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FEATURES OF THE KINETICS OF CHEMICAL REACTIONS OF HIGH-MOLECULAR-WEIGHT COMPOUNDS

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I. INTRODUCTION

The study of the kinetics of homogeneous reactions of macromolecules has recently received much attention from several investigators [1-37]. The interest in this problem is due to the search for ways of controlling the chemical changes in polymers and of carrying out directed reactions to obtain chemical derivatives with desired properties.

By comparing the kinetic parameters of reactions of functional groups included in the polymer chain with the analogous parameters of the same groups in low-molecular-weight compounds, it is possible to suggest a series of factors which lower the pre-exponential term of the Arrhenius equation for large molecules [1]. Firstly, from the kinetic theory, with increase in the dimensions (mass) of the molecule the rate of the Brownian movement of the molecules falls. Secondly, the high viscosity of the polymeric solutions decreases the number of collisions of the reacting groups. Thirdly, there is the great steric factor due to the screening of the functional groups by coiling of the polymeric chains.

When there is regular attention of the functional groups in the polymeric chain, the interaction of neighbouring groups (of two which have not reacted or which have reacted with those which have not yet entered into reaction, etc.) can affect the energy of activation.

This review shows the influence of the inclusion of a functional group in a polymeric chain and the interaction of regularly alternating functional groups on the kinetic parameters of reactions of macromolecules.

II. INFLUENCE OF THE INCLUSION OF A FUNCTIONAL GROUP IN A POLYMERIC CHAIN ON THE KINETIC PARAMETERS FOR THE REACTIONS OF THIS GROUP

There are many experimental results which show that the inclusion of a functional group in a polymeric chain does not significantly change either the activation energy or the pre-exponential term of the Arrhenius equation for reactions of this group with low-molecular-weight agents. Thus, Fuoss and coworkers [2], in studying the formation of quaternary salts of poly(vinylpyridine) and low-molecular pyridine compounds obtained the following constants for reaction rates and activation energies (Table 1).

The reaction was effected in tetramethylene sulphone; the alkyl halide used was n-butyl bromide.

TABLE 1. Kinetic parameters of the Menshutkin reaction for poly(vinylpyridine) and low-molecular-weight pyridines.

	$10^3 K_2$			E_a
	25°	50°	75°	
Pyridine C_5H_5N	0.463	3.70	23.1	16.04
4-Isopropylpyridine $C_3H_7C_5H_4N$	0.904	6.95	39.7	15.6
Poly(vinypyridine) (first stage of reaction)	0.64	5.4	29.4	15.7
4-Picoline $CH_3C_5H_4N$	0.83	6.58	40.1	15.95

Table 1 shows that the inclusion of pyridine in the polymeric chain affects neither the activation energy nor the reaction rate constant. Analogous results were obtained when propylene carbonate [4 methyl-1,2-dioxolan-2-one (Ed. of Translation)] [3], 2,4-dimethylsulpholane [2,4-dimethyltetramethylene sulphone (Ed. of Translation)] [4] or a mixture of propylene carbonate and diphenyl ether [5] was used as solvent.

Loucheux and Banderet[6] investigated the kinetic parameters of the reactions of macromolecules with one or several groups. In the range of functional group concentrations from 10^{-6} to 10^{-8} (per 1 cm^3) the rate of reaction of monoanhydride with aniline is the same for both the functional group of a macromolecule and the low-molecular-weight anhydride. The rate of reaction is independent of the viscosity of the solution even beyond the gelling point.

Moens and Smets[7] found that the rate constants and the Arrhenius parameters for the alkaline hydrolysis of poly(diethylacrylamide) were identical with those for diethyl isobutyramide (Table 2).

TABLE 2. Alkaline hydrolysis of amides.

	$10^4 K_2$, OH, s^{-1}			E_a	log PZ
	60°	70°	80°		
Poly(diethylacrylamide)	0.14	0.415	1.15	22.05	9.47
Diethylisobutyramide	0.20	0.51	1.24	21.70	9.07

In the alkaline hydrolysis of amides[8] the Arrhenius parameters for polyacrylamide and isobutyramide are identical (E_a = 14.16 kcal $mole^{-1}$ and log PZ = 5.63 for the first stage of the hydrolysis of polyacrylamide and E_a = 14.2 kcal $mole^{-1}$ and log PZ = 5.56 for the hydrolysis of isobutyramide).

Similar results are obtained in the acid of poly-(*N*-ethylacrylamide) and *NN'*-diethylisobutyramide: the activation energy for the first is 24.6 kcal $mole^{-1}$ and the number of effective collisions was characterised by log PZ = 9.49; for the model low-molecular-weight compound E_a = 23.7 kcal $mole^{-1}$ and log PZ = 9.20.

Conix and Smets[9] obtained the following results in the hydrolysis of low- and high-molecular-weight lactams (Table 3).

TABLE 3. Hydrolysis of lactams.

	E_a, kcal $mole^{-1}$	log PZ
Poly-(*N*-vinylpyrrolidone)	25±1	11.7
N-Isopropyl-2-methylpyrrolidone	27±0.5	12.3
Copolymer of vinylpyrrolidone and maleic acid (68 : 32)	16±1	6.3
Pyrrolidone-*N*-acetic acid	17±0.5	7.3

By studying the acetylation of cellulose and the reverse reaction of hydrolysis, Hiller[10] showed that the rate of reaction and activation energy in the acetylation of the primary hydroxyl groups in cellulose were of the same order as for the analogous reactions of butanol.

Salomon and coworkers[11,12] note that the activity of the chloride of natural rubber, which contains 20–30% allyl chloride, with respect to aniline is identical with that of low-molecular-weight allyl chlorides.

Losev and Trostyanskaya[13] state that in solutions, reaction between a polymer and a monomer proceeds at a rate similar to that for reaction of two low-molecular-weight substances.

Billmeyer[1] explains as follows the similarity between the kinetic parameters of the reactions of the functional groups in polymers and low-molecular-weight compounds in polycondensations.

Firstly, the mobility of the functional groups in a polymeric chain is considerably greater than the mobility of the chain itself. The functional groups move easily within a considerable region as a result of the change in configurations of the neighbouring parts of the chain. The frequency of the collision of these groups with their neighbours is comparable with the frequency of the collisions of low-molecular-weight compounds.

Secondly, in addition to the lower rate of diffusion, due to the high viscosity of the solutions of polymers and the increase in the time needed for the approach of the reacting groups, there is also an increase in the time for these groups being together and consequently in the effective collision number.

Thirdly, a screening effect can appear only in dilute solutions; at high concentrations the chains of the macromolecules are so greatly entangled that the chain proper, from the point of view of the screening of the functional groups forming part of it, has no advantage over the chains of other molecules.

Probably the same factors lead to the similarity between the kinetic parameters of the reactions of functional groups in polymers and in low-molecular-weight compounds as cited above.

III. INFLUENCE OF THE INTERACTION OF FUNCTIONAL GROUPS IN A POLYMERIC CHAIN ON THE REACTION KINETICS

The similarity of the kinetic parameters of the reactions of functional groups in high polymers and low-molecular-weight compounds can be upset if during the reaction the molecule of high polymer becomes charged and the charged groups are situated beside functional non-reacting groups.

Fuoss and coworkers[14] investigated the kinetics of the Menshutkin reaction for poly(vinylpyridine). The general kinetics of the reaction do not correspond with the kinetics of the reactions of low-molecular-weight pyridines. As the pyridine group forms part of the molecular chains, the successive reaction to form quaternary salts should take place at small distances from the groups that have already reacted. In solvents of high dielectric constant a considerable proportion of the bromide ions leaves the site of the pyridinium ions, creating a positive electric field of high intensity at the polymeric chain. As a result, after one-third of all the groups have reacted each remaining group will have an average of one charged neighbouring group, and when one-half of all the groups have reacted the remaining groups will have two charged neighbour groups. Thanks to the field of the positive charge of the nitrogen which reacted first, the rate constant falls to one-tenth of its initial value at the group of the neighbouring nitrogen.

Moens and Smets[7] showed the influence of the accumulation of charge on a macromolecule during the course of

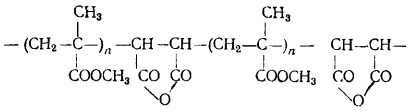
the reaction on the kinetic parameters of the alkaline hydrolysis of polyacrylamides. The hydrolysis can be divided into two clearly defined stages, the first being rapid, with a rate similar to that for the hydrolysis of the model low-molecular-weight compound, and the second being slow. During the initial stage the reaction is first order, but after reaching ~ 40% conversion the rate constant falls.

At low degrees of hydrolysis the molecule has a convolute configuration. At ~ 40% conversion the chain is uncoiled owing to electrostatic repulsion of the carboxyl groups present in a single molecule. The accumulation of charge on the macromolecule leads to an increase in the rigidity of the chain, a change in its configuration, and a diminution in the rate constant.

Kargin and coworkers [15] showed the influence of the electrostatic factor on the kinetic parameters of the hydrolysis of ethyl acetate, which is catalysed by poly(styrenesulphonic acid) (PSSA). Toluenesulphonic acid (TSA) served as a low-molecular analogue of PSSA. In the presence of PSSA the rate of hydrolysis was 1.3–1.8 times as great. The difference in the rates of reactions catalysed by PSSA and by TSA increases as the catalyst concentration is reduced.

The high activity of PSSA is explained by the increase in the concentration of protons (in the form of oxonium ions H_3O^+) close to the polymer chains. In the oxonium cloud around the macroanion the activity coefficients of the H_3O^+ ions are greater than in the TSA solution, where the H_3O^+ ions are distributed uniformly throughout the entire volume. During this, the increase in the rate of hydrolysis in the oxonium cloud is not compensated by the fall in the reaction rate in the regions of the solution denuded of H_3O^+ ions. Naturally, the more dilute the solution the more marked this effect.

Loucheux and Banderet [6] investigated the reaction of aniline with a copolymer of methyl methacrylate and maleic anhydride in which the anhydride groups were not adjacent:



The greater the number of anhydride groups in the macromolecule, the less the rate of reaction, all other conditions being equal. This occurs because, in a non-polar solvent (benzene), the macromolecule with a low concentration of anhydride groups mixes well with the solvent. An increase in the number of anhydride groups in the macromolecule increases its polarity, which leads to a complication of the polymeric chain into more intimate tangles. As a result, the anhydride groups become less accessible and the rate of reaction decreases.

The kinetic similarity of the reaction of polymers and low-molecular-weight compounds fails when an intramolecular reaction is possible for a polyfunctional polymer. Arcus [16] showed this by the example of the alkaline hydrolysis of poly(methyl methacrylate). At the start of the reaction the polymer contains only amido-groups which are mono-functional. During the reaction carboxyl groups appear as well as the amido-groups, and because both are fixed in a polymeric chain hydrogen bonds are formed between them, increasing the activation energy for hydrolysis of the amido-groups, as a result of which the reaction rate is sharply depressed. When each amido-group has two carboxyl groups as neighbours, the reaction ceases. Under those conditions the low-molecular-weight amides are hydrolysed to completion. Smets [8] considers that it is not hydrogen bonds but electrostatic repulsion and steric hindrance which lead to the progressive retardation of the alkaline hydrolysis of the alkaline hydrolysis of polyacrylamide.

Moens and Smets [7] observed the effect of intramolecular chemical reaction of functional groups on the kinetic parameters of their reactions by the example of the acid hydrolysis of poly(vinylamides). They thought that the hydrolysis was accompanied by imidisation, which lowers the reaction rate and raises the activation energy by 3.5 kcal.

Smets and Petit [38] observed an increase in the activation energy due to the association of functional groups in a monofunctional polymer. Thus in the acetylation of poly(vinyl alcohol) at a sulphuric acid concentration of 0.5 N and 0.05 N the activation energy was 9.5 and 15 kcal respectively. The increase in E_a by 5.5 kcal in the second case is due to the association of hydroxyl groups.

In polyfunctional polymers the kinetic parameters can be affected by catalytic action shown by one functional group to another.

Moens and Smets [7] compared the alkaline hydrolysis of polyacrylamide with the hydrolysis of low-molecular-weight amides (Table 4).

As Table 4 shows, the rate of reaction of the functional groups in the polymer is greater than that in the low-molecular-weight compounds. Morawetz explains this by the specific catalysis of the carboxyl groups in the first stage of the reaction.

TABLE 4. Hydrolysis of amides.

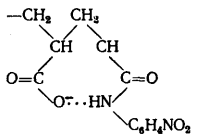
	$10^4 K_2$, OH, mole^{-1} s^{-1}					E_a	log PZ
	55°	65°	70°	75°	85°		
Polyacrylamide	6.66	—	18.6	—	38.8	13.7	5.99
Isobutyramide	1.16	2.36	—	3.95	—	14.2	5.56
Glutaramide	—	3.80	—	6.94	12.7	14.8	6.01
Acrylamide	1.47	3.70	—	6.66	13.8	16.6	7.24
Propionamide	5.24	9.98	—	17.7	—	14.6	6.10

The nature of the intramolecular catalysis of hydrolytic reactions was studied in detail by Bender and coworkers using the example of acid and alkaline hydrolysis of phthalamic acid [39,40] and the hydrolysis of methyl phthalate [41]. Kinetic comparison of several low- and high-molecular-weight compounds showed a great difference between the intramolecular and intermolecular hydrolysis [42].

Smets and Petit [38] observed the catalytic action of a hydroxyl group situated directly next to an acetyl group in the hydrolysis of poly(vinylacetal).

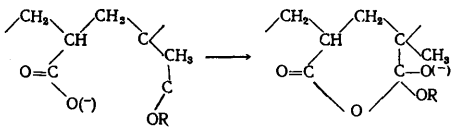
Schaefgen and Sarasohn [17] carried out the quantitative thermal decomposition of poly(butyl acrylate) into 2-methylprop-1-ene and poly(acrylic acid). Initially the reaction follows a statistical law. When 9.4 ± 2% has been converted, there is a rapid autocatalytic splitting-off of ester groups owing to the action of neighbouring carboxylic groups.

The investigations of Morawetz and coworkers [18,19] showed that the introduction of methacryl-*p*-nitroanilido--groups into a polyacid molecule makes these groups a thousand times more stable to sodium hydroxide, in comparison with the *p*-nitroanilides of trimethylacetic and glutaric acids. The stabilisation results from ring formation:



from an increase in the steric effect, and from an increase in the electrostatic repulsion. This explanation is confirmed by the accelerating effect of the addition of small quantities of Ba^{2+} ions, which, by bonding the carboxylate groups, free the anilide groups.

The hydrolysis of *p*-nitrophenylmethacrylic groups, introduced into the chain of poly(acrylic acid) to the extent of ~ 1%, goes a million times faster than the hydrolysis of *p*-nitrophenyl trimethylacetate [20,21]. Morawetz explains this by the selective catalytic action of a neighbouring carboxylate ion with the formation of an intermediate complex:

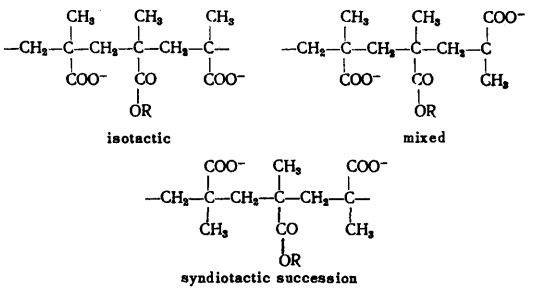


Smets and De Loecker [22] investigated the hydrolysis of copolymers of methacrylic acid and methyl methacrylate, at various ratios of the components. Under similar conditions the copolymer of methyl methacrylate and vinylpyrrolidone is hydrolysed 1000 times more slowly since with the latter the catalytic action of carboxyl groups is absent.

Smets and Hesbain [23] studied the hydrolysis of polyacrylamide and of copolymers of acrylamide and acrylic acid in an acetate buffer solution. The presence of the carboxyl group along with the amide in the copolymer increases the rate of hydrolysis three thousand times compared with the rate of hydrolysis of polyacrylamide.

The kinetic parameters of functional groups in a macromolecule are greatly affected by the stereoregularity of their distribution, when the polymer is polyfunctional — or when the reacting groups display a catalytic action on neighbouring functional groups, not taking part in the reaction. Thus, Glavis [24] showed, by the example of the alkaline hydrolysis of poly(methyl methacrylate)s of different tacticity, that the standard (atactic) and syndiotactic polymers are hydrolysed comparatively slowly but the isotactic polymers very rapidly and to a much greater degree. Smets [8] carried out the hydrolysis of atactic and isotactic copolymers of methacrylic acid with its ester (72% acid). The isotactic copolymer is hydrolysed 10–15 times more rapidly than the atactic and to a greater extent (40% instead of 20%).

The hydrolysis of a copolymer of methacrylic acid with 1–2% *p*-nitrophenyl methacrylate with isotactic succession of the carboxyl and ester groups is 12 times faster than that for a mixed succession [25]:



Smets and De Loecker [26,27] investigated the hydrolysis of copolymers of methacrylic acid with methyl methcrylate of the same chemical structure but different tacticity. The rate constants of the hydrolysis of a syndiotactic copolymer were four to five times those for the atactic. The syndiotactic copolymer is hydrolysed in a single stage, after which the reaction stops; the atactic copolymer in two stages with a ratio of the rates $K_1 : K_2 = 1 : 6$.

A comparison with the hydrolysis of a copolymer of methylmethacrylic acid and *N*-vinylpyrrolidone shows clearly that the ester and carboxyl groups interact with one another, which leads to a drop in the energy of activiation from 23 to 16 kcal.

Chapman [28] studied the acid hydrolysis of very crystalline isotactic and amorphous atactic poly-(*NN*-dimethylacrylamide)s. The isotactic polymer is hydrolysed more rapidly, since owing to the intramolecular nature of the hydrolysis the activation energy is reduced from 29 to 22.6 kcal. On the basis of his investigations Chapman proposes a method for determining the degree of tacticity by hydrolytic measurements.

Smets and Van Humbeeck [29] studied the hydrolysis of copolymers of acrylic acid and ethyl ethacrylate containing 50, 67, 77, and 85% of the acid. The hydrolysis rate is directly proportional to the concentration of the acid–ester–acid triad and the isotactic polymer is hydrolysed three to five times more rapidly than the atactic, and to a greater extent. The hydrolysis of copolymers of acrylic acid and t-butyl acrylate and of polymers of poly-(t-butyl acrylate) is independent of their stereoregularity, since the intramolecular interaction of the functional groups is ruled out by the strong steric effect.

Fujii and coworkers [30–32] showed the influence of stereoregularity on the kinetic parameters of the reactions of polymers by the example of hydrolysis of poly(vinyl acetate) and the acetalisation of poly(vinyl alcohol).

The kinetic similarity of the reaction of polymers and of low-molecular compounds breaks down when the functional groups or double bonds can bring about electronic interaction along the polymeric chain.

Cunneen [42–44] showed a diminution in the reactivity of double bonds relative to electrophilic agents on going from low-molecular monoalkenes to 1,5-polyenes, for example, of the reaction of polyisoprene and cyclohexene with ethanethiol, 3-methylbutane-1-thiol, thiophenol, thioglycollic acid [43], propane-1,3-dithiol and hexane-1,6-dithiol [44], and thioacetic and chlorothioacetic acids [45]. The reactivity is reduced in the order: cyclohexene > dihydromyrcene > > squalene > natural rubber.

We have found complete inertness of *cis*- and *trans*-polyisoprenes towards ethyl thioglycollate, whereas its addition to isopentene proceeds very readily [46].

Bateman and coworkers [47] note a fall in the reactivity of double bonds in polyisoprene compared with low-molecular-weight alkenes in hydrogenation.

We assume that the fall in reactivity of double bonds in 1,5-polyene systems in relation to electrophilic reagents is connected with the interaction of double bonds regularly alternating in the 1,5 positions. We have already considered the mechanism of this interaction [47]. Such an interaction of double bonds in diene polymers leads to the development of a series of reactions of these polymers by an intramolecular chain mechanism [46,48].

Alfrey and Lloyd [33] showed an intramolecular chain mechanism in the dehydrochlorination of poly(vinyl chloride). The act of reaction in one monomer unit converts a neighbouring unit into an allyl structure with an enhanced tendency to dehydrochlorination, which should lead to the chain development of the process and to the formation of a block of conjugated bonds.

There are several theoretical works on the kinetics of reactions of macromolecules in which the mean number of reacting functional groups is determined as a function of time under the condition that the reactivity of each group depends on how many of the neighbouring groups (one, two, or none) have already reacted [14,33-37].

The features noted do not, of course, exhaust all the specific characteristics of the kinetics of the reactions of polymers. The tasks of future investigations in this interesting and little studied field are the accumulation of information on the influence of the solvent on the course of the polymeric reactions, and also on the influence of secondary structures in solutions of polymers on the topochemical and kinetic features of the reactions.

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