Russian Chemical Reviews **72** (3) 217 – 231 (2003) © 2003 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2003v072n03ABEH000752

Chain chemical reactions at low temperatures

D P Kiryukhin, I M Barkalov

Contents

I.	Introduction	217
II.	Chain reactions in crystals	218
III.	Chain reactions in glasses	221
IV.	Autowave processes	225
V.	Cosmochemical aspects of low-temperature reactions	229
VI.	Conclusion	230

Abstract. The review generalises results of studies on chain cryochemical polymerisation and copolymerisation, oxidation, chlorination and hydrobromination of saturated hydrocarbons and alkenes in the crystalline and glassy state. Chain chemical reactions that occur at liquid helium temperature with a measurable, temperature-independent rate are considered; high-intensity autowave modes of low-temperature reactions in solid phase are discussed. The bibliography includes 111 references.

I. Introduction

Chain chemical reactions were discovered and their study was started at the beginning of the 20th century. The term 'chain reaction' appeared in 1913 when Bodenstein was studying the reaction of hydrogen with chlorine. The application of the chain reaction theory turned out to be exceptionally fruitful for understanding the kinetics and mechanisms of many processes, including natural ones. Chain processes that had originally been discovered in the gas phase were later observed in liquid and solid phases. A fundamental contribution to the development of the quantitative theory of chain processes was made by Academician N N Semenov and his disciples, and also by Professor S Hinshelwood (Semenov and Hinshelwood were awarded the Nobel prize in chemistry for these works in 1956). Chain reactions were classified into the following basic types: non-branched, branched and degenerate branched; furthermore, the following steps of a chain process were distinguished: chain initiation, chain growth, chain branching and chain termination. The history of the creation and development of the theory of chain reactions is described in detail in the monograph by Emanuel *et al.*[1]

Until recently, the obstacles to studies on chemical reactions at low and ultralow temperatures (4.2 – 77 K) were the traditional theory of the chemical reaction mechanism. The requirement that an activation barrier has to be overcome in each elementary event postulated by this theory precludes any noticeable chemical transformations in the vicinity of absolute zero temperature. The thousand-year experience of the mankind showed that cooling prevents any complex chemical transformations.

The classical picture of the elementary event of a chemical reaction is based on the following postulates: (1) the activation energy barrier is necessary to be overcome in order to start a reaction between reactants; (2) the reactants get the energy they need to overcome the activation barrier from intermolecular interactions; (3) the time required for the reactants to accumulate this energy (the characteristic time of an elementary event) is determined by the temperature of the environment. It is easy to show that these postulates totally exclude the possibility for a chain chemical reaction to occur near absolute zero. However, a considerable fraction of matter in the Universe exists in the cold of the cosmic space. It is hard to believe that this matter has been scattering since the Big Bang without undergoing any chemical evolution.

The natural chemical transformations in solids only become noticeable on a geological time scale; they also involve liquid and gas phases, mechanical destruction, as well as high pressures and temperatures. The combustion of solid fuels, explosions and sintering processes were always considered as reactions occurring at interfaces between a solid and a gas or liquid. It should be noted that it is most thermodynamically favourable to perform the majority of important industrial processes, *e.g.*, synthesis of ammonia from nitrogen and hydrogen, at the lowest possible temperatures. Low-temperature synthesis is also preferable because, for complex chemical processes, only those of the possible transformation channels 'survive' which have the lowest activation energy.

In the 1930s, polymerisation of crystalline monomers was reported.[2–4] It was found, for example, that transparent trioxane undergoes polymerisation in the presence of formaldehyde vapour to give polyoxymethylene fibres oriented along one of the crystallographic axes. The formation of polymers was observed[3,4] upon freezing of acetaldehyde (m.p. 150 K). This was a step to the low-temperature synthesis. It was found that chain reactions can occur in solid matter even at low temperatures, although this is forbidden.

The concept that chain chemical reactions are impossible near absolute zero was discarded after a low-temperature threshold of the rate of a chemical reaction had been revealed experimentally in studies on the polymerisation mechanism of solid formaldehyde at 4 – 100 K.[5–7] Subsequently, the low-temperature reaction rate threshold was found to exist for many chain and non-chain chemical processes.[8] It was found that certain chemical reactions can occur with a measurable temperature-independent rate at

D P Kiryukhin, I M Barkalov Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-096) 515 54 20. Tel. (7-096) 522 32 46. E-mail: kir@icp.ac.ru (D P Kiryukhin).
Tel. (7-096) 522 19 73. E-mail: barkalov@icp.ac.ru (I M Barkalov)

Received 18 November 2002
Uspekhi Khimii **72** (3) 245 – 261 (2003); translated by S S Veselyi

liquid helium temperature. Just after the low-temperature reaction rate threshold had been discovered, it was suggested that the mechanism of this phenomenon could be interpreted within the framework of the molecular tunnelling concept. Later, this idea was developed with intrermolecular oscillations taken into account.[8–12]

The scope of studies on chain cryochemical reactions expanded considerably after the discovery of transformations in autowave modes that occur upon local brittle destruction of solid samples subjected to radiolysis or photolysis at 4.2–77 K.[13–15] When a sufficiently extended sample undergoes local brittle destruction, a chemical reaction starts on the newly formed surface. The temperature or density gradients that appear during the reaction create stresses that favour subsequent layer-by-layer destruction of the solid sample. Owing to this positive feedback, an autowave of the chemical transformation spreads along the sample, *i.e.*, a kind of mechanoenergetic chain is realised.[13–15] The autowave mode is observed for many reactions (chlorination of hydrocarbons, hydrobromination of alkenes, polymerisation) in the temperature range 4–77 K. This concept allowed us to put forward new ideas regarding the mechanisms of the 'cold' chemical evolution of matter in the Universe.[15]

In the present work, we generalise experimental data of studies on chain cryochemical processes that have led to the discovery of the low-temperature threshold of the chemical reaction rate and also the autowave and self-oscillating modes of low-temperature transformations. Consideration of general trends of the evolution in this field of chemistry is certainly interesting; however, our review pays the most attention to studies performed over the last years.

II. Chain reactions in crystals

1. Polymerisation of solid formaldehyde

In the 1960s, studies on the solid-phase polymerisation were developed intensely. However, most of these studies were phenomenological, and the theoretical conclusions and hypotheses were rather speculative than based on experimental results. Initially, it was assumed [16] that the strict orientation of monomer molecules in the crystal can predefine the regularity of chains of the macromolecules formed, and hence the 'precursors' of reactants in the crystal will favour the realisation of unusually fast chemical transformation mechanisms. As early as in 1960, N N Semenov proposed the energy chain mechanism for the solid-phase polymerisation.[16] The idea was that the energy evolved in each elementary event of the polymer chain growth does not dissipate as heat, but is consumed for overcoming the activation barrier in the next event. A variant of such collective interaction is the exciton movement along the chain of monomer molecules in the crystal. In this case, the polymer chain growth will occur at a rate equal to the exciton propagation rate.[17]

The reader can find vast experimental data collected to date in a number of reviews.[18–22] Let us outline the main conclusions of studies carried out during that period. When a polymer is formed, the mean distances between the fragments of the monomer crystal lattice change (*i.e.*, the intermolecular distances are replaced by the lengths of chemical bonds). Two extreme cases are possible: (1) the monomer crystal structure defines the structure of the resulting polymer (diacetylene derivatives, trioxane); (2) the polymer is formed as a separate phase in extended defects of the crystal lattice, which leads to subsequent destruction of the monomer crystal (acrylamide). In addition, many intermediate cases exist.

It is hard to imagine that the decay of the growing macroradicals can occur by recombination or disproportionation in a crystal where the translational movement is quite limited. The previously developed ideas of 'polychronous kinetics' were found to be also applicable when considering the polymerisation in a crystal.[23,24] As the polymer chain grows in a solid, the access of the monomer to the active site is hampered and kinetic inhibition of the process occurs; this is called polymer chain 'freezing' (the opposite process is called 'revival').

The main results of studies on the radiation-induced polymerisation of solid formaldehyde at 5–150 K were described by Kiryukhin.[25] The dependences of the formaldehyde polymerisation rate (m.p. 155 K) and the radiation-chemical yield of the polymer [$G(-M)$] on temperature were studied in the temperature range 4.2–140 K. It was found that these dependences become weaker as the temperature is decreased, and are no more observed in the range 5–20 K (Fig. 1). Even at 5–20 K, polymerisation occurs with high radiation-chemical yield $G(-M) = 1000$ which is typical of chain processes.† This is the first experimental proof of the existence of long polymeric chains formed upon conversions in the vicinity of absolute zero temperature ($\sim$1000 monomer units at 4.2 K). The non-steady-state process kinetics was studied and the elementary polymerisation rate constants were determined. In the temperature range 80–140 K, the time required for the chain to lengthen by one unit increases with a decrease in temperature according to the Arrhenius law, with an activation energy of $\sim$10 kJ mol^{-1}, and no longer depends on temperature upon deeper cooling, *i.e.*, a low-temperature threshold of the chain chemical reaction is observed.[7] The formaldehyde polymerisation is a typical chemical reaction: a number of planar triangular molecules of the monomer are transformed to a long $-CH_2-O-CH_2-O-$ chain; obviously, the formation of chemical bonds in the macromolecules being formed should increase considerably the density of the compound.

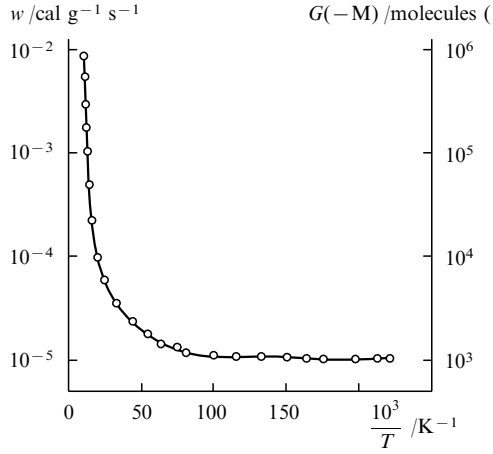


Figure 1. Temperature dependences of the rate (w) and radiation-chemical yield [$G(-M)$] of formaldehyde polymerisation under γ-irradiation.[25]

Studies of low-temperature photoinitiated solid-phase formaldehyde polymerisation were also carried out. It was reported [26,27] that a polymeric phase was formed in crystalline and amorphous formaldehyde containing an additive of β-naphthol as a result of photoinitiation at temperatures above 20 K. Low-temperature transformations in amorphous formaldehyde–chlorine mixtures were studied.[28–30] Photolysis of chlorine under these conditions was carried out by an excimer laser (λ = 308 nm) or an arc mercury lamp (λ = 365 nm). In the temperature range 10–77 K, the formation of oligomers containing 5–7 monomeric units was observed. At temperatures above 90 K, the chain length increased twofold. These values are much lower than those of the polymer formed upon radiolysis of crystalline formaldehyde (chain length 10^3–10^6); this is probably due to the molecular disorder in the amorphous compound.

† The radiation-chemical yield of active sites (g) that initiate polymerisation is usually 1 (per 100 eV of absorbed energy); in this case, $G(-M)$ equals the kinetic length (ν) of the polymeric chains: $\nu = G(-M)/g = 1000$.

Polymerisation of crystalline acetaldehyde (the nearest homologue of formaldehyde) and glyoxal (the simplest dialdehyde) occurs with much lower rates; at $T < 77$ K, no long polymeric chains are formed from these monomers.[25,31] Subsequent search for cryochemical chain reactions involved two-component polycrystalline systems.[32–37]

2. Solid-phase hydrobromination and chlorination of ethylene

The photochemical hydrobromination of alkenes at temperatures above 77 K has been reported in detail.[32,33] A detailed study of the kinetics and mechanism of radiation hydrobromination of ethylene in the temperature range 4.2–90 K revealed long kinetic transformation chains in the low-temperature range ($v \approx 300$ chain units at 20 K).[34,35] This process is yet another example of a low-temperature rate threshold of a chain chemical reaction. The elementary events of chain growth in hydrobromination and deuterobromination were compared in the following systems: C_2H_4-HBr, C_2H_4-DBr, C_2D_4-HBr and C_2D_4-DBr. This made it possible to determine more precisely the chain growth mechanism in the hydrobromination of ethylene at ultralow temperatures. It was found that it is the approach of heavy species (including intermolecular oscillations) rather than the tunnelling transfer of the hydrogen atom that limits the rate of the low-temperature chain growth.

A method to obtain reactive cryocrystals was reported; the activation-free growth of chains ~300 units long at 17–45 K was studied for ethylene photochlorination as an example.[36] The role of the spatial packing of reactants in solid-phase chain chemical reactions at ultralow temperatures was considered by Misochko.[37] Three limiting cases were discussed: (1) growth of one-dimensional chains along a specific direction in a mixed crystal with alternating arrangement of reactants; (2) chain growth in a random binary mixture of reactants; (3) chain growth with long-range migration of 'hot' atoms. In the first case, where the products formed in the reaction gradually replace the reactants in the lattice sites without any considerable displacement of the neighbouring molecules, chains up to ~300 units long can grow. In the second case, the mean chain length is determined by the number of molecules in the first coordination sphere which are accessible to any reactive species. The chain growth ends in the stabilisation of radicals; the mean chain length is 3–7 units. If chain growth involves 'hot' atoms, the latter can migrate to a far distance from the cage and thus increase the efficient number of sites that separate successive chain units.

Thus, data on the radiation-induced formaldehyde polymerisation and ethylene hydrobromination and on the ethylene photochlorination in crystalline state have shown that chain processes can occur at temperatures near absolute zero. These experiments promoted theoretical studies aimed at the development of the concept of the elementary event of a chemical reaction in a solid.[8,12,36–41]

3. Low-temperature oxidation

Studies on the gas-phase and liquid-phase oxidation of various compounds have contributed markedly to the development of the chain reaction theory.[1] In particular, the possibility, in principle, of radiation-induced oxidation of sulfur dioxide with molecular oxygen under low temperature conditions (at 77 K and in the post-radiation effect mode, *i.e.*, upon heating of a pre-radiated system) was shown experimentally.[42] The radiation-induced oxidation of SO_2 is of interest in the context of decontamination of gaseous industrial exhausts and the possibility of obtaining sulfuric acid. Therefore, it is important to evaluate the efficiency of the non-traditional environmentally safe method for the SO_3 synthesis at low temperatures where undesirable admixtures can be frozen-out. Studies of the low-temperature oxidation of sulfur dioxide showed that the basic process occurs by a chain mechanism during γ-irradiation at 77 K; the initial radiation-chemical yield is 30. The optimum starting molar ratio $SO_2:O_2$ which provides the maximum conversion of sulfur dioxide is 1 : 4. In the post-radiation mode, the conversion is no greater than 1%.

4. Low-temperature radiation-induced conversions of hydrogen cyanide and cyanogen bromide

Hydrogen cyanide (prussic acid) is a compound that is rather common in the outer space: HCN molecules have been detected in comets, in protoplanet formations, in giant clouds of interstellar dust and in other galactical structures. In principle, the HCN molecule may be regarded as the basis of pre-biological chemical evolution, since hydrogen cyanide is a precursor of purines, pyrimidines and amino acids.[43–47] Stahler[48] suggested that the chain length of azapolyene macromolecules formed upon HCN polymerisation may be used as a kind of clock to determine the age of interstellar clouds. Other astrophysical aspects of the chemical conversions of hydrogen cyanide are also being developed intensely.[49,50]

It seemed interesting to study the chemical behaviour of this simple molecule under conditions that are close to those in outer space (low temperatures and radiation) and the role it plays in the 'cold' chemical evolution of the Universe. Below we present the results of experiments carried out in a number of studies.[51–54]

Cooling of liquid HCN to 77 K converts it to the crystalline state. On heating of hydrogen cyanide cooled to 77 K, a 'crystal–crystal' phase transition occurs (248 K) followed by melting (260 K). The heat of melting of HCN is 8.4 ± 0.4 kJ mol^{-1}.

When solid HCN undergoes radiolysis (with doses of 1–800 kGy) at 77 K, the active sites of radical and radical ion nature are stabilised in the crystal.[54] On subsequent heating of the system, a brown polymer $(-HC=N-)_n$, which contains conjugated double bonds, and crystals of the tetramer (1,2-diaminomaleonitrile) are formed in the solid phase. At low temperatures, the polymerisation rates of crystalline HCN are low, and chain polymerisation at 77 K under γ-radiation is not observed. A polymer is formed at temperatures near the melting point of the monomer.

The ESR spectrum of the polymer represents a singlet typical of polyconjugated systems. Within the framework of the suggested radical transformation scheme,[54] the brown colour of the polymer may be explained by the formation of the $-HC=N-HC=N-$ conjugation chain. The formation of needle-like crystals of 1,2-diaminomaleonitrile (tetramer of hydrogen cyanide) may be[53] due to the formation of an intermediate biradical, *viz.*, aminocyanocarbene; dimerisation of the latter results in the tetramer. The fact that 1,2-diaminomaleonitrile is formed under conditions that are close to those in outer space (low temperatures and radiation) seems very important to us, since this compound may play a key role in pre-biological organic synthesis because its hydrolysis directly gives an amino acid.

Crystalline cyanogen bromide does not contain N···H hydrogen bonds typical of crystalline HCN. It was of interest to compare the ability of this compound and hydrogen cyanide to undergo cryopolymerisation. Polymerisation of BrCN following radiolysis at 77 K occurs upon unfreezing in the temperature range 220–230 K and near the monomer melting point (324 K).[55] The heats of melting of BrCN (11.6 kJ mol^{-1}) and of polymerisation (86.0 ± 2.0 kJ mol^{-1}) have been determined. The dependence of the polymer yield from cyanogen bromide on the pre-irradiation dose has an unusual shape with an extremum. At doses in the range 0–900 kGy, the polymer yield increases monotonically to reach a maximum value of ~9% at 900 kGy. A subsequent increase in the irradiation dose decreases the yield to ~4% at 1200 kGy; at higher doses, the yield remains nearly constant up to a dose of 2000 kGy. It is assumed[55] that the suppression of the polymerisation of cyanogen bromide at high pre-irradiation doses results from the progressive degradation of the matrix structure. Such radiation-induced degradation may increase rather strongly the molecular mobility near the monomer melting point. As a result, the rate of polymer chain termination may increase, which would result in degeneration of the chain

process and hence decrease the polymer yield. Thus, the absence of intermolecular chains with strong N···H hydrogen bonds in crystalline cyanogen bromide predetermines a difference in the dynamics of the cryopolymerisation of BrCN and HCN and decreases the radiation resistance of BrCN.

5. Cryopolymerisation of ketene

Work on the mechanism of cryochemical chain reactions involved studies on the radiation-induced polymerisation of carbonyl-containing compounds (formaldehyde, acetaldehyde, glyoxal, *etc.*).[25] Ketene ($H_2C=C=O$) is of considerable interest for studying the features of the low-temperature polymerisation of such compounds. Since the ketene molecule contains cumulated heterochain double bonds, its linear polymerisation may occur by three different pathways to give a polyketone, a polyacetal or a polyester.

Polyketones are formed in the presence of cationic catalysts (*e.g.*, $AlBr_3$) at -60 °C,[56] whereas polyesters and polyacetals are formed with anionic catalysts ($AlEt_3$).[57] Radical initiators do not cause ketene polymerisation.

In addition to soluble linear macromolecules, polymerisation can give insoluble cross-linked structures, since each ketene molecule contains two double bonds.

On cooling to 77 K, ketene is completely converted to the crystalline state. When such a sample is heated, the calorimetric curve displays only an endothermic peak, which corresponds to the melting of crystalline ketene at 140 K (Fig. 2, curve *1*). The heat of melting of ketene determined from calorimetric measurements is 4.0 ± 0.4 kJ mol^{-1}.

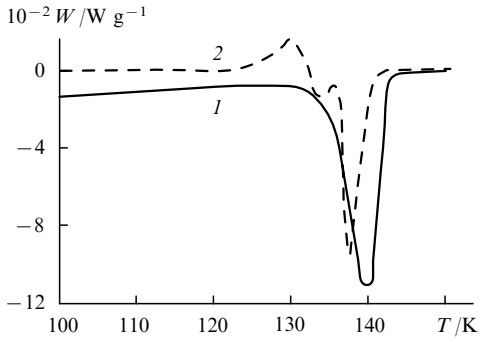


Figure 2. Calorimetric curves of ketene unfreezing;[25] (*1*) non-irradiated sample; (*2*) sample exposed to γ-irradiation with a dose of 300 kGy (here and in Figs 4 and 5, W is the heat evolution rate).

Heating of crystalline ketene pre-γ-irradiated at 77 K results in the solid-phase polymerisation of the monomer, which starts near the melting point and occurs near the melting point, as well. An increase in the pre-irradiation dose decreases the measured temperature of the beginning of polymerisation. For example, at a dose of 300 kGy, the temperature of the beginning of the reaction is about 30 K lower than the melting point of the monomer (Fig. 2, curve *2*). The polymer yield increases with an increase in the pre-irradiation dose and reaches 17% at a dose of 350 kGy.

The thermal effect of ketene polymerisation in this reaction mode as determined from the comparison of the gravimetric yield of the polymer with data from calorimetric measurements is 18.1 ± 1.8 kJ mol^{-1}. The resulting polymer is yellow; on heating to room temperature, it gradually turns dark-orange. It is partially soluble in ethyl methyl ketone. The ratio between the soluble and insoluble polymer fractions depends on the time of exposure of the sample at room temperature. For example, the solubility of the polymer obtained after pre-irradiation of the monomer with a dose of 350 kGy is 85%. If a sealed tube containing this polymer and non-consumed monomer is kept for 20–30 min at ~20 °C, the soluble polymer fraction decreases to 60%. Hence, post-polymerisation of ketene gives a partially cross-linked polymer; this polymer undergoes additional structuring at room temperature in the presence of the monomer, and the proportion of the cross-linked fraction in it increases. This indicates that the polymer retains double bonds which are involved in cross-linking of the macromolecules.

Analysis of the IR spectra of the polymer (the ratio of the band intensities characterising the C=C and C=O bonds in the regions of 1600 and 1720 cm^{-1}, respectively) suggests that ketene polymerisation mainly involves cleavage of the C=O bonds.

The preferential cleavage of C=O bonds during the post-radiation polymerisation of ketene is additionally evidenced by the measured thermal effect of the reaction, which is 18 kJ mol^{-1}. This is close to the thermal effect of polymerisation[58] occurring with the cleavage of C=O double bonds [the experimentally determined heat of polymerisation of acetaldehyde is 10.5 kJ mol^{-1} and that of glyoxal is 21.0 kJ mol^{-1} (see Ref. 25)]. The thermal effects of polymerisation involving the cleavage of C=C bonds are much higher, *viz.*, about 50–80 kJ mol^{-1}.

The cross-linking of the polymer on its storage at room temperature probably occurs through C=O bonds, since the IR band intensities corresponding to the stretching vibrations of these bonds decrease during this process.

Thus, the low-temperature post-radiation polymerisation of crystalline ketene mainly involves the cleavage of C=O bonds to give a polyester. The retention of C=O bonds enables the cross-linking of the polymer.

6. Carbon suboxide

Unusual features were observed in the low-temperature polymerisation of carbon suboxide (tricarbon dioxide) C_3O_2 (m.p. 160 K).[59,60] Calorimetric measurements showed that no radiation-induced polymerisation of solid C_3O_2 with measurable yields in the temperature range 77–160 K could be detected. Similarly, no polymerisation of the monomer was observed in the radiolysis of liquid carbon suboxide. However, it was found that heating of C_3O_2 samples which have been exposed to preliminary γ-irradiation at 77 K resulted in efficient post-polymerisation. The calorimetric curve of unfreezing of samples pre-exposed to radiolysis shows that the heat evolution due to the polymerisation of C_3O_2 is observed starting from the melting point of the monomer. In the temperature range 180–260 K, polymerisation occurs with a very low rate; its rate increases significantly upon subsequent heating, reaches a maximum and then decreases as the monomer is consumed. Probably, radiolysis of crystalline carbon suboxide at 77 K and subsequent heating produce oligomeric active sites (containing 3–5 monomer units); the probability of their decay is low both in the solid and liquid phases. It is these sites that are responsible for the efficient liquid-phase post-radiation polymerisation of C_3O_2. The chain growth in this reaction occurs by the cationic mechanism.[25,60]

Yet another interesting feature of the post-polymerisation of carbon suboxide is the auto-acceleration of the process at constant temperature. The post-polymerisation of C_3O_2 was studied calorimetrically (Fig. 3) at 297 K.[59] At this temperature, the process rate first increases with time, *i.e.*, auto-acceleration of the reaction is observed, and then decreases to zero because the monomer is exhausted. This phenomenon is unusual because the number of active sites 'preformed' during preliminary irradiation can only decrease. Probably, the most likely reason for the auto-acceleration is branching of the chain reaction in an elementary event of monomer addition. Without specifying the particular branching mechanism, let us note that the specific features of the electron structure of the C_3O_2 molecule allow us to speak of both physical and energetic branching. Anyway, the issue of the auto-acceleration mechanism remains open as yet.

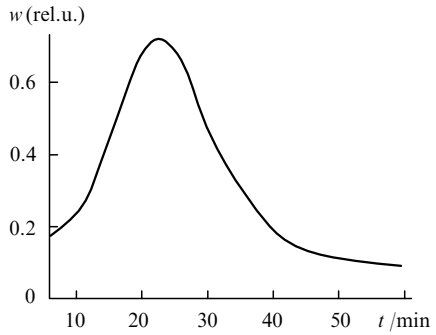


Figure 3. Variation of the post-polymerisation rate (w) of C_3O_2 at 297 K with time; the pre-irradiation dose is 10 kGy.[59]

7. Cryocopolymerisation of dienes and α-alkenes with sulfur dioxide

Certain dienes, such as butadiene, isoprene and 2,3-dimethylbutadiene, efficiently copolymerise with sulfur dioxide to give copolymers with the 1 : 1 composition.[61] Two main mechanisms of the formation of alternating copolymers are possible in such two-component systems. One of them is based on the assumption that two monomers are added sequentially. The alternation of monomer units is due to the considerably higher rate constants of the cross-growth of chains in comparison with the addition constants for each of the monomers. The other mechanism assumes that the copolymer is formed by the mutual addition of binary charge-transfer complexes, which are formed upon mixing of the monomers. The results of studies on the alternating copolymerisation were reported by Golubev [62] for a broad range of such systems.

A specific feature of alternating copolymerisation is that copolymers with the 1 : 1 composition are formed, no matter what the composition of the original monomer mixture. However, the reaction has specific features at low temperatures, which not always comply with the common concept of liquid-phase processes. In fact, solid-phase chemical transformations and copolymerisation in particular depend considerably on the complex phase state of the solid reactant mixture, and are sometimes determined by this composition.[22] As a rule, radiolysis of solid organic mixtures at 77 K results only in the accumulation of stabilised active sites, which are released from the traps upon subsequent heating of the system in the absence of irradiation and initiate the chain chemical transformations. When the system melts, all the growing active sites usually decay, and the polymerisation processes stop. Thus, both phase transitions and chain copolymerisation occur in the temperature range from 77 K to the melting point region of the multicomponent system.[21]

Experimental results obtained by Kichigina *et al.*[63] indicate that the phase composition of an isoprene – SO_2 system affects both the copolymer composition and the dynamics of post-radiation copolymerisation. On sufficiently rapid cooling of a liquid solution of these monomers to 77 K, the system vitrifies; however, it can also be obtained in polycrystalline state upon 'annealing'. The eutectic mixture formed in the system is not equimolar. If isoprene is copolymerised with SO_2 in the post-radiation effect mode at these low temperatures and with an excess of one of the monomers, the isoprene and SO_2 molecules are incorporated in the chain not in strict sequence but with violated alternation of units in the copolymer, as deduced from the results of elemental analysis and the heats of polymerisation.

The processes of post-radiation copolymerisation of a number of dienes and alkenes (ethylene, but-1-ene, cyclopentene, hex-1-ene, oct-1-ene, *etc.*) with sulfur dioxide, occurring both on heating of samples irradiated at 77 K and spontaneously (upon mutual dissolution of the compounds) were compared.[64] It was concluded that the possibility of the formation of donor-acceptor complexes of SO_2 with a monomer is not a sufficient condition, as it is necessary that the structure and composition of the resulting complex favour subsequent polymerisation. A vivid example is provided by comparison of the following two-component systems: cyclopentene – SO_2 and cyclohexene – SO_2. Spontaneous polymerisation is only observed in mixtures of cyclopentene with SO_2; neither spontaneous nor radiation-induced polymerisation is observed in the case of cyclohexene.

8. Quenched high-pressure phases

The radiation-induced polymerisation of crystalline acrylamide starts in areas containing extended defects and occurs at interfaces between the amorphous polymer and the crystalline monomer. In the eutectic mixture acrylamide – water, the chain polymerisation in the quenched high pressure phase was found to be hindered very strongly when the samples that had been exposed to radiolysis at 77 K were heated.[65] The most likely reason for the inhibition of this process is the small size of eutectical acrylamide crystals, the contacts between which are disturbed as the metastable ice phase passes into the equilibrium phase, with the accompanying sharp increase in the volume of the system and its strong dispersion. In fact, if the sample under study represents monomer microcrystals that have virtually no contacts between each other (which hinders strongly the transfer of the growing polymer chain from one crystal to another) and the linear size of these crystals does not exceed 100 molecules (the length of polymer chains is ~ 100 units), the polymerisation in such a sample will be hampered strongly in comparison with a monolithic sample (at equal concentrations of active sites). The estimated size of such crystals is ~ 0.1 μm.

III. Chain reactions in glasses

Amorphous bodies feature only short-range ordering where only the mutual arrangement of a few molecules is correlated. Owing to the absence of long-range order, amorphous bodies are isotropic, *i.e.*, their macroscopic properties do not depend on direction. At temperatures above the melting point, the compound is in a thermodynamically stable liquid state, while on cooling below the melting point it is transformed to another equilibrium state, *i.e.*, a crystal. However, sufficiently fast cooling can give a liquid in a non-equilibrium supercooled state; its subsequent cooling below the glass transition point (T_g) results in yet another non-equilibrium solid amorphous state, which is commonly referred to as glass. It fact, the transition from the supercooled liquid state to the glassy state occurs within a narrow temperature range. The glass-transition point is not a thermodynamic characteristics of a compound and may vary widely depending on conditions of the the sample preparation and the measurement procedure used. Species in a glass are only capable of oscillation and small-scale rotational movement. The translational mobility typical of liquids is lost almost completely.

In our subsequent discussion, the following fact is very important: both the transition from the supercooled liquid state to the glassy state and the reverse transition (called devitrification) are accompanied by an abrupt change in the properties of the compound, such as viscosity, elastic modulus, thermal expansion factor, *etc*. Certainly, the most impressive phenomenon is the huge jump of viscosity (by 10 – 12 orders of magnitude) in the narrow glass-transition range.[66] From the chemical viewpoint, this means that the molecular mobility, which defines the dynamics of a chemical conversion, changes abruptly in this region. The nature of the chemical process should change considerably when the glass softening region is passed owing to the abrupt change in the mobilities of the reactants (in this case, the mobilities of molecules change stepwise on increasing or decreasing the temperature by only a few degrees).

Radiolysis of glassy matrices gives rise to reactive radical or ionic species which are stabilised in more or less deep traps and which may preserve reactivities for a long time. The absence of molecular mobility in the glass prevents mutual recombination of such stabilised radicals. When the matrix is heated and the glass

passes to the supercooled liquid state (devitrification), the translational mobility increases abruptly and, as a consequence, recombination of the accumulated radicals occurs. In the systems where the radicals released upon devitrification can initiate a chain reaction, efficient chain radical processes are realised (see below).

Polymerisation reactions (radical, ionic, copolymerisation, graft polymerisation) occurring quite intensely upon devitrification of glassy matrices that have undergone radiolysis at 77 K are described in detail in a review by Barkalov and Kiryukhin.[66]

1. Chlorination during matrix devitrification

Specific features of low-temperature radiation-induced chlorination in glassy matrices were studied in a system butyl chloride – molecular chlorine (T_g = 100 K). The reaction was studied (i) directly under γ-irradiation and (ii) in the post-radiation effect mode on heating of pre-irradiated samples.[67,68]

The radiation-induced chlorination of butyl chloride, in both the glassy and supercooled liquid state near the devitrification point (98 – 107 K), is characterised by a long life time (τ) of active sites ($\sim$1500 s). As the temperature is increased, the chain growth rate in the supercooled liquid reaches a maximum at 114 K; when the system passes to a thermodynamically stable liquid and the viscosity of the medium decreases, the probability of chain termination increases (τ < 100 s). This decreases the overall rate of the process in the temperature range 115 – 150 K.

When glassy solutions of chlorine in butyl chloride pre-exposed to γ-irradiation at 77 K are heated in a calorimeter, heat evolution is observed because of chlorination. As the pre-irradiation dose is increased, the heat evolution due to chlorination is detected at progressively lower temperatures. After irradiation with a dose of 100 kGy, the reaction starts at 80 K.

The ESR spectra recorded during the irradiation of the system at 77 K manifest two types of paramagnetic centres, *viz*., alkyl radicals ($R_A^{\bullet}$) and Cl_2^- species. The most likely mechanism of the formation of the $R_A^{\bullet}$ radical involves the dissociative capture of a slow electron:

$$Me(CH_2)_2CH_2Cl + e^- \longrightarrow Me(CH_2)_2CH_2^{\bullet} + Cl^-. \quad (1)$$

The formation of Cl_2^- species probably results from direct electron addition:

$$Cl_2 + e^- \longrightarrow Cl_2^-. \quad (2)$$

The chain chlorination in the temperature range 90 – 110 K occurs by the classical mechanism:

$$R_A^{\bullet} + Cl_2 \longrightarrow RCl + Cl^{\bullet}, \quad (3)$$

$$Cl^{\bullet} + RH \longrightarrow R_A^{\bullet} + HCl. \quad (4)$$

The behaviour of the Cl^- species formed upon radiolysis is quite unusual: in the presence of these species, chlorine atoms are captured from the chain at 80 – 100 K according to the reaction:

$$Cl^- + Cl^{\bullet} \longrightarrow Cl_2^-. \quad (5)$$

As a consequence, the efficiency of the low-temperature radiation-induced chlorination decreases. It is this that differs radiation-induced chlorination from photochemical chlorination. In fact, photolysis does not produce Cl^- species, and at equal concentrations of alkyl active sites $R_A^{\bullet}$ the process occurs more intensely in those samples which have undergone photolysis.

Measurements of the rate of the process directly during γ-irradiation and in the post-effect mode (on heating of pre-irradiated samples) gave the following rate constant for the limiting step of chain growth [reaction (4)] in the temperature range 98 – 114 K:[67,68]

$$k_4 = 10^{12} \exp\left(-\frac{25000}{RT}\right) \text{ litre mol}^{-1} \text{ s}.$$

Thus, the chain reaction of chlorination of chloroparaffins (both in the glassy and supercooled liquid state near the devitrification region) features long life times of active sites. With an increase in temperature, the chain growth rate reaches a maximum in the supercooled liquid; when the system passes to the thermodynamically stable state and the viscosity of the medium decreases, the probability of chain termination increases. Hence, similarly to polymerisation processes,[66] the suppression of chain termination reactions and simultaneous provision of efficient chain growth (this is the mode which is automatically realised near the devitrification region) makes it possible to increase considerably the overall reaction rate.

2. Hydrobromination of alkenes

The solid-phase hydrobromination of ethylene occurs in an equimolar crystalline complex. Mozhaev *et al*.[69] studied low-temperature radiation-induced hydrobromination of alkanes (for allyl chloride as an example) in the glassy state.

On cooling to 77 K, an allyl chloride – HBr system passes to the glassy state (T_g = 88 K) for all the reagent ratios used (1 : 1, 10 : 1 and 60 : 1). Spontaneous hydrobromination in this system occurs only in the liquid state (in the temperature range 182 – 220 K); for the allyl chloride : HBr ratio = 1 : 1, the conversion is 50% in this temperature range. The degree of conversion was determined calorimetrically. Complete conversion of HBr in thermoactivated hydrobromination occurs only in the presence of an excess of allyl chloride. For example, complete conversion of hydrogen bromide is observed in the allyl chloride – HBr system with 10 : 1 composition. The thermal effect of the reaction (ΔH) determined in a series of experiments is 71.4 ± 2.0 kJ mol^{-1}. This value is in good agreement with the thermal effect of ethylene hydrobromination and the calculated ΔH value.[34]

Hydrobromination in the allyl chloride – HBr system can give either 2-bromo-1-chloropropane (addition in accordance with the Markownikoff rule) or 3-bromo-1-chloropropane (anti-Markownikoff addition). The difference between the thermal effects of these two reaction pathways is determined by the different strengths of C – H bonds in the methyl and methylene groups. In fact, the strengths of the C – Br bonds in 1-bromopropane and 2-bromopropane are the same,[69] whereas the energies of the C – H bonds in propane at the C(1) and C(2) atoms are 412 and 395 kJ mol^{-1}, respectively.

Thus, the thermal effect of the Markownikoff addition of bromine is 17 kJ mol^{-1} higher than that of the anti-Markownikoff addition. Hence, the experimentally measured thermal effect of spontaneous hydrobromination of allyl chloride (which is the same as that of the hydrobromination of ethylene) corresponds to the Markownikoff addition of HBr to give 2-bromo-1-chloropropane.

During radiolysis of the allyl chloride – HBr system (^{60}Co γ-irradiation) at 77 K, active sites are stabilised in the matrix; they initiate efficient chain hydrobromination when the sample is unfrozen. This reaction occurs when the molecular mobility increases abruptly, *viz*., in the devitrification region of the system (in the temperature range 87 – 95 K). The degree of conversion depends on the pre-irradiation dose; for example, it increases from 12% to 25% as the dose is increased from 1.5 to 20 kGy. A decrease in the HBr concentration in the original mixture increases the degree of conversion. In allyl chloride – HBr systems with 20 : 1 and 60 : 1 compositions that have been pre-γ-irradiated with a dose of 10 kGy, complete HBr conversion is observed. Naturally, no spontaneous addition occurs on heating of such samples to 200 K. The thermal effect of the post-radiation reaction (ΔH) determined in a series of experiments[69] is 55.4 ± 2.0 kJ mol^{-1}. Hence, the post-radiation addition of HBr to allyl chloride results in 3-bromo-1-chloropropane (anti-Markownikoff addition); the thermal effect of the reaction coincides with the calculated[69] ΔH value.

3. Hydrobromination of allene

Chain addition at low temperatures has also been studied for the first representative of hydrocarbons containing cumulated C=C bonds, *viz*., allene ($H_2C=C=CH_2$).[70]

On stirring the allene–HBr equimolar mixture at $\leqslant$190 K followed by freezing to 77 K, the system passes to the glassy state ($T_g \approx 80$ K). Unlike the equimolar mixture, samples with allene–HBr molar ratios of 1:5, 1:2 or 5:1 pass to the crystalline state upon stirring and cooling to 77 K. An eutectic mixture is formed in the case of the allene–HBr molar ratio of 1:2, and the calorimetric curve shows only the melting of the eutectics around $\sim$120 K. In the other reaction mixtures containing a larger excess of one of the components, melting of the excess component is observed as well. Subsequent heating of samples results in spontaneous hydrobromination; calorimetric curves show exothermic reactions at a temperature of $\geqslant$170 K. The hydrobromination rate increases with an increase in the HBr content in the mixture. The maximum reaction rates in mixtures with allene–HBr molar ratios of 1:2 and 1:5 are observed at 260 and 230 K, respectively.

Spontaneous hydrobromination of allene in this temperature range obeys the Markownikoff rule. In all the systems studied, 2-bromopropene [MeC(Br)=CH_2] is the major reaction product, irrespective of the original ratio of the reactants. Analysis of absorption IR spectra of the reaction products allows two conclusions to be made. First, spontaneous hydrobromination of allene results in the cleavage of only one C=C bond, since the IR spectrum of the reaction products displays absorption bands near 1650 cm^{-1}, which correspond to the stretching vibrations of the C=C bond. Second, the absorption IR spectra of 2-bromopropene, unlike those of allyl bromide, contain bands originating from the presence of a methyl group in the regions of 800 cm^{-1} (skeleton C–Me vibrations) and $\sim$1380 cm^{-1} (symmetric deformation vibrations of the C–H bond in the methyl group).

The yield of the allene spontaneous hydrobromination product (the reaction occurs in the dark; the heating rate is $\sim$1 deg min^{-1}) depends on the original molar ratio of the reactants: it is $\sim$25% (allene : HBr = 1:1) or $\sim$60% (allene : HBr = 1:2 or 1:5). The thermal effect of the reaction (ΔH) determined in a series of experiments [70] was 70.0 ± 0.7 kJ mol^{-1}.

It should be noted that the conclusion that only one C=C bond is cleaved in the allene molecule during spontaneous hydrobromination under these reaction conditions is confirmed experimentally. Studies of the reaction of allyl bromide (3-bromopropene) and 2-bromopropene with HBr showed that no spontaneous hydrobromination of these compounds occurs in the temperature range 77– 290 K.[70]

Studies of the radiation-induced hydrobromination of allene were carried out for the same systems (with the molar ratios allene : HBr = 1:1, 1:2, 5:1) that have been used in studies of the spontaneous reaction. When the allene–HBr equimolar mixture pre-exposed to γ-irradiation with a dose of 2 kGy at 77 K was heated, intense heat evolution due to hydrobromination was observed in the temperature range of system devitrification (82–90 K).

When the allene–HBr system pre-exposed to γ-irradiation at 77 K with 1:2 molar ratio of the reactants was heated, hydrobromination was detected in the temperature ranges 85–95 K and 105–110 K. Subsequent heating results in melting of the remaining eutectic mixture.

If an excess of allene is originally present in the system (molar ratio allene : HBr = 5:1), post-radiation hydrobromination is observed in the temperature range 90–115 K. Subsequent heating of the sample results in melting of the excess allene. It should be noted that the heat of melting of the excess allene remains the same in both systems, *viz*., intact and subjected to radiolysis. Hence, hydrobromination involves only the amount of allene which corresponds to its content in the eutectic mixture.

Thus, the post-radiation hydrobromination of allene, unlike spontaneous hydrobromination, occurs at much lower temperatures (80–120 K). Analysis of hydrobromination products in allene–HBr systems (with original molar ratios of the reactants 1:1, 1:2 and 5:1) makes it possible to conclude that one allene C=C bond is cleaved in the first step, and subsequent hydrobromination involves the cleavage of the second C=C bond.The post-radiation hydrobromination of allene at low temperatures occurs as the anti-Markownikoff addition to give allyl bromide and also a product of more extensive hydrobromination of allene, *viz*., 1,3-dibromopropane. The absorption IR spectrum of the reaction products is a superposition of two spectra, *i.e*., those of allyl bromide and 1,3-dibromopropane.

Since the boiling points of allyl bromide and 1,3-dibromopropane differ considerably (344 and 439 K, respectively), it is easy to separate these products. It was found that if the composition of the original mixture is 1:1, then the overall product yield is $\sim$50%, while the yield of 1,3-dibromopropane is $\sim$14%; if the allene : HBr ratio is 1:2, the overall yield is 70%, while the yield of 1,3-dibromopropane is $\sim$50%. The IR spectra of the reaction products that were isolated match completely the spectra of allyl bromide and 1,3-dibromopropane recorded previously.

Thus, the hydrobromination of allene in the temperature range 80–120 K during unfreezing of the allene–HBr system pre-exposed to radiolysis at 77 K occurs as the anti-Markownikoff addition, irrespective of the original ratio of the reactants. In the first stage, allyl bromide is formed; it then undergoes hydrobromination to give 1,3-dibromopropane. The content of allyl bromide and 1,3-dibromopropane in the reaction products depends on the original composition of the reaction mixture and on the pre-irradiation dose.

4. Cryopolymerisation of epichlorohydrin

Epichlorohydrin (ECH) passes to the glassy state on cooling to 77 K at a rate of 50–100 deg min^{-1}. The calorimetric heating curve for ECH (Fig. 4, curve *1*) displays the transition from the glassy state to the supercooled liquid state (T_g = 130 K), crystallisation in the temperature range 150–170 K and melting of the monomer (at 210 K).[71] The heat of melting of ECH determined from these calorimetric measurements is 10.0 ± 0.5 kJ mol^{-1}.

Preliminary γ-irradiation of ECH at 77 K followed by heating results in polymerisation of the monomer.[71] The most intense polymerisation is observed in the devitrification region (see Fig. 4, curves *2*, *3*). As the pre-irradiation dose is increased, the post-polymerisation of ECH during heating is detected carolimetrically at progressively lower temperatures. At sufficiently high pre-irradiation doses (> 300 kGy), the calorimetric curve shows that the polymerisation rate first increases with an increase in temperature, then decreases slightly and eventually increases abruptly in the glass softening region (see Fig. 4, curve *3*). This pattern is probably a consequence of the kinetic non-uniformity of the growing active sites. The 'freezing' and 'revival' of growing polymer chains during solid-phase polymerisation,[23] the decay

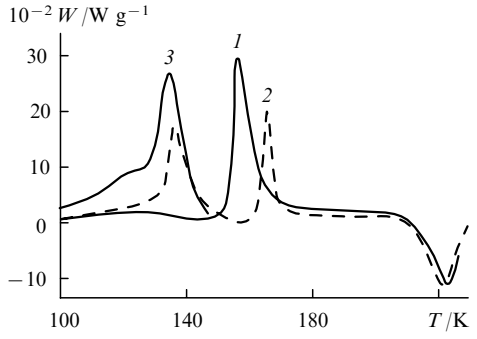


Figure 4. Calorimetric curves of epichlorohydrin heating;[25] non-irradiated sample (*1*); samples exposed to γ-irradiation with doses of 57 kGy (*2*) and 310 kGy (*3*). The irradiation was carried out at 77 K.

of stabilised active sites and a number of other processes may be interpreted within the framework of the 'polychronous kinetics' concept.[24] In the glass softening temperature range, where the molecular mobility increases abruptly, the post-polymerisation of ECH (like that of the majority of other monomers) occurs efficiently.

In order to elucidate the specific features of the reaction mechanism, Kichigina *et al.*[71] studied the effect of certain additives (pyridine, hydroquinone, ethanol) on the post-polymerisation of ECH. The addition of ~4% pyridine (a typical inhibitor of cationic polymerisation) to the system suppressed completely the ECH post-polymerisation. On the other hand, the addition of hydroquinone (a typical inhibitor of radical polymerisation) did not affect the ECH post-polymerisation. The yield of the polymer from samples containing hydroquinone was almost the same as in the case of pure ECH. Hence, the post-radiation polymerisation of ECH in the temperature range 85–150 K occurs according to the cationic mechanism. It is of note that a polymer is also formed in the region of the system devitrification during the radiation polymerisation of ECH in a glassy matrix of dichloromethane, which is a typical solvent for cationic polymerisation.

Ethanol was found to exert an unusual effect on the post-radiation polymerisation of ECH. The addition of ethanol (to a concentration of 5%) does not virtually affect the post-polymerisation in the temperature range 77–120 K and suppresses strongly the polymerisation in the devitrification region (130–150 K). Ethanol is a weaker inhibitor of cationic polymerisation than pyridine. This is probably the reason why it suppresses the ECH polymerisation in this way. At low temperatures, far from the devitrification region where the matrix is sufficiently rigid, ethanol does not affect polymerisation. In the devitrification region, where softening of the matrix occurs with an abrupt decrease in the viscosity and hence an increase in molecular mobility, ethanol suppresses the cationic polymerisation of ECH. In this case, the yield of the polymer is 5% for the irradiation dose of 150 kGy (for the pure monomer, the yield of the polymer is 12% for the same irradiation dose).

The dynamics of the post-radiation polymerisation of crystalline ECH differs considerably from that of the glassy monomer. Crystalline ECH is obtained by 'annealing' a sample in a calorimeter: glassy ECH is heated to the pre-melting region and then frozen to 77 K.[71] Unlike the glassy monomer, insignificant heat evolution associated with polymerisation is only observed in the pre-melting region for the crystalline sample pre-exposed to radiolysis. At equal pre-irradiation doses at 77 K (170 kGy), the yield of the polymer from crystalline ECH is 3%, while that from glassy ECH is 12%.

It is well known that the epoxide ring is highly resistant against high-energy ionising radiation.[72,73] Efficient chain polymerisation of ethylene oxide could be carried out only by heating a glassy solution of the monomer in butyl chloride pre-exposed to radiolysis at 77 K.[74] In the case of ECH, post-polymerisation during devitrification makes it possible to carry out the reaction without the use of glass-forming solvents, since the monomer itself readily passes to the glassy state on cooling to 77 K. This analogy may be extended. As shown previously,[75] heating of a pre-irradiated glassy ethylene oxide–hydrogen cyanide mixture results in their copolymerisation. It was found that a solution of HCN in ECH (molar ratio 1 : 3) passes to the glassy state on cooling to 77 K (the glass softening temperature is ~130 K). Cooling of this solution pre-irradiated at temperatures in the glass softening region results in copolymerisation of ECH with HCN. The brown reaction product is soluble in ECH. Its IR spectrum displays a band near 1680 cm^{-1} characteristic of the stretching vibrations of the C=N bond, which indicates that HCN molecules are involved in the copolymer.

5. Polymerisation of ketene in glassy matrices

Solutions of ketene (25 mol.%) in butyl chloride pass to the glassy state on cooling to 77 K (Fig. 5*a*, curve *1*).[76] Heating of this glassy system pre-γ-irradiated at 77 K results in ketene polymerisation in the devitrification temperature range (T_g = 95 K) (see Fig. 5*a*, curve *2*). Subsequent heating results in crystallisation, which (due to the presence of the polymer) is shifted to a higher temperature range with respect to the crystallisation of a non-irradiated sample; in addition, melting of the mixture occurs (see Fig. 5*a*).

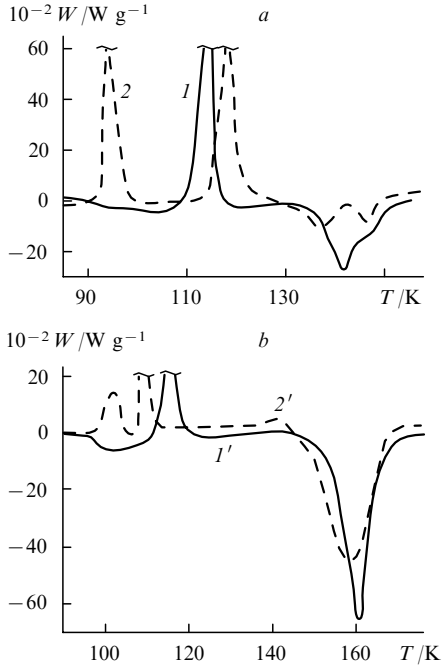


Figure 5. Calorimetric curves of the unfreezing of ketene solutions in butyl chloride (25 mol.%) (*a*) and in diethyl ether (33 mol.%) (*b*);[76] non-irradiated solutions (*1*, *1′*); solutions γ-irradiated with doses of 250 kGy (*2*) and 330 kGy (*2′*).

The dependence of the yield of the polymer on the pre-irradiation dose is shown in Fig. 6. In the case of ketene polymerisation in a glassy butyl chloride matrix, the yield of the polymer reached the limit of ~20% at a dose of 50 kGy (see Fig. 6, curve *2*). The resulting polymer is yellow; it is partially soluble in ethyl methyl ketone. Its solubility increases with an increase in the pre-irradiation dose: the soluble polymer fraction is 10% at a dose of 10 kGy and 75% at 250 kGy. The polymer was isolated without exposure at room temperature.[76]

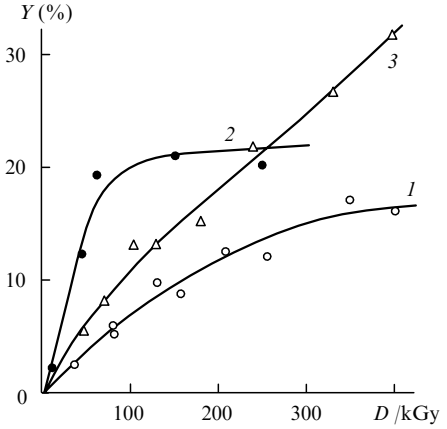


Figure 6. Dependence of the yield (*Y*) of the ketene polymerisation product on the dose (*D*) of preliminary γ-irradiation;[76] (*1*) ketene, (*2*) solution of ketene (25 mol.%) in butyl chloride, (*3*) solution of ketene (33 mol.%) in diethyl ether.

The specific heat of ketene polymerisation in a glassy matrix of butyl chloride differs considerably from the heat of polymerisation of crystalline ketene. The mean specific heat of ketene polymerisation in the devitrification region of the system determined in a series of experiments is 74 ± 3 kJ mol^{-1}, which is almost fourfold larger than the specific heat of polymerisation obtained for crystalline ketene.

The IR spectrum of polyketene resulting from the reaction in the ketene – butyl chloride system also differs considerably from that of the polymerisation product of crystalline ketene. The former contains an intense absorption band characteristic of the stretching vibrations of the C=O bond and a weak band corresponding to the C=C bond. The absorption IR spectra and the specific heat of ketene polymerisation (which is close to the heat of cleavage of the C=C bond) suggest that the cryopolymerisation of a glassy solution of ketene in butyl chloride predominantly occurs with the cleavage of C=C bonds.

It should be noted that previous studies of low-temperature post-radiation polymerisation of various monomers (cyclopentadiene,[77] ethylene oxide,[78] acetaldehyde[79]) in a butyl chloride glass-forming matrix pointed to a cationic reaction mechanism. It is likely that the cryopolymerisation of ketene in butyl chloride also occurs by the cationic mechanism with the cleavage of the C=C bond.

Post-radiation cryopolymerisation of a solution of ketene (33 mol.%) in diethyl ether was studied.[76] On cooling to 77 K, this solution, like the ketene – butyl chloride system, passes to the glassy state. The calorimetric curve of heating displays devitrification of the system (T_g = 100 K), crystallisation (110 – 120 K) and melting of the mixture (150 K) (see Fig. 5*b*, curve *1′*).

After γ-irradiation at 77 K followed by heating of the irradiated sample, as in the ketene – butyl chloride system, the calorimetric curve displays ketene polymerisation in the devitrification temperature range (see Fig. 5*b*, curve *2′*). However, unlike the ketene – butyl chloride system, the formation of a polymer in the devitrification region of the ketene – diethyl ether system shifts crystallisation to a lower temperature range (105 – 110 K). Post-polymerisation of ketene occurs not only in the devitrification temperature range but also during subsequent heating near the melting point of the system (see Fig. 5*b*, curve *2′*).

The yield of the polymer increases almost linearly with an increase in the pre-radiation dose to 200 kGy and equals ~35% at a dose of 400 kGy (see Fig. 6, curve *3*). The isolated polymer was yellow; it was completely soluble in ethyl methyl ketone.

The IR spectrum of the ketene polymerisation product formed in this system is virtually completely the same as that of the polymer obtained by cryopolymerisation of crystalline ketene. The specific heat of ketene polymerisation in a diethyl ether glassy matrix is 21 ± 2 kJ mol^{-1}, which is close to the specific heat of polymerisation of pure ketene. These data suggest that, as for pure ketene, its polymerisation in a diethyl ether matrix probably occurs by an anionic mechanism involving the preferential cleavage of C=O bonds and formation of a polyester.

Analysis of experimental data[76] demonstrates clearly that the low-temperature post-radiation polymerisation of ketene can occur by both the anionic and cationic mechanism depending on the conditions of the process. Using solvents typical of cationic (butyl chloride) or anionic polymerisation (diethyl ether) as the glass-forming matrix, it is possible to govern the predominant reaction pathway.

6. Cryoozonolysis of perfluoroalkenes

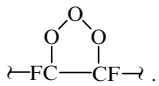
Cryochemical methods have favoured a considerable progress in the studies on perfluoroalkenes. First, it became possible to conduct experiments with pure ozone (which was isolated by low-temperature rectification). Second, the use of low-temperature kinetic calorimetry[80] made it possible to follow the temperature and rate parameters of chemical processes involved in the cryoozonolysis of perfluoroalkenes.

The low-temperature ozonolysis of neat tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) in the absence of oxygen was studied.[81,82] It was found that for equimolar perfluoroalkene : O_3 ratios and at low temperatures (140 – 230 K) ozone adds quantitatively to the double bond to give the corresponding ozonides. The cryoozonolysis products are stable up to temperatures of 250 – 290 K. They decompose at higher temperatures; however, the ozonide from TFE is more stable than the ozonide from HFP. The resulting decomposition products of TFE and HFP ozonides initiate the polymerisation of TFE and a number of other monomers.[83]

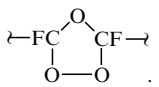
The previously developed technique to prepare samples and perform experiments, which prevents the reaction from occurring in uncontrolled explosive mode, allowed the low-temperature ozonolysis of some other perfluoroalkenes, *e.g.*, perfluoro-4-methylpent-2-ene (HFP dimer, or DHFP) and perfluoro-2,4-dimethyl-3-ethylpent-2-ene (HFP trimer, or THFP) to be studied as well.[83,84]

On cooling to 77 K, the HFP dimer passes to the glassy state (T_g = 110 K). On cooling the sample containing equimolar amounts of DHFP and O_3, an exothermic reaction of ozone with DHFP occurs starting from ~210 K. The cryoozonolysis rate increases with an increase in temperature to reach a maximum near ~240 – 250 K. The overall activation energy of the reaction in the temperature range 210 – 240 K is 90 ± 5 kJ mol^{-1}. On further increase in temperature, the rate of the process decreases because the reactants are depleted. The thermal effect of DHFP ozonolysis determined in a series of calorimetric measurements is 505 ± 5 kJ mol^{-1}.

As with TFE and HFP, the ozonolysis of DHFP at low temperatures according to the well-known three-step Criegee mechanism[85] gives the corresponding carbonyl-containing compounds and the DHFP ozonide. Initially, the reaction of ozone with DHFP gives the so-called molozonide



This ozonide is unstable and decomposes quickly to a bipolar ion $-FC^+-O-O^- \rightharpoondown FC^+—O—O^-$ and a carbonyl compound $-FC=O \rightharpoondown FC=O$. The resulting intermediates readily reassemble in a different manner to give a more stable ozonide



Like TFE and HFP ozonides, DHFP ozonide initiates polymerisation of a number of monomers, *e.g.*, TFE, methyl methacrylate, acrylonitrile, and also copolymerisation of tetrafluoroethylene with hexafluoropropylene. It should be noted that the use of the ozonides obtained for the initiation of the polymerisation of fluoromonomers has important advantages over the use of other initiators.[86] DHFP ozonide is non-explosive and storage-stable. The use of perfluoroozonides makes it possible to polymerise TFE under atmospheric pressure and at room temperature with technologically acceptable rates. In principle, such initiators allow continuous polymerisation of fluoromonomers in the gas phase to be performed. The equipment required for the process is simplified considerably because gaseous TFE is used under ordinary pressure; furthermore, the synthesis becomes much more environmentally safe, because no emulsions or water are used.

IV. Autowave processes

In our discussion of the mechanism of an elementary act of a chemical reaction at temperatures near absolute zero (radiation-induced and photochemical polymerisation of formaldehyde, photochlorination of ethylene in a spatially ordered crystalline structure, radiation-induced hydrobromination of ethylene,

etc.[25–33]), we did not touch upon the mechanism of the chemical transformation chain. However, in addition to the obscure issue of the mechanism of overcoming the activation barrier, yet another important problem remained open, *viz.*, that of the mechanism of the displacement of reagents in an elementary act of attachment of monomeric unit. It should be reminded that in the formation of a macromolecule each van der Waals distance between the monomers in a crystal decreases to the lengths of chemical bonds as a result of the reaction.

The consideration of the mechanochemical aspect of the radiation cryochemistry of solids was stimulated by the discovery of the chain reaction initiation upon local sample destruction.[87]

When destruction of a solid occurs, the mechanical energy of its elastic deformation is concentrated in the vicinity of the newly formed surface. It is well known that upon such energy transformation, the properties of substances on the newly formed surface change considerably in comparison with their bulk properties.[88,89] Brittle destruction is accompanied by a number of physicochemical phenomena: emission of electrons and ions, luminescence, generation of radicals, sharp acceleration of transfer processes on the split surfaces.[90–92] It seemed logical that the transition of the reaction from the homogeneous mode to the considerably heterogeneous mode by performing brittle destruction of the sample would 'switch on' the non-equilibrium mechanism of energy transfer to active sites previously stabilised in the solid matrix, and initiate chemical transformations at low temperatures.

Let us consider yet another circumstance that prompted the researchers to reconsider the generally accepted concepts. In the studies performed before, both the kinetic models that describe solid-phase radiation-chemical transformations and the experimental techniques were based on the assumptions about the system uniformity and homogeneity of the chemical reaction. This stage was quite logical, as it is difficult to reveal and study specific features of non-uniform chemical transformation modes by calorimetric and spectroscopic techniques that deal with integral signals. There have always been doubts as to the applicability of zero-dimensional kinetic models in the radiation chemistry of solids, since it is well known that an irradiated sample is never homogeneous on the microscopic scale. The main results obtained at this step of the studies were generalised in a number of reviews.[13–15]

Polymerisation and copolymerisation are the most interesting processes during which it is possible to observe low-temperature transformation autowaves. Their principal difference from previously studied chain reactions of chlorination and hydrobromination of hydrocarbons is that polymerisation produces long material chains. It is reasonable to expect that this predetermines certain features of the reaction, *e.g.*, an increase in the life time of active polymerisation sites due to the limited molecular mobility in the network formed by a polymeric product. Furthermore, the formation of long polymeric chains under low and ultralow temperature conditions is of undoubted interest for the explanation of the processes of 'cold' chemical evolution of matter in the Universe.

1. Polymerisation autowave of crystalline acetaldehyde

The propagation of the polymerisation front in solid radiolysed acetaldehyde at comparatively high temperatures (117–147 K) close to the monomer melting point (150 K) was observed by thermography and by shooting a film.[93] This phenomenon was interpreted within the framework of the classical thermal mechanism of burning. The propagation rate of the reaction front was 1–3 cm s^{-1} at the temperatures specified above and upon preirradiation with doses of 5–100 kGy. Using just one heat transfer equation and a number of assumptions, Pshezhetskii and Tupikov[93] calculated the time required to add one monomeric unit to a polymeric chain (10^{-8} s). The kinetics of this reaction has been studied in detail by the calorimetric method in a slow temperature scanning mode and directly under γ-irradiation in the absence of noticeable sample overheating.[25] The rate constant of chain growth in the crystalline monomer was determined at 130–140 K:

$$k \approx 3 \times 10^{17} \exp\left(-\frac{46000}{RT}\right) \text{ litre mol}^{-1}\ \text{s}^{-1};$$

it was found that the time required for the addition of one monomer unit is as short as 0.1–0.01 s. In view of this, a question appeared whether the theory of burning was rightfully used[93] to describe the process of the layer-by-layer propagation of the polymerisation front.

The development of the concept of autowave processes stimulated Kichigina *et al.*[94] to analyse specific features of the polymerisation of crystalline acetaldehyde on a new qualitative level. This reaction is of particular interest owing to two factors. First, the discovery of the autowave mode during the polymerisation of acetaldehyde would allow one to state that a cryochemical wave is possible in a one-component system. Second, the thermal effect of this reaction is virtually an order of magnitude lower than those of systems studied previously.

The main concepts regarding the mechanochemical feedback in the autowave process[13–15] were confirmed by a study of this system. The polymerisation wave, which appears as a result of local brittle destruction of crystalline pre-radiolysed acetaldehyde in the temperature range 4.2–77 K, was observed in bulk (cylindrical) and thin-film samples immersed in a nitrogen or helium bath.[94]

The principal features of the structure of the running polymerisation fronts in acetaldehyde are similar to those found for other cryochemical reactions (Fig. 7). These include an indistinctly expressed stage of inert heating and the abrupt reaction 'turn-on' at considerably lower temperatures than in the case of thermoactivated processes. However, unlike the systems studied before, more time is required for the temperature decrease after the polymerisation front has passed. The characteristic time of this decrease is 2–3 times longer than the thermal inertia of the system. Hence, the polymerisation reaction is not 'turned off' after the wave front has passed, and part of the polymer is formed behind the front.

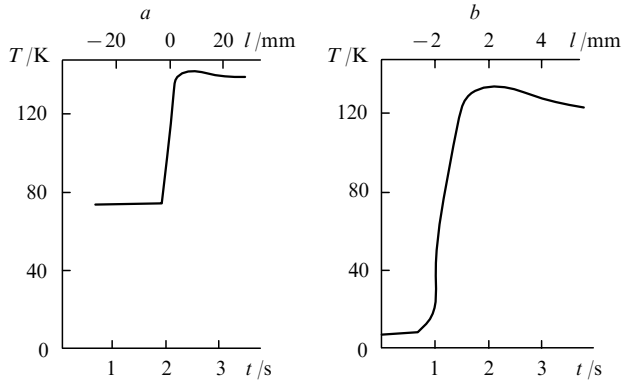


Figure 7. Time and spatial scanning of characteristic temperature profiles of the propagation waves of acetaldehyde polymerisation at 77 K (*a*) and 4.2 K (*b*).[94]
The γ-irradiation dose is 700 kGy; the wave propagation rates are 26 (*a*) and 4 mm s^{-1} (*b*).

When the front passes through a sample immersed into a helium bath, the maximum temperature in the polymerisation front does not exceed 130 K, which is much lower than the monomer melting temperature (150 K). Thus, this system may be used to analyse the changes in the structure and phase state of a crystalline sample caused by the passage of a cryopolymerisation mechanochemical wave through the sample. According to the concept developed in a series of studies,[13–15] the front of a chemical reaction is a mechanical dispersion zone that moves

through a solid reagent. The cinegrams obtained by Kichigina *et al.*[94] for the polymerisation of acetaldehyde show that a polycrystalline sample becomes transparent after the wave has passed. It may be assumed that, as the polymerisation wave passes, amorphisation of polycrystalline acetaldehyde occurs due to both the formation of an amorphous polymer phase and mechanical dispersion.[94]

This assumption was checked by the calorimetric method, which allows determination of the ratio of amorphous and glassy phases in a solid matrix, based on changes in the thermal effect of melting. In order to perform this analysis, a cylindrical sample of acetaldehyde through which an autowave has passed in liquid helium was transferred to a liquid nitrogen bath and then cut into several parts at different heights. Each of the parts was placed in a separate calorimeter at 77 K and its calorimetric curve of unfreezing was recorded. It was found that the crystalline phase was absent in the entire sample after the wave has passed. The calorimetric experiments only manifested a jump of the thermal capacity which accompanies devitrification, whereas the thermal effect of melting was not observed. However, if the process is carried out not in the autowave mode but by slow heating of the entire sample in a calorimeter (without brittle destruction that initiates an autowave), then the nonconsumed monomer maintains its crystallinity. This confirms that the passage of a mechanochemical wave through a crystalline sample results in its amorphisation.

The autowave propagation rate depends on the pre-irradiation dose. For samples immersed into liquid nitrogen, the propagation rate of the polymerisation autowave increases linearly with an increase in the irradiation dose up to 1200 kGy. It was logical to assume that the increase in the wave propagation rate resulted from the accumulation of active sites. However, active sites (radical ions and radicals) are accumulated linearly during the radiolysis of polycrystalline acetaldehyde at 77 K as the irradiation dose increases to 50 kGy; after that, the process slows down and ceases completely at doses above 650 kGy.

The increase in the wave propagation rate with an increase in the irradiation dose may be explained as follows. The low-temperature radiolysis of acetaldehyde gives rise to methane and carbon monoxide, which exist in a condensed state at 77 K. When the reaction front passes, these radiolysis products turn into gases (the melting points of CH_4 and CO are 111 and 81 K, respectively). The gases evolved can facilitate brittle dispersion of the sample and thus accelerate the movement of the running transformation front.[94]

2. Acetaldehyde polymerisation autowave in a glassy matrix

Pure acetaldehyde could not be transformed to the glassy state even by fast cooling. Solutions of acetaldehyde (up to 30 mass %) in butyl chloride are completely transformed to the glassy state on cooling. As the content of acetaldehyde in the original solution is increased (>30 mass %), a crystalline phase appears in samples cooled to 77 K (the cooling rate is ~ 150 K min^{-1}). Such samples are mixtures of a glassy and crystalline phases.

On slow cooling (in a calorimeter) of the acetaldehyde – butyl chloride system radiolysed at 77 K, efficient polymerisation of the monomer occurs in the devitrification region. Convincing proof of the cationic mechanism of the post-polymerisation of acetaldehyde in a glassy butyl chloride matrix has been obtained.[25]

An autowave polymerisation mode initiated by local brittle destruction was realised in a glassy acetaldehyde – butyl chloride system pre-irradiated at 77 K.[95] It is interesting to compare the characteristics of the cryopolymerisation waves for crystalline and glassy acetaldehyde samples. The main parameters of the autowave polymerisation process are qualitatively the same in polycrystalline and glassy matrices, but differences are observed as well.

The maximum temperature at the running wave front in a glassy system is 110 – 130 K; in the case of crystalline acetaldehyde, it may reach 150 K. The critical dose of pre-irradiation, *i.e.*, the dose starting from which autowave propagation of the process is ensured, is 60 kGy for the glassy system, whereas in the crystalline monomer, it is above 300 kGy.[79]

There is a minimum threshold concentration of acetaldehyde in the original solution that still supports the autowave mode. In fact, the reaction cannot be run in autowave propagation mode in samples containing less than 20 mass % of acetaldehyde at a pre-irradiation dose of 300 kGy.

It is reasonable to relate the observed differences between the cryopolymerisation waves in the crystalline and glassy acetaldehyde with differences in the reaction mechanisms (ionic mechanism in glass and radical mechanism in crystal) and in the strength characteristics of the systems in question. It should be reminded that the devitrification temperature of the acetaldehyde – butyl chloride system ($T_g = 95$ K) is much lower than the melting point of crystalline acetaldehyde (150 K).

Thus, while autowave modes have previously been observed for reactions that were believed to involve radical processes, the acetaldehyde – butyl chloride system features a polymerisation autowave which occurs by a cationic mechanism.

3. Cyclopentadiene cryopolymerisation autowave

It has been shown previously[77] that the post-radiation polymerisation of cyclopentadiene vitrified in a butyl chloride matrix occurs by a cationic mechanism in the devitrification temperature range of the system ($T_g = 97$ K). These results gave grounds for the search for autowave modes in this system. The local brittle destruction of a cyclopentadiene sample in a glassy butyl chloride matrix pre-radiolysed at 77 K initiates polymerisation that propagates through the sample as an autowave.[96] As in other autowave processes, this reaction 'switches on' at 77 K, and the temperature at the wave front quickly reaches a maximum value. However, considerable time is required for the decrease in temperature after the front has passed, just as in the case of the acetaldehyde cryopolymerisation wave. The polymerisation is not 'turned off' after the wave front has passed, and part of the polymer is formed behind the front. The mean degree of conversion calculated from the adiabatic heating at the reaction wave front is $\sim 25\%$, whereas the yield of the polymer determined gravimetrically is $\sim 55\%$.

Thus, unlike the autowave processes that give low-molecular-mass products (chlorination and hydrobromination), considerable additional conversion occurs behind the wave front in the case of polymerisation. It may be assumed that the low degree of conversion, *e.g.*, in the butyl chloride – chlorine system, is due to the heating of the wave front to the devitrification temperature, where the molecular mobility increases abruptly; this results in the efficient decay of active sites due to recombination. On the contrary, the limited molecular mobilities of active sites during the polymerisation increase the life time of these sites and hence the degree of conversion.

The velocity of the cyclopentadiene polymerisation autowave increases linearly with an increase in the pre-irradiation dose up to 1200 kGy. Most likely, this behaviour of the wave rate does not result from the dynamics of the accumulation of cationic active sites, since their concentration ceases to increase at much lower doses. It has been shown in special experiments that the radiolysis of the cyclopentadiene – butyl chloride system at 77 K produces a gas mixture with an overall radiation yield of ~ 1 molecule per 100 eV of absorbed energy.[96] The fraction of hydrogen in this mixture is $\sim 75\%$. The passage of the polymerisation wave through a sample (heating to 110 – 130 K occurs at the wave front) results in intense evolution of dissolved and frozen gases from the glass and their transfer to the gas phase. The pressure of the gas micro-bubbles may favour the brittle destruction of the system. An increase in the pre-irradiation dose increases the quantity of evolved gases almost linearly; hence, brittle destruction should be facilitated. Analysis of the cinegrams of the reaction propagation through the sample confirms this assumption qualitatively.

At high pre-irradiation doses, strong swelling of a sample upon passage of the polymerisation wave is observed; as a result, its volume increases almost twofold after the process has ended. At low pre-irradiation doses and hence smaller amounts of gaseous radiolysis products, no swelling of the sample occurs upon passage of the wave.

Depending on the autowave 'startup' conditions, the character of the autowave process may differ considerably. For the same pre-irradiation doses, the propagation rate of the polymerisation wave initiated in the lower part of the sample is much higher than if the wave is initiated in the upper part. It is of note that if the wave is initiated in the lower part of the sample, the temperature profile of the running wave is steeper. This fact can also be explained by the role of radiolytic gases. When the polymerisation wave propagates from above downwards, the gaseous products can exit to the evacuated space above the sample. However, if the reaction is initiated in the bottom part of the sample, the gases evolved at the wave front have no free way to exit; as a result, the disjoining pressure of the gases increases and accelerates the front movement.

Yet another reason for the linear increase in the wave propagation rate with an increase in the pre-irradiation dose is possible.[97] Part of the irradiation energy absorbed during the low-temperature radiolysis can be accumulated by means of lattice deformations and formation of metastable phases. Under certain conditions, this accumulated energy will facilitate the brittle destruction of the system. When the wave is launched in the top part of the sample, there are conditions for its 'relief'; however, when it is launched in the bottom part of the sample, 'relief' is hindered considerably owing to the permanent solid 'plug' created by the top part of the sample. In the latter case, the deformation energy accumulated during radiolysis is spent more efficiently, which accelerates the movement of the wave.

The IR spectra of the polymer isolated after the passage of the polymerisation wave coincide completely with the spectra of the product obtained in the post-radiation polymerisation mode during devitrification. However, the conversion of the monomer is much higher if polymerisation is carried out in the autowave mode. The maximum yield of the polymer is 20% for post-polymerisation during devitrification (at a pre-irradiation dose of 50 – 500 kGy) and from 30% at a dose of 100 kGy to 55% at a dose of 1200 kGy in the autowave mode. The molecular mass of polycyclopentadiene obtained in the autowave mode decreases from 10^6 to 10^4 with an increase in the pre-irradiation dose, but it is by almost an order of magnitude higher than the molecular mass of the polymer formed upon post-radiation polymerisation during devitrification.[77] This difference may result from the fact that polymerisation in the autowave mode commences at lower temperatures (almost at 77 K) than thermally activated post-polymerisation (T_g = 97 K).

It should be noted that the 'explosive' polymerisation of cyclopentadiene was observed in films obtained from molecular beams of the monomer and $TiCl_4$ as a catalyst, after pricking the film with a metal needle at 77 K.[98,99] In these experiments, the reaction propagated through the sample at high rate. The highest propagation rates of cryochemical reactions initiated by local brittle destruction of samples pre-radiolysed at 77 K were achieved by Kiryukhin *et al.*[100] These facts suggest that such cryochemical processes may involve a detonation mechanism. It is possible that the 'gas-free detonation' mechanism is realised in this case. According to this mechanism, the shock wave appears and is then supported by the system owing to changes in the density of the compound during the conversion.[100] A model of an autowave process that occurs due to appearance of a density gradient in the reacting layer upon formation of reaction products was suggested.[101 – 103] These calculations allowed evaluation of the size of the fragmentation grain of the reactant matrix. The resulting value ($\sim$10 μm) agrees well with experimental data for autowave modes of cryochemical transformations in thin-film samples.

4. Autowave of acetaldehyde – HCN cryocopolymerisation

The autowave mode has also been realised for cryocopolymerisation.[104] On cooling to 77 K, an HCN – acetaldehyde mixture containing 25 mol.% of hydrogen cyanide passes to the glassy state. Its devitrification temperature (transition to the supercooled liquid state) is 90 K, the crystallisation temperature is 110 – 115 K, and the melting point is 140 K. The local brittle destruction of such a sample pre-radiolysed at 77 K gives rise to an autowave of copolymerisation of acetaldehyde with HCN. The copolymerisation wave front rapidly propagates over the entire sample from the top downwards (this may be observed visually by the changes in the sample colour). The maximum temperature at the wave front increases from 125 K at an irradiation dose of 15 kGy to 148 K at a dose of 140 kGy; the yield of the copolymer increases similarly.

The dependence of the propagation rate of the cryocopolymerisation autowave front on the pre-irradiation dose was found to be unusual (Fig. 8, curve *2*). It should first be noted that, as in the systems studied previously in which the autowave low-temperature transformation mode was observed, the acetaldehyde – HCN system features a critical dose of preliminary γ-irradiation below which autowave cryocopolymerisation is not initiated. In this case, the threshold γ-irradiation dose is $\sim$15 kGy. The propagation rate of the acetaldehyde – HCN copolymerisation wave front increases with an increase in the pre-irradiation dose to $\sim$8 cm s^{-1} at 100 kGy. If the irradiation dose is increased, the propagation rate of the copolymerisation wave front decreases.[104]

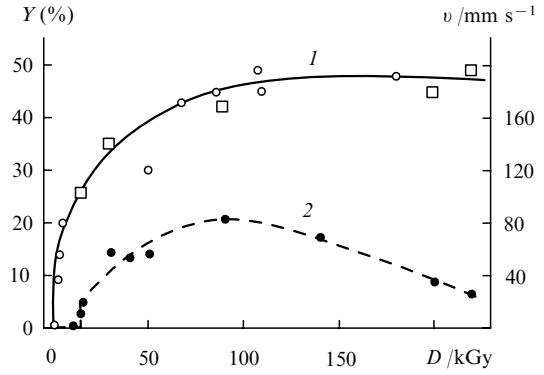


Figure 8. Dependence of the yield (*Y*) of the copolymer (*1*) and the rate (υ) of the copolymerisation propagation wave front (*2*) on the pre-irradiation dose (*D*).[104]
The open squares show the values for the reaction in the thermoactivated post-radiation effect mode.[105]

The model of the autowave phenomena studied is based on a concept of the existence of a positive feedback between (i) the heat evolved in an exothermic reaction and (ii) destruction of the matrix. As follows from this concept, the chemical reactivity of a radiolysed system is determined not only by the concentration of active sites but also by the potential mechanical energy accumulated in the sample and the strength parameters of the matrix. In fact, autowave transformation modes have been realised at 4.2 K whereas the thermally activated mode requires much higher temperatures for these reactions to occur (near the melting point or the system devitrification temperature). The linear relationship between the propagation rate of the transformation wave and the concentration of the active sites accumulated during radiolysis is violated considerably. It was assumed [104] that the slowing down of the acetaldehyde – HCN copolymerisation propagation wave at doses above 100 kGy results from changes in the accumulating properties of this matrix during the radiolysis.

After the passage of the copolymerisation wave at 77 K, the sample was unfrozen to room temperature and the copolymerisa-

tion yield was determined.[105, 106] On increasing the pre-irradiation dose, the copolymerisation yield increases to reach a maximum value of 45% – 50% (see Fig. 8, curve *1*). Figure 8 also shows the dependences of the yield of the copolymer on the irradiation dose during thermally activated post-polymerisation.[105, 106] During slow unfreezing of a pre-irradiated acetaldehyde – HCN system in a calorimeter, post-polymerisation occurs in the devitrification temperature range. The dependences of the yield of the copolymer on the irradiation dose are similar for both reaction modes.

The copolymer obtained in the autowave mode is colourless; it is completely soluble in ethyl methyl ketone, and its molecular mass decreases with an increase in the pre-irradiation dose.[105] On the contrary, the content of nitrogen in the copolymer increases with an increase in the pre-irradiation dose (Table 1). Based on these experimental results and the data on the yield of the copolymer at different irradiation doses, it is possible to calculate the mean number of HCN and acetaldehyde molecules in one polymeric macromolecule and the concentration of polymeric chains in the system during the reaction. The calculated values are listed in Table 1.[104] It is of note that the number of macromolecules formed increases monotonically with an increase in the pre-irradiation dose; this number is larger than that of the initiating active sites accumulated during pre-radiolysis, especially at high doses.[107 – 109] These data are evidence of the existence of chain transfer.

Table 1. Characteristics of acetaldehyde – hydrogen cyanide copolymers.[104]

Pre-irradiation dose /kGy	Molecular mass	Nitrogen content (mol.%)	Mean number of units in a macromolecule		Number of macromolecules, $10^{-19}A$ /g^{-1}
			HCN units	MeCHO units	
15	13 500	0.8	2.4	306	1.2
40	9 000	1.28	2.6	204	2.6
50	7 800	1.59	2.8	176	3.2
90	5 000	3.95	4.5	111	5.6
140	4 000	–	–	–	7.8
200	2 200	–	–	–	13.3
220	2 200	18.6	9.1	34	14.8

The principal difference between the autowave polymerisation mode described above and classical liquid-phase processes is that in the former case the reaction initiation rate at the wave front quickly attains a maximum value (in approximately 0.1 s) and then decreases (the active sites accumulated during irradiation are consumed during the process). The observed characteristics of copolymerisation are evidently due to this feature of the process kinetics.

It should be noted that autowave copolymerisation does not give cross-linked insoluble fractions formed as a result of a thermally activated reaction (slow heating of pre-irradiated samples) at different acetaldehyde : HCN starting ratios.

A scheme of thermally activated copolymerisation of acetaldehyde and HCN was suggested, which involved a combination of two mechanisms (cationic and radical).[106] At low pre-irradiation doses, the copolymer is mostly formed by the cationic mechanism. As the pre-irradiation dose is increased, the radical mechanism starts to predominate, and the fraction of HCN in the copolymer increases. Taking into account that the characteristics of the copolymers obtained in different reaction modes (autowave and thermoactivated) are similar, it may be assumed that a similar mechanism is realised in the autowave cryocopolymerisation of acetaldehyde with HCN.

V. Cosmochemical aspects of low-temperature reactions

It is very likely that a very long period of chemical evolution of compounds preceded the origination of living matter and its subsequent biological evolution. This pre-biological development provided 'building materials' for the creation and development of living substance: the formation and accumulation of progressively more complex molecular structures, *viz*., amino acids, nucleotides, polysaccharides, *etc*., that could subsequently be utilised as a basis for building the main elements of the living cell in the process of biological evolution.

It is hard to imagine, based on the generally accepted concepts about the dynamics of chemical transformations, that a sufficient amount of the 'building material' could have been formed in a specific place over any period when favourable physical conditions existed on the Earth (temperatures within 250 – 450 K, pressure within 1 – 1000 bar, virtual absence of radiation fields). Probably, the main obstacle was that there had never existed a sufficiently long time interval during which the required conditions were maintained. Previously, the idea was put forward that the cosmic time and space scales may be used to describe the pre-biological evolution process (see, *e.g*., the monograph by Zigel'[110]). However, the common concepts about the dynamics of chemical transformations hampered the development of this idea. The impossibility of chemical reactions at temperatures near absolute zero had to be doubted after it had been established experimentally that chain polymerisation of solid formaldehyde can occur at temperatures within 4 – 100 K. Later, low-temperature chain processes were also observed for a number of other chemical transformations.

The autowave cryopolymerisation processes considered above demonstrate that macromolecules can be formed under conditions similar to those in outer space, *i.e*., at low temperatures and in weak radiation fields. It is quite rightful to apply the ideas considered in the present review to the explanation of the processes of 'cold' chemical evolution in the Universe, *i.e*., formation of progressively more complex molecules from elements under conditions of interstellar dust and cold planets.

Since the time of their origination in the 'big bang',[110, 111] the matter in the Universe may have passed through a number of cycles involving strong heating. The end of any such cycle may have served as a starting point for the subsequent chemical evolution of matter. Certainly, matter only existed as chemical elements during any heating cycle. Subsequent cosmic processes resulted in a more or less fast temperature decrease almost to absolute zero. The formation of molecules from elements and their subsequent complication could only occur during such cooling. For example, molecular gases were formed: hydrogen, oxygen, nitrogen, carbon monoxide. If these gases froze on interstellar dust particles, then, according to the classical concept, their subsequent chemical transformations were quite doubtful, even on the cosmic time scale. On the other hand, 'oceans' of ammonia and methane have been discovered on many outer planets and their satellites. In addition, the interstellar space also contains large amounts of these gases and water.

We can attempt to describe the formation of such compounds as ammonia and methane from a frozen mixture of elements that originally existed on the surface of cold planets and their satellites in the following way. The thermal stress in the solid planet cover was a means for its continuous destruction. The multiple brittle destruction events of the frozen element mixture pre-activated by radiation may have resulted in the chemical binding of the components. This scenario may have been realised in interstellar clouds, *i.e*., huge suspensions of dust grains in a gas. It is believed[8, 48] that space dust particles contain silica or graphite nuclei coated with a 'coat' of 'dirty ice', *viz*., a mixture of frozen gases.

The next stage of chemical evolution, during which solid ammonia and hydrocarbons were transformed to the simplest

amines due to the positive feedback between brittle destruction and chemical reactions on the freshly formed surface, is also quite believable. The fact that long polymeric chains are formed upon brittle destruction under conditions of cosmic cold may be regarded as proven experimentally for the polymerisation of formaldehyde and acetaldehyde.

The information presented above is also of interest in relation to other cosmochemical problems. Hydrogen cyanide is a widespread molecular compound in outer space, specifically, in huge clouds of interstellar dust, in comets and in other galactic structures. The HCN molecule is generally considered to be the basis for further chemical evolution, because its transformations provide a direct route to proteins and other large molecules. The chemical behaviour of this simple molecule under conditions that are close to those in outer space (low temperatures and radiation) and the role it plays in the 'cold' chemical evolution of the Universe are of considerable interest for researchers.

VI. Conclusion

Studies on the cryochemical reactions in crystals have made it possible to observe experimentally chain processes at temperatures near absolute zero. These results, which are beyond the scope of the classical concepts of chemical kinetics, have stimulated studies on the mechanisms of 'non-Arrhenius' elementary events of chemical transformations.[8, 12, 35–41] However, there are not so many reactions that occur by the chain mechanism at $T < 77$ K: radiation-induced polymerisation and photopolymerisation of formaldehyde [5, 25, 27, 30] and acetaldehyde;[25, 31] photochlorination of ethylene in a spatially ordered structure,[36] radiation-induced hydrobromination of ethylene,[34, 35] and others.[20–22, 26]

The next step important in principle which favoured the expansion of studies at low temperatures involved the discovery and investigation of the autowave modes of chemical transformations initiated by local brittle destruction of solid samples at 4.2–77 K.[13–15, 87] Results of recent studies suggest that autowave processes are rather widespread in the cryochemical transformations of solids. Autowave modes of cryochemical transformations have been observed for polymerisation and copolymerisation, chlorination and hydrobromination of saturated and unsaturated hydrocarbons.[25] The realisation of high chemical transformation rates at such low temperatures is also very attractive.[100] The results obtained open up new approaches to the explanation of the mechanism of chain cryochemical reactions; these approaches take the potential energy accumulated by a solid and the high reactivity of surfaces formed upon brittle destruction in an autowave transformation mode into account.

If a chemical reaction is carried out during matrix devitrification, transformations of the reactants can be studied at temperatures much lower than the melting points of these compounds.[25] Obviously, a chain reaction in a crystal lattice is hindered owing to the low translational mobility of the reactants and the necessity of destruction of the lattice. On the other hand, the selection of an appropriate vitrifying matrix makes it possible to perform a reaction at very low temperatures.[22, 66] The interest in such low-temperature chemical processes is due to the fact that, as the temperature is decreased, selection from among the possible reaction pathways occurs: those reactions that have the lowest activation energy 'survive'.

Thus, a decrease in the reaction temperature should increase the selectivity of the process. Furthermore, the entropy factors that are so important in the thermodynamics of chemical reactions become less important at lower temperatures; therefore, the equilibria of transformations are shifted in favour of exothermic reactions, even if the latter give rise to highly ordered systems.

The data presented in this review are of interest because they can help explain the 'cold' chemical evolution of matter in the Universe.

References

1. N M Emanuel, G E Zaikov, V A Kritsman *Tsepnye Reaktsii. Istoricheskii Aspekt* (Chain Reaction. Historical Aspect) (Moscow: Nauka, 1989)
2. H W Kolschutter, L Sprenger *Z. Phys. Chem.* **16** 282 (1932)
3. M S Travers *Trans. Faraday Soc.* **32** 246 (1936)
4. M Letort *C. R. Hebd. Seances Acad. Sci.* **202** 767 (1936)
5. D P Kiryukhin, A M Kaplan, I M Barkalov, V I Gol'danskii *Vysokomol. Soedin., Ser. A* **14** 2115 (1972) [a]
6. V I Gol'danskii, M D Frank-Kamenetskii, I M Barkalov *Dokl. Akad. Nauk SSSR* **211** 632 (1973) [b]
7. V I Gol'danskii, I M Barkalov, A M Kaplan, D P Kiryukhin, A D Abkin, M A Bruk, G N Gerasimov, V I Muromtsev, E I Finkel'shtein *Vestn. Akad. Nauk SSSR* (7) 141 (1978) [c]
8. V I Gol'danskii, L I Trakhtenberg, V N Flerov *Tunnel'nye Yavleniya v Khimicheskoi Fizike* (Tunnel Effects in Chemical Physics) (Moscow: Nauka, 1986)
9. M Ya Ovchinnikova *Chem. Phys.* **36** 85 (1979)
10. V A Benderskii, V I Goldanskii, A A Ovchinnikov *Chem. Phys. Lett.* **73** 492 (1980)
11. L I Trakhtenberg, V L Klochikhin, S Ya Pshezhetzky *Chem. Phys.* **69** 121 (1982)
12. V A Benderskii, D E Makarov, C A Wight *Chemical Dynamics at Low Temperature* (New York: Wiley-Interscience, 1994)
13. V V Barelko, I M Barkalov, V I Goldanskii, D P Kiryukhin, A M Zanin *Adv. Chem. Phys.* **74** 339 (1988)
14. V V Barelko, I M Barkalov, V I Gol'danskii, A M Zanin, D P Kiryukhin *Usp. Khim.* **59** 353 (1990) [*Russ. Chem. Rev.* **59** 205 (1990)]
15. D P Kiryukhin, V V Barelko, I M Barkalov *Khim. Vys. Energ.* **33** 165 (1999) [d]
16. N N Semenov *Khim. Tekhnol. Polim.* (7–8) 196 (1960)
17. E I Adirovich *Dokl. Akad. Nauk SSSR* **136** 117 (1961) [b]
18. V S Ivanov *Radiatsionnaya Polimerizatsiya* (Radiation-Induced Polymerisation) (Moscow: Khimiya, 1967)
19. V I Gol'danskii *Usp. Khim.* **44** 2121 (1975) [*Russ. Chem. Rev.* **44** 1019 (1975)]
20. D P Kiryukhin, I M Barkalov *Khim. Fiz.* **12** 774 (1993) [e]
21. I M Barkalov, D P Kiryukhin *Usp. Khim.* **63** 514 (1994) [*Russ. Chem. Rev.* **63** 491 (1994)]
22. I M Barkalov, D P Kiryukhin *Int. Rev. Phys. Chem.* **19** 1 (2000)
23. A M Kaplan, D P Kiryukhin, I M Barkalov, V I Gol'danskii *Dokl. Akad. Nauk SSSR* **190** 1387 (1970) [b]
24. A I Mikhailov, S I Kuzina *Eur. Polym. J.* **26** 105 (1990)
25. D P Kiryukhin, Doctoral Thesis in Chemical Sciences, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 1999
26. G N Gerasimov, A D Abkin *Khim. Fiz.* **3** 176 (1984) [e]
27. S M Dolotov,O A Yuzhakova, G N Gerasimov, A D Abkin *Vysokomol. Soedin., Ser. B* **22** 575 (1980) [a]
28. E S Mansueto, C Y Ju, C A Wight *J. Phys. Chem.* **93** 2143 (1989)
29. E S Mansueto, C A Wight *J. Am. Chem. Soc.* **111** 1900 (1989)
30. E Ya Misochko, V A Bendersky, V I Gol'danskii, E V Kononikhina *Dokl. Akad. Nauk SSSR* **316** 403 (1991) [b]
31. E S Mansueto, C A Wight *J. Phys. Chem.* **96** 1502 (1992)
32. G B Sergeev, V A Batyuk *Kriokhimiya* (Cryochemistry) (Moscow: Khimiya, 1978)
33. G B Sergeev, V V Smirnov *Molekulyarnoe Galogenirovanie Olefinov* (Molecular Halogenation of Alkenes) (Moscow: Moscow State University, 1985)
34. D P Kiryukhin, I M Barkalov, V I Gol'danskii *Dokl. Akad. Nauk SSSR* **238** 388 (1978) [b]
35. D P Kiryukhin, I M Barkalov, V I Goldanskii *J. Chim. Phys.* **76** 1013 (1979)
36. E Ya Misochko, C A Wight, E V Vetoshkin, V A Benderskii *Izv. Akad. Nauk, Ser. Khim.* 687 (1993) [f]
37. E Ya Misochko *Khim. Vys. Energ.* **29** 429 (1995) [d]
38. M V Bazilevskii, G N Gerasimov, S I Petrochenko *Khim. Fiz.* **3** 162 (1984) [e]
39. L I Trakhtenberg, Doctoral Thesis in Physical and Mathematical Sciences, L Ya Karpov Research Physical Chemical Institute, Moscow, 1986

40. S F Timashev, L I Trakhtenberg *Zh. Fiz. Khim.* **67** 448 (1993) [g]
41. L I Trakhtenberg *Khim. Fiz.* **14** 96 (1995) [e]
42. D P Kiryukhin, A M Zanin *Khim. Vys. Energ.* **27** 59 (1993) [d]
43. M Calvin *Chemical Evolution* (Oxford: Oxford University Press, 1969)
44. M A Sanchez, J P Ferris, L E Orgel *Science* **154** 784 (1966)
45. J P Ferris, E H Edelson *J. Org. Chem.* **43** 3989 (1978)
46. J P Ferris, P C Joshi, E H Edelson, J G Lawless *J. Mol. Evol.* **11** 293 (1978)
47. J P Ferris, W J Hagan *Tetrahedron* **40** 1093 (1984)
48. S W Stahler *Astrophys. J.* **281** 209 (1984)
49. C Meisse, E T Arakawa, B N Khare,W R Thompson, C Sagan *Bull. Am. Astron. Soc.* **23** 1189 (1991)
50. C Sagan, C F Cyba *Bull. Am. Astron. Soc.* **23** 1211 (1991)
51. P S Mozhaev, D P Kiryukhin, G A Kichigina, I M Barkalov *Mendeleev Commun.* 17 (1994)
52. P S Mozhaev, G A Kichigina, D P Kiryukhin, I M Barkalov *Khim. Vys. Energ.* **29** 19 (1995) [d]
53. P S Mozhaev, G A Kichigina, Z G Aliev, D P Kiryukhin, L O Atovmyan, I M Barkalov *Dokl. Akad. Nauk* **335** 747 (1994) [b]
54. S I Kuzina, A P Pivovarov, D P Kiryukhin, P S Mozhaev, A I Mikhailov, I M Barkalov *Khim. Vys. Energ.* **36** 19 (2002) [d]
55. G A Kichigina, P S Mozhaev, D P Kiryukhin, I M Barkalov *Mendeleev Commun.* 159 (1998)
56. G Natta, G Mazzanti, G Pregalia, M Binaghi, M Peraldo *J. Am. Chem. Soc.* **82** 4742 (1960)
57. G Natta, G Mazzanti, P Corradini, I W Bassi *Makromol. Chem.* **B37** 156 (1960)
58. J Furukawa, T Saegusa *Polymerization of Aldehyde and Oxides* (New York: Wiley, 1963)
59. D P Kiryukhin, I M Barkalov, V I Gol'danskii *Vysokomol. Soedin., Ser. A* **18** 759 (1976) [a]
60. I M Barkalov, I P Kim, A I Mikhailov, D P Kiryukhin *J. Polym. Sci., Polym. Chem. Ed.* **18** 1551 (1980)
61. V A Kabanov, V P Zubov, Yu D Semchikov *Kompleksno-Radikal'naya Polimerizatsiya* (Complex Radical Polymerisation) (Moscow: Khimiya, 1987)
62. V B Golubev *Vysokomol. Soedin., Ser. A* **36** 298 (1994) [a]
63. G A Kichigina, D P Kiryukhin, I M Barkalov *Vysokomol. Soedin., Ser. A* **42** 1275 (2000) [a]
64. I P Kim, G A Kichigina, D P Kiryukhin, I M Barkalov *Khim. Vys. Energ.* **35** 368 (2001) [d]
65. D P Kiryukhin, O I Barkalov, I M Barkalov *Khim. Vys. Energ.* **29** 271 (1995) [d]
66. I M Barkalov, D P Kiryukhin *Int. Rev. Phys. Chem.* **11** 263 (1992)
67. D P Kiryukhin, I M Barkalov, V I Gol'danskii *Khim. Vys. Energ.* **11** 438 (1977) [d]
68. S V Demidov, A M Zanin, D P Kiryukhin, A I Mikhailov, I M Barkalov *Dokl. Akad. Nauk SSSR* **277** 394 (1984) [b]
69. P S Mozhaev, G A Kichigina, D P Kiryukhin, I M Barkalov *Mendeleev Commun.* 64 (1993)
70. G A Kichigina, D P Kiryukhin, I M Barkalov *Khim. Vys. Energ.* (in the press) [d]
71. G A Kichigina, D P Kiryukhin, P S Mozhaev, I M Barkalov *Khim. Vys. Energ.* **35** 109 (2001) [d]
72. A A Kozlov, V N Doroshenko, A P Meleshevich *Vysokomol. Soedin., Ser. A* **25** 1505 (1983) [a]
73. A P Meleshevich, A A Kozlov, V N Doroshenko *Teoret. Eksp. Khim.* **20** 492 (1984) [h]
74. M R Muidinov, G A Kichigina, D P Kiryukhin, I M Barkalov *Khim. Vys. Energ.* **17** 249 (1983) [d]
75. D P Kiryukhin, G A Kichigina, I M Barkalov *Vysokomol. Soedin., Ser. B* **40** 1044 (1998) [a]
76. G A Kichigina, D P Kiryukhin, I M Barkalov *Vysokomol. Soedin., Ser. A* **44** 1069 (2002) [a]
77. M R Muidinov, G A Kichigina, D P Kiryukhin, I M Barkalov *Vysokomol. Soedin., Ser. A* **25** 818 (1983) [a]
78. I M Barkalov, D P Kiryukhin, G A Kichigina *Eur. Polym. J.* **20** 1013 (1984)
79. G A Kichigina, A M Zanin, D P Kiryukhin, I M Barkalov *Vysokomol. Soedin., Ser. B* **30** 672 (1988) [a]
80. I M Barkalov, D P Kiryukhin *Int. Rev. Phys. Chem.* **13** 337 (1994)
81. I L Ismoilov, Sh B Atakulov, M R Muidinov, D P Kiryukhin, I M Barkalov *Dokl. Akad. Nauk SSSR* **295** 1159 (1987) [b]
82. I L Ismoilov, D P Kiryukhin, I M Barkalov, S T Teshabaev *Khim. Fiz.* **8** 98 (1989) [e]
83. D P Kiryukhin, I M Barkalov, I L Ismoilov *Zh. Prikl. Khim.* **74** 682 (2001) [i]
84. D P Kiryukhin, I M Barkalov, I L Ismoilov *Zh. Prikl. Khim.* **74** 1688 (2001) [i]
85. R Criegee *Angew. Chem.* **14** 596 (1975)
86. Yu A Panshin, S G Malkevich, Ts G Dunaevskaya *Ftoroplasty* (Fluoroplastics) (Leningrad: Khimiya, 1978)
87. A M Zanin, D P Kiryukhin, I M Barkalov, V I Gol'danskii *Pis'ma Zh. Eksp. Teor. Fiz.* **33** 336 (1981) [j]
88. V R Regel', A I Slutsker, E E Tomashevskii *Kineticheskaya Priroda Prochnosti Tverdykh Tel* (Kinetic Nature of the Strength of Solids) (Moscow: Nauka, 1974)
89. N K Baramboim *Mekhanokhimiya Vysokomolekulyarnykh Soedinenii* (Mechanochemistry of High-Molecular-Mass Compounds) (Moscow: Khimiya, 1978)
90. D Broek *Elementary Engineering Fracture Mechanics* (Leyden: Noordhoff, 1974)
91. G Heinicke *Tribochemistry* (Berlin: Akademie Verlag, 1984)
92. P Yu Butyagin *Usp. Khim.* **63** 1031 (1994) [*Russ. Chem. Rev.* **63** 965 (1994)]
93. V S Pshezhetskii, V I Tupikov *Geterotsepnye Vysokomolekulyarnye Soedineniya* (Heterochain High-Molecular-Mass Compounds) (Moscow: Nauka, 1964)
94. G A Kichigina, A M Zanin, D P Kiryukhin, I M Barkalov, V I Gol'danskii *Khim. Fiz.* **7** 543 (1988) [e]
95. D P Kiryukhin, I M Barkalov *Vysokomol. Soedin., Ser. B* **42** 1604 (2000) [a]
96. G A Kichigina, D P Kiryukhin, A M Zanin, I M Barkalov *Vysokomol. Soedin., Ser. A* **32** 1094 (1990) [a]
97. D P Kiryukhin, V V Barelko, I M Barkalov *Dokl. Akad. Nauk SSSR* **306** 654 (1989) [b]
98. V A Kabanov, V G Sergeev G M Lukovkin, V D Baranovskii *Dokl. Akad. Nauk SSSR* **266** 1410 (1982) [b]
99. G B Sergeev, V S Komarov, V N Bekhterev *Vysokomol. Soedin., Ser. A* **24** 2589 (1982) [a]
100. D P Kiryukhin, P S Mozhaev, V V Barelko *Khim. Fiz.* **11** 264 (1992) [e]
101. A Pumir, V V Barelko *Eur. Phys. J. B* **10** 379 (1999)
102. A Pumir, V V Barelko *Eur. Phys. J. B* **16** 137 (2000)
103. A Pumir, V V Barelko *Eur. Phys. J. B* **22** 71 (2001)
104. D P Kiryukhin, G A Kichigina, P S Mozhaev, I M Barkalov *Vysokomol. Soedin., Ser. A* **40** 236 (1998) [a]
105. D P Kiryukhin, G A Kichigina, P S Mozhaev, I M Barkalov *Vysokomol. Soedin., Ser. A* **39** 1109 (1997) [a]
106. D P Kiryukhin, G A Kichigina, P S Mozhaev, I M Barkalov *Eur. Polym. J.* **33** 1685 (1997)
107. S I Kuzina, P S Mozhaev, D P Kiryukhin, A I Mikhailov, I M Barkalov *Izv. Akad. Nauk, Ser. Khim.* 859 (1996) [f]
108. S I Kuzina, H S Mozhaev, D P Kiryukhin, A I Mikhailov, I M Barkalov *Mendeleev Commun.* 34 (1996)
109. S I Kuzina, D P Kiryukhin, A P Pivovarov, A I Mikhailov *Khim. Vys. Energ.* **32** 330 (1998) [d]
110. A Yu Zigel' *Veshchestvo Vselennoi* (The Matter of the Universe) (Moscow: Khimiya, 1982)
111. Ya B Zel'dovich, I D Novikov *Stroenie i Evolyutsiya Vselennoi* (Structure and Evolution of the Universe) (Moscow: Nauka, 1975)

[a] — *Polym. Sci. (Engl. Transl.)*
[b] — *Dokl. Chem. (Engl. Transl.)*
[c] — *Herald Russ. Acad. Sci. (Engl. Transl.)*
[d] — *High Energy Chem. (Engl. Transl.)*
[e] — *Chem. Phys. Rep. (Engl. Transl.)*
[f] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[g] — *Russ. Phys. Chem. J. (Engl. Transl.)*
[h] — *Theor. Exp. Chem. (Engl. Transl.)*
[i] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[j] — *J. Exp. Theor. Phys. Lett. (Engl. Transl.)*