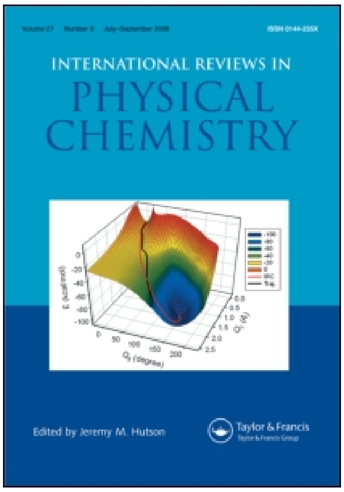

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Chemical reactions in the process of matrix devitrification

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To cite this Article Barkalov, I. M. and Kiryukhin, D. P.(1992) 'Chemical reactions in the process of matrix devitrification', International Reviews in Physical Chemistry, 11: 2, 263 — 288
To link to this Article: DOI: 10.1080/01442359209353272
URL: http://dx.doi.org/10.1080/01442359209353272

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1992, VOL. 11, NO. 2, 263–288

Chemical reactions in the process of matrix devitrification

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Chemical reactions and physical processes occurring during matrix devitrification are studied to reveal important factors concerning low-temperature, isotropic, amorphous structures. Reactions in this regime allow active observation of supercooled reagents well below their melting temperatures. It is possible to selectively carry out and observe chain reactions in the vitrifying matrix, whereas in crystal lattices such reactions are hindered due to low translational reagent mobility effects. Very low-temperature reactions allow selectivity of pathways in the vitrifying medium; entropy effects are minimized and exothermic pathways are favoured.

1. Introduction

"In effect, a macroscopic glass is a Universe of regions at different stages of evolution." (Phillips, J. C., 1982, *Physics Today*, February, 27.)

In amorphous bodies, the three-dimensional periodicity of the structure, i.e. the main characteristic of the crystal state, is absent. However, there is a short-range order in an amorphous body when the mutual arrangement of several molecules is intercorrelated. Due to the absence of the long-range order amorphous bodies are isotropic: their macroscopic properties do not depend on the direction. At temperatures above the melting point T_m the substance passes to another equilibrium state—a crystal one (see figure 1). However, upon sufficiently fast cooling the state of non-equilibrium supercooled liquid is reached. Further cooling of this state down to below the vitrification point T_g leads also to the non-equilibrium solid amorphous state, often called merely 'glass' (figure 1). The vitrification point is rather a lame name, although commonly accepted. In fact, transition from a supercooled liquid to the glass state occurs usually in a narrow temperature interval. T_g itself is not a thermodynamic characteristic of the substance and may vary over a wide range depending on the conditions of measurements that are connected with sharp retardation of the structure rearrangement in the short-range order of a liquid. In the glass state the particles can make only vibrational and smallscale rotational movements. Translational mobility, characteristic of the liquid state, is practically lost here.

Although the vitrified state of the substance is metastable (specific volume and enthalpy of glass is higher then that of an equilibrium crystal), it can survive for a long period of time. Such natural glasses as obsidian, amber and others exist for millions of years. The theoretical description of the glass state markedly lags behind the modern theory of crystals. It can be easily understood from the human point of view: a strict order can be easily described and put into its proper place in the human consciousness, but it is Chaos that gives birth to Life. The requirements of practice (fibre optics, metallic glasses) have particularly intensified the efforts of physicists and there is hope that theoretical efforts will make it possible to overtake the far-advanced vanguard of experiment.

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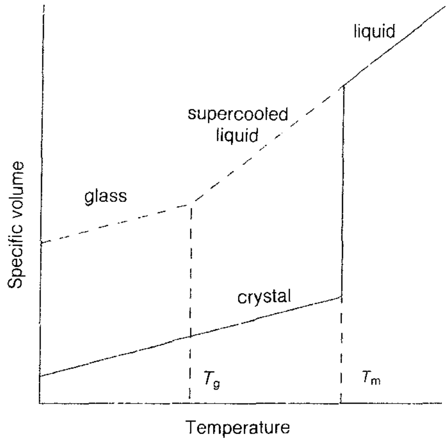

Figure 1. Temperature dependence of the specific volume for crystal and glass phases (the scheme).

Very important is also the fact that transition from a supercooled liquid to the glass state or a back transition (devitrification) is followed by a sharp change of the properties: *viscosity is changed by 10–15 orders*, an elasticity modulus—by a factor of 10–1000, a temperature expansion coefficient by a factor of 10–100, etc. The most impressive here is of course a gigantic jump of viscosity in a narrow temperature range of vitrification. For a chemist it is clear that molecular mobility determining the dynamics of chemical conversion changes sharply in this region. We are used to the fact that the dynamics of the process (in the absence of catalysis) can be varied only by the temperature of the medium in which the chemical reaction occurs. The character of temperature dependence of the chemical reaction rate has become very familiar: $K = Z\exp(-E/RT)$, where K is the rate constant of an elementary act, Z is the pre-exponential factor, whose temperature dependence can be ignored in most cases, and E is the activation energy of the reaction. Thus the character of the chemical process is not described by this traditional equation in the region of glass softening and should change drastically due to rather a sharp change of the mobility of reagents. Meanwhile, a great change in the mobility of molecules is reached by temperature variations of a few degrees. The next chapter is devoted to the first steps in the study of these unusual chemical processes.

2. Decay of radicals stabilized in the glass matrix

The radiolysis of organic glasses leads to formation of active species of radical and ionic nature that are stabilized in more or less deep traps and can keep reactive for a long time. The absence of molecular mobility in the glass inhibits mutual recombination of such stabilized radicals. This fact acounts for rather high limiting concentrations of radicals that can be achieved in low-temperature radiolysis. Heating of such a matrix and the transition of the glass to the supercooled liquid state (devitrification) leads to a sharp increase in translational mobility and, as a consequence, to recombination of accumulated radicals. It should be noted that an analogous picture is observed also for polycrystal matrices: their melting should lead to an effective recombination of stabilized radicals.

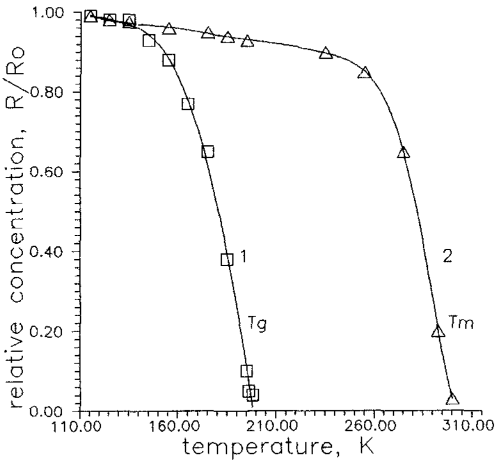

Figure 2. Defreezing curves: (1) and (2) glass and crystal 1,1-dicyclohexyldodecane [1].

Already in early investigations the above-given picture was fully confirmed experimentally. Typical results of such investigations [1] are shown in figure 2. The so-called 'defreezing curves' have been obtained for various organic substances, both glass and crystalline, radiolysed at $T \leqslant 100$ K. The concentration of stabilized radicals (an electron spin resonance (ESR) method) and its relative change along with a temperature rise have been also measured. For the same compound (1,1-dicyclohexyldodecane) prepared as a glass and as a crystal, an effective recombination of accumulated radicals takes place in one case at T_g, in another case at T_m (see figure 2).

We should mention here also one more very interesting physical state of a solid—a 'gasocrystal' one. A whole class of crystals formed by almost spherical molecules appear to have a specific transition from the crystal to the 'gasocrystal' state when the molecules preserve only the positions of gravity centres in the crystal lattice, while the rotary and partially translational movements are released. This form, with a low entropy of melting has the properties of an exceptionally viscous liquid. The crystals we are speaking about have been called *plastic crystals* by Timmerman [2].

It seems natural that the transition of a matrix to the gasocrystal state should lead to a sharp increase of the mobility of reagents and an acceleration of the rate of chemical reactions. Really, as is seen from figure 3, an effective recombination of the stabilized radicals [1] is detected in the region of such a phase transition.

Therefore, the radicals stabilized in glasses because of insufficient translational mobility can meet each other and recombine at T_g or in the transition to the gasocrystal state. As this chemical reaction is followed by a marked heat release (at recombination of alkyl radicals 80–90 kcal mol^{-1} are released), it may also be controlled with a scanning calorimeter [3,4]. Simultaneously, the use of this low-temperature calorimeter allows us to control the variation of the phase state of the matrix under investigation.

Let us examine this process in more detail on an example of the study of recombination dynamics of stabilized radicals in radiolyzed methanol [5]. Pure methanol is crystallized on freezing and no amorphous state is formed. However, addition of small amounts of salts such as $CoCl_2$ soluble in methanol leads to these solutions turning into glass at sufficiently fast cooling. When glass methanol is heated in the calorimeter (with $CoCl_2$), a sharp change in heat capacity of the system in the

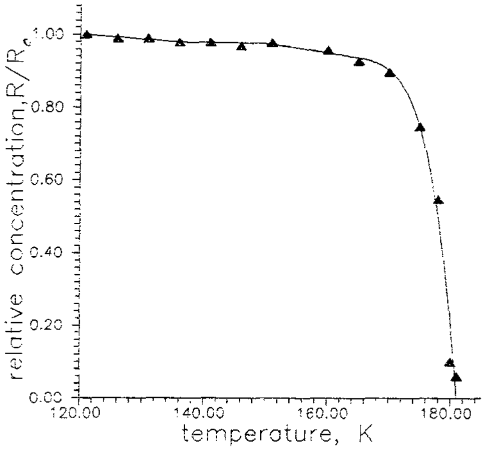

Figure 3. A defreezing curve of a cyclohexane plastic crystal. The phase transition temperature 'crystal I–crystal II' is 186·1 K, the melting temperature 279·8 K [1].

range of 110–115 K is observed, which is connected with glass softening and its transition to a viscous supercooled liquid. At further increase of temperature, the thermodynamically unstable supercooled liquid is crystallized: an exothermic peak is registered by the calorimeter. Crystal methanol during further heating is melted (an endothermic peak). With an increase of $CoCl_2$ concentration in methanol the solution viscosity increases, and crystallization of an overcooled liquid is more and more hampered. Already for a 10% solution its crystallization, as well as melting, is not detected (see figure 4).

Radiolysis of glass solution of $CoCl_2$ in methanol at 77 K leads to accumulation of stabilized radicals. As has been shown above, when the system is passing to the supercooled liquid state, these stabilized radicals recombine effectively, which is confirmed by an ESR technique. This recombination process can also be registered by a

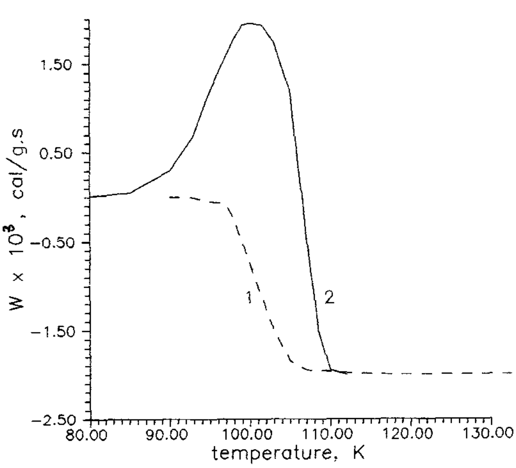

Figure 4. Calorimetric curve of defreezing before (1) and after (2) ^{60}Co γ-rays irradiation with $D \approx 1$ MGy dose at 77 K of a 10% $CoCl_2$ solution in methanol [5]. The rate of defreezing $0{\cdot}012\ K\,s^{-1}$.

calorimetric technique by its heat release. Actually, in the vitrification temperature range the irradiated samples have heat release that grows with a previous irradiation dose. At a dose of 1 MGy a contribution into heat release from the charge recombination may be ignored as their concentration is small as compared with that of the stabilized radicals [6]. Radicals $\dot{C}H_2OH$ accumulated at low-temperature methanol radiolysis recombine to give ethylene glycol. In recombination, $70 \pm 8\,\mathrm{kcal\,mol^{-1}}$ are released. Based on measured heat release (figure 4) we may estimate a concentration of the stabilized radicals $\dot{C}H_2OH$. ESR and calorimetric techniques have appeared to give practically the same results.

Thus on sharp increase of the translational mobility that takes place in a narrow temperature interval of glass transition to a supercooled liquid, the radicals of comparatively small sizes recombine effectively. Strictly speaking only those radicals recombine whose mobility in a viscous supercooled liquid is high enough for them to meet each other. As will be shown later, an effective chain chemical process is observed in the systems where the radicals released during vitrification can initiate a chain reaction.

3. Radical polymerization

As early as 1962 it was shown that vinylacetate can be produced both in the glass and crystalline states. Polymerization rate for glass vinylacetate under similar conditions appeared to be an order of magnitude higher than for crystalline one [7]. High rates of postradiation polymerization were detected for a series of glass solutions of monomers in paraffin oil and other glass-forming solutions [8,9]. However, a significant drawback of all the early works was the use of a traditional gravimetric technique for determination of a polymer yield and, hence, a polymerization rate. The polymer yield in the vitrification region was estimated, for instance, by the measurements at room temperature after destruction of the matrix. To perform quantitative kinetic measurements it was necessary, at first, to create techniques that could allow us to control the process directly at the moment of its occurring. In every particular case it was also necessary to perform a phase analysis of the two-component system 'reagent–vitrifying matrix' to determine the limits of solubility at vitrifying temperatures of the system and, at last, at the vitrifying temperature region itself. Further successes in the study of the chain reaction mechanism in matrix devitrification were connected with development and use of kinetic calorimetry that successfully solved the above experimental tasks [3,4].

The use of the calorimetric technique allowed us to establish that the polymerization in a series of radiolyzed glass systems proceeded on their defreezing in the temperature range of matrix devitrification [10–12]. Let us consider in more detail the polymerization in the 'acrylic acid–ethanol' glass system [13].

A 17% acrylic acid solution in ethanol was established to pass completely to the glass state on freezing down to 77 K. As this glass was defrozen in the calorimeter, the system passed to a supercooled liquid state with $T_g \simeq 103\,\mathrm{K}$. The latter on further heating passed to the thermodynamically stable liquid region (without crystallization and subsequent melting). Direct calorimetric measurements in the γ-ray field showed that no polymerization took place in this system at $T \leqslant T_g$. The calorimetric curve produced in the defreezing of a radiolyzed glass solution showed intensive heat release just after the devitrification sample, which was connected with polymerization of acrylic acid (see figure 5). The total polymer yield reached here 80%.

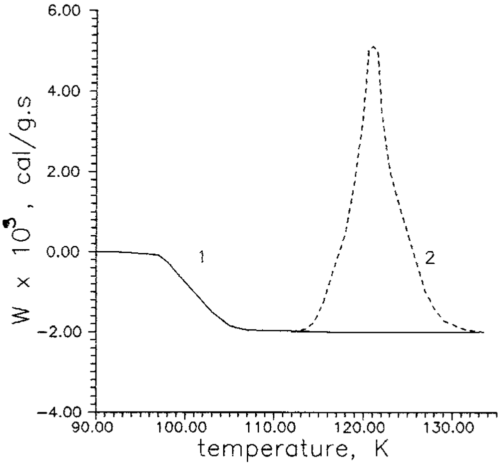

Figure 5. Calorimetric curve of defreezing: (1) of a glass solution of a 17% acrylic acid in ethanol; (2) the same solution irradiated by ^{60}Co γ-rays at 777 K with a 20 kGy dose. The rate of defreezing 0·018 K s^{-1}.

In accordance with the ESR spectra at $T \geqslant 108$ K a transition of monomeric radicals and radicals of an alcoholic matrix formed in radiolysis into the radicals of a propagatint polymer chain $R{-}C_\beta H_2{-}\dot{C}_\alpha H{-}COOH$ takes place. A detailed analysis of the evolution of ESR spectra of these radicals and their conformational conversions was made in [14]. Along with the starting of the polymer chain, recombination of a part of the monomer radicals takes place, nearly half of them turning into propagating polymer radicals. On further heating, in the temperature range where a polymerization of acrylic acid proceeds intensively the concentration of growing polymer radicals remains constant. More recent study of the polymerization dynamics in this system by the Mössbauer label (ferrocene 0·4% wt., enriched up to 90% by isotope ^{57}Fe) confirms the correctness of the main conclusions [15].

Therefore, in a rather narrow temperature interval in the matrix devitrification region the polymerization proceeds practically without chain termination. The radicals stabilized in glass during radiolysis acquire translational mobility while passing through the devitrification region and begin recombining. Simultaneously the reaction of addition of radicals in the double monomer bond occurs. The growing radicals are formed, whose mobility in a viscous supercooled liquid is so small that their collision and recombination are practically not observed. Meanwhile, a supply of small monomer molecules to such growing centres occurs readily, and their growing is continued. This unique situation, as will be clear from the following, is widely used in various polymerization processes.

3.1. *Kinetic peculiarities of the process*

The use of kinetic calorimetry in combination with an ESR method has allowed the quantitative description of the polymerization dynamics in matrix devitrification. In the course of slow scanning of the temperature region of the transition all three elementary polymerization stages can be divided in time:

(1) initiation—when the radicals being released partly recombine and partly turn into growing centres (here it is very simple to determine the number of propagating macromolecules and effectiveness of initiation);

(2) propagation of polymer chains—the concentration of propagating polymer chains remains constant (one may determine the propagating constant);
(3) termination of polymer radicals become rather mobile and decay.

For the process of acrylic acid polymerization during devitrification of an alcoholic matrix in the temperature interval of 110–120 K the propagation constant has been found:

$$K_p \simeq 5\times10^{-3}\exp(-10\,700/RT)\,\mathrm{cm}^3\,\mathrm{s}^{-1}.$$

The overestimated values of Arrhenius parameters and their change with the dose rate of pre-irradiation testify to the cooperative character of the process revealing itself in a compensational effect [16].

The polymerization method in matrix devitrification has been used to determine the main kinetic parameters of low-temperature polymerization of tetrafluoroethylene [17]. Perfluoro-2,4-dimethyl-3-ethylpentene-2 has been chosen as a vitrifying matrix. Solutions of tetrafluoroethylene in this solvent vitrify readily, and, when these samples are defrozen, the calorimetric curve shows only a devitrification 'step' corresponding to the transition of a glass solution into a supercooled liquid (figure 6). When the tetrafluoroethylene concentration in the solution increases, the transition of a glass to a supercooled liquid is shifted monotonously as is seen in figure 6, to the region of lower temperatures.

Postpolymerization of tetrafluoroethylene in radiolyzed glass solutions is recorded in a narrow temperature range in the region of devitrification of the systems. Here the temperature region of polymerization decreases (figure 6) together with the rise of the initial concentration of tetrafluoroethylene in the solution and the lowering of a glass point. A total polymer yield is also decreased in this case.

After reaching the maximum the rate of tetrafluoroethylene polymerization drops fast. This rate decrease cannot be connected with a monomer production as its conversion on reaching the maximum is not higher than 10–20%. Therefore, this rate decrease is caused by an effective termination of polymer chains. It is shown that the

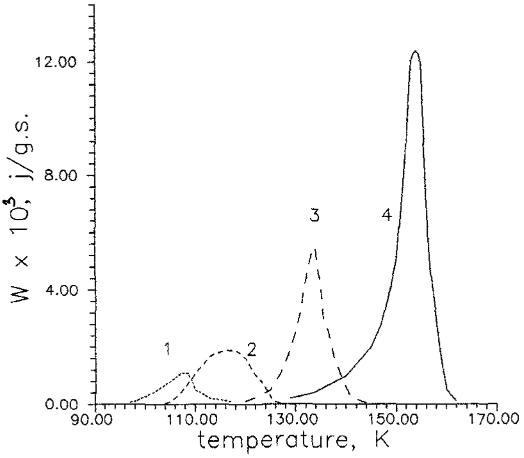

Figure 6. Calorimetric curve of defreezing of radiolyzed tetrafluoroethylene glass solutions with different initial concentration: (1) 25%, $T_g=103$ K; (2) 17%, $T_g=117$ K; (3) 9%, $T_g=133$ K; (4) 1%, $T_g=149$ K. The rate of defreezing is 0·02 K s^{-1}.

chain termination occurs on addition of a propagating macroradical to a double bond of a solvent to give a poorly active stable radical that is unable to further chain propagating [18]. Then a decrease of the polymerization rate (W) in time must be described by the equation:

$$W = -\mathrm{d}[M]/\mathrm{d}t = K_p[M][R_p]_0 \exp(-K_t t), \tag{1}$$

where K_p and K_t are the constants of propagation and termination polymer chain, respectively; $[R_p]_0$ is the maximum concentration of the propagating macroradicals in the system; $[M]$ is the current monomer concentration. Therefore, the rate decrease for each experiment represented in figure 6 should give a line in the coordinates $-\ln W$ against t, while the K_t value can be determined by the slope of the curves.

Actually, a decrease of the polymerization rate for all the peaks shown in figure 6 is readily rectified in the given coordinates (figure 7). As, upon the change of the initial concentration of tetrafluoroethylene, the calorimetric peaks of polymerization are observed in different temperature regions, the K_t values are determined by the slope of the curve (figure 7) for different temperatures. Based on these data we have obtained a temperature dependence of K_t. Thus, for the temperature interval of 110–155 K we have $K_t = 0{\cdot}1 \exp(-800/RT)\,\mathrm{s}^{-1}$. Having integrated the equation (1) we obtain an expression for varying the polymer yield in time. From this expression it is easy to obtain a limiting yield Q_∞ (at $t \to \infty$) of the polymer formed on reaching the maximum polymerization rate: $Q_\infty = 1 - \exp([R_p]_0 K_p/K_t)$. The value of Q_∞ can be easily determined by calorimetric measurements. Thus the $K_p[R_p]_0$ value has been calculated from every experiment and the temperature dependence of the propagation rate constant determined. The propagation activation energy $E_p = 14\,650 \pm 2100\,\mathrm{J\,mol^{-1}}$.

It should be noted that the postpolymerization technique in devitrification which has been subsequently widely used to study the kinetic measurements for different elementary polymerization processes will be given in the paragraphs to follow.

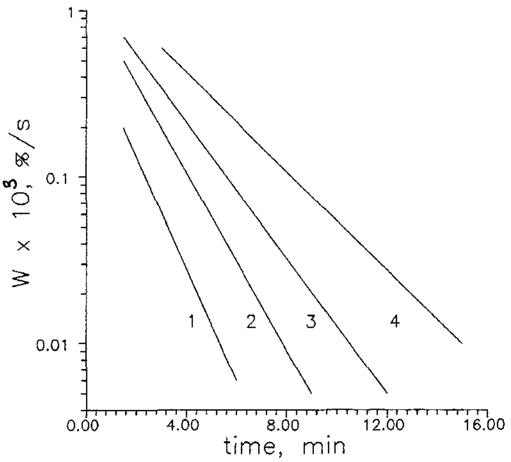

Figure 7. Variation of the tetrafluoroethylene polymerization rate, W, in time (see in the text equation (1) for the rate decrease) for different initial monomer concentrations: (1) 1%, (2) 2%, (3) 17%, (4) 25%.

3.2. *Chain transfer*

Thus, an intensive polymerization is observed in the process of defreezing of glass monomers during devitrification of the system and its transition to the state of viscous supercooled liquid. Characteristic of this process are large, in comparison with a usual liquid, times of mutual contact of reagents and absence of termination of propagating polymer chains in a certain temperature range. It seems likely that under such conditions polymer products with rather high molecular masses should form. In reality, nothing of the kind is observed. We may suppose that even at these low temperatures the reaction of chain transfer through monomer or solvent may play a marked role limiting the polymer chain length due to the large time of mutual contact of reagents. The chain transfer is thought to be a reaction of, for instance, detachment of hydrogen from the monomer or solvent by a propagating macroradical to form an inert macromolecule and a radical initiating propagating of a new polymer chain.

In [23] a study was undertaken of polymerization on devitrification of radiolysed glass solutions of acrylic acid, acrylamide and methylacrylate in ethanol. If the stage of chain transfer plays an important role in the polymerization process, then an average length of a kinetic chain will be sufficiently greater than an average length of a polymer chain. As has been said above, the ESR method allows us to measure directly the concentration of propagating polymer radicals for the systems in question. Therefore, knowing the polymer yield and the number of propagating macroradicals it is easy to determine an average length of a kinetic chain (P_k). This value should be compared with an average length of a polymer chain (P_p) obtained by viscosimetric measurements of molecular mass for polymers produced. It was found out that in case of acrylamide polymerization P_k is one hundred times as large as P_p. Such an inconsistency can be understood only in terms of an effective chain transfer.

Therefore, the destruction of polymer chain in a narrow temperature range is absent in the process of polymerization during devitrification, and the chain transfer can also proceed effectively there. [24] Actually reports on a remarkably sensitive system with kinetic chains of $\geqslant 10^7$. This is a glass solution of acrylamide in glycerine. When this solution, radiolyzed at 77 K, is being defrozen, the transition from a glass to an

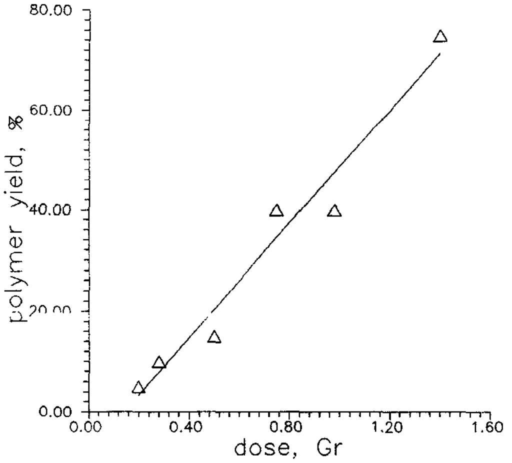

Figure 8. A relation between the polymer yield and a pre-irradiation dose at 77 K for a glass 15% solution of acrylamide in glycerine.

supercooled liquid is observed at $T_g \cong 190\,\mathrm{K}$. The subsequently effective monomer polymerization proceeds in the temperature range of 220–260 K. To realize the polymerization in this system an extremely small dose of irradiation, about 0·3 Gy, is needed. The dependence of the total polymer yield on the dose of preirradiation for this system is shown in figure 8. The polymer yield has been calculated by calorimetric measurements and by an amount of the polymer produced in the reaction. The difference between these two methods of yield determination is not more than ±5%.

An ESR technique has been used to record the number of propagating polymer radicals and to calculate their radiation-chemical yield. The system has been found to form about $0{\cdot}6 \pm 0{\cdot}2$ macroradicals per 100 eV accumulated energy. Therefore, the kinetic chain length is 10^7, i.e. one act of chain generation leads to conversion of more than 10 million monomer molecules. We don't known any other polymerization processes even at room temperature that are so sensitive to initiating radiation.

3.3. *Radicals activity in the propagating polymer chain*

It was established [25] that in the polymerization during devitrification of alcoholic solutions the reactivities of acrylic and methacrylic derivatives differ sharply. The main factor responsible for low translational mobility of macroradicals in a supercooled liquid (the temperature range of live-chain polymerization) is an interaction of a macroradical with alcohol molecules which is due to a specific non-equilibrium conformation of a propagating centre [13, 14]. It was found out that no non-equilibrium conformation of a propagating radical formed in a polymerization of methacrylic acid and its analogous derivatives is not higher than 3–5%. The relative concentrations of propagating polymer radicals for all the monomers investigated appeared to be very close. Therefore, a sharp difference between the rates of polymerization for acrylic and methacrylic derivatives is not connected with the difference in the effectiveness of initiation.

As the polymer chain is propagating, its translational mobility falls sharply, hence, the possibility of termination falls too. Figures 9–11 show that the concentration of propagating polymer radicals of acrylic acid and its derivatives remains constant in a

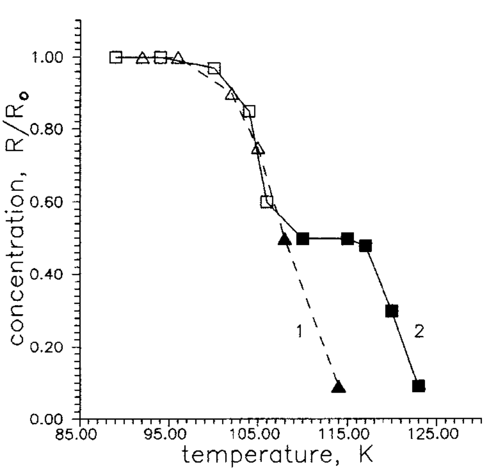

Figure 9. Variation of the relative concentration of radicals during defreezing of radiolyzed glass solutions (17%): (1) of metharylic and (2) acrylic acids. Dark points propagating radicals. An initial concentration of radicals $R_0 \simeq 1 \times 10^{18}\,\mathrm{cm}^{-3}$.

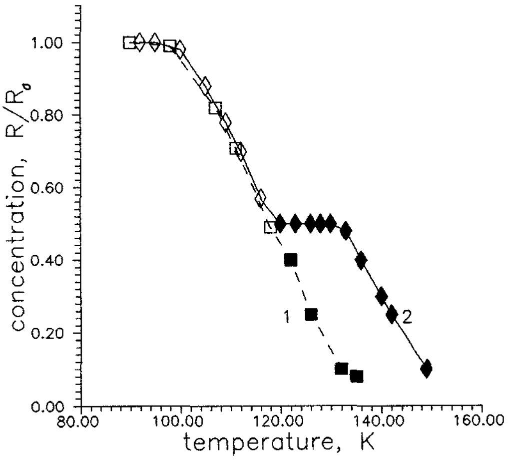

Figure 10. Variation of the relative concentration of radicals during defreezing of radiolysed glass solutions (17%): (1) of metharylamide and (2) acrylamide. Dark points are propagating radicals. An initial concentration of radicals is $R_0 \simeq 1 \times 10^{18}\,\text{cm}^{-3}$.

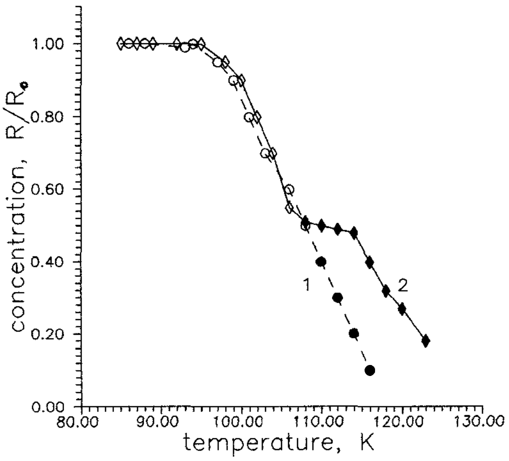

Figure 11. Variation of the relative concentration of radicals during defreezing of radiolysed glass solutions (17%): methyl ethers (1) of metharylic and (2) acrylic acids. Dark points are propagating radicals. An initial concentration of radicals is $R_0 \simeq 1 \times 10^{18}\,\text{cm}^{-3}$.

certain temperature range. The same temperature range also shows an effective polymerization.

Quite another picture is observed in the case of methacrylic acid and its derivatives. The arising propagating radicals possess sufficient translational mobility, are not stabilized and readily recombine (figures 9–11). To learn the reason of such a sharp difference in termination rates we studied the structure of ESR spectra and found the conformation of terminal propagating macroradicals by hyperfine splitting on β-protons. The propagating radicals of acrylic acid and its derivatives appeared to have a specific conformation different from that characteristic of polymerization of monomers in the crystalline state [26]. The ESR spectra of propagating macroradicals in the polymerization of methacrylic acid in a supercooled alcohol and its own crystalline

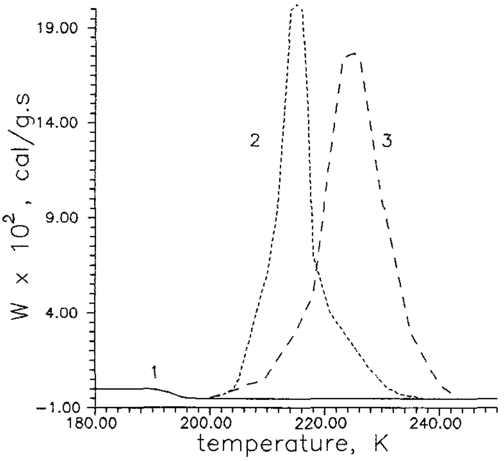

Figure 12. Calorimetric curve of defreezing: (1) of a glass solution of a 15% acrylic acid in glycerine; 15% solution in glycerine of acrylic (2) and methacrylic (3) acids pre-irradiated by ^{60}Co γ-rays at 77 K with a 1 kGy dose. The rate of defreezing 0·018 K s^{-1}. An initial concentration of radicals $R_0 \simeq 1 \times 10^{18}$ cm^{-3}.

matrices are practically identical and are accounted for by hyperfine interaction (splitting $\Delta H = 20$ e) with the protons of a rotating CH_3 group and one of the polymer chain β-protons.

It follows that the presence of a CH_3 group in the vicinity of the reacting centre interferes with the interaction of a propagating macroradical with an alcohol matrix: no alcohol 'coat' is formed to prevent their recombination. It is obviously the main reason of sharp differences in the rates of polymerization of acrylic and methacrylic monomers in devitrification of their alcoholic solutions.

Thus, as distinct from the usual liquid-phase polymerization, the polymerization in devitrification gives a sharp difference in the polymerization activity of acrylic and methacrylic monomers, which is connected with a stronger interaction of propagating acrylic macroradicals with the medium. It was natural to assume that the polymerization abilities of acrylic and methacrylic monomers should become closer with an increase of the matrix devitrification temperature (i.e. the region where the postpolymerization proceeds effectively). This assumption was confirmed experimentally [27]. The postpolymerization in devitrification of acrylic and methacrylic derivatives dissolved in glycerine was studied. On cooling, these solutions fully passed to the glass state, while at defreezing they devitrified at $T_g \approx 190$ K. As is seen from figure 12, the postpolymerization in devitrification of radiolyzed glycerine solutions of acrylic and methacrylic acids proceeds quite effectively. Thus, the sharp difference in the reactivity of acrylic and methacrylic monomers is registered only in the region of rather low temperatures.

4. Ionic polymerization

A sharp change of the matrix physical properties in the transition through the devitrification region cannot but affect the dynamics of polymer chain development by the cationic or anionic mechanism. As the low-temperature radiolysis in glasses leads to stabilization of not only radicals but captured electrons and holes as well, the possibility for the reaction to proceed by the ionic or by the radical mechanism seems to be the same. Here we should mention shortly the history of study of the radiation-induced polymerization by the ionic mechanism. There is evidently nothing to prevent the examination of this process, since it is the ions that are the main initial products of the radiolysis. However, by the time when the radiation polymerization by the radical mechanism had been already extensively studied, the ionic radiation-induced polymerization in the liquid phase at room temperature failed to be carried out. Many painstaking efforts were needed to understand that the water traces in monomers and solvents were the strongest inhibitors of this process. The application of complicated techniques of preliminary dewatering of reagents led at last to a success.

We might suppose that in case of a postpolymerization regime in devitrification of the matrix no special methods of drying the monomer and the solvent were required as the polymerization proceeded at quite low temperatures. In this temperature region the lifetime of ions increased, and the water traces were isolated in their own crystal phase and could not inhibit the polymerization.

4.1. *Polymerization of cyclopentadiene*

The choice of cyclopentadiene was caused by the fact that earlier [28] we observed its cationic polymerization under ^{60}Co γ-radiation at 195 K. When cooled to 77 K the pure monomer fully passed to the crystal state. When such a sample was heated in a calorimeter, we observed only an endothermic melting peak at 180 K. The melting heat was $8{\cdot}0 \pm 0{\cdot}3\,\mathrm{kJ\,mol^{-1}}$. No postpolymerization of a polycrystalline radiolyzed cyclopentadiene sample was observed.

Butyl chloride was chosen as a vitrifying matrix since the centres of the cationic nature arising on radiolysis were readily stabilized in it. On fast cooling, the cyclopentadiene solutions in butyl chloride passed fully to the glass state. At 97 K this glass passed to a viscous supercooled liquid that crystallized on heating at $\cong 128$ K, and then melted at 140 K.

Heating of a γ-irradiated at 77 K glass solution of cyclopentadiene (20%) in butyl chloride results in an effective monomer polymerization [29, 30]. Heat release connected with a cyclopentadiene polymerization is observed in a narrow temperature region just after the transition of the system from a glass to a supercooled liquid (figure 13). No polymerization is observed upon crystallization and melting of the system. For 95–110 K, the specific heat of the polymerization, found in a series of experiments, was $\Delta H = 58{\cdot}8 \pm 4\,\mathrm{kJ\,mol^{-1}}$. Note that the polymer yield increased with an increase of a pre-irradiation dose reaching the limiting value at rather small doses of $\simeq 30$ kGy. The kinetics of accumulation of stabilized centres of the ionic nature in the course of low-temperature radiolysis has the same character.

To prove the ionic character of the cyclopentadiene postpolymerization under these conditions we studied an affect of preliminary photo bleaching of a radiolyzed sample. With this purpose in view, the radiolyzed sample was illuminated with a mercury lamp within several hours at 77 K. In the course of such bleaching the dark colouring of the sample connected with the presence of stabilized charges gradually disappeared and it became colourless. The concentration of stabilized radicals in the sample, however, as a result of that bleaching, practically did not change. Upon heating of the bleached sample in a calorimeter, no heat release connected with cyclopentadiene postpolymerization was observed, and no polymer was formed after heating. Hence, no radical polymerization of a monomer took place under those conditions. Here, cations and cation-radicals stabilized in the low-temperature radiolysis of butyl chloride [31] were obviously the centres initiating the cyclopentadiene postpolymerization.

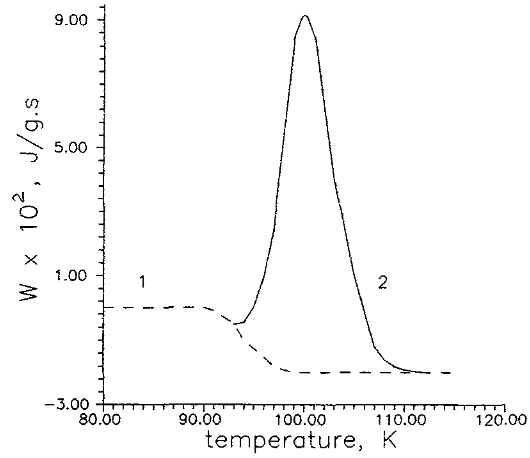

Figure 13. Calorimetric curve of defreezing: (1) 20% solution of cyclopentadiene in butyl chloride and (2) of the same solution, but pre-irradiated at 77 K with a 50 kGy dose. The rate of defreezing is 0·018 K s^{-1}.

The compounds containing atoms with a lone electron pair, e.g., alcohols, are known to inhibit the cationic polymerization. Actually, in the case of a cyclopentadiene postpolymerization in devitrification of a butyl chloride matrix, an introduction of small quantities of a typical, cationic inhibitor, ethanol, into the system (1–5%) leads to suppression of the polymerization.

Thus the use of the postpolymerization method in matrix devitrification allows one to carry out an effective cationic polymerization of cyclopentadiene. The peculiarity of this process is the absence of any special requirements to the drying of a monomer and a solvent.

4.2. *Polymerization of ethylene oxide*

Ethylene oxide is readily polymerized with the opening of the epoxy cycle by the cationic or anionic mechanism in the presence of a large number of catalysts. However, the epoxy cycle appeared to be rather stable to the action of high-energy radiations. The attempts to carry out a radiation polymerization of ethylene oxide in the solid and liquid phases proved unsuccessful and led only to formation of polymer traces, while the radiation yield of monomer molecules consumption for polymer formation did not exceed $G(-M)\simeq 10$ [32]. A radiation-initiated effective polymerization of ethylene turned out well using a postpolymerization regime in devitrification of the butyl chloride matrix [30, 33].

Solutions of ethylene oxide fully pass to the glass state on their freezing in butyl chloride (from 0 to 80%). As distinct from a crystal monomer, heating of γ-irradiated at 77 K glass solutions of ethylene oxide in butyl chloride leads to an effective polymerization. Heat release connected with the ethylene oxide postpolymerization occurs in the temperature range of glass softening at ≃96 K. Here the total polymer yield is to a great extent dependent on the concentration of ethylene oxide in the initial solution (figure 14). A sharp increase of the polymer yield at low initial concentrations of ethylene oxide in the starting solution is assumed to be caused by an increase of an average chain length.

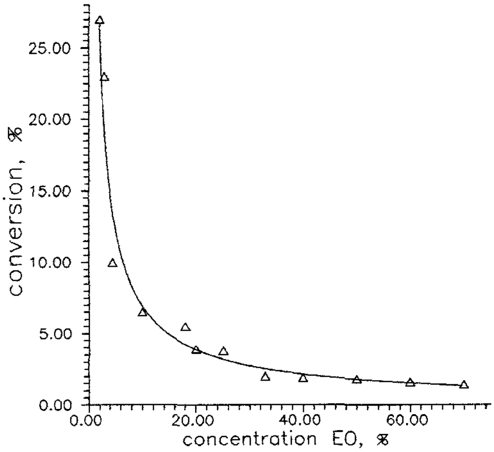

Figure 14. A relation between the polymer yield and the concentration of ethylene oxide in a glass solution of butyl chloride. A pre-irradiation dose 80 kGy at 77 K.

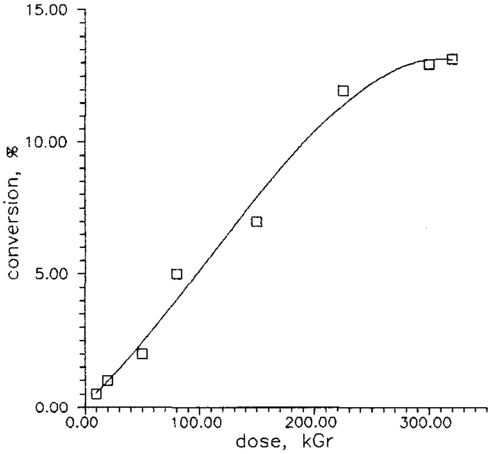

Figure 15. A relation between the polymer yield and a pre-irradiated dose at 77 K. The concentration of ethylene oxide in the initial solution of butyl chloride is 17%.

As the dose of pre-irradiation grows, the polymer yield practically linearly increases up to the dose of 350 kGy (figure 15). The following confirmations of the cationic mechanism of ethylene oxide polymerization have been obtained in the given conditions.

(1) Photobleaching of radiolyzed samples (similar to that described above for glass solutions of cyclopentadiene) leads to a sharp suppression of postpolymerization.
(2) Additions of small quantities of ethanol and pyridine (typical cationic inhibitors) fully inhibit postpolymerization.
(3) Additions of $\simeq 2\%$ hydroquinone—a typical inhibitor of radical polymerization—in the starting solution do not affect the process of postpolymerization in devitrification.

In case of radical postpolymerization in matrix devitrification, as has been mentioned above, in a certain temperature interval, no termination of growing polymer chains occurs, hence, naturally, an increase of the period of time during which the system is within this temperature interval (a decrease of heating rate) leads to the growth of the integral polymer yield. In case of ionic postpolymerization, a decrease of the heating rate of γ-irradiated samples in the calorimeter from 0·6 to 0·009 K min^{-1} does not result in any marked increase of polymer yield. The polymerization of ethylene oxide proceeds in a very narrow temperature interval of 10 K, the total activation energy of the process being $E \cong 58{\cdot}5\,\mathrm{kJ\,mol^{-1}}$. Hence, the process is limited by defreezing of the matrix molecular mobility in glass softening.

Infrared spectra of the polymer isolated that are similar to those known in the literature have been obtained. Thus, as distinct from other ways of radiation polymerization of ethylene oxide, the use of a postpolymerization method in matrix devitrification makes it possible to carry out an effective polymerization of ethylene oxide with the opening of an epoxy cycle. The postpolymerization proceeds by the cationic mechanism and does not require any special methods of drying a monomer and a solvent.

Therefore, the polymerization by the ionic mechanism, as well as the radical polymerization in devitrification, proceeds in a certain temperature range without chain termination. In the case of the ionic mechanism, however, this temperature interval is even narrower, as the process is only limited by defreezing of the matrix molecular mobility.

5. Copolymerization

When the copolymerization is carried out in the liquid and gas phases, the copolymer composition is determined by mutual reactivity of comonomers, a homogeneous copolymer resulting only at the initial polymerization stage. As one of the monomers is consumed, the resulting copolymer, as a rule, is enriched with a less reactive monomer, the polymer chains having a heterogeneous composition.

The copolymerization in devitrification for systems 'monomer-complexing agent' was studied in [34–38]. A complex with charge transfer, for example, gives sulphur dioxide with dimethyl-butadiene, the latter system on fast cooling forming glass. During defreezing of such a radiolyzed glass an intensive copolymerization is observed in the devitrification region. Here an alternating copolymer of a 1 : 1 composition is formed. The alternating mechanism consists in addition of a complex of monomers to the end of the propagation chain [38]. Thus, in these systems the homopolymerization of a monomer complex is investigated, and no specific influence of the reaction conditions on the composition of a copolymer formed is detected.

As has been mentioned above, a comparatively high viscosity of the supercooled liquid state resulting on matrix devitrification is a distinctive feature of this state. The time of mutual contact of reacting particles in this highly viscous supercooled liquid is much greater than in the gas or liquid phases, while the frequencies of monomer addition to the active centre of a propagating polymer chain in the order of magnitude is comparable with the frequencies of translational movements [13]. Taking this into consideration it is expected that the copolymer composition obtained under these conditions can be regulated by the composition of the initial mixture of monomers and it is possible to get a homogeneous, by its composition, copolymer at any degree of conversion.

Copolymerization during devitrification of radiolysed alcohol solutions in the absence of complex formation was studied in [39]. The copolymerization was studied for two pairs of copolymers: acrylic acid with acrylamide and acrylamide with methylacrylate. At a total concentration of comonomers in ethanol of 17% the solution, on cooling, turns to the glass state. During heating this glass passes to a supercooled liquid at $T_g \simeq 102$ K that does not crystallize passing to an equilibrium liquid. When changing the monomers ratio (their summary concentration in solution being constant) in a wide range the form of the calorimetric curve does not change. Thus within the whole temperature interval of 77–300 K and the change of monomers ratios from 1 : 8 to 8 : 1, they remain uniformly distributed over the whole volume of the sample like it is in a liquid solution.

On devitrification of such radiolysed solutions, an intensive heat release connected with the proceeding of copolymerization is observed. The copolymer yield increases monotonously with an increase of a preirradiation dose and reaches $\simeq 95\%$. The copolymerization can be interrupted at any required degree by fast ($\simeq 250$ K min^{-1}) heating of the sample up to room temperature. It turns out that on changing the copolymer yield from 1 to 90% the composition of the copolymer formed practically does not change (figure 16). Meanwhile, the copolymer composition in systems 'acrylamide–acrylic acid' and 'acrylamide–methylacrylate' may be varied simply by changing the monomer ratio in the solution. That means that the copolymer composition depends only on the initial solution composition. This conclusion was confirmed experimentally.

Thus the process of copolymerization in an supercooled viscous liquid produced on devitrification of alcohol solutions of monomers makes it possible to produce homogeneous copolymers and to control their composition. In a viscous supercooled liquid, the composition of a copolymer formed is determined by an initial concentration of the comonomer and not by their mutual reactivity. As the time of mutual contact of reagents under these conditions is considerably greater than in an ordinary equilibrium liquid, the addition of a monomer to an active centre of a propagating polymer chain

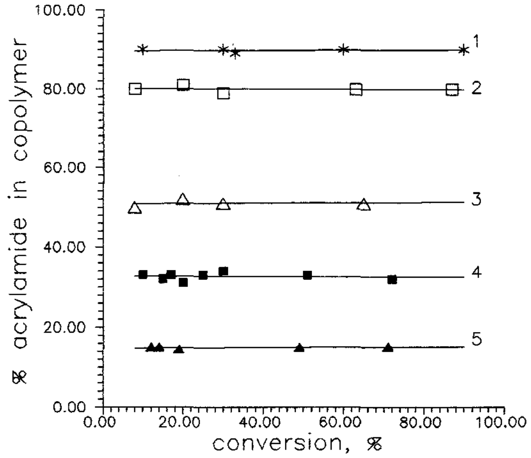

Figure 16. Acrylamide content in copolymer against conversion degree for a 17% solution of comonomers in ethanol. Copolymerization in vitrification, a pre-irradiation dose at 77 K 0·85 kGy. Acrylamide–acrylic acid ratio: (1) 9 : 1; (2) 4 : 1; (3) 1 : 1; (4) 1 : 2; (5) 1 : 5.

takes place practically at each collision. This is what accounts for the coincidence of the composition of the initial solution and the copolymer.

It is this increase of the mutual contact time of reagents in the supercooled liquid that allows us to hope that during devitrification the compounds usually not looked upon as monomers can be involved into copolymerization. An interesting example of such a copolymerization during devitrification is the system 'acetone–acrylic acid' [40]. The polymerization of acetone by a carbonyl group was first reported in [41]. Later on polyacetone was also produced by a solid-phase radiation-induced polymerization [42]. This polymer proved to be very unstable and quickly decomposed to a monomer even at room temperature. Thermostable copolymers of acetone with acrylic acid were obtained using a copolymerization technique in devitrification [40].

On slow defreezing in the calorimeter of a glass solution of acrylic acid in acetone irradiated at 77 K a heat release connected with the polymerization was observed immediately after the system had passed to a supercooled liquid (≈ 110 K). After defreezing up to room temperature the separation of a polymer was carried out that completely excluded the possibility of physical retention of unreacted acetone. The quantity of unreacted acrylic acid was determined by titration, the polymer yield was calculated according to the quantity of acrylic acid coming into the polymer. In diluted acetone solutions of acrylic acid the yield of the polymer separated reached 250%. Therefore, the polymer product contained two acetone molecules per one molecule of acrylic acid. With an increase of the acrylic acid concentration in the initial solution the polymer yield decreased fast down to 130–140% and then in a wide range of concentrations did not depend on the composition of the initial solution. Introduction binding of acetone in the copolymer composition was also observed when the system was irradiated in the liquid state at 195 K [43]. Various mechanisms of acetone connection with a polymer product were examined. The copolymerization of an acetone enol form was assumed to be most probable.

Thus the specificity of a supercooled liquid state, reflecting itself in a considerable increase of the mutual contact time of reagents leads to a radical change in the notions of mutual reactivity of comonomers. That opens new experimental possibilities of influence on a copolymerization process.

6. Graft polymerization

Not only low-molecular compounds, but also polymers may be used as devitrifying matrices. As will be clear from the following, for glass monomer solutions in a polymer matrix qualitatively the same picture is observed as for the polymerization at devitrification of low-molecular matrices. However, whereas in the case of the polymerization in divitrification of alcohol monomer solutions, in order to decrease the probability of propagating chain termination, it was necessary that macroradicals formed before passing to a supercooled liquid; in the case of a polymer matrix this condition was satisfied automatically.

On freezing down to 77 K, polyisobutene passes to the glass state [43]. At low concentrations the monomers dissolved in it, e.g., acrylonitrile, pass to the glass state without phase separation. No melting peak of an individual monomer can be observed on a calorimetric curve of devitrification of such a solution, although the calorimeter sensitivity is quite satisfactory (figure 17). Therefore, for these monomer concentrations the system is a solution over all the temperature range. At higher concentrations, a part of the dissolved monomer during freezing forms a separate phase, the calorimetric

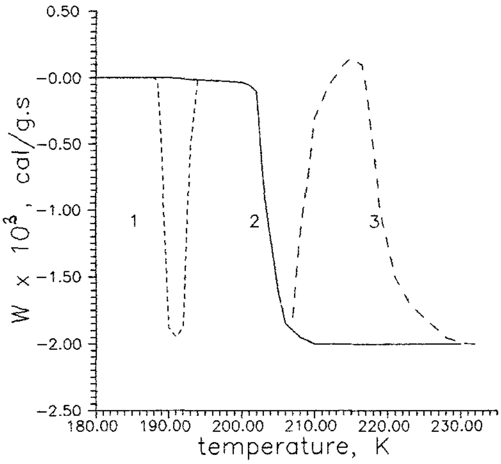

Figure 17. Calorimetric curves of defreezing: (1) of a 2% solution of acrylonitrile in polyisobutylene, (2) of polyisobutylene, (3) of a 1% solution of acrylonitrile in polyisobutylene irradiated at 77 K with a 50 kGy dose.

curve showing a melting peak of the monomer (figure 17). It should be noted that the calorimetric technique in the present case is very convenient to determine the monomer solubility limit in a polymer at such low temperatures.

As for the monomers glassed in an alcohol matrix, an intensive polymerization (figure 17) is registered also for radiolyzed glass solutions of monomers in a polymer in the devitrification region. In the course of a low-temperature radiolysis of such systems, there occurs mainly a stabilization of macroradicals in a polymer matrix. In the transition of a polymer matrix from the glass to the viscous-elastic state the stabilized macroradicals acquire sufficient mobility to initiate a polymerization of an introduced monomer, i.e. a graft polymerization takes place.

The use of the graft technique in polymer matrix devitrification proves to be very convenient for readily polymerized monomers, such as tetrafluoroethylene [44,45]. The ordinary methods of joint radiolysis of a monomer and a polymer are hindered as in this case the monomer homopolymerization becomes a predominating process.

7. Chlorination of saturated hydrocarbons

Chain chlorination of paraffin hydrocarbons and their chloroderivatives in the gas and liquid phase in photo and radiational initiation has been studied in every detail [46]. However, all these investigations did not affect the specificities of the processes in solid and viscous media. It has appeared that the specific characteristics of the chain process in matrix devitrification demonstrated above are qualitatively preserved for the reactions, such as chlorination of paraffins.

7.1. *Radiation chlorination in the transition of the system from a glass to a liquid*

The specificity of low-temperature radiation chlorination in glass matrices was studied for the system 'butyl chloride–molecular chlorine' [47]. Consider the calorimetric analysis of the phase composition of the system. In the temperature range of 77–200 K the solid has no phase conversions and melts at 172 K. Butyl chloride on fast cooling down to 77 K fully passes to the glass state, the transition from the glass to the supercooled liquid state being observed on defreezing in the 96–98 K range. At further temperature increase, there occurs crystallization of the sample, and then its melting at 150 K. Dissolution of molecular chlorine in butyl chloride is performed in the dark at 180 K, and no chemical reaction proceeds at that time. This solution also passes to the glass state on freezing. The simplest picture of phase conversions is observed for the solution with the ratio of one mole of chlorine per three moles of butyl chloride. This solution does not crystallize after devitrification and, hence, does not melt. Therefore, ther is no phase separation at such ratios in a vitrifying solution. This fact is quite important, since in the case of a homogeneous one-phase system the interpretation of kinetic data is simplified significantly. That is why the solution of this very concentration is chosen for further kinetic investigations. A heat effect of the $C_4H_9Cl + Cl_2 \rightarrow C_4H_8Cl_2 + HCl$ reaction in the field of ^{60}Co γ-radiation at 114 K was determined in a series of separate experiments. It appeared to be $Q = 33 + 3\ \mathrm{kcal\,mol^{-1}}$ of chlorine used. This value was further used to calculate the kinetic curves based on calorimetric measurements.

Radiation chlorination of butyl chloride proceeds, although with low rate, already at the temperature below the devitrification region. When the system passes from the glass to the supercooled liquid state, the reaction rate is accelerated considerably. A distinctive feature of the processes in this temperature range is a practically linear increase of the chlorination rate with time. This is quite understandable, as in a viscous supercooled liquid in the course of irradiation the concentration of active centres rises, the destruction of the latter being hindered. Really, when the initiated γ-radiation is switched off, the reaction rate decreases, but very slowly, with time. The characteristic time of chlorination rate decreases was determined after switching off of γ-radiation, $\tau \simeq 1500$ s. Therefore, the life time of active centres under these conditions is great. It is this fact that accounts for the non-steady-state character of the process kinetics—the accumulation of active centres during radiolysis leads to an increase of the process rate with time.

The most intensive is chlorination at 114 K. On further temperature increase the supercooled liquid viscosity decreases considerably, which results in a sharp decrease of the lifetime of active centres. Already at 127 K, after switching off ionizing radiation, the steady-state rate of the process is reached. An increase of the probability of chain termination leads to a decrease of the total rate of the process with a temperature increase.

Radiation-induced low-temperature chlorination of butyl chloride can be described by the following simple scheme:

$$ClRH \rightarrow ClR^{\cdot} + H, \tag{1}$$

$$ClR^{\cdot} + Cl_2 \rightarrow ClRCl + Cl, \tag{2}$$

$$Cl + ClRH \rightarrow ClR^{\cdot} + HCl, \tag{3}$$

$$\left.\begin{array}{l} Cl \rightarrow \\ ClR \rightarrow \end{array}\right\} \text{termination.} \qquad (4,5)$$

In the temperature range of 98–114 K the termination of kinetic curves proceeds very slowly, $1/\tau \simeq 6{\cdot}6 \times 10^{-4}\ \mathrm{s^{-1}}$. According to the data [48], for photochemical chlorination of C_2H_5Cl in some temperature range the reaction rate constant (2) may be several orders of magnitude higher than the reaction rate constant (3). Therefore, reaction (3) will limit the process under study. For the initial rate of the process, when chain termination may be ignored, the following expression is derived:

$$W_0 = \mathrm{d}[\mathrm{ClRH}]/\mathrm{d}t \simeq k_3 g I t [\mathrm{ClRH}],$$

where g is the radiation yield of the centres initiating chlorination, and I is the γ-radiation intensity. Using this expression for the initial regions of the kinetic curves the value and temperature dependence of k_3 are determined. This dependence is shown in figure 18. Assuming $g \simeq 1$ for the interval of 98–114 K we get the following expression for $k_3 \simeq 10^{11} \exp(-5600/RT)\,\mathrm{l\,mol\,s}$.

At higher temperatures, as was already mentioned, the termination rate increases sharply, and the steady-state rate of the process is reached quickly. Assuming that the termination of kinetic chains occurs mainly by reaction (5), we deduce the following for the steady-state chlorination rate:

$$W_{\mathrm{st}} = -\mathrm{d}[\mathrm{ClRH}]/\mathrm{d}t = k_3 g I [\mathrm{ClRH}]/k_4.$$

An analogous expression for the steady-state rate, with the same assumptions, was used in [49] to describe the process of radiation induced liquid-phase chlorination of tetradecane. Actually, in this temperature range the reaction rate quickly reaches the steady-state value and becomes independent of time. A series of experimental measurements in the range of 107–150 K led to the expression of the termination rate constant:

$$k_4 \simeq 10^{12} \exp(-7400/RT)\,\mathrm{s}^{-1}.$$

Therefore, the total activation energy of the chlorination process is $E = E_3 - E_4 = 5{,}6 - 7{,}4 = -1{\cdot}8\,\mathrm{kcal\,mol}^{-1}$. This very value characterizes the gross-process rate within this temperature interval (figure 18, line 3).

Thus, just like in the case of polymerization, the chain reaction of chloroparaffins chlorination in the supercooled liquid is characterized by a long lifetime of active centres. With a temperature increase in a supercooled liquid the propagation rate

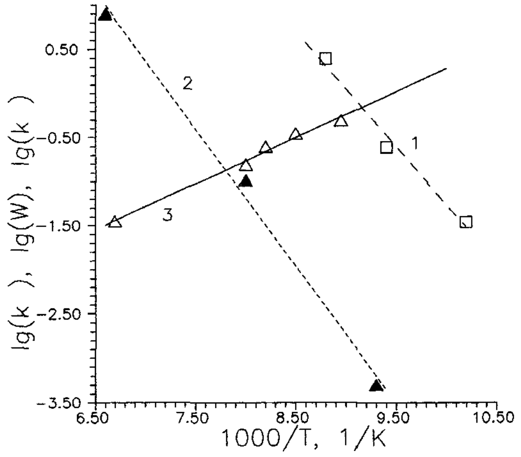

Figure 18. Temperature dependences of $k_3(\mathrm{l\,(mol\,s)}^{-1})$ (1), $k_4(\mathrm{l\,s}^{-1})$ (2) and the rates of radiation chlorination of butyl chloride in a 4% chlorine conversion $W(\times 10\,\mathrm{cal\,(mol\,s)}^{-1})$ (3). Dose rate $3\,\mathrm{Gy\,s}^{-1}$.

reaches a maximum, and when the system passes to a thermodynamically stable liquid and the medium viscosity drops sharply, the probability of chain termination rises. So we may conclude that suppression of chain termination while simultaneously ensuring an effective propagation of the chains—the regime that is automatically realized near the devitrification region of the system—makes it possible to increase the total reaction rate.

7.2. *Postradiation chlorination in matrix devitrification*

Kinetics of post-radiation chlorination for glass solution of chlorine in butyl chloride as well as the dynamics of conversion of active centres in this system were investigated in [50]. The investigations were carried out for solutions of molecular chlorine in butyl chlorine with the composition 1 : 3 (mol ratio). This system, as was mentioned above, passes completely to a glass on freezing, while on defreezing, the calorimetric curve registers only a transition from a glass to a supercooled liquid.

During heating in the calorimeter of γ-irradiated at 77 K glass solution of chlorine in butyl chloride a heat release connected with a process of chlorination is observed (figure 19). With an increase of a pre-irradiation dose the heat increase connected with chlorination begins at lower temperatures. For pre-irradiation doses of $\geqslant 100$ kGy the reaction already begins from ≈ 80 K. However, at such high doses the further reaction proceeds in the regime of heat explosion (figure 19, curve 4).

An ESR spectrum of active centres stabilized in the course of radiolysis of the system at 77 K is a superposition of the spectra of paramagnetic centres of two types. These are alkyl radicals R_a and ion-radicals $^{-}Cl_2$. The most probable process of R_a formation is a dissociative capture of a slow electron [51]:

$$H_3C\text{–}(CH_2)_2\text{–}CH_2Cl + \bar{e} \rightarrow H_3C\text{–}(CH_2)_2\text{–}\dot{C}H_2 + Cl^-.$$

Formation of Cl_2^- particles should be evidently connected with direct acceptance of $\bar{e}$:

$$Cl_2 + \bar{e} \rightarrow Cl_2^-.$$

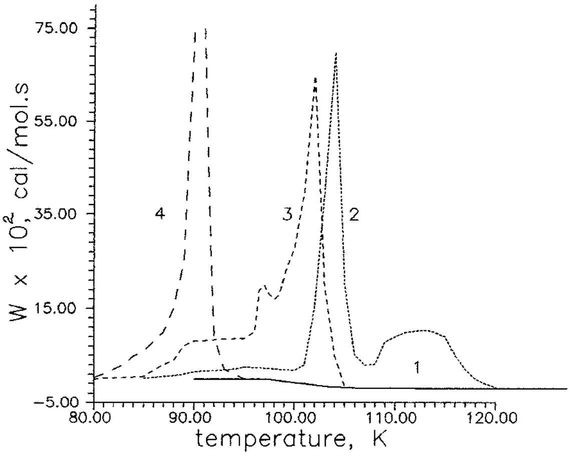

Figure 19. Calorimetric curves of defreezing of γ-irradiated at 77 K glass system 'butyl chloride–chlorine' (mol ratio 3 : 1): (1) an initial sample; (2) a sample irradiated with a dose of 4 kGy; (3) a sample bleached with light $\lambda > 700$ nm $\Phi = 10^{21}$ q cm^{-2} after irradiation with a 4 kGy dose; (4) a sample irradiated with a 202 kGy dose. Rate of defreezing 0·2 K min^{-1}.

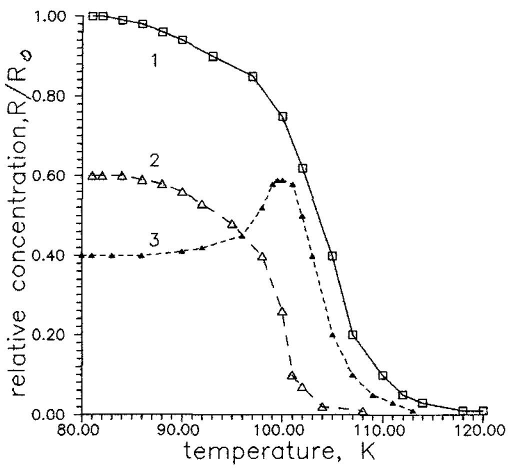

Figure 20. The temperature dependence of the relative concentration of paramagnetic centres in heating the radiolysed system 'chlorine–butyl chloride': (1) a total concentration of paramagnetic centres; (2) concentration of alkyl radicals R_a; (3) concentration of particles Cl_2^-. The sample irradiated at 77 K with a 5 kGy dose.

Really, on photolysis of this system by light with $\lambda > 360$ nm no formation of a particle Cl_2^- occurs, stabilized are only R_a radicals:

$$Cl_2 \xrightarrow{h\nu} 2Cl, \qquad Cl + H_3C\text{–}(CH_2)_2\text{–}CH_2Cl \rightarrow R_a + HCl.$$

To elucidate the mechanism of post-radiation chlorination a process of concentration variation of stabilized paramagnetic centres was studied during heating of the sample from 77 to 120 K. The sum concentration of the centres on heating up to ≈ 95 K decreases by only 20–30% (figure 20). In the temperature range of 95–105 K there is a sharp decrease of the concentration of alkyl radicals R_a, while the concentration of Cl_2^- increases and reaches its maximum at $T \approx 100$ K (figure 20).

In the temperature range of 80–100 K the fact that ion-radicals Cl_2^- do not participate in chlorination is evidently accounted for by the capture of chlorine atoms from the chlorination chain by non-paramagnetic chlorine atoms from the system by the reaction: $Cl + Cl^- \rightarrow Cl_2^-$. In this process about 30–40% of chlorine atoms participating in chlorination are captured.

When the system passes to a supercooled liquid, a sufficient molecular mobility is created for the more stable Cl_2^- particles to take part in the process of chlorination. Really, the maximum rate of the process is registered in this temperature region. Reactions of a Cl_2^- particle with organic molecules in the liquid phase were studied in [52].

The value and temperature dependence of the chain development constant k_3 for the temperature range of 80–96 K were determined: $k_3 \simeq 8 \times 10^{11} \exp(-6000/RT)(\text{mol s})^{-1}$, which is in a good agreement with the above constant determined directly in irradiation.

Cl_2^- is known to have an absorption band in the range of $\lambda = 700$–900 nm with a maximum at $\lambda = 750$ nm [53]. Bleaching of the radiolyzed system by this light leads to a decrease of Cl_2^- concentration with a simultaneous increase of the concentration of R_a radicals. Therefore, the reaction proceeds on photobleaching:

$$Cl_2^- \xrightarrow{h\nu} Cl + Cl^-.$$

A chlorine atom arising in this reaction leads to formation of an alkyl radical.

Thus, ions Cl^- and Cl_2^- diminish the effectiveness of the low-temperature radiation-induced chlorination considerably. Cl^- ions inhibit the process by capturing chlorine atoms from the chain and forming a less reactive particle Cl_2^-. A considerable difference between the low-temperature radiation and photo-chlorination is also connected with the same fact.

8. Conclusions

We hope that all the above that may be thought to be just another story of new 'rich lands' will prove to the reader the non-trivial peculiarities of low-temperature chemistry. It should also be mentioned that the method of carrying out a chemical reaction during matrix devitrification allows us to study actively the conversion of reagents at temperatures that are much lower than their melting point. In a crystal lattice a chain reaction is hindered due to the low translational mobility of reagents and the necessity of destruction of the lattice itself. At the same time, the selection of an appropriate vitrifying matrix makes it possible to carry out a chain reaction at quite low temperatures (much lower than melting points of their crystals). The chemical process carried out at the lowest possible temperatures is of exceptional interest as there is a certain choice between all possible reaction paths with a temperature decrease. At low temperatures, only the channel having the lowest activation energy will 'survive'.

Thus a decrease of the reaction temperature should result in high selectivity of the process. Besides, with a temperature decrease the entropy factors that are so important for the thermodynamics of chemical reactions should play here more and more insignificant roles, hence the equilibrium of all conversions should shift towards exothermic reactions, even those where high-order systems are formed.

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