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Cryopolymerisation

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Abstract. The mechanism of cryochemical chain reactions is examined in relation to polymerisation. The study of such processes in crystals has led to the discovery of a low-temperature limit to the rates of chemical reactions. Polymerisation occurring under the conditions of a sharp change (by 5–6 orders of magnitude) in the molecular mobility of the medium in the region of the devitrification of the matrix has been investigated in vitreous systems. Unusual mechanoenergetic chains of chemical reactions have been observed in the study of systems immersed in liquid helium. The chemical reaction is initiated by a local brittle fracture and is propagated along the specimen in the form of an autowave. Auto-oscillations of the rate of cryopolymerisation have been observed under certain conditions. The bibliography includes 132 references.

I. Introduction

It is difficult to imagine an effective chemical reaction in a solid without a significant mass transfer of the reactants and products. At first sight it might turn out that chemical reactions in a solid occur in nature only on the geological time scale and even then not without the participation of liquid and gas phases, mechanical breakdown, and high pressures and temperatures.

Indeed, the classical picture of the elementary step in a chemical reaction is based on the following postulates: (1) an activation barrier must be overcome for the interaction reactions to be initiated; (2) reactants receive the energy required to overcome the activation barrier as a result of intermolecular interactions; (3) the time necessary for the reactions to accumulate this energy (the characteristic time of the elementary step) is determined by the temperature of the medium. It is easy to show that these postulates exclude the possibility of a chemical process in the vicinity of the absolute zero of temperature.

In the 1930s, communications were published in which the polymerisation of crystalline monomers was reported. It was found that crystalline trioxane polymerises in the presence of formaldehyde vapour with formation of polyoxymethylene fibres oriented along one of the crystallographic axes. The formation of rubber-like polymers of acetaldehyde was observed at the same time at the instant of its freezing (crystallisation) and fusion. The latter processes occur at low temperatures. Thus it was found that chain reactions can take place in a solid also at low temperatures.

Later investigators found new ways of initiating chemical reactions in the solid. One of them is based on the use of γ-radiation. Initiation of active centres, more or less uniform throughout the volume of the solid phase, takes place under these conditions and all the complications associated with the diffusion of the initiator molecules within the crystals are fully eliminated. However, the main advantage of radiation initiation is that its effectiveness is independent of temperature (in contrast to chemical initiation). The latter factor made it possible to proceed to the study of the polymerisation of solid monomers at low and ultralow temperatures.

All this led in the 1960s to a vigorous development of studies on solid-phase polymerisation. However, at the time most of the investigations were phenomenological in nature and theoretical generalisations and hypotheses were novel rather than experimentally well-founded.

It was found initially that the rigorous orientation of the monomer molecules in space, which is characteristic of crystals, may be reflected in the regularity of the macromolecules formed. Furthermore, hopes arose that the 'ordered military ranks' of the reactants in the crystal would promote the rapid occurrence of the process. In 1960, Semenov [1] proposed the energy chain mechanism for solid-phase polymerisation. The idea was that the energy evolved in each elementary chain propagation step is not scattered by being converted into heat, but, by virtue of the collective interaction of the monomeric 'precursors' in the crystal, ensures that the activation barrier is overcome in the next such step. One of the variants of the collective interaction may involve the movement of an exciton along the 'precursor'. In this case, the polymer chain may grow at the rate of propagation of the exciton. (The exciton chain model has been examined in detail by Adirovich [2].)

Here we shall not dwell on the analysis of the extensive factual data, with which the reader may become acquainted in the relevant communications, [1,3–8] and only the principal conclusions will be quoted. The formation of a polymer in a crystal of the initial monomer alters the average distances between the individual

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fragments, whereupon the spatial orientation of the monomer units may be changed. There is a wide variety of numerous systems in which these geometrical factors play a significant role. The transfer of classical ideas about the reaction mechanisms in the gas and liquid phases to solid-phase reactions proved fruitless; new ideas were needed.

In view of the extremely restricted translational displacements in a crystal, it is difficult to imagine the destruction of growing macroradicals as a result of recombination or disproportionation. In this case, the polymer chain gradually ceases to grow owing to progressive difficulties in the supply of the monomer to the growing active centre — a kinetic arrest of the process ('setting and revival' of the polymer chain) is observed.[9] This served as a basis for the development of the theory of 'polychronic kinetics'.[10]

The idea that chemical reactions are impossible near the absolute zero changed after *the low temperature limit to the rates of chemical reactions had been established* experimentally. This phenomenon was observed in the study of the mechanism of the polymerisation of solid formaldehyde in the temperature range 4–100 K.[11] The existence of the low-temperature limit to the rate was subsequently confirmed for a series of chain and nonchain chemical reactions.[12] Systems in which the chemical reaction takes place even at the temperature of liquid helium were found experimentally. Although the rate of such a reaction is low, it is nevertheless measureable and is independent of temperature.

Immediately after the discovery of the phenomenon of the low-temperature limit to the rate, it was suggested that its mechanism be interpreted within the framework of the concept of molecular tunnelling. This idea was subsequently developed taking into account the role of intermolecular vibrations.[12–15]

The present review describes only a small portion of the enormous amount of data concerning the mechanisms of solid-phase reactions.

II. Crystals

1. Formaldehyde

The possibility of the radiation polymerisation of solid formaldehyde at temperatures close to that of liquid nitrogen has been reported.[16–18] However, these studies were qualitative. Indeed, the yield of the polymer was determined only after the heating and fusion of the irradiated solid monomer (the rate of the process was determined by dividing the mass of the polymer isolated by the irradiation time of the system). This naturally did not allow the determination of the true rates of polymerisation at 77 K. Subsequently, it was found that, when the irradiated polycrystalline formaldehyde is heated, effective postpolymerisation takes place, masking completely the effect occurring directly during the radiolysis of the specimen at 77 K. Only the use of kinetic calorimetry made it possible to investigate these processes separately. The principal results of investigations of the solid-phase polymerisation of formaldehyde in the temperature range 5–150 K are presented below.[11,19–26]

The method for the purification and drying of gaseous formaldehyde, which has been thoroughly elaborated, made it possible to eliminate the problem of the reproducibility of kinetic measurements.[27] Calorimetric analysis showed that frozen formaldehyde forms a polycrystalline mass rapidly ($\sim$200 K min^{-1}) or slowly ($\sim$0.3 K min^{-1}) and undergoes no phase transitions of any kind in the temperature range 4.2–155 K. It melts at 155 K and its heat of fusion is $\Delta H = 1.80 \pm 0.05$ kcal mol^{-1}. The enthalpy of the polymerisation of solid formaldehyde was found to be 8.5 ± 1.0 kcal mol^{-1} and this value was used subsequently to calculate the rate of polymerisation.

The radiation polymerisation of formaldehyde proceeds extremely effectively, so that thermal explosion is observed when heat is removed inadequately.[16,17] For this reason, all the kinetic measurements were performed under conditions as close to isothermal conditions as possible, which was achieved by increasing the heat exchange area and by reducing the γ-radiation dose rate. After exposure to γ-radiation, the rate of heat evolution associated with polymerisation reaches a steady value during a period equal to the characteristic time of the calorimetric apparatus used in the experiments (Fig. 1).

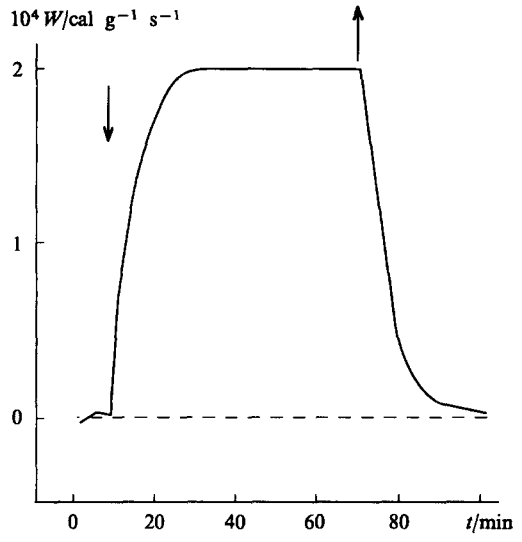


Figure 1. Variation of the rate of heat evolution in the polymerisation of formaldehyde in the field of γ-radiation. Temperature 100 K; dose rate 1.4×10^{-4} Gy s^{-1}. The arrows indicate the instants when γ-radiation was switched on and off. The dashed line represents the analogous experiment with polyformaldehyde.

However, the steady rate of polymerisation does not persist for a long time and an appreciable decrease in the rate is observed already for degrees of conversion of $\sim$0.5%. The reason for the decrease can be only the kinetic arrest of the process when the access of the monomer to the growing polymer centre is hindered.

Experimental proof that the kinetic chain termination reaction is first order in the polymerisation process has been obtained. It is natural to attribute linear termination to the kinetic arrest of the growth of the polymer chain ('setting') and not to the destruction of active centres, because, when the temperature rises outside the radiation zone, effective postpolymerisation is observed, i.e. the chains which have set are 'revived'.

The radiation-chemical yield of the polymer is $G(-M) \geqslant 10^6$ molecules per 100 eV of the absorbed energy of the γ-radiation in the early stages of the process. One may assume that this is the highest recorded quantity for radiation polymerisation.

The temperature dependence of the steady rate in the range 80–150 K is described satisfactorily by the Arrhenius equation (the activation energy is 2.0 ± 0.6 kcal mol^{-1}). At temperatures above 140 K, the rate of polymerisation falls, apparently owing to the increase in the chain termination rate constant near the melting point of the monomer crystals. A negative activation energy for the polymerisation of formaldehyde ($E = -0.5$ kcal mol^{-1}) has been reported.[16,17] This value is clearly erroneous if only because the authors of the above communications observed the phenomenon of thermal explosion, which is impossible for a negative temperature dependence of the rate of polymerisation.

The following expression for the chain propagation rate constant has been obtained in the temperature range 8–140 K:

$$k_p \approx 0.03 \exp\left(-\frac{2000 \pm 100}{RT}\right).$$

On passing to the liquid phase, the steady rate of polymerisation of formaldehyde falls sharply (almost by a factor of 10). This is naturally associated with the significant increase in the rate of termination of polymer chains in the liquid phase compared with that in the crystal lattice.

The high radiation yield of the polymerisation of solid formaldehyde at the temperature of liquid nitrogen made it possible to proceed to the investigation of its polymerisation at still lower temperatures (5–80 K). The temperature dependence of the rate of polymerisation was studied. With decrease in temperature (below 80 K), the temperature dependence of the rate of polymerisation diminishes and then ceases altogether. A more marked deviation of the rate from the Arrhenius law is observed. However, even at 5 K polymerisation still occurs with a radiation yield $G(-M) \approx 1000$, which is characteristic of chain processes. Thus, the occurrence of a chain reaction at such low temperatures was observed for the first time by a direct method for the given process.

The characteristic chain propagation times in solid formaldehyde have also been measured in the temperature range 5–80 K. Two identical calorimetric experiments were performed: one with solid formaldehyde and another with polyoxymethylene. In the experiment with polyoxymethylene, the evolution of heat is associated solely with the heating of the system owing to the absorption of γ-radiation. Since γ-radiation is absorbed equally by the polymer and the monomer, in the experiments with the monomer the overall heat evolution due to the absorption of γ-radiation and the polymerisation reaction was detected.

Figure 2 presents the results of these measurements. The characteristic time of the process τ (the average kinetic chain propagation time) was determined by fitting the following relation to the rate of increase in the rate of polymerisation after exposure to initiating radiation:

$$W = W_{st}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right].$$

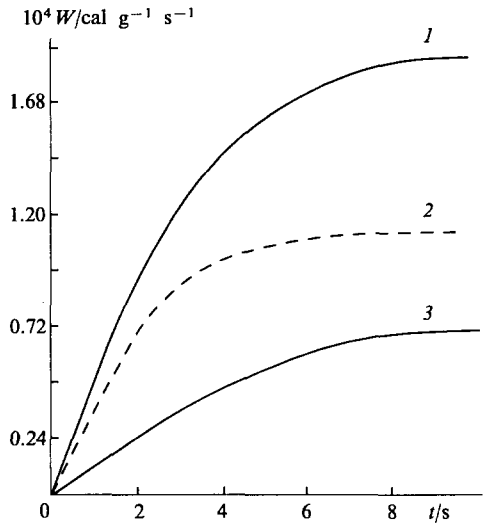


Figure 2. Time variation of the rate of heat evolution in the field of γ-radiation for formaldehyde (curve *1*) and polyformaldehyde (curve *2*) and variation of the rate of polymerisation of formaldehyde (curve *3*) (difference between the rates represented by curves *1* and *2*). Polymer sample 0.25 g; dose rate 0.45 Gy s^{-1}; temperature 5 K.

The intrinsic chain propagation characteristic time at temperatures below 10 K approached 10 s. The temperature dependence of the chain propagation time was obtained from the results of a series of similar experiments carried out at different temperatures. From the measured chain propagation characteristic times, one can proceed to the time required for the step involving an increment by one monomer unit:

$$\tau_o = \frac{\tau g}{G(-M)},$$

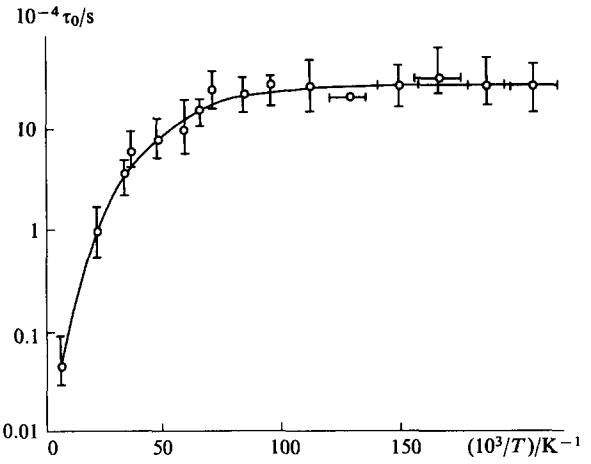


Figure 3. Temperature variation of the time required for the addition of one monomer unit in the polymerisation of formaldehyde.

where g is the radiation yield of the active centres initiating the polymerisation (usually $g \approx 1$). With decrease in temperature, a more marked deviation of the rate of polymerisation from the Arrhenius law is observed — the time required for the addition of one unit tends to the constant value $\tau_0 = 0.01$ s (Fig. 3), while extrapolation of the data for 80–140 K on the basis of the Arrhenius law would yield a value at 5 K, which would be much too high ($\tau_0 \approx 10^{100}$ years!).

A low-inertia calorimetric apparatus was used to investigate the possibility of polymerising formaldehyde at 5 K in the absence of radiation, but the reaction was carried out in this case under conditions where γ-radiation was switched off rapidly. After γ-radiation has been stopped, a decrease in the rate of polymerisation is observed with a characteristic time $\tau \approx 15$ s, which is significantly longer than the time corresponding to the inertia of the calorimeter (Fig. 4).

Thus it was shown clearly that the polymerisation chain continues to be propagated at helium temperatures also in the absence of a radiation field. Therefore the hypothesis that the

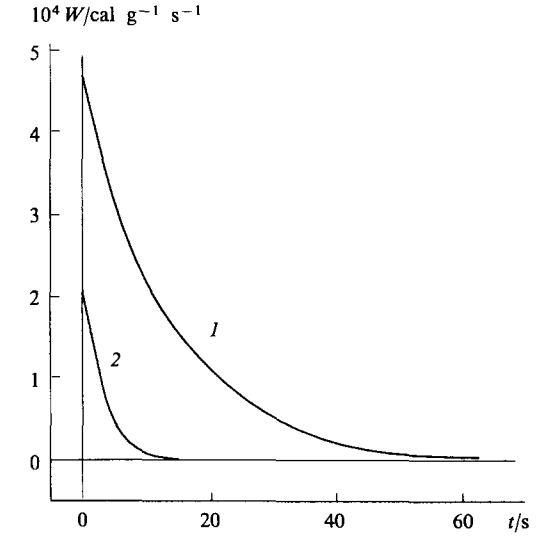


Figure 4. The postpolymerisation of formaldehyde after switching off γ-radiation: (*1*) monomer in the calorimetric cell; (*2*) analogous experiment with the polymer. Formaldehyde sample 0.25 g; temperature 5 K; dose rate 6 Gy s^{-1}.

radiant energy is used to activate each elementary addition step is incorrect. At the same time the hypotheses postulating that chain propagation takes place as a result of the transfer of short-lived excited states, that polymerisation takes place in tracks, etc. have to be abandoned. This significantly narrows the range of the possible hypotheses concerning the mechanism of the observed phenomenon.

The polyformaldehyde obtained by the radiation polymerisation of formaldehyde at 77 K has a supermolecular structure comprising monolithic crystalline domains.[28] The formation of this morphological type was not observed either on crystallisation of this polymer from solutions or melts or on crystallisation during synthesis.[29-31] Analysis of the IR spectra in the range 800–1300 cm^{-1}, where the vibration bands sensitive to changes in the angles of internal rotation of the CHO chain are located, demonstrated an unusual conformation of the chains in the polymer obtained by solid-phase polymerisation.

The known modifications of polyformaldehyde, named in accordance with the type of crystal lattice—hexagonal (I) and orthorhombic (II)—are characterised by a sequence of monomer units having the *gauche, gauche*-conformation with internal rotation angles of 77° (I) and 63° (II).[32] Such differences between the angles of internal rotation of the polymer chains do not lead to significant differences between the IR spectra. On the other hand, the spectrum of the polymer specimen obtained by solid-phase polymerisation contains bands additional to the absorption bands of the known modifications (I) and (II).[28] This finding shows that some of the monomer units of the polymer chains in the specimen are in a conformation different from the *gauche, gauche*-conformation. This can be only the uncoiled *trans*-conformation, since the coiled *cis*-conformation is prohibited by steric hindrance. One can therefore postulate that the chains in the new structural modification of the polymer are characterised by sequences of monomer units with the *gauche, trans*-conformation.

The new structural modification of the polymer, obtained by the solid-phase polymerisation of formaldehyde, proved to be metastable. Judging from the changes in the IR spectra, it passes to the known modification I on recrystallisation from melts and solutions and also under the influence of pressure. We may also note that a stable modification is formed in the radiation polymerisation of liquid formaldehyde.

The polymerisation of a monomer crystal entails a change in both the average distances between individual fragments (the intermolecular distances are replaced by chemical bond lengths) and in the spatial orientation of the monomer units. We may note two extreme cases: (1) the structure of the monomer crystal determines to a large extent the structure of the polymer (derivatives of conjugated diacetylenes, trioxane); (2) the polymer arises as an independent phase in the extended lattice defects, which leads to further fracture of the monomer crystal; the polymer phase is amorphous (acrylamide). There is a large number of intermediate cases between these extremes.

The polymerisation of crystalline acrylamide begins in the region of the extended defects and proceeds on the interface between the amorphous polymer and the crystalline monomer.[33] A decrease in the size of the crystals facilitates the polymerisation process. The average rates of polymerisation in fine defective acrylamide crystals are higher than in large perfect crystals.

An example of the first of the extreme cases listed above is the so called topochemical polymerisation.[34] A polymer phase, the crystallographic directions of the axes of which are determined by the directions of the axes of the initial crystal, is formed in such processes. The polymerisation in large crystals of monomers of this kind is faster than in small crystals, while the presence of noncrystallising additives reduces the rate of the process.

In this connection, it appeared important to elucidate the influence of the size of the formaldehyde crystals and of their defectiveness on the kinetics of the low-temperature radiation polymerisation. It was found[35] that the kinetics of the radiation polymerisation of formaldehyde depend significantly on their crystal size. The rate of polymerisation in small defective crystals is almost 20 times lower than in slowly grown large crystals. It is natural to assume that the decrease in the yield of the polymer on passing to highly defective formaldehyde crystals is associated with the decrease in the length of the kinetic chains in the polymerisation process, i.e. that the solid-phase polymerisation of formaldehyde takes place at a high rate only within large and perfect crystals.

Photoinitiation has also been used in the study of the low-temperature solid-phase polymerisation of formaldehyde. Thus the polymerisation of crystalline and amorphous formaldehyde at temperatures above 20 K on photoexcitation of added β-naphthol has been reported.[36,37] Such initiation entails the transfer of a proton from β-naphthol to formaldehyde with formation of a cation as the chain-transfer agent.

The low-temperature reactions of formaldehyde in amorphous formaldehyde–chlorine mixtures have been investigated.[38-40] Chlorine was photolysed by using an excimer laser (λ = 308 nm) or a mercury arc lamp (λ = 365 nm). The formation of oligomers with a chain length corresponding to 5–7 units was observed in the temperature range 10–77 K, whilst at temperatures $\geqslant$90 K the chain length increased by a factor of 2. The molecular mass of the polymer obtained in this way is much lower than that of the polymer formed in the crystal (chain length 10^3–10^6). This is caused by the molecular disorder in the amorphous state.

In order to account for the low-temperature limit to the rate of chain propagation, the concept of molecular tunnelling was introduced.[23,24] These investigations stimulated many studies on the theoretical development of ideas concerning the elementary chemical step in a solid†.

2. Acetaldehyde

Acetaldehyde is the closest homologue of formaldehyde. Rubber-like acetaldehyde polymers were first obtained by Travers[41] and Letort.[42] Pshezhetskii et al.[43] observed with the aid of thermographic and cine-film techniques the propagation of the polymerisation front in solid radiolysed acetaldehyde at relatively high temperatures (117–147 K) close to the melting point of the monomer (T_m = 150 K). Having made a series of assumptions and having restricted the treatment to one thermal conductivity equation, the authors[43] obtained an extremely short time for the addition of one monomer unit to the polymer chain (10^{-8} s). Such high rates stimulated further investigations of this system by the calorimetric method under slow temperature scanning conditions and directly in the field of γ-radiation under isothermal conditions.[44]

Even at the maximum rate of cooling of the liquid monomer to 77 K (~100 K min^{-1}), the latter does not form a vitreous state. As in formaldehyde, in polycrystalline acetaldehyde there are no phase transitions of any kind, the compound melting at 150 K (ΔH = 1.40 ± 0.07 kcal mol^{-1}).

Figure 5 presents the typical time dependence of the rate of polymerisation (rate of heat evolution) of solid acetaldehyde in the field of γ-radiation, indicating a distinct autoacceleration of the polymerisation process. Evidently, the autoacceleration is associated with the accumulation of active centres during the radiolysis of the solid monomer, i.e. with the increase in the rate of initiation. The expression for the time variation of the rate of the process is

$$W = -\frac{d[M]}{d[t]} = k_p g I t [M]_0 \exp(-0.5 k_p g I t^2),$$

where k_p is the polymer chain propagation rate constant, I the intensity of the radiation, and $[M]_0$ the initial monomer concentration. Two corollaries arise from this: (1) the experimental

† For further details, see the monograph of Gol'danskii et al.[12]

relation $W = f(t)$ (Fig. 5) should become linear in terms of the $\ln(W/t)$ against t coordinates; (2) the time required for the attainment of the maximum rate t_{max} is $k_p g I^{-0.5}$, which makes it possible to calculate k_p. This kinetic scheme does not take into account the possibility of the kinetic arrest of the growing chains, but it describes satisfactorily the relation obtained. Indeed, the function illustrated in Fig. 5 becomes satisfactorily linear in the appropriate coordinates.

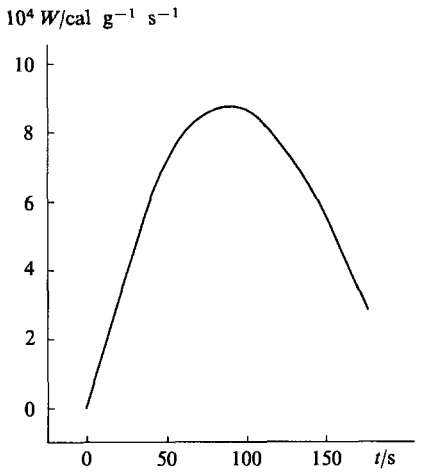


Figure 5. Time variation of the rate of heat evolution (polymerisation) in solid acetaldehyde in the field of γ-radiation. Dose rate 0.6 Gy s^{-1}; temperature 136 K.

A series of experiments, analogous to that described above, were then carried out at different temperatures, which made it possible to determine the chain propagation rate constant. The temperature variation of k_p in the range 130 – 144 K is described by an expression of the type

$$k_p = 5 \times 10^{-4} \exp\left(-\frac{11000}{RT}\right),$$

i.e. the average time required for the addition of the monomer unit in this temperature range is 0.1 – 0.001 s.

It is noteworthy that the activation energy (11 kcal mol^{-1}) is much higher for acetaldehyde than for formaldehyde (2 kcal mol^{-1}) in the same temperature range. However, we are apparently dealing here with an effective activation energy because its high values are compensated by the high values of the pre-exponential factor, which is characteristic of reactions occurring near the melting point.

Thus, in contrast to its nearest homologue, acetaldehyde hardly polymerises even at 77 K. An intense thermoactivated post-effect is characteristic of solid acetaldehyde, as for formaldehyde.

3. Glyoxal and tricarbon dioxide

We shall consider the polymerisation of crystalline glyoxal $(HCO)_2$.[45] In contrast to formaldehyde, the mechanism of the polymerisation of this monomer has been little investigated.[46] Calorimetric analysis showed that phase transitions of any kind do not occur in solid glyoxal in the temperature range 80 – 288 K. Glyoxal melts at 288 K and its heat of fusion is ΔH = 3.0 kcal mol^{-1}. The slightest traces of moisture lead to spontaneous polymerisation near the melting point of the monomer, which is clearly recorded on the calorimetric heating curve.

The rate of polymerisation of solid glyoxal in the field of γ-radiation slowly reaches a steady value and, with the initiating radiation switched off, it decreases with the characteristic time τ = 1300 s.

The heat of polymerisation of glyoxal is 5 ± 1 kcal mol^{-1}. This quantity is the mean of the heats of polymerisation of formaldehyde (8.5 kcal mol^{-1}) and acetaldehyde (2.5 kcal mol^{-1}). A series of measurements of the process dynamics at different temperatures made it possible, as in the case of other monomers, to determine the principal kinetic parameters. The chain propagation rate constant for the solid-phase polymerisation of glyoxal is different from that for formaldehyde.

$$k_p \approx 10^{-17} \exp\left(-\frac{4000}{RT}\right).$$

At 170 K, the rate of polymerisation of glyoxal becomes negligible. However, the postpolymerisation of this monomer can be observed even at temperatures slightly above 100 K. The supermolecular and molecular structures of the polymer formed depend significantly on the temperature at which glyoxal is polymerised. The particles of the polymer obtained at 100 – 170 K have a polygonal shape and exhibit double refraction, which indicates oriented growth of the polymer chains. The polymers obtained at higher temperatures (200 – 280 K) do not have this property. In both cases, the polymer is amorphous, because the formation of a three-dimensional network prevents crystallisation.

At low temperatures, predominantly one aldehyde group participates in the polymerisation of glyoxal. The IR spectrum contains an intense band due to the aldehyde group (1740 cm^{-1}). The spectrum of the polymer obtained at higher temperatures contains an absorption band due to hydroxy-groups in the range 3200 – 3400 cm^{-1}. Apparently, the polymerisation of the simplest dialdehyde proceeds via the mechanism of aldol condensation with formation of $-[CH(CHO)-CH(OH)]_n-$ chains. Since aldol condensation is characterised by a large volume of activation for chain propagation (compared with the formation of a polyacetal chain), this reaction becomes possible at high temperatures. Thus the closest analogues of the formaldehyde — glyoxal and acetaldehyde — polymerise in the crystalline state at comparatively high temperatures, the rate of their polymerisation decreases in conformity with the Arrhenius law, and a low-temperature plateau is not observed.

Continuing the search for monomers capable of chain polymerisation in the vicinity of the absolute zero of temperature, we considered a fairly exotic monomer — tricarbon dioxide O=C=C=C=O. The polymerisation of this monomer on thermal[47] and radiation[48] initiation as well as photoinitiation[49] has been reported in the literature. In all the studies, the investigators dealt with a complex set of reactions occurring in parallel, which hindered significantly the understanding of the polymerisation mechanism. When this reaction is carried out at low temperatures, the set of possible reaction pathways becomes significantly smaller. We shall consider the results of these investigations.[50, 51]

The phase state of solid C_3O_2 has been subjected to calorimetric analysis. At 130 – 135 K a phase transition, apparently of the crystal – crystal type, takes place with ΔH = 1.4 ± 0.2 cal g^{-1}. Tricarbon dioxide melts at 160 K with the heat of fusion ΔH = 20.3 ± 1.7 cal g^{-1}. The enthalpy of polymerisation of C_3O_2 has been determined for the temperature range 160 – 310 K in a series of experiments; ΔH was 35 ± 5 kcal mol^{-1}.

The calorimetric experiments showed that the occurrence of the radiation polymerisation of C_3O_2 with measureable yields cannot be detected in the solid phase over the entire temperature range. This means that the radiation yield of the polymerisation reaction does not exceed $G(-M) \approx 100$ molecules per 100 eV of the absorbed energy.

The postpolymerisation of C_3O_2 specimens irradiated with different doses was investigated at 77 K. Evolution of heat due to the polymerisation of C_3O_2 begins to be observed on the calorimetric heating curve for the radiolysed specimen starting from the melting point of the monomer. In the temperature range 180 – 260 K, the polymerisation takes place at a low rate.

On further heating, the rate of polymerisation rises sharply, reaches a maximum, and then falls owing to the consumption of the monomer. The monomer specimen was heated in the experiments to 310 K, whereupon the overall yield of the polymer was 80% – 100%.[50]

The postpolymerisation was studied calorimetrically at a constant temperature of 297 ± 1 K (Fig. 6). It was found that the rate of the process initially increases with time, autoacceleration is observed, and then falls to zero owing to the exhaustion of the monomer. These experiments show that the active centres stored during the low-temperature radiolysis are retained in the postpolymerisation of not only solid but also liquid C_3O_2.

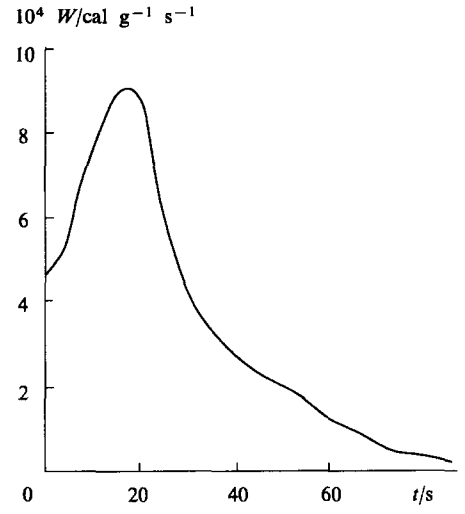


Figure 6. Time variation of the rate of heat evolution (postpolymerisation) in C_3O_2 at 297 K. Preliminary irradiation dose 10 kGy.

Unfortunately there are no experimental data of any kind concerning the nature of the active centres propagating the polymerisation. However, one can postulate that, as in the gas phase,[48] the polymerisation is propagated by ions. Apparently the long lifetime of the active centres, which are retained even in the liquid, is due to the following causes. The primary centres stabilised during the solid-phase radiolysis initiate the polymerisation of the monomer in its melting temperature range, forming oligomeric growing centres. The lifetime of such centres rises sharply owing to the appearance of steric hindrance, so that even in the liquid phase their concentration is sufficiently high to ensure effective polymerisation.

Another interesting feature of the postpolymerisation of C_3O_2 is the autoacceleration of the process at a constant temperature (Fig. 6). This phenomenon is unusual if only because the number of active centres generated during the preliminary irradiation can only decrease. The most probable cause of the autoacceleration is the increase in the rate of initiation apparently as a consequence of the branching of the chain reaction in the elementary monomer addition step. Without specifying in detail the branching mechanism, we may note that one may consider both material and energy branching. In one way or another, the question of the mechanism of the autoacceleration still remains open.

Thus the search for cryochemical chain polymerisation processes among the closest analogues of formaldehyde proved unsuccessful. The only example of a chain process occurring in the vicinity of the absolute zero of temperature and demonstrating the existence of a low-temperature limit to the rate still remains the polymerisation of formaldehyde. The next logical step was to switch the search to the chain reactions of compounds of other classes.

4. Hydrogen cyanide

It has been suggested that liquid hydrocyanic acid polymerises via an anionic mechanism under the influence of γ-radiation, affording a complex mixture of nitrogen compounds.[52] Furthermore, HCN is an extremely common molecular formation in the giant clouds of interstellar dust, in comets, and in other galactic structures. In general, the HCN molecule has come to be regarded as the basis of the prebiological chemical evolution, since its reactions constitute a direct pathway to the formation of purines, pyrimidines, and aminoacids.[53–57] It has been suggested[58] that the chain length of the cyanopolyene macromolecules arising on condensation of HCN be employed as an internal clock for the determination of the age of interstellar clouds. Other astrophysical aspects of the chemical reactions of hydrogen cyanide are developing vigorously.[59,60]

The chemical behaviour of this simple molecule under conditions approaching those in cosmic space (low temperatures and radiation) and its role in the 'cold' chemical evolution of the universe are of interest. The principal results of a series of experiments carried out on these lines recently are presented below.[61,62]

When hydrocyanic acid is cooled to 77 K, it passes to a crystalline state and, when it is heated, a phase transition of the crystal–crystal type (248 K) and fusion at 260 K (ΔH = 2.1 ± 0.1 kcal mol^{-1}) take place.

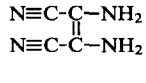
Calorimetric measurements directly in the field of γ-radiation at 77 K demonstrated the absence of appreciable heat evolution associated with a chain polymerisation reaction. When hydrocyanic acid radiolysed at 77 K is heated to room temperature, the formation of a polymer is observed. The heat change associated with the polymerisation of hydrocyanic acid is detected only in the fusion region. The yield of the polymer formed on heating to room temperature HCN specimens irradiated at 77 K increases with the preliminary irradiation dose and reaches 2.5% for a dose of 725 kGy. It is of interest that the radiation polymerisation of liquid HCN at 273 K proceeds significantly less effectively.

Prolonged maintenance of hydrocyanic acid in evacuated sealed tubes at room temperature does not lead to any changes in its colour or to the formation of polymeric products. But storage at room temperature of HCN specimens radiolysed at 77 K alters the colour (from pale-brown to almost black) and leads to the formation of polymeric products. The yield of polymer increases with increase in storage time, reaching 33.5% after 750 h.

Analysis of the IR absorption spectra of the freshly prepared polymer showed that, together with the absorption bands due to the stretching vibrations of the C≡N bond (2100–2200 cm^{-1}), which are also observed in the spectrum of monomeric HCN, absorption bands in the ranges 1600–1700 and 1200–1250 cm^{-1} appear in the spectrum. They are apparently due to the stretching vibrations of the C=N and C–N bonds respectively. When the system is maintained at room temperature, structure formation in the polymeric product together with an increase in its amount take place. A redistribution of the band intensities in the regions of 1250 and 2200 cm^{-1} is observed in the IR spectrum and the background in the range 1700–2200 cm^{-1} intensifies, but all the principal absorption bands are retained.

The polymer gives rise to a singlet EPR spectrum, characteristic of polyconjugated systems. The electrical conductivity of the polymer is typical for the majority of dielectric materials: $\sigma = 3 \times 10^6 \Omega^{-1}$ cm^{-1}. The appearance of colour in the polymeric product and its variation (up to black) during the radical reaction can be accounted for as a consequence of the formation of the –C=N–C=N– conjugation chain.

The appearance of the acicular crystals of the tetrameric hydrocyanic acid may be associated[63] with the formation of an intermediate biradical — aminocyanocarbene, the dimerisation of which actually leads to the appearance of the tetramer — 1,2-diaminomaleic acid dinitrile:



Indeed, photolysis of a vitreous solution of the lithium salt of the toluene-*p*-sulfonylhydrazone of 1-cyanoformamide in 2-methyltetrahydrofuran at 77 K led to the formation of a yellow product — aminocyanocarbene.[64] The biradical

$$H_2N-\overset{\delta+}{\ddot{C}}-C\overset{\delta-}{\equiv}N \quad ,$$

exists in the singlet state.

The formation of appreciable amounts of the tetramer in our experiments on radiation polymerisation suggests the operation of the mechanism described above. Aminocyanocarbene apparently initiates further propagation of the hydrogen cyanide polymerisation chain, which leads to the formation of the polymeric product.

In the first place, it was necessary to discover when the tetramer crystals are formed: during the heating of the hydrocyanic acid radiolysed at 77 K, in the solid phase, or after its fusion. The radiolysed solid HCN specimen was therefore placed in vacuo and the unreacted monomer was sublimed at a temperature below the melting point (260 K). The residue obtained after such prolonged sublimation (2.5% of the initial mass) consisted of a mixture of the polymer and the crystalline tetramer. A noteworthy feature of fundamental importance is that these products were formed in the solid phase.

X-Ray diffraction analysis of the crystals selected from the residue obtained after the sublimation of the unreacted monomer described above showed that the crystals belonged to the monoclinic system.[65] The bond lengths and bond angles in the $(HCN)_4$ molecule have the standard values. The molecule is planar with localised triple $C\equiv N$ and double $C=C$ bonds and possesses an intrinsic plane of symmetry. Shortened intermolecular contacts or other specific interactions are absent from the crystal.

Thus it has been shown experimentally that crystals of 1,2-diaminomaleic acid dinitrile are formed together with a conjugated polymer of the type $-C=N-C=N-$ during the sublimation of the solid hydrocyanic acid matrix radiolysed at 77 K. These crystals are formed on recombination of biradicals of the aminocyanocarbene type, which are stabilised in the matrix during the low-temperature radiolysis. When the matrix sublimes in the vicinity of its melting point, these biradicals acquire molecular mobility and recombine.

In our experiments, 1,2-diaminomaleic acid dinitrile was formed with a radiation yield $G \approx 2$ molecules per gram per 100 eV of the absorbed energy. Such a yield is typical for the products of a primary radiation-induced reaction (for example, of the radicals). Consequently, 1,2-diaminomaleic acid dinitrile cannot be formed as a result of consecutive radiation-induced reactions. We suggest that dimers are formed in the solid HCN matrix via $C\equiv N\cdots H$ hydrogen bonds. The primary radiation excitation of these dimers actually leads to aminocyanocarbene. In one way or another, the formation of 1,2-diaminomaleic acid dinitrile under conditions approaching those in cosmic space appears to us to be extremely important because this compound may play a key role in prebiological organic synthesis, since the hydrolysis of 1,2-diaminomaleic acid dinitrile leads to the formation of an aminoacid.

From the standpoint of the problem of the cold chemical evolution of matter in cosmic space and the formation of complex polymeric macromolecules, the polymerisation of the closest analogue of HCN — cyanogen $(CN)_2$ — is of no less interest. It was found that the low-temperature radiation polymerisation of $(CN)_2$ proceeds less effectively than that of hydrogen cyanide. After $(CN)_2$ had been irradiated at 77 K with doses up to 10^3 kGy and was subsequently heated, the yield of the polymer was only 0.1%. However, polymerisation of this monomer in various solvents (alcohol, butyl chloride) leads to a severalfold increase in the yield. A significant increase in the yield of the polymer was also observed in the polymerisation of HCN in the presence of acetylene.

III. Glasses

Amorphous bodies are characterised by the presence of short-range order alone. Owing to the absence of long-range order, the macroscopic properties of amorphous bodies are independent of direction. However, on sufficiently rapid cooling, it is possible to obtain the state of a nonequilibrium supercooled liquid. Further cooling of the substance in this state below the glass point T_g leads to the formation of a nonequilibrium solid amorphous state frequently referred to as a glass. In reality, the transition from the supercooled liquid to the vitreous state usually occurs over a narrow temperature range. The glass point is not a thermodynamic characteristic of the substance and, depending on the conditions in the preparation of the specimen and the method of measurement employed, it can vary within a fairly wide range. In the vitreous state, the species comprising the substance are capable of only vibrational and small-scale rotational motions. The translational mobility, characteristic of the liquid state is almost completely lost in the vitreous state.

The fact that transitions from the supercooled liquid to the glass state and conversely (devitrification) are accompanied by a sharp alteration in properties is extremely important: the viscosity changes by 10–15 orders of magnitude, the modulus of elasticity changes by a factor of 10–1000, the coefficient of thermal expansion changes by a factor of 10–100, etc. The gigantic jump in viscosity over the narrow vitrification temperature range is naturally the most impressive. For the chemist, this means that the molecular mobility, which determines the dynamics of the chemical reaction, changes sharply in this region. The nature of the chemical process should change on passage through the glass softening region owing to the extremely sharp alteration of the mobilities of the reactants. The mobility of molecules changes very markedly following a very slight alteration in temperature (by only a few degrees).

Reactive radical and ionic species are formed on radiolysis of vitreous matrices, are stabilised in deeper or shallower traps, and can retain their reactivity for a very long time. The absence of molecular mobility in the glass prevents the mutual recombination of such stabilised radicals. When the matrix is heated and devitrified, the translational mobility increases sharply, which entails the recombination of the accumulated radicals.

Thus, following a sharp increase in translational mobility, which occurs over the narrow temperature range in the transition from the glass to the supercooled liquid, relatively small radicals undergo effective recombination. It is more accurate to say that those radicals recombine whose mobility is sufficient to ensure their encounter in a viscous supercooled liquid. In systems where radicals liberated on devitrification are capable of initiating a chain reaction, a chemical chain process does occur effectively, as will be shown below.

1. Radical polymerisation

Vinyl acetate can be obtained in both vitreous and crystalline states. The rate of polymerisation of vitreous vinyl acetate is an order of magnitude higher than that of the crystalline substance under identical conditions.[66] High rates of post-radiation polymerisation have been noted for a series of vitreous solutions of monomers in liquid paraffin and other glass-forming solvents.[67,68]

The use of the calorimetric method of measurement established that the polymerisation process in many radiolysed vitreous systems occurs when they are heated in the temperature range corresponding to the devitrification of the matrix.[69–71] We shall consider in greater detail the study of polymerisation in the acrylic acid–ethanol vitreous system.[72]

It has been established that, on cooling to 77 K, a 17% solution of acrylic acid in ethanol passes to the vitreous state. During the heating of the glass in the calorimeter, a transition of the system from the vitreous to the supercooled liquid state ($T_g \approx 103$ K) is observed. On further heating, the supercooled

liquid passes to the region of a thermodynamically stable liquid (without crystallisation and subsequent fusion). Direct calorimetric measurements in the field of γ-radiation showed that there is hardly any polymerisation in this system at $T \leqslant T_g$. Immediately after the devitrification step, intense heat evolution, associated with the polymerisation of acrylic acid, is observed on the calorimetric curve. The overall yield of the polymer then reaches 80%. EPR spectra recorded at 108 K indicate the conversion of the monomeric radicals and the radicals of the alcohol matrix, formed during radiolysis, into the radicals of the growing polymer chain.

The EPR spectra of these radicals and their conformational transformations have been analysed in detail.[73] Together with the initiation of the polymer chain, some of the monomeric radicals recombine and only half of them are converted into polymeric radicals. On further heating in the temperature range where acrylic acid polymerises vigorously, the concentration of the growing polymeric radicals remains unchanged. Later studies of the polymerisation dynamics in this system with the aid of Mössbauer spectroscopy confirmed the validity of the principal conclusions.[74]

It follows from the foregoing that the polymerisation process proceeds virtually without chain termination over a comparatively narrow temperature range in the region corresponding to the devitrification of the matrix. The radicals stabilised in the glass during radiolysis acquire translational mobility on passage through the devitrification region and begin to recombine. They also add simultaneously to the double bond of the monomer. *n*-Meric growing radicals, the mobility of which is so low in a viscous supercooled liquid that their encounters and recombination are hardly noticeable, are produced. Furthermore, the small monomer molecules are readily supplied to such *n*-meric growing centres and their termination-free propagation is observed. This unique situation has been widely used in various polymerisation processes.

The method involving polymerisation on devitrification of the matrix has been applied to the determination of the principal kinetic parameters (rate of chain propagation, activation energy) of the low-temperature polymerisation of tetrafluoroethylene.[75] Perfluoro-3-ethyl-2,4-dimethylpent-2-ene served as the vitrifying matrix. Solutions of tetrafluoroethylene in this solvent pass fully to the vitreous state on cooling. With increase in the tetrafluoroethylene concentration in the solution, the glass point shifts monotonically into the region of lower temperatures with a corresponding decrease in the temperature range of the polymerisation process.

It has been shown that chain termination occurs when the growing macroradical adds to the double bond of the solvent, whereupon a relatively inactive stable radical, incapable of further chain propagation, is produced.[76]

We may note that the method involving postpolymerisation on devitrification was subsequently used widely in the study of the kinetics and mechanisms of low-temperature polymerisation processes (see, for example, Barkalov[77] and Barkalov and Kiryukhin[78] and the literature quoted therein, as well as other communications by Barkalov and coworkers[79–81]). It would seem that the polymerisation process carried out on devitrification of the matrix should lead to the formation of polymers with an extremely high molecular mass. In reality this is not observed. Presumably even at such low temperatures chain transfer through the monomer or the solvent plays an appreciable role in limiting the length of the polymer chain owing to the long time of the mutual contact of the reactants. Here chain transfer is understood, for example, as the reaction involving the abstraction of hydrogen from the monomer or the solvent by the growing macroradical with formation of an inert macroradical and a radical which initiates the propagation of a new polymer chain.

Indeed, the results of a study of the polymerisation of acrylamide in a vitreous solution of acrylamide in glycerol have been published.[82] Kinetic chains with a length $\geqslant 10^7$ occur in this system. Effective polymerisation during heating takes place in the temperature range 220–260 K immediately after the softening of the glass. The initiation of polymerisation in this system requires an extremely low radiation dose—only 0.3 Gy. The number of growing polymeric radicals was measured by the EPR method and their radiation-chemical yield was calculated. It was found that a single chain initiation step leads to the reaction of more than ten million monomer molecules.

During polymerisation on devitrification of alcohol solutions, the reactivities of acrylic and methacrylic derivatives differ sharply.[83] Whereas the yield of the polymer reaches 80% in the polymerisation during the vitrification of alcohol solutions of acrylic acid, its amide, and its methyl ester, the yield of the polymer for methacrylic acid and its analogous derivatives does not exceed 3%–5% under identical conditions. Bearing in mind that the relative concentrations of the growing polymeric radicals proved to be similar for all the monomers investigated, one may conclude that the sharp difference between the rates of polymerisation of acrylic and methacrylic derivatives is not associated with the difference between the initiation efficiencies.

Figure 7 presents the temperature dependences of the relative concentrations of the radicals during the heating of radiolysed vitreous solutions. Evidently the concentration of the growing polymeric radicals for acrylic acid and its derivatives is constant within a certain temperature range. In this temperature range, acrylic acid undergoes effective polymerisation. In the case of methacrylic acid and its derivatives, a completely different picture is observed. The *n*-meric radicals initiated possess sufficient translational mobility, are not stabilised, and recombine rapidly.

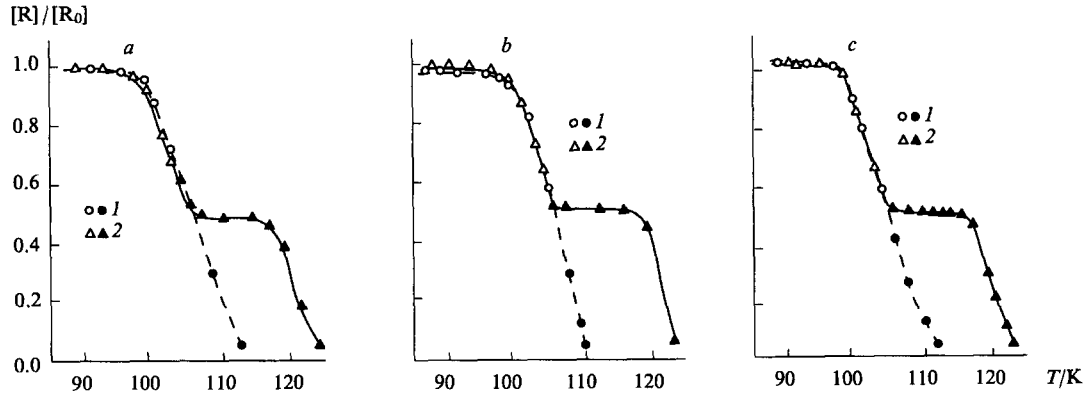


Figure 7. Variation of the relative concentration of radicals during the heating of radiolysed vitreous solutions: (*a*) methacrylic (*1*) and acrylic (*2*) acids; (*b*) methacrylamide (*1*) and acrylamide (*2*); (*c*) methyl methacrylate (*1*) and methyl acrylate (*2*). Filled symbols—growing *n*-meric radicals; initial radical concentration 1×10^{18} cm^{-3}.

In order to elucidate the causes of such a sharp difference between the rates of chain termination in the polymerisation reactions of acrylic and methacrylic acids, a study was made of the structure of the EPR spectra and the conformation of the growing terminal macroradicals was determined from the hyperfine splitting of the β-proton. The main factor responsible for the low translational mobility of macroradicals in a supercooled liquid is known to be their interaction with the alcohol molecules, which is indicated by the specific nonequilibrium conformation of the growing centre.[72,73] It was found that the presence of the CH_3 group near the reaction centre in the case of methacrylic acid prevents the interaction of the growing macroradical with the alcohol matrix, thereby preserving its mobility. This is apparently the main cause of the sharp difference between the rates of polymerisation of acrylic and methacrylic monomers on devitrification of their alcohol solution.

Thus, in contrast to the usual liquid-phase polymerisation, a sharp difference between the capacities of acrylic and methacrylic monomers for polymerisation is observed in polymerisation on devitrification, which is associated with the stronger interaction of the growing acrylic macroradicals with the medium. This difference between the reactivities of acrylic and methacrylic monomers is manifested only at fairly low temperatures.

2. Ionic polymerisation

The change in the physical properties of the matrix on passage through the devitrification region cannot fail to be reflected also in the dynamics of the propagation of the polymer chain via a cationic or anionic mechanism, since not only radicals but also trapped electrons and holes are stabilised during low-temperature radiolysis in glasses, i.e. the occurrence of the polymerisation process via an ionic mechanism is just as likely as its occurrence via a radical mechanism. The lifetime of the ions increases in the low-temperature region, while impurity water is segregated as its own crystalline phase and does not inhibit the polymerisation. Thus one may postulate that special methods for the drying of the monomer and the solvent are not needed under the conditions of postpolymerisation on devitrification of the matrix.

Cyclopentadiene was selected as the object for the study of low-temperature ionic polymerisation. The choice of cyclopentadiene was dictated by the fact that it had been earlier observed[84] that it undergoes cationic polymerisation on exposure to γ-radiation. Butyl chloride served as the vitrifying matrix in which the cationic centres arising on radiolysis are satisfactorily stabilised. On rapid cooling, solutions of cyclopentadiene in butyl chloride pass fully to the vitreous state. At 97 K, the glass is converted into a viscous supercooled liquid, which crystallises on heating and then melts at 140 K. Heating of a vitreous solution of cyclopentadiene in butyl chloride, γ-irradiated at 77 K, leads to the effective polymerisation of the monomer.[85,86] The heat evolution associated with the polymerisation of cyclopentadiene is observed over a narrow temperature range immediately after the transition of the system from the vitreous to the supercooled liquid state. On crystallisation and fusion of the system, polymerisation does not occur. The yield of the polymer increases with increasing preliminary irradiation dose and reaches a limiting value for extremely low doses (~30 kGy), which is characteristic of the accumulation of stabilised ionic centres in the course of the low-temperature radiolysis.

Epoxyethane is known to polymerise readily with the opening of the epoxide ring via a cationic or ionic mechanism in the presence of a large number of different catalysts. However, the epoxide ring proved to be extremely resistant to the action of high-energy radiation. The attempts to carry out the radiation polymerisation of epoxyethane in the solid and liquid phases were unsuccessful.[87] The effective polymerisation of epoxyethane with radiation initiation was achieved only by employing the post-polymerisation regime on devitrification of a butyl chloride matrix.[86,88] In contrast to the crystalline monomer, heating of vitreous solutions of epoxyethane in butyl chloride γ-irradiated at 77 K leads to effective polymerisation. The heat evolution associated with the postpolymerisation of epoxyethane is observed in the temperature range corresponding to the softening of the glass (~96 K).

The following evidence has been obtained for a cationic mechanism of the polymerisation of epoxyethane on devitrification of the matrix: (1) optical bleaching of the radiolysed specimens leads to a marked suppression of the postpolymerisation process; (2) the addition of small amounts of ethanol or pyridine (typical cationic inhibitors) fully inhibits the post-polymerisation; (3) the addition of hydroquinone (a typical inhibitor of radical polymerisation) to the initial solution does not affect the post-polymerisation reaction on devitrification.

Thus the use of the method of postpolymerisation on devitrification of the matrix makes it possible to achieve effective cationic polymerisation. A characteristic feature of this process is the lack of any special requirements as regards the drying of the monomer and the solvent.

3. Copolymerisation

On copolymerisation in the liquid and gas phases, the composition of the copolymer is determined by the reactivities of the comonomers (a homogeneous copolymer is obtained only in the initial stage of the polymerisation reaction). As the more reactive monomer is consumed, the resulting copolymer begins to be enriched, as a rule, in the less reactive monomer and the polymer chains acquire an inhomogeneous composition.

A characteristic feature of the supercooled liquid state obtained after the devitrification of the matrix is its comparatively high viscosity. In a highly viscous system of this kind, the duration of mutual contact between the reacting species is much longer than in the gas and liquid phases. It was therefore to be expected that the composition of the copolymer obtained under such conditions could be regulated by varying the composition of the initial mixture of monomers and that a homogeneous copolymer could be obtained for any degree of conversion.

Copolymerisation on devitrification in monomer–complex-forming agent systems has been investigated by Zubov and coworkers,[89–93] while similar copolymerisation in the absence of a complex-forming agent has been investigated by Bol'shakov et al.[94] It has been shown experimentally that copolymerisation in a supercooled viscous liquid makes it possible to obtain homogeneous copolymers and to regulate their composition.

It may be hoped that an increase in the time of contact between the reactants in the supercooled liquid will make it possible to involve compounds in copolymerisation which are not usually regarded as comonomers. In this connection, it is of interest to consider the copolymerisation of acetone with acrylic acid.[95] Heat evolution associated with copolymerisation was observed immediately after the transition of the system to a supercooled liquid state (110 K) on slow heating in a calorimeter of a vitreous solution of acrylic acid irradiated at 77 K.

In dilute acetone solutions of acrylic acid, the yield of the polymer isolated reached 250% relative to acrylic acid. Consequently the polymeric product contained two acetone molecules per acrylic acid molecule. Analysis of various mechanisms for the incorporation of acetone in the polymeric product showed that the copolymerisation of acrylic acid with the enolic form of acetone is most probable.

Thus the specific features of the supercooled liquid state, manifested by a significant increase in the contact time between the reactants, lead to a radical alteration of ideas concerning the reactivity of comonomers.

4. Graft polymerisation

Not only low-molecular-mass compounds but also polymers can be used as the vitrifying matrix. The use of the grafting method with devitrification of a polymer matrix proved effective for readily polymerising monomers such as tetrafluoroethylene.[96,97] The usual methods for the joint radiolysis of the monomer and

polymer in order to achieve graft polymerisation are difficult to use because the homopolymerisation of the monomer becomes the dominant process under these conditions.

IV. Other metastable systems

A large series of studies have been carried out also for other metastable solid systems. The low-temperature polymerisation of various monomers by condensing the monomer and the initiator onto a cooled surface (the molecular beam method) was achieved in 1959.[98-100] The initiators employed were metal couples (magnesium, potassium, sodium) and certain oxides and salts. In their presence, acrylamide, styrene, acrylonitrile, methyl methacrylate, and a series of other monomers polymerised at high rates. The low-temperature polymerisation occurred mainly in the vicinity of phase transitions, where the necessary mobility of the molecules was attained. The results of these studies have been surveyed in a review.[100]

Recently, the molecular beam method has been applied successfully in the low-temperature (77 K) polymerisation of frozen cocondensates initiated by a local mechanical action.[101-109] The polymerisation of cyclopentadiene and styrene in the presence of $TiCl_4$ has been investigated. The local mechanical action on the molecular mixtures of the monomer and the initiator involved impact by a steel needle with the aid of an electromagnetic gun. After the application of the mechanical impact, a rapid propagation of the polymerisation reaction through the specimen was observed at low temperatures. The dependence of the mechanical stresses in the low-temperature cocondensates of the monomer and the initiator on the conditions in the formation of the specimens and their role in the initiation of rapid polymerisation were demonstrated. These phenomena will be examined below in greater detail.

Photoinitiation has been used in a series of studies[105-109] of polymerisation and polycondensation at low temperatures. This procedure generally requires the application of photosensitisers; the systems obtained under these conditions are usually heterogeneous. It has been shown that in certain systems (with cinnamic acid derivatives and anthracene as sensitisers), the rate of addition at low temperatures ceases to depend on temperature and the polymerisation proceeds without activation as far as 4.2 K.

The photosensitised chain polymerisation reactions of acrylonitrile, formaldehyde, and xylene at low temperatures have been investigated. The sensitisers employed were *N,N'*-tetramethyl-*p*-phenylenediamine and β-naphthol and the specimens were prepared by the joint vacuum condensation of the monomer and the sensitiser onto an optical support. These reactions proceed as a result of the direct transformation of part of the radiant energy into the energy of the motion of the species along the reaction coordinate. Furthermore, it has been suggested that a proportion of the chemical energy is converted into mechanical stresses, which, for a certain structure of the solid system, induce the mutual approach of the reacting species and chain propagation at the very low temperatures employed.

Communications of this series report polymerisation at temperatures much lower than the glass point and the reactions are distinguished by a high yield of the polymer.

V. Autowaves

The mechanical energy of the elastic deformation of a solid at the instant of its disruption is concentrated in the region directly adjoining the newly formed surface. This energy transformation process is known to give rise to significant changes in the physicochemical properties of the substance on the freshly formed surface compared with the bulk-phase properties.[110]

Brittle breakdown is accompanied by phenomena such as the emission of electrons and ions, luminescence, the formation of radicals, and a sharp acceleration of transport processes on the cleavage surfaces. It appeared likely that the transition of the process from a homogeneous to a significantly heterogeneous regime via the brittle fracture of the specimen would include a nonequilibrium mechanism of energy transfer to the active centres previously stabilised in the solid matrix and would initiate the chemical reaction at low temperatures.

The ideas described above stimulated the study of the sensitivity of solid-phase processes to local perturbations which have been either introduced or have arisen spontaneously. These investigations led to the observation of highly intense autowave regimes in low-temperature solid-phase reactions. The principal conclusions have been surveyed in reviews.[111,112] The logic of the development of these studies will be traced below.

The objects of study were systems in which the spontaneous development of reaction chains is impossible in the solid state at radiolysis temperatures of 77 and 4.2 K, and the first task was to elucidate the activating role of the brittle fracture of the system. It was possible to show that the formation of the primary crack plays the role of an initiating device which switches on the positive feedback mechanism ensuring a self-supporting process regime. The following self-activation mechanism has been proposed. The chemical reaction arising on the cleavage planes and in the adjoining regions disturbs the monolithic nature of the sections of the solid matrix not involved in the reaction, thereby preparing the next layer for the reaction to take place. Such breakdown of monolithic structure can occur, for example, as a consequence of the appearance of temperature or density gradients during the reaction, which create stresses disrupting the specimen.

Autowave phenomena are known to be characteristic of systems described by nonlinear branched-chain models. Autowave reaction regimes should arise in sufficiently long specimens in response to a locally introduced perturbation. In the first experiments,[113] it was already possible to initiate the spontaneous propagation of the reaction wave throughout the specimen on formation of a local cleavage plane. The structure of the travelling front of the cryochemical reaction proved to be completely atypical for classical thermal self-propagation processes.

The qualitative picture of the propagation of the wave involved the concept of the movement in the solid specimen of a narrow zone highly truncated by an extensive network of freshly formed cracks. The chemical reaction arises in precisely this zone on the surface of the cracks (or close to it) and creates in its turn conditions for continuation of the breakdown in the adjoining layer of the solid matrix. Such layer-by-layer dispersion of the specimen is referred to as the travelling stress field. A stress of this kind may be caused, as already stated, either by the difference between the densities of the starting materials and the final products (isothermal mechanism) or by the appearance in the specimen of 'steep' temperature gradients as a result of the exothermicity of the reaction (nonisothermal mechanism). Naturally both factors can also operate simultaneously.

The studies carried out indicate the wide occurrence of autowave phenomena in cryochemical solid state reactions and the identity of their physical mechanism in a wide range of chemical systems. This gave grounds for the assumption that autowave reaction regimes can prove useful in the creation of new nontraditional chemical technologies. Indeed, the principal technological tasks (activation of the chemical system, supply of energy, and mixing of the reactants) are performed jointly by employing the energy of the autowave chemical proceses. The occurrence of very high rates of the chemical reaction in the autowave regime at low temperatures is also extremely attractive.

1. Acetaldehyde

The autowave polymerisation regime arises in polycrystalline acetaldehyde already at 4.2–77 K. Its principal characteristics have been investigated.[114] The polymerisation wave in the crystalline monomer was observed in massive (cylindrical) and thin-walled specimens immersed in both nitrogen and helium baths. The reaction wave was excited in response to the local brittle fracture of the frozen acetaldehyde.

Propagation of the polymerisation front in solid radiolysed acetaldehyde at relatively high temperatures (117–147 K), close to the melting point of the monomer (150 K), was observed with the aid of thermography and cine-filming.[43] This phenomenon was interpreted within the framework of the classical thermal combustion mechanism. The rate of propagation of the reaction front at these temperatures was 1–3 cm s^{-1} for preliminary irradiation doses of 5–100 kGy.

The development of ideas concerning autowave processes made it possible to analyse the characteristics of the polymerisation of acetaldehyde at a new qualitative level. Acetaldehyde is of special interest in connection with two factors. First, the autowave regime in the polymerisation of acetaldehyde is an example of the appearance of a cryochemical wave in a one-component system. Second, the heat of this reaction is almost an order of magnitude lower than for the systems investigated previously. This created preconditions for the development of ideas concerning the role of the isothermal and nonisothermal mechanisms and their inter-action in the autowave process.

When the autowave passed through the specimen in the helium bath, the maximum temperature in the front did not exceed 130 K, i.e. was significantly lower than the melting point of the monomer (Fig. 8). Thus here there are all the conditions for the analysis of the changes in the structure and phase state of the crystalline specimen induced by the passage of the mechanochemical cryo-wave through it. According to the ideas developed, the chemical reaction front represents a mechanical dispersion zone moving through the solid reactant. One may postulate that the passage of such a wave through the specimen results in its dispersion.

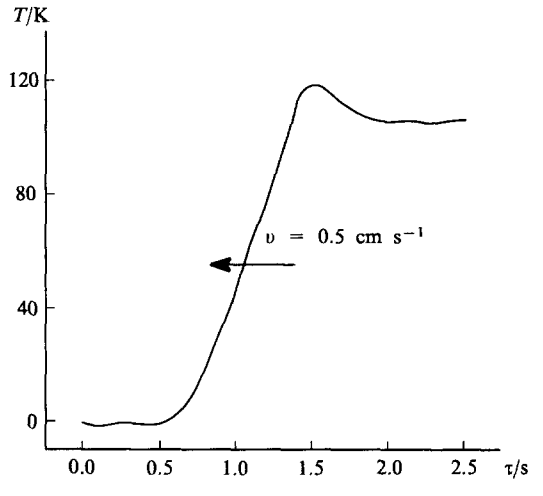


Figure 8. Time variation of the temperature profile of the acetaldehyde polymerisation travelling wave at 4.2 K. Preliminary γ-irradiation dose 700 kGy.

This hypothesis was tested by calorimetric analysis. To carry out such an analysis, the acetaldehyde specimen was transferred to a bath of liquid nitrogen after the passage of the auto-wave through it (in liquid helium) and was then cut up into several portions. Each of these was placed separately in a calorimeter at 77 K and the calorimetric heating curve was recorded. It was found that after the passage of the wave there was no crystalline phase in the specimen. Only a heat capacity jump, accompanying devitrification, was detected in the calorimetric experiments, and the signal corresponding to the heat of fusion was absent. When the process was carried out not in the autowave regime but in a regime involving the slow heating of the entire specimen in the calorimeter (without the brittle fracture initiating the autowave), the unreacted monomer retained its crystallinity. Thus the passage of the mechanochemical wave through the crystalline specimen does indeed lead to its conversion into an amorphous form.

The rate of propagation of the autowave depends on the preliminary γ-irradiation dose. As in the systems investigated previously,[111] there is a critical dose necessary for the attainment of the autowave regime. The magnitude of this dose increases with decrease in the thermostat temperature from 77 to 4.2 K. For specimens immersed in liquid nitrogen, the rate of propagation of the polymerisation wave increases linearly with the irradiation dose. It is logical to postulate that the increase in the rate of propagation of the wave with increasing irradiation dose is associated with the increased concentration of the active centres. However, the accumulation of paramagnetic centres (radical-ions and radicals) during the radiolysis of polycrystalline acetaldehyde at 77 K takes place linearly only in the region of small doses (only up to ~50 kGy) and then slows down. After the attainment of ~650 kGy, the stabilised active centres altogether cease to accumulate.

Even on rapid cooling, pure acetaldehyde cannot be converted into a vitreous state and its polymerisation in such a state has not therefore been investigated. A study has been made[115] of the polymerisation of a solid vitreous solution of acetaldehyde in butyl chloride. Local brittle fracture initiated the autowave polymerisation regime. The principal parameters of the autowave polymerisation process in the polycrystalline and vitreous matrices agreed only qualitatively. On the other hand, in quantitative terms, the critical dose of the preliminary γ-irradiation, above which it is possible to generate an autowave in glass, is 60 kGy, while in crystalline acetaldehyde it exceeds 300 kGy.

2. Cyclopentadiene

In the phenomenological description of the autowave processes considered above, the nature of the active centres arising on brittle fracture of the system were not specified in concrete terms. Since the majority of the cryochemical autowaves have been observed for typical radical chain reactions, it was of interest to establish the autowave regime for a typical ionic chain reaction.

Cyclopentadiene polymerises only via an ionic mechanism and this is why it was selected for the investigation of the characteristics of the autowave regimes in cryochemical reactions of this type.[116] It is noteworthy that the 'explosive' polymerisation reaction of cyclopentadiene was observed in films obtained by freezing them from molecular beams comprising the monomer and the catalyst ($TiCl_4$) and then pricking the film with a metallic needle at 77 K.[101]

On rapid cooling to 77 K, a solution of cyclopentadiene in butyl chloride passes to the vitreous state. On local brittle fracture of the radiolysed specimen immersed in liquid nitrogen, the polymerisation reaction, propagated through the specimen in the form of an autowave, begins. The velocity of the polymerisation wave and the form of its temperature profile depend significantly on the preliminary irradiation dose. The velocity of the wave increases with increasing dose, while the temperature profile of the wave becomes increasingly sharp.

The velocity of the polymerisation wave increases linearly with increasing preliminary irradiation dose up to 1200 kGy. This type of dependence of the velocity of the wave is evidently not associated with the dynamics of the accumulation of the cationic active centres, because such accumulation ceases for significantly lower doses.

The molecular mass and the yield of the polycyclopentadiene obtained in the autowave regime are higher than in thermo-activated postpolymerisation. The latter factor may prove useful in the development of technological regimes for the synthesis of polymers.

VI. Oscillations in the rate of reaction

Oscillations in the rate of reaction is an unusual phenomenon as regards the classical ideas concerning the nature of a chemical process. Many investigators are engaged nowadays in the study of its mechanism.[117-122]

The present authors encountered auto-oscillations in the rates of cryochemical reactions for the first time in a study of the solid-phase radiation-induced hydrobromination of ethylene.[123] The post-radiation process (for example, polymerisation), occurring under conditions where the temperature of the thermostat is scanned, is initiated by the active centres gradually liberated with increase in the temperature of the matrix. A definite number of active centres stabilised in the matrix are generated on γ-irradiation. The irradiation takes place at a fairly low temperature, the centres formed are stabilised in the matrix, and the reaction is not initiated. Only on raising the temperature of the medium are the active centres liberated and initiate the chemical reaction.

We shall consider the establishment of auto-oscillatory regimes in low-temperature radiation-induced thermokinetic chemical chain reactions.[123-128] For reactions occurring under isothermal conditions, the negative feedback necessary for the occurrence of oscillations in the reaction rate can be brought into operation only by chemical autocatalysis. For exothermic chain reactions, the heat evolved may play the role of the negative feedback under certain conditions. The evolution of heat can increase the temperature of the medium and hence the rate of the chemical reaction. Thus the evolution of heat can perform a function analogous to autocatalysis.

Cryochemical reactions are responsible for the appearance of thermokinetic oscillations: the defectiveness of solid matrices and their low heat capacities promote the appearance of non-uniformities in the temperature field. Thermokinetic models of the auto-oscillations in the rates of chemical reactions have been considered by Sal'nikov[129,130] and a detailed description of such reaction conditions may be found in monographs.[117,121,122] We shall consider certain examples of the auto-oscillatory regimes in cryochemical reactions in vitreous and crystalline matrices.

As an illustration, we may quote the results of a study of the polymerisation of crystalline heptyl acrylate. The process takes place during the heating of specimens γ-radiolysed at 77 K in both auto-oscillatory and the usual regimes. On rapid cooling of heptyl acrylate to 77 K, the monomer passes to the vitreous state. Heating of such specimens in a calorimeter makes it possible to observe the transition from the vitreous to the supercooled liquid (~138 K) state and then the crystallisation of the supercooled liquid in the temperature range 140–205 K and fusion of the monomer crystals at 205–210 K. If, however, the monomer is initially annealed at 205 K and then cooled to 77 K, then it passes fully to the crystalline state. The calorimetric heating curve for such specimens shows only the endothermic peak due to the fusion of the monomer at 208 K (Fig. 9). The postpolymerisation process was in fact investigated in precisely such specimens.

In order to accumulate the polymerisation active centres, the monomer was γ-irradiated at 77 K with a dose of 5–100 kGy. The calorimetric heating curves of the specimens subjected to preliminary irradiation are presented in Fig. 9 (curves *2–4*). The polymerisation reaction, recorded from the evolution of heat, begins at temperatures 15–20 K below the melting point of the monomer, where the molecules acquire translational mobility.

The rate of polymerisation exhibits a marked temperature dependence along the initial section and rapidly attains a maximum. After this, a sharp decrease and a further increase in the rate of the process are observed. Ultimately, several acceleration and retardation periods occur. The oscillations in the rate of reaction have a decaying amplitude. An increase in the preliminary irradiation dose shifts the onset of the process into the region of lower temperatures and increases the amplitude of the oscillations in the rate (cf. curves *2* and *3* in Fig. 9). When the preliminary

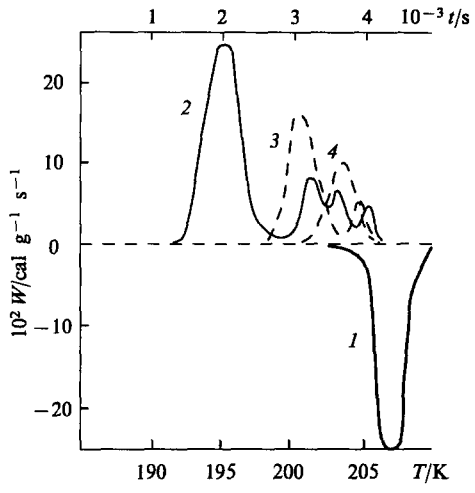


Figure 9. Calorimetric heating curve for nonirradiated heptyl acrylate (curve *1*) and variation of the rate of heat evolution on heating heptyl acrylate γ-irradiated at 77 K using different doses (kGy): (*2*) 100; (*3*) 17.5; (*4*) 5.

irradiation dose is sufficiently low, oscillations in the rate of post-polymerisation are no longer observed (curve *4*). The mathematical model of the postpolymerisation process proposed by Nefedov et al.[125] permits a qualitative explanation of the observed features of the polymerisation reaction of crystalline heptyl acrylate.

Oscillatory regimes in low-temperature radiation-initiated chain reactions have been observed also for polymerisation on devitrification of the matrix. As an example, we shall consider various regimes in the post-radiation polymerisation of acetaldehyde in a vitreous butyl chloride matrix.

On cooling to 77 K, a solution of acetaldehyde in butyl chloride passes fully to the vitreous state. When such a system is heated in a calorimeter in the temperature range 94–97 K, a transition from the vitreous to the supercooled liquid state is observed. This is followed by crystallisation (112–115 K) and then fusion (145 K). When the same system, subjected to preliminary γ-irradiation at 77 K, is heated, heat evolution due to the post-polymerisation of acetaldehyde is observed in the devitrification region. Various process regimes are possible depending on the conditions in the transfer of heat from the calorimetric cell.

Polymerisation can occur in the absence of appreciable superheating of the test substance in the cell relative to the calorimeter block (stationary conditions). For this regime to be achieved, it is necessary to establish a fairly rapid removal of heat from the cell. This can be done experimentally by altering a series of parameters. It is essential to decrease the rate of heating of the specimen, to improve the heat removal conditions by increasing the ratio of the surface of the specimen to its volume (by reducing the mass of the initial sample), and to reduce the preliminary irradiation dose, which leads to a diminution of the concentration of the active centres stabilised in the system, i.e. to a decrease in the rate of heat evolution due to the polymerisation reaction.

During the heating of the specimen in the absence of appreciable superheating of the latter in the cell, the rate of post-polymerisation of acetaldehyde increases with increasing temperature, reaches a maximum, and diminishes smoothly owing to the consumption of the monomer and the active centres for the reaction stored during the preliminary radiolysis (Fig. 10, curve *1*). The initial section of the calorimetric curve can be expressed satisfactorily in a linear form in terms of the Arrhenius variables under these conditions (the activation energy is 6 kcal mol^{-1}).

Another extreme case is the thermal explosion regime. It is observed when the conditions in the elimination of heat from the cell are impaired: an increase in the mass of the substance in the

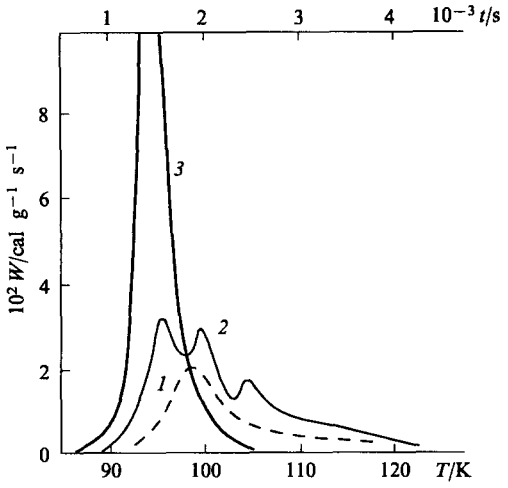


Figure 10. Variation of the rate of heat evolution in the devitrification region during the postpolymerisation of acetaldehyde (AA) in a butyl chloride (BC) matrix in different specimens: (*1*) 0.097 g of AA + 0.367 g of BC; (*2*) 0.138 g of AA + 0.549 g of BC; (*3*) 0.175 g of AA + 0.672 g of BC. Preliminary γ-irradiation dose at 77 K 120 kGy (curves *1* and *2*) and 300 kGy (curve *3*); *T*—temperature of the calorimeter block.

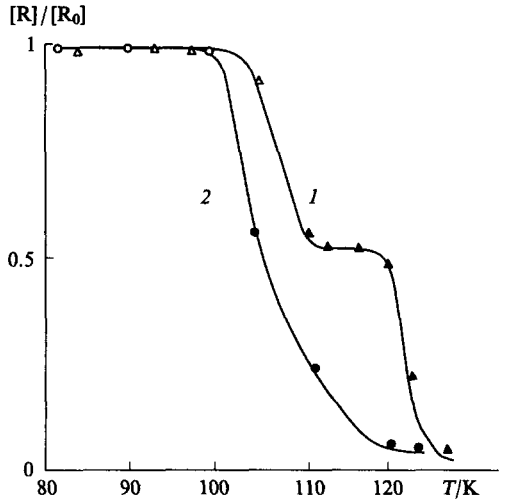


Figure 11. Variation of the relative concentration of radicals during the heating of 17% solutions of acrylic acid in ethanol irradiated at 77 K using doses of 20 kGy (curve *1*) and 50 kGy (curve *2*). Heating rate of the specimens 0.2 K min^{-1} (curve *1*) and 0.5 K min^{-1} (curve *2*). The filled symbols refer to the concentration of the growing polymer chain.

cell, in the rate of heating of the specimen, and in the preliminary irradiation dose (Fig. 10, curve *3*). Under the conditions of moderate heat removal, an oscillatory process regime has been recorded—several cycles involving an increase and a decrease in the rate of reaction were observed during the experiment (Fig. 10, curve *2*).

Thus, depending on the reaction conditions, different process regimes are realised: the stationary regime (in the absence of appreciable superheating of the test substance in the specimen), thermal explosion, and the oscillatory regime. Analysis of experimental data leads to the conclusion that the oscillations in rate in the acetaldehyde–butyl chloride system are associated with the thermokinetic mechanism described above. The following estimates of the limits of the existence of oscillatory regimes may be quoted: (1) $T_{th} < T_c < T_{th} + \Delta T$, where T_c is the temperature to which the reaction mixture has been superheated in the oscillatory regime in the cell relative to the thermostat temperature T_{th}, and ΔT represents the pre-explosion heating ($\Delta T = RT^2/E$); (2) $\tau > n\tau_{os}$, where τ is the average lifetime of the active centres ($\tau = 1/k$ in the case of unimolecular chain termination, $\tau = 1/k_t R_t$ in the case of bimolecular termination, k_t is the termination reaction rate constant, and R_t is the initial concentration of the polymerisation active centres), τ_{os} is the period of the oscillations, and n is the number of oscillation cycles. When the reaction takes place under stationary conditions (in the absence of appreciable superheating in the specimen), the growing macroradicals do not recombine in the temperature range 110–120 K; only the propagation of the polymer chain takes place (Fig. 11, curve *1*). When the quasi-isothermal regime is infringed and oscillations arise in the rate of postpolymerisation, the growing macroradicals are destroyed (Fig. 11, curve *2*). At high rates of heating of the system (~600 K min^{-1}), the growing polymer chains are not formed at all owing to the destruction of the active centres at an early stage in the process.

The different chemical reaction regimes are of interest in connection with the possibility of increasing the selectivity of complex processes and of expanding the technological procedures for controlling cryochemical synthesis. The thermal instability arising in the operation of chemical reactors is usually an undesirable phenomenon leading to a decrease in the quality of the production and possible breakdowns. The understanding of the process mechanism makes it possible to suppress the auto-oscillations and to maintain a stationary regime. However, oscillatory regimes may also prove convenient—they afford a significantly greater average yield of the product than stationary regimes. Such advantages are manifested particularly strikingly when the target product is an intermediate in a complex chemical chain reaction.[131]

As an example of the influence of various reaction regimes on the properties of the final product, we shall consider the low-temperature radiation polymerisation of 1,3-bis(dimethylamino)-isopropyl methacrylate.[132] Depending on the conditions in the removal of heat from the reaction volume, different polymerisation process regimes were realised on devitrification of the matrix: stationary, oscillatory, and thermal explosion.

In the case of the auto-oscillatory postpolymerisation regime, the mass-average molecular mass of the polymer diminishes from 2.8×10^6 to 1.4×10^6 with increase in the preliminary irradiation dose from 10 to 118 kGy. In the stationary regime, the molecular mass diminishes from 1.5×10^6 to 0.3×10^6. The high molecular mass of the polymer obtained in the oscillatory regime is evidently due to the fact that local superheating results in an increase in the mobility of the growing polymer chains, so that their bimolecular termination predominates.

Polymers with a different supermolecular structure, characterised by the presence of microheterogeneities, are obtained in the thermal explosion regime.[132] A more detailed analysis of the polymeric products obtained in this series of studies showed that the appearance of nonstationary conditions in the low-temperature polymerisation process (oscillatory regime and thermal explosion) leads to the broadening of the polymer molecular mass distribution in the direction of higher molecular masses.

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