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Characteristics of the structure and properties of low-temperature fractions recovered from the powder ultradispersed polytetrafluoroethylene by sublimation



L.N. Ignatieva^{a,*}, O.M. Gorbenko^a, V.G. Kuryavii^a, N.N. Savchenko^a, A.D. Pavlov^a,
D.V. Mashtalyar^a, V.M. Bouznic^b

^a Institute of Chemistry FEB RAS, 159, Pr. 100-letya Vladivostoka, Vladivostok 690022, Russia

^b A.A. Baikov Institute of Metallurgy and Materials Science, 49, Leninskii Pr., Moscow 119334, Russia

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ABSTRACT

Low-molecular fractions were recovered through sublimation of the ultradispersed powder polytetrafluoroethylene (UPTFE) under isothermal conditions and specified temperatures. The present paper describes the results of study of the fractions recovered at 50–100 °C with an increment of 10°. The studies revealed that the obtained fractions were in general characterized by a film structure, a paraffin-like phase composition with different crystalline structures, and a layered packing. Films of the fraction isolated at 50 °C have pores; those isolated at 60 °C had fibers. The molecular structures are represented by a short chain of molecules consisting of CF₂ fragments with end –CF=CF₂ groups. The chain length increases from 5 to 15 fragments along with the increasing temperature of the fraction isolation. The beginning and the process of decomposition of fractions depend on the temperature, at which the fraction of interest was obtained.

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1. Introduction

Polytetrafluoroethylene (PTFE) is an actively studied and extensively used material. The demands of novel technologies call for the necessity of improvement of its functioning parameters through modification and fabrication of new products on its basis. For this purpose, different treatment methods are applied: thermal, mechanical, radiation, laser, etc. [1–3]. In the Institute of Chemistry FEBRAS, the powder of ultradispersed polytetrafluoroethylene (UPTFE, FORUM trademark) fabricated through PTFE treatment by the pyrolytic method, has been developed and patented [4]. The studies of the powder by a set of physical methods revealed more complex, as compared to PTFE, molecular, phase, and morphological structure as well as thermal characteristics radically different from those of PTFE [2,5–7]. Further studies showed that the UPTFE consisted of fractions with different molecular weights: this enabled us to recover low-molecular (70 °C), intermediate-molecular (180 °C), and high-molecular (430 °C) fractions [7], each of them having specific features and, accordingly, other fields of practical application [8–10]. The low-molecular (70 °C) fraction is very different from intermediate-, and

high-molecular ones. The obtained results served as the basis for a finer material isolation into the low-molecular fraction, whose study was of substantial interest. We assumed that the fractions isolated at lower and higher temperatures than the 70°-fraction could have its own characteristics opening up new possibilities for their further application. The present paper describes the fabrication and results of study of low-temperature fractions of UPTFE recovered at 50, 60, 70, 80, 90, and 100 °C (Fig. 1).

2. Results and discussion

2.1. Peculiarities of molecular structure of UPTFE fractions recovered at 50–100 °C

In general, IR-spectra of UPTFE and fractions recovered at 50–100 °C manifest a close similarity to that of the standard PTFE [11]. The bands corresponding to the stretching vibrations of CF₂-groups (1211 and 1154 cm⁻¹) and the ν(CC) vibration manifested as a bend at ~1233 cm⁻¹ are the most intensive. The low-frequency range contains deformation and out-of-plane vibrations of CF₂-groups: rolling γ_ω(CF₂) vibrations are manifested at 640 cm⁻¹, the bands at 555 and 516 cm⁻¹ characterize deformation and pendulum vibrations of CF₂-groups, see Ref. [11].

However, in the UPTFE IR spectrum one observes the bands at 1786 and 985 cm⁻¹ absent in that of PTFE: these bands

* Corresponding author. Tel.: +7 4232 311889; fax: +7 4232 311889.
E-mail address: ignatieva@ich.dvo.ru (L.N. Ignatieva).

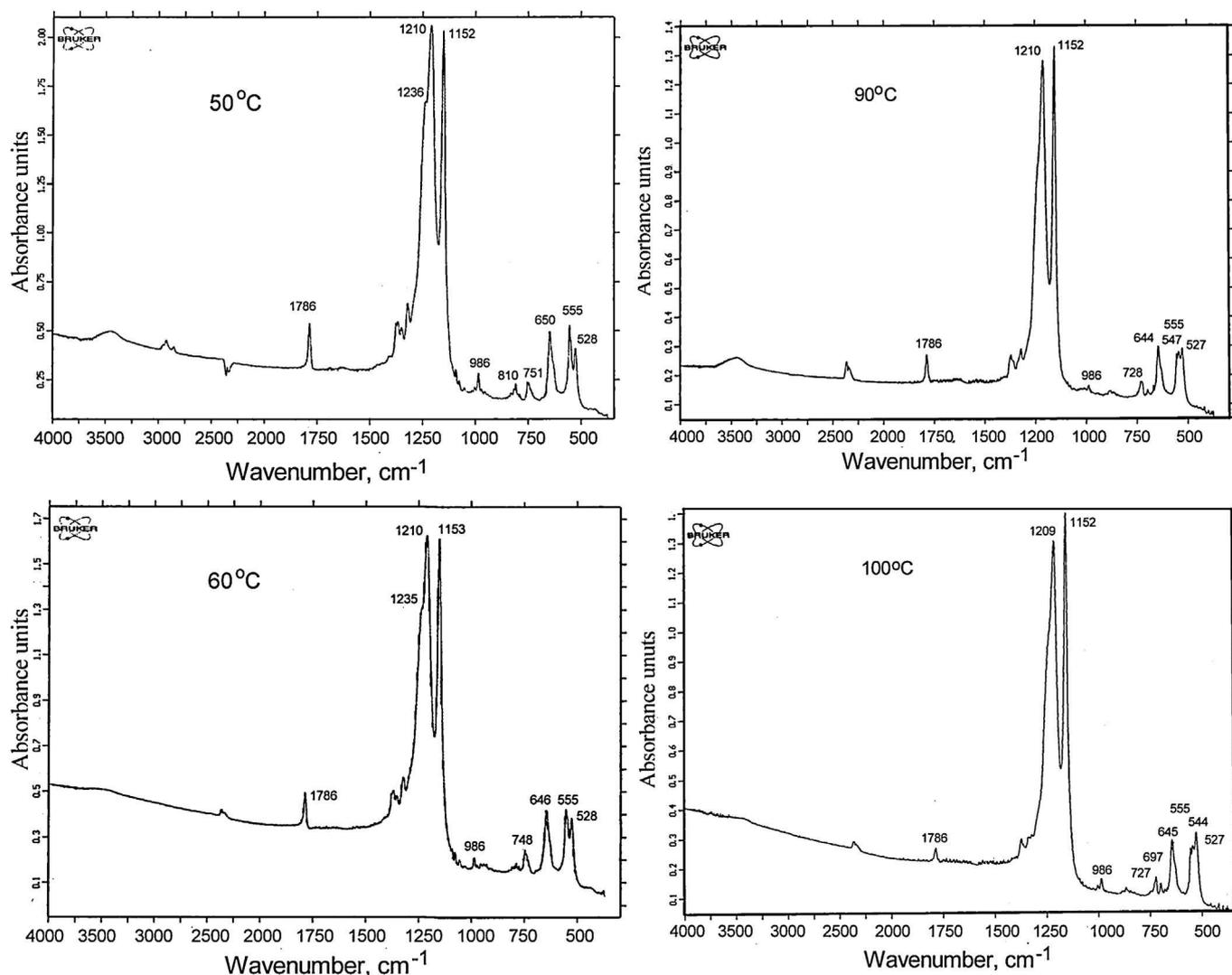


Fig. 1. IR absorption spectra of fractions recovered at 50, 60, 90, and 100 °C.

interpretation was made in Refs. [2,5]. They correspond to vibrations of end olefin groups $-\text{CF}=\text{CF}_2$ and side trifluoromethyl groups $-\text{CF}-\text{CF}_3$. The performed assignments were corroborated by the data of quantum chemistry calculations of model molecules C_nF_{2n} and $\text{C}_n\text{F}_{2n+2}$ [12,14]. The above bands are observed in IR-spectra of the fractions under examination as well. One should also mention that in all the above fractions spectra just single band is observed around 640 cm^{-1} , in opposite to the doublet at $640, 625\text{ cm}^{-1}$ clearly manifested in IR-spectra of UPTFE and PTFE. PTFE and UPTFE molecules are known [7,11] to comprise chains twisted into spirals and consisting of CF_2 fragments. There are also the chain parts with transitions between left- and right-rotatory spirals. The presence of a doublet is attributed to changes in the spiral conformation of PTFE macromolecules and their packing. It is believed that the band at 640 cm^{-1} is related to the presence of a regular spiral, whereas the band at 625 cm^{-1} is related to the defect structure, i.e., the chain parts, in which transitions between left- and right-rotatory spirals take place. Absence of the band at 625 cm^{-1} in IR-spectra of low-temperature fractions indicates to absence of the above transitions that in this case can be related to a short-chain structure of the formations under study. However, upon detailed examination, in the IR-spectrum of the fraction recovered at 70 °C , one can distinguish the emergence of asymmetry of the band at 640 cm^{-1} that becomes more expressed

along with the increase of the fraction recovery temperature. Besides, in IR-spectra one can visualize the decrease of the intensity of the band characterizing vibrations of end groups ($-\text{CF}=\text{CF}_2$) along with the increase of the fraction recovery temperature. Based on the fraction obtaining technique, the observed changes in their IR-spectra can be expected and, most probably, are related to changes in the polymer chain lengths (C_nF_{2n} and $\text{C}_n\text{F}_{2n+2}$).

Changes in the fractions compositions are clearly seen on chromatograms (Fig. 2): while in the sample recovered at 50 °C molecules with 7 and 8 fluorocarbon fragments are predominant, the 100 °C -fraction contains virtually none of such fragments. In the latter one, molecules with 12–13 fragments are predominant, and longer chains emerge as well. In the initial UPTFE, as was shown in the chromatogram analysis, the molecules up to 70 fragments are identified [13].

The obtained data demonstrate that the process of PTFE heating is accompanied by sublimation of short-chain fragments, and each higher-temperature fraction is characterized by the increase of the percentage of longer chains in its structure. On a qualitative level, one can expect a correlation between C_n (C_n – the number of fluorocarbon fragments) and the intensity of the band corresponding to vibrations of the end group $-\text{CF}=\text{CF}_2$, which is rather high in spectra of low-temperature fractions and observed there at

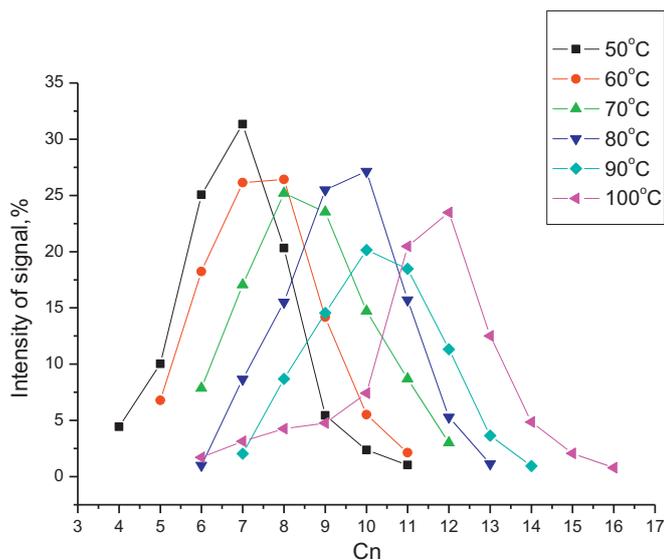


Fig. 2. Chromatograms of fractions recovered at different temperatures (50–100 °C).

1786 cm^{-1} . If one assumes that the absolute intensity of this band depends on the number of end groups, then the information on the chain length can be obtained. The absolute intensity of the band of a powder sample is rather difficult to measure in IR-spectra: here it is more convenient to use the ratio of intensities of the bands characterizing chain fragments CF_2 (1154 cm^{-1}) and the end group $\text{CF}=\text{CF}_2$ (1786 cm^{-1}). Fig. 3a demonstrates the presence of the experimental dependence of I_{1154}/I_{1786} on the fraction recovery temperature. The grounds of this dependence validity can be found in the data of quantum chemistry calculations performed for $\text{CF}_3-(\text{CF}_2)_{n-3}-\text{CF}=\text{CF}_2$ molecules ($n = 6-14$). In these calculations, the most energy-efficient configurations of unbranched chain molecules C_nF_{2n} are used. Fig. 3b presents the correlation between the molecule length (number of fluorocarbon fragments, C_n) and the value of the ratio of peak band intensities at 1154 and 1786 cm^{-1} in IR-spectra of the molecules under examination revealed using quantum chemistry calculations. Calculations of IR-spectra of fluorocarbon molecules were made according to methods [12,14].

2.2. Phase composition of UPTFE fractions recovered at temperatures 50–100 °C

Low-molecular composition of the samples under examination allows anticipating the difference in their phase composition from

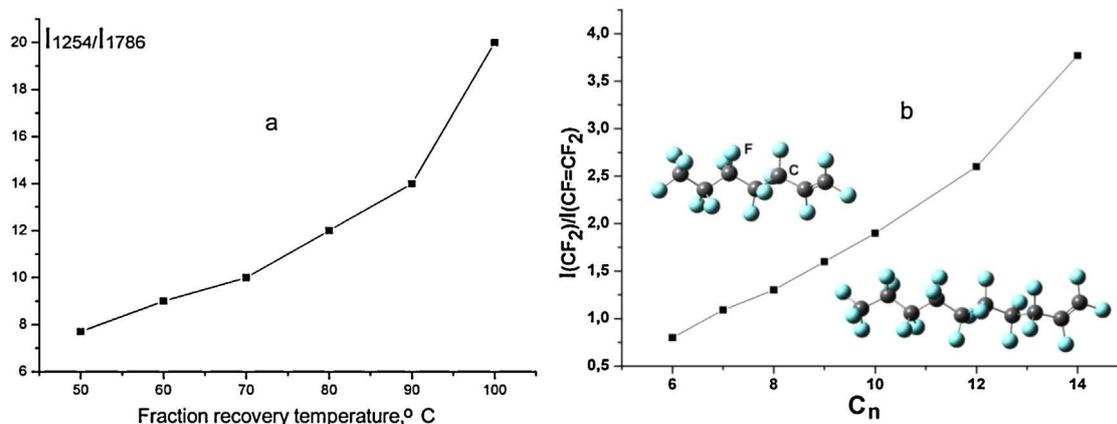


Fig. 3. Dependence of the ratio of band peak intensities at 1154 and 1786 cm^{-1} in IR-spectra of fractions recovered at different temperatures: a – experimental values; b – calculated values.

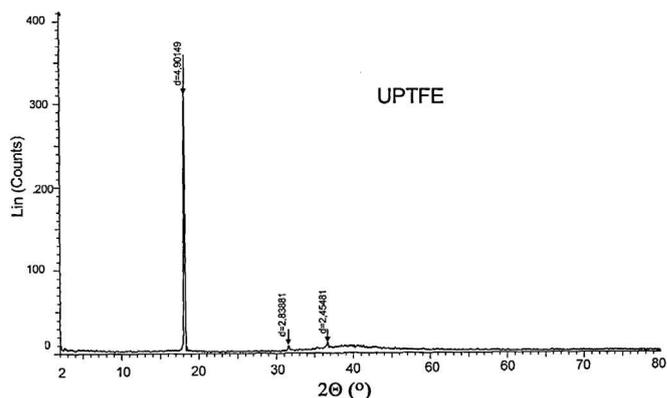


Fig. 4. X-ray picture of the UPTFE-FORUM.

that of the initial UPTFE. The comparison of diffractograms of the recovered fractions with that of the initial product (UPTFE-FORUM) indicates to these differences (Figs. 4–6).

The UPTFE-FORUM picture is characterized by the presence of an intensive peak at $2\theta = 18^\circ$ indicating to high degree of crystallinity of the initial product [7]. At $2\theta = 40^\circ$ one observes a diffraction halo, whose presence is a clear indication to disorientation of spiral-like molecules in the structure of the sample under study. FORUM comprises a form of PTFE with a complete angle disorder of the spiral. The angle disordering is accompanied by the shift disordering of adjacent molecules along the spiral axis [15]. In general, FORUM is essentially crystalline (90%) and belongs to the hexagonal syngony [15,16].

In X-ray pictures of the fractions under examination (Fig. 5), unlike the initial UPTFE product, in the small-angle range one observes a set of distinct reflections near $2\theta = 11.5^\circ$, 7° , and 4° , and the intensity of the peak at $2\theta = 18^\circ$, characteristic for the UPTFE X-ray picture, changes significantly between the fractions. This peak is scarcely seen on the X-ray picture of the fraction recovered at 50°C . The intensity of the peak at $2\theta = 18^\circ$ increases along with the increase of the fraction recovery temperature. One can assume that the crystal phase characteristic for the initial material is generally preserved, and its percentage increases along with the fraction recovery temperature increase. The presence of the diffraction area at $2\theta = 40^\circ$ in all X-ray pictures enables one to assume the preservation of the characteristic for UPTFE type of disorientation in the structure of the recovered samples.

Analysis of the X-ray picture of the 70° -fraction performed earlier in Refs. [16,17] demonstrated that the system had a typical

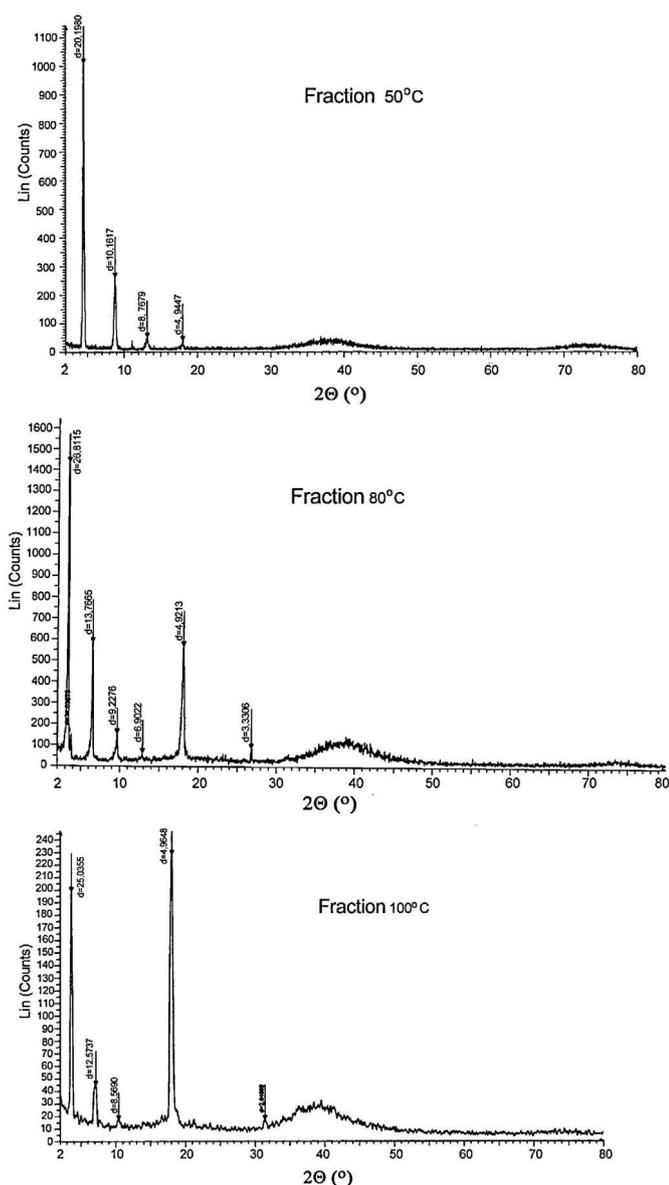


Fig. 5. X-ray pictures of fractions recovered at 50, 80, and 100 °C.

layered paraffin-like structure [18] with a clearly expressed layer periodicity (four orders of reflection are perfectly resolved in the X-ray picture). Reflections in relatively small diffraction angles correspond to the layered packing of perfluorinated paraffins (in particular, the peak at $2\theta = 4.0^\circ$ corresponds to a periodicity of 23 Å of the perfluorinated n-alkane, n-C₁₀F₂₂). The fraction X-ray picture is similar to that of the n-alkane, n-C₁₆F₃₄. The structure of fraction molecules inside the layer is 2D-pseudo-hexagonal, and chains are directed perpendicularly to the layer plane (typical situation for odd n-alkanes [18]). There is no correlation between chains in the transversal direction: random rotational shift of molecules relatively to their own axis characteristic for rotary bodies having the cylindrical symmetry. The attempt to identify this complex crystallographic lattice yielded the conclusion that this lattice had a monoclinic syngony with the following parameters: $a = 25.103 \text{ \AA}$, $b = 12.464 \text{ \AA}$, $c = 5.712 \text{ \AA}$, $\beta = 96.23$, $V = 1776.4 \text{ \AA}^3$, $FM = 34.7$.

X-ray pictures of all the fractions are similar, except that of the 50 °C-fraction, in which the crystallinity peak at $2\theta = 18^\circ$ is virtually absent. The change in the molecular weight of macromolecules

constituting the samples under study and the peculiarities of changes in the molecular structure must be reflected in their crystal structure. One should mention that the peak positions at the small angles somewhat change from fraction to fraction; whereas the peak intensity ratios change substantially (see Fig. 5). An intensive peak near $2\theta = 4.0^\circ$ is observed in X-ray pictures of all the fractions indicating to the preservation of the layered packing of perfluorinated paraffins. The periodicity, as judged from the d value, changes from 20 up to 27 Å. Changes in d are also traced for peaks located near $2\theta = 6\text{--}8^\circ$ (from 10 to 14 Å) and $2\theta = 9\text{--}11^\circ$ (from 6 to 9 Å).

2.3. Morphology of low-molecular UPTFE fractions recovered at 50–100 °C

The results presented above demonstrate that the low-molecular fractions under examination have a number of differences from each other related to the peculiarities of their molecular structure and phase composition, which, in its turn, must be reflected in the molecule buildup in the process of material formation. Taking into account the data of Ref. [7], one expected a general film structure of the fractions. It is natural to assume, with the above data, that each fraction would have morphological peculiarities. For instance, one can expect that the morphology of the fraction recovered at 50 °C would differ from that of other fractions. Indeed, this fraction, as seen from Fig. 6, is composed of porous films (Fig. 6a and b), rod-like nanoparticles (Fig. 6c), and oval nanoparticles (Fig. 6d). The pore size in films is 5–10 nm. The estimated film thickness determined from its end face, manifested during the film bend, is not more than 10 nm. Oval particles are of a size of $300 \text{ nm} \times 150 \text{ nm}$. Most probably, oval particles are of the same nature as rods, but have unformed rounded edges. Such formations (rods, oval particles) are seen in significant quantities only in the 50 °C-fraction: this very fraction, as was shown above, is characterized by predominance of the shortest-chain molecules (7, 6, 5) and virtual absence of the peak at $2\theta = 18^\circ$ on the diffractogram, characteristic for the UPTFE-FORUM crystalline phase.

The fraction recovered at 60 °C is also composed of films (Fig. 7a and b) of a thickness of 10–50 nm. The sample does not contain rods, but includes prolonged and branched fiber structures (Fig. 7c) of a length up to 5 μm and a diameter of 50–70 nm. The same fibers were observed in the images of the 70 °C-fraction. The fraction recovered at 70 °C was thoroughly investigated in Ref. [10]. According to the SEM data, this fraction has a film structure as well. The film thickness is $30\text{--}50 \pm 5 \text{ nm}$. During studies of the material by the SEM method, the fraction material could evaporate under effect of the microscope electronic beam, especially at a prolonged examination of the specific surface part. Since the latter complicates obtaining quality SEM images of the fraction at large magnifications, the authors of Ref. [10] used in addition the method of atomic force microscopy (AFM), which does not have the above disadvantage and does not require the sample sputtering with a conducting material that might bring an artifact. The AFM studies results were in full agreement with those obtained by the SEM method.

The fractions recovered at 80 and 90 °C were also characterized by a film structure. The film thickness grows (up to 1 μm), fibers–nanofibrils were not found in these fractions. The same tendency was observed for the sample obtained at 100 °C. The sample is composed of film parts (Fig. 8), whose thickness varies from 10 nm up to 3 μm . There are neither rods nor fibers in this fraction images. Possibly, just very small molecules can form such structures: rods of up to 6–7 fluorocarbon fragments, fibers of up to 9–10 fragments.

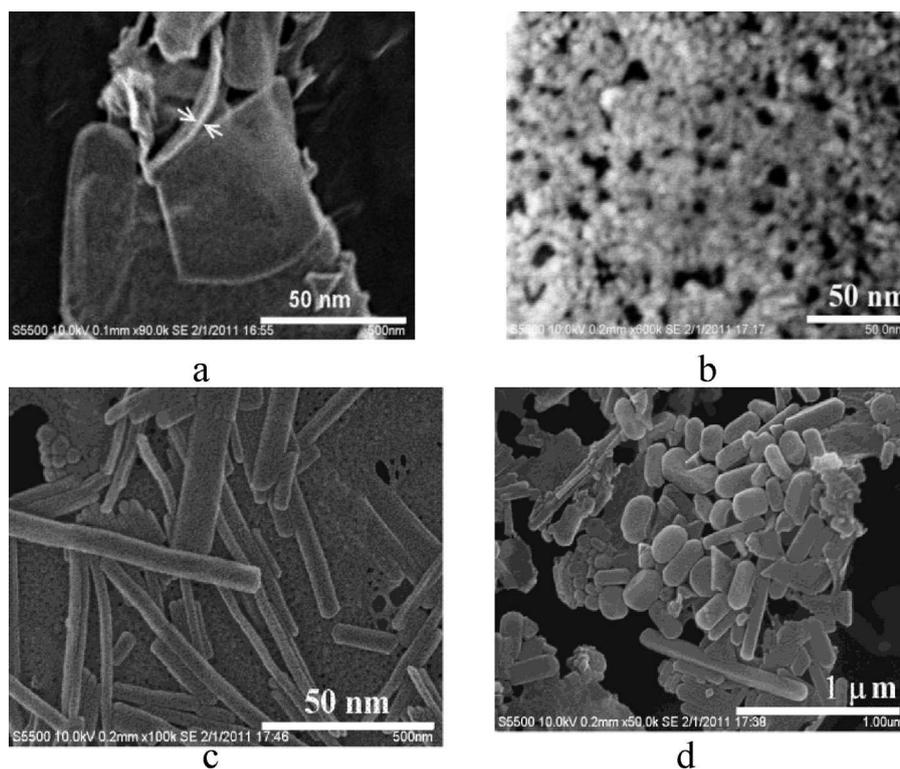


Fig. 6. SEM-images of the UPTFE fraction recovered at 50 °C. Length of rods: 200–1000 nm, width of rods: 100–150 nm.

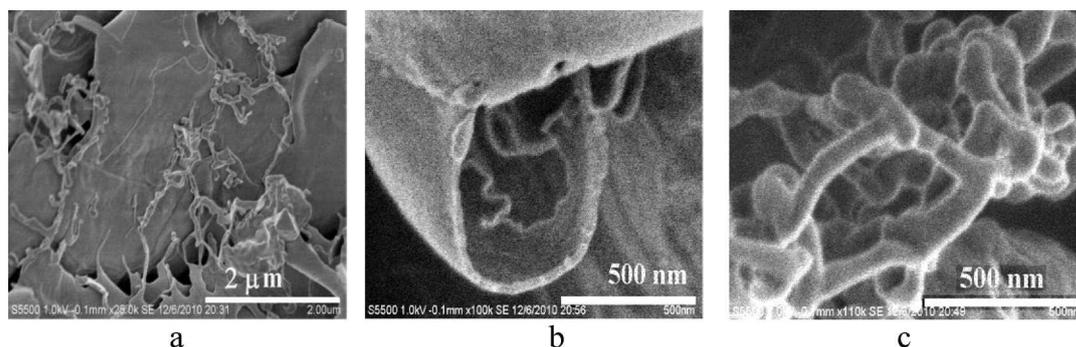


Fig. 7. SEM-images of the UPTFE fraction recovered at 60 °C.

2.4. Peculiarities of thermal behavior of fractions recovered at 50–100 °C

The peculiarities of the phase composition and the molecular structure must result in the fact that the thermal behavior of the

whole set of fractions (50–100 °C) would differ from that of the initial FORUM material, as well as differences in the thermal behavior between fractions are possible.

The fraction corresponding to the beginning of FORUM material sublimation is that recovered at 50 °C. As seen from Fig. 9, upon

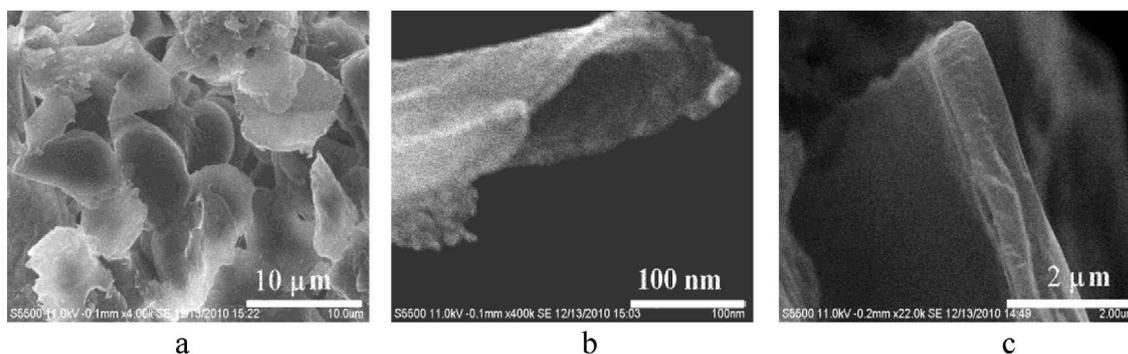


Fig. 8. SEM-images of the UPTFE temperature fraction recovered at 100 °C.

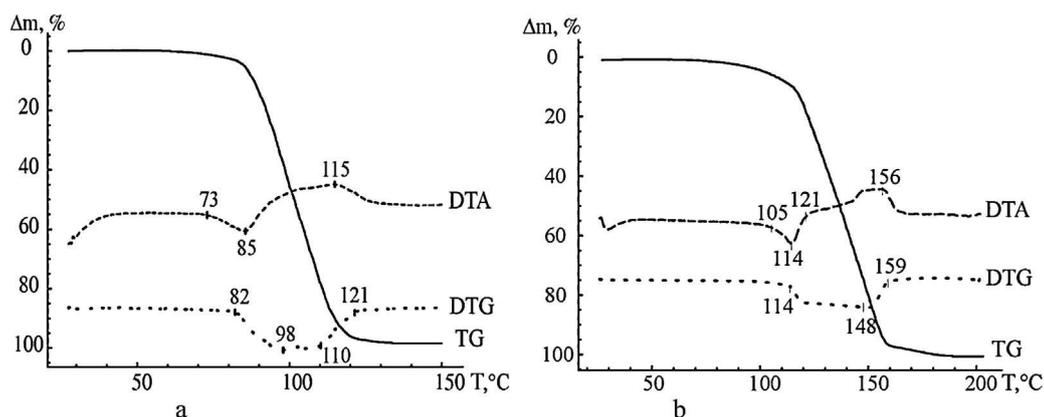


Fig. 9. Derivatograph data for the samples recovered at temperatures: a – 50 °C; b – 60 °C.

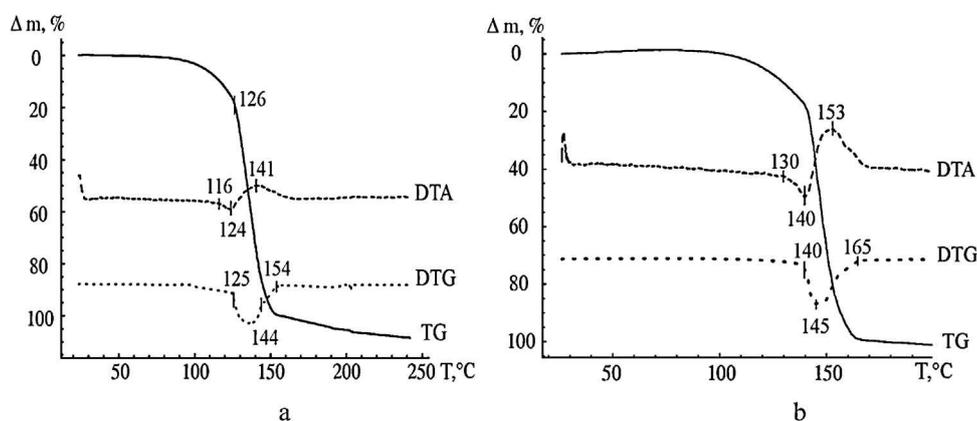


Fig. 10. Derivatograph data for the samples recovered at temperatures: a – 90 °C; b – 100 °C.

heating this fraction starts to lose weight at a temperature of ~80 °C, while the decomposition process stops after 120 °C. On the DTA curve one can see a diffuse endothermic effect with a maximum at 85 °C. Visualization of the sample state upon heating up to this temperature demonstrated that there occurred the sample softening and transition into a liquid-viscous state, which allows assumption that the observed effect is related to the sample melting. The character of DTG and TG curves slope upon the sample heating above the mentioned temperature indicates to a dramatic increase of the rate of the weight loss for the sample under study. It is understandable, because the removal of polymer thermal decomposition products from the liquid state proceeds with higher rate than that from the solid phase. Prior to the melting start temperature, there is virtually no loss of the sample weight. In other words, the sample does not contain lighter fractions (even in small amounts) anymore: they are removed to the gaseous phase before heating.

The endothermic effect corresponding to the sample melting is observed in all the derivatograms of the studied series of samples.

The melting temperatures increase along with the increase of the fraction recovery temperature (Table 1). Since all the fractions are low-molecular and each of them contains molecules of different lengths, the melting temperature increase results in the fact that higher-temperature fractions (80, 90, and 100 °C) start to lose weight prior to the sample melting (Fig. 10).

On all the DTA curves of the examined samples, one observes an exothermic effect (around 150 °C). For the fraction recovered at 70 °C, the heating process was carried out in air and in argon atmosphere. The exothermic effect with a maximum at 155 °C observed on the DTA curve in air was not observed in argon atmosphere. The latter enables one to assume that this effect can be related to oxidation of the sample thermal decomposition products. The calculated activation energy of process (for the fraction recovered at 70 °C) is equal to 7.15 kJ/mol. Such a low activation energy value is related to low molecular weight of the macromolecules of polymer product.

Analysis of the data summarized in Table 1 shows that the temperatures of the decomposition start for fractions recovered at

Table 1
Thermal characteristics of fractions recovered in the range (T, °C) 50–100 °C.

T of fraction recovery	T of melting	T of weight loss start	T of 2nd decomposition stage start (DTG)	T of decomposition end (DTG)	Reaction temperature range
50	85	82.34		121.41	39.07
60	101	96		131.60	34.86
70	114	90	114.00	159.00	45.00
80	124	90	125	154.00	28.60
90	130	90	138	154.17	16.17
100	140	110	139	164.60	25.00

different temperatures increase from 82 up to 110 °C. The same tendency characterizes the temperatures of the decomposition process end, but, since the processes of fractions decomposition are different, changes in the values of the decomposition temperature range do not reveal any expressed regularities.

3. Conclusions

To sum up, low-molecular fractions of the UPTFE-FORUM material recovered from 50 up to 100 °C are in general characterized by film structure, paraffin-like phase composition and layered packing preserved until the recovery temperature of 100 °C. The molecular structure is represented by a short-chain structure of molecules with end $-\text{CF}=\text{CF}_2$ groups. The chain length increases along with the fraction recovery temperature increase from 5 up to 14 fluorocarbon fragments. The same tendency is traced for the fractions crystallinity degree as well (this is concerned with the crystallinity type of the initial UPTFE-FORUM material). Decomposition of all the samples upon heating proceeds through melting. The melting temperatures increase along with the fraction recovery temperature from 80 up to 140 °C. With respect to the thermal behavior, fractions can be conditionally divided into two types: those that start to sublime upon melting (50–60 °C) and those that start to lose weight prior to the sample melting (80–100 °C).

Each of the fractions can be recovered and used as an individual material employing its specific properties, for instance, the presence of pores or fibers. The whole set of fractions recovered at 50–100 °C can be considered as a fluorocarbon paraffin. But one should take into account that this is a family of paraffins having the different crystalline structures. By continuing the process of fractions recovery through the UPTFE temperature increase, one can obtain a modified product, in which paraffin-like fluorocarbon fractions are absent.

4. Experimental

4.1. Fraction recovery and study techniques

To obtain low-molecular fractions, a laboratory installation was assembled: it was operated under accumulation conditions, which enabled us to recover fractions (50, 60, 70, 80, 90, and 100 °C) with low temperature increment (10 °C) at low installation productivity. The fractions recovery was realized through sublimation of the UPTFE powder under isothermal conditions and specified temperatures. Since, as had been established during thermogravimetric studies, the weight loss of an UPTFE sample began around 50 °C, the fractions recovery was started at 50 °C. The polymer products recovered at a specific temperature are condensed on the cooled receiver. Recovery of each fraction was carried out until the moment when the polymer product stopped to emerge on the cooled receiver and the reactor flask neck. Sublimation of the polymer product is a slow process. The powder remained upon sampling of each fraction was further heated, and new portions of sublimate were sampled with 10° increments.

The samples IR absorption spectra were recorded at room temperature on an IFS EQUINOX 55S spectrometer in the range 4000–350 cm^{-1} with the frequency registration error not higher than 0.5 cm^{-1} . The samples were ground until a finely dispersed state and pressed into tablets with KBr.

The fractions chromatography analysis was carried out on a Shimadzu GCMS-QP2010 chromatography-mass spectrometer equipped with a PY-2020iD pyrolyzer. Samples of a mass of $\sim 0.1 \mu\text{g}$ were placed into a pyrolyzer chamber in special disposable capsules. The process was conducted in helium atmosphere. The sample was held for 30 s at 50 °C to oust oxygen from the chamber and the sample. The above technique was applied for all the fractions recovered from UPTFE at 50, 60, 70, 80, 90, and 100 °C. For the samples components identification, Wiley 8 and NIST 08 mass spectra libraries were used.

The fractions morphology was studied on a Hitachi S5500 high-resolution scanning electron microscope (SEM). The sample was fixed on a sticky carbon Scotch tape and sputtered with gold.

The X-ray pictures of the low-molecular fraction and FORUM powder under study were recorded on D8 ADVANCE diffractometer in accordance with the Bragg-Brentano method without rotation, in the $\text{CuK}\alpha$ radiation. The samples were not preliminarily ground for X-ray analysis.

The thermal properties of UPTFE fractions were studied using a Shimadzu DTG-60H thermogravimetry/differential thermal analyzer in air in corundum crucibles with lids. The heating rate was 2.5 °C/min.

Quantum chemistry calculations were performed within the scopes of the Hartree-Fock method (HF, basis 6-31G). The GAUSSIAN-03 program was used for calculations. The used technique was thoroughly grounded in Refs. [12,14,19].

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