

Structure of Polytetrafluoroethylene Powders Obtained by Photochemical Polymerization of Gaseous Monomer

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Abstract—A set of physical methods is used to study the molecular, supramolecular, and topologic structure of polytetrafluoroethylene (PTFE) powders obtained from the gaseous phase of a monomer, tetrafluoroethylene (TFE) (C₂F₄), under ultraviolet irradiation in the presence of different initiators. Morphological diversity of particles forming powders is found; the effect of technological modes on the regularities of the morphological powder structure is established. The method of nuclear magnetic resonance (¹⁹F NMR) of broad lines allowed detecting the difference in the rotational dynamics of fragments of macromolecular chains in samples synthesized under different conditions.

Keywords: polytetrafluoroethylene, photochemical polymerization, structure, NMR, SEM, XRD, IR spectroscopy, DTA/TGA.

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INTRODUCTION

PTFE powders find application in a number of industries as materials for antifriction, antiwear, hydrophobic, protective, and biocompatible coatings. The area and effectiveness of their application are largely determined by the powder particle size and morphology, which, in turn, depend on the method of their synthesis and the applied processing methods [1–3].

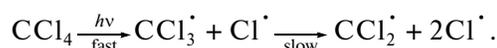
In most cases, powders are obtained by synthesis from the monomer (TFE—C₂F₄) used in industrial production [3] or thermal processing of PTFE [1, 2]. As shown by the studies [1], powdered PTFE products have a considerably different molecular, supramolecular, and morphological structure.

The aim of the work was to study the structure of PTFE powders obtained by UV photopolymerization of gaseous TFE using the scanning and transmission electron microscopy (SEM and TEM) techniques, laser scattering, X-ray diffractometry, derivatographic techniques, and IR and NMR spectroscopy.

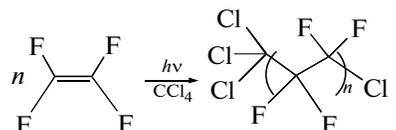
SAMPLE SYNTHESIS TECHNIQUES AND STUDY METHODS

The highly dispersed PTFE powder was synthesized using the earlier developed and patented tech-

nique [4]. Its originality consists in photochemical polymerization of gaseous PTFE using tetrachloromethane as the main initiator. The UV irradiation source was a quartz–mercury lamp. Tetrachloromethane is decomposed forming radicals under UV irradiation:



Radicals take part in the growth of a polymer chain without impairing its chemical and physicochemical properties. The amount of tetrachloromethane is 4–10 wt % of loaded TFE. This reaction can be schematically represented as follows:



The photochemical polymerization reaction was carried out in a stainless steel reactor equipped with a quartz lantern with a quartz–mercury lamp.

Samples of T-4-95MN and T-4-95ChN powders were obtained for studies using different manufacturing methods. The process was carried out in three stages: (1) photochemical polymerization yielding raw polymer using different initiators; (2) sieving and

Results of studies of sample no. 1 using the X-ray diffraction technique

2θ	I/I_0	$d/n, \text{\AA}$	hkl
18.0	100.0	4.97	1 0 0
31.51	1.0	2.87	1 1 0
36.58	<1.0	2.49	2 0 0
49.04	<1.0	1.88	2 1 0
56.17	<1.0	1.66	3 0 0
65.70	<1.0	1.44	2 2 0
68.90	<1.0	1.38	3 1 0
72.58	<1.0	1.30	0 0 15

evacuation of raw polymer; (3) sieving, compounding, and packaging of the ready product.

When T-4-95MN powders were obtained, the initiator used was a mixture of tetrafluorodichloroacetone and trifluorotrichloroacetone, while in the case of T-4-95ChN powders it was tetrachloromethane. Polymerization was carried out at a temperature below 250°C for 40–70 min. Sample no. 1 (T-4-95ChN) represents a white powder with a relative low bulk density of 218 g/dm³. Sample no. 2 was obtained by thermal treatment of sample no. 1 at the temperature of 260°C for 5 h, which allowed increasing the bulk density to 605 g/dm³.

Sample no. 3 (T-4-95MN) has the bulk density of 653 g/dm³. Sample no. 4 (T-4-95MN) is a raw polymer obtained by photochemical polymerization without any further processing stages (heating, evacuation); its bulk density is 512 g/dm³. Sample no. 5 was obtained without application of initiators.

The morphological structure of samples was determined using a Carl Zeiss NVision 40 scanning electron microscope and a JEOL JEM-1011 transmission microscope with the accelerating voltage of 80 kV. The function of the particle size distribution was determined using a Fritsch Particle Sizer Analysette 22 setup.

X-ray diffraction studies were carried out using a Shimadzu XRD-6000 setup at room temperature in the Bragg angle range of 3°–110° (2 θ) with the step of 0.02°. Measurements were carried out in the reflection mode using the CuK α radiation ($\lambda = 0.154$ nm).

Differential thermal analysis (DTA) was performed using a NETZCSH STA 449C setup in the temperature range of 20–600°C with the heating rate of 5°C/min in platinum crucibles with a lid with a calibrated hole providing the given vapor pressure of decomposition products. The upper limiting measurement temperature was determined by the end of decomposition and evolution of gases; it was 500–650°C. The sample mass used in the studies was 0.6 \pm 0.1 mg.

IR spectra of samples were measured using tablets pressed with KBr using a NEXUS spectrometer (ThermoNicolet) in the range of 400–4000 cm⁻¹. The

accuracy of band determination was not more than 2 cm⁻¹.

The studies using the NMR spectroscopy technique were carried out using an AVANCE 400 solid-state spectrometer (Bruker) with the operating frequency for protons being 400 MHz, which corresponds to the magnetic field voltage of 9.4 T. Measurements were carried out using a gradient sensor with ¹⁹F nuclei at the operating frequency of 376.5 MHz in the temperature range of –40 to 70°C. A single pulse with the duration of 2 μ s with eight repetitions was used for measurement of spectra. Samples were placed in a standard 5 mm ampoule.

MORPHOLOGICAL STRUCTURE OF SAMPLES

As seen in Fig. 1a, sample no. 1 contains spherical monoparticles with the diameter of 2 to 5 μ m and formations of shapeless particles with the size of several hundred nanometers; these particles form aggregates with the size of up to 10 μ m resembling structures of the swallow nest type. Apart from aggregate formations, small particles cover the monoparticle surface. The particle size distribution function of sample no. 1 is a four-mode curve with different intensity of components and maxima at 0.7, 3, 5, and 15 μ m with the intensity ratio of 0.7 : 0.6 : 0.4 : 1. The minimum particle size was 0.5 μ m, and the size range of 0.5–5 μ m covers more than 70% of all powder particles. Shapelessness of associate formations and small particles probably prevents compact packing, which is what determines the low bulk density of this powder. Aggregates appear to be rather strong formations; in any case, they are not broken by the air stream used in the analyzer.

As seen from the presented photomicrograph (Fig. 1b), spherical monoparticles are predominant in sample no. 2; the fraction of shapeless formations of small particles is much lower. The observed fact can be explained by the fact that the shapeless fraction consists of low-molecular fluoropolymer fractions, which is removed by thermal treatment and passes into the gaseous state. Monoparticles are formed by high-molecular components; they are more stable to thermal exposure. They have a spherical shape, which is convenient for compact packing and therefore their bulk density is much higher.

Figure 1c presents the image of sample no. 3. The size distribution function is represented by a four-mode curve with the component intensity ratio of 1 : 1 : 1 : 0.3 and with maxima at 0.7, 3, 10, and 40 μ m. The minimum particle size was 0.5 μ m, and the average diameter was 5.9 μ m. More than 70% of particles have a size below 7 μ m.

As seen in Fig. 1d, the change of the initiator affects the morphological structure of the powder: here, the amount of shapeless particles is much lower and monoparticles are predominant. As follows from the size dis-

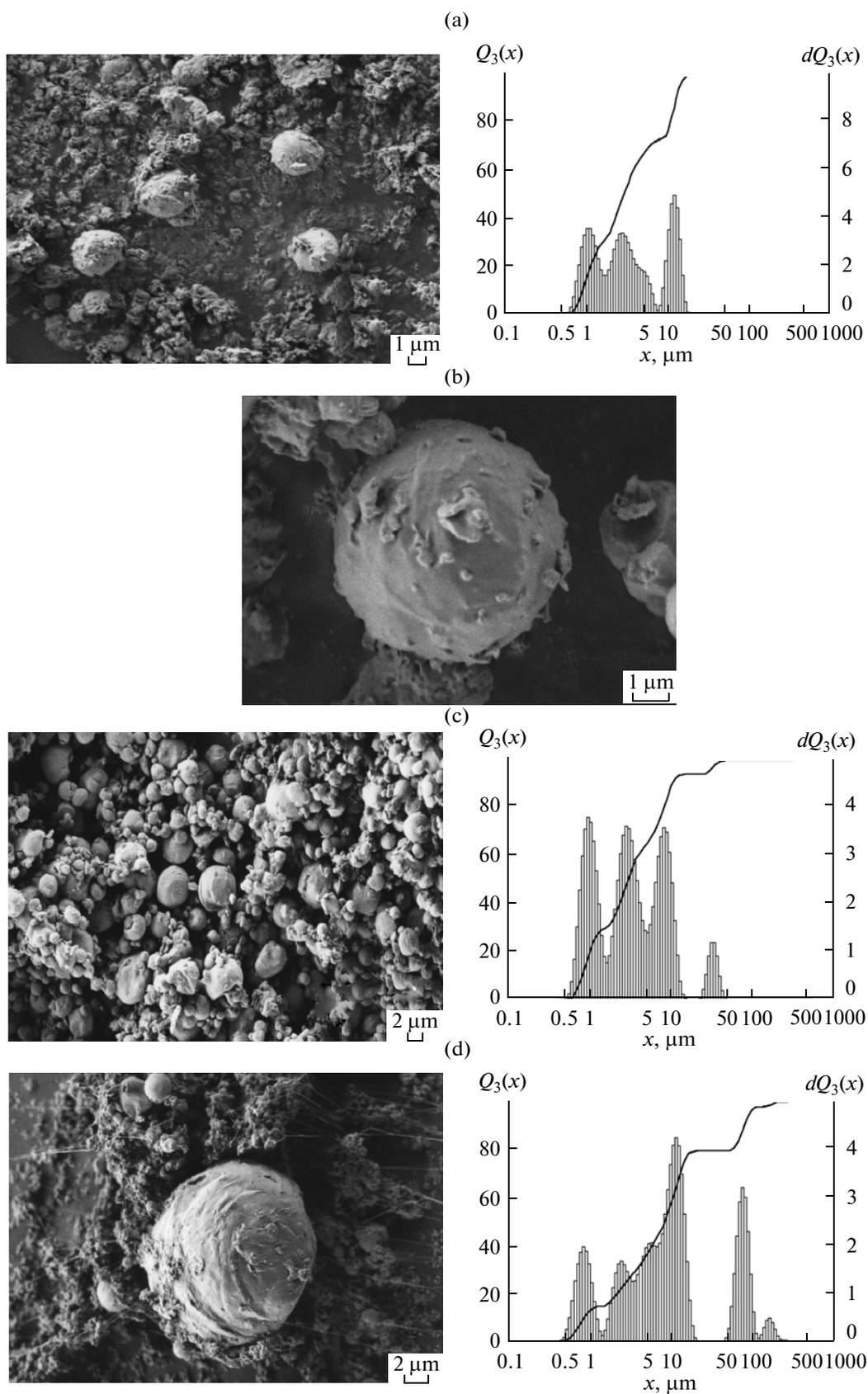


Fig. 1. SEM and size distribution functions of samples: (a) no. 1, (c) no. 3, (d) no. 5; (b) SEM of sample no. 2 obtained by thermal treatment of sample no. 1.

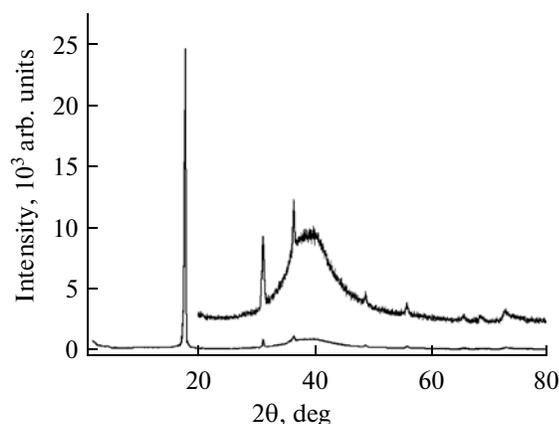


Fig. 2. X-ray diffractogram of sample no. 1.

tribution function, the scatter of spherical monoparticles is greater than in samples no. 1 and no. 2. In this case, two particle modes are observed with the size of 3 and 7 μm . Large formations are also found with the size of up to 30 μm . Sample no. 4 contains both monoparticles and formations of small particles.

Sample no. 5 is characterized by the highest number of morphological forms (Fig. 1d). It contains spherical monoparticles with the greatest diameter scatter, complex formations of small particles, and filamentary structures (with the length of up to 10 μm and diameter of about 0.1 μm). The particle size distribution function appears to be a six-mode curve with the component intensity ratio of 0.5 : 0.4 : 0.5 : 1 : 0.8 : 0.1 and with maxima at 0.7, 4, 7, 15, 85, and 200 μm , respectively. The minimum particle size is 0.5 μm , and the average diameter is 26.9 μm . The size range of 1–50 μm includes more than 70% of the objects.

Let us compare the morphological structure of the studied samples with that of the FORUM powder obtained from gaseous products of pyrolysis of Fluoroplast-4. The gaseous medium used to obtain it has a multicomponent composition. It contains, along with monomers C_2F_4 , also other molecular fluorocarbon structures [5]. It would be logical to expect a greater morphological nonuniformity of FORUM powders as compared to that of the studied samples on account of the complexity of the gaseous medium. However, the opposite is observed: the main structure corresponds to spherical monoparticles with the size of 0.2–1.2 μm . These form agglomerates with the size of up to 5 μm and larger agglomerates (up to 40 μm). While monoparticles are stable systems, complex structures are unstable and are destroyed by an air medium or by exposure to ultrasound in a liquid medium.

The greater diversity of particle shapes and sizes in the studied samples is possibly due to the fact that the effect of UV irradiation differs despite the inhomogeneity of the initial gas medium, especially when solid particles producing a shadowing effect appear in the reactor. The employed polymerization process takes a

long time (several hours), as opposed to the condensation time when the FORUM product is manufactured, which may result in a higher probability of appearance of monoparticles of different size and shape.

X-RAY DIFFRACTION STUDIES

Diffractograms of all samples have a shape similar to that of sample no. 1 (Fig. 2) and also of FORUM powders. In all cases, crystalline reflexes characteristic for PTFE were found (table); the most intense peak is at $d/n = 4.90 \text{ \AA}$ (18.01°). Two diffuse halos are observed: an intense one in the range of 30° – 50° and a low-intensity one at 72° . The first (intense) halo is related to the presence of disordered formations with a structure different from that of usual amorphous polymer regions [6]; the low-intensity halo corresponds to the translation disordering of fluorocarbon PTFE macromolecules [7]. The ratios of the squares of interplane distances of the first, second, and third crystalline peaks are $(d_{100})^2 : (d_{110})^2 : (d_{200})^2 = 1 : 3 : 4$, which points to the hexagonal structure of the crystalline phase. The indexing of the diffraction maxima manifests the presence only of the reflexes characterized by the zero value of the third Miller index ($hk0$), which is explained by the rotation disordering of CF_2 groups along the hexagonal axis of the crystalline phase (symmetry group $p6mm$) [7]. This is the difference between such samples as the FORUM powders and the commercial PTFE powders of the F-4 grade.

The degree of crystallinity was estimated on the basis of the ratio of areas of reflexes corresponding to disordered and crystalline regions. First, the overall area was found (less incoherent scattering) and then the integral intensity of peaks corresponding to the crystalline phase was measured. The area of the amorphous halo was determined as the difference between the overall and crystalline components. According to the calculations performed, the degree of crystallinity of all samples is $\sim 31\%$ and the scatter does not go beyond the experimental error.

The diffractogram of sample no. 2 is similar with the only difference that the intense reflex is narrower and the intensity of maxima characteristic of the crystalline phase increases somewhat. Similar diffractograms were also observed for other samples.

STUDIES OF THERMAL PROPERTIES OF FLUOROPOLYMERS

Figure 3 shows thermogravimetric (TG) curves of the studied samples. One can see that the mass loss of sample no. 1 occurs in two stages: the first one in the range of 180 – 430°C and the second one in the range of 430 – 580°C . The temperature of the mass loss start is lower than in the case of Fluoroplast-4 ($>400^\circ\text{C}$), which can be attributed to the presence in the sample of fractions with a lower molecular mass of macromolecules. Two stages of thermal destruction are most

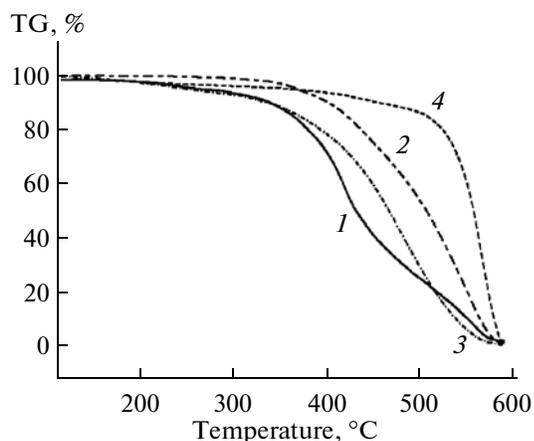


Fig. 3. TG curves of samples: (1) no. 1, (2) no. 2, (3) no. 3, (4) no. 5.

probably related to two fluoropolymer fractions with different thermal characteristics owing to different molecular mass. The share of the first (low-molecular) fraction is about 50%. In sample no. 2, the mass loss is observed at a temperature above 350°C and occurs in a single stage. Since this sample is obtained by the heating of sample no. 1, one can assume that the low-molecular structure is sublimated in the course of thermal treatment. It is found in the microscopic studies that the share of shapeless structures of small particles is reduced, so one can assume that it is these that form the low-molecular fraction. The highest thermal stability close to that of Fluoroplast-4 is observed in sample no. 5, though it contains phases with a different morphological structure. The share of the low-molecular components that start losing weight at 180°C is not more than 10% of the total mass.

The temperature dependences of the curves of differential scanning calorimetry (DSC) (Fig. 4) of the studied samples are similar: an endothermic effect is observed at low temperatures and an exothermic one is found in the high-temperature range. The first one is related to polymer melting and the second one is related to oxidative processes. At the same time, the polymer melting temperature changes from sample to sample: the minimum value is characteristic of sample no. 1 (268.8°C) (this is lower than in the case of Fluoroplast-4 (327°C)) because of the lower molecular weight of sample macromolecules. In sample no. 2, from which the low-molecular fraction is removed, melting is observed at the temperature of 286°C, and the melting temperature of sample no. 5 is 324°C, which is close to the values typical of industrial samples.

MOLECULAR STRUCTURE OF FLUOROPOLYMERS ACCORDING TO SPECTROSCOPIC DATA

IR spectra of the studied samples (Fig. 5) have the shape characteristic of PTFE [9], with the difference

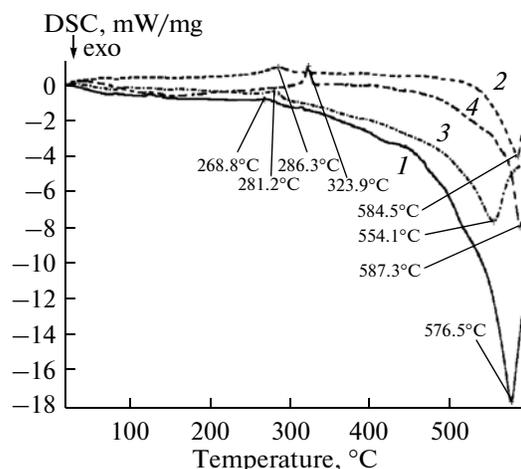


Fig. 4. DSC curves of the studied samples: (1) no. 1, (2) no. 2, (3) no. 3, (4) no. 5.

that weak bands are observed in the range of 2400 and 1700 cm^{-1} , which may be due to signals of initiator molecules remaining in the sample.

The most intense absorption bands at 1211 and 1154 cm^{-1} are characteristic of C–F valence vibrations in $-\text{CF}_2$ groups. The low-frequency region con-

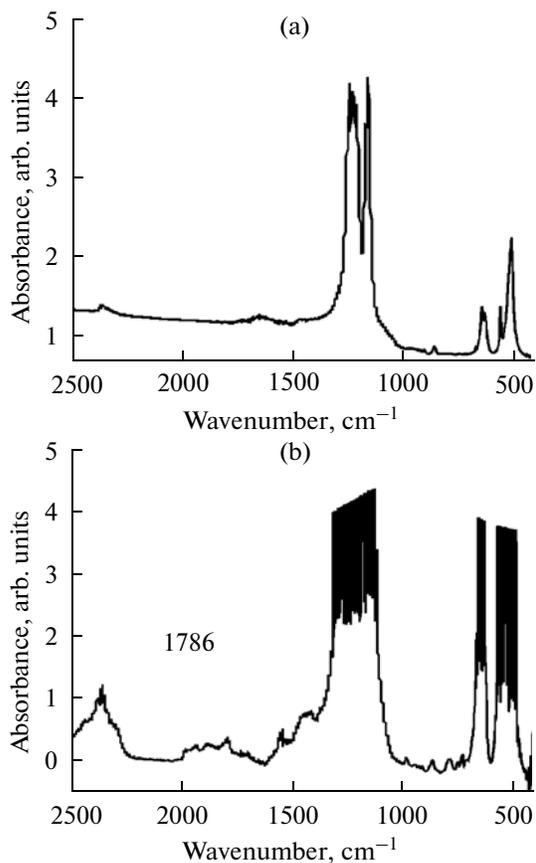


Fig. 5. IR spectra (at considerable magnification) of samples: (a) no. 1, (b) no. 5.

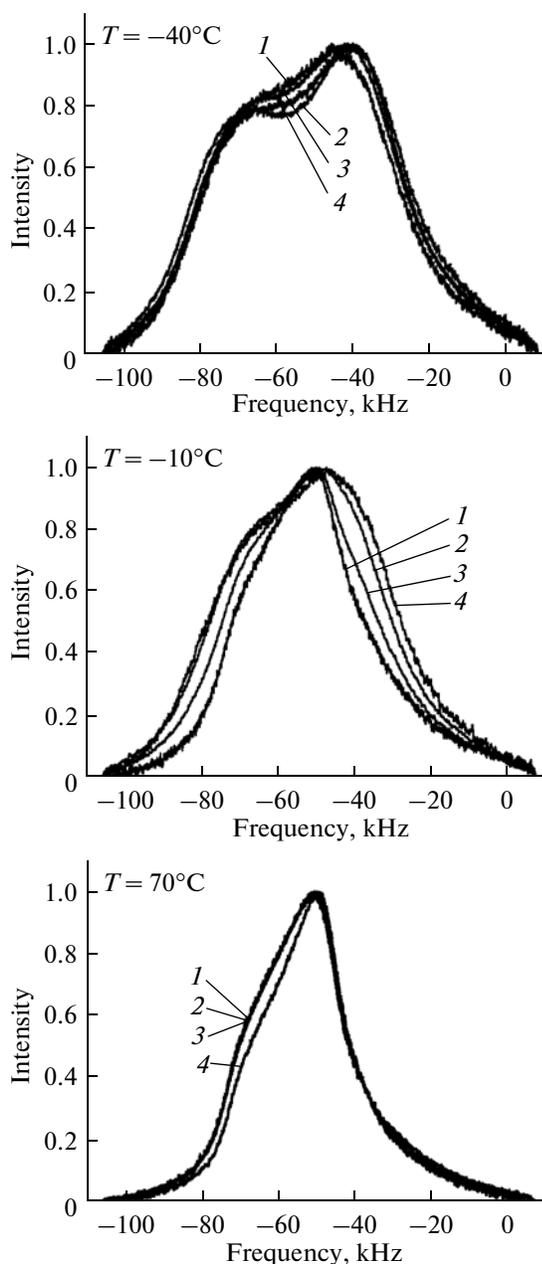


Fig. 6. Dependence of the shape of ^{19}F NMR lines for samples (1) no. 1, (2) no. 2, (3) no. 3, and (4) no. 5 at the temperatures of -40°C , -10°C , and 70°C .

tains bands corresponding to wagging vibrations $\gamma_{\omega}(\text{CF}_2)$. The bands at 639 cm^{-1} and also those at 555 and 516 cm^{-1} are related to deformation and pendulum oscillations of the $-\text{CF}_2$ groups, respectively. The ratio of intensities of these bands for all the studied samples remains practically the same.

The spectrum of sample no. 5 obtained at high polymer concentrations in the studied tablets manifests low-intensity bands at 1786 and 986 cm^{-1} responsible for vibrations of the $-\text{CF}=\text{CF}_2$ terminal groups and nonterminal trifluoromethyl groups (CF_3). These

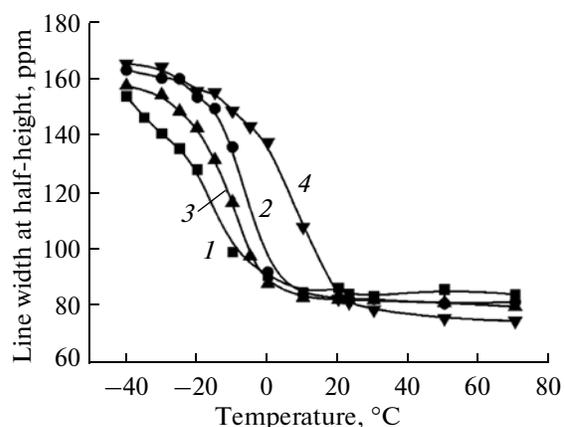


Fig. 7. Temperature dependences of resonance line width for the studied samples: (1) no. 1, (2) no. 2, (3) no. 3, (4) no. 5.

groups are typical of the spectra of low-molecular fractions of the FORUM powder [9].

The line shape and width of the low-resolution ^{19}F NMR spectra of the studied fluoropolymers demonstrate the temperature dependence related to the averaging of the dipole–dipole interaction of magnetic moments of fluorine nuclei under the heating of the sample (Fig. 6). The averaging is due to mobility of molecular fragments of macromolecular PTFE chains. The low-temperature spectrum is represented by a line with the width of 145 ppm (55 kHz) at the half-height, with a pronounced asymmetry, while at the temperature of -40°C , it corresponds to a broad line with a doublet structure element related to the regularities of the dipole–dipole interaction of magnetic nuclei [10]. In the course of the sample heating, the line becomes narrower, but preserves its asymmetry, which is in all probability related to anisotropy of the chemical shift of the fluorine nucleus owing to the regularities of the electron distribution of a fluorocarbon bond in CF_2 groups.

The temperature dependences of the resonance line width at half the maximum intensity differ significantly from sample to sample (Fig. 7). A decrease in the temperature of the spectral line narrowing reflects a higher mobility of molecular groups. The fact that the line narrowing is incomplete points to the reorientation character of fragment movement. The temperature range of the transition region reflects the degree of dynamic inhomogeneity of molecular fragments in the polymer. One can see that the highest mobility is characteristic of sample no. 1, in which the narrowing is already observed at -35°C , which is typical of low-molecular fractions. Sublimation of this fraction observed when sample no. 2 is obtained is confirmed by an increase in initiation of the spectral line narrowing and a decrease in the temperature range of the transition region. In other words, the sample predominantly contains a high-molecular

component and is more dynamically uniform. The greatest difference in the temperature behavior of the line width curve is characteristic of sample no. 5: firstly, it is less mobile; secondly, its temperature dependence contains two pronounced spectrum narrowing regions (-20 to $+20^{\circ}\text{C}$ and $+20$ to $+45^{\circ}\text{C}$). This sample features the highest number of morphological phases also characterized by dynamic mobility of molecular fragments.

CONCLUSIONS

The technology of photochemical polymerization of PTFE results in obtaining fluoropolymer powders with the particle morphology differing from that of PTFE samples obtained using industrial technologies. The studied products contain spherical monoparticles of significant size (up to $10\ \mu\text{m}$), which is much higher than in the case of powders obtained by thermal treatment of PTFE. Along with spherical monoparticles, shapeless associative formations of small particles (hundreds of nanometers) are observed. All samples are characterized by polymodal size distribution functions. The type of employed initiator, as well as the sample treatment after synthesis, affects the morphological sample composition and content of fractions with different molecular weights. This is especially pronounced in variation of sample melting temperatures in DSC studies. Judging by the data of X-ray diffractometry, the crystal component of the studied samples is insignificant.

Temperature studies of ^{19}F NMR spectra manifest a considerable difference in mobility of chain macromolecules of samples in relation to the synthesis technology.

ACKNOWLEDGMENTS

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