Conformation of perfluoroalkyl radicals in the solid phase

1. Terminal $\sim CF_2{}^{\cdot}CF_2$ radical stabilized at 77 K in matrices of linear perfluoroalkanes and polytetrafluoroethylene

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An equilibrium conformation of the perfluoroalkyl $\sim CF_2{}^{\cdot}CF_2$ radical at 77 K in matrices of polytetrafluoroethylene and *n*-perfluoroalkanes was studied. Upon cooling from 300 to 77 K at temperatures below 200 K, the ESR spectrum of this radical changes, and the well-resolved hyperfine structure appears. The hyperfine splitting constants on nuclei of two nonequivalent F_β atoms were determined: 2.2 and 1.1 mT, respectively. The $A_\parallel$ and $A_\perp$ values for the F_α atoms are 22.5 and 3.3 mT, respectively. The conformational angle between the axis of the orbital of an unpaired electron and projection of the C_β—C_γ bond is 5.6°.

Key words: polytetrafluoroethylene, linear perfluorododecane, radiolysis, photolysis, ESR spectra, $\sim CF_2C{}^{\cdot}F_2$ radical, conformation, hyperfine structure.

Synthesis and modification of fluorocarbon polymers, in particular, polytetrafluoroethylene (PTFE), occur, as a rule, according to the radical mechanism. Therefore, data on the structure of "terminal" free radicals $\sim CF_2{}^{\cdot}CF_2$ leading the chain during polymerization are of great interest.[1–12] Terminal radicals were studied in processes of low-temperature mechanical destruction of polymers,[3] solid-phase[4,5] and liquid-phase polymerization of tetrafluoroethylene (TFE),[13,14] polymerization of TFE in the adsorbed state,[6] and photodestruction of peroxide radicals in γ-irradiated PTFE.[7–9]

The ESR spectrum of the terminal $\sim CF_2{}^{\cdot}CF_2$ radical (R_t) at 77 K consists of two parts: an intense central singlet and lateral peaks with a splitting constant of ~40 mT.[10] The presence of the terminal radical in the ESR spectra of γ-irradiated *n*-C_6F_{14} [15] and *n*-C_8F_{18} [16] was determined mainly by the characteristic lateral peaks. The study of the kinetics of accumulation of R_t becomes complex, on the one hand, because of a low intensity of the peaks as compared to that of the central singlet and, on the other hand, due to the superimposition on these signals of the components of the ESR spectrum of the "middle" $\sim CF_2C{}^{\cdot}FCF_2\sim$ (R_m) radical that is also formed during radiolysis of *n*-perfluoroalkanes (*n*-PFA).

It has been mentioned[8] that the hyperfine structure (HFS) appears in the central signal in the ESR spectrum of the terminal radical in PTFE at registration temperatures below 170 K.

In this work, we studied the ESR spectrum of the terminal radical and established its equilibrium conformation at 77 K for several crystalline *n*-PFA (*n*-C_6F_{14}, *n*-C_8F_{18}, *n*-$C_{12}F_{26}$, and *n*-$C_{16}F_{34}$) and PTFE.

Experimental

Samples of linear perfluoroalkanes containing not less than 99.9% of the main product and samples of fibrous PTFE powder (F-4 trade mark) were used. These PTFE samples are characterized by high crystallinity.

ESR spectra were recorded on an EPR-21 radiospectrometer (N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences). Radiolysis of pre-degassed samples was carried out by γ-beams (^{60}Co source) *in vacuo* in sealed ampoules of SK-4B glass. Photolysis of samples was carried out by the light of a high-pressure mercury light (DRSh-1000) at 77 and 300 K.

Results and Discussion

The ESR spectrum of *n*-PFA γ-irradiated at 77 K is the superimposition of signals of several paramagnetic centers (PC) (Fig. 1, *a*). The spectrum exhibits peaks with splitting constants of (21.5±0.6) and (44.4±0.6) mT with one and two F_α atoms, respectively, which are characteristic of the stabilized perfluoroalkyl $\sim CF_2{}^{\cdot}CFCF_2\sim$ and $\sim CF_2{}^{\cdot}CF_2$ radicals. In addition to signals of these radicals, the spectrum contains the components of the quadruple spectrum with splittings of 14.4 mT belonging to the ${}^{\cdot}CF_3$ radical.

As seen in Fig. 1, in the ESR spectrum of *n*-PFA γ-irradiated at 77 K, HFS with remote lines with splitting of ≈1.1 mT is detected in the central singlet. Their intensities increase in parallel with the intensities of characteristic lines from the terminal radical with splitting of (44.4±0.6) mT, which indicates most likely their belonging to this radical.

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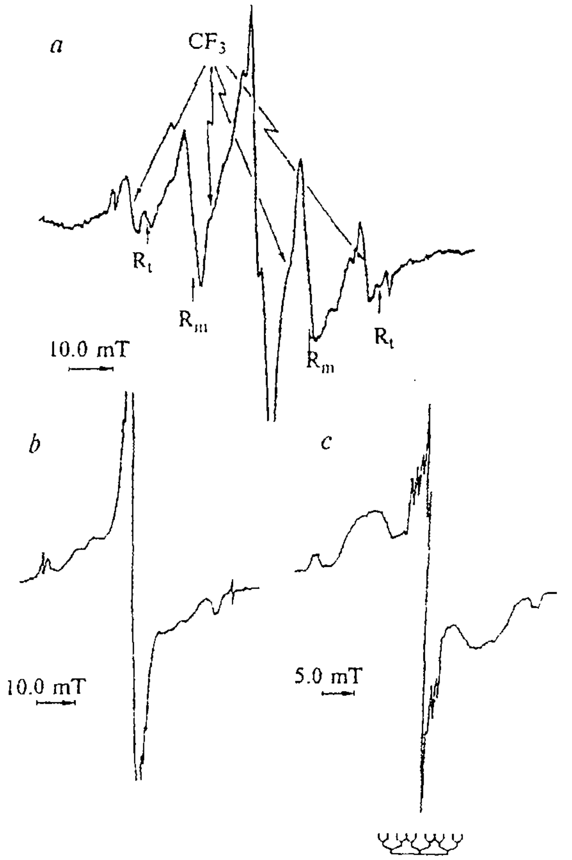

Fig. 1. ESR spectra of n-C_6F_{14} (*a*) and n-$C_{12}F_{26}$ (*b*, *c*) samples irradiated at 77 K by doses of 16.7 (*a*) and 3900 kGy (*b*, *c*). ESR spectra were recorded before (*a*, *b*) and after heating to 215 K (*c*). The characteristic lines in the spectrum of $C^{\cdot}F_3$, $\sim CF_2C^{\cdot}FCF_2\sim$ (R_m), and $\sim CF_2C^{\cdot}F_2$ (R_t) radicals are shown by arrows.

When n-PFA irradiated at 77 K is heated to 215 K, a decrease in the fraction of PC contributing to the central part of the ESR spectrum is observed. The ratio of intensities of lateral components of the spectrum of R_t and the signal from the R_m radical remains almost unchanged (see Fig. 1, *b*, *c*). Therefore, in the central part of the spectrum, other PC with lower thermal stability than those of the terminal and middle radicals are detected along with R_t. When n-PFA irradiated at 77 K is heated to room temperature, only internal radicals remain stable. Despite the difference in thermal stabilities of PC stabilizing in n-PFA γ-irradiated at 77 K, no individual spectrum of terminal radicals was obtained during freezing out.

The parameters of the ESR spectra of terminal and internal radicals in samples of low-molecular n-PFA and PTFE γ-irradiated at 77 K virtually coincide.

However, unlike the ESR spectra of irradiated n-PFA, in which terminal radicals predominate (see Fig. 1, *b*), in the ESR spectrum of PTFE irradiated at 77 K, their fraction is low, and the concentration is almost an order of magnitude lower than that of the $\sim CF_2C^{\cdot}FCF_2\sim$ radicals.[7] Therefore, terminal radicals in PTFE were generated similarly to the method described previously[8] by photolysis of peroxide radicals $\sim CF_2CF(OO^{\cdot})CF_2\sim$ obtained by the oxidation of perfluoroalkyl radicals in preliminarily γ-irradiated PTFE. Using this procedure, we achieved a sufficiently high concentration of terminal radicals without admixtures of other PC. It should be noted that the well-resolved central part of the spectrum of the terminal radical is observed only for samples of high-crystallinity PTFE.

It is known that the ESR spectrum of the peroxide $\sim CF_2CF_2OO^{\cdot}$ radical at 77 K has the shape of an anisotropic singlet. At 300 K, this spectrum is reversibly transformed into a symmetrical singlet, *i.e.*, at this temperature, $\sim CF_2CF_2OO^{\cdot}$ executes fast reorientation motions with frequencies $\nu_m \geq 10^8$ s^{-1} (see Ref. 3), averaging of the anisotropy of the g-factor being observed at 77 K.

The same considerations can concern motions of the terminal alkyl radicals (Fig. 2). The ESR spectra observed at 300 K are recorded under conditions of fast reorientation mobility. When the sample is cooled, the HF-components of the spectra of the terminal radical begin to broaden. The triplet form of the central part of the spectrum is retained to 200 K. The further decrease in temperature sharply changes the shape of the spectrum (see Fig. 2, *f*—*h*). Triplet splitting increases from ΔH_{T_1} = 9.7 mT (300 K) to ΔH_{T_2} = 22.5 mT (77 K). Additional HFS lines appear in the central part of the spectrum at the sides of triplet components. In addition, the central component of the spectrum is also split to gain an even character. Finally, at 77 K, the central part of the spectrum of the terminal radical in PTFE contains 10 HFS lines with splitting $\Delta H_{10} \approx 1.1$ mT (see Fig. 2, *h*) similarly to the ESR spectrum of n-PFA γ-irradiated at 77 K.

As a rule, a decrease in the registration temperature results in broadening of the HF-component. As a result, in the majority of cases at low temperatures and in the solid phase, ESR spectra of fluorine-containing alkyl radicals bear very poor information. As seen in Fig. 2, by contrast, well-resolved HFS appears in the ESR spectrum upon cooling of the PTFE sample to temperatures below 200 K. This temperature anomaly is most likely related to the phase transition in PTFE. The PTFE macromolecule looks like a coil. According to the data in Ref. 17, at ~176 K, the coil chain is uncoiled in the amorphous region. The changes in the ESR spectra observed at these temperatures indicate a great interrelation between the HFS spectrum and the conformational structure of the radical.

As known, the values of hyperfine coupling (HFC) on the F_α nuclei can be described by the correlation:

$$a_{F_\alpha} = A_0 + B(3\cos^2\omega - 1), \qquad (1)$$

where A_0 and B are constants of isotropic and anisotropic HFC, ω is the angle between the direction of the C_α—F_α bond and external magnetic field. Under condi-

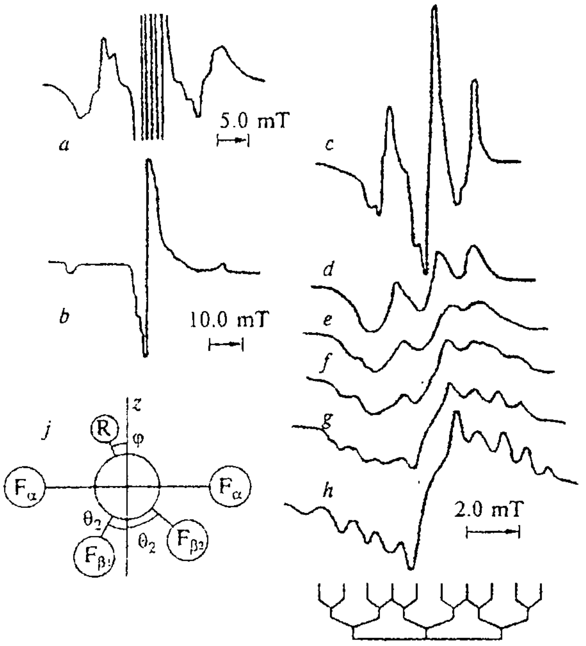

Fig. 2. ESR spectra of the ~$CF_2C^{\cdot}F_2$ radical in PTFE at *T*/K = 295 (*a*), 77 (*b*), 295 (*c*), 240 (*d*), 200 (*e*), 180 (*f*), 150 (*g*), and 77 (*h*); *c—h* were recorded at a field scan 2.5-fold lower; projections of bonds of this radical (*j*) on the plane perpendicular to the line connecting C_α and C_β atoms. The ~$CF_2C^{\cdot}F_2$ radical was obtained by photolysis of peroxide ~$CF_2CF(OO^{\cdot})CF_2$~ radicals in PTFE at 77 K.

tions of fast reorientations at 300 K, anisotropic HFC are averaged, and only the isotropic component appears in the spectrum ($\Delta H_{T_1} \approx A_0$). The splitting value (close to ΔH_{T_1} = 9.7 mT) in the triplet at 300 K can be determined from the ESR spectra of the terminal radical presented previously.[11] As shown below, only the value A_0 = 9.7 mT describes satisfactorily the ESR spectrum of the terminal radical in *n*-PFA and PTFE observed at 77 K. The F_α HFC constant, which is close to 9.7 mT (~9.0 mT), is also observed in the ESR spectrum of the $CF_2C^{\cdot}FCF_2$~ radical in the 295—540 K temperature range. When the sample is heated to temperatures >400 K[8] or for the strong extension of the polymer chain,[11] in the spectrum of the terminal radical, HFC anisotropy is averaged and, most likely, the constant of isotropic HFC decreases as well. Therefore, under these conditions of registration, the A_0 value (see Refs. 8 and 11) is lower than $A_0 \approx$ 9.7 mT. When rotations are frozen, the parallel and perpendicular components of the HF-components[19] with the splittings

$$A_{\parallel}(F_\alpha) = A_0 + 2B;\ A_{\perp}(F_\alpha) = A_0 - B \qquad (2)$$

should appear in the spectrum.

The external component of the triplet structure of the ESR spectrum at 77 K is identical to the parallel component (*i.e.*, $A_{\parallel}(F_\alpha)$ = 22.5 mT). From Eq. (2) we obtain B = 6.4 mT and $A_{\perp}(F_\alpha)$ = 3.3 mT. Therefore, the perpendicular components of the components caused by HFC with nuclei of the F_α atoms should be observed in the central part of the spectrum.

At fast reorientation motions, the F_β atoms often exchange sites and, hence, they are equivalent. Upon freezing, the equivalence of the F_β atom is distorted, and the HFC values are determined by the correlations

$$a_{F_{\beta i}} = Q'_\beta \cos^2\theta_i, \qquad (3)$$

where $Q'_\beta = Q_\beta\rho$; Q_β is constant; ρ is the spin density of an unpaired electron at the C_α atom, and θ_i is the angle between the projection of the $C_\beta—F_{\beta i}$ bond and the axis of the orbital of an unpaired electron. The central part of the spectrum of R_t has an even character and, hence, the *n*-PFA molecule and the polymeric PTFE chain adopt the conformation in which the F_β are really nonequivalent. Ten lines of the central part of the spectrum can be considered as a triplet of quadruplets (see Fig. 2, *h*). The isotropic central part (m_z = 0) and perpendicular components of the HFS components on two F_α nuclei (*i.e.*, $\Delta H_{T_3} = A_{\perp}(F_\alpha)$) are responsible for the structure of the spectrum with splitting ΔH_{T_3} = 3.3 mT. The quadruplet structure with splitting ΔH_4 = 1.1 mT is due to nonequivalent F_β atoms, and the equidistant lines in the spectrum indicate that the HFC constants (*a*) with the F_β atoms are $a_{F_{\beta1}} = 2a_{F_{\beta2}}$. The ten-component HFS of the central part of the spectrum can be obtained under the condition that $\Delta H_4 = 1/3A_{\perp}(F_\alpha) = a_{F_{\beta2}} = \Delta H_{10} \approx$ 1.1 mT. The experimental data indicate that this correlation is satisfactorily fulfilled:

$A_{\parallel}(F_\alpha)$	22.5	ω = 0°, 180°
$A_{\perp}(F_\alpha)$	3.3	ω = 90°
$a_{F_{\beta1}}$	2.2	φ = 5.6°, θ = 54.4°
$a_{F_{\beta2}}$	1.1	φ = 5.6°, θ = 65.6°

Here *A* and *a* (in mT) are HFC constants; ω is the angle between the direction of the $C_\alpha—F_\alpha$ bond and external magnetic field; φ is the angle between the projection of the $C_\beta—C_\gamma$ bond and the axis of the orbital of a lone electron; θ is the angle between the projection of the $C_\beta—F_{\beta i}$ bond and the axis of the orbital of a lone electron. The edge components of quadruplets are broadened and, hence, their intensity is lower than that of the middle components (it can be observed best of all for the 1st and 10th components). The solution of Eq. (3) for the spectrum of R_t has two roots and, hence, two sets of conformational angles and values of the HFC constant Q'_β:

1) Q'_β(I) = 6.5 mT, φ(I) = 5.6°,

2) Q'_β(II) = 2.3 mT, φ(II) = 73.6°,

where φ is the angle between the projections of the axis of the orbital of an unpaired electron and the $C_\beta—C_\gamma$ bond on the plane perpendicular to the line connecting the C_α and C_β atoms. The conformational angle φ is related to the θ_1 and θ_2 angles by the equations: θ_1 =

$\pi/3 - \varphi$; $\theta_2 = \pi/3 + \varphi$, where θ_1 and θ_2 are the angles between the axis of the orbital of a lone electron and projection of the $C_\beta{-}F_{\beta 1}$ and $C_\beta{-}F_{\beta 2}$ bonds, respectively. The projections of the bonds in the terminal radical on the plane perpendicular to the $C_\alpha{-}C_\beta$ bond are presented in Fig. 2. Under conditions of fast reorientations in the polymer molecule and *n*-PFA, HFC are averaged. Both roots of Eq. (3) result in the value $(a_{F\beta})_{av}$ = 1.65 mT, which is close, in fact, to the value experimentally obtained in PTFE at 300 K: $(a_{F\beta})_{av}$ = 1.6 mT.

To choose one of these roots, we analyzed the spectrum of the terminal radical formed upon the solid-phase polymerization of TFE. Splitting observed in the triplet of (4.3±0.1) mT[4,12] and (4.0±0.3) mT[6] is due to terminal radicals with equivalent F_β. According to Eq. (3), for this radical at angles $\varphi = 90°$ and $\theta_1 = \theta_2 = 30°$, the Q'_β constant is equal to 5.8 mT. Comparison of the values of $Q'_\beta(\mathrm{I})$ and $Q'_\beta(\mathrm{II})$ constants for R_t in PTFE with the calculated value (5.8 mT) shows that the root $Q'_\beta(\mathrm{I})$ = 6.5 mT should be used for the solution of Eq. (3). Close Q'_β values were obtained for some low-molecular fluorine-containing[20,21] and hydrocarbon alkyl radicals.[10]

Thus, taking into account the conformational structure, we can explain many experimental data on ESR spectra of terminal radicals. The values of constants (A_0, B, Q'_β) calculated for the radicals indicated above agree satisfactorily with each other. Therefore, they can be used for the determination of the conformational structure of other fluorine-substituted radicals as well.

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