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Degradation of γ-irradiated linear perfluoroalkanes at high dosage

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Abstract

The effects of the carbon backbone chain length on the EPR spectra of linear perfluoro-*n*-alkanes (PFAs) γ-irradiated at 77 K was studied for the short chain *n*-C_6F_{14}, *n*-C_8F_{16}, *n*-$C_{12}F_{26}$, and *n*-$C_{16}F_{34}$ molecules as well as the polymer polytetrafluoroethylene (PTFE). The experimental data show that the processes occurring during radiolysis of perfluoro-*n*-alkanes and polytetrafluoroethylene are very similar. EPR spectra of irradiated perfluoro-*n*-alkanes at low radiation dose show superimposed signals from three radicals: $–F_2CC^{\bullet}FCF_2–$, $–CF_2C^{\bullet}F_2$ and $F_3C^{\bullet}$. The signal intensity decreases with perfluoro-*n*-alkanes chain length. At doses above 2.0 MGy, a constant increase in concentration of the radicals $–F_2CC^{\bullet}FCF_2–$ and $–CF_2C^{\bullet}F_2$ is observed with decreasing chain length. The concentration of these radicals formed during radiolysis of PFA is described by the ratio: $[–CF_2C^{\bullet}F_2]/[–F_2CC^{\bullet}FCF_2–] \approx 3/(n-2)$, where n is the number of carbon atoms in the linear perfluoroalkanes. Density functional theory was used to calculate the structures of the radicals and C–F bond energies in model perfluoro-*n*-alkanes as well as the EPR spectra of the associated radicals. This data is used to provide further insight into the radiation stability of PTFE. Four topographical structures of polytetrafluoroethylene, one amorphous and three crystalline, were identified by thermomechanical analysis. In the crystal phase, γ-irradiation results in their transformation to the amorphous form. The helical structure of individual perfluroalkanes readily distorts on removal of a fluorine and this will have an impact on the overall structure of the material. Such structural reorganization can lead to loss of the mechanical stability of polytetrafluoroethylene.

Keywords: Linear short chain perfluoroalkanes; Polytetrafluoroethylene; γ-Irradiation; EPR spectra; Stabilized radicals; Decomposition mechanism; Density functional theory

1. Introduction

The structure of fluorinated carbon polymers changes in two different ways upon radiolysis. Perfluorinated polymers, for example, polytetrafluoroethylene (PTFE), copolymers of tetrafluoroethylene and hexafluoropropylene, and copolymers of tetrafluoroethylene and perfluoroalkylvinyl ethers, undergo rapid destruction. Hydrogen containing fluorocarbon polymers, for example copolymers of vinylfluoride, rapidly cross-link and form a network. Because of the technological importance of PTFE, there has been a substantial amount of work on its radiation [1–8] chemistry. Recent work has focused on the stability of PTFE under VUV irradiation for spacecraft applications [9]. In this work, PTFE was irradiated under vacuum conditions and the resulting polymer was studied by X-ray photoelectron spectroscopy (XPS). The results showed a loss of F atoms as the F/C ratio decreased from 1.98 to 1.65 after 2 h of irradiation. A similar study of polyvinyl fluoride has been carried out [10]. In addition, CO_2 laser ablation of PTFE after γ-irradiation led to enhanced fiber formation as compared to polymers that were not irradiated [11].

The contrast between the high chemical and thermal stability of PTFE [5,6] and its very low radiation stability [4] is of real interest as there are potential technological uses for such polymers in high radiation environments. Studies of PTFE degradation due to radiation damage are complicated by its insolubility and by the complexity of the resulting radiolysis products. The description of the molecular heterogeneity of

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polymers is usually based on the properties of dilute solutions of linear polymers, for example swelling in certain solvents. Such methods can be used to analyze only very soluble polymers but for insoluble polymers such as PTFE, these methods are inapplicable. Thus, one has to use model systems for PTFE radiolysis such as the linear perfluoroalkanes.

The radiation stability of polytetrafluoroethylene (PTFE) in air is two orders lower than that of polyethylene [4] and the mechanism of PTFE radiolysis leading to destruction has not been established. This is a consequence of the competition between radical formation and reaction of the radical sites with O_2 which leads to oxidative degradation. For radiolysis in air at 27 °C a dose of 1 MGy is necessary for a 50% reduction of durability in polyethylene [4]. For a 50% reduction of PTFE durability, only 10 kGy is necessary, two orders of magnitude less than for polyethylene. This suggests that the perfluorinated radicals formed on irradiation react more rapidly with the oxygen present in air. Thus, currently, there is no effective way to protect this polymer again radiation. The EPR spectra of polytetrafluoroethylene (PTFE) irradiated at 77 K in vacuo shows superimposed signals of several paramagnetic species. These spectra are due to the components of signals from $–F_2CC^{\bullet}FCF_2–$ "chain centered" [12] as well as $–CF_2C^{\bullet}FCF=CFCF_2–$ allylic radical centers [13,14]. There are inconsistent data in the literature with respect to signals from $–F_2CC^{\bullet}F_2$ terminal radicals in the EPR spectrum of irradiated PTFE. According to Ref. [12], the terminal radicals are formed by cleavage of C–C bonds both at 77 K, and at 300 K. In samples irradiated in vacuo at 300 K by doses of 0.1–1.0 MGy, the concentration of the terminal radicals is 10 times less than the concentration of the "chain centered" radicals [15,16]. As reported in Ref. [17], the EPR spectrum of PTFE irradiated at 77 K does not show terminal radicals but consists primarily of the "chain centered" radicals. In contrast the spectrum of linear short chain perfluoroalkanes irradiated at 77 K in vacuo shows both "chain centered" and "end" radicals [18]. Good EPR spectral resolution of polycrystalline perfluoroalkanes irradiated at 77 K permitted identification of all of 10 lines with hyperfine splittings of 1.1 mT in the central part of the terminal radical spectrum [18]. In the EPR spectrum of irradiated perfluoroalkanes, the intensity of the terminal radical signals is more intense than in the samples of irradiated PTFE.

In the present work the influence of the carbon chain length on bond cleavage due to γ-irradiation at 77 K in vacuo of linear perfluoroalkanes is investigated.

2. Experimental

The linear perfluoroalkanes, C_6F_{14}, C_8F_{18}, $C_{12}F_{26}$, $C_{16}F_{34}$ and high-molecular weight PTFE were studied. The perfluoroalkanes were >99.9% pure and were procured from the Perm Branch of Federal State Unitary Enterprise "Russian Scientific Center" "Applied Chemistry" Commercial PTFE from JSC "Halogen" was used. Samples of the perfluoroalkanes and PTFE in SK-4B tubes were evacuated to a low pressure (10^{-3} mm) at 77 K prior to irradiation with γ-rays of ^{60}Co. EPR spectra were recorded with a PS100X spectrometer and their simulation was achieved with the EPRTOOLS program of the NPP "Adani" Company. The EPR spectrum at each dose, was integrated to determine a total concentration of radicals. Absolute concentrations are good to ±25% and relative concentrations are good to ±10%.

3. Results and discussion

3.1. Experimental results

The low-molecular weight products (CF_4, C_2F_6, C_3F_8) from the radiolysis of PTFE [19] are formed in only low yield ($G = 0.3$) [20]. The main radiolysis products of perfluoroalkanes are smaller linear perfluoroalkanes of various chain lengths. At doses of 0.1–3 MGy, these linear molecules constitute 90 ± 3% of the products. Their proportion decreases with increasing irradiation dose. At 19 MGy, they constitute 80 ± 4% of the products. Upon perfluoroalkane radiolysis appreciable quantities of fluoroalkenes (>3%) are formed at doses above 1 MGy. The presence of fluoroalkenes is confirmed by characteristic lines in the UV spectra of irradiated perfluoroalkanes [18,21]. About 100 eV of absorbed radiation energy is required to break two molecules of liquid (n-C_6F_{14}, n-C_8F_{18}) or solid (n-$C_{12}F_{26}$, n-$C_{16}F_{34}$) perfluoroalkanes during radiolysis up to a dose of 50 Mrad at 27 °C [20]. Increasing the perfluoroalkane chain length from C6 to C16 does not affect the products of radiolysis for smaller perfluoroalkanes such as CF_4, C_2F_6, C_3F_8, n-C_4F_{10}, n-C_5F_{12}, and n-$C_{n-2}F_{2(n-2)+2}$ up to $n = 16$; c-C_3F_6; and perfluoroalkenes with internal double bonds such as C_5F_{10} and $CF_3CF=CFCF_3$ or with terminal double bonds such as C_2F_4, C_3F_6, and $F_2C=CFC_2F_5$. The quantity of radiolysis products does decrease over this range by approximately 20%. Such a decrease in the amount of products of radiolysis of perfluoroalkanes, for example, for n-$C_{16}F_{34}$ is probably related to "cage" effects as the amount of recombination competes with loss of the radicals. These data show that the products of radiolysis of perfluoroalkane molecules do not depend strongly on their chain length.

The EPR spectrum of perfluoroalkanes irradiated at low dose (<0.1 MGy) at 77 K shows superimposed signals from three radical centers ($CF_3^{\bullet}$, $–CF_2CF_2^{\bullet}$, and $–CF_2CF^{\bullet}CF_2–$) as previously observed and identified at low dosage (see Fig. 2 of Ref. [18]). The EPR parameters of the radicals formed upon radiolysis of perfluoroalkanes and PTFE are given in Table 1. The parameters are consistent with those from EPR studies of fluorinated radicals in single crystals [22]. The low and high field EPR lines (denoted by a (*) in Fig. 1a) are separated by 44.0 mT and were assigned to the $–CF_2CF_2^{\bullet}$ radical center following reference [18], with overlap of the high and low EPR lines of a quadruplet belonging to the $CF_3^{\bullet}$ radical. The next inner high and low peaks (denoted by a † in Fig. 1a) are separated by 20.87 mT and are the high and low field peaks of a broadened doublet assigned to a $–CF_2CF^{\bullet}CF_2–$ radical center. Increasing the perfluoroalkane chain length from C6 to C16 has minimal effect on the resulting parameters of the EPR spectra although the spectra do change in appearance as shown in Fig. 1 because the

Table 1
Experimental EPR hyperfine parameters of the free radicals formed by radiolysis at 77 K of polytetrafluoroethylene and short-chain linear perfluoroalkanes as reported in Refs. [11,12]

Radical	Compounds	$A^F_{\parallel}$ (mT)[a]	$A^F_{\perp}$ (mT)[a]	$a^F_{\beta(1)}$ (mT)	$a^F_{\beta(2)}$ (mT)	I_r(mT)[b]
$-CF_2C^{\bullet}F_2$[c]	PFA	22.5	3.3	2.2	1.1	45.0
$-F_2CC^{\bullet}FCF_2-$[d]	PFA	14.1	5.7	5.7	2.8	24.0
	PTFE	23.8		7.2	1.8	24.0
$C^{\bullet}F_3$	PFA	14.4[e]				

[a] Parallel ($A^F_{\parallel}$) and perpendicular ($A^F_{\perp}$) components of hyperfine coupling constant with fluorine atom.

[b] I_r = separation between the highest and lowest EPR lines of $-CF_2C^{\bullet}F_2$ (45.0 mT) and $-F_2CC^{\bullet}FCF_2-$ radicals (24.0 mT).

[c] $a^F_{\beta(1)}$ = || component and $a^F_{\beta(2)} = \perp$ component.

[d] $a^F_{\beta(1)} = a^F_{\beta(3)}$, $a^F_{\beta(2)} = a^F_{\beta(4)}$.

[e] Hyperfine coupling constant with three fluorine atoms.

terminal and "chain centered" radicals accumulate at different rates. In addition, as the chain length increases, the EPR parameters for the β fluorine couplings for the $-CF_2CF^{\bullet}CF_2-$ are site dependent due to differing numbers of additional CF_2 or CF_3 substituents on the β carbons. This results in a broadening of the powder EPR spectrum and subsequent loss of resolution. However, at high dose (>2 MGy) the spectra changes due to a change in the ratio of the radicals. It is especially apparent in the transition from low-molecular weight perfluoroalkane to high-molecular weight PTFE. Upon radiolysis of two types of PTFE (F-4, F-4D) with different molecular weight, the radical yield is the same as a function of radiation dose.

At room temperature, in the solid phase, the radicals $-F_2CC^{\bullet}FCF_2-$ formed by irradiation of the perfluoroalkanes n-$C_{12}F_{26}$ and n-$C_{16}F_{34}$ are stable as found in irradiated PTFE. The concentration of radicals $-F_2CC^{\bullet}FCF_2-$, stabilized at 27 °C depends on the dose of irradiation. At a dose of 0.14 MGy, 10^{18} of radicals are stabilized in 1 g of PTFE. For a molecular weight of 10^6, there is then ~1 radical/PTFE molecule. Heating of the irradiated polymer leads to recombination of radicals at temperatures of (60–120 °C) and (200–250 °C). At 320 °C, no radicals are observed.

Paramagnetic species accumulate nearly linear with doses up to 1.0 MGy (Fig. 2). At higher doses, the accumulation rate decreases from linear and from 5.0 to 20 MGy, the radical accumulation rate does not change. Increasing the dose rate from 2.8 to 28 kGy/h, does not vary the accumulation rate. Lengthening the perfluoroalkane chain from 6 to 16 carbon atoms does not affect the concentration of the paramagnetic species formed by radiolysis at 77 K. In the four perfluoroalkanes investigated, the rate of accumulation with dose of the paramagnetic species is nearly the same (Fig. 2). The radiation

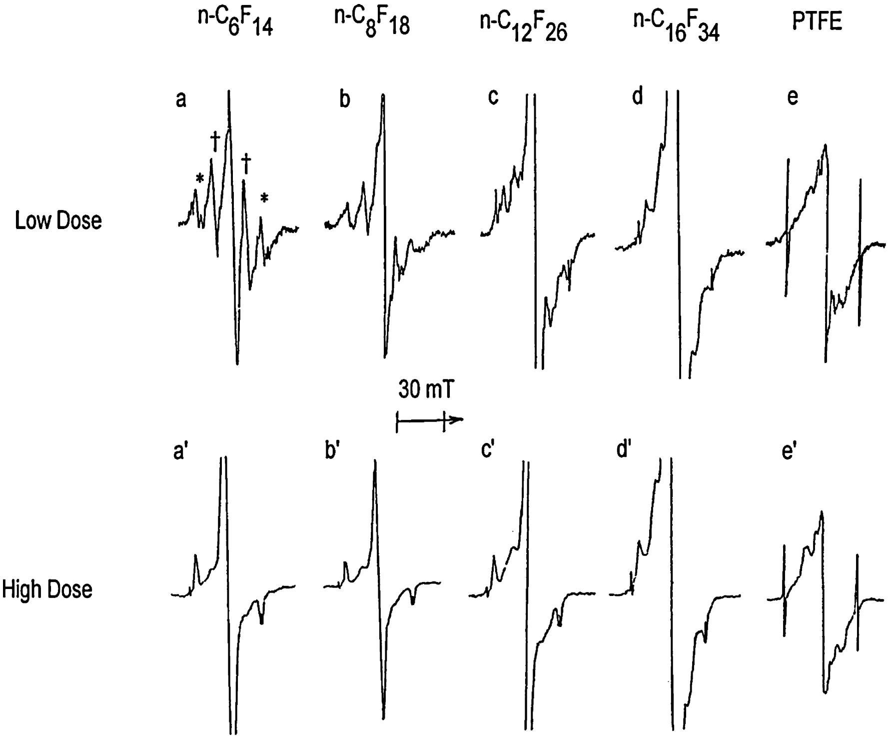


Fig. 1. The EPR spectra as a function of radiation dose of n-C_6F_{14} (a and a′), n-C_8F_{18} (b and b′), n-$C_{12}F_{26}$ (c and c′), n-$C_{16}F_{34}$ (d and d′) and PTFE (e and e′) γ-irradiated at 77 K with low dose [0.0167 MGy (a–c), 0.04 MGy (d), 0.8 MGy (e)] and high dose [6.82 MGy (a′ and b′), 2.8 MGy (c′ and d′), 5.44 MGy (e′)].

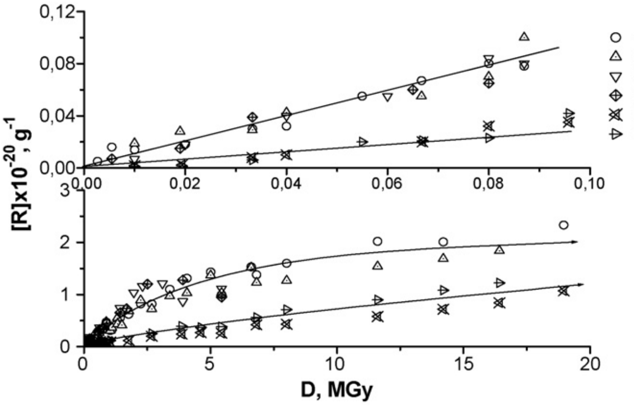


Fig. 2. The total concentration of radicals [R] formed vs. radiation dose (MGy) at 77 K of n-C_6F_{14} (1), n-C_8F_{18} (2), n-$C_{12}F_{26}$ (3), n-$C_{16}F_{34}$ (4) and PTFE indicated by the symbols (5) and (6). The upper plot is an expansion of the low dose region near the origin from 0 to 0.10 MGy.

yields calculated from the initial part of the curve in Fig. 2 are 1.6 for the perfluoroalkanes and 0.4 for PTFE in units of paramagnetic species per 100 eV of adsorbed radiation energy.

Under similar conditions during radiolysis of n-C_7H_{16} and polyethylene (PE), the concentration of radicals formed as a function of dose was recorded (Fig. 3) with a yield of 13 paramagnetic species per 100 eV. This yield of radicals during the radiolysis of hydrocarbon analogues is almost one order of magnitude greater than that of perfluoroalkanes. In Ref. [18], the low yield of radicals from irradiation of perfluoroalkanes as compared to their hydrocarbon analogues was attributed to recombination of the stabilized radicals when fluorine atoms were formed during radiolysis or to the absence of fluorine atom separation from the perfluoroalkane molecules. Comparing the n-C_7H_{16} and PE data in Fig. 3 shows that during the radiolysis of the hydrocarbon analogues (PE (1) and n-C_7H_{16} (2)), the radical yield is the same for both the molecule and the polymer.

To determine the growth rate of each alkyl radicals, we focused on their characteristic EPR lines. For this, the intensity of the lines separated by 45 and 24 mT were chosen for radicals $-CF_2C^{\bullet}F_2$ and $-F_2CC^{\bullet}FCF_2-$ respectively, following the previous assignment [18]. Upon increasing irradiation dosage beyond 1.0 MGy, spin–spin broadening of the lines is observed as shown in Fig. 1 (a′–e′). The dependence of the ratio of the intensity of $-CF_2C^{\bullet}F_2$ radicals to the intensity of $-F_2CC^{\bullet}FCF_2-$ radicals on irradiation dose is given in Fig. 4. At low dose (<1 MGy), the growth of $-F_2CC^{\bullet}F_2$ radical are observed. Above approximately 2 MGy, the ratio of the intensity of $-CF_2C^{\bullet}F_2$ radicals to the intensity of $-F_2CC^{\bullet}FCF_2-$ radicals does not depend on dose. This independence on dose appears at doses of approximately 3, 2, 1.6, 1 and 0.2 MGy for n-C_6F_{14}, n-C_8F_{18}, n-$C_{12}F_{26}$, n-$C_{16}F_{34}$ and PTFE, respectively. Thus, the longer the perfluoroalkane chain, the lower is the required irradiation dosage to reach this limit.

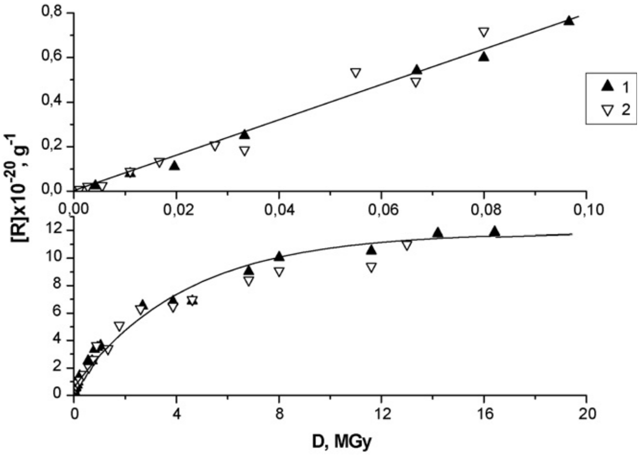


Fig. 3. The total concentration of radicals [R] formed vs. radiation dose (MGy) during γ-irradiation at 77 K of PE (1) and n-C_7H_{16} (2). The upper plot is an expansion of the low dose region near the origin from 0 to 0.10 MGy.

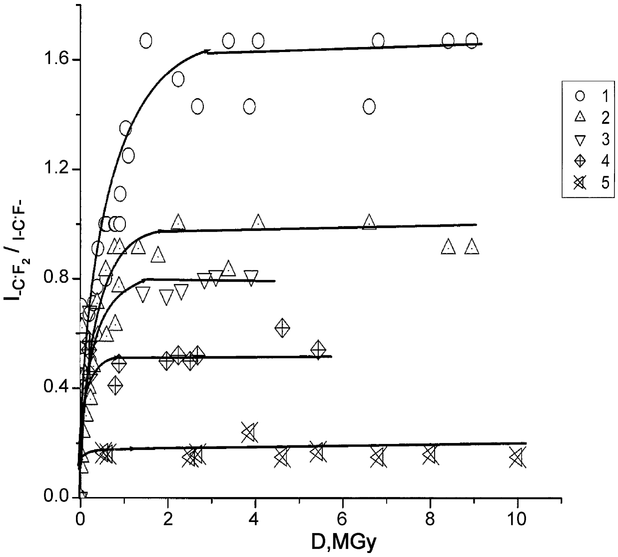


Fig. 4. Dependence of the EPR spectral intensity of the $-CF_2C^{\bullet}F_2$ and $-F_2CC^{\bullet}FCF_2-$ radicals with irradiation dose at 77 K for n-C_6F_{14} (1), n-C_8F_{18} (2), n-$C_{12}F_{26}$ (3), n-$C_{16}F_{34}$ (4) and PTFE (5).

For the perfluoroalkanes, n-C_6F_{14}, n-C_8F_{18}, n-$C_{12}F_{26}$ and n-$C_{16}F_{34}$, the ratio of the intensity of $-CF_2C^{\bullet}F_2$ radicals to the intensity of $-F_2CC^{\bullet}FCF_2-$ radicals is approximately 0.75, 0.5, 0.3 and 0.2, respectively. Our analysis shows that during radiolysis of perfluoroalkanes at 77 K, the concentration ratio of the alkyl radicals $[-CF_2C^{\bullet}F_2]/[-F_2CC^{\bullet}FCF_2-]$ is related linearly to $3/(n-2)$, where n is the number of carbon atoms in the perfluoroalkane as shown in Fig. 5. The value $3/(n-2)$ was derived by dividing the number of fluorine atoms (6) of two terminal $-CF_3$ groups by the total number of fluorine atoms of the $-CF_2$- groups, i.e., $6/[(2n+2)-6] = 3/(n-2)$. Thus, the fraction of terminal radicals $-CF_2C^{\bullet}F_2$ in the EPR spectrum of perfluoroalkane molecules irradiated at 77 K at a dosage >2 MGy is directly related to the number of fluorine atoms of trifluoro methyl groups in the PFA molecules. Thus we can conclude that the observed radical amounts are consistent with terminal radicals formed by breaking the C–F bond of the terminal CF_3 group and that the chain-centered radicals formed by cleavage of a C–F bond in a $-CF_2-$ group. Irradiation of perfluoroalkanes at high dosage does not lead to C–C bond

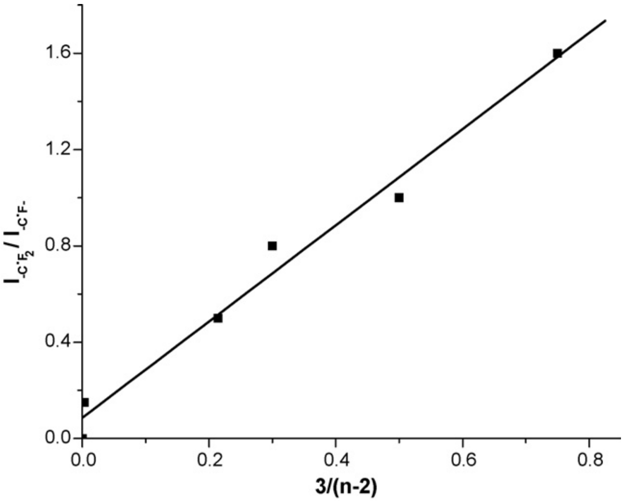


Fig. 5. Dependence of the ratio of the EPR spectral intensity of the –$CF_2C^\bullet F_2$ and –$F_2CC^\bullet FCF_2$– radicals as a function of 3/(n − 2), where n is the number of carbon atoms of irradiated perfluoroalkane molecules at high radiation dose (>2 MGy).

cleavage on a time scale that can be observed by our EPR experiments. For high-molecular weight PTFE with a molecular mass of 10^6, we calculate a value of 3/(n − 2) ≈ 10^{-4}. Thus, –$CF_2C^\bullet F_2$ terminal radicals would be extremely difficult to observe in the spectra of PTFE irradiated at 77 K.

Thermomechanical spectroscopy (TMS) is a diagnostic tool for obtaining information about the molecular-topographical structures of insoluble polymers. The influence of γ-radiation on the molecular-topographical structure of PTFE before and after irradiation was investigated by this method [23]. Before irradiation, the variation of a thermomechanical curve of PTFE shows its amorphous-crystal structure. In the range of temperatures from −100 to 500 °C, the lowest temperature structural relaxation is found only near room temperature. The previously reported [6] relaxation transition at $T_g = 123$ °C has been shown to be incorrect. Four topographical structures of PTFE were identified: amorphous ($T_g = 17$ °C) and three crystal blocks; high-melting ($T_{m1} = 334$ °C), intermediate-melting ($T_{m2} = 374$ °C) and low-melting crystal modifications ($T_{m3} = 411$ °C) consistent with the phase behavior of PTFE [23–26]. In the crystal phase, γ-irradiation reduces the molecular mass of the crystalline chains of the low-melting modifications and also results in the disappearance of intermediate- and high-temperature melting crystal phases as a result of their transformation into the amorphous state [23]. During radiolysis of PTFE, both the free volume and molecular-mass characteristics remain nearly constant in the pseudo-mesh structure of the amorphous block. The effects of irradiation on the crystal phase of PTFE are more appreciable because of the more regular and denser packing of the chains. The irradiation results in changes in the morphology of PTFE [23]. As discussed above, cleavage of C–F bonds is the basic radical process of the radiolysis of PTFE. This probably plays a major role in the destruction of the crystal structure.

3.2. *Quantum chemical results*

Density functional theory was used to predict the C–F bond energies to better understand the radiation process. The molecules were optimized using the B3LYP exchange-correlation functional [27] with the polarized double-ζ DZVP2 basis set [28] using the program Gaussian-03 on a Cray XD1 computer. Frequencies were calculated to show that the optimized structures were minima. The bond energies were calculated from the isodesmic reaction

$$CF_4 + R_f^* \rightarrow CF_3^* + R_fF$$

as the C–F bond energy in CF_4 is well-established as 128.3 kcal/mol at 0 K and 129.6 kcal/mol at 298 K [29,30]. Such an approach has been shown to yield good relative bond energies at the MP2 level for hydrofluorocarbons [31,32]. The terminal C–F bond energies are always stronger than the interior C–F bond energies by about 10 kcal/mol consistent with the C–F bond energies in other fluorinated compounds. The C–F bond energies for $C_{12}F_{26}$ starting from the CF_3 terminal and proceeding to the center of the molecule are 123.8, 115.0, 113.9, 113.6, 113.6, and 113.7 kcal/mol for the structures shown in Fig. 6. (Fig. 6 shows the structures of all of

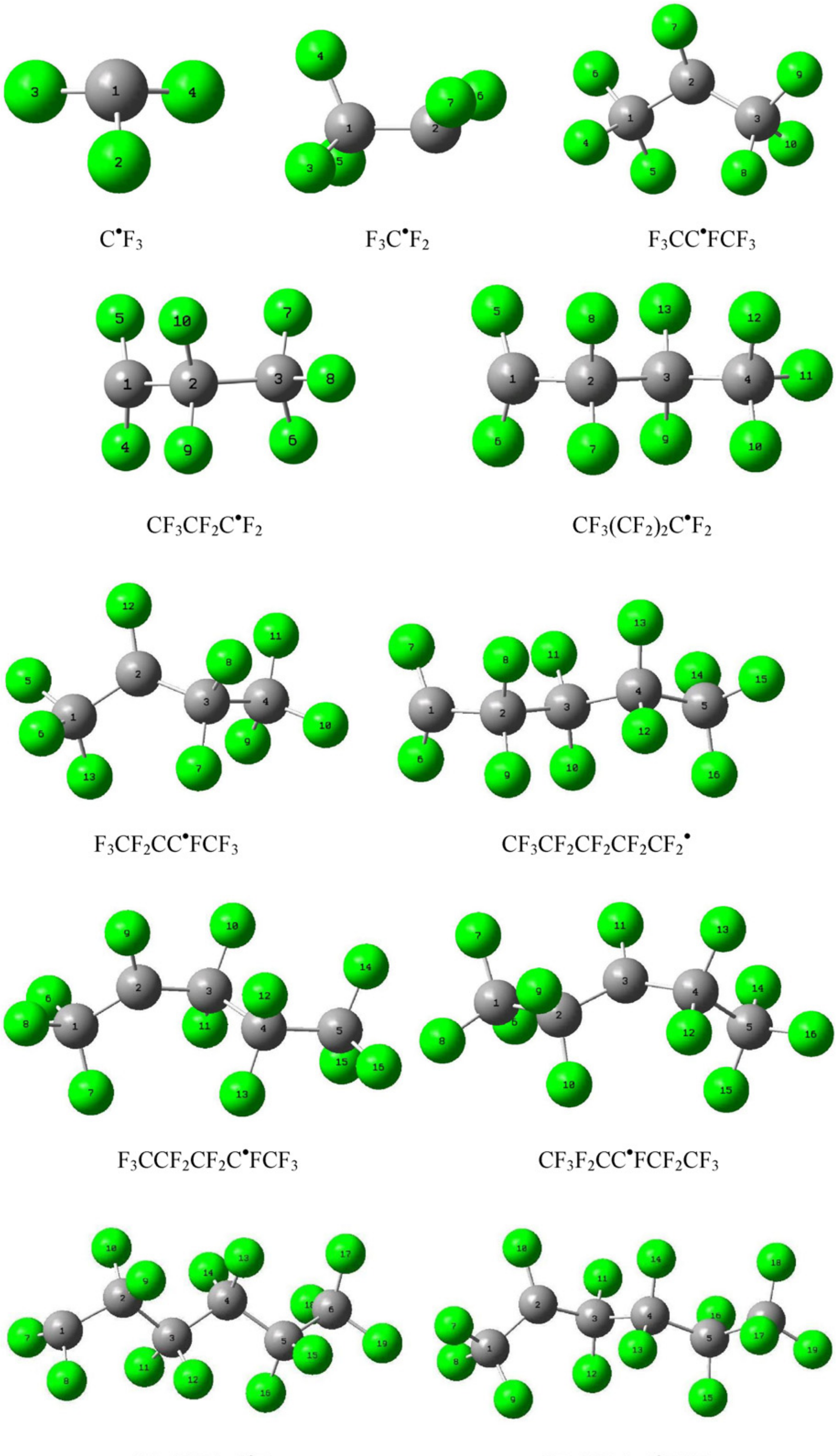
Table 2
Calculated DFT EPR hyperfine parameters (mT) of fluroocarbon radicals

Radical	$A_\parallel^{F}$ [a]	$A_\perp^{F}$ [a]	$a_{\parallel\beta(1)}^{F}$ [b]	$a_{\beta(1)\perp}^{F}$ [b]	$a_{\parallel\beta(2)}^{F}$ [b]	$a_{\beta(2)\perp}^{F}$ [b]
$C^\bullet F_3$	14.6[c]	14.6[c]				
$CF_3C^\bullet F_2$	25.4	1.6				
$CF_3CF_2C^\bullet F_2$	25.3	1.5	1.5	0.7		
$CF_3(CF_2)_2C^\bullet F_2$	25.2	1.3	1.8	0.8		
$CF_3CF_2CF_2CF_2CF_2^\bullet$	25.3	1.5	1.8	0.8		
$CF_3(CF_2)_4C^\bullet F_2$	25.3	1.4	1.8	0.8		
$CF_3(CF_2)_5C^\bullet F_2$	25.3	1.4	1.8	0.8		
$CF_3(CF_2)_6C^\bullet F_2$	25.1	1.6	5.4	0.9		
$CF_3(CF_2)_{10}C^\bullet F_2$	25.1	1.6	5.4	0.9		
Average CF_2	25.3	1.5	2.8	0.8		
$F_3CC^\bullet FCF_3$	27.5	−1.1				
$F_3CF_2CC^\bullet FCF_3$	27.5	−1.5	5.9	1.6	3.9	1.0
$F_3CCF_2CF_2C^\bullet FCF_3$	27.5	−1.5	6.3	1.8	3.8	1.0
$CF_3F_2CC^\bullet FCF_2CF_3$	27.3	−1.5	10.0	2.8	3.6	0.6
$CF_3(CF_2)_3C^\bullet FCF_3$	27.7	−1.4	5.6	1.6	4.4	1.3
$CF_3CF_2CF_2C^\bullet FCF_2CF_3$	27.4	−1.5	9.6	2.8	3.8	0.1
$CF_3(CF_2)_4C^\bullet FCF_3$	26.9	−1.2	12.5	3.0	4.2	0.7
$CF_3(CF_2)_3C^\bullet FCF_2CF_3$	27.3	−1.5	9.7	2.8	3.8	0.7
$CF_3(CF_2)_2C^\bullet F(CF_2)_2CF_3$	27.2	−1.5	9.4	2.7	3.6	0.7
$CF_3(CF_2)_5C^\bullet FCF_3$	27.6	−1.5	6.4	1.8	3.5	0.9
$CF_3(CF_2)_4C^\bullet FCF_2CF_3$	27.3	−1.5	9.8	2.8	3.7	0.7
$CF_3(CF_2)_3C^\bullet F(CF_2)_2CF_3$	27.2	−1.5	9.5	2.8	3.7	0.7
$CF_3(CF_2)_9C^\bullet FCF_3$	27.5	−1.5	6.8	2.0	3.4	0.8
$CF_3(CF_2)_8C^\bullet FCF_2CF_3$	27.1	−1.5	9.2	2.6	3.6	0.7
$CF_3(CF_2)_7C^\bullet F(CF_2)_2CF_3$	27.2	−1.5	9.5	2.8	3.7	0.7
$CF_3(CF_2)_6C^\bullet F(CF_2)_3CF_3$	27.0	−1.5	9.4	2.7	3.6	0.7
$CF_3(CF_2)_5C^\bullet F(CF_2)_4CF_3$	27.0	−1.5	9.4	2.7	3.6	0.7
Average CF	27.3	−1.5	8.7	2.5	3.7	0.8

[a] Parallel ($A_\parallel^F$) and perpendicular ($A_\perp^F$) components of hyperfine coupling constant with fluorine atom.

[b] $a_{\beta(1)}^F = \|$ component and $a_{\beta(2)}^F = \perp$ component. $a_{\beta(1)}^F = a_{\beta(3)}^F$, $a_{\beta(2)}^F = a_{\beta(4)}^F$.

[c] Isotropic hyperfine coupling constant with three fluorine atoms.



$C^{\bullet}F_3$ $F_3C^{\bullet}F_2$ $F_3CC^{\bullet}FCF_3$

$CF_3CF_2C^{\bullet}F_2$ $CF_3(CF_2)_2C^{\bullet}F_2$

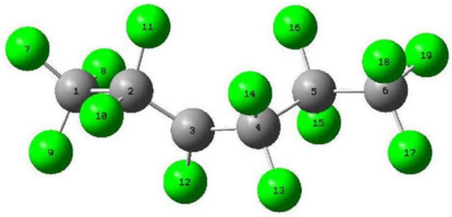
$F_3CF_2CC^{\bullet}FCF_3$ $CF_3CF_2CF_2CF_2CF_2^{\bullet}$

$F_3CCF_2CF_2C^{\bullet}FCF_3$ $CF_3F_2CC^{\bullet}FCF_2CF_3$

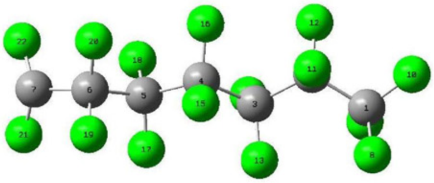
$CF_3(CF_2)_4C^{\bullet}F_2$ $CF_3(CF_2)_3C^{\bullet}FCF_3$

Fig. 6. DFT optimized structures of the perfluro-*n*-alkane radicals generated by breaking a C–F bond in the parent perfluro-*n*-alkane.

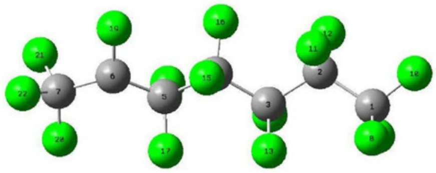
the perfluoro-*n*-alkane radicals in this study.) For comparison, the C–F bond energies in the same order are 123.4, 115.2, and 113.5 kcal/mol for C_6F_{14}; 123.6, 116.0, 113.7, and 113.5 kcal/mol for C_7F_{16}; and 123.8, 115.2, 113.7, and 113.6 kcal/mol for C_8F_{18}. Although, the initial structure of the perfluoroalkanes is helical consistent with calculations on other flurocarbons [33,34] and with the crystal structure of PTFE, removal of a fluorine leads to changes in the basic structure with a loss of helicity as shown in Fig. 6, which, as discussed below, can have an impact on the overall structure and stability. The loss of helicity becomes more pronounced as one generates radicals further from the terminal CF_3 group.



$CF_3CF_2CF_2C^{\bullet}FCF_2CF_3$



$CF_3(CF_2)_5C^{\bullet}F_2$



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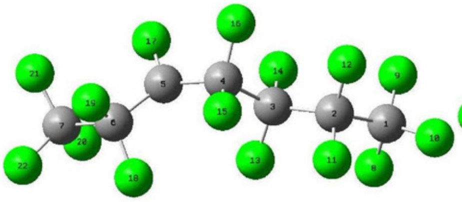
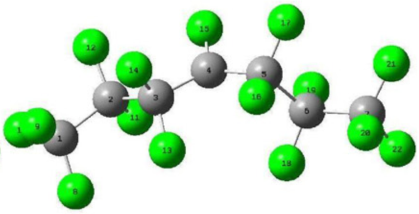
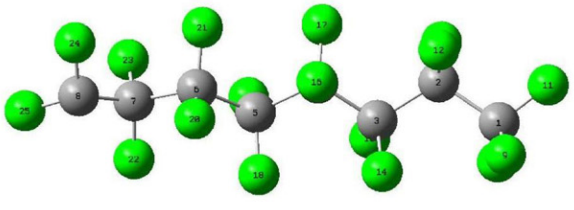


$CF_3(CF2)_3C^{\bullet}FCF_2CF_3$



$CF_3(CF_2)_2C^{\bullet}F(CF_2)_2CF_3$



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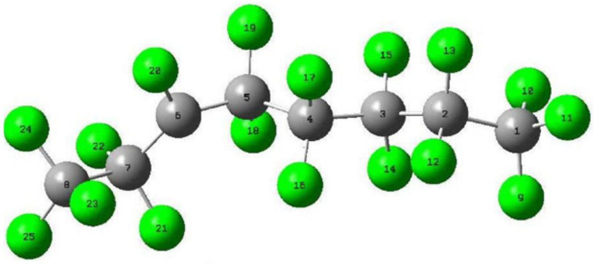
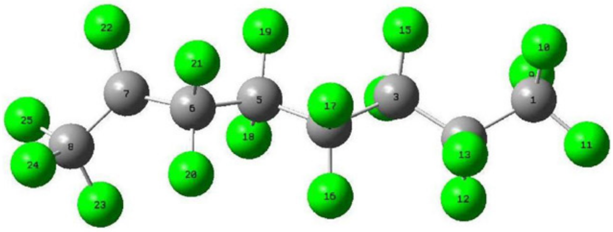
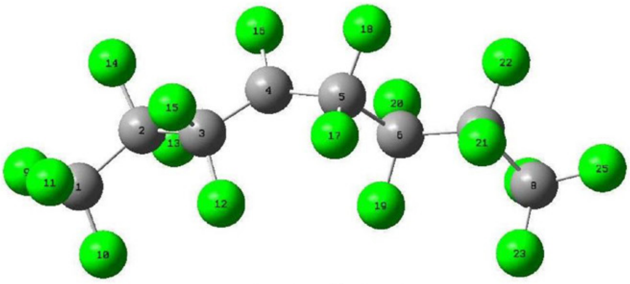


$CF_3(CF_2)_4C^{\bullet}FCF_2CF_3$



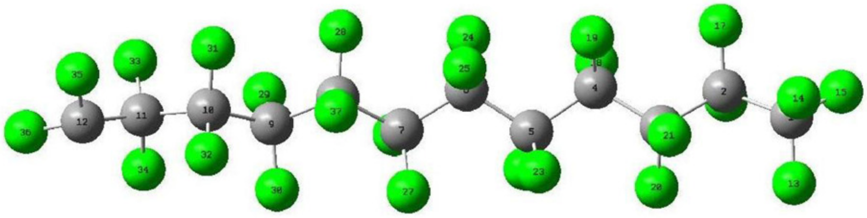
$CF_3(CF_2)_5C^{\bullet}FCF_3$



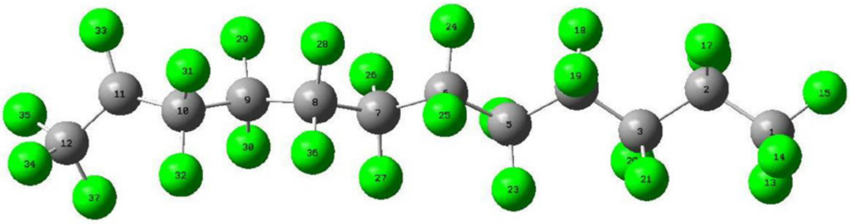
$CF_3(CF_2)_3C^{\bullet}F(CF_2)_2CF_3$

Fig. 6. (*Continued*)

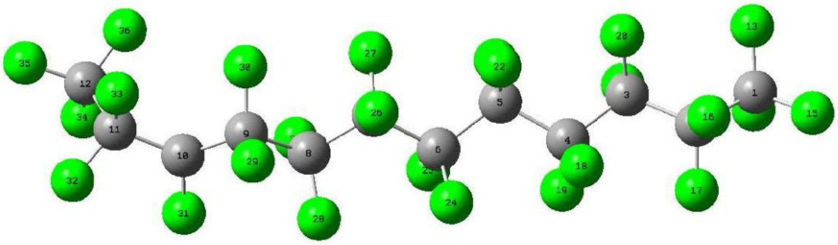
DFT calculations of the EPR hyperfine parameters (Table 2) for a range of perfluororadicals C_nF_{2n+1} for $n = 1, 2, 3, 4, 5, 6, 7, 8$, and 12 representing the $^{\bullet}CF_3$, $–CF_2{}^{\bullet}CF_2$ and $–F_2C^{\bullet}CFCF_2–$ centers show excellent agreement with the experimental values given in Table 1. Experimentally, the $^{\bullet}CF_3$ radical is rapidly rotating at 77 K, so only the isotropic fluorine coupling is measured. The observed 14.4 mT experimental isotropic coupling is in



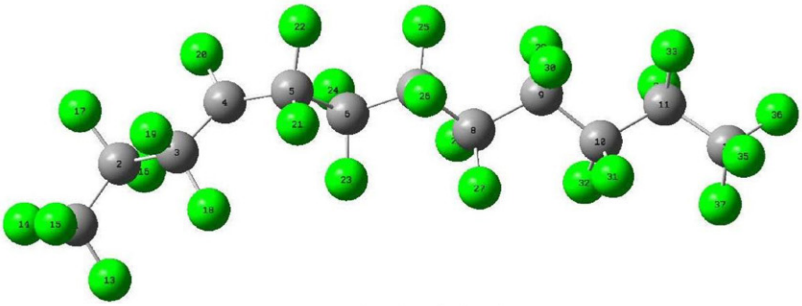
$CF_3(CF_2)_{10}C^{\bullet}F_2$



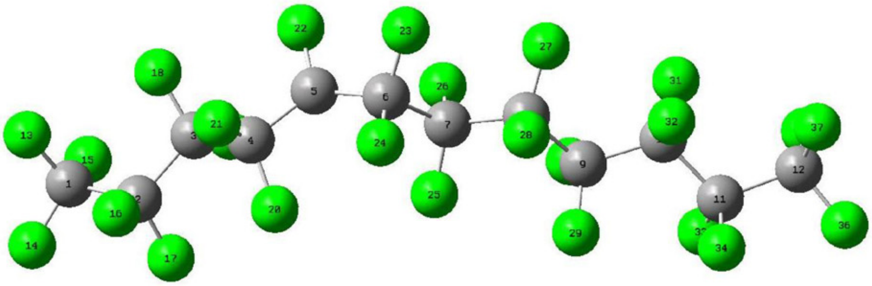
$CF_3(CF_2)_9C^{\bullet}FCF_3$



$CF_3(CF_2)_8C^{\bullet}FCF_2CF_3$

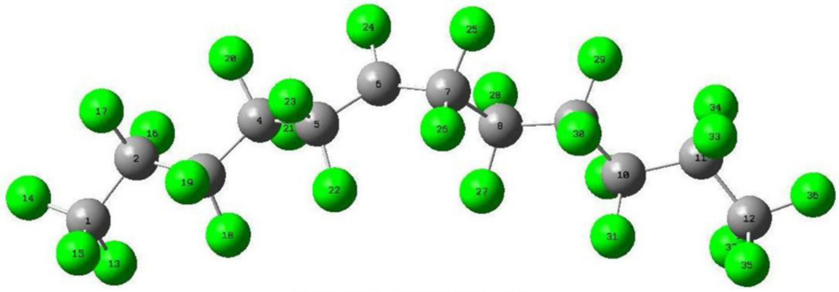


$CF_3(CF_2)_7C^{\bullet}F(CF_2)_2CF_3$

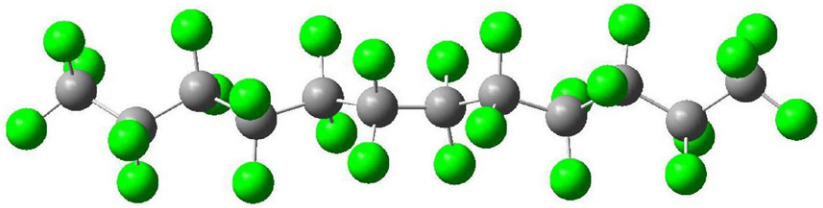


$CF_3(CF_2)_6C^{\bullet}F(CF_2)_3CF_3$

Fig. 6. (*Continued*)



$CF_3(CF_2)_5C^{\bullet}F(CF_2)_4CF_3$



$C_{12}F_{26}$

Fig. 6. (*Continued*).

excellent agreement with the DFT calculated 14.6 mT coupling for CF_3.

The experimental value for $A^F_{\|}$ for the $–CF_2C^{\bullet}F_2$ radicals derived from PTFE is 22.5 mT and the calculated value is 25.3 mT in excellent agreement. The calculated value for $A^F_{\perp}$ is smaller than the experimental value by about a factor of two, 1.5 mT (calculated) as compared to 3.3 mT (experimental). The average calculated values for $a^F_{\|\beta(1)}$ and $a^F_{\perp\beta(1)}$ are in excellent agreement with the experimental values.

For the $–F_2C^{\bullet}CFCF_2–$ radical, excellent agreement exists for the experimental value for the radical that occurs in PTFE of 23.8 for $A^F_{\|}$ and the average value of 27.3 mT predicted by DFT for the range of fluorocarbon radicals from C2 to C12. We also predict a small average value of -1.5 mT for $A^F_{\perp}$ which would be difficult to detect experimentally as found. The average calculated values for $a^F_{\|\beta(1)}$ and $a^F_{\|\beta(2)}$ of 8.7 mT and 3.7 mT are also in excellent agreement with the experimental values of 7.2 mT and 1.8 mT for the radical derived from PTFE. The predicted $a^F_{\perp\beta}$ values are smaller and would be difficult to observe. The DFT calculations show that the α^F and β^F couplings do not depend strongly on chain length. In addition, they do not depend strongly on the location of the radical in the chain except that the values for $A^F_{\perp}$ which have a small dependence on the location of the radical in the chain, being smaller the closer the radical is to the terminal CF_3 group. The major difference between the experimental results for the $–F_2C^{\bullet}CFCF_2–$ radicals from PTFE and PFA is that the value for $A^F_{\|}$ is substantially smaller and that for $A^F_{\perp}$ is substantially larger in PFA than in PTFE. The calculated results are not consistent with the PFA values. We explain these differences as being due to a time averaged structure in PFA at 77 K that does not occur in PTFE. As discussed below, conformational averaging in fluorocarbon radicals can have a dramatic effect on the values of the EPR hyperfine parameters. Of course, the calculated values are for a rigid structure at 0 K. The consistency between the calculated values and those for the radicals derived PTFE suggests that the structures in the PTFE radicals are similar to those in the calculated radicals. The α-fluorine isotropic coupling for $–F_2C^{\bullet}CFCF_2–$ in both PFA and PTFE can be estimated by averaging $A^F_{\|}$ and two times $A^F_{\perp}$. The estimated value for both is –8.5 mT (assuming values of 0.8 mT for $A^F_{\perp}$ for PTFE) showing that differences in the values of $A^F_{\|}$ and $A^F_{\perp}$ could be due to averaging of the conformations in the different matrices.

It has been well established [22] that fluorine containing radicals undergo molecular motion over a wide temperature range and exhibit a conformation at low temperatures dependent on the surrounding matrix. Two relevant examples are the $^{\bullet}CF_2CONH_2$ [35] and the $-O_2CC_{\beta}F_2{}^{\bullet}C_{\alpha}FCO_2-$ [36,37] radicals. The $^{\bullet}CF_2CONH_2$ radical exhibits a rapid in-phase motion of the CF_2 group above and below the CON Plane [35] making a dihedral angle of 9° with respect to the CON plane; at 77 K the fluorine coupling along the p_z orbital ($A_{\|}$) equals 20.2 mT, whereas at 300 K—the coupling equals 18.1 mT due to motional averaging. In the case of the $^-O_2CC_{\beta}F_2{}^{\bullet}C_{\alpha}FCO_2^-$ radical, the motion is coupled. The torsional oscillation of the $C_{\beta}F_2$ group does not occur independent of the torsional motion of the $C_{\alpha}F$ group [36,37]. Measurement of the α- and β-hyperfine couplings shows that torsional motion results from a counterclockwise rotation by 70° to the direction normal to the plane of the radical while the $CF_{2(\beta)}$ group moves about 30° clockwise. Thus, in one conformation the $p_{x'}$ orbital on the β_1 fluorine directly overlaps with the α fluorine p_z orbital while the p_x orbital on the β_2 fluorine lies in a nodal plane of the α fluorine p_z orbital. Thus the α fluorine coupling along the p_z orbital can vary from 21.7 mT (77 K) to 15.0 mT at 300 K. In

Table 3
The radiation-chemical yields of products for polymer radiolysis

Compounds	The radiation-chemical yields, G (per on 100 eV of adsorbed dose)
	Paramagnetic species
PTFE	0.4
n-C_6F_{14} to n-$C_{16}F_{34}$	1.6
Polyethylene	13
n-C_7H_{16}	13
	Destruction of molecules
PTFE	Irradiation and sintering in a vacuum: 0.02 [8,43] Irradiation in vacuum, sintering in air: 0.07 [8,43] Irradiation and sintering in air: 0.01–0.02 [8,43] TMS using results of the average numerical ($\bar{M}_g$) weight molecular mass in amorphous block: 0.20 [23] TMS using results of the weight molecular mass of PTFE ($\bar{\bar{M}}_w$) averaged over the topographical blocks: 0.04 [23]
CF_4–n-C_5F_{12}	1–5 [42,44,45]
CH_4–n-C_5H_{12}	6–10 [46,47]
Polyethylene	0.77 [4]
Polymethacrylate	1.6 [4]
Polyisobutylene	3 [4]
Cellulose	6–10 [4]
Polysulfones	9–12 [4]
	Formation of gaseous molecules
PTFE	0.051 [4]
Polyethylene	2.03 [4]

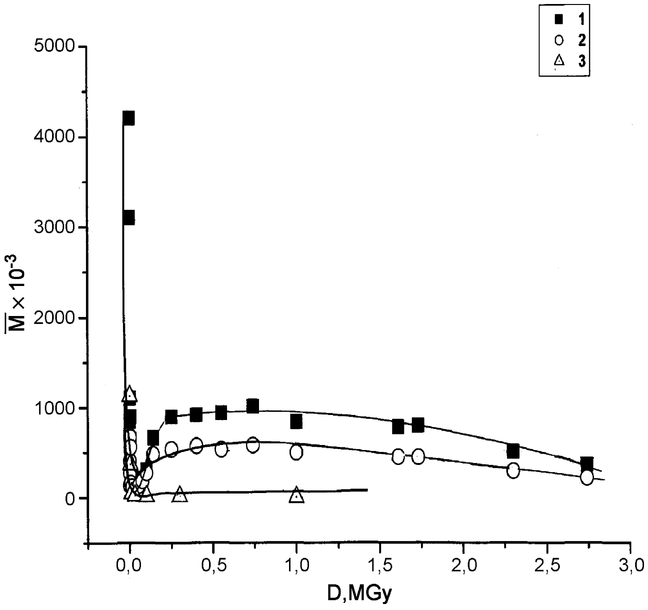


Fig. 7. Change of the weight molecular mass averaged over four topographical blocks of PTFE ($\bar{\bar{M}}_w$) (1) and the average numerical weight molecular mass of PTFE in the amorphous block ($\bar{M}_{g_n}$) (2) with irradiation dose at 27 °C. The molecular weight change of PTFE (3) during radiolysis at room temperature from Ref. [4].

addition the β_1 coupling along x' equals 12.2 mT while the β_2 coupling along x equals 1.1 mT. In a second conformation, these roles are reversed. Depending on the conformation that occurs in a matrix, the β fluorine couplings can vary between 12.2 and 1.1 mT values along the x direction. Likewise a coupling along the p_z direction of the α fluorine can be lower than the predicted gas phase value for a minimum energy configuration. The observed value will depend on the averaging that occurs at the temperature of the measurement.

3.3. Mechanism of polytetrafluoroethylene radiolysis

A mechanism of cation-radical formation has been proposed [38] which is consistent with the results of PTFE radiolysis at high pressure [38–40]. After polymer ionization, radical formation proceeds in two stages. First, there is a cleavage of C–C bonds of the ionized macromolecule with formation of fluorovinylcation-radicals. Second, the recombination of fluorovinylcation-radicals with electrons leads to the formation of allyl radicals, which can react with fluorine atoms leading to double bond formation. However, as was noted in Ref. [5], unsaturated products are not formed during radiolysis of PTFE in vacuum. The very low radiation-chemical yield of unsaturated products is only observed during irradiation of PTFE in air [7] when oxygen is present which leads the presence of oxygenated radicals [32]. These data show that the cation-radical mechanism cannot explain the radiation destruction of PTFE.

On the basis of on our results, it is more likely that C–F bond cleavage is playing the major role, at least on the time scales of the EPR experiments, consistent with the mechanism described in Refs. [18,21]. C–F bond cleavage with formation of $–CF_2CF^{\bullet}CF_2–$ centers was also observed in XPS studies of VUV irradiated PTFE [9]. These latter authors also suggest the formation of carbocation centers due to loss of F^- which would not be observed by EPR. However, carbocation centers will only be formed under the most extreme VUV conditions due to the formation of a fluorocarbocation and an anion. For example, the formation of the CF_3^+/F^- and $C_2F_5^+/F^-$ ion pairs from CF_4 and C_2F_6 respectively require about 11.3 ± 0.5 eV [41] which is at the upper limit of the VUV experimental range (115 nm = 10.8 eV) in the XPS study. In perfluoro-n-alkanes and PTFE, the calculated radiation-chemical yield for paramagnetic centers, is almost an order of magnitude less than in their hydrocarbon analogues (see Table 3). The low yield of radicals could well be the result of reactions with fluorine atoms, which can add to the stabilized radicals.

3.4. Source of radiation damage in PTFE

In order to determine the degree of radiation destruction of macromolecular polymers, it is necessary to determine the molecular mass before and after radiolysis. For the radiolysis of PTFE, the changes in molecular mass are usually deduced by indirect methods [5,6]. A search of the literature revealed poor consistency of the available data. In fact, it has not yet proven possible to determine the average molecular weight of PTFE by direct methods. This polymer cannot be transferred into either a soluble or a plastic state. Recently [23], the molecular mass of PTFE was deduced before and after irradiation in vacuo by the TMS method.

Radiation induced degradation of PTFE is accompanied by an increase in the molecular weight. The change in the average numerical weight molecular mass in the amorphous block of PTFE ($\bar{M}_{g_n}$) averaged over four topographical blocks of molecular mass of PTFE ($\bar{\bar{M}}_\mathrm{w}$) are shown in Fig. 7. Curve 3 in Fig. 7 is from Ref. [4] and shows the molecular weight change of PTFE during radiolysis at room temperature. As shown in Fig. 1, the molecular weight undergoes an appreciable change in the dose of <10 kGy during the radiolysis of PTFE. The radiation yields of degradation (G_d) calculated from the initial part of the curves in Fig. 7 are 0.2 for $\bar{M}_{g_n}$ and 0.04 for $\bar{\bar{M}}_\mathrm{w}$ chain cleavage per 100 eV of absorbed radiation energy. In Table 3, we give the values of G_d determined from the data of Refs. [8,42] using the Alexander–Charlesby–Ross equation [4]:

$$G_\mathrm{d} = (0.965 \times 10^5)\left(\frac{1}{D}\right)\left(\frac{1}{M^D - M}\right)$$

where D is the adsorbed dose (in kGy), M and M^D are the average molecular weights of the polymer before and after irradiaton with the dose D. The value of the radiation-chemical yield for the PTFE destruction calculated from literature data [7,43] indicates <0.1 chain cleavage for 100 eV of absorbed energy. During PTFE radiolysis, the values of $G_\mathrm{d} = 0.2$ (in air) and $G_\mathrm{d} = 0.1$ (in vacuum) were obtained as described in Ref. [23]. As shown in Table 3, the radiation-chemical stability of PTFE is one order greater than that of polyethylene and two orders greater than those for cellulose and polysulfones. In addition, the linear perfluoroalkanes, the low-molecular analogues of PTFE, have greater radiation stability ($G_\mathrm{d} = 1$–5) molecules destroyed per 100 eV adsorbed radiation energy [42,45,46]) than their hydrocarbon analogues ($G_\mathrm{d} = 6$–10) molecules destroyed per 100 eV adsorbed radiation energy [46,47]). In PTFE, the radiation-chemical yield of paramagnetic centers is very low ($G_\mathrm{d} = 0.4$) [48] as compared to polyethylene ($G_\mathrm{d} = 13$). On the basis of all of this data, PTFE should be a radiation-resistant polymer in vacuum.

Because the individual macromolecules of PTFE are not particularly susceptible to radiation destruction, some other mechanism must be important. We hypothesize that PTFE readily undergoes structural-topographical transitions upon radiation in vacuo, i.e., the generation of a radical leads to a significant change in the structure of the individual chains which disrupts the crystallinity of the bulk polymer. As shown in Fig. 6, generation of the radical sites in the perfluorcarbon radicals leads to kinking in the chains which will force disruption of the crystal structure. This is confirmed by the agreement with the calculated EPR hyperfine parameters for the perfuoro-*n*-alkanes and those found in PTFE radicals. The formation of the radicals will then lead to extensive reorganization of the supra-molecular structure of the polymer leading to considerable changes in the crystal structure. The change in the crystal structure results in loss of PTFE's favorable mechanical properties. It is well established that the properties of crystalline PTFE are strongly related to the degree of helicity of the polymer and that changes in this parameter alone are enough to dramatically affect the phase diagram of PTFE [26]. The phase diagram for PTFE is dominated by changes in the helicity which does not involve kinking of the chains. The formation of radicals leads to substantially more changes than just the helicity of the chain so the crystal structure and hence the properties are dramatically affected. Thus, kinking of the perflurocarbon-*n*-alkane chains in PTFE leads to a loss of mechanical stability. Although the individual chains in PTFE do not form radicals as easily as other organic polymers, once a radical is formed, the structure dramatically changes leading to the result that, among the known polymers, PTFE has the least mechanical stability towards high energy radiation.

Acknowledgement

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