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Radiation-Chemical Synthesis of Tetrafluoroethylene Telomers and Their Use for Preparation of Thin Protective Fluoropolymer Coatings

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Abstract—The specific features and possibilities of preparation of protective coatings and composite materials based on fluoromonomers using high-energy rays (^{60}Co γ-rays, fast electrons) were analyzed. The emphasis was placed on synthesis and application of tetrafluoroethylene telomers in acetone. The structure and properties of telomers were examined by IR and NMR spectroscopy, as well as by X-ray diffraction analysis and diathermy. The radiation initiation allows preparation of new products with a broad spectrum of functional properties and opens wider prospects for technological application of fluoromonomers.

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Polytetrafluoroethylene combines a set of valuable properties with some drawbacks limiting its application. In particular, polytetrafluoroethylene is insoluble in virtually all known solvents, is hard to process, and exhibits weak adhesion. Also, deposition of thin controlled polytetrafluoroethylene coatings poses certain problems. These drawbacks are partly associated with a high molecular weight of polytetrafluoroethylene. Fluoropolymer coatings are typically deposited from suspensions containing emulsifiers, stabilizers, whose residues contaminate the resulting coatings and worsen their properties. Preparation of a defect-free coating may be a difficult task involving deposition of numerous consecutive layers.

A solution to these problems, in particular, that of preparation of thin fluoropolymer coatings, can be found in the use of low-molecular-weight fluorine-containing polymers. They can be synthesized by telomerization. (It should be reminded that telomerization is a special type of polymerization run in the presence of chain transfer agents, which yields a mixture of low-molecular-weight homologues, telomers, characterized by the degree of polymerization ≤10–20). Under the initiating γ-radiation exposure telomerization does not require special reaction initiators. In this case, the reaction is initiated by solvent radicals formed under radiation exposure, and solvent molecules can act as chain transfer agents, telogens. Further advantages offered by radiation-chemical synthesis of telomers consist in that the reaction initiation rate is temperature-independent and that, in the absence in the reaction system of emulsifiers and catalysts (except for initiators), high-purity products can be obtained in an environment-friendly manner. The corresponding procedures can be implemented in a fairly easy way as regards preparation of products and deposition of thin coatings. Telomers are synthesized in a liquid phase, which allows deposition of coatings by traditional methods using sprayers, brushes, etc.

Telomerization of Tetrafluoroethylene

The systems research efforts with respect to radiation-chemical processes, undertaken by the

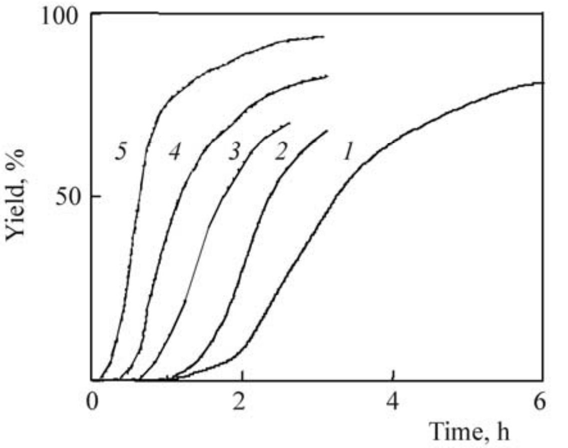

Fig. 1. Kinetic curves of the yield of tetrafluoroethylene telomers at different γ-radiation dose rates, Gy s^{-1}: (*1*) 0.08; (*2*) 0.14; (*3*) 0.28; (*4*) 0.39; and (*5*) 0.82. Initial monomer concentration 0.4 M.

Institute of Chemical Physics Problems, Russian Academy of Sciences, demonstrated that solutions of tetrafluoroethylene telomers can be obtained with the use of ionizing radiation (^{60}Co γ-rays) [1–3]. These solutions are suitable for preparation of thin coatings with the properties similar to those of polytetrafluoroethylene coatings. The flowsheet for telomer synthesis and preparation of coatings includes the following stages: preparation of a monomer solution (removal of atmospheric oxygen and saturation of the solution with the monomer); radiation-induced polymerization of tetrafluoroethylene in solution; deposition of the coating; and final surface treatment.

Radiation-induced telomerization of tetrafluoroethylene solutions is a vigorous process yielding a transparent, slightly viscous, solution. The measurements of the rate of the process in time showed that, under initiating γ-radiation exposure, the telomerization rate gradually increases and reaches saturation. When γ-radiation is “switched off,” the rate of the process rapidly decreases to zero; when it is once again “switched on”, no autoacceleration is observed, and the rate of the process rapidly regains the previous value. This suggests that the autoacceleration of the process, observed when the initiating radiation was “switched on” for the first time, is evidently associated with the presence of weak inhibitor traces in the system, rather than with accumulation of reactive centers in the initial stage of the reaction.

Figure 1 shows the plots of the yield of the product vs. time for different γ-radiation dose rates *I*. It is seen that virtually 100% yield of the product is achieved within several hours of the process (2–6 h, depending on the radiation dose rate). With increasing dose rate the process rate w tends to increase. The calorimetric measurements by the technique described in [1] showed that the steady-state rate of the process varies as $w \sim I^{0.5}$. This suggests a square-law kinetic chain termination in the system examined.

Telomerization follows a radical mechanism, as suggested by its active suppression by typical radical inhibitors (oxygen and hydroquinone). The average molecular weight of the telomer was estimated at 550 from the measured heat effects of condensation and the molecular-weight distribution determined by gel-permeation chromatography.

The following mechanism of radiation-induced telomerization of tetrafluoroethylene in acetone was suggested:

(1) chain initiation with radicals yielded by radiolysis of the monomer or solvent (•H, •CH_3, •CH_2COCH_3);

(2) chain propagation

$$\bullet R + C_2F_2 \rightarrow \bullet R{-}CF_2{-}CF_2;$$

(3) chain transfer via solvent

$$R(C_2F_4)_n + CH_3COCH_3 \rightarrow R(C_2F_4)_nH\bullet + CH_2COCH_3$$

(the arising radical •CH_2COCH_3 once again initiates the telomerization chain propagation); and

(4) chain termination via recombination of the •R—CF_2—CF_2, •CH_3, and •CH_2COCH_3 radicals.

The chain transfer reaction in this system is highly efficient, as suggested by the following simple comparison. The radiation yield (the amount of the monomer spent) is 10^3 molecules per 100 eV energy taken up, which allows estimating the kinetic chain length at $\nu_c \approx 10^3$ monomer molecules. At the same time, the measured molecular weight of the telomer suggests that it contains ν_m= 5–6 monomer units (ν_m is the “material” chain length). Hence, there are $\nu_c/\nu_m \approx$ 200 telomer molecules per primary radical yielded by radiolysis. In terms of the considered scheme, the empirical formula of the telomer can be represented as $R^1(C_2F_4)_nR^2$, where R^1 and R^2 = H, CH_3, CH_2COCH_3 with n = 5–6.

The rate of the process and the properties of the resulting telomer solutions depend on the tetrafluoroethylene concentration in the initial solution. The

Characteristics of the telomer solution of tetrafluoroethylene in acetone

Monomer concentration in the initial solution, wt %	Weight average molecular weight of telomer, M_w	Repetitive solubility in acetone, wt %	Notes
0.35	300	78	Transparent solution
0.63	310	64	The same
1.5	600	40	Opalescent solution
2.0	610	30	The same
3.3	540	18	Jelly-like solution
4.38	650	9.5	The same
7.2	840	–	Dense jelly-like solution
24	–	0	The same

steady-state rate of telomerization tends to increase with increasing monomer concentration in the initial solution. Hence, the reaction order with respect to the monomer concentration exceeds unity. This is evidently due to participation of the monomer in the chain initiation [1]. The table lists selected characteristics of the telomer solutions for various initial tetrafluoroethylene concentrations upon completion of the process (100% yield of the product). Detailed IR- and NMR-spectroscopic examinations [4] of the composition and structure of the products formed in the telomer solution of tetrafluoroethylene in acetone showed the following.

The IR absorption spectrum of the telomer solution of tetrafluoroethylene (Fig. 2; the spectrum of neat acetone is given for comparison) contains bands at 1154, 642, 625, and 555 cm^{-1} characteristic for solid polytetrafluoroethylene [5]. The most intense band (1154 cm^{-1}) is associated with the stretching C–F vibrations in the CF_2 group of the polytetrafluoroethylene chain. (Another intense band in the IR spectrum of polytetrafluoroethylene, observed at 1212 cm^{-1}, is obscured by the band associated with acetone). The fluorocarbon chains in polytetrafluoroethylene assume a helical conformation, and some chain segments are the sites of transitions between the right- and left-handed helices at room temperature, whose number varies with temperature [6]. This structural feature of polytetrafluoroethylene macromolecules is manifested in the IR spectra via bands at 640 and 625 cm^{-1}. Both these bands are observed in the IR spectrum of a telomer solution as well. The band at 555 cm^{-1}, also observed in the spectra of polytetrafluoroethylene, is associated with the bending vibrations of the CF_2 group. Along with these lines, a broadened inflection obscured by the line of acetone is observed at 519 cm^{-1}, which can be associated with the band at 514 cm^{-1}, characteristic for out-of-plane vibrations of the CF_2 group. This band serves as indicator of the crystaslline ordering of the polymer macromolecules.

Thus, the IR-spectroscopic data for tetrafluoroethylene telomer solutions suggest that they contain chain helices consisting of CF_2 moieties. The quantum-chemical calculations for oligomer fluorocarbon chains [7] showed that the macromolecule assumes a helical conformation if there are over five CF_2 units in the oligomer. Also, the chain structure has a defect (a band at 625 cm^{-1}) associated with transitions between the right- and left-handed segments of the molecular chains, which also suggests the presence in the telomer solution of chains containing more than five CF_2 units. The presence of fairly long molecular chains was

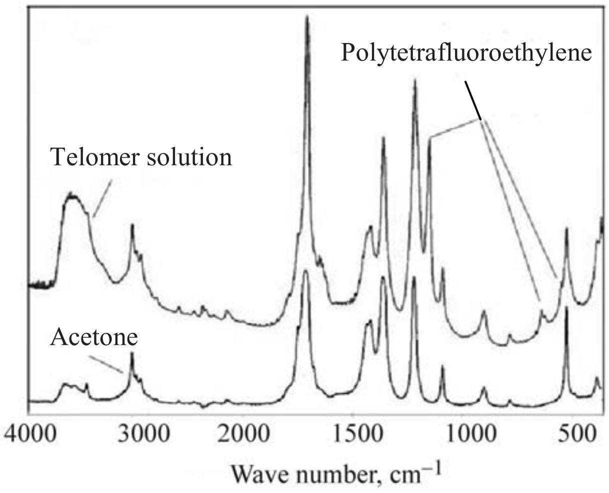

Fig. 2. IR absorption spectra of telomer solution of tetrafluoroethylene in acetone.

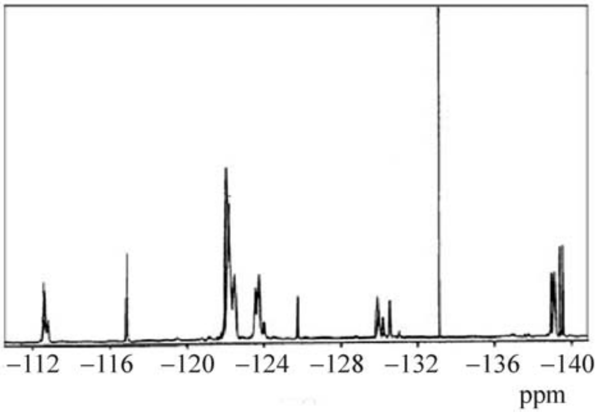

Fig. 3. ^{19}F NMR spectrum of the telomer solution of tetrafluoroethylene in acetone.

confirmed by Kiruykhin et al. [1] who revealed a fairly broad molecular-weight distribution, in particular, for the high-molecular-weight region.

An NMR-spectroscopic study [4] provided further, more detailed, information on the structure of fluorinated molecular moieties in the telomer solutions. The ^{19}F NMR spectrum (Fig. 3) contains a large number of resonance lines with different multiplicities, ranging from –110 to –140 ppm. Also, the spectrum contains singlet signals corresponding to different chemical shifts. For example, the NMR spectrum taken after prolonged storage of the sample at room temperature does not contain a singlet at –82.9 ppm, and new signals appear at –77.6 and –141 ppm. Hence, the telomer solution is the site of formation of new fluorocarbon compounds, rather than a static system. Along with narrow (~1-Hz) spectral lines, the spectrum contains 50-Hz and broader components. This broadening may be associated with the presence of fluorocarbon oligomers containing different numbers of CF_2 groups.

The ratio of the integrated intensities of the lines in the ^{19}F NMR spectra suggests that the main products (no less than 90%) of tetrafluoroethylene telomerization in acetone are telomers whose structure, as mentioned above, can be represented as $R^1(C_2F_4)_nR^2$ with R^1 and R^2 = H, CH_3, CH_2COCH_3 with $n = 5–6$. Also, the following products can be formed: 4,4,5,5-tetrafluoropentanone-2; perfluoroacetone, or trifluoroacetone; $CF_3–CH_2–X$, where X = $(O=C)–CH_3X$; perfluorocyclobutane C_4F_8 or prefluorocyclohexane C_6F_{12}; and $HCF_2–(CF_{2–n}H_n)_xR$, where $n = 0–1$, $x = 3–5$, R = $–(C=O)–CH_3$. It was found that the telomer structure is independent of the irradiation dose within 2.5–20 kGy. The resulting telomer solutions are unstable systems whose composition can vary with time depending on the actual conditions.

Thin Coatings Based on Tetrafluoroethylene Telomers

Buznik et al. [8] examined the molecular and morphological structures of the fluoropolymer product prepared by deposition from tetrafluoroethylene telomer solutions in acetone onto various substrates (glass, metal, wood). Evaporation of acetone leaves behind a white fluoropolymer product on the substrate surface. The IR- and NMR-spectroscopic, as well as atomic-force microscopic examinations and X-ray phase analysis, showed that the molecular structure of this product is close to that of high-molecular-weight commercial polytetrafluoroethylene F-4. The substance on the substrate surface consists of helical chains comprised of CF_2 groups, but these chains are shorter and include terminal $CH_3–C(=O)–CH_2–$ groups. The helix contains more than five CF_2 units, since otherwise the chains cannot form helices.

The X-ray powder diffraction patterns of the product provide the following information on the ordering of the macromolecules. These patterns strongly depend on the preparation technology and history of samples, but in all cases they contain an intense peak corresponding to the Bragg's angle of 18°, as well as a diffuse halo at 30°–50° [9, 10]. The X-ray diffraction patterns of the samples characterized by high degrees of crystallinity also contain further narrow peaks characteristic for crystalline phases. The halo is associated with special forms of disordering of the macromolecules whose topology is different from those of amorphous and crystalline phases [10]. The X-ray diffraction pattern of the powder (Fig. 4) contains the above-mentioned peak and a halo; other peaks characteristic for crystalline polytetrafluoroethylene (shown with points in Fig. 4) are virtually completely obscured by noise. Hence, there is a small proportion of a crystalline phase in the sample. It should be noted that the main peak to halo intensity ratio for the powder is much smaller than that for samples of commercial polytetrafluoroethylene and Forum product (ultradispersed polytetrafluoroethylene). This evidences a stronger topological disordering in the sample examined. The diffuse peaks observed at $2\theta = 9°$ and 12°–26° are apparently associated with an amorphous phase in which the nature of topological disorder differs from that in the phases corresponding to the halo at 30°–50°.

The morphological structure of the fluoropolymer product yielded by drying of the telomer solution on the substrate, specifically, of the coating formed on a silicon wafer, was examined by atomic-force microscopy (AFM). The resulting AFM images were compared with those for F-4 commercial polytetrafluoroethylene (Fig. 5). The F-4 coating is comprised of lamella stacks (Figs. 5a, 5b), whose edges egress to the surface as mutually parallel stacks of extended structures. Such pattern is characteristic for crystalline fluoropolymers.

The sample of interest exhibits a basically different morphology (Figs. 5c, 5d). The coating surface is represented by irregularly shaped block moieties widely varying in size (from 100 to 1500 nm). This pattern is more typical for disordered (amorphous) fluoropolymers. The coating is not continuous, as evidenced by dark uncoated domains seen in the image obtained in the amplitude modulation mode (Fig. 5c). At the same time, the phase contrast image (Fig. 5d) is indicative of lamellar structural elements. Selected

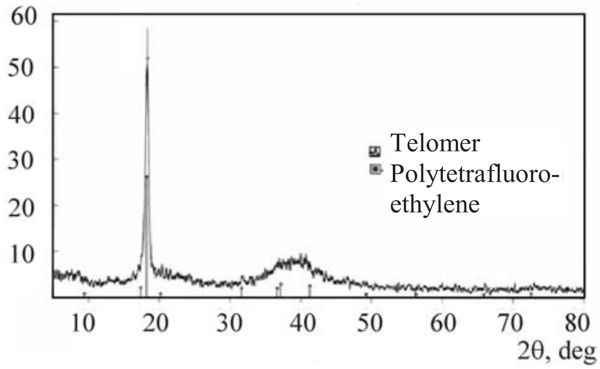

Fig. 4. X-ray diffraction pattern of the powdered material obtained upon drying of the telomer solution of tetrafluoroethylene in acetone. Points designate the positions of the crystalline reflexes for polytetrafluoroethylene.

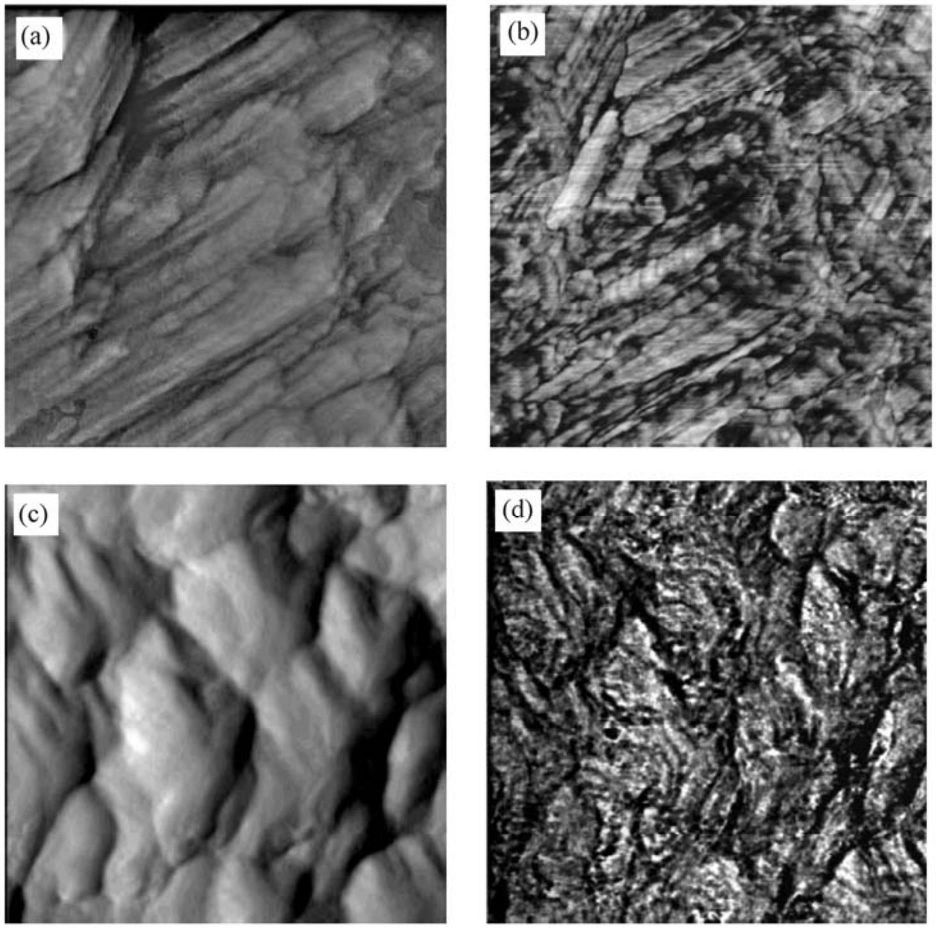

Fig. 5. AFM image of the coating based on (a, b) F-4 fluoroplastic and (c, d) telomer solution of tetrafluoroethylene: (a, c) amplitude modulation and (b, d) phase contrast mode.

domains of the coating deposited from a solution of fluorinated telomer are characterized by nearly parallel alignment of lamellas in the stacks. This can be associated with egress to the surface of the edges of the stacks, but the same may also be true of individual fibrous structures aligned in one direction. However, by contrast to F-4, this is not explicit alignment in a well-defined direction. This allows a presumption that the examined sample contains crystalline ordering elements characteristic for polytetrafluoroethylene.

The thermal analysis data for the fluoropolymer product obtained in an argon atmosphere and in air are absolutely identical, which suggests that thermal degradation of this product does not involve oxidation processes. Thermal degradation of the sample in an argon atmosphere proceeds in three stages: at temperatures within 100–305°C, 305–450°C, and 450–560°C (Fig. 6). The process onset temperature is much lower than that in the case of F-4 commercial fluoroplastic, for which an appreciable mass loss is observed at 500–550°C. A substantial broadening of the temperature range of degradation for the product can be associated with phases characterized by different heat resistances. Possibly, these phases have different molecular weights. In the first stage, the mass loss rate for the sample is 1.9–2.2% min^{-1} with the mass loss of 64.4%, and in the second stage, it is appreciably lower, 0.5% min^{-1}, with the mass loss of 20.4%. The remaining mass of the sample (13.8%) is lost in the third stage at a rate of 0.65% min^{-1}.

As known, the temperatures corresponding to heat effects in polymers (melting, mass loss onset) depend on the molecular weight [11]. In low-molecular-weight phases of the polymer, the onset of the processes is observed at lower temperatures. Hence, the first stage of thermal degradation of the fluoropolymer product most likely involves the low-molecular-weight fraction, and subsequent heating causes degradation of the high-molecular-weight fractions.

The temperature dependence obtained by differential scanning calorimetry also exhibits specific features within the temperature ranges mentioned. The first temperature range is characterized by a weak and extended exothermic peak, and the two other ranges, by broad exothermic peaks. These broadened patterns are most likely associated with a wide scatter of the molecular weights of different phases of the polymer of interest.

Heating of the tetrafluoroethylene telomer samples to 180–200°C causes a loss of terminal acetone moieties of the macromolecule, softening of the fluoropolymer, and its spread over the substrate surface.

This yields a continuous 1–5-μm-thick fluoropolymer film, whose structure and properties are close to those of polytetrafluoroethylene.

Thus, tetrafluoroethylene telomer solutions are suitable for preparation of thin protective hydrophobic coatings on various materials and articles [2, 3, 12, 13]. Deposition of the coatings does not create

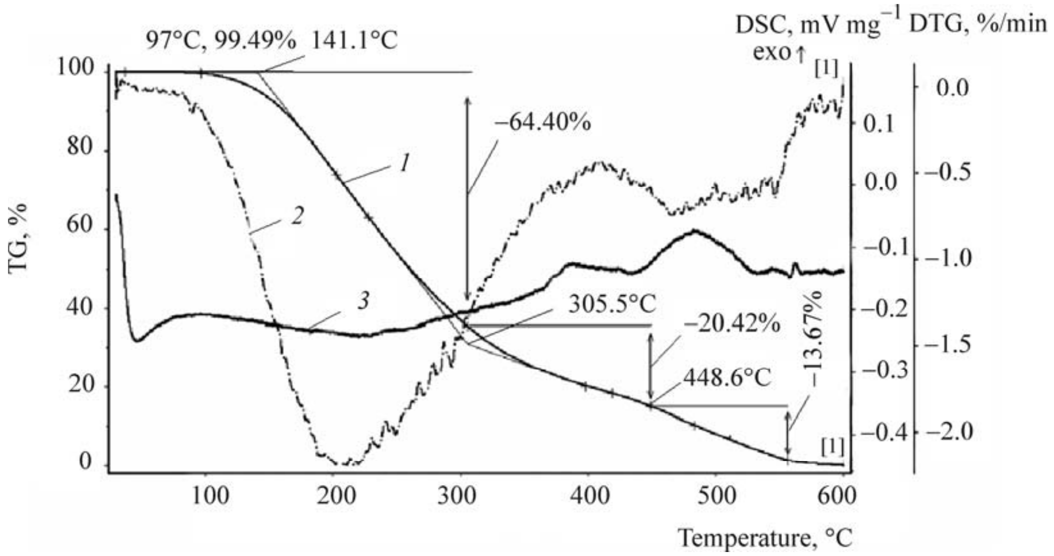

Fig. 6. Thermogravimetric and differential scanning calorimetric curves for a fluoropolymer material obtained in an argon atmosphere: (*1*) thermogravimetry (TG), mass loss; (*2*) differential thermogravimetry (DTG); and (*3*) differential scanning calorimetry (DSC).

technological difficulties and utilizes traditional techniques (brushing, immersing, spraying). Tetrafluoroethylene telomer solutions are suitable for impregnation of fabrics, wood, asbestos, cement, building brick, facing materials, as well as metal, ceramic, and other items, in order to impart them chemical stability, as well as hydrophobic and antifriction properties and wear resistance. Small thickness of the films allows preparation of transparent coatings with good thermal conductivities. The method being developed can be implemented as a simple continuous process.

ACKNOWLEDGMENTS

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