Detection and investigation of oscillations of the rate of radiation-induced solid-state chain reactions at low temperatures

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The data on the detection and investigation of rate oscillations of radiation-induced (^{60}Co γ-radiation) cryochemical solid-state chain reactions are reviewed. Self oscillation regimes were observed for various reactions (ethylene hydrobromination, polymerization, and copolymerization) in the crystalline and glassy states both in the field of γ-radiation and as the post-effect recorded when the samples were warmed. The recent experimental data on the unusual oscillations of the polymerization rate of crystalline formaldehyde at 5—30 K are discussed. The mechanical factor (brittle disintegration) is proposed to be responsible for these oscillations.

Key words: self oscillations, kinetics, cryochemistry, radiation chemistry, solid-state chain reactions, calorimetry.

The glow of phosphorus vapor by the oxidation in the presence of air reported by Robert Boyle in 1680 can be considered as one of the first observations of the oscillation chemical reaction. Diverse chemical oscillation reactions in the gas, liquid, and solid phases that occur under the homogeneous and heterogeneous conditions are known to the present time. Several monographs[1—6] contain a detailed description of the development and results of studies in the area of chemical oscillations. Undoubtedly, the observation by Belousov of oscillations of the ratio of cerium(IV) and cerium(III) ion concentration during citric acid oxidation with bromate catalyzed by cerium ions created incentives for investigations of oscillation reactions.[7] This reaction was further studied[1] in detail by Zhabotinsky, and this class of concentration oscillation reactions was named a Belousov—Zhabotinsky (BZ) reaction.

The present review describes the oscillation processes in cryochemical chain solid-state radiation-initiated (^{60}Co γ-radiation) reactions discovered in studied at the Institute of Problems of Chemical Physics (Russian Academy of Sciences). One of the substantial advantages of the radiation method for the initiation of chemical reactions is the temperature-independent rate of initiation of the reaction: active sites of the reactions (radicals, ions), unlike initiation with specially introduced substances, can be formed at any temperatures. Thus, the use of the radiation-chemical method of initiation makes it possible to generate high concentrations of active sites relatively uniformly distributed over the whole volume of the sample, and they can easily be controlled by the power of the radiation dose. These sites can initiate various chemical reactions (polymerization and copolymerization, chlorination and hydrobromination, oxidation, and other) at various temperatures and diverse phase states of the reaction medium: solid (crystalline) or glassy (viscous, liquid).

The concepts of low probability of the occurrence of chain chemical reactions under the conditions of rigid spatial fixation and low mobility of reactants in the solid phase at low and superlow temperature were rejected as early as in the middle of the XX century. The studies led to the discovery of chain radiation-initiated reactions near absolute temperature zero. A large comprehensive information on specific features of the occurrence of a wide range of chemical reactions at low and superlow temperature was accumulated. The low-temperature limit of the chemical reaction rate; "congelation" and "revival" of polymer chains; autowave and self oscillation regimes of cryochemical reactions; fast reactions of halogenation, hydrohalogenation, and nitration of olefins near the boiling temperature of liquid nitrogen (77 K); spontaneous formation of free radicals in low-temperature reactions of halogens with olefins; and a series of other important phenomena were discovered and studied.[8] Concepts of tunneling of particles; dispersion of rate constants of elementary steps (polychronous kinetics); participation of molecular complexes in cryochemical reactions proceeding *via* the molecular, ionic, and radical mechanisms; the action of the positive feedback between the brittle disintegration process and the chemical reaction with allowance for the potential energy accumulated by the solid body, *etc.* are used to explain kinetic regularities of low-temperature sol-

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id-state reactions. A new direction is being actively developed in the recent time: cryochemistry of atoms and nanoparticles of metals, or cryonanochemistry.[9]

The self-sustaining regimes described above are not infrequently found for the processes occurring in the crystalline[10—14] and glassy[15—17] states in a wide temperature range (down to temperatures close to absolute zero). They can be observed both directly in the γ-radiation field[10,11,13,17] and as the post-effect when pre-irradiated samples are warmed.[12—16] In the next sections, we will consider oscillation processes initiated by the ^{60}Co γ-radiation in the solid phase at low and superlow temperatures for chain unbranched reactions of hydrobromination of ethylene, chlorination of hydrocarbons, and polymerization and copolymerization of various monomers. Kinetic chain length for these reactions ranges from 10^3 to 10^5. The oscillation chain reactions of γ-irradiated solid organic compounds at usual (ambient) temperatures are unknown to the author. However, the self oscillation processes in the liquid phase were observed and studied. Concentration oscillations of the radiolysis products of the solutions appear upon the action of the ionizing radiation on aqueous and alcoholic solutions of various compounds ($MgCl_2$ and other alkaline and alkaline-earth metal halides, phosphomolybdenic and silicotungstic heteroacids, and phthalocyanine complexes of Co^{II}, VO^{2+}, Zn^{II}, Mg^{2+}, and Mn^{II}).[18—23] In these systems, similar processes can be initiated by both ionising radiation and light.

The detailed study of the low-temperature photochemical hydrobromination of olefins in the solid state resulted in the observation of the chain reaction at the boiling temperature of liquid nitrogen.[8,24] Based on the obtained experimental data, Nikolay Semenov proposed that the fast photochemical reaction of ethylene hydrobromination at 77 K is a unique chain explosion in which the number of active sites entering the reaction increases due to the heat evolved upon the reaction.[25] He concluded that regularities of the chain and heat explosions are closely interwoven in chain low-temperature reactions, although the possibility of the appearance of oscillation processes was not considered in this case.

Oscillations of the rate of cryochemical transformations in the γ-radiation field

Rate oscillations in radiation-initiated cryochemical transformations were observed for the first time in the study of the chain solid-state hydrobromination of ethylene.[10] The rate oscillations of the chemical reaction were detected at a temperature of the thermostat of 85 K when γ-radiation that initiated the reaction was switched-on (Fig. 1). The reaction rate was measured with a differential diathermic calorimeter placed directly in the γ-radiation field. The rate oscillations decay in time as the reactants are consumed. The total conversion of the reactants was 40% for the experiment presented in Fig. 1, *a*. No oscillations of the reaction rate are observed when γ-radiation is switched-on repeatedly. The oscillation regime needs the temperature of the thermostat higher than 75 K and the power of the used ionizing radiation dose higher than 0.2 Gy s^{-1}, which exceeds a certain value of the initiation rate of the reaction. Figure 1, *b* shows the experimental results obtained under the same conditions as the data presented in Fig. 1, *a* but with the γ-radiation dose power decreased to $4 \cdot 10^{-4}$ Gy s^{-1}. It is seen that no self oscillations of the hydrobromination rate appear.

In isothermal systems the feedback mechanism necessary for the appearance of oscillations is caused by chemical autocatalysis. In exothermic reactions the heat evolved in the reaction can play the same role. Heat evolution can increase the temperature of the medium and, hence, the chemical reaction rate. Thus, the heat can perform the function analogous to autocatalysis. It follows from this that exothermic reactions can proceed periodically even when their kinetics is not autocatalytic. The term "thermokinetic oscillations" was introduced to define interrelated oscillations of the temperature and concentrations of the reactants in chemical systems.[5,26—28] Detailed description of such regimes of the reactions can be found in

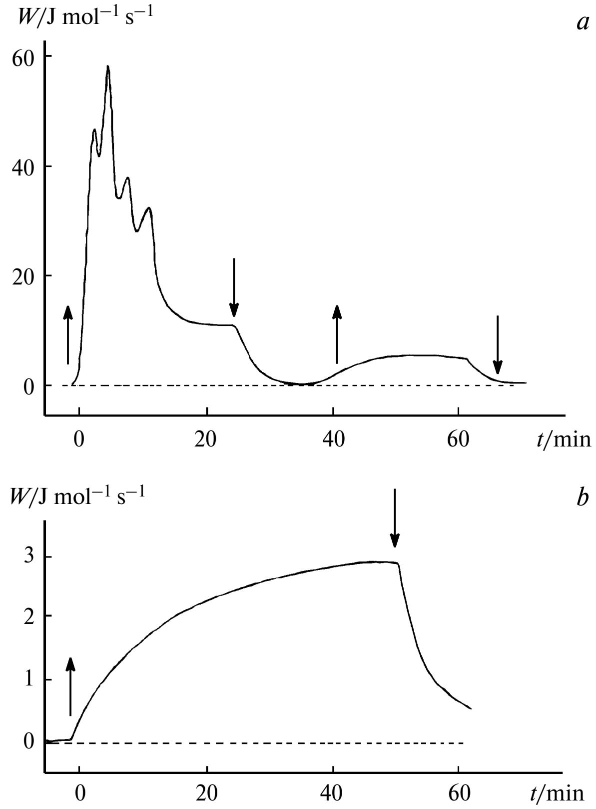

Fig. 1. Change in the rate of radiation hydrobromination of ethylene at the temperature of the thermostat (85 K) and the γ-radiation dose power 0.3 (*a*) and $4 \cdot 10^{-4}$ Gy s^{-1} (*b*). Arrows show the moments of switching-on and switching-off of γ-radiation.

a number of works.[2,29] The main success in the study of thermokinetic phenomena is associated with reactions of homogeneous gas-phase oxidation ("cold flames")[2] and with the study of stability of regimes of the work of chemical reactors.[29]

The mechanism of the chain unbranched reaction of ethylene hydrobromination is so simple (see, *e.g.*, Refs 8, 30, and 31) that the step of autocatalysis is not observed in the system under study. In this system the reaction rate oscillations can be only thermokinetic at which one of the parameters that oscillate is temperature. Since two species participate in the reaction of chain propagation during hydrobromination, only the temperature and concentration of one or two active species can undergo oscillations.

From the moment of switching-on γ-radiation, the reaction rate (heat evolution rate) increases in time due to an increase in the concentration of active sites. In the absence of sufficient heat removal, some overheating of the sample over the thermostat is possible. The value of overheating increases with an increase in the reaction rate. However, the decay rate of active site increases and the total concentration of active sites decreases with temperature. This decrease results in a decrease in the rate of the process and, as a consequence, in a decrease in the value of overheating of the sample over the thermostat. The decrease in the value of overheating again brings the system to the temperature region where the active sites can be accumulated to a higher concentration, which again induces an increase in the reaction rate. Thus, self oscillations of the process rate observed for the radiation solid-state hydrobromination of ethylene are of thermokinetic nature.

Evidently, the self oscillation regime can appear only in the case of rather intensive heat release. For low initiation rates (small dose powers), the overheating of the sample is low and, as can be seen experimentally, the self oscillation regime degenerates.

The appearance of self oscillations in the system $HBr—C_2H_4$ is most probable at temperatures higher than 70 K, because the total reaction rate increases sharply with temperature in this range (activation energy ~17 kJ mol^{-1}). At lower temperatures (<70 K) the hydrobromination rate has a weak temperature dependence (activation energy ~0.75 kJ mol^{-1}), and attempts to detect self oscillations in this temperature range failed.

Validity of these assumptions was checked in experiments where the conditions of heat removal from the sample were deliberately deteriorated by increasing a weighed sample of the substance and decreasing the ratio of the sample surface to its volume. This resulted in the appearance of self oscillations, which can develop not only in time but also in the space.

The radiation chain hydrobromination of ethylene proceeds *via* the following steps (Scheme 1).

Scheme 1

Chain initiation

$$HBr \xrightarrow{\gamma} H + Br,$$

Chain propagation

$$Br + C_2H_4 \longrightarrow C_2H_4Br$$

$$C_2H_4Br + HBr \longrightarrow C_2H_5Br + Br,$$

Monomolecular chain termination

$$C_2H_4Br + L \longrightarrow C_2H_4BrL,$$

Bimolecular chain termination

$$Br + C_2H_4Br \longrightarrow C_2H_4Br_2$$

L is radical trap.

Note that in the solid state this reaction involves an equimolar complex $C_2H_4 \cdot HBr$ (for details, see, *e.g.*, Refs 8, 30, and 31). Then the non-isothermal kinetics of the reaction can be described by differential equations that take into account the consumption of the initial reactant M (complex $C_2H_4 \cdot HBr$)

$$\dot{M} = -k(T)RM, \qquad (1)$$

the balance of active sites R

$$\dot{R} = gJ - k_1(T)R - k_2(T)R^2, \qquad (2)$$

and the heat balance

$$c\rho\dot{T} = Qk(T)RM - \alpha(S/V)(T - T_0), \qquad (3)$$

where $\dot{M}$, $\dot{R}$, and $\dot{T}$ are differentials with respect to t; T and T_0 are the temperature of the thermostat and reactor, respectively; Q is the heat effect of the reaction; α is the coefficient of heat conductivity of the walls; S/V is the geometric factor expressing the ratio of the surface area of the reactor to its volume; c and ρ are the heat capacity and the density of the substance in the reactor, respectively, which are considered constant; J is the power of the initiating radiation dose; g is the radiation-chemical yield of active sites; $k(T)$, $k_1(T)$, and $k_2(T)$ are the reaction rate constants, whose temperature dependences in the range 50—90 K are described by the Arrhenius equations with the activation energies E, E_1, and E_2, respectively.

This system of equations should be solved under the following initial conditions:

$$t = 0\colon M = M_0,\ R = 0,\ T = T_0. \qquad (4)$$

The detailed studies[11] of this system of equations* (see also Ref. 32, pp. 197—200) showed that the stationary points of the system have the character of "saddle," "node,"

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* The close thermokinetic model was also considered in Refs 26 and 27. In the present review, specific features of low-temperature solid-state reactions and the specifics of the radiation initiation of the reaction were taken into account. The mechanism of self oscillations is of general character and can be encountered in other problems and systems (see Refs 5, 28, 29, 32, and 33).

or "focus." It is shown that in the whole region of instability of the stationary point of the "focus" or "node" type the system has the stable limiting cycle on the phase plane, *i.e.*, the self oscillation solution periodical in time. In another region of parameters, into which the system finds itself as the initial reactant is consumed or at a low power of the γ-radiation dose (initiation reaction rate), the stationary state is established that corresponds to the smooth non-oscillation consumption of the initial reactant (see Fig. 1). Finally, there is a region where the system has no stationary states and where the temperature increases unrestrictedly within the finite time: thermal explosion.

Thus, an analysis of the proposed model makes it possible to qualitatively describe the self oscillation regime of the reaction occurring in the γ-radiation field. The regime is related to the non-isothermal character of the process due to heat release during the reaction and a change in the concentration of active sites. The appearance of the oscillation regime of the reaction is independent of the character of termination of kinetic chains. It would be interesting to compare the critical conditions of transition between different regions of the reaction (stationary, oscillation, thermal explosion) with the experimental measurements and to use a mathematical model for the solution of the inverse problem of determination of parameters of the model by its identification with experiment.

The possibility to generate thermokinetic self oscillations by the initiation with the light or ionizing radiation was considered using as an example the simplest chain unbranched reaction of hydrogen atom substitution in any hydrocarbon by chlorine atoms.[33] A comparison of the theoretical analysis with the available experimental data shows that thermokinetic self oscillations for this reaction are impossible in either gaseous or liquid phases because of the insufficiently high heat effect and, correspondingly, impossibility to attain rather high adiabatic temperature.[33] On the contrary, thermokinetic oscillations can occur in the solid phase at low temperatures, because the heat capacity of solid decreases with the temperature decreases and a rather high adiabatic temperature can be reached. Therefore, thermokinetic oscillations for chain unbranched reactions can be observed most easily at low temperatures (dozens of Kelvin degrees). The analysis of the chlorination of hydrocarbons showed[33] that the search for self oscillations in the gas and liquid phases is hopeless; however, at the same time, thermokinetic self oscillations can be observed with high probability in the solid phase under the corresponding conditions.

Rate oscillations in post-radiation reactions

The post-radiation process (for instance, polymerization), which proceeds in the regime of scanning of the thermostat temperature, is initiated by a gradual release of active sites with an increase in the temperature of the matrix. A certain number of active sites stabilized in the matrix is generated by a fixed dose of γ-radiation. Irradiation is carried out at rather low temperature, and the sites formed are stabilized in the matrix and do not initiate the reaction. The active sites are released and initiate the chemical transformation only with an increase in the temperature of the medium. The rate of liberation of active sites is the Arrhenius function of the temperature with the activation energy determining the depth of traps, which accumulate active sites during the process of low-temperature radiolysis. The active sites liberated with temperature participate in the reaction and decay either due to the spatial isolation on the traps, which differ from radiation traps (monomolecular mechanism of decay), or due to bimolecular recombination.

A mathematical model of post-radiation polymerization is analogous to the earlier considered thermokinetic model for the reactions occurring directly under the action of radiation. This model should be supplemented by the equation describing the liberation of the stabilized active sites N upon heating of the system $\mathrm{d}N/\mathrm{d}t = -Nk_0(T)$, where k_0 is the rate constant with the activation energy E_0. The qualitative analysis of this model performed under the assumption of slow temperature change and slow consumption of both the initial reactant and stabilized active sites suggests that the self oscillation regime of the reaction is possible.[12]

Consider as an example various regimes of post-radiation polymerization of acetaldehyde in the glassy matrix of butyl chloride.[15] A solution of acetaldehyde in butyl chloride (mole ratio 1 : 4) on cooling to 77 K is gradually transformed into the glassy state. When this system is warmed in a calorimeter at temperatures ranging from 94 to 97 K transition from the glassy state to the overcooled liquid (devitrification) is observed followed by crystallization (112—115 K) and melting (145 K).

Heat release in the devitrification region caused by the post-polymerization of acetaldehyde is observed upon warming the same system pre-irradiated with γ-rays at 77 K. Various regimes of the process are possible, depending on the conditions of the removal of the heat of the reaction from the calorimetric cell.

Polymerization can occur in the absence of noticeable overheatings of the substance in the cell over the calorimeter block (stationary regime). To accomplish this regime, it is necessary to maintain rather intensive heat removal from the reaction cell. This can experimentally be accomplished by changing a number of parameters: (1) a decrease in the warming rate of the sample, (2) the improvement of the heat removal conditions due to an increase in the sample surface to its volume (decrease in the initial weighed sample), and (3) a decrease in the preliminary irradiation dose, which decreases the concentration of stabilized active sites in the system, *i.e.*, decreases the heat release rate due to polymerization. When the sample is warmed in the absence of noticeable overheatings of the sample in the cell, the post-polymerization rate of acetaldehyde increases with temperature, reaches a maximum, and smoothly decreases because of the exhaustion of the monomer and active reaction sites formed upon irradiation (Fig. 2, curve *1*). In this case, the initial region of the calorimetric curve is well described by the Arrhenius equation with the activation energy $E = 25$ kJ mol^{-1}.

Another ultimate case is the thermal explosion regime. This regime is observed when the conditions become unfavorable for heat removal from the cell. An increase in the substance weighted sample in the cell, in the heating rate of the sample, or in the dose of preliminary irradiation (see Fig. 2, curve *2*) can bring about these conditions. When heat removal was of intermediate intensity, the oscillation regime of the process was detected, and several cycles of increasing and decreasing reaction rates were experimentally observed (Fig. 2, curve *3*).

Thus, depending on the reaction conditions, various regimes of the process are possible: the stationary regime in the absence of noticeably overheatings of the substance in the sample, thermal explosion, and the oscillating regime. An analysis of the experimental data suggests that in this system rate oscillations are related to the thermokinetic mechanism described above. The following simple correlations can be used to evaluate the boundaries of the existence of oscillation regimes:

(1) $T_t < T_c < T_t + \Delta T$, where T_c is the temperature of overheating of the reaction mixture in the oscillation regime in the cell over the temperature of the thermostat T_t, and ΔT is the pre-explosion warming ($\Delta T = RT^2/E$);

(2) $\tau > n\tau_{os}$, where τ is the average lifetime of active sites ($\tau = 1/k$ in the case of monomolecular chain termination and $\tau = 1/kA_0$ is the case of bimolecular termination, A_0 is the initial concentration of active sites of polymerization), τ_{os} is the oscillation period, and n is the number of oscillation cycles.

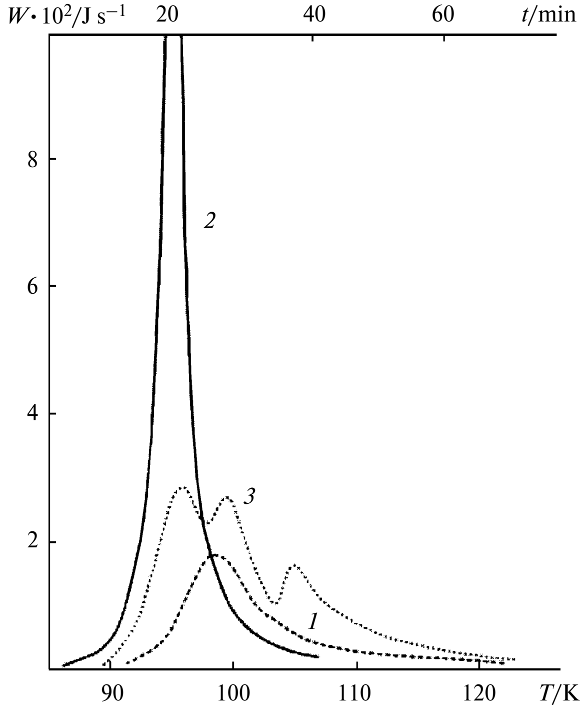

Fig. 2. Change in the heat evolution rate in the region of devitrification during post-polymerization of acetaldehyde (AA) in the butyl chloride (BC) matrix in the samples containing 0.097 g of AA and 0.367 g of BC (*1*); 0.138 g of AA and 0.549 g of BC (*2*); and 0.175 g of AA and 0.672 g of BC (*3*). The dose of preliminary γ-irradiation at 77 K was 120 (*1*, *2*) and 300 kGy (*3*). *T* is the temperature of the calorimeter block.

The examples listed above can be supplemented by other cases of oscilaltion of the low-temperature post-radiation polymerization rate observed under specific reaction conditions (warming rate, sample weight, preliminary irradiation dose, *etc.*). Among these are the polymerization of crystalline heptyl acrylate[12] and methyl acrylate,[34] vitrifying glycidyl esters and their solutions in ethanol, glassy 1,3-bis(dimethylamino)isopropyl methacrylate,[35] crystalline and glassy (in an ethanolic solution) acrylic acid,[16] ketene in a glassy solution of butyl chloride.[36]

The self oscillation regimes of the reaction were observed for the low-temperature chlorination of saturated hydrocarbons in the pre-photolyzed glassy systems.[37—39] Several peaks of increasing and decreasing reaction rates (four—seven reaction pulses with a period 3—5 s) are observed for a mixture of chlorine with methylcyclopentane at certain parameters (mole ratio of the reactants 1 : 2, concentration of the radical $2 \cdot 10^{17}$—$5 \cdot 10^{17}$ cm^{-3}) after the compression pulse initiating the transformation. The appearance of self oscillations is explained by an increase in an excessive deformation energy of the matrix *G* at low temperatures, which accelerates the reaction and decreases *G* on heating leading to the retardation of the reaction.

Oscillations of the rate of post-radiation formaldehyde polymerization at 5—50 K

Unusual rate oscillations were observed at 5—50 K for the post-radiation polymerization of formaldehyde (FA). Unlike the earlier observed thermokinetic oscillation regimes of cryochemical reactions, the rate oscillations of FA post-polymerization at such low temperatures are induced by the mechanical factor (brittle disintegration).

An effective chain reaction near absolute temperature zero was observed in the study of radiation-initiated (^{60}Co γ-radiation) FA polymerization.[40] The radiation-chemical yield of the polymer $G(-M)$ is close in value to the chain length and equal to 10^3 molecules per 100 eV of the absorbed radiation energy at 5 K. The rate of radiation-initiated FA polymerization (m.p. 150 K) decreases according to the Arrhenius law with the activation energy

~10 kJ mol^{-1} with the temperature decreasing in the range 140—80 K, whereas in the range 50—5 K it is nearly independent of the temperature. The low-temperature limit of the chemical reaction rate is observed.[41]

The polymerization of FA at such low temperatures occurs not only in the field of ionizing radiation but also outside the irradiation zone. When γ-radiation is switched-of, the decrease in the polymerization rate at 5 K proceeds with the characteristic time $\tau \approx 15$ s (average time of the polymer chain growth).[42] However, active sites responsible for the polymerization process do not decay, and the kinetic termination of the polymerization chain is observed. In fact, on heating of the pre-irradiated FA sample, efficient post-polymerization occurs outside the irradiation zone.

On warming the FA samples pre-irradiated in the range 50—90 K, the polymerization rate increases with temperature, decreases, and then increases again and decreases to zero when the monomer begins to melt because of the decay of active sites (Fig. 3, curves *1—3*). Two regions of post-polymerization are observed: low-temperature region *A* and high-temperature region *B*. The temperature boundary of the detected post-polymerization in region *A* decreases with a decrease in the irradiation temperature (Fig. 1, curve *3*). The temperature boundaries of region *B* are independent of the temperature of preliminary irradiation but are determined by the integral irradiation dose. As the dose of preliminary irradiation increases, post-polymerization in region *B* occurs more efficiently at lower and lower temperatures.

It turned out that optical bleaching (irradiation with a DRSh-1000 mercury lamp) resulting in the decay of ions stabilized in the matrix more efficiently suppresses polymerization in region *A* and weakly affects the process in region *B*. Accordingly, it can be assumed that the post-polymerization of FA at low temperatures <70 K occurs due to the presence of stabilized ions, whereas the radical mechanism of the process becomes predominant at higher temperatures.[43]

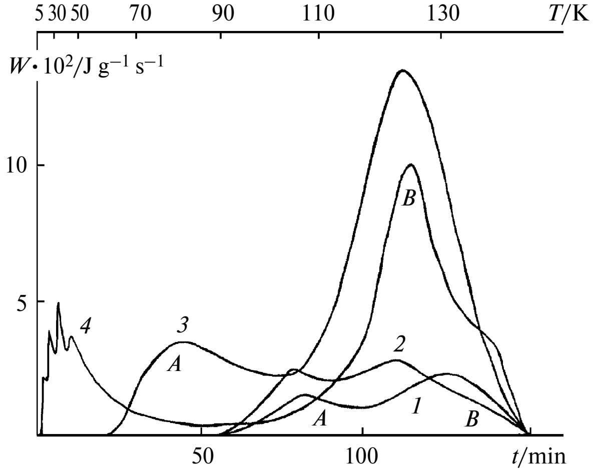

Fig. 3. Change in the rate of post-polymerization (heat release) (*W*) of solid FA on warming the samples irradiated at temperatures 90 (*1*, *2*), 58 (*3*), and 5 K (*4*) with the doses 4.5 (*1*), 14 (*2*), 480 (*3*), and 200 Gy (*4*). *A* and *B* are the low-and high-temperature regions of post-polymerization, respectively (see the text).

Another pattern of changing the FA post-polymerization rate is observed on warming the samples preliminarily γ-irradiated at 5 K. Several sharp peaks corresponding to an increase and a decrease in the process rate appear on warming the sample pre-irradiated with a dose of 200 Gy in the temperature range 5—50 K (see Fig. 3, curve *4*). The smooth increase in the FA post-polymerization rate is detected with the further increase in temperature (region *B*). Thus, the oscillation regime of monomer polymerization is observed on heating FA crystals pre-heated at 5 K in the temperature range 5—30 K.

The principal distinction of the observed oscillation regime of FA post-polymerization in the temperature range 5—50 K is that the activation energy in this temperature range is nearly zero (the reaction rate is temperature independent).[40,41] Therefore, oscillations of the FA post-polymerization rate cannot be of thermokinetic origin.

A sharp increase in the chemical transformation rate at the moment of brittle disintegration at low temperatures (4.2—77 K) was observed for reactions of various classes.[44,45] The local brittle disintegration of the solid sample containing the supercritical concentration of active reaction sites, which are formed due to the preliminary irradiation with the necessary γ-irradiation dose, results in the appearance of a running wave of the cryochemical reaction over the whole sample. The process is caused by the action of the positive feedback between the transformation of the sample and its brittle disintegration: the chemical reaction that appears upon the violation of continuity of the solid sample (because of the appearance of temperature or density gradients during the reaction) induces a further development of the disintegration process. This, in turn, stimulates the chemical reaction to occur *etc.* A unique mechanoenergetic chain is observed.

However, at the concentrations of active sites lower than critical values (low pre-irradiation doses) the wave development of the process degenerates. No self reaction regime takes place at low irradiation doses, no progressive multiplication of cracks appears, and no wave of the chemical transformation is observed. Only the reactants are transformed (increase in the reaction rate) in the zone of freshly formed cracks, which artificially appear when the sample is warmed.[44,46]

It can be assumed that oscillations of the FA post-polymerization rate in the range 5—50 K are due to a series of consequent local crackings of the sample during heating. Crystalline FA disintegrates on warming because of temperature gradients in the sample, resulting in an increase in the reaction rate on the freshly formed surfaces of the crystal. However, the self-sustaining regime of the process does not appear, because the positive feedback between brittle disintegration and the chemical reaction is not formed since the surface of the formed cracks is not large enough. Accordingly, the reaction rate decreases. On further heating the local brittle disintegration occurs again, and the reaction rate increases once more. The maximum value of the reaction rate (peak) depends on the effective surface area of the freshly formed cracks at the moment of brittle disintegration. Unlike the earlier known oscillation regimes of chemical reactions (concentration, thermokinetic), the oscillations of the FA post-polymerization rate at such low temperatures are induced by the mechanical factor (brittle disintegration).

Various regimes of chemical transformations are of significant interest because of the possibility to increase the selectivity of complicated processes and to extend technical facilities that control cryochemical synthesis. Thermal instabilities arising when chemical reactors are in operation usually decrease the quality of the product and result in breakdowns. Understanding of the mechanism of the process makes it possible to avoid thermal explosions, to suppress self oscillations, and to maintain the stationary regime. However, oscillation regimes can be favorable, giving a substantially higher average yield of the product than that in the stationary regime.[47] Such advantages are especially pronounced when the target product is an intermediate compound in the complicated chain chemical transformation.[48]

The influence of various reaction regimes on the properties of the final product can be examplified by the radiation low-temperature polymerization of 1,3-bis(dimethylamino)isopropyl methacrylate. The polymer formed is used in biomedicine and ecology.[35] Depending on the conditions of heat removal of polymerization from the reaction volume, various regimes of the process were implemented during matrix devitrification: stationary, oscillation, and thermal explosion.

The dependence of the average-weight molecular weight of the polymer on the preliminary irradiation dose (dose power 1.4 Gy s^{-1}) at various regimes of post-polymerization is presented in Fig. 4. In the case of the self oscillation regime of post-polymerization, the average-weight molecular weight M_w of the polymer decreases from $2.8 \cdot 10^6$ to $1.4 \cdot 10^6$ as the pre-irradiation dose increases from 10 to 118 kGy. In the case of the stationary post-polymerization regime, the value of M_w decreases from $1.5 \cdot 10^6$ to $0.3 \cdot 10^6$. The substantial increase in the molecular weight on going from the stationary to oscillation regime is evidently due to an increase in the mobility of growing polymer chains under the conditions of local overheatings and, as a consequence, their bimolecular termination becomes the main reaction. The same explanation pertains to the increase in the molecular weight.

The regime of thermal explosion results in the formation of the polymer with another supermolecular structure, which is characterized by microheterogeneity.[35] More detailed analysis of the polymer products obtained in this series of investigations showed that the appearance of nonstationarity during the process of low-temperature polymerization (oscillation regime and thermal explosion) extends the molecular weight distribution of the polymer toward high molecular weights.

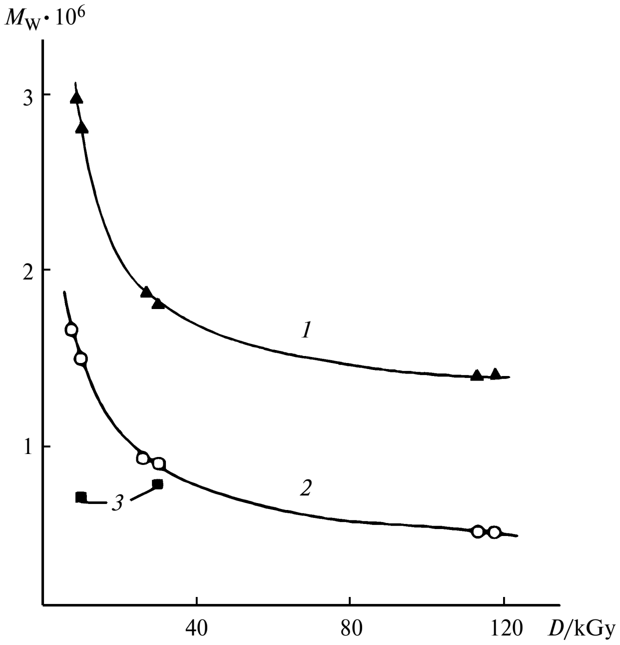

Fig. 4. Average-weight molecular weight (M_w) of the polymer obtained by the low-temperature polymerization of 1,3-bis-(dimethylamino)isopropyl methacrylate *vs* dose (D) of preliminary irradiation in various regimes of the process: self oscillations (*1*), stationary (*2*), and heat explosion (*3*). The γ-radiation dose power is 1.4 Gy s^{-1}.

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