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Kinetic Study of the Degradation and Stabilisation of Polymers

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The kinetics and the mechanism of the thermal, thermo-oxidative, photo-oxidative, and hydrolytic degradation of polymers are surveyed. Critical phenomena in the thermal degradation of poly(vinyl chloride) are described. Specific aspects of radical reactions in the solid phase are discussed. A list of 151 references is included.

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I. INTRODUCTION

During recent years many studies have been published on the degradation and the stabilisation of polymers. The scientific and practical value of such investigation is obvious, since lengthening the life of plastic articles is equivalent to increasing the production of such articles. The summarising papers by Emanuel',[1-5] based on the application of various kinetic methods, are especially promising in the study of the mechanism of the ageing of polymers and in the search for ways of stabilising them.

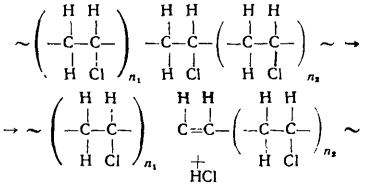
Detailed study of the kinetics and the mechanism of the degradation of polymers will permit (i) development of theoretically based accelerated methods for estimating the "lifetime" of polymers and polymeric articles under storage, processing, and service conditions, (ii) preparation of effective stabilisers for polymers and assessment of their efficiency, (iii) prolongation (or shortening†) of the useful life of polymer articles, and (iv) assessment of the effect of various additives on the stability of polymers.

Four modes of degradation of polymers—thermal, thermo-oxidative, photo-oxidative, and hydrolytic—are especially important both theoretically and practically. Overall the degradation (ageing) of polymers is a complicated radical, ionic, and molecular process involving many consecutive and simultaneous reactions.

II. THERMAL DEGRADATION

Among work on the thermal degradation of polymers a special place is occupied by studies of the degradation of poly(vinyl chloride) (p.v.c.).[6-9] This polymer is widely used in various branches of industry, but its instability when heated makes its processing and use in articles difficult.

Hydrogen chloride is evolved by the decomposition of poly(vinyl chloride):



(1)

† This is important for "one-off" uses of polymers (e.g. packaging materials) from the point of view of conservation of the environment and the regeneration of waste products.

The polymer becomes discoloured (owing to the formation of polyconjugated systems) and its physicomechanical properties change. The decomposition exhibits the principal features of a radical–chain process (rate of dehydrochlorination increased by radical initiators, and decreased by inhibitors of radical reactions)[9]. The proportionality of the rate of evolution of hydrogen chloride to the square root of the concentration of added initiators[9], indicates that destruction of the active centres involved occurs by recombination or disproportionation[7]. Degradation is initiated by the bimolecular interaction of structures P'Cl containing a labile chlorine atom with hydrogen atoms in the polymer PH to form a molecule of hydrogen chloride and two macroradicals P$^{\cdot}$ and P''$^{\cdot}$:

$$PH + P'Cl \rightarrow P^{\cdot} + P''^{\cdot} + HCl \quad . \qquad (2)$$

Molecular detachment of hydrogen chloride from the poly(vinyl chloride) molecule (reaction 1) cannot be completely excluded[7-9].

During thermal degradation in the presence of the hydrogen chloride evolved, reactions (1) and (2) are accompanied by the autocatalytic reaction

$$HCl + PH \xrightarrow{k} 2\,HCl + Pr$$

where Pr is the reaction product (macromolecules with a double bond) and k the effective rate constant. The occurrence of this reaction gives rise to critical phenomena[8,9]. The concentration of hydrogen chloride is determined in general not only by its rate of formation but also by its rate of removal from the specimen by diffusion. The variation in its concentration inside the polymer film $c(x,t)$ can therefore be described by the equation

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} + W_0 + kc,$$

where W_0 is the rate of the uncatalysed formation of hydrogen chloride, D its diffusion coefficient in the film, and k the effective autocatalysis constant. Hence the flux of hydrogen chloride through the boundary surfaces of the film ($x = 0$, $x = l$) referred to unit volume (the rate of formation of hydrogen chloride determined experimentally) can be calculated as

$$W_{HCl} = \frac{2D}{l}\frac{dc}{dx} = \sum_{n=0}^{\infty} \frac{8W_0D\left[e^{\left[k-\frac{(2n+1)^2\pi^2D}{l^2}\right]t} - 1\right]}{l^2\left[k - \frac{(2n+1)^2\pi^2D}{l^2}\right]} \qquad (3)$$

For thin films (with $\pi^2D/l^2 \gg k$ and $t > l^2/\pi^2D$) Eqn. (3) becomes

$$W_{HCl} = \frac{8W_0D}{l^2}\sum_{n=0}^{\infty}\frac{1}{\frac{(2n+1)^2\pi^2D}{l^2} - k}.$$

The rate of evolution increases as the film becomes thicker. When $\pi^2D/l^2 = k$, we have

$$W_{HCl} = \frac{8W_0Dt}{l^2},$$

i.e. W_{HCl} increases linearly with time. The presence of autocatalysis when $k > \pi^2D/l^2$ should produce an exponential increase in rate of evolution of hydrogen chloride during the process:

$$W_{HCl} = \frac{8D}{l^2}\frac{W_0e^{kt}}{k}.$$

Calculation shows [9] that at 200°C the critical film thickness (corresponding to the transition from a steady-state to an autocatalytic process) is 0.018 cm.

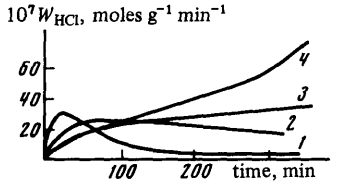


Figure 1. Rates of formation of hydrogen chloride (at 200°C) calculated by means of Eqn. (3) for poly(vinyl chloride) films of different thicknesses (mm): 1) 0.06; 2) 0.14; 3) 0.18; 4) 0.19.

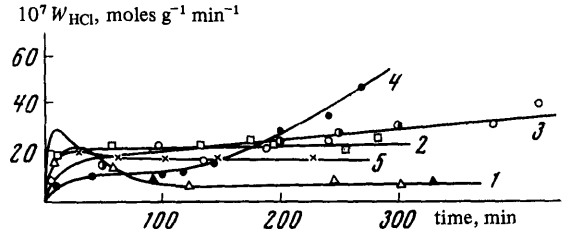


Figure 2. Rates of formation of hydrogen chloride (at 200°C) for poly(vinyl chloride) films of different thicknesses (mm): 1) 0.06; 2) 0.14; 3) 0.18; 4) 0.19; 5) finely divided powder.

Figs. 1 and 2 show good agreement between curves calculated by means of Eqn. (3), with $D = 3.3 \times 10^{-7}$ cm^2 min^{-1} and $k = 0.0103$ min^{-1}, and those obtained experimentally (at 200°C). The results demonstrate a novel type of critical phenomena in degradation processes, due to competition between catalysis by the final reaction product and its diffusion from the polymer [6-9]. It is evident from Figs. 1 and 2 that autocatalysis is absent only with very thin films and finely powdered poly(vinyl chloride). The occurrence of such critical phenomena in the thermal degradation of the polymer is the reason for the irreproducibility of the experimental results obtained by different workers.

The introduction of stabilisers to combine with hydrogen chloride (acceptors) should increase its rate of removal and hence the critical dimensions of the specimen. In the presence of an acceptor A we have

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} + W_0 + k_{eff}c,$$

where $k_{eff} = k - k_A[A]$ is the effective autocatalysis constant, k_A being the rate constant for interaction between hydrogen chloride and the acceptor, and [A] the concentration of the latter. At acceptor concentrations $[A]_{cr} \geq k/k_A$ degradation will occur under steady-state conditions whatever the size of the specimen. Taking into account the thickness of the film yields

$$[A]_{cr} = \frac{k - \frac{\pi^2}{l^2}D}{k_A},$$

i.e. the critical acceptor concentration is lower the thinner the film. This equation can be used to calculate k_A, an important quantitative parameter of hydrogen-chloride acceptors.

Thus prediction of the useful life of articles made of poly(vinyl chloride) must take into account not only the temperature and the concentration of the added stabiliser–acceptor but also the critical size of the article and the critical concentration of the stabiliser under service conditions.

III. THERMO-OXIDATIVE DEGRADATION

Significant progress in the degradation and stabilisation of polymers has recently been made particularly by kinetic investigations. The oxidation of polymers comprises in principle the same primary steps as that of simpler compounds, so that many features of their oxidation can be explained by the generally accepted scheme [10,11]. Denoting the oxidisable compound as RH (e.g. a hydrocarbon), we can write for the initial stages [10] (where R'OOR' is an initiator)

$$R'OOR' \xrightarrow{W_i} [2R'O'] \xrightarrow{e} R'O^{\cdot} \xrightarrow{RH} R^{\cdot};$$
$$R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot};$$
$$RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot};$$
$$ROOH \xrightarrow{k_3} RO^{\cdot} + {}^{\cdot}OH;$$
$$R^{\cdot} + R^{\cdot} \xrightarrow{k_4}$$
$$R^{\cdot} + RO_2^{\cdot} \xrightarrow{k_5} \text{Inactive products};$$
$$RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_6}$$

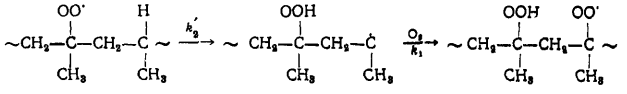
and in the presence of an inhibitor InH we have

$$RO_2^{\cdot} + InH \xrightarrow{k_7} ROOH + In^{\cdot}; \quad (4)$$
$$R^{\cdot} + InH \xrightarrow{k_7'} RH + In^{\cdot}. \quad (5)$$

However, conditions for the development of a chain reaction in a solid polymer differ markedly from those in a liquid organic compound. Recent kinetic studies of the oxidation of several (primarily carbon-chain) polymers have revealed facts that cannot be interpreted in terms of the classical scheme. Such solid-phase processes can be described quantitatively [12] by a step-by-step model of the

chain oxidation of polymers with a two-centre chain reaction and a stepwise mechanism of migration of the free valency and destruction of free radicals on collision.

According to this model the oxidation of a polymer PH involves the formation of solitary hydroperoxides POOH and adjoining peroxides $(POOH)_2$, among which the latter break down considerably more rapidly into radicals [13]. Adjacent hydroperoxy-groups are formed when a peroxy-radical attacks a β-carbon–hydrogen bond, and the resulting alkyl radical adds oxygen:



The ratio of the yields of (POOH) and $(POOH)_2$ depends on the oxygen pressure.

An important role in the mechanism of the solid-phase oxidation of polymers is played by chain-propagation reactions involving alkyl radicals‡:

$$P^{\cdot} + PH \xrightarrow{k_2''} PH + P^{\cdot},$$

which tend to move the free valency through the specimen.

As oxygen diffuses slowly and is relatively sparingly soluble in the polymer [16–20], the conversion of alkyl into peroxide macroradicals is a slow process, and the $[P^{\cdot}]/[PO_2^{\cdot}]$ ratio in the polymer is quite high, which is of great importance for solving the problem of stabilisation. Inhibitors (phenols, amines, anthracene) terminate chains in an oxidisable polymer by reacting not only with peroxide but also with alkyl radicals [21–23]. For this reason inhibitors that react mainly with alkyl radicals (iminoxyl radicals, anthracene, or quinol) inhibit the oxidation of a polymer far more efficiently than that of a hydrocarbon [23,24]. Whereas chain termination during oxidation of a polymer in solution takes place only by reaction (4), reaction (5) plays an important part in the solid polymer [25].

Thus stepwise migration of the free valency in the solid oxidisable polymer occurs by two primary processes:

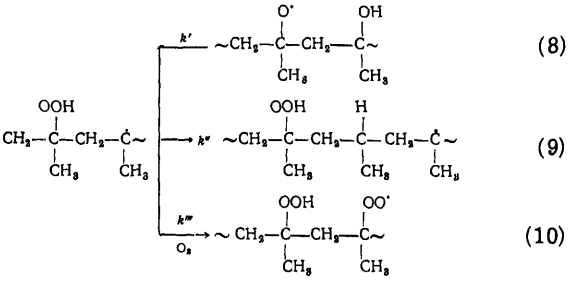
$$P^{\cdot} + PH \xrightarrow{k_2''} PH + P^{\cdot}; \qquad (6)$$

$$PO_2^{\cdot} + PH \xrightarrow{k_5} POOH + P^{\cdot}. \qquad (7)$$

During the interval between these two processes the free valency moves a distance d as a consequence of the thermal motion of the segments of the macromolecules [12]. The more mobile the segments the more rapid the migration of the active centre; the latter is determined also by the rate of the chemical reactions (6) and (7). Two such active centres are destroyed when they enter a space of $4\pi d^3/3$, where they may be brought together by the thermal mobility of the segments and interact, the rate of recombination being greater the higher the concentration of active particles, the more vigorous the movement of the segments, and the more rapid the migration of active centres through the polymer specimen [12]. The meeting of two active centres in the polymer cannot be regarded as the encounter of independent particles; k_4, k_5, and k_6 depend on the reaction conditions (pressure of oxygen, structure of polymer, solubility of oxygen, and other factors determining the composition of the radicals).

A step-by-step mechanism of migration of the free valency in the polymer predominates when the diffusion of free radicals is slow. In solution, the melt, and in the swollen polymer, where diffusion of macromolecules and their segments is facilitated, a diffusion mechanism may be a more efficient mode of migration of the free valency [26–30].

It is quite likely that, besides the "direct" step-by-step mechanism leading to formation of a block of hydroperoxy-groups on the polymer chain, $P^{\cdot}$ or $PO_2^{\cdot}$ radicals may attack hydroperoxy-groups that have just been formed [31,32]. Results obtained for the oxidation of isotactic polypropylene—a low yield of stable hydroperoxides (20–40% on the rate of absorption of oxygen at 130°C), the shortness of surviving hydroperoxide blocks, the formation of degradation products of low molecular weight even in the initial stages, and the proportionality of the rate of formation of such products to the concentration not of hydroperoxide but of free radicals—support [31] the latter mechanism (chain propagation by the breakdown of a considerable proportion of hydroperoxy-groups immediately after their formation). Furthermore [33] the rate constants for reaction of these radicals with a hydroperoxide are considerably larger than those for their interaction with P–H. Thus the free valency is located beside the newly formed hydroperoxy-group after abstraction of a hydrogen atom by a $PO_2^{\cdot}$ radical from a neighbouring unit of the macromolecule§; it may attack a hydroperoxy-group or the next unit of its own or a neighbouring macromolecule, or add oxygen to form a new $PO_2^{\cdot}$ radical [35–36]:



(8)

(9)

(10)

The first process leads to destruction of the hydroperoxide just formed, whereas the latter two processes remove the reaction centre and stabilise this group, to give a yield of stabilised hydroperoxide of [35]

$$\alpha = \frac{k'' + k'''[O_2]}{k' + k'' + k'''[O_2]},$$

$$\frac{1}{\alpha} = 1 + \frac{k'}{k'''([O_2] + k''/k''')}.$$

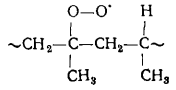
These equations show that α should depend on the oxygen pressure. The latter formula permits determination of the ratio k''/k''' of the rates of the second and third processes.

As a result of this first process hydroxyl and carboxyl groups appear within the hydroperoxide block, in both α- and β-positions with respect to tertiary and secondary hydroperoxy-groups. This process leads to rupture of the chain. The second process disturbs the regular arrangement of hydroperoxy-groups. Since the ratio of the sum of the rates of (8) and (9) to the rates of reaction (10) will depend on the concentration of molecular oxygen in the polymer, the composition of the block and the properties of the polymer hydroperoxides will depend on the oxygen pressure. Taking into account all three processes involving the $PO_2^{\cdot}$ radical, we are able to explain many experimental aspects of the oxidation of polyalkenes [31–35].

‡ The role of such reactions was shown earlier [14,15] in the co-oxidation of simpler organic compounds.

§ The $PO_2^{\cdot}$ macroradicals formed by oxidation of a polymer react mainly with a neighbouring unit in their own macromolecule [32,34].

Products of low molecular weight can be formed also by the direct decompositon of a single radical



Competition between two reactions of chain propagation—the unimolecular isomerisation and breakdown of peroxy-radicals (to form many different products with rupture of the initial carbon skeleton)

$$RO_2^{\cdot} \rightarrow R'HO + R''O^{\cdot},$$

and the bimolecular reaction

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$$

with formation of a hydroperoxide as sole primary product—governs the composition of the oxidation products of simple organic compounds [10,11,37]. Since the corresponding activation energies are ~20 and ~10 kcal mole^{-1}, the proportion of unimolecular reactions (yielding simple degradation products) will increase with rise in temperature, and the contribution of unimolecular reactions to the oxidation of compounds of low molecular weight is usually negligible below 100°C. However, the relative proportions of the two reaction paths is determined not only by the temperature but also by the frequency of the collisions necessary for a bimolecular process. This may be responsible for the significantly larger contribution to the solid-phase oxidation of polymers made by unimolecular reactions leading to the formation of simple reaction products.

The above conditions mark the limits within which the step-by-step mechanism of migration of the free valency plays a decisive part in the oxidation of polymers. The role of this mechanism should diminish as low-molecular products accumulate, and the free valency will migrate mainly by means of reaction products possessing sufficient mobility in the polymer matrix [38]. Denoting by rH the low-molecular-degradation products, we can represent displacement of the free valency as

$$P^{\cdot} + rH \xrightarrow{k_2''} PH + r^{\cdot}.$$

The resulting low-molecular radical r$^{\cdot}$ (alkyl or, in the presence of molecular oxygen, peroxy) moves a distance

$$\lambda = \sqrt{6D_0\tau}$$

during its lifetime τ. At temperatures above 100°C the diffusion coefficient D_0 for rH and r$^{\cdot}$ lies in the range $10^{-6}-10^{-8}$ cm^2 s^{-1}, so that λ may reach several micrometres [38-40]. Destruction of the radical r$^{\cdot}$ by the reaction

$$r^{\cdot} + PH \xrightarrow{k_3''} rH + P \qquad (11)$$

is equivalent to the macroradical P$^{\cdot}$ "jumping" a distance $\lambda = (6D_0\tau)^{1/2}$, the frequency of such jumps being $\nu = k_2''[rH]$. [34] The coefficient for chemical diffusion of the radical P$^{\cdot}$ is

$$D_1 = D_0 k_2''[rH]\tau.$$

On the assumption that r$^{\cdot}$ is removed solely by reaction (11), we obtain $\tau = 1/k_3''[PH]$, and then $D_1 = D_0 k_2''[rH]/k_3''[PH]$. With $D_0 \simeq 10^{-7}$ cm^2 s^{-1}, [rH] $\simeq 6 \times 10^{-6}$ mole cm^{-1}, and $k_2''/k_3'' \simeq 1-100$¶ we have $D_1 \simeq 10^{-8}-10^{-10}$ cm^2 s^{-1}. Such a rate of migration of the free valency ensures propagation of the oxidation chain in the solid polymer, since in many cases [38] the rate provided by the step-by-step mechanism is far lower.

The recombination of radicals may also be due to the involvement of low-molecular degradation products [38-41]:

$$\left.\begin{array}{l} r^{\cdot} + P^{\cdot} \xrightarrow{k_4'} \\ r^{\cdot} + r^{\cdot} \xrightarrow{k_5'} \end{array}\right| \longrightarrow \text{Stable products.}$$

Provided that $k_4' \simeq k_5'$, we have

$$-\frac{d[P^{\cdot}]}{dt} = 2k_4' \frac{k_2''[rH]}{k_3''[PH] + k_4'[P^{\cdot}]}[P]^2.$$

When $k_4'[P^{\cdot}] \ll k_3''[PH]$, we find that

$$-\frac{d[P^{\cdot}]}{dt} = 8\pi d_1 D_0 \frac{k_2''[rH]}{k_3''[PH]}[P^{\cdot}]^2,$$

where d_1 is the sum of the radii of the colliding particles. Substituting the values $d_1 \simeq 5 \times 10^{-8}$ cm, $D_0 \simeq 10^{-7}$ cm^2 s^{-1}, $k_2''/k_3'' \simeq 200$, [rH] $= 5 \times 10^{-6}$ and [PH] $= 0.025$ mole cm^{-3}, we obtain a chain-termination rate constant of 3.5×10^9 cm^3 mole^{-1} s^{-1} (the corresponding experimental values is 9×10^9).

Another important feature of a crystalline polymer is a complicated supermolecular structure comprising alternating regions differing in degree of ordering of the polymer chain. In general we must regard a polymer specimen as consisting of various microregions of varying reactivity. The relative arrangement and dimensions of such regions, as well as the specific volumes of the various structural components, depend on many factors. The stability of a polymer is considerably influenced by the degree of ordering of the polymer chains in the solid [19,31,42-44].

The rate of interaction of a gas A with a polymer comprises the reaction velocities in the individual structural components:

$$W_a = \sum_j \rho_j W_{aj},$$

where ρ_j is the specific volume of the jth structural component and W_{aj} the rate of reaction in this component. For a second-order reaction

$$W_{aj} = k_{aj}c_j[A]_j = k_{aj}c_j\gamma_{aj}^{-1}p_a,$$

where k_{aj} is the rate constant, c_j the polymer concentration, γ_{aj} the solubility coefficient of A (all for the jth component), and $p_a = \gamma_{aj}[A]_j$ is the partial pressure of A outside the polymer. When a chain reaction occurs in an individual structural unit, the process is complicated by the migration of active centres through the boundary of this unit. Oxidation does not usually involve the crystalline regions of a polymer [43]: the solubility of oxygen is low in regions having an undistorted crystal lattice [16,18], while the reactivity of the macromolecules is diminished in these segments, since the lattice prevents formation of the optimum configuration of the activated complex [45].

It has been shown for the oxidation of polypropylene that finely spherulitic specimens are oxidised more rapidly than coarsely spherulitic specimens at different stages of the process. In the former case the reaction is probably localised mainly in the interspherulitic material. In a coarsely spherulitic polymer, where the proportion of such material is insignificant, the process occurs predominantly in the interfibre portions within the spherulite. During extensive oxidation, when radicals decay mainly by

¶ The reality of these postulates was validated in Ref. 38.

quadratic termination†, the escape of radicals from amorphous layers into the crystalline material plays a subordinate role, and the rates of oxidation of specimens having the same "crystallinity" differ insignificantly.

The observed difference between rates of oxidation of specimens differing in supermolecular structure is more strongly marked the lower the reaction temperature, and it disappears at the melting point. The presence of inhomogeneities in a polymer, as well as differences in the solubility of an inhibitor in regions of the polymer differing in degree of organisation[16-19], demands a special study of non-uniformly inhibited polymers[46-50]. Such cases are indeed found, since a non-uniform distribution of an inhibitor may result from technical defects in the preparation of the specimen.

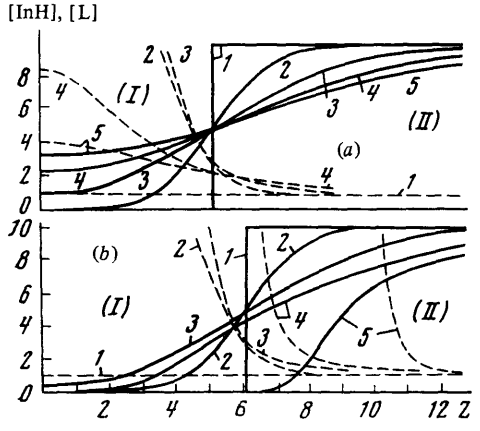


Figure 3. Distribution of relative concentrations of inhibitor [InH] (full curves) and of active centres [L] (broken curves) along a unidimensional specimen of length Z with section (I) initially uninhibited ([InH] = 0) and section (II) initially inhibited ($[InH]^{I,0}_{II,0} = 10$) for: *a*) smaller section (I); *b*) larger section (I) after different times of oxidation τ (in relative units): 1) 0; 2) 1; 3) 5; 4) 10 (12.5 in case *b*); 5) 15 (17.5).

If the inhibitor is initially absent from some part of the specimen, and neither inhibitor nor active degradation centres are able to diffuse, an autocatalytic reaction should occur in this portion independent of its size. But diffusion of inhibitor into the uninhibited region (and of active centres outwards) may result either in decay of the reaction or of gradual extension of the autocatalytic reaction throughout the specimen. Hence diffusion of inhibitor and of active centres must in general be considered when the initial distribution of inhibitor in the oxidisable specimen is non-uniform. Fig. 3 illustrates the theoretically calculated concentration distributions of inhibitor and of active centre [InH] and [L] along a unidimensional specimen after various time intervals. In both cases (*a*) and (*b*) both inhibitor and active-centre concentrations increase initially on the originally uninhibited segment. However, a difference then develops: if the size of the uninhibited portion Z is smaller than a limiting value Z_{cr}, the reaction dies out; if $Z > Z_{cr}$, a front is formed, and the reaction extends throughout the specimen. The critical value Z_{cr} depends on the concentration of inhibitor in the specimen $[InH]_{II,0}$ and on the ratio of the diffusion coefficients of inhibitor and of active centre. Both cases have been achieved in practice (Fig. 4)[47,48]. Fig. 5 shows the dependence of the induction period in the oxidation of polypropylene on the concentration of a diamine either uniformly or non-uniformly distributed in the polymer. The inflexion on curve *1* corresponds to the critical inhibitor concentration required to halt the process[50]. The inflexion on curve *2*, representing non-uniform inhibition, corresponds to the concentration at which the critical size of the uninhibited part of the polymer becomes equal to the actual size of the largest of the central segments of the powder particles devoid of inhibitor.

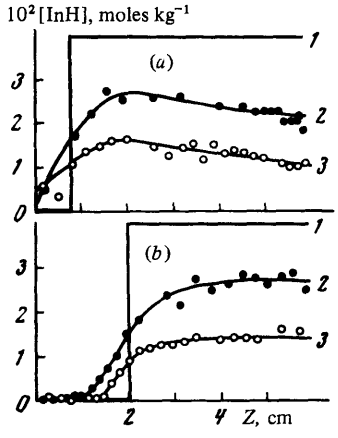


Figure 4. Distribution of actual concentrations of methylenebis-2-(4-methyl-6-t-butylphenol) [InH] in atactic polypropylene (size of specimen Z), with initially uninhibited portions of: *a*) 0.8 cm; *b*) 2 cm and initial inhibitor concentration in inhibited portion $[InH]_{II,0} = 0.04$ mole kg^{-1}, after oxidation in air at 190°C for different periods (min): 1) 0; 2) 150; 3) 300.

The investigation of oxidation processes in polymers at low temperatures is of great interest for the storage and performance of articles. Polymers are processed at high temperatures (as melts), under which conditions the specific features of low-temperature solid-phase oxidation[12,30-32,51] disappear, and new problems connected with the mechanism of high-temperature oxidation appear[51-53]. In spite of the precautions adopted in technology (e.g. processing in an atmosphere of an inert gas) the properties of the polymer change during processing, since degradation or cross-linking of the polymer chains takes place.

† In the early stages (at a low rate of initiation of radicals), when the concentration of radicals is small, decay occurs linearly, by migration of the free valency into the crystalline phase. In a finely spherulitic polymer the crystallites are too small for the radicals that have entered them to be able to react with oxygen.

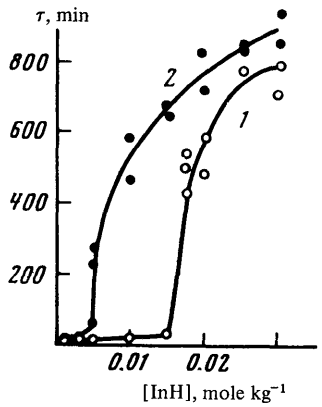


Figure 5. Dependence of induction period τ on concentration of dimethylbis-*p*-phenylaminophenoxysilane (S-1) [InH] in the oxidation of isotactic polypropylene of particle size 0.03 mm in oxygen (300 mmHg) at 200°C: 1) inhibitor applied to surface of pellets to give a non-uniform distribution; 2) pellets then heated in a vacuum at 100°C to give a uniform distribution of inhibitor.

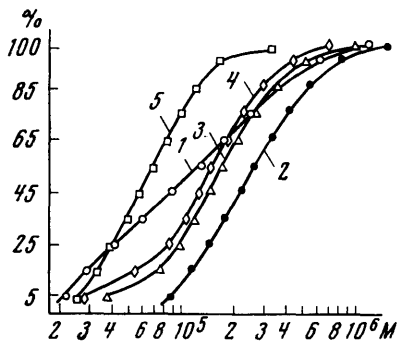


Figure 6. Dependence of molecular mass M distribution function on number of processings: 1) initial medium-pressure polyethylene; 2) polymer after first processing; 3) after second processing; 4) after third processing; 5) after thermal oxidation.

One of the most sensitive methods for recording the degradation and the cross-linking of macromolecules is analysis of the molecular-mass distribution function MMD.[29,53-56] For example, significant changes in molecular weight during multiple extrusions of (action of high temperatures and shear stresses on) high-density medium-pressure polyethylene are revealed[29] by analysis of the MMD function (Fig. 6). After the first processing the distribution curve of the initial polymer, which possesses a comparatively wide distribution (curve *1*), contracts and shifts to higher molecular weights (curve *2*). Subsequent processings produce the reverse process (curves *3* and *4*): they result in degradative processes leading to a decrease in molecular weight. In the absence of mechanical action on the polymer (subjected only to thermal oxidation) the latter undergoes only degradation (curve *5*). Degradation is probably[29] associated with thermal oxidation, whereas mechanical action is responsible for cross-linking.

Another effective method for studying ageing processes is use of a paramagnetic probe[57-67]. It consists essentially in measuring the electron spin resonance spectra of stable radicals introduced into the polymer, and calculating the appropriate parameters. The form of e.s.r. spectrum indicates structural features of the polymer matrix[57]. The following points must be borne in mind when the method is used[57].

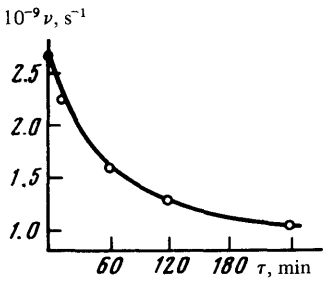


Figure 7. Dependence of rotational frequency ν of probe radical on time of oxidation of polypropylene in oxygen (400 mmHg) at 130°C.

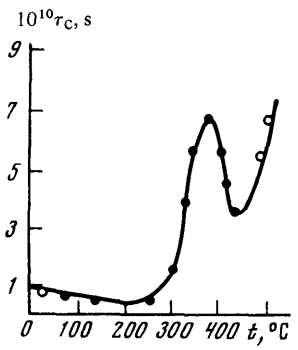


Figure 8. Dependence of correlation time of probe $\tau_c = \nu^{-1}$ on limiting temperature of initial heating of methylvinylsiloxane rubber.

Firstly, the rotational and translational mobility of stable radicals introduced into polymers indicates the intensity of molecular movements of the polymer matrix. Degradation is accompanied by a change in the molecular mobility of segments of the polymer chains, which is apparent in a change in the frequency of rotation of the probe radical. For example, a decrease in frequency during thermo-oxidative degradation (Fig. 7) corresponds to decreases in movements of segments in the amorphous phase of the polymer. In this case cross-linking occurs during oxidation. A more complicated case is illustrated by Fig. 8, where the ratio of the contributions of degradation and cross-linking changes several times with rise in temperature.

Secondly, stable radicals simulate the behaviour of simple compounds in a polymer (initiators, inhibitors, etc.), their rotational and translational mobility, and their local sites and local concentrations, which is important for calculating elementary constants for the reactions of macromolecules with simple substances.

Information obtained from study of the kinetics and the mechanism of the thermo-oxidative degradation of polymers is used [21-23] in selecting the most effective antioxidants, among which derivatives of phenols and amines are of considerable interest, as before. Among the attributes which the most efficient stabilisers should possess are (i) high rate constants of reaction with radicals (primarily peroxy and alkyl [10])

$$InH + PO_2^{\cdot}\ (P^{\cdot}) \rightarrow POOH\ (PH) + In^{\cdot} \qquad (12)$$

(ii) a relatively inactive radical In$^{\cdot}$ formed by the action of P$^{\cdot}$ or $PO_2^{\cdot}$ on InH, [10] (iii) reaction products that are preferably effective stabilisers [21-23], and (iv) more than one functional group in the molecule [21-23,68]. Highly efficient new antioxidants have recently been prepared [for polyalkenes, polyoxymethylene, polystyrene, polychlorides, synthetic rubbers, cellulose ethers, poly(vinyl chloride), and other polymers]—the S series of stabilisers [69-72] (stabiliser S-1 is dimethylbis-*p*-phenylaminophenoxysilane).

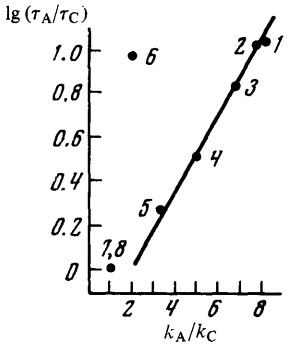


Figure 9. Dependence of $\lg(\tau_A/\tau_C)$ on k_A/k_C for: 1) *NN'*-dioctyl-*p*-phenylenediamine; 2) *NN'*-di-isopentyl-*p*-phenylenediamine; 3) *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine; 4) *NN'*-bis-α-methylbenzyl-*p*-phenylenediamine; 5) *N*-α-methylbenzylanisidine; 6) *NN'*-dibutylthiourea; 7) thiobis-2-(4-methyl-6-t-butylphenol); 8) methyl oleate.

Another important problem is to protect polymers from the action of ozone. Kinetic investigations [73] have established correlations between the rate of reaction of ozone with the test antiozonant under model conditions and the efficiency of the latter in rubbers (Fig. 9):

$$\lg\frac{\tau_A}{\tau_c} = N + M\frac{k_A}{k_c},$$

where N and M are constants, τ_A and τ_C are the induction periods for ozonisation of rubber containing the antiozonant A and of a control compound (model alkene) respectively, and k_A and k_C are the rate constants for reaction of ozone with A and with the control. The above relation not only simplifies and accelerates the testing of new potential ozonants (since little time is required to measure the rate constants for reaction with ozone) but also guides the preparation of new antiozonants.

The efficiency of the usual stabilisers (amines, phenols, and phosphorus-containing and sulphur-containing compounds) in polymers decreases with rise in temperature independently of their mechanism of action; at 270–300°C they become completely ineffective [74,75]. The reasons are that at high temperatures the In$^{\cdot}$ radicals formed by reactions (4) and (5) become reactive and capable of propagating chains, the inhibitor itself is readily oxidised, and the In–H bond is weak, so that the inhibitor becomes an initiator yielding free radicals.

Finely divided metals (M), generated by decomposition of their organic salts (e.g. oxalates) in polymer compositions during the service life of articles, are effective stabilisers against thermo-oxidative degradation at temperatures above 300°C. [76-79] The rate at which such metals react with oxygen exceeds considerably the rate at which oxygen reacts with the polymer and with the radicals formed by the degradation of polymers:

$$W_{M+O_2} \gg W_{PH+O_2},\ W_{P^{\cdot}+O_2}.$$

Thus oxygen plays almost no part in chain initiation and propagation, but is entirely absorbed by reaction with the metal.

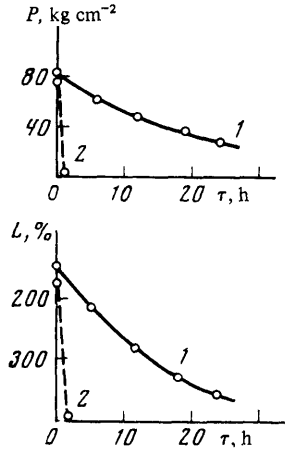


Figure 10. Variation in strength P and relative elongation L at rupture of SKTV-2 silicone rubber during ageing in air at 350°C: 1) specimen stabilised with finely divided copper; 2) control specimen stabilised with iron sesquioxide.

The lifetime of a polymer τ_p depends on the thickness of the specimen l and the solubility of oxygen in the polymer σ_x:

$$\tau_p = K\frac{l^2[M]}{D\sigma_x},$$

where K is a constant determined by the stoichiometry of the process and D is the diffusion coefficient of molecular oxygen. Figs. 10 and 11 show that specimens stabilised by finely divided metals retain their properties several

times longer. This method of stabilisation is suitable not only for polyorganosiloxanes but in principle for all polymers for which the relation $W_{M + O_2} > W_{PH + O_2}$ is satisfied (Fig. 12) under the working conditions of articles made from them.

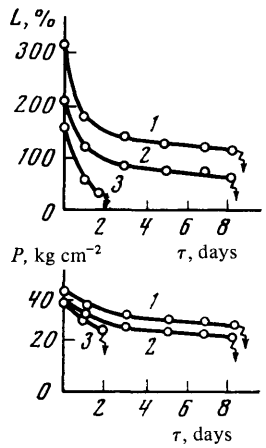


Figure 11. Variation in strength P and relative elongation L at break of siloxane rubber during ageing in air at 350°C: 1) specimen stabilised with finely divided copper; 2) specimen stabilised with finely divided iron; 3) standard specimen stabilised with titanium dioxide. The arrows show the beginning of rapid breakdown of the polymer; those on curves *1* and *2* correspond to exhaustion of the stabiliser.

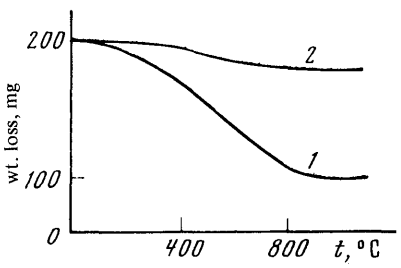


Figure 12. Thermogravimetric curves for a carbonised fibre: 1) unstabilised specimen; 2) specimen stabilised with finely divided copper.

IV. PHOTO-OXIDATIVE DEGRADATION

The photo-oxidation of a polymer comprises a complicated set of physical and chemical processes occurring under the influence of light [80-97]. It is extremely important to be able to calculate the absolute rate of photo-oxidation of a solid polymer, since this will enable the life of articles to be predicted. This was first accomplished for the photo-oxidation of polypropylene [80-82], where analysis of all possible reactions revealed a chain reaction with degenerate branching at hydroperoxides and with quadratic chain termination. Oxidation can be represented by the scheme

$$X \xrightarrow{h\nu} PO_2^{\cdot};$$

$$POOH + h\nu \xrightarrow{\varphi} PO^{\cdot} + {}^{\cdot}OH \xrightarrow{2O_2 + 2PH} 2PO_2^{\cdot} + H_2O + K;$$

$$K + h\nu \xrightarrow{2O_2} PO_2^{\cdot};$$

$$PO_2^{\cdot} + PH \xrightarrow{\frac{k_2}{O_2}} POOH + PO_2^{\cdot};$$

$$PO_2^{\cdot} + PO_2^{\cdot} \xrightarrow{k_6} K + POH + O_2;$$

where X represents impurities in a polymer PH and K is a ketone, while φ is the quantum efficiency of the photochemical reaction. This scheme yields for the concentration of carbonyl compounds formed during photo-oxidation the formula

$$\frac{[K]}{[POOH]_\infty} = \alpha t - 2\left(3 - e^{-\frac{\alpha t}{4}}\right)\left(1 - e^{-\frac{\alpha t}{4}}\right),$$

where

$$\alpha = \int I \varepsilon d\lambda, \quad [POOH]_\infty = \frac{4k_2^2[PH]^2}{\alpha k_6}.$$

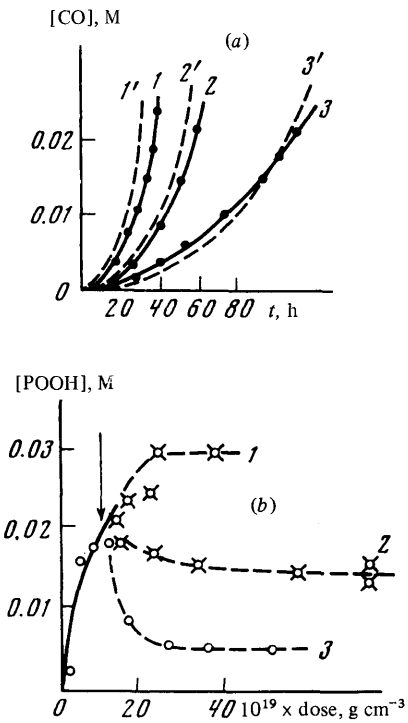


Figure 13. Comparison of experimental results (curves with points) with calculated values (broken curves, primed) for the photo-oxidation of polyalkenes. (*a*) Kinetic curves for the accumulation of carbonyl compounds under the influence of light of different wavelengths (nm): 1,1′) 280; 2,2′) 295; 3,3′) 305. (*b*) Kinetic curves for the accumulation of hydroperoxides during the photo-oxidation of polypropylene containing Methylox antioxidant (0.1 mole kg^{-1}), where the relative light intensity was changed at the time indicated by the arrow from 4 to: 1) 0.7; 2) 1.4; 3) 4 (by this time the Methylox was exhausted).

The data used in the calculation‡ included the intensity I, the absorption coefficient ϵ and the spectral distribution of the light source, and the absorption spectrum and the quantum efficiency of photodecomposition of the hydroperoxide; values of $k_2/k_6^{1/2}$ were taken from work on the dark initiated oxidation of the polymer. Fig. 13 shows good agreement between calculation and experiment, which confirms the reliability of the suggested scheme. Such agreement opens up the possibility of using polypropylene as a model polymer in investigating the mechanism of the action of photostabilisers.

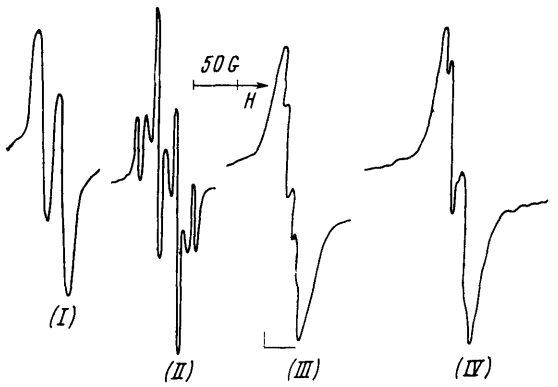
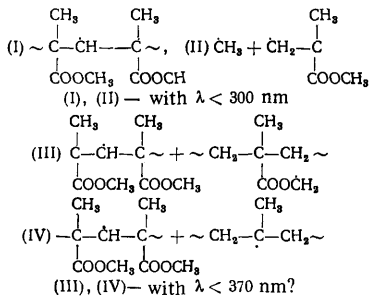
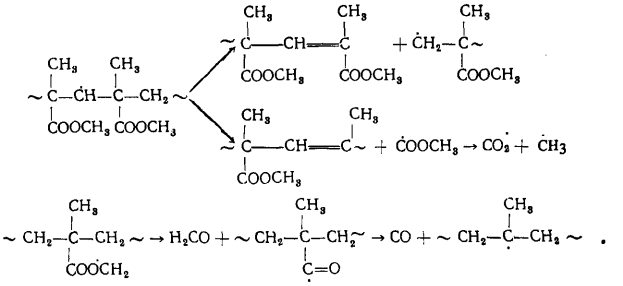


Figure 14. Electron spin resonance spectra of certain radicals obtained in the photo-oxidation of poly(methyl methacrylate):



The action of light on a polymer usually gives rise at once to several chemical processes occurring at different rates. To determine the contributions made by each of these reactions it is extremely important to know the quantum efficiencies of the remaining processes [83-85,90-92]. With poly(methyl methacrylate), whose ester groups are responsible for absorption, the principal photochemical process was the rupture of ester groups with a quantum efficiency close to unity [88,91,92]; this was accompanied by the transformation of methylene groups, chain cleavage, and the accumulation of radicals in order of diminishing quantum efficiency (respectively ~0.1, 0.012, and 0.001). Many details of the mechanism of the photo-oxidation of this polymer have been elucidated from the quantum efficiencies together with the application of ultraviolet, infrared, and e.s.r. spectroscopy to its kinetic investigation [91-93]. Fig. 14 illustrates the e.s.r. spectra of intermediate free radicals recorded in the polymer, in which the main photochemical reactions are



Photoconversion in cellulose triacetate is also due to the absorption of light by ester groups. The breakdown of such groups and of ether groups and the accumulation of carbonyl compounds, hydroxy-groups, and acetic acid have respectively quantum efficiencies of 0.015, 0.01, 0.005, 0.005, and 0.005.

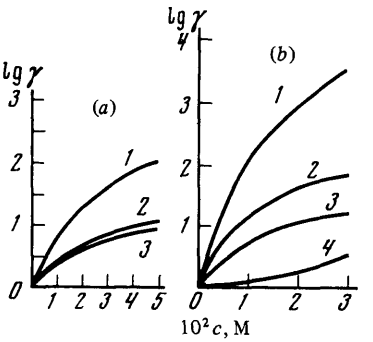
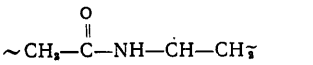


Figure 15. Coefficient of inhibition of the oxidation of diphenylmethane γ photosensitised by benzophenone (λ = 365 nm) as a function of the concentration of the photostabiliser: *a*) 2-hydroxy-4-octyloxybenzophenone; *b*) 2-(2-hydroxy-5-methylphenyl)benzotriazole: 1) total effect; and contributions made by: 2) shielding; 3) quenching; 4) inhibition.

The absorption of light by polyhexanamide is most effective in causing the absorption of oxygen (φ = 0.06); [90] rupture of the chain and evolution of carbon monoxide have φ = 0.015; and the quantum efficiencies of the accumulation of carbonyl and carboxyl groups are respectively 0.009 and 0.005. Under the influence of light

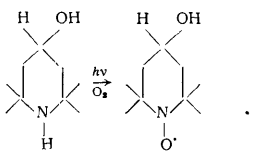


radicals decompose with the formation of ~$[CH_2]_5-\dot{C}=O$ radicals, which are then converted into ~$CH_2-\dot{C}H_2$ and ~$CH_2-\dot{C}H-CH_2$~ radicals [94].

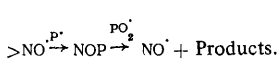
‡ The calculations were based on the usual equations of homogeneous chemical kinetics, since the photo-oxidation of polypropylene was investigated at temperatures above the glass point T_{gl}. However, processes occurring in a polymer below this temperature exhibit kinetic peculiarities—inhibition of chemical conversion during the process and kinetic arrest of the reaction [80].

Photostabilisers act by three main mechanisms: they absorb photochemically active light, quench excited states, and inhibit dark oxidation [88]. For two typical ultraviolet absorbers Fig. 15 shows the concentration dependence of the total reaction inhibition coefficient and the contributions made by shielding, quenching, and inhibition. Since the quantum efficiency is approximately unity for poly(methyl methacrylate), the photoreaction is so rapid that deactivation cannot occur, and therefore the efficiency of photostabilisers is here determined solely by their ability to absorb light. In cellulose triacetate, ester groups are decomposed with a quantum efficiency of 0.015, deactivation processes are competitive, and the photostabilisers that protect poly(methyl methacrylate) by a shielding mechanism act in cellulose triacetate by a quenching mechanism.

In the photo-oxidation of several polymers (e.g. polyhexanamide [88,90]) in the kinetic range in air, only a proportion of alkyl radicals are converted into peroxy-radicals. Thus such polymers can be stabilised by inhibitors that react with both types of radicals. Considerable inhibition is observed in the presence of stable nitroxyl radicals, which react only with alkyl radicals, and of chelate complexes of metals of variable valency, whose activity increases as the partial pressure of oxygen falls. In this connection great interest attaches to highly efficient new photostabilisers—secondary and tertiary aliphatic amines, derivatives of piperidine [22,87-102]—possessing neither shielding nor inhibiting effects and exerting only a weak quenching action. These compounds function [87] by photosensitised conversion of the amines into nitroxyl radicals, which are known to act as photostabilisers:

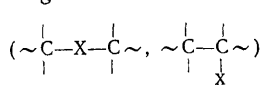


Prolonged inhibition is observed in the presence of such compounds (the stoichiometric coefficient may [63] exceed 10). The nitroxyl radical is regenerated from its reaction product with the alkyl radical by the action of a peroxy-radical:



V. HYDROLYTIC DEGRADATION

Polymers containing heteroatoms X in main and side chains



are hydrolytically unstable§. Hydrolytic degradation of a polymer involves diffusion of the active medium into the polymer and reactions involving chemically unstable bonds [103,104]. Several investigations are being undertaken in conformity with this—(i) use of simple model compounds to study the mechanisms of the conversion of hydrolytically unstable bonds of polymers in active media, (ii) determination of the main types of breakdown undergone by molecules of various polymers, (iii) establishment of the laws of the diffusion of active media into polymeric materials, and (iv) investigation of the mechanisms of the degradation of polymeric material in active media.

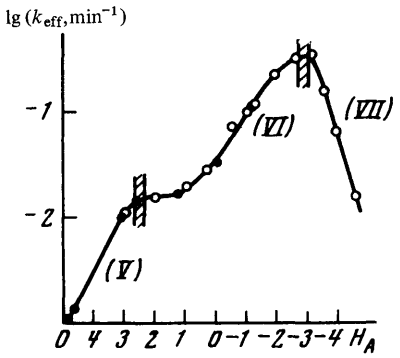
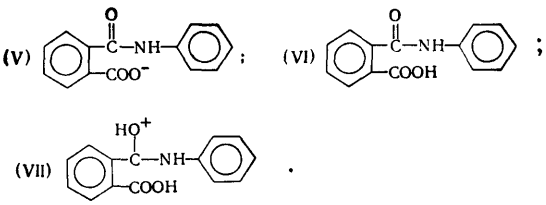


Figure 16. Dependence of effective hydrolysis rate constant k_{eff} of phthalanilic acid (at 25°C) on the acidity function H_A. The forms of the acid predominating on the various sections of the curve are



Quite detailed studies have now been made of the breakdown in acid and alkaline media of amide and imide [105-118], ether and ester [119-124], acetal [125-128], glycosidic [129-135], and siloxane [136,137] bonds. Fig. 16 illustrates the variation of $\lg k_{eff}$ with the acidity function H_A for the hydrolysis of phthalanilic acid as a model of non-cyclised units in polymers. The complexity of the dependence is explained by a mechanism in which unreactive forms are produced by protonation of the carbonyl oxygen of the amide bonds and by dissociation of the carboxy-group. The unionised form is reactive, able to react either with a carboxy-group (intramolecular catalysis along the segment H_A = 4–1) or with an oxonium ion (specific acid catalysis in more acidic solutions)¶.

Mechanisms of the hydrolytic degradation of various bonds have been surveyed [103,104]. Two types of decomposition—random and depolymerisation—can occur in polymer molecules. In the first type all hydrolytically unstable bonds are equally reactive, so that there should be no difference between a polymer and its simple analogue. In depolymerisation the effective rate constant depends on the molecular weight. In practice the two types of decomposition generally occur together [125-128].

Thus the hydrolytic degradation of polymers under homogeneous conditions can be characterised by a few true rate constants depending on the type and character of the decomposition [103,104]. In order to establish the mechanism of the degradation of polymeric materials in active media,

§ Polymers containing fluorine constitute an exception.

¶ A result of practical importance is the enhancement of the stability of amides in concentrated acids.

however, we must know how the medium diffuses in the polymer and the degree of dissociation of the electrolyte into ions [138-151]. In polymers that dissolve readily in water, e.g. poly(vinyl alcohol) (solubility 80% by mass), acids migrate with diffusion coefficients closely similar to those in aqueous solutions [144-147]. Selective sorption of electrolyte and water is observed in moderately soluble polymers, e.g. ethylcellulose (solubility 2% by mass). Fig. 17 shows the variation in the concentrations of water and hydrogen chloride during the diffusion of the vapour from 28% hydrochloric acid in ethylcellulose films at 45 °C. The active medium diffuses on a single front, but the concentration ratio of water and hydrogen chloride in the polymer is approximately ten times the ratio for the gaseous phase [150].

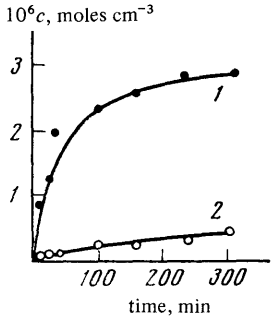


Figure 17. Variation in concentration during the diffusion of the vapour of 28% hydrochloric acid into an ethylcellulose film at 45 °C: 1) H_2O; 2) HCl.

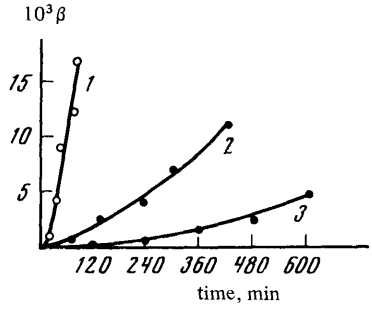


Figure 18. Time variation of degree of conversion β of ester bonds during degradation, in 53% sulphuric acid at 116 °C, of poly(ethylene terephthalate) films varying in thickness (μm): 1) 5 ± 1; 2) 20 ± 2; 3) 80 ± 5.

Water and sulphuric acid diffuse at significantly different rates in sparingly water-soluble polymers, e.g. poly(ethylene terephthalate): the diffusion coefficient of water exceeds that of sulphuric acid by a factor of 10^5. [118,124] In the chemical degradation of polymers the rate of diffusion of the active medium is frequently comparable with the rate of the chemical reaction, and degradation takes place within a reaction zone whose size increases with time, ultimately reaching the size of the article. Fig. 18 illustrates the time dependence of the degree of conversion of ester bonds during the degradation of poly(ethylene terephthalate) films in 53% sulphuric acid at 116 °C. [118,120,121] With a thin film (5 μm) the rate is constant after 30 min, since the acid has saturated the polymer. With films 20 and 80 μm thick the rate increases with time, as the quantity of acid in the films increases. The equations obtained kinetically permit quantitative prediction of the chemical stability of poly(ethylene terephthalate) over wide ranges of acid concentration, temperature, and time [118,120,121].

A correct interpretation of kinetic data for structurally non-uniform polymer materials requires information on the accessibility of functional groups. Hydrogen–deuterium exchange provides a convenient method for determining such accessibility in polymers having mobile hydrogen atoms [138-143]. The accessibility of amide bonds in polyhexanamide, for example, is a function of temperature (Fig. 19): at 150 °C all such bonds, including those in crystalline regions, are accessible to hydrogen–deuterium exchange.

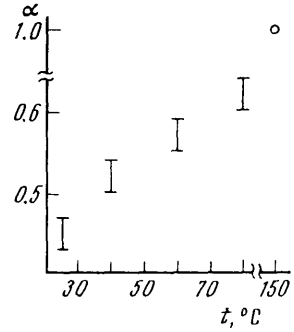


Figure 19. Temperature dependence of accessibility α of amide bonds in polyhexanamide films.

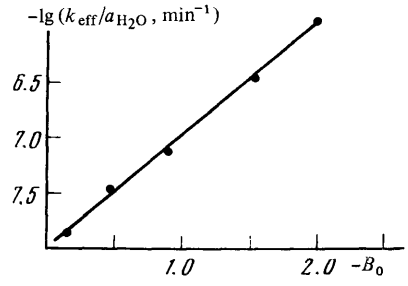


Figure 20. Dependence of $\lg(k_{eff}/a_{H_2O})$ on alkalinity function B_0 of aqueous potassium hydroxide for the degradation of poly(ethylene terephthalate) films 68 ± 2 μm thick.

In concentrated solutions the rate of chemical reaction far exceeds the rate of diffusion of molecules of the active medium into the polymer, and degradation takes place in a thin surface layer. An example is the breakdown of poly(ethylene terephthalate) film in aqueous alkalis [118,122,123].

The reaction is zero order with respect to the polymer, and the absence from the infrared multiple diffuse total internal reflection spectra of absorption bands due to decomposition products suggests that the depth of reaction approximates to a monolayer. Degradation of this type is characterised by two laws: (i) the effective rate constant is simply related to the thermodynamic parameters—the activity of water and the alkalinity function—of the aggressive medium (Fig. 20); and (ii) degree of crystallinity and orientation have hardly any effect on the kinetic parameters.

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The results discussed above, obtained from kinetic studies of various types of polymer degradation (thermal, thermo-oxidative, photo-oxidative, and hydrolytic), apply to polymers in an unstressed state. This covers by no means all the degradation processes encountered in practice. Development of a theory of the degradation of polymeric materials in a stressed state is an urgent task of the science of polymer degradation.

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