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Polymerization of Condensed Monomers in a Shock Wave

In recent years a large number of works have been carried out devoted to the study of chemical processes in gases caused by shock waves (^{1}). Owing to the homogeneous and very rapid heating of a gas, it is possible to create conditions that make it possible to study thermodynamically nonequilibrium processes, relaxation phenomena, and other effects associated with high-temperature reactions in gases.

Shock waves are, as is known, a very specific phenomenon, due to the fact that at high pressures the speed of sound increases with compression. As a result, an ordinary compression sound wave, as its amplitude increases, becomes increasingly steep, until a certain discontinuity arises in the state of the substance ahead of and behind the wave, called the shock-wave front. If, during compression by a shock wave, the substance does not undergo any transformations, the front of a stationary shock wave in this case is a region with a jump in pressure, temperature, density, and other parameters, with a width of several molecular mean free paths. If, however, the substance upon compression undergoes some transformation, the width of the shock-wave front in this substance (the transition region) increases. A transformation in a shock wave will take place if the reaction time is less than the duration of the action of the shock wave. When a shock wave passes through a gas, relatively weak pressures cause strong compression of the gas and a large increase in temperature (^{2}). As a result, excitation, ionization of atoms, dissociation of molecules, and the occurrence of high-temperature reactions arise in the gas compressed by the shock wave.

When a shock wave passes through a condensed substance, the nature of the resulting consequences will be different. To increase the density of a condensed substance it is necessary to overcome repulsive forces, the magnitude of which increases as atoms approach one another. Therefore, under strong compression of a condensed substance, an enormous internal pressure of a nonthermal character arises in it. With a further increase in pressure, a thermal component of the internal pressure also appears; however, for waves with pressures below 10^5

atm, the thermal pressure will be less than the elastic pressure. The state of the condensed substance behind the shock-wave front will be characterized by strong compression and a comparatively small rise in temperature. Thus, for example, when a shock wave passes through water, a pressure at the front of $5 \cdot 10^4$ atm corresponds to a decrease in the initial volume by a factor of 1.5 and to an increase in the temperature at the front by 200° ([3], [4]). If the substance has greater compressibility than water, the temperature will be higher. After the passage of the wave, the residual temperature will be substantially lower than the temperature at the front.* Thus, the state of a condensed substance compressed by a shock wave is substantially—

differs sharply from the state of a gas behind a shock wave. Whereas reactions in gases caused by shock waves have been widely investigated, chemical reactions induced by a shock wave in condensed media had previously been studied mainly in connection with problems of combustion and detonation. Meanwhile, it may be expected that, when a shock wave passes through a solid or liquid substance, quite different chemical processes may arise, distinct from those occurring in combustion.

It is not excluded that many physicochemical processes that are sterically forbidden or hindered in the ordinary state of a substance can proceed with great ease in the unusual state in which the substance finds itself in a shock wave.

It seemed desirable to us to test this supposition concerning the effect of shock waves on physicochemical processes using solid-phase polymerization as an example. In a number of cases, polymerization of solid monomers proceeds at enormous rates at temperatures near the melting point or the points of phase transitions.

As early as 1943, Letort and Duval (5) reported the polymerization of acetaldehyde at the moment of melting of its crystals, with rates equal to the rate of melting. Subsequently, V. A. Kargin and V. A. Kabanov with co-workers observed similar flashes of polymerization during phase transitions for a whole series of frozen monomers with a molecularly dispersed catalyst (6). According to the ideas developed by these authors, formation of a polymer in a solid crystalline matrix requires a combination of a definite geometrical ordering of the initial monomer with increased mobility, realized near phase transitions. However, for a whole series of monomers, rapid solid-phase polymerization also occurs at temperatures very far from the points of phase transitions (7,8).

According to the hypothesis of N. N. Semenov (9), the ordering of monomer units in a crystal ensures directed transfer of energy, making possible the realization of an energy chain. The wide variety of regularities observed in solid-phase

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* If the wave passes through a porous or loose substance, the increase in the temperature of the substance after passage of the wave may be considerably greater.

polymerization—sometimes general, and sometimes dependent on the nature of initiation (the action of light, radiation, catalysts, elevated temperature, etc.)—testifies to the complexity of the processes united under the single name "solid-phase polymerization." As yet there is no unified theory of this phenomenon, and therefore it seemed especially interesting to us to investigate whether polymerization occurs in condensed media compressed by a shock wave, whose action is reducible neither to any of the methods just mentioned nor to the methods of mechanical or mechanochemical action that we shall touch on below.

Usually shock waves are produced as a result of the detonation of some explosive substance, by the collision of two bodies possessing a large relative velocity, by a powerful electric discharge, etc. In the present work, charges of various explosive substances (e.s.) were used as a shock-wave generator. The pressure of shock compression could be varied by using different barrier materials placed between the e.s. and the sample under test. A special scheme was used for preserving shock-compressed materials. The solid monomer was placed in a metal ampoule, which was surrounded by a set of materials of different dynamic rigidity for a smoother release of the shock load. This is necessary, since abrupt pressure release gives rise to large tensile stresses leading to destruction of the ampoules and the sample. The shock wave passing through the sample was plane, which was ensured by the design of the charge. At a time from 0.5 to 1.5 min after the explosion, the ampoule with the shock-compressed sample was cooled to room temperature. The ampoule was opened and the yield of polymer was determined. Preliminary results were reported by us earlier (10).

By the present time, a number of monomers listed in Table 1 have been investigated.

As can be seen from the data in Table 1, the phenomenon of polymerization in a shock wave is observed for various classes of monomers. Polymer formation has been noted in monomers polymerizing both by a radical mechanism (acrylamide) and with an ionic character of chain growth (trioxane). A particularly high yield (up to 60% of the monomer) was recorded for acrylamide. The polymerization in a shock wave of such a very difficultly polymerizing monomer as tolane should be noted especially.

Table 1

No.	Substance	M.p., °C	Degree of polymerization, %	Note
1	Trioxane	+62	5–6	Decomposes under strong compression

No.	Substance	M.p., °C	Degree of polymerization, %	Note
2	Acrylamide	+84	up to 60	Polymer is partially crosslinked
3	Potassium acrylate	solid	6%	
4	Methacrylamide	+110	10.7	
5	Tolane	+58	7	Polymer is soluble in benzene
6	Salicylaldehyde	−10	2	Experiment was carried out at −78°
7	Stilbene	+80	traces	Usually does not polymerize
8	Diphenylbutadiene	+120	3-4	Polymer is insoluble in ordinary solvents

A series of special measurements showed that the observed phenomenon of polymerization in a shock wave cannot be caused by heating of the assembly with the ampoule after passage of the shock wave.

The temperature after passage of the unloading wave did not exceed the melting temperature of the monomer (62° for trioxane and 84° for acrylamide). In addition, for the case of acrylamide, the possibility of melting of the monomer as a result of heating of the ampoule after passage of the unloading wave and of trivial thermal initiation of polymerization in the liquid phase was ruled out by comparative experiments in which 0.1% hydroquinone was added to the acrylamide. This additive, which completely stops polymerization in the liquid phase, did not change the yield of polymer in the shock wave.

Measurements were also made of the polymer yield at different initial temperatures of the monomer, and no change was observed in the amount of polymer formed over a wide range of initial temperatures of the substance (+25°, −190°).

Thus, it may be considered established that the described phenomenon of polymerization in a shock wave is not reducible to trivial thermal polymerization.

By varying the amplitude of the shock wave, we tried to establish the pressure range in which polymerization occurs in the monomer. In the case of acrylamide it was shown that, under the conditions of the experiment, polymerization is observed at pressures of (1.5–3.5) $\cdot 10^4$ atm. At higher shock-wave amplitudes the monomer becomes carbonized and undergoes destruction. Apparently, the indicated pressure range in the general case depends on the compression time of the substance and a number of other factors. Under the conditions of our experiments this time was about 10^{-5} sec.

At the shock-wave amplitudes indicated above, the molecular weight of the polyacrylamide obtained varied from $1.5 \cdot 10^5$ to 10^6, which corresponds to approximately 10^4 units. As yet, no relationship has been established between the magnitude of the molecular weight and the characteristics of the shock wave.

There are grounds to suppose that, to explain the phenomenon we observed, N. N. Semenov' s hypothesis ([9]) on the occurrence of solid-phase polymerization by the mechanism of an energy chain may be applied. The energy chain is realized owing to the presence in the monomer crystal of "preforms," i.e., regions with an orientation of monomer molecules that promotes polymer formation. Under these conditions, the scattering of the activation energy once expended (together with the heat of polymerization) can ···

the transfer of energy along the polymer chain growing along the "blank" must predominate. This process must occur extremely rapidly and be characterized by a total activation energy equal to the activation energy for chain initiation (in the radiation case $E = 0$). It is not excluded that the polymerization in a shock wave described above is one of the cases of such an energetic chain reaction. The independence of the amount of polymer formed from the initial temperature of the monomer argues in favor of the fact that the polymerization process in a shock wave can be described with the aid of a collective-excitation mechanism. One of the reasons limiting the growth of a polymer chain is usually the difference in the densities of the monomer and of the polymer formed. Since the mean distances between monomer molecules in a crystal are greater than those between analogous groups in the polymer, formation of a polymer chain requires overcoming cohesive forces. In this connection, the conditions of strong compression experienced by a monomer in a shock wave must be extremely favorable for the formation of a polymer chain, since the external action of the shock wave decreases the intermolecular distances in the monomer, and therefore, when a polymer chain is formed, the need to perform work against the elastic forces of the crystal lattice disappears. Since, thus, polymerization in a shock wave differs very strongly from other polymerization processes, it may be assumed that in a shock wave the steric difficulties that impede the polymerization and copolymerization of a number of substances will be reduced, and in this connection polymers with new physicochemical properties may be obtained.

Recently, the phenomenon of polymerization as a result of mechanochemical effects has been discovered ([11,12]). This interesting phenomenon consists in the fact that, when a powdered monomer is ground or crushed in the presence of catalysts, active centers arise which, upon subsequent heating, lead to the formation of polymer. The literature has also mentioned polymerization under the action of mechanical impacts (13). Trioxane crystals treated by impacts (apparently, by a rebound hammer) were then subjected to thermal post-polymerization, analogous to the post-polymerization observed after irradiation of crystals of this monomer. However, both the mechanochemical and the mechanical methods merely initiate the polymerization process. It should be noted that in our experiments polymerization is completely effected by the shock wave, without requiring the involvement of any other agents. This is not post-polymerization of a monomer subjected to the action of a shock wave, but precisely polymerization in a shock wave.

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Note: Figure translations are in progress. See original paper for figures.

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