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Chemical Degradation of Polymers in Corrosive Liquid Media

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The physicochemical foundations of the degradation of polymeric materials in corrosive liquid media are examined and the characteristics of the polymer degradation processes, the mechanisms of reactions of chemically unstable bonds, and the principal types of decomposition of polymeric molecules as well as the characteristics of the diffusion of corrosive media into polymeric materials are discussed. Kinetic equations have been obtained for the principal types of chemical degradation of polymeric materials under heterogeneous conditions.
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I. INTRODUCTION

As a result of the wide-scale application of polymers in the chemical and petrochemical industries, in medicine, in the building industry, and in various branches of modern engineering, much attention has been devoted to their degradation processes in corrosive media. In many instances these processes are undesirable, because they lead to loss of valuable practical properties of polymeric articles. In other cases they are used for numerous chemical transformations, the etching of polymers, the dissipation of polymers in living organisms, etc.

The problems of the chemical stability of polymers have been the subject of numerous investigations, but the latter have not as a rule involved a theoretical analysis of the experimental data and are in many instances empirical in nature. The inadequacy of the theoretical studies in the field of chemical degradation of polymers and the availability of a large amount of experimental data make it necessary to discover quantitative relations in the first place.

Corrosive media can be divided into two groups in terms of the type of their action[1,2]:

1. Physically corrosive media giving rise to reversible changes in the polymer.

2. Chemically corrosive media (acid–base and oxidative) under the influence of which the polymer undergoes irreversible changes†.

Naturally, certain media (for example many organic acids) can behave simultaneously as both physically and chemically corrosive media.

Concepts such as chemical ageing, corrosion, chemical degradation, and longevity of the material are nowadays used in the literature and in standards[2] to characterise the decomposition of polymeric materials under the influence of corrosive media.

The term "ageing" was taken from biology and is widely applied in science and engineering. The ageing of polymers is understood as the set of physical and chemical processes occurring in the polymer in corrosive media and giving rise to changes in the properties of polymeric materials. These changes usually lead to the impairment of the practical properties of the polymer.

The term "corrosion" was borrowed from metals science; chemical corrosion of metals is understood as the interaction of the metallic surface with the surrounding corrosive medium. The decomposition of polymeric materials in corrosive media usually occurs in a reaction zone the size of which may vary from several monolayers to the entire bulk of the polymeric article. Therefore the term "corrosion" as applied to polymers is too narrow and cannot be recommended.

Chemical degradation is usually understood as all the processes leading to a change in the chemical structure of polymeric materials. Thus chemical degradation constitutes the set of the following chemical processes occurring in the polymer in corrosive media and altering its molecular weight:

(a) depolymerisation—the abstraction of the monomer from the end of the macromolecule;

(b) polymer-analogue decomposition of the monomer—the abstraction of a group of atoms from the macromolecule with retention of the initial degree of polymerisation;

(c) decomposition of the main chain leading to a decrease of the degree of polymerisation;

(d) cross-linking—reactions involving the formation of chemical bonds between the macromolecules and leading to the appearance of branched and network structures.

The chemical degradation of polymers under the influence of oxidants is a complex process including, as a rule, radical, molecular, and ionic chemical reactions; degradation under the influence of acids and bases consists largely of hydrolytic, solvolytic, or abstraction reactions.

The criteria of the chemical resistance of polymeric materials to the action of corrosive media have been defined in a number of standards[2]. Longevity should be understood as the period during which the properties of the polymeric material change under particular conditions of its employment to the level specified in the technical documentation.

The study of the kinetics of chemical degradation is extremely difficult both as regards the determination of

† Biochemical media are also included here.

correct experimental data and the determination of the kinetic parameters of the individual fundamental steps. For a successful solution of this problem, it is necessary to discover in the first place whether the chemical degradation process can be resolved into a series of simpler processes (for example diffusion of the corrosive medium into the polymer and chemical reaction of the functional groups) in order to investigate them separately; secondly, one must find out to what extent these processes can be simulated using low-molecular-weight analogues. Such simulation is necessary, because one cannot always separate the chemical reaction step from diffusion phenomena and, furthermore, it is always interesting to compare the calculated kinetic and diffusion parameters of the chemical degradation process with the corresponding parameters of model processes.

The aim of the present review is to examine the physicochemical foundations of the degradation of polymeric materials in corrosive media, whereby one can characterise the chemical degradation process in terms of kinetic and diffusion parameters and to predict the chemical stability of polymeric materials under the conditions of their employment. We do not aim to quote all the known facts and data concerning the chemical degradation of polymers. An attempt has been made in the review to examine at a quantitative level the degradation processes of polymeric materials in corrosive media. The review deals mainly with the degradation of polymers under the influence of acids and bases, which is most frequently encountered in practice.

II. THE CHARACTERISTICS OF POLYMER DEGRADATION PROCESSES

Flory [3] formulated the main principles of the independence of the reactivities of the functional groups in oligomers and polymers of molecular weight for various types of reactions. The functional groups in the polymer must have the same reactivities as in a low-molecular-weight model compound when the following conditions are observed:

(a) the reaction proceeds in a homogeneous medium in which the initial reactants and products are soluble;

(b) one type of functional group of the polymer is involved in each fundamental step, and the molecules of all the remaining reactants are small and fairly mobile;

(c) the low-molecular-weight analogue is chosen taking into account the steric hindrance which may arise when the conformation of the macromolecule changes during the reaction.

Alfrey [4] noted that identical reactivities of the functional groups in the polymer and in the low-molecular-weight analogue may be observed even if one of the above conditions does not hold.

However, many instances are now known where the reactivities of various groups in the polymer are anomalous owing to the specific influence of the polymeric state [5-7]. We shall consider for simplicity the homogenous catalytic degradation of a polymer via the following mechanism:

$$\sim R + Cat \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sim X; \qquad (I)$$

$$\sim X + R' \xrightarrow{k_3} P + Cat, \qquad (II)$$

where R is a functional group in the polymer, Cat the catalyst, X an intermediate state, R′ a reactant (for example H_2O in hydrolysis), and P the reaction product.

The viscosity of polymer solutions may be several orders of magnitude greater than that of solutions of low-molecular-weight analogues; furthermore, the functional groups in polymers are as a rule distributed close to one another. Therefore, in comparing the reactivities of the group R in the polymer and in the low-molecular-weight analogue (chosen taking into account the steric hindrance arising during the change in the conformation of the macromolecule during the reaction), one must elucidate the influence of the macroviscosity of the solution and of the interaction of the functional groups on the degradation reactions (I) and (II).

1. A QUANTITATIVE ESTIMATE OF THE INFLUENCE OF THE MACROVISCOSITY OF THE SOLUTION ON THE DEGRADATION KINETICS

The influence of the macroviscosity of the solution on the kinetics of the degradation of small molecules has already been examined [8-10]. If, for example, the rate of the reaction of R with Cat is high compared with the rate diffusion of Cat to R, then the concentration of Cat in the immediate vicinity of R may be reduced, which creates a concentration gradient causing a diffusional flux of the species directed towards R. In the steady state the velocity of this flux becomes equal to the rate of the reaction of R with Cat. According to Plate [6], we obtain

$$k_{eff} = \frac{4\pi\rho D k_{true} \cdot \beta}{k_{true} + 4\pi\rho D\beta}, \qquad (1)$$

where $k$eff and $k$true are respectively the effective and true rate constants, ρ is the distance between the centres of the reacting species, β a proportionality coefficient having the dimension molecule^{-1}, and D the diffusion coefficient of Cat or the reactant R′ in the medium. One should note that, even when the functional group in the polymer completely lacks mobility, the frequency of the collisions of R with Cat does not change significantly.

Conditions governing the reaction in kinetic or diffusion regions can be readily obtained from Eqn.(1):

when $k\text{true} \ll 4\pi\rho D\beta$, $k\text{eff} = k\text{true}$,

i.e. there is an equilibrium statistical distribution of the species in solution (the kinetic region of the reaction);

when $k\text{true} \gg 4\pi\rho D\beta$, $k\text{eff} = 4\pi\rho D\beta$,

i.e. there is a sharp breakdown of the equilibrium statistical distribution of the species in solution (diffusion region of the reaction).

At the usual temperatures in non-viscous media, we have $D\text{cat} \simeq 10^{-6}-10^{-5}$ cm^2 s^{-1} (Table 1) and the values of ρ for typical functional groups and catalysts amount to seversl angstroms. Consequently, $4\pi\rho D\beta \simeq 10^{-12}-10^{-11}$ cm^3 mol.$^{-1}$ s^{-1} or 10^9-10^{10} litre mole^{-1} s^{-1}. Thus reactions with $k\text{true} > 10^8$ litre mole^{-1} s^{-1} occur in the diffusion region. The reactions of the proton, the hydroxide, ion [9], and enzymes [10] with the functional groups of the reactants, i.e. stage (1) of the polymer degradation process, do in fact occur in this region.

The rate of reactions with $k\text{true} < 10^8$ litre mole^{-1} s^{-1} is not limited by diffusion and such reactions occur in the kinetic region. These include the decomposition of the ionised forms of the functional groups and of the majority of enzyme–substrate complexes involving the formation of the reaction products [stage (II) of the polymer degradation process]. In the majority of cases the rate of this

stage limits rate of the entire degradation process. On passing to viscous systems, ρ hardly changes, while D decreases with increase of the viscosity of the system. For example, D changes with increase of the viscosity of electrolyte solutions in accordance with the equation [11]

$$D = D_0\left(\frac{\eta_0}{\eta}\right)\left(1-\frac{e^3q}{4\epsilon kT}\right), \qquad (2)$$

where D_0 and η_0 are the diffusion coefficient and the viscosity at infinite dilution respectively, e is the electronic charge, ϵ the dielectric constant of the medium, q a variable quantity which depends on the electrolyte concentration, and k the Boltzmann constant.

Table 1. Diffusion coefficients of acids in water.

Catalyst	$10^6D_{25°}$, $cm^2\ s^{-1}$	References
HCl	30.0	13
H_2SO_4	12.0	11
H_3PO_4	8.7	14

It is noteworthy that Eqn.(2) is inapplicable to very viscous media. In solid polymers, $D_{250} \simeq 10^{-9}-10^{-8}$ $cm^2\ s^{-1}$ for water [12] and $4\pi\rho D\beta \simeq 10^5-10^6$ litre $mole^{-1}\ s^{-1}$. These data lead to the conclusion that, even in very viscous media (solid polymers), the rate of state (II) is not limited by diffusion, i.e. this stage occurs in the kinetic region (we have in view a microkinetic treatment in contrast to a macrokinetic treatment, to which the last part of the review is devoted).

Thus the macroviscosity of the reaction medium influences significantly the rate of reaction between catalysts and the functional groups of the reactants and has almost no effect of the decomposition of the complexes of the functional groups with catalysts, resulting in the formation of products. On the other hand, in most cases the latter reaction in fact constitutes the rate-limiting stage of the entire degradation process.

2. A QUANTITATIVE ESTIMATE OF THE INFLUENCE OF THE INTERACTION OF FUNCTIONAL GROUPS ON THEIR REACTIVITY IN THE POLYMER

If the functional groups in the polymeric molecules are distributed at distances which virtually rule out their mutual influence, then the kinetic parameters of the degradation reactions of polymers and their low-molecular-weight analogues are similar, i.e. the principle of independence of reactivity of molecular weight is valid. Table 2 lists the kinetic parameters for the degradation of polymers and their low-molecular-weight analogues; within the limits of experimental error, these parameters are similar. It is interesting to note that the reactivity ($k$eff) of acrylic polymers in the H–D exchange reaction is approximately two orders of magnitude lower than that of the corresponding low-molecular-weight analogues (Table 3); according to Scarpa et al. [21], this is due to the decrease of the dissociation constant of water near amide groups relative to the solution.

However, functional groups are frequently distributed close to one another (at distances <10 Å) and this is in fact the cause of the anomalous reactivity of the functional groups in polymers. The following types of the anomalous reactivity of the functional groups in polymers have been distinguished: (a) the effect of an adjoining group which may be either of the long-range type (the "chain effect") or of the short-range type (i.e. the influence of groups located in the immediate vicinity of the given functional group); (b) conformational effects—effects due to the change in reactivity caused by the changes in the form of the macromolecule in the given reaction medium or in the course of the reaction.

Table 2. Kinetic parameters of the degradation reactions of polymers and their low-molecular-weight analogues.

Polymer and its low-molecular-weight analogue	Solvent-catalyst	$k_{true}(25°)$, s^{-1}	E, kcal $mole^{-1}$	$\lg A^*$ (s^{-1})	References
Polycaproamide	$H_2O-H_2SO_4$	$8.3\cdot10^{-8}$	20±1	7.2	15
Cyclic caprolactam trimer		$8.3\cdot10^{-8}$	20±1	7.4	
Cellulose	H_2O—HCl	$1.1\cdot10^{-8}$	30±1	14.2	16
	$H_2O-H_2SO_4$				
	$H_2O-HClO_4$	$1.6\cdot10^{-8}$	30±1	14.0	
Cellobiose	$H_2O-H_3PO_4$				
Poly-*NN*-diethylacrylamide	H_2O— buffer	$2.5\cdot10^{-7}$	22.0	9.5	17
		$(3.1\cdot10^{-9})$	(24.6)	(9.5)	
NN-Diethylisobutyramide		$2.0\cdot10^{-7}$	21.7	9.1	(18)
		$(8.0\cdot10^{-9})$	(23.7)	(9.5)	
Polyacrylamide	»	$2.0\cdot10^{-5}$	14.2	5.6	19
Isobutyramide		$2.0\cdot10^{-5}$	14.2	5.6	
Poly-*N*-vinyl-2-pyrrolidinone	»	$3.1\cdot10^{-7}$	25±1	11.7	20
N-Isopropyl-5-methyl-2-pyrrolidinone		$4.0\cdot10^{-8}$	27±0.5	12.3	

*A = pre-exponential factor.

Table 3. Kinetics parameters of the H–D exchange reaction in polymers and their low-molecular-weight analogues.

Polymer and its low-molecular-weight analogue	Solvent-catalyst	$k^*_{true}(25°)$, s^{-1}	E, kcal $mole^{-1}$	$\lg A$ (s^{-1})	Refs.
Polyisopropylpropionamide	D_2O—DCl	$5.0\cdot10^{-5}$	20.0	10.3	21
N-Isopropylpropionamide	D_2O—KOD	$2.5\cdot10^{-3}$	20.0	12.0	
Poly-*N*-aminomethacryloyl-L-lysine	—	$6.6\cdot10^{-5}$	19.0	9.8	22
ε-Aminoisobutyryl-L-lysine		$2.5\cdot10^{-3}$	16.0	9.1	
Polymethylpropionamide	—	$4.0\cdot10^{-4}$	18.0	9.7	23
N-Methylacetamide		$1.0\cdot10^{-2}$	17.0	10.4	

*The rate constant at the minimum in the relation between $\lg k_{eff}$ and pD.

These effects can probably be accounted for by polar, resonance, and steric effects [24], which are well known in organic chemistry, just as the mechanism of the hydrolytic action of chymotrypsin has been explained with the aid of explicit chemical analogues [25].

a. The Long-range Effects of Neighbours of the Group

As a rule, this effect is illustrated by comparing the reactivities of monomers having a system of conjugated double bonds and of a model compound having a single double bond. We shall consider the manifestation of the

chain effect in the dehydrochlorination of poly(vinyl chloride) (PVC) at high temperatures. The dehydrochlorination process is known to occur in steps, the double bonds formed activating the next dehydrochlorination step (allylic activation). An attempt has been made [26] to subdivide the complex dehydrochlorination process into two reactions: (1) the random formation of isolated double bonds and (2) the growth of the system of conjugated bonds as a result of allylic activation.

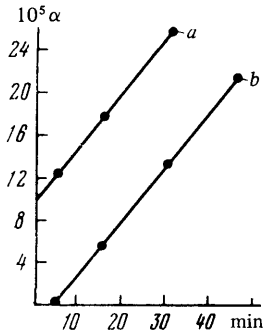


Figure 1. The rate of dehydrochlorination of PVC (*a*) and chlorinated PVC (*b*) at 175°C; α is the number of breaks per mole of the polymer [26].

Fig. 1 presents the rates of dehydrochlorination of PVC (a) and chlorinated PVC (b) at 175°C. Evidently the formation of isolated double bonds is independent of the nature of the PVC specimen and proceeds at the same rate ($k_1 = 8.6 \times 10^{-8}$ s^{-1}). In the general case the overall PVC dehydrochlorination process can be described by the following equation without taking into account the destruction of kinetic chains in the initial stages:

$$\frac{d[HCl]}{dt} = k_1 + k_2 X_t,$$

where $k_2 = (W_{PVC} - W_{CPVC})/X_0 = 9.3 \times 10^{-4}$ s^{-1}, W_{PVC} and W_{CPVC} are the rates of dehydrochlorination of PVC and chlorinated PVC respectively, and X_0 and X_t are respectively the numbers of double bonds in PVC at the initial instant and at time t.

Table 4. Kinetic parameters of the dehydrochlorination reaction of model compounds for PVC in the gas phase [27].

Model compound	Temp. range, °C	$10^{11}k_{117°}$, s^{-1}	E, kcal mole^{-1}	lg A
2-Chlorobutane	347—394	3.6	49	13
2,4-Dichloropentane	347—397	3.3	49	13
2,4,6-Trichloroheptane	346—386	3.4	51	14
4-Chloropent-2-ene	296—345	859	41	12
6-Chlorohepta-2,4-diene	302—347	45 900	35	10
3-Chloropent-1-ene	319—380	8.9	51	15

It is interesting to compare the constants obtained with the results [27] for compounds simulating PVC (Table 4).

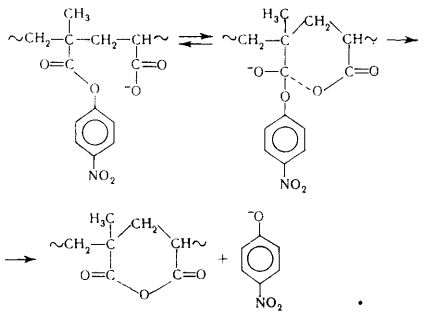
The presence of a double bond at the end of the macromolecule does not have an appreciable influence on the dehydrochlorination reaction (3-chloropent-1-ene); the double bond in the 2- or 4-position greatly accelerates the dehydrochlorination reaction and 4-chloropent-2-ene and particularly 6-chlorohepta-2,4-diene can simulate the allylic activation effect. It is noteworthy that the rate constant for the dehydrochlorination of the latter compound is 10^4 times higher than the rate constant for alkyl chlorides.

Thus the formation of isolated double bonds and the growth of the system of conjugated bonds as a result of allylic activation can be simulated by the dehydrochlorination reactions of alkyl chlorides and 6-chlorohepta-2,4-diene respectively.

b. The Short-range Effect of a Neighbouring Group

Effects of this type occur when the substituent adjoining the given functional group favours or hinders the formation of the activated complex.

For example, the hydrolysis of the copolymer of acrylic acid and *p*-nitrophenyl methacrylate proceeds more readily than that of *p*-nitrophenyl acetate, since in the former case a six-membered activated complex is formed easily following the attack by the carboxylate ion on the ester linkage [28]:



(III)

At 0°C and pH 6 the rate constants for the intramolecular (copolymer of acrylic acid and *p*-nitrophenyl methacrylate) and intramolecular (*p*-nitrophenyl acetate or acetate ion) hydrolysis are respectively 2×10^{-3} s^{-1} and 6.5×10^{-7} litre mole^{-1} s^{-1}.

The question of the influence of neighbouring groups on the given functional group has been examined theoretically [29-35]. Functional groups of three types may be present in a polymeric molecule under the conditions of a low degree of conversion:

1) groups whose nearest neighbours have not reacted;
2) groups having one neighbour which has reacted;
3) groups having two neighbours which have reacted.

The rates of reaction of functional groups under the conditions of an excess concentration of the catalyst are defined by the equation

$$-\frac{dx}{dt} = k_0 N_0 + k_1 N_1 + k_2 N_2,$$

where k_0, k_1, and k_2 are respectively the rate constants for reactions of type 1, 2, and 3 functional groups and N_0, N_1, and N_2 are the mole fractions of the corresponding types of functional groups. The solution of the system of the corresponding differential equations relating the change in N_n of a sequence of n groups which have reacted to the corresponding concentrations of functional groups

of different types, the rate constants, and time leads to the following expressions [29]:

$$N_0 = \exp\left\{-\left(2\frac{k_1}{k_0}+1\right)k_0t - 2\left(\frac{k_1}{k_0}-1\right)[(\exp -k_0t)-1]\right\};$$

$$N_1 = [\exp k_0t - 1]\exp\left\{-\left(2\frac{k_1}{k_0}+1\right)k_0t - 2\left(\frac{k_1}{k_0}-1\right)[(\exp -k_0t)-1]\right\}.$$

The solution for N_2 is complex: for example, when $k_1/k_0 = 1$, we have

$$N_2 = \frac{2}{\left(\frac{k_2}{k_0}-2\right)\left(\frac{k_2}{k_0}-3\right)}\left[\left(\frac{k_2}{k_0}-3\right)\exp(-2k_0t) - \left(\frac{k_2}{k_0}-2\right)\exp(-3k_0t) + \exp(-k_2t)\right].$$

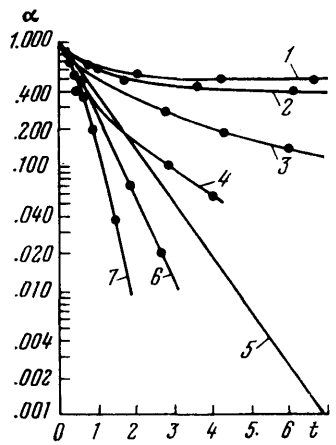


Figure 2. Variation of the degree of conversion of the functional groups in the polymer with time for different reaction rate constants [31]; respective values of the rate constants k_0, k_1, and k_2: 1) 1.0, 4×10^{-2}, 4×10^{-4}; 2) 1.0, 0.2, 1×10^{-2}; 3) 1.0, 0.5, 0.2; 4) 1.0, 1.8, 0.5; 5) 1.0, 1.0, 1.0; 6) 1.0, 1.8, 1.5; 7) 1.0, 2.0, 5.0.

Fig. 2 illustrates the variation of the degree of conversion of the functional groups in the polymer with time for different reaction rate constants obtained by Arends [31]:

$k_0 = k_1 = k_2$ (linear relation),
$k_0 = 1$, $k_1 < 1$, $k_2 < 1$ (self-inhibition),
$k_0 = 1$, $k_1 > 1$, $k_2 > 1$ (self-acceleration).

The second case, where the degradation process does not reach completion owing to self-inhibition, i.e. there is a certain limiting degree of conversion, is encountered most frequently. A statistical approach to the solution of this problem has been adopted [31-33].

The limiting degrees of conversion of functional groups in the polymer (α) for different ratios k_0/k_1 are listed below [35]:

α	0.667	0.632	0.606	0.600	0.586	0.577	0.50
$\frac{k_1}{k_0}$	1	0.5	0.25	0.20	0.10	0.05	0.01

The kinetics of the alkaline hydrolysis of polyacrylamide have been thoroughly investigated in the same study [35]. In order to describe the experimental data, the authors made the mechanism more involved by assuming that the carboxylate group formed can influence not only the neighbouring group but also the next amide group.

They quote the following data for the influence of the carboxylate groups on the reactivity of the amide linkages in the alkaline hydrolysis of polyacrylamide at 60°C: [35]

	—A—A—A—	—A—A—C—A—A—	—C—A—A—C	—C—A—C—
10^4k, litre mole^{-1} s^{-1}	10.8	3	2	0.05
$\Delta G^{\neq}$, kcal mole^{-1}	0	0.7	1.0	3.0

A = amide group, C = carboxylate group

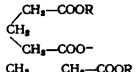
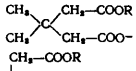
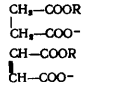
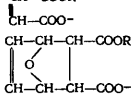
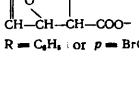
The increase of the free energy of activation owing to the influence of the neighbouring carboxylate groups was determined from the formula

$$\Delta G = \frac{e^2R}{\varepsilon \cdot \bar{r} \cdot k},$$

where R is the gas content and $\bar{r}$ the average distance between the amide linkage and the carboxylate group, assumed to be 3.5 Å.

When the effect of a neighbouring group is considered, it is important to discover (a) what changes in the reactivity of the given functional group may be expected as a result of its approach to the neighbouring functional group, and (b) the mechanism of the action of the neighbouring functional groups. We shall consider as an example the intramolecular alkaline hydrolysis of monophenyl esters of dicarboxylic acids [36,37].

Table 5. The influence of structure on the reactivity of monophenyl esters of dicarboxylic acids in the intramolecular hydrolytic reaction in an alkaline medium [36,37].

No.	Reactants	Relative rate constant
I		1.0
II		20
III		230
IV		10 000
V	 R = C_6H_5 or p = BrC_6H_4	53 000

The data presented in Table 5 show that the bicyclic compound (V) reacts 53 times faster than monophenyl glutarate (I), i.e. in a series of low-molecular-weight compounds it is possible to attain greater differences between reactivities than in the example quoted above.

The intramolecular reactions cannot be accelerated by the following factors [38,39]:

(a) A local increase of the concentration of reactant near the bond being hydrolysed during the intramolecular reaction. For example, the effective concentration of carboxylate groups near the ester linkage in the hydrolysis of the copolymer of acrylic acid and p-nitrophenyl methacrylate may be estimated from the ratio $k$intramol./$k$intermol.. It amounts to 3×10^3 mole litre^{-1}, which is much larger than the concentrations actually reached.

(b) A favourable mutual orientation of the reacting groups, since the kinetic differences between the intramolecular and intermolecular reactions cannot be reduced to the entropy effect alone.

Changes in solvation can make a considerable contribution to the acceleration of certain intramolecular reactions (including "polymerisation" reactions). For the formation of the activated complex via the intramolecular hydrolytic reaction of monophenyl esters of dicarboxylic acids, it is necessary that the water molecules hydrolysing the charged carboxylate group should be removed. Examination of molecular models shows that in the ester (V) this group cannot be hydrated by water on the side where the ester linkage is attacked. Therefore, during the above intramolecular reaction, energy is not required for the removal of water from the hydration shell.

It is also possible to draw the following analogy. The catalytic properties of the proton, expressed in terms of the acidity function, increase as water molecules are eliminated from its hydration shell. In non-aqueous solvents, for example acetic acid, nitromethane, and sulpholane, the acidity function is several orders of magnitude higher than in aqueous solution at the same sulphuric acid concentration[40]. These effects are probably the cause of the high rates of intramolecular reactions in both polymers and in their low-molecular-weight analogues.

c. Conformational Effects

Depending on the temperature and the composition of the solution, the macromolecules can exist in different conformations where the functional groups differ in reactivity. This is associated with the change in the relative disposition of the functional groups and in addition with their different accessibilities to the external reactant. This case obtains in the alkaline hydrolysis of polyacrylamide, where the formation of carboxylate groups leads to a transition of the macromolecule from the globular to the uncoiled form; unfortunately a kinetic assessment of this effect has not been made. Similar effects are characteristic of polymeric molecules with a pronounced secondary structure (polypeptides, polyorganosiloxanes, etc.).

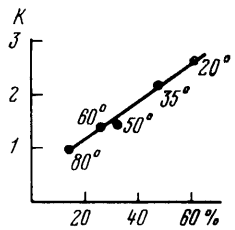


Figure 3. Variation of the ratio of the rate constants for the $^1H \rightarrow {}^3H$ exchange reaction involving AMP and poly-A with the fraction of bases in poly-A participating in the stacking interaction[41].

The $^1H \rightarrow {}^3H$ exchange reaction has been investigated in polyriboadenylic acid (poly-A) and its low-molecular-weight fragment—adenosine 5-monophosphate (AMP)—at pH 7.1.[41] In neutral solutions below 0°C, the poly-A molecules have the conformation of rigid rods consisting of helices of the same type. The stabilisation of these helices is determined primarily by the stacking interaction via the π electrons of the purine rings and hydrogen bonds. With increase of temperature, the interaction between the bases weakens and the polymer molecules become more labile. The AMP molecules retain their structure at all temperatures.

Fig. 3 illustrates the variation of the ratio K of the rate constants for the $^1H \rightarrow {}^3H$ exchange reaction involving AMP and poly-A with the fraction of the bases in poly-A participating in the stacking interaction. The latter quantity was determined by an independent procedure. The observed proportionality between K and the fraction can be regarded as evidence that the stacking interaction causes the retardation of the exchange of hydrogen atoms in the C—H bonds of the adenyl residues.

Thus the anomalous reactivity of "polymeric" functional groups, caused by the primary structure (the short- and long-range effects of the neighbouring group), can probably be determined and simulated with the aid of low-molecular-weight analogues. The anomalous reactivity caused by the secondary structure (conformational effects) is specific to the polymeric state.

III. THE MECHANISMS OF REACTIONS OF CHEMICALLY UNSTABLE BONDS OF VARIOUS POLYMERS IN CORROSIVE MEDIA

Solutions of acids and bases catalyse chemical degradation reactions of monomers. By the mechanism of the catalytic action of acids and bases, we mean the set of data concerning the equilibrium between the ionised and unionised forms of the substance in the reaction medium and the mechanism of the slow fundamental stages limiting the rate of the process.

1. THE MEASURE OF THE CATALYTIC EFFECT OF CORROSIVE MEDIA

The catalytic effect of acids and bases is usually estimated in terms of the capacity of the medium to behave as a donor of protons or hydroxyls. In dilute aqueous solutions of acids and bases, the pH may serve as a quantitative measure of the catalytic effect. However, at electrolyte concentrations in excess of 0.1 M the deviation from ideal solutions becomes appreciable, so that a rigorous quantitative determination of the activity of the proton or the hydroxyl becomes impossible. Hammett[42] proposed an empirical approach to the determination of the acidity of solutions of acids with the aid of indicators.

For the protolytic equilibrium

$$In + H^+ \rightleftarrows InH^+,$$

the dissociation constant of the conjugate acid of the indicator InH^+ can be expressed as follows:

$$K_{InH^+} = \frac{a_{H^+} f_{In}}{f_{InH^+}} \cdot \frac{c_{In}}{c_{InH^+}},$$

where a is the activity, f the activity coefficient, and c the concentration. The concentrations of the ionised and

unionised forms of the indicator are determined spectrophotometrically. Knowing K_{InH^+}, the quantity

$$h_x = a_{H^+}\frac{f_{In}}{f_{InH^+}}, \quad (3)$$

called the acidity of the medium, can be calculated. By analogy with pH, the acidity function is $H_X = ph_X$. More than ten acidity functions, defined with the aid of different classes of indicators, are now known and according to Hammett none of them have any advantages over the others[43].

Thus, since the acidity is determined not only by the capacity of the medium to give up protons but also by the capacity of the indicators to combine with protons, the absolute acidity of the medium cannot be determined by the indicator method, although definite progress has been made in this field during recent years.

Yates et al.[44] calculated a_{H^+} for aqueous solutions of sulphuric and perchloric acids by Eqn.(3) and the activity coefficients were determined by the solubility method. The values of a_{H^+} thus obtained agree with the results determined by electrochemical methods using the ferrocene–ferrocenium system as the reference electrode. Several alkalinity functions are also known for solutions of bases[45,46].

2. CLASSIFICATION OF THE MECHANISMS OF HYDROLYSIS

The mechanisms of the hydrolysis of various compounds have been classified by Ingold[47] on the basis of two main features:

1. Type of catalysis (A—acid, B—base).
2. The molecularity of the rate-limiting stage.

We shall consider the principal relations for uni- and bi-molecular processes.

A. The Unimolecular Mechanism

Consider a reaction via the mechanism

$$R + Cat \overset{K_X}{\rightleftarrows} X;$$

$$X \rightleftarrows M^{\neq} \xrightarrow{k_{true}} P + Cat,$$

where $M^{\neq}$ is the activated complex. The rate of reaction can be formulated as follows:

$$W = k_{eff}c_0 = k_{true}\cdot\frac{a_{\neq}}{f^{\neq}} = k_{true}\,c_X\,\frac{f_X}{f^{\neq}}.$$

Taking into account the equilibrium constant for the formation of X and assuming that X is the Arrhenius complex and that the rate of decomposition of the complex into the catalyst and the substrate is higher than the rate of formation of the reaction product, we obtain

$$c_R = \frac{K_X c_X}{a_{Cat}}\cdot\frac{f_X}{f_R}.$$

Taking into account the material balance equation

$$c_0 = c_R + c_X,$$

we find the general equation for the unimolecular process:

$$k_{eff} = \frac{k_{true}\cdot\dfrac{f_X}{f^{\neq}}}{1+\dfrac{K_X f_X}{a_{Cat}\,f_R}}. \quad (4)$$

If the mechanism of the ionisation of the substrate is known, then, using Hammett's postulate

$$\frac{f_X}{f_R} = \frac{f_{X'}}{f_{In}} = \text{const}$$

we introduce into Eqn.(4) the corresponding acidity or alkalinity. Furthermore, the complex X and the activated complex usually have the same composition, charge, and structure, i.e. $f_X/f^{\neq} = \text{const.}$, which greatly simplifies Eqn.(4):

$$k_{eff} = \frac{k_{true}}{1+\dfrac{K_X}{h_X}}. \quad (5)$$

The values of c_X have now been determined by independent methods in a number of studies[48] and the validity of Eqn. (5) has been demonstrated.

B. The Bimolecular Mechanism

In reactions involving a bimolecular mechanism, the activated complex includes the reactant, the catalyst, and, in hydrolytic reactions, a water molecule. In some cases the activated complex is formed when X interacts with a water molecule and in others when the reactant interacts with the complex of the catalyst and a water molecule, for example the hydronium ion.

The rate of reaction can be defined by two identical equations:

$$W = k_{eff}\,c_0 = k_{true}\frac{a_{\neq}}{f^{\neq}} = \begin{cases} k_{true}\dfrac{a_R\cdot a_{Cat.H_2O}}{f^{\neq}} \\ k_{true}\dfrac{a_{R.Cat.}\cdot a_{H_2O}}{f^{\neq}} \end{cases}.$$

These equations cannot be solved in a general form, since there are as yet no reasonable quantitative methods for estimate $f^{\neq}$. However, there are many empirical approaches. We shall consider briefly some of them, assuming for simplicity that the concentration of R is much higher than of the complex X.

In Bunnett's approach[49], specific hydration numbers are assigned to all the species in the reaction medium. After formulating the equation

$$R\cdot(H_2O)_s + Cat\,(H_2O)_n \overset{K_X}{\rightleftarrows} X\,(H_2O)_p + (s+n-p)\cdot H_2O,$$

$$X\cdot(H_2O)_p + (H_2O)_r \rightleftarrows M^{\neq}(H_2O)_t \xrightarrow{k_{true}} \text{products},$$

and taking into account the indicator equilibrium

$$In\,(H_2O)_b + Cat\,(H_2O)_n \rightleftarrows In\cdot Cat\,(H_2O)_c + (b+n-c)\cdot H_2O,$$

we obtain

$$k_{eff} = \frac{k_{true}}{K_X}\cdot h_X\,\frac{f_{R(H_2O)_s}\cdot f_{In\,Cat(H_2O)_c}}{f^{\neq}_{M(H_2O)_t}\cdot f_{In(H_2O)_b}}\cdot a_{H_2O}^{(b-c)-(s-p)+r}. \quad (6)$$

Using Hammett's postulate and assuming that $f_{In\,Cat(H_2O)c}/f^{\neq}_{M(H_2O)t}$ is independent of the composition of the medium because the complex of the reactant and the catalyst (or of the indicator and the catalyst) and the activated complex have the same charge and similar structures, we obtain

$$k_{eff} = \frac{k_{true}}{K_X}\cdot h_x\cdot a^r_{H_2O}. \quad (7)$$

Bunnett treated in terms of this equation numerous data for the hydrolysis of various compounds[49]. However, Eqn.(7) is frequently inapplicable when the catalyst concentration range is fairly wide. Strictly speaking, one cannot assume that the ratio $f_{\text{In Cat}(H_2O)c}/f^{\neq}_{M(H_2O)t}$ is constant in Eqn.(6), because the two complexes should have different compositions (differ hydration numbers); however, the lack of knowledge of this ratio is compensated by an empirical parameter r, formally expressing the number of water molecules involved in the activated complex.

Vinnik's approach[50] consists in the hypothesis that an intermediate complex M (of R and H_3O^+) is formed in aqueous solutions of strong acids and decomposes unimolecularly into the reaction products. It is assumed that the activity coefficient ratio $f_M/f^{\neq}$ is constant and the activity coefficients of the activated complex and the complex M are given by the equation

$$f_M = f^{\neq} = f_R^{\beta} f_{H_3O^+}^{\alpha} \text{ const},$$

where α and β are parameters independent of the medium,

$$k_{\text{eff}} = \frac{k_{\text{true}}}{K_X} \cdot c_{H_3O} + f_R^{(1-\beta)} f_{H_3O^+}^{(1-\alpha)},$$

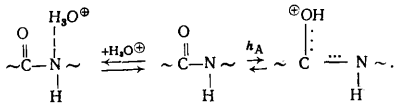
and f_R can be determined from solubility data. Thus the problem reduced to the determination of the parameters α and β alone.

In recent years Vinnik[51] formulated a general rule for the determination of the mechanism of the rate-limiting step in catalytic hydrolysis in aqueous solutions: the activity of the activated complex must be expressed in terms of the concentrations of different forms of the reactants in such a way that the multiplier involving the activity coefficients which appears in the kinetic equation does not vary with the concentration of the acid. Using extensive experimental data, Vinnik divided all the hydrolytic reactions in aqueous solutions of strong acids into four groups. In reactions of groups I and II, the activated complex is produced from the unionised form of the reactant, the hydronium ion, and the nucleophilic agent—water molecule (group I) or anion (group II). In the reactions of the other groups, the activated complex is produced from the protonated form of the reactant with or without the participation of a water molecule (group III) or with participation of the anion (group IV).

Thus, whereas a simple general equation, obtained within the framework of reasonable assumptions is available for unimolecular processes, such an equation does not exist for bimolecular processes and in each specific case additional information is necessary for the choice of the mechanism.

We shall consider the mechanisms of the decomposition of chemically unstable bonds in polymers.

The amide linkage. A characteristic feature of the hydrolytic reactions of compounds with an amide linkage in acid media is a maximum in the effective rate constant as a function of the concentration of the acid. Fig.4 illustrates the variation of $\lg k_{\text{eff},25^\circ}$ for the hydrolysis of the cyclic caproamide trimer (a polymer model) as a function of the amide acidity function of aqueous solutions of sulphuric acid H_A.[15,52] The values of $\lg k_{\text{eff},25^\circ}$ for the hydrolysis of the polymer with M_V = 20 000 lie almost on the same curve. According to the proposed mechanism, the rate-limiting step of the process is the attack by the hydronium ion on the amide nitrogen atom; the protonation of the carbonyl oxygen leads to the formation of the unreactive form:



The variation of k_{eff} with thermodynamic parameter is described satisfactorily by the equation

$$k_{\text{eff}} = \frac{k_{\text{true}}\, c_{H_3O^+}}{1 + \frac{h_A}{K_{BH^+}}}. \qquad (8)$$

The continuous line in Fig.4 was calculated theoretically from this equation.

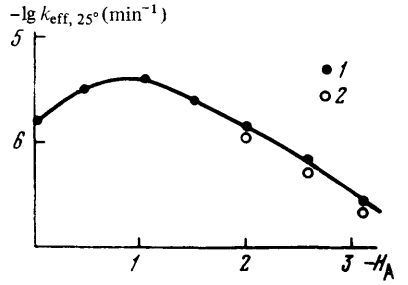


Figure 4. Variation of $\lg k_{\text{eff}},25^\circ$ for the hydrolysis of the cyclic caproamide trimer (1) and polycaproamide having $\bar{M}_V$ = 20 000 (2) with the amide acidity function of aqueous sulphuric acid solutions[15].

Thus the hydrolysis of compounds with an amide bond is described by the A-2 mechanism. Attention should be drawn to two facts of practical importance:

1. The hydrolytic stability of compounds with an amide linkage increases greatly in concentrated solutions of acids.

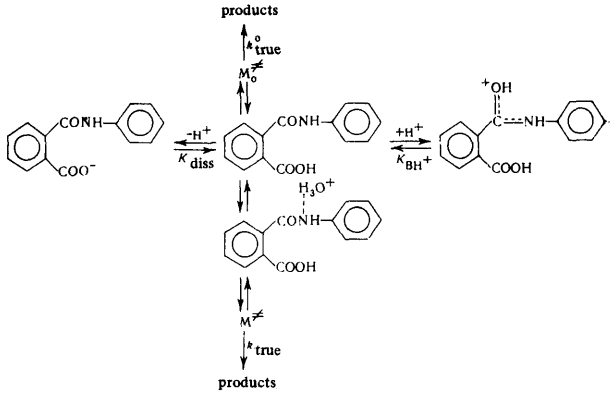
2. In polycaproamide the amide linkages are kinetically independent, since the five methylene groups completely prevent the transmission of the mutual polar influence of the amide linkages.

The study of the hydrolysis of o-substituted aromatic amides, simulating the non-cyclised units in heterocyclochain polymers, is of considerable interest. The presence of o-substituents is responsible for a number of characteristic features of the acid hydrolysis of these amides, namely the hydrolytic reaction may be accompanied by the cyclisation reaction and in dilute acid solutions intramolecular catalysis may occur.

Fig.5 illustrates the variation of $\lg k_{\text{eff}},25^\circ$ with H_A for the hydrolysis and cyclisation of 2-benzamidophenol and the hydrolysis of 2-phenylbenzoxazole—the model compounds for polybenzoxazole[53]. Kinetic analysis of the results showed that the variation of k_{eff} is described by Eqn.(8) for all three reactions.

Fig.6 presents kinetic data for the acid hydrolysis of N-phenylphthalamic acid—the model of aromatic polyamidoacids[54]. In order to interpret the experimental data, a mechanism was adopted according to which unreactive forms are produced on protonation of the

carbonyl oxygen of the amide linkage and on dissociation of the carboxy-group. The reactive species is the unionised form, which may react either with the carboxy-group (intramolecular catalysis) or with a hydronium ion (specific acid catalysis).



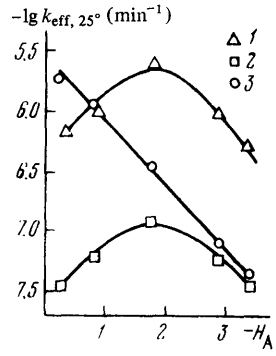


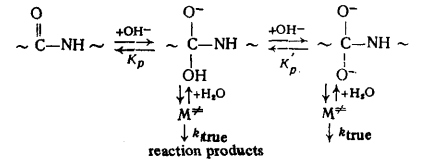
Figure 5. Variation of $\lg k_{eff}$ with the amide acidity function of aqueous sulphuric acid solution for the hydrolysis (1) and cyclisation (2) of 2-benzamidophenol and the hydrolysis of 2-phenylbenzoxazole (3).[53]

The general expression for k_{eff} is

$$k_{eff} = \frac{k_{true}\, c_{H_3O^+} + k^0_{true}}{1 + \frac{K_{diss}}{h_A} + \frac{h_A}{K_{BH^+}}},$$

where k_{true} and k^0_{true} are the true rate constants for hydrolysis via the specific acid and intramolecular catalytic mechanisms and K_{diss} is the dissociation constant of *N*-phenylphthalamic acid.

In alkaline media there is also a complex profile of changes in the alkaline hydrolysis of compounds with amide linkages. Fig. 7 illustrates the variation of $\lg k_{eff,25°}$ for the hydrolysis of *N*-methylacetamide with the alkalinity function of aqueous KOH solutions[55]. It has been shown by infrared spectroscopy that amides may exist both in the unionised form and as singly and doubly charged ions. The rate-limiting step in the process involves the interaction of these ions with a water molecule:



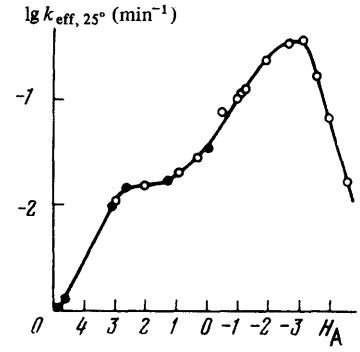


Figure 6. Variation of $\lg k_{eff,25°}$ with the amide acidity function of aqueous sulphuric acid solutions for the hydrolysis of *N*-phenylphthalamic acid[54].

The kinetic equation for the hydrolysis is

$$k_{eff} = \frac{k_{true}\, a^2_{H_2O}\, K_p \cdot \frac{1}{b_0} + k'_{true} a_{H_2O}}{1 + K'_p \frac{a_{H_2O}}{b_0} + K_p K'_p \frac{a_{H_2O}}{b_0^2}}, \qquad (9)$$

where b_0 is the alkalinity of the medium.

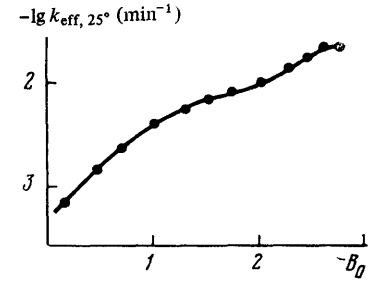


Figure 7. Variation of $\lg k_{eff,25°}$ with the alkalinity function of aqueous potassium hydroxide solutions for the hydrolysis of *N*-methylacetamide[55].

The validity of this equation has been demonstrated by an independent procedure involving a comparison of the changes in k_{eff} with the concentrations of the ionised forms of the amide[56].

The ester linkage. Numerous studies have been made on the acid hydrolysis of compounds with ester linkages, but there is as yet no unanimous view concerning the mechanism of the hydrolysis. The possible mechanisms of the hydrolytic reactions have been analysed in detail[51]. The hydrolysis of compounds with ester linkages in alkaline media proceeds via a mechanism[51] analogous to that described above for compounds with amide linkages.

The imide linkage. The hydrolysis of compounds with imide linkages takes place in acid and alkaline media via mechanisms analogous to those described for amides.

The acetal linkage. Compounds with acetal linkages are known to be stable in alkalis and to be readily hydrolysed in acids. The acid-catalysed hydrolysis of acetals is an example of the A-1 monomolecular mechanism[58,59]. The experimental data are described by the equation

$$k_{\text{eff}} = \frac{k_{\text{true}}}{K_{\text{BH+}}} \cdot h_0,$$

where h_0 is the Hammett acidity function.

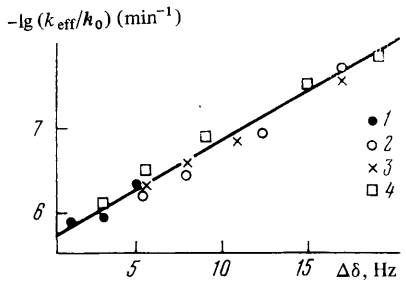
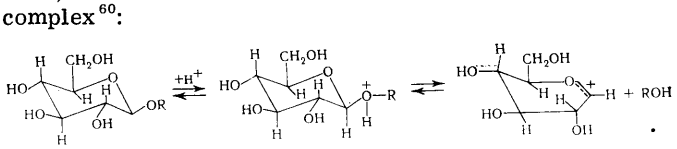


Figure 8. Experimental data represented by a plot of $\lg(k_{\text{eff}}/k_0)$ against $\Delta\delta$ for the hydrolysis of cellobiose in aqueous acid solutions: 1) HCl; 2) $HClO_4$; 3) H_2SO_4; 4) H_3PO_4.[61]

In the hydrolysis of cyclic hemiacetals (glycosides) the principle of correspondence between the structure of the protonated species and the activated complex does not hold. For example, the rate-limiting stage in the hydrolysis of cellobiose, a model of cellulose, includes a slow transition from the chair conformation (protonated form) to the half-chair conformation in the activated complex[60]:



The ratio $f_X/f^{\neq}$ in Eqn. (4) cannot then be regarded as constant. Evidently it will be larger the stronger the interaction between the cellobiose molecule and the medium.

The change in the activity coefficient ratio $f_{RH^+}/f^{\neq}$ can be estimated from the chemical shifts $\Delta\delta$ of the protons at the carbon atom in the 2-position[61]. The change in k_{eff} for the hydrolysis of cellobiose is described by the equation

$$\lg \frac{k_{\text{eff}}}{h_0} = \lg \frac{k_{\text{true}}}{K_{\text{BH+}}} + p \cdot \Delta\delta,$$

where p is a proportionality coefficient. Fig. 8 presents experimental data in terms of the variables of this equation for aqueous solutions of different acids.

For the other linkages encountered in polymers, the evidence adduced for the hydrolytic mechanisms is not rigorous.

IV. PRINCIPAL TYPES OF DECOMPOSITION OF POLYMERIC MOLECULES

The structure of polymeric molecules determines the type of their decomposition. On the one hand, chemically unstable bonds can be equally reactive and, on the other, terminal bonds can exhibit enhanced reactivity, which complicates the chemical degradation process. Furthermore, polymers may contain bonds with enhanced reactivity—"weak bonds".

The kinetics (changes in the number of molecules and in the mass of the polymer) have been examined theoretically[62] for the principal types of decomposition of polymeric molecules in degradation processes. We shall consider the main types of decomposition of polymeric molecules in chemical degradation reactions.

a. Random Decomposition

This type of decomposition is frequently encountered in chemical degradation processes and can be illustrated by the examples in Tables 2 both for the reactions of the main polymer chain and for the polymer-analogue reactions involving the abstraction of groups of atoms without a change in the degree of polymerisation.

In cellulose the terminal hemiacetal linkages are somewhat more reactive than the "non-terminal" linkages. This is seen from a comparison of the rate constants for the acid-catalysed hydrolysis of cellulose and cellobiose (Table 2) and also from data[63] showing that the reactivities of the two hemiacetal linkages in cellotriose differ by 1.5. However, the difference between the reactivities of the terminal and non-terminal linkages is slight and the acid-catalysed hydrolysis of cellulose under homogeneous conditions can therefore be regarded as a random process to a first approximation.

b. Depolymerisation Decomposition

This type of decomposition is encountered extremely rarely in a pure form in chemical degradation processes; it is usually combined with the random decomposition of the polymer chain.

c. Decomposition of the Mixed Type

A typical example of such decomposition is the acid-catalysed degradation of polyoxymethylene, which is accompanied by the cleavage of the chain with formation of fragments having terminal hydroxy-groups and by the depolymerisation of these fragments.

d. The Cleavage of the Polymer Chain

The maximum in the reactivity of polyoxymethylene oligomers with terminal methoxy-groups (POM-OCH_3) in the acid-catalysed degradation process (Table 6) leads to the conclusion[64] that the terminal acetal linkages are more reactive than the non-terminal linkages and that the acid-catalysed degradation process includes two consecutive stages: (1) slow decomposition of the terminal acetal linkage in the oligomer; (2) rapid depolymerisation of the hemiacetal formed.

Table 6. Aliphatic reaction constants σ^* and the rate constants for the degradation of the $CH_3(OCH_2)_nOCH_3$ oligomers in aqueous sulphuric acid solutions[64].

n	R_1^a	R^a	$\Sigma\sigma^*$	$\lg K_{25°}^b$	n	R_1^a	R^a	$\Sigma\sigma^*$	$\lg K_{25°}^b$
1	CH_3	CH_3	0	−2.82	3	»	$(CH_2O)_2CH_3$	0.15	−2.64
2	»	CH_2OCH_3	0.52	−2.18	4	»	$(CH_2O)_3CH_3$	0.05	−2.74

[a] Substituents near the reaction centre.
[b] $k25° = (k\text{true}/K_{BH^+})25°$, where $k\text{true}$ is the true rate constant for the decomposition of the protonated form of the reactant and K_{BH^+} is the basicity constant of the reactant.

The results are described satisfactorily by the Taft equation (Fig. 9) and make it possible to select methylal ($n = 1$) as a model of the terminal acetal linkage in POM-OCH_3 polymers.

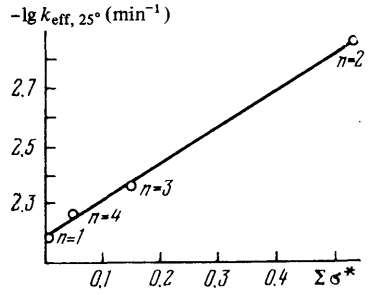


Figure 9. Correlation based on the Taft equation of the experimental data for the degradation of polyoxymethylene oligomers with terminal methoxy-groups in aqueous sulphuric acid solutions[64].

The reactivities of certain acetal linkages have been determined[65] from the change in the molecular weight of POM-OCH_3 in the course of degradation in a water–hexafluoroacetone solution of HCl. Table 7 shows that the terminal acetal linkages are approximately five times more reactive than the "non-terminal" linkages.

e. The Depolymerisation Reaction

This reaction occurs when the polyoxymethylene molecule contains terminal hydroxy-groups (POM-OH), which serve as active centres for the depolymerisation reaction.

Table 7. The rate constants for the decomposition of terminal and non-terminal acetal linkages and for depolymerisation in the acid-catalysed degradation of POM-OCH_3 in water–hexafluoroacetone solutions of HCl at 25°C.

	k, litre mole^{-1} min^{-1}		
water concn., M	decomposition of terminal bonds	decomposition of non-terminal bonds (random process)	depolymerisation
8.99	$(1.1\pm0.2)\cdot10$	2±0.4	$(3\pm1)\cdot10$
55.5	$(3.1\pm0.2)\cdot10^{-3}$	—	6±1

In stepwise depolymerisation of polymers with an exponential molecular weight distribution, the molecular weight remains almost constant, i.e. $(dM_n/dt)_{dep} \simeq 0$. When the decomposition of the polymeric molecules is a random process followed by depolymerisation (the length of the kinetic depolymerisation chain is much smaller than the number-average degree of polymerisation), we therefore obtain the following system of equations:

$$\frac{dm}{dt} = -2k_{rand}N - 2k_{dep}N; \quad (10)$$

$$\frac{dN}{dt} = k_{rand}m - 3k_{rand}N - \frac{2k_{dep}N^2}{m}, \quad (11)$$

where m and N are respectively the mass of the polymer and the number of molecules at time t, k_{rand} and k_{dep} are respectively the rate constants for random and depolymerisation decomposition. For the initial conditions $m = m_0$ and $N = 0$ with $t = 0$, Eqns. (10) and (11) have the following solution:

$$m = m_0 \exp\left\{\left(\frac{2k_{rand}}{k_{rand}} + 1\right)[\ln(2 - \exp - k_{rand}t) - k_{rand}t]\right\},$$

from which it is possible to calculate the depolymerisation rate constant (Table 7).

This relation between the rate constants for the decomposition of the terminal and non-terminal acetal linkages and for depolymerisation is responsible for the virtually identical effective rate constants determined from the accumulation of formaldehyde in the degradation of POM with different terminal groups in water–hexafluoroacetone solutions of HCl (Table 8). Thus the acid-catalysed degradation of POM in water–hexafluoroacetone solutions takes place in a complex manner; during the initial period, the random dissociations and the decomposition of the terminal acetal linkages lead to the formation of a considerable number of POM-OH molecules, which depolymerise with liberation of formaldehyde, the amount of POM-OH being almost independent of the molecular weight of the initial polymer and the nature of its terminal group.

It is noteworthy that the random decomposition and depolymerisation reactions have different mechanisms. The acetal linkage is decomposed via the A-1 mechanism[59,66], while the depolymerisation reaction proceeds via the A-2 mechanism[67]. Thus the relation between the

rate constants for these reactions changes when there is an appreciable alteration of the acid concentration. An equation describing the variation of the effective rate constants for the degradation of POM-OH, determined from the accumulation of formaldehyde, in aqueous sulphuric acid solutions (5–50 wt.%) has been derived [67]:

$$k_{\text{eff}} = k_{\text{dep(true)}}\, c_{H_3O^+} \left(\frac{1}{M_{n_0}} + \frac{k_{\text{rand(true)}}\, h_0}{K_{BH^+}\, k_{\text{term(true)}}\, c_{H_3O^+}} \right),$$

where $k$dep(true) is the true depolymerisation rate constant and $k$term(true) the true rate constant for the destruction of active depolymerisation centres in consequence of the degradation of the polymer chain. When

$$\frac{k_{\text{dep(true)}}}{\overline{M}_{n_0}} \gg \frac{k_{\text{dep(true)}} k_{\text{rand(true)}}}{K_{BH^+}\, k_{\text{term(true)}}} \cdot \frac{h_0}{c_{H_3O^+}}$$

only the depolymerisation reaction takes place and is determined by the initial concentration of the OH terminal groups in POM-OH. This condition holds in dilute sulphuric acid solutions (<5 wt.%) for POM-OH ($\overline{M}_V$ = 7000). With increase of the acid concentration, the depolymerisation reaction, determined by the terminal groups formed on random cleavage of the polymer chain, begins to play a major role and when

$$\frac{k_{\text{dep(true)}}}{\overline{M}_{n_0}} \ll \frac{k_{\text{dep(true)}} k_{\text{rand(true)}}}{K_{BH^+}\, k_{\text{term(true)}}} \cdot \frac{h_0}{c_{H_3O^+}}$$

we obtain

$$k_{\text{eff}} = \frac{k_{\text{rand(true)}} k_{\text{dep(true)}}}{K_{BH^+}\, k_{\text{term(true)}}} \cdot h_0,$$

i.e. the acid-catalysed degradation process obeys the A-1 mechanism.

Table 8. The effective rate constants for the degradation of POM having different molecular weights and different terminal groups in 4.4×10^{-3} M HCl solution (8.99 M H_2O in hexafluoroacetone at 30°C [65]).

Polymer	$\overline{M}_V$	$10^2 k_{\text{eff}}$, min^{-1}	Polymer	$\overline{M}_V$	$10^2 k_{\text{eff}}$, min^{-1}
POM-OCH_3	1 500	3.8	POM-$OOCCH_3$	50 000	3.4
	6 500	3.6		100 000	3.4
	10 500	3.7	POM-OH	7 000	19*
	19 500	3.9		220 000	3.5

*Initially there is a large number of depolymerisation centres.

The type of decomposition of the molecules in the solid polymer may differ from that in solution. For example, according to one of the models, cellulose molecules have a folded conformation in the protofibrils and in each fold there are about eight elementary units [68]. On the basis of this structure, Manley and coworkers [69] suggested that the hemiacetal linkage at the tops of the folds exhibit an enhanced reactivity. To confirm this, experiments were performed on the acid-catalysed degradation of different types of cellulose under heterogeneous conditions and molecular weight distribution (MWD) curves were obtained for the acid-soluble degradation products and for the insoluble residue at different time intervals up to 70% conversion. In the course of the degradation process, the cellulose molecules broke down into fragments with an average degree of polymerisation of about 8 regardless of the type of polymer and the MWD of the unreacted component of the cellulose did not change. The results confirm the hypothesis of the presence in cellulose of at least two types of linkage differing appreciably in their reactivities; hemiacetal linkages at the tops of the folds are more reactive than the hemiacetal linkages in the remaining portions of the folds.

Thus in the decomposition of polymers in corrosive media there is a possibility in the general case of sets of bonds having different reactivities. This in fact determines the type of decomposition of polymeric molecules.

V. DIFFUSION OF CORROSIVE MEDIA INTO POLYMERIC MATERIALS

In order to determine the mechanism of the degradation of polymeric materials in corrosive media, it is necessary to know how the corrosive medium diffuses into the polymer and what is its state within the polymer, i.e. to what extent the electrolyte is dissociated into ions and how much the latter are solvated by the solvent.

Since the diffusion of corrosive media into polymers is of considerable theoretical and practical interest (for example in connection with the prediction of the protective properties of polymeric coatings, the permeability of biological membranes, etc.), it will be necessary to consider in this section the general characteristics of the diffusion of corrosive media into polymeric materials. There is at present no general quantitative theory relating the diffusion coefficients of electrolytes in polymers to any structural parameters of the latter. Polymers are usually divided into two classes: hydrophilic and hydrophobic; the principal characteristics of the diffusion of electrolyte solutions into such polymers have been described in a number of studies [70–72].

It is useful to examine the diffusion of electrolytes into polymers as a function of their content of the solvent, for example water. Polymers can be divided arbitrarily into three groups:

(a) polymers readily dissolving water (50–80 wt.%);

(b) polymers dissolving water to a limited extent (1–50 wt.%);

(c) polymers dissolving water sparingly (<1 wt.%).

One should bear in mind that polymers in groups (a) and (b) are as a rule hydrophilic and those in group (c) are hydrophobic.

Polymers of Group (a)

A typical polymer of this group is poly(vinyl alcohol); the solubility of water in this polymer lies in the range 60–80% depending on the method of synthesis. The influence of the polymer on the diffusing species is slight and largely reduces to the bending of the polymer molecules by the diffusing substance. The Mackie–Meares theory [73], which takes into account such bending, makes it possible to calculate the diffusion coefficients fairly rigorously. As a rule electrolytes dissociate into ions in such polymers to the same extent as in aqueous solutions [74]. If the electrolyte in the polymer matrix is not completely dissociated, then in the general case the effective diffusion coefficient depends on the electrolyte concentration. This effect is associated with the different mobilities of ions and undissociated molecules in the polymer matrix [74].

its time variation is described by one of the adsorption equations.

(c) The attainment of a steady concentration of the diffusing substances on the surface of the polymeric article is determined by certain mass-transfer laws, the simplest of which is

$$j = \beta (c_S - c_V),$$

where j is the flux of the diffusing substance, c_S and c_V are respectively the concentration of the substance on the surface and in the bulk of the corrosive solution, and β is the mass-transfer coefficient.

Solution of the Equations for Polymeric Articles of Different Shapes

Most of the practical problems reduce to the description of degradation processes in bodies of simple shape. Polymeric films and coatings are modelled by layers of infinite extent, fibres are modelled by a cylinder, etc. The solutions of Eqns.(12)–(14) for a layer of infinite extent will be considered below. Depending on the ratio of the rates of diffusion and chemical reaction, chemical degradation can proceed under different conditions:

(a) the rate of diffusion of the corrosive medium is comparable to the rate of the chemical reaction (the degradation process takes place in a reaction zone whose size increases with time, and reaches in the limit the dimensions of the polymeric article), i.e. the reaction takes place in the internal diffusion-kinetic region.

(b) The rate of diffusion of the corrosive medium greatly exceeds the rate of the chemical reaction. After the entire polymer has swollen in the corrosive medium, the degradation process takes place throughout the bulk of the polymer, i.e. in the internal kinetic region.

(c) The rate of diffusion of the corrosive medium is much lower than the rate of the chemical reaction. In this case the degradation process takes place in a thin surface reaction layer, which is usually described as reaction from the surface of the article, i.e. in the external diffusion-kinetic region.

b. Internal Diffusion-kinetic Region

The simultaneous solution of Eqns.(12)–(14) constitutes a difficult mathematical problem, which can only be solved with the aid of a computer.

Consideration of the diffusion of the corrosive medium in polymers showed that the diffusion of the solvent is frequently much faster than the direct diffusion of the catalyst (acid or base), i.e. $D_{solv} > D_{cat}$; one can therefore assume that the concentration of the solvent in the reaction zone of the polymeric article is constant and equal to its solubility in the polymer (c^0_{solv}), i.e.

$$c_{solv} = c^0_{solv}. \qquad (17)$$

Thus the problem simplifies and reduces to the solution of Eqns.(12) and (13), the first of which assumes the following form when account is taken of Eqn.(17):

$$\frac{dc_n}{dt} = k c_n c^0_{solv}\, c_{Cat} = k_{eff} \cdot c_{Cat}, \qquad (18)$$

where

$$k_{eff} = k\, c^0_n\, c^0_{solv}.$$

For simplicity, we shall confine ourselves to only one term in Eqn.(13) and shall put $c_i = c_n$.

Consider the case where $K_p \to \infty$, i.e. the functional groups formed during degradation react almost completely with the catalyst. When account is taken of the fact that this reaction proceeds much faster than the degradation reaction, Eqn.(13) becomes

$$\frac{\partial c_{Cat}}{\partial t} = D_{Cat} \frac{\partial^2 c_{Cat}}{\partial x^2} - k_{eff}\, c_{Cat}, \qquad (19)$$

where x is the diffusion coordinate.

The solution of Eqn.(19) subject to the boundary conditions $c_{cat} = c^0_{cat}$ when $x = 0$ and l and the initial condition $c_{cat} = 0$ when $t = 0$ and $0 \leq x \leq l$ is the following:

$$c_{Cat}(x, t) = c^0_{Cat}\left\{1 - \frac{4}{\pi} \sum_{m=1}^{\infty} \frac{\sin b_m x}{(2m-1)(b_m^2 D_{Cat} + 1)} \times \right.$$
$$\left. \times [k_{eff} + b^2 m D_{Cat} \exp - (b_m^2 D_{Cat} + k_{eff})\, t]\right\}, \qquad (20)$$

where $b_m = \pi(2m-1)/l$, c^0_{cat} is the solubility of the catalyst in the polymer, and l is the thickness of the film.

After substituting Eqn.(20) in Eqn.(18) and after double integration from 0 to t and from 0 to $l/2$, we obtain

$$c_n = k_{eff} c^0_{Cat} t \left\{1 - \frac{8}{\pi l} \sum_{m=1}^{\infty} \frac{k_{eff} t (b_m^2 D_{Cat} + k_{eff}) + b_m^2 D_{Cat} [1 - \exp - (b_m^2 D_{Cat} + k_{eff})\, t]}{(2m-1)\, b_m (b_m^2 D_{Cat} + k_{eff})^2\, t}\right\}. \qquad (21)$$

Analysis of Eqn.(21) makes it possible to distinguish two cases:

(a) $b_m^2 D_{cat} > k_{eff}$. In this case it is sufficient to retain only the first term of the series. A detailed solution in this instance will be described below.

(b) $b_m^2 D_{cat} < k_{eff}$. Restriction to only the first term of the series is not permissible and one must bear in mind that, for fairly large values of t,

$$c_n = k_{eff} c^0_{Cat}\, t. \qquad (22)$$

This case will also be analysed below.

When $K_p \to 0$, i.e. the functional groups formed during the reaction do not interact with the catalyst, Eqn.(19) becomes

$$\frac{\partial c_{Cat}}{\partial t} = D_{Cat} \cdot \frac{\partial^2 c_{Cat}}{\partial x^2}.$$

It solution, subject to analogous boundary and initial conditions, is

$$c_{Cat}(x, t) = c^0_{Cat}\left(1 - \frac{4}{\pi} \sum_{m=1}^{\infty} \frac{\sin b_m x}{2m-1} \exp - b_m^2 D_{Cat}\, t\right). \qquad (23)$$

After substituting Eqn.(23) in Eqn.(18) and after integrating between the same limits as for Eqn.(21), we obtain

$$c_n = k_{eff} c^0_{Cat}\, t \left\{1 - \frac{8}{\pi^2} \sum_{m=1}^{\infty} [1 - \exp - (2m-1)^2 y] \frac{1}{(2m-1)^4 y}\right\}, \qquad (24)$$

where

$$y = \frac{\pi^2 D_{Cat}\, t}{l^2}.$$

When $y < 1$, this case obtains during the initial period of the degradation reaction for films of any thickness:

$$c_n = k_{eff} c^0_{Cat}\, t \frac{8}{\pi^2} \varphi(y), \qquad (25)$$

where

$$\varphi(y) = \sum_{m=1}^{\infty} \frac{\exp - (2m-1)^2 y - 1 + (2m-1)^2 y}{(2m-1)^4 y}.$$

Polymers of Group (b)

These include, for example, polycaproamide, epoxy-resin, and ethylcellulose. The solubility of water in these polymers at 25°C is about 7–9 wt.% for the first two and 2 wt.% for the last[12].

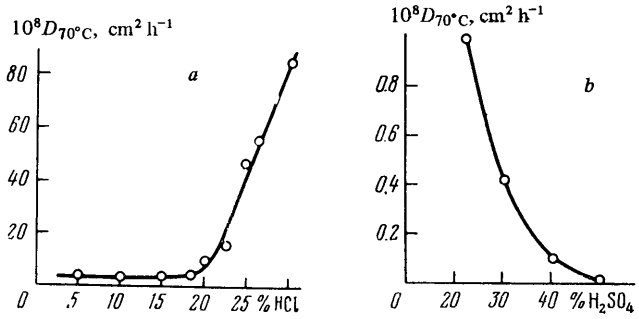


Figure 10. Variation of the diffusion coefficients of hydrochloric (*a*) and sulphuric (*b*) acids in epoxy-resin as a function of acid concentration[72].

Differences are observed in the behaviour in these polymers of electrolytes having high and low vapour pressures. Fig. 10 illustrates the variation of the diffusion coefficients of hydrochloric and sulphuric acids in epoxy-resin at 70°C as a function of the acid concentration[72].

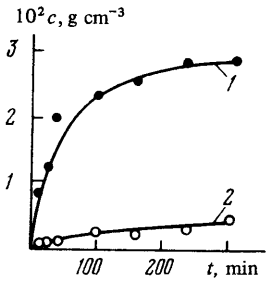


Figure 11. Variation of the concentration of water (1) and HCl (2) during the diffusion of the vapour of 28% hydrochloric acid into an ethylcellulose film at 35°C.[76]

Shterenzon et al.[75] believe that hydrogen chloride can exist in two-forms in polyethylene: in the non-hydrated form and as hydrates, the diffusion coefficient of the former being much higher. With decrease of the water content, there is a change in the ratio of the hydrated and non-hydrated forms of hydrogen chloride, which leads to an increase of the effective diffusion coefficient and in concentrated hydrochloric acid solutions the latter approaches that of gaseous hydrogen chloride.

In sulphuric acid solutions, diffusion coefficient and the water content in the polymer vary in parallel. In contrast to polymers of group (a), the polymers considered here sorb selectively the electrolyte and water.

Fig. 11 illustrates the variation of the concentration of water and HCl during the diffusion of the vapour of 28% hydrochloric acid solution into an ethylcellulose film at 35°C. The diffusion of the components of the corrosive medium proceeds with similar diffusion coefficients, but the ratio of the concentrations of water and HCl in the polymer is approximately ten times greater than in the gas phase[76].

Electrolytes are dissociated into ions in polymers of this kind, but quantitative data on the degree of dissociation are not available.

Polymers of Group (c)

This group includes the majority of industrially important polymers. Electrolytes with a high vapour pressure diffuse with diffusion coefficients close to those for polymers of groups (a) and (b). Electrolytes with a low vapour pressure diffuse into these polymers at very low rates[77].

VI. THE INFLUENCE OF THE SOLID STATE OF THE POLYMER ON THE DEGRADATION PROCESS

The degradation reactions in solid polymers have a number of characteristics which are associated both with the specific features of the structures of polymeric materials and with the specific features of the kinetics of heterogeneous reactions. We shall consider the characteristics of the structures of polymeric materials.

1. THE INHOMOGENEITY OF THE STRUCTURES AND PROPERTIES OF POLYMERS

The structural characteristics and properties of polymeric materials are almost always anisotropic with respect to volume, which is frequently referred to as spatial gradients[78]. For single-phase systems, the following examples of structural gradients may be quoted:

(a) vitreous and viscoelastic sections (copolymers of methyl methacrylate and methyl acrylate);

(b) strongly and weakly cross-linked regions (vulcanised elastomers);

(c) oriented and non-oriented regions (crystallising polymers);

(d) regions with different MWD (fractionated during shear flow);

(e) regions with different degrees of order in single-phase amorphous polymers (association).

The following structural gradients are characteristic of heterophase systems:

(a) amorphous and crystalline regions (crystalline polymers);

(b) regions with different degrees of microheterogeneity (stereoregular polymers);

(c) regions with different steric (*cis–trans* groups) or chemical structures (statistical copolymers).

In real polymeric materials there are in addition a wide variety of structural gradients established by added organic and inorganic substances: stabilisers, plasticisers, pore-forming agents, fillers (fibreglass in laminated glass plastics and carbon black in rubbers), dyes, etc.

The above structural gradients are responsible for the anisotropy of the chemical and diffusion properties of polymeric materials. At present there are no rigorous quantitative data concerning the influence of structural factors on the diffusion of corrosive media, on the one hand, and on the reactivity of the functional groups in polymeric materials, on the other. Isolated data on these problems have been published[79,80].

2. KINETICS OF THE DEGRADATION OF POLYMERS

The degradation of polymers in liquid corrosive media proceeds via the following principal stages:

(1) adsorption of the corrosive medium on the surface of the polymeric article;

(2) diffusion of the corrosive medium into the bulk of the polymeric article;

(3) chemical reaction of the corrosive medium with the chemically unstable bonds of the polymer;

(4) diffusion of the degradation products to the surface of the polymeric article;

(5) desorption of the degradation products from the surface of the polymeric article.

Examination of all the stages of the degradation process is difficult, because it is usually assumed that one or at most two stages are slow compared with the others, and therefore limit the rate of the entire degradation process. Stages (1) and (5) are usually faster than stages (2)–(4). The diffusion of the degradation products to the surface of the polymeric articles does not usually play a significant role in the estimation of the changes in the useful properties of the polymer during the degradation of polymeric articles, but it may limit, for example, the rate of biological degradation of the polymer in a living organism.

a. Fundamental Equations

In the general case (assuming that the law of mass action holds), the rate of decomposition of chemically unstable bonds in a polymer under the influence of a corrosive medium is

$$W = \frac{d c_n}{d t} = k (c_n^0 - c_n)\, c_{Cat}\, c_{solv}, \qquad (12)$$

where c_n^0 is the initial concentration of the chemically unstable bonds in the polymer, c_n the concentration of the dissociated bonds, c_{cat} the concentration of the catalyst in the polymer, and c_{solv} the concentration of the solvent in the polymer.

The concentration of the catalyst (for example an acid or a base) in the polymer can be found from Fick's equation:

$$\frac{\partial c_{Cat}}{\partial t} = D_{Cat} \nabla^2 c_{Cat} - \sum_i^0 c_{Cat}\, c_i\, K_{pi}, \qquad (13)$$

where ∇^2 is the Laplace operator, c_i the concentration of the functional groups in the polymer capable of involvement in complex-formation or substitution reactions, and K_{pi} are the equilibrium constants for the complex-formation or substitution reactions. The second term on the right-hand side of Eqn. (13) takes into account the possibility of reactions such as protonation, the conversion of carboxy-groups, etc.

If the solvent is consumed in the steps involving the decomposition of the chemically unstable bonds in the polymer (for example, water is consumed in hydrolytic reactions), then the concentration of the solvent can be found from the equation

$$\frac{\partial c_{solv}}{\partial t} = D_{solv} \nabla^2 c_{solv} - k (c_n^0 - c_n)\, c_{Cat}\, c_{solv}. \qquad (14)$$

In order to formulate these equations, a number of assumptions must be justified:

(a) the polymer–corrosive medium system is as a rule extremely dilute with respect to the corrosive medium, i.e. one may assume that D_{cat} and D_{solv} are independent of the concentrations of the corresponding components in the polymer. When the corrosive medium is very soluble in the polymer, it is necessary to use the equation taking into account the relation between D and the concentration of the diffusant.

(b) k is constant. This is true for low solubilities of the corrosive medium in the polymer. In general, the influence of the corrosive medium on k can be reduced, to a first approximation, to the influence of the solvent on the rate of the chemical reaction and may be predicted on the basis of the existing theories[10].

(c) The decomposition of the chemically unstable bonds is almost irreversible. This condition holds for the degradation process in a thin surface layer, or in a reaction zone up to low degrees of conversion (<0.02). The concentration of the chemically unstable bonds then remains almost constant and $c_n^0 - c_n \simeq c_n^0$.

(d) The properties of the polymer are homogeneous with respect to volume. In reality there are regions in the polymer where the reactivity may be different (different values of k) and which exhibit a different capacity to sorb corrosive media and allow them to diffuse (different c_0 and D). The rigorous expression for the overall rate of the degradation process should therefore assume the following form:

$$W_\Sigma = \sum_i [k (c_n^0 - c_n)\, c_{Cat}\, c_{solv}]_i\, V_i, \qquad (15)$$

where V_i is the relative volume of each region. The use of Eqn. (14) involves considerable difficulties, so that in most cases one has to employ the concept of the average rate. We shall define it as the ratio of the overall rate of the process to the total volume of the polymeric article:

$$\overline{W} = \frac{\sum_i [k (c_n^0 - c_n)\, c_{Cat}\, c_{solv}]_i\, V_i}{\sum_i V_i}. \qquad (16)$$

This quantity will in fact be used subsequently except in special instances. Eqns. (13) and (14) can be formulated similarly.

Thus the problem of the determination of the rate of decomposition of chemically unstable bonds in the polymer under the influence of corrosive media reduces to the simultaneous solution of Eqns. (12)–(14).

Boundary Conditions

The following boundary conditions are usually encountered:

(a) the concentration of the diffusing substances on the surface of the polymeric article is constant. In practice this condition holds when a solution with a constant concentration of the diffusing corrosive medium flows rapidly around the article.

(b) The concentration of the diffusing substances on the surface of the polymeric article is a function of time, and

The following simple relation has been established with the aid of computer calculations:

$$\varphi(y) = 0.589y^{1/2},$$

so that

$$c_n = \frac{4}{\pi^{1/2}} k_{\text{eff}}\, c^0_{\text{Cat}}\, D^{1/2}_{\text{Cat}}\, t^{1/2} l^{-1}, \qquad (26)$$

i.e. during the initial period of the degradation the concentration of the ruptured bonds depends on the rate constant for the chemical reaction, the diffusion coefficient, the solubility of the catalyst, the thickness of the film, and time.

c. Internal Kinetic Region

The kinetic equation for this region can be obtained from Eqn. (24) with $y \gg 1$. This case obtains either for very thin films or very long times when the film has been saturated by the catalyst solution:

$$c_n = k_{\text{eff}}\, c^0_{\text{Cat}} t \left[1 - \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{(2m-1)^4 y}\right]. \qquad (27)$$

In this case one can restrict the treatment to the first term of the series, whereupon

$$c_n = k_{\text{eff}}\, c^0_{\text{Cat}} t. \qquad (28)$$

Thus the concentration of the ruptured bonds corresponding to low degrees of conversion is proportional to the rate constant for the chemical reaction, the catalyst concentration under saturation conditions, and the reaction time.

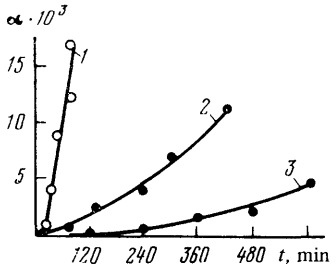


Figure 12. Time variation of the degree of conversion of ester linkages in the degradation of PETP films of different thickness in 53% H_2SO_4 at 116°C; film thickness (μm): 1) 5 ± 1; 2) 20 ± 2; 3) 80 ± 5.[81]

Fig. 12 illustrates the variation of the degree of conversion of the ester linkages α during the degradation of poly(ethylene terephthalate) (PETP) films of different thickness as a function of time[81]. For films 5 μm thick, there is a linear relation between α and time t starting from 30 min (by this time, the film has been saturated with the catalyst solution). Using Eqn. (28), we find the product $k_{\text{eff}} c^0_{\text{cat}}$. D_{cat} is determined from Eqn. (26) (Fig. 13).

We shall now consider certain characteristics of the degradation processes in the internal diffusion-kinetic and kinetic regions.

The Accessibility of the Functional Groups in Polymer Degradation Reactions

In polymeric materials with inhomogeneous structures (this applies primarily to heterophase systems), difficulties are frequently encountered in the definition of the terms "reactivity" and "accessibility" of the functional groups, because both terms are used to define the ability of the polymer to enter into a chemical reaction.

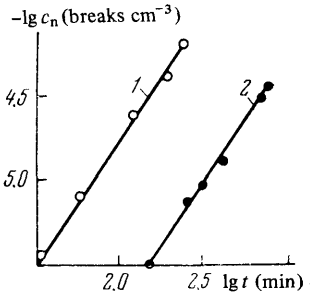


Figure 13. Variation of lg c_n with lg t for the degradation of PETP films of different thickness (1) in 53% H_2SO_4 at 116°C; thickness (l, μm): 1) 20 ± 2; 2) 80 ± 5.[81]

As already stated, the reactivity of the functional groups of the polymer can be accounted for on the basis of polar, resonance, and steric effects, and in most cases can be predicted quantitatively with the aid of correlation equations or by studying the kinetics of low-molecular-weight model reactions under corresponding conditions. Although there are as yet no rigorous quantitative data, presumably there should be no significant differences between the reactivities of the functional groups in regions with different structural inhomogeneities.

The accessibility of the "polymer" functional groups to molecules with which they should react is usually expressed quantitatively by the ratio $d = N/N_0$, where N_0 and N are respectively the total number of functional groups and the number of the accessible groups. It is reasonable to suppose that d will depend on the external conditions and on the method of determination. One should bear in mind that the "inaccessible" functional groups are involved in degradation reactions, but the rates of these reactions are low owing to the low concentration of the corrosive medium around these groups.

For polymers with mobile hydrogen atoms, a convenient method whereby the accessibility of the functional groups can be determined is provided by the H–D reaction, because during this reaction there is no change in the concentration of functional groups. The H–D exchange reaction has been investigated in detail in polycaproamide films[82,83]. The accessibility of the amide linkages is a function of temperature (Fig. 14). At 150°C all the amide linkages, including those in crystalline regions, are accessible to the H–D exchange reaction.

Most of the studies have dealt with the influence of the structure of cellulose on its reactivity in acid-catalysed degradation reaction[84]. The structure of the accessible regions in cellulose belonging to the structural type I has

been studied in detail [85]. Small amounts of diethylaminoethyl substituents were introduced into the cellulose virtually without any alteration of the polymer structure (X-ray diffraction analysis was carried out); such substituents could be easily determined quantitatively in the soluble and insoluble products of the acid-catalysed hydrolysis by gas-liquid chromatography, which permits the determination of diethylaminoethyl groups in the 2-*O*-, 3-*O*-, and 6-*O*-positions of the D-glucopyranose residues.

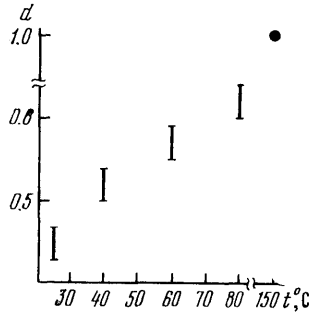


Figure 14. Temperature variation of the accessibility of the amide linkages in polycaproamide films.

The hydrolytic reaction takes place on the surface of the fibrils and there are two different types of accessible surfaces, called the "crystalline" and "disordered segments". According to BeMiller [86], the significant difference between the first-order rate constant for the formation of substituted D-glucopyranose residues in the acid-catalysed hydrolysis of cellulose at 25°C in 2.5 *N* HCl (Table 9) is due to the greater accessibility of the glycosidic linkages to protonation in the disordered segments and the greater ease of the transition from the chair to the half-chair conformation in these regions (the rate-limiting stage of the hydrolytic process).

Table 9. The first-order rate constants for the formation of various substituted D-glucopyranose residues in the acid-catalysed hydrolysis of cellulose at 25°C in 2.5 *N* HCl. [85]

D-Glucopyranose residue	Disordered segments; 10^3k, s^{-1}	Crystalline segments; 10^6k, s^{-1}	D-Glucopyranose residue	Disordered segments; 10^3k, s^{-1}	Crystalline segments; 10^6k, s^{-1}
Unsubstituted	1.1	6.5	3-*O*-Substituted	1.9	38.6
2-*O*-Substituted	4.8	15.8	6-*O*-Substituted	3.9	16,7

The distribution of the accessible surface between the disordered and crystalline segments, based on the content of the 2-*O*-substituted D-glucopyranose residues in these regions, is in the ratio 0.26 : 0.74 during the initial period of the reaction, changing to 0.36 : 0.64 as hydrolysis proceeds, because cellulose undergoes recrystallisation.

The surfaces of the crystalline and disordered segments of the fibrils are illustrated schematically in Fig. 15.

In the crystalline regions (surfaces A and B), the segments are oriented and the hydroxy-groups are located in regularly repeating positions, the hydroxy-group in the 3-position being linked by a strong hydrogen bond to the oxygen in the ring of the neighbouring D-glucopyranose unit (Fig. 16). The bulk of the crystal structure defects due to twisting and bending of the fibrils and the presence of internal strain are concentrated in the disordered regions (surfaces C). The hydrogen bons 3-OH...5-O in these regions are least stable, which is the cause of the increase of the rate constant for the formation of 3-*O*-substituted D-glucopyranose residues.

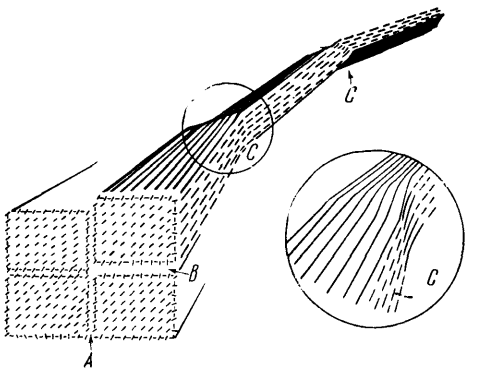


Figure 15. Schematic representation of the surfaces of the crystalline and disordered segments of cellulose fibrils [86].

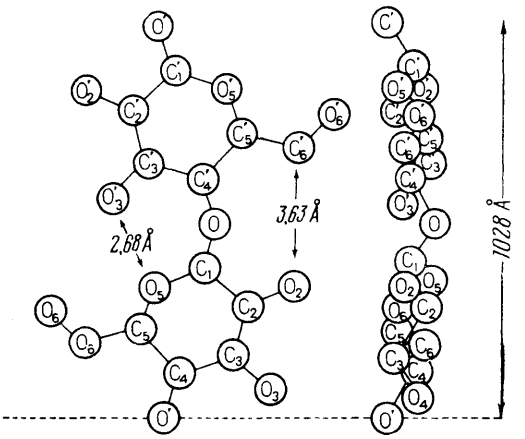


Figure 16. The conformation of the cellobiose segment of a crystalline cellulose chain [86].

Comparison of the Reactivities of the Functional Groups of Polymers in the Solid State and in Solution

Using as an example the degradation of cellulose derivatives, it is of interest to compare the kinetic parameters obtained for the solid state (degradation of ethylcellulose films in hydrochloric acid vapour) [76] and in solution (degradation of methylcellulose in aqueous hydrochloric

acid solution)[61]. In the former case, the rate constants were calculated by Eqn.(28); ethylcellulose is an amorphous polymer and it was assumed that all the glycosidic linkages are equally accessible. In the latter case the rate constant under the conditions of an excess of hydrochloric acid was calculated from the equation for first-order kinetics but was referred to a single catalyst concentration (Table 10).

Table 10. Kinetic parameters of the acid-catalysed degradation reactions of methyl- and ethyl-cellulose.

Polymer	$k_{85°}$, mole min^{-1} cm^{-3}	E, kcal mole^{-1}	$\Delta S^{\neq}$ e.u.
Methylcellulose	$5.0\cdot10^{-6}$	30	4
Ethylcellulose	$1.2\cdot10^{-1}$	5.5	50

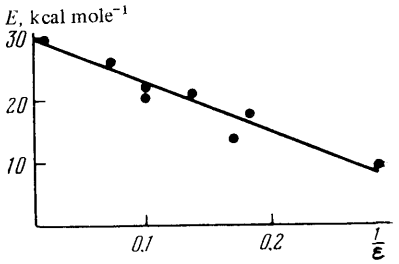


Figure 17. Variation of E with $1/\epsilon$ for the degradation of cellulose derivatives in various media[76].

To a first approximation, one may assume that the degradation of ethylcellulose takes place in "solution"; it is of interest to discover which properties of the solution are primarily responsible for the change in the kinetic parameters. Fig. 17 illustrates the variation of the activation energy for the degradation of cellulose ethers in various media as a function of the reciprocal of the dielectric constant[76]. The activation energy varies in opposition to $1/\epsilon$. Hence it follows that the chemical degradation processes in the solid state can be apparently simulated by reactions in solvents with similar physical parameters. To what extent this approach is valid will be established in the future when sufficient examples have accumulated.

d. The External Diffusion-kinetic Region

The degradation process in this region starts from the surface of the polymeric article. In this case we have

$$\frac{dc_n^S}{dt} = k(c_n^0 - c_n)^S c_{Cat}^S c_{solv}^S.$$

The superscript S denotes concentrations in the surface layer.

Regardless of the type of decomposition of the polymeric molecules, we have $(c_n^0 - c_n)^S \simeq (c_n^0)^S$. The state of the solvent and catalyst molecules in the surface layer has not been discussed in the literature. To a first approximation, one may assume that, under the conditions of adequate mixing, the thermodynamic parameters of the solvent and the catalyst in the surface layer and in the bulk of the liquid phase will be similar, so that

$$c_n^S = k_{eff}^S c_{Cat}^V c_{solv}^V,$$

where $k_{eff}^S = k(c_n^0)^S$ and the superscript V denotes bulk-phase concentration.

We shall consider how the mass of the polymer changes during degradation in this instance. Regardless of the type of decomposition of the polymer molecules, one can formulate an expression for the mass of the monomers formed:

$$m = k_{eff}^S c_{Cat}^V c_{solv}^V t\, S,$$

where S is the area of the polymer film. The thickness of the polymer film varies in accordance with the equation

$$x = l - \frac{k_{eff}^S c_{Cat}^V c_{solv}^V t}{\rho},$$

where ρ is the density of the polymer. The total decomposition time of the film is

$$\tau = \frac{m_0}{k_{eff}^S c_{Cat}^V c_{solv}^V S}.$$

The change in the mass of the polymer m_{pol} is described by the equation

$$m_{pol} = m_{pol}^0\left(1 - \frac{t}{\tau}\right) = m_{pol}^0\left(1 - \frac{k_{eff}^S c_{Cat}^V c_{solv}^V S t}{m_{pol}^0}\right). \qquad (29)$$

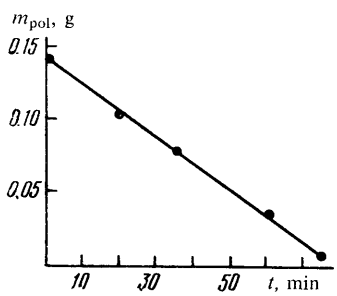


Figure 18. Time variation of the mass of the polymer in the degradation of a PETP film in 22.1% KOH solution at 88.2°C (l = 68 ± 8 μm, S = 14 cm^2).[57]

When the degradation process takes place in the external diffusion-kinetic region, one must bear in mind that the polymer molecules in the surface layers have properties differing from those in the bulk of the specimen (molecular weight, degree of crystallinity, orientation, etc.). We have no data for the reactivities of polymer molecules in the surface layer. Progress in this field will be achieved by studying monolayers deposited directly on to the corrosive medium.

The change in the mass of PETP film during degradation is illustrated in Fig. 18. The following experimental observations have been made[57]:

(a) the reaction is of zero order with respect to the polymer;

(b) the molecular weight of the polymer film does not change until the end of the process;

(c) the multiple distorted total internal reflection infrared spectra contain no absorption bands due to the carboxy-groups formed in the decomposition of the ester linkages;

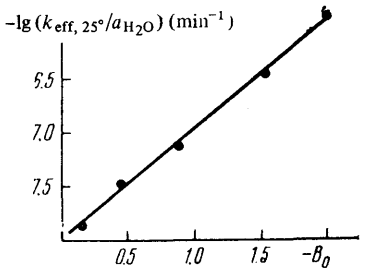


Figure 19. Variation of $\lg k_{\text{eff},25°}/a_{H_2O}$ with the alkalinity function of aqueous potassium hydroxide solution for the degradation of PETP films 68 ± 2 μm thick [57].

(d) the values of k_{eff}^{S} calculated by Eqn. (29) vary as a function of the thermodynamic parameters of the medium in accordance with Eqn. (9) (Fig. 19), which describes the hydrolysis of low-molecular-weight compounds in aqueous solutions of alkalis.

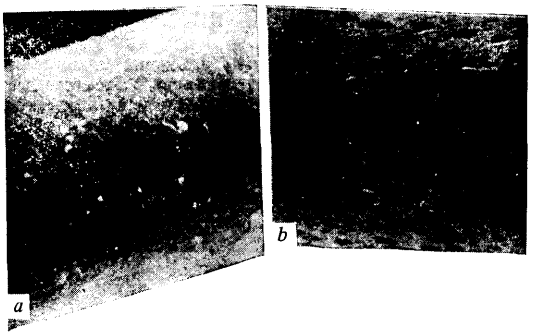


Figure 20. Photomicrographs (× 2100) [× 3000 in the Russian original] of PETP fibres during degradation in 22.1% KOH solution at 88.2°C: *a*) before degradation; *b*) after 5 min.

All these findings suggest that the reaction layer approaches a monolayer. The surface area of the films was estimated from profilograms. The variation of the surface area during the degradation process is illustrated in Fig. 20. Photomicrographs of PETP fibres were obtained under a scanning microscope. In degradation of this type, structural gradients (degree of crystallinity and orientation) had almost no influence on the kinetic parameters.

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The concepts described above and the examples discussed reveal the fundamental characteristics of polymer degradation processes in corrosive media. The review deals with the degradation reactions in polymeric materials in an unstrained state in corrosive media which have been most thoroughly investigated—aqueous solutions of acids and bases. These constitute only some of the degradation processes encountered in practice. The creation and development of a theory of the chemical degradation of polymeric materials in the strained state in different corrosive media is one of the immediate tasks in the modern science of polymer degradation.

REFERENCES

1. GOST 17050-71, "Starenie Polimernykh Materialov. Terminy i Opredeleniya" (The Ageing of Polymeric Materials. Terminology and Definitions).
2. Yu. S. Zuev, "Razrushenie Polimerov pod Deistviem Agressivnykh Sred" (The Decomposition of Polymers Under the Influence of Corrosive Media), Izd. Khimiya, Moscow, 1972.
3. P. I. Flory, "Principles of Polymer Chemistry", New York, Interscience, 1953, p. 47.
4. T. Alfrey, Jnr., Symposium, "Khimicheskie Reaktsii Polimerov" (Chemical Reactions of Polymers) (Translated into Russian), Izd. Mir, Moscow, 1967, Vol. 1, p. 9.
5. H. Morawetz, Symposium, "Khimicheskie Reaktsii Polimerov" (Chemical Reactions of Polymers) (Translated into Russian), Izd. Mir, Moscow, 1967, Vol. 1, p. 16.
6. N. A. Plate, "Kinetika i Mekhanizm Obrazovaniya i Prevrashcheniya Makromolekul" (Kinetics and Mechanism of the Formations and Transformation of Macromolecules), Izd. Nauka, Moscow, 1968, p. 250.
7. I. A. Tutorskii, Uspekhi Khim., 35, 191 (1966) [Russ. Chem. Rev., No. 1 (1966)].
8. R. M. Noyes, "Progress in Reaction Kinetics", Oxford–London–New York–Paris, 1961, Vol. 1, p. 129.
9. A. M. North, "The Collision Theory of Chemical Reactions in Liquids", New York, Wiley, 1964.
10. S. G. Entelis and R. P. Tiger, "Kinetika Reaktsii v Zhidkoi Faze" (Kinetics of Liquid-phase Reactions), Izd. Khimiya, Moscow, 1973, p. 17.
11. E. A. Moelwyn-Hughes, "Physical Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1962, Vol. II, p. 789.
12. I. A. Barrie, "Diffusion in Polymers" (Edited by I. Grank and G. S. Park), Acad. Press, London–New York, 1968, p. 274
13. O. W. Edwards and E. O. Huffman, J. Phys. Chem., 63, 1830 (1959).
14. "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, 1955, p. 2026.
15. P. P. Nechaev, Yu. V. Moiseev, and G. E. Zaikov, Vysokomol. Soed., 14A, 1048 (1972).
16. N. A. Khalturinskii, Yu. V. Moiseev, G. E. Zaikov, and M. I. Vinnik, Dokl. Akad. Nauk SSSR, 198, 149 (1971).
17. I. Moens and G. Smets, J. Polymer Sci., 2, 931 (1947).
18. G. Smets and W. Van Humbeeck, J. Polymer Sci., A-1, 1, 1227 (1963).
19. G. Smets, Macromol. Chem., 34, 190 (1959).
20. A. Conix and G. Smets, J. Polymer Sci., 15, 221 (1955).

21. J.S.Scarpa, D.D.Mueller, and J.M.Klotz, J.Amer. Chem.Soc., 89, 6024 (1967).
22. Y.Kakuda, N.Perry, and D.D.Mueller, J.Amer. Chem.Soc., 93, 5992 (1971).
23. A.Hvidt and R.Corret, J.Amer.Chem.Soc., 92, 5546 (1970).
24. R.W.Taft, Jnr., "Separation of Polar, Steric, and Resonance Effects in Reactivity", Chapter in "Steric Effects in Organic Chemistry" (Edited by M.S.Newman) (Translated into Russian), Inostr. Lit., Moscow, 1960, p.562.
25. R.B.Malcolm, Nature, 195, 202 (1962).
26. K.S.Minsker, Al.Al.Berlin, D.B.Kazanchenko, and R.G.Abdullina, Dokl.Akad.Nauk SSSR, 203, 881 (1972).
27. V.Chyty, B.Obereigner, and D.Zim, "Conference on Chemical Transformations of Polymers, Bratislava, June, 1968", p.15.
28. M.L.Bender and M.C.Nevew, J.Amer.Chem.Soc., 80, 5388 (1958).
29. T.Alfrey and W.G.Leoyd, J.Chem.Phys., 38, 318 (1963).
30. J.B.Keller, J.Chem.Phys., 37, 2584 (1962); 38, 325 (1963).
31. C.B.Arends, J.Chem.Phys., 38, 322 (1963).
32. L.Lazare, J.Chem.Phys., 39, 727 (1963).
33. D.A.McQuarrie, J.P.McTaque, and H.Reiss, Biopolymers, 3, 657 (1965).
34. L.V.Noa, A.L.Toom, N.B.Vasil'ev, A.D.Litmanovich, and N.A.Plate, Vysokomol.Soed., 15A, 877 (1973).
35. M.Hianchi and R.Senju, Polymer J., 3, 370 (1972).
36. T.C.Bruice and U.K.Pandit, J.Amer.Chem.Soc., 82, 5858 (1960).
37. T.C.Bruice and U.K.Paudit, Proc.Nat.Acad.Sci. U.S.A., 46, 402 (1960).
38. M.L.Bender, "The Mechanism of the Catalysis of Nucleophilic Reactions of Carboxylic Acid Derivatives" (Translated into Russian), Izd.Mir, Moscow, 1964, p.175.
39. W.P.Jencks, "Catalysis in Chemistry and Ezymology" (Translated into Russian), Izd.Mir, Moscow, 1972, p.21.
40. R.W.Alder, G.R.Chalkley, and M.C.Whiting, Chem. Comm., 405 (1966).
41. R.N.Maslova, E.A.Lesnik, and Ya.V.Varshavskii, Mol.Biol., 3, 728 (1969).
42. L.P.Hammett, Chem.Rev., 16, 67 (1935).
43. L.P.Hammett, "Fundamentals of Physical Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1972, p.353.
44. K.Yates, H.War, G.Welch, and R.A.McCleland, J.Amer.Chem.Soc., 95, 418 (1973).
45. C.H.Rochester, "Acidity Functions", Acad.Press, London–New York, 1970.
46. M.I.Vinnik and Y.V.Moiseev, Tetrahedron, 19, 1441 (1963).
47. C.K.Ingold, "Structure and Mechanisms in Organic Chemistry" (Translated into Russian), Inostr.Lit., Moscow, 1959.
48. N.M.Emanuel' and D.G.Knorre, "Kurs Khimicheskoi Kinetiki" (A Course of Chemical Kinetics), Izd.Vysshaya Shkola, Moscow, 1969.
49. J.F.Bunnett, J.Amer.Chem.Soc., 82, 499 (1960); 83, 4978 (1961).
50. M.I.Vinnik, I.M.Medvetskaya, L.R.Andreeva, and A.E.Tiger, Zhur.Fiz.Khim., 41, 252 (1967) [Russ. J.Phys.Chem., No.1 (1967)].
51. M.I.Vinnik, Izv.Akad.Nauk SSSR, Ser.Khim., 998 (1973).
52. P.P.Nechaev, Candidate's Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1975.
53. V.N.Kulagin, T.P.Esakova, Yu.V.Moiseev, G.M.Tseitlin, E.V.Brin, G.E.Zaikov, and V.V.Korshak, Izv.Akad.Nauk SSSR, Ser.Khim., 1770 (1974).
54. P.P.Nechaev, Yu.V.Moiseev, E.V.Kamzolkina, Z.V.Gerashchenko, Ya.S.Vygodskii, and G.E.Zaikov, Izv.Akad.Nauk SSSR, Ser.Khim., 2723 (1972).
55. Yu.V.Moiseev, E.Ya.Bakhrak, and M.I.Vinnik, Zhur.Fiz.Khim., 37, 784 (1963) [Russ.J.Phys. Chem., No.4 (1963)].
56. Yu.V.Moiseev, G.I.Batyukov, and M.I.Vinnik, Zhur.Fiz.Khim., 37, 510 (1963) [Russ.J.Phys. Chem., No.3 (1963)].
57. T.E.Rudakova, Yu.V.Moiseev, A.E.Chalykh, and G.E.Zaikov, Vysokomol.Soed., 14A, 449 (1972).
58. F.A.Long and M.A.Paul, Chem.Rev., 57, 935 (1957).
59. D.McIntyre and F.A.Long, J.Amer.Chem.Soc., 76, 3240 (1954).
60. I.T.Edward, Chem.Ind.(London), 1102 (1955).
61. N.A.Khalturinskii, Candidate's Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1972.
62. Al.Al.Berlin and N.S.Enikolopov, Vysokomol.Soed., A10, 1475 (1968).
63. M.S.Feather and J.F.Harris, J.Amer.Chem.Soc., 89, 5661 (1967).
64. L.V.Ivanova, Yu.V.Moiseev, and G.E.Zaikov, Izv. Akad.Nauk SSSR, Ser.Khim., 2501 (1970).
65. L.V.Ivanova, Yu.V.Moiseev, G.E.Zaikov, and Al.Al.Berlin, Vysokomol.Soed., 16A, 1831 (1974).
66. L.V.Ivanova, Yu.V.Moiseev, G.E.Zaikov, and V.V.Ivanov, Izv.Akad.Nauk SSSR, Ser.Khim., 2236 (1970).
67. L.V.Ivanova, Yu.V.Moiseev, and G.E.Zaikov, Vysokomol.Soed., 14A, 1057 (1972).
68. R.St.J.Manley, J.Polymer Sci., A-2, 9, 1025 (1971).
69. M.Chang, T.C.Pound, and R.St.J.Manley, J. Polymer Sci., Polymer Phys.Ed., 11, 399 (1973).
70. B.Dolezel, "Corrosion of Plastics and Rubbers" (Translated into Russian), Izd.Khimiya, Moscow, 1962.
71. A.L.Shterenzon, Yu.E.Lobanov, and S.F.Konovalova, Vysokomol.Soed., 9, 1668 (1964).
72. A.L.Shevchenko, Doctoral Thesis, Institute of the Petrochemical and Gas Industry, Moscow, 1972.
73. J.S.Mackie and P.Meares, Proc.Roy.Soc., A232, 510 (1955).
74. A.L.Iordanskii, Yu.V.Moiseev, V.S.Markin, and G.E.Zaikov, Vysokomol.Soed., 14A, 801 (1972).
75. A.L.Shterenzon, S.A.Reitlinger, and L.P.Topina, Vysokomol.Soed., 11, 4 (1969).
76. M.I.Artsis, A.E.Chalykh, N.A.Khalturinskii, Yu.V.Moiseev, and G.E.Zaikov, Vysokomol.Soed., 17A, 128 (1975).
77. A.L.Glass and I.Smith, J.Paint Technol., 38, 203 (1966).
78. M.Shen and M.Bever, J.Mater.Sci., 7, 741 (1972).
79. S.W.Lasoski and W.H.Cobbs, J.Polymer Sci., 36, 21 (1962).
80. G.Farrow, D.A.S.Raveng, and I.M.Ward, Polymer, 3, 17 (1962).

81. T.E.Rudakova, Yu.V.Moiseev, V.Ch.Pal'vanov, and G.E.Zaikov, Dokl.Akad.Nauk SSSR, **210**, 395 (1973).
82. P.Schmidt and B.Schneider, Coll.Czech.Chem. Comm., **31**, 1896 (1966).
83. R.Puffer and J.Sebenda, Coll.Czech.Chem.Comm., **29**, 75 (1964).
84. S.Haworth, D.M.Jones, J.G.Roberts, and B.F.Sagar, Carbohydr.Res., **10**, 1 (1969).
85. S.P.Rowland and E.J.Roberts, J.Polymer Sci., A-1, 10, 2447 (1972).
86. J.N.BeMiller, Adv.Carbohydr.Chem., **22**, 25 (1957).

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