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

Features of the Molecular–Topological Structure of γ-Irradiated Powdered Tetrafluoroethylene–Perfluoro(propyl vinyl ether) Copolymer

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Abstract—With the use of thermomechanical spectrometry in two modes, coaxial, when the load application vector is coplanar with the compacting pressure vector (semicrystalline copolymer) during the measurement of the deformation of a copolymer of tetrafluoroethylene with perfluoro(propyl vinyl ether), and mutually perpendicular (completely amorphous copolymer), it has been established that the axial compression of the copolymer brought its topological structure to an absolutely anisotropic state. After γ-irradiation, the semicrystalline structure of the copolymer was retained regardless of the radiation dose. The minimum values of the glass transition temperature of the amorphous block and the degree of crystallinity were observed in the copolymer irradiated to a dose of 150 kGy. The molecular weight distribution functions of interjunction chains in the networks of the amorphous blocks of the initial copolymer and its γ-irradiated analogs are bimodal.

INTRODUCTION

Methodologically, a study of the molecular–topological structure of powdered fluorine-containing polymers by thermomechanical spectrometry (TMS) implies their uniaxial extrusion at an optimized pressure [1–3]. In this case, as a rule, amorphous and amorphous–crystalline polymers lose their isotropic structure to transform to an anisotropic structure [1, 2]. As a result of a structural rearrangement, for example, in poly(vinylidene fluoride) [1], a copolymer of tetrafluoroethylene with ethylene [2], and polytetrafluoroethylene (PTFE) [3], not only their degree of crystallinity decreases, but also the spatial orientation of crystallites changes: a certain portion of them, which quantitatively depends on compacting pressure, becomes oriented by its axial plane in a plane perpendicular to the compacting pressure vector. The anisotropic topological structure thus obtained is a reason for a technological defect: the cracking of cylindrical billets in the PTFE agglomeration procedure [3].

Based on experimental data [1–3], a technique was developed for evaluating the degree of anisotropy of a topological structure—the TMS determination of the degree of crystallinity in a fluorine-containing polymer sample in the two modes of analysis: coaxial, when the load application vector is coplanar with the compacting pressure vector (II) on the measurement of polymer deformation in a thermal analyzer, and mutually perpendicular (⊥). The ratio of the degree of crystallinity determined by analysis in the former mode to an analogous value found in the latter mode was taken as the degree of anisotropy of a topological structure ($K_{an} = \varphi_{g(II)}/\varphi_{g(\perp)}$). The effect of γ-irradiation dose on the degrees of anisotropy of the topological structures of fluoroplastics and on the molecular-relaxation characteristics of chains in the structures of topological blocks in γ-irradiated fluoroplastics was studied with the use of the powdered samples of a copolymer of tetrafluoroethylene with ethylene [2] and PTFE [3] as examples. The results of the study made it possible to propose a method for eliminating a technological defect of the cracking of cylindrical billets in the procedure of PTFE agglomeration by γ-irradiation [3]. However, the influence of γ-radiation dose on the degree of anisotropy of the topological structure of fluoroplastics was found not always unambiguous, and it should be studied in more detail; this is the subject matter of this work.

The aim of this work was to examine the effect of the γ-irradiation of a copolymer of tetrafluoroethylene and perfluoro(propyl vinyl ether) on its molecular–topological structure.

EXPERIMENTAL

The commercial powdered copolymer of tetrafluoroethylene and perfluoro(propyl vinyl ether) (PFA) of Ftoroplast F-50 brand produced at the Kirovo-Chepetsk Chemical Works was used in this study.

The TMS method used in this work is based on the thermomechanical analysis (TMA) of polymers, and it makes it possible to perform the comprehensive molecular–topological testing of structurally different polymers in the course of a single experiment in the regime of rapid analysis for all practical purposes. The analytical capabilities of TMS and the characteristics measured directly and calculated from the results of a single experiment were described elsewhere [4–6]. The TMS method has been widely used previously for investigating the influence of radiolysis on the structure of fluorine-containing polymers [7–10].

Thermomechanical analysis was carried out by the penetration of a hemispherical quartz probe with a radius of 1.0 mm into the copolymer. The powdered copolymer was pressed in a matrix mold. The samples for TMA were pellets with a diameter of 6 mm and a height of 3 mm. They were placed in the heat chamber of a standard UIP-70M thermal analyzer and cooled to 173 K at a rate of 5 K/min with the simultaneous recording of a thermomechanical curve (TMC). The accuracy of temperature or deformation measurements was ±0.05 K and ±5 nm, respectively [11]. The reproducibility of the results of analysis in the measurements of molecular weights and free volumes was about ±10%. The other data were reproduced in the ranges of errors from ±5 to 10%, but error was as high as 20% in certain cases because of the heterogeneity of materials and differences in their thermal prehistory.

The radiolysis of the copolymer with ^{60}Co γ-rays was performed in glass ampoules on a Gammatok-100 source at 300 K. The irradiation dose rate was 0.5 kGy/h. The powdered PFA samples after γ-irradiation were pressed into pellets for TMA.

The EPR spectra were measured at 77 K on a portable PS100.X radiospectrometer with the automatic processing of EPR spectra (NPP Adani, Minsk, Belarus). For the EPR analysis of the γ-irradiated copolymer powders, a PFA sample was initially evacuated to a residual pressure of 0.13 Pa and then irradiated with ^{60}Co γ-rays in an ampule made from SK-4B glass, which does not give an EPR signal upon radiolysis at 77 K.

RESULTS AND DISCUSSION

Molecular–Topological Structure of PFA

Figure 1a shows the TMA curve of the copolymer. Its shape is characteristic of a polyblock polymer with a semicrystalline structure. In a temperature range of 173–268 K, it occurred in a crystal-vitrified state and expanded with temperature at a constant rate (straight line AB), which is characterized by the linear thermal expansion (or compression on cooling) coefficient $\alpha_1 = 12.8 \times 10^{-5}$ K^{-1}.

At $T_g = 268$ K, the segmental mobility began to freeze out in the copolymer and a TMC transition region began to be formed as an envelope of deformation jumps (H_i). They occur in the loaded polymer due to a continuous decrease in the physical network modulus upon the completion of the segmental relaxation of interjunction homologs with mass M_i and weight fraction φ_i. According to the physical network theory and thermomechanical spectrometry data [12–14], it begins with the relaxation of the shortest segments (Kuhn's segments) and completes at $T_\infty = 526$ K with a transition to a state of the flow of homologs with the highest molecular weight. In this case, the molecular weight M_i, which is proportional to $T_i - T_g$, corresponds to a deformation jump (H_i) that determines its weight fraction φ_i in accordance with the equation $\varphi_i = [H_{(i+1)} - H_i]/H_\infty$. Here, the quantity H_∞ is equal to the total thermomechanical (penetration) deformation at T_∞. The molecular weight M_i is related to ΔT_i by the following Kargin–Slonimskii–Ol'khov relationship [11, 15]: log $M_i = 2.3 + 11\Delta T_i/(100 + \Delta T_i)$. Thus, the TMC transition region of the copolymer having the coordinates φ_i (ordinate) and M_i (abscissa) is a pseudo-integral molecular weight distribution (MWD) curve of interjunction chains in the pseudo-network of the amorphous block. Criteria for this attribution of this topological (supramolecular) organization element of PFA are, first, the attainment of a rubbery deformation plateau (straight line CD) and, second, the correspondence of a ratio of expansion rates in this zone ($\alpha_2 = 35.7 \times 10^{-5}$ K^{-1}) to α_1 to the inequality $\alpha_2/\alpha_1 < 6$ [16].

The calculated values of the number-average ($\overline{M_{g_n}}$) and weight-average ($\overline{M_{g_w}}$) molecular weights of the interjunction chains of block pseudonetworks are $\overline{M_{c_n}} = 46\,800$, $\overline{M_{g_w}} = 83\,900$, and $K = 1.79$, where K is the polydispersity index. The shape of the curve in the transition region (shaded region) indicates a bimodal curve of the MWD of interjunction chains (Fig. 2a).

The pseudonetwork structure of the amorphous block is formed by crystallized segments of PFA macromolecules as branching points. Their heat resistance is responsible for the thermal stability of the rubbery plateau of the amorphous block in a temperature range from $T_\infty = 526$ K to the initial melting temperature of
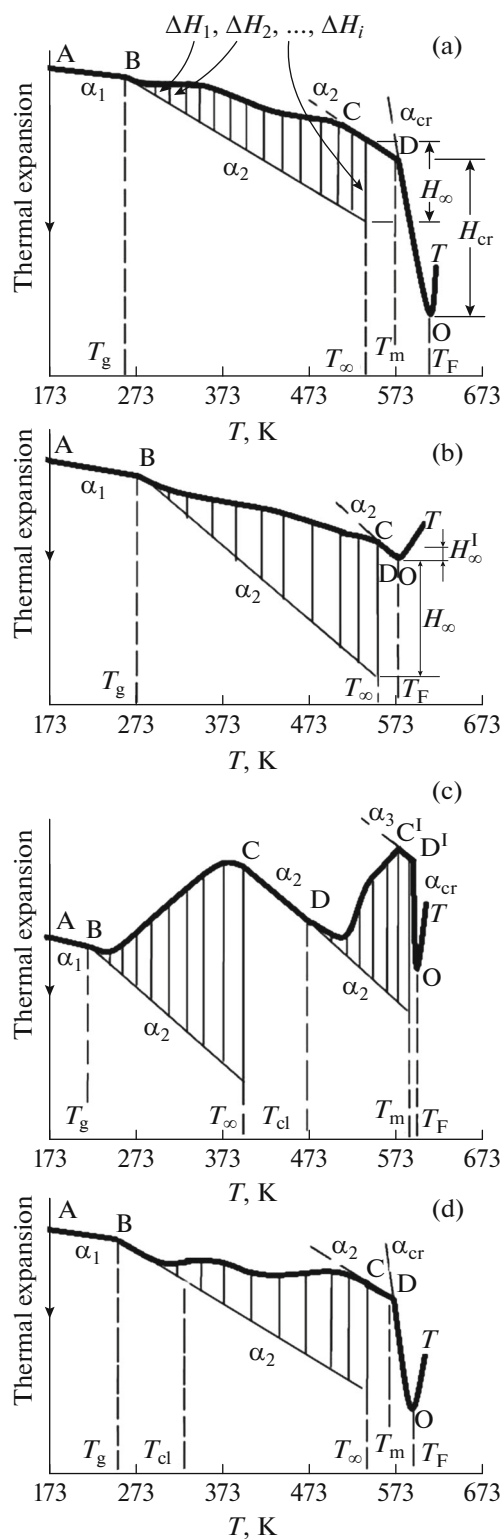
Fig. 1. Thermomechanical curves of PFA (a, b) before and after γ-radiolysis at doses of (c) 150 kGy and (d) 600 kGy. The curves were measured at the (a, c, d) coaxial and (b) mutually perpendicular orientations of the compacting pressure and thermomechanical load vectors.
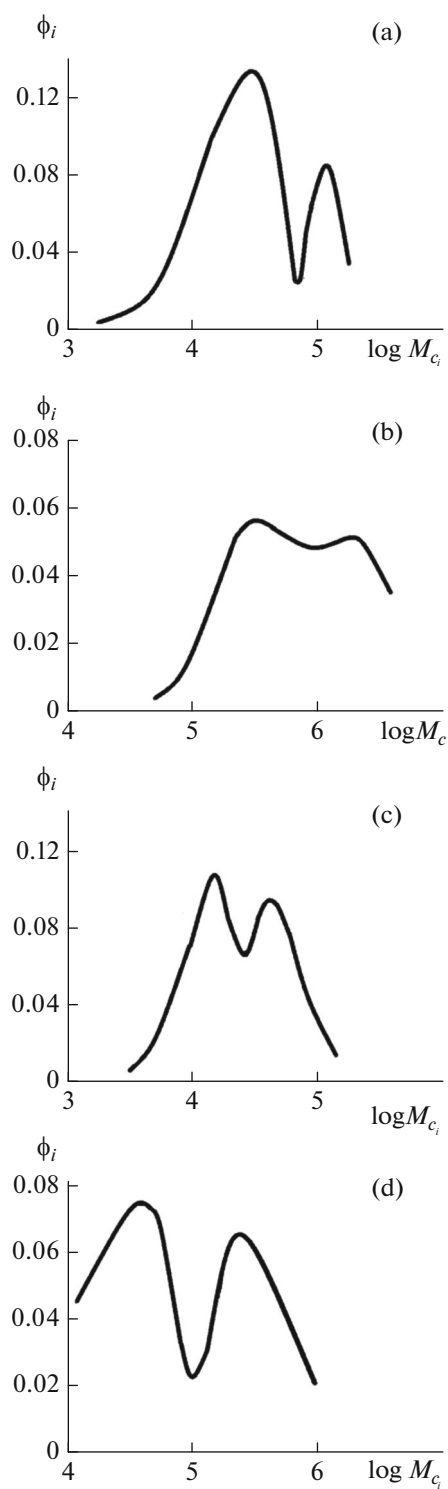

Fig. 2. Molecular-weight distribution functions of inter-junction chains in the pseudonetwork of the amorphous block of PFA (a, b) before and after γ-irradiation to doses of (c) 150 kGy and (d) 600 kGy. TMA was carried out with the coaxial (a, c, d) and (b) mutually perpendicular orientations of the vectors.

crystallites at $T_m = 550$ K. At a temperature higher than T_m, the rate of expansion of the polymer sharply increased due to an increase in its specific volume upon melting. The rate of expansion under steady-state conditions is $\alpha_{cr} = 285.7 \times 10^{-5}$ K^{-1}; this value exceeds the threshold ratio $\alpha_{cr}/\alpha_1 \geq 6$ [16].

The molecular weight of the crystallized fragments of the copolymer macromolecules is proportional to $\Delta T = T_m - T_F$ and equal to $\sim 13\,200$. The free-molecule flow of PFA comes into play at a temperature at point O ($T_F = 583$ K) (curve OT).

The weight concentration ratio between amorphized and crystallized chains in PFA is 0.47 : 0.53. It is evident that in contrast to the homopolymer of tetrafluoroethylene (PTFE) in the structure of which a crystalline state predominates (to 0.70) under similar TMA conditions [7], the fraction of the crystalline phase decreased to $\varphi_c = 0.47$ in PFA containing about 4 mol % perfluoro(propyl vinyl ether). Thus, the incorporation of perfluoro(propyl vinyl ether) molecules into the composition of a tetrafluoroethylene polymer leads to a decrease in the crystallinity of its topological structure.

The rigid-chain nature of the amorphized fragments of the copolymer macromolecules, in which the free volume is $V_f = 0.184$ at T_g, provides an opportunity to calculate the molecular weight of PFA under the assumption of no more than a single its intersection by the pass-through chains of both topological blocks from the following block weight averaging equation:

$$\overline{\overline{M_w}} = \overline{M_{g_n}}\varphi_a + \overline{M_w^{cr}}\varphi_{cr} = 46\,400.$$

Figure 1b shows the TMC of the copolymer measured in the same temperature range but with a mutually perpendicular orientation of vectors. In this case, a probe does not detect all of the crystals whose longitudinal axis was directed in parallel to the thermomechanical load vector as an anomalously expanding structural fragment. It responded to only the deformation of their amorphized state and expansion on the melting of crystals with another orientation of the longitudinal axis. The shape of the TMC in Fig. 1b is indicative of the completely amorphous diblock structure of the copolymer ($\alpha_2/\alpha_1 < 6$), and the copolymer occurred in a glassy state in the temperature range of 173–273 K, being expanded with temperature (straight line AB) at a rate of $\alpha_1 = 10.8 \times 10^{-5}$ K^{-1}. The transition region (BC curve) of the TMC afforded the following values of the averaged molecular weights of interjunction chains in the pseudonetwork of the low-temperature amorphous block: $\overline{M_{g_n}} = 323600$, $\overline{M_{g_w}} = 1711200$, and $K = 1.85$. Figure 2b shows their MWD function.

The thermally stable state—the plateau of the rubbery deformation of the block pseudonetwork (straight line CD, $\alpha_2 = 50.5 \times 10^{-5}$ K^{-1}) occurred in a narrow temperature range from $T_\infty = T_g^I = 560$ K to $T_F = 570$ K. The molecular weight of chains in the cluster units of the high-temperature amorphous block was also small. It was proportional to $\Delta T = T_g^I - T_F$ and equal to $\overline{M_{C_w}^I} = 5\,300$. The weight fraction of these segments of macromolecules was no higher than 2% $\varphi_\alpha^I = H'_\infty/(H_\infty + H'_\infty)$.

The weight-average molecular weight of completely amorphous PFA averaged over blocks was $\overline{\overline{M_w}} = \overline{M_{c_w}}\varphi_a + \overline{M_{C_w}^I}\varphi_a^I = 1694100$.

With $V_f \sim 0.325$ (at T_g), this value is close to the true molecular weight of the copolymer. The value $\overline{\overline{M_w}} = 46\,400$ determined on the coaxial orientation of vectors (at $V_f = 0.184$) is an effective quantity because of the repeated intersection of its topological blocks by PFA macromolecules.

Thus, the TMS analysis of the molecular–topological structure of powdered PFA performed in two test modes showed a significant tendency of the crystalline elements of its topological structure toward complete orientation under the action of axial compression with the formation of an absolute anisotropic structure: $K_{an} = \varphi_{cr(II)}/\varphi_{cr(\perp)} = 0$.

Molecular–Topological Structure of PFA after γ-Irradiation

Figure 1c shows the TMC of the copolymer γ-irradiated at a dose of 150 kGy, measured under the conditions of the coaxial orientation of vectors. It is characteristic of a topologically triblock polymer with an amorphous–crystalline structure, in which the pseudonetwork structure of an amorphous block whose points are associative cluster structures (cluster block, $T_g^I = 475$ K) and crystalline units (crystalline block, $T_m = 581$ K) coexist in a temperature range of 173–673 K. In a temperature range of 173–216 K, PFA occurred as a mixture of glassy, cluster, and crystalline states. At $T_g = 216$ K, the segmental mobility in interjunction chains began to freeze out and a TMC transition region (curve BC) began to be formed: a transition from expansion in the glassy state (straight line AB) at a rate of $\alpha_1 = 4.65 \times 10^{-5}$ K^{-1} to expansion in the rubbery state at a rate of $\alpha_2 = 15.6 \times 10^{-5}$ K^{-1}. An analysis of the transition region of the TMC gave the following values of the averaged molecular-weight characteristics of interjunction chains in the network of the amorphous block: $\overline{M_{g_n}} = 18630$, $\overline{M_{g_w}} = 31680$, and $K = 1.70$. Figure 2c shows their MWD function.

The region of a thermally stable state of the network structure of the amorphous block (straight line CD) ended at $T_g^I = 475$ K with the onset of the segmental relaxation of chains in the cluster block of PFA. In this process, the deformation of the block net-

work formed the transition region (curve DC'). An analysis of this region makes it possible to calculate the averaged molecular weight characteristics of chains in the pseudonetwork structure of the cluster block: $\overline{M_{c_w}^I} = 35350$, $\overline{M_{C_w}^I} = 48910$, and $K = 1.38$.

The region of the high-temperature thermally stable state of the PFA network after the thermal degradation of its cluster block begins at a temperature at the point C' and ends at $T_m = 581$ K by its thermal decay in the course of the melting of the copolymer crystalline phase at a rate of $\alpha_{cr} = 800 \times 10^{-5}$ K^{-1}. The extension of the copolymer in the region of the high-temperature rubbery plateau (straight line C'D') occurred at a rate of $\alpha_3 = 25.6 \times 10^{-5}$ K^{-1}. The molecular weight of the crystallized chain segments was $\overline{M_w^{cr}} = 630$. The weight concentration ratio between chains in the structures of the amorphous, cluster, and crystalline blocks of the γ-irradiated PFA was 0.40 : 0.41 : 0.19. The free-molecule flow of PFA came into play at $T_F = 585$ K (point T). The molecular weight of the copolymer γ-irradiated to a dose of 150 kGy averaged over the blocks is $\overline{\overline{M_w}} = 32840$.

Figure 1d shows the TMC of the copolymer γ-irradiated to a dose of 600 kGy. Its topological structure measured in the mode of the coaxial orientation of vectors is analogous to that of the copolymer before radiolysis (Fig. 1c). It is characteristic of a polyblock semicrystalline polymer, in which one amorphous (shaded region) and one crystalline topological blocks were detected in a temperature range of 173−673 K. Below the temperature $T_g = 257$ K, the polymer occurred in a glassy−crystalline state and expanded with temperature in this region (straight line AB) at a rate of $\alpha_1 = 13.9 \times 10^{-5}$ K^{-1}. Above this temperature, the segmental mobility unfreezed and the interjunction chains of the transition region deformed (curve BC). Its treatment as a pseudointegral MWD curve of interjunction chains in the pseudonetwork of the low-temperature block gave the number-average and weight-average molecular weights of interjunction chains as $\overline{M_{c_n}} = 55900$ and $\overline{M_{c_w}} = 110670$, respectively. Figure 2d shows their MWD function.

At the temperature at point C ($T_\infty = 557$ K), the polymer passed into the region of the thermally stable rubbery expansion of the network structure of the block—the rubbery plateau (straight line CD). In this region, it expanded with temperature at a rate of $\alpha_2 = 37.0 \times 10^{-5}$ K^{-1} ($\alpha_1/\alpha_2 < 6$). The crystallized segments of PFA macromolecules act as the branching points of the amorphous block pseudonetwork. Their melting begins at $T_m = 586$ K and is accompanied by expansion at a rate of $\alpha_{cr} = 133.3 \times 10^{-5}$ K^{-1}. At the temperature at point O ($T_F = 606$ K), the free molecular flow of PFA comes into play (curve OT). The molecular weight of the crystallized segments of mac-

romolecules is proportional to $\Delta T = T_m - T_F$ and equal to $\overline{\overline{M_w^{cr}}} \sim 15850$. The weight concentration ratio between the amorphized and crystallized chains in the PFA sample γ-irradiated to a dose of 600 kGy is 0.71 : 0.29. In contrast to the radiolysis of PTFE when polymer macromolecules lose the ability to form crystalline blocks of a topological structure at doses above 140 kGy [3], the crystalline modifications of PFA remained intact upon the γ-irradiation of the copolymer even at a radiation dose of 600 kGy. The block-averaged weight-average molecular weight of the copolymer irradiated to a dose of 600 kGy is $\overline{\overline{M_w}} = 83180$.

Figure 3a shows the EPR spectrum of the paramagnetic centers trapped during the γ-irradiation of PFA cooled to 77 K. It is broad, and its shape is difficult to interpret. On the sides, two narrow lines at a distance of 50.5 mT due to atomic hydrogen that resulted from the radiolysis of a glass ampoule were detected in the spectrum. Furthermore, intense signals on the sides of the spectrum at a distance of 22.5 mT (they are marked with asterisk in Fig. 3) and in the central section of the general spectrum were detected. The nature of the appearance of these lines should be additionally studied. Analyzing the spectrum, we managed to recognize lines typical of radicals containing α-fluorine atoms. The character of their spectra in PFA suggests that the tensor of anisotropic hyperfine coupling with α-fluorine atoms has axial symmetry (the g-factor is isotropic). In this case, the interaction of an unpaired electron in the $2p\pi$ orbital of the fluorine atom with the fluorine nucleus makes the main contribution to anisotropic hyperfine coupling. For the axisymmetric spectrum with one α-fluorine atom, the EPR spectrum has characteristic points based on which it is possible to determine isotropic and anisotropic hyperfine coupling constants [17]. The distance between lines due to the paramagnetic centers whose axes are oriented along the applied magnetic field is $A_\parallel = |a + 2b|m_i$, and the distance between lines due to the radicals whose axes are perpendicular to the applied magnetic field is $A_\perp = |a - b|m_i$ (a and b are the isotropic and anisotropic hyperfine coupling constants, respectively, and m_i is the nuclear spin projection on the direction of the external magnetic field).

Figure 3a shows distances between the corresponding lines $A_\parallel = 45.8$ mT and $A_\perp = 14.0$ mT, which most likely characterize the spectrum of $>CFOCF_2CF_2C \cdot F_2$ radicals trapped in irradiated PFA. The isotropic and anisotropic hyperfine coupling constants calculated for this radical are $a = 12.3$ mT and $b = 5.3$ mT. For a comparative analysis with the spectrum of PFA, Fig. 3b shows the EPR spectrum of Ftoroplast F-10, another perfluorinated copolymer of tetrafluoroethylene with perfluoro(methyl vinyl ether). In the spectrum of this copolymer, it is also possible to recognize
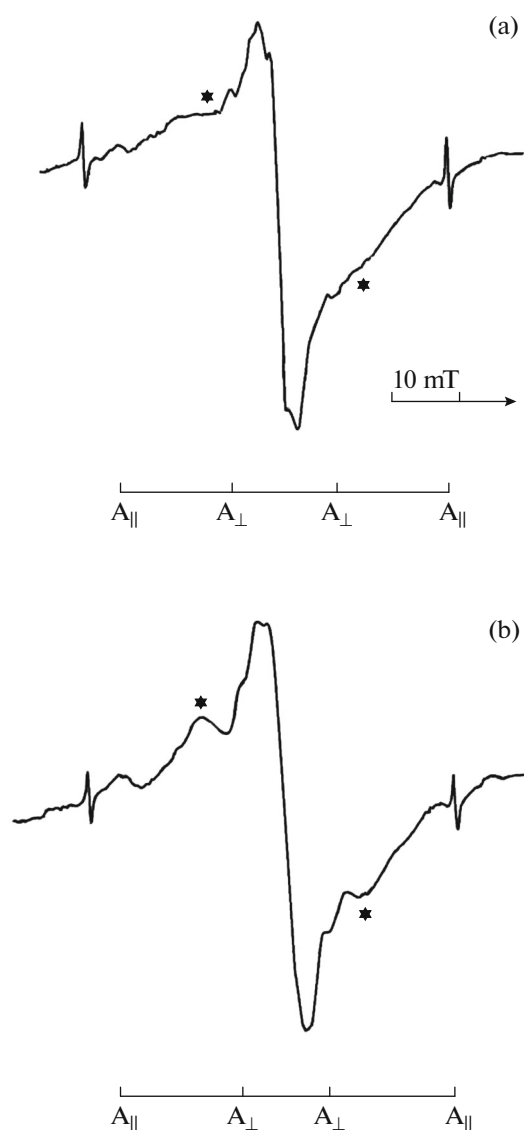
Fig. 3. EPR spectra of the γ-irradiated samples of (a) PFA and (b) the Ftoroplast F-10 copolymer of tetrafluoroethylene and perfluoro(propyl vinyl ether). The dose of γ-irradiation at 77 K was 600 kGy. The spectral EPR lines with a width of 22.5 mT are marked with asterisks.

characteristic lines corresponding to the axially symmetrical EPR spectrum of >CFOC˙F$_2$ radicals. The isotropic and anisotropic hyperfine coupling constants for these radicals are $a = 11.5$ mT and $b = 5.6$ mT. Faucitano et al. [18] obtained similar values of hyperfine coupling constants ($a = 11.7$ mT and $b = 5.4$ mT) by analyzing the EPR spectra of γ-irradiated perfluoropolyethers. As is evident, in the case of γ-irradiation of TFE copolymers with perfluoro(alkyl vinyl ethers), radicals that are produced via the detachment of a fluorine atom or a perfluoroalkyl group from side segments of copolymer macromolecules and contain two α-fluorine atoms are detected in the EPR spectra.

It is well known [9, 19] that the ~F$_2$CF$_2$C˙ radicals which are formed upon C−C bond breaking are not trapped in the matrices of linear perfluoroalkanes and PTFE. In the EPR spectra of samples irradiated at 77 and 300 K, only the ~F$_2$CF$_2$C˙ radicals generated via F atom detachment from the terminal F$_3$C groups were detected. The proportion of the ~F$_2$CF$_2$C˙ radicals stabilized in linear high-molecular-weight PFA with an enormous number of carbon atoms (n), such as PTFE with a molecular weight of $>10^6$, is $3/(n − 2) \approx 10^{-4}$, which is almost one thousand times smaller than that of the central radicals ~F$_2$CFC˙FCF$_2$~. Therefore, the lines of the terminal radicals ~F$_2$CFC˙FCF$_2$~ are almost absent from the spectrum of irradiated PTFE. The revealed effects of the chain length of linear perfluoroalkanes and PTFE on their γ-radiolysis can be used for describing the mechanisms of the radiolysis of other perfluoropolymers, in which the main chain of a macromolecule is analogous to the PTFE chain containing exceptionally fluorine atoms in addition to carbon atoms. The macromolecular structure of PFA can also be represented as ~F$_2$CFC(R$_f$)CF$_2$~, where the side segment R$_f$ consists of the OCF$_2$CF$_2$CF$_3$ group. It is likely that the ~F$_2$CF$_2$C˙ radicals generated during radiolysis as a result of C−C bond breaking in the main chain of PFA are not trapped in the PFA matrix at 77 K because of the cage effect. On the other hand, the terminal ~F$_2$CF$_2$C˙ radicals can be formed as a result of F−C bond breaking in the terminal F$_3$C groups of the PFA macromolecule. However, as in the case of PTFE radiolysis, their fraction is small so that their EPR spectral lines can hardly appear in the general spectrum of the γ-irradiated copolymer against the background of the spectra of other radicals. Thus, the radicals trapped in the PFA copolymer γ-irradiated at 77 K can result from the detachment of a fluorine atom or a −OCF$_2$CF$_2$CF$_3$ group from the PFA macromolecule with the formation of the central ~F$_2$CFC˙FCF$_2$~ radicals or from a reaction that occurred in the side group >CFOCF$_2$CF$_2$CF$_3$ of the macromolecule. The axially symmetrical lines marked in Fig. 3a are the spectra of radicals with two α-fluorine atoms, and they can be attributed to the >CFOCF$_2$CF$_2$C˙F$_2$ radicals formed via the detachment of a fluorine atom from the terminal F$_3$C groups of the PFA macromolecule.

CONCLUSIONS

The comparative analysis of the molecular relaxation characteristics of PFA before and after γ-irradiation to doses of 150 and 600 kGy (see table) has led to the following conclusions:

an optimized pressure of ~20 MPa, at which the initial powdered copolymer and its γ-irradiated coun-

Composition of topological blocks of PFA before and after γ-irradiation

Determined parameter	TMA mode*	TMA mode**		
	dose, kGy			
	0	0	150	600
Amorphous block of pseudonetwork matrix				
T_g, K	273	268	216	257
T_∞, K	560	526	393	557
$\alpha_1 \times 10^5$, K^{-1}	10.8	12.8	4.65	13.9
$\alpha_2 \times 10^5$, K^{-1}	50.5	35.7	15.6	37.0
V_f	0.325	0.184		
$\overline{M_{c_n}} \times 10^{-3}$	323.6	46.8	18.630	55.9
$\overline{M_{c_w}} \times 10^{-3}$	1711.2	83.9	31.680	110.67
K	1.85	1.79	1.7	1.29
φ_a	1.0	0.47	0.4	0.71
Crystalline modification—branching point				
T_m, K		550	581	586
$\alpha_{cr} \times 10^5$, K^{-1}		285.7	800	133.3
$\overline{M_w^{cr}}$		13.2	0.63	15.85
φ_{cr}		0.53	0.19	0.29
High-temperature amorphous block (cluster) of pseudonetwork matrix				
T_g^I,	560		475	
$\alpha_3 \times 10^5$, K^{-1}			25.6	
$\overline{M_{C_n}^I} \times 10^{-3}$			35.35	
$\overline{M_{C_w}^I} \times 10^{-3}$	5.3		48.91	
K			1.38	
φ_α^I	0.01		0.41	
Block-averaged parameters				
$\overline{\overline{M_w}} \times 10^{-3}$	1694.1	46.4	32.84	83.18
T_F, K	570	583	585	606

 * TMA was carried out with the mutually perpendicular orientation of load vectors during the polymer strain relief in a thermal analyzer and compacting pressure relief.
** The load vector occurs in the same plane with the compacting pressure vector during the polymer strain relief in a thermal analyzer.

terpart were pressed before TMA, is sufficient for the formation of a monolithic PFA sample, which was not destroyed with increasing temperature and under the action of a thermomechanical load of 0.5 g;

thermomechanical analysis was conducted in two modes, the coaxial mode when the load application vector is coplanar with the compacting pressure vector during the measurement of copolymer deformation in a thermal analyzer (II) and the mutually perpendicular mode ($\perp$);

in the TMA in the mutually perpendicular vector orientation mode, the shape of TMCs indicates that the copolymer has a completely amorphous diblock structure. The cluster units of the high-temperature amorphous block comprise a small fraction (near 1%) of the topological structure of the pseudonetwork of the amorphous block of PFA;

the TMC measured with the coaxial orientation of vectors is characteristic of a diblock semicrystalline copolymer, in which the crystallized segments of PFA macromolecules act as branching points in the pseudonetwork of the amorphous block through their tie chains;

it has been established that PFA acquires an absolutely anisotropic structure as a result of axial compression. The ratio of the PFA crystallinity determined in the analysis in the mutually perpendicular orientation mode to that found in the coaxial mode is zero;

it has been assumed that $>CF-OCF_2CF_2C^\cdot F_2$ radicals with an axisymmetric EPR spectrum are generated and trapped during the course of γ-irradiation of PFA at 77 K; this spectrum exhibits characteristic points at distances of 45.8 and 14.0 mT;

the semicrystalline structure of PFA remains almost unchanged by radiolysis. The minimum values of the glass transition temperature of the amorphous block and the crystallinity have been observed the PFA powder irradiated to a dose of 150 kGy. The MWD function of the interjunction chains of the network of the amorphous block of the virgin PFA and its γ-irradiated counterparts is bimodal.

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