=== **RADIATION CHEMISTRY** ===

Low-Temperature Post-Irradiation Polymerization of Fluoroolefins in Glassy Perfluoroalkane Matrix

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Abstract—The kinetics of post-irradiation polymerization of olefins, such as tetrafluoroethylene (TFE), vinylidene fluoride (VDF), chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), and ethylene, in the glassy matrix of branched perfluoroalkane $C_{10}F_{22}$ (PFA) were investigated by low-temperature calorimetry. An olefin solution in PFA transforms into the glassy or the crystalline state upon cooling to 77 K, depending on the monomer concentrations in the initial monomer−PFA mixture. At monomer concentrations (mol/kg) of ≤ 2.5 (TFE), ≤ 1.7 (HFP), ≤ 1.3 (CTFE), and ≤ 1.3 (VDF) in the initial mixture, the fluoroolefins pass completely into the glassy state. The ability of fluoroolefins to polymerize depends on their physical state, and the effective post-irradiation polymerization in the glassy state occurs in the glass transition region of the sample, reaching a high degree of conversion. Hexafluropropylene irradiated in the glassy state in the PFA matrix at 77 K does not polymerize. By their reactivity in polymerization in the glassy state, the olefins can be arranged in the order: TFE > VDF > CTFE > $C_2H_4 \gg$ HFP.

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Radiolysis of perfluoroolefins differs from that of both their hydrocarbon analogues and perfluoroalkanes. The effect of ionizing radiation on perfluoroalkanes results in the prevalent rupture of C−C, rather than C−F, bonds [1−4]. In the case of radiolysis of pure hydrocarbonaceous olefins, the most characteristic primary process is the detachment of the hydrogen atom [5, 6]. The specific feature of the primary radiolysis of perfluoroalkenes is double bond scission, as well as polymerization. The most documented representative of perfluoroalkenes is tetrafluoroethylene (TFE). None of the studies on the radiolysis [7] or photolysis [8, 9] of TFE has experimentally revealed the abstraction of the fluorine atom from the excited TFE molecule. Of the products of the gas-phase radiolysis of TFE, *cyclo*-C_3F_4 ($G = 1.8$), *cyclo*-C_4F_6 ($G = 0.15$), C_3F_6 ($G = 0.3$), *iso*-C_4F_8 ($G = 2.0$), and polymer were detected [7]. The polymer and perfluorocyclopropanes were also found to be the main products of TFE photolysis [8, 9]. This fact suggests that the mechanism of the primary TFE photolysis and radiolysis reactions is the same. It includes the formation of difluorocarbene during the photolysis of TFE followed by its addition to a TFE molecule yielding the transient product $−C_3F_6−$, which subsequently undergoes dimerization. However, it has been assumed [7] that the formation of the main products of TFE radiolysis involves the addition reaction of an excited TFE molecule to a ground-state TFE molecule to give $−C_4F_8−$ as a transient. The main outcome of the action of ionizing radiation on perfluoroolefins is the formation of a polymer [10]. As a result of radiation polymerization of TFE with β- [11] and γ-rays [12] in the liquid [13, 14] and gas [15] phases or in different media [16, 17], two specific features of this process were revealed: first, the extreme ease of TFE polymerization, which was characterized by a high radiation-chemical yield reaching 10^6 molecule/100 eV [18], and, second, the long-term posteffect characterized by a high rate of polymerization [10]. The replacement of a fluorine atom in the TFE molecule with chlorine results in a dramatic reduction in the polymerization rate. The radiation-chemical yield of polymerization of chlorotrifluoroethylene (CTFE) is 5.5×10^4 molecule/100 eV [18]. The substitution of the trifluoromethyl group for a fluorine atom in the TFE molecule leads to an even more dramatic decline in the rate of polymerization and almost complete degeneration of the chain polymerization mechanism [12]. In the case of irradiation of hexafluoropropylene (HFP), the radiation-chemical yield is 13 molecule/100 eV [18]. The introduction of two trifluoromethyl groups into the TFE molecule leads to the complete inability of the olefin to enter homopolymerization. Perfluoroisobutylene does not polymerize even at a dose of 2.5 MGy [18]. The solid-state polymerization of TFE has been examined in a variety of studies [14, 19–23]. By means of ESR spectroscopy, radiothermoluminescence, gravimetry and other techniques, it was shown that polytetrafluoroethylene is produced in the solid phase with a relatively

low radiation-chemical yield; in the case of radiolysis of crystalline TFE and subsequent heating above the melting point, it was possible to obtain the polymer in as low an amount as 1–2% [14, 19, 21]. The low molecular mobility of the monomer in the crystal lattice precludes the formation of relatively long polymer chains, as well as effective chain termination processes in the melting range. However, the mobility dramatically increases upon the devitrification of monomer solutions and thereby ensures the effective chain propagation with simultaneous suppression of the termination processes; thus, quite a high rate of conversion is achieved [24]. A high rate of post-irradiation polymerization is observed in the cases of polymerization of TFE [22, 23] and CTFE [25] in a glassy matrix of HFP oligomers; as a result, a high conversion of the monomers is attained.

Analysis of the published data allows us to distinguish the following three principal features of the radiolysis of fluorinated olefins: (1) the scission of the double bond by the action of ionizing radiation and the formation of carbene, (2) the addition of fluorine atoms or small radicals to the double bond of fluoroolefins yielding radicals, and (3) the polymerization of fluoroolefins at a rate, which strongly depends on the number of fluorine atoms in fluoroolefin molecules, branching, and the physical state of the monomer.

The objective of this work was to study the influence of the nature of fluorinated olefins on the kinetics of their low temperature post-irradiation polymerization in a glassy perfluoroalkane matrix.

EXPERIMENTAL

Commercial fluoroolefins tetrafluoroethylene, vinylidene fluoride (VDF), chlorotrifluoroethylene, and hexafluoropropylene and unsubstituted ethylene purchased from OAO Galogen were used as monomers. The monomers were purified for the removal of inhibitors and impurities by passing though a sulfuric acid solution (30%) and an activated-charcoal column. The branched perfluoroalkane $C_{10}F_{22}$ manufactured by the Kirovo-Chepetsk chemical plant was used as received,

The picture of phase transformations in the system in question and the polymerization kinetics were studied by means of kinetic calorimetry [26] with the use of special calorimetric glass cells. Polymerization was conducted in the absence of oxygen (the samples were deoxygenated in a vacuum unit to a residual pressure of 0.133 Pa). To initiate polymerization, the sample were irradiated with ^{60}Co γ-rays on a Gammatok source at 77 K. The absorbed dose rate determined with a ferrous sulfate dosimeter was 10 kGy/h.

The specimens designed for ESR studies were prepared by sealing a certain amount of the substance to be examined in an ampule made from SK-4B glass,

which does not give an ESR signal upon radiolysis after outgassing to a residual pressure of 0.133 Pa. The ESR spectra were recorded on an EPR 21-I radiospectrometer and a PS100.X compact radiospectrometer with automated processing of ESR spectra. Automated recording was run by the EPRWIN software program. The theoretical ESR spectra were calculated and simulated with the use of the EPRTOOLS program. The programs EPRWIN and EPRTOOLL were designed at NPP Adani (Minsk).

The polymerization of olefins irradiated in the glassy PFA matrix was monitored as follows. The yield of the polymer was determined relative to the glassy portion of the monomer dissolved in the glassy PFA matrix. Heat release due to postpolymerization of the samples irradiated at 77 K was measured calorimetrically during their heating. The following values were compared: (1) the monomer conversion Q_k as determined from the calorimetric data on heat evolution in the glass transition region of the system; (2) the polymer yield Q_g determined gravimetrically after the removal of the unreacted monomer at room temperature; (3) the yield of the polymer produced immediately during irradiation at 77 K, which was determined as the difference of the two above quantities, $Q_\gamma = Q_g - Q_k$ (the unreacted monomers were removed in a vacuum of ~0.133 Pa); and (4) the polymer yield Q_w determined gravimetrically after the removal of PFA that was not linked to the polymer. The free PFA was removed by long-term evacuation of the sample at 373 K to a constant mass.

RESULTS AND DISCUSSION

Since the polymerizing ability of fluoroalkenes at low temperatures is substantially dependent on their physical state [24], a detailed calorimetric analysis of the monomer−PFA samples at different monomer concentrations was performed first. When cooled to 77 K, the test olefins in the pure form appear only in the crystalline state and their calorimetric thawing curve displays only the endothermic peak due to melting. The heats of melting of the monomers determined in the set of experiments are as follows (kJ/mol) : 6.9 ± 0.2 (TFE), 4.7 ± 0.2 (VDF), 4.9 ± 0.1 (HFP), 4.9 ± 0.23 (CTFE), and 2.9 ± 0.13 (C_2H_4).

During their cooling to 77 K, the monomer−PFA samples form a mixture of a glassy monomer solution in PFA with the residual monomer that does not enter the glassy solution and forms the crystalline phase of its own, depending on the monomer concentration in the sample. Calorimetric measurements of the crystallization and melting of the monomer make it possible to determine the proportion of the monomer that composes the crystalline phase of its own and the monomer concentration in the glassy solution [24]. Figure 1 (curves $1-4$) shows the plots of the concentrations of the glassy monomers in the PFA matrix ($[c]_p$) versus the monomer concentrations in the initial
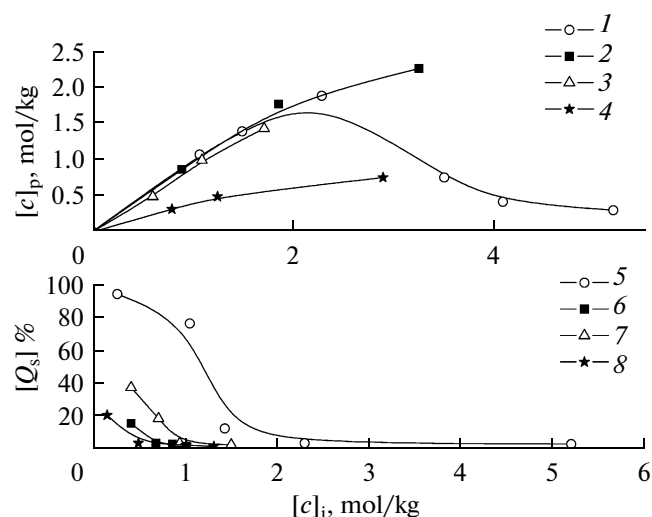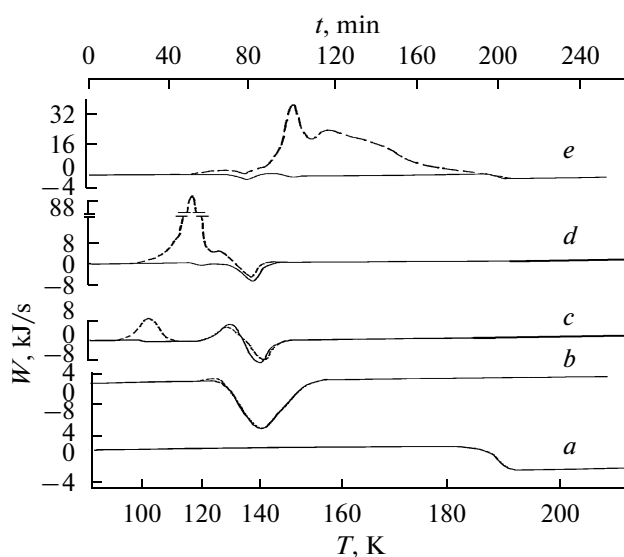
Fig. 1. Dependence of (*1–4*) the monomer concentration in glassy solutions $[c]_p$ and (*5–8*) the polymer yield upon the monomer concentration in the initial mixture $[c]_i$ for (*1, 5*) TFE–PFA, (*2, 6*) CTFE–PFA, (*3, 5*) VDF–PFA, and (*4, 8*) C_2H_4–PFA samples. The absorbed doses in radiolysis at 77 K are (*5*) 85, (*6*) 125, (*7*) 100, and (*8*) 150 kGy.

Fig. 2. Calorimetric thawing curves after cooling to 77 K for (*a*) a perfluoroalkane sample and tetrafluoroethylene solutions in the perfluoroalkane having TFE concentrations of (*b*) 10.0, (*c*) 3.7, (*d*) 3.0, and (*e*) 1.4 mol/kg; the dashes curves refer to the samples irradiated at 77 K to doses of (*b*) 40, (*c*) 83, (*d*) 120, and (*e*) 5 kGy.

monomer–PFA mixtures ($[c]_i$). It is seen that the concentration of the monomer in the glassy solution depends not only on its concentration in the initial mixture but also on the monomer nature. At monomer concentrations in the initial monomer–PFA mixture of ≤2.5 (TFE), ≤1.7 (HFP), ≤1.3 (CTFE), and ≤1.3 (VDF) mol/kg, fluoroolefins completely pass to the glassy state upon their cooling from 300 to 77 K. In samples with identical amounts of monomers in the initial monomer–PFA mixture, the concentration of C_2H_4 in the glassy solution was always lower than that of fluoroolefins.

Curves *5–8* in Fig. 1 show the dependence of the conversion of the monomers upon their concentration in the initial monomer–PFA mixture. It is seen that the most effective post-irradiation polymerization of the monomers occurs in the samples with monomer concentrations of ≤2.0 (TFE), ≤1.0 (VDF), ≤0.8 (CTFE), and ≤0.5 (C_2H_4) mol/kg.

The specifics of the low-temperature post-irradiation polymerization of fluoroalkenes in the vitrifiable PFA matrix were considered for TFE polymerization as an example. The calorimetric heating curves for TFE–PFA samples at different TFE concentrations are presented in Fig. 2.

When cooled to 77 K, PFA passes to the glassy state. The calorimetric thawing curve of the sample exhibits only a heat capacity change as the step at ~200 K due to devitrification of PFA (Fig. 2a). Solid TFE does not experience any phase transformation, it melts at 142 K [21]. At a TFE molality of >6.13 mol/kg in PFA, the TFE–PFA sample at 77 K is a mixture of crystalline TFE and glassy PFA. The calorimetric thawing curve of this sample displays the endothermic peak due to TFE melting; however, there is no PFA devitrification step, a situation that is due to the dissolution of PFA in liquid TFE (Fig. 2, curve *b*). As the TFE concentration in the initial mixture is decreased to 3.7 mol/kg, a certain portion of TFE dissolved in PFA transfers to the glassy phase and the remaining portion of the monomer forms the crystalline phase of its own. In this case, the calorimetric thawing curve (Fig. 2, curve *c*) exhibits the step of softening of the TFE solution in PFA at ~106 K. As the temperature further increases, the dissolved portion of TFE crystallizes from the overcooled liquid solution (exotherm at 120 K) and then melts (endotherm at 142 K).

At a TFE concentration in the system below 3.7 mol/kg, the sample is a homogeneous transparent glass at liquid nitrogen temperature. When such samples are unfrozen in the calorimeter, the TFE melting peak is almost undetectable (Fig. 2, curve *d*); 3–5% of TFE occurs in the crystalline state. The calorimetric curve exhibits only the step attributed to the devitrification of the glassy TFE solution in PFA. Note that the sample should be cooled quite slowly in order to prepare such solutions.

The glass transition temperature (T_g) of glassy monomer solutions in PFA monotonically shifts toward lower temperatures with an increase in the monomer concentration. This change is the most illustrative for the solutions of fluoroolefins (Fig. 3, curves *1–3*), rather than the ethylene solution (curve *4*), in PFA.

The thawing of the glassy solutions of TFE in PFA irradiated at 77 K is accompanied by post-irradiation polymerization of the monomer.

The efficiency of the postpolymerization dramatically increases when TFE occurs in the glassy state (at a concentration of $[c]_i < 2.5$ mol/kg, the samples contain less than 5% of TFE in the crystalline state at 77 K. As the TFE content in the system increases ($[c]_i > 2.5$ mol/kg), a higher amount of the monomer is separated into the crystalline phase of its own and the post-irradiation polymerization is suppressed.

At a high TFE content in the system ($[c]_i \geq 6.13$ mol/kg), post-irradiation polymerization occurs almost exceptionally in the crystalline phase of TFE (dashed line in Fig. 2, curve *b*). The yield of the polymer at doses of preliminary irradiation of 100–200 kGy is ~1–2%, as in the crystalline monomer [21].

The calorimetric data show that the post-irradiation polymerization in the TFE–PFA samples with a monomer concentration of 3.0–5.0 mol/kg occurs in the glass transition temperature region of the glassy solution (dashed line in Fig. 2, curve *c*). It is in this region that a molecular mobility sufficient for chain propagation is developed. When the temperature is further increased, monomer crystallization takes place, the mobility of monomer molecules abruptly drops, and the post-irradiation polymerization stops. Active sites decay during melting, and the further elevation of the temperature does not lead to the resumption of the process.

In the case of a low TFE content, ($[c]_i \leq 2.5$ mol/kg), post-irradiation polymerization proceeds more effectively and is observed over a wide temperature range (dashed line in Fig 2, curve *e*). The polymer yield in experiments under these conditions substantially depends on the sample thawing rate. For example, an increase in the thawing rate of samples with identical concentrations that have received the same dose leads to suppression of post-irradiation polymerization.

To obtain kinetic information from the calorimetric data, we first determined the specific heat of polymerization of the monomers in the PFA matrix. For this purpose, the integral heat release due to polymerization and the conversions of the monomers were determined in a set of experiments. The heats of polymerization for TFE, CTFE, and VDF were $150 + 20$, 125 ± 20, and 130 ± 19 kJ/mol, respectively. The obtained values of the specific heat of polymerization for TFE and CTFE in the glassy PFA matrix agree well with the heat of polymerization of liquid TFE and CTFE [27, 28].

Figure 1 (curve *5*) presents the dependence of the degree of TFE conversion Q_k, as determined from calorimetric data, upon the monomer concentration ($[c]_i$) in the TFE–PFA sample. A comparison of curves *1* and *5* in Fig. 1 shows that the high rate of post-
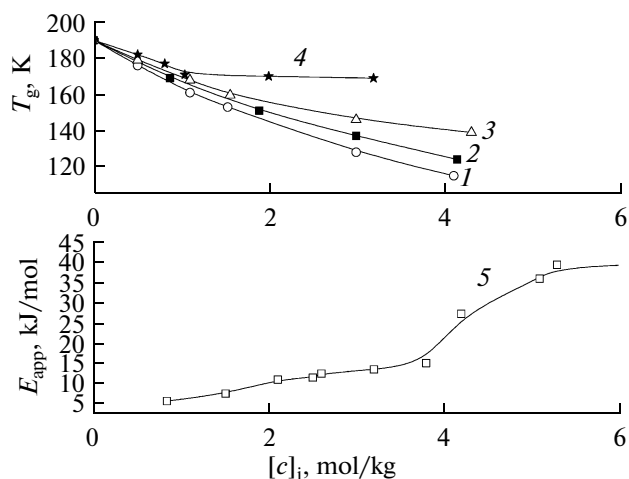

Fig. 3. Dependence of (*1–4*) the glass transition temperature T_g and (*5*) the apparent activation energy E_{app} on the monomer content in the initial mixture $[c]_i$ of (*1, 5*) TFE–PFA, (*2*) CTFE–PFA, (*3*) VDF–PFA, and (*4*) C_2H_4–PFA samples. The absorbed dose in the radiolysis of the TFE–PFA sample at 77 K is 85 kGy.

irradiation polymerization is observed in the samples in which TFE occurs only in the glassy state.

The initial portions of the calorimetric curves for post-irradiation polymerization (dashed curves in Fig. 2) yield fairly good straight lines on the Arrhenius plots $\log W = f(1/T)$, thereby making it possible to determine the apparent activation energy of post-irradiation polymerization E_{app}. Figure 3 (curve *5*) presents the dependence of E_{app} on the TFE concentration in TFE–PFA samples at identical parameters of the reactions It is seen that $E_{app} = 8.4 \pm 12.6$ kJ/mol at a low TFE content in the samples when the polymerization occurs during the devitrification of the glassy solution. As the TFE concentration in the system increases, E_{app} increases, reaching 41.9 kJ/mol, a value that is typical of the post-irradiation polymerization of crystalline TFE [21]. The low values of the activation energy for the samples with a low TFE concentration suggest the absence of diffusion constraints during the process upon devitrification of the matrix.

At low monomer concentrations in a TFE–PFA sample, the whole of the sample passes to the glassy state upon freezing and the monomer molecules surrounded by PFA form small aggregates. In this state, the translational arrival of monomer molecules at the propagating active site is facilitated and post-irradiation polymerization proceeds effectively.

An increase in the TFE content in PFA leads to the formation of a rather loose matrix upon freezing, which is composed of larger aggregates of TFE molecules that form the crystal lattice of their own, and makes the supercooled solution of TFE in PFA produced via devitrification capable of crystallization
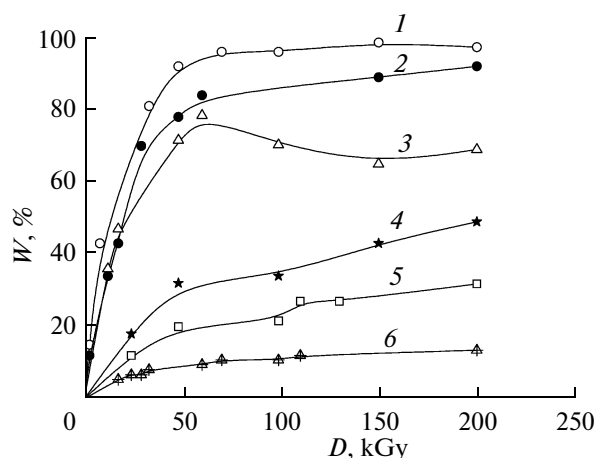
Fig. 4. Dependence of (*1, 4*) the total polymer yield Q_w (*2, 5*) the yield of PTFE Q_g, and (*3, 6*) the PTFE yield Q_k calculated from calorimetric curves of post-irradiation polymerization. The TFE concentrations in the TFE–PFA system are (*1–3*) 2.0 and (*4–6*) 3.15 mol/kg.

Fig. 5. Temperature dependence of the concentration of paramagnetic centers in (*1*) TFE solution in PFA and (*2*) PFA irradiated at 77 K. The TFE concentration in PFA is $[c]_i = 22.5$ mol/kg. The initial concentration of paramagnetic centers $[R]_o$ is 35×10^{17} g^{-1}, the holding time at each temperature is 10 min.
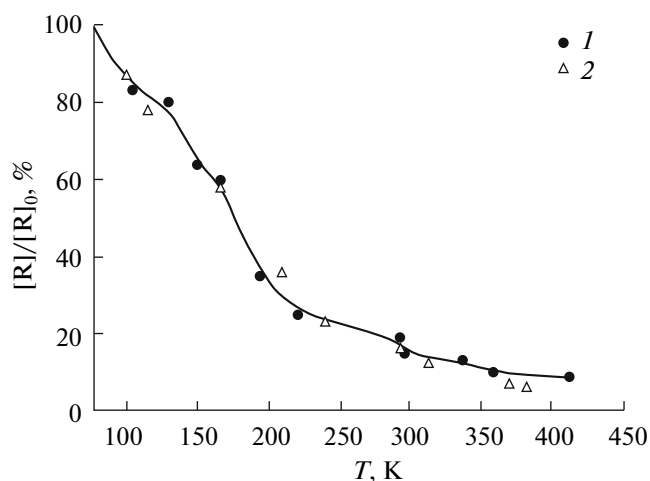
(Fig. 2, curve *c*). When the supercooled solution crystallizes, the molecular mobility sharply drops and post-irradiation polymerization is practically ceased.

If the TFE concentration in the initial solution is further increased, the matrix is made so loose by cooling that almost the entire amount of the monomer passes to the crystalline phase and the post-irradiation polymerization occurs in the crystal lattice of the TFE itself; i.e., it is very ineffective (Fig. 2, curve *b*).

In the case of a low TFE content ($[c]_i \le 2.0$ mol/kg), the monomer entirely occurs in the glassy state and the glass transition temperature at which the most intense polymerization is observed lies above the melting point of the monomer. As a result, the growth of polymer chains occurs in a wide temperature range and the total yield of the polymer reaches 90–100% (Fig. 4, curve *1*).

In the case when a portion of TFE forms the crystalline phase of its own in the system (TFE concentration of $[c]_i > 2.5$ mol/kg), post-irradiation polymerization proceeds until the melting of the crystalline phase of TFE (Fig. 3, curve *d*) because all propagation sites decay in the melt. As a result, the total yield of the polymer is low, reaching a limiting value of 10% at a dose of 50 kGy (Fig. 4, curve *4*).

At low doses of preliminary irradiation, the polymer yields determined gravimetrically (Q_g) and from the measured heat of post-irradiation polymerization (Q_k) almost coincide, although a noticeable discrepancy is observed with an increase in the dose (Fig. 4; curves *2, 3*). The reason behind this divergence is understandable, namely, the polymer can be produced during irradiation of the samples at 77 K. Indeed, from the results of direct calorimetric measurements at 77 K

it follows that Q_γ for the polymer is ~1% upon irradiation at a dose of 10 kGy and the radiation-chemical yield of polymerization G(-M) does not exceed 100 molecule/100 eV.

It is interesting that the addition of a small amount of vinyl chloride to the TFE–PFA system leads to an increase in the relative amount of the crystalline phase of TFE; as a result, the efficiency of its post-irradiation polymerization noticeably decreases. For example, the polymer yield (90%) observed upon TFE polymerization in the sample TFE (1.4 mol/kg)–PFA (1 kg) is reduced to 12% when a small amount (0.03 mol/kg) of vinyl chloride is admixed to the sample. In the presence of this amount of vinyl chloride in the glassy TFE–PFA solution, the proportion of the crystalline phase of TFE increases by a factor of 6. Such an increase in the amount of the crystalline TFE phase results in the suppression of the post-irradiation polymerization of TFE.

Figure 5 (curve *1*) illustrates the kinetics of the decay of paramagnetic centers (PMCs) during the thawing of the TFE–PFA sample with $[c]_i$(TFE) = 3.7 mol/kg irradiated at 77 K. A change in the PMC concentration in this sample is similar to that in neat PFA radiolyzed at 77 K (Fig. 5, curve *2*). In addition, the ESR spectrum of the TFE–PFA sample displays the same broad singlet as in the case of irradiated PFA. There are no ESR signals attributed to PMCs of the monomer or propagating polymer radicals. The absence of these signals is associated with a low concentration of paramagnetic species produced from TFE as compared to the concentration of PMCs resulting from matrix molecules. This situation can be due to two factors. First, the rise in the PMC concen-

tration during the radiolysis of crystalline TFE at 77 K comes to saturation at a dose of ~150 kGy, whereas the concentration of PMCs in PFA increases linearly until a dose of 830 kGy [29]. Therefore, the PMCs produced from PFA must prevail at high radiation doses absorbed by the TFE−PFA samples. Second, the concentration of TFE in the TFE−PFA samples in which effective polymerization is observed is very low ($([c]_i < 2.5$ mol/kg). As a result, the proportion of PMCs produced from TFE molecules will be much lower than that generated by PFA in the irradiated TFE−PFA sample.

Since post-irradiation polymerization of fluoroolefins in the glassy monomer−PFA solutions effectively proceeds at the glass transition temperatures of the solutions (which lie well above the melting temperature of the relevant monomer) and all active sites decay at the melting points of irradiated crystalline olefins (TFE, CTFE, VDF), it should be assumed that the paramagnetic species generated by PFA are actively involved in the processes of post-irradiation polymerization of the fluoroolefins in a glassy solution. In addition, the above data on the kinetics of PMC buildup depending on the dose and the decay of PMCs depending on the temperature in the monomer−PFA systems indicate the prevalence of the PFA paramagnetic centers.

It is noteworthy that the post-irradiation polymerization of the monomers has not been observed during the devitrification of glassy monomer−PFA solutions containing long-lived radicals generated by radiolysis of the PFA itself; that is, these radicals, which have a long lifetime in the liquid, do not take part in low-temperature post-irradiation polymerization. Consequently, the paramagnetic species involved in post-irradiation polymerization during the devitrification of glassy solutions are not stabilized in the liquid perfluoroalkane.

Figure 6 presents the plots of the polymer yield versus the dose of preliminary irradiation of glassy CTFE−PFA (curve 1) and VDF−PFA (curve 2) solutions at 77 K. It is seen that the yield of the polymer increases with the dose and high monomer conversions can be achieved at relatively low doses. The apparent activation energy of CTFE polymerization in the glassy CTFE−PFA solution containing 0.32 mol/kg of CTFE is 25.2 ± 4.2 kJ/mol.

Note that hexafluoropropylene irradiated in both (crystalline and glassy) states does not undergo polymerization. As any fluoroolefin radical, the radicals produced during HFP radiolysis can initiate the polymerization of HFP. However, an unreactive propagating radical is produced in the first events of chain growth and the chain is terminated [30]. These radicals are characterized by a low chemical activity and quite a long lifetime in the liquid. Thus, the inability of HFP to enter homopolymerization (according to published data [31], only lower oligomers—dimers, trimers, and tetramers—are produced in the radiolysis of
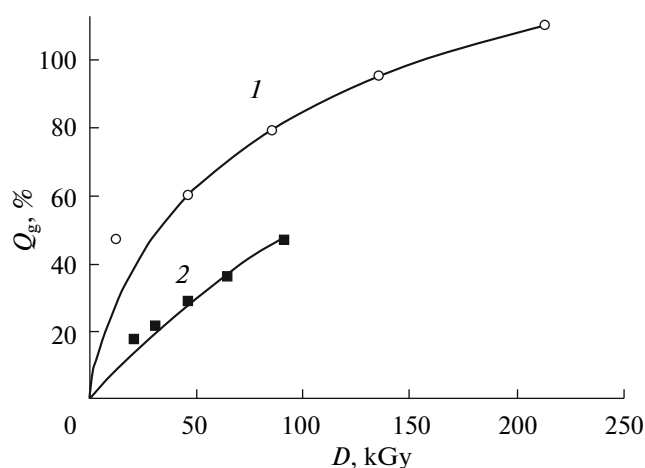

Fig. 6. Dose dependence of the polymer yield in the radiolysis of the (1) CTFE−PFA and (2) VDF−PFA systems at 77 K. The monomer concentrations ($[c]_i$) in the TFE−PFA are (1) 11.1 and (2) 60.0 mol/kg.

both crystalline and liquid hexafluoropropylene) can be associated with the formation of the inactive propagating oligomer radical. Despite this passive behavior in the homopolymerization reaction, HFP is quite active in the radical copolymerization with other vinyl monomers [32]. Obviously, alternation of the monomers in the terminal units of the growing radical takes place during copolymerization and the probability of the formation of the inactive propagating HFP derived radical is either reduced or eliminated altogether.

A comparison of the total polymer yield Q_g and the yield of polytetrafluoroethylene Q_k leads to the conclusion that a certain portion of PFA is linked in the polymer chain (Fig. 4). The perfluoroalkane is engaged to the polymer chain at the step of initiation or termination of the polymer chain. The presence of PFA units in the polymer chain revealed during the post-irradiation polymerization of some monomers in the glassy PFA matrix suggests that the PMCs or PFA take part in polymerization. This conclusion is supported by the following data.

(1) There is a difference between the polymer yield Q_w and the monomer conversion Q_g in the TFE−PFA and CTFE−PFA samples, which is due to the involvement of PFA in the polymer chain. The limiting values for the TFE−PFA ([TFE] = 3.15 mol/kg) sample are $Q_w \approx 40\%$ and $Q_k \approx Q_g \approx 28\%$ (Fig. 4; curves 4, 6). On the basis of these data, it was calculated that there are approximately two PFA molecules per 40 TFE units in the macromolecule produced from this sample. At a lower TFE concentration ($[c]_i = 2.0$ mol/kg), the monomer conversion is $Q_w \approx 99\%$ and $Q_g \approx 90\%$ (Fig. 4; curves 1, 3). In this case, the number of TFE units in the product macromolecule increases to ~160 according to similar estimates. Thus, post-irradiation polymerization of TFE−PFA samples with a

low TFE concentration when the monomer entirely occurs in the glassy state results in longer polymer chains than in the case of the TFE−PFA samples in which a portion of the monomer forms its own crystalline phase. This factor is also responsible for the increase in the total polymer yield. Using the kinetic data and assuming that the product macromolecule is endcapped at both sides by PFA molecules, which have a molecular mass of 538, we can estimate the ratio of monomer to PFA molecules in the CTFE polymer chain. For example, the CTFE−PFA sample having a monomer concentration of $[c]_i = 0.86$ mol/kg gives the product with two PFA units per 15 CTFE units after irradiation to a dose of 12.5 Mrad. Note that the ratio of PFA to perfluoroolefin units in the final product can vary over a wide range depending on the conditions of the process.

(2) Radiation polymerization of vinyl chloride in the glassy PFA matrix was conducted. Since PFA dissolves well in the freon $C_2F_4Br_2$ and the product poly(vinyl chloride) (PVC) is barely soluble in it, this Freon was used as a selective solvent for the removal of the unreacted portion of PFA from the polymeric product. The polymeric product obtained in the post-irradiation polymerization of vinyl chloride during the warming of the VC−PFA sample with a monomer concentration of $[c]_i = 1.52$ mol/kg irradiated at 77 K to a dose of 150 kGy was studied. The polymer produced during the post-irradiation polymerization of vinyl chloride in the glassy PFA matrix was thoroughly washed with Freon and dried in a vacuum, and its absorption spectrum was recorded. The IR spectrum displays an absorption band at 540 cm^{-1} characteristic of PFA, which indicates that PFA has entered into the structure of the product macromolecule (the most intense IR absorption bands of PFA at 1100−1300 cm^{-1} almost coincide with the PVC bands in this region). After thorough washing with freon and drying in a vacuum, the product was analyzed for fluorine. The polymer contained fluorine in an amount of 21 + 3%. The observed introduction of PFA units into the polymer chain during post-irradiation polymerization can occur at the steps of initiation and termination of polymer chains. Indeed, as has been mentioned above, post-irradiation polymerization most effectively proceeds at temperatures well above the melting point of the monomer and the reaction is initiated by PFA radicals alone. With the use of the obtained kinetic data, it is possible to determine the ratio between the −CH$_2$−CHCl− and −CF$_2$− units in the product macromolecule. For example, this ratio obtained from the experimentally found values of $Q_w = 28\%$ and $Q_k = 18.5\%$ is approximately 1.5; i.e., there are about 0.7 −CF$_2$− groups per vinyl chloride unit in the polymer molecule.

In conclusion, analysis of the experimental data on the efficiency of polymerization in the glassy state in the perfluoroalkane matrix enables us to arrange the test olefins in the following order: TFE > VDF > CTFE > C$_2$H$_4$ ≫ HFP.

REFERENCES

1. Scanlon, N.D. and Hanrahan, R.J., *J. Fluorine Chem.*, 1980, vol. 16, no. 3, p. 199.
2. Askew, W.C., *Diss. Abstr.*, 1966, vol. 27, p. 1458.
3. Mailen, J.C., *Diss. Abstr.*, 1965, vol. 25, p. 5812.
4. Askew, W.C., Reed, T.M., and Mallen, J.C., *Radiat. Res.*, 1968, vol. 33, p. 282.
5. Saraeva, V.V., *Radioliz uglevodorodov v zhidkoi faze* (Radiolysis of Hydrocarbons in the Liquid Phase), Moscow: Mosk. Gos. Univ., 1986.
6. Pshezhetskii, S.Ya., Kotov, A.G., Milinchuk, V.K., Roginskii, V.A., and Tupikov, V.M., *EPR svobodnykh radikalov v radiatsionnoi khimii* (ESR of Free Radicals in Radiation Chemistry), Moscow: Khimiya, 1972.
7. Barchenkova, A.I., Baberkin, A.S., and Volkova, E.V., *Khim. Vys. Energ.*, 1969, vol. 3, no. 5, p. 2684.
8. Atkinson, B., *J. Chem. Soc.*, 1962, no. 7, p. 268.
9. Cohen, N. and Heicklen, J., *J. Chem. Phys.*, 1965, vol. 45, p. 871.
10. Ivanov, V.S., *Radiatsionnaya khimiya polimerov* (Radiation Chemistry of Polymers), Leningrad: Khimiya, 1988.
11. Volkova, E.V., Fokin, A.V., Zimakov, P.V., and Belikova, V.M., in *Trudy Vtorogo Vsesoyuznogo soveshchaniya po radiatsionnoi khimii* (Proc. of Second All-Union Meeting on Radiation Chemistry), Moscow: Akad. Nauk SSSR, 1962, p. 464.
12. Manno, P.J., *Nucleonics*, 1964, vol. 22, no. 6, p. 64.
13. Volkova, E.V., Fokin, A.V., and Belikova, V.M., *Zh. Vses. Khim. O-va im. D.I. Mendeleeva*, 1961, vol. 6, no. 1, p. 113.
14. Tabata, Y., Shibano, H., and Oshima, K., *J. Polym. Sci., Part C*, 1967, no. 16, p. 2403.
15. Cordischi, D., Site, A.D., Lenzi, M., and Mele, A., *La Chem. L'Ind.*, 1962, vol. 44, no. 10, p. 1101.
16. Tabata, Y., Ito, W., Oshima, K., and Takagi, J., *J. Macromol. Sci.*, 1970, vol. A4, p. 815.
17. Fujioka, S., Shinohara, Y., and Nakamura, T., *J. Chem. Soc. Jpn. Ind. Chem. Sect.*, 1970, vol. 73, p. 824.
18. Volkova, E.V., Zimakov, P.V., Fokin, A.V., Sorokin, A.D., Belikova, V.M., Bulygina, L.A., Skobina, A.I., and Krasnousov, L.A., in *Radiatsionnaya khimiya polimerov* (Radiation Chemistry of Polymers), Moscow: Nauka, 1966, p. 109.
19. Muromtsev, V.I., Bruk, M.A., Asaturyan, R.A., Akhvlediani, I.G., and Abkin, A.D., *Khim. Vys. Energ.*, 1968, vol. 2, no. 4, p. 369.
20. Chuiko, K.K., Bruk, M.A., Abkin, A.D., Aslankina, T.S., Gol'der, G.A., Golikov, V.P., and Muromtsev, V.I., *Vysokomol. Soedin., Ser. B*, 1972, vol. 14, no. 9, p. 635.
21. Allayarov, S.R., Kiryukhin, D.P., Asamov, M.K., and Barkalov, I.M., *Khim. Vys. Energ.*, 1980, vol. 14, no. 6, p. 509.
22. Allayarov, S.R., Kiryukhin, D.P., Asamov, M.K., and Barkalov, I.M., *Vysokomol. Soedin., Ser. A*, 1982, vol. 24, no. 3, p. 486.

23. Allayarov, S.R., Bol'shakov, A.I., and Barkalov, I.M., *Vysokomol. Soedin., Ser. A*, 1987, vol. 29, no. 2, p. 364.

24. Barkalov, I.M., *Usp. Khim.*, 1980, vol. 49, no. 2, p. 362.

25. Allayarov, S.R., Barkalov, I.M., and Kiryukhin, D.P., *Khim. Vys. Energ.*, 1987, vol. 21, no. 2, p. 138.

26. Barkalov, I.M. and Kiryukhin, D.P., *Int. Rev. Phys. Chim.*, 1994, vol. 13, no. 2, p. 337.

27. *Vinyl Polymerization*, Ham, G., Ed., New York: Marcel Dekker, 1969.

28. Volokhonovich, I.E., Pirogov, O.N., Kleimenov, N.A., and Markevich, A.M., *Vysokomol. Soedin., Ser. B*, 1974, vol. 16, no. 4, p. 253.

29. Allayarov, S.R., Demidov, S.V., Kiryukhin, D.P., Mikhailov, A.I., and Barkalov, I.M., *Khim. Vys. Energ.*, 1983, vol. 17, no. 2, p. 178.

30. Allayarov, S.R., Barkalov, I.M., Kuzina, S.I., Loginova, N.N., and Mikhailov, A.I., *Khim. Vys. Energ.*, 1988, vol. 22, no. 4, p. 333.

31. Skobina, A.I. and Volkova, E.V., in *Radiatsionnaya khimiya polimerov* (Radiation Chemistry of Polymers), Moscow: Nauka, 1966, p. 126.

32. Kuzieva, Kh., *Ftorsoderzhashchie polimery* (Fluorinated Polymers), Tashkent: Fan, 1978.