ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 3, pp. 666–676. © Pleiades Publishing, Ltd., 2009.
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Morphology and Structure of Micro- and Nanosize Polytetrafluoroethylene Powders Prepared by the Gas-Phase Method

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Received February 1, 2008

Abstract—Formation of fluoropolymer nanoaerosols and micropowders in the gas products of polytetrafluoroethylene pyrolysis and the hierarchical self-organization of ultradispersed powders were revealed. The features of the molecular and supramolecular structures of powders were analyzed. Low- and high-molecular-weight fractions of the fluoropolymers, constituting the powder particles were identified, and a method for their partitioning was proposed.

DOI: 10.1134/S1070363209030487

INTRODUCTION

Powder materials occupy specific segments of the world manufacture and market and in certain cases underlie entire branches, which concerns, e.g., powder metallurgy. In particular, powder materials are suitable as components of composite materials. The properties of composites are strongly dependent not only on the chemical composition but also on the powder particle size and shape, as well as on some other factors. This stimulates the researchers' interest in preparation of specific powders, above all, those with a minimal particle size.

Polytetrafluoroethylene synthesized as a powder is suitable as a commercial product or as raw material for preparation of granules or bulk fluoroplastic stocks to be used for manufacture of various items. Commercial powdered polytetrafluoroethylene is basically manufactured by the emulsion and suspension technologies, which imply polymerization of gaseous tetrafluoroethylene in an aqueous medium under specific process conditions with addition of initiators [1]. Such procedures yield 50–500-μm particles. Jet milling of powders allows reducing the particle size to 10–50 μm [1], but often smaller particle size of powders is dictated by practical needs.

Micro- and nanosize powders can be synthesized by either of two methods, the "top–bottom" method, in which the bulk sample is ground by a certain technique, and the "bottom–top" method, in which nanosize moieties are assembled from smaller formations, atoms and/or molecules. In the case of fluoropolymers, the first method finds only limited use because of enhanced mechanical and other characteristics of these polymers.

Extensive application in preparation of inorganic, in particular metal, powders is found by the gas-phase synthesis method [2], classed with the "bottom–top" methods. In the case of fluoropolymers, in particular, polytetrafluoroethylene, the use of this technology was prevented by several factors. First, it was believed that heating causes thermal degradation of polytetrafluoroethylene with predominant (by over 90%) elimination of gaseous monomer C_2F_4 which is not prone to polymerization under ordinary conditions [1, 3] and whose polymerization requires complex technologies implemented at special industrial enterprises. Second, organic polymers belong to "soft" materials, whose structure and properties undergo severe modification in response to minor external impacts, and this complicates selection of the best range of the process parameters for synthesis. Third, polymers are characterized by more complex compared to inorganic systems mechanisms of thermal degradation and formation of aerosols and particles in the gas phase. In metal systems, the “bricks” constituting the nanoparticles in the gas phase are represented by one kind of metal atoms, and in polymeric systems the “building material” has a more complex nature. Polymeric particles are formed from molecules, each of which is comprised of at least two kinds of atoms. The molecules differ in size and helix twist and exhibit isomerism; there exist other factors responsible for their distinctions. The number of channels for formation of polymeric particles is larger than that in metal powders, and it is very difficult to predict the topology of polymeric micro- and nanoparticles in the case of fluoropolymers. An additional difficulty is associated with the fact that there is covalent bonding inside the molecular "bricks" and a different bonding type (e.g., Van der Waals, polarization) among them, which is specifically responsible for the supramolecular structure of the polymer particles. For these reasons, the mechanism of formation of products from the gas phase and their structural features are difficult to understand and theoretically interpret.

The research efforts undertaken by the Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, Vladivostok, demonstrated that preparation of a polytetrafluoroethylene powder from the pyrolysis products of this polymer is possible in principle and, moreover, is economically and technologically justified for commercial application. The method of preparation of the powder, as well as the product itself and the facility for its manufacture were patented [4–6], and the Forum product (an ultradispersed organofluorine material) received a trade mark registration [7]. Pilot-scale production was organized within the framework of the Institute.

An advantage offered by this method consists in that it operates with the waste generated by manufacture of commercial polytetrafluoroethylene and products thereof as the raw material. An efficient processing technology for this polymer waste still remains to be developed, which poses not only an economic but also an environmental problem, namely, that of utilization of waste accumulated at industrial enterprises.

Here, we discuss the issues related to synthesis of polytetrafluoroethylene powders from gaseous pyrolysis products of fluoropolymers and their structure. These data in part were presented earlier [8], and here we report the latest results and discuss the new aspects to better understand the mechanism of formation and structural features of the powders.

Nature of Formation of Nanoaerosols in Gaseous Polytetrafluoroethylene Pyrolysis Products

As already mentioned, there has long existed an opinion that heating causes degradation of polytetrafluoroethylene with predominant elimination of the tetrafluoroethylene monomer which does not undergo polymerization in the gas phase without initiators or radiation exposure. However, it was found that, under certain conditions, a "mist” is formed in the medium of gaseous polytetrafluoroethylene pyrolysis products, and a white powder is formed on the reactor walls. Light scattering on the resulting particles, responsible for the "mist" phenomenon, is possible only in the case when the particle size is comparable with a quarter of the light wavelength. The aerosol particles are yielded by the reaction of molecular radicals, polytetrafluoroethylene pyrolysis products, with the monomer molecules. The conditions of formation of radicals are governed by the pyrolysis temperature, and those of their interaction in the gas medium are controlled by pressure, as well as by the design characteristics of the reactor.

We will start analyzing the formation of nanoaerosols with discussing the gas medium preparation aspects. As for thermal degradation of polytetrafluoroethylene, it was predicted theoretically (see, e.g., [3, 9, 10]) that it is stable up to 300°C. Above this temperature, the softening of polytetrafluoroethylene, associated with its melting, is observed, and at higher temperatures under prolonged keeping, appreciable degradation. In particular, near 800°C the degradation is accompanied by formation of the C_2F_4 monomer (97 %) [9]. Relevant mass-spectrometric examinations showed that, in the case of pyrolysis of the fluoroplastic at 357–410°C, the gas phase contains C_2F_4, C_3F_6, and C_3F_5 moieties in the 1:0.04:0.02 ratio throughout the experiment [8]. The spectrum of the pyrolysis products and the ratio of the components are strongly dependent on the temperature mode of the process but, whatever the temperature conditions, this is clearly a multicomponent gas medium. The relevant IR spectra (Fig. 1) are also indicative of a broad spectrum of gaseous products formed.

The earliest studies on aerosol formation in polytetrafluoroethylene pyrolysis products [11, 12]

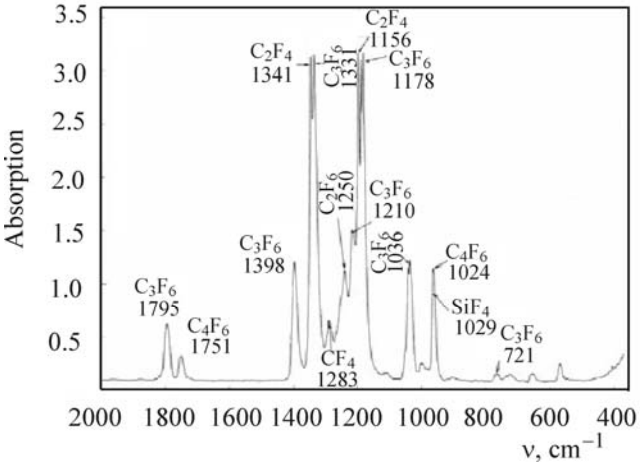

Fig. 1. IR absorption spectrum of the gaseous products from thermal degradation of polytetrafluoroethylene.

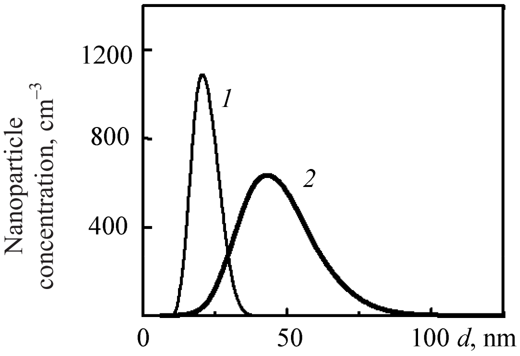

Fig. 2. Radial distribution function for the nanoaerosol particles in relation to the pyrolysis time [11]: (*1*) 70 min (mean particle diameter d_{mean} = 21 nm) and (*2*) 365 nm (d_{mean} = 44 nm). Pyrolysis temperature 496°C, nucleation temperature 60°C.

showed that the medium size of the nanoaerosol particles varies with the process conditions, namely, temperature and time of pyrolysis of the initial product and the difference between the pyrolysis and nucleation temperatures (Fig. 2). The radial distribution function for the aerosol particles within 3–200 nm was determined with a diffuse spectrometer developed at the Institute of Chemical Kinetics and Burning, Siberian Division, Russian Academy of Sciences [12]. The operation of the spectrometer is underlain by the dependence of the diffusion coefficient on the microparticle size. Increase in the pyrolysis time not only causes an increase in the mean size of the aerosol particles but is also responsible for a wider radial distribution. The observed aerosol particles are several tens of nanometers in size, which fully justifies the term “nanoaerosols” in their case.

The plot of the aerosol particle diameter vs. pyrolysis time for the initial product at constant degradation (496°C) and nucleation (60°C) temperatures (Fig. 3) shows that, within 6 h, the particle diameter increases threefold, which corresponds to the diameter growth at a rate of 4.4 nm h^{-1}. The aerosol particle diameter changed with time in the experiment with the same pyrolyzed sample until its virtually exhaustive consumption. The experimental facility provided a constant temperature of the gas medium throughout the experiment, which suggests that an increase in the nanoaerosol particle size should be associated with the time variation of the surface structure of the polymer being heated. Presumably, evaporation causes a change in the nature of the polymer surface, thereby decreasing the work function of the gaseous products and increasing their concentration. The above-said is supported by the data on modification of the morphology of the polytetrafluoroethylene plate surface upon prolonged heating at high temperatures: A smooth surface of the polymer plate gets loose upon heating at 350°C. The surface roughness is comparable in size with the diameter of the powder particles formed in the gas medium of the pyrolysis products. Such surface structure of the polymer can promote degradation of the polymer without destruction of the macromolecules. This was presumed by Grigorov [13] in the framework of a theory predicting that, at appropriate surface geometry, solid particles can be detached from the polymer block, without changing the molecular structure of the polymer, and get into the gas medium of the pyrolysis products. This can be specifically responsible for the appearance of large particles comparable in size with powder particles of the end product, formed upon prolonged heating at high temperatures. An increase in the concentration of the products in the gas phase should also cause the nanoparticle diameter to increase.

Variation of the degradation temperature within 400–580°C at a constant nucleation temperature (60°C) induced more than 15-fold change in the median particle diameter. To eliminate the time factor, the measurements were carried out with freshly prepared samples for each degradation temperature within one hour. The observed variability of the diameter suggests the fluctuation nature of the aerosols; their concentra-

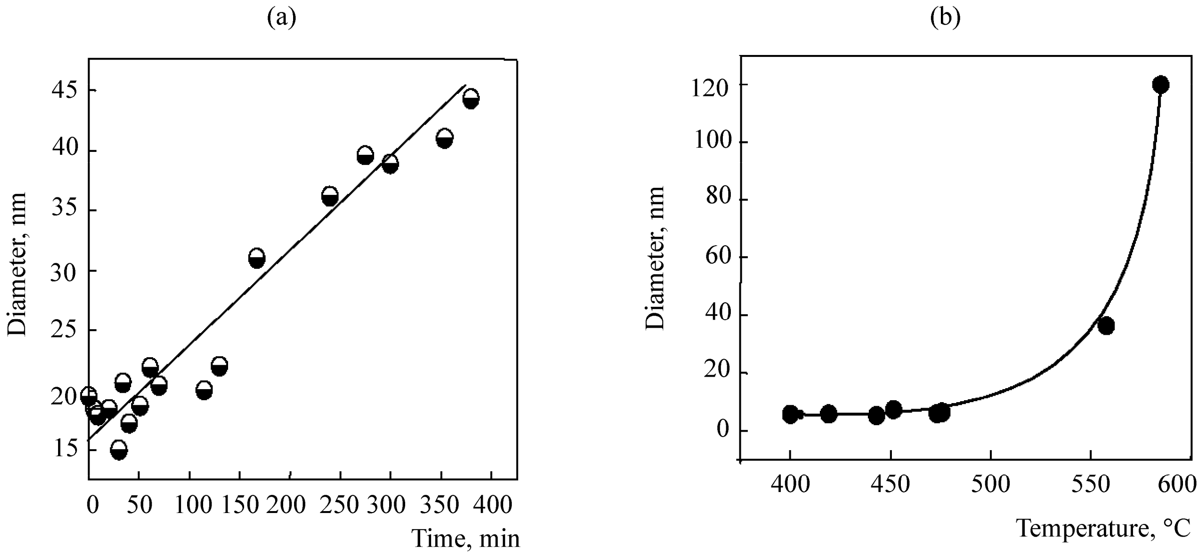

Fig. 3. Nanoaerosol particle size vs. (a) time and (b) temperature of pyrolysis of the initial polytetrafluoroethylene [11].

tion varies with time as well. The overall rate of nucleation by all the channels possible for the thermal degradation products of polytetrafluoroethylene tends to increase with increasing degradation temperature (at a constant nucleation temperature). This seems quite natural, since an increase in the pyrolysis temperature causes the partial content of the components (at a constant nucleation temperature) to increase, which results in more intensive nucleation.

Presumably, the nanoaerosols in the gas medium of the polytetrafluoroethylene pyrolysis products are formed by the following mechanism. The fluorocarbon gas medium of the pyrolysis products contains a broad spectrum of radicals and molecules, which affords multichannel nucleation. The nucleation kinetics is determined by the density fluctuations of the radicals in the gas phase, and this stage of aerosol formation is accompanied by polymerization. This can be paralleled by degradation of the C_2F_4 monomer molecules into polymerization-active structures, which in turn provides an additional nucleation channel. Considering a large proportion of the monomers in the pyrolysis products, this can be an efficient nucleation channel, which will intensify formation of nanoaerosols. In the fluorocarbon molecules medium, the nanoaerosol particles grow in size due to condensation of the molecular formations on them. Condensation can occur both on nanoaerosol particles and on the reactor walls. Clearly, by varying the process characteristics (pyrolysis temperature and time, temperature and pressure of the gas phase of the fluorocarbon products, etc.) it will be possible to control the size of the nanoaerosol particles and, thereby, the structure of the ultradispersed polytetrafluoroethylene particles.

Rebrov et al. [14] studied preparation of fluoropolymer coatings by treatment of the surface with polytetrafluoroethylene pyrolysis products under ultrasonication in a vacuum (using the facility available from the Institute of Thermal Physics, Siberian Division, Russian Academy of Sciences). Those experiments demonstrated that the structure of the fluoropolymer coatings depends on the process conditions, presence/absence of the carrier gas (in the case of interest, helium) and the substrate temperature. The electron microscopic images (Fig. 4) suggest formation of a fairly loose coating whose surface area exceeds 1500 times that of the initial substrate. The morphology of the coating particles deposited onto a cold substrate with the use of helium more closely corresponds to that of the crystalline formations, and the morphology of the coatings prepared under different conditions, to that of amorphous formations.

The IR spectra of the samples of the coatings prepared by deposition of the polytetrafluoroethylene pyrolysis products onto cold (50–150°C) copper substrate with the use of helium have a structure characteristic for polytetrafluoroethylene, but also exhibit some peculiar features. For example, there is a band at 1784 cm^{-1}, which can be associated with the terminal $–CF=CF_2$ groups in the macromolecule. A high intensity of this band suggests a large content of

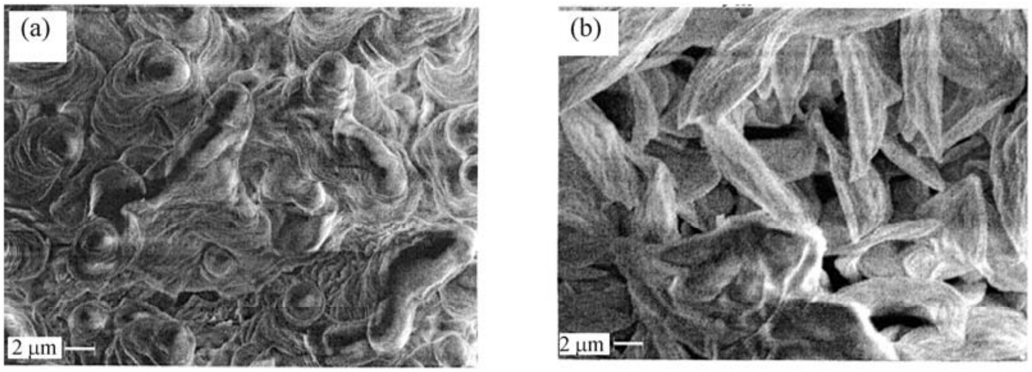

Fig. 4. Electron microscopic images of the coatings on a copper substrate, formed by a stream of polytetrafluoroethylene pyrolysis products at different process conditions: (a) substrate temperature 290°C, without carrier gas and (b) substrate temperature 50–150°C, with carrier gas (helium; concentration 50%) [14].

these groups, which is due to a low molecular weight of the macromolecules in comparison with commercial polytetrafluoroethylene samples. The spectrum does not contain a band at 625 cm^{-1}, associated with the defects due to the change from left- to right-hand twist of the macromolecular helices. The lack of bands at 700–800 cm^{-1}, corresponding to the amorphous phase, suggests a high degree of crystallinity of the coating. The coatings deposited onto substrates at higher temperatures (> 290°C) exhibit a stronger structural disordering. For example, along with the already mentioned bands, the spectra of the coatings prepared on a cold substrate contain additional lines. The band of 987 cm^{-1} is associated with side trifluoromethyl CF_3 groups. Also, there is a band at 625 cm^{-1} corresponding to transitions between the left- and right-handed helices. The most important feature is the appearance of bands at 720–780 cm^{-1} corresponding to the amorphous fractions of the polymer. It should be noted that the coatings deposited without carrier gas exhibit stronger disordering of the fluoropolymer chains. For example, trifluormethyl groups are observed even in the spectrum of the coating deposited onto a cold substrate.

Morphology and Hierarchical Organization of Ultradispersed Polytetrafluoroethylenes Powder

Electron microscopic examinations showed that the ultradispersed polytetrafluoroethylene powder particles have a close to spherical shape (Fig. 5). It should be noted that these examinations required surface metallization of the particles, which distorted their actual form. Along with these particles (hereinafter, monoparticles), there are aggregates of monoparticles, and also larger agglomerates formed by the aggregates and monoparticles. The occurrence of these formations was confirmed by the particle size measurements on a Symhftec HELOS - H1084 facility whose operation is based on laser radiation scattering by powder particles [15].

A dry powder is supplied to the measurement chamber by a controlled-power air stream, which allows examination of the powder particles aggregation in relation to the air stream characteristics.

The particle size distribution function (Fig. 5) has several peaks corresponding to monoparticles, aggregates, and agglomerates. The monoparticles are 0.1–1.0 μm in size; the upper limit cannot be determined more precisely because of superposition with the distribution function of the aggregates. The statistical mean value of the monoparticle size was estimated at 0.55 μm; the aggregates are 1–5 μm in size (the function has a maximum at 2.5 μm); and the agglomerates are over 10 μm in size. The particle size distribution function varies with the air stream pressure, which suggests that the air stream may cause decomposition of the aggregates and agglomerates.

The kinetic features of formation of agglomerates were examined on the facility designed at the Institute of the Atmosphere Optics, Siberian Division, Russian Academy of Sciences. This facility generates turbulent air streams in a closed space, which cause decomposition of the aggregates and agglomerates into monoparticles whose size is recorded. After the turbulent stream is “switched off,” the size of the resulting complex systems is measured.

The particle size distribution functions obtained at the beginning of experiment clearly suggest the

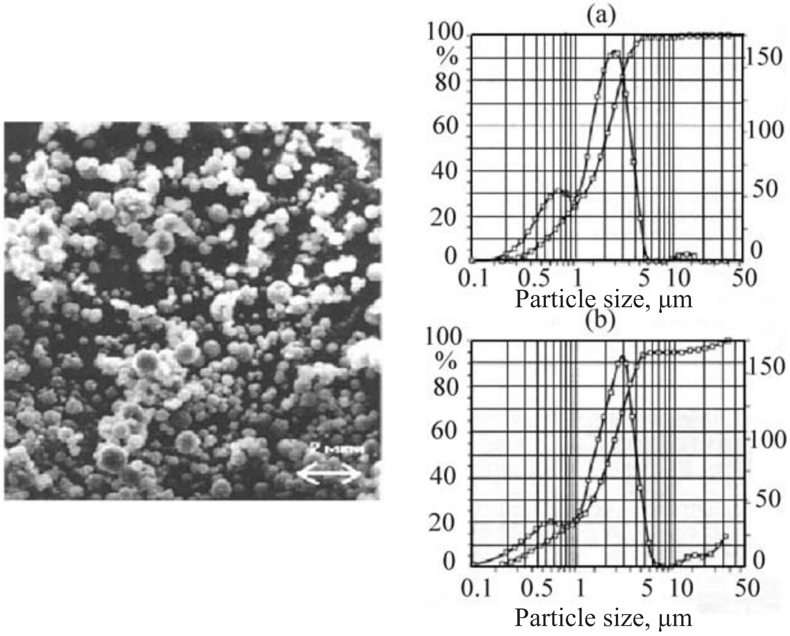

Fig. 5. (Left) Electron microscopic images of ultradispersed polytetrafluoroethylene particles and (right) particle size distribution in relation to the air stream pressure [15].

absence of aggregates of monoparticles. The function recorded without turbulent streams in the measurement chamber contains a peak corresponding to formation of agglomerates. The radial distribution function gets close to that in Fig. 4.

The corresponding atomic-force microscopic images show that the shape of the particles is not perfectly spherical (Fig. 6). This is most clearly demonstrated by the image presented in Fig. 6c for a particle comprised of merged blocks from tens to

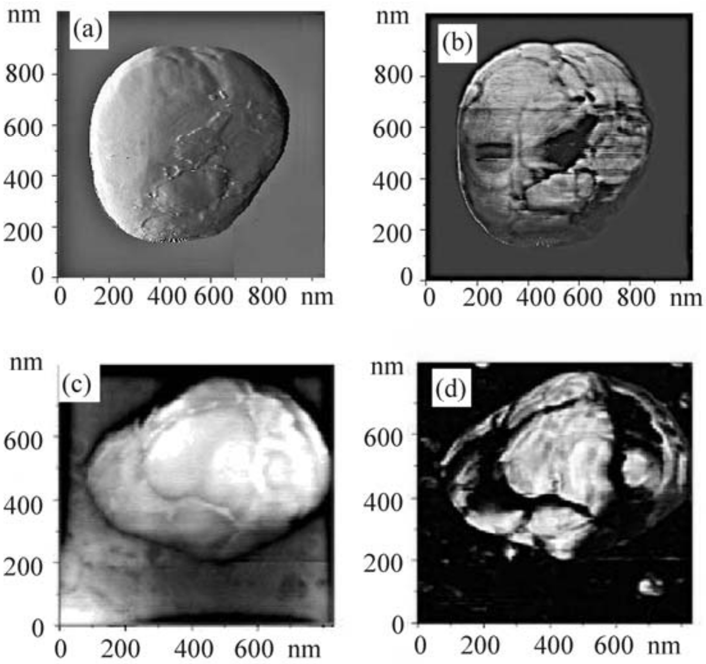

Fig. 6. Atomic-force image of an ultadispersed polytetrafluoroethylene powder monoparticle [6]: (a, b) block monoparticles and (c, d) continuous nanoparticles. (Top) Amplitude modulation and (bottom) phase contrast mode. Image size 1.2×1.2 μm.

hundred nanometers in size. The phase-contrast images exhibit light and dark domains which may correspond to fluoropolymers of different structures. Relevant examinations showed that the monoparticles consist of high- and low-molecular-weight fractions. These are high-molecular-weight blocks fastened together by a low-molecular-weight polymer. Along with block monoparticles, there are particles with a continuous structure. The presence of two types, block and continuous, of monoparticles was confirmed by relevant transmission electron microscopic data [6]. It should be noted that continuous particles have a ~10-nm-thick low-molecular-weight polymer coating.

The above-said suggests the following mechanism of formation of the monoparticles. The molecular radicals form dimers and larger oligomers; in other words, macromolecules are formed. The latter produce nanoaerosols observed in the gas medium, whose evolution can follow two pathways: (1) the nanoparticles grow in size to monoparticles, thereby yielding continuous formations, and (2) the nanoparticles merge into block monoparticles. The merging is underlain by covalent and intermolecular bonding, which provides for mechanical strength of the block monoparticles. Also possible are intermediate mechanisms of formation of monoparticles and of their aggregates. The specific routes of self-organization of the particles depend on the thermodynamic conditions. At the same time, different molecular radicals are prone to self-organization by their respective channels into films or bulk particles.

On this basis, a multilevel hierarchical scheme of self-organization of polytetrafluoroethylene pyrolysis products can be proposed. The first level includes the molecular radicals several angstroms in size; the second level, nanosize blocks (nanoaerosols), several tens nanometers in size; the third level, monoparticles, both block and continuous, 100–700 nm in size; the fourth level, aggregates of weakly bound low-strength monoparticles 500–5000 nm in size; and the fifth level, even more weakly bound agglomerates of monoparticles and aggregates, 10000–30000 nm in size.

Thermal Properties of Ultradispersed Polytetrafluoroethylene

The structure of ultradispersed polytetrafluoroethylene prepared by the gas-phase method differs from that of commercial block samples, which is naturally responsible for different physicochemical, in particular, thermal properties of the polymers.

Derivatographic examinations demonstrated that the behavior of commercial fluoroplastic-4 differs substantially from that of Forum ultradispersed powder (Fig. 7). The mass loss onset temperature for F-4 is above 485°C, and the entire temperature range covers one hundred degrees. The DTG curve of this sample has two peaks, at 515 and 555°C, which suggests

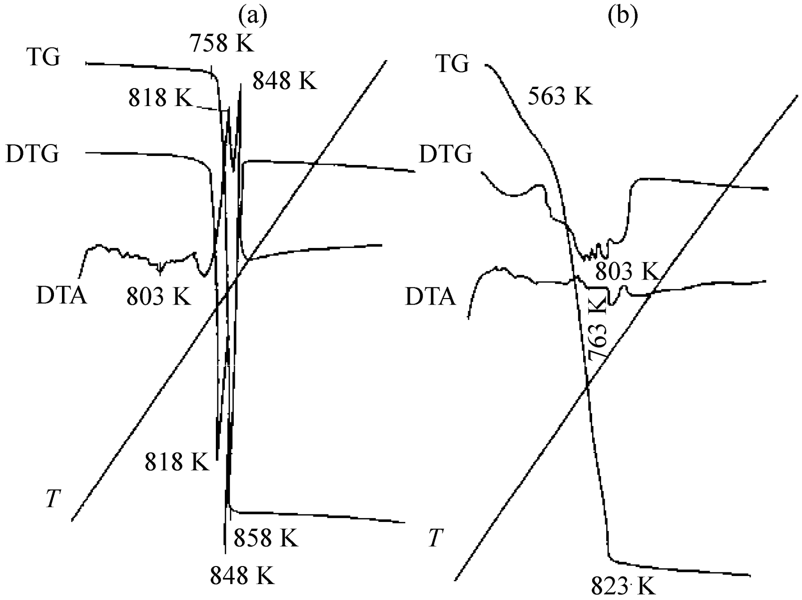

Fig. 7. Derivatogram of (a) F-4 fluoroplastic and (b) Forum ultardispersed powder [6]: (TG) thermogravimetric curve; (DTG) differential thermogravimetric curve; (DTA) differential thermal analysis curve; and (*T*) temperature.

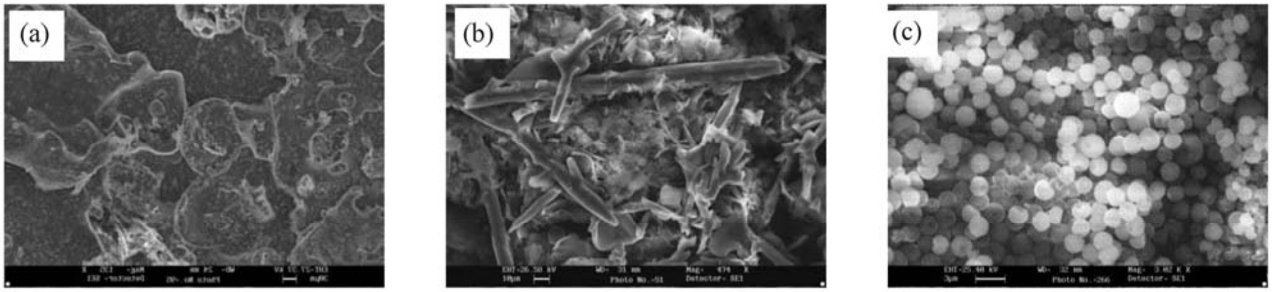

Fig. 8. Electron microscopic images of the products of Forum pyrolysis at different temperatures: (a) 70 (b) 150, and (c) 300°C [19]. Labels designate 30, 10, and 2 μm, respectively.

stepwise thermal degradation. The DTA curve exhibits an endothermic effect near 315°C, which can be reasonably associated with melting of the sample. Two exothermic (525 and 575°C) peaks in the DTA curve are associated with oxidation processes [10, 16].

The Forum powder exhibits a basically different pattern. The mass loss onset temperature is 60–70°C, and the polymer degradation covers a much broader temperature range (333–823 K); the TG curve contains distinct areas corresponding to slow and fast thermal degradation. Such pattern is due to the presence in the powdered polymer of phases with different thermal stabilities. The degradation temperature varies with the molecular weight of the macromolecules, which makes reasonable regarding the material as comprised of fractions with different molecular weights. Near 300°C, no endothermic anomaly is observed that could be associated with melting of the polymer whose macromolecules are characterized by a wide molecular weight distribution.

The mass-spectrometric data for the pyrolysis products of commercial polytetrafluoroethylene are strongly dependent on the conditions of the process. At temperatures above 400°C, pyrolysis of commercial polytetrafluoroethylene yields C_2F_4, C_3F_6, and C_3F_5 moieties. If heat treatment is accompanied by radiolysis (γ-ray exposure), the CF, CF_2, CF_3, C_2F_3, C_2F_5, C_3F_3, and C_4F_7 moieties are formed additionally [17]. At high temperatures, pyrolysis in the gas media [18] yields 15 molecular moieties.

The mass-spectrometric analysis of the Forum product at 144°C revealed an unusually large number of gaseous components, over 45 [16]. Along with fluorocarbon components, there are oxide and hydride compounds in low concentrations, whose formation was made possible by the access of air during pyrolysis in the Forum preparation technology. Quantitatively, the principal components are C_3F_5 and CF_3 (peak intensity of 100 and 97.4, respectively). As to the C_2F_4 monomer, its concentration corresponds to the intensity of 30. Fairly large formations, e.g., $C_{18}F_{35}$, with the mass number of 881 were revealed, though in low concentrations.

Another feature distinguishing the thermal behavior of the Forum powder from that of commercial polytetrafluoroethylene samples is the lack of phase transitions at 19 and 30°C, despite the fact that a fairly broad peak is observed in the temperature dependence of the heat capacity at 21°C [16]. Phase transitions are associated with reorganization of the crystalline components of the polymer. At room temperature the crystal structure of Forum fluoropolymer corresponds to a high-temperature phase, for which reason phase transitions are not observed. The revealed low-temperature anomaly is most likely due to the reorganization in the amorphous phase of the product.

Preparation of Low-Temperature Fractions of Polytetrafluoroethylene

Thermal degradation of the Forum product covers a broad temperature range because of the existence of two phases with different molecular weights, whose sublimation temperatures are also different, which enables partitioning of the materials into fractions by repeated heat treatment. Upon heating the product to temperatures corresponding to the loss of the low-molecular-weight fraction, followed by keeping the polymer under these conditions, the polymer contains only the high-molecular-weight fraction. It should be noted that pyrolysis of Forum yields a broad spectrum of molecular fluorocarbon moieties, which may produce various structural and morphological forms of fluorocarbon polymers.

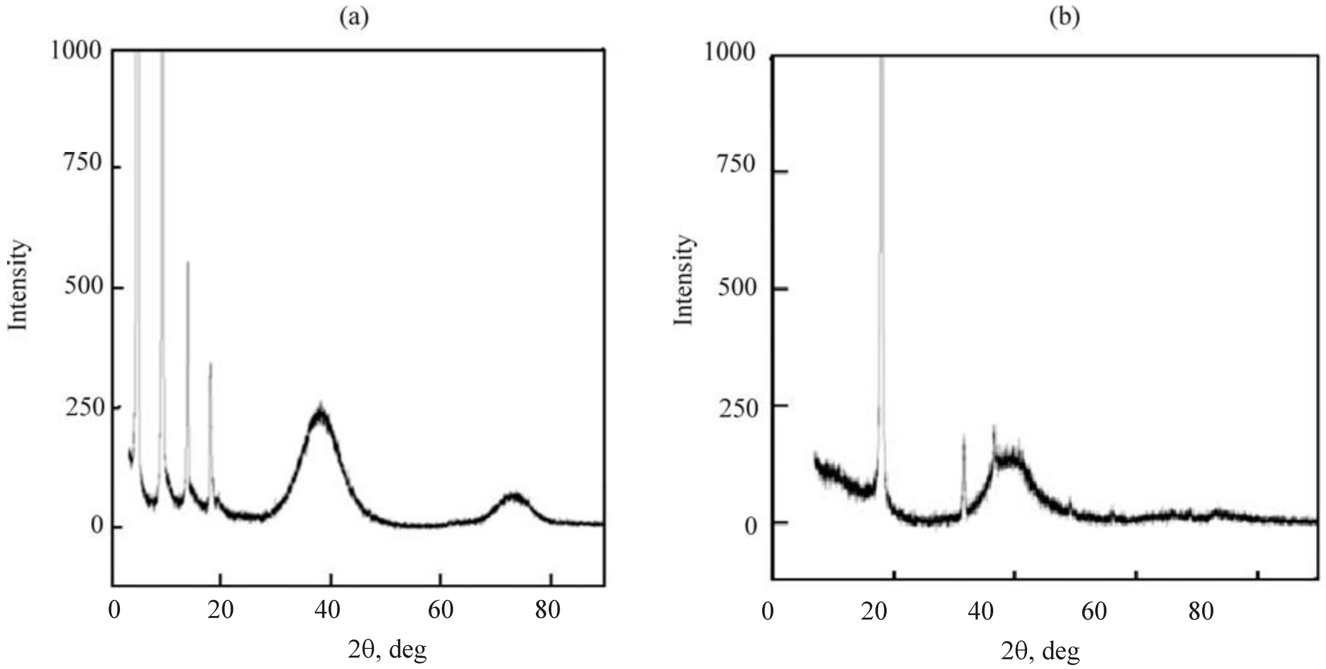

Fig. 9. X-ray diffraction pattern of (a) low-temperature, 70°C, and (b) high-temperature, 300°C, fractions of ultardispersed polytetrafluoroethylene powder [20].

Examinations of the products of Forum pyrolysis at 70, 140, and 300°C showed that they have considerably different morphological structures [19]. The first group products are films with the microsize areas and nanosize thicknesses (Fig. 8). Second group samples contain 10–300-μm-long multilayered tubes 2–20-μm in diameter (rolled up planar moieties), and other formations. The third group products are represented by virtually calibrated spheres ca. 1 μm in size.

A possible reason to the revealed distinctions in the morphological structures of the particles is that the gaseous products of pyrolysis at different temperatures are characterized by different ratios of the molecular fragments, each of which is prone to building specific morphological formations. For example, examination of the plasmochemically deposited coatings showed [8] that the CF_3 и C_2F_5 fragments form films.

The structures of the fractions are also different [20, 21]. The X-ray diffraction pattern of the powder prepared at high temperatures is absolutely identical to that of commercial polytetrafluoroethylene. At the same time, the low-temperature fraction is characterized by a different diffraction pattern (Fig. 9):

No crystalline peaks are observed at large Bragg's angles; there are two prominent diffuse halos and a number of distinct reflexes at small Bragg's angles. This diffraction pattern can be associated with layered formations.

The thermal characteristics of the fractions differ substantially (Fig. 10). For the low-temperature fractions, the onset of mass loss is observed at 50°C, and its termination, near 150°C. There is a smooth mass loss, but the rates at the beginning and the end of the process are different, as manifested in the asymmetry of the minimum in the DTG curve. This may be due to more intensive degradation of the polymer after melting. The DTA curve exhibits an anomaly with a minimum at 83°C, which can be associated with melting of the polymer.

The mass loss of the high-temperature fraction occurs within 120–300°C in two stages, with a borderline near 215°C. In same range the DTA curve exhibits an anomaly associated with melting of the fluoropolymer.

As mentioned above, the distinctions in the thermal properties are due to the difference in the molecular weight, as confirmed by relevant NMR and IR spectroscopic data. The macromolecules of the low-temperature fraction contain terminal olefin groups and middle trifluoromethyl groups. An appreciable inten-

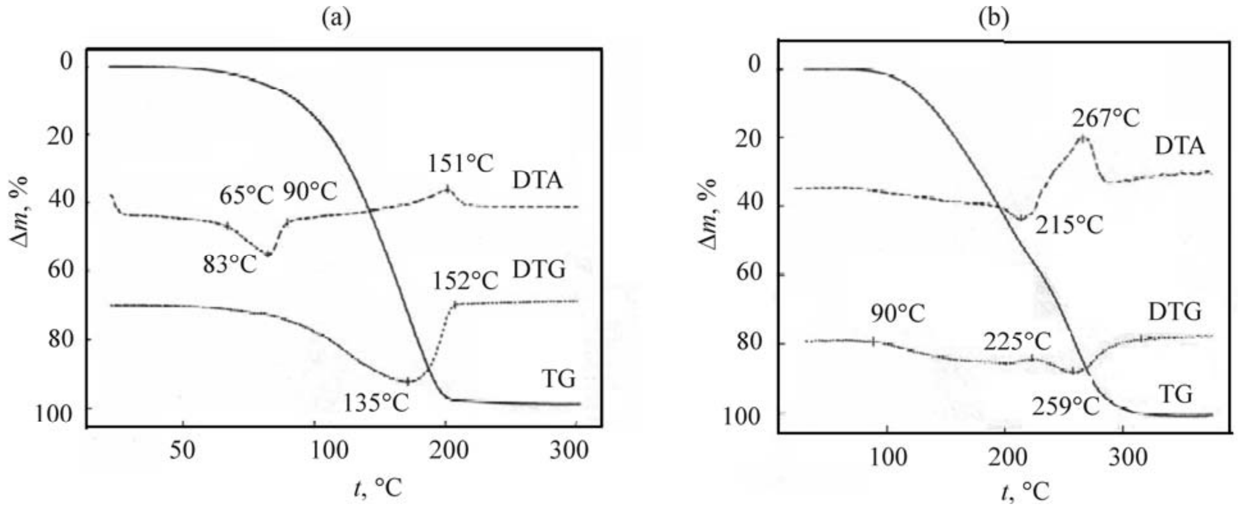

Fig. 10. Derivatographic data for the samples of (a) low- and (b) high-temperature fractions of ultradispered polytetrafluoroethylene powder.

sity of the spectral signals suggests their significant amount and, correspondingly, small size of the molecular chains. The spectra of the high-temperature fractions do not contain these signals, and this suggests a significant size of the macromolecules.

It should be noted that an advantage offered by the low-molecular-weight fraction consists in its solubility in supercritical carbon dioxide.

CONCLUSIONS

Nano- and microsize fluoropolymer particles can be formed from the gas phase of the polytetrafluoroethylene pyrolysis products. The size of the fluoropolymer nanoaerosol particles can be controlled by temperature and time of pyrolysis of the initial polymer.

The powder monoparticles can have a continuous or a block structure. The powder prepared by the gas-phase method contains two fluoropolymer types corresponding to the low- and high-molecular-weight fractions, respectively. These fractions can be partitioned by repeated heat treatment of the product.

ACKNOWLEDGMENTS

The authors are grateful for helpful cooperation in joint researches on the subject discussed to colleagues: O.M. Gorbenko, L.N. Ignat’eva, and A.K. Tsvetnikov from the Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences; M. P. Anisimov and I. N. Mikhalin from the Institute of Catalysis, Siberian Division, Russian Academy of Sciences; and P. P. Semyannikov from the Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences.

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