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Kinetics and Mechanism of the Oxidation of Polymers in a Stressed State

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The characteristics of the kinetics and mechanism of the chain oxidation of stressed polymers are considered as a result of structural and conformational changes occurring in polymer matrices under the influence of mechanical stresses. Attention has been concentrated on the kinetics of the autoxidation of polyolefins subjected to the influence of stretching stresses and the kinetics of the ozonisation and autoxidation of stressed raw and cured rubbers. The results of studies on the kinetics of individual stages of the chain process, namely initiation, propagation, degenerate branching, and termination of kinetic chains in stressed polyolefins, are surveyed; the effects of orientational stretching in the kinetics of the oxidation of polyolefins are considered. The relation between the kinetics of oxidation, durability, and the mechanism of the decomposition of oriented specimens subjected to an external mechanical load is discussed. The method of defectoscopy of polymers subjected to the simultaneous influence of mechanical stresses and an oxidising medium, based on the local character of the oxidation of stressed polymers, is considered.
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I. INTRODUCTION

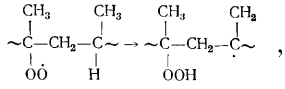
The use of polymeric materials as a rule involves the operation of mechanical stresses applied either from the outside or internal stresses arising during the conversion of the polymer into a finished article and also in the course of the ageing of the polymer. Chemical reactions leading to the ageing of polymers therefore usually take place in stressed polymer matrices. A characteristic feature of chemical reactions in solid polymers is a relation between the reaction kinetics and the structural-physical parameters of the matrix, which differ significantly for the unstressed and stressed specimens. The task of predicting the durability of polymeric articles and the search for the optimal ways of stabilising polymers require the knowledge of and allowance for the influence of mechanical stresses on the kinetics and mechanism of ageing processes. Since the publication of the first study in which the accelerating influence of mechanical stresses on the rate of oxidation of vulcanised rubbers was demonstrated (the authors called this phenomenon mechanical activation[1,2]), more than 30 years have elapsed and extensive and varied experimental data concerning the influence of mechanical stresses on the kinetics of the oxidation of polymers of different classes by molecular oxygen and ozone have accumulated. In the present review an attempt is made to analyse and survey these data.

The structural microheterogeneity of solid polymers, even those in the amorphous state (see, for example, Jech[3] and Arzhakov et al.[4] as well as Lebedev's review[5]) has important kinetic consequences.

1. The microheterogeneity of the distribution of the reactants in the matrix leads to the possibility that their local concentrations differ significantly from the average values and the experimental rate constants calculated in relation to the average concentrations differ appreciably from the true values. The microheterogeneity in the distribution of the reactants can also be one of the causes of the manifestation of polychromatic kinetics characteristic of reactions in solid matrices: the reactions take place at a higher rate in regions with higher local concentrations and, as these regions become exhausted, those with lower local concentrations are "manifested". Formally, this will be described as a distribution with respect to the reaction rate constants. The microheterogeneity of the distribution of reactants is shown most distinctly in amorphous-crystalline polymers. For example, a stable nitroxy-radical is localised exclusively in the amorphous phase of polypropylene (PP)[6]. Antioxidants are also localised in the amorphous regions and the solubility of antioxidants in isotropic PP depends on its supermolecular structure: 80% of antioxidants are dissolved within spherulites and in the interfibril and defective intrafibril regions, while 20% are localised at the interspherulite interfaces[7]. Allowance for the heterogeneity of the distribution of antioxidant molecules in the polymer matrix is extremely important for the practical stabilisation of polymers.

2. The most important structural-physical parameter of a solid polymer for kinetics is the distribution with respect to the frequencies and amplitudes of molecular movements, which also leads to a distribution with respect to the reaction rate constants. This problem has been analysed in detail in a review[8]. The relation between the kinetics and molecular mobility is determined, firstly, by the dependence of the rate of diffusional encounters between the reactant molecules on the molecular mobility of the polymer, and, secondly, by the influence of the molecular dynamics directly on the chemical reactions step (see, for example, Girva and co-workers[6,9,10]). The possible physical mechanisms of the influence of molecular mobility on the reactivity have been discussed[8].

3. Finally the relation between the reaction kinetics and the set of polymer conformations, specific to reactions in polymer matrices, is due to the fact that many reactions in polymers take place intramolecularly. An example may be provided by the radical substitution reaction



(I)

which is a reaction involving the propagation of kinetic chains in the chain oxidation of polyolefins, leading to the migration of a free valence in the specimen. The ratio of the rate constants for the intramolecular and intermolecular reactions (I) in 2,4-dimethylpentane, a low-molecular-weight

analogue of polypropylene, at 100 °C is approximately two orders of magnitude[11]. An important structural requirement for the intramolecular transfer of a hydrogen atom from a carbon atom to a peroxy-radical is the formation of six-membered (or larger) rings in the transition state. In general, the abstraction of a hydrogen atom by a free radical requires that the bond ruptured should be located on the axis of the unpaired electron at a distance of 1.5–2 Å from the latter, i.e. that the pre-start state of the reactant should be located on the reaction coordinate[8]. Evidently the probability of the appearance of such a pre-start state and the probability of the formation of a transition complex having the optimum structure depend on the local conformation of the reaction centre. In polymers structural relaxation takes place slowly and the local mobility of a section of the macromolecule depends on its local conformation[12], so that one can expect a dependence of the kinetics of intramolecular reactions on the set of conformations of the polymer. Examples of such a relation will be considered below.

The conformations of macromolecules can influence, albeit to a smaller extent, also the rates of intermolecular reactions; for example, the rate constant for the abstraction of a hydrogen atom by the t-butoxy-radical in atactic PP at 45 °C is lower by a factor of two than in 2,2,4-trimethylpentane[13], which is associated with the steric hindrance to the reaction in the polymer; such hindrance should depend on the conformations of the macromolecules.

Under the influence of mechanical stresses, all the structural-physical parameters of the matrix significant for the kinetics of chemical reactions change in polymers. We shall consider mainly the effect of stretching stresses, which has been studied in greatest detail.

In the first place we shall note that two types of elasticity—predominantly entropic and predominantly energetic—are characteristic of polymers as a medium consisting of long and flexible chain molecules. The appearance in the polymer of entropic stresses is associated with the deviation of the conformations of the macromolecules from the statistically most probable conformations†. Energetic stresses are determined by the distortion of the valence angles and by the change in the lengths of the chemical bonds.

The calculated moduli of elasticity for various types of deformation of macromolecules have been published[14]. For the "pure" extension of a C=C bond, the modulus of elasticity is 740 GPa, for the extension of a "zig-zag" chain it is 180–340 GPa, and for the bending of a C=C bond and the hindered rotation of helices the moduli are 80 and 4–7 GPa respectively. The moduli of elasticity corresponding to the entropic and energetic stresses differ by two orders of magnitude. The deformation of polymers under the influence of external stretching stresses therefore initially takes place as a result of conformational rearrangements, which lead to the appearance of internal entropic stresses, and only after their completion does the distortion of valence angles and bonds, leading to the weakening of chemical bonds in the macromolecular skeleton, begin.

As will be shown below, entropic stresses become fixed ("frozen") in the amorphous phase of oriented amorphous-crystalline polymers if the latter are not subjected to a special heat treatment inducing the relaxation of the stress (annealing). Energetic stresses in amorphous-crystalline polymers arise after the application of an additional external load to oriented specimens, particularly in the region of plastic deformations.

† As a consequence of the presence of barriers to internal rotation, a purely entropic elasticity does not exist in polymers just as an ideal gas does not exist. We are only concerned with the question which component of elastic forces—entropic or energetic—is dominant.

II. THE INFLUENCE OF MECHANICAL STRETCHING STRESSES ON THE STRUCTURAL-PHYSICAL PARAMETERS OF POLYMER MATRICES

1. The Change in the Supermolecular Structure of Polymers under the Influence of a Stretching Load

Under the influence of stretching stresses, high and reversible (in the case of rubbers) deformations develop in amorphous highly elastic polymers (raw and cured rubbers) and the macromolecules are subjected to an orientation, which relaxes after the removal of the load (the preferred directions in the disposition of the macromolecular axes relative to the stretching axis appear). An enforced elasticity is manifested in vitreous amorphous polymers and an orientation arises which persists after the removal of the load at temperatures not exceeding the glass point. In isotropic amorphous-crystalline polymers the stretching stresses lead to profound structural rearrangements; the spherulitic structure is transformed into a fibrillar structure.

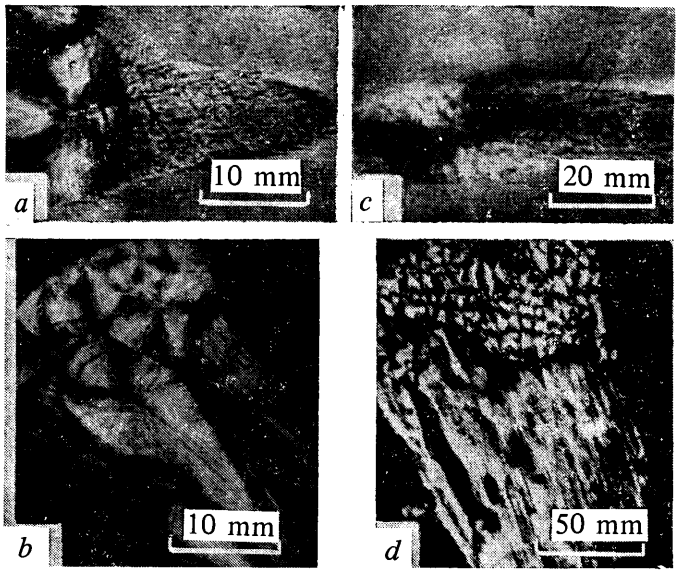


Figure 1. Stages in the deformation of a spherulite and the structure of the neck in isotactic PS[15].

The photomicrographs in Fig. 1 illustrate different stages in the deformation of a single spherulite in isotactic polystyrene (PS)[15]. The deformation of the spherulite takes place abruptly with formation of a "microneck" and a distinct interface persists between the deformed and undeformed parts of the spherulite. After the conversion of the entire spherulite into the "microneck", uniform deformation of the resulting oriented structure takes place and the formation of the microfibrillar structure is completed. In contrast to the

spherulitic structure, the microfibrillar structure is characterised by a distinct anisotropy of its properties. The microfibrils distributed along the direction of the extension contain alternating regions with crystalline and amorphous orders whose dimensions depend on the stretching (and annealing) conditions. The linkages between individual crystallites within the fibrils are formed by "crossing" macromolecules and also by a network of engagements between macromolecules, each of which returns to its "own" crystallite. In the transverse direction the individual microfibrils are linked by cohesive forces and crossing chains whose number is significantly lower than in the intrafibril regions. The transverse strength of monoaxially oriented polymer specimens is therefore much lower than their longitudinal strength.

As a result of the structural rearrangements induced by mechanical stresses, the proportions of the low-molecular-weight compounds in polymers and their solubilities change and there is a significant alteration of the molecular-dynamic properties of the matrices and the set of their conformations.

2. The Change in the Solubilities of Low-Molecular-Weight Compounds in Stressed Polymers

For elastomers, this question has been discussed in greatest detail[16] for rubbers stressed in a complex manner. Under the conditions of static compression, mechanical stresses lead to an anomalous transport of low-molecular-weight substances (plasticisers and inhibitors). The situation is different when elastomers are acted upon by stretching stresses: for deformations which do not induce the crystallisation of raw rubber (less than 200%), the permeability and diffusion characteristics hardly change[17,18]; for greater deformations, the crystallisation of raw rubber results in a significant decrease of the sorption and diffusion coefficients of low-molecular-weight compounds[17].

For vitreous amorphous and amorphous-crystalline polymers, the dependence of the permeability parameters on the stretching stress is complex[19–23]. In the region of stresses corresponding to the elastic deformations of the polymer, the degree of sorption of low-molecular-weight substances increases with increase of the stress owing to the increased fraction of the free volume in the specimen (in the majority of amorphous-crystalline polymers the Poisson coefficient is less than 0.5). In the region of stresses corresponding to plastic deformations, the sorption of low-molecular-weight compounds decreases appreciably with increase of deformation as a consequence of the decreasing density of the amorphous component[21]. The authors[21] based their interpretation of the experimental results on the model of impermeable microfibrils distributed in the bulk of the interfibrillar amorphous component. Despite the approximate nature of this model, in most cases its application is justified by the fact that the solubilities of low-molecular-weight compounds in amorphous-crystalline polymers are proportional to the fraction of the amorphous phase[24,25].

The study of the influence of mechanical stresses on the permeability parameters for oxygen is naturally of greatest interest for the elucidation of the kinetics of oxidation processes. There are few such data in the literature. It has been shown[25] that the solubility of oxygen in PP is proportional to the fraction of the amorphous phase and depends on the supermolecular structure of the polymer. However, one should note that the concept of the impermeability of the crystalline phase of amorphous-crystalline polymers to oxygen is not entirely correct. For example, in the radiation-induced initiation of radicals in the crystalline phase of PP in an oxygen atmosphere, all the alkyl radicals are converted into peroxy-radicals, i.e. oxygen diffuses into the crystalline phase of the PP (and into the even looser crystalline phase of poly-4-methylpent-1-ene). This is not observed in polyethylene (PE): the dense crystalline regions of this polymer are impermeable to oxygen[24] (for further details, see the relevant review[26]—pp.22–30). The solubilities of oxygen in unannealed (subjected to an entropic stress) and annealed (unstressed) oriented films of isotactic PP have been compared[27]. The solubility in the unstressed oriented films proved to be higher by a factor of 1.5–2.5 than in the annealed films. However, the influence of mechanical stresses on the sorption characteristics of the polymer is significantly weaker than their influence on the molecular-dynamic and diffusion parameters.

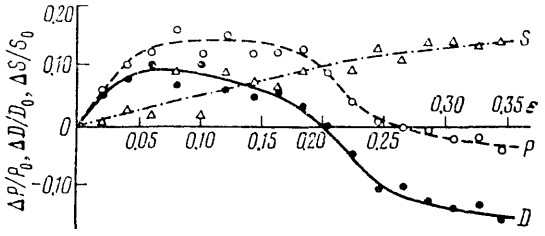


Figure 2. The relative changes in the sorption (S), diffusion (D), and permeability (P) coefficients for CO_2 in PE films as a function of the degree of deformation ε of an isotropic film[21].

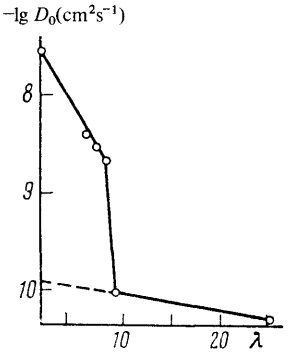


Figure 3. Variation of the diffusion coefficient of CH_2Cl_2 in PE with the degree of orientational extension λ.[21]

3. The Changes in the Molecular Dynamics and Diffusion Parameters in Oriented and Stressed Polymers.

The deformation of elastomers (in the absence of crystallisation) does not change appreciably their diffusion characteristics[17], while the diffusion characteristics of amorphous-crystalline polymers can change by several orders of magnitude on deformation. In the region of small reversible elastic deformations of PE (Fig.2), the diffusion coefficients of gases increase somewhat (like the increase in the degree of

sorption, this is also evidently associated with the increase in free volume), but, after the appearance of the plastic component of the deformation, the diffusion coefficient falls sharply (Figs.2 and 3)[21]; for example, threefold orientation stretching of PE leads to a decrease of the diffusion coefficient of gases by a factor of 40–50. The most marked diminution of the diffusion coefficient takes place over a narrow range of degrees of stretching apparently corresponding to the termination of the formation of a microfibrillar structure[21]. An analogous dependence on the degree of stretching has been observed for the diffusion coefficients of nitrogen and methane in oriented PP (Fig.4)[28].

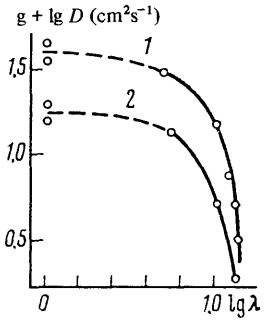


Figure 4. Variation of the diffusion coefficients of nitrogen (curve *1*) and methane (curve *2*) in PP with the degree of extension λ.[28]

One should note that the influence of the deformation of the polymer on the diffusion coefficients of low-molecular-weight substances is greater the greater the size of the diffusant molecule[20].

The change in the polymer permeability parameters on orientational extension is associated with the presence of unstressed extended fragments of the micromolecules in the amorphous phase. The more complete was the preceding relaxation of the amorphous phase, the smaller were the changes in the sorption and diffusion coefficients for the same degree of extension; an increase of the extension temperature or annealing of the oriented polymer above the extension temperature therefore diminish appreciably the changes in the permeability parameters[21].

The changes in the translational diffusion coefficient of low-molecular-weight substances in stressed oriented polymers, apart from the molecular-dynamic polymers, have purely geometrical causes: during their migration, the species must move round impermeable or relatively impermeable crystallites (or microfibrils), which leads to an increase in the length of the diffusional transport path. The contribution of the purely geometrical causes to the change in the translational diffusion coefficients on deformation of the polymer can be isolated by the paramagnetic probe method. The influence of the degree of extension of PP on the rotational and translational mobility of a stable nitroxy-radical, namely the 2,2,6,6-tetramethylpiperidin-1-oxy-radical, has been investigated[29].

Data for the dependence of the translational and rotational diffusion coefficients of this radical in PP on the degree of extension at 80° and 130 °C are presented in Table 1. Evidently at 80 °C, where $\lambda = 7$, the translational diffusion coefficient in the specimen decreases by a factor of 8 compared with the isotropic polymer, while the rotational diffusion coefficient diminishes less than by a factor of 2. These data refer to specimens in which the probe radical has been introduced before extension; on the other hand, if the radical is introduced into specimens which have already been oriented, then, up to $\lambda = 7$, the rotational frequencies do not change at all relative to the isotropic polymer, since the radical enters the "softest" and accessible regions of the specimen. Nevertheless the translational diffusion coefficient of the radical falls compared with its value in the isotropic polymer, which is evidently due solely to geometrical obstacles, which increase as the polymer is oriented. The data obtained made it possible to estimate the coefficient γ, which takes into account the increase, due to the geometrical obstacles arising in the orientational extension, of the path traversed by the radical: $\gamma = 1.4$ and 2.1 for specimens with $\lambda = 4.5$ and 7 respectively. Consequently, for specimens with $\lambda = 7$, all the changes in the translational diffusion coefficient greater than by a factor of two are due to the decrease of the segmental mobility of the macromolecules.

Table 1. Dependence of the translational (D_t) and rotational (D_r) diffusion coefficients of the probe radical on the degree of extension of PP at 80° and 130 °C.[29]

λ	$10^9 D_t$, $cm^2 s^{-1}$	$10^{-8} D_r$, s^{-1}	$10^7 D_t$, $cm^2 s^{-1}$	$10^{-9} D_r$, s^{-1}
	80° C		130° C	
0	5.4	7.9	2.9	7.2
4.5	1.9	6.6	1.7	4.7
7.0	0.7	4.6	1.9	2.8
10.0	—	4.3	—	2.0

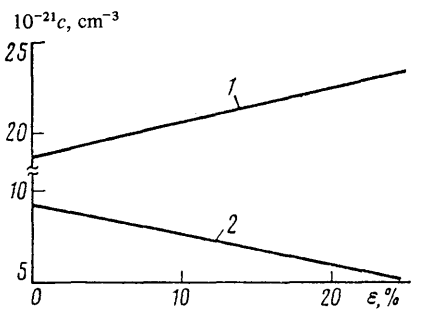


Figure 5. Variation of the concentrations of the *trans*-conformation (line *1*) and the *gauche*-conformation (line *2*) in oriented PE ($\lambda = 10$) under the conditions of additional deformation along the stretching axis[38].

We may note that at room temperature the rotation of the radical in PP is significantly hindered and is relatively insensitive to the stress[29]. The low sensitivity of the rotational mobility of the radical to the external load applied to PP at room temperature is apparently associated with the same factor[30,31]: the maximum changes in the rotational correlation time of the probe in the range of stresses from 0 to 250 MPa do not exceed 9%. Furthermore, NMR spectroscopy has revealed significant changes in the segmental mobility of the molecules of oriented PP subjected to an external load[32].

4. The Change in the Set of Conformations of Micromolecules under the Influence of a Stretching Load.

The change in the molecular dynamics of polymers, to which a load has been applied and which are subjected to orientation, takes place as a result of a change in the set of conformations: the depletion of the specimen in the mobile coiled conformations and its enrichment in the relatively immobile extended conformations (i.e. a decrease of the entropy of the system)[33-39]. Fig.5 illustrates the changes in the concentrations of the *gauche*- and *trans*-isomers when a load is applied to oriented PE (according to the data of Pakhomov et al.[38]). The dependence of the contents of various conformers in the polymer chain on the degree of its extension has been studied theoretically[39]. It was shown that in the initial stage of the extension the chain is stretched mainly as a result of the reorientation of its elements: the coiled G-isomers are distributed more uniformly along the chain, preferentially in the vicinity of extended T-isomers as neighbours, and the fraction of G-isomers begins to fall appreciably only for fairly high degrees of extension (Table 2). The relative positions of the coiled isomers are characterised by the concentrations of triads containing one *trans*-isomer and two coiled isomers (Fig.5). The most stable triads, containing the G-isomers in the extended chain, are the TGT and GTG′ triads, which is natural, since precisely these triads cause the smallest shortening of the chain for the given number of G-isomers (they are incorporated in a "kink" in the PE chain). It has been shown experimentally[38] that, in the region of elastic deformations of PE, the extension of amorphous layers from 40 to 60 Å leads to a more than 30% decrease of the number of TGT and GTG′ triads; on further extension, the specimen breaks. It is natural to suppose that the synchronous disappearance of the above triads is associated with the straightening out of the "kink", i.e. with a simultaneous conversion of two G-isomers into T-isomers; this is also indicated by the activation energy for the deformation (~ 8 kcal mol^{-1}), exceeding by a factor greater than two the height of the barrier to internal rotation in the PE chain.

Table 2.

$\varkappa$	α_{TG}	α_{GG}	α_{G}
0	0.94	0.68	0.80
1	0.90	0.70	0.81
2	0.86	0.72	0.82

Note. α are the degrees of extension of the chain for which the concentrations of the isomers and diads containing the G isomers decrease by a factor of two compared with the unstretched chain ($\alpha = 0$) and $\varkappa = E/kT$ is the thermodynamic rigidity of the chain[39].

It has been shown[39] that the decrease of the concentration of the TGT and GTG′ triads begins for fairly high degrees of extension of the chain (~ 0.9). The fact that the number of these conformers diminishes by more than a third in pre-rupture PE deformations means that the fraction of chains stretched to this extent is more than one third of the total number of crossing chains; the long range of the degrees of deformation (~ 50%) in which the concentration of these triads diminishes enabled the authors[39] to postulate that in some of the chains there is additional stretching of the fully extended *trans*-chains as a result of the deformation of the valence angles.

It must be emphasised that the above investigators[39] based their calculation on the PE chain model in which the conformation extended to the maximum extent consists of a flat zig-zag. As a consequence of the interaction of the methyl groups, the flat zig-zag does not occur in PP and the conformation extended to the maximum of extent consists of a sequence of TGT triads corresponding to the α-helix in PP crystals.

It follows from the above that the statistical weight of the mobile coiled conformations diminishes following the extension of polymer chains. The corresponding calculations have been carried out for the PE chain[40]. From these results, it was possible to estimate the contribution of the entropic elasticity to the forces tending to contract the extended polymer chain. In terms of order of magnitude, these forces are close to the energetic contribution by the elastic forces of the "kink" isomers (associated with the existence of a barrier to internal rotation) but have the opposite sign.

The variation of the free energy F of the partly extended chain as a function of the distance between its ends is illustrated in Fig.6[14] (p.129). The minimum free energy of the chain corresponds to a distance between its ends $r = (n-n_k)\sqrt{2}/3a$, where n is the total number of C–C bonds, n_k is the number of "kink" isomers, and a is the length of the C–C bond. If the ends of the chain are displaced from the equilibrium positions, then elastic forces arise which are associated with the hindered rotation of the *gauche*-bonds outside the plane of the zig-zag of the PE chain and the deformation of the *trans*-bonds in the plane of the zig-zag.

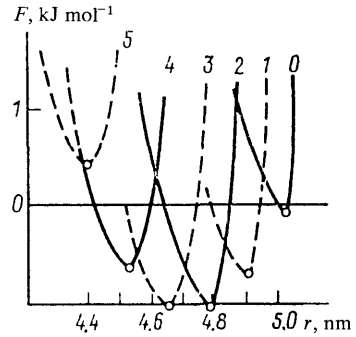


Figure 6. Variation of the free energy F of a partly extended PE chain with the distance r between its ends; the numerals against the curves represent the numbers of kink isomers[14] (p.129).

The modulus of the chain containing different conformers is specified by the expression

$$1/\bar{E} = \sum_i x_i/E_i ,$$

where E_i are the moduli of the individual conformers and x_i are their volume fractions. The smaller the content of *gauche*-conformers in the chain the greater the rigidity of the latter; the presence of only five "kink" isomers in the PE chain reduces the modulus from 200 to 9.5 GPa. It is seen from Fig.6 that, when the chain is extended, there are transitions between individual conformational states and the transition to the more extended conformation removes the axial stress from the section of the chain considered, i.e. it is a thermodynamically favourable process.

The results of a calculation by Darinskii and Neelov[39] and Pechhold[40] are extremely important for the interpretation of the experimental data obtained in the study of the kinetics of the oxidation of oriented and stressed polyolefins.

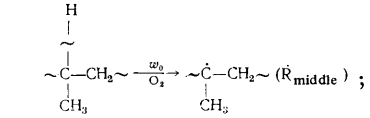
III. KINETICS AND MECHANISM OF THE OXIDATION OF STRESSED POLYMERS.

The discovery in 1950 by Kuz'minskii and co-workers of the phenomenon of the mechanical activation of the oxidation of raw and cured rubbers[1,2,41], the wisely familiar acceleration of the ozone-induced cracking of resins under a mechanical stress (see, for example, Refs.42–53), and the acceleration of the degradation of the C–C bonds in the macromolecular skeleton of mechanically stressed polymers[54] led to the idea that the oxidation reaction is as a rule accelerated under the influence of mechanical stresses. The onset of the breakdown of these traditional ideas dates back to the middle 1970's when studies on different polymeric objects and by different methods, showing that the acceleration of chemical reactions and particularly the oxidation reactions under the influence of mechanical stresses is by no means a universal phenomenon, were published independently and almost simultaneously[55–68]. This is associated with the fact that oxidation is usually a complex chain process whose individual stages vary differently in the stressed polymer. We shall consider the influence of mechanical stresses (1) on the kinetics of the oxidation of polyolefins under the influence of molecular oxygen and ozone and (2) on the kinetics of the ozonisation and oxidation of raw and cured rubbers.

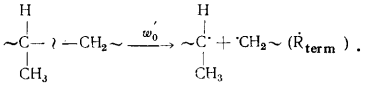
1. Kinetics and Mechanism of the Thermo-oxidation of Stressed Polyolefins under the Influence of Molecular Oxygen

The generally accepted mechanism of the chain oxidation of polyolefins is presented below.

Initiation:



(0)

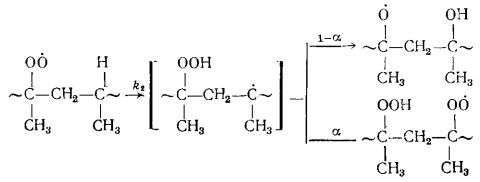


(0′)*

Chain propagation:

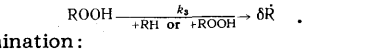


(1)



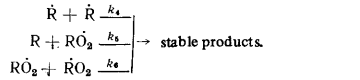
(2)*

Branching:



(3)*

Chain termination:



(4)
(5)
(6)

The asterisk denotes stages in which polymer chains may be degraded. The mechanism includes four main stages: initiation, propagation, degenerate branching, and termination of kinetic chains. The changes in the overall kinetics of the oxidation in stressed polyolefins occur as a result of the influence of mechanical stresses on the rate of each of the above stages. We shall consider in succession the data available at present concerning the influence of stretching stresses on the rate of each stage.

(a) Primary initiation. The primary initiation of radicals in stressed polyolefins can take place via two main pathways: reaction (0)—"direct" interaction of oxygen with macromolecules leading to the rupture of a C–H bond and the formation of internal alkyl macroradicals (this is the "usual" initiation stage in unstressed systems in which various admixtures such as the residues of the polymerisation catalysts apparently play a significant role[69]) and reaction (0′)—the rupture of C–C bonds in the macromolecular skeleton with formation of terminal macroradicals (this reaction proceeds only in stressed polymers).

The influence of structural stresses on the rate of reaction (0)—the rupture of C–H bonds under the influence of various hydrogen acceptors—has been investigated[62,63] for model compounds—unstressed and stressed cyclic paraffins. It has been shown[62] that the reaction of stressed cyclic paraffins with olefin is accelerated relative to the unstressed six-membered ring: by a factor of 48 for the eight-membered ring, by a factor of 89 for the nine-membered ring, and by a factor of 6 for the less stressed twelve-membered ring. An attempt has been made[64] at a quantitative interpretation of these results. The rate constant for the reaction with ozone depends on the excess energy of the ring subjected to stretching stresses, in conformity with the expression

$$\ln (k_i/k_0) = \gamma (E^{\alpha}_{\text{exc}}/RT) \ .$$

The authors[64] suggested that, in any reaction accompanied by the rehybridisation of the sp^3 carbon atom to the sp^2 state and hence by an increase of the valence angle, a stretching stress should reduce the activation energy: the increase of the valence angle under the influence of the stretching stress increases the energy of the molecule in the initial state by $E_{\text{init}} = 0.5C(\Delta\alpha)^2$. where C is a constant and $\Delta\alpha$ the radiation of the valence angle from the optimum value. During the abstraction of a hydrogen atom, the deviation of the angle from the optimum value diminishes and $E^{\neq}$ is therefore lower than E_{init}, which leads to a decrease of E_{act}. The above is valid also for reactions involving the abstraction of a hydrogen atom from polyolefin molecules.

This hypothesis has been tested experimentally[65] for the reaction of ozone with PP, high-density polyethylene (HDPE), and low-density polyethylene (LDPE). It was shown that the rate of accumulation of carbonyl groups in PP and PE increases linearly with increase of the stress. The rate of relaxation of the stress under the conditions of constant deformation differs significantly in oxygen and in ozone, the difference increasing with increasing stress, which indicates an increase of the rate of ozone-induced degradation of the macromolecule as the stress becomes more pronounced.

Studies on the ozone oxidation of the surfaces of isotropic PP films with different thermal histories[66] demonstrated the faster "combustion" of the bonds corresponding to the long-wavelength wing of the 973 cm^{-1} band in the absorption spectrum of PP. The authors interpreted this as a result of the faster reaction with ozone of the most overstressed C–H bonds. However, the long-wavelength wing of the band can correspond to bonds in other conformations rather than the overstressed bonds[70] and the result obtained by

Krisyuk[66] is thus a consequence of the different reactivities of different conformers. At the present time there are insufficient data for the solution of this problem.

The results of the above studies[62,64-66] have been surveyed by Popov et al.,[31] who demonstrated that the orientation and external load applied to oriented specimens have effects of different sign on the rate of the ozone oxidation of PP and PE. It was shown that the observed effects cannot be accounted for by a change in the degree of orientation, the degree of crystallinity, and the molecular dynamics of the polymers under load. Popov et al.[31] concluded that the main cause of the acceleration of the reactions of ozone with PP and PE under load is the stress-induced decrease of the activation energy for the abstraction of a hydrogen atom from the polymer chain. Unfortunately, the investigators[31,65,66] inferred the acceleration of reaction (0) in stressed polymers from the increase of the rate of acceleration of secondary products (carbonyl groups, breaks in macromolecules), which are produced as a result of subsequent reactions of the alkyl macroradicals generated in reaction (0).

However, the author's view[31,65,66] is apparently valid: additional (albeit also indirect) confirmation of the acceleration of reaction (0) in stressed PP has been obtained recently[71] (Fig.7). In the uninhibited oxidation of PP subjected to an external load there is a range of stresses in which the durability of the polymer is determined by the rate of the thermo-oxidative chain degradation and depends only slightly on the load[59,72,73] (Fig.7, curve *1*). In the inhibited specimen the chain oxidation process is suppressed, as a result of which in the region of low stresses its durability increases by more than an order of magnitude compared with the uninhibited specimen and is determined by the inhibitor consumption time, which depends on the rate of initiation (after the consumption of the inhibitor, the oxidative chain degradation leads to rapid decomposition of the specimen).

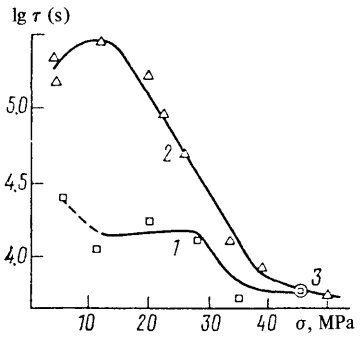


Figure 7. Isotherms of the durability in air of oriented PP ($\lambda = 7$), both uninhibited (curve *1*) and inhibited (curve *2*); inhibitor—Ionox; [InH] = 3×10^{-3} mol kg^{-1}; point *3* corresponds to the durability of the inhibited specimen *in vacuo*[71].

Fig.7 (curve *2*) shows that in the range of stresses 15–35 MPa the durability of the polymer falls exponentially with increase of the applied stress, which may indicate an increase of the rate of initiation [it will be shown below that in the range of stresses indicated the oxidation is initiated via reaction (0)]#. The causes of the increase of the rates of reaction may be associated with the fact that the rehybridisation of a carbon atom from the sp^3 to the sp^2 state as a result of the hydrogen atom abstraction reaction entails an increase in the length of the macromolecular fragment, which promotes the relaxation of part of the stress, and not with the deformation of the valence angles in the pre-start state (the absolute values of the applied stresses are fairly low—see Fig.7).

The second initiation reaction [reaction (0') involving the dissociation of a C–C bond in the macromolecular skeleton], leading to the formation of terminal macroradicals, takes place only in stressed polymers. Its rate increases exponentially with increase of the applied stress, as shown in numerous studies of Zhurkov's Leningrad School (see, for example, Regel' et al.[54]).

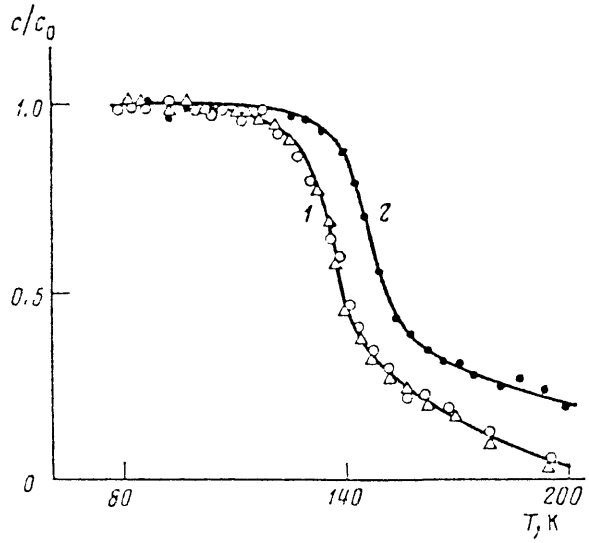


Figure 8. "Heating" curves for the reaction between $\dot{R}$ and NO in isotropic PP specimens (curve *1*) and specimens oriented with $\lambda = 9$ (curve *2*).[77]

(b) Propagation of the kinetic chains. The first kinetic chain propagation reaction involves the addition of oxygen to alkyl macroradicals [reaction (1)]. In polymers this reaction proceeds under microdiffusional conditions[74-76] and its rate is controlled by the rate of microdiffusion of oxygen via the polymer matrix. The decrease of the translational mobility of gases in PP as a result of orientational extension (see Fig.4 and Tochin et al.[28]) should lead to a decrease of the rate of reaction (1) in oriented PP. It follows from the data of Yakimchenko et al.[77] that this is indeed observed.

An unambiguous interpretation of these results is hindered by the fact that the oxidation under load is of a distinctly local character (see below): the concentration of the inhibitor in the region of the future break can be partly made good as a result of diffusional "suction" from neighbouring regions where it is consumed more slowly, the translational diffusion coefficient of the antioxidant depending on the applied stress[117].

The above investigators[77] studied the rate of reaction between $\dot{R}$ and NO (modelling the reaction of $\dot{R}$ and O_2) in isotropic and oriented PP. Fig. 8 presents the "heating" curve for this reaction in isotropic and oriented ($\lambda = 9$) PP specimens and Fig. 9 presents the kinetic curve for the destruction of the radicals $\dot{R}$ at a fixed temperature. Evidently alkyl radicals are destroyed more slowly in oriented PP than in the isotropic polymer. This is consistent with the shift of the spectrum of free energies of activation towards higher values.

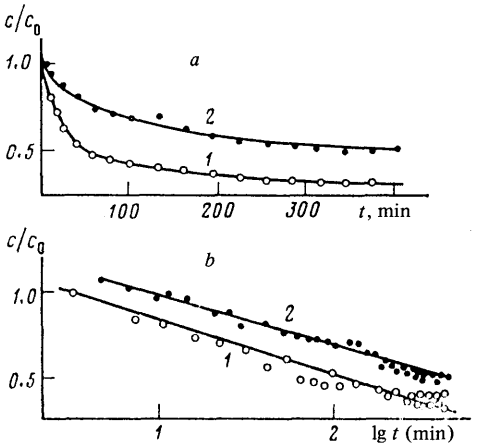


Figure 9. Kinetic curves for the destruction of alkyl radicals by the reaction between $\dot{R}$ and NO in PP (*a*) and the corresponding semilogarithmic plots (*b*)[77]; for legend, see Fig. 8.

The application of an additional load to oriented specimens can entail a change in the diffusion coefficients of oxygen relative to the unstressed oriented specimens and the corresponding change in the rate of reaction (1); however, according to Iasuda and Peterlin[20,21], in the region of reversible deformations the scale of these changes is significantly smaller than on transition of the polymer from the isotropic to the oriented state. It may be expected that, in PP specimens maintained under isometric conditions (with the ends fixed), i.e. in the state of elastic deformation at the oxidation temperature (130 °C), the diffusion coefficient of oxygen is somewhat greater than in specimens subjected to shrinkage (for a degree of extension $\lambda = 9$ at 130 °C, the shrinkage is ~ 20%). However, the relevant experimental data are not available in the literature.

The changes in the translational diffusion coefficient of a bulky stable nitroxy-radical (the 4-methyl-2-spiro-cyclohexyl-2,3,3,4-tetrahydrofurano-1,2,3,4-tetrahydroquinoline-nitroxy-radical) in oriented PP subjected to a monoaxial load ($\lambda = 6$) at 120 °C have been investigated[74]. It was observed that, in a certain range of stresses, the diffusion coefficient of the radical increases with increase of the stress and then falls sharply, the difference between the maximum and minimum diffusion coefficients of the radical observed in the investigation amounting to approximately one order of magnitude. We have already mentioned that the influence of the deformation of the polymer on the diffusion coefficients of low-molecular-weight substances is greater the larger the size of the diffusant molecule. *D* decreases exponentially with increase of *V**, where *V** is the product of the cross-section of the diffusant molecule and the length of the jump in the activated diffusion model[20]. Naturally, for the diffusion of oxygen, the dependence of the diffusion coefficient on the load is significantly less (for example, the orientational stretching of PP to $\lambda = 7$ decreases the translational diffusion coefficient of a very large nitroxy-radical, namely the 2,2,6,6-tetramethylpiperidinoxy-radical, by a factor of approximately 100 at room temperature[29]), while the diffusion coefficient of nitrogen falls only severalfold under these conditions[28].

Thus one can assume that the influence of the external load on the diffusion coefficient of oxygen in oriented specimens [and hence also on the rate of reaction (1)] is small. It may be expected that, under the conditions of plastic deformation, the rate of reaction (1) increases. (It is known, for example, that, in the absence of a mechanical influence at 77 K, alkyl radicals are not converted into peroxy-radicals in an oxygen atmosphere; on the other hand, when various polymers are vibromilled at 77 K in an atmosphere of oxygen, peroxy-radicals are formed, which is evidently associated with the enforced acceleration of the diffusion of oxygen in the specimen[78].)

At fairly high oxygen pressures the rate of reaction (1) influences the kinetics of the oxidation of polyolefins only indirectly (see below) because the rate-limiting stage in the propagation of kinetic chains is reaction (2).

In polyolefins reaction (2) can proceed intramolecularly and intermolecularly. In PE and its low-molecular-weight analogues the main pathway in reaction (2) is apparently intermolecular. Indeed, according to Ivanchenko et al.,[79] the rate constant for the abstraction of a hydrogen atom from the PE macromolecule in solution (in the presence of the cumenylperoxy-radical as the acceptor) at 115 °C amounts to 0.12 litre mol^{-1} s^{-1}, which corresponds to a lifetime of the peroxy-radical in PE, relative to the intermolecular chain transfer reaction, of ~ 2.5×10^{-2} s. (Account is taken of the fact that the reactivity of the secondary peroxy-radical in PE is ~ 3 times higher the reactivity of the tertiary cumenylperoxy-radical, and the concentration of the reactive C–H bonds in block PE is 142 mol kg^{-1}.[80] This estimate for the "ideal" intermolecular reaction (2) was made without taking into account the specific features of the reactions in the solid phase where the constant may be significantly lower.)

The lifetime of the peroxy-radical of PE, in relation to the intramolecular radical substitution reaction, can be estimated from data obtained in a study[81] whose authors investigated the transition $RO_2^{\cdot} \rightarrow R^{\cdot}$ in PE–urea complexes, where it proceeds strictly intramolecularly. Extrapolation of the above data[81] to 115 °C yields the lifetime of the peroxy-radical PE in relation to the "ideal" intramolecular reaction (2), which amounts to ~ 3×10^2 s, i.e. higher by almost four orders of magnitude than the lifetime in relation to the intermolecular reaction. Such differences are apparently caused by the low probability of the activated complex with the optimum linear structure in the section of the chain having the *trans*-zig-zag conformation in PE–urea complexes. Examination of the possibility of reaction (2) in the *trans*-zig-zag PE model shows that the formation of a linear activated complex requires the distortion of the *trans*-zig-zag as a consequence of a change in the angles of internal rotation or the distortion of the valence angles. This factor probably determines the high activation energy for the intramolecular reaction (2) in the PE–urea complex (24.6 kcal mol^{-1}[81]), while in n-decane the activation energy for the abstraction of a hydrogen atom by the cumenylperoxy-radical is 17.5 kcal mol^{-1}.[80]

The preferentially intermolecular course of reaction (2) in PE is also indicated by the large fraction of the monomeric (not linked by hydrogen bonds) hydroperoxide formed on oxidation: whereas mainly bound hydroperoxide is formed in substituted poly-α-olefins (PP, poly-4-methylpent-1-ene-P-4-MP-1) on oxidation, in PE the concentration of the free hydroperoxide exceeds that of the bound form[82].

A necessary condition for the intermolecular transfer of kinetic chains is molecular mobility which ensures the encounter of the peroxy-macroradical with a neighbouring macromolecule. As shown in Sections II.3 and II.4, orientational stretching decreases the segmental mobility of the macromolecules in the amorphous phase, which can influence the rate of reaction (2). Indeed, according to the data of Rapoport et al.,[82] in the radiation-induced oxidation of PE at room temperature the parameter $k_2/k_6^{1/2}$ in oriented PE is lower by a factor of ~ 1.5 than in the isotropic monomer; this is evidently associated with a decrease of k_2, because the destruction of radicals is also controlled by molecular dynamics and for oriented PE the constant k_6 should be lower than for the isotropic polymer (see below).

In contrast to PE, in substituted poly-α-olefins and their low-molecular-weight analogues, reaction (2) proceeds mainly intramolecularly[11,83-85]. Examination of the probability of the intramolecular reaction (2) of a model of the PP macromolecule showed[55] that the reaction is virtually impossible if the radical is localised in the section of the macromolecule having an extended TGT conformation (the same as in PP crystallites): in this case the peroxy-radical is shielded from the neighbouring tertiary C–H bonds of the same macromolecule. Reaction (2) becomes sterically feasible only if the reaction centre undergoes the TGT → TGG evolution.

The formation of the conformation necessary for the reaction can be formally regarded as the "encounter" of a radical in the TGT conformation with a G conformer "diffusing" in the macromolecule. In reality the diffusion process constitutes a concerted transition of the type $\mathrm{TGTGTGT} \underset{k_{-r}}{\overset{k_r}{\rightleftharpoons}} \mathrm{TGGTGGT}$. The cooperative nature of the transition is due to the fact that the TT and GGG conformations in PP are forbidden (the former as a consequence of the "overlap" of the methyl groups and the latter due to the effect of the excluded volume). Attention should be drawn to the fact that the number of G conformers on the right-side of the scheme presented exceeds their number on the left-hand side, i.e. conformational transitions of this kind require the presence of "superfluous" G conformers in the macromolecule (compared with their number in the fully extended helical TGT sequence). The number of *gauche*-conformers in a given section of the macromolecule is determined by the ratio of its contour length to the distance between its ends and for each macromolecule in the amorphous phase of an amorphous-crystalline polymer is specified "genetically" at the instant of crystallisation or orientational extension.

Formally, reaction (2) can be considered from the standpoint proposed[86,87] for the kinetic description of bimolecular solid-phase reactions. Reaction (2) is described as a result of the reaction in the radical–GG conformer pair:

$$\mathrm{GG} + \mathrm{R\dot{O}_2} \underset{k_{-r}}{\overset{k_r}{\rightleftharpoons}} [\mathrm{R\dot{O}_2}(\mathrm{GG})] \xrightarrow{k_x} \mathrm{ROOH}\ .$$

Assuming that $k_r \cong k_{-r}$, we obtain the following expression for the rate of reaction (2) in the quasi-stationary approximation:

$$w_2 = \frac{k_x k_r}{k_x + k_r} [\mathrm{GG}] [\mathrm{R\dot{O}_2}] \equiv k_{\mathrm{eff}} [\mathrm{GG}] [\mathrm{R\dot{O}_2}]\ .$$

If the rate-limiting stage is the "encounter" of the GG conformer with the radical, then $k_{\mathrm{eff}} \cong k_r$; if the reaction in the pair is rate-limiting (i.e. not every collision of the radical with the GG conformer results in reaction), then $k_{\mathrm{eff}} \cong k_x$; in the intermediate case k_r and k_x are added together in accordance with the law of kinetic resistances.

In any case the rate of the intramolecular reaction (2) is proportional to the concentration of the GG conformers in the macromolecule. In the amorphous phase of amorphous-crystalline polymers there is always a distribution of sections of the macromolecules with respect to the contour length and hence a distribution with respect to the concentrations of the GG conformers§. In the oxidation of amorphous-crystalline polymers one should therefore observe a distribution with respect to the constants k_2 and the latter, determined on the basis of the overall kinetics of the oxidation reaction[89,90] (and incidentally also the constants k_1 and k_6) are effective average quantities for the given distribution.

The lowest constant k_2 is to be expected in the crystalline phase of PP where the unreactive TGT conformation predominates and constitutes "the elementary unit" of the helix and the characteristic reaction time is probably the expectation time for the formation of a defect in the helix at the site of the location of the radical. Reaction (2) in the crystalline phase of PP has been investigated[91] in the temperature range 270–300 K; an estimate of the effective value of k_2^{cr} from the results of this investigation yields ~ 2×10^{-5} s^{-1}, which is lower approximately by three orders of magnitude than k_{eff} for the amorphous phase of PP[89,90]. Such differences between the rates of reaction (2) in the crystalline and amorphous phases of PP are apparently a result of the "conformational inhibition" of the reaction in the crystalline phase[61]. The existence of a distribution with respect to the constants k_2 in PP is indicated by the results of a study[92] in which the kinetics of the destruction *in vacuo* of the peroxy-radicals of PP, obtained by γ-radiolysis at −78 °C and at room temperature, were investigated. The authors[91] fitted sets of three (irradiation at −78 °C) or two (irradiation at room temperature) exponential functions to the kinetic curves obtained. The plots of c/c_0 against lg τ, based on the results of the above study[92], are straight lines which may be evidence in support of the existence of a distribution function for the reactive species with respect to the constants k_2; the lowest constant k_2 agrees in order of magnitude with the value determined[91] for the crystalline phase of PP.

In the orientation stretching of polymers and following the application of an additional load to them, the conformers are redistributed (there is a decrease of the fraction of GG pairs and an increase of the fraction of TG pairs) and the overall concentration of the coiled conformers decreases (see below). As was to be expected, this results in a decrease of the average effective value of the constant k_2[89] by (a factor of 3–4 in oriented PP compared with the isotropic polymer). Although the absolute changes in the effective constant k_2 in oriented PP are small, the shift of the distribution towards lower values of the constants for the extended chains,

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§ Attempts to establish the character of the distribution of sections of macromolecules with respect to length have been made[88]. Histograms of the concentrations of the free radicals formed in the stepwise deformation of PA-6 fibres were constructed. Unfortunately the results obtained are not unambiguous because it is still not clear whether there is a direct correlation between the concentration of the free radicals detected and the concentration of the ruptured macromolecules.

enriched in the unreactive TGT conformers, plays a decisive role in the strength of the material and its change during oxidative degradation, which are very important characteristics.

(c) Reaction (2) and the variation of the strength characteristics of PP in the oxidation process. The strength properties of amorphous-crystalline polymers are determined by the "tail" of the distribution of sections of the macromolecules in the amorphous phase with respect to lengths, which corresponds to the shortest and therefore the most extended chains incorporating the smallest number of coiled *gauche*-conformers. According to Kaush and De Vries[88], the fraction of fully extended macromolecules in PA-6 fibres, responsible for the modulus of elasticity and the strength properties of the specimen, is 1.1%, while 98.6% is the fraction of chains in the unextended state (see the preceding footnote concerning these results). The greater the degree of extension, the higher the fraction of the short-chain "tail" of the distribution, the greater the number of the fully extended macromolecules, and the higher the initial strength of PP[58]. It follows from the above that the probability of the intramolecular reaction (2) involving such macromolecules should be a minimum; reaction (2) in polyolefins results in the formation of hydroperoxy-groups whose thermal decomposition is usually accompanied by the degradation of the macromolecules and serves as the main source of the decrease of the molecular weight in autoxidation[93,94]. If reaction (2) proceeds intramolecularly, a hydroperoxide block is formed. According to Shlyapnikova and Shlyapnikov[94], the probability of the degradation of the macromolecule on decomposition of the hydroperoxide increases with increase of the length of the block:

$$\rho_d = 1-(1-\rho_1)^{\nu_{bl}},$$

where ρ_1 is the probability of the decomposition of a single hydroperoxy-group without the degradation of the macromolecule and ν_{bl} is the length of the block.

The presence of extended conformers prevents the intramolecular propagation of the kinetic oxidation chain; the more extended the chain, the smaller the number of GG conformers in it, and the lower the probability of the intramolecular reaction (2). Short hydroperoxide blocks or isolated hydroperoxy-groups would therefore be expected to form on the extended macromolecules [as a result of the intramolecular reaction (2), whose rate constant has been shown, in relation to low-molecular-weight analogues of PP, to be significantly lower even in the liquid phase than the intramolecular constant k_2 (Mill and Montorsi[11]]; the intermolecular reaction should be even slower in the solid polymer, where its rate is limited by the rate of encounters of the reactants, one of which is the stressed polymer chain, and, apart from diffusion-dependent obstacles, there is also steric hindrance to the reaction[13].

The isolated hydroperoxy-groups are decomposed several times more slowly than the block groups[84]. Consequently both the formation and the decomposition of the hydroperoxy-groups are retarded on extended macromolecules, which should lead to a sharp fall of the rate of the oxidative degradation of the extended macromolecules compared with the degradation of the coiled macromolecules. Since extended macromolecules are in fact responsible for the strength properties of the polymer, for the same degree of oxidation one should expect a smaller diminution of the strength of the specimens having a higher concentration of extended macromolecules, i.e. specimens which are more highly oriented. It has been shown[55] that this is indeed the case (Fig.10).

Formally, the amorphous phase of oriented PP can be divided into two unequal parts: in the larger part enriched in the coiled conformations (the "soft" part), there is rapid intramolecular propagation of the kinetic chains leading to the formation of hydroperoxide blocks, and degradative processes develop (this part of the polymer is responsible for the overall kinetics of the absorption of oxygen), while in the smaller ("hard") part, enriched in the extended conformations, the intramolecular propagation of kinetic chains is inhibited and their oxidative degradation is much slower; the absorption of oxygen by these macromolecules does not contribute appreciably to the overall oxidation kinetics but they are in fact responsible for the retention of the strength properties of the specimens undergoing oxidation. The retention of non-degraded extended macromolecules even for high degrees of oxidation of oriented PP has been confirmed in experiments involving the measurement of the repeated durability of unannealed and annealed PP specimens[61] (see below).

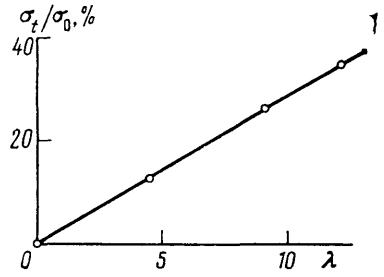


Figure 10. Dependence of the relative strength of PP on the degree of extension for absorption of O_2 at a concentration of 0.5 mol kg^{-1}.[55]

Thus a mechanical stress, leading to a decrease of the diffusional mobility of the polymer matrix and altering the set of conformations of the macromolecules in favour of the extended isomers, causes a decrease of the effective rates of both propagation reactions of the kinetic oxidation chains [reactions (1) and (2)].

(d) The branching of kinetic chains. The degenerate branching of kinetic chains in polyolefins takes place as a result of the thermal decomposition of the hydroperoxy-groups into radicals. Since side groups are decomposed in this reaction, a mechanical stress should not influence significantly the decomposition rate constant. Nevertheless, the rate of degenerate branching of kinetic chains in oriented PP proved to be significantly lower than in the isotropic polymer[57,95]. This is associated with the decrease of the yield of the branching agent—the hydroperoxide (calculated per mole of the absorbed oxygen).

Fig.11 presents the kinetic curves for the accumulation of hydroperoxide in the autoxidation of PP specimens with different degrees of orientational extension. Evidently a decreasing concentration of the accumulated hydroperoxide corresponds to the same amount of absorbed oxygen in the specimens with an increasing degree of extension. It has been shown[57] that this is not associated with the increase of the rate of the thermal decomposition of the hydroperoxide in the oriented specimens. The observed effect is caused by the induced decomposition of the hydroperoxy-group

under the influence of the alkyl macroradical present in it in the β-position—the isomerisation of the β-hydroperoxyalkyl radical [see the scheme below illustrating the sequence of reactions (2)]. The addition of oxygen to the alkyl macroradical, resulting in the formation of a "stable" hydroperoxy-group, competes with the isomerisation reaction. Within the framework of this mechanism, the yield of the hydroperoxide per mole of absorbed oxygen (α) is defined by the expression

$$\alpha = k_1[O_2]/(k_1[O_2] + k_5) ,$$

i.e. depends on the rate of reaction (1). Thus the rate of reaction (1) diminishes as a result of the orientational stretching of PP: the induced decomposition of the hydroperoxide begins to complete successfully with the addition of oxygen to the alkyl macroradical, which leads to a decrease of the parameter α. In this case the kinetic chain propagation reaction [reaction (2)] results in the preferential formation of an alcoholic hydroxy-group and an alkoxy-macroradical and not the branching agent (hydroperoxide) and an alkyl macroradical. The validity of the proposed interpretation is confirmed by the dependence of α on the oxygen pressure in the oxidation reaction[96-98].

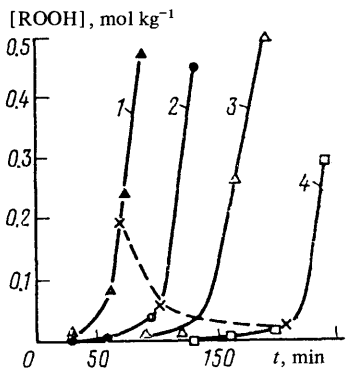


Figure 11. Kinetic curves for the accumulation of hydroperoxide in the autoxidation of PP with different degrees of extension (130 °C, p_{O_2} = 600 mmHg)[27]; the points corresponding to the absorption of oxygen at a concentration of 0.5 mol kg^{-1} are joined by a dashed line; λ: 1) 0; 2) 4.5; 3) 7; 4) 9.

The decrease of the yield of the hydroperoxide per mole of the absorbed oxygen in oriented PP specimens should lead to an increase of the induction period of the autoxidation relation, which has been observed experimentally[58] (see below).

(e) Termination of kinetic chains. In solid polymers the rate of destruction of macroradicals is limited by the rate of their encounters and is sensitive to the intensity of molecular movements[8]. In order to account for the experimentally observed high rates of destruction of macroradicals in solid polymers, the dependence of the rates of destruction on molecular mobility of the system, the anomalously high activation energies for the degradation process, and the compensation effect, several models have been proposed and have been examined critically[8].

In the amorphous phase of the isotropic PP the rate of destruction of peroxy-radicals ($k_6 \cong 10$ litre mol^{-1} s^{-1})[88,99] exceeds by 2–3 orders of magnitude that observed in the crystalline phase of PP even at room temperature[100] (the constant k_6 is undoubtedly an effective quantity; the activation energy is E_6^{PP} = 28.5 kcal mol^{-1}). Orientational stretching, which leads to a decrease of the average segmental mobility in the amorphous phase of the polymer, induces a decrease of the rate of destruction of the radicals[89,101,102]. The data for PP[89] are presented in Fig.12. They correspond to the destruction of radicals in elastically deformed and entropically stressed PP. An entirely different dependence of the rate of destruction of radicals on the stress is to be expected in the case where the polymer undergoes plastic deformations: the enforced mixing of macromolecules under the influence of mechanical stresses increases the rate of their encounters and the rate of their destruction[103-105]. The destruction of radicals in the crystalline phase of PE and PP fibres at the instant of deformation of the crystallites¶ has been observed[104] (Fig.13).

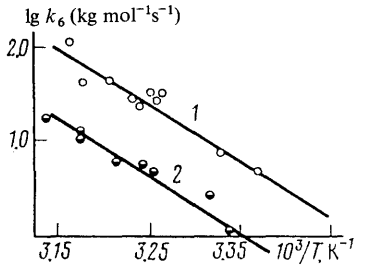


Figure 12. Temperature variation of the rate constant for the destruction of peroxy-radicals in PP: 1) isotropic; 2) oriented (λ = 8)[88].

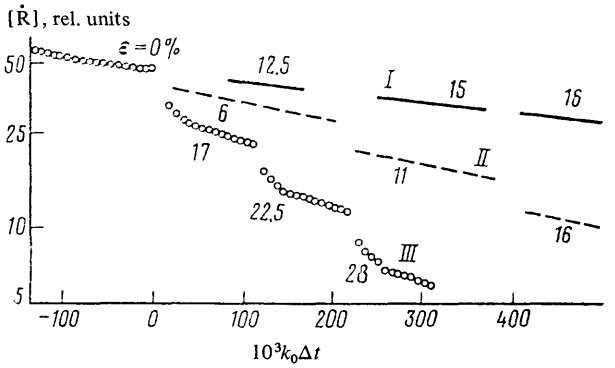


Figure 13. The influence of the degree of deformation of polymers ε on the destruction of radicals in irradiated and heat-treated PA-6 (I), PP (II), and PE (III) fibres; the reduced time is plotted along the abscissa axis; k_0 = rate constant for the destruction of radicals with zero deformation; Δt = time from the onset of deformation[14] (p.240).

¶ This is most probably associated with the formation and migration of defects in the crystal structure at the instant of deformation of the specimen.

An analogous effect has been investigated by Radtsig and Rainov[105], who showed that the reaction involving the destruction of the peroxy-radicals of polystyrene (PS) (which proceeds with a kinetic arrest at a temperature below T_g) can be restarted if the polymer is subjected to a brief plastic deformation at 77 K: the migrations of the macroradicals and macromolecules alter the local environment of the macroradicals and restore the initial distribution of the radicals with respect to reactivity. Thus the plastic deformation of the polymer should promote an increase of the rate of destruction of the macroradical. In PP this effect can be enhanced also by the fact that, as will be shown below, in the region of plastic deformations the initiation of kinetic chains proceeds preferentially via reaction (0) with formation of terminal macroradicals, which are more mobile and reactive than the internal macroradicals.

The results of the study of the influence of the stretching stresses on individual stages of the chain oxidation show that in the region of both elastic and plastic deformations the stresses accelerate the initiation reactions (0) and (0') and inhibit the kinetic chain propagation reaction (2), while reaction (1) and the kinetic chain termination reaction (6) are inhibited in the region of elastic deformations and are accelerated in the region of plastic deformations; the reaction involving the degenerate branching of the kinetic chains [reaction (3)] is inhibited in the region of elastic deformations.

The influence of stretching stresses on the rate of the overall oxidation depends on the role which each of the above stages plays in the overall chain process.

2. The Influence of Stretching Mechanical Stresses on the Overall Rate of Oxidation of Polyolefins

We shall consider initially the effects of orientational extension in the kinetics of the oxidation of polyolefins and then the effects of an external load applied to the oriented specimens and hence the problem of the durability and mechanism of the decomposition of polyolefins subjected to the joint action of mechanical stresses and an oxidising medium.

(a) The effects of orientational extension in the overall kinetics of the oxidation of polyolefins. This process has been studied in detail in a series of investigations[27,55-58,60,82,89,95,98,106] and has been examined critically in a review[26]. Here we shall deal briefly with the main results. Fig.14 presents the kinetic curves, for the absorption of oxygen in the autoxidation of unannealed and annealed PP films with different degrees of extension, and their linear forms. The kinetic parameters of the oxidation process are compared in Table 3 with the structural-mechanical parameters of the oriented specimens. The kinetics of the oxidation of the oriented PP are characterised by the following main features:

(1) the induction period in the oxidation of unannealed PP specimens increases exponentially with increasing degree of extension (Fig.14a) (an analogous relation has been observed for polyamide fibres[107]); (2) the differences between the initial rates of oxidation (reflected in the increase of the induction period with the degree of orientation) persist along the autocatalytic sections of the kinetic curves: the slopes of the linear forms of the curves diminish with increasing degree of extension (Fig.14c); (3) the maximum rates of oxidation are independent of the degree of extension; (4) starting with a specific duration of oxidation, the kinetic curves for the absorption of oxygen can be satisfactorily fitted by parabolas and the linear forms of the kinetic curves do not pass through the origin of coordinates [it has been suggested that the time interval t_0 obtained by extrapolating the linear forms of the curves (Fig.14c) to the abscissa axis be referred to as the true induction period of the uninhibited oxidation of PP[106]]; during the period t_0, the oxidation of the polymer develops at a very low rate; (5) annealing leads to the smoothing out of the differences between the oriented and isotropic specimens.

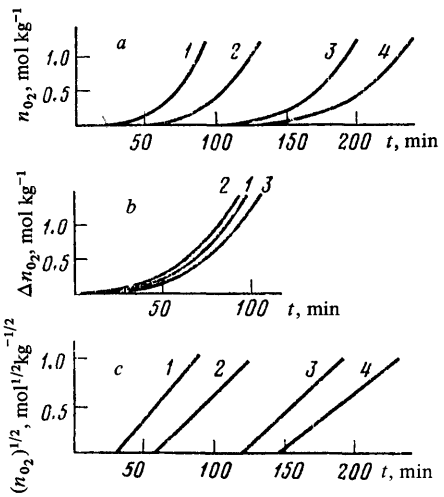


Figure 14. Kinetic curves for the absorption of oxygen in the autoxidation of PP: *a*) unannealed specimens; *b*) annealed specimens; *c*) linear plots corresponding to the kinetic curves; λ: 1) 0; 2) 4.5; 3) 9; 4) 12 (130 °C, p_{O_2} = 600 mmHg)[58].

The following main conclusions have been reached on the basis of the data presented.

1. The decrease of the initial rate of oxidation (the increase of the induction period) as a result of the orientational extension is not associated with a change in the degree of crystallinity, as is usually assumed (see, for example, Winslow et al.[108]): during annealing, the degree of crystallinity increases appreciably (from 64 to 76%), while the induction period of the oxidation reaction actually diminishes.

2. The changes in the oxidation kinetics are due to the presence of stressed extended macromolecules in the amorphous phase: annealing, leading to the relaxation of the internal stresses and the restoration of the compact conformations of the macromolecule[58,108], eliminates the differences between the oriented and isotropic specimens. Chemical relaxation of internal stresses, associated with the rupture of the extended macromolecules during the oxidation process itself, leads to the same result (this explains the equality of the maximum rates of oxidation for specimens with different degrees of extension).

Thus the main effect of orientational extension in the kinetics of the oxidation of PP is a significant increase of the induction period of the autoxidation reaction. An analogous phenomenon has been observed in the oxidation of oriented poly-4-methylpent-1-ene (P-4-MP-1)[110]. Differences between the kinetics of the absorption of oxygen by isotropic and oriented specimens were not observed in the autoxidation of PE at 130 °C,[82] which is natural because at this temperature relaxation processes take place vigorously in PE.

The data presented in the previous Section concerning the changes in the kinetic parameters of the individual stages of the chain oxidation of stressed PP show that, when PP is oriented, the effective rate constants for the propagation and termination of kinetic chains (k_2 and k_6) decrease in such a way that the parameter $k_2/k_6^{1/2}$, which determines the rate of the oxidation reaction at an advanced stage, diminishes slightly (by a factor of ~ 1.5 in the specimen with $\lambda = 4.5$, obtained by stretching an isotropic specimen subjected to preliminary oxidation). The changes in the initial rate of reaction exceed significantly the changes in the parameters $k_2/k_6^{1/2}$ (for example, the induction period of the oxidation reaction involving the specimen with $\lambda = 12$ increases by a factor greater than 4 compared with the isotropic specimen—see Table 3).

Table 3. Relation between the structural-mechanical parameters of oriented PP specimens and the kinetic parameters of their autoxidation (130 °C, p_{O_2} = 600 mmHg).[58]

λ	$10^3_s{}^{10}r_{corr}$,	α_{cr}, %	σ, MPa	E, MPa	τ_{ind}, min	10^6b, $mol^{1/2}kg^{-1/2}s^{-1}$	10^4w_{max}, $mol\ kg^{-1}s^{-1}$
0	5.4/5.4	58/70	0	2	40/30	2.8/2.1	6.9/4.9
4.5	5.7/5.4	66/74	13	40	75/30	2.4/—	6.2/4.5
9.0	7.9/5.4	64/76	86	290	140/35	2.1/—	6.2/4.5
12.0	9.3/5.4	65/71	215	660	170/40	1.9/—	6.2/5.0

Note. The values for the unannealed and annealed specimens are given in the numerator and denominator respectively. Notation: τ_{corr} is the correlation time of the rotational movement of the probe radicals (the 2,2,6,6-tetramethylpiperidin-1-oxy-radical) at 60 °C, α_{cr} the degree of crystallinity, σ the stress in the orientational extension, $E = (2\lambda + 1)(d\sigma/d\lambda)$ the conventional rigidity, τ_{ind} the induction period of the autoxidation reaction, b the slope of the linear form of the kinetic curve for the absorption of oxygen in Fig. 14c, and w_{max} the maximum rate of absorption of oxygen.

The causes of the change in the induction period of the oxidation reaction during the orientational extension of PP have been examined[95,106]. However, before proceeding to their discussion, one must deal briefly with the question why an induction period arises at all in the uninhibited oxidation of PP and P-4-MP-1 or, in other words, why the kinetics of the initial stage of the oxidation reaction differ from the characteristics of the reaction at an advanced stage.

The derivation of kinetic information about the process occurring during the induction period presents considerable experimental difficulties, because the rates and degrees of oxidation are then very low. The absence of the necessary kinetic information does not at present permit unambiguous answers to the question posed. It has been shown[106] that the kinetic features characteristic of reactions with degenerate branching and quadratic termination of the kinetic chains are established only after the accumulation in the specimens of specific concentrations of the hydroperoxide (2×10^{-2} mol per kg of the amorphous phase, 80 °C, 760 mmHg O_2), which are approximately equal for the isotropic and oriented specimens (Fig. 15). It has been suggested[106] that at lower concentrations the hydroperoxide in PP has a low initiating capacity and is not the main source of radicals; the initiation reaction proceeds via the direct interaction between oxygen and the macromolecules [reaction (0)].

The results obtained recently in the study of the kinetics of the autoxidation of PP at elevated oxygen pressures[111] may serve as confirmation of the ideas described: it was found that the induction period decreases with increasing oxygen pressure over the entire range of pressures (from 0.02 to 4.24 MPa), while the maximum rate of accumulation of carbonyl groups virtually ceases to depend on the oxygen pressure already at $p_{O_2} \cong 0.45$ MPa. The activation energy for the induction period in the range 60–90 °C proved to be 24 kcal mol^{-1}. The low initiating capacity of the hydroperoxide formed in the initial stage of the oxidation reaction may be associated with the fact that its decomposition proceeds either as the unimolecular reaction

$$ROOH \xrightarrow{k_{s1}} R\dot{O} + \dot{O}H$$

(activation energy 35 kcal mol^{-1}, low values of k_3) or via the reaction

$$ROOH + RH \xrightarrow{k_{s2}} [R\dot{O} + \dot{R}] + H_2O \rightarrow \delta\dot{R}\ ,$$

in which rapidly recombining alkyl and alkoxy-macroradicals are formed (low degree of liberation of radicals from the cage, low values of δ). At higher concentrations the hydroperoxide apparently decomposes in intermolecular pairs linked by a hydrogen bond:

$$ROOH + ROOH \xrightarrow{k_{s3}} [R\dot{O}_2 + R\dot{O}] + H_2O \rightarrow \delta'\dot{R}\ .$$

The maximum rate of initiation corresponds to this reaction[86]. The increase of the initiation rate constant approximately by an order of magnitude with increase of the hydroperoxide concentration is observed also in the liquid phase: in the initial stage of the oxidation of n-decane and in the decomposition of t-butyl hydroperoxide[112].

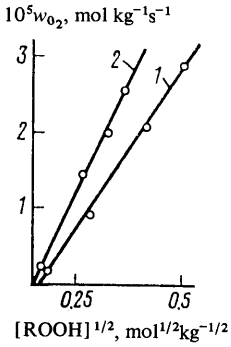


Figure 15. Dependence of the rate of absorption of oxygen on the concentration of the hydroperoxide for isotropic (line *1*) and oriented ($\lambda = 9$) (line *2*) PP films (80 °C, p_{O_2} = 760 mmHg)[107].

An alternative hypothesis concerning the causes of the induction period in the uninhibited oxidation of PP has been put forward[113]. It has been shown[114,115] by the EPR method that the rate of destruction of peroxy-radicals decreases with increase of the hydroperoxide concentration in PP subjected to preliminary oxidation: at room temperature k_6 falls from 170 to 5.2 kg mol^{-1} s^{-1} with increase of the hydroperoxide concentrations from 2.5×10^{-3} to 1×10^{-1} mol kg^{-1}, but, after the accumulation of hydroperoxide to give a concentration of 4×10^{-2} mol kg^{-1}, the constant k_6 changes only slightly. If it is assumed that the constant k_2 remains

unchanged during oxidation, then the changes in k_6 lead to an increase of the parameter $k_2/k_6^{1/2}$ with the degree of oxidation.

In principle, this can explain the difference between the kinetics of the initial stage and the advanced reaction. However, the induction period in the oxidation of PP is observed also at high temperatures (130 °C and above) where the constants k_6 are close to the "chemical" rate constant for the destruction of tertiary radicals in the liquid phase even for the oxidised polymer and it is difficult to expect higher values of k_6 in the initial stage. We therefore believe that the hypothesis of a low initiating capacity of the hydroperoxide formed in the initial oxidation stage is more likely. In one way or another, the establishment of the kinetic features characteristic of the advanced reaction is associated with the accumulation in the specimens of a hydroperoxide up to a specific concentration, which is virtually the same for isotropic and oriented specimens (Fig.15).

It was shown in Section III.1 that the rate of formation of the hydroperoxide falls when PP is oriented as a consequence of the decrease of the yield of the hydroperoxide per mole of absorbed oxygen. This factor is apparently the main cause of the increase of the induction period in the oxidation of PP subjected to orientational extension[95,106]. The decrease of the yield of the hydroperoxide is a consequence, in its turn, of the structural-physical changes occurring during the orientational stretching and is associated with the decrease of the rate of microdiffusion of oxygen in the polymer. This results in an increase of the rate of the induced decomposition of the hydroperoxide, which takes place without branching of the kinetic chains. We emphasise yet again that the oxidation of the entropically stressed specimens is slower than that of the unstressed specimens. The relaxation of stresses and the restoration of the compact conformations of the macromolecules in the amorphous phase of the oriented specimens smooth out the structural-physical differences between the isotropic and oriented specimens and increase the rate of oxidation of the latter (Table 3). This has important and interesting consequences for the kinetics of the oxidation and the durability of the specimens subjected to an external stretching load.

(b) The kinetics of the oxidation, durability, and mechanism of the decomposition of polyolefins subjected to an external stretching load. The mechanical load alters the structure of the molecular-dynamic properties of polymer matrices (see Section II); it is therefore natural to expect that the kinetics of the oxidation of polymers subjected to an external load will differ from the kinetics of the oxidation of specimens without an applied load. A series of studies devoted to this question have been carried out on oriented PP[59,72,73,116,117]. The specimens were maintained under different loads until rupture under the conditions of vigorous thermo-oxidative degradation and the durability of the polymer was compared with the concentrations and proportions of the oxidation products in the ruptured specimens. It was shown that, in the oxidation of PP subjected to an external stretching load, there exists a range of stresses in which the durability of the polymer depends only slightly on the load[59] and can actually increase as the latter is increased[117], but under these conditions the durability *in vacuo* is smaller by many orders of magnitude, i.e. is determined wholly by the rate of the thermo-oxidative degradation processes[71-73]. As an illustration, Fig.16 presents (on the basis of the data of Livanova et al.[73]), the durability isotherms (*a*) and curves relating to the rate of the steady creep to the stress (*b*) in oxygen and *in vacuo* for different PP specimens. The durability isotherms can be arbitrarily divided into three sections: along section I, the durability is determined by the rate of the thermo-oxidative chain degradation, along section II, by the sum of the rates of the mechanoinitiated and oxidative degradation, and along section III, solely by the rate of the mechanodegradation of the macromolecules carrying the load (which diminishes in a certain range with increase of the stress as a consequence of processes involving the orientational strengthening of the polymer). Accordingly, the durability increases significantly along section I after the introduction of inhibitors[60,71], while along section III it remains unchanged (Fig.7).

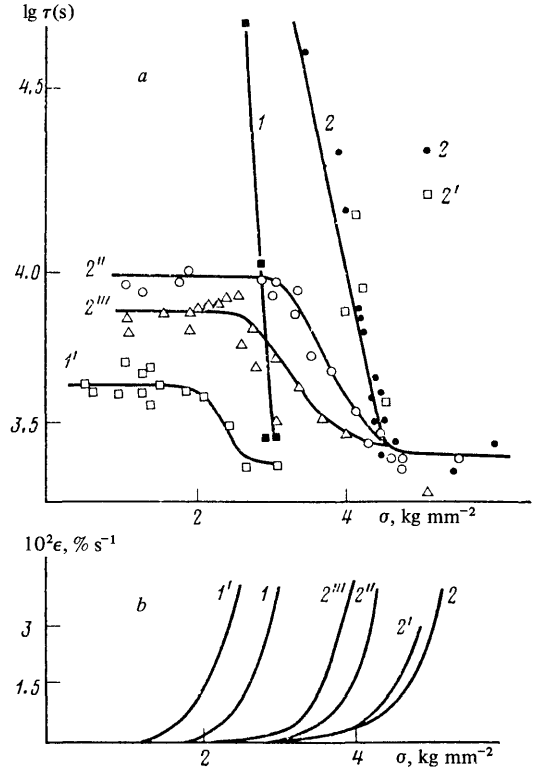


Figure 16. Durability isotherms (*a*) and the dependence of the rate of steady creep on the stress (*b*) at 130 °C for $\lambda = 5$ (curves *1* and *1'*) and 7 (curves *2* and *2'*–*2'''*) in oxygen (curves *1'*, *2''*, and *2'''*) and *in vacuo* (curves *1*, *2*, and *2'*) for unannealed (curves *1*, *1'*, *2*, and *2'*) and annealed (curves *2'* and *2'''*) specimens[73].

Fundamentally new results have been obtained[60,116] in a study of the concentration and distribution of the oxidation products in PP specimens oxidised under an external load. More than 100 specimens differing in the degree of extension, the initial structure (unannealed and annealed), and in the external stress ($\sigma = 5$–70 MPa) were investigated. In these studies the distribution of the oxidation products in the film was determined by scanning the specimen with a beam of infrared light focussed on to an area of 1 mm^2. We shall now describe the main results.

1. With increase of the applied stress, the transition from elastic deformations to creep deformations entails a change in the concentration and composition of the oxidation products

in the zone of the rupture of the specimens, indicating a change in the initiation mechanism: initiation via reaction (0) is gradually replaced by initiation via reaction (0'). This is accompanied by a decrease of the length of the kinetic oxidation chains and, under the conditions of fairly high stresses, the oxidation reaction passes from the chain to the non-chain regime. Fig.17 presents (on the basis of the data of Rapoport and co-workers[60,116]) the infrared spectra of the ruptured specimens in the region of the vibrations of the carbonyl and hydroxy-groups. For stresses corresponding to elastic deformations, the shape of the absorption band of the carbonyl groups in the stressed PP hardly differs from that of the band in the spectrum of the polymer oxidised without an external load; the band maximum at 1710 cm^{-1} corresponds to the C=O stretching vibrations in ketones (Fig.17*a*, spectrum *1*). With increase of the stress, the maximum shift towards higher frequencies, whereas for stresses corresponding to plastic deformations the maximum is observed at 1740 cm^{-1}, which indicates the predominant formation of aldehyde groups (Fig.17*a*, spectrum *3*).

The changes in the spectrum of the carbonyl groups occurring as the deformation regime is altered are accompanied by a sharp diminution of the concentration of hydroxy- and hydroperoxy-groups. In specimens oxidised under the conditions of plastic flow, where the aldehyde groups are virtually the only carbonyl oxidation products, the hydroperoxide cannot be determined iodometrically and the ratio of the concentrations of the aldehyde and hydroxy-groups is ~ 1:1, which corresponds to the ratio which should be obtained in the disproportionation of peroxy-radicals, one of which must be a terminal radical. This implies that in the region of plastic deformations the oxidation reaction virtually passes to a non-chain regime and consists in the formation, oxidation, and destruction of terminal macroradicals.

The data obtained indicate a change in the initiation mechanism: for small stresses, the initiation proceeds via reaction (0) and leads to the formation of middle macroradicals, whose subsequent chain reactions give rise to ketone, aldehyde, hydroperoxy-, and other groups. With increase of the stress, the mechanoinitiated rupture of C–C bonds, leading to the formation of terminal macroradicals, begins to play an increasing role. Evidently this is accompanied by a sharp increase of the rate of termination of the kinetic chains: the terminal radicals are more mobile than the middle radicals formed via reaction (0) and their destruction takes place in the plastically deformed matrix, which, as shown in section III.1, accelerates the process. The non-chain character of the oxidation under the conditions of high stresses is confirmed by the absence of the influence of inhibitors on the durability time in this region of stresses (Fig.7).

2. The fact that the oxidation process under a mechanical stress is local in character, observed by Rapoport and co-workers[60,116], is very important. At the site of the future break in the film, an oxidation centre arises and spreads in the specimen over a distance which depends on the stress in the oxidation reaction and on the structure of the specimen. This results in the establishment of a concentration gradient of oxygen-containing groups in the rupture zone. In the group of spectra *b* and *c* in Fig.17 the lower spectra correspond to the rupture zone of the specimens and the upper spectra to the "matrix" (sites remote from the rupture zone). For a fixed stress, the concentration gradient in the unannealed specimens is always greater than in the annealed specimens (Fig.18, curves *1* and *1a*). For specimens with a fixed structure, the concentration gradient increases sharply with increase of the stress in the oxidation process (Fig.18, curves *1–3*). As a result, the concentration of carbonyl groups, averaged over an area of 1 mm^2 in the rupture zone,

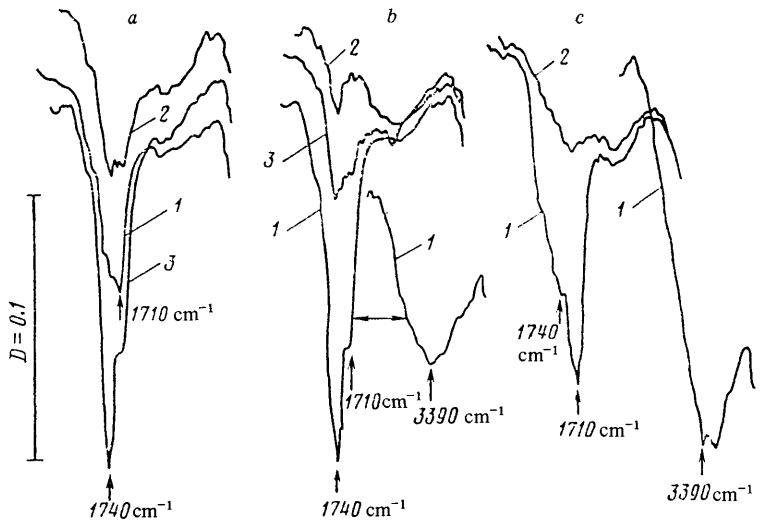


Figure 17. Infrared spectra of PP specimens subjected to an external load up to rupture; *a*) $\lambda = 7$, annealed specimen [σ(MPa): 1) 10; 2) 13; 3) 20]; *b*) the same specimen, $\sigma = 20$ MPa [1) rupture zone; 2) and 3) matrix]; *c*) $\lambda = 4$, unannealed specimen [1) rupture zone; 2) matrix][60,116].

decreases with increasing stress (Fig.19). For example, in unannealed specimens a change of the stress from 10 to 40 MPa (the region of elastic deformations) results in a decrease of the concentration of carbonyl groups in the rupture zone by a factor of 20. The same effect is observed in the annealed specimens. The durability of the specimens in the range of applied stresses 10–40 MPa are very similar. The data presented imply that the average rate of oxidation in the rupture zone diminishes with increasing stress. Since the rate of the initiation reactions increases with increasing stress and the rate of destruction of radicals falls in the region of elastic deformations (Section III.1), the decrease of the overall rate of oxidation with increasing stress can be a result of a decrease of the rate of propagation of kinetic chains induced by the additional enrichment of the amorphous phase of the polymer in macromolecules with extended conformations.

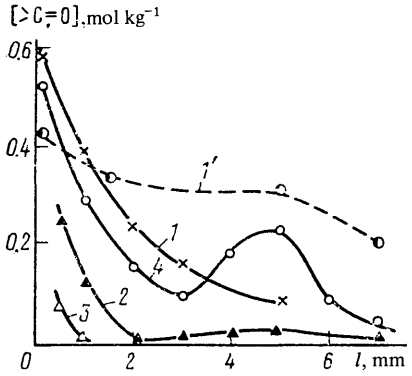


Figure 18. Carbonyl group concentration profile in PP specimens oxidised until rupture: 1)–4) unannealed specimen; 1') annealed specimen; oxidation temperature (°C): 1) and 1') 130; 2)–4) 120; λ: 1)–3) 8.5; 4) 4; σ (MPa): 1) and 1') 10; 2) 20; 3) 29; 4) 5.[60]

In the region of plastic deformations, the concentration of the non-chain oxidation products increases with the stress (Fig.19), which is associated with the increase of the rate of the mechanical initiation of the oxidation reaction. The decrease of the rate of propagation of kinetic chains under load and the increase of the rate of their rupture in the region of plastic deformations actually lead to the transition of the oxidation reaction to the non-chain regime.

3. In the rupture zone of the specimen, not only the concentrations but also the compositions of the carbonyl-containing groups can differ in the "matrix": starting from a specific stress, aldehyde groups predominate in the region remote from the rupture zone, while in the rupture zone ketones as well as aldehydes are often detected (Fig.17*b*). This is apparently associated with the fact that the rupture is preceded by the formation of a large number of microcracks, with relaxation of stress above and below such cracks; the oxidation process develops at these sites in an unstressed polymer, has a chain mechanism, and is accompanied by the formation of ketones. Comparison of spectra *2* and *3* in group *b* (Fig.17) shows that the compositions of the oxidation products differ at individual points in the matrix: in spectra *2* only aldehydes can be detected, while in spectra *3* ketones appear as well. On the basis of the data presented by Rapoport[60], it has been suggested that, at the "point" corresponding to spectrum *3*, a zone corresponding to the release of the load has appeared, which led to the development of chain oxidation and the formation of ketones. The appearance of release of load zones in the stressed polymer is associated with the formation of microcracks. The acceleration of the oxidation on the inner side of the arc-shaped microcracks, formed in the diffusional oxidation of annealed oriented PP specimens, has been observed[118]. Rapoport[60] suggested that the difference between the compositions and concentrations of the oxidation products formed in the stressed zones and in the zones where the load has been released be used as a basis for a method of defectoscopy for stressed PP undergoing oxidation; this possibility has been realised experimentally[116].

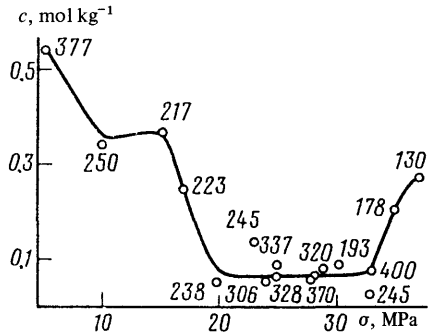


Figure 19. Dependence of the concentration of carbonyl groups in the rupture zone on the stress during oxidation; λ = 7.5; unannealed specimen; oxidation temperature 120 °C; the numbers against the points represent the lifetimes of the specimens in minutes[117].

4. It must be specially emphasised that oxygen-containing groups accumulate at significantly different concentrations at the instant of rupture in the matrices of specimens of different structures undergoing oxidation when subjected to different stresses. For example, the rupture of unannealed specimens frequently occurs when the matrix remote from the rupture zone is still in the induction period of the oxidation reaction (Fig.18, curves *2* and *3*); in the rupture zone profound oxidative degradation takes place under these conditions. On the other hand, at the instant of the rupture of annealed specimens the matrix is highly oxidised (Fig.18, curve *1'*). It is striking that the durabilities of the unannealed and annealed specimens are similar. It is even more striking that their repeated durabilities (the periods before rupture following a second application of the load to parts of the ruptured specimens) are also similar although in the annealed specimens the matrix has been oxidised to a much greater extent from the very beginning of the experiment. Rapoport et al.[116] consider the possible causes of the above effects: (a) the strictly local character of the oxidation of the unannealed stressed specimens; (b) the smoothing out of the structural differences between the annealed and unannealed specimens in the zone of a developing major crack; (c) profound oxidative degradation occurring in the annealed polymer without involving the extended macromolecules carrying the load, which are degraded more slowly and

in accordance with the same kinetic laws as the extended macromolecules in the unannealed polymer. This is an important argument in support of the ideas developed in Section III.1.

5. The significant differences between the concentrations of the oxygen-containing groups accumulating in the matrices of different specimens towards the instant of rupture show how carefully one must approach the development of criteria for macroscopic decomposition: it is very frequently suggested that the accumulation of carbonyl groups up to a specific concentration in the bulk of the specimens be employed as such a criterion for PP[119]; the results of Rapoport et al.[116] show that, as a consequence of the spatial localisation of the oxidation process in stressed PP, the employment of such a criterion would lead to major errors. It follows from the data obtained[116] that, in the study of the kinetics of the rupture of stressed polymers, one should not employ methods yielding values of the measured quantity averaged throughout the specimen.

The spatial localisation of the oxidation process observed in a stressed polymer[60,116] and the dependence of the reaction regime on the size of the stress posed new problems for investigators engaged in predicting the durability of polymer articles under operating conditions (when the polymer is subjected to the joint action of mechanical stresses, oxidising agents, ultraviolet light, etc.). Evidently, in describing the kinetics of such localised processes, one cannot employ the usual mathematical procedures developed for solid-phase reactions (even when account is taken of the distributions with respect to the rate constants). A key question becomes that of the causes and the instant of the spatial localisation of the oxidative degradation. It must be elucidated whether the localisation obtains from the very beginning of the oxidation of the stressed polymer or whether the process proceeds for a time uniformly throughout the bulk of the specimen. We believe that the localisation of the oxidation reaction is an "after-effect" of the opening of the sides of the microcracks and is associated with the acceleration of the oxidation process in the relaxed zones above and below the lips of the microcracks; up to this instant, the degradation can be regarded as proceeding "uniformly" throughout the bulk of the stressed polymer and the formation of a decomposition centre can be treated as a result of the accumulation of random ruptures. In the description of the kinetics of this process, one can therefore use successfully the method described in the literature[120,121].

We shall enumerate briefly the principal results of the studies of Rapoport and co-workers[60,116]: (1) a change in the mechanism of the initiation of the oxidation with increase of mechanical stress has been observed; (2) a change in the reaction regime—a transition from chain to non-chain oxidation—has been noted; (3) the limits of the ability of inhibitors to increase the durability of stressed polymers have been established; (4) the development of the oxidation process from a centre in the stressed polymer, requiring the application of local methods for the experimental study of the kinetics of the decomposition reaction, has been observed; (5) the possibility of the defectoscopy of the polymer undergoing oxidation under the influence of an external load, based on the difference between the concentrations and compositions of the oxidation products formed in the region of the crack and in the "undamaged matrix", has been demonstrated.

Two studies dealing with the kinetics of the oxidation of non-oriented PE[122] and PP[123] specimens subjected to an external load were published in 1982. In the first study[122] PE specimens in the form of "blades", whose widths in the wide and narrow parts differed by a factor of three, which corresponded to stresses differing by a factor of three in relation to the initial section, were oxidised. The ranges of the experimental stresses were 2.9–4 MPa at 70 °C and 1.9–3.1 MPa at 90 °C. The oxidation kinetics were followed from the accumulation of carbonyl groups in the wide and narrow parts of the specimens. For the highest and lowest stresses, no differences were observed between the rates of formation of carbonyl groups in the wide and narrow parts while for intermediate stresses the degree of oxidation of the wide parts of the specimens was always greater; the major crack and the degree of decomposition of the specimens increased in precisely this region, although the true stress was greater in the narrow part. In other words the specimens were not ruptured at the site of the maximum stress but at the sites of the minimum deformation, where the thermo-oxidative degradation developed faster. The results of this study[122] fully confirm the results and conclusions in other investigations[82,60,116]. The lower rate of oxidation of stressed PE in the narrow part is associated with orientation effects and its nature is apparently the same as that of the decrease of the rate of the radiation-induced oxidation of oriented PE[82]. A decrease of the rate of the photochemical oxidation of isotropic PP subjected to an external load has been observed[123].

Thus, under the conditions of orientational extension and an external load, the overall rate of the chain oxidation of polyolefins as a rule diminishes. For stresses which result in a transition of the reaction to a non-chain regime, the overall rate of oxidation increases with increase of the stress as a consequence of the increase of the rate of the mechanical initiation of the radicals.

3. The Influence of Mechanical Stresses on the Kinetics of the Oxidation of Raw and Cured Rubbers by Molecular Oxygen and Ozone

The influence of an external load on the ozone-induced ageing of polyolefins has been studied in the investigations[31,65,66] discussed above in Section III.1. In this Section we shall deal with the specific features of the oxidation of stressed raw and cured rubbers.

The majority of elastomers contain double bonds, which make them more reactive than polyolefins. Elastomers are rapidly oxidised in air and particularly in an ozone–oxygen mixture, which leads to the loss of their operating properties. In recent years this question has attracted increasing attention by investigators in connection with the pollution of the atmosphere and the increase of the content of corrosive components in air. The kinetics of oxidation processes in elastomers are influenced significantly by mechanical stresses[124,125], which was pointed out as early as 1950 by Kuz'minskii[1,2], who called this phenomenon "mechanical activation". The effect of mechanical activation was not related to the breaks in macromolecules, i.e. to mechanical degradation; on repeated deformations (amplitude 75%, frequency 250 cycles min^{-1}), the effect of mechanical activation proved to be much greater than in static deformations (degree of deformation 75%). However, there was no reason to attribute this effect solely to the mechanical activation of oxidation processes, because a dynamic load accelerated equally the rupture of vulcanised elastomers in oxygen and in an inert atmosphere; the effect was more likely to have been associated with the formation and development of microcracks.

Subsequently it was found that mechanical stresses can not only activate but can also inhibit chemical reactions in stressed elastomers[67,126] and the activation effect has been attributed to the decrease of the activation energy for oxidative and thermal processes, while the inhibition effect was attributed to the decrease of the pre-exponential factor.

The existing ideas about the mechanism of the ozone-induced cracking of stressed elastomers have been examined critically in Zuev's book[53]. In this review we are interested in the influence of mechanical stresses on the kinetics of the oxidative degradation of elastomers.

In the ozone-induced ageing of unsaturated vulcanised elastomers, the double bond dissociates. The influence of structural stresses on this process has been investigated on model compounds—cyclo-olefins[64], and a calculation[127] made it possible to explain quantitatively the results obtained by Popov and Zaikov[64]. During the dissociation of the double bond, a steric change takes place in the ~ C(1)–C(2)=C(3)–C(4) ~ unit associated with the rehybridisation of the C(2) and C(3) atoms from the sp^2 state to the sp^3 state; the C(2)–C(3) bond length increases from 1.333 to 1.534 Å, the valence angle decreases from 122.2° to 112.2°, and the angle of internal rotation diminishes from 0° to 60°. Fig.20 illustrates the changes in the distance l between the C(1) and C(4) atoms, not linked by valence bonds, as a function of the reaction coordinate for the *cis*- and *trans*-fragments ~ C(1)–C(2)=C(3)–C(4) ~. For the *trans*-configuration, the C(1)–C(4) distance only increases in the course of the reaction; for the *cis*-isomer, the above distance passes through a minimum. The rate of the ozonisation reaction should therefore be sensitive to the mechanical stress; stretching stresses should accelerate the reaction for the *trans*-configuration of the fragment and should inhibit it for the *cis*-configuration (in the latter case the energy of the transition complex can increase more under the influence of the stretching stress than the energy of the initial state, which should result in an increase of the activation energy for the ozonisation of the *cis*-isomer of raw rubber).

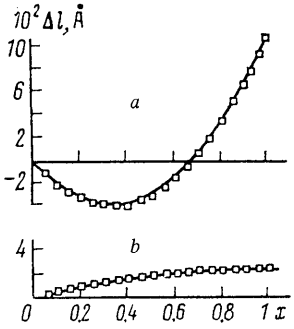


Figure 20. The changes in the C(1)–C(4) distances in the *cis*-forms (*a*) and *trans*-forms (*b*) of the ~ C(1)–C(2)=C(3)–C(4) ~ fragments in the $sp^2 \rightarrow sp^3$ transition of the C(2) and C(3) atoms[68]; x = reaction coordinate.

The ideas described served as a basis for the interpretation of the results obtained in the ozonisation of the unsaturated polymers obtained by vulcanising the *cis*- and *trans*-isomers of raw rubbers[68,128]; stretching stresses did indeed increase the rate of ozonisation of *trans*-1,4-polybutadiene, inhibited the ozonisation of *cis*-1,4-polyisoprene (for degrees of deformation exceeding 20%), and did not change the rate of reaction involving 1,2-polybutadiene in which the double bond is localised in a side group. From the standpoint considered here, the authors[68,128] proposed a new explanation for the existence of a critical deformation in the ozone-induced cracking of stressed cured rubbers, which had been known a long time but had not found an adequate interpretation. In the oxidation of elastomers, oxygen-containing functional groups accumulate in the latter and their decomposition is activated in the statically deformed cured rubbers[41].

The data presented in this review show that mechanical stresses interfere with the chain oxidation process at all its stages and can alter significantly the kinetics and even the regime of the oxidative degradation. Mechanical stresses can also lead to a very pronounced spatial localisation of the oxidation process in polymer specimens. They are frequently frozen in the material during its conversion into the finished article, are generated in the article during its use, and finally arise in the ageing process when the latter takes place in a diffusion regime. The oxidation of specimens uniformly throughout their bulk under real conditions is apparently more likely to be the exception rather than the rule. This poses new problems for investigators concerned with its prediction of the durabilities of polymer articles under real operating conditions, because the methods of homogeneous kinetics are inapplicable in this instance.

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