Exposed to radiation, fluorocarbon polymers, depending on their composition, undergo changes in two different directions. Fully halogenated polymers such as polytetrafluoroethylene (PTFE), polytrifluorochloroethylene, and copolymers of tetrafluoroethylene with hexafluoropropylene or with perfluoroalkylvinyl ethers undergo rapid degradation. Polymers that contain a certain amount of hydrogen, such as, for example, copolymers of vinylidene fluoride, undergo rapid structure formation with the development of a three-dimensional structure. Intermediate cases are rarely encountered.

PTFE can be placed in a separate category on account of the large number of studies devoted to it [1–8] but also the incomplete information about it as a result of the absence of suitable solvents and reliable data on molecular weights.

The discrepancy between the high chemical and heat resistance of PTFE [5, 6] and its very low radiation resistance [4] remains the subject of keen debate. To this day, a mechanism of PTFE radiolysis that explains the degradative nature of this process has not clearly been determined.

The study of the radiation degradation of PTFE is extremely difficult on account of its insolubility and the complexity of analysis of the radiolysis products. Existing methods for determining the molecular inhomogeneity of polymers are based mainly on using the properties of weak solutions of the polymers if they are of linear structure and on investigating the process of swelling in specially selected solvents in polymers of three-dimensional structure. Naturally, only polymers with good solubility can be analysed by such methods. For insoluble polymers such as PTFE, these methods are unacceptable. Good models for investigating the mechanism of radiolysis of PTFE may be linear perfluoroalkanes (PFAs), the degradation products of which are easily analysed by normal methods. However, description of the mechanism of radiolysis of PTFE using PFA radiolysis data requires knowledge of the influence on radiolysis of a several thousandfold carbon chain elongation of PFA.

INFLUENCE OF CHAIN LENGTH AND AGGREGATE STATE ON THE MECHANISM OF RADIOLYSIS OF LINEAR PERFLUOROALKANES

Increase in the chain length of PFA from \( C(6) \) to \( C(16) \) does not affect the qualitative composition of the molecular products of radiolysis \([C_F_4, C_2F_6, C_3F_8, n-C_6F_{14}, n-C_8F_{12}, n-C_6F_{14}, n-C_5F_{12}, n-C_4F_{10}, n-C_3F_{8}, n-C_2F_{6}, F_2C=CFCF_3, F_2C=CF_2F_2, F_2C=CF_2F_3, n-C_4F_{10}, n-C_3F_{10}, n-C_2F_{12}, n-C_5F_{12}, F_2C=CFCF_3, C_5F_{12}, C_4F_{10}, C_3F_{10}, C_2F_{12}, n-C_4F_{14}, n-C_3F_{14}, n-C_2F_{14}, n-C_5F_{14}, C_6F_{14}, C_7F_{14}, F_2C=CFCF_3, F_2C=CF_2F_2, F_2C=CF_2F_3] \) and with end double bonds \([C_6F_{14}, C_7F_{14}, C_8F_{14}, F_2C=CFCF_3, C_5F_{12}, C_4F_{10}, n-C_3F_{10}, n-C_2F_{12}, n-C_5F_{12}, F_2C=CFCF_3, C_5F_{12}, C_4F_{10}, C_3F_{10}, C_2F_{12}, n-C_4F_{14}, n-C_3F_{14}, n-C_2F_{14}, n-C_5F_{14}, C_6F_{14}, C_7F_{14}, F_2C=CFCF_3, F_2C=CF_2F_2, F_2C=CF_2F_3] \) compounds that are higher boiling than the initial PFA compound. However, the amount of radiolysis products in this case decreases roughly by 20%. Reduction in the product yield in \( n-C_{18}F_{34} \) appears to be due to \( \sim F_2C_2C^* \) "cage" effects which prevent the removal of the heavier \( \sim F_2C_2C^* \) radicals from the "cage" during C–C bond rupture. On changing from PFAs to their polymeric analogues, the "cage" effect increases and, finally, during radiolysis of PTFE, low molecular weight products \([C_6F_{14}, F_2C=CFCF_3, C_5F_{12}, n-C_4F_{14}, n-C_3F_{14}, n-C_2F_{14}, n-C_5F_{14}, C_6F_{14}, C_7F_{14}, F_2C=CFCF_3, F_2C=CF_2F_2, F_2C=CF_2F_3, n-C_4F_{14}, n-C_3F_{14}, n-C_2F_{14}, n-C_5F_{14}, C_6F_{14}, C_7F_{14}, F_2C=CFCF_3, F_2C=CF_2F_2, F_2C=CF_2F_3] \) are formed in a low radiation yield \((G = 0.3) \).

The main PFA radiolysis products are linear PFAs with different chain lengths, and their proportion with a radiation dose of 10–300 Mrad amounts to 90 ± 3%. Their proportion decreases with further increase...
in the radiation dose, and at 1900 Mrad they amount to 80 ± 4%. The formation of an appreciable amount of fluoroolefins (over 3%) during the radiolysis of PFAs was found at radiation doses of over 100 Mrad, and their presence was confirmed by the characteristic lines in the IR spectra [11, 12]. The low content of olefin analogue in the radiolysis products of both PFAs and PTFE indicates that perfluoroalkyl radicals are incapable of disproportionation with fluorine atom detachment.

In the course of the radiolysis at 300 K of liquid perfluoroalkane \( n \text{C}_6 \text{F}_{14} \), \( n \text{C}_8 \text{F}_{18} \) or solid perfluoroalkane \( n \text{C}_{12} \text{F}_{26} \), \( n \text{C}_{16} \text{F}_{34} \), for every 100 eV of absorbed energy at a radiation dose of 50 Mrad there are roughly two decomposed PFA molecules [10]. As follows from available data, in contrast to PTFE [4], linear PFAs possess greater radiation resistance \( (G = 1–5 [13–16]) \) than their hydrocarbon analogues \( (G = 6–10 [17, 18]) \).

Thus, the radiolysis of PFA molecules is not dependent on their chain length, and the main products of their radiolysis are linear PFAs formed on C–C bond rupture.

PFA chain elongation from 6 to 16 carbon atoms has no effect on the concentration of paramagnetic centres [PCs] stabilised in the course of radiolysis at 77 K [10]. The kinetics of accumulation of PCs during the radiolysis of two PTFE grades (F-4, F-4D) differing in molecular weights [19] also matches entirely. The radiation chemical yield of PCs, calculated from the initial section of the curve of PC accumulation in PFAs and PTFE, amounts to \( G = 1.6 \text{ PC/10}^2 \text{ eV} \) and \( G = 0.4 \text{ PC/10}^2 \text{ eV} \) respectively.

The EPR spectrum of PFA irradiated at 77 K comprises the superimposition of signals from three radicals [11, 12]. In the spectrum, peaks characteristic of stabilised radicals \(-\text{CF}_2\text{-C}^*\text{-CF}_2-\) and \(-\text{CF}_2\text{C}^*\text{CF}_2-\) are recorded. The main spatial parameters of the carbon skeleton of these radicals [20–22] are very consistent with the spiral configuration of the PFA molecules in crystals. Besides signals of these radicals, components of a quadruplet spectrum belonging to the \( F_3\text{C} \) radical are present. Increase in the chain length of PFA from 6 to 16 carbon atoms does not affect the parameters of the EPR spectra, but the form of the spectra changes, indicating a change in the ratio of the amount of radicals, and this is particularly marked on switching from low molecular weight PFAs to the polymer.

The ratio of the signal intensity of \(-\text{F}_2\text{CF}_2\text{C}^*\) radicals to the signal intensity of \(-\text{F}_2\text{CFC}^*\text{CF}_2-\) in PFAs is in good agreement with the equation

\[
\frac{[-\text{F}_2\text{CF}_2\text{C}^*]}{[-\text{F}_2\text{CFC}^*\text{CF}_2-]} = \frac{3}{n-2} \tag{1}
\]

where \( n \) is the number of carbon atoms in a PFA molecule [16]. Analysis of this equation showed that the proportion of \(-\text{F}_2\text{CF}_2\text{C}^*\) radicals in the spectrum of PFA irradiated at 77 K is directly proportional to the number of fluorine atoms of the \( F_3\text{C} \) groups of a PFA molecule.

EPR spectra of PTFE irradiated at 77 K comprise the superimposition of the signals of several PCs. The components of signals of “middle” [23] \(-\text{F}_2\text{CFC}^*\text{CF}_2-\) and allyl \(-\text{F}_2\text{CFC}^*\text{CF}^*\text{CF}_2-\) macroradicals [24, 25], and also spectra of positive and negative charges captured by different kinds of trap [26], can be recorded in the PTFE. There are contradictory data in the literature concerning the presence of a signal of \(-\text{F}_2\text{CF}_2\text{C}^* -\text{macroradicals} [27]. On the other hand, as confirmed by Astakhov and co-workers [28–30], end macroradicals are not recorded in the EPR spectrum of PTFE irradiated at 77 K. Recent investigations have shown [16] that \(-\text{F}_2\text{CF}_2\text{C}^*\) radicals formed on C–C bond rupture are not stabilised in the matrices of PFA and PTFE. In the EPR spectra of specimens irradiated at 77 and 300 K, only \(-\text{F}_2\text{CF}_2\text{C}^*\) radicals are recorded, formed as a result of F atom detachment from the end \( F_3\text{C} \) groups. The proportion of stabilised \(-\text{F}_2\text{CF}_2\text{C}^*\) radicals in high molecular weight PFA, such as PTFE with a molecular weight of \( 10^6 \), amounts to \( 3/(n-2) = 10^{-4} \), which is almost 1000 times lower than the proportion of \(-\text{F}_2\text{CFC}^*\text{CF}_2-\) radicals. Therefore, there is practically no \(-\text{F}_2\text{CF}_2\text{C}^*\) radical spectrum in the spectrum of irradiated PTFE.

The found laws governing the influence of the chain length of PFAs on their radiolysis can be used to describe the mechanism of radiolysis of PTFE.

**EFFECT OF GAMMA-RADIATION ON THE MOLECULAR TOPOLOGICAL STRUCTURE OF POLYTETRAFLUOROETHYLENE**

Thermomechanical spectroscopy (TMS) – a new solutionless means of identifying the molecular topological structure of polymers – was developed at the Institute of Chemical Physics Problems of the Russian Academy of Sciences. In reference [31], the TMS method was used to study the molecular topological structure of PTFE before and after exposure to gamma-radiation. The nature of the thermomechanical curve of non-irradiated PTFE indicates its amorphous–crystalline structure. At temperatures ranging from \(-100^\circ\text{C}\) to \(500^\circ\text{C}\), the lowest-temperature relaxation transition was found only close to room temperature. The relaxation transition at \( T_g \) is 123°C that was claimed in reference
of the low-temperature modification and results in the lowers the molecular weight of the crystallised chains unchanged. In the crystalline phase, gamma-radiation structure of the amorphous block remain practically weight characteristics in the pseudo-three-dimensional of PTFE, both the free volume and the molecular weight of PTFE, the effects of irradiation on its properties are and dense packing of chains in the crystalline phase as a result of their transformation into amorphous phase. Thus, by virtue of the more regular crystalline phases as a result of their transformation into disappearance of the intermediate and high-temperature crystalline phases as a result of their transformation into amorphous phase. Thus, by virtue of the more regular dense packing of chains in the crystalline phase of PTFE, the effects of irradiation on its properties are more appreciable.

It was shown [31] that irradiation leads to profound changes in the morphology of PTFE. As the main radical process during the radiolysis of PTFE is splitting out of the fluorine atom, it is its reactions that may play the key role in breakdown of the crystalline structure. In connection with this, the next logical step is to clarify the role of the formation of fluorine and a radical centre during the radiolysis of PTFE in the mechanism of breakdown of the polymer. To this end, the most suitable method proved to be quantum-chemical calculation of the geometry of a PFA molecule and perfluoroalkyl radicals.

QUANTUM-CHEMICAL CALCULATION (QCC) OF THE GEOMETRY OF A MOLECULE AND RADICALS OF PERFLUOROALKANES FOR THE MODELLING OF A MACROMOLECULE OF IRRADIATED POLYTETRAFLUORETHYLENE

From general positions of molecular orbital (MO) theory it follows that the stability of the ion radicals should increase with increasing length of the PFA chain on account of the higher capacity of a long molecule to dissipate energy. However, semi-empirical QCCs of \( C_nF_{n+2} \) molecules with \( n = 8-20 \) showed that in the free state their anion radicals have longer central C–C bonds of 1.88–1.90 Å, although the existence of such a bond is theoretically impossible. For example, a C–C bond of 1.90 Å length was found experimentally in polymers of fullerences \( \text{RbC}_{60} \) [32]. As in QCC, experiment indicates that the anion radicals of PFA break down.

According to data of semi-empirical QCCs, the conversion by radiolysis of \( C_nF_{n+2} \) molecules with \( n = 8-20 \) leads to rupture of one of the C–C bonds. The difference in energies of the ground and excited states of the molecules amounts to 1.44–1.46 kcal/mol and hardly depends on the carbon chain length of the PFAs.

Comparison of the results of non-empirical and semi-empirical QCCs of linear PFAs revealed an unexpected behaviour pattern. According to data of non-empirical QCCs, \( C_nF_{n+2} \) molecules with \( n = 10 \) have a spiral structure with C–C–C–C torsion angles of 160–161°. According to data of semi-empirical QCCs by the parametric model 3 (PM3), modified neglect of differential overlap (MNDO), and Austin model 1 (AM1) methods, these same molecules have two stable conformations: a spiral conformation with C–C–C–C torsion angles of 159–162°, and a plane conformation with C–C–C–C torsion angles of 180°. At present there are no experimental data on the conformation of perfluoroalkanes with \( n = 10 \). Therefore, it is not possible to compare the data obtained with experiment.

The changes occurring with a PTFE macromolecule as a result of the formation of a \( -\text{CF}_2-C^*C=\text{CF}_2- \) radical were modelled using quantum-chemical calculation [33] of the geometry of an \( n\text{C}_{20}F_{42} \) molecule and an \( F_2\text{C}(\text{CF}_2)_8\text{FC}^*(\text{CF}_2)_9\text{CF}_3 \) radical, which is formed by the splitting out of a fluorine atom from the tenth carbon atom in the chain of the given PFA.

As a result of repulsion between the unbound fluorine radicals of PFAs on account of their large Van der Waals radius (1.4 Å), the PTFE molecule in the crystalline state has the shape of a spiral [34]. Comparison of the results of different quantum-chemical calculations showed that the spiral structure of the \( C_{20}F_{42} \) molecule (Figure 1(a)) is reproduced by all semi-empirical methods. In this case, the best agreement of experimental and calculated geometry of molecules is achieved in calculations by the PM3 method. The three-dimensional structure of the \( F_2\text{C}(\text{CF}_2)_8\text{FC}^*(\text{CF}_2)_9\text{CF}_3 \) radical (Figure 1(b)) differs from the structure of the \( n\text{C}_{20}F_{42} \) molecule. The results obtained indicate that the transformation of the \( C_{20}F_{42} \) molecule into a \( C_{20}F_{41}^* \) radical is accompanied with strong rearrangement of the molecular structure. In the solid phase, such reorganisation should be accompanied with a strong change in crystalline structure. It can be assumed that \( -\text{CF}_2-C^*C=\text{CF}_2- \) radicals formed during the radiolysis of PTFE comprise one of the main sources of breakdown of the crystalline structure of the polymer.

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Figure 1. Structure of \( C_{20}F_{42} \) molecule (a) and \( C_{20}F_{41}^* \) radical (b) according to data of quantum-chemical calculations
MECHANISM OF RADIOLYSIS OF POLYTETRAFLUOROETHYLENE

In spite of the large number of studies devoted to the radiolysis of PTFE, it proved impossible to find the value of the radiation yield of degradation of PTFE in vacuum. The radiation resistance of PTFE has been judged hitherto only from indirect radiolysis parameters associated with degradation of the PTFE chain. According to data in reference [4], the value of the absorbed dose of ionising radiation (in air at 300 K) with which the strength is halved is two orders of magnitude lower for PTFE (1 Mrad) than for PE (100 Mrad). Comparison of the strength of PTFE with that of other polymers also shows that PTFE possesses the lowest resistance to high-energy radiation among known polymers. Thus, PTFE has been termed “the most non-radiation-resistant synthetic polymer”. At the same time it is known that linear perfluoroalkanes (low molecular weight analogues of PTFE) possess greater radiation resistance \( G = 1–5 \) ([13–16]) than their hydrocarbon analogues \( G = 6–10 \) ([17, 18]). Furthermore, if degradation of the PTFE chain were effective, then low-temperature (77 K) radiolysis would produce a high yield of \( \sim\text{F}_2\text{CFC}^-\text{CF}_2^- \) and \( \sim\text{F}_2\text{CF}_2\text{C}^-\text{CF}_2^- \) macroradicals which are thermally “ultrastable”. In practice [35], the PC yield in PTFE is very low \( G = 0.25 \), and it is more than an order of magnitude lower than in PE \( G = 5.8 \).

Specialists in the field of radiation chemistry who are engaged in studying polymers quite often fail to realise that, in the process of radiation chemical reactions, the physical state of the specimen may change significantly. Radiation chemical reactions are very often examined purely from a chemical point of view, thereby neglecting the influence of the physical state. This also seems to apply to the radiolysis of PTFE.

To determine the degree of radiation degradation of the PTFE chain, it is necessary to measure the molecular weight (MW) before and after radiolysis. Data on the change in molecular weight of PTFE during radiolysis have normally been obtained using special indirect methods [5, 6]. Unfortunately, analysis of the literature indicates the poor convergence of available data. This is natural, as no one as yet has managed to characterise the weight of PTFE macromolecules directly, by virtue of the fact that they cannot be converted either to a soluble or to a viscous-flow state. Therefore, the notion of the MW for PTFE is purely virtual, and it makes sense to speak of and analyse the molecular weight characteristics only in topological blocks, and by block summation, obtaining information about its molecular weight. In reference [31], TMS was used to determine the MW in all topological structures of PTFE before and after gamma-radiation.

The PTFE degradation yield \( G \) (chain ruptures per 100 eV of absorbed energy), calculated from the initial section of the curves of the dependences of the block-average molecular weight on radiation dose, does not exceed \( G = 0.2 \) in air and \( G = 0.1 \) in vacuum. The magnitude of the PTFE degradation yield calculated from MW data in the literature \([7, 36]\) amounts to less than 0.1. Degradation yields of this magnitude indicate that PTFE possesses radiation chemical stability. The chain degradation yield in PTFE is almost an order of magnitude lower than that in PE, and two orders of magnitude lower than that in cellulose and polysulphones (Table 1).

Thus, PTFE, along with excellent heat and chemical stability, also possesses radiation chemical resistance.

Although macromolecules of PTFE are not prone to degradation during radiolysis, this polymer is characterised by structural and topological changes. The \( \sim\text{CF}_2^-\text{C}^*\text{CF}_2^- \) macroradicals formed in the course of radiolysis may be initiators of structural topological transformations in PTFE. Their formation from macromolecules is accompanied with strong rearrangement of the molecular (Figure 1) and supermolecular structure of the polymer. In solid phase, such reorganisation seems to be accompanied with strong changes in crystalline structure and its amorphisation, which leads to loss of mechanical properties of the PTFE. Therefore, PTFE possesses the lowest mechanical resistance to high-energy radiation among known polymers.

Generalising the results of high-pressure radiolysis of PTFE, Astakhov et al. [28–30] proposed a mechanism of free radical formation that consists of two stages after ionisation: at the first stage, decomposition of the C–C bond in an ionised fragment of the macromolecule occurs, accompanied with disproportionation of the breakdown products; at the second stage, breakdown of the C–F bond occurs by the recombinant of the electron with the fluorovinyl cation radical formed. Thus, a cation radical mechanism of radiation degradation of PTFE was proposed. By this mechanism, at the end of each PTFE macromolecule, after its degradation, an allyl radical is formed, by the recombinant of which with fluorine atoms a double bond should be formed. As a result, during the radiolysis of PTFE, the yield of unsaturated bonds should be equal to the degradation yield of PTFE chains. However, as noted above [5], in the radiolysis of PTFE in vacuum, products with unsaturated bonds are not formed. They are formed only during the irradiation of PTFE in air [7].

According to the mechanism described in references [11] and [12], in the radiation degradation of PTFE the main role is played by radiolytic fluorine atoms formed by the rupture of the C–F bond. The radiation chemical yield of PCs, calculated from the initial section of the curve of PC accumulation in PFA and PTFE, is almost an order of magnitude lower than that in hydrocarbon analogues (Table 1). The observed low yield of radicals led to the idea of the recombinant of radicals stabilised
in PFA with radiolytic fluorine atoms. On the other hand, radiolytic fluorine atoms, reacting with the radical pair \( \sim F_2 CF_2 C\cdots\cdot CF_2 CF_2 \sim \) formed by C–C bond rupture in PTFE, ensure the breakdown of the macromolecule. Thus, the radiation degradation of PTFE can occur through the recombination of the “caged” \( \sim F_2 CF_2 C\cdots\cdot CF_2 CF_2 \sim \) radicals with radiolytic fluorine atoms.

### REFERENCES

33. S. R. Allayarov et al., Khimiya Vysokikh Energii, 2004 (in print).

(No date given)