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THE CHEMICAL ACTION OF ULTRASONIC WAVES ON MACROMOLECULES

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INTRODUCTION

The chemical action of ultrasonic waves on macromolecules has been studied by a number of workers. It is determined chiefly by processes of polymerisation or depolymerisation of these compounds, and the study of such processes has revealed a characteristic, strictly specific effect of ultrasonic vibrations on macromolecular structures (long-chain and branched). This in turn raises certain questions about the structure of solutions of macromolecules and the nature of their mechano-chemical reactions, which have been widely studied[1-5], and it also justifies an independent examination of the problems.

In view of our recently published article[6], it is unnecessary to give a detailed account of the general problems of the mechanism of the chemical action of ultrasonic waves, and we shall restrict ourselves to a short summary of the principal theories.

Most workers consider that the chemical action of ultrasonic waves results chiefly from cavitation phenomena produced in the liquid medium exposed to the waves[7-10]. Cavitation is greatly facilitated by the presence of gas-bubble nuclei in the liquid under study.

Cavitation phenomena in a liquid are associated with the production of mechanical forces which bring about rupture of the chemical bonds. There are indications that these forces are produced by the collapse (annihilation) of the cavitation bubbles which takes place in the compression phase along the propagation path of the ultrasonic wave[11,12] (mechanical cavitation theory).

According to other workers[13,14], the chemical processes may be brought about by mechanical forces which develop when the characteristic pulsation frequency of the gas bubbles in the liquid coincides with the ultrasonic frequency used (resonance cavitation theory). A similar suggestion is that the ultrasonic chemical processes are thermal in nature[15,16], in view of the possible development of large quantities of heat in the resonating gas bubbles.

Finally, the photoelectrochemical cavitation theory, based on the theoretical suggestions of Frenkel'[17], has gained wide acceptance. According to this theory, high electrical potential differences are set up in the cavity during the initial period of its development and lead to electronic breakdown of the cavity. The production of freely moving electrical charges in the cavity should result in the activation or ionisation of the molecules of gas or vapour present. There are grounds for considering that the initiation of chemical processes in ultrasonic fields is brought about chiefly by solvent molecules or gas atoms which have been activated or ionised in the cavity[18-21].

To some extent the photoelectrochemical cavitation theory has made it possible to clarify the nature of the primary products which bring about the various ultrasonic chemical reactions. This is particularly true of the analysis of such reactions in aqueous medium, which is almost the only medium in which observations have been made on oxidation and reduction reactions and the decomposition and synthesis of inorganic and organic substances[22-27]. The explanation

is that water is the most favourable medium for the production of electrical voltages in the cavitation bubbles formed by the action of ultrasonic waves. Furthermore, it is generally accepted that the initiation of chemical reactions in an aqueous medium irradiated by ultrasonic waves is brought about by the breakdown products of the water molecules – atomic hydrogen and free hydroxyl radicals. The breakdown of water molecules to form the extremely reactive, H· and OH· radicals takes place in the cavity as a result of the ionisation of the molecules by the moving charges.

In addition to water molecules, molecules of any gases present are also activated or ionised in the cavity under the action of the electrical charge, as indicated by the following facts. When distilled water saturated with hydrogen and nitrogen is exposed to ultrasonic waves, ammonia is produced[28]; when distilled water saturated with CO and H_2 is exposed, formaldehyde is formed, and in the presence of CO, H_2, and N_2, hydrocyanic acid is formed. The synthesis of an extremely complex substance with empirical formula $C_{10}H_7O_3Cl_2$ by the action of ultrasonic waves on water containing methylene chloride[29] apparently takes place by the same mechanism.

There are a number of other examples which indicate the important part played in the initiation of chemical reactions by molecules which, having entered the cavity in the gaseous state, are there activated or ionised[30].

The question of the possible appearance of electrical potential differences in cavities produced not in aqueous media but in organic solvents, particularly in non-polar solvents, is still unresolved. The problem arises since processes of polymerisation and depolymerisation of macromolecules under the action of ultrasonic waves take place not only in water but also in polar and non-polar organic liquids. In the theory of the action of ultrasonic waves on macromolecules, greatest attention has naturally been given to the part played in the depolymerising effect by the mechanical forces arising from the propagation of the acoustic energy in the liquid.

I. THE DEPOLYMERISING EFFECT OF ULTRASONIC WAVES AND CAVITATION PHENOMENA

The depolymerising action of ultrasonic waves on solutions of starch, gum arabic, and other macromolecular compounds was established by Szalay as early as 1933 [31]. The degradation of these compounds was accompanied by a decrease in the viscosity of the test solutions. In certain cases, however, this viscosity decrease was temporary and reversible; the viscosity of the solution returned to its original value on standing[32-35]. In other words, the action of the ultrasonic waves on the colloidal solutions led to the isothermal phenomenon known as thixotropy.

As a rule, the prolonged exposure of solutions of macromolecules to ultrasonic waves leads to a permanent, irreversible decrease in viscosity, indicating a breakdown in the molecular structure as a result of the rupture of valency bonds. The irreversible decrease in the viscosity of long-chain molecules was observed by Schmid and Rommel[36-39], who exposed dilute solutions of polyvinyl acetate, polyacrylic ester and nitrocellulose in organic solvents to the action of ultrasonic waves. The viscosity of the exposed solutions remained low even after the solvent had been carefully evaporated by heating and the residue redissolved.

These authors also noted similar phenomena under conditions which excluded oxidation processes and cavitation phenomena. They reported that degradation of long-chain molecules (nitrocellulose and polystyrene in toluene) was observed in a liquid exposed to ultrasonic waves, both in the absence of oxygen and under a constant external pressure of ~15 atm. It is known that the application of an external pressure of 4–5 atm to a liquid irradiated at the intensities used by the authors is sufficient to suppress cavitation.

In explaining the depolymerising effect of ultrasonic waves, Schmid considers two idealised cases: 1) the long-chain molecule is firmly fixed in the solution, and 2) the long-chain molecule may move freely in the solution. As an example, he analysed the behaviour of polystyrene in an ultrasonic field by representing the molecule as a long fibre, free from frictional forces, to which isolated spheres (benzene rings) with a radius of 3 Å are attached at equal distances from one another.

When the macromolecules are firmly fixed in the ultrasonic field, frictional forces should arise between the rapidly moving solvent molecules and these macromolecules. In this case the frictional forces may be calculated using Stokes' formula

$$f_0 = P_n 6\pi r \eta V_s, \qquad (1)$$

where η is the viscosity of the solvent, r the radius of the benzene ring, V_s the maximum rate at which the solvent molecules move as a result of the accelerations applied to them in the ultrasonic field, and P_n the number of links in the macromolecule.

Eqn. (1) may be written in the form

$$f_0 = \alpha P_n. \qquad (2)$$

Using the experimental data given by Jellinek and White[40]: $V_s = 50$ cm sec^{-1}, $r = 3$ Å, $\eta = 0.0062$ (in c.g.s. units), $P_n = 3000$, and hence $f_0 = 5.37 \times 10^{-4}$ dynes. According to de Boer's data[41], this value of f_0 is sufficient to break the C–C bond.

The forces acting on a macromolecule in an ultrasonic field will be smaller, by several orders of magnitude, if it is assumed that these molecules are free to move with the solvent molecules in the solution. These forces may be found from the formula

$$f_0 = P_n \frac{m}{N} \omega V_s, \qquad (3)$$

where m is the molecular weight of the monomer, N is Avogadro's number, $\omega = 2\pi/T$, and $T = 2.1 \times 10^{-6}$ sec (period of the ultrasonic wave). If the amplitude (A) of the acceleration in the vibrational motion is ωV_s, then the force acting on the macromolecule may be expressed by Eqn. (3).

Under the experimental conditions given above, $\frac{m}{N}\omega V_s$ will be equal to 2.77×10^{-14} dynes. In other words, in dilute solutions when there is no interaction between the dissolved molecules, the depolymerising effect should be zero, which is not in fact observed.

A slightly different treatment is given by Mark[42], from the following considerations. According to modern theory, long-chain molecules in dilute solution in suitable solvents are not extended to form straight chains, nor rolled up to form balls. The most probable configuration is a sinuous wavy structure. In solution, the separate links of the sinuous molecule undergo independent mechanical vibration and rotation at comparatively high rates (micro-Brownian intramolecular motion). The small links in the molecular

chain change position in a period of 10^{-3} sec. The chaotic movement of the molecules as a whole (macro-Brownian motion) is much slower. The average speed of the macromolecules amounts to 0.5–1.0 μ per second.

In an ultrasonic field, according to Mark, the movement of the whole macromolecule is much less than that of the solvent molecules, and according to his calculations, the frictional forces between the two greatly exceed the strengths of the chemical bonds C–C, C=C, and C=O. In accordance with spectroscopic data, these strengths are $4.5 \times \times 10^{-5}$ dynes, 5.77×10^{-5} dynes, and 9.77×10^{-5} dynes respectively. The frictional force between the macromolecules and solvent molecules (for speeds of the latter equal to 40 cm sec^{-1}) was estimated by Mark to be $2-3 \times 10^{-4}$ dynes per bond. This indicates that the application of ultrasonic waves to macromolecules containing the above groups should result in immediate breakdown to small molecules.

Schmid's experimental data show, however, that even on prolonged exposure to ultrasonic waves, only a very small fraction of the above-mentioned groups, when incorporated in a long-chain molecule, are in fact broken — approximately 5 per 1000. Mark therefore considers that most of the separate links of the macromolecule rotate freely around the line of the valency bond and follow the rapid vibrational movements of the solvent in the ultrasonic field, without offering any resistance to these movements. It is only rarely, in isolated places, that a considerable frictional force arises, capable of breaking the bond between the atoms.

It should be noted that the rotation of the separate links of high-polymer compounds is not free, but greatly restricted by interaction between the individual links of the molecule[43].

In addition, according to the theories of Kargin and Sogolova[44], Slonimskii et al.[45] (see also Kuz'minskii[46]), the stress produced in the micro-regions of the specimen (solid or liquid), at relatively small deformations, is not distributed uniformly and may be concentrated at isolated points, leading to the rupture of isolated covalent bonds in the macromolecule. This can apparently take place either in the compression or rarefaction regions along the propagation path of the ultrasonic wave, since the wave-length of the latter is much greater than the length of the macromolecule.

The views of Schmid and Mark have aroused considerable discussion, the only point not disputed being the equation put forward by Schmid to describe the kinetics of the breakdown of macromolecules in an ultrasonic field. This equation resulted from an analysis of the following experimental facts.

From a study of the influence of ultrasonic waves on solutions of separate fractions of polystyrene in toluene (molecular weight of 1st fraction 850 000, 2nd fraction 350 000, 3rd fraction 195 000), Schmid and Rommel established that during the first few minutes of the exposure the depolymerisation process is fairly rapid, after which the rate decreases and finally becomes zero as the molecular weight of the polymer approaches 30 000. The rate of depolymerisation is higher, the higher the original molecular weight, or, more precisely, the longer the initial length of the polymer studied. Analogous data have been obtained by Mostafa[47] (Fig. 1).

The same feature was observed by Schmid and Rommel in their investigation of the action of ultrasonic waves on dilute solutions of polyvinyl acetate, polymethyl-acrylate, nitrocellulose, and rubber.

The existence of a limiting degree of polymerisation was also established by Okuyama[48], and by Sato, Okuyama, and Chujo[49], who studied the action of ultrasonic waves on solutions of polyvinyl alcohol (initial molecular weight 77 000). The degree of polymerisation of the polymers studied, according to measurements of the diffusion and viscosity coefficients, reached limiting values after 90–120 minutes' exposure (frequency of vibrations 450 kc/s, intensity of ultrasonic waves 20 W/cm^2).

Schmid expressed this mathematically in the form

$$\frac{dx}{dt} = k(P_t - P_e) \qquad (4)$$

where x is the number of chemical bonds broken in unit volume for a given time of exposure, $\frac{dx}{dt}$ the rate of depolymerisation, P_t the degree of polymerisation of the long-chain molecule at time t, and P_e the limiting degree of polymerisation of the macromolecule when it undergoes no further depolymerisation under the influence of ultrasonic waves. This means that the rate of depolymerisation is independent of the chemical composition of the polymer; it depends on the difference between the initial and limiting degrees of polymerisation, and on the concentration of the irradiated polymer.

At very high degrees of polymerisation, Schmid observed a decrease in the rate of depolymerisation of the irradiated polymer. The decrease was particularly marked when the concentration of the macromolecules and the viscosity of the solution were high. In gels, the depolymerising effect was not observed at all.

Henglein[50] states that Schmid's equation is true for dilute solutions with concentrations up to 0.02 M, and that for higher concentrations the following equation is more satisfactory:

$$\frac{dx}{dt} = K \log \frac{P}{P_0}. \qquad (5)$$

Henglein suggests that ultrasonic depolymerisation may be brought about by the production of pulsating cavitation bubbles in the irradiated liquid. In the liquid close to these bubbles, velocity gradients may be produced resulting in the breakdown of the macromolecules. At high polymer concentrations, the oscillations of the bubbles are damped fairly rapidly, and Henglein suggests that this is associated with a decrease in the depolymerising effect of the ultrasonic waves under these conditions.

Weissler[51-53] claims that the depolymerisation of macromolecules is related to cavitation phenomena in the liquid. He observed the depolymerisation of polystyrene in toluene, and of hydroxyethylcellulose in water (frequency 175 kc/s) only when cavitation took place. According to his data, the molecular weight of the irradiated polymer decreased to one-tenth of its initial value.

In a degassed liquid, in which cavitation is difficult, Weissler observed no decrease in the molecular weight of the polymers (Fig. 2). His observations indicate that the depolymerisation of the macromolecules in the ultrasonic field is not related to the oxidation phenomena which take place in an aqueous medium exposed to ultrasonic waves (in the presence of oxygen). The depolymerisation of hydroxyethylcellulose in water was observed irrespective of

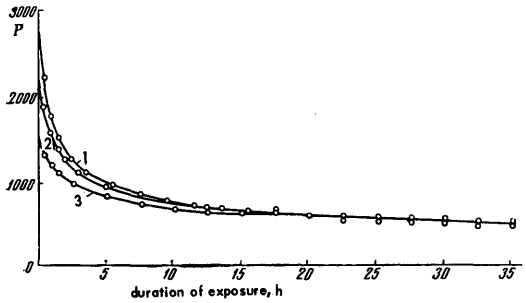


Fig. 1. Ultrasonic depolymerisation of polystyrene in benzene for different initial degrees of polymerisation P. 1) $P = 3260$; 2) $P = 2460$; 3) P 1505 (ultrasonic frequency 750 kc/s, intensity 12 W/cm^2)

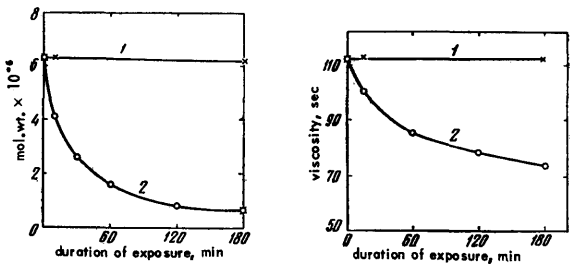


Fig. 2. a) Ultrasonic depolymerisation of polystyrene in toluene; b) ultrasonic depolymerisation of hydroxyethylcellulose in water. 1) Degassed solution; 2) in the presence of air.

whether the irradiated solution was saturated with air or helium.

Analogous conclusions were reached by Prudhomme and Grabar[54,55], who also studied the influence of ultrasonic waves on polystyrene in toluene and on carboxymethylcellulose in water (frequency 960 kc/s, intensity 6.8 W/cm^2). They observed the depolymerisation of the long-chain molecules when the irradiated liquid was saturated with gases that facilitate cavitation. In degassed liquid, or in liquid saturated with carbon dioxide, no depolymerisation took place.

More detailed studies on these lines were carried out by Brett and Jellinek[56]. According to their data, small cavitation bubbles and so-called cavitation noises are produced comparatively easily in irradiated benzene in the presence of nitrogen, hydrogen, argon, or methane, whereas cavitation is extremely slight in benzene saturated with ammonia or carbon dioxide, and is not observed at all in the presence of SO_2, even at ultrasonic intensities of 10 W/cm^2.

The above authors point out a definite correlation between the solubility of a gas in benzene and the intensity of the cavitation. The higher the solubility of the gas, the more readily it forms a molecularly dispersed solution, and the lower the tendency for the formation of bubble nuclei leading to cavitation.

Table 1 shows that various gases differ considerably in their solubility in benzene.

In this way the authors try to show that certain gases (N_2, H_2, O_2 and methane) intensify the ultrasonic depolymerisation of polystyrene in benzene, while NH_3, CO_2 or SO_2 inhibit this process. The same feature was observed by Gebert[57], who studied the action of ultrasonic waves on aqueous solutions of apple pectin in the presence of these gases.

The existence of a relationship between cavitation phenomena and the depolymerising action of ultrasonic waves was pointed out by Gaertner[58]. It is known that in the frequency range 400–1000 kc/s, the cavitation starts at comparatively low ultrasonic intensities (0.3–0.5 W/cm^2). At high frequencies (~ 2000 kc/s), more intense ultrasonic vibrations are required to produce cavitation. In accordance with this, Gaertner observed that on going to higher frequencies, the depolymerisation of long-chain molecules took place at intensities which always ensured cavitation. At a frequency of 2500 kc/s, the depolymerising effect (and also the cavitation) appeared only at very high intensities — 1.8 kW/cm^2.

TABLE 1. Solubility of various gases in benzene.

Gas	N_2	O_2	H_2	CO_2	NH_3	SO_2	CH_4	Air
Solubility of gas in ml/litre	0.10	0.219	0.07	2.40	9.95	8.8	0.54	0.140

There are reports, however, that cavitation only intensifies the degradation of macromolecules produced by mechano-hydrodynamic phenomena occurring in the liquid medium exposed to the ultrasonic waves. This possibility was admitted by Melville and Murray[59], who observed that the action of ultrasonic waves decreased the molecular weight of polystyrene in benzene from 700 000 to 260 000, with previous degassing of the solution. When the same solution was exposed to ultrasonic waves in the presence of air, the molecular weight of the polymer decreased to 47 000. According to the authors, the increase in the depolymerising effect in this case is due to the appearance of cavitation bubbles with resonance dimensions.

The intensifying action of cavitation on the rate of depolymerisation was later admitted by Schmid and coworkers[60]. However, they did not detect a relationship between the depolymerising effect and the frequency of the ultrasonic waves in the range 10–284 kc/s.

Schmid and Poppe[61] exclude the possibility that the breakdown of the polymer is due to resonance between the frequency of the molecular vibrations and the frequency of the ultrasonic waves being propagated in the liquid. The frequency of the ultrasonic vibrations (10^5–10^8) is usually smaller, by many orders of magnitude, than that of the molecular vibrations, estimated at 10^{14} c/s. The length of the ultrasonic waves in the liquid (1 mm to 1 cm) is many times greater than the length of the longest long-chain molecule, which is measured in microns.

Recently, attention has again been turned to the problem arising from the fact that the depolymerising action occurs under conditions excluding cavitation[47,62-63]. The authors of these papers excluded cavitation not only by removing the gases from the irradiated liquid, but also by using high frequencies.

According to Neppiras and Noltingk[64], there exists a limiting frequency (approximately 10 000 kc/s) above which no cavitation takes place. This limit depends on the initial dimensions of the bubbles in the liquid, on the amplitude of the ultrasonic wave pressure, and on the hydrostatic pressure in the liquid (see also other papers[65-67]). Gaertner states that there exist optimum frequencies at which cavitation is most intense, and that the cavitation is suppressed at frequencies exceeding 1000 or 2000 kc/s.

In agreement with this, Mostafa[63] found that the maximum degradation of polystyrene in benzene was observed at 1000 kc/s (intensity 12.5 W/cm²) (Fig.3). At higher frequencies, the rate of depolymerisation decreases considerably, but degradation of the macromolecules is still observed, even at frequencies of 2000 kc/s, at which, he believes, cavitation phenomena are absent. The same author also observed some degradation at these frequencies even in cases where the test solutions were degassed beforehand, which contradicts Weissler's findings[53]. In Mostafa's opinion, however, this discrepancy is due to the fact that Weissler observed the depolymerising effect at "medium" frequencies (400 kc/s) and comparatively low ultrasonic intensities (4 W/cm²). According to Mostafa, some degradation of macromolecules, albeit slight, still appears clearly at very high frequencies, i.e. in the absence of cavitation, probably as a result of resonance phenomena, and he believes that this is supported by the relationship which he has found between K in Eqn. (5) and the frequency of the ultrasonic waves.

From a practical point of view, the important feature is that cavitation phenomena are almost the only source of the mechanical forces which bring about the characteristic degradation of macromolecules when exposed to ultrasonic waves.

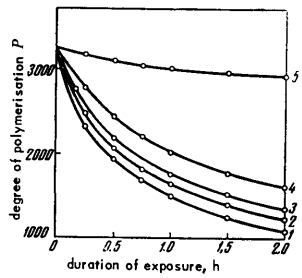


Fig. 3. Depolymerisation of 1% polystyrene in benzene under the action of ultrasonic waves of different frequency.
1) 1.0 Mc/s; 2) 1.25 Mc/s; 3) 0.75 Mc/s; 4) 1.25 Mc/s; 5) 2.0 Mc/s

II. THE HOMOGENISATION OF MACROMOLECULAR COMPOUNDS. THE FORMATION OF MACRORADICALS AND THEIR RECOMBINATION IN AN ULTRASONIC FIELD

One of the characteristic and remarkable phenomena produced by ultrasonic waves is a decrease in the polydispersity of the polymer under investigation. The homogenisation of a non-fractionated specimen of polymethyl-methacrylate under the influence of ultrasonic vibrations was first observed by Schmid, Paret, and Pfleiderer[60]. A specimen with uniform degree of polymerisation was obtained as the limiting degree of polymerisation P of the irradiated polymer was reached.

In a study of the influence of ultrasonic waves on aqueous solutions of polyvinyl alcohol, Sato, Okuyama, and Chujo[49] also discovered that the irradiated solutions become more uniform with respect to molecular weight. This phenomenon was not observed for depolymerisation brought about by heating or by oxidation with potassium permanganate. The authors suggest that in the last two cases, there is a high probability of rupture of the chemical bond at any part of the molecular chain, as a result of which the polymerisation products form a mixture of "fragments" of different molecular weight. In ultrasonic depolymerisation, however, the curve showing the molecular-weight distribution becomes narrower and sharper (Fig. 4) and the maximum is shifted to lower molecular weights.

The same authors believe that the action of ultrasonic waves leads to rupture of the molecule to form two equal parts, which in turn are broken into two equal parts, so that prolonged exposure leads to an almost uniformly dispersed polymer solution.

The question then arises of whether the ultrasonic depolymerisation is brought about by the rupture of weak bonds in the polymerised particles. In a study of this problem Melville and Murray[59] examined the rate of depolymerisation of polymethyl-methacrylate and two polymethyl--methacrylate–acrylonitrile copolymers differing in the molar ratios of methyl methacrylate and acrylonitrile (411 : 1 and 40 : 1). If it is considered that the bond rupture takes place at the points where the methyl methacrylate and acrylonitrile are joined, as has been shown for thermal depolymerisation[68], then these polymers should differ in the rate of depolymerisation under ultrasonic irradiation. Experiment showed, however, that there was no significant difference between the rates of breakdown of the irradiated copolymers (Table 2).

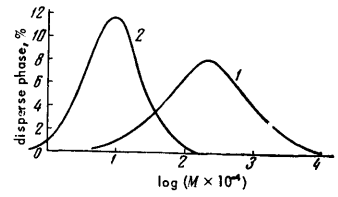


Fig. 4. Molecular-weight distribution curves. 1) Before irradiation; 2) after irradiation.

According to Schmid, Schneider, and Henglein[69], the predominant importance of mechanical forces in ultrasonic depolymerisation is indicated by the following effect. In the case of extremely long macromolecules, for which P is much greater than P_e, there is the possibility of rupture of bonds located at different points along the length of the molecular chain. As a result, the irradiated solution may contain molecular fragments of different length, which should lead to an increase in the polydispersity of the polymer at the beginning of the exposure period. In such cases, homogenisation of the solution takes place at a later stage of the exposure. This effect was detected experimentally[69]

TABLE 2. Molecular weight of polymers before and after ultrasonic irradiation (solvent—benzene, time of irradiation 350 min).

Polymer	Molecular weight of polymers	
	before irradiation	after irradiation
Methyl methacrylate	725 000	544 000±40 000
»	725 000	460 000±40 000
Methyl methacrylate—acrylonitrile	615 000	385 000±25 000
»	615 000	395 000±25 000

during the irradiation of fractionated polymethyl-methacrylate (mol. wt. 1.9×10^6). The authors calculated the molecular weight using Kuhn's equation, $Z_\eta = kM^a$. They also used the equation of Schulz and Blaschke[70], which makes it possible to determine the viscosity number directly from the measured specific viscosity:

$$Z_\eta = \frac{\eta_{sp}/c}{1 + k\eta_{sp}}.$$

The values of k and α for fractionated polymethacrylate were taken from the work of Schulz[71] and Meyerhoff and Schulz[72].

In the study of ultrasonic depolymerisation, the choice of values for the constants in the Staudinger and Kuhn equation becomes extremely difficult. The quantities α and k should remain constant for any degree of polymerisation of a given polymer, and for the calculation of these quantities it is necessary to determine the molecular weight by cryoscopic or ebullioscopic methods using the monomer or a low-molecular fraction of the polymer. According to many workers, however, the quantity k depends on the value of M.[62,73]

TABLE 3. Dependence of quantity of iodine consumed on the number of bonds broken in the irradiated polymer. (Polymer concentration 0.5 mole of monomer/litre; gas present argon).

Iodine concentration, 10^{-6} g-atoms × × litre^{-1}	Duration of exposure, min	Degree of polymerisation before irradiation, $P_0 \times 10^{-4}$	Degree of polymerisation after irradiation, $P_1 \times 10^{-3}$	Number of bonds broken, 10^{-6} moles/litre × litre^{-1} a	I_2 consumed 10^{-6} g-atoms × litre^{-1} b	b/a
41.1	25	1.90	2.40	1.82	4.00	2.20
21.4	25	1.90	2.30	1.91	4.32	2.25
10.8	15	1.90	2.75	1.55	3.02	1.95
5.0	8	1.90	4.60	0.83	1.75	2.11
1.8	5	1.90	7.50	0.40	0.91	2.27

The difficulties associated with the choice of k in calculating the degree of polymerisation of long-chain molecules explain the fact that P_e (and the number of bonds broken) for the same polymer is given different values by different authors[38,69,74-76].

More satisfactory data are apparently obtained by direct chemical determination of the number of molecular fragments formed as a result of rupture of the valency bonds. According to the theories developed by Kargin, Slonimskii, Sogolova, Baramboim, and others[1,2,77-81], extensive mechanical interaction not only causes the macromolecules to be displaced relative to one another, but also brings about mechanical rupture, accompanied by the appearance of free valencies at the ends of the broken polymeric chains. The rearrangement of polymer structure which develops under the influence of the high stresses is the essential feature of the process referred to by the authors as "chemical flow". The formation of macroradicals in this process brings about a number of chemical reactions such as mechano-chemical polymerisation, intensification of oxidation processes, ageing phenomena, etc.

It is useful to examine from this point of view the phenomena resulting from exposure to ultrasonic waves, since possible new methods controlling and directing these processes are then revealed.

Henglein[82] (see also Berlin[5]) considers that the rupture of a C–C bond in a long-chain molecule may give decomposition products in different physical states. In the so-called homolytic scission, two free radicals are formed:

$$P_{n+m} \rightarrow P_n^{\cdot} + P_m^{\cdot}.$$

In heterolytic scission, the products are ions of opposite charge:

$$P_{n+m} \rightarrow P_n^{+} + P_m^{-}.$$

Cases are also possible where the decomposition products become stable "fragments" of the broken macromolecule:

$$P_{n+m} \rightarrow P_n + P_m.$$

Experiment has shown that rupture of a C–C bond in an ultrasonic field results for the most part in the formation of long-chain radicals, which can be detected by their reaction with substances capable of indicating the presence of free radicals in solution.

When polyacrylic esters in benzene were exposed to ultrasonic waves in the presence of iodine, for example, the iodine reacted with the radicals formed. When the halogen was added after irradiation of the solution, no I_2 entered the long-chain molecule, indicating that the radical is short-lived[83].

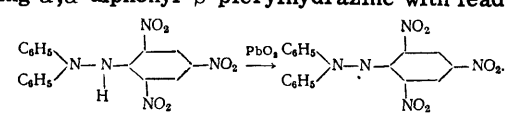
According to Henglein[83], the amount of I_2 reacting depends on the degree of polymerisation of the long-chain molecules exposed to the ultrasonic waves. The lower the degree of polymerisation, the lower the rate of depolymerisation under the ultrasonic irradiation, and the smaller the quantity of I_2 combining with the irradiated polymer. The author used the isotope I^{131}; if the reaction between I_2 and the irradiated polymer is

$$I_2 + P_{m+n} \rightarrow P_n^{\cdot} + P_m^{\cdot} + I_2 \rightarrow P_n I + P_m I,$$

then the number of I atoms which react should be double the number of bonds broken, as was in fact observed (Table 3).

When the polymer is exposed to ultrasonic waves in the presence of oxygen, only a very small fraction of the long-chain radicals formed combine with iodine, indicating that the C-radicals react more readily with oxygen than with iodine.

The free radicals produced in ultrasonic intermediate reactions have been detected by using the stable α,α-diphenyl-β-picrylhydrazyl radical (DPPH), obtained by oxidising α,α-diphenyl-β-picrylhydrazine with lead dioxide:

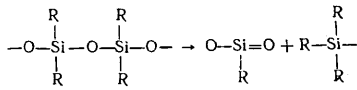


This compound (DPPH) is soluble in many organic solvents, and according to Bawn and Mellish[84], reacts readily with other free radicals. DPPH solutions have a violet colour and an intense absorption maximum at 520 mμ. This maximum decreases or disappears when the DPPH reacts with other free radicals in the solution.

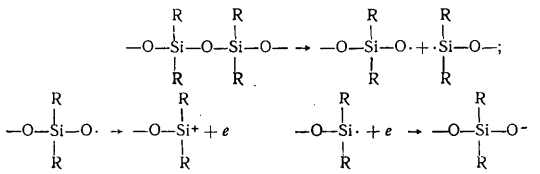
Henglein observed a decrease in the absorption maximum at 520 mμ when DPPH and the polymer under investigation were exposed simultaneously to ultrasonic waves, the decrease in the optical density of the DPPH solution being proportional to the number of broken C–C bonds in the macromolecule. On the basis of these studies, Henglein confirmed that the only macromolecules depolymerised under ultrasonic irradiation were those with degree of polymerisation above a definite value P_c. At P_c, no decrease in the quantity of DPPH was observed, i.e. the rate of depolymerisation at the limiting degree of polymerisation is zero. According to Henglein after the degree of polymerisation had reached 260, the exposure of polyacrylic esters to ultrasonic waves did not result in breakdown to form radicals capable of reacting with DPPH.

DPPH has also been used to detect the formation of long-chain free radicals when polystyrene and polyisobutylene in organic solvents are exposed to ultrasonic waves[86]. When a 3% solution of polyisobutylene in isooctane or benzene was exposed for 15 min, sufficient free radicals were produced to decolourise ~ 10 mg DPPH in 100 ml. The same authors also used DPPH to show that ultrasonic depolymerisation is apparently not always accompanied by the formation of long-chain free radicals. For example, no decrease in the quantity of DPPH was observed during the irradiation of 3% solutions of polydimethylsiloxane in benzene, *n*-heptane, or isooctane, although a considerable decrease in the viscosity of the solutions was brought about.

It may be suggested that under the influence of ultrasonic waves, polysiloxanes are split into compounds which, unlike long-chain radicals, do not react with DPPH. The authors believe that rupture of the Si–O bond may be accompanied by intramolecular disproportionation to produce two stable macromolecular fragments:



They also suggest that rupture of the Si–O bond leads to the formation of two radicals which can ionise:



The possibility of such processes was pointed out by Berlin[86], who believed that radical-ion formation may be observed where relatively unstable ionic bonds are present in the polymeric molecule,

$$\ldots\sim RCOOM\ldots\vdots\ldots OCOR_1\ldots\simeq\ldots\rightarrow\ldots\simeq\ldots RCOOM^+ + \sim R_1COO^-,$$

while long-chain radicals are formed for the most part when the polymeric chains contain covalent bonds only:

$$\ldots\sim R{-}CH_2\overset{\cdot}{\underset{\cdot}{\vdots}}CH_2{-}R_1\ldots\simeq\ldots\rightarrow\infty RCH_2^{\cdot} + {\cdot}CH_2R_1\ldots\simeq\ldots$$

Experimental proof of the possibility of heterolytic rupture of the Si–O bond is provided by the following observations made by the above mentioned authors. They exposed polysiloxane in benzene to the action of ultrasonic waves, in the presence of methanol labelled with C^{14}. Methanol reacts readily with $\geq C^+$ ions and probably also with $\geq Si^+$ ions, and this apparently explains the inclusion of the radioactive methanol in the fragments of the broken polymer. This inclusion is not prevented by the presence of DPPH in the irradiated solution. They state that labelled methanol does not react with the products of the ultrasonic rupture of polyisobutylene and polystyrene in organic solvents, which indicates that the C–C bond rupture in these compounds is homolytic. No methanol is taken up by these molecules, irrespective of whether or not DPPH is present in the solution.

On the assumption that one molecule of methanol is taken up for every bond broken in the polysiloxane, the authors calculated the number of bonds broken in the ultrasonic field, and obtained the value 19×10^{-7} moles of broken bonds per gram of polymer, which may prove sufficient to bring about extensive physicochemical changes in the system.

The authors obtained a similar low figure (8×10^{-7} per gram of substance) for the number of bonds broken in polyisobutylene exposed to ultrasonic waves, calculated from the quantity of DPPH disappearing, on the assumption that each broken bond uses up 2 molecules of DPPH.

If it is assumed that under the action of ultrasonic waves, the polysiloxane molecules split to form ions, then in organic solvents with low dielectric constants (particularly non-polar solvents), they should remain extremely close to one another. In the authors' opinion, this may (in the absence of methanol) facilitate the disproportionation and the production of stable long-chain fragments. This process apparently takes place rapidly, since the addition of the radioactive methanol immediately after ultrasonic irradiation is not accompanied by reaction with the breakdown products of the polysiloxane.

The formation of stable molecular "fragments" as a result of disproportionation can also take place when certain other polymers are exposed to ultrasonic waves, if substances capable of inactivating the long-chain radicals are not present in the solution. In the absence of such substances (I_2, O_2, DPPH, etc.), the long-chain radicals may also recombine. Studies on those lines have been carried out by Henglein[83,87], who determined the rate of scission of an irradiated polymer in the presence and in the absence of I_2. The difference in the values was used to estimate the number of radicals inactivated as a result of recombination and hence the probability of this process

$$w_k = \frac{\text{number of radicals inactivated by recombination}}{\text{number of radicals formed}}$$

If polymers in the presence of I_2 split from P_0 to P_1. and in the absence of I_2 from P_0 to P_1', then the corresponding number of broken bonds, in moles per litre, will be

$$x = c_\rho\left(\frac{1}{P_1}-\frac{1}{P_0}\right) \text{ and } x_1 = c_\rho\left(\frac{1}{P_1'}-\frac{1}{P_0}\right).$$

It may be assumed that the number of radicals inactivated by recombination amounts to $x-x_1=\Delta x$, and it can be shown that

$$\frac{\Delta x}{x} = \frac{\Delta P_1}{P_1'}\frac{P_0}{P_0-P_1}, \text{ where } \Delta P_1 = P_1'-P_1.$$

Assuming that P_0/P_0-P_1 is close to unity, Henglein obtained

$$\frac{\Delta x}{x} = \frac{\Delta P_1}{P_1'}.$$

From the Staudinger equation, he proposed the following formula:

$$\frac{\Delta P_1}{P_1'} = \frac{\Delta Z_{\eta_1}}{Z_{\eta_1}} \frac{1}{\alpha},$$

which is obtained by taking account of the fact that $Z_{\eta_1'} - Z_{\eta_1}$ is small compared to $Z_{\eta_1'}$.

The viscosity number Z_{η_1} was calculated according to Schulz and Blaschke, from the specific viscosity of the solution. The values of α for the polymethyl-methacrylate and polystyrene in benzene were taken from the literature [70,71].

Henglein worked with polymer solutions free from oxygen, which was displaced by argon. According to his data, the specific viscosity ($\eta_{1\,sp}$) of the polymethyl-methacrylate irradiated in the presence of I_2 differed from the value for the polymer exposed in the absence of I_2:

$$\eta_{1\,sp} = 0.837; \quad Z_{\eta_1} = 0.140;$$
$$\eta_{1\,sp}' = 0.922; \quad Z_{\eta_1'} = 0.152.$$

A greater difference was observed between the values of $\eta_{1\,sp}$ and $\eta_{1\,sp}'$ for irradiated solutions of polystyrene in benzene:

$$\eta_{1\,sp} = 0.927; \quad Z_{\eta_1} = 0.148;$$
$$\eta_{1\,sp}' = 1.167; \quad Z_{\eta_1'} = 0.177.$$

From this Henglein concluded that w_k is greater for polystyrene than for polymethyl-methacrylate.

III. THE FORMATION OF COPOLYMERS BY THE ACTION OF ULTRASONIC WAVES AND THE INFLUENCE OF THE LATTER ON THE RATE OF POLYMERISATION PROCESSES

The combination of macroradicals should be accompanied by copolymerisation processes when a mixture of polymers is exposed to ultrasonic waves. Thus Henglein showed that the value of w_k (the probability of radical combination) of an irradiated mixture of polystyrene and polymethyl-methacrylate dissolved in benzene is different from the value of w_k for the separate polymers in the same solution. Studies were made at identical concentrations (2.5 g per litre) of the polymers, which had almost identical degrees of polymerisation: P_0 for polystyrene = 1.0×10^4; P_0 for polymethyl-methacrylate = 1.3×10^4. The irradiated mixture of these polymers had $\eta_{1\,sp} = 0.916$ and $\eta_{1\,sp}' = 1.090$ ($Z_{\eta_1} = 0.160$, $Z_{\eta_1'} = 0.186$), which indicated that, under the influence of the ultrasonic waves, the polystyrene radicals recombine with polymethyl-methacrylate radicals to form block- or graft-copolymers:

$$R\text{----}R \rightarrow R_n^{\cdot} + R_m^{\cdot}; \quad Q\text{----}Q \rightarrow Q_n^{\cdot} + Q_m^{\cdot};$$
$$Q_n^{\cdot} + R_n^{\cdot} \rightarrow Q_n R_n, \text{ etc.}$$

Other experimental evidence for this process was obtained by the same author.

It is known that polymethyl-methacrylate is precipitated from a benzene solution containing polymethyl-methacrylate and polystyrene when carbon disulphide is added, and in this way it is possible to separate one polymer from the other. According to Henglein, however, no precipitate is obtained if the solution is first exposed to ultrasonic waves; the solution merely becomes turbid. In his opinion, this effect indicates a change in the structure of the polymers, namely the formation of graft-copolymers, which tend to form a colloidal solution in the presence of CS_2.

The tendency of graft-copolymers to form colloidal solutions in the presence of precipitants in which one of the components of the copolymer is soluble, is, according to Henglein, an exceptional phenomenon.

No graft-polymer formation takes place if the polymer mixture is exposed to the ultrasonic field in the presence of substances which inactivate the long-chain radicals — intermediate products of ultrasonic polymerisation (Table 4).

Table 4 shows that the combination of polymeric radicals of the same kind is influenced to a greater extent by DPPH and I_2 than by oxygen, which is inconsistent with the fact, established by the same author, that O_2 is a more powerful inactivator of long-chain radicals than DPPH or iodine.

According to Henglein, when a mixture of polymethyl-methacrylate and polystyrene is exposed to ultrasonic waves in the presence of O_2, the long-chain peroxy radicals formed,

$$P_n^{\cdot} + O_2 \rightarrow P_n\text{–O–O}^{\cdot} \text{ and } Q_n^{\cdot} + O_2 \rightarrow Q_n\text{–O–O}^{\cdot}$$

recombine as follows:

$$P_n\text{–O–O}^{\cdot} + Q_n^{\cdot} \rightarrow P_n\text{–O–O–}Q_n \text{ or}$$
$$P_n\text{–O–O}^{\cdot} + Q_n\text{–O–O}^{\cdot} \rightarrow P_n\text{–O–O–}Q_n + O_2.$$

The formation of graft-polymers is suppressed if, at identical concentration of the reacting components (polystyrene and polymethyl-methacrylate), one of these (polymethyl-methacrylate) has a comparatively low degree of polymerisation P (Table 5). This is explained as follows. The polystyrene, with large value of P, forms more long-chain radicals under the influence of ultrasonic waves than polymethyl-methacrylate. Under these conditions the long-chain radicals from the polystyrene will react with one another, and thus suppress the process of graft-copolymer formation.

Other investigators developed the idea that polymerisation processes in an ultrasonic field are brought about by the production of free radicals.

Thus the ultrasonic polymerisation of styrene in the presence of polystyrene, according to Berlin and El'tsefon [88], results from the fact that long-chain radicals — the products of scission of the polystyrene molecules — appear in the irradiated solution. According to these authors, the process is activated considerably when water is added to the

TABLE 4. Precipitation with CS_2 of polymethyl–methacrylate from an irradiated benzene solution of a mixture of polymethyl-methacrylate (1.5 g/litre, and polystyrene (1.5 g/litre). (P_0 of polystyrene = $= 1.0 \times 10^4$; P_0 of polymethyl–methacrylate = 1.3×10^4).

Duration of exposure, min	% of polymethyl–methacrylate precipitated in the presence of various substances capable of inactivating long-chain radicals			
	– *	I_2, 10^{-4} M	DPPH, 10^{-4} M	Air
5	0	93	—	60
10	0	98	90	60
60	0	97	—	80

* Solution saturated with argon.

TABLE 5. Precipitation with CS_2 of polymethylmethacrylate, with different degrees of polymerisation P, from benzene solutions of a mixture of polymethylmethacrylate (1.5 g/litre) and polystyrene (1.5 g/litre) (P for polystyrene = 1.0×10^4).

Degree of polymerisation of polymethylmethacrylate, P	Precipitate of polymethylmethacrylate formed during exposure for:	
	5 min	10 min
$1.3 \cdot 10^4$	0	0
$1.5 \cdot 10^3$	52	0
$4.3 \cdot 10^2$	80	35

irradiated reaction mixture. In this case the water molecules act as sources of free hydroxyl radicals, which, according to Berlin, accelerate the polymerisation of styrene.

Polymerisation reactions are shown by acrylonitrile in aqueous medium under the influence of ultrasonic waves [89]. The authors suggest that the polymerisation of the acrylonitrile takes place not only as a result of conversion of monomer to a radical form, but also as a result of a characteristic autocatalytic effect, by which the polyacrylonitrile molecules produced are depolymerised under the influence of the ultrasonic vibrations to form long-chain radicals which are able to increase their polymeric chain. Oxygen, which blocks the unsaturated end groups of the long-chain radical, is a fairly powerful inhibitor of the polymerisation of acrylonitrile.

TABLE 6. Dependence of the rate of polymerisation of acrylamide on the modulation frequency of the ultrasonic waves.

Modulation frequency, c/s	Duration of impulse, μ sec	Duration of exposure, min	Effective duration of exposure, min	Polymer formed, mg	η_{sp}/c (c = 1 g × × litre^{-1})	Rate of polymerisation, mole litre^{-1} × × min^{-1} × 10^{-4}
Unmodulated frequency	—	5	5	111	0.462	77
»	—	5	5	90	0.443	63
7	36.0	20	5	129	0.659	90
26	9.6	20	5	96	0.541	67
112	2.2	20	5	65	0.550	45
340	0.73	20	5	45	0.711	31
1200	0.21	40	10	10	—	3.5

The inhibiting action of oxygen may be intensified during ultrasonic depolymerisation in an aqueous medium as a result of its activation in the cavities.

The part played by cavitation in ultrasonic polymerisation is pointed out by Henglein [90]. According to his data, the rate of polymerisation of acrylamide in water saturated with argon depends on the duration of the ultrasonic impulse or on the modulation frequency of the ultrasonic vibrations (Table 6).

Table 6 shows that the rate of polymerisation decreases with decrease in the duration of the ultrasonic impulse, which also makes cavitation extremely difficult.

According to Henglein and Schulz [91], the rate and degree of polymerisation depend on the nature of the gas with which the solution is saturated. In the presence of nitrogen carefully purified from oxygen, the ultrasonic polymerisation of acrylamide starts with practically no induction period. The rate of polymerisation of acrylamide is also high when argon and nitrogen are present in the irradiated solution; the ultrasonic polymerisation is suppressed by oxygen and hydroquinone, which block the radicals produced.

Methacrylic acid is also polymerised in aqueous medium exposed to ultrasonic waves [92]. The data of these investigators show that the polymerisation effect is again dependent on the nature of the gas present in the water. Thus after 15 minutes' exposure in the presence of air, 1.8% of the methacrylic acid is polymerised, in the presence of nitrogen 12.7% is polymerised, and in the degassed solution the polymerisation process does not start at all.

Ultrasonic waves accelerate emulsion polymerisation. This has been observed in the preparation of copolymers of butadiene (CH_2=CH–CH=CH_2) and styrene (C_6H_5–CH=CH_2) [93] (see also Kudryavtsev [94]). 37.5 g of butadiene and 14.5 g of styrene in 90 ml of distilled water were irradiated, using soap as emulsifier and potassium persulphate as water—soluble initiator. The authors ascribe the increase in the rate of emulsion polymerisation and the decrease in the induction time of the reaction to the rapid removal of free oxygen from the mixture under the influence of the ultrasonic vibrations. In their view, the decrease in the induction period may be related to the activation of the polymerised styrene molecules by the ultrasonic waves, which should lead to an increase in the number of long-chain free radicals in the irradiated system. Finally, they suggest that any impurities acting as inhibitors of emulsion polymerisation may be oxidised in the ultrasonic field.

The acceleration of emulsion polymerisation in an ultrasonic field has been observed by other workers. For example, Sato and Harisaki [95] established that the action of ultrasonic vibrations increases the reaction yield in the emulsion polymerisation of vinyl acetate (CH_3COO–CH=CH_2). The initiator used was ammonium persulphate $(NH_4)_2S_2O_8$, and oleates were used as emulsifiers.

These examples indicate that water is a very favourable medium for the acceleration and possibly also the initiation of ultrasonic polymerisation of synthetic polymers. The medium is favourable not only for occurrence of cavitation phenomena and the related mechanical forces, but also for the electrochemical processes which take place in the cavities and result in the production of activated and ionised molecules of the solvent (water) and any gases present. These processes have to be taken into account, particularly in analysis of the depolymerising and polymerising action of ultrasonic vibrations on aqueous solutions of highly polymerised materials extracted from plant and animal cells, such as polysaccharides, nucleic acids, nucleoproteins, hyaluronic acids, etc. [96-102]

These macromolecules may be depolymerised under the influence of ultrasonic waves, and, under certain conditions, the opposite effect of increase in the molecular weight may be observed, apparently accompanied by an increase in the degree of branching. Such studies are of interest in examining the relationship between the biological function and structure of bio-polymers, and require a separate discussion.

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There is now sufficient information to indicate that modern mechano-chemistry has available a new form of energy — — ultrasonic energy — which is capable of bringing about almost all the reactions known in this field.

A clear picture has been obtained of the part played by a number of factors, such as the nature of the solvent and any

gases present, the physical parameters of the polymeric molecules, their concentration, etc., in bringing about the process known in mechano-chemistry as "destruction–combination" under the influence of ultrasonic waves.

Further study of ultrasonic macromolecular reactions promises the discovery of new principles in macromolecular chemistry and the extension of its practical applications.

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DEVELOPMENTS IN THE CHLORINATION OF SATURATED HYDROCARBONS

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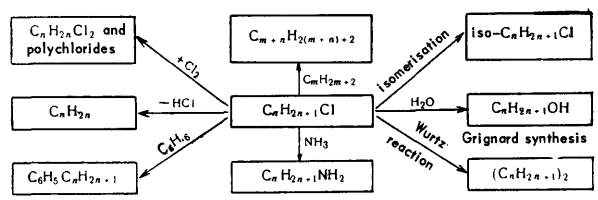
INTRODUCTION

The present article is a review of work published on the chlorination of saturated hydrocarbons in the USSR and abroad from 1947 to 1958.

Ellis[1] has reviewed the literature in this field up to 1934, and Hass and McBee[2] and Nelles[3] have also considered certain aspects of the chlorination of saturated hydrocarbons in their reviews. The literature from 1937 to 1947 has been reviewed by Solodar' and Markin[4].

A considerable expansion of the chemical industry in the USSR is planned for the period 1958–1965, particular attention being directed towards the necessity of utilising natural and industrial petroleum gases as raw material for the chemical industry. The saturated hydrocarbons in natural and industrial gases can be converted into useful products by various methods, chiefly by chlorination.

Diagram of possible conversions of alkyl halides



Chlorinated hydrocarbons find very wide application in industry and agriculture as solvents, refrigerants, synthetic intermediates, insecticides, herbicides, etc. At the present time the production of chlorinated hydrocarbons is growing continuously; thus in the USA the production of chlorine, hydrogen chloride, and chlorine-containing chemicals increased considerably in 1955 by comparison with 1954 [5] (Table 1).

TABLE 1. Production of chlorinated hydrocarbons in the USA (tons).

Product	1953	1954	1955	1956
Cl_2	—	2 622 298	3 091 628	—
HCl	—	672 889	764 419	—
CH_3Cl	18 300	—	16 500	—
CH_2Cl_2	28 000	—	31 000	—
$CHCl_3$	11 500	—	18 300	—
CCl_4	117 000	—	130 500	136 200
$C_2H_4Cl_2$	—	—	213 600	249 700
C_2H_3Cl	234 000	—	245 900	28 600

Chlorinated hydrocarbons may be obtained by various methods, the chief being:

1. Hydrochlorination and chlorination of unsaturated hydrocarbons:

$$C_nH_{2n} + HCl \rightarrow C_nH_{2n+1}Cl.$$

2. Chlorination of saturated hydrocarbons:

$$C_nH_{2n+2} + Cl_2 \rightarrow C_nH_{2n+1}Cl + HCl.$$