullet} + PH \longrightarrow H_2O + P^{\bullet},$$

$$2P^{\bullet} \xrightarrow{k_2} \text{termination}.$$

By applying the condition of steady-state concentration of radicals to these block schemes, one can obtain a series of equations:

(a) for the concentration of the radicals translating the free valence

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

(g_s is the concentration of G in s-zones);
(b) for the rate of s,v-transfer

$$V_{tr} = k'_{tr}[PH][R_m^{\bullet}] = k_{tr}[R_m^{\bullet}] = k_{tr}k_m \frac{[R_s^{\bullet}]}{k_{-m} + k_{tr}} = \frac{k_{tr}k_m \delta k_{0s} g_s}{2k_{2s}(k_{-m} + k_{tr})}$$

(V_{tr} is equal to the rate of termination of the reaction v-chains, $V_{tr} = 2k_2[P^{\bullet}]^2$);
(c) for the concentration of radicals that attack hydroperoxide

$$[P^{\bullet}] = \left(\frac{V_{tr}}{2k_2}\right)^{0.5};$$

(d) for the rate of chain decomposition of hydroperoxide in v-zones

$$-\frac{dg_v}{dt} = k_1[P^{\bullet}]g_v = k'_e g_s^{0.5} g_v.$$

Taking into account the facts that the current concentration of the hydroperoxide dissociating in s-zones is described by an exponential equation

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

and that the content of hydroperoxide in s-zones is low compared to that in v-zones, the latter being nearly equal to its concentration in the amorphous phase ($g_v \approx g$), we obtain the following expression for the rate of hydroperoxide decomposition:

$$-\frac{dg}{dt} = k'_e g_{s0}^{0.5} g \exp(-0.5 k_{0s} t) = k_e g \exp(-0.5 k_{0s} t). \quad (14)$$

Integration of Eqn (14) leads to an equation describing the curve of anaerobic decomposition of hydroperoxide:

$$g = g_0 \exp\left\{\frac{k_e}{0.5 k_{0s}} [\exp(-0.5 k_{0s} t) - 1]\right\}. \quad (15)$$

At $t \to 0$, formula (15) is approximated by a first-order equation

$$g = g_0 \exp(-k_e t), \quad (16)$$

while at $t \to \infty$, it describes termination of the process in the presence of unconsumed hydroperoxide:

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

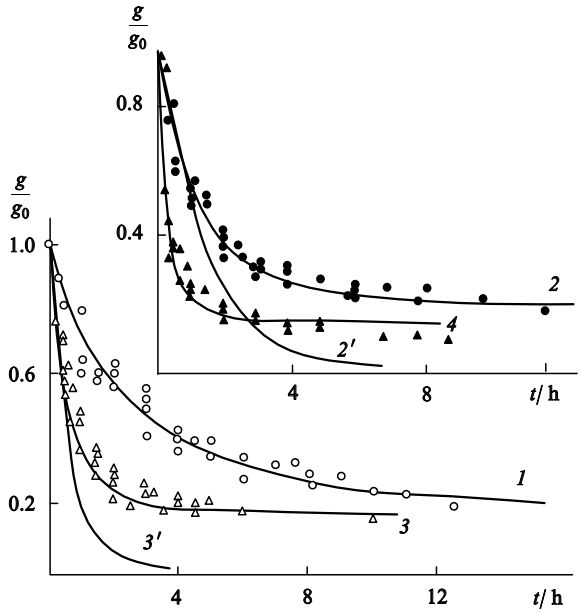


Figure 8. Curves for the consumption of polypropylene hydroperoxide in evacuated samples at temperatures /K: 383 (*1*); 393 (*2*, *2′*); 403 (*3*, *3′*); 413 (*4*). Curves *2′* and *3′* were calculated from a first-order equation for rate constants of 2.0×10^{-4} and 4.2×10^{-4} s^{-1}, respectively.

Eqn (15) derived theoretically is in good agreement with experimental results, which is illustrated by the data presented in Fig. 8. The effective rate constants for chain decomposition at 383, 393, 403 and 413 K are equal to 0.865×10^{-4}, 2.00×10^{-4}, 4.20×10^{-4} and 10.00×10^{-4} s^{-1}, respectively and are described by the general formula

$$k_e = 3.9 \times 10^9 \exp\left(-\frac{E_e}{RT}\right), \quad (17)$$

where $E_e = 100 \pm 5$ kJ mol^{-1} The rate constants for spontaneous decomposition at the same temperatures are 1.14×10^{-4}, 2.48×10^{-4}, 5.06×10^{-4} and 10.00×10^{-4} s^{-1}, respectively, and are described by the following formula

$$k_{0s} = 6.5 \times 10^8 \exp\left(-\frac{E_{0s}}{RT}\right), \quad (18)$$

where $E_{0s} = 93.6 \pm 5$ kJ mol^{-1}. For comparison, curves *2′* and *3′* calculated from formula (16) are presented in Fig. 8. It can be seen that these curves begin to deviate from the experimental points rather early; therefore, they lead to overestimated rates at large degrees of conversion, whereas theoretical curves *2* and *3*, which are in agreement with experimental results, attest to almost complete termination of the process.

It should be noted that the first adequate description of the initial stage of anaerobic decomposition of hydroperoxide, which is characterised by Eqn (16), has been given only recently.[6] This stage has long been regarded as a stage of spontaneous decomposition of hydroperoxide.[14] Later, after its chain mechanism had been proved,[15,26] this stage has been believed to be a superposition of spontaneous and chain reactions having a one and one half order with respect to hydroperoxide. However, in both cases the initial stage of the anaerobic decomposition of hydroperoxide was considered within the framework of a homogeneous model. Since the results obtained earlier[4–6,25] indicate that this process occurs by a heterophase mechanism, we shall attempt to demonstrate that the regularities of the hydroperoxide decomposition accelerated by an admixture initiator are also quite consistent with the heterophase model.

The dependence of the initial rate of hydroperoxide decomposition on the concentration of dibenzoyl peroxide present as an admixture[15,26] evidences that the process includes a chain constituent characterised by quadratic termination of reaction chains:

$$V_0 = k_d g_0 + k_{ind} g_0 (k_b c_0)^{0.5}, \quad (19)$$

where g_0 and c_0 are initial concentrations of hydroperoxide and BP, respectively ($c_0 < 0.05$ mol kg^{-1}), k_d is the rate constant for spontaneous decomposition of hydroperoxide, and k_b is the effective rate constant for the decomposition of BP.

Experimental values of k_d at 365 K obtained in the absence of BP and by extrapolating dependence (19) to $c_0 = 0$ are in agreement with each other and amount to $(1.8-1.9) \times 10^{-5}$ s^{-1}. With the assumption that a polymeric medium being oxidised can be regarded as a homogeneous liquid, the following expression was proposed[15,26] to describe the rate of the process occurring without BP:

$$-\frac{dg}{dt} = k_d g + k'_e g^{1.5}, \quad (20)$$

The first term in this expression corresponds to spontaneous decomposition, while the second term reflects chain decomposition. At the same time, the rate constant for the chain reaction at 365 K calculated from formula (17) found by us, $k_e = 1.9 \times 10^{-5}$ s^{-1}, exactly coincides with the value of k_d in Eqn (19). In addition, Eqn (20) is at variance in its physical meaning with expression (15), which implies that the contribution of spontaneous decomposition of hydroperoxide is negligibly small compared to the contribution of the chain reaction.

Let us consider this situation in terms of a heterophase reaction mechanism. Recall that BP molecules rapidly migrate between the zones of chain sponge micelles,

$$BP_v \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} BP_s$$

and dissociate in s-zones,

$$BP_s \xrightarrow{k_{bs}} 2r_s^{\bullet}.$$

The condition for the equilibrium in the interzone exchange of BP molecules has the following form

$$c_s = \frac{k_s}{k_{-s}} c_v = K_e c_v = \frac{K_e c}{\beta}, \quad (21)$$

where c_s, c_v and c are concentrations of BP in s- and v-zones and in the amorphous phase of PP, respectively; β is the fraction of the amorphous phase in the polymer, and K_e is the equilibrium constant.

Owing to dissociation of BP, benzoyloxyl radicals with a free valence on the oxygen atom are generated in s-zones of the polymeric-chain sponge. The reactivity of these radicals with respect to the hydrogen atoms in OOH groups is known to be hundreds or thousands times higher than that towards CH groups.[27] Therefore, at the initial stage of the process, capture of benzoyloxyl radicals by hydroperoxides should be the predominant reaction in s-zones containing hydroperoxides.

$$r_s^{\bullet} + G_s \longrightarrow rH + POO_s^{\bullet},$$

$$POO_s^{\bullet} \longrightarrow {}^{\bullet}POOH_s \longrightarrow \varepsilon + HO_s^{\bullet},$$

$$HO_s^{\bullet} + PH_s \longrightarrow H_2O + P_s^{\bullet}.$$

Taking these transformations into account within the above s-scheme for decomposition of hydroperoxide, it is not difficult to derive an expression for the concentration of radicals that are leaders in the s,v-transfer of valence

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

as well as for the rate of s,v-transfer

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

Then using the v-scheme considered above and applying the condition of equality of the rates of v-chain generation and termination $V_{tr} = 2k_2 [P^{\cdot}]^2$, we find the concentration of the radicals that induce the decomposition of hydroperoxide

$$[P^{\cdot}] = \left(\frac{V_{tr}}{2k_2}\right)^{0.5},$$

and the rate of chain reaction

$$-\frac{dg}{dt} = k_1 [P^{\cdot}] g = \frac{k_1 g [k_{tr} k_m (\delta k_{0s} g_s + 2 k_{bs} c_s)]^{0.5}}{[4 k_2 k_{2s} (k_{-m} + k_{tr})]^{0.5}}. \quad (22)$$

To pass from the specific rate of decomposition of BP

$$-\frac{dc_s}{dt} = 2 k_{bs} c_s \quad (23)$$

to the empirical rate dc/dt, we express the number of moles of BP in s-zones as $p_s = m_s c_s$ (where m_s is the mass of s-zones) and take into account the fact that the loss of p moles of BP in a specimen is equal to the loss of the corresponding number of moles in s-zones (oxygen completely inhibits chain decomposition of BP in polypropylene).[28] Then

$$-\frac{dc}{dt} = -\frac{1}{m}\frac{dp}{dt} = -\frac{1}{m}\frac{dp_s}{dt} = -\frac{m_s}{m}\frac{dc_s}{dt}.$$

By substituting expressions (23) and (21) in this equation, we obtain

$$-\frac{dc}{dt} = \frac{2 k_{bs} m_s K_e c}{\beta m} = k_b c. \quad (24)$$

The effective rate constant for decomposition of BP included in Eqn (24),

$$k_b = \frac{2 k_{bs} m_s K_e}{\beta m}$$

in conformity with the known formula,

$$k_b = 8.4 \times 10^{13} \exp \frac{-124000}{RT} \ s^{-1}$$

is equal to $1.2 \times 10^{-4}\ s^{-1}$.
This value is consistent with the statement that the parameter

$$2 k_{bs} = \frac{k_b m \beta}{m_s K_e}$$

is much greater than the k_b constant, because

$$\frac{m}{m_s} \gg 1 \text{ and } K_e < 1.$$

From this it follows that in Eqn (22), the rate of radical generation due to dissociation of BP is substantially higher than that due to dissociation of hydroperoxide. According to formula (18), the rate constant for spontaneous decomposition of hydroperoxide at 365 K, k_{0s}, is equal to $2.6 \times 10^{-5}\ s^{-1}$. In other words, for a fairly wide range of initial concentrations of BP, Eqn (22) is transformed into the following equation

$$-\left(\frac{dg}{dt}\right)_0 = k_{ind} g_0 (k_b c_0)^{0.5};$$

and only in the region of very low c_0, is it extrapolated to relation (14), which also characterises chain decomposition of hydroperoxide with quadratic termination of reaction v-chains.

Thus, the heterophase scheme for hydroperoxide decomposition stimulated by dibenzoyl peroxide provides an explanation of the kinetic results obtained in previous studies [15, 26] and discloses the intimate connection between the mechanism of this process and the mechanism of non-sensitised chain reaction. In addition, this scheme makes it possible to account for the formation of water in the chain process, which has not been reflected in the homogeneous scheme at all.

V. The mechanism of the influence of ionol on the rate of anaerobic decomposition of polypropylene hydroperoxide

In an early paper,[29] some interesting features of the fast and slow kinetic stages in the unified process of decomposition of polypropylene hydroperoxide in the presence of ionol have been found. The researchers used low-molecular-weight syndiotactic PP (M_n = 13 500), which was oxidised at 373 K, in order to accumulate hydroperoxide, by passing oxygen through its solution in chlorobenzene containing an initiator.

In the absence of oxygen, decomposition of the hydroperoxide thus accumulated occurred in two stages, the first of which was fast, while the second stage was slow. The rate of the second stage of hydroperoxide decomposition, unlike that found for PP samples oxidised in the bulk (Fig. 8), was quite measurable.

The rate of the fast stage did not depend on the concentrations of hydroperoxide and ionol. In fact, at T = 408 K and at the following concentrations of reagents, G/IH (mol litre^{-1}) 0.0078/0.001, 0.0034/0.001, 0.27/0.1 and 0.005/0.012, the rate constants k_{e1} for this stage were 19.8×10^{-4}, 15.1×10^{-4}, 19.8×10^{-4} and $18.2 \times 10^{-4}\ s^{-1}$, respectively; at T = 393 K and at concentrations G/IH (mol litre^{-1}) of 0.034/0.000, 0.011/0.001, 0.0078/0.001 and 0.27/0.01, the rate constants k_{e1} were 5.01×10^{-4}, 6.3×10^{-4}, 6.41×10^{-4} and $6.13 \times 10^{-4}\ s^{-1}$, respectively.

Conversely, the rate constant for the second stage k_{e2} (which is formally a first-order rate constant) depended on the initial concentration of hydroperoxide g_0, as has also been observed in the homogeneous chain reaction; however, unlike the latter case, the constant k_{e2} did not change when ionol was present in small or medium concentrations (up to 0.05 mol litre^{-1}). Only at a very high content of ionol (0.124 mol litre^{-1}), the rate of the second stage lost its chain constituent, and the constant k_{e2} assumed its minimum value equal to that observed in the absence of ionol and at the lowest concentration g_0.

It was suggested [29] that at the first stage, hydroperoxide decomposition follows a chain mechanism, which is characterised by a specific mode of propagation of reaction chains along the polymer. However, it was not explained why the fraction of the rapidly decomposing hydroperoxide diminished from 0.8–0.9 to 0.25 upon the introduction of ionol in a concentration of up to 0.124 mol litre^{-1}.

From our viewpoint, the reaction studied in Ref. 29 actually follows a chain mechanism, its specific features reflecting the specific state of the reaction matrix, namely, the chain-sponge micellar structure of the oxidised PP. It should be noted that the local concentration of hydroperoxide in s-zones, g_{s0}, which appears in Eqn (14), reaches the level of saturation during the oxidation of PP. As has been found in a previous study,[6] this is accompanied by the constant k_e reaching its maximum value, equal to $11.0 \times 10^{-4}\ s^{-1}$, at 403 K. Eqn (17) makes it possible to calculate the constants k_e at 408 and 393 K (the effective activation energy E_a is 100 kJ mol^{-1}). The values of 16×10^{-4} and $5.15 \times 10^{-4}\ s^{-1}$ thus obtained coincide with those found for k_{e1} in Ref. 29. This indicates that the limiting degree of filling of s-zones with hydroperoxide was achieved in the oxidation in

solution carried out in this study. This is why the rate constant for the initial stage of chain decomposition k_e was independent of the initial concentration g_0 calculated with respect to the whole specimen [Eqns (14) and (16)].

Regarding the specific character of the fast stage of the process in the presence of ionol, we recall that ionol substantially narrows the concentration range in which the fast stage occurs, but does not change the magnitude of k_{e1}. Within the framework of the heterophase model, this can be accounted for by the fact that ionol, which has no influence on the mechanism of the transfer of radicals from s-zones to v-zones, decreases the number of radicals transferred due to the appearance of the additional catalytic pathway for destruction of the hydroperoxide accumulated in s-zones.

All the foregoing can be expressed as an s_i-scheme by introducing the reactions involving ionol into the s-scheme described above:

$$G_s \xrightarrow{k_{0s}} 0.5\,\delta\,(PO_s^{\cdot} + HO_s^{\cdot}),$$

$$HO_s^{\cdot} + PH_s \xrightarrow{k_{4s}} P_s^{\cdot} + H_2O,$$

$$PO_s^{\cdot} + IH_s \xrightarrow{k_{5s}} I_s^{\cdot} + POH,$$

$$I_s^{\cdot} + G_s \xrightarrow{k_{6s}} POO_s^{\cdot} + IH_s,$$

$$POO_s^{\cdot} + IH_s \xrightarrow{k_{-6s}} G_s + I_s^{\cdot},$$

$$POO_s^{\cdot} + IH_s \xrightarrow{k_{7s}} POOIH_s^{\cdot} \longrightarrow POH + IO_s^{\cdot},$$

$$IO_s^{\cdot} + G_s \xrightarrow{k_{8s}} IOH + POO_s^{\cdot},$$

$$POO_s^{\cdot} \xrightarrow{k_{9s}} HO_s^{\cdot} + \text{products},$$

$$P_s^{\cdot} \xrightarrow{k_{1s}} R_s^{\cdot},$$

$$R_s^{\cdot} \xrightarrow{k_{2s}} R_{1s}^{\cdot},$$

$$R_s^{\cdot} + R_{1s}^{\cdot} \xrightarrow{k_{3s}} \text{products}.$$

This scheme reflects a number of characteristic features of the reactants. The reactions of ionol with alkyl radicals $P_s^{\cdot}$, $R_s^{\cdot}$ and $R_{1s}^{\cdot}$ were not included in the scheme, because all alkylphenols exhibit fairly low reactivities towards radicals derived from polyalkenes[14] (even bisphenol 2246, which is more reactive, does not have any influence on the concentration of PP radicals, which eliminate propene during the induction period of the PP oxidation).[30]

The scheme takes into account the interaction of phenoxyl with hydroperoxide[15,16] and both routes known from the literature for the attack of a phenol molecule by $POO^{\cdot}$ radicals: to yield phenoxyl and σ-complex. In the micropores of chain-sponge micelles, unlike liquid solutions, there exist molecular force fields, which, as noted above, hamper reversible dissociation of σ-complexes and thus enable their subsequent transformations. In the present case, σ-complex is converted into the alkoxyl radical $IO^{\cdot}$ with a quinoid structure.

This scheme also takes into account the fact that $HO_s^{\cdot}$ radicals are highly reactive and interact with the polymer more quickly. Since they are adsorbed on the walls of s-micropores, the conditions for their reaction with ionol are less favourable than those of $PO_s^{\cdot}$ radicals.

Finally, due to the high local concentration of hydroperoxide in the s-zones of the samples used in Ref. 29, the s-scheme did not include recombination

$$I_s^{\cdot} + POO_s^{\cdot} \longrightarrow POOI,$$

the rate of which at the initial stage of the process is believed to be negligibly small compared to the rate of the reaction

$$I_s^{\cdot} + G_s \longrightarrow IH_s + POO_s^{\cdot}.$$

If the condition of a steady-state concentration of radicals is applied to the s_i-scheme, it can be easily seen that the expression for the concentration of radicals

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

which has been obtained previously based on the s-scheme for the process occurring without ionol (see Section IV), also holds in the present case. The concentration of s-phenoxyl radicals corresponding to the s_i-scheme does not depend on the concentration of G_s

$$[I_s^{\cdot}] = \frac{0.5\,\delta k_{0s}}{k_{6s}} + \frac{0.5\,\delta k_{0s} k_{-6s}\,[IH_s]}{k_{6s} k_{9s}}, \qquad (25)$$

the concentration of s-peroxyl radicals is equal to

$$[POO_s^{\cdot}] = \frac{0.5\,\delta k_{0s} g_s}{k_{9s}},$$

and the overall rate for decomposition of s-hydroperoxide is the sum of several terms,

$$-\frac{dg_s}{dt} = k_{0s} g_s + k_{6s}[I_s^{\cdot}] g_s + k_{8s}[IO_s^{\cdot}] g_s - k_{-6s}[POO_s^{\cdot}][IH_s] =$$

$$= k_{0s} g_s + 0.5\,\delta k_{0s} g_s + \frac{0.5\,\delta k_{0s} g_s k_{7s}}{k_{9s}}\,[IH_s],$$

the second term being much smaller than the first term characterising the spontaneous decomposition of G_s ($\delta < 1$). By integrating this expression and taking into account the condition of interzone equilibrium

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

(where c_{is} ($[IH_s]$) and c_i ($[IH]$) are the concentrations of ionol in s-zones and in the non-crystalline phase of PP, respectively, K_{ei} is the equilibrium constant, and β is the fraction of the amorphous phase in the polymer), we obtain the equation for the consumption of s-hydroperoxide with allowance for the chain contribution catalysed by ionol:

$$g_s = g_{s0} \exp\left[-(k_{0s} + b_i c_i)\, t\right], \qquad (26)$$

where b_i is a complex constant.

When we pass to the mechanism of chain decomposition of hydroperoxide in v-zones, it is noteworthy that, according to the study discussed above,[29] ionol exerts no influence on the constant k_{e1} over the whole range of concentrations c_i studied and has an influence on the constant k_{e2} only at a fairly high c_i value, 0.124 mol kg^{-1}. Therefore, it was suggested[29] that the reaction chains of hydroperoxide decomposition are mostly realised through the migration of the free valence along the polymer chains and that the intermolecular attack of hydroperoxide by $P^{\cdot}$ radicals yielding free peroxyl radicals is impossible. In this case, the v-scheme considered above assumes the following form

$$P^{\cdot} + G \longrightarrow {}^{\cdot}POOH \longrightarrow H_2O + P^{\cdot} + \text{products},$$
$$2P^{\cdot} \longrightarrow \text{termination}$$

(the $OH^{\cdot}$ radical arising reacts with the neighbouring CH group of the same macromolecule). This scheme corresponds to a fairly loose packing of polymer chains in the chain-sponge micellar structure.

The structural looseness, *i.e.* an enhanced volume tension of the chain sponge in the PP specimens oxidised in solution, is stabilised due to fixing of the stretched chains on the crystallite

framework. It is known that syndiotactic and isotactic PP readily crystallise; and crystallising polyalkenes do not form molecular solutions in hydrocarbons at $T < T_{melt}$.[31] They are able to be dispersed in a liquid to some extent to form a colloidal solution, in case where polymer–polymer type molecular contacts arise in the system leading to the simultaneous formation of crystal nuclei.[32]

Thus, in all probability, the PP matrix subjected to oxidation in the study considered above[29] consisted of disseminations of chain-sponge micelles swelled in chlorobenzene into colloidal particles reinforced by a lattice of crystallites linked to one another. The lattice of crystallites was relatively strong and did not change upon drying and heating of the suspension.

It is the framework strength of the lattice of crystallites that accounts for the stabilisation of the structural looseness of chain-sponge micelles and for the fact that the rates of decomposition of hydroperoxide in PP occurring as a colloidal suspension in chlorobenzene and in PP films are virtually identical.[29]

The reaction v-scheme for hydroperoxide decomposition, modified with allowance for the results discussed above,[29] includes the same steps of generation and termination of reaction v-chains, which were considered in Section IV. Therefore, Eqn (26) presented above can be included in the expression for the rate of the chain reaction, which was proposed in Section IV:

$$-\frac{dg}{dt} = k_1[P^{\cdot}]g = k'_e g_s^{0.5} g = k_e g \exp[-0.5(k_{0s} + b_i c_i)t]. \qquad (27)$$

The pre-exponential factor k_e in Eqn (27) has the same structure as that in Eqn (14), and the exponential part contains an additional constant, $b_i c_i$, associated with chain decomposition of hydroperoxide in s-zones.

Integration of Eqn (27) leads to a formula, which describes the curve for decomposition of hydroperoxide

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

At $t \to 0$, *i.e.* in the initial stage of the reaction, this formula is transformed in a first-order equation

$$\ln\frac{g}{g_0} = -k_e t\,,$$

or

$$g = g_0 \exp(-k_e t)\,,$$

which coincides with Eqn (16) and includes only the constant k_e, which does not depend on the content of ionol.

At a high degree of conversion ($t \to \infty$), this initial formula is transformed in the following expression

$$\ln\frac{g_\infty}{g_0} = -\frac{k_e}{0.5\,(k_{0s} + b_i c_i)}\,,$$

or

$$g_\infty = g_0 \exp\left[-\frac{k_e}{0.5\,(k_{0s} + b_i c_i)}\right],$$

which characterises a 'kinetic step'; the larger the ionol concentration (c_i) in the samples and the more pronounced is the catalytic influence of ionol on the decomposition of hydroperoxide in s-zones, the higher is this step.

Now we shall consider characteristic features of the homophase stage of decomposition of PP hydroperoxide.

In the study discussed above,[29] the fast stage of the process was followed by its slow stage rather than by its kinetic termination. The rate of the slow stage remained constant at low and medium concentrations of ionol (up to 0.05 mol kg^{-1}). The fact that the rate of the reaction characterised by k_{e2} can be reliably measured, although it is relatively low, distinguishes these samples from the samples oxidised in the bulk in which the second stage of the process occurs at an extremely low rate (see Fig. 8).

In the first stage of the process, the rate of hydroperoxide decomposition in the samples, which were studied in Ref. 29, was also higher than that in PP oxidised in the bulk (the temperature being the same). Obviously, the higher reactivity of the polymer oxidised in suspension should be attributed to the loose packing of the polymer chains in the chain-sponge micellar structure.

The loose structure of the micellar material in combination with high flexibility of the polymer chains increases the degree to which v-zones (which accumulate the greater part of the hydroperoxide formed upon oxidation) are ready to undergo thermofluctuational excitation, which ensures widening of v-micropores to the size of s-micropores. Consequently, the frequency of these excitation acts increases and the probability of dissociation of hydroperoxide groups within the intensely oscillating micropores increases correspondingly.

Thermofluctuational excitation of this sort is favourable for the beginning of the second stage of hydroperoxide decomposition, which can be characterised as a heterogeneous-homophase stage. The contribution of this stage becomes predominant after heterophase s,v-transfer of radicals has ceased due to the exhaustion of hydroperoxide groups within s-zones.

There is always a certain probability of the flickering growth of v-micropores in the chain-sponge zones; this probability is especially high when the polymer occurs in the highly elastic or molten state.[5,6] The process of generation of free radicals in this stage can be represented by the following scheme

$$G_v \underset{k_{-f}}{\overset{k_f}{\rightleftharpoons}} G_f \xrightarrow{k_{0f}} (PO_f^{\bullet} + HO_f^{\bullet}) \longrightarrow \delta_f P^{\bullet},$$

in which the constants k_f, k_{-f} and k_{0f} correspond to the heterogeneous steps of excitation, deactivation and dissociation of hydroperoxide groups conjugated with the steps of fluctuation of micropores; the symbol δ_f denotes the fraction of radicals leaving an oscillating micropore.

An equation for the rate of chain heterogeneous-homophase reaction follows from this scheme in combination with the reaction v-scheme considered in Section IV:

$$-\left(\frac{dg}{dt}\right)_c = k_1[P^{\cdot}]g = k_1 g^{1.5}\left[\frac{\delta k_{0f} k_f}{2k_2(k_{-f} + k_{0f})}\right]^{0.5}.$$

Taking into account the fact that the occurrence of this reaction suggests a relatively large contribution of fluctuational dissociative decomposition of hydroperoxide in v-zones, we obtain the following expression for the overall rate of decomposition:

$$-\frac{dg}{dt} = k_{d,f} g + k_{c,f} g^{1.5}, \qquad (28)$$

where $k_{d,f}$ and $k_{c,f}$ are complex rate constants for non-chain and chain v-reactions, respectively.

The fact that the process actually obeys Eqn (28) is indicated by the typical dependence of the formal first-order rate constant on the initial concentration of hydroperoxide, which was found in Ref. 29:

$$k_{e2} = k_{d,f} + k_{c,f} g_0^{0.5}.$$

Note that Eqn (28) looks like Eqn (20) obtained for a homogeneous reaction; however, in contrast to the interpretation reported previously,[15,26] it characterises the slow stage of decomposition of a polymeric hydroperoxide rather than its fast stage.

According to the data obtained in Ref. 29, the chain constituent of the rate $k_{c,f} g_0^{0.5}$ is suppressed by ionol only when its concentration is very high, $c_i = 0.124$ mol kg^{-1}. This can be explained by the fact that ionol is extremely inert with respect to alkyl polymeric radicals $P^{\cdot}$ and that the probability of its interaction with $PO_f^{\bullet}$ and $HO_f^{\bullet}$ radicals, hanging on the walls of a micropore excited by thermofluctuation, is low.

VI. Specific features of the influence of ionol on the chain decomposition of polypropylene hydroperoxide in the presence of oxygen

The presence of dissolved oxygen in the oxidised PP samples containing ionol dramatically changes the situation; in this case, the heterogeneous-homophase process is brought to the fore. As shown in the previous section, this process is limited by the slow rate of heterogeneous generation of radicals, occurring directly in those structural zones of chain-sponge micelles, which accumulate the major part of hydroperoxide resulting from the oxidation of PP. The chain decomposition of hydroperoxide initiated in the absence of oxygen is decelerated by ionol only when its concentration is very high, because the reactivity of alkyl radicals towards ionol is negligibly small.

The situation changes in the presence of oxygen, which converts alkyl radicals into peroxyl radicals and thus sharply increases the rate of their interaction with ionol and simultaneously switches the process to the catalytic decomposition of hydroperoxide.

An example of this change in the kinetic regime of a reaction has been reported by Chien and Boss,[21] who studied the kinetics of hydroperoxide decomposition in films, which were prepared from a melt and then oxidised (G_1) or obtained from colloidal PP oxidised in chlorobenzene (G_2). The introduction of ionol into these specimens caused the appearance of induction periods in their oxidation carried out by heating under an atmosphere of oxygen ($P_{O_2} = 1$ atm), the duration of these periods being substantially different for the specimens prepared in different ways. The rates of hydroperoxide decomposition during the induction periods were also different. The films of the polymer oxidised in a colloidal solution were the most active. This is not surprising, since chain-sponge micelles in these films possess the most pronounced fluctuation-dynamic properties (see Section V).

Figure 9 shows the plot for the consumption of G_1 (curve *1*) in samples with weak fluctuation dynamics ($T = 403$ K, $g_0 = 0.150$ mol litre^{-1}, $c_{i0} = 0.013$ mol litre^{-1}). It can be compared with the curve for the consumption of peroxyl radicals (curve *2*) and with the curves recorded after completion of the induction period for the absorption of oxygen (*3*) and for the accumulation of hydroperoxides and polymeric peroxyl radicals (*4* and *5*, respectively).

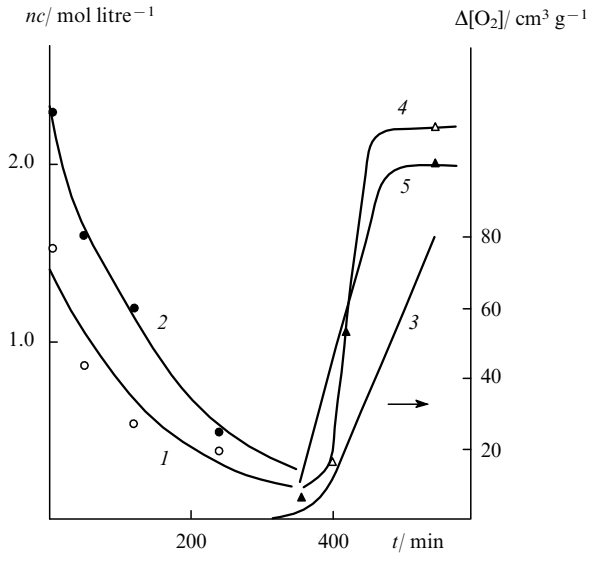


Figure 9. Kinetic curves for autooxidation of PP during the induction period (*1*, *2*) and after it (*3*–*5*) at 403 K ($P_{O_2} = 1$ atm): consumption of hydroperoxide (*1*); consumption of phenoxyl radicals derived from ionol (*2*); consumption of oxygen (*3*); accumulation of hydroperoxide (*4*); accumulation of peroxyl radicals (*5*). The factor *n* for curves *1*, *4* is 10; that for *2*, *5* is 10^6.

During the induction period, which lasted for 350 min, the amount of oxygen absorbed did not exceed the sensitivity threshold of the analytical instrument used. In this stage, the kinetic curve for the consumption of ionol (which is not shown in Fig. 9) and the curve for the consumption of phenoxyl radicals are described by exponential equations $c_i = c_{i0}\exp(-k_i t)$ and $[\Gamma] = [\Gamma]_0 \exp(-k_i t)$, respectively, with identical coefficients $k_i = 1 \times 10^{-4}$ s^{-1}. This combination of kinetic curves implies that the condition of a quasi-steady-state concentration of phenoxyl radicals derived from ionol is ensured almost from the very beginning of the process and that phenoxyl radicals do not participate in the steps of bimolecular destruction and do not react with oxygen.

During the induction period, the concentration of POO$^{\cdot}$ radicals was lower than the limit of sensitivity of the EPR spectrometer ($\leqslant 10^{-8}$ mol litre^{-1}), but when the induction period was over, it quickly reached a steady-state value of $\sim 2 \times 10^{-6}$ mol litre^{-1}, which could be measured reliably.

No analytical function has been suggested[21] to describe the curve of consumption of G_1; however, with allowance for the usual 10% error in the determination of hydroperoxide concentration, a calculated curve can be constructed (curve *1* in Fig. 9), which follows an exponential law with the same k_i value that characterises consumption of ionol and phenoxyl radicals:

$$g = g_0 \exp(-k_i t) \qquad (29)$$

(the value $g_0 = 0.14$ mol litre^{-1} was taken as the initial concentration). A transformed version of this equation plotted on semilogarithmic coordinates is shown in Fig. 10 (straight line *1*), together with the plots obtained by us, which describe the consumption of hydroperoxide in the presence of air and tri-*tert*-butylphenol. Our experiments were aimed at obtaining a more precise pattern for the scattering of experimental points, because the number of points obtained in the study cited[21] was insufficient.

In our experiments, weighed portions of finely grained PP powder (~ 1 mg each) were oxidised in air at 413 K until the concentration of hydroperoxide was $g_0 = 0.14$ mol kg^{-1}. Tri-*tert*-butylphenol was introduced in the oxidised powder as a solution in chloroform. After 40 min of storage, the solvent was evaporated and its last traces were removed *in vacuo*. Decomposition of the hydroperoxide was studied by heating the samples in air and using the spectrophotometric version of iodometric analysis.[4–6,25] The curves obtained for the consumption of hydroperoxide at phenol to polypropylene ratios of 1 : 1 and 2 : 1 by weight were identical.

The experimental points on the straight lines *2*, *3*, *4* and *5* (Fig. 10) were obtained at 372, 383, 393 and 403 K, respectively. For comparison, the initial section of the transform of the curve

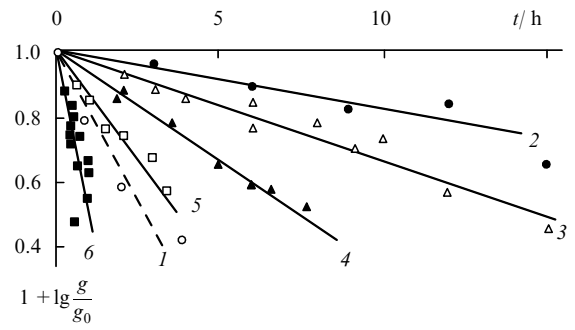


Figure 10. Constants from the curves for the consumption of hydroperoxide in the presence (*1*–*5*) and in the absence (*6*) of oxygen in PP samples containing ionol (*1*), tri-*tert*-butylphenol (*2*–*5*) and containing no antioxidant (*6*) at temperatures/ K: 372 (*2*); 383 (*3*); 393 (*4*); 403 (*1*, *5*, *6*).

for decomposition of hydroperoxide at 403 K in the absence of oxygen is also presented (straight line *6*). Comparison of the scatter of experimental points in our experiments with that observed in the previous study [21] (straight line *1*) makes it possible to conclude that the use of exponential functions (29) is acceptable in all cases. The effective rate constants k_i calculated from the slopes of the straight lines *2–5* are the following: 0.85×10^{-5}, 2.0×10^{-5}, 4.26×10^{-5} and 8.5×10^{-5} s^{-1}. They can be described by the following common expression

$$k_i = 6.0 \times 10^7 \exp\left(-\frac{E_i}{RT}\right),$$

where $E_i = 91.5$ kJ mol^{-1}. It is significant that at 403 K, the rate constant for the decomposition of hydroperoxide in the presence of ionol k_i is equal to 1×10^{-4} s^{-1}, which differs only slightly from the value of 0.85×10^{-5} s^{-1} found for the process involving tri-*tert*-butylphenol. Both of these constants are markedly smaller than the constant characterising the chain decomposition of hydroperoxide in the absence of oxygen and alkylphenol (Fig. 10, straight line *6*), which is equal to 4.2×10^{-4} s^{-1}. However, the decrease in the decomposition rate cannot be attributed to the partial reduction of hydroperoxide caused by chain oxidation of PP or by the interaction of peroxyl radicals with an inhibitor, since the current concentrations g, c_i and $[I^{\cdot}]$ are directly proportional to one another over the whole induction period. It is also significant that in this stage of the process, the chain consumption of oxygen is largely depressed (Fig. 9, curve *3*), and the synchronous consumption of hydroperoxide and ionol characterised by identical exponential factor $\exp(-k_i t)$ takes place when the concentration g_0 is ten times higher than c_{i0}, *i.e.* under conditions when the formation of hydroperoxide in the steps of chain termination can by no means override the four-fold deceleration of its decomposition (Fig. 10, straight lines *1* and *6*).

The kinetic law for the consumption of hydroperoxide, proposed by Chien and Boss,[21] corresponds formally to a non-chain homogeneous reaction. However, the effective rate constant for this process falls in the range of rate constants for the heterophase stage of chain anaerobic decomposition [6] and is many times higher than the rate constant for the heterogeneous-homophase stage of the non-chain constituent. The latter reaches only a value of 4×10^{-5} s^{-1} at 408 K or 1.5×10^{-5} s^{-1} at 393 K even for fluctuatonally active samples containing hydroperoxide G_2,[29] and in films with G_1 it cannot be reliably measured at all (Sections IV and V).

The dramatic increase in the rate of hydroperoxide decomposition in the presence of oxygen with respect to the rate of the second (homophase) stage of the anaerobic reaction is, most probably, due to oxidation of alkyl macroradicals to peroxyl radicals. This process has no influence on the generation of radicals by the mechanism of thermofluctuational excitation of v-micropores but it sharply accelerates the interaction of polymer radicals with alkylphenols and results in the appearance of a new chain pathway to the decomposition of hydroperoxide. Recall that we had to introduce a new reaction in order to explain the characteristic features of the anaerobic decomposition of hydroperoxide in the presence of ionol, and this reaction was actually included in the s_i-scheme described in Section V. According to the s_i-scheme, the new chain reaction of hydroperoxide decomposition is induced by alkoxyl radicals with a quinoid structure of the six-membered carbon ring, which are formed from ionol.

The characteristic features of the decomposition of PP hydroperoxide under oxidative conditions, considered in this Section, also indicate that this new chain reaction should be taken into account. This conclusion is also confirmed by the fact, established independently, that in the specimens with G_2, the process is accelerated by oxygen to even a greater degree. For example, it was found [29] that complete consumption of G_2 and of ionol-derived phenoxyl radicals under an oxygen atmosphere at $T = 393$ K ($g_0 = 0.156$ mol litre^{-1}, $c_{i0} = 0.17$ mol litre^{-1}) is observed in approximately 20 min, whereas in samples with G_1 this occurs after 350 min, *i.e.* the half-transformation period decreases from 116 min to 5–10 min, despite the fact that G_2 decomposes at a lower temperature. The effective rate constant for the reaction under these conditions ($\sim 23 \times 10^{-4}$ s^{-1}) is markedly larger than the rate constant for the initial stage of chain anaerobic reaction in identical samples (see Section V).

Thus, the influence of oxygen leads phenomenolly to the replacement of two macroscopic kinetic stages of the anaerobic process by a single stage; this is due to a substantial acceleration, which is dissimilar for G_1 and G_2, of the ionol-catalysed decomposition of hydroperoxide in a process occurring by a chain mechanism.

The generation of the reaction v-chains under oxidative conditions occurs predominantly according to a homophase route: *via* thermofluctuational excitation of v-micropores, which accumulate hydroperoxide. Ionol, which intercepts all the reaction chains and behaves as an efficient inhibitor of autooxidation of PP, participates simultaneously in the reaction chains of hydroperoxide decomposition.

It should be emphasised that the regularities of the decomposition of PP hydroperoxide both in the presence and in the absence of oxygen considered above rule out the possibility of any significant contribution of the molecular reaction of alkylphenol with hydroperoxide (and thus preclude an increase in the probability of degenerate branching in the presence of an inhibitor). In addition, the fact that the catalytic function of ionol is retained during the whole induction period indicates that some mechanism for its regeneration exists.

Taking the above into account, the following v_i-scheme can be proposed for the transformations that occur in v-zones of chain-sponge micelles of PP beginning with thermofluctuational excitation of v-micropores.

$$G \underset{k_{-f}}{\overset{k_f}{\rightleftharpoons}} G_f \xrightarrow{k_{0f}} \delta_f P^{\cdot},$$

$$P^{\cdot} + O_2 \longrightarrow POO^{\cdot},$$

$$POO^{\cdot} + IH \xrightarrow{k_1} POOIH^{\cdot} \longrightarrow POH + IO^{\cdot},$$

$$IO^{\cdot} + G \xrightarrow{k_2} IOH + POO^{\cdot},$$

$$POO^{\cdot} + IH \xrightarrow{k_3} G + I^{\cdot},$$

$$POO^{\cdot} + I^{\cdot} \xrightarrow{k_4} POOI.$$

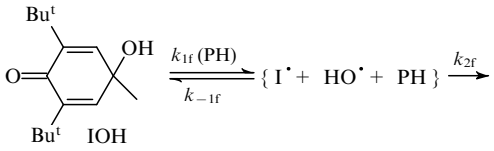
According to this scheme, the reaction chains of hydroperoxide decomposition propagate in the same way as those in the s_i-scheme considered above, *i.e.* through intermediate formation of a σ-complex from phenol and a peroxyl radical and of a quinoid alkoxyl (the rate constants for these stages are k_1 and k_2, respectively). However, chain termination in the v_i-scheme, unlike that in the s_i-scheme, occurs on ionol and its rate (characterised by constant k_3) is directly proportional to the rate of chain propagation in the decomposition of hydroperoxide. The latter is determined by the processes characterised by rate constant k_1. It is this direct proportionality that accounts for the fact that ionol, which sharply decreases the concentration of peroxyl radicals and brings the rate of chain autooxidation of PP

$$POO^{\cdot} + PH \longrightarrow G + P^{\cdot},$$
$$P^{\cdot} + O_2 \longrightarrow POO^{\cdot}$$

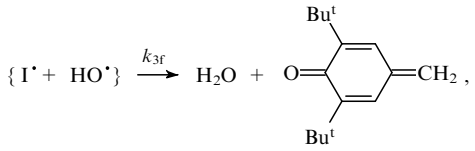
to a negligibly small value, ensures the catalytic development of chain decomposition of PP hydroperoxide.

Regeneration of the initial ionol (and tri-*tert*-butylphenol) from the product of its transformation, a quinoid alcohol, should follow a pathway ensuring regeneration of ionol from the quinoid compound Ir (see Sections II and III) in the steps of thermofluctuational excitation of v-micropores. These steps occur as

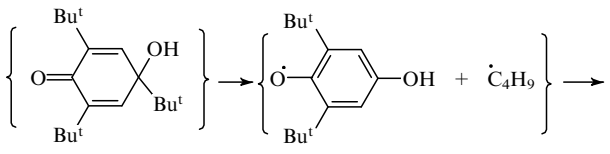
'latent radical' or 'intra-cage' processes and include dissociation of the quinoid alcohol and subsequent dehydrogenation of macromolecules:



where $P^{=}$ is a fragment of the polymer containing a double bond. Simultaneously, partial loss of phenol should occur in the disproportionation steps occurring in parallel. In the case of ionol, this leads to a methylenequinone



which undergoes subsequent transformations, while in the case of tri-*tert*-butylphenol, this process involves elimination of *tert*-butyl radicals to give a quinone and other products



By applying the condition of steady-state concentration to the reactive species appearing in the v_i-scheme (radicals and alcohols IOH), one can derive an expression for the equality of the chain generation and chain termination rates

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

[here δ_f is the yield of radicals in the fluctuation decomposition of hydroperoxide in v-zones, and $\alpha_f = k_f/(k_{-f} + k_{0f})$] and for the rate of hydroperoxide decomposition

$$-\frac{dg}{dt} = \alpha_f k_{0f} g + k_1 [POO^{\bullet}][IH] - 2k_3 [POO^{\bullet}][IH] =$$

$$= \alpha_f k_{0f} g + \frac{k_1 \delta_f \alpha_f k_{0f} g}{2k_3} - \delta_f \alpha_f k_{0f} g = k_i g.$$

The latter expression implies that this process obeys first-order kinetics with respect to hydroperoxide and zero-order kinetics with respect to alkylphenol

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

The rate of the consumption of phenol, according to the v_i-scheme, is

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

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

$$= \left[0.5 + \frac{0.5 k_1 k_{3f}}{(k_{2f} + k_{3f}) k_3}\right] \delta_f \alpha_f k_{0f} g = k_{ii} g .$$

By integrating the expression

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

we obtain the equation

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

for the initial instant $c_i = c_{i0}$ ($t = 0$), this equation assumes the following form

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

If at $t \to \infty$, $c_i = 0$, then

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

which is in full agreement with the results obtained by Chien and Boss.[21]

As noted above, a quasi-equilibrium concentration of phenoxyl radicals in the process under consideration is established very quickly. The kinetics of their consumption is described by the theoretical formula

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

which should be valid from the instant at which a quasi-steady-state concentration of phenoxyl radicals is established until the induction period in the PP oxidation is completed. This theoretical expression, like the previous ones, describes adequately the experimental results obtained in Ref. 21. Therefore, it can be concluded that the heterogeneous-homophase chain reaction model properly reflects the empirical regularities of the oxidative decomposition of polypropylene hydroperoxide in the presence of a phenolic antioxidant.

It is noteworthy that the mechanism of partial regeneration of phenol from the quinoid alcohol formed upon its chain transformation, which is similar to the mechanism of regeneration of ionol from the product of the reaction of phenol with dibenzoyl peroxide (Section II), is apparently fairly abundant. This has been supported by an independent experiment that we have carried out with the methyl ether of the quinoid alcohol, prepared from ionol by a procedure described previously.[33]

When this ether was introduced into cellulose triacetate films together with dibenzoyl peroxide, it exerted qualitatively the same influence on the rate of BP decomposition as did alkylphenols (see Sections II and III). Fig. 11 shows the linear transforms of the curves for anaerobic decomposition of BP ($c_0 = 0.66$ mol kg^{-1}, $T = 371$ K) at initial concentrations of the methoxy-quinoid compound of 0.08 mol kg^{-1} (straight line *1*) and 0.32 mol kg^{-1} (straight line *2*). Even when the difference between the initial concentrations is so large, the effective rate constant for this reaction, as has also been observed for mixtures with phenols, remains virtually unchanged during the whole process. As in systems containing phenols, the rate of the chain reaction of BP induced by polymer radicals reaches a minimum when the concentration of the quinoid ether is $\sim$0.08 mol kg^{-1}. At quinoid ether concentrations of 0, 0.08 and 0.32 mol kg^{-1}, the effective rate constants for the decomposition of BP were 2.7×10^{-4}, 1.5×10^{-4} and 1.58×10^{-4} s^{-1}, whereas the rate constant for non-chain decomposition of BP was 7.5×10^{-5} s^{-1}. Thus, the non-phenolic quinoid compound exerts a prolonged inhibitory influence on the decomposition of BP induced by macroradicals and, conversely, exhibits a catalytic effect in the concentration range in which the influence of macroradicals is suppressed. The

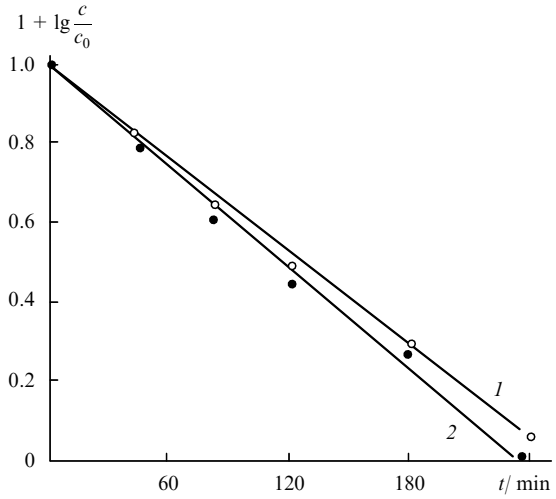


Figure 11. Constants from the curves for the consumption of BP at c_0 = 0.66 mol kg^{-1} and a temperature of 371 K in evacuated CTA films in the presence of 0.08 (*1*) and 0.32 mol kg^{-1} (*2*) of a methoxyquinoid ionol derivative (3,5-di-*tert*-butyl-1-methyl-1-methoxycyclohexadien-4-one).

concentration of this ether, like those of phenols, appears in the expression for the effective rate constant of the reaction of BP as a parameter. This confirms the fact that the quinoid compound is quickly transformed into the corresponding phenol by a thermofluctuation mechanism.

VII. The mechanism of the initiated chain process involving ionol during the induction period of the oxidation of polyalkenes

The data presented above make it possible to consider the chemical aspect of the inhibited oxidation of polyalkenes during the induction period from a new standpoint. A lot of experimental results and theoretical studies have been accumulated in this field; however, as a rule, they do not go beyond homogeneous reaction models.[14–16]

One of the two methodological approaches to the solution of this problem is based on the use of initiators that have been tested in liquid-phase reactions.[15,16] In the case of liquid-phase oxidation, this method makes it possible to determine, using relatively simple experiments, the character and specific features of the influence of a particular inhibitor on the rate of oxygen absorption and on the duration of the induction period, after which the action of the inhibitor ends.

Another approach involves investigation of the inhibited oxidation of a polymer containing no specially added initiator.[14]

In this Section, we consider oxidation of polymers in the presence of an initiator added as an admixture; attention is focused on the regularities of the absorption of oxygen during the induction period. The fact that oxygen absorption does occur at a certain rate during the induction period of inhibited oxidation of polyalkenes in the presence of an initiator has been long known; however, it has not yet received any acceptable explanation. Among other reasons, this is due to the fact that the rate of oxygen absorption in this stage is lower than that in the stage of the polymer oxidation itself (after completion of the induction period). In determining the efficiency of inhibitors or the rate of generation of oxidation chains, researchers have believed that it was sufficient to choose conditions under which the rate of the consumption of an inhibitor did not depend on its concentration. It has been assumed that under these conditions, slow absorption of oxygen during the induction period of the polymer oxidation can be neglected.[15,16,28] Meanwhile, insight into the mechanism of the transformation of alkylphenols with allowance for the specific features of functioning of the chain-sponge structure in polymers, should aid greatly the refinement of general views on the mechanism of oxidative transformations involving inhibitors.

To construct a kinetic model of the process occurring during the induction period, we used experimental data reported by Chien and Wang,[28] who have carried out oxidation of polypropylene, poly(but-1-ene), and poly(4-methylpent-1-ene) (under an oxygen pressure of 1 atm) using dibenzoyl peroxide as the initiator and ionol as the inhibitor. Although the workers did not consider the reason why oxygen is absorbed noticeably during the induction period, they presented, among other results, fairly detailed data on the rate of the absorption of oxygen (V) and the rate of the consumption of ionol (V_i) during this stage of the reaction.

The process of oxidation of these polymers, which are partly crystalline, involved only their amorphous regions and was limited to a very early stage, corresponding to a degree of BP conversion of 0.6% to 2%.

The values $V_i = c_{i0}/t_{ind}$ (c_{i0} is the initial concentration of ionol and t_{ind} is the induction period) measured in the temperature range between 344 and 378 K, as well as the V values remained constant for the concentrations of BP used up to the instant when the oxidation process sharply accelerated due to exhaustion of ionol.

The workers proved definitely that no chain transformation of BP proceeded under oxidative conditions and found the temperature dependence of the coefficient A

$$A = \frac{c_{i0}}{c_0\,[1 - \exp(-k_d\,t_{ind})]}. \qquad (30)$$

Since the discussion was carried out within the framework of a liquid-phase model, they considered A to be a parameter characterising the influence of the inhibitor on the yield of radicals in spontaneous reaction of BP.

However, comparison of the rates of consumption of ionol and oxygen during the induction period makes it possible to give a different interpretation of this coefficient. The results of this comparison are presented in Fig. 12 in which straight lines *1*, *2*

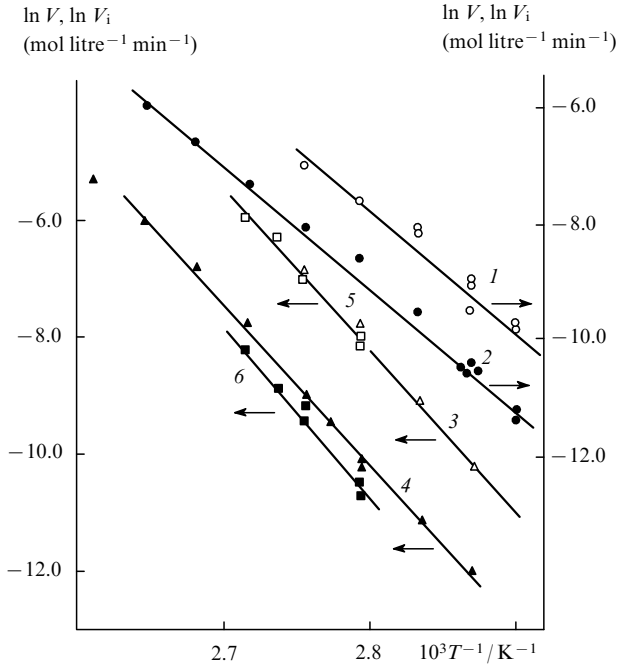


Figure 12. Temperature dependences of the rates of oxygen (*1*, *3*, *5*) and ionol (*2*, *4*, *6*) consumption during the induction period of oxidation of polypropylene (*1*, *2*), poly(but-1-ene) (*3*, *4*) and poly(4-methylpent-1-ene) (*5*, *6*), initiated by dibenzoyl peroxide.

and *3* plotted on the Arrhenius coordinates refer to the variation of the rate of oxygen absorption, while straight lines *2*, *4* and *6* refer to the rate of consumption of ionol. These temperature dependences remain linear as c_{i0} varies from 3.4×10^{-3} to 72.6×10^{-3} mol litre^{-1}, which is a consequence of the fact that these rates do not depend on the concentration of ionol. The identical slopes of the straight lines characterising consumption of oxygen and ionol during oxidation of each polymer indicate that the effective activation energies of the two macroscopic processes are identical ($E_i = E_{O_2}$). In the case of PP (straight lines *1* and *2*; $c_0 = 0.127$ mol litre^{-1}), this energy is equal to 127 kJ mol^{-1}, while for polybut-1-ene (straight lines *3* and *4*; $c_0 = 0.376$ mol litre^{-1}) and for polymethylpentene (straight lines *5* and *6*; $c_0 = 0.33$ mol litre^{-1}), it is 231.0 kJ mol^{-1}. The number of oxygen molecules absorbed per ionol molecule consumed remains constant over the whole temperature range studied. The V/V_i ratios are 3.65, 8.0 and 13.5 for PP, poly(but-1-ene) and poly(4-methylpent-1-ene), respectively.

It can be seen that the stoichiometric V/V_i ratio depends on the chemical structure of the polymer and can be so great that this cannot be due to oxidation of only the ionol added. Therefore, the process occurring during the induction period can be regarded as initiated chain co-oxidation of the alkylphenol and the polymer. In this case, formula (30) characterises variation of the amount of ionol consumed in the chains of its co-oxidation with the polymer per BP molecule decomposed spontaneously rather than the influence of ionol and temperature on the emergence of radicals from the 'cage' of spontaneously decomposing BP.

According to Ref. 28, the rate constant of the spontaneous decomposition of BP k_d is $8.4 \times 10^{13} \exp(-124\,650/RT)$ s^{-1} in PP and poly(but-1-ene) and $7 \times 10^{13} \exp(-123\,000/RT)$ s^{-1} in poly(4-methylpent-1-ene). The activation energy for the decomposition of BP (E_d = 123 to 125 kJ mol^{-1}) during the oxidation of these polymers is much less than the activation energy for their co-oxidation with ionol (172–231 kJ mol^{-1}). Therefore, the temperature dependence of A found previously,[28] which corresponded to an extremely low degree of BP decomposition (from 0.6% to 2% over the time t_{ind}), characterises the ratio between the rates

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

where $V_i = c_{i0}/t_{ind}$ and $V_{d0} = k_d\,c_0$.

The structural-kinetic model of the co-oxidation can be constructed quite easily taking into account considerations presented in the above Sections and also the facts that the systems in question contain initially no hydroperoxide, able to decompose in v-zones of the chain-sponge matrix by the mechanism of fluctuational excitation of v-micropores, and that BP molecules decompose to give radicals in the s-zones

$$BP_v \rightleftharpoons BP_s,$$

$$BP_s \xrightarrow{k_{0s}} 2\,\delta\,r_s^{\bullet},$$

$$r_s^{\bullet} \xrightarrow{k_{1s}} P_s^{\bullet} \longrightarrow R_s^{\bullet},$$

$$R_s^{\bullet} \xrightarrow{k_{2s}} R_{1s}^{\bullet},$$

$$R_{1s}^{\bullet} + r_s^{\bullet} \longrightarrow Rr.$$

This s-scheme differs from that considered above by the presence of a stage of recombination of s-benzoyloxyl radicals with $R_{1s}^{\bullet}$ macroradicals. This recombination was discovered in a study of the material balance of phenyl-containing compounds in the reaction between BP and PP.[34]

According to the s-scheme suggested, the steady-state concentration of radicals that accomplish the interzone s,v-transfer of free valence is equal to

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

The acts of s,v-transfer themselves should occur with a low frequency, having no influence on $[R_s^{\bullet}]$ (this is ensured by the rigidity of the chain-sponge framework):

$$R_s^{\bullet} \underset{k_{-m}}{\overset{k_m}{\rightleftharpoons}} R_m^{\bullet},$$

$$R_m^{\bullet} + O_{2s} \xrightarrow{k_{tr}} ROO_m^{\bullet},$$

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

The quinoid alkoxyl radicals, which appear in this way in v-zones, initiate chain oxidation of macromolecules, ionol being also involved in this process:

$$IO^{\bullet} + PH \xrightarrow{k_5} IOH + P^{\bullet},$$

$$P^{\bullet} + O_2 \longrightarrow POO^{\bullet},$$

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

$$POO^{\bullet} + IH \xrightarrow{k_3} G + I^{\bullet},$$

$$POO^{\bullet} + I^{\bullet} \xrightarrow{k_4} POOI.$$

Here we follow the numbering of rate constants k_1, k_3 and k_4 accepted in the previous Section. It is suggested that the steps of ionol regeneration and consumption, characterised by the rate constants for the 'latent radical' stages in the transformation of the alcohol IOH (k_{1f}, k_{-1f}, k_{2f} and k_{3f}), are also retained in this case.

Within the framework of the present heterophase scheme, the fact that the rates of generation and termination of reaction v-chains are equal is represented by the following expression

$$V_{tr} = \frac{k_{tr}\,k_m\,\delta\,k_{0s}\,c_s\,[O_{2s}]}{k_{2s}\,(k_{-m} + k_{tr}\,[O_{2s}])} = 2\,k_3\,[POO^{\bullet}][IH]. \qquad (31)$$

Assuming that these chains are sufficiently long, which permits the use of the approximate equality

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

we obtain the steady-state concentration condition for the quinoid alcohol

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

Now we substitute the product [IOH][PH], found from the above relation, in the equation for the rate of ionol consumption

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

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

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

Then we neglect the consumption of ionol in the chain termination steps (with rate constant k_3) and find, using formula (31), the $[POO^{\bullet}][IH]$ product for a system saturated with oxygen ($k_{-m} \ll k_{tr}[O_{2s}]$); thus

$$V_i = -\frac{dc_i}{dt} = \frac{0.5 k_{3f} k_1 k_m \delta k_{0s} c_s}{(k_{2f} + k_{3f}) k_3 k_{2s}}.$$

Taking into account the interzone equilibrium of BP [Eqn (1)], we finally obtain

$$V_i = \beta k_i c,$$

where k_i is the complex constant and $\beta = k_{3f}/(k_{2f} + k_{3f})$.

From the same heterophase scheme subject to the conditions listed above, we obtain the following expression for the rate of oxygen consumption

$$V = -\frac{d[O_2]}{dt} = k_5 [IO^{\cdot}] [PH] = k_1 [POO^{\cdot}] [IH] = \frac{0.5 k_1 k_m \delta k_{0s} c_s}{k_3 k_{2s}} = k_i c.$$

Thus, it can be seen that the theory of heterophase transformation in a system based on a polymer containing relatively large amounts of alkylphenol and oxygen in addition to an initiator leads to the rates of the consumption of inhibitor (V_i) and oxygen (V), which do not depend on their concentrations and are directly proportional to one another:

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

This implies that the fact that V is substantially greater than V_i is associated with regeneration of alkylphenol. Thus, the observed increase in the V/V_i ratio from 3.65 to 13.5 means that the efficiency of regeneration (β^{-1}) increases in the sequence: polypropylene > poly(but-1-ene) > polymethylpentene and is probably a result of the increase in the number of reactive hydrogen atoms on the surfaces of thermofluctuationally excited v-micropores. The larger is the number of these hydrogen atoms surrounded by arising $HO^{\cdot}$ and $I^{\cdot}$ radicals, the lower is the probability of mutual disproportionation of radicals and the higher is the probability of dehydrogenation of macromolecules by the 'latent radical' mechanism.

It should be specially emphasised that regeneration of alkylphenol is exactly an 'intracage' latent radical reaction occurring over the life span of a micropore grown to the required size. The emergence of radicals from such a micropore into the bulk of v-zones of the chain sponge occurs at a negligibly low rate and has no influence on the steady-state concentrations of v-radicals. In this connection, it is also noteworthy that the temperature dependence of

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

reported previously [28] is not associated with the process, considered in the same study, of thermally activated diffusional insertion of ionol into a 'cage' formed upon spontaneous decomposition of the initiator. In conformity with the concept of chain co-oxidation of ionol and polyalkene, this dependence characterises the stoichiometry of chain co-oxidation. The reaction model proposed by us reveals the structure of coefficient A, which is described by the equation

$$A = \frac{V_i}{V_{d0}} = \frac{0.5 \delta \beta k_1 k_m}{k_3 k_{2s}}.$$

The coefficient β appearing in this formula depends only slightly if at all on the temperature, which follows from the fact that the E_{O_2} and E_i values are equal for all the polymers studied.[28] Therefore, the main contribution to the temperature dependence of A is made by the steps of migration of the terminal macroradicals $R_s^{\cdot}$ from the framework walls into the bulk of s-micropores (the rate constant k_m). The size of the corresponding mediator fragment

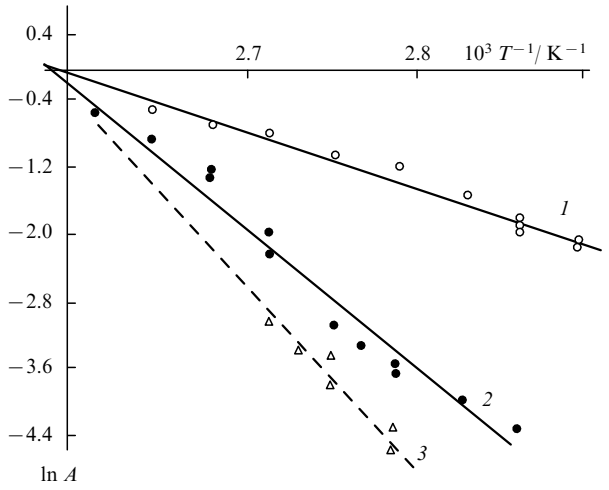


Figure 13. Temperature dependences of coefficients A in Arrhenius coordinates for polypropylene (*1*), poly(but-1-ene) (*2*) and poly(4-methylpent-1-ene) (*3*).

($R_s^{\cdot} \rightleftarrows R_m^{\cdot}$) increases in the order: polypropylene < poly(but-1-ene) < polymethylpentene; therefore it is natural to expect that the restrictions to this migration will also increase in the same sequence. The temperature dependences of coefficients A plotted on the Arrhenius coordinates indicate that the activation energy E_A increases from 50 kJ mol^{-1} for PP to 128 kJ mol^{-1} for poly(but-1-ene) and to even a larger value for poly(4-methylpent-1-ene) (Fig. 13).

In the absence of an adequate theoretical base, Chien and Wang [28] could not construct the plots presented in Fig. 13. Meanwhile, it follows from these plots that in the case of PP, the parameter A is equal to 1 at 388 K, while at 405 K, it exceeds 2 ($\ln 2 = 0.693$). It is clear that dissociation of a BP molecule cannot yield more than two free radicals; thus, an A value, larger than 2, denudes of its physical meaning the suggestion made in Ref. 28 that the coefficient A characterises the output of radicals in the steps of generation of oxidation chains.

Since the physical sense of the coefficient A has changed, the interpretation of the coefficient f, determined by the procedures used for homogeneous reactions, should also change. When the inhibitor method is used, the coefficient f is calculated from the formula

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

where W_{i0} is the rate of homogeneous generation of radicals, and δ is a coefficient characterising the output of radicals in the steps of dissociation of the initiator. In this case, the parameter f characterises the number of oxidative chains terminated by one molecule of the inhibitor. At the same time, by definition, f is inversely proportional to the parameter A:

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

Thus, as applied to polymers, this coefficient is also a particular characteristic of the chain co-oxidation of the inhibitor with the polymer. The instant when the inhibitor in the polymer is exhausted, which is detected by a sharp increase in the rate of oxygen absorption, corresponds to the end of the co-oxidation period and to the transition to the stage of oxidation of the polymer itself.

The application of the homogeneous reaction model to the oxidation of a polymer during the induction period gives rise to some inconsistencies. Let us consider, for example, a study [35]

dealing with oxidation of PP in the presence of ionol with dicumyl peroxide as the initiator (P_{O_2} = 1 atm, T = 388 K). In this study, the coefficient f was found to be

$$f = \frac{W_i}{V_i} = 1$$

(W_i is the constant rate of radical generation found by the inhibitor method, and V_i is the rate of ionol consumption). Since at a constant W_i, the inhibitor was consumed at an invariant rate, it was concluded[35] that all the chains were terminated at the inhibitor and that there were no side reactions leading to its consumption; and the equality $f = 1$ corresponded to one oxidation chain terminated at one ionol molecule (recall that according to the data presented in Fig. 13, $A = 1$ at T = 388 K). However, the workers had to note that the f value obtained differed from the value $f = 2$, typical of the liquid phase, and they also presented a number of facts proving that bimolecular destruction of the ionol-based phenoxyl radicals ($I^{\cdot} + I^{\cdot} \rightarrow$ products) occurred in the PP matrix. However, the data discussed in Section VI indicate that this mechanism is by no means consistent with the actual kinetics of the destruction of phenoxyl radicals.

VIII. Chain co-oxidation of alkylphenol with polyalkene in the absence of an initiator

We shall analyse the co-oxidation occurring in the absence of an initiator using the v-scheme considered in the previous Section and taking into account the fact that the rate of radical generation in v-zones is negligibly small. Under these conditions, initiation can occur in s-zones, which serve as a heterophase source of radicals, *via* either direct oxidation of polymer s-chains or oxidation of molecules of an inhibitor if they are sufficiently reactive.

To consider the former possibility, let us examine the s-scheme, which previously has made it possible to give kinetic description for the initial stage of autooxidation of PP in the absence of an initiator and an inhibitor.[4,25] According to this scheme, radicals are generated in supermicropores of chain-sponge s-zones upon the interaction of the CH bonds in the polymer chains with the oxygen adsorbed on the walls of s-micropores.

$$PH_s + O_{2s} \xrightarrow{k_{0s,p}} \delta P_s^{\cdot}.$$

Subsequent transformations of s-macroradicals occur in the same way as was described in Sections II and V

$$P_s^{\cdot} \xrightarrow{k_{1s}} R_s^{\cdot},$$

$$R_s^{\cdot} \xrightarrow{k_{2s}} R_{1s}^{\cdot},$$

$$R_s^{\cdot} + R_{1s}^{\cdot} \xrightarrow{k_{3s}} \text{products}.$$

The expression for the concentration of mediator radicals, which follows from this scheme, has the form

$$[R_s^{\cdot}] = \frac{\delta k_{0s,p}}{2k_{2s}} [PH_s][O_{2s}],$$

whereas the s,v-translation of valence, involving these radicals, is described by the scheme

$$R_s^{\cdot} \underset{k_{-m}}{\overset{k_m}{\rightleftharpoons}} R_m^{\cdot},$$

$$R_m^{\cdot} + O_2 \xrightarrow{k_{tr}} ROO_m^{\cdot},$$

$$ROO_m^{\cdot} + IH \longrightarrow ROOIH^{\cdot} \longrightarrow ROH + IO^{\cdot}.$$

The scheme for the reaction v-chains of the co-oxidation of alkylphenol and polymer

$$IO^{\cdot} + PH \xrightarrow{k_5} IOH + P^{\cdot},$$

$$P^{\cdot} + O_2 \longrightarrow POO^{\cdot},$$

$$POO^{\cdot} + IH \xrightarrow{k_1} POOIH^{\cdot} \longrightarrow POH + IO^{\cdot},$$

$$POO^{\cdot} + IH \xrightarrow{k_3} G + I^{\cdot},$$

$$POO^{\cdot} + I^{\cdot} \xrightarrow{k_4} POOI$$

is retained without changes. So is the scheme of the latent radical transformations of the quinoid alcohol IOH, which ensure partial regeneration of the initial phenol.

This combination of s- and v-schemes indicates that the macroradicals occurring within individual zones are non-equivalent with respect to oxidation and interaction with the inhibitor: in supermicropores, the rates of these processes are low, whereas in v-zones, on the contrary, they are high. This selectivity, which is associated with the predominant accumulation of low-molecular-weight compounds (including oxygen and the inhibitor) in the grains of sponge micelles filled with narrow micropores, is obviously a general phenomenon.[1–6,11–13,25] An example of this non-equivalent behaviour has been considered in the description of the transformations of ionol in the s-chains of initiated destruction of macromolecules and in the v-chains of arylation of CTA and PC (Section II). A number of similar facts have been reported. For example, it is quite characteristic that the number of polymer chains cleaved per unit time in the oxidation of molten polystyrene at 473 K (P_{O_2} = 150 mm Hg) in the presence of bisphenol 2246 as an inhibitor remains virtually unchanged over a period of 26 h.[36,37] This phenomenon is observed during the induction period if the concentration of the inhibitor is high; in the case of a low inhibitor concentration ($c_i \rightarrow 0$), it is observed after the induction period has been completed. In the oxidation of rubber in the presence of ionol[38] and in the oxidation of PP in the presence of bisphenol 2246 (437 K, P_{O_2} = 300 mm Hg),[30] the concentration of inhibitor also has no influence on the rate of the polymer destruction during the induction period.

Thus, the heterophase scheme suggested for the non-initiated co-oxidation of alkylphenol and the polymer conforms to the general features observed for the induction period of the process and takes into account the specific features of co-oxidation in a heterogeneous chain-sponge micellar matrix considered previously.

By applying the condition of steady-state concentration of radicals to each unit of the overall scheme of the process considered, it is easy to obtain an expression for the rate of the s,v-transfer of free valence

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

If the polymer has been saturated with oxygen ($k_{-m} \ll k_{tr}[O_{2s}]$), this expression assumes the following form

$$V_{tr} = \frac{\delta k_{0s,p} k_m [PH_s][O_{2s}]}{2k_{2s}}. \quad (32)$$

The V_{tr} value, which is simultaneously the rate of generation of the reaction v-chains, is equal to the rate of their termination.

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

Under the conditions considered, the rate of consumption of alkylphenol does not depend on its concentration but depends on the oxygen pressure:

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

$$\approx \beta k_1 [POO^{\cdot}][IH] = \frac{\beta k_1 V_{tr}}{k_3} =$$

$$= \frac{\beta k_1 \delta k_{0s,p} k_m}{4 k_3 k_{2s}} [PH_s][O_{2s}] = \beta k_{i,p} P_{O_2} . \quad (33)$$

Here $[O_{2s}] = K_{O_2}[O_{2v}] = K_{O_2} \gamma P_{O_2}$, where K_{O_2} is the equilibrium constant for the oxygen exchange between the zones, γ is the Henry constant, $\beta = k_{3f}/(k_{2f} + k_{3f})$ is the efficiency of the consumption of quinoid alcohol in the steps of regeneration of phenol (see Sections VI and VII), and $k_{i,p}$ is the complex constant.

According to this scheme, the rate of oxygen absorption

$$V = -\frac{d[O_2]}{dt} \approx k_5 [IO^{\cdot}][PH] = k_1 [POO^{\cdot}][IH] = k_{i,p} P_{O_2}$$

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

It is these regularities that have been established back in early studies dealing with the mechanism of antioxidative stabilisation with phenols, which have been regarded as weak inhibitors. Processes involving inhibitors of this type are characterised by an approximately zero order with respect to the inhibitor, the first order with respect to oxygen, and the linear dependence of the duration of the induction period on the inhibitor concentration. The following antioxidants were studied: 2,6-bis(1,1-dimethylhexyl)-4-methylphenol (at 473 K and at P_{O_2} = 300 mm Hg, the value of t_{ind} increased linearly from 9.5 min at $c_i = 0$ to 373 min at c_i = 0.20 mol kg^{-1}),[39,40] 2,4,6-tri-*tert*-butylphenol (the effective activation energy for the consumption of phenol in the 453 – 473 K range: E_i = 151 kJ mol^{-1}),[41] 2,6-di-*tert*-butyl-4-phenylphenol (E_i = 126 kJ mol^{-1}),[41] and a bis-phenol with spatially separated OH groups — 4,4′-methylenebis(2,6-di-*tert*-butylphenol) (the t_{ind} value increased linearly from 9.5 min at $c_i = 0$ to 250 min at c_i = 0.025 mol kg^{-1}).[41]

One more feature peculiar to the phenols listed above is that their consumption is not accompanied by the formation of water; the appearance of water becomes noticeable only at the very end of the induction period. This important fact indicates that the rates of decomposition of peroxyl radicals (with evolution of OH$^{\cdot}$) and of the polymeric hydroperoxide formed in small amounts are negligibly small. The fact that the rates of consumption of oxygen and inhibitor remain constant over the whole induction period also implies that hydroperoxide scarcely makes any contribution to the radical generation at the stage of co-oxidation of the polymer and phenol.[42]

The heterophase scheme accepted by us does not include reactions of decomposition of POO$^{\cdot}$ radicals or hydroperoxide groups; this reflects the fact that the concentration of peroxyl radicals sharply decreases when the polymer contains even a minor amount of an inhibitor.

Additional evidence for the chain mechanism of the co-oxidation of polyalkenes and alkylphenols is provided by the substantial deceleration of this process in the presence of dialkyl sulfides.

1. The mechanism of co-oxidation inhibited by dialkyl sulfide

Analysis of the characteristic features of transformations of antioxidants in the polymer-chain zones of sponge micelles causes one to consider the problem of the mechanism of joint action of phenolic antioxidants and dialkyl sulfides. It is known that the latter do not possess any substantial inhibitory activity but extend markedly the induction period in the co-oxidation of a polymer with a 'weak' phenol and change the kinetics of the phenol consumption.[41,43]

The reasons for the non-additive influence of phenol and dialkyl sulfide have been considered in the literature in terms of the concept of non-radical decomposition of a hydroperoxide by a dialkyl sulfide. It is believed that dialkyl sulfide destroys hydroperoxide without formation of free radicals and thus decreases dramatically the rate of degenerate branching of oxidation chains, the probability of which during the induction period in the presence of a 'weak' phenol is thought to be relatively high. As shown above, hydroperoxide can hardly act as a branching agent at the stage of co-oxidation, if for no other reason than its fairly low concentration. However, even in the samples in which hydroperoxide has been specially accumulated prior to the reaction, the branching factor of oxidation chains in the presence of alkylphenol is equal to zero (Sections V and VI), and the transformation reduces only to oxidative chain decomposition of hydroperoxide.

Thus, the question of the mechanism of direct interaction of dialkyl sulfide and hydroperoxide, which has not yet been ultimately resolved due to its complexity,[14] becomes a separate problem. It is significant for us that dialkyl sulfide, which is not an inhibitor for the polymer oxidation itself, inhibits its co-oxidation of alkylphenol. In other words, dialkyl sulfide acts as if it extended the period during which alkylphenol is efficient. This is indicated, for example, by the character of kinetic curves for the consumption of 2,6-bis(1,1-dimethylhexyl)-4-methylphenol and bisphenol 2246 obtained for oxidation at 473 K (P_{O_2} = 300 mm Hg).[14,43] It can be seen from Fig. 14 that the rates of consumption of monophenol (the initial concentration was 0.16 mol kg^{-1}) and bisphenol (the initial concentration was 0.08 mol kg^{-1}) in the presence of 0.08 mol kg^{-1} of a sulfide are lower than those in the absence of the sulfide. This is observed even at the very beginning of the reaction when a change in the yield of radicals in the steps of hydroperoxide decomposition under the influence of both phenol and sulfide is out of the question. As has already been noted, influence of this sort is not manifested even at high concentrations of hydroperoxide (Sections V and VI).

In addition, we mention important results,[30] according to which in the oxidation of molten PP (473 K, P_{O_2} = 300 mm Hg), the rate of evolution of propene remains constant over 100 min in the induction period; this rate is the same in the presence of 0.025

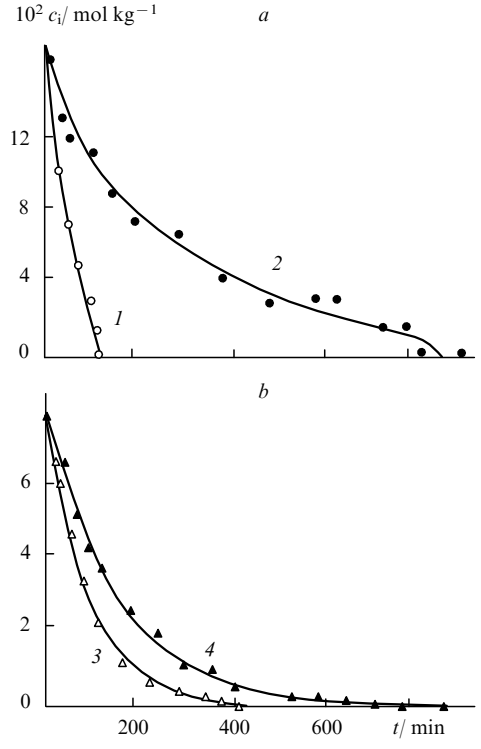


Figure 14. Curves for the consumption of 2,6-bis(1,1-dimethylhexyl)-4-methylphenol (*a*) and 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (*b*) during the induction period of the oxidation of polypropylene (473 K, P_{O_2} = 300 mm Hg) in the absence (*1*, *3*) and in the presence (*2*, *4*) of 0.08 mol kg^{-1} of didecyl sulfide.

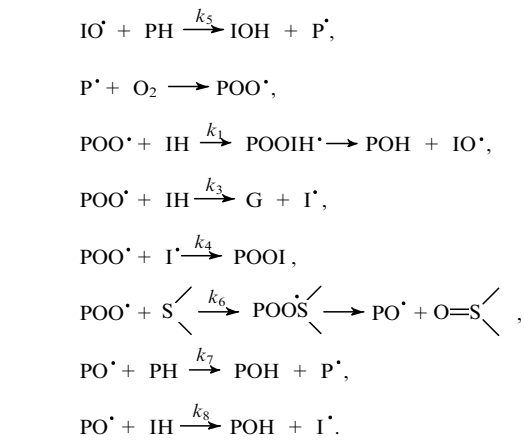
or 0.05 mol kg^{-1} of bisphenol 2246; it also does not change when 0.08 mol kg^{-1} of didecyl sulfide or dilauryl thiodipropionate are introduced in the reaction mixture. In other words, under these conditions, the concentration of depolymerising terminal macroradicals remains constant over a period of 100 min, and the process of degenerate branching involving hydroperoxide and phenol can be neglected.

At the same time, gas-chromatographic analysis has shown that the introduction of dialkyl sulfides in the PP being oxidised leads to a substantial increase in the yield of ethylene,[30] which indicates that sulfides interact with polymeric peroxyl radicals. When dialkyl sulfides are involved in co-oxidation with PP, they do not extend markedly the induction period. However, in the presence of a 'weak' phenol, a synergistic effect is manifested, and the induction period can become much longer. The mechanism of this phenomenon can be understood by taking into account the known [30] fact that dialkyl sulfides react with peroxyl radicals; this leads to a decrease in the concentration of peroxyl radicals, which induce the chain consumption of alkylphenol.

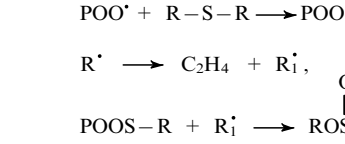
For this purpose, dialkyl sulfide should ensure the conversion of peroxyl into a polymeric alkoxyl, which then reacts predominantly with the inhibitor:



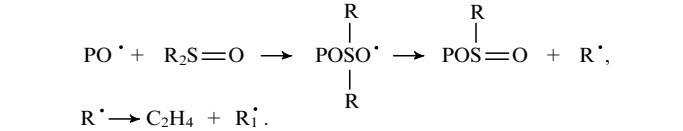
With allowance for the assumptions made, the scheme for the reaction v-chains of co-oxidation of the polymer, phenol, and sulfide assumes the following form:



In the absence of phenol, the role of dialkyl sulfide reduces to its consumption with the rate constant k_6 in the transformation of peroxyl radicals into alkoxyl radicals, which then produce oxidisable alkyl radicals $P^{\cdot}$ in a stage with the constant k_7. This results in the reduction of $POO^{\cdot}$. The overall sequence of reactions does not lead to a change in the concentration of peroxyl radicals; therefore, the consumption of dialkyl sulfide has no influence on the rate of oxidation of the polymer. The transformation of sulfide yielding ethylene, which either follows a replacement mechanism [30]



or occurs as a reaction of the alkoxyl radical formed with sulfoxide



is not shown in the scheme. These processes seem to be energetically and sterically less favourable than the stage characterised by constant k_6, which involves rupture of the weak peroxide bond and formation of a strong S–O bond. Therefore, the formation of ethylene can be regarded as a side process. Besides, it does not influence the kinetic picture of the co-oxidation with phenol, because $R_1^{\cdot}$ radicals are oxidised to peroxyl radicals, which qualitatively do not differ from polymeric peroxyl radicals.

The co-oxidation v-scheme under consideration includes a stage in which phenol interacts with $PO^{\cdot}$ radicals and terminates the reaction chains involving dialkyl sulfide. Thus, the sulfide assumes an inhibitory function, which was lacking initially.

However, when the concentration of phenol is sufficiently high, the oxidative chains predominate again due to an increase in the rates of reactions characterised by constants k_1 and k_5. This ensures a co-oxidation route independent of the presence of dialkyl sulfide.

By applying the condition of steady-state radical concentration to the v-scheme described above and resorting to the above assumption that regeneration of phenol occurs by a latent-radical mechanism, we can obtain quite easily an expression for the rate of consumption of the inhibitor

$$V_i = -\frac{dc_i}{dt} \approx \beta k_1 [POO^{\cdot}] c_i = \\ = \frac{0.5 \beta k_1 c_i V_{tr}}{k_3 c_i + k_6 k_8 c_i c_S / (k_7 [PH] + k_8 c_i)},$$

where c_s is the concentration of dialkyl sulfide. This equation can be brought to identical forms at opposite concentration ratios

$$\frac{c_i}{c_S} \ll 1 \text{ and } \frac{c_i}{c_S} \gg 1 .$$

In fact, when the concentration c_i is low, so that the inequality $k_7[PH] \gg k_8 c_i$ holds, the second term in the denominator of the main fraction in the expression for V_i can be neglected. Conversely, if the concentration c_i is high, then $k_7[PH] < k_8 c_i$; but the inequality $k_3 c_i > k_6 c_S$ is also valid. The final results are identical in both cases

$$V_i = \frac{0.5 \beta k_1 V_{tr}}{k_3},$$

i.e. dialkyl sulfide has no influence on the rate of the process.

However, when the ratio of concentrations is intermediate

$$\frac{c_i}{c_S} \approx 1$$

and the inequality $k_7[PH] < k_8 c_i$ holds in combination with $k_3 c_i < k_6 c_S$, then the expression for the rate of consumption of the inhibitor assumes the following form

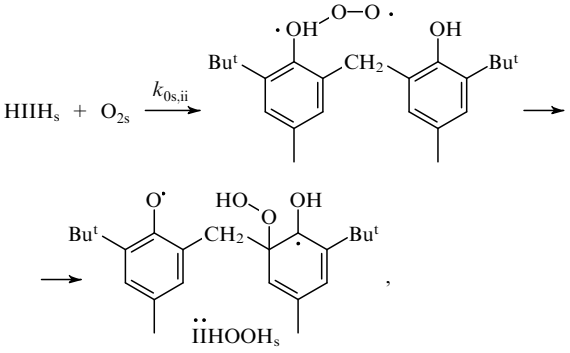
$$V_i = \frac{0.5 \beta k_1 c_i V_{tr}}{k_6 c_S}.$$

Consequently, within a certain time interval, the process is first order with respect to phenol, which is in agreement with Eqn (32) describing the rate of translation of radicals V_{tr} to the v-zones of sponge micelles. The rate of consumption of the 'weak' phenol decreases, since the inhibitory activity of dialkyl sulfide induced by phenol is fully manifested under these conditions. Comparison of dependences *1* and *2* in Fig. 14 indicates that the kinetic law for the consumption of the inhibitor has actually changed in agreement with the theoretical prediction, which follows from the heterophase model of the induction period of the process.

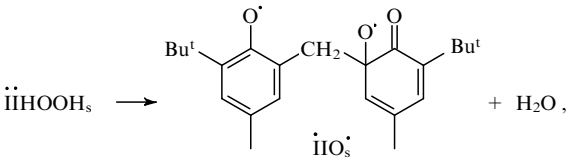
2. Characteristic features of co-oxidation with 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol)

The influence of dialkyl sulfides on the duration of the induction period of the oxidation of polyalkenes mixed with bisphenol 2246, which is considered to be a strong inhibitor,[14] is less pronounced. The deceleration of consumption of bisphenol is also manifested to a lesser degree than that for a weak phenol (Fig. 14, curves *3* and *4*). Molecules of bisphenol 2246 differ from molecules of 'weak' phenols, on the one hand, by less efficient shielding of the OH groups by the neighbouring alkyl substituents (and, hence, their higher accessibility to attacking radicals and to oxygen molecules) and, on the other hand, by specific mutual arrangement of the benzene nuclei (see Section III). For these reasons, direct oxidation of bisphenol 2246 occurring in s-zones of the polymer-chain sponge to yield radicals is facilitated (Scheme 1).

Scheme 1



$$\ddot{\text{I}}\text{IHOOH}_s \longrightarrow \text{HIIOOH (intramolecular disproportionation)},$$



$$\cdot\text{IIO}_s^{\bullet} + \text{PH}_s \longrightarrow \cdot\text{IIOH} + \text{P}_s^{\bullet},$$

$$\text{P}_s \xrightarrow{k_{1s}} \text{R}_s^{\bullet},$$

$$\text{R}_s^{\bullet} \xrightarrow{k_{2s}} \text{R}_{1s}^{\bullet},$$

$$\text{R}_s^{\bullet} + \text{R}_{1s}^{\bullet} \xrightarrow{k_{3s}} \text{products},$$

$$\text{R}_{1s}^{\bullet} + \cdot\text{IIOH}_s \longrightarrow \text{R}^{=} + \text{HIIOH}.$$

Therefore, when bisphenol 2246 is present at a sufficiently high concentration, the products of its oxidation act as the main initiator of co-oxidation. This has been observed by Pudov *et al.*,[30] who have found that over a period of 100 min after the beginning of the process, the rate of evolution of propene (resulting from depolymerisation of PP) increases up to a constant value, which is the same for different concentrations of HIIH (0.025 and 0.05 mol kg^{-1}), and this occurs during the induction period. According to the s_{ii} scheme, the constant initial rate of propene evolution is explained by the fact that bisphenol 2246 not only initiates the formation and depolymerisation of alkyl macroradicals $R_{1s}^{\bullet}$ but also ensures that a constant concentration of these species is maintained through their disproportionation with the bisphenol-derived phenoxyl radicals $\cdot$IIOH, which arise in the steps of radical generation. The fact that the rate of propene evolution increases up to a constant value during the induction period can be attributed to dissociation of the peroxide initiator of a quinoid structure HIIOOH formed from the bis-phenol, the concentration of which reaches a steady-state value.

In conformity with the s_{ii}-scheme, the steady-state concentration of mediator radicals, responsible for the interzone s,v-transfer of radicals, is

$$[\text{R}_s^{\bullet}] = \frac{\lambda\, c_{ii}\, P_{O_2}}{2\, k_{2s}},$$

where λ is a complex value characterising the efficiency of the initiator action of bisphenol, and c_{ii} is its concentration.

The transfer of free valence from s-zones into v-zones, as in the case of phenols considered previously, occurs *via* intermediate formation of active quinoid alkoxyl radicals

$$\text{R}_s^{\bullet} \underset{k_{-m}}{\overset{k_m}{\rightleftharpoons}} \text{R}_m^{\bullet},$$

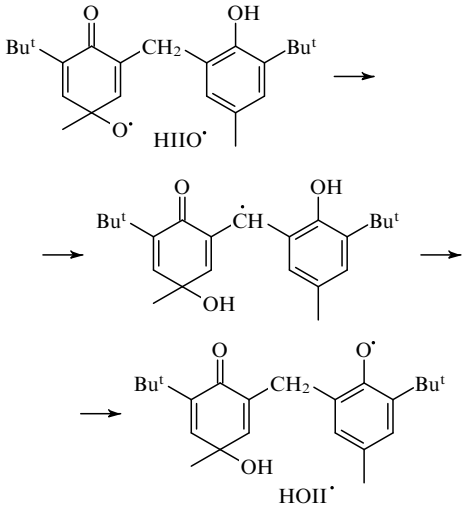
$$\text{R}_m^{\bullet} + \text{O}_{2s} \xrightarrow{k_{tr}} \text{ROO}_m^{\bullet},$$

$$\text{ROO}_m^{\bullet} + \text{HIIH}_s \longrightarrow \text{ROO}\dot{\text{I}}\text{HIH}_m \longrightarrow \text{ROH} + \text{HIIO}_m^{\bullet}.$$

This alkoxyl radical migrates to the v-zones of the polymer and initiates co-oxidation in these zones.

It is known [14, 40, 44] that in the presence of bisphenol 2246, the induction period (more precisely, the period of co-oxidation) is much longer, and the influence of dialkyl sulfides is substantially less pronounced than in the case of 'weak' monophenols. Both of these effects may be due to the specific structure of the bisphenol molecule, which ensures large probability of isomerisation of active alkoxyl into inactive phenoxyl *via* an intermediate radical of the benzyl type (Scheme 2).

Scheme 2



Competition between the steps of isomerisation and s,v-translation

$$\text{HIIO}_m^{\bullet} \xrightarrow{k'_{tr}} \text{HIIO}^{\bullet},$$

$$\text{HIIO}_m^{\bullet} \xrightarrow{k_{is}} \text{HOII}^{\bullet}$$

leads to a substantial decrease in the rate of generation of reaction v-chains. In a system saturated with oxygen, this rate is equal to

$$V_{tr} = k'_{tr}[\text{HIIO}_m^{\bullet}] = \frac{\delta_{ii}, \lambda\, c_{ii} P_{O_2}}{2\, k_{2s}} = \frac{\delta_{ii}}{2k_{2s}}, \qquad (34)$$

where

$$\delta_{ii} = \frac{k_m\, k'_{tr}}{k'_{tr} + k_{is}} < k_m.$$

A similar isomerisation of phenoxyl radicals makes a contribution to the termination of co-oxidation chains in v-zones of the polymer:

$$HIIO^{\bullet} + PH \xrightarrow{k_5} HIIOH + P^{\bullet},$$

$$P^{\bullet} + O_2 \longrightarrow POO^{\bullet},$$

$$POO^{\bullet} + HIIH \xrightarrow{k_1} POO\dot{I}HIH \longrightarrow POH + HIIO^{\bullet},$$

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

$$HII^{\bullet} \longrightarrow IIH^{\bullet} \text{ (isomerisation of phenoxyl into σ-complex, see Section III)},$$

$$POO^{\bullet} + IIH^{\bullet} \longrightarrow G + II \text{ (cyclic quinoid compound)},$$

$$HIIO^{\bullet} \xrightarrow{k_9} HOII^{\bullet},$$

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

It is assumed that here, as in the case of monophenols, partial regeneration of the initial bisphenol from the quinoid alcohol HIIOH occurs by the latent radical mechanism.

Since an additional route for the termination of the reaction v-chains exists, this process occurs at a lower concentration of the peroxyl radicals $POO^{\bullet}$. This concentration can be found from the condition of equality of the rates of v-chain generation and termination:

$$V_{tr} = 2k_3[POO^{\bullet}]c_{ii} + 2k_9[HIIO^{\bullet}] =$$

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

For this reason, and also due to the fact that radicals lose their reactivity during s,v-translation [in Eqn (34), $\delta_{ii} < k_m$], the rate of consumption of bisphenol becomes much lower than that of monophenols [Eqn (33)].

$$V_{ii} = -\frac{dc_{ii}}{dt} \approx \beta k_1[POO^{\bullet}]c_{ii} = \frac{\beta k_1\delta_{ii}\lambda c_{ii}P_{O_2}}{(2k_3 + 2k_1k_9/k_5[PH])2k_{2s}}.$$

Simultaneously, the induction period of the polymer oxidation becomes longer, and the opportunity for the synergistic action of a dialkyl sulfide decreases.

Thus, within the framework of the heterophase model, the induction period is distinguished as a macroscopic stage involving chain co-oxidation of the inhibitor and the polymer. At this stage, alkylphenol actively participates in the chain process and is mostly consumed in the steps of propagation of co-oxidation chains rather than in the steps of termination of oxidation chains. This period is finished when the concentration of the inhibitor decreases and the concentration of peroxyl radicals increases to a degree at which the rate of oxygen absorption is determined only by the steps of oxidation of the polymer itself[4–6, 25]

$$POO^{\bullet} + PH \longrightarrow POOH + P^{\bullet},$$

$$P^{\bullet} + O_2 \longrightarrow POO^{\bullet},$$

$$POO^{\bullet} \longrightarrow {}^{\bullet}POOH \longrightarrow HO^{\bullet} + \text{products},$$

$$HO^{\bullet} + PH \longrightarrow P^{\bullet} + H_2O,$$

and by bimolecular chain termination steps

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

The fact that both in the presence of an inhibitor and after its complete exhaustion the oxidation process does not switch to a regime with non-degenerate (non-stationary) branchings of reaction chains is of primary importance. The transition from co-oxidation to the oxidation of the polymer itself occurs when the condition of steady-state concentration of peroxyl radicals is fulfilled. This requirement is also retained when the regime of co-oxidation changes from the zero order to an apparent first order with respect to phenol following the introduction of dialkyl sulfide into the system.

It should be noted that the extension of the induction period, which accompanies the change in the regime, is often manifested quite clearly in the $t_{ind}(c_{i0})$ plots, the concentration of phenol at the inflection point in the curve being interpreted as the critical concentration corresponding to the transition from a non-stationary branched chain process to stationary oxidation.[14] The fact that the stage with non-stationary branching does exist was confirmed[14] by the observation that at a relatively high temperature ($\sim$473 K), the lifetime of hydroperoxide is limited to several seconds. However, the chain heterophase mechanism of anaerobic decomposition of hydroperoxide was not taken into account.

In the absence of oxygen, decomposition of hydroperoxide follows a chain mechanism, the contribution of spontaneous decomposition to the overall hydroperoxide consumption, as has been shown in Section IV, being negligibly small.[5,6] Despite the fact that according to Eqn (18), the life span of hydroperoxide within s-micropores at T $\approx$ 473 K is tens of seconds, the lifetime of the main bulk of hydroperoxide in the dissociated state, which is localised in the narrow micropores of v-zones of the chain sponge is much higher. For example, it is remarkable that in the absence of oxygen at 453 K, polystyrene hydroperoxide decomposes by half over a period of 12–15 min, while under conditions of oxidation of molten polystyrene† at 473 or 453 K it is accumulated, together with other products, for 30 or 100 min, respectively[45] and does not decompose noticeably until it begins to react with accumulated products of the polymer oxidation. After that, the accumulation of hydroperoxide ceases, and its concentration decreases.

The data considered in the present and previous Sections indicate that the explanation of the 'critical' concentration of phenols proposed previously[14] was inadequate. In terms of our structural-kinetic reaction model, the inflection in the $t_{ind}(c_{i0})$ curve caused by the presence of dialkyl sulfide is due to the decrease in the rate of consumption of phenol in the co-oxidation following its transition from the zero order to the first order with respect to the inhibitor, when in the absence of non-stationary branching of the reaction chains, a quasi-steady-state concentration of peroxyl radicals is retained.

When the process obeys a zero-order kinetics, the rate of consumption of the inhibitor is constant

$$-\frac{dc_i}{dt} = V_i = \frac{c_{i0}}{t_{ind,i}} = \text{const}.$$

Thus, the time required for its complete consumption (*i.e.* the period co-oxidation) is equal to

$$t_{ind,i} = \frac{c_{i0}}{V_i}.$$

If we add the time t_0 for the propagation of reaction after the inhibitor has been exhausted to the above value, we obtain the dependence of the induction period on the initial concentration of phenol

$$t_{ind} = t_0 + t_{ind,i} = t_0 + \frac{c_{i0}}{V_i}.$$

The linear dependence $t_{ind}(c_{i0})$ holds over a wide range of monophenol concentrations.[39–41] The length of the linear sections decreases appreciably in the presence of dialkyl sulfide. In this case, t_{ind} rapidly increases starting from a certain 'critical' $c_{i0,cr}$ value. A similar behaviour has also been observed in the presence of bisphenol 2246. In these systems, co-oxidation at $c_{i0} > c_{i0,cr}$ (and $c_{ii0} > c_{ii0,cr}$) obeys first-order kinetics and is characterised by an exponential equation

† In the presence of oxygen, the mechanism of hydroperoxide decomposition basically changes.

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

or

$$\ln \frac{c_{i0}}{c_i} = k_i t .$$

This equation is valid until the $c_{i0,cr}$ value is attained. After that, the law for the termination of reaction chains changes, and their bimolecular termination in the subsequent steps begins:

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

In this case, the total induction period is characterised by the sum

$$t_{ind} = t_0 + \frac{1}{k_i} \ln \frac{c_{i0}}{c_{i,cr}} .$$

This relation holds fairly frequently.[14]

The above structural-kinetic model for the co-oxidation of the phenol and a polymer makes it possible to elucidate more precisely the physical meaning of the antagonistic influence of monophenol and bisphenol 2246 simultaneously introduced in a polymer.[14, 39, 40] Although in this case, the overall content of inhibitors is larger, the induction period in the presence of these mixtures is shorter than that observed with bisphenol 2246 alone. The authors cited explained this phenomenon by a specific influence of monophenol and bisphenol on the emergence of radicals from the 'cage' of the hydroperoxide, which decomposes spontaneously. They believed that the monophenol destroys one of the radicals in a primary radical pair but prevents the destruction of the second radical; thus, the overall yield of radicals should increase. However, in the presence of bis-phenol 2246, which contains two functional groups, the yield of radicals increases to a lesser extent than in the presence of a monophenol or does not increase at all.

However, in contrast to these views, the data presented in Sections V and VI indicate that a typical monophenol, ionol, does not lead to any substantial increase in the yield of radicals from hydroperoxide. The kinetic model considered above makes it possible to give a simple explanation to the antagonistic effect.

Monophenol increases the rate of generation of co-oxidation v-chains by accelerating the injection of free valence from s-zones to v-zones of the polymeric-chain sponge. In this case, the term 'reaction cage' refers to a system of supermicropores in the structural s-zones rather than to a homogeneous environment consisting of macromolecular segments and resembling a structureless liquid.

Monophenol reacts with the mediator peroxyl radical and is thus converted into a quinoid alkoxyl

$$ROO^{\bullet}_m + IH_s \longrightarrow ROOIH^{\bullet} \longrightarrow ROH + IO^{\bullet} ,$$

which cannot isomerise into the inactive phenoxyl. In this case, $\delta_i = k_m$, whereas in the reaction involving bisphenol 2246, $\delta_{ii} < k_m$ [Eqn (34)].

The competition between monophenol and bis-phenol for the s,v-transfer of radicals results in an increase in the rate of generation of the co-oxidation chains in v-zones of the polymeric matrix and thus shortens the induction period.

In conclusion, note that in the presence of sterically hindered monophenols considered in previous studies,[41,43] no transition to the first-order kinetics was observed over the whole range of monophenol concentrations studied. However, it cannot be ruled out that this transition would be possible in the presence of phenols in which the steric hindrance from the alkyl substituents is weaker or at a sufficiently high concentration c_i. For example, this situation can arise if the reversible dissociation of a complex of phenol with oxygen

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

competes with the following reaction

$$(I^{\bullet} \ldots HOO^{\bullet})_s + IH_s \longrightarrow I^{\bullet}_s + HOOIH^{\bullet}_s ,$$

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

Diminution of steric hindrance can also be favourable for the appearance of an additional pathway to the termination of co-oxidation chains.

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

The reasons considered above might also account for the known fact that 4,4′-methylenebis(2-methyl-6-*tert*-butylphenol), which contains spatially separated OH groups in the molecule and is considered[14] to be a weak antioxidant, is actually as effective as bisphenol 2246.[46] The termination steps mentioned above can also be among the reasons for the synergistic effect exhibited by antioxidant mixtures.

IX. Conclusion

A certain relationship between the microheterogeneous structure of the non-crystalline polymeric matrix and chemical transformations in the polymers has been mentioned in the literature long ago; this has been reflected in the polychromatic[47] (or polychromic)[48] kinetic model. However, individual studies in which this relationship was only stated, have not yet been united in a separate branch of the chemical physics of polymers. Description of kinetic polychromatism has reduced only to one or another variant of the formal mathematical scheme based on general physical views, without disclosing the in-depth causes for its origin.

It is clear that construction of adequate chemico-physical models for polymeric transformations requires inevitably that the supermolecular organisation of the polymeric reaction medium be known in detail. The microheterogeneous chain-sponge structure of polymer chains increases substantially the number of factors, which are able to influence in a particular way a chemical process involving them (compared to the number of factors influencing processes in a homogeneous liquid) and hampers the theoretical studies. Construction of structural kinetic reaction models[10] is helpful in overcoming the arising difficulties (which is especially significant in the initial stage of the development of the theory).

The models for chain processes presented in this review have been constructed with allowance for the fine structure of polymer chain-sponge micelles, which contain a sponge framework possessing a certain degree of mobility. In these models, the notion of mobility is associated with the property of micropores to change their sizes under the influence of thermofluctuational motion of cooperated units of flexible polymer chains within the microporous sponge structure rather than with the abstract concept of 'molecular segmental mobility'.

The method of structural-kinetic modelling made it possible to discover important regimes of chain reactions, such as heterogeneous-heterophase and heterogeneous-homophase regimes, and to refine the concept of 'latent radical' (intracage) processes occurring inside a thermofluctuationally excited micropore, which has expanded to the size of a supermicropore.

The construction and analysis of various reaction models proved the validity of the general concept of the chemistry of the microheterogeneous polymeric-chain sponge. This concept provides extensive possibilities for further specification of the mechanism of elementary chemical steps occurring in a fluctuating sponge material. In addition, it requires that researchers change their attitude to some generally accepted views concerning the homogeneous character of non-crystalline polymers (in terms of the homogeneous model, a kinetically unstable unit, which is formed and destroyed by fluctuations, has a 'short-range' order in the arrangement of segments, and resembles the areas with a short-range order in liquids, is considered as the only structural element).[49]

In particular, the interpretation of the self-acceleration stage in the oxidation of polyalkenes within the framework of the non-stationary branched chain mechanism should be rejected.

It is also believed[14] that the absence of substantial deviations from the first-order kinetics indicates that the inhibitor is mostly consumed in its direct interaction with oxygen and in the steps of termination of the oxidation chains thus generated. However, in reality, as shown in our review, the greater part of phenol is consumed *via* its chain co-oxidation with the polymer, no matter what particular order — zero or first — with respect to the inhibitor is obeyed by the process.

The criterion used in the inhibitor method for determination of the rate of generation of oxidation chains in homogeneous liquids [15] also loses its fundamental significance when applied to polymers. The zero order for consumption of an inhibitor in a microheterogeneous chain-sponge medium does not imply any longer, as it does in a homogeneous liquid, that the inhibitor is not involved in any step other than termination of reaction chains. The inhibitor molecules, which occur in a polymeric matrix and scavenge all the reaction chains, can liberate fairly reactive radicals, together with inactive ones. Thus, the inhibitor becomes an active participant in the co-oxidation with the polymer.

The structured character of the chain-sponge polymeric matrix also causes the need to determine separately the non-equivalent rates of radical generation, firstly, in quasi-steady-state zones consisting of relatively immobile supermicropores, secondly, in dynamically more active zones in which the oxidation chains of macromolecules propagate, and, thirdly, at the stage of the interzone transfer of radicals. Simultaneously, this gives rise to the problem of development of experimental methods for determining the rate constants for the elementary reactions, which characterise heterogeneous steps in the polymeric-chain sponge.

This review is a logical continuation of the studies performed by Academician N M Emmanuel and his school dealing with oxidation processes in the condensed phase.[50–54]

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