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Radiation-Induced Destruction of Polytetrafluoroethylene: New Concept

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Abstract

Four topological structures of polytetrafluoroethylene (PTFE) have been found by using thermomechanical spectroscopy (TMS): amorphous structure and three crystalline (high-melting, intermediate, and low-melting) modifications. Gamma irradiation of PTFE showed that both free volume and molecular mass remain practically unaffected in the pseudoreticular structure of the amorphous block. In the crystalline phase, gamma irradiation reduces the molecular weight of the crystallized chains of the low-temperature modification; the intermediate and high-temperature crystalline phases disappear as a result of their transformation into the amorphous structure. Quantum-chemical simulation of the $F_3C(CF_2)_9FC^{\bullet}(CF_2)_8CF_3$ radical and perfluoroalkane n-$C_{20}F_{42}$ molecule demonstrated that elimination of a fluorine atom results in a substantial rearrangement of the molecular structure of PTFE. In the solid, a rearrangement like that is accompanied by dramatic changes and strains in the crystalline structure of perfluoroalkane and PTFE, contributing to the loss of its mechanical strength.

INTRODUCTION

Irradiation changes fluorocarbon polymers in two different directions depending on their composition. Completely halogenated polymers as polytetrafluoroethylene (PTFE), polytrifluorochloroethylene, and tetrafluoroethylene copolymers with hexafluoropropylene or with perfluoroalkylvinyl ethers undergo fast destruction. Polymers with hydrogen atoms such as vinylidene fluoride copolymers are quickly structured to form a three-dimensional network. Intermediate cases are rare occurrences.

While PTFE has been discussed in a great many of publications [1–8], full data on its properties and molecular weights are yet unavailable because of the lack of proper solvents.

High chemical and thermal stability of PTFE [5, 6] and its very low radiation stability [4] are still being vigorously debated. To the present day, there is no clear concept on the mechanism of PTFE radiolysis to explain the destructive character of this process.

Research into radiative destruction of PTFE is methodologically hindered because of its insolubility and difficulties in analyzing radiolysis products. Current methods for determining molecular nonhomogeneity of polymers mostly use the properties of their dilute solutions for linear polymers and swelling in specially selected solvents for cross-linked polymers. These methods are naturally applicable to highly soluble polymers alone. For insoluble polymers such as PTFE, these methods are unacceptable. Linear perfluoroalkanes (PFAs), whose destruction products can easily be analyzed by conventional procedures, are good models to study the mechanism of PTFE radiolysis. For this, however, we need to know how (several thousand fold) extension of the PFA carbon chain will affect radiolysis.

CHAIN LENGTH AND PHYSICAL STATE EFFECTS ON THE MECHANISM OF RADIOLYSIS OF LINEAR PERFLUOROALKANES

Extension of the PFA chain length from C_6 to C_{16} has no effect on the composition of the molecular products of radiolysis: CF_4, C_2F_6, C_3F_8, n-C_4F_{10}, n-C_5F_{12}, n-C_6F_{14}, *cis*-C_3F_6; internal (C_5F_{10}, $CF_3CF{=}CFCF_3$) and terminal

(C_2F_4, C_3F_6, $F_2C{=}CFC_2F_5$) perfluoroalkenes; and compounds with higher boiling points than those of the PFA substrate. However, the yield of radiolysis products decreases by approximately 20 %. For n-$C_{16}F_{34}$, this is probably due to the "cage" effects of ~$F_2CF_2C^\bullet$ ...$^\bullet CF_2CF_2$~, which hinder the removal of the heavier ~$F_2CF_2C^\bullet$ radicals from the "cage" during C-C bond cleavage. For the polymer analogue of PFA, the "cage" effect is even more pronounced, resulting in a low radiation yield ($G = 0.3$ [10]) of low-molecular products (CF_4, C_2F_6, C_3F_8, SiF_4 [9]) during radiolysis of PTFE.

Linear PFAs with varying chain lengths are the main products of PFA radiolysis, amounting to (90 ± 3) % for a radiation dose of 10–300 Mrad. As the dose increases (1900 Mrad), percent of these products decreases to (80 ± 4) %. Radiolysis of PFA forms more than 3 % fluoroolefins when radiation doses exceed 100 Mrad, as confirmed by the characteristic lines in the IR spectra [11, 12]. The low content of the olefinic analogue among the radiolysis products of PFA and PTFE is due to the inability of perfluoroalkyl radicals to disproportionate by elimination of an F atom.

Radiolysis of liquid (n-C_6F_{14}, n-C_8F_{18}) or solid (n-$C_{12}F_{26}$, n-$C_{16}F_{34}$) perfluoroalkanes at 300 K splits approximately two PFA molecules per 100 eV of absorbed energy for a radiation dose of 50 Mrad [10]. As follows from the available data, linear PFAs, unlike PTFE [4], exhibit higher radiation resistance ($G = 1$–5 [13–16]) than their hydrocarbon analogues ($G = 6$–10 [17, 18]).

Thus radiolysis of PFA molecules is independent of the chain length, and linear PFA arising from C–C bond cleavage are the major products of radiolysis.

Extension of the PFA chain from 6 to 16 carbon atoms has no effect on the concentration of the paramagnetic centres (PC) stabilised in the course of radiolysis at 77 K [10]. The kinetics of PC accumulation in the course of radiolysis of PTFE grades (F-4, F-4D) differing in molecular mass [19] are also in perfect agreement with each other. The radiation-chemical yield of PC calculated from the initial region of the PC accumulation curve in PFA and PTFE is 1.6 and 0.4 PC/10^2 eV, respectively.

The EPR spectrum of PFA irradiated at 77 K represents a superposition of signals from three radicals [11, 12]. The spectrum contains peaks characteristic of the stabilised $-CF_2-C^\bullet F-CF_2-$ and $-CF_2C^\bullet F_2$ radicals. The basic dimensions of the carbon skeleton of these radicals [20–22] are in good agreement with the helical configuration of the PFA molecule in crystal. In addition to the signals of these radicals, there are components of the quadruplet spectrum of the $F_3C^\bullet$ radical. An increase from 6 to 16 carbon atoms in the PFA chain length affects the shape, but not the parameters, of the EPR spectra, indicating that the proportion of the radicals has changed, this effect being particularly pronounced in going from low-molecular PFAs to polymers.

The signal intensity ratio between the ~$F_2CF_2C^\bullet$ and ~$F_2CFC^\bullet CF_2$~ radicals in PFA obeys an equation

$$[\sim F_2CF_2C^\bullet]/[\sim F_2CFC^\bullet CF_2\sim] \cdot 3/(n-2) \qquad (1)$$

where n is the number of carbon atoms in the PFA molecule [16]. Analysis of this equation suggested that the fraction of ~$F_2CF_2C^\bullet$ radicals in the spectrum of PFA irradiated at 77 K is directly proportional to the number of the fluorine atoms of the F_3C groups in the PFA molecule.

The EPR spectra of PTFE irradiated at 77 K represent a superposition of the signals of several PC. They can involve the components of the signals of the "middle" (~$F_2CFC^\bullet CF_2$~ [23]) and allylic (~$F_2CFC^\bullet CF{=}CFCF_2$~ [24, 25]) polymer radicals, and the signals of the positive and negative charges captured by various kinds of traps [26]. The presence of a signal of ~$F_2CF_2C^\bullet$ polymer radicals in the EPR spectrum of irradiated PTFE is a matter of great controversy. According to [23], terminal polymer radicals are formed during C–C bond cleavage in the course of PTFE radiolysis both at 77 K and 300 K, and their concentration in the range 10–100 Mrad in vacuum is about 10 times lower than the concentration of the "middle" polymer radicals [27]. On the other hand, it was argued [28–30] that no terminal polymer radicals were registered in the EPR spectrum of PTFE irradiated at 77 K. Recent studies showed [16] that the ~$F_2CF_2C^\bullet$ radicals arising from C–C bond cleavage are not stabilised in

PFA and PTFE matrices. The EPR spectra of the samples irradiated at 77 and 300 K contain only the $\sim F_2CF_2C^{\bullet}$ radicals formed by F atom elimination from the terminal F_3C groups. The fraction of the stabilised $\sim F_2CF_2C^{\bullet}$ radicals in a high-molecular PFA such as PTFE with a molecular mass of $3/(n - 2) \approx 10^{-4}$, which is nearly one thousands of the fraction of the $\sim F_2CFC^{\bullet}FCF_2\sim$ radicals. That is why the spectrum of irradiated PTFE is practically free from the spectrum of the $\sim F_2CF_2C^{\bullet}$ radicals.

The chain length effects of PFAs on radiolysis can be useful to describe the mechanism of PTFE radiolysis. Theoretical verification of this assumption is currently underway.

GAMMA RADIATION EFFECT ON THE MOLECULAR TOPOLOGY OF POLYTETRAFLUOROETHYLENE

Thermomechanical spectroscopy (TMS) is a new solution-free method of diagnostics of the molecular topology of polymers worked out at the Semenov Institute of Chemical Physics, RAS. A TMS study of the molecular topology of PTFE before and after gamma irradiation is reported in [31]. The thermomechanical curve of non-irradiated PTFE demonstrates that this polymer has an amorphous-crystalline structure. In the temperature range from −100 to 500 °C, the lowest temperature relaxation transition is found only in the region of ambient temperature. The relaxation transition at T_c = 123 °C reported in [6] did not find support. Four topological structures of PTFE have been found by the TMS method: amorphous (T_c = 17 °C) and three crystalline [high-melting (T_m = 334 °C), intermediate (T_m = 374 °C), and low-melting (T_m = 41 °C)] modifications. In the course of gamma irradiation of PTFE, both the free volume and the molecular mass remained practically unaffected in the pseudoreticular structure of the amorphous form. In the crystalline phase, gamma radiation reduced the molecular mass of the crystallized chains of the low-temperature modification; the intermediate and high-temperature crystalline phases disappeared as a result of their transformation into the amorphous phase. Thus the radiation effect on the properties of the crystalline phase of PTFE is more pronounced in view of its more regular and close packing of chains.

It was demonstrated [31] that irradiation changes drastically the morphology of PTFE. Since elimination of a fluorine atom is the key radical process in the course of PTFE radiolysis, the consequences of this process can play a crucial role during destruction of the crystal structure. Therefore, the next logical step was to understand the effect of the radical centre, arising in the process of PTFE radiolysis, on the structure of the polymer macromolecule. A quantum chemical calculation (QCC) of molecular geometry of PFAs and perfluoroalkyl radicals appeared to be most suitable for this purpose.

QUANTUM-CHEMICAL CALCULATIONS OF MOLECULAR AND RADICAL GEOMETRIES OF LINEAR PERFLUOROALKANES FOR SIMULATING THE IRRADIATED POLYTETRAFLUOROETHYLENE MACROMOLECULE

From general molecular-orbital theory it follows that the stability of radical ions must increase with the chain length of PFA due to the higher energy-dissipating capacity of a long molecule. However, semi-empirical QCC of C_nF_{n+2} ($n = 8-20$) molecules demonstrated that their free radical anions have very long central C−C bonds: 1.88−1.90 Å. The existence of a bond of this type is theoretically conceivable. For example, a C−C bond of 1.90 Å in length has been found experimentally in fullerene RbC_{60} polymers [32]. Nevertheless, it was shown empirically that PFA radical anions are subject to decomposition.

According to semi-empirical QCC, transformation of C_nF_{n+2} ($n = 8-20$) molecules into the excited state destabilizes them and is accompanied by cleavage of one of the C−C bonds. The energy difference between the ground and excited states of molecules is 144−146 kcal/mol and is almost independent of the length of the carbon chain of PFAs.

A comparison of the results of *ab initio* and semi-empirical QCC has revealed an unexpected tendency. According to *ab initio* QCC, C_nF_{n+2} molecules with $n = 10$ have a spiral structure with C−C−C−C torsion angles of 160−161°. According to PM-3, MNDO, and AM-1

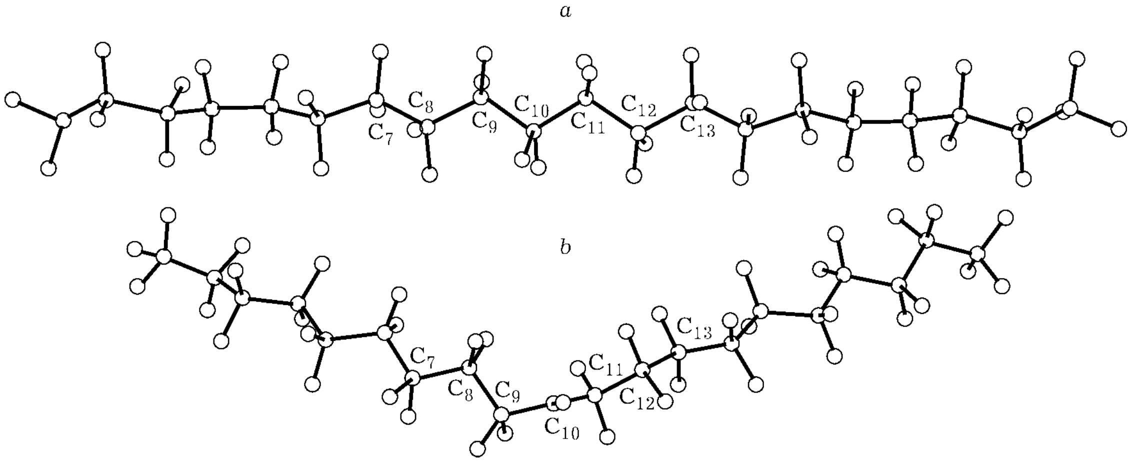

Fig. 1. Structure of the $C_{20}F_{42}$ molecule (*a*) and $C_{20}F_{41}^{\bullet}$ radical (*b*) according to quantum-chemical calculations.

semi-empirical QCC, the same molecules have two stable conformations: a helical conformation with C–C–C–C torsion angles of 159–162° and a flat conformation with C-C-C-C torsion angles of 180°. There are no experimental data on the conformations of perfluoroalkanes with $n = 10$. Therefore, the data cannot be verified experimentally.

The transformations of the PTFE macromolecule induced by the formation of a $-CF_2-C^{\bullet}F-CF_2-$ radical were simulated by QCC [33] of the geometry of the n-$C_{20}F_{42}$ molecule and $F_3C(CF_2)_8FC^{\bullet}(CF_2)_9CF_3$ radical formed by fluorine atom elimination from the tenth carbon atom in the backbone of this PFA.

The PTFE molecule has a helical form in the crystalline state due to the repulsion between the nonbonded fluorine atoms because of their large van der Waals radius (1.4 Å) [34]. Comparison of QCC data demonstrated that the helical structure of the $C_{20}F_{42}$ molecule (Fig. 1, *a)* is reproduced by all semi-empirical methods. The best agreement between the experimental and calculated molecular geometries is achieved in PM-3 calculations. The spatial structure of the $F_3C(CF_2)_8FC^{\bullet}(CF_2)_9CF_3$ radical (see Fig. 1, *b)* differs from that of the n-$C_{20}F_{42}$ molecule. These results suggest that the transformation of the $C_{20}F_{42}$ molecule into the $C_{20}F_{41}^{\bullet}$ radical is accompanied by a drastic rearrangement of molecular structure. In the solid, a rearrangement of this kind must be accompanied by dramatic changes in the crystal structure. It is assumed that the $-CF_2-C^{\bullet}F-CF_2$ radicals formed in the course of PTFE radiolysis may be one of the major factors responsible for crystal structure destruction of the polymer.

MECHANISM OF POLYTETRAFLUOROETHYLENE RADIOLYSIS

Although many publications are devoted to PTFE radiolysis, no data on the vacuum radiation yield of PTFE destruction have been found in the literature. Previously, the radiation resistance of PTFE was evaluated from the indirect parameters of radiolysis related to destruction of the PTFE backbone chain. According to [4], the absorbed dose of ionizing radiation (at 300 K in air) at which polymer hardness decreases by a factor of two is two orders of magnitude smaller for PTFE (1 Mrad) than for PE (100 Mrad). Comparison of the hardness of PTFE with that of other polymers also suggests that PTFE shows the least stability against high-energy radiation among known polymers. Hence PTFE was labelled as "the most radiation-unstable synthetic polymer." At the same time, it is common knowledge that linear perfluoroalkanes (low-molecular analogues of PTFE) possess greater radiation resistance ($G = 1–5$ [13–16]) than their hydrocarbon analogues ($G = 6–10$ [17, 18]). Moreover, if PTFE chain destruction had been effective, low-temperature (77 K) radiolysis would have given high yields of thermally "superstable" $\sim F_2CFC^{\bullet}CF_2\sim$ and $\sim F_2CF_2C^{\bullet}$ polymer radicals. In practice [35], however, the yield of PC in PTFE is very low ($G = 0.25$),

TABLE 1

Radiochemical yield of radiolysis products

Performance	Comment	
Radiochemical yield of PMC, ea/100 eV:		
PTFE	0.4 [16]	
n-C_6F_{14} – n-$C_{16}F_{34}$	1.6 [16]	
PE	13 [16]	
n-C_7H_{16}	13 [16]	
The same, of destruction, molecules/100 eV:		
PTFE	0.02*	Irradiation and sintering in vacuum
	0.07*	Irradiation in vacuum, air sintering
	0.01–0.02*	Air irradiation and sintering
	0.20**	From the results of M_s
	0.04**	From the results of M_w
CF_4 – n-C_5F_{12}	1–5 [13–15]	
CH_4 – n-C_5H_{12}	6–10 [17, 18]	
PE	0.77 [4]	
Polymethylmethacrylate	1.6 [4]	
Polyisobutylene	3 [4]	
Cellulose	6–10 [4]	
Polysulfones	9–12 [4]	
Yield of gaseous molecules, ea/100 eV:		
PTFE	0.051 [4]	
PE	2.03 [4]	

* Calculated from data on PTFE molecular weight before and after irradiation [7, 36].

** Investigation conducted by thermomechanical spectroscopy.

more than an order of magnitude smaller than that in PE ($G = 5.8$).

Experts in radiation chemistry who are engaged in polymer research often neglect that the physical state of a sample can change considerably during radiochemical reactions, which are treated as chemical reactions. Probably, this is also true of PTFE radiolysis.

To determine the degree of radiation destruction of the PTFE chain, molecular weight (MW) measurements should be performed before and after radiolysis. Data on variation of MW during PTFE radiolysis were generally obtained by specific indirect techniques [5, 6]. Unfortunately, literature analysis has revealed poor convergence of data. Indeed, PTFE macromolecules cannot be transferred into solution or viscous fluid state, and their mass, therefore, can never be determined by direct methods. As MW is an essentially virtual notion for PTFE, it is reasonable to analyze the molecular weight of its topological units, deriving MW data by block summation. Previously [31], TMS was effectively used to determine MW for all topological structures of PTFE before and after gamma irradiation.

When calculated from the initial region of the radiation dose dependences of block-averaged MW, the PTFE destruction yield did not exceed 0.2 chain splits in air and 0.1 chain splits in vacuum per 100 eV of absorbed energy. The same value calculated from the literature data on MW [7, 36] is less than 0.1. The fact that these values are practically identical is testimony to the radiochemical stability of PTFE. For PTFE, the chain destruction yield is more than an order of magnitude higher than that of PE and more than two orders of magnitude higher than the yields of cellulose and polysulfones (Table 1).

Hence PTFE shows high thermal and chemical stability along with radiochemical stability.

Although PTFE macromolecules are not prone to destruction in the course of radiolysis, they typically undergo structural and topological conversions. The $-CF_2-C^{\bullet}F-CF_2-$ polymer radicals formed during radiolysis can act as initiators of structural and topological transformations inside PTFE. Their formation from macromolecules is accompanied by drastic rearrangements of the molecular (see Fig. 1) and supermolecular structures of the polymer. In the solid phase, a rearrangement like that may be accompanied by dramatic changes in the crystal structure and by amorphization of the latter, resulting in a loss of the mechanical characteristics of PTFE. Thus PTFE shows the least mechanical stability to high-energy radiation among known polymers.

In their reviews of data on high-pressure radiolysis of PTFE [28–30], the authors suggested the following two-stage mechanism of the process that forms free radicals after ionization. The first stage involves C–C bond cleavage in the ionized fragment of the macromolecule followed by disproportionation of disintegration products; the second stage is C–F bond cleavage that takes place during recombination of an electron with the resulting fluorovinyl radical cation. Thus the radical cation mechanism of radiation destruction of PTFE has been suggested. According to this mechanism, an allylic radical is formed at the end of each PTFE macromolecule upon its destruction. Recombination of this radical with fluorine atoms must form a double bond. Eventually, the yield of unsaturated bonds during PTFE radiolysis should be equal to the chain destruction yield of PTFE. However, as noted in [5], products with unsaturated bonds do not form during vacuum radiolysis of PTFE. They form only in the course of air irradiation of PTFE [7].

According to the mechanism described in [11, 12], radiolytic fluorine atoms formed during C–F bond cleavage play a leading part in the process of radiation destruction of PTFE. The radiochemical yield of PC calculated from the initial region of the curve of PC accumulation for PFA and PTFE is almost an order of magnitude smaller than for the hydrocarbon analogues (see Table 1). The observable low yield of the radicals may be related with the destruction of radicals stabilised by radiolytic fluorine atoms in PFA. On the other hand, the latter react with the $\sim F_2CF_2C^{\bullet}...^{\bullet}CF_2CF_2\sim$ radical pair arising from C–C bond cleavage to ensure disintegration of the macromolecule. Thus radiation destruction of PTFE may proceed by recombination of the $\sim F_2CF_2C^{\bullet}$ $...^{\bullet}CF_2CF_2\sim$ “cage” radicals with radiolytic fluorine atoms.

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