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The Polymerisation of Solid Monomers Under Conditions of Deformation at a High Pressure

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The polymerisation of solid monomers deformed under high pressure has been examined. The anomalously high reactivity of the substances under these conditions, and the reasons for it, have been discussed. The possibilities provided by the methods of formal kinetics for the description and study of the mechanism of polymerisation have been demonstrated for the polymerisation of acrylamide.
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I. INTRODUCTION

The formation of macromolecular compounds with shear deformation of the solid monomers under a high pressure was first detected by Enikolopov, Zharov, and Kapustyan in 1964.

In the first studies[1], for ten monomers of different character, it was shown that shear deformation and high pressures (SD + HP) are powerful factors stimulating the polymerisation of solid monomers. In a short time, studies in this field have extended and have led to considerable progress in the investigation of the reactivity of solid monomers and the regular features of polymerisation under SD + HP conditions. Compounds of various classes have now been studied: alkene derivatives, compounds of the acetylene series, nitriles, heterocyclic compounds, aromatic hydrocarbons, etc., corresponding to more than one hundred individual substances. Most of these substances can form macromolecular compounds under SD + HP conditions[1-25]. The study of the polymerisation has revealed unusual features in the chemical processes, for example the anomalously high reaction rates and the dependence of the kinetics of polymerisation on the magnitude of the shear deformation.

About one hundred papers have been published on the formation of polymers under SD + HP conditions. Most of the work in this field has been carried out by Soviet scientists. In recent years, a number of studies in this area have been carried out by the Japanese workers Ogo and Okuri[11,12,16].

II. CHARACTERISTIC FEATURES OF THE TRANSFORMATIONS AND REACTIVITY OF ORGANIC COMPOUNDS DEFORMED AT HIGH PRESSURES

Experiments under SD + HP conditions are carried out on an apparatus of the anvil type[26-28], whose operational principles were first realised by Bridgman, and which is based on the fact that the compression of a solid specimen between two plates does not lead to flow of the substance if a sufficiently thin specimen is taken. A version of this apparatus is given in Fig.1. The solid reaction mixture is placed between the anvils, which are made of ball-bearing steel or VK-6 hard alloy and which have the form of truncated cones. The thickness of the specimen depends on the nature of the substance and the area of the working surface of the anvils; for an anvil area of 1 cm^2, the weight of the original specimen is 5–10 mg. The anvils are compressed by means of a press capable of creating a load of up to 100 tons; a pressure of up to 10 GPa is produced in the specimen. After the pressure has been established, the specimen is deformed by rotating the lower anvil, which is on a platform placed on a supporting ball bearing. The platform is rotated by an electric motor and reducing gear. The shear forces are measured using an assembly consisting of a spring element, levers, and a mechanotron, the signal from which is passed to a recorder. The anvils can be kept at a constant temperature in the range 77–500 K.

Experiments have shown[1-25] that under SD + HP conditions, polymers can be formed by organic compounds of various classes: a) compounds with one $-C=C-$ bond: hydrocarbons (ethylene, styrene, α-methylstyrene, etc.), esters (alkyl acrylates, alkyl methacrylates), acids (acrylic, methacrylic, crotonic, etc.)[1,7], anhydrides[6], amides, imides[5], and nitriles[17,20], chloro-compounds (dichloro- and trichloropropenes, etc.)[15]; b) compounds with conjugated double bonds: butadiene, cyclopentadiene[7,14], 1,1,2-trichlorobutadiene[15], etc.; c) compounds with a triple bond: derivatives of acetylene (*p*-diethynylbenzene, tolan[1], derivatives of diacetylene[16], etc.), nitriles (malononitrile, cyanacetamide, terephthalodinitrile, 4-cyanopyridine, etc.)[17-19]; d) heterocyclic compounds: trioxan, hexamethyltrisiloxane[1,7], thiophene, pyridine[20,21]; e) aromatic compounds: benzene[25], napthalene, anthracene, phenanthrene[19,20,22], quinones, etc.[23,24]

The study of a large number of organic compounds indicates that if the molecules of a substance contain the groups $-C\equiv C-$, $-C=C-$, $-C=N-$, heterocyclic rings, or aromatic rings, then the conditions produced when the specimen is deformed can induce the formation of macromolecular compounds. Compounds with different reactivities can react: monomers which readily form polymers by different mechanisms in both the liquid and solid phases (acrylamide, styrene, etc.[1,30]); compounds which in other conditions do not give macromolecular products in the solid state (methyl methacrylate[8], maleic anhydride[1,6]); and substances which polymerise with difficulty (nitriles[20], derivatives of acetylene[1,7], whose polymerisation takes place only under severe conditions at high temperatures.

Parallel transformations in addition to the main reaction are often observed under SD + HP conditions. Polymerisation may be accompanied by Diels–Alder reactions[14], and the substances may react with atmospheric oxygen and moisture at the moment of deformation. If the compound contains two or more functional groups capable of reacting under SD + HP conditions, cross-linked insoluble polymers are formed[14,15,18,29]. The influence of side reactions can be decreased by selecting a range of pressures at which polymerisation takes place without complications; the products are analogous to the polymers synthesised under ordinary conditions. Styrene, methyl methacrylate, and trichlorobutadiene are converted into polymers which have the same structures as the corresponding polymers obtained by radical polymerisation[8,15,30]. Trioxan forms a polymer whose infrared spectrum is identical to that of polyoxymethylene obtained by radiation polymerisation[7]. Derivatives of maleimide give polymers corresponding to those obtained by radiation polymerisation[5].

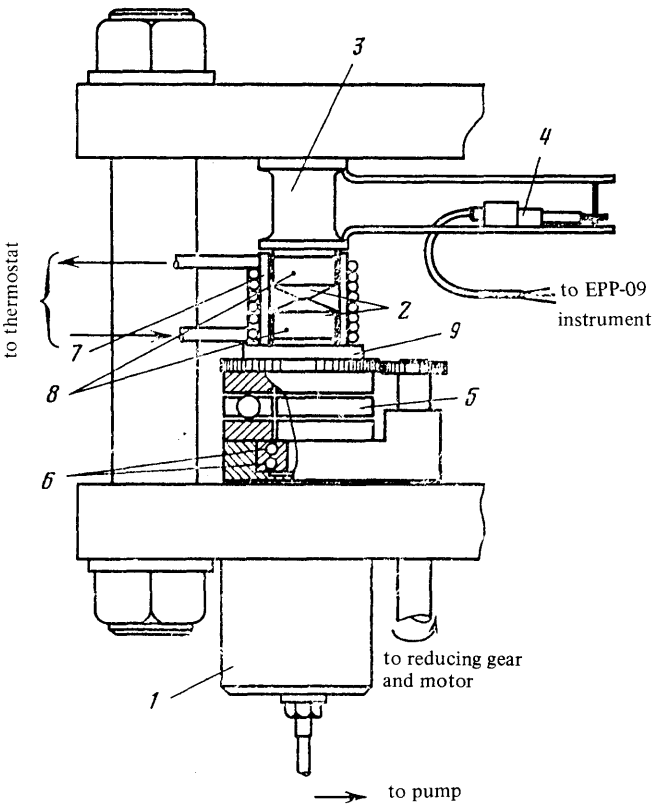


Figure 1. Apparatus for studying the transformations of substances under SD + HP conditions[28]: *1*) cylinder of hydraulic press; *2*) anvils; *3*) spring element; *4*) mechanotron; *5*) supporting ball bearing; *6*) radial ball bearing; *7*) constant-temperature jacket; *8*) positions for thermocouples; *9*) step bearing of heat insulator.

The reactivity of compounds under SD + HP conditions is such that high degrees of transformation are achieved in anvil rotation times measured in seconds[3,4,7]; the deformation of the solid specimen is a necessary condition for the chemical reaction. Treatment of the reaction mixture at the same pressures for times which are 10^2–10^3 times the duration of the experiments under SD + HP conditions does not lead to any significant transformation[1,7].

A general feature of chemical processes under SD + HP conditions is that the extent of the transformation depends on the magnitude of the shear deformation (usually expressed in terms of the angle of rotation of the anvil). The nature of the curves giving the dependence of the degree of conversion on the angle of rotation may vary, but the conversion always increases with increase in the deformation (Fig.2). The yield of reaction products increases with increase in pressure. With decrease in temperature, the rate of transformation decreases; the temperature coefficient of the reaction is small, however, and polymerisation can take place even at liquid-nitrogen temperature (acrylamide, butadiene, etc.)[6,7,14,31].

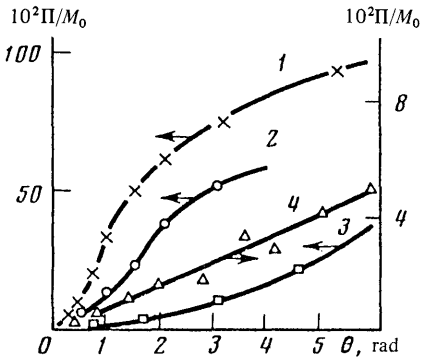


Figure 2. Dependence of the yield of polymer (Π/M_0) on the angle of rotation (θ) of the anvils (2000 MPa, 293 K)[7]: *1*) acrylamide, *2*) methacrylamide, *3*) maleic anhydride, *4*) trioxan (1000 MPa).

Other characteristic features of the formation of macromolecular compounds under SD + HP conditions are conveniently considered for specific examples.

1) Acrylamide. This monomer polymerises readily under SD + HP conditions, beginning at a pressure of several hundred MPa[4,6,31,32]. The study of the transformations of this monomer has resolved the question of when polymerisation takes place: whether the polymer is formed at the moment of deformation, or whether the growth of the polymer chains takes place after the SD + HP experiment is complete, as a result of the initiation of active centres, accumulated in the substance during its deformation. Which of these possibilities is realised was established[32] by measuring the shear stress of the specimen during deformation. Fig.3 gives the observed dependence of the shear stress (τ) on the angle of rotation of the anvil (θ) and on the quantity of polymer formed in the specimen (Π/M_0). The curves in Fig.3 show the accumulation of polymer in the specimen at the moment of deformation. Moreover, according to the results of the same study[32], for the mixture of acrylamide and polyacrylamide prepared by mechanical mixing or partial polymerisation, the values of τ correspond to the dependence of Π/M_0 given in Fig.3*b*. Thus polymerisation takes place at the moment of deformation of acrylamide, and the contribution of post-polymerisation is insignificant or non-existent.

2) *Styrene*[30]. The structure of the polymer obtained by the deformation of solid styrene at a pressure of 1000 MPa is extremely close to that of the polymer synthesised by radical polymerisation. With increase in pressure, however, the structure of the polymer formed under SD + HP conditions changes: there is a decrease in the proportion of units in the regular, predominantly syndiotactic, groups characteristic of ordinary polystyrene, and an increase in the proportion of units in short and irregular blocks. This phenomenon may be related to "head to head" connection or chain branching, and may be the consequence of the rupture of benzene rings. Side reactions taking place in parallel at pressures above 4000 MPa give a product made up of short polystyrene blocks, which are joined to one another by groups with an irregular structure.

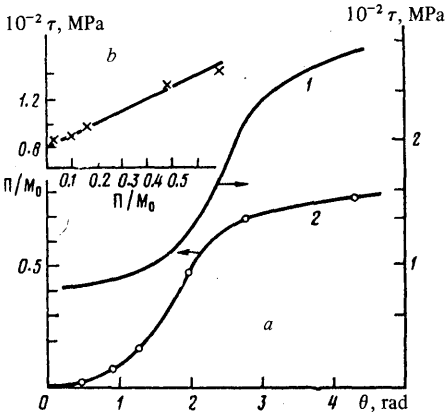


Figure 3. Relationship between the shear stress of the specimen τ, the degree of transformation Π/M_0, and the angle of rotation of the anvils θ;[32] *a*) dependence of the shear stress and the degree of transformation on the angle of rotation; *b*) dependence of the shear stress on the concentration of polymer in the specimen.

Thus with increase in pressure in SD + HP experiments there may be a change in the structure of the resultant macromolecular compound as a result of side reactions which are not revealed at low pressures.

3) *Trioxan*. The study of the polymerisation of trioxan has shown[7] that this monomer is polymerised with great difficulty under SD + HP conditions. At pressures of 3000–4000 MPa and θ = 4–5 rad, the yield of polymer did not exceed 1%. At lower pressures (1000–1500 MPa), no polymer was detected. If however trioxan is treated beforehand with ionising radiation, that is if ionic active centres are introduced, then this monomer polymerises readily on deformation even at a pressure of 1000 MPa to give polyoxymethylene (see Fig. 2).

The formation of polyoxymethylene under SD + HP conditions from trioxan containing ionic active centres indicates that the formation of the macromolecules is not due only to the production of the active centres and that it is the deformation of the solid monomer than ensures the necessary conditions for the chain process of growth of the polymer molecules.

Compounds whose polymerisation is difficult or not detected at all under ordinary conditions are of particular interest.

1. Polymerisation of Nitriles and Aromatic Compounds

Nitriles under ordinary conditions undergo poly-addition either under the influence of large doses of ionising radiation or in the presence of Lewis acids with cocatalysts. The passivity of the cyano-group with respect to polymerisation is explained by the fact that the formation of sequences of $-C=N-$bonds in many cases is a thermodynamically unfavourable process[33].

Under SD + HP conditions, however, solid nitriles can react to form sequences of $-C=N-$ bonds; the polymers obtained are brown or black, and give an EPR signal in the form of the singlet characteristic of polyconjugated systems[19]. The change in the colour of the nitriles on polymerisation made it possible to use a micro-apparatus with transparent diamond anvils to follow visually the transformations of the nitriles during deformation[18]. These observations, made for tetracyanoethylene, malononitrile, and terephthalodinitrile, made it possible to record the breakdown of the crystalline blocks in the field of the shear stresses, to observe the displacement zones in the substance, and, which is most important, to detect the development of the polymerisation process as the deformation of the specimen increased[18].

The transformations of other nitriles under SD + HP conditions was studied using ordinary apparatus[17–20]. The reactivity of these compounds varies over a wide range[7,18]. The least reactive are derivatives of compounds of the aliphatic series: stearonitrile and palmitonitrile do not react even at 10000 MPa; succinonitrile is polymerised at this pressure, but at higher values of the deformation. Increase in the number of CN groups in the molecule, and additional functional groups such as $-C=C-$, NO_2, aromatic rings, etc. increase the reactivity of a compound to a considerable extent: benzonitrile reacts at 8000 MPa, *p*-nitrobenzonitrile at 5500 MPa, fumaronitrile at 3000 MPa, malononitrile at 1000 MPa, etc.[18] Under deformation conditions, both functional groups often react. Thus 4-cyanopyridine and benzonitrile react both at the $C\equiv N$ group and with opening of the aromatic ring. If the molecule contains a group more reactive than CN, for example the $-C=C-$ group in acrylonitrile, the polymerisation takes place primarily through this group[20].

Thus the transformations of nitriles are accompanied by the formation of products with a high molecular mass. The production of the structure of the polymeric molecules in the general case, however, is due not only to the successive attachment of CN groups to one another but also to the reaction of other functional groups ($-C=C-$, amide, NO_2, etc.)[18].

Aromatic hydrocarbons under SD + HP conditions undergo unusual transformations, whose chief characteristic is the opening of the aromatic rings[4]. It is known that aromatic fragments of molecules are among the most stable in chemical reactions. Very high pressures of tens of thousands of MPa generally do not bring about the transformation of aromatic hydrocarbons[34].

Benzene, pyridine, and thiophene are classical examples of aromatic compounds. All these substances at 8000–10000 MPa under shear deformation conditions undergo transformations accompanied by rupture of the aromatic ring and the formation of macromolecular compounds[9,20,35,36]. For example, benzene is converted into a brown polymer which does not melt and which is insoluble in common solvents; the infrared spectrum of the product does not contain absorption bands characteristic of aromatic derivatives, and is identical to the spectrum of the polyacetylene obtained on Ziegler–Natta catalysts, that is under SD + HP conditions, benzene is converted into a polymer made up of sequences of $-C=C-$ bonds[25,36]. The formation of polyene structures under SD + HP conditions is unique. The opening of the benzene rings under other conditions has been reported; it can take

place, for example, under the influence of radiation[37], ultrasonic waves[38], and shock waves[39], but the formation of sequences of −C=C− bonds is not observed.

Polynuclear compounds with isolated or condensed rings (naphthalene, biphenyl, anthracene, phenanthrene, etc.) under SD + HP conditions also form macromolecular compounds by rupture of the aromatic ring[20,36]. As with nitriles, the pressures at which aromatic compounds begin to react are characteristic of each substance[7]. Thus anthracene begins to polymerise at a pressure of 2000 MPa and above, naphthalene at 4000 MPa, biphenyl at 8000 MPa, and bibenzyl at 2,3-dimethylnaphthalene at 10000 MPa (durene does not react at these pressures[36]).

The reactivity of hydrocarbons under SD + HP conditions depends on the number of aromatic rings in the molecule, on the way in which they are connected, and on the nature of the substituents[35,36]. The stability of an aromatic derivative decreases with increase in the number of rings (benzene is more stable than naphthalene, naphthalene is more stable than anthracene, and biphenyl is more stable than terphenyl). For a given number of rings, the reactivity of the hydrocarbons depends on the way in which the rings are connected; anthracene reacts at lower pressures than phenanthrene, and phenanthrene reacts before terphenyl. Compounds with isolated rings are more stable than those with condensed rings: biphenyl is more stable than naphthalene, etc. The reactivity is influenced strongly by aliphatic groups. Dimethylnaphthalene, bibenzyl, and durene are much more stable in SD + HP conditions than their non-substituted analogues. The stability of these compounds in a field of mechanical stresses cannot be explained within the framework of the usual concepts of organic chemistry, since CH_3 or CH_2 groups have practically no influence on the stability of an aromatic ring. It has been suggested[7,35] that mechanical stresses may be "concentrated" in chemical bonds in different ways; mobile aliphatic groups prevent the "concentration" of the mechanical stresses in the molecule or its fragments, leading to a decrease in the reactivity of the substances under SD + HP conditions.

2. Estimation of the Rate Constants of Polymer Chain Growth

Chemical reactions under SD + HP conditions take place in times measured in seconds or fractions of a second, that is the reaction rates are very high. In a number of cases it has been possible to estimate the lower limit of the reaction rate constant[7,42].

Table 1. Rate constants for the growth of polymer chains (mole litre^{-1} s^{-1}) calculated for the liquid phase and observed for DS + HP.

Monomer	p, MPa	T, K	t, s	P	k_p (calc.)	k_p (SD + HP)	Refs.
Styrene	1000	195	1	1000	1.6	$\geqslant 10^2$	[7, 30]
Acrylamide	1000	150	1	1000	1.5	$\geqslant 10^2$	[3, 7]
Butadiene	2000	150	1	200	10^{-3}	$\geqslant 20$	[7, 29]

The lower limit of the rate constant is calculated using the obvious inequality[7]:

$$k_p \geqslant P/M_0 t$$

relating the rate constant of the propagation of the polymer chains (k_p, litre mole^{-1} s^{-1}) to the concentration of monomer (M_0, M), the degree of polymerisation (P), and the reaction time (t, s). By substituting the experiment time and the degree of polymerisation in the inequality obtained, it is possible to calculate the lower limit of the rate constant of polymer chain propagation. These estimates have been carried out for various polymerisation reactions (Table 1). The examples given in Table 1 indicate that under SD + HP conditions, the polymerisation rate constants are greater by 2–5 orders of magnitude than the corresponding rate constants for polymerisation in the liquid phase. In other words, on deformation of the solid monomers the reaction of the double bonds with the radicals is stimulated.

Table 2. Degree of transformation, yields of product, and rate constants for the dimerisation and trimerisation of cyclopentadiene[42].

T, K	p, MPa	t, h	$10^2 M/M_0$	$10^2 2M_2/M_0$	$10^2 3M_3/M_0$	k_d, litre mole^{-1}s^{-1}	k_t/k_d
Experiments in the liquid phase*							
353	500	1	8.35	91.3	0.32	$2.4\cdot10^{-3}$	$1.5\cdot10^{-3}$
353	0.1	5	31.7	68.2	0.076	$9.0\cdot10^{-5}$	$1.05\cdot10^{-3}$
293	0.1	170	56.9	43.1	0.0021	$7.2\cdot10^{-7}$	$6.7\cdot10^{-1}$
Experiments under SD + HP conditions**							
153	4000	0.02***	45.5	47.3	7.2	—	$2.5\cdot10^{-1}$

* 10% solution in toluene used.
** Pure cyclopentadiene.
*** Angle of rotation of anvils equal to 2.6 rad.

The reaction rate constants under SD + HP conditions were also estimated quantitatively in a study of the dimerisation of cyclopentadiene[42]. In the liquid phase this reaction is accompanied by the formation of small quantities of oligomers, mainly trimers, so that the kinetics of dimerisation are described by equations which take account of the formation of the trimers[29,42]:

$$-\frac{dM_1}{dt} = \frac{1}{2}\frac{dM_2}{dt} = k_d M_1^3 \quad , \tag{1}$$

$$\frac{dM_3}{dt} = k_t M_1 M_2 \tag{2}$$

where M_1, M_2, M_3 are the concentrations of the monomer, dimer, and trimer, M; and k_d and k_t are the dimerisation and trimerisation constants respectively. Some of the experimental results, and also the constants k_d and k_t calculated using the equations obtained by solving the differential equations (1) and (2)[7,29], are given in Table 2. When the reaction is carried out under SD + HP conditions, the trimerisation rate constant increases considerably relative to the dimerisation rate constant. Comparison of the dimerisation rate constants calculated for the liquid phase and observed under SD + HP conditions gives an interesting result. k_d for the liquid-phase reaction (at the temperature and pressure of the SD + HP experiment) was calculated from the known values of the activation energy[40] and the volume effect of the formation of the activated complex[41]. The calculated rate was 2×10^{-9} mass % min^{-1}, whereas the rate observed under SD + HP conditions is not less than 15–20 mass % min^{-1}, that is it is 10^{10} times greater[42].

Thus the estimates of the reaction rate constants under SD + HP conditions indicate that the substances show an anomalously high reactivity under conditions of deformation in the compressed state.

3. The Role of Heat Production Under SD + HP Conditions

The deformation of solid specimens involves considerable mechanical work, most of which is converted into heat; the solution of the problems related to the estimation of the heat production in a substance is therefore important for the interpretation of the results of SD + HP experiments, and in particular for the determination of the factors responsible for the high reactivity. Calculations and direct measurements of the temperature of specimens have shown[7,49] that the total heat production in a substance on deformation in an apparatus of the anvil type is slight, and cannot be responsible for the high rate of the chemical transformations.

Another mechanism which can be introduced to explain the high reactivity of the compounds is based on the concept of "hot spots". It is suggested[7] that at the moment of deformation in the specimen there exist zones in which there is a sharp increase in temperature as a consequence of the non-uniformity of the specimen, the separation of the plastic flow of the substance, or other factors. The size of these zones is obviously greater by many orders of magnitude than that of the molecules, and the temperature in these "hot spots" cannot exceed the melting point of the substance at the given pressure[44].

To resolve the question of the existence of these molten zones under SD + HP conditions and their role as places where the reactions take place, a study was made of the influence of pressure on the rate constants of the iso- and syndiotactic addition of the growing polymer radical to the double bond of methyl methacrylate (k_i and k_s) in the liquid-phase polymerisation[45] and the polymerisation of this monomer under SD + HP conditions[8]. The difference in the volume effects of activation $\delta\Delta V^{\neq} = \Delta V_i^{\neq} - \Delta V_s^{\neq} = -0.3$ cm^3 mole^{-1} (liquid-phase polymerisation, pressure range 8000–1050 MPa) and the difference in the activation energy $E_i - E_s$, which was found to be 1.1 kcal mole^{-1} at both ordinary and high pressures, were determined. For SD + HP conditions, it was found that $\delta\Delta V^{\neq} = -0.08$ cm^3 mole^{-1}.[8] The values of $\delta\Delta V^{\neq}$ and $E_i - E_s$ obtained were used to verify the concept of "hot spots".

If the reaction takes place in the zones of the molten monomer, the change in lg (k_i/k_s) with change in pressure under SD + HP conditions should be determined by the quantity $|\delta\Delta V^{\neq}| > 0.3$ cm^3 mole^{-1}, since increase in pressure is accompanied by an increase in the temperature of the molten zones as a result of the increase in the melting point with increase in pressure. Thus the value $\delta\Delta V^{\neq} = -0.08$ cm^3 mole^{-1} found under SD + HP conditions does not agree with the suggestion that molten zones exist.

The applicability of the concept of "hot spots" can also be verified by another method, by comparing the values of k_i/k_s. This ratio is appreciably higher under SD + HP conditions than for polymerisation in the liquid phase[7]. To explain this difference, it is necessary to assume that the heat production in the monomer on deformation takes place up to a temperature ~ 100 K higher than the melting point of methyl methacrylate at the given pressure, but this contradicts existing ideas about local heat production[44]. Thus under SD + HP conditions, either no local molten zones of monomer are produced, or this phenomenon does not make a significant contribution to the chemical process.

4. Copolymerisation Reactions

A number of studies have been carried out for reaction mixtures consisting of two monomers[46–49]. When specimens of mixtures of acrylamide and methacrylamide with the eutectic composition (87% acrylamide and 13% methacrylamide) were deformed, a reaction was observed, accompanied by the formation of polymeric products (pressure range 500–1500 MPa, temperature 293 K). Gel-permeation chromatography indicated that copolymers are formed[46]. An interesting feature is that the rate of the copolymerisation of acrylamide and methacrylamide is greater than the rates of polymerisation of pure acrylamide and methacrylamide.

The study of the copolymerisation of mixtures of maleic anhydride and acenaphthene under SD + HP conditions[47,49] showed that the nature of the dependence of the composition of the copolymer on the composition of the original mixture is the same as that for the liquid-phase copolymerisation of the same monomers in acetone solution. The composition of the copolymer remains unchanged with change in the composition of the original mixture (with increase in the proportion of maleic anhydride from 20% to 85%). This was attributed[47] to the reaction of maleic anhydride and acenaphthene to form a charge-transfer complex, which polymerises rapidly and forms a copolymer of definite composition.

Copolymerisation reactions are often sensitive to both the mechanism of polymerisation and the phase state of the original mixture of the monomers. These reactions include the copolymerisation of styrene and methyl methacrylate, so that this reaction has been studied in detail under SD + HP conditions[6,48,49]. The experiments were carried out at 2000 MPa, 195 K, and angles of rotation of the anvils to give a yield of copolymer not exceeding 10%. Studies of the infrared and NMR spectra of copolymers of styrene and methyl methacrylate (obtained under SD + HP conditions, in the liquid phase, and with radiation-initiated polymerisation of the solid monomers), fractionation of the polymeric products, and subsequent analysis of the fractions gave the following results[48]: 1) under SD + HP conditions, mixtures of styrene and methyl methacrylate react to give copolymers; 2) the nature of the distribution of the units of styrene and methyl methacrylate is the same for the copolymer macromolecules obtained by radical copolymerisation and the copolymers obtained under SD + HP conditions; 3) the copolymers obtained by solid-phase polymerisation show a distribution of the units approaching that found for a mixture of homopolymers of styrene and methyl methacrylate; 4) the dependence of the yield of copolymer on the composition of the original mixture, obtained under SD + HP conditions, is close to that for the liquid-phase copolymerisation (the form of this dependence is quite different for the solid-phase copolymerisation).

Thus in spite of the fact that the original solid mixtures of monomers are non-uniform, their deformation is accompanied by effective mixing of the components and the formation of copolymers with uniform compositions. Moreover, the composition of the copolymers and the distribution of the monomeric units in the polymer chain are close to those which are observed in the copolymers obtained by liquid-phase radical polymerisation. From these factors, it was concluded[48] that the state of a substance under SD + HP conditions, according to a number of its properties, is close to the liquid state (a quasi-liquid state).

III. KINETICS AND MECHANISM OF POLYMERISATION UNDER CONDITIONS OF SHEAR DEFORMATION AND HIGH PRESSURES

To determine the mechanism and characteristic features of the kinetics of polymerisation reactions with SD + HP, a series of investigations was carried out, involving the detailed study of the polymerisation of acrylamide, and including studies of the physical state of the substance

during its deformation[50-52,54] and a series of kinetic measurements and calculations undertaken to investigate the mechanism of polymerisation[3,32] and to find the rate constants of the elementary stages of the polymerisation of acrylamide[7,53,55].

These studies established a number of general regular features of polymerisation under SD + HP conditions. It was found that the yield of polymer at constant pressure and temperature depends on the magnitude of the deformation and is independent of the rate of deformation of the specimen[3,7]. The kinetic curves are *S*-shaped (Fig. 4), and the point of inflection corresponds to the range in which there is a change from internal displacement of the layers of substance to the surface slip of the anvils over the specimen[7]. It can be seen from Fig. 4 that with increase in pressure, the position of the point of inflection is displaced to the range of higher degrees of conversion, due to the increase in the strength of the adhesion of the specimen to the material of the anvils. The calculations were carried out using data relating to the range in which the angle of rotation of the anvils corresponded to the magnitude of the deformation of acrylamide[7]. The molecular mass of polyacrylamide at first increases with increase in the deformation, reaches a maximum for 2–8% conversion (depending on the conditions of the experiment), and then decreases (Fig. 5).

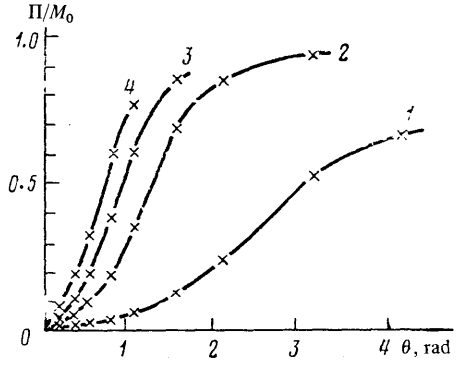


Figure 4. Dependence of the yield of polyacrylamide on the angle of rotation of the anvils at 293 K and different pressures[7]: *1*) 1000, *2*) 2000, *3*) 2500, *4*) 3000 MPa.

A study of the kinetics of the dependence of the polymerisation of acrylamide on the radical acceptors added to the monomer and experiments with previously irradiated specimens (treatment with γ-rays from a ^{60}Co source)[32] indicated that the polymerisation of acrylamide takes place by a radical mechanism. The increase in the rate of polymerisation is proportional to the increase in the concentration of polymer in the specimen[32]. The mechanism of the increase in the rate of polymerisation with increase in the concentration of the polymer is not clear. The appearance of polymer leads to an increase in the shear stress applied to the specimen (see for example Fig. 3a), and this may lead to an increase in the reaction rate, since the shear stress applied to the reaction mixture under SD + HP conditions influences the rate of the chemical process[56]. It is also extremely probable that the appearance of polymer molecules in the specimen facilitates the production of regions in which the mechanical stresses leading to the generation of active centres for polymerisation are concentrated[32].

On the basis of the regular features observed, a mechanism was proposed for the polymerisation of acrylamide[7,53,55]; the following assumptions were made: a) all the elementary stages of polymerisation (initiation, propagation, and bimolecular termination of the chain) take place during the deformation of the specimen; the collision of the reagent molecules takes place only as a result of the movement of the layers of the substance relative to one another on shear deformation. Thus the independent variable in the equations describing the elementary stages should be not time but the magnitude of the deformation of the substance; b) the production of active centres (radicals) takes place mechanochemically in a medium of the monomer in regions where mechanical stresses are concentrated, and the number of such regions is proportional to the quantity of polymer formed. The differential equations are written as follows[53]:

$$\frac{dR}{dx} = k_i' M_0 + k_i \Pi - k_t R^2 \qquad (3)$$

$$-\frac{dM}{dx} = \frac{d\Pi}{dx} = k_p M_0 R \qquad (4)$$

where x is the magnitude of the shear deformation ($x = r\theta/z$); r the radius of the differential zone of the specimen, cm; θ the angle of rotation of the anvil, rad; z the height of the specimen, cm; M, Π, and R the concentrations of the monomer, polymer, and radicals, M; k_i' and k_i the rate constants of the initiation in the pure monomer and in the presence of polymer; and k_p and k_t the rate constants of the propagation and termination of the polymer chains.

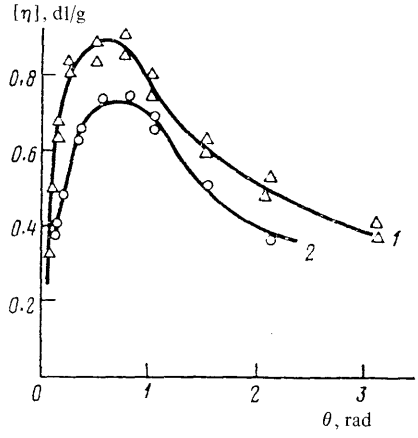


Figure 5. Dependence of the characteristic viscosity [η] of polyacrylamide on the angle of rotation of the anvils at 293 K[7]: *1*) 1000, *2*) 2000 MPa.

Solution of Eqns. (3) and (4) using the principle of stationary character gives the expression[7,53]:

$$\frac{\bar{\Pi}}{M_0} = \frac{k_p^2 k_i}{8 k_t} M_0 \frac{(r_2^2 + r_1^2)}{z^2} \theta^2 \qquad (5)$$

where $\bar{\Pi}$ is the average concentration of the polymer in the annular zone of the specimen bounded by the radii r_1 and r_2.

Fig. 6 gives the dependence on θ obtained at different pressures for different radial zones of the specimen. The experimental data obtained lie effectively on straight lines on these coordinates.

Eqn.(5) has been used[53] to verify the dependence of the yield of polymer on the radius of the anvil. Fig.7 gives the dependence of $(\Pi/M)^{1/2}$ on θ, obtained by averaging the results of 16 experimental series for anvils with diameters of 10 mm and 20 mm. The slopes of the straight lines corresponding to experiments with anvils of different diameter differ by a factor of two, and the yields of polymer differ accordingly by a factor of four. According to Eqn.(5), the yields of polymer for a fixed angle of rotation and the same specimen thickness should also differ by a factor of four; thus these results indicate good agreement between theory and experiment.

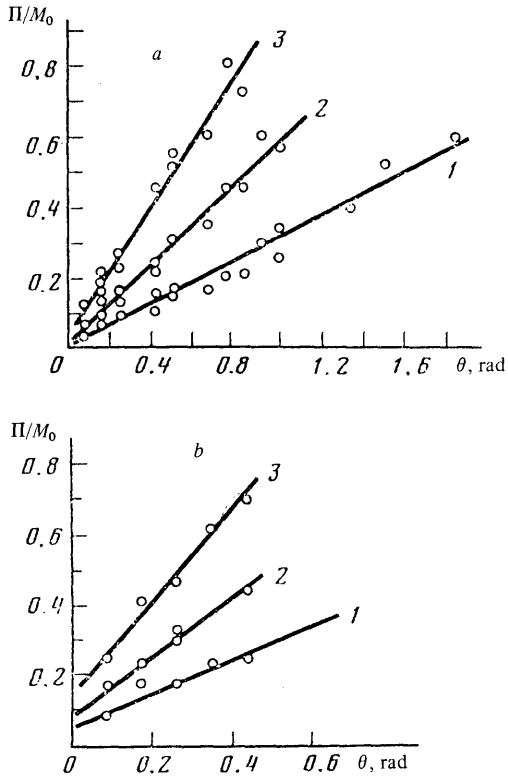


Figure 6. Dependence of (Π/M_0) on θ, obtained for different zones of the specimen at different pressures[53]: *a*) 1000, *b*) 3000 MPa; *1, 2, 3*) radial zones of specimens with diameters from 0 to 10 mm, from 10 mm to 15 mm, and from 15 mm to 20 mm respectively.

In the work cited[53], the experimental data on the molecular masses were treated using an equation relating the mean-molecular mass of the resulting polymer M_m to the angle of rotation of the anvils θ. The degree of polymerisation $\bar{P}$, the average for the entire specimen, is defined as $\bar{P} = G/N$, where G is the mass of the polymer, and N the total number of polymer particles. Solution of this equation[7] gave the equation:

$$\frac{1}{\bar{p}} = \frac{4}{15}\frac{k_i\theta\rho}{z} \qquad (6)$$

where ρ is the radius of the working surface of the anvil.

Fig.8 gives the dependence of $1/M_m$ on θ for pressures of 1000 MPa and 2000 MPa and for temperatures of 293 K and 195 K. Data corresponding to degrees of transformation of 3% and above[53] were used, that is the descending branch of the dependence of the molecular mass on the angle of rotation of the anvil was treated. According to Eqn.(6), the slope of the straight lines is proportional to k_i; thus the rate of formation of the radicals in the specimen increases with increase in pressure and temperature.

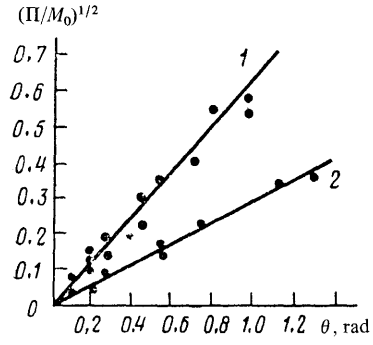


Figure 7. Dependence of (Π/M_0) on θ, obtained on anvils of different diameter[53] at 1000 MPa and 293 K: *1*) 20 mm, *2*) 10 mm.

Table 3. Rate constants and their ratio for the elementary stages of the polymerisation of acrylamide for SD + HP[7].

Conditions	$10^4\, k_p k_i/k_t$	$10^4\, k_i$	k_p/k_t
2000 MPa, 293 K	0.59	0.75	0.88
1000 MPa, 293 K	0.48	0.52	0.58
1000 MPa, 195 K	0.42	0.2	0.45

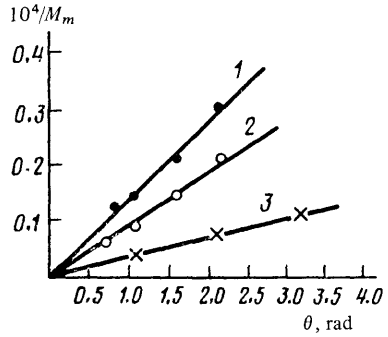


Figure 8. Dependence of the reciprocal of the molecular mass of polyacrylamide on the angle of rotation of the anvils under different conditions[53]: *1*) 2000 MPa, 293 K; *2*) 1000 MPa, 293 K; 3) 1000 MPa, 195 K.

The proposed mechanism of polymerisation and the mathematical m treatment of the experimental data carried out using the principle of stationary character make it possible to describe the dependence of P on θ and of π/M_0 on θ. This mechanism makes it possible to explain why the molecular mass of the polymer decreases at degrees of transformation greater than 3–5%; the decrease in molecular mass is due to the rapid increase in the concentration of active centres for polymerisation as the reaction proceeds[7].

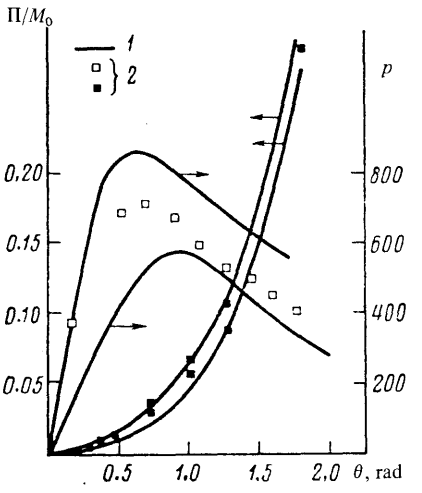


Figure 9. Dependence of the yield and degree of polymerisation of polyacrylamide on the angle of rotation of the anvils[7]: *1*) calculated curves, *2*) experimental data.

Eqns.(5) and (6) made it possible to calculate the rate constants of the elementary reactions and their ratios[7,53] (Table 3). Although Eqns.(5) and (6) describe the principal kinetic data satisfactorily, they do not explain, even qualitatively, the production of the maximum on the curves giving the dependence of the molecular masses on θ. It has been suggested[7,55] that the increase in the molecular mass of the polymer at low degrees of deformation is related to the non-stationary character of the process in the initial stage of the polymerisation. To verify this suggestion, the system of equations was solved without using the principle of stationary character[7,55]. The differential equations (3) and (4) were solved by numerical methods using the experimentally determined values of k_i and k_p^2/k_t (see Table 3) with variation of the quantity k_t/k_p. It was necessary, using the values of k_p^2/k_t and k_i, to select k_t/k_p to obtain curves giving the dependence of Π/M_0 on θ, of P on θ, and of P on Π/M_0 close to the experimental curves.

Fig.9 gives the experimental and calculated dependence of Π/M_0 on θ and of P on θ.[7] The theoretical curves calculated for $k_t/k_p = 10–20$ coincide to within 20–30% with the experimental curves for all degrees of conversion. Thus the results confirm that the polymerisation is non-stationary in the early stages of the deformation of acrylamide.

IV. CONCLUSION

The experimental data obtained indicate that under shear deformation conditions at a high pressure, solid organic compounds of different classes can polymerise at anomalously high rates, and can react by reaction paths which are not followed under ordinary conditions.

Measurements and calculations indicate that the rate constants of polymerisation with SD + HP may be 10^5 or more times the analogous constants characterising the liquid-phase reactions at the same temperatures and pressures. Under deformation conditions there may be a marked change in the selectivity of the chemical process. In a number of cases, side reactions which do not take place to a significant extent under ordinary conditions take place at rates comparable with that of the main reaction.

The reasons for the high reactivity of substances under SD + HP conditions have been insufficiently studied. Nevertheless, it should be noted that the dependence of the principal kinetic parameters (the degree of transformation, the concentration of radicals, the molecular mass of the polymer, etc.) on the shear deformation indicates that the duration of the elementary stages of the reaction of the interacting particles is very short, and the number of elementary acts is a function of the shear deformation. To explain this characteristic feature of processes under SD + HP conditions, two alternative mechanisms can be proposed. According to the first, under SD + HP conditions, strained and hence chemically activated bonds are produced in the reagent molecules and subsequently react with other molecules or their fragments in collisions, brought about by the motion of the substance on deformation. In the other possible mechanism, the bond, molecular fragment, molecule, or micro-region of the solid reagent, strained as a result of deformation, on subsequent deformation "ejects" the stored energy (relaxation); the potential energy of elastic deformation is converted into the vibrational energy of the molecules and individual bonds, which consequently show a high reactivity.

It is difficult at present to decide which of these mechanisms predominates under SD + HP conditions, since both explain the anomalously high rates of transformation and the weak temperature dependence of the reaction rate. In the first case, the mechanical stress applied to the bond can lower the activation energy of the reaction, and in the second case the high vibrational temperatures ensure high rates of transformation and are revealed in low values of the apparent activation energies. The elucidation of the mechanism responsible for the high reactivity of substances, and the determination of the reasons for the mixing of heterogeneous solid mixtures under SD + HP conditions at a level close to the molecular level, are important tasks in physicochemical studies under SD + HP conditions.

Another important problem is the determination of the types of chemical transformation which can take place during the deformation of solid reagents. At the present time, about twenty types of chemical reaction have been detected under SD + HP conditions. These include the addition to a $-C=C-$ bond of small molecules and functional groups (water, ammonia, the carboxyl group, the amide group, etc.), Diels–Alder reactions, the decomposition of peroxides, esterification, etc. These studies have shown that there are chemical processes favoured by SD + HP conditions, and on the other hand there are types of transformation which take place with difficulty or not at all on deformation of the compressed reagents. The reactions for SD + HP conditions are favourable include primarily the synthesis of macromolecular compounds. The largest number of studies carried out with SD + HP have been devoted to transformations of

this type. For these reasons, the results of the study of polymerisation processes with SD + HP are providing (and undoubtedly will continue to provide, in further extensions of these studies) a phenomenological and theoretical base for the development of the chemistry of solid organic compounds under conditions of deformation at high pressure in the compressed state.

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