RUSSIAN CHEMICAL REVIEWS
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December 1979

Translated from *Uspekhi Khimii*, 48, 2113-2163 (1979) U.D.C. 547.912.22

Some Problems of the Chemical Physics of the Ageing and Stabilisation of Polymers

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The ageing and stabilisation of polymers involves the chemical physics of coupled radical-chain, ionic, and molecular transformations in complex multicomponent systems which make up the polymeric material. In the present review the question of the ageing and stabilisation of polymers is formulated as a multifactor problem, where the study of the changes in the properties of the material under various conditions can be treated from a single standpoint, and the mechanism is represented by a set of interrelated elementary processes. Some new results and views are considered.
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I. INTRODUCTION

Ten years ago the field of the ageing and stabilisation of polymers was defined as the "chemistry and physics of coupled radical-chain, ionic, and molecular transformations in complex multicomponent systems"[1]. Since then numerous investigations of the detailed mechanism of the ageing processes of polymers and their kinetics as well as studies designed to develop rational stabilisation principles have been carried out[2-6].

Much scope has been found for the application in this field of the theoretical and experimental methods characteristic of chemical physics to the investigation of new phenomena and relations which are of enormous practical importance. A well-founded possibility of formulating the question of ageing and stabilisation of polymers as a multifactor problem, where the study of the changes in the properties of the polymeric material under various conditions can be treated from a single view point, became possible. This field acquired special significance as an important

branch of the chemistry of the solid state with allowance for the specific features of the chemical reactions of macromolecules.

In the course of the development of the first attempts at the identification of the active species responsible for ageing, numerous studies devoted to the elementary steps of the chemical reactions involves these species were carried out and their quantitative kinetic characteristics were determined. New experimental techniques made possible the determination of fine details of the structure of the active centres and at the same time raised the level and importance of the study of the elementary reactions in polymers.

The time is approaching when the ageing process will be treated quantitatively as a set of interrelated elementary reactions no longer in relation to individual model systems but in all cases on the basis of kinetic parameters of elementary processes compiled in tables and handbooks.

The principal task of chemistry, which is to establish relations between the structure of substances and their reactivity, acquires a new significance in the field of the ageing of stabilisation of polymers as the problem of the determination of relations between the changes in the properties of polymers during ageing and the kinetics of the chemical reactions in the polymer.

New principles of the stabilisation of polymers, based on the knowledge of the detailed mechanism of the ageing process, have arisen. New tasks in the field of the ageing and stabilisation of polymers arise in connection with their use in space apparatus and research, in medicine, in the building industry, and in many fields of modern engineering.

The present review deals with certain new results and views referring to the chemical-physical study of the ageing and stabilisation of polymeric materials.

II. THE AGEING OF POLYMERS AS A MULTIFACTOR PROBLEM

The polymeric material in the initial state possesses a definite set of properties y_i which vary with time during ageing, i.e. are functions of time.

The ageing of a polymer consists of a set of its chemical and physical transformations in the course of storage and use. The polymer is then subjected to the action of a wide variety of chemical and physical factors x_i: heat, light, penetrating radiation, oxygen, moisture, corrosive chemical compounds, and mechanical stresses. The operation of these factors creates conditions for the initiation and development of chemical reactions responsible for the ageing of the polymer. For a time the changes in the properties of the polymer may be insignificant from the standpoint of its suitability for practical use (the material is stable). The stability of the material can be characterised quantitatively by its useful life, i.e. the time during which the article or material loses its suitability for practical use under specified influences.

We shall assume that the properties of the material are characterised by a point Y in the space of properties (Fig. 1) at a given instance. The coordinates of this space y_i are quantitative characteristics of the properties, for example, the density, composition, physicomechanical characteristics, dielectric constant, absorption spectrum, etc. The conditions in the practical utilisation of the material can also be characterised by a point in the space of conditions whose coordinates x_i are quantitative characteristics of the conditions: temperature, intensity, and spectral composition of the radiation acting on the polymer, mechanical stress, moisture content, oxygen pressure, etc. The material is suitable for use as long as it possesses the required set of properties, i.e. as long as the point Y does not leave in the course of ageing a certain region of practical suitability ϵ_0 whose dimensions and form may be various depending on the requirements which must be met by the material.

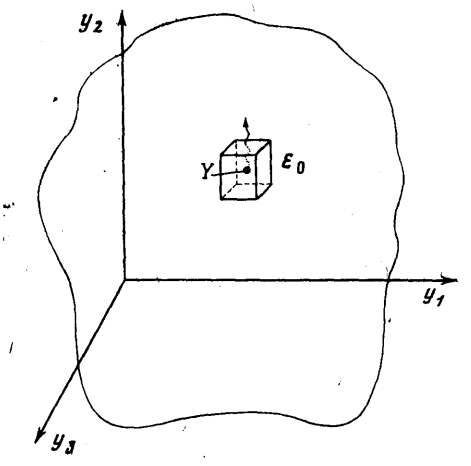


Figure 1. A qualitative picture of the time variation of the set of properties of a polymer y (special case—a point in three-dimensional space). ϵ_0 represents the region of the practical suitability of the polymer.

From the standpoint of chemical physics, the ageing of a polymeric material must be regarded as a process described by a single system of equations suitable for any conditions:

$$Y = f(X, t). \quad (1)$$

The introduction of the characteristics of the conditions into this system of equations makes it possible to determine how the properties of the polymer vary under these conditions. As a result, one can determine the instant when the point Y leaves the limits of any region ϵ_0, i.e. when the material ceases to satisfy the requirements imposed on it.

Thus the useful life of the polymeric materials is determined not only by its physicochemical properties, but also by the conditions under which it is used (X) and the requirements which it must meet whilst being used (ϵ_0).

1. Criteria of the Constancy of the Properties of Polymers

A quantitative treatment of the constancy of the properties of polymers in practice is exceptionally important. Indeed, if it were possible to devise rigorous criteria of the constancy of the properties of polymers, it would be easy to answer the question how far degradation can proceed without the polymer losing its initial properties in practice.

The study of the ageing and stabilisation processes of polymers involves slight chemical transformations in the material which may lead to considerable changes in the physical properties of the specimen.

It is frequently assumed that the properties of a substance virtually do not change if the number of elementary points of damage S (chain rupture, the appearance of new functional groups as a result of chemical reactions) is small compared with the total number of molecules n present in the specimen, i.e. if the condition

$$S/n \ll 1. \tag{2}$$

is fulfilled. If it is assumed that the degree of damage (degradation) δ is defined as the number of breaks per chemical bond in the main chain of the linear polymer molecule, then

$$\delta = \frac{S}{npz}, \tag{3}$$

where $p = M/m$ is the degree of polymerisation (the ratio of the molecular weight of the polymer to the molecular weight of the monomeric unit, which is equal to the number of monomeric units in the macromolecule) and z is the number of bonds in the main chain per monomeric unit. Hence

$$\frac{S}{n} = \delta pz = \delta \frac{M}{m} z, \tag{4}$$

and the condition for the constancy of the properties of the polymer becomes

$$\delta \frac{M}{m} z \ll 1, \text{ or } \delta M \ll \frac{m}{z}. \tag{5}$$

Evidently, for a given type of linear chain, the permissible degree of degradation is smaller the greater the molecular weight.

The use of this criterion leads to the conclusion that polymer materials should have much less constant properties than low-molecular-weight compounds. As an example, we shall compare the capacity for degradation of the polymethylene chains in low-pressure polyethylene ($M = 420\,000$) and in lubricating oil ($M = 420$). In both cases $z = 2$ and $m/z = 14$. We shall assume that 0.01% of all the carbon chains are ruptured in both specimens, i.e. $\delta = 10^{-4}$. We then find $\delta M = 10^{-4} \times 4.2 \times 10^2 = 4.2 \times 10^{-2} \ll 14$ for the lubricating oil, i.e. its properties remain virtually constant. On the other hand, for polyethylene we have

$$\delta M = 10^{-4} \cdot 4.2 \cdot 10^5 = 42 > 14. \tag{6}$$

Hence it follows that the condition for the constancy of the properties is not fulfilled in the latter case.

The significance of the results obtained is that only a small proportion of the molecules were damaged in the lubricating oil, while in the polymer there were several breaks in each macromolecular chain. Indeed $S/n = \delta Mz/m = 10^{-4} \times 420 \times 2/28 \simeq 3 \times 10^{-3}$ for the lubricating oil, while $S/n \simeq 3$ for the polymer.

The simplest criterion of the constancy of the properties of a polymer examined above is by no means universal; it can be used in characterising those properties of the polymer which are determined not only by its chemical structure, but also by the size of its macromolecules. These are, for example, the intrinsic viscosity of the polymer and the light scattering parameters of its dilute solutions. These properties are normally employed for analytical purposes in order to determine the changes in the molecular weight of the polymer during its degradation.

Properties of the polymer of practical importance usually vary with the molecular weight in a complex manner. For example, the stability of the majority of polymers with high degrees of polymerisation usually ceases to depend on the molecular weight, while the glass point, the brittle temperature, and the modulus of elasticity can assume extremum values (Fig. 2). For such a complex dependence of the properties of the polymeric material on its molecular weight, the simplest criterion of their constancy becomes inapplicable. The presence of a region where the properties of the polymer are independent of its molecular weight may result in the properties remaining unchanged for fairly high degrees of degradation. The properties of a polymeric material with a high molecular weight are therefore more stable.

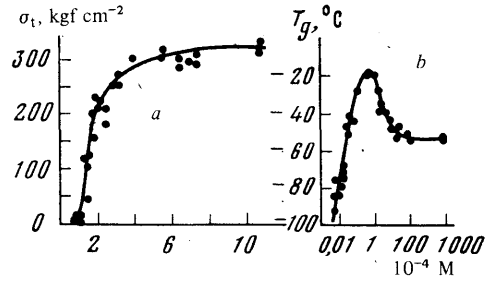


Figure 2. Dependence of the molecular weight M on the tensile strength σ_p of vulcanised natural rubber (a) and on the glass point T_g of poly(ethylene oxide)[7] (b).

It has been established that the reciprocals of many properties of polymeric materials are linearly related to the quantity which is the reciprocal of the molecular weight or the degree of polymerisation[7]:

$$\frac{1}{y} = A\left(1 + \frac{\mu}{M}\right), \tag{7}$$

where y is a characteristic of the properties of the material, for example, breaking strain, while A and μ are parameters. In this case the degree of the change in the property y can be adopted as a criterion of its constancy:

$$\frac{y_0 - y}{y} \ll 1. \tag{8}$$

The degree of damage of the polymer δ is related to its molecular weight by the expression

$$M = \frac{M_0}{1 + \delta M_0}, \tag{9}$$

where M_0 is the molecular weight of the initial polymer. We find from Eqns. (7)–(9)

$$\delta\mu M_0/(M_0 + \mu) \ll 1. \tag{10}$$

Hence the criterion of the constancy of the properties of the material is

$$\delta \ll (M_0 + \mu)/M_0\mu. \tag{11}$$

It follows from Eqn. (11) that for low-molecular-weight compounds ($M_0 \ll \mu$):

$$\delta \ll 1/M_0, \tag{12}$$

i.e. the properties of the substance are less stable the higher its molecular weight. For high molecular weights ($M_0 \gg \mu$), the stability of the material ceases to depend on the molecular weight:

$$\delta \ll 1/\mu. \qquad (13)$$

Unfortunately such criteria, relating the degree of degradation of the polymer to the change in its properties, are also not general. For example, they do not characterise the change in the molecular weight distribution or composition of the polymeric material and do not take into account the change in its molecular structure. In order to determine the extent of the change in the properties of polymeric specimens, one must therefore employ several methods. For example, one may point to methods for the determination of thermal stability from the change in the pressure in the system (manometric method) and from the weight loss (thermogravimetric method), methods based on the study of the change in physicomechanical properties, as well as procedures for the estimation of stability employing data obtained in the study of the polymer degradation products, etc.

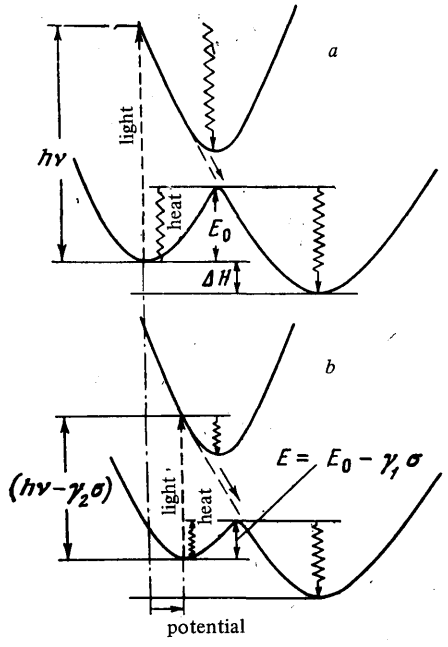


Figure 3. A qualitative picture of the cross-section through the potential surfaces along the elementary chemical reaction coordinate (*a*) and its variation under the influence of mechanical stresses (*b*).

2. The Elementary Step in the Chemical Reaction

In a quantum-mechanical treatment the elementary step of a chemical reaction in a polymeric material, as well as any other system, reduces to the movement of the initial species on the potential energy surface along the reaction coordinate.

Fig. 3 presents a qualitative picture of a section through the potential energy surface for the thermal, photochemical, and mechanical degradation of the polymer. The thermal transition is carried out adiabatically. The phototransition can include a non-adiabatic process stage associated with the absorption of a quantum with the energy $h\nu_0$. When the macromolecule is acted upon by mechanical stresses σ, the minima on the potential curves approach one another, which reduces the values of E and $h\nu$ for which the reaction can take place (in the zeroth approximation the decrease is linear). The rate constant for the elementary step then becomes

$$k = k_0 \exp\left(-\frac{E-\gamma\sigma}{RT}\right), \qquad (14)$$

where γ is a proportionality coefficient, which depends on the form of the potential curves. Since the lifetime of the material, i.e. the time which must elapse before degradation, is

$$\tau_p \propto 1/k,$$

we obtain from Eqn. (14)

$$\tau_p = \tau_0 \exp\left(\frac{E-\gamma\sigma}{RT}\right), \qquad (15)$$

i.e. the familiar Zhurkov equation.

This picture is characteristic of the influence of a field of mechanical forces on any elementary step of the chemical reaction regardless of its nature. When the influence of mechanical stresses on the stability of a polymeric material as a whole or its lifetime is estimated, account must be taken of this influence not on one but on all the elementary steps of the chemical reaction in the ageing process. The linear relationship between the logarithm of the lifetime and the stress

$$\ln\tau_p = \ln\tau_0 + (E-\gamma\sigma)/RT \qquad (16)$$

is therefore an effective characteristic of the process and usually holds over a narrow range of stresses, where the rate of the process is limited virtually by one elementary step. Over a wide range of variation of stresses, this relation is more complex, since the rate-limiting stage of the ageing process can vary with the stress.

3. The Nature of the Active Centres

Molecular reactions are not as a rule important in the mechanism of the ageing of polymers. In practice one must usually take into account reactions involving three types of active species: free radicals, excited species, and to a lesser extent ions.

Free radicals play the main role in the ageing of polymeric materials. This is because reactions involving either the homolytic dissociation of the main chain of the molecule or the homolytic abstraction of atoms or radicals from side groups are characteristic of the majority of polymers.

Ions are formed in polymers usually only in the stage involving the initiation of radiation-induced processes and in processes associated with the degradation of polymers in corrosive media. Data for the formation of ions in the mechanical degradation of polymers on friction and on breakdown of the polymeric material lead to the conclusion that ions play an insignificant role in these processes, their concentrations are low, and they are formed in

secondary reactions associated with the acquisition of electric charge by the polymeric material as the macroparticles move relative to one another. On the other hand, the chemical changes in the material, for example, its mechanical breakdown, are determined by radical and not ionic processes[8].

Electronically excited molecules in the lowest excited singlet (S_1) or lowest triplet (T_0) states play the greatest role in the photochemical ageing of polymers. Two-quantum photochemical processes occurring with participation of the highest triplet states can also be important[9]. The dependence of the quantum yield of a number of photochemical processes on the wavelength of the radiation acting on the polymer indicates the important role of the highest excited singlet states[10].

Together with electronically excited molecules, certain labile species in the excited state can participate in the photochemical ageing process. Thus thermal and photochemical decomposition of certain molecules can lead to the formation of excited ("hot") free radicals[11], which interact more effectively with the medium than the usual ("cold") free radicals. For high intensities of the light during photoageing, free radicals can absorb light quanta and pass to an electronically excited state[12]. The problem of the possible increase of the rate of the chain propagation reaction as a result of the absorption of a light quantum by the free radical is discussed in the literature[13].

The structure and properties of radical active centres involved in the ageing of the polymeric material are various. Table 1 presents typical examples of active centres of this class and demonstrates their role in the ageing process.

EPR has played a particularly important role in the study of radical active centres. It extended enormously the possibilities for the study of the structure of these centres and for the determination of their role in the ageing process.

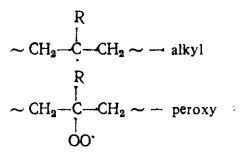
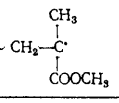
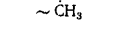
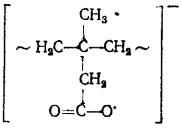
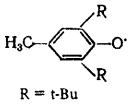
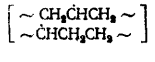
Numerous EPR spectra of the "central" and "terminal" macroradicals of different types are now known (Figs. 4 and 5). The complex structure of the spectrum makes it possible to identify the structure of the macroradical. For example, the spectrum of the central macroradical of polypropylene (Fig. 4) consists of eight components with a splitting of 21 ± 1 G. Hence it follows that in all probability the spectrum refers to the radicals



because here the β-positions relative to the unpaired electron contain seven equivalent protons. Another example is the terminal macroradical of polyformaldehyde whose spectrum consists of a triplet with a splitting of 20 ± 1 G (Fig. 5). Since this type of spectrum corresponds to the interaction of the unpaired electron with two protons, it may be imagined that the given radical has one of two possible structures:



Table 1. Radical active centres and their role in the ageing process.

Type of radical active centre	Example	Formation pathways	Role in ageing process	Influence on direction and rate of ageing process
Central macroradical		chain propagation		
		oxidation of alkyl radicals	chain propagation, cross-linking, and polymer-analogue reactions	change in the structure of side chain, cross-linking, and change in MWD
Terminal macroradical		breaks in macromolecules and depolymerisation	cross-linking and depolymerisation	change in molecular weight and MWD
Low-molecular-weight radical		decomposition of macro-radicals	migration of free valence лентности	formation of volatile products
Radical-ion		exposure to penetrating radiation and two-quantum photoprocesses	chain initiation	increase of rate of ageing
Inhibitor radicals	 R = t-Bu	reactions involving stabilisers	chain termination and propagation	decrease of rate of ageing
Variable-valence metal ions	Fe^{3+}	catalyst residues, contaminations, and organometallic stabilisers	chain initiation and termination	change in rate of ageing
Radical pairs		decomposition of molecules	destruction in the cage and formation of free radicals	change in rate of ageing

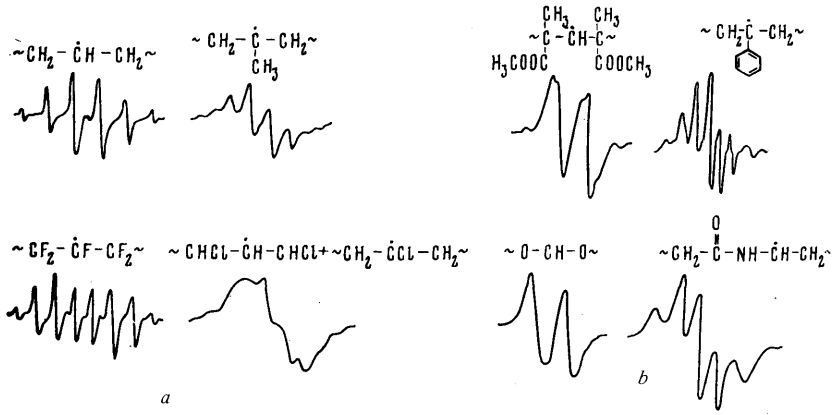


Figure 4. EPR spectra of central macroradicals: *a*) formed under the influence of γ-radiation of polyethylene, polypropylene, Teflon, and poly(vinyl chloride); *b*) formed from poly(methyl methacrylate), polystyrene, polyformaldehyde, and Kapron following the application of mechanical and radiation influences and light.

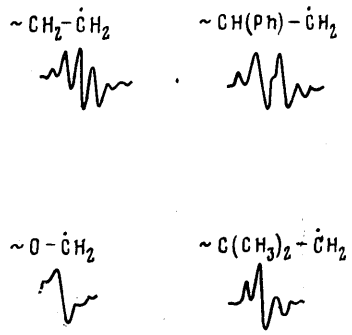


Figure 5. EPR spectra of the terminal macroradicals formed on mechanical degradation and under the influence of radiation for polyethylene, polystyrene, and polyformaldehyde, and polyisobutylene.

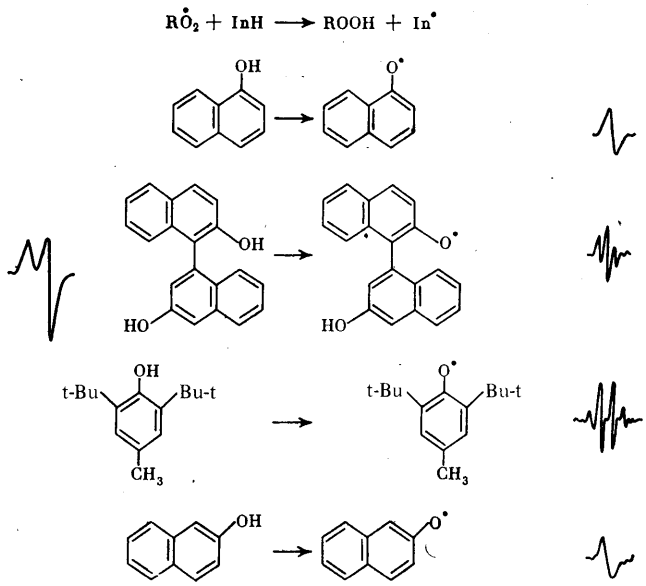


Figure 6. Schematic illustration of the replacement of the radicals $\dot{R}O_2$ by the inhibitor radical (polypropylene, melt); 200°C, p_{O_2} = 400 mmHg.

A number of workers have devoted particular attention to the interactions of macroradicals with inhibitors and other additives or admixtures present in real polymeric systems. The structures of an enormous number of inhibitor radicals (phenoxy-, nitrogen, and nitroxy-) and their behaviour in the oxidation of the corresponding polymers have been investigated. The scheme presented in Fig. 6 illustrates the conversion of the radicals $\dot{R}O_2$ into the radicals of phenolic inhibitors which occurs in a polypropylene melt at 200°C. Fig. 7 illustrates the EPR spectrum of the inhibitor radical in solid polypropylene [14].

Fig. 8 presents the kinetics of the variation of the concentration of α-naphthol radicals in the oxidation of a polypropylene melt. Evidently during the induction period (curve *2* describes the time variation of Δp_{O_2}) the change in the concentration of inhibitor radicals is autocatalytic. Next a sharp decrease of the amount of In· in the system is observed. The kinetic curve shown agrees satisfactorily with the fact that the inhibitor is consumed as a result of the reaction and the concentration of $\dot{R}O_2$ increases.

EPR makes it possible to record a special type of active radical centres—radical pairs. In low-molecular-weight substances EPR permitted the determination of the distance between the unpaired electrons for such stabilised pairs, which usually amounts to 4–7 Å.

Since radical pairs represent in essence the triplet state arising in the interaction of two unpaired electrons, the EPR spectrum reveals the occurrence of two types of transitions between energy levels: with $\Delta M_S = 1$ (transitions in the usual magnetic fields, $g \simeq 2$) and forbidden transitions with $\Delta M_S = 2$ (in "half" fields, $g \simeq 4$) (Fig. 9).

Table 2 presents certain results of the study of the radical pairs in solid polymers at 77 K.

The study of radical pairs in polymers by EPR makes it possible to infer both the nature of the radical components and the mechanism of the elementary step in degradation and structure formation during ageing. For example, analysis of the EPR spectrum for $\Delta M_S = 2$ in γ-irradiated polyethylene led to the conclusion that a pair with the structure

$$\sim CH_2-\dot{C}H-CH_2\sim$$
$$\sim CH_2-\dot{C}H-CH_2\sim$$

is formed and not $\sim\dot{C}H_2\dot{C}H_2\sim$. Evidently such pairs are the kinetic precursors of the cross-links being produced.

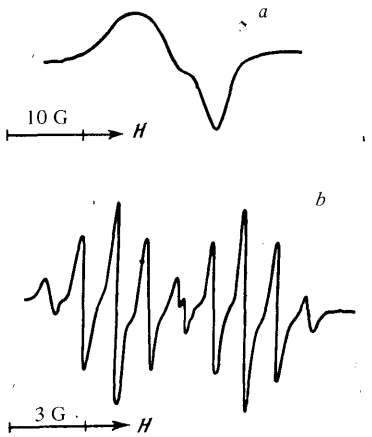
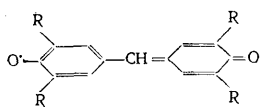


Figure 7. EPR spectrum of the inhibitor radical



(R = t-Bu) in solid polypropylene at 25 °C (*a*) and the spectrum of the same radical in benzene at 25 °C (*b*). In the solid polymer the spectrum is greatly broadened and the hyperfine structure disappears owing to the decrease of the rotation frequencies of the radical [14].

All the foregoing considerations referred to the identification of radical active centres arising in the degradation of polymers. Unfortunately, owing to the lack of special methods, similar to EPR, it is much more difficult to identify active centres in degradation via an ionic mechanism. In this field there have been virtually no systematic studies, with the exception of those which yielded data on the degradation of certain natural polymers in solution.

4. General Characteristics of the Ageing Process

Eqns. (1) are suitable for the description of the ageing process under any conditions. In principle, this problem is susceptible to solution in a general form by modern computer techniques. The thermal degradation, photodegradation, mechanical degradation, oxidation, hydrolytic degradation, etc. processes usually examined are limiting cases of a single ageing process in which the change of the properties of the material is determined by only one factor.

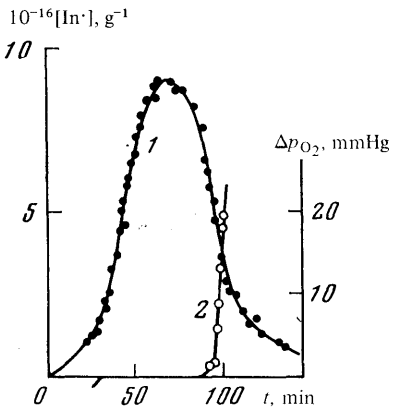


Figure 8. Kinetics of the variation of the concentrations of α-naphthol radicals in the oxidation of fused polypropylene: 1) variation of [In]; 2) kinetics of the absorption of oxygen [15].

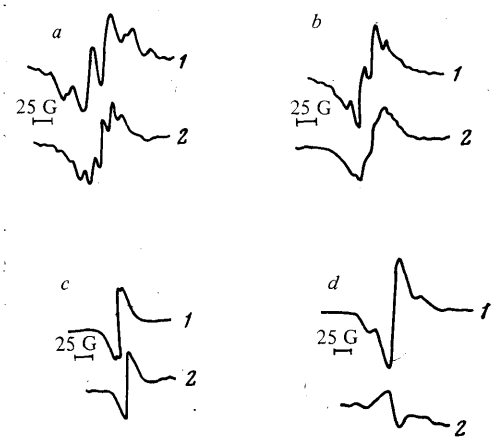


Figure 9. EPR spectra of transitions where $\Delta M_S = 1$ (curve *1*) and $\Delta M_S = 2$ (curve *2*) for polyethylene (*a*), polypropylene (*b*), polyoxymethylene (*c*), and polystyrene (*d*) irradiated with accelerated electrons at 77 K. [16]

In the general case the ageing process includes three main stages (Table 3):

(1) initiation—stage involving the formation of active centres;

(2) the development of ageing—the main stage determining the change in the properties of the polymeric material;

(3) the stage involving the destruction of active centres for ageing.

Table 2. EPR data for radical pairs in solid polymers at 77 K.[16]

Polymer	Ratio of integral intensities $\Delta M_S = 2$ and $\Delta M_S = 1$ in EPR spectra ($\Delta M_S = 2/\Delta M_S = 1 \times 10^5$)	HFS of spectra with $\Delta M_S = 2$
Polyethylene	6.1	16 G
Polypropylene	12.7	15 G
Polyoxymethylene	6.1	unresolved
Poly(ethylene oxide)	1.8	"
Poly(vinyl alcohol)	2.9	"
Cellulose	1.3	"

The physicochemical nature of the initiation stage can be various: in photoageing it is an elementary process with participation of light quanta and molecules in an excited state, while in the radiation-induced process it is a reaction involving ions. In mechanical degradation the initiation stage consists in the dissociation of molecules under the influence of mechanical forces with formation of free radicals.

The development of the ageing process takes place virtually independently of the nature of the initiation. For example, photoageing and radiation-induced ageing proceeds via the same elementary reactions as thermal ageing. External conditions determine in the first place the initiation stage (the formation of free radicals, ions, and excited species). Certain influences affect also the further development of ageing. For example, the presence of oxygen converts any process into an oxidation reaction (thermal degradation becomes thermal oxidation, photolysis becomes photochemical oxidation, and mechanical degradation becomes oxidation in the field of mechanical forces). Temperature influences all the elementary stages with the exception of processes whose activation energy is virtually zero.

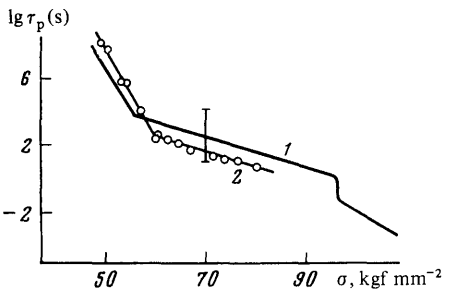
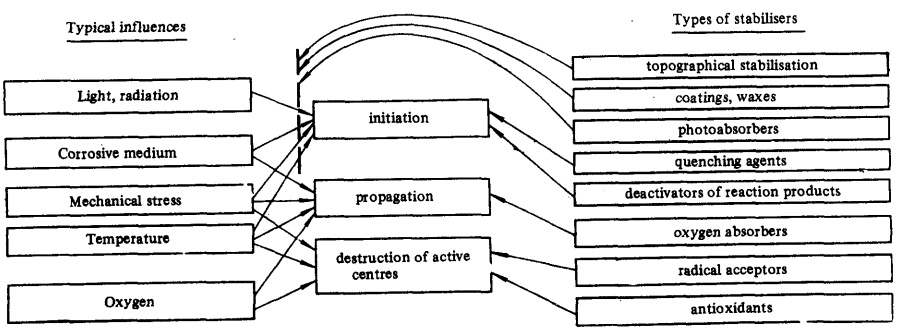


Figure 10. Comparison of the theoretical temperature dependence of the lifetime of polypropylene (calculation based on the radical-chain decomposition mechanism) (curve *1*) with experimental data (curve *2*). The vertical line indicates the error of the calculation.

The complex mechanism of the ageing of polymers makes the relatively simple relations governing a chemical process limited by a single elementary step unsuitable for the description of the ageing process over a wide range variation of conditions. For example, Fig. 10 shows that the semilogarithmic form of the relation between the lifetime of polypropylene and applied stress is not linear as required by Zhurkov's equation. This result has been explained[17] on the basis of a radical-chain mechanism of thermal mechanical degradation including chain initiation stages via the dissociation of the strained bonds of the macromolecules, depolymerisation, chain transfer with formation of a central radical, decomposition of the central radical under the influence of stresses, migration

Table 3. The principal stages in the ageing and stabilisation of a polymeric material.



of the free valence along the central radical, and chain termination:

$$\left.\begin{array}{l} PH \xrightarrow{k_1(\sigma)} 2R^{\cdot}_{term} \\ R^{\cdot}_{term} \xrightarrow{k_2} R^{\cdot}_{term} + M \\ R^{\cdot}_{term} + PH \xrightarrow{k_3} PH + R^{\cdot}_{cent} \\ R^{\cdot}_{cent} \xrightarrow{k_4(\sigma)} R^{\cdot}_{term} + PH \\ R^{\cdot}_{cent} \xrightarrow{k_5(\sigma)} R^{\cdot}_{term} \\ 2R^{\cdot}_{term} \xrightarrow{k_6} PH \end{array}\right\}. \qquad (17)$$

where M is the monomer and PH the polymer. Account was taken of the influence of the applied stress, in accordance with Zhurkov's equation, on the elementary steps in the decomposition of the polymer (k_1) and the macroradical (k_4 and k_5).

For small stresses, Eqn.(15) should hold; under these conditions, τ_0 and F are effective quantities and do not refer to any one elementary stage of the process:

$$\tau_p = a\sqrt{\frac{k_6}{k_1 k_3^2}}\exp\left(\frac{-\gamma\sigma}{RT}\right), \qquad (18)$$

where a is a proportionality coefficient which depends on temperature. Accordingly, the pre-exponential factor for this process is not the average period of the thermal vibrations of the atoms, as in Eqn.(15), but is determined by the ratio of the pre-exponential factors associated with the rate constants for the elementary thermal degradation reactions.

Over a wide range of stresses, Eqn.(18) ceases to hold, because for large stresses the degradation process is so fast that there is insufficient time for the establishment of a quasi-stationary concentration of radicals. Calculation shows that, under these conditions, the plot of the logarithm of the lifetime against stress should be curved. This type of relation has been observed experimentally in the study of the thermal mechanical degradation of polypropylene[17].

Fig. 10 compares the experimental data with the results of a computer calculation using the known rate constants for the elementary reactions in the kinetic scheme (17). Not only a qualitative but also a quantitative agreement between calculation and experiment is evident; the break in both relations corresponds to approximately the same applied stresses.

The hypothesis of a radical-chain mechanism of thermal mechanical degradation suggests that inhibitors of free radical reactions, which increase the stability of the polymer on thermal degradation, should also increase its lifetime on application of a mechanical load. Indeed, when a stable nitroxy-radical, which functions as an acceptor of alkyl radicals, is introduced, the lifetime of nitrocellulose increases significantly (Fig. 11*a*).[18] On the other hand, an increase of the rate of initiation of the ageing process should decrease the lifetime of the polymers. An appreciable decrease of the lifetime of stressed polycarbonate, in which an additional amount of free radicals was produced as a result of the thermal decomposition of the benzoyl peroxide introduced into the polymer or via the photolysis of added iron(III) chloride, has been observed[79] (Fig. 11*b*).

For low stresses, the main source of radicals is the decomposition of initiators; the lifetime of the polymer in their presence decreases greatly and depends only slightly on the applied stress. For large stresses, free radicals are generated mainly as a result of the mechanical degradation of macromolecules, so that the lifetime of the polymer hardly changes after the introduction of additives.

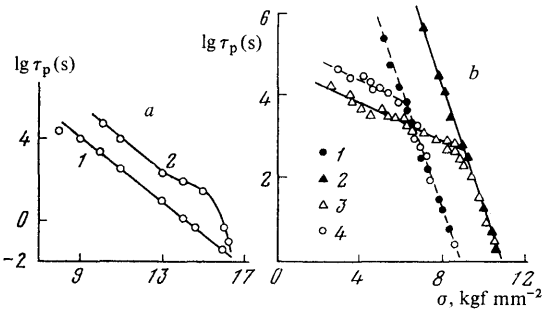


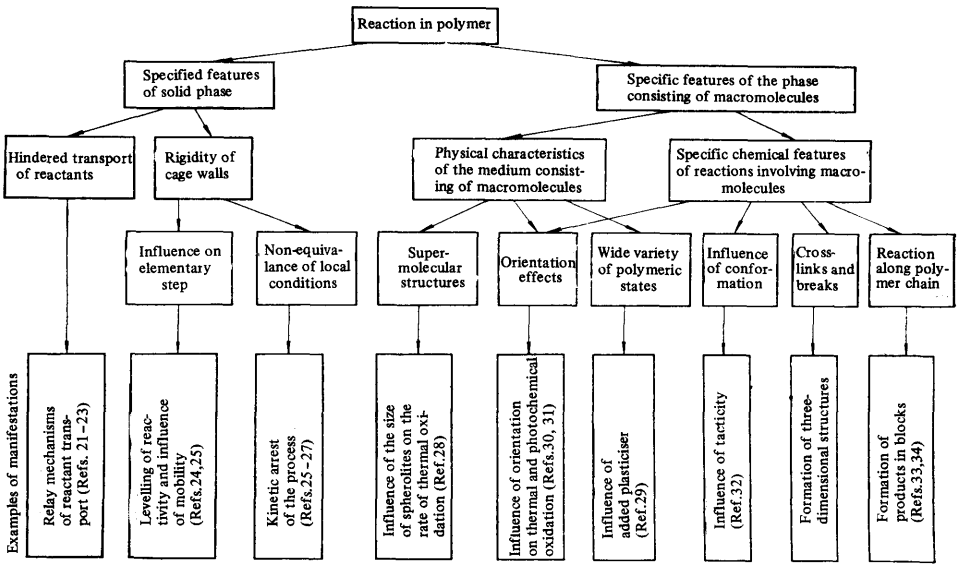
Figure 11. Variation of the lifetime of the polymer as a result of the introduction of inhibitors (*a*) and initiators (*b*) of radical reactions: *a*) nitrocellulose [1) pure; 2) with added 0.3% of 4-ethyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical]; *b*) polycarbonate [1) and 2) pure; 3) with added 0.34% $FeCl_3$ under the influence of the light from a mercury lamp; 4) with added 0.5% of phenyl peroxide; 2) and 3) 20°C; 1) and 4) 70°C].

The internal stresses arising the specimen, for example, during its hardening, can also alter the rate of ageing of the polymer. For example, cross-linked polyester-urethanes, obtained at 30°C, decomposes with an activation energy $E = 21-23$ kcal mole^{-1}, while the specimens synthesised at 60°C decompose much more slowly with $E = 46-50$ kcal mole^{-1}. It has been shown that this difference is associated with the competition between the urethane formation reaction and the relaxation of the internal stresses in the specimen as a result of conformational transitions[20]. At low temperatures there is insufficient time for the occurrence of the conformational transitions during synthesis, so that a polymer with strained bonds is formed, which facilitates its thermal degradation. At elevated temperatures there is sufficient time for relaxation processes during the synthesis of cross-linked polyurethanes, the number of strained bonds formed is very small, and the resulting polymer has a higher thermal stability.

III. CHARACTERISTICS OF THE CHEMICAL REACTIONS IN THE POLYMER MATRIX

As a subdivision of the chemistry of the solid state, the field of the ageing and stabilisation of polymers deals with the study of complex coupled radical-chain, ionic, and molecular reactions under the conditions of polymer matrices involving in the chemical process the very polymer molecules forming the matrix. Table 4 illustrates the principal features of the chemical reactions in the polymer matrix (PM). They have distinctive features as both solid-phase reactions and reactions of high-molecular-weight compounds.

Table 4. Characteristics of the chemical reaction in the polymer matrix.



As in any solid-phase process, the kinetics of the reactions in the polymer matrix are influenced significantly by the transport of reactants and the stability of the cell walls surrounding the reactive centres. The first factor is particularly important in cases where the reactive centre is localised on a macromolecule. The diffusion of such centres is hindered and complex models, including many macromolecules or intermediate labile centres—the so-called models of the relay migration of the active centre—have been considered to explain processes with participation of such centres[21-23].

The stability of the cage environment of the active centre leads to two qualitatively different effects. On the one hand, the contact time between the reactants which have entered a single cage is much greater than in the liquid phase, which can reduce many types of steric hindrance and can lead to an appreciable degree of levelling of the reactivities of the species in the solid phase compared with the liquid phase[24,25]. On the other hand, the polymeric material usually contains defects, many of the formations in which can exist for a fairly long time. As a result of the wide variety of these defects, the occurrence of elementary chemical reactions under kinetically non-equivalent conditions is typical for a polymer matrix. This is manifested by the kinetic arrest of certain chemical reactions under conditions where the reactants have still not been exhausted[25,26] and also by the obligatory occurrence of certain photochemical processes which cannot be inhibited despite the virtually complete quenching of the luminescence of the excited species propagating the process[27].

The polymer matrix cannot be regarded as a normal solid matrix. The polymeric material has as a rule a complex structure, because it is possible to distinguish in it a number of regions differing in the degree of order in the arrangement of the polymer chains and hence in the chemical reactivity. The most ordered regions, with a structure close to that of an ideal crystal, are characterised by the minimum free energy and close packing of the polymer chains and have a comparatively low reactivity. Crystalline regions with different structural defects, for example, dislocations, can exhibit a greater permeability with respect to small molecules and a somewhat higher reactivity. Finally, the least ordered amorphous regions are characterised by a low chain packing density, an increased concentration of impurities, and the maximum reactivity.

Because of this, the ageing of a polymeric material is influenced by its supermolecular structure[28]. Small amounts of added plasticiser alter the structure of the polymer matrix and change sharply the rate constant for the processes occurring in it[29]. Orientation effects, which result in a change of the physicomechanical properties of the polymeric material and of the rate and direction of the chemical reaction, are characteristic of the polymer matrix[30,31]. In the course of the ageing of the polymeric material, degradation processes and cross-linking reactions of the macromolecules, which are characteristic of high-molecular-weight compounds only and which lead to a change of the molecular weight distribution and sometimes to the formation of cross-linked three-dimensional structures, take place in the polymeric material in the course of its ageing.

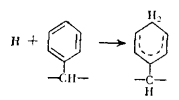
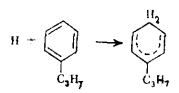
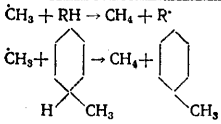
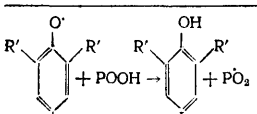
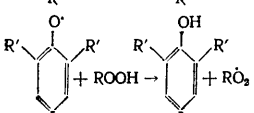
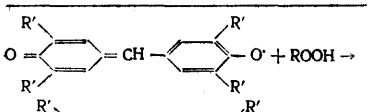
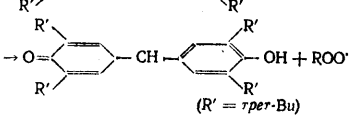
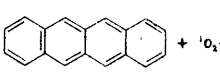
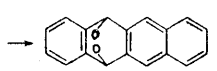
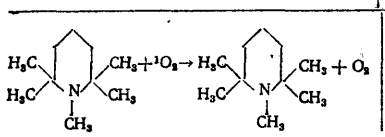
The kinetics of reactions in which high-molecular-weight compounds participate are influenced also by the conformations of the latter[32]. Furthermore, there are data indicating the development of the reaction along the polymer chain, which leads to the formation of reaction products in blocks, in the form of long sequences along the macromolecular chain[33,34].

1. The Influence of the Molecular Mobility of the Polymer Matrix on the Rate Constants for the Elementary Reactions Occurring in It

The dynamics of the molecular movements of the polymer exerts a significant influence on the kinetics of chemical reactions. This is caused by the change in the translational diffusion coefficients of the low-molecular-weight

reactants and the frequencies and amplitudes of segmental movements of the macromolecules and macroradicals, resulting in a change of the frequency of encounters of the reacting species. Furthermore, the molecular mobility of the medium influences directly the elementary step of the chemical reaction.

Table 5. The rate constants for chemical reactions in solid polymers and in the liquid phase.

Reaction	Polymer or solvent	t, °C	k, litre mole^{-1} s^{-1}	Refs.
	polystyrene	25	$1\cdot10^{4}$	35
	n-heptane	23	$3.3\cdot10^{8}$	36
$\dot{C}H_3 + RH \rightarrow CH_4 + R^{\cdot}$	polypropylene	100	0.2	37
	n-heptane	100	$3.8\cdot10^{3}$	36
	polypropylene	25	$4.5\cdot10^{-3}$	38
 (R′ = *tert*-Bu)	benzene	25	0.11	39
	polypropylene	25	$3.0\cdot10^{-5}$	14
 (R′ = *tert*-Bu)	benzene	25	$5.6\cdot10^{-4}$	
	polystyrene	20	$2.0\cdot10^{5}$	40
	methylene chloride	20	$1.8\cdot10^{7}$	
	polystyrene	20	$1.0\cdot10^{6}$	41
	methylene chloride	20	$5.4\cdot10^{7}$	

The rate constants for a number of bimolecular reactions in solid polymers are significantly lower than in the liquid phase. Certain examples of this kind are listed in Table 5. The decrease of the rate constants on passing to solid polymers is not associated solely with diffusion-dependent obstacles. The rate constants for the encounters between the reactants, estimated from the diffusion coefficients of the low-molecular-weight substances, exceed by several orders of magnitude the experimental rate constants for the reactions, i.e. these reactions are not diffusion-controlled.

The molecular mobility of the medium is known to influence the kinetics of the destruction of macroradicals in solid polymers which entails a decrease of the rate of destruction on passing from the amorphous to the crystalline phase [41-43], a decrease of the rate constant for destruction in oriented specimens compared with non-oriented specimens [44,45], an increase of the stability of the macroradicals on cross-linking of the polymer [46,47], an increase of the rate of destruction of macroradicals in three-dimensional polymers with the increase of the length of the oligomeric block [48], etc.

Molecular mobility can be varied in a controlled manner by changing the external pressure and by introducing chemically inert solvents into the polymer (plasticisation).

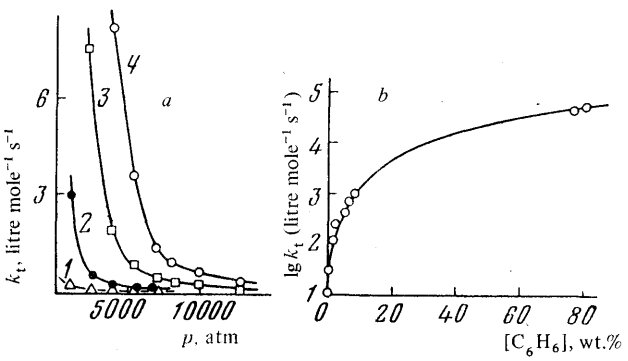


Figure 12. The influence of pressure (*a*) and plasticisation (*b*) on the rate constants for the destruction of free radicals in the polymer: *a*) poly(methyl metacrylate) [temperature (°C): 1) 80; 2) 100; 3) 120; 4) 130]; *b*) polystyrene with benzene as plasticising agent; $T = -10$°C.

In amorphous polymers at temperatures above T_g the radical recombination rate constants k_t decrease with increasing pressure p (Fig. 12*a*) [49-52]. At temperatures below T_g the influence of pressure on k_t is comparatively small. The strongest effect is observed for low values of p; at a pressure higher than a critical value p_{cr} the constant k_t depends only slightly on p. For $p < p_{cr}$, the dependence of k_t on p is described by the relation [53]:

$$k_t = k_t^0 \exp\left(-\frac{E + pV^*}{RT}\right), \qquad (19)$$

where V^* is the activation volume; here E sometimes changes to p. Pressure apparently influences the kinetics of the destruction of the macroradicals by altering the molecular mobility of the medium. With increase of

pressure, there is an increase of the density of the polymer and a decrease of the intensity of molecular movements, which is manifested, for example, by an increase of T_g, a decrease of the free volume and the melting point of the polymer, etc.

Eqn. (19) shows that an increase of p affects k_t in the same way as a decrease of temperature. The glass point is apparently attained at $p = p_{cr}$.

The plasticisation of the polymers has a significant influence on the kinetics of the destruction of macroradicals. The destruction of peroxy-radicals in polystyrene[23] (Fig. 12*b*) and polypropylene[54,55] is accelerated by small amounts of added chemically inert solvents. The accelerating effect can be explained only by the increase of molecular mobility in the polymer.

According to Roginskii and Miller[55], the variation of k_6 in solid polypropylene in the presence of *o*-dichlorobenzene is correlated with the frequency of the rotation of the paramagnetic probe characterising the mobility. Plasticisation of the polymer also leads to an increase of the liberation of radicals from the cage on decomposition of the initiator[14,55,56] and to an increase of the rate of chain oxidation of polypropylene[55].

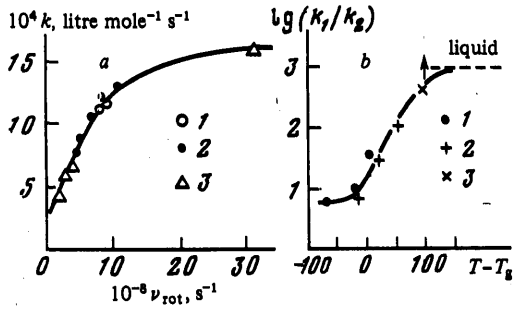


Figure 13. Relation between the rate constants for chemical reactions and the molecular mobility of the medium: *a*) rate constant for the reaction of 4-benzyloxy-2,2,6,6-tetramethylpiperidinyloxy-radical with 4,6-di-t-butyl phenol in various polymeric matrices plasticised with benzene (60°C) [1) polyethylene; 2) polypropylene; 3) polystyrene]; *b*) the ratio of the rate constants for the quenching of singlet oxygen by nickel dibutyldithiocarbamate and nickel ortho-ethoxy-(3,5-di-t-butyl-4-hydroxybenzyl)phosphonate [*O*-ethyl 3,5-di-t-butyl-4-hydroxybenzylphosphonate?] at different temperatures in different polymer matrices: 1) polystyrene; 2) BMK-5 copolymer; 3) polybutadiene.

The influence of molecular mobility on the reactions of phenoxy-radicals with the hydroperoxides of polyolefins[14,38] and of nitroxy-radicals with phenols in solid polyolefins has also been considered. The rates of these reactions are independent of the nature of the polymer and increase following the addition of aromatic solvents, whose role reduces to an increase of molecular mobility. Here the increase of the rate constant is correlated with the increase of the frequency of rotation of the paramagnetic probe[38,57] (Fig. 13*a*). Another phenomenon characteristic of the solid polymer matrix, the levelling of reactivity compared with the liquid phase for a series of compounds undergoing the same reaction, is also associated with the decrease of the molecular mobility of the medium in the polymer matrix.

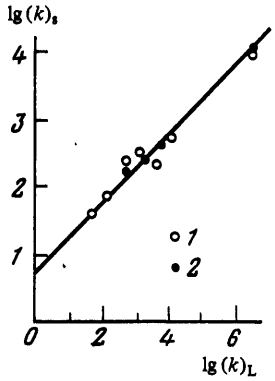


Figure 14. Logarithmic form of the dependence of the efficiency of the quenching of singlet oxygen by a number of quenching agents at different classes in polystyrene (1) and the butyl methacrylate–methacrylic acid copolymer (2) on the efficiency of the quenching by the same agents in liquid solution.

The levelling phenomenon was first observed for the reaction of a number of antioxidants with free radicals in solid polymers[24]. An analogous effect has been observed in processes with participation of singlet oxygen $^1O_2$.[40] Fig. 14 illustrates the logarithmic form of the relation between the efficiency of the quenching of $^1O_2$ by a number of quenching agents of different chemical types in a solid polymer on the efficiency of the same compounds in a liquid solution for two different polymer matrices (polystyrene and the butyl methacrylate–methacrylic acid copolymer). Evidently the range of differences between the efficiencies for the given series of quenching agents is over five orders of magnitude in the liquid phase and less than three orders of magnitude in the solid phase.

The relation between the observed phenomenon and the molecular mobility of the medium is demonstrated in Fig. 13*b*.[58] The degree of levelling presented in the figure is defined as the ratio of the quenching constants for two quenching agents with different efficiencies. The difference between the experimental temperature and the glass point of the matrix is a measure of the molecular mobility of the medium. Evidently the data obtained for different polymer matrices fit the same relation despite the fact that their absolute glass points differ by hundreds of degrees. The levelling of reactivity is apparently determined solely by the mobility of the medium and is independent of the chemical nature of the polymer.

The levelling phenomenon can be explained quantitatively by a change in the nature of the movement of a pair of reacting species in the solid matrix compared with the liquid phase[59]. It has been found that, for isotypical reactions, whose rate is limited by steric hindrance, the relative reactivities of the species in the solid polymer

(k_S) and in the liquid phase (k_L) are linked by the relation

$$\frac{(k_1)_S}{(k_2)_S} = \sqrt{\frac{(k_1)_L}{(k_2)_L}}. \quad (20)$$

Eqn. (20) is of considerable practical importance, since it is possible to select with its aid various stabilisers for polymeric materials (antioxidants and quenching agents) on the basis of much less laborious experiments, carried out in model liquid-phase systems.

2. The Influence of the Molecular Mobility of the Medium on the Kinetics of Reactions in Polymers

The equivalence of the local properties of the environment of the reactive centres and hence the sterically different activities of these centres is characteristic of polymers as structurally inhomogeneous systems. Chemical reactions occur in the first place in those regions where the conditions are most favourable. As a result, the concentration of active centres in these regions diminishes and there is a corresponding decrease of the effective rate constant for the reaction averaged with respect to the entire specimen. Different kinds of relaxation processes, which alter the local conditions around the reactive centres causing the migration of these centres to regions favouring chemical reaction, act in the opposite direction.

We shall introduce the concept of characteristic times of processes occurring in the polymer matrix. The chemical reaction time τ_{chem} can be characterised by a quantity which is the reciprocal of the rate of change of the relative concentration of the reactants (c/c_0):

$$\tau_{chem} = \left(\frac{d(c/c_0)}{dt}\right)^{-1}. \quad (21)$$

The duration of relaxation processes τ_c, which restore the equilibrium distribution of the local properties around the reaction centres disturbed by the chemical process, can be characterised by the correlation time of the reacting species with respect to all local properties of the medium which determine the reactivity of these species. If

$$\tau_{chem} \gg \tau_c, \quad (22)$$

the relaxation processes are so fast that the chemical reaction virtually does not alter the equilibrium distribution of the reactants and any reacting species has average properties throughout the entire process. Consequently the process as a whole will be described by a single average rate constant, as in classical liquid- or gas-phase kinetics. If condition (22) is not fulfilled, the reacting species will exist under non-equivalent conditions during the chemical process and the effective rate constant for the chemical reaction will gradually decrease.

The rate of change of the macroscopic concentration of the reacting substances is described by an integrodifferential equation which assumes the following form for the simplest unimolecular reaction:

$$\frac{d[A]}{dt} = -\int k(u) A(u) du, \quad (23)$$

where $k(u)$ is the rate constant for the chemical reaction and the local conditions characterised by the parameter u; the form of the function $k(u)$ is independent of time, since it determines the relation between the probability of the chemical reaction and the local properties of the medium; $A(u)$, the density of the distribution of the concentration of substance A with respect to the parameter u, varies in time owing to both the chemical reaction of substance A, described by Eqn. (23), and the relaxation and diffusion processes which alter the local properties of the medium around the reaction centre.

Eqn. (23) is converted into the classical expression when the local properties of the medium do not influence the probability of the chemical reaction:

$$k(u) = K^0 = \text{const} \quad (24)$$

or if the function $A(u)$ can be represented by the product of the concentration of substance A and the time-invariant characteristic form of the distribution of the local properties of the medium $\rho(u)$, i.e. if

$$A(u) = [A]\,\rho(u). \quad (25)$$

In such cases the rate of decrease of the macroscopic concentration of substance A is described, as in the liquid or gas phase, by the exponential relation

$$[A] = [A]_0 e^{-k_0 t} \quad (26)$$

or

$$[A] = [A]_0 e^{-\int k(u)\rho(u)du \cdot t}.$$

In all remaining cases the process inhibition is greater.

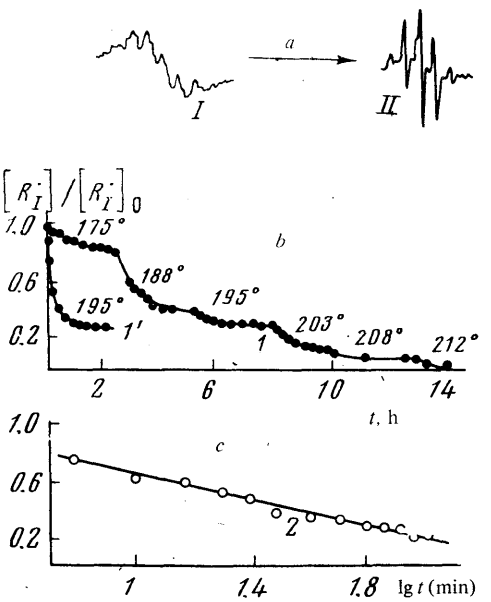


Figure 15. *a*) EPR spectrum of polymethacrylic acid (PMAA) macroradicals with the free valence localised at a tertiary carbon atom of the main chain (I) and of the terminal macroradicals (II) formed as a result of the thermal decomposition of the radicals (I); *b*) kinetic curves (curves *1* and *1'*) for the thermal decomposition of radicals (I) in PMAA in the temperature range 175–212 K; 2) a modification of the kinetic curve *1'* obtained by plotting $[\dot{R}_I]/[R_I]_0$ against lg*t* at 195 K.

Such inhibition is fairly common in chemical processes occurring in polymer matrices at temperatures below the glass point under conditions such that the molecular mobility of the medium is low. For a comparatively low degree of conversion, the reaction is inhibited but does not come to a complete stop. The inverse semilogarithmic $A/A_0 - \lg t$ form of the kinetic curve for the variation of the concentrations of the reactants is usually a straight line up to high degrees of conversion of the substance (Fig. 15)[66].

The phenomenon of such kinetic arrest of the reaction has now been observed in many processes in solid polymers: the destruction of the radicals involved in radical pairs[60], the oxidation of radicals[61], postpolymerisation[62], inhibited oxidation[63], oxidation by singlet oxygen[64], thermal isomerisation and photoisomerisation[65], decomposition of macroradicals with chain rupture[66], and dark cyclisation of spiropyrans[67]. These results can usually be described on the basis of the idea that, throughout the process, the reacting species are as it were frozen under different, but constant during the entire process, local conditions, i.e. $\tau_{chem} \ll \tau_C$. The equations of classical kinetics are then applicable only to species under identical conditions, i.e. for a distribution density $A(u)$. The inverse semilogarithmic plot is linear if it is assumed that the initial distribution $A(u)$ with respect to the free energy of activation for the process $\Delta G = E_a + IS$ is rectangular:

$$(A(u))_{t=0} = 1/S_0 \text{ when } 0 < u < S_0;$$
$$(A(u))_{t=0} = 0 \quad \text{when} \quad 0 > u > S_0. \qquad (27)$$

The solution of Eqn. (23) can then be written as follows:

$$[A] = -\frac{[A]_0}{S}\left[\ln(1.76k_0) - S_0 + \ln t - \frac{E_a}{RT}\right]. \qquad (28)$$

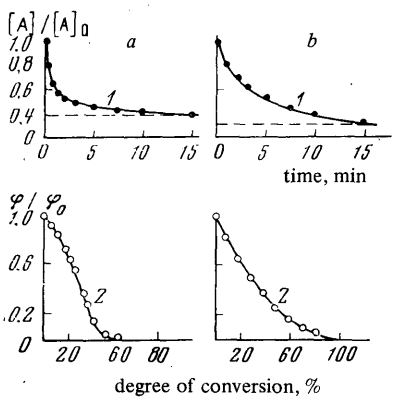


Figure 16. The photochemical reaction (λ = 365 nm) of anthracene in poly(methyl methacrylate): *a*) vacuum; *b*) air; 1) process kinetics; 2) dependence of the quantum yield on the degree of conversion of anthracene.

It has been shown that the semilogarithmic plot should remain linear for a rectangular distribution and for any law governing the consumption of A for reaction orders between first and third[68]. The change in the order of the reaction involving the consumption of A alters only the coefficient of the pre-exponential factor k_0 in Eqn. (28).

A characteristic feature of the kinetics of reactions in a solid polymer, the "stepwise" kinetics involving a kinetic arrest, can be used to regulate the corresponding processes. By changing the conditions, the temperature, and the viscosity, it is possible to accelerate greatly the inhibited process. On the other hand, without allowing the conditions to be altered, it is possible to avoid undesirable ageing reactions.

The decrease of the effective rate constant for the chemical reaction in the polymer matrix gives rise to the possibility of the "kinetic stabilisation" of substances fulfilling various functions in the polymeric material. For this purpose, one introduces into the polymer the substance at a concentration greater than necessary and the part of the substance under conditions favourable for chemical reaction is decomposed. The remaining additive is preserved by virtue of the kinetic arrest of reactions in polymers.

Anisimov[69] introduced anthracene into poly(methyl methacrylate) (PMMA) and illuminated the specimen with light at λ = 365 nm. Part of the anthracene was consumed as a result of the photochemical reaction; the remainder was as it were stabilised in the polymer (Fig. 16).

Hydrocarbons with condensed rings, of which anthracene is a representative, are widely used as luminescent labels for the recording of information, i.e. as photochromic materials. The kinetic stabilisation of these compounds in a polymer matrix is therefore of practical importance.

IV. QUANTITATIVE CHARACTERISTICS OF THE ELEMENTARY STAGES OF THE AGEING PROCESS

During recent years, apart from the study of the kinetics of the overall ageing process, numerous measurements have been made of the rate constants for the individual elementary stages of the complex process. The methods of their measurement in solid polymers do not differ in principle from those used in the liquid phase. The data obtained refer mainly to the thermal oxidation of polymers.

The rate of initiation w_i was measured with the aid of different versions of the method of inhibitors[63,70,71], based on the determination of the rate of consumption of a radical acceptor (X) taken at a concentration sufficient to cause the termination of all the oxidation chains. The independence of the rate of consumption of the acceptor of its concentration is an experimental criterion of the fulfilment of this condition:

$$w_i = n\frac{d[X]}{dt},$$

where n is the number of chains terminated by one acceptor molecule. Phenolic and amine inhibitors as well as stable radicals, mainly nitroxy-radicals, have been used as acceptors.

A method based on the determination of the induction period of the inhibited oxidation is also employed[72]. Some of the rate constants for the initiation of the reactions in solid polymeric media are listed in Table 6.

The parameters $k_p/\sqrt{k_t}$, which is the ratio of the rate constants for the chain propagation reaction (k_p) and the square root of the rate constant for the chain termination reaction (k_t) and characterises the oxidisability of the

polymer, is determined from the rate of the chain initiation of the oxidation process (w_i = const.); one can use as initiators not only specially added low-molecular-weight substances but also a "natural initiator"—a polymer hydroperoxide [10].

Table 6. The rate constants for initiation (k_i) in the decomposition of radical initiators in solid polymers.

Initiator*	Polymer	k_i, s^{-1}	References
AIBN	polypropylene	$5.1\cdot10^{17}$ exp (—37 000/*RT*)	70
AIBN	polystyrene	$8.4\cdot10^{13}$ exp (—30 800/*RT*)	63
CPC	polystyrene	$4.6\cdot10^{14}$ exp (—29 600/*RT*)	63
Benzoyl peroxide	polybut-1-ene	$1.5\cdot10^{-6}$ (80° C)	73
Cumenyl peroxide	polyethylene	$1.4\cdot10^{-6}$ (115° C)	74
Butyryl peroxide	polystyrene	$1.3\cdot10^{-7}$ (80° C)	75
Polymeric hydroperoxide	polypropylene	$1.0\cdot10^{13}$ exp (—30 500/*RT*)	70
Polymeric hydroperoxide	polyethylene	$1.6\cdot10^{14}$ exp (—35 000/*RT*)	76
2-t-Butylperoxy-2,4,6-tri-t-butylcyclohexa-3,5-dienone	polyprolyene	$4.5\cdot10^{16}$ exp (—35 500/*RT*)	77

*Notation: AIBN = azobisisobutyronitrile; CPC = cyclohexyl peroxydicarbonate.

Table 7. The chain propagation (k_p) and termination (k_t) rate constants in the oxidation of solid polymers.

Polymer	*t*, °C	$k_p/\sqrt{k_t}$, $kg^{1/2}\ mole^{-1/2}\ s^{-1/2}$	k_t, kg mole^{-1} s^{-1}	k_p, kg mole^{-1} s^{-1}
Polypropylene (atactic)	80	$1.8\cdot10^{-3}$ [79]	$1.2\cdot10^{3}$ [79]	0.055 [79]
Polypropylene (isotactic)	80	$8.1\cdot10^{-4}$ [70]	$3.5\cdot10^{3}$ [55]	0.1 [70]
Polyethylene	80	$4\cdot10^{-5}$ [60]	$4.8\cdot10^{4}$ [61]	$7.7\cdot10^{-3}$ *
Polybut-1-ene	80	$6.5\cdot10^{-4}$ [73]	—	—
Poly-4-methylpent-1-ene	80	$4\cdot10^{-4}$ [73]	—	—
Polystyrene	20	—	7.7 [61]	$0.7\div3\cdot10^{-4}$ ** [61]
Poly(methyl methacrylate)	20	—	0.5 [23]	$8\cdot10^{-4}\div8\cdot10^{-6}$ ** [69]

*Calculated from the data of Shilov and Denisov [80] and Davis et al. [81].
**Values obtained from data for the "stepwise" kinetics of the transformation $R\dot{O}_2 \rightarrow \dot{R}$ in an inert atmosphere.

The rate of absorption of oxygen W is related as follows to w_i and $k_p/\sqrt{k_t}$:

$$W = (k_p/\sqrt{k_t})\,[RH]\,\sqrt{w_i} + m w_i,$$

where m is the number of oxygen molecules absorbed in the oxidation chain initiation and termination steps.

The absolute rate constant for chain termination is determined either from the absolute concentration of peroxy-radicals in the initiated process [78,79]

$$k_t = \frac{w_i}{[R\dot{O}_2]^2},$$

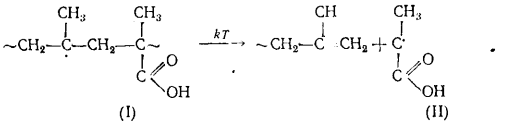
or by fitting an expression to the rate of destruction of radicals after brief exposure to light [54]:

$$\frac{[R\dot{O}_2]_0}{[R\dot{O}_2]} = 1 + k_t\,[R\dot{O}_2]_0\,t.$$

The latter method does not require a preliminary determination of w_i and the kinetic law governing the destruction of the radicals is established directly in the experiment. Table 7 lists the rate constants and the kinetic parameters $k_p/\sqrt{k_t}$ determined by these methods.

Together with the determination of the rate constants for the main stages of the chain thermal oxidation process, the detailed mechanism of the reactions of many macroradicals propagating the ageing process has now been investigated. It has been shown by EPR that the macroradicals of poly(methacrylic acid), generated at 77 K and having the free valence located at a tertiary carbon atom of the main chain as in (I) (Fig. 15*a*), are converted, on raising the temperature, into terminal radicals stable at room temperature, which are formed on thermal decomposition of (I).

The rate constants for the decomposition of the macroradicals of poly(methacrylic acid) with rupture of the main macromolecular chain were measured for the first time by Davydov et al. [66]:



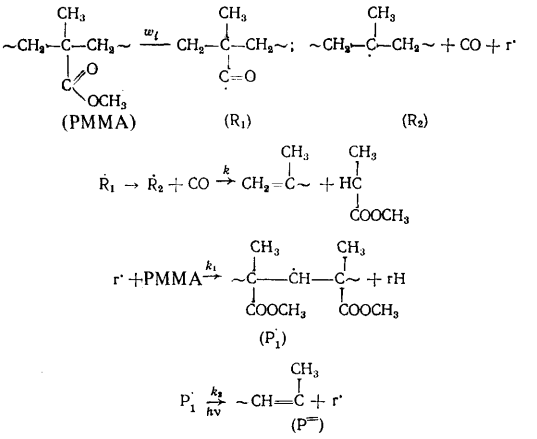
(I) (II)

Above 212 K, this process is described by a first order equation with rate constants defined by expressions of the type

$$k = 10^{13\pm1}e^{-16500/RT}\ (s^{-1}).$$

On the other hand, at lower temperatures the molecular mobility in poly(methacrylic acid) decreases and, on converting radicals (I) into radicals (II), the reaction undergoes a kinetic arrest (Fig. 15), which can be interpreted qualitatively on the assumption of a rectangular distribution of the rate constants for the decomposition of radicals (I) with respect to activation energies, which has the parameters E_{min} = 13 kcal mole^{-1}, E_{max} = 16.1 kcal mole^{-1}, and $\lg k_0\ (s^{-1}) = 13.7$.

The free radical mechanism of the photolysis and thermally initiated and photoinitiated conversion of PMMA has been investigated at temperatures below 50 °C [82–85] where depolymerisation virtually does not occur. Six macroradicals were identified and the mechanism of their thermal reaction and photoreaction was investigated:



(PMMA) (R_1) (R_2)

(P_1)

($P^{=}$)

$$r^{\cdot} + P^{=} \rightarrow \sim\overset{\overset{H}{|}}{C}-\overset{\overset{r}{|}}{C}-CH_3$$

$$(P_2^{\cdot})$$

$$P_2^{\cdot} + P^{=} \xrightarrow{k_4} P_{2(1)}^{\cdot}$$

$$\cdots\cdots\cdots\cdots$$

$$P_{2(i)}^{\cdot} + P^{=} \rightarrow P_2^{\cdot}(i+1)$$

$$P_{2(i+1)}^{\cdot} \xrightarrow[h\nu]{k_4} P^{=} + r$$

$$r^{\cdot} \xrightarrow{k_5} \text{destruction.}$$

Here $P^{=}$ is a polymer molecule containing a double bond, $P_{2(i)}$ is a polymer radical containing i double bonds, and $r^{\cdot}$ is a low-molecular-weight radical.

The calculation of the rate of accumulation of C=C bonds based on this scheme agrees with the empirical equation

$$[P^{=}] = [P^{=}]_{\infty}(1 - e^{-w_0 t/[P^{=}]_{\infty}}),$$

where $[P^{=}]_{\infty} = 1.6$ M and w_0 is the initial rate of formation of C=C bonds and of consumption of ester groups. All the free radicals were recorded by EPR and the regions of their thermal and photochemical stability were investigated.

V. CERTAIN NEW METHODS FOR THE INVESTIGATION OF FREE RADICALS

The wide-scale application of EPR in the chemical physics of polymers is in most cases limited by the difficulties associated with the elucidation of the complex EPR spectra of real polymer specimens. Although modern quantum chemistry and the use of computers make it possible to obtain information from the analysis of EPR signals, in the case of specially complex signals or spectra consisting of a superposition of signals due to different chemical centres, the methods of theoretical analysis are relatively ineffective [86].

The EPR signals of the vast majority of organic free radicals have virtually the same g-factor in the region $g_0 \simeq 2$, by differing $\Delta g \simeq 10^{-4}-10^{-5}$. The distance between the centres of such signals in units of the magnetic field $\delta H \simeq \Delta g H_0/g_0$ is approximately 1 G in the usual EPR spectrometers ($H_0 \simeq 3 \times 10^3$ G; 3 cm range). On the other hand, the intrinsic line width of organic radicals in polymers is not less than 3–10 G, so that the signals are usually superimposed.

Submillimetre EPR spectroscopy was used recently for the first time to investigate free radicals [87]. The magnetic field strength in such a spectrometer reaches 50 000 G (2 mm range). The distance between the signals of organic radicals is then found to be 10–20 G (on average 15 times greater than in the usual microwave spectrometer) and it is possible to record and analyse the spectra of individual radicals.

Fig. 17 presents the EPR spectra of macroradicals in polytetrafluoroethylene γ-irradiated in the presence of oxygen and then kept in the light [88]. It is evident that, in contrast to the EPR spectrum belonging to the usual 3 cm range, which contains relatively little information, the spectrum in the 2 mm range makes it possible to distinguish terminal alkyl, allyl, and terminal peroxy-radicals. Fig. 17*b* shows that the new method makes it possible to distinguish even terminal and central peroxy-radicals.

Thus there is a unique possibility of investigating the kinetics of complex free radical processes involving several kinds of free radicals.

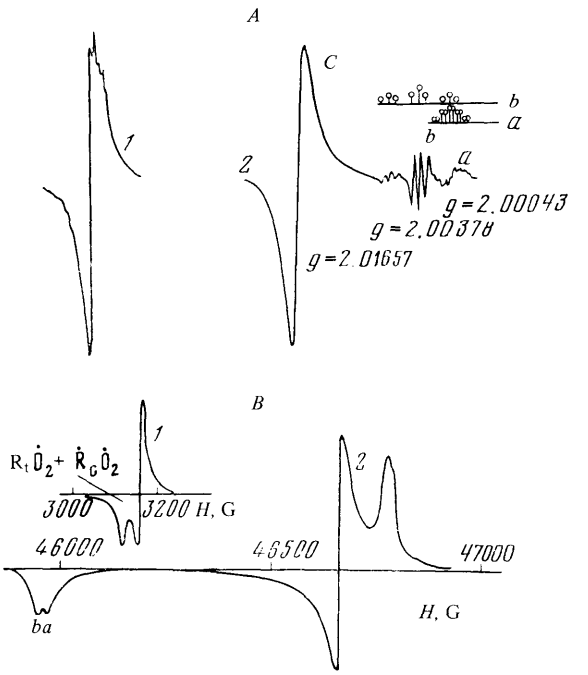


Figure 17. Comparison of the EPR spectra of polytetrafluoroethylene radicals obtained with the aid of 3 cm (curve *1*) and 2 mm (curve *2*) microwave spectrometers: *A*) allyl radicals (*a*), alkyl radicals (*b*), and peroxy-radicals (*c*); *B*) central R_cO_2 radical (a) and terminal R_tO_2 radical (b).

Under the real conditions in the ageing of polymers, the concentrations of the free radicals formed in the latter are too low to be detected by EPR. The application of the spin-trapping method is therefore apparently promising in this connection. The method has been used successfully in recent times for the investigation of radical processes in the liquid phase [89–91].

The principal idea of the spin trapping method consists in the conversion of an active short-lived radical $r^{\cdot}$ as a result of its addition to a specially selected acceptor T (spin-trapping agent) into a much more stable radical $rT^{\cdot}$ (the spin adduct):

$$r^{\cdot} + T \xrightarrow{k_1} rT^{\cdot}.$$

The latter can be accumulated in concentrations sufficient for its detection by EPR. In order to estimate the ratio of the steady-state concentrations of the active radical (in the absence of T) in the spin adduct, we shall consider the simplest kinetic scheme for the transformations of the

radicals in the presence of T:

$$\text{Initiation} \xrightarrow{w_i} r^{\cdot},$$
$$r^{\cdot} + r^{\cdot} \xrightarrow{k_t} \text{products},$$
$$r^{\cdot} + T \xrightarrow{k_1} rT^{\cdot},$$
$$r^{\cdot} + rT^{\cdot} \xrightarrow{k_t'} \text{products},$$
$$rT^{\cdot} + rT^{\cdot} \xrightarrow{k_t''} \text{products}.$$

In the absence of the spin-trapping agent the stationary concentration of the active radicals is

$$[r^{\cdot}]_{st} = \sqrt{w_i/k_t}. \quad (29)$$

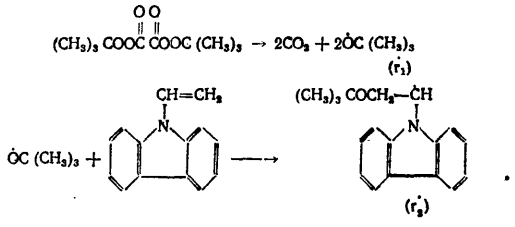
In the presence of a sufficient concentration of the spin-trapping agent $\{k_1[T] \gg k_t[r^{\cdot}]\}$, in the case where the spin adduct is sufficiently stable $\{k_t''[rT^{\cdot}] \ll k_t'[r^{\cdot}]\}$, we have

$$[rT^{\cdot}]_{st} = \frac{k_1}{k_t'}[T]. \quad (30)$$

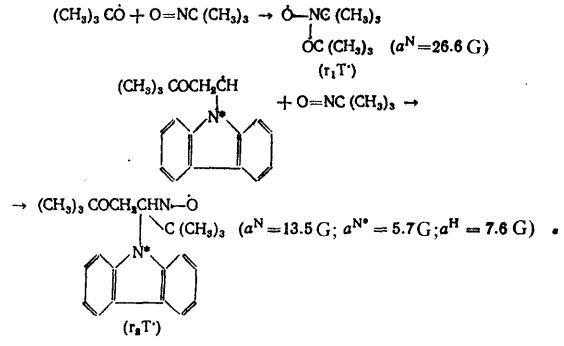
For low rate of initiation, we usually have $[rT^{\cdot}]_{st} \gg [r^{\cdot}]_{st}$.

The spin-trapping method not only makes it possible to detect free radicals, but, by analysing the EPR spectra of the spin adducts, one can determine the nature of the active radicals r$^{\cdot}$ combined. Various compounds with multiple bonds are used as spin-trapping agents—mainly nitroso-compounds and nitrones as well as thiocarbonyl compounds, nitro-compounds, quinones, acetylene derivatives, nitrile *N*-oxides, etc.

As an example we shall consider the results of the investigation by the spin-trapping method of the mechanism and kinetics of the polymerisation of *N*-vinylcarbazole initiated by di-t-butyl peroxyoxalate[89]:



In the presence of 2-methyl-2-nitrosopropane (T) the active radicals $r_1^{\cdot}$ and $r_2^{\cdot}$ add to the spin-trapping agent and give rise to two types of spin adducts $r_1T^{\cdot}$ and $r_2T^{\cdot}$ with markedly different EPR spectra (Fig. 18):



Analysis of the EPR spectrum of the spin adduct $r_2T^{\cdot}$ indicates the direction of the reaction involving the addition of the initiator radical to the monomer.

VI. RELATION BETWEEN THE CHANGES IN THE PROPERTIES OF POLYMERS OF PRACTICAL IMPORTANCE AND THE KINETICS OF AGEING

On the basis of individual elementary reactions, it is now possible to determine the complete process mechanism and to describe the kinetics of the variation of polymer properties of practical importance under any operating conditions.

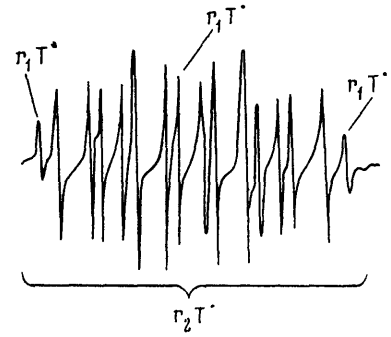


Figure 18. EPR spectrum recorded in the polymerisation of *N*-vinylcarbazole (0.52 M) initiated by di-t-butyl peroxyoxalate (4.3×10^{-2} M) in the presence of 2-methyl-2-nitrosopropane (2.3×10^{-2} M) as the spin-trapping agent; solvent—*p*-xylene; 25 °C.

The mechanism of the photochemical oxidation of polyolefins (ПН) has been investigated in greatest detail[92]. This process is a chain reaction with degenerate photobranching by the hydroperoxide and quadratic chain termination. The mechanism of the photochemical oxidation can be formulated as follows in a general form:

$$\text{ПН} \xrightarrow{h\nu} \text{П}\dot{\text{O}}_2$$
$$\text{П}\dot{\text{O}}_2 + \text{ПН} \xrightarrow{O_2,\ k_p} \text{ПООН} + \text{П}\dot{\text{O}}_2 \text{ — chain propagation,}$$
$$\left.\begin{aligned} &\text{ПООН} \xrightarrow{h\nu} \text{П}\dot{\text{O}} + \dot{\text{O}}\text{H} \rightarrow 2\text{П}\dot{\text{O}}_2 \\ &[\text{C=O}] \xrightarrow{h\nu} f\text{П}\dot{\text{O}}_2 \end{aligned}\right\} \text{chain branching,}$$
$$\text{П}\dot{\text{O}}_2 + \text{П}\dot{\text{O}}_2 \xrightarrow{k_t} [\text{C=O}] \text{ — chain termination.}$$

Here [C=O] represents carbonyl compounds, f is the probability of the formation of its free radical in the [C=O]-photochemical decomposition step.

The following system of differential kinetic equations corresponds to this scheme:

$$\left.\begin{aligned} \frac{d[\text{П}\dot{\text{O}}_2]}{dt} &= 2\alpha[\text{ПООН}] - k_t[\text{П}\dot{\text{O}}_2]^2 + \alpha' f[\text{C=O}]; \\ \frac{d[\text{ПООН}]}{dt} &= k_p[\text{ПН}][\text{П}\dot{\text{O}}_2] - \alpha[\text{ПООН}]; \\ \frac{d[\text{C=O}]}{dt} &= \alpha[\text{ПООН}] - \alpha'[\text{C=O}] + \frac{k_t}{2}[\text{П}\dot{\text{O}}_2]^2, \end{aligned}\right\} \quad (31)$$

where α and α' are the probabilities of the photochemical decomposition of the hydroperoxide and carbonyl compounds, which are defined by the following relation for thin

specimens:

$$\alpha = \int \varphi\varepsilon(\lambda) I(\lambda)\, d\lambda; \qquad (32)$$

where $\epsilon(\lambda)$ is the absorption spectrum of the decomposing compound, φ the decomposition quantum yield, and $I(\lambda)$ the spectrum of the radiation incident on the specimen.

In terms of dimensionless coordinates, the system of equations is

$$\left.\begin{aligned}
&\frac{d\rho}{d\tau} = (\pi - 4\rho^2 + k_2 f K)\, k_1;\\
&\frac{d\pi}{d\tau} = \rho - \pi/2;\\
&\frac{dK}{d\tau} = 2\rho^2 - k_2 K + \frac{\pi}{2};\\
&\rho = k_t [\Pi O_2^\cdot]/4k_p [\Pi H];\ \pi = [\Pi OOH]/[\Pi OOH]_\infty;\ K = [C{=}O]/[\Pi OOH]_\infty;\\
&k_1 = k_p [\Pi H]/2\alpha;\ k_2 = \alpha'/2\alpha;\ \tau = 2\alpha t;\\
&[\Pi OOH]_\infty = 2k_p^2 [\Pi H]^2/k_t\alpha.
\end{aligned}\right\} \qquad (33)$$

It follows from Eqns. (33) that, under quasi-stationary conditions with respect to $[\Pi O_2^\cdot]$, for different light intensities, and for the same spectral composition, the process kinetics should be described by a single relation in terms of the variables $[C{=}O]/[\Pi OOH]_\infty$ and αt. Fig. 19 illustrates the logarithmic form of this relation calculated using the rate constants for the elementary reactions determined independently. The experimental data fit satisfactorily on the calculated curve [93].

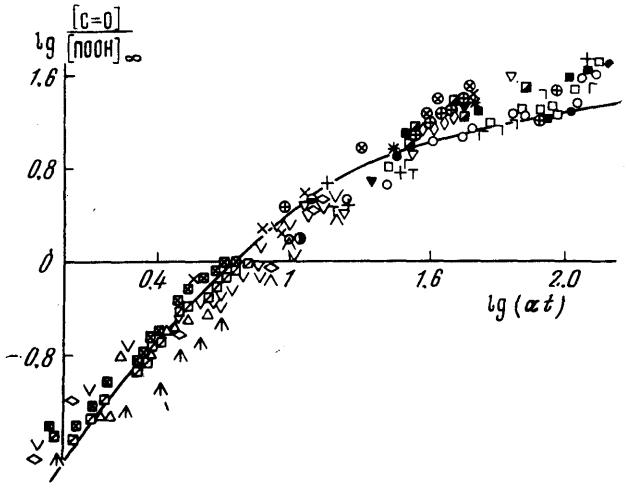


Figure 19. Logarithmic forms of the kinetic curves for the accumulation of carbonyl compounds in the photochemical oxidation of various polypropylene specimens; continuous line—calculation.

When polymeric materials are used in practice, an important factor is not the kinetics of the accumulation of the polymer oxidation products, but the change in characteristics of practical importance, for example, physicomechanical characteristics, the relative elongation on rupture, the tensile strength, etc. These characteristics are not unambiguously related to the composition of the polymer and depend to a large extent on its physical structure. It has been shown for the photochemical oxidation of polypropylene that the change in these characteristics is determined by the kinetics of the chemical reactions occurring in the polymer.

Fig. 20 illustrates the kinetic curves for the variation of the relative elongation on rupture (ϵ, %) in the course of the photochemical oxidation of various polypropylene specimens. Despite the fact that these curves are of different forms, they nevertheless have one feature in common: the change in the relative elongation on photochemical oxidation depends only on the amount of light incident on the polymer and not on its intensity; for high light intensities, the change in the properties takes place less effectively [93]. This is due to the fact that, in the case of quadratic chain termination for low light intensities, the effective oxidation chain length is greater than for high light intensities. Accordingly, at low light intensities there is a high yield of the branching product—the hydroperoxide, as a result of which all the degradation processes per quantum of the incident light take place more effectively.

The relations obtained for different light intensities can be combined into a single one if the number of radicals Ω formed in the polymer during oxidation, and not the amount of light incident on the polymer, is plotted along the abscissa axis (Fig. 2). In conformity with this mechanism, the number of radicals is determined as the sum of the steps involving the photochemical decomposition of the branching products—hydroperoxides and carbonyl compounds:

$$\Omega = \int_0^t (2\alpha [\Pi OOH] + f\alpha' [C{=}O])\, dt. \qquad (34)$$

Sometimes, for example, in the case of oriented polypropylene or polypropylene thermally stabilised by phenols, Ω can be calculated even if the overall kinetic mechanism of the photochemical process is unknown. This makes it possible to describe the kinetics of the change in the mechanical properties of polypropylene when the process mechanism is not completely known.

Thus the dynamics of the change in the physicomechanical properties of the polymer is related to the kinetics of the chemical ageing process and calculations on such dynamics can be performed on the basis of the measurement of its kinetic characteristics.

VII. PRINCIPLES OF THE STABILISATION OF POLYMERIC MATERIALS FROM THE STANDPOINT OF THE MECHANISM OF AGEING

The known methods for the stabilisation of polymeric materials can be divided in accordance with the stage of the ageing process on which they act (Table 3). The simplest procedure involves the mechanism of the action of stabilisers which prevent the initiation of ageing. These are, for example, waxes and coatings which prevent the penetration of chemical agents into the polymer and photoabsorbers—substances which absorb photochemically active light. Such stabilisers act in the surface layer of the polymeric material.

Substances which reduce the probability of the formation of an active centre in the initiation stage constitute a large group of stabilisers. These include agents which quench excited states ("quenchers")—substances which

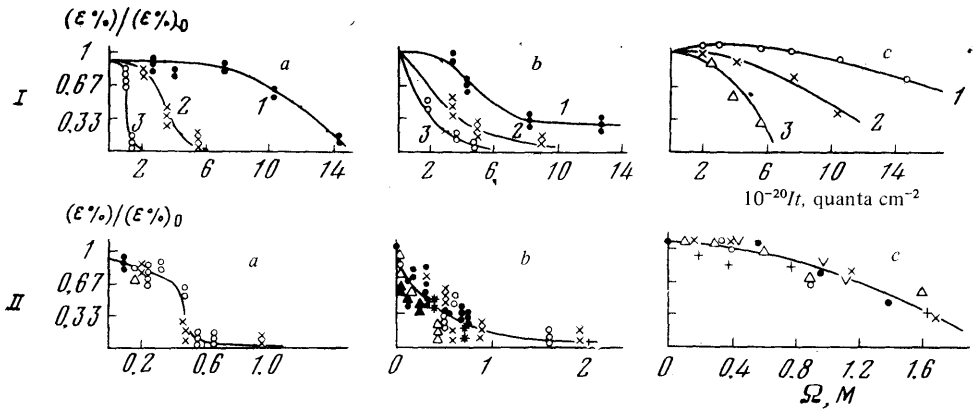


Figure 20. Variation of the relative elongation on rupture (ϵ, %) for polypropylene in the course of its photochemical oxidation: I) dependence on the light It incident on the specimen; II) dependence on the dose Ω of the radicals formed in the specimen in a given period; *a*) isotropic specimen; *b*) oriented annealed specimen; *c*) oriented specimen (950%). Light intensity $\eta = 254$ nm: 1) $\times 10^{15}$ quanta cm^{-2} s^{-1}; 2) 0.7×10^{15} quanta cm^{-2} s^{-1}; 3) 0.24×10^{15} quanta cm^{-2} s^{-1}.

react with various admixtures catalysing the decomposition of polymers. Stabilisers which deactivate chemically active reaction products, for example, substances which decompose hydroperoxides (the branching products of the chain thermal oxidation process) are of particular importance.

Stabilisers which influence the stage involving the development of the ageing process, for example, the oxidation chain propagation stage, include substances which prevent the penetration of oxygen into the polymeric material or reduce its concentration in the material. In the absence of oxygen the chemical composition of the product arising in the chain propagation stage changes, unstable branching products are not formed, and the ageing process is retarded. As an example of such stabilisers, one may quote finely dispersed metals and substances giving rise to them, which are used as stabilisers of thermostable materials [94].

The class of stabilisers which accelerate the stage involving the destruction of active centres, for example, free radical acceptors or inhibitors of free radical process InH are most widely used in practice and have been studied in greatest detail. By interacting with active radicals, they lead to the formation of relatively inactive inhibitor radicals In$^{\cdot}$.

The antiradical activity of such inhibitors (stabilisers) is usually characterised by the rate constant for their interaction with the active radical (k_7). [95] Their efficiency is determined also by the activity of the radical In$^{\cdot}$, which is characterised by the ratio k_{10}/k_p of the rate constants for the reactions

$$RO_2^{\cdot} + RH \xrightarrow{k_p} ROOH + R^{\cdot} \quad ,$$

$$In^{\cdot} + RH \xrightarrow{k_{10}} InH + R^{\cdot} \quad .$$

The lower this ratio the greater the inhibiting effect of the inhibitor.

In the thermal oxidation of polymers the practical efficiency of active radical acceptors is not only determined by the constants k_7 and k_{10} but depends also on the possibility of the additional initiation of the ageing process as a result of the interaction of the radical In$^{\cdot}$ with the hydroperoxide [96] and the decomposition of the quinolide peroxides formed in the reaction of the active radical with the stabiliser radical [97].

The set of these factors is taken into account in a special automated method for testing chemical compounds for their suitability as stabilisers of polymeric materials, which was developed recently in the Sector of the Kinetics of Chemical and Biological Processes of the Institute of Chemical Physics of the USSR Academy of Sciences. The measuring system includes a highly sensitive differential manometric apparatus with continuous recording of the rate of oxidation. At the same time the experimental data are automatically transmitted via a communication link to a BESM-6 computer, where they are interpreted. The mathematical solution of the problem consists of two dialogues incorporating approximately ten programs for the treatment of the data. The investigator controls the treatment directly from the laboratory via a "Videoton-340" display. Both the intermediate and final results of the calculations are displayed on the Videoton screen. The results are presented in the form of Tables and graphs executed with the aid of external devices of the computer. For control and storage, the initial information is coded by means of a Teleprinter on perforated tape. The system is designed for the simultaneous operation of four experimental sets of apparatus.

VIII. A NEW EFFECTIVE METHOD FOR THE STABILISATION OF POLYMERS—A "DEPOT" OF STABILISERS

Many stabilisers cannot be used at the required concentrations for different reasons. For example, certain stabilisers impart an undesirable colour to the polymeric material and thermal stabilisers can prove to be also effective photosensitisers. Free radicals formed from the stabilisers in some cases enter into reactions which promote the decomposition of the polymer. Furthermore, the stabiliser can be consumed in useless side reactions.

It is therefore desirable to create stabilising compositions in such a way that the effective inhibitor acts in accordance with the principle of *in statu nascendi*, i.e. that its main bulk should remain in the bound state, a kind of "depot", and that the active form of the stabiliser is released from the latter gradually or when necessary. A quantitative criterion of the effectiveness of the inhibitor *in statu nascendi* can be found by analysing a simplified kinetic scheme for the action of such inhibitors Z on an initiated chain process:

$\xrightarrow{w_i}$ r· — initiation of active radical;

$Z \xrightarrow{k}$ R· — the formation of a "depot" of the active form of the inhibitor R which functions as the stabiliser (for simplicity, a stabiliser in a radical form is considered);

$R^{\cdot} + r^{\cdot} \xrightarrow{k_7}$ — inhibition reaction;

$R^{\cdot} \xrightarrow{k_{10}} r^{\cdot}$ — regeneration of the active radical via a reaction with participation of the inhibitor.

If the concentration of the stabiliser is fairly high and the active centres are destroyed only on interaction with it, then the efficiency of the stabilisation by such a stabiliser can be characterised by the ratio of the rates of initiation and consumption of the active form of the inhibitor:

$$\psi = \frac{w_i}{d[\dot{R}]/dt} \simeq \frac{w_i}{k[Z]} \quad (\text{when } k_{10} \gg k). \tag{35}$$

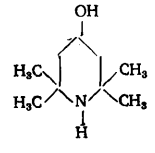
If an inhibitor is introduced initially at a concentration $[Z]_0$, then its efficiency ψ is defined by the expression

$$\psi_0 = \frac{w_i}{w_i + 2k_{10}[Z]_0}. \tag{36}$$

Since by hypothesis $k_{10} \gg k$, it follows that $\psi > \psi_0$. The ratio $\psi/\psi_0 = Q$ can serve as a criterion of the usefulness of the inhibitor *in statu nascendi*:

$$Q = \frac{\psi}{\psi_0} = \frac{w_i + 2k_{10}[Z]_0}{k[Z]_0} \simeq \frac{2k_{10}}{k}. \tag{37}$$

It has been shown recently that sterically hindered piperidines protect polymers from the action of light via the "depot" mechanism[98]. The mechanism of their light stabilising activity remained obscure for a long time. In the literature it was only noted that these compounds should not act via any one of the known mechanisms. In reality it was found that the stabilisers are not the piperidines themselves, being converted in the course of the ageing of the polymer into a mixture of nitroxy-radicals and other compounds which act as inhibitors. Fig. 21*a* presents kinetic curves for the photochemical oxidation of the butadiene–acrylonitrile copolymer. The initial section of the kinetic curve *2* for the oxidation in the presence of 2,2,6,6-tetramethyl-4-hydroxypiperidine



coincides with the curve for the unstabilised specimen (curve *1*) and the rate of oxidation falls only after some time has elapsed. During this period, stabile nitroxy-radicals accumulate in the specimen (curve *3*). The introduction into the polymer of a mixture of piperidine and radicals lowers the rate of the photochemical oxidation process from the very beginning. The addition to the polymer of nitroxy-radicals alone at the same concentration has little influence on the oxidation kinetics owing to the rapid consumption of the stable radicals.

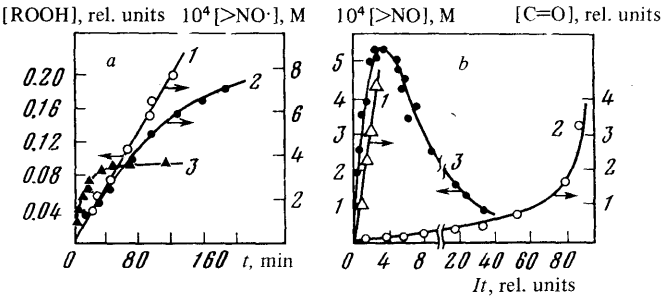


Figure 21. Kinetic curves for photochemical oxidation in the presence of 4-hydroxy-2,2,6,6-tetramethylpiperidine (NH); λ = 280 nm: *a*) butadiene–acrylonitrile copolymer (SKN-26). Accumulation of alcohols: 1) without stabiliser; 2) 2×10^{-1} M NH; 3) accumulation of NO in the specimen containing 2×10^{-1} M NH; *b*) polypropylene. Formation of carbonyl compounds: 1) without stabiliser; 2) 3.2×10^{-2} M NH; 3) variation of the concentration of NO.

The mechanism of the stabilising action of sterically hindered piperidines is more complex than that considered above. It can be described qualitatively as follows:

$\xrightarrow{w_i} \dot{r}$ — photoinitiation;

$>NH \xrightarrow{+\dot{r}_1, +\dot{r}O_2} >N\dot{O} + \dot{r}$ — generation of the stabiliser and the active radical;

$>NO + \dot{r} \rightarrow S$

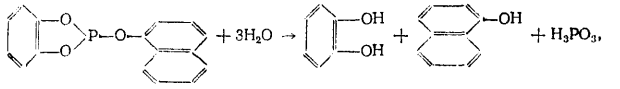
$S + r\dot{O}_2 \rightarrow >NO_2$ — inhibition and regeneration of stabiliser;

$>N\dot{O} \xrightarrow{h\nu} \dot{r}$ — generation of active radicals.

Here S is an intermediate product. The stage of the generation of the stabiliser involving the formation of nitroxy-radicals $>N\dot{O}$, which can proceed with participation of singlet oxygen or peroxy-radicals, and the reactions involving the regeneration of the active form as a result of the apparent conversion of the nitroxy-radical into hydroxylamine and an ether from which the nitroxy-radical can be reformed in its turn, are important. The possibility of the regeneration of the inhibitor of the system makes piperidines and nitroxy-radicals extremely effective polymer stabilisers.

Fig. 21*b* shows how the concentration of the nitroxy-radical formed from sterically hindered piperidine changes in the course of the photochemical oxidation of polypropylene. Evidently, throughout the reaction period, the concentration of nitroxy-radicals in the specimen is lower almost by two orders of magnitude than the initial concentration of piperidine. The introduction of nitroxy-radicals into the polymer at a high concentration at the beginning of the process is in the present instance undesirable owing to

the development of an intense colour in the specimen. The function of a "depot" can also be fulfilled by phosphite esters, whose hydrolysis leads to the formation of the corresponding phenols or catechols[99]:



as well as clathrate compounds from which the stabiliser is liberated on thermal or photochemical decomposition.

Not only compounds from which the stabiliser is synthesised during ageing but also the undamaged portion of the polymer from which the stabiliser diffuses to the degradation zone can be used as a "depot" of stabilisers. This phenomenon was recently observed in a study of the photochemical oxidation of polybutadiene films.

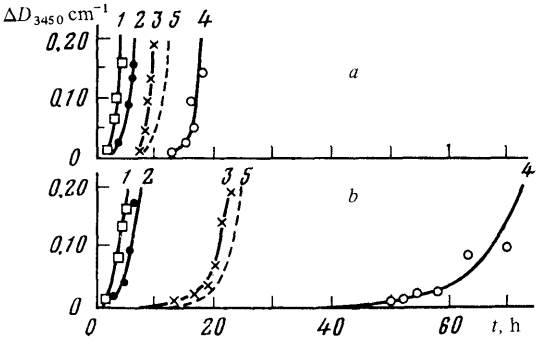


Figure 22. Kinetic curves for the photochemical oxidation of polybutadiene films 20 μm (*a*) and 60 μm (*b*) thick, without additives (curve *1*) and stabilised by additives; 2) 4-heptyloxy-2-hydroxybenzophenone UVA (3.6×10^{-2} M); 3) 2,6-di-t-butyl-4-methylphenol A (5×10^{-2} M); 4) their mixture with the same UVA and A concentrations (wavelength 254 nm); 5) calculated curves for films containing a mixture of UVA and an antioxidant corresponding to their additive activity.

In the presence of a u.v. absorber, light does not penetrate into the bulk of the polymeric specimen. Photochemical oxidation takes place only in the surface layer, which results in the consumption of the antioxidant (A). The concentration gradient of A rises and the antioxidant diffuses from the bulk of the polymer to the surface layer. Since deep layers serve as a source of the inhibitor, thick specimens are oxidised more slowly than thin specimens (Fig. 22). It has been shown recently that this phenomenon is the principal cause of the synergism observed in the stabilisation of polymers by mixtures of u.v. absorbers (UVA) and antioxidants, which interact with free radicals[100,101].

The problem of the influence of diffusion of A on the duration of the induction period in the oxidation reaction (T_{ind}) has been solved[101] for the unbranched chain photochemical oxidation reaction via the mechanism

$$S + h\nu \xrightarrow{PH,\ O_2} P\dot{O}_2 \quad ,$$

$$P\dot{O}_2 + PH \xrightarrow{k_2} POOH + P\dot{O}_2 \quad ,$$

$$P\dot{O}_2 + P\dot{O}_2 \xrightarrow{k_3} \text{chain termination},$$

$$P\dot{O}_2 + A \xrightarrow{k_4} \text{chain termination}.$$

Here S is the photosensitiser. The system of diffusion-kinetic equations describing the kinetics of the consumption of A and of the formation of $P\dot{O}_2$ in different sections of the polymer (x) during the induction period is as follows:

$$\left.\begin{aligned}
&\frac{\partial [PO_2(x,t)]}{\partial t} = -k_4 [A(x,t)]\,[PO_2(x,t)] + w_0 e^{-\alpha x} + D_{PO_2} \frac{\partial^2 [PO_2(x,t)]}{\partial x^2}\ ;\\
&\frac{\partial [A(x,t)]}{\partial t} = -k_4 [A(x,t)]\,[PO_2(x,t)] + D_A \frac{\partial^2 [A(x,t)]}{\partial x^2}\ ;\\
&0 < x < l;\ 0 < t < T_{ind};\\
&[PO_2(x,t)]_{t=0} = 0;\ [A(x,t)]_{t=0} = [A]_0;\\
&\left.\frac{\partial [A(x,t)]}{\partial x}\right|_{x=0} = \left.\frac{\partial [PO_2(x,t)]}{\partial x}\right|_{x=0} = 0;\\
&\left.\frac{\partial [A(x,t)]}{\partial x}\right|_{x=l} = \left.\frac{\partial [PO_2(x,t)]}{\partial x}\right|_{x=l},
\end{aligned}\right\} \quad (38)$$

where $\alpha = [A]_\epsilon$ is the UVA absorption index, D_i the diffusion coefficient, l the film thickness, and w_0 the rate of formation of free radicals on the surface of the film (for $x = 0$). The characteristic reaction conditions obtained by solving Eqns. (38) are illustrated in Figs. 23*a* to 23*c*.

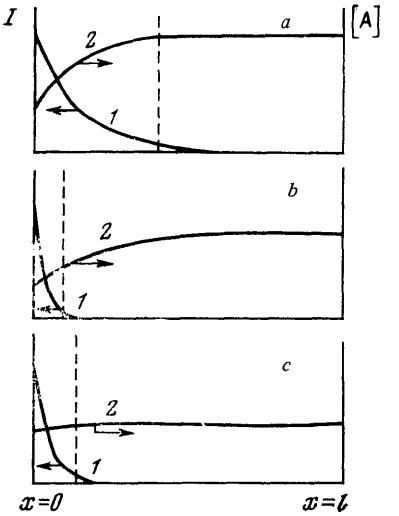


Figure 23. Distribution of light intensity (curve *1*) and antioxidant concentration (curve *2*) in the thickness of a polymer film for photochemical oxidation processes under different conditions: *a*) static; *b*) diffusion-controlled; *c*) rapid diffusion. The dashed line indicates the section in which the reaction is 20 times slower than on the surface. The photochemical reaction zone is located between this line and the surface ($x = 0$).

Under local conditions ($T_{ind} \ll l^2/\pi^2 D_a$, $T_{ind} \ll \alpha^2 l^4/\pi^2 T_A$), we have

$$T_{ind} = a[A_0]/I,$$

where I is the light intensity and a a constant. During the period T_{ind}, the diffusion of A is very slight and does not affect T_{ind}. Each layer reacts independently. The distribution of A in the film thickness at time t is therefore determined by the distribution of light intensity (Fig. 23*a*).

Under diffusion-controlled conditions ($1/\pi^2 D_A \alpha^2 \ll T_{ind} \ll l^2/\pi^2 D$, $\alpha l \gg 1$), we have

$$T_{ind} = bD_A \alpha^2 [A]_0^2/I^2. \quad (39)$$

In contrast to the local conditions, under these conditions there is an exchange of the antioxidant between neighbouring layers. As a result, $+d[A]/dt$ varies more smoothly than I along the thickness of the film (Fig. 23*b*).

Under rapid diffusion conditions ($T_{ind} \gg l^2/\pi^2 D_A$, $T_{ind} \gg 1/\pi^2 L_A \alpha^2$), we have

$$T_{ind} = a[A]_0 \alpha l/I, \quad (40)$$

i.e. [A] is virtually constant throughout the thickness of the film (Fig. 23*c*). Under these conditions, as under local conditions, the kinetics of the transformation of A are independent of D_A. T_{ind} is greater than under local conditions by a factor of αl. This is the maximum synergistic effect within the framework of the diffusion mechanism.

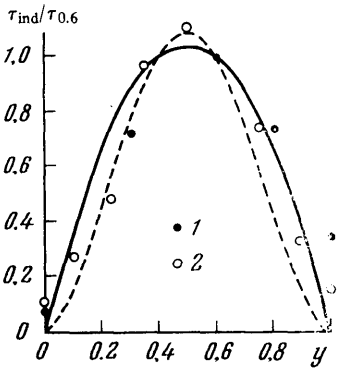


Figure 24. Dependence of the relative induction periods for the oxidation reaction $T_{ind}/\tau_{0.6}$ ($\tau_{0.6}$ is the induction period for $y = 0.6$) on the fraction of A: 1) in a mixture of 2,6-di-t-butyl-4-methylphenol and 4-heptyloxy-2-hydroxybenzophenone on irradiation of polybutadiene films 60 μm thick with light at 254 nm ($c\Sigma = 8.6 \times 10^{-2}$ M); 2) in a mixture of 2,2-methylenebis-(6-t-butyl-4-methylphenol) and 2-hydroxy-4-octyloxybenzophenone on irradiation of polychloroprene films[102]. Curves—calculation by Eqn.(41) (continuous curve) and by Eqn.(42) (dashed curve), normalised with respect to the experimental point corresponding to $y = 0.6$.

Analysis[100,101] showed that, for specified A and UVA concentrations, the synergistic effect can depend on I, D_A, and l, and the existence of such relations has been confirmed experimentally. The diffusion mechanism also made it possible to obtain the dependence of T_{ind} on the composition of the mixture of stabilisers. Under rapid diffusion conditions, we have

$$T_{ind} \sim c_\Sigma y(1-y) \quad (41)$$

and under diffusion-controlled conditions

$$T_{ind} \sim [c_\Sigma y(1-y)]^2, \quad (42)$$

where $c\Sigma$ is the overall concentration of stabilisers and y the mole fraction of A in the mixture. Fig. 24 shows that Eqns. (41) and (42) reflect correctly, in qualitative terms, the form of the dependence of T_{ind} on the composition of the synergistic mixture.

Thus the diffusion mechanism explains the observed dependence of the synergistic effect on the composition of the mixture of stabilisers, I, D_A, and α. The principles of the selection of synergistic mixtures for different polymers and different operating conditions as well as the requirements which must be met by the thicknesses of the specimens and the conditions under which the tests of the resistance to light by polymers stabilised with synergistic mixtures have to be accelerated acquire theoretical justification. On the basis of this mechanism, the resistance to light will be presumably significantly influenced by the irradiation conditions. Under conditions of periodic irradiation, the synergistic effect will be greater than under conditions of continuous irradiation; in particular, an increased resistance to light should be promoted by the nightly interruption of irradiation. During the night, diffusion will increase [A] in the surface zone of the polymer where [A] was consumed during the day. It is also possible to account for the synergism between the effect of the UVA and substances causing a non-radical decomposition of hydroperoxides. On the basis of the diffusion mechanism, a quantitative mechanism of the synergistic effect is possible.

IX. THE AGEING OF POLYMERS UNDER SPECIAL OPERATING CONDITIONS

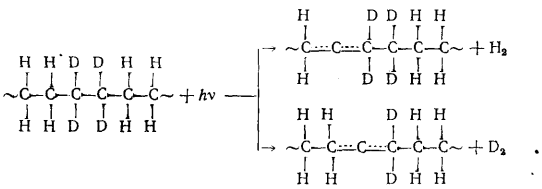
1. The Influence of Vacuum Ultraviolet Radiation on Polymers

In Space, a polymeric material is acted upon by vacuum ultraviolet (v.u.v.) radiation ($\lambda < 200$ nm). Such radiation constitutes a significant proportion of the spectrum of solar radiation, but does not reach the surface of the Earth, since it is absorbed by the ozone layer of the atmosphere.

The degradation of polymers under the influence of the v.u.v. differs from that under the influence of the softer u.v. with $\lambda > 200$ nm as well as the harder γ-radiation[103-106]. For example, polyolefins scarcely absorb light at a wavelength $\lambda > 200$ nm and their photodegradation under the influence of radiation in this spectral region therefore proceeds as a result of the absorption of light by impurities, which play the role of photosensitisers. The action of γ-rays on polyolefins is determined by the comparatively slow secondary electrons, which generate positively charged ions, free electrons, and excited molecules in the singlet and triplet states in the given substance. Secondary processes give rise to hydrogen atoms and free macroradicals, which initiate the radical degradation of the polymer.

The absorption maximum of polyolefins lies in the v.u.v. region. As a result of the absorption of a quantum of v.u.v. light with an energy insufficient for photoionisation, a polyolefin (polyethylene) molecule is transformed to an excited singlet state (in contrast to γ-radiolysis, the

probability of the formation of triplet molecules is extremely small). This state is unstable and the molecule decomposes mainly into molecular hydrogen and a polymer molecule containing a double bond of the *trans*-vinylene type. The hydrogen molecule is apparently abstracted from a single carbon atom, since the fraction of HD in the photolysis (λ = 147 nm) of the ethylene–deuteroethylene copolymer is small:



2. Degradation of Polymers in the Tissues of a Living Organism

In the last decade polymers have found extensive applications in medicine (cardiovascular surgery, surgery of the internal organs and tissues, traumatology, orthopaedic surgery, blood substitutes, agents prolonging the action of drugs, etc.). On contact with the tissues of the organism, polymeric materials undergo a change in properties to some extent and can influence the vital activity of the organism. The interaction of the polymer with the organism is a many-factor process, the understanding of which requires the investigation of processes involving the decomposition of implanted polymers, the metabolism of the decomposition products of the polymers and additives, and the genetic consequences of the action of polymers and their decomposition products on the organism.

In the general case implanted polymers are involved in three processes.

1. The sorption by the polymer of the components of the surrounding medium (water, salts, proteins, and lipids). For example, the sorption of lipids by cardiac valves made of polyorganosiloxanes leads to failure of the valves.

2. Desorption of low-molecular-weight compounds (catalysts, stabilisers, and fillers) from the polymers.

3. The decomposition of polymers as a result of degradation (thermal and mechanical energy, water, salts, enzymes) and dissolution. For example, the presence of low-molecular-weight oligomers, in equilibrium with the polymer, is characteristic of polycondensation polymers. The dissolution of these oligomers in the surrounding medium decreases the mass of the implanted material.

The macrokinetic features of the decomposition of polymers in the tissues of the living organism have been investigated[107,108]. Two main types of degradation of polymers in the organism are known—on the surface and in the bulk of the implanted material.

For the majority of hydrophobic polymers, the rate of decomposition of chemically unstable bonds under the influence of salts and enzymes greatly exceeds the rate of diffusion of these components in the polymer[107]. The degradation reaction proceeds in the surface of the implanted material at the rate

$$\frac{dn}{dt} = k^S C_m^S C_{cat}^S \cdot S, \qquad (43)$$

where n is the number of unstable bonds which have decomposed and C_m^S and C_{cat}^S are the surface concentrations of the chemically unstable bonds and the catalyst.

In the case of a simple fibre the change in the radius r, the mass m, and the breaking stress σ in the course of degradation, unaccompanied by the cracking of the surface, are described by the equations

$$\frac{r}{r_0} = 1 - k_{eff}^S \frac{t}{r_0 \rho}, \qquad (44)$$

$$\left(\frac{m}{m_0}\right)^{1/3} = \left(\frac{\sigma}{\sigma_0}\right)^{1/3} = 1 - k_{eff}^S \frac{t}{r_0 \rho}, \qquad (45)$$

where $k_{eff}^S = kC_m^S C_{cat}^S$ and ρ is the density of the polymer.

The degradation of poly(ethylene terephthalate) fibres in human subcutaneous cellular tissue has been investigated[108]. Fig. 25 *a* shows that relation (45) holds satisfactorily. The experimental data make it possible to predict the time τ of the complete decomposition of the implanted material:

$$\tau = r_0 \rho / k_{eff}, \qquad (46)$$

which in the given instance is 30 ± 3 years.

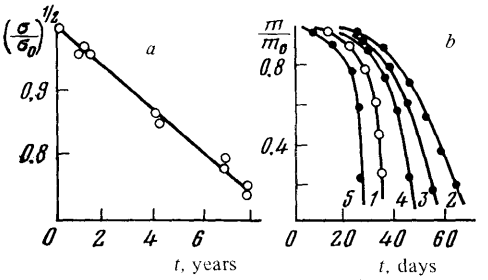


Figure 25. *a*) Variation of the relative breaking stress for a simple poly(ethylene terephthalate) fibre with r_{init} = 11 μm on the implantation time in the subcutaneous cellular tissue of man; *b*) kinetic curves for the variation of the mass m/m_0 of a polyglycolide fibre in the subcutaneous cellular tissue of rabbit (curve *1*), in water (curve *2*), and in phosphate buffer solutions at different concentrations: 1) 0.1 M; 4) 0.5 M; 5) 1.0 M; pH 7.4; 37°C.

In the degradation of the bulk phase of amorphous polymers, where the accessibility of all the chemically unstable bonds is as a rule the same, the degree of conversion with respect to the bonds and with respect to mass varies in accordance with the laws of homogeneous kinetics[107].

In amorphous-crystalline polymers the accessibilities of chemically unstable bonds in the amorphous regions and in the crystallites are different. The degradation of polyglycolide (degree of crystallinity approximately 80%) takes place under kinetic conditions in the amorphous regions and on the lateral surface of the crystallites.

Fig. 25 *b* presents kinetic curves for the variation of the degree of conversion with respect to mass in the degradation of polyglycolide filaments in water, phosphate buffers of different concentrations, and in the subcutaneous cellular tissue of rabbits. Evidently phosphate ions greatly accelerate the degradation process and, for example in 1 M solution, the degradation of polyglycolide is faster than in the tissues of the living organism.

The variation of the mass of polyglycolide is described by the equation

$$\frac{m}{m_0} = \varphi_{cr} - \varphi_{am}[1 - \exp(-k_{eff}^{V} c_{cat}^{V} t)]^2 + \varphi_{cr}\left(1 - \frac{k_{eff}^{V-S} c_{cat}^{V-S} t}{N b_0 \rho}\right)^2, \quad (47)$$

where φ_{am} and φ_{cr} are the volume fractions of the amorphous and crystalline phases respectively, k_{eff}^{V} and k_{eff}^{V-S} are the effective rate constants for the degradation in the amorphous regions and on the surface of crystallites with a diameter b_0, and N is the number of crystallites per cross-section of the elementary filament.

The study of the characteristics of the degradation of polymer materials in the living organism makes it possible to predict the time required for the complete decomposition of the implanted materials.

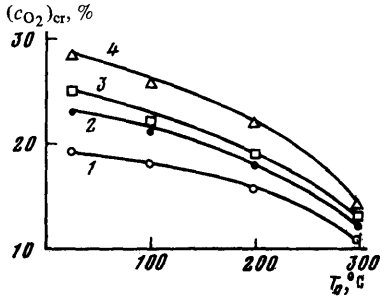


Figure 26. Decrease of the oxygen index $(c_{O_2})_{cr}$ with increase of the initial temperature T_0 of polystyrene specimens with added bromine-containing inhibitor (%): 1) 0; 2) 5; 3) 10; 4) 15.

3. Combustion of Polymers

The extensive use of polymeric materials in the building, textile, furniture, and other industries has greatly increased the importance of the problem of reducing the combustibility of polymers. Many of the commonest polymers—polystyrene, poly(methyl methacrylate), polyurethane, polyethylene, and natural and synthetic rubber—are highly combustible and readily ignite.

In order to estimate the degree of combustibility of the material, it is necessary to determine the conditions under which combustion is stable and the conditions under which it is quenched, i.e. it is necessary to find the critical conditions for combustion. These critical conditions are quoted in the literature: the minimum concentration of oxygen $(c_{O_2})_{cr}$, the minimum size of the specimen d_{cr}, the minimum pressure p_{cr}, the minimum temperature T_{cr}, etc. All these critical conditions are interrelated. For example, Fig. 26 [109] illustrates the decrease of $(c_{O_2})_{cr}$ with increase of the initial temperature of a polystyrene specimen—pure and with added bromine-containing inhibitor.

The oxygen index (OI)—the minimum concentration of oxygen $(c_{O_2})_{cr}$ at which combustion can still occur—is most often used to estimate the combustibility of the material. An advantage of the OI is its satisfactory reproducibility. However, the combustibility of the given material in air is of greatest interest, so that the characteristic based on the change in the composition of the atmosphere is not always suitable.

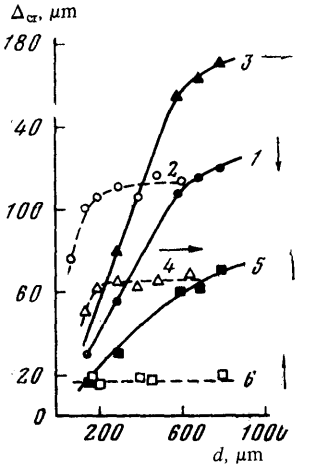


Figure 27. Dependence of the minimum thickness Δ_{cr} of PMMA films on the diameter d of copper wires (curves *1*, *3*, and *5*) and glass fibres (curves *2*, *4*, and *6*) in combustion from above downwards (curves *1* and *2*), horizontally (curves *3* and *4*), and from below upwards (curves *5* and *6*).

Table 8. Conditions for the quenching of the combustion of polymer films [poly(methyl methacrylate) on copper wire and glass fibres]. Test of the applicability of the Zel'dovich–Peclet number to polymer films.

Support	Direction of combustion	d, μm	Δ_{cr}, μm	w_{cr}, cm s^{-1}	L, cm	$10^5(dm/dt)_{cr}/\Delta_{cr}$, g cm s^{-1}
Copper	from above downwards	150	30	1.29	0.19	7.2
		300	55	0.70	0.30	8.3
		700	115	0.35	0.64	8.6
	horizontally	150	40	1.31	0.29	8.6
		300	80	0.70	0.53	10.0
		700	165	0.36	1.23	9.4
Glass	from above downwards	250	110	0.30	0.37	11.6
		350	110	0.21	0.29	10.3
		500	110	0.16	0.23	9.9
	horizontally	250	65	0.64	0.34	9.4
		350	65	0.46	0.32	7.2

Combustibility can be characterised by the minimum size of the specimen capable of combustion. This criterion is widely used for gaseous systems (particularly in the design of fire breaks), but is more rarely employed in the combustion of polymers. Fig. 27 and Table 8 illustrate the dependence of the minimum thickness Δ_{cr} of PMMA films on copper wires and glass fibres on the diameter d of the wire or fibre for different orientations of the specimen [110]. These results are of interest for the study of the combustion of insulating coatings on electric wires and also for the combustion of glass plastics. With increase of

the diameter of the wire, the quantity Δ_{cr} initially increases rapidly and then the relation $\Delta_{cr}(d)$ is weakened. For glass fibres, the $\Delta_{cr}(d)$ curves has a plateau. It might have been expected that thinner films would be capable of combustion on glass fibres than on copper wires. However, this is true only for a large diameter; for small values of d, thinner films can actually burn on copper than on glass. This is due to the fact that, for large diameters of the wire, the copper support removes heat from the burning polymeric films more effectively than the glass support and, for small values of d, the dominant factor is the supply of heat from the flame to the polymer via the wire.

By analogy with the Zel'dovich criterion for the quenching of homogeneous gaseous mixtures,

$$Pe = Pe_{cr} = ud_{cr}/a_T = \text{const} \quad (48)$$

(where Pe is the Peclet number, d_{cr} the critical diameter of the tube, a_T the thermal diffusivity of the fresh mixture, and u the linear rate of combustion), it was shown [110] that the product

$$\dot{m}_{cr} \cdot \Delta_{cr} = \rho w_{cr} \frac{\Delta_{cr}}{L}, \quad (49)$$

where m_{cr} and w_{cr} are the critical mass and linear rate of combustion, ρ the density of the polymer, and L the length of the pyrolysis zone (the distance from the flame barrier to the section where the film is fully gasified) can be used as a quantity characterising the stability of the combustion of polymer films. It follows from Table 8 that, when the thermal diffusivity of the support changes by more than two orders of magnitude (copper–glass) and the diameter of the wire (fibre) changes by a factor of 5, the quantity Δ_{cr} changes by a factor of 5.5, w_{cr} changes by a factor of 8, and the product $M_{cr}\Delta_{cr}$ changes only by a factor of 1.6.

The combustion of a polymer in a centrifuge has been studied [111]. Here the load factor a can serve as a critical parameter. It was observed that in the propagation of the flame along the acceleration vector, the ignition of paper takes place at an acceleration $a_{cr} = 5g$; on the other hand, if the flame is propagated in the opposite direction, ignition occurs at a much higher acceleration ($a_{cr} = 100g$), since in this case the hot combustion products flow in the direction of the propagation of the flame and heat ahead of the combustion front.

The knowledge of the critical combustion conditions makes it possible to arrange polymeric materials in a series based on decreasing combustibility with a particular degree of reliability. Only few polymeric materials have a low combustibility and do not require the addition of combustion inhibitors. Such materials include Teflon, rigid poly(vinyl chloride) (PVC) as well as synthetic fibres—Cordelan [based on PVC and poly(vinyl alcohol)] Nomex, and Kevlar (based on aromatic amine polymers).

However, for the majority of polymeric materials, the problem of the reduction of combustibility still remains extremely urgent. It is fairly difficult, since an increase of fire resistance usually has a number of undesirable consequences. For example, the majority of combustion inhibitors increase the toxicity of the combustion products. The amount of inhibitor which must be introduced to reduce significantly the combustibility of the polymer is usually extremely large. Thus self-extinguishing compositions based on polyethylene can be obtained only in the presence of at least 20–30 wt.% of the inhibitor.

Additives introduced in the form of mechanical admixtures are sometimes classified as chemically active and inert, although there is no sharp boundary between them. Mineral fillers such as SiO_2, chalk, kaolin, $Al_2O_3.3H_2O$, etc. may be referred to by convention as inert, while active fillers include Sb_2O_3 and alkali metal, barium, zinc, etc. borates and metaborates.

Chloralkanes (with a chlorine content up to 70%) alkyl and aryl phosphates and their halogeno-derivatives, etc. are used as plasticisers which reduce combustibility. In the chemical modification of a polymer carried out to reduce its combustibility halogens and phosphorus are introduced into its structure. A variant of this method involves the modification of the surface layers of the polymer only (halogenation, chlorosulphonation, etc.).

In the development of methods for suppressing the combustion of polymers one usually endeavours to achieve the following aims:

1. The reduction of the heat of combustion of polymeric materials following the introduction of thermodynamically inert additives. Particularly effective additives decompose with a fairly large endothermic heat change within the limits of the condensed phase of the polymer, which lowers the temperature of the surface of the latter and the rate of its combustion.

2. The formation on the polymer surface of a dense carbon residue under the influence of inhibitors, which prevents the supply of heat from the flame to the surface of the polymer and the diffusion of the polymer gasification products to the combustion zone. Readily fusible inhibitors, forming a layer of inert melt on the surface of the polymer, can act similarly.

3. The inhibition by additives (or their reaction products) of the chain oxidation reactions in the flame over the polymer surface.

X. CHEMICAL DEGRADATION AS A METHOD FOR THE MODIFICATION OF THE SURFACES OF POLYMERS

In many cases the operating properties of polymeric articles (for example, fibres and films) are determined by the properties of their surface. Chemical degradation permits a specific modification of the properties of the surfaces of polymers. It is important that the reaction should then involve only those macromolecules which are directly on the surface.

Under real conditions, the modification reaction takes place in a surface layer whose size depends on the ratio of the rate of diffusion of catalysts and reactants to the rate of decomposition of the chemically unstable bonds of the functional groups of the polymer.

The rate of decomposition of chemically unstable polymer bonds is

$$\frac{\partial c_n}{\partial t} = k(c_m^0 - c_n)\, c_{cat} c_{react}, \quad (50)$$

where c_m^0 is the initial concentration of the chemically unstable bonds, c_n the concentration of the bonds which have been ruptured, and c_{cat} and c_{react} are the concentrations in the catalyst and the reactant in the polymer respectively.

The changes in the concentrations of the catalyst and reactant in the polymer are described by the equations

$$\frac{\partial c_{cat}}{\partial t} = D_{cat}\nabla^2 c_{cat} - \sum_i k_i c_{cat} c_i, \quad (51)$$

$$\frac{\partial c_{\text{react}}}{\partial t} = D_{\text{react}}\nabla^2 c_{\text{react}} - k(c_m^0 - c_n)c_{\text{cat}}c_{\text{react}}, \quad (52)$$

where c_i is the concentration of the functional groups in the polymer capable of reacting with the catalyst with a rate constant k_i, D the diffusion coefficient, and ∇^2 the Laplace operator.

In the general case Eqns. (50)–(52) do not have an analytical solution but they can be solved on a computer. The equations are simplified if, for example, the reactant is water (hydrolytic reaction). In the diffusion of catalysts with a low vapour pressure into hydrophobic polymers we then have $D_{H_2O} \gg L_{cat}$ and the concentration of the reactant in the reaction layer is constant and equal to $c^0_{H_2O}$. In the case of catalysts with a high vapour pressure the diffusion of the catalyst and the solvent can be characterised by a single diffusion coefficient, since $D_{H_2O} \simeq D_{cat}$.

The case where the degradation proceeds under steady-state conditions in which the catalyst and reactant concentration gradients in the reaction layer are constant in time is frequently encountered. If the macromolecules decompose at random, the fragments formed on the polymer surface flake off and decompose in solution, i.e. $c^0_m - c_n \simeq c^0_m$. In this case the solution is

$$c_n = k_{\text{eff}}\, c^0_{\text{cat(surf)}} \cdot t \sqrt{\frac{D_{\text{cat}}}{k_{\text{eff}}}} \tanh\left(\frac{L}{2}\sqrt{\frac{k_{\text{eff}}}{D_{\text{cat}}}}\right), \quad (53)$$

where L is the thickness of the reaction layer on the surface of the polymeric article and $c^0_{\text{cat(surf)}}$ the concentration of the catalyst at the polymer–medium interface.

If the rate of decomposition of chemically unstable bonds is much greater than the rate of diffusion,

$$\frac{L}{2}\sqrt{\frac{k_{\text{eff}}}{D_{\text{cat}}}} \gg 1,$$

then

$$c_n = k_{\text{eff(surf)}} c^0_{\text{cat(surf)}} t, \quad (54)$$

where $k_{\text{eff(surf)}} = k_{\text{eff}}\sqrt{D_{\text{cat}}/k_{\text{eff}}}$ and the degradation reaction proceeds virtually on the surface of the polymeric article. This condition holds, for example, in the degradation of poly(ethylene terephthalate) (PETP) in concentrated KOH solutions [112].

The relative change in thickness (l) and mass (m) of the PETP film in concentrated solutions of alkalis is described by the equation

$$\frac{l}{l_0} = \frac{m}{m_0} = \left(1 - \frac{t}{\tau}\right), \quad (55)$$

where $\tau = l_0\rho / k_{\text{eff(surf)}} c^0_{\text{cat(surf)}}$ is the time required for the total decomposition of the polymer and ρ is the density of the polymer.

We shall now consider examples of the employment of the chemical degradation of polymer for the improvement of the properties of their surfaces.

1. The Preparation of Poly(ethylene terephthalate) Films with a Rough Surface

Films with a rough surface are used in modern computers, in radioelectronic, video-recording, and sound recording apparatus, in electrotechnical industry, and in cartography.

According to the generally accepted etching mechanism, a rough surface is formed when the amorphous phase is etched away and the bared crystallites form microrugosities [113]. Rudakova et al. [112] showed for the first time that, in degradative etching on the surface, a roughness arises as a result of the exposure of microdefects (for example, micropores) as the surface layer of the polymer is decomposed. As a result of the wedging pressure, the microdefects then initiate the growth of cracks. The number of micropores is non-uniform with respect to the thickness of the specimen, decreasing with increasing degree of crystallinity. It is to be expected that the surface with the greatest degree of roughness would be obtained in the etching of amorphous polymers.

Fig. 29 illustrates the dependence of the roughness factor Ra on the thickness of the layer λ removed from the surface of PETP films with different degrees of crystallinity. Evidently the maximum value of Ra is observed for amorphous PETP films following the decomposition of a 25–30 μm layer.

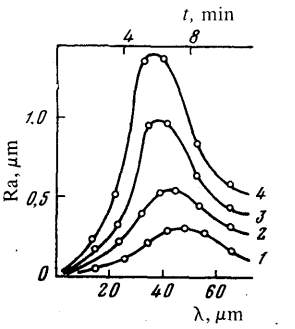
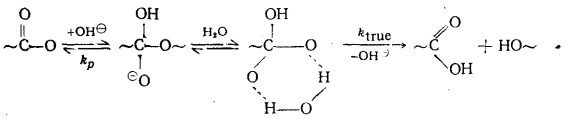


Figure 28. Dependence of the roughness factor Ra for poly(ethylene terephthalate) films treated with 49% KOH (108 °C) on the size of the decomposed layer λ and the degree of crystallinity (%): 1) 58; 2) 40; 3) 30; 4) 5.

Hydrolysis of the ester linkages in PETP proceeds via the mechanism [112]



The variation of k_{eff} with the thermodynamic parameters of the medium is described by the equation

$$K_{\text{eff}} = \frac{k_{\text{true}}\, a_{H_2O}}{1 + K_p/b_0}, \quad (56)$$

where K_p is the equilibrium constant for the addition of a hydroxide ion to the carbonyl carbon atom, b_0 the alkalinity, a parameter proportional to a_{OH^-}, a_{H_2O} the activity of water, and k_{true} the true rate constant.

The overall equation describing the variation of l with time, temperature, and the thermodynamic parameters of the medium is

$$l = l_0 - \frac{A \exp(-E/RT)\, a_{H_2O}\, t}{(1 + K_p/b_0)\,\rho}. \quad (57)$$

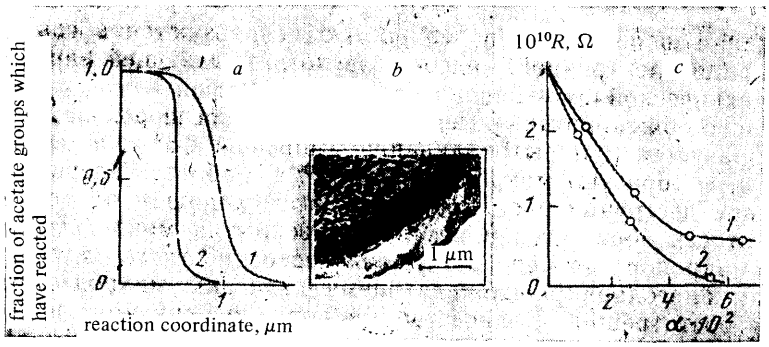


Figure 29. Preparation of diacetate filaments with reduced susceptibility to acquisition of an electrostatic charge: *a*) migration of the reaction front calculated by equations with $t/\tau = 0.1$ (τ is the time corresponding to the end of reaction) in solutions of different alkalis [1) NaOH; 2) $(C_4H_9)_4NOH$]; *b*) photomicrograph of a cross-section of the diacetate filament; *c*) dependence of the resistance of diacetate filaments R on the degree of conversion of the acetate groups in the filament α.

For this form of degradation, the degree of crystallinity of PETP has almost no influence on the kinetic parameters and Eqn. (57) makes it possible to find the optimum conditions for the etching of PETP films.

2. Preparation of Fibres with Reduced Susceptibility to the Acquisition of an Electrostatic Charge

A disadvantage of synthetic and artificial polyester fibres is their high susceptibility to the acquisition of an electrostatic charge. The employment of antistatic agents is frequently undesirable, since many of them can be readily eluted from the polymer and act as irritants to the skin and the mucous membrane of the eye.

Surface degradation is used successfully to reduce the susceptibility of artificial and synthetic fibres to the acquisition of an electrostatic charge. For example, such susceptibility of fabrics can be diminished if the hydrophobic ester groups in the surface layer of cellulose diacetate or triacetate filaments is replaced by the hydrophilic hydroxy-group of the regenerated cellulose. The conditions under which the rate of hydrolysis of the ester linkages is much higher than the rate of diffusion of the alkali into the filaments have been determined[114]. This is achieved (Fig. 29) by (1) using concentrated solutions of strong alkalis, i.e. by increasing k_{eff} for D_{cat} [Eqn. (53)] and (2) by employing alkali with a large bulky cation, for example $(C_4H_9)_4NOH$, i.e. by diminishing D_{cat} for a constant rate of hydrolysis, Both procedures lead to an appreciable reduction of the susceptibility of cellulose to the acquisition of an electrostatic charge.

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Thus, over an extremely short period, the field of the ageing and stabilisation of polymers has become an important branch of the fundamental and applied chemical science, which is concerned with the study of the chemical changes in polymers and polymeric materials and with the development of rational methods for controlling these changes.

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