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Chemical Chain Reactions in the Devitrification of the Matrix

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The results of studies of the mechanisms of chain reactions occurring in the devitrification of vitreous matrices are surveyed and the characteristics of the kinetics and the mechanisms of the chain reactions accompanying the devitrification process are examined: chlorination of hydrocarbons, polymerisation, copolymerisation, and graft polymerisation. The possible applied aspects of chain reactions in the devitrification of the matrix are also considered.
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I. INTRODUCTION

With decrease of temperature, the short-range order structure in a low-molecular-weight liquid or in a polymer varies continuously at a rate which depends on the relaxation time of the system. The rate of this rearrangement decreases as the temperature is reduced and at a certain temperature, called the glass point (T_g), the structure of the liquid or polymer is fixed and the substances passes to the vitreous state.

We may isolate two main factors which determine the probability of the conversion of a liquid into a glass rather than a crystal: a sufficiently high rate of cooling of the melt and a high viscosity in the range of crystallisation temperatures. A high viscosity of the melt retards the migration of the structural units and the relaxation time increases. Therefore at sufficiently high rates of cooling the equilibrium structure of the liquid corresponding to temperatures $T \geq T_g$ is "frozen". However, if the rate of cooling is reduced, the same liquid can be crystallised. On the other hand, typically crystallisable substances can be obtained, in principle, in a vitreous state at very high rates of cooling.

The ability of organic low- and high-molecular-weight compounds, to the reactions of which this review is devoted, to pass to the vitreous state is associated as a rule with a fairly intense intermolecular interaction in the liquid. The vitreous state is formed readily by alcohols (particularly dihydric and trihydric), amines, branched paraffins, and high-molecular-weight compounds.

The vitreous state is thermodynamically unstable but is in practice extremely stable owing to kinetic obstacles to the migration of structural units. When a vitreous substance is heated slowly in the devitrification region, there is a transition to a supercooled liquid thermodynamically unstable at the given temperature. This transition is accompanied by a fairly sharp increase in heat capacity. On the other hand, the viscosity of the system falls under these conditions. For a vitreous substance at $T \leq T_g$, the viscosity exceeds 10^{14} P, while transition to a supercooled liquid entails a fall of the viscosity to 10^7 P for silica and 10^2 P for alcohol. Naturally the sharp change in molecular mobility in the medium over a narrow temperature change should lead to extremely specific features of the mechanism of a chain reaction occurring under these conditions.

Among the chain reactions developing against the background of such a rearrangement of the matrix, polymerisation has aroused most interest among investigators. As early as 1962, it was shown[1] that vinyl acetate can be obtained in both vitreous and crystalline states. On the other hand, the rates of polymerisation under identical conditions proved to be higher by an order of magnitude for vitreous vinyl acetate than for the crystalline substance. High rates of polymerisation of vinyl monomers have been noted for the postradiation polymerisation in vitreous solutions in liquid paraffin and other solvents capable of forming a glass. The results of this series of investigations have been described in reviews[2,3]. Extremely high rates of polymerisation on devitrification of the matrix have been demonstrated for a large number of vitreous solutions of various vinyl monomers. Chapiro[2] suggested that such high rates of polymerisation at comparatively low temperatures ($T_g \cong -100°$ to -150 °C) are associated with the fact that in a vitreous matrix the monomer exists in the form of liquid microdrops incapable of forming crystals. Therefore, in spite of the very low temperatures, polymerisation takes place in a liquid monomer. However, if this hypothesis were valid, then the temperature dependence of the rate of polymerisation would undergo no sharp changes on passing through the matrix vitrification region. Nevertheless, it was shown in Chapiro's later study[3] that in all the instances investigated there is a sharp maximum in the rate in the region of the devitrification of the matrix.

In general a significant deficiency of all the early studies was the use of the traditional gravimetric method for the determination of the yield of the polymer and of the corresponding rate of polymerisation. As a result of the application of this method, the yield of the polymer, for example, at temperatures in the devitrification region, was inferred from measurements carried out at room temperature after the disintegration of the matrix. On the other hand, quantitative kinetic studies, necessary to understand the mechanisms of the chain reactions on devitrification, required primarily the development of methods whereby one could follow the process directly at the instant of its occurrence and not after its completion and disintegration of the surrounding matrix. In the first place, direct measurements of the rates of reaction, the rate constants for the elementary steps, and their temperature variations were necessary. Phase analysis of the two-component "monomer–vitrifying matrix" system, the

determination of the limits of miscibility at the glass temperatures of the system, and finally the determination of the vitrification region itself were needed in each specific instance.

Further advances in the study of the mechanisms of chain reactions on devitrification are associated mainly with the employment of the calorimetric technique in which the above methodological problems have been solved successfully. The application of the EPR method, which made it possible to follow the conversion of the active centres in radical processes directly at the instant of their occurrence, both qualitatively and quantitatively, also proved to be very fruitful. The latest advances in research into the characteristics of chain reactions on devitrification, associated mainly with the application of calorimetry and EPR, will be examined in this review.

II. DESTRUCTION OF RADICALS

Stabilised active centres accumulate in vitreous substances during their low-temperature radiolysis ($T < T_g$). Translational migrations (leading, for example, to the encounter and recombination of radicals) are greatly hindered in both crystalline and vitreous solids. This factor is in fact responsible for the comparatively high limiting concentrations of radicals which can be attained in the low-temperature radiolysis. On the other hand, the transition of the matrix to the liquid state on fusion of the crystals or to a supercooled liquid on devitrification leads to a sharp decrease of the viscosity of the system and an increase of the rate of translational movements and consequently of the rate of recombination of the radicals accumulated.

We shall consider this process in greater detail in relation to the destruction of stabilised radicals in radiolysed methanol[4]. On freezing, pure methanol crystallises and the vitreous state is not observed. However, the addition of small amounts of salts soluble in methanol such as $CoCl_2$, leads to the transition of these solutions to the vitreous state when the rate of cooling is sufficiently high. The use of differential scanning calorimetry[5] makes it possible to follow the phase transformations of the given system. When a solution of $CoCl_2$ in methanol is heated in the calorimeter in the region of the devitrification of the system (110–115 K), a sharp change in the heat capacity of the system is observed—there is a "step" (Fig.1, curve *a*). The solution then passes from the vitreous to the supercooled liquid state. On further increase of temperature, the thermodynamically unstable supercooled liquid crystallises. The crystallisation is accompanied by the evolution of heat (exothermic peak on curve *a* in Fig.1). Further heating leads to the fusion of methanol (endothermic peak). With increase of the $CoCl_2$ concentration in methanol, the viscosity of the solution apparently increases and the crystallisation of the supercooled liquid becomes increasingly more difficult. Thus, whereas approximately half of the methanol crystallises for a 2% concentration of $CoCl_2$, in 10% solution appreciable crystallisation and hence also fusion are no longer observed (Fig.1, curve *b*).

The radiolysis of such a vitreous $CoCl_2$ solution in methanol at 77 K leads to the accumulation of stabilised radicals. Measurement of the concentration of radicals by EPR shows that the stabilised radicals recombine effectively when the matrix passes from the vitreous to the liquid state. This recombination process can be followed also calorimetrically on the basis of the heat evolution accompanying it. Indeed heat evolution in irradiated specimens is observed precisely in the temperature range of the devitrification process (Fig.1, shaded exothermic peak) and the amount of evolved heat increases with increase of the dose until the attainment of a limiting concentration of radicals. The observed heat evolution is related precisely to the recombination of radicals. For a dose of approximately 100 Mrad, when the limiting concentration of radicals is attained, the contribution of charge recombination to the heat evolution can be neglected, because the concentration of charges is small compared with that of the radicals[6].

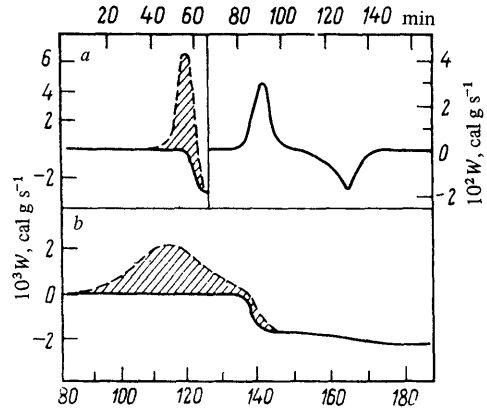


Figure 1. Calorimetric heating curves before (continuous lines) and after (dashed lines) irradiation of 2% (*a*) and 10% (*b*) solutions of $CoCl_2$ and CH_3OH with a dose of 100 Mrad at 77 K. Shaded regions—heat evolution associated with the recombination of radicals.

The radicals $^{\cdot}CH_2OH$, which are stabilised and accumulate in the low-temperature radiolysis, recombine with formation of ethylene glycol. On recombination, 70 ± 8 kcal mol^{-1} is evolved. The concentration of stabilised $^{\cdot}CH_2OH$ radicals can be calculated from the measured heat evolution. It was found that the EPR method and calorimetry yield virtually concordant results.

Thus, following the sharp change in the translational mobility of molecules, which occurs on transition from the vitreous to the supercooled liquid state, relatively small radicals recombine effectively. This takes place in systems where there exists virtually only one possible interaction channel—the recombination of radicals. In systems where the radicals liberated on devitrification are capable of initiating a chain reaction a different behaviour is observed, as will be shown below.

III. POLYMERISATION

As mentioned in the introduction, it has been shown in relation to a large number of examples that the polymerisation of vinyl monomers is sharply accelerated on devitrification of the matrix. The calorimetric method, which makes it possible to measure the rate of polymerisation directly at the instant of its occurrence, has been used successfully in an attempt to elucidate the causes of such acceleration of the polymerisation process. It has been shown by the calorimetric method[7] that the polymerisation of vitreous vinyl acetate and butylene dimethacrylate does not occur in the low-temperature radiolysis ($T < T_g$) and takes place only when the irradiated specimen

is heated in its devitrification region. It has also been established by the calorimetric technique[8] that the polymerisation of monomers in a vitrifying polymeric matrix proceeds vigorously immediately after the devitrification of the system.

Butyl methacrylate forms a complex with anhydrous zinc chloride, which passes to the vitreous state on freezing. The application of the calorimetric method in combination with EPR in the study of the postpolymerisation in the devitrification of this complex demonstrated the growth of radical chains after devitrification without termination[9]. The sharp inhibition of the termination of polymer chains in the supercooled liquid in the vicinity of the devitrification region itself provides a qualitative explanation of the high rates of polymerisation under these conditions. However, the problem of the rate of chain growth under such conditions remained open. In order to understand the mechanism of the polymerisation process on devitrification it was necessary to compare the propagation rate constants in the supercooled liquid, in the intrinsic crystal lattice of the monomer, and in the thermodynamically stable liquid.

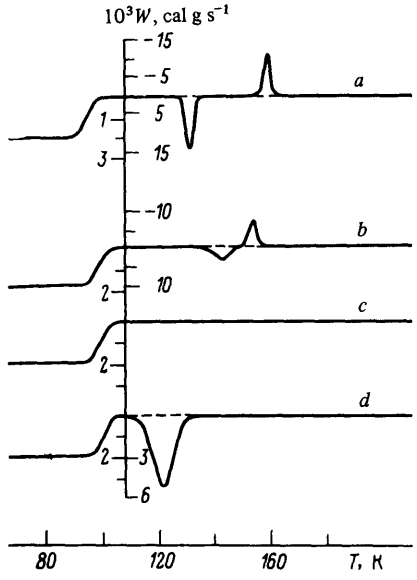


Figure 2. Calorimetric heating curves for pure ethanol (*a*), 10% (*b*) and 17% (*c*) acrylic acid solutions in ethanol, and a 17% acrylic acid solution in ethanol irradiated with ^{60}Co γ-rays for a dose of 2 Mrad at 77 K (*d*).

A system comprising a solution of acrylic acid in ethanol was studied[10] in order to solve these problems. Fig.2 shows that, when rapidly frozen (~100 K min^{-1}) solutions of acrylic acid in ethanol are warmed, the calorimeter reveals a characteristic change in heat capacity, a "step" associated with the transition of the system from the vitreous to the supercooled liquid state. On further increase of temperature in pure ethanol and dilute solutions (≤10 wt.%) of acrylic acid, the supercooled liquid crystallises and the calorimetric curve shows the corresponding heat evolution (Figs.2*a* and 2*b*). At higher temperatures the crystallised system melts (endothermic peak). With increase of acrylic acid concentration, the crystallisation of the supercooled solution after its devitrification becomes increasingly difficult and, in the presence of 17 wt.% of acrylic acid in alcohol, the solution does not crystallise at all (Fig.2*c*). All further studies were carried out[10] precisely for this simpler system—a non-crystallising 17% vitreous solution of acrylic acid in alcohol. Direct calorimetric measurements in the field of ^{60}Co γ-radiation showed that there is virtually no polymerisation in the vitreous solution of acrylic acid in alcohol at $T < T_g$. The calorimetric curve, obtained on heating the vitreous solution irradiated by ^{60}Co γ-rays at 77 K, shows an intense heat evolution, associated with polymerisation of acrylic acid, immediately after the devitrification step (i.e. after the transition to the supercooled liquid state) (Fig.2*d*). The overall yield of the polymer then reaches 80%.

At approximately 108 K the EPR spectra indicate the conversion of the monomeric radicals and the radicals of the alcohol matrix R_M, formed on radiolysis, into the radicals of the growing polymer chain R–$C_\beta H_2$–$\dot{C}_\alpha$H–COOH (R_p) (Fig.3).[10] In the supercooled liquid this radical assumes a non-equilibrium conformation with an angle $\phi \cong 75°$ between the axis of the unpaired electron orbital and the projection of the R–C_β bond on to a plane perpendicular to the C_β–C_α bond; the EPR spectrum then consists of a doublet of triplets (Fig.3*b*). On raising the temperature to 120 K, the destruction of R_p begins, because the growing macroradicals now acquired sufficient translational mobility. Under these conditions they apparently "roll up", become surrounded by the polymer units, acquire a conformation normal for the polymer matrix with $\phi = 15°$, and give rise to a triplet EPR spectrum (Fig.3*c*).[11] The conformational transformations at the end of the growing radical in such systems has been examined in greater detail by Bol'shakov et al.[12]

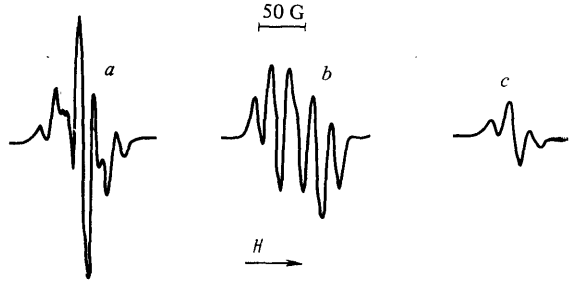


Figure 3. EPR spectra of a 17% acrylic acid solution in ethanol γ-irradiated with a dose of 2 Mrad at 77 K: *a*) at 77 K (R_M); *b*) specimen heated to 110 K (R_p); *c*) at 121 K.

Chain initiation is accompanied by the recombination of some of the monomeric radicals and only approximately half of them are converted into growing polymer radicals. On further increase of temperature, in the temperature range where acrylic acid is vigorously polymerised, the concentration of growing polymer radicals remains unchanged. Thus, over a comparatively narrow temperature range in the region of the devitrification of the matrix, the polymerisation process proceeds virtually without chain termination. This extremely important conclusion was convincingly confirmed experimentally for a whole series of systems[9,10,13,14].

Rates of polymerisation of the kind observed in a supercooled alcoholic solution of acrylic acid are reached in solid acrylic acid only at temperatures higher by 70–80 °C [15] and there is no termination of macroradicals in either case. This comparison clearly demonstrates the decisive role of the intermolecular interactions of the matrix. The translational mobility of the monomeric radicals, which is close to the mobility of the monomeric molecules, was estimated from the initial sections of the curves for the destruction of the radicals[15]. It proved to be $\nu_t \cong 2\times10^{-2}$ s^{-1}, while the frequency of the addition of monomeric molecules to the active centre is $\nu_p \cong 1.3\times10^{-3}$ s^{-1}. The frequencies of the reorientational mobility in this system are $\nu_r \cong 10^8$ s^{-1}. Thus $\nu_r \gg \nu_t > \nu_p$, i.e. the types of molecular mobility examined do not limit the polymer chain growth step.

However, the Arrhenius parameters of the propagation rate constant are very high[10]. The chain propagation rate constant in the temperature range 110–120 K has been estimated for the postpolymerisation of acrylic acid in the devitrification of the alcohol matrix[16]:

$$k_p \simeq 5\cdot10^{-3}\exp(-10700/RT),\ \text{cm}^3\ \text{s}^{-1}\ .$$

The high Arrhenius parameters and their variation with increasing preliminary irradiation dose[10] indicate a cooperative nature of the process manifested by the compensation effect[17]. Consequently the monomer addition step continues to be limited by some third type of molecular movement.

After the mutual approach of the monomeric molecule and the active centre as a result of the translational and reorientational migrations, the rate-limiting stage is apparently the steric deformation of the molecules in the addition step[1c,12], for which mainly barriers to intermolecular interactions are overcome.

The monomeric radicals formed in the low-temperature radiolysis of glasses, should be destroyed when the matrix passes to the supercooled liquid state, unless they have attained during the growth process a critical length, which, when exceeded, precludes bimolecular recombination. Naturally, the rate of heating of the system by radiolysis will have a significant influence on the process mechanism: depending on the rate of heating, there either is or is not sufficient time for the monomeric radicals to be stabilised by conversion into growing polymer radicals[13]. Indeed constant heating of the system prevents the "setting" of the polymer chains and a fairly low rate of heating ensures the stabilisation of growing macroradicals[14].

On comparatively rapid (~2 K min^{-1}) heating of radiolysed vitreous butyl methacrylate, a polymer is hardly formed, while on slow heating (~0.05 K min^{-1}), virtually complete conversion is observed[13]. The postpolymerisation of pure butyl methacrylate during its devitrification is a radical process occurring in the absence of the destruction of radicals and chain transfer, i.e. proceeding via the mechanism of "living chains"[13].

A characteristic feature of the polymerisation of allylamine on devitrification of the matrix is the suppression of the "allylic termination" typical for the polymerisation of this monomer in the liquid state, this leads to the formation of a product with a very high molecular weight in such systems[18].

The nature of the chain process occurring on devitrification of the matrix depends significantly on the rigidity of the latter, the width of the devitrification temperature range, and the differences between the viscosities of the medium in the vitreous and supercooled liquid states. Thus it has been shown[19] that the radiation-induced polymerisation of vinyl chloride takes place solely in long-chain paraffin matrices, whereas in glasses consisting of low-molecular-weight paraffins a polymer is not formed. It has been suggested[20] that the supermolecular structure of the glass has a decisive influence on the development of polymerisation in the glass; in glasses comprising long-chain molecules the supermolecular formations consist of "packets" in which particularly favourable conditions may arise for the growth of polymer chains.

The polymerisation of vinyl chloride, vitrified in liquid paraffin, has been investigated on the basis of the changes in the energy losses by the ultrasonic emitter in the course of the radiolysis of the system at 77 K.[20] A change in the resistance to waves was observed in the course of the radiolysis, which the authors attributed to the formation of a polymer in the vitreous matrix at 77 K ($T_g \cong 183$ K for this system). Unfortunately the technique employed in the above study[20] did not permit the estimation of the amount of polymer formed at such low temperatures. Nevertheless, the

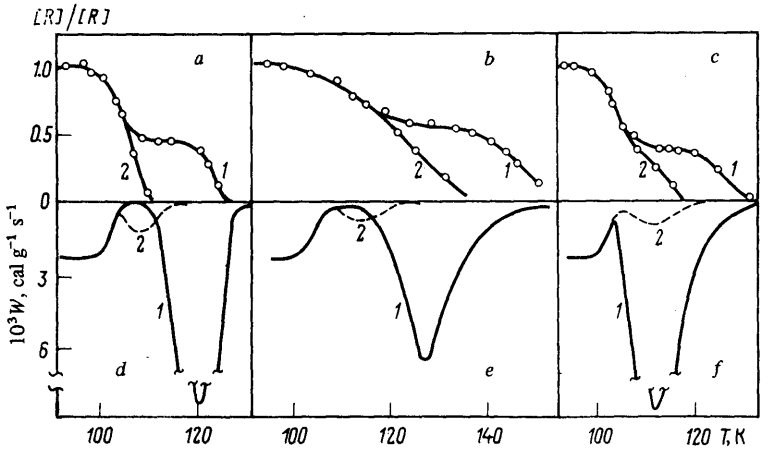


Figure 4. Temperature dependence of the stationary concentration of radicals [R_{st}] (*a*–*c*) and of the rate of polymerisation (*d*–*f*)(calorimetric heating curves) in γ-irradiated solutions (17 wt.%): *1a*) and *1d*) acrylic acid; *1b*) and *1e*) acrylamide; *1c*) and *1f*) methyl acrylate; *2a*) and *2d*) methacrylic acid; *2b*) and *2e*) methacrylamide; *2c*) and *2f*) methyl methacrylate.

main bulk of the polymer in these systems is formed on devitrification of the matrix[2]. The growth of polymer chains in the vitreous matrix at temperatures much smaller than T_g is believed[20] to take place in the region of extended defects in the glass, at the boundary between the ordered elements of the type of packets and the disordered medium.

Infrared spectroscopy has been used to investigate the characteristics of the chain propagation and termination reactions in the polymerisation of vinyl chloride vitrified in liquid paraffin[21]. It was established that, under isothermal conditions, the polymerisation is retarded in the system investigated, a further increase of temperature resulting in its acceleration. The phenomenon is extremely similar to the problem of the "setting" and "reviving" of polymer chains, first established[22] for solid-phase polymerisation.

It has been shown that, in postpolymerisation in supercooled alcoholic solutions, the reactivities of acrylic and methacrylic derivatives differ sharply[23]. Whereas on raising the temperature of vitrified alcoholic solutions of acrylic acid, acrylamide, and methyl acrylate, the yield of the polymer is 80%, the corresponding yield for their methacrylic analogues—methacrylic acid, methacrylamide, and methyl methacrylate—does not exceed 3–5% under identical conditions (Figs.4*d*–4*f*, cf. curves *1* and *2*).[23]

When solutions irradiated at 77 K are heated above T_g, the chain initiation and propagation are accompanied by the partial recombination of the radicals. The first monomer addition step, leading to the formation of an oligomeric radical, can be detected from the EPR spectra. For acrylic and methacrylic derivatives, the relative concentrations of the oligomeric radicals proved to be similar (Figs.4*a*–4*c*). Consequently the sharp difference between the rates of polymerisation of acrylic and methacrylic derivatives is not associated with the difference between the efficiencies of the initiation processes. With increase of the length of the growing polymer chain, its translational mobility falls and hence there is also a decrease of the probability of the destruction of the chain by recombination. For acrylic derivatives the concentration of the growing polymer radicals remains constant over a temperature range (Figs.4*a*–4*c*) and the polymer chain grows virtually without termination (Figs.4*d*–4*f*). On the other hand, a completely different picture is observed for methacrylic derivatives, The oligomeric radicals R_{ol} possess a fairly high translational mobility, are not stabilised, and recombine rapidly (Figs.4*a*–4*c*, curve *2*).

In order to elucidate the causes of such a sharp difference, the EPR spectra were analysed and the conformations of the terminal macroradicals in acrylic and methacrylic derivatives were determined from the hyperfine splitting by β-protons[23]. As a result of the interaction with the alcohol matrix, the terminal macroradicals of acrylic monomers exist in a specific conformation (Fig.5*a*, spectrum *2*), which differs from the conformation characteristic of the polymerisation of monomers in the crystalline state[10]. Methacrylic monomers do not give rise to a specific conformation and the terminal macroradicals have the same conformation as in their polymerisation in the crystal lattice of the monomer. The EPR spectra of the growing macroradicals are virtually identical in the polymerisation of methacrylic acid in a supercooled alcohol matrix (Fig.5*b*) and in its own crystal matrix (Fig.5*c*). Hence it follows that the presence of the CH_3 group near the reaction centre prevents the interaction of the growing macroradicals with the alcohol matrix, which leads to an increase of the probability of chain termination and to a decrease of the yield of the polymer. On the other hand, for acrylic monomers, the growing macroradical is associated with the alcohol molecules surrounding it, which leads to the formation of a specific conformation and the "coat" formed prevents its destruction. This is apparently the main cause of the sharp difference between the characteristics of the polymerisation of acrylic and methacrylic monomers[24]. On the other hand, the difference between the propagation rate constants is small and cannot account for the large difference in behaviour. Thus in a liquid medium $k_p = 1.45 \times 10^6 \exp(-4700/RT)$ for methyl acrylate and $k_p = 5.35 \times 10^5 \exp(-4700/RT)$ litre mol^{-1} s^{-1} for methyl methacrylate[25].

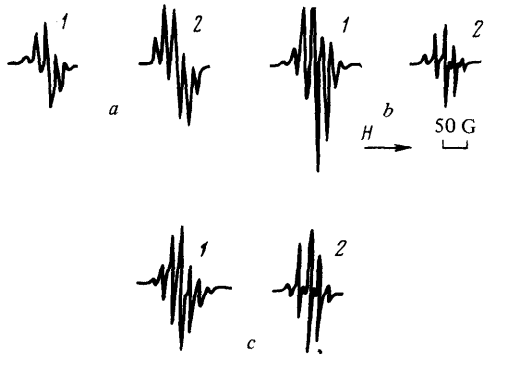


Figure 5. EPR spectra of 17% solutions γ-irradiated with a dose of 2 Mrad at 77 K: *a*) acrylic acid in ethanol at 77 K (curve *1*) and 120 K (curve *2*); *b*) methacrylic acid in ethanol at 77 K (curve *1*) and 112 K (curve *2*); *c*) spectrum of a polycrystalline methacrylic acid specimen at 77 K (curve *1*) and of the growing radical at 300 K (curve *2*).

Thus, in contrast to the usual liquid-phase polymerisation, a sharp difference is observed in the capacities of acrylic and methacrylic monomers for polymerisation on devitrification, which is associated with the more intense interaction with the growing acrylic macroradicals with the medium.

On heating irradiated vitreous monomers or their solutions, the following picture is thus observed: in the vicinity of the devitrification region the matrix is softened to such an extent that the conversion of monomeric radicals into the oligomeric radicals of the growing chain becomes possible. However, the characteristic times for the elementary chain propagation step are in this region extremely long and the chain growth is limited by the supply of the monomer to the growing active centre. With increase of temperature, the viscosity of the system is significantly reduced on passing to the supercooled liquid state, which facilitates the supply of the comparatively small monomer molecules to the growing polymer radical. At the same time, the viscosity of the supercooled liquid is still sufficiently high to prevent the bimolecular destruction of the macroradicals of the growing polymer chains. In this temperature range the polymerisation develops in accordance with the "living chain" mechanism. At high temperatures the matrix softens to such an extent that the bimolecular destruction of the growing macroradicals becomes possible and leads to the cessation of polymerisation. Such ideas concerning the mechanism of the polymerisation process on transition of radiolysed vitreous solutions of monomers to the supercooled liquid state proved to be applicable to a wide range of systems.

The polymerisation processes occurring on devitrification of the matrix by an ionic mechanism have also been investigated in fair detail. Not only radicals but also trapped electrons are known to be stabilised in glasses on low-temperature radiolysis. It has been found that there exist conditions under which ionic active centres stabilised in glasses can initiate ionic polymerisation. The anionic postpolymerisation of acrylonitrile has been observed on heating its vitrified solutions in methyltetrahydrofuran[26], dimethylformamide, and triethylamine[3] after the latter have been subjected to low-temperature radiolysis. The polymerisation process in these systems reached a maximum immediately after the transition of the system from the vitreous to the supercooled liquid state.

The polymerisation of the above systems at temperatures exceeding T_g was not observed, but it was possible to observe postpolymerisation via an ionic mechanism. It was found that the addition of acetone during the heating of vitreous acrylonitrile solutions fully suppresses its anionic polymerisation. It is noteworthy that, in a study of this system, the authors[26] noted for the first time the decisive role of the rate of heating of the radiolysed glass, showing that, when the system is heated slowly, a much greater amount of polymer is produced.

The anionic mechanism of postpolymerisation on devitrification has been demonstrated most clearly in the study of the polymerisation of nitroethylene vitrified in a methyltetrahydrofuran glass[27]. Electrons stabilised in the low-temperature radiolysis of glasses can be ejected from traps by visible and ultraviolet light, whereupon they recombine with holes. This optical "bleaching" method was first used to suppress ionic polymerisation[28] in order to demonstrate the ionic mechanism of the polymerisation of solid acrylonitrile. By subjecting nitroethylene glasses in methyltetrahydrofuran radiolysed at 77 K to optical bleaching before heating, the authors[27] showed that the postpolymerisation of this monomer is fully suppressed on devitrification of the matrix.

A cationic mechanism of the polymer chain propagation has been observed in the postpolymerisation of styrene vitrified in hexachlorobutadiene and methylene chloride[26]. Under comparable conditions, the amount of polymer formed in the above systems is smaller by an order of magnitude than in the anionic polymerisation of acrylonitrile on devitrification. However, here too a sharp maximum of the rate of polymerisation is observed in the region of the devitrification of the system. A qualitatively identical picture has been found for the polymerisation of a whole series of other systems on devitrification[29]. Cationic polymerisation on devitrification has also been observed for the postpolymerisation of isobutene vitrified in a poly(vinyl chloride) matrix[26].

Thus one must conclude that the characteristics of the polymerisation process on devitrification of the matrix, namely (1) the formation, before the transition of the system from the vitreous to the supercooled liquid state, of growing active centres sufficiently long to prevent their destruction and (2) the occurrence of the polymerisation reaction over a narrow temperature range above T_g without the termination of the growing active centres, are associated mainly with the specific physical nature of the rearrangement of the matrix on devitrification and are qualitatively the same for the radical and ionic mechanisms of chain propagation.

IV. GRAFT POLYMERISATION

Not only low-molecular-weight compounds but also polymers can be used as vitrifying matrices. As will be shown below, the same qualitative behaviour has been observed for vitreous solutions of a monomer in a polymer matrix as in the post-polymerisation of acrylic acid in an alcohol matrix. However, whereas the formation of macroradicals before the transition to the supercooled liquid state was necessary for polymerisation on devitrification of alcoholic solutions of the monomer in order to reduce the probability of the termination of the growing chains, when polymers are used as matrices, this condition is fulfilled automatically.

On cooling to 77 K, polyisobutylene passes to the vitreous state (Fig. 6*a*).[8] At low concentrations the monomers dissolved in it, for example acrylonitrile (the monomers were introduced into polyisobutylene by swelling it in the monomer vapour at room temperature), pass to the vitreous state without phase separation. The calorimetric heating curve for such solutions does not show peaks corresponding to the fusion of the individual monomers, although the sensitivity of the calorimeter was quite sufficient. Consequently, at these monomer concentrations the system consists of a solution over the entire temperature range. At higher temperatures part of the monomer becomes segregated as a separate phase on cooling and the calorimetric curve shows a monomer fusion peak (Fig. 6*b*). We may note that the calorimetric method is in this case convenient for the determination of the limiting solubility of the monomer in the polymer at the low temperatures employed.

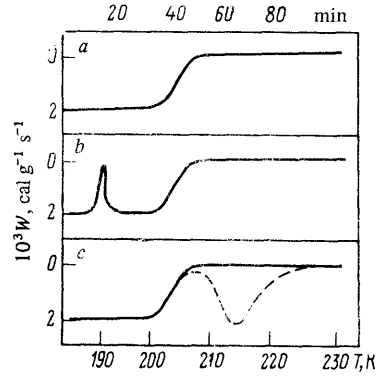


Figure 6. Calorimetric heating curves: *a*) polyisobutylene; *b*) 2% acrylonitrile solution in polyisobutylene; *c*) 1% acrylonitrile solution in polyisobutylene irradiated with 5 Mrad dose at 77 K.

As for monomers vitrified in an alcohol matrix, intense polymerisation is observed in radiolysed vitreous solutions of a monomer in a polymer on their devitrification (Fig. 6*c*). It can be easily shown that, in the low-temperature radiolysis of such vitreous solutions (monomer concentration 1–2%), mainly macroradicals of the polymer matrix are formed and stabilised. On devitrification, they acquire a sufficient mobility for the initiation of the polymerisation of the monomer introduced. Thus the polymerisation of the polymer matrix is initiated by macroradicals under the given conditions, i.e. graft polymerisation takes place. Since the monomer was first dissolved in the polymer matrix, polymers grafted in the bulk phase are formed.

In contrast to the usual methods of radiation-induced graft polymerisation—joint radiolysis of the polymer and the monomer (as a rule at temperatures higher than T_g for the polymer) and postpolymerisation of monomers on a radiolysed polymer matrix (*in vacuo* or in the presence of oxygen)[30,31]—graft polymerisation on devitrification makes it possible to employ most efficiently the macroradicals formed on radiolysis for the initiation of the grafted chains. The above factor is associated with the fact that, near T_g for the polymer matrix, conditions are created under which the destruction of the macroradicals formed is still difficult, while the supply of small monomer molecules to the growing active centres proceeds readily. This explains the high rates of graft copolymerisation observed under these conditions.

Intense graft polymerisation on devitrification of monomer solutions in polyisobutylene has been observed for a whole series of vinyl monomers: styrene, methyl acrylate, methyl methacrylate, etc.[8] Intense grafting of acrylonitrile, dissolved in poly(vinyl chloride), has been observed in the devitrification of the polymer matrix[32]. In the grafting of acrylonitrile, effective cross-linking of the macromolecules of the polymer matrix was also observed on devitrification of polyisobutylene as a result of the involvement of the C≡N group in the reaction[8]. Subsequently the grafting of acrylonitrile was used to cross-link polyethylene, and the cross-linking of macromolecules as a result of the dissociation of the C≡N groups of the grafted chains was demonstrated experimentally[33].

Radiation-induced graft polymerisation of readily polymerisable monomers such as tetrafluoroethylene by the method involving the joint irradiation of the monomer and polymer is extremely difficult. The point is that under these conditions the homopolymerisation of the monomer becomes the dominant process. Grafting on to polymers subjected to preliminary irradiation is also ineffective (for example, only 2–3% of tetrafluoroethylene can be grafted onto polyethylene[34]). The yield of the graft polymer can be increased only by employing polyethylene with an extremely high surface area and by carrying out the reaction at reduced temperatures[35]. However, under these conditions too the rate of reaction is low. The method of postradiation grafting on devitrification proved to be the most satisfactory in this instance[36].

To achieve partial dissolution of tetrafluoroethylene in powdered polyethylene (grain size 10–20 μm) and to fill the micropores in the polymer grains by the monomer, the polymer was first kept in liquid tetrafluoroethylene under a small pressure. The system was then cooled to 77 K and radiolysed. The calorimetric heating curve for this system (Fig.7) shows that the heat evolution associated with the graft polymerisation of tetrafluoroethylene is recorded starting from approximately 225 K. The grafting process takes place most effectively in the range 230–250 K, i.e. in the region of the devitrification of the amorphous portions of the polyethylene matrix. The yield of the graft polymer then reaches 200–300% (relative to the weight of the initial polyethylene). The graft polymer is soluble in boiling xylene and its infrared spectra clearly reveal absorption bands at 1160–1200 cm^{-1}, which are absent from the spectrum of polyethylene and are characteristic of polytetrafluoroethylene[36].

This method of grafting tetrafluoroethylene on devitrification of the matrix could be extended also to other polymeric supports. Treatment of polypropylene and ethylenepropylene rubber in liquid tetrafluoroethylene leads to the partial dissolution of the monomer in the polymer. When such a solution is cooled, it passes to the vitreous state without phase separation. When specimens of this kind, subjected to low-temperature radiolysis, are heated, vigorous polymerisation takes place on devitrification of the matrix[37].

Thus, when polymers are used as vitrifying matrices, the same qualitative picture is observed as for low-molecular-weight matrices with the sole difference that graft copolymers are formed. The advantages of the method of postradiation grafting on devitrification of the polymer matrix are as follows: (1) decrease of the irradiation dose required to obtain a specific yield of the graft polymer relative to the usual methods; (2) the formation of polymers grafted in the bulk phase—in the usual methods grafting takes place as a rule in the surface layer; (3) the possibility of grafting readily polymerisable monomers such as tetrafluoroethylene.

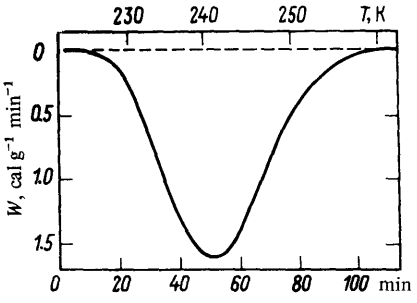


Figure 7. Postradiation grafting of tetrafluoroethylene in the devitrification of a polyethylene matrix. Irradiation dose 5 Mrad at 77 K.

V. COPOLYMERISATION

When the copolymerisation reaction is carried out in liquid and gas phases, the composition of the copolymer is determined by the relative reactivities of the comonomers and a homogeneous copolymer is obtained only in the initial stage of the copolymerisation. As one of the monomers is consumed, the resulting copolymer is as a rule enriched in the less reactive monomer and the polymer chains have an inhomogeneous composition.

As already mentioned above, a characteristic feature of the supercooled liquid state obtained on devitrification is a comparatively high viscosity. This feature must be manifested in some way in altering, compared with the usual liquids, the capacity of monomers for polymerisation. The preceding section presented examples of the sharp differences between the polymerisation capacities of acrylic and methacrylic derivatives on devitrification, while on polymerisation in the liquid state the propagation rate constants for these monomers were comparable as regards order of magnitude. Hence it was natural to expect that copolymerisation on devitrification can lead to a composition of the copolymer different than in the liquid phase copolymerisation.

The copolymerisation of methyl methacrylate with styrene on devitrification of an aniline matrix has been investigated[38]. A 30% solution of the monomer in aniline was devitrified at approximately 170 K. The copolymerisation was carried out by irradiating the system at 178 K, i.e. already in the supercooled liquid state. The authors claim that the composition

of the copolymer formed under these conditions is identical to that obtained on radical polymerisation, but they do not quote experimental data confirming this[38]. Subsequently these results were not confirmed either.

A series of studies on the mechanism of alternating copolymerisation in a vitreous system were carried out at Moscow State University[39-43]. Copolymerisation on devitrification in systems such as methyl methacrylate and methyl acrylate in the presence of $ZnCl_2$ and other complex-forming agents[39], butyl acrylate and 2,3-dimethylbutadiene, also in the presence of a complex forming agent[40], maleic anhydride and dimethylbutadiene[41], and sulphur dioxide together with a series of electron-donating monomers[43] takes place with formation of alternating copolymers. The introduction of a complex-forming agent into these systems entails a sharp increase of the cross chain propagation rate constant. Thus the copolymerisation proceeds via a mechanism involving the consecutive addition of monomers to the end of the growing chain. The cause of this mechanism is the possibility of donor–acceptor interactions between the chain growth radical and the monomer[41].

Another cause of the formation of an alternating copolymer is the formation of a charge-transfer complex between two monomeric species. Its reactivity is higher than that of each monomeric species and the alternation is thus explained by the homopolymerisation of this complex[43]. Sulphur dioxide probably forms a charge-transfer complex with dimethylbutadiene; on cooling, the system passes to the vitreous state. When a radiolysed glass of this kind is heated in the range $T_g \cong 113-133$ K, vigorous copolymerisation is observed. A 1:1 alternating copolymer is formed and its composition is almost independent of that of the initial mixture. The mechanism of the alternation consists in the addition of the complex formed by the monomers to the end of the growing chain[43].

The copolymerisation on devitrification of radiolysed alcoholic solutions of monomers in the absence of complex formation has been studied by Bol'shakov et al.[44] It was investigated for two pairs of comonomers: acrylic acid with acrylamide and acrylamide with methyl acrylate. For an overall concentration of comonomers in ethanol of 17 wt.%, the solution passes fully to the vitreous state on cooling. On subsequent heating, the solution devitrifies at $T_g \cong 102$ K and the supercooled liquid does not crystallise. When the monomer ratio is altered (but the overall concentration of the monomers in ethanol remains at 77 wt.%) over a wide range, the form of the calorimetric curve remains unaltered; consequently, over the entire temperature range from 77 to 300 K, when the monomer ratio is altered from 1:8 to 8:1, the monomers remain uniformly distributed throughout the bulk of the specimen, as in a liquid solution.

On devitrification of radiolysed solutions of this kind, vigorous heat evolution, associated with the copolymerisation, is observed. The yield of the copolymer increases monotonically with increasing preliminary irradiation dose and reaches approximately 95%. The copolymerisation could be interrupted, after the attainment of any required extent, by heating the specimen rapidly (at approximately 250 K min^{-1}) to room temperature. When the yield of the copolymer was altered from 1 to 90%, its composition hardly changed (Fig.8). Nevertheless, the composition of the copolymer in the systems investigated by Bol'shakov et al.[44] could be varied by altering the initial ratio of the monomers in solution. This means that the composition of the copolymer depends solely on that of the initial solution. For a solution of acrylic acid and acrylamide in ethanol, the composition of the resulting copolymer fully corresponds to that of the initial solution, while the composition of the copolymer obtained on radiation-induced copolymerisation of these monomers in the liquid phase at room temperature is determined by their relative reactivities, the copolymerisation constants being $r_1 = 0.25$ and $r_2 = 0.77$ respectively[45].

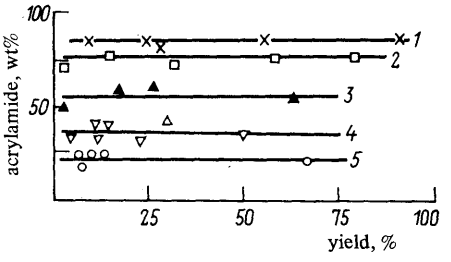


Figure 8. Dependence of the content of acrylamide in the copolymer on the degree of conversion for a 17% solution in ethanol; acrylamide : acrylic acid ratio (by weight): 1) 9:1; 2) 4:1; 3) 1:1; 4) 1:2; 5) 1:5.

The composition of the copolymer has also been found to be independent of the degree of conversion in the copolymerisation on devitrification of an alcoholic solution of acrylamide and methyl acrylate. However, up to an 80% content of acrylamide in the initial solution of this system, its content in the copolymer remains smaller throughout than in the initial mixture although it does continue to increase[44].

In the viscous supercooled liquid formed on devitrification of the solutions, the time of the mutual contact between the reacting species is much longer than in gas and liquid phases and the frequencies of the addition of the monomer to the active centre of the growing polymer chain are comparable in order of magnitude to the frequencies of the translational migrations of the monomers in the system[10]. Thus the increased viscosity of the supercooled liquid leads to a sharp increase of the time of mutual contact between the comonomers. On the other hand, the rate of growth of the polymer chain is not limited by diffusion under these conditions, because the frequency of the addition of the monomer to the growing macroradical is not limited by the rate of the translational migrations[10]. Presumably the increase of the time of mutual contact between the growing macroradical and the monomer in the systems indicated actually leads to the addition of the monomer in virtually every collision, in contrast to the behaviour observed in the usual liquids; this is in fact responsible for the identity of the compositions of the initial solution and the copolymer.

Such increase of the time of mutual contact between the reactants and the supercooled liquid gives rise to the hope that compounds which are not usually regarded as monomers can be involved in copolymerisation on devitrification. An interesting example of such copolymerisation and devitrification is provided by the acetone–acrylic acid system[46]. The polymerisation of acetone via the carbonyl group was first reported by Kargin et al.[47] Polyacetone was later obtained also by solid-phase radiation-induced polymerisation[48]. This polymer proved to be very unstable and decomposed rapidly to the monomer even at room temperature. Thermostable acetone–acrylic acid copolymers have been obtained by copolymerisation on devitrification[49]. When solutions of acrylic acid in acetone are cooled rapidly, partly or fully

vitreous specimens are formed. The amount of the vitreous phase then depends on the rate of cooling and on the concentration of the monomer in the solution. A fully vitrified specimen can be obtained by cooling a 10% solution of acrylic acid in acetone at a rate of 150 K min^{-1}. The calorimetric heating curve for such a specimen reveals devitrification at approximately 110 K; next, at approximately 133 K, a eutectic mixture crystallises from the supercooled liquid and then melts at 165 K.

When a vitreous solution of acrylic acid in acetone irradiated at 77 K is heated slowly in the calorimeter, heat evolution associated with polymerisation is observed immediately after the system passes to the supercooled liquid state. The conditions governing the formation of the polymer fully ruled out the possibility of the physical retention of acetone by the polymer matrix. The amount of unreacted acrylic acid was determined by titration and the yield of the polymer was calculated in relation to the amount of acrylic acid in the polymer. Fig. 9 illustrates the dependence of the yield of the polymer on the concentration of acrylic acid in the initial solution. In dilute solutions the yield of the polymer reaches 250%, which corresponds to the composition of the polymer: two acetone molecules per acrylic acid unit. With increase of the concentration of acrylic acid, the yield of the polymer falls rapidly to 130–140% and is then almost independent of the composition of the initial solution.

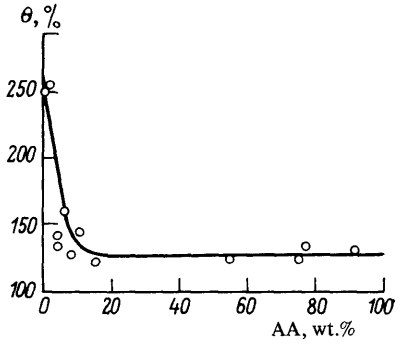
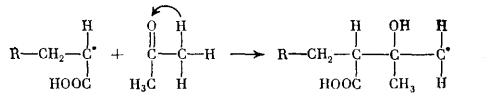
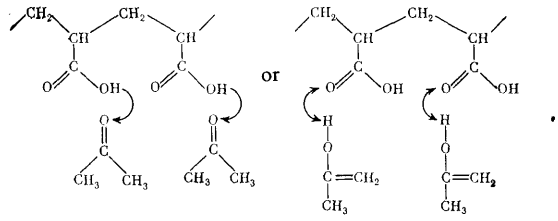


Figure 9. Dependence of the yield of the acrylic acid–acetone copolymer (θ) on the initial acrylic acid (AA) concentration in acetone. The yield of the polymer is referred to the acrylic acid which has reacted.

The incorporation of acetone into the composition of the polymer is observed also when the system is irradiated in the liquid state at 195 K.[50] 100% conversion is rapidly attained in the first stage of the polymerisation. This rapid stage is followed by a fairly slow stage, in which the conversion reaches 140–150% with respect to the acrylic acid which has reacted. It is extremely interesting that the incorporation of acetone into the copolymer is fully suppressed by traces of water. At the same time, traces of water do not have this kind of inhibiting influence on the homopolymerisation of acrylic acid. Two mechanisms, explaining the incorporation of acetone into the polymer formed have been proposed: (1) copolymerisation of acrylic acid and the enolic form of acetone:



[this mechanism is similar to that proposed previously for the polymerisation of acetaldehyde with formation of poly(vinyl alcohol)[51,52]]; (2) the formation of associated species comprising one or other tautomeric form of acetone and polyacrylic acid:



VI. CHLORINATION OF HYDROCARBONS

The chlorination of paraffinic hydrocarbons and their chloro-derivatives in the gas and liquid phases on radiation initiation and photoinitiation has been investigated in fair detail[53]. However, the characteristic features of the mechanism of these processes in solid and viscous media have been hardly studied. Investigations carried out recently have shown that the characteristics of the chain process occurring on devitrification of the matrix, demonstrated in relation to the polymerisation reaction, are maintained qualitatively also in reactions such as the chlorination of paraffins.

The characteristic features of low-temperature radiation-induced chlorination in vitrifying matrices have been studied for the butyl chloride–molecular chlorine system[54]. Solid chlorine undergoes no phase transformations and melts at 172 K (Fig. 10*a*). Butyl chloride passes to the vitreous state on fairly rapid cooling and, when such a specimen is heated, devitrification is observed at 96 K (Fig. 10*b*). On further increase of temperature, butyl chloride crystallises and then melts at a temperature as low as 150 K. A solution of chlorine in butyl chloride was prepared in the dark and no chemical reaction was observed. On cooling, this solution also passes to the vitreous state. The simplest phase transformations are observed on dissolution of one mole of Cl_2 in three moles of C_4H_5Cl—after devitrification the solution does not crystallise and does not melt (Fig. 10*c*). Consequently, for these proportions of the reactants, phase separation does not occur in the vitrifying solution. This finding is extremely important, because the interpretation of kinetic data for homogeneous one-component systems is significantly simplified.

The heat of the radiation-induced chlorination in the system investigated is 33 kcal per mole of chlorine. The relations presented in Fig. 11 shows that the radiation-induced chlorination takes place with acceleration at 114 K. The retardation of the process and the subsequent fall of the rate are associated with the consumption of the initial chlorine.

The radiation-induced chlorination of butyl chloride takes place in the solid phase, i.e. at temperatures below the devitrification region. When the system passes from the vitreous to the supercooled liquid state, the rate of reaction rises (Fig. 11). A characteristic feature of the process in this temperature range is a virtually linear increase of the rate of chlorination as a function of time. When the initiating γ-radiation is switched off, the rate of the process gradually falls. The characteristic time of the decrease of the rate of

chlorination after switching off γ-irradiation has been determined as $\tau_0 \cong 1500$ s. Such a slow decrease of the rate indicates a long lifetime of the active centres in the supercooled liquid at the temperatures indicated. This finding is in fact responsible for the non-stationary process kinetics—the accumulation of active centres in the course of the radiolysis entails an increase of the rate of the process with time in the initial stage.

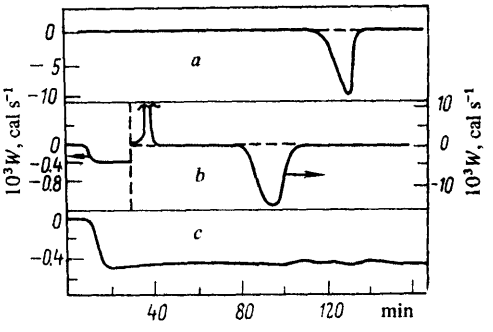


Figure 10. Calorimetric heating curves: *a*) chlorine (3.7×10^{-3} M); *b*) butyl chloride (5.26×10^{-3} M); *c*) chlorine solution (8.7×10^{-4} M) in butyl chloride (2.4×10^{-3} M).

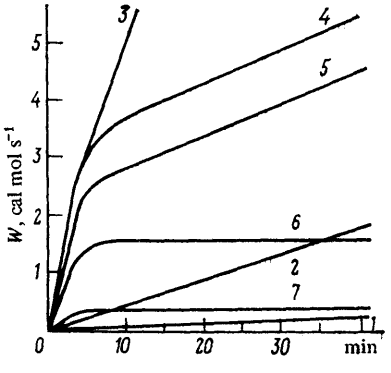


Figure 11. Time variation of the rate of radiation-induced chlorination of butyl chloride at different temperatures (K): 1) 98; 2) 107; 3) 113; 4) 118; 5) 122; 6) 127; 7) 150. Dose rate 30 rad s^{-1}.

The kinetics of the process change significantly with increase of temperature (Fig.11). The process takes place most vigorously at 114 K. On further increase of temperature, the matrix softens, which leads to a sharp decrease of the lifetime of the active centres. At 127 K a constant rate of the process is established immediately (more precisely after the characteristic time of the calorimetric apparatus has elapsed) when the ionising radiation is switched off. The increase probability of chain termination lowers the overall rate of the process over the increase of temperature.

The radiation-induced chlorination of butyl chloride on devitrification of the matrix can be described by the following simple scheme:

$$ClRH \overset{\gamma}{\rightsquigarrow} ClR^{\cdot} + H^{\cdot}, \quad (1)$$

$$ClR^{\cdot} + Cl_2 \rightarrow ClRCl + Cl^{\cdot}, \quad (2)$$

$$Cl^{\cdot} + ClRH \rightarrow ClR^{\cdot} + HCl, \quad (3)$$

$$\left.\begin{matrix} Cl^{\cdot} \\ ClR^{\cdot} \end{matrix}\right\} \rightarrow \text{termination}. \quad \begin{matrix} (4) \\ (5) \end{matrix}$$

In the temperature range 98–114 K the termination of the kinetic chains is extremely slow ($1/\tau_0 \cong 6.6 \times 10^{-4}$ s^{-1}). Judging from the data of Eckling and Goldfinger[55], the rate constant for reaction (2) in the photochemical chlorination of C_2H_5Cl in the temperature range in which we are interested can exceed by several orders of magnitude the rate constant for reaction (3). Consequently, reaction (3) will limit the rate of the given process. For the initial rate of the process (when chain termination can be neglected), we obtain the following expression[54]:

$$w_0 = -d[ClRH]/dt \simeq k_3 g I t [ClRH], \quad (6)$$

where g is the radiation yield of the centres initiating the chlorination and I the intensity of the γ-radiation.

Using this expression, the temperature variation of k_3 was determined from the initial sections of curves *1–3* in Fig.11. This relation is illustrated in Fig.12 (curve *1*). Assuming that $g \cong 1$ in Eqn.(6), we can estimate the constant k_3, which has the following value in the range 98–114 K:

$$k_3 \simeq 10^{11} \cdot \exp(-5600/RT) \text{ litre mol}^{-1} \text{ s}^{-1}. \quad (7)$$

As already mentioned, at higher temperatures the rate of termination increases sharply and a stationary rate of the chlorination process is established. Assuming that the kinetic chains are terminated mainly by reaction (5), the following expression is obtained for the stationary rate of chlorination:

$$w_{st} = -d[ClRH]/dt = k_3/k_4 g I [ClRH]. \quad (8)$$

An analogous expression for the stationary rate has been used[56] after the same assumptions to describe the radiation-induced liquid-phase chlorination of tetradecane. Indeed, in conformity with Eqn.(8), the rate in this temperature range rapidly attains a stationary value and ceases to depend on time (Fig.11, curves *6* and *7*). On substituting Eqn.(8) the values of k_3 calculated by Eqn.(7) and the value of w_{st} (Fig.11, curves *6* and *7*), we obtain $k_4 = 7$ s^{-1} (for 150 K) and $k_4 = 0.05$ s^{-1} (for 127 K). Taking into account the experimental value $k_0 = k_4 = 6.6 \times 10^{-4}$ s^{-1} for 107 K, we obtain the temperature variation of k_4 in the range 150–107 K (Fig.12, curve *2*) and the following expression for the termination rate constant:

$$k \simeq 10^{12} \cdot \exp(-7400/RT), \text{ s}^{-1}.$$

It follows from Eqn.(8) that the activation energy for the overall process $E_{OV} = E_3 - E_4 - 5.6 - 7.4 = -1.8$ kcal mol^{-1}. A similar activation energy in fact characterises the rate of the overall process in this temperature range (Fig.12, curve *3*).

Thus, as in polymerisation, the chain chlorination of chloroalkanes in the supercooled liquid state is characterised by a long lifetime of the active centres. With increase of temperature in the supercooled liquid, the rate of chain propagation reaches a maximum and, when the liquid passes to the thermodynamically stable state and the viscosity of the medium falls sharply, the probability of termination increases. Consequently the suppression of the chain termination process combined with the attainment of conditions ensuring

effective chain growth—conditions which are automatically obtained in the vicinity of the region of devitrification of the system—make it possible to increase significantly the overall rate of reaction.

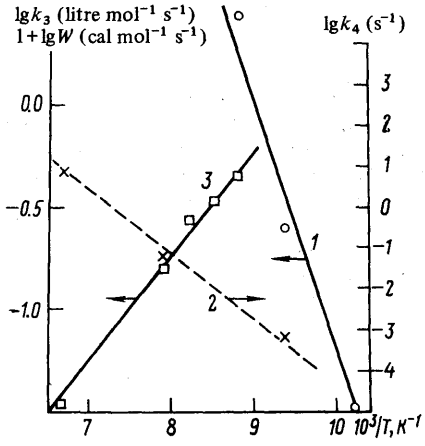


Figure 12. Temperature variation of the rate constants k_3 (line *1*) and k_4 (line *2*) and of the rate of radiation-induced chlorination of butyl chloride for a 4% degree of conversion of chlorine (curve *3*).

Possibly other low-temperature chain processes, such as, for example, hydrohalogenation and halogenation of olefins, the interaction of N_2O_4 with unsaturated compounds, etc.[57,58] under conditions corresponding to the devitrification of the matrix will be characterised by the suppression of chain termination with simultaneous attainment of conditions ensuring vigorous chain propagation.

VII. APPLIED ASPECTS

Graft polymerisation on devitrification of the matrix permits an effective use of the active centres and hence of the expensive ionising radiation energy which generates them. The employment of this process for the grafting of tetrafluoroethylene appears to be most promising. The prospect of the modification of polymeric materials and articles by grafting to impart to them properties close to the unique properties of polytetrafluoroethylene is extremely attractive. The grafted layer of polytetrafluoroethylene can significantly lower the coefficient of friction of the polymer surface and increase its thermal and chemical stabilities. The use of tetrafluoroethylene grafts in order to regenerate PTFE waste is also promising[59,60]. In all these processes the method of graft polymerisation on devitrification of matrices can be used successfully.

A new class of polymerisable oligomers—oligocarbonate-acrylates—is characterised by high rates of radiation-induced hardening[61,64]. All the oligocarbonate-acrylates investigated pass to the vitreous state on rapid cooling. When the oligomers irradiated in the vitreous state are heated, intense postpolymerisation is observed after the system passes to the supercooled liquid state (Fig.13). The efficiency of the method is so high that a dose of only 100 krad is sufficient for the required degree of hardening[61,63].

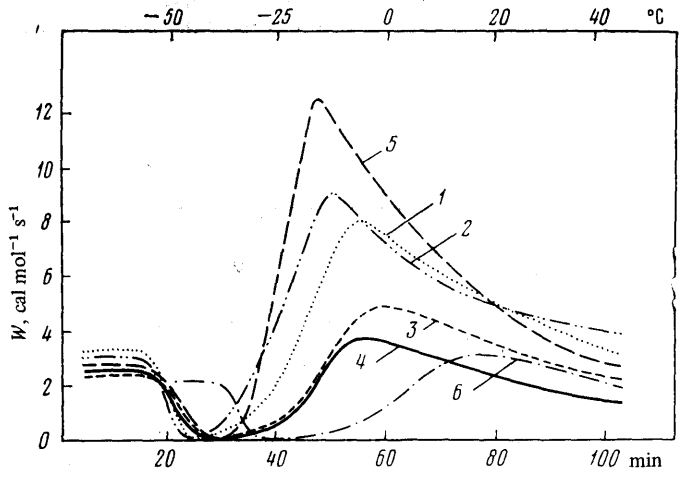


Figure 13. Calorimetric heating curves for oligocarbonate-acrylates irradiated with an 8 krad dose of ^{60}Co γ-rays at 77 K: 1) OKM-3; 2) OKM-4; 3) OKA-2; 4) OKM-1; 5) OKM-2; 6) OKM-7.

For low doses of the preliminary irradiation (1–5 krad), the presence of atmospheric oxygen dissolved in the oligomer causes sharp inhibition of the process and the appearance of an induction period. However, when the preliminary irradiation dose is increased to 50–100 krad, the inhibiting effect of oxygen ceases to influence the kinetics of the hardening process. This effect is probably associated with the increase of the rate of initiation of the process. The absence of an inhibiting influence of oxygen in a closed system even for a dose of 50–100 krad is of interest. Indeed, the elimination of the stickiness of the surface layers (insufficient hardening due to inhibition by oxygen) constitutes a serious problem in the radiation-induced hardening of coatings based on polymerisable oligomers.

The selection of the appropriate vitrifying matrix makes it possible to carry out the chain reaction at extremely low temperatures—as a rule significantly below the melting points of the reactants. On the other hand, the occurrence of a chain reaction in the crystal lattice is hindered by the low translational mobility of the reactants. Furthermore a chain reaction at the lowest possible temperature is of interest because a decrease of temperature entails a kind of selection of the possible reaction channels. Indeed, the channel with the lowest activation energy "survives" at low temperatures. Thus a decrease of the reaction temperature should lead to a high process selectivity. Furthermore, with decrease of temperature, the entropy factors, which are so important in the thermodynamics of chemical reactions, play a continuously decreasing role and the equilibrium in all the reactions is therefore displaced towards exothermic reactions, even those in which highly ordered systems are produced. On the other hand, the employment of vitrifying matrices permits chain reactions at temperatures close to 77–100 K.

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