ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 3, pp. 578–588. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © L.N. Nikitin, M.O. Gallyamov, E.E. Said-Galiev, A.R. Khokhlov, V.M. Buznik, 2009, published in Rossiiskii Khimicheskii Zhurnal, 2009, Vol. 52, No. 3, pp. 56–65.

# Supercritical Carbon Dioxide: A Reactive Medium for Chemical Processes Involving Fluoropolymers

**L. N. Nikitin[a], M. O. Gallyamov[b], E. E. Said-Galiev[a],
A. R. Khokhlov[b], and V. M. Buznik[c]**

[a] *Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences,
ul. Vavilova 28, Moscow, 119991 Russia
e-mail: link@ineos.ac.ru; thor@ineos.ac.ru*

[b] *Faculty of Chemistry, Moscow State University, Vorob'evy gory 1, Moscow, 119992 Russia
e-mail: khokhlov@polly.phys.msu.ru*

[c] *Baikov Institute of Metallurgy and Materials Science, Leninskii pr. 49, Moscow, 119991 Russia
e-mail: bouznik@ngs.ru*

Received February 1, 2008

**Abstract**—The application of supercritical carbon dioxide for deposition of fluoropolymer coatings on various substrates and formation of superhydrophobic surfaces and composite core-shell microparticles was discussed.

**DOI:** 10.1134/S1070363209030396

## INTRODUCTION

Substances in the supercritical state have diversified technological application. Among them, special interest is attracted by supercritical carbon dioxide as a candidate medium to replace numerous environmentally unsafe solvents, in particular, those used in synthesis and modification of polymers [1–3], as well as in extraction, chromatography, etc. [4]. Supercritical $CO_2$ is incombustible, nontoxic, and relatively inert in chemical processes, and these physicochemical properties are specifically responsible for its extensive application [1–3]. It should also be noted that a transition of carbon dioxide to the supercritical state occurs at fairly low pressures (7.38 MPa) and temperatures (31.1°C). This allows reuse of this solvent without further purification, and the target product needs no treatment to remove $CO_2$ (because of its transition to the gas phase with decreasing pressure and/or temperatures). A specific feature of supercritical media is that pressure and/or temperature variations cause smooth modification of their properties (density, viscosity, dielectric properties, dissolving power, etc.), which provides an additional opportunity to affect the route of chemical or physical processes.

Supercritical carbon dioxide is not oxidized and is inert to free radicals, which makes it suitable as solvent for various chemical applications involving polymerization and polycondensation [5, 6]. Low viscosity (up to ~100 times lower than that of liquids) and high diffusion coefficient (~100 times higher than that of liquids) makes it applicable for modifying polymers, including fluoropolymers [7–22].

As known, fluoropolymers find extensive industrial and engineering application [23, 24]. However, they combine valuable properties with an essential drawback, difficult technological implementation. This stimulates a permanent search for techniques utilizing fluoropolymers as part of various technologies that apply nonclassical methods.

Here, we discuss the specific features and advantages offered by supercritical $CO_2$ as a reactive medium for deposition of fluoropolymer nanolayers onto various substrates, intended for preparation of superhydrophobic surfaces and development of core-shell microparticles. These research efforts are of special significance, since most of fluoropolymers is insoluble in conventional solvents, which makes standard technologies utilizing solutions inapplicable in their case.

## Deposition of Nanometer-Size Fluoropolymer Layers

Deposition of thin coatings from polymer solutions onto substrates is usually complicated by nonequilibrium solvent drying, which can result in uncontrollable increase in the local concentrations and manifestation of surface tension forces. Moreover, when coatings are deposited from nonvolatile, difficultly removable solvents, the latter can be retained in polymer films, thereby deteriorating the quality of coatings and reproducibility of the results. In this respect, supercritical carbon dioxide offers certain advantages as solvent: When $CO_2$ (a gas at atmospheric pressure) is removed from the coating, a drying up film is not formed, which precludes reorganization of the polymer layers being deposited, and also the problem of residual solvent is avoided. This makes supercritical $CO_2$ a promising solvent for deposition of ultrathin polymer layers.

The solubility of polymers in supercritical $CO_2$ is pressure- and temperature-dependent: It typically increases with increasing pressure and varies with temperature in a more complex manner. For example, at pressures of up to ~15 MPa some polymers exhibit a decrease in solubility with increasing temperature, and an increase in solubility with increasing pressure and temperature. Such temperature dependence of the solubility is typically associated with competition of two factors: a decrease in the density of medium with increasing temperature at a constant pressure and an increase in saturated vapor pressure of the solute under heating. The former process dominates at pressures of up to ~15 MPa, and the latter, at increased pressures [25]. Among fluorine-containing polymers, polyfluoroacrylates are soluble [26]; polyperfluoropropylene oxide [4, 27–31] and perfluoroethers are partly soluble in supercritical $CO_2$, and other fluorinated polymers are also characterized by certain solubility [33–36].

Most of the published data on application of supercritical $CO_2$ as a carrier of polymer molecules in preparation of thin coatings were obtained with the use of the Rapid Expansion of Supercritical Solutions (RESS) method. Here, we will focus on the method of preparation of thin coatings by controlled deterioration of the thermodynamic quality of supercritical solvent. This method consists in preparation of a polymer solution in a reactor with a solvent in supercritical state, into which a substrate is introduced, whereupon the temperature and pressure are decreased. This causes the solubility of the polymer in the medium of interest to decrease, and in this “bad” solvent the polymer molecules are deposited onto accessible surfaces, including the substrate surface.

Relevant studies are few, but, in our opinion, they are indicative of the promise offered by this fairly simple method. For example, Novick et al. [37] examined deposition of thin perfluoroether-based coatings from solution in liquid carbon dioxide onto solid substrates. Liquid $CO_2$, similar to supercritical $CO_2$, is an efficient solvent for thin film formation. Its low viscosity and small surface tension favor penetration of the dissolved polymer into surface pores and defects. Like in the case of supercritical $CO_2$, variation of the temperature and pressure allows controlling the balance of the interaction of the solvent, polymer, and substrate and choosing the best conditions for preparation of defect-free coatings with the desired thickness and maximal uniformity. This method enables preparation of 3.5–35-nm-thick coatings.

Wang et al. [38] carried out deposition of ultrathin (2-nm on the average) protective coatings prepared from fluorinated alternating methyl vinyl ester–maleic acid anhydride copolymer onto multiwall carbon nanotubes in supercritical $CO_2$. By varying pressure it was possible to prepare coatings from high-molecular-weight fractions of the copolymer, with low-molecular-weight fractions removed in the course of the process. Those results are of much significance for development of new nanomaterials.

Hoggan et al. [39] deposited thin perfluorooctyl methacrylate–*tert*-butyl methacrylate copolymer coatings from liquid $CO_2$ onto a rotating silicon substrate. This allowed preparation of 0.1–3-μm coatings, of which those thinner than 1 μm were highly nonuniform.

Thin protective polymeric coatings were deposited from polyvinyl diphenyl and polyvinylidene fluoride solutions in supercritical $CO_2$ onto metal powder samples and silicon substrates. An atomic-force microscopic (AFM) examination of the morphology of the deposited structures by Glebov et al. [40] showed that the coatings on silicon substrates are distinguished by nonuniform thickness. Also, those experiments revealed protector properties of coatings deposited onto metal powders.

Cho et al. [41] carried out deposition of mono- and submonolayers (up to 1.5 nm) of a styrene–dimethylsiloxane copolymer onto polystyrene surface in supercritical $CO_2$. Those experiments showed that the thickness of the coating can be controlled by varying the process conditions (pressure, temperature). The deposition of the coatings was ascertained from increase in the water contact angle for polystyrene and from X-ray photoelectron spectroscopic data.

In our opinion, of much interest are the data reported by Puniredd and Srinivasan [42] who deposited polyamidoamine dendrimer and pyromellitic acid dianhydride coatings as alternating layers onto modified silicon or quartz substrates in supercritical $CO_2$. Those experiments showed that alternating layers can be grown up to the desired thickness. The layers are covalently bound to one another and to the substrate.

Let us discuss in more detail studies demonstrating the progress achieved in development of thin high-quality fluorinated polymer coatings deposited onto various substrates.

Fluoropolymers soluble in supercritical $CO_2$ include commercial Teflon AF materials available from DuPont. Polymers of this type can be fairly easily dissolved under laboratory and industrial conditions and are characterized by high chemical stability, which makes them suitable for preparation of protective coatings. We examined Teflon AF 2400, a copolymer of tetrafluoroethylene with 4,5-diflouoro-2,2-bis(trifluoromethyl)-1,3-dioxolane (87 mol % dioxolane moieties, relative molecular weight $10^5$, density 1.6 g $cm^{-3}$, glass transition temperature 250°C) [10]. We carried out dissolution and redeposition of this material onto various substrates, with AFM monitoring of the morphology of the deposited structures. Those experiments showed that highly uniform defect-free nanometer-size fluoropolymer films can be deposited from supercritical $CO_2$.

Also, much promise for preparation of thin coatings is shown by ultradispersed polytetrafluoroethylene (Forum trade mark) comprising spherical particles with the average statistical diameter of ~500 nm. Mica (muscovite) and highly oriented pyrolytic graphite (pyrographite) served as substrates for deposition of thin polymeric layers. These substrates were used for preparation of atomically smooth surfaces with angstrom level roughness by splitting of interlayer sites. These materials differ in the physicochemical properties: mica is polar, hydrophilic, has a high surface energy, and is charged in aqueous media, and graphite is nonpolar and more hydrophobic.

Studies by Rindfleisch et al. [43], as well as our studies, showed that the solubility region for Teflon AF 2400 and ultradispersed polytetrafluoroethylene in supercritical $CO_2$ is above 65°C at pressures of 50–70 MPa. The thin-film coating deposition technique [10, 12, 15] implies keeping a weighed portion of the polymer and the substrate in supercritical $CO_2$ in an autoclave at temperatures and pressures at which the polymer is soluble. After the equilibrium state is achieved for the polymer solution in liquid $CO_2$, the temperature in the autoclave is decreased at a constant volume (isochoric process), which causes the pressure to decrease as well. As a result, the polymer molecules lose solubility and are deposited onto the inner surface of the autoclave and onto the substrate. Upon completion of the polymer deposition, the autoclave is degassed, and the substrate is taken out.

Figures 1 and 2 show the AFM images of thin-film Teflon AF 2400 coatings deposited onto pyrographite and mica. The coatings deposited on pyrographite are characterized by nanometer thickness and high uniformity (0.4–0.6-nm roughness) unachievable with traditional methods of coating preparation with the use of liquid solvents or even with the RESS method. This suggests dense packing of the macromolecules in the coating. These films are qualitatively close to several monolayer-thick Langmuir-Blodgett films. However, the latter are often unstable and prone to reorganization [44, 45], by contrast to the films obtained by the above-described method. The films are resistant to local mechanical loads from the AFM probe not only in air but also in liquid media, e.g., in ethanol. The surface morphologies of films deposited onto pyrographite and mica are different. In the case of mica, formation of coatings is accompanied by structural reorganization of the macromolecules, which causes the thickness to increase to 60 nm and roughness, to 15 nm (Fig. 2a). Under milder dissolution conditions it is possible to prepare coating with a thickness of up to 4–7 nm and a roughness of up to 2 nm. The coating formed on the mica surface is nonuniform, and individual particles can be distinguished in the images (see Fig. 2b).

The above-described technique is also suitable for preparation of ultrarthin 2–3.5-nm polymer coatings from ultradispersed polytetrafluoroethylene on a mica substrate, and 2–8-nm coatings, on a pyrographite substrate (Fig. 3). Like in the case of Teflon AF 2400, the morphology of the deposited coating is strongly affected by the nature of the substrate. For example,

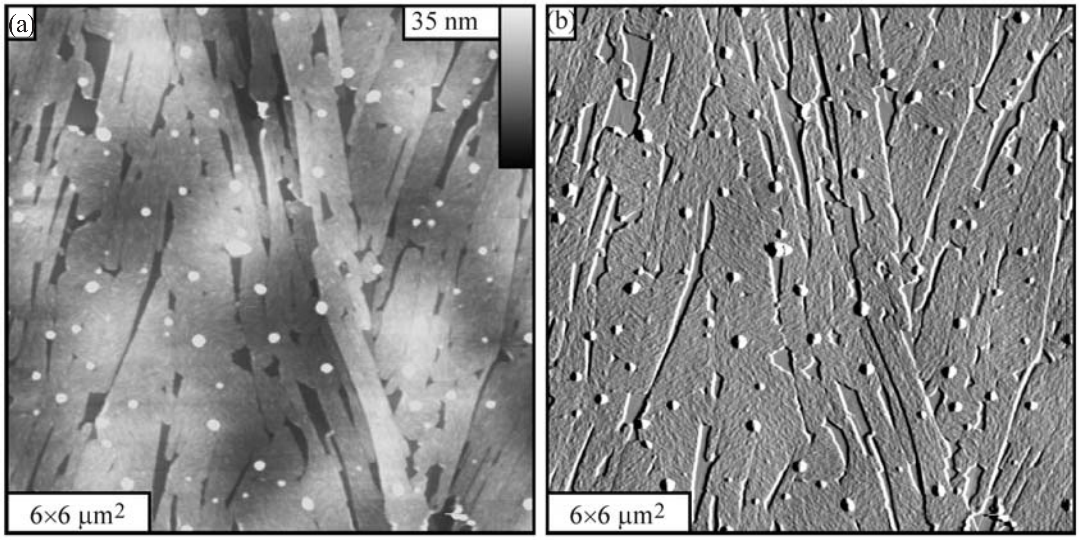

**Fig. 1.** AFM image of a Teflon AF film formed on a pyrographite substrate. Film preparation conditions: polymer and substrate exposure to supercritical $CO_2$ at 65°C, 75 MPa. AFM image obtained (a) in the tapping mode in air and (b) after mathematical processing by the "lighting" technique (to make the fine structure more prominent).

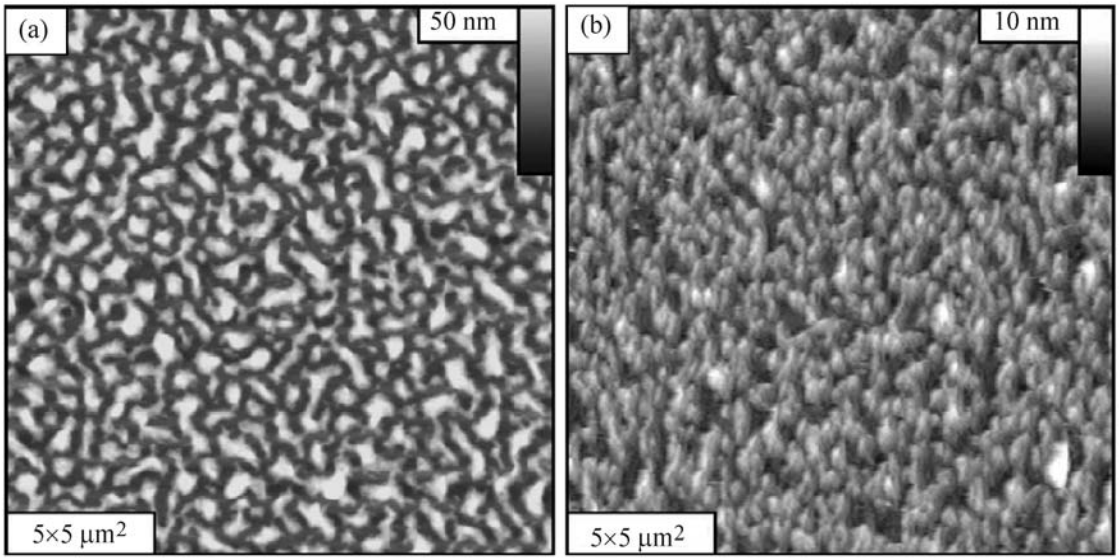

**Fig. 2.** AFM image of a Teflon AF film formed on a mica surface. Film preparation conditions: polymer and substrate exposure to supercritical $CO_2$ at (a) 65°C, 80 MPa for 6 h and (b) 40°C, 50 MPa for 3 h, followed by cooling to 25°C and decompression. The AFM images were obtained in the contact mode in air.

Figs. 3a and 3b reveal clear distinctions between the films deposited onto mica and pyrographite surfaces under identical conditions. Deposition onto the mica surface yields a more structured film with a more uniform height of the deposited structures (2.5–3.0 nm) above the substrate level. It should be noted that ultradispersed polytetrafluoroethylene films formed on pyrographite are less uniform and more defective than Teflon AF 2400 films. However, polytetrafluoro-ethylene films on the mica surface are more uniform than the films prepared from copolymer products which undergo reorganization on the substrate.

Thus, the use of supercritical $CO_2$ allows minimizing the reorganization of the film structure, induced by surface tension forces in a drying up liquid solvent droplet. This allows elucidation of the factors responsible for stability of nanometer-size thin poly-

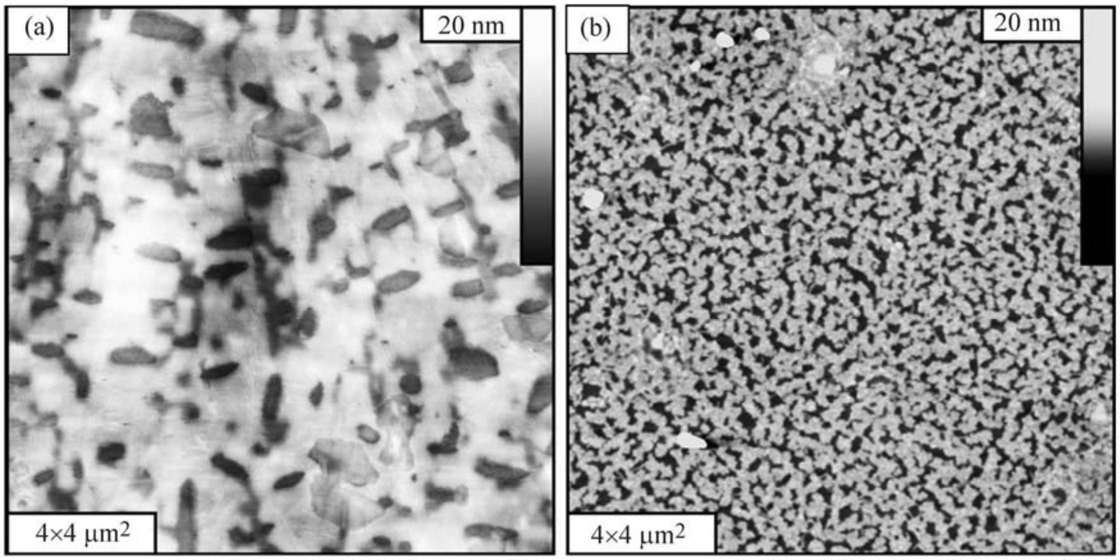

**Fig. 3.** AFM image of ultradispersed polytetrafluoroethylene films deposited onto (a) pyrographite and (b) mica substrate. Film preparation conditions: polymer and substrate exposure to supercritical $CO_2$ at 65°C, 75 MPa for 3 h, followed by cooling to 55°C and decompression. The AFM images were obtained in the tapping mode in air.

mer films in relation to the nature of the substrate and the polymer. Such studies are of much interest both from the fundamental and practical (optical, electronic, and medical applications) viewpoints.

### Preparation of Superhydrophobic Coatings

Deposition of uniform fluorine-containing polymer coatings from their solutions in supercritical carbon dioxide onto rough substrates imparts superhydrophobic properties to their surfaces, i.e., increases the water contact angle to 150° and over. Furthermore, modified surfaces exhibit a small contact angle hysteresis (several degrees). This facilitates removal of water droplets from the surfaces together with the particles of possible contaminants.

As known, the maximal water contact angle for smooth surfaces of hydrophobic materials does not exceed 120° and can be essentially increased via increasing roughness. There are two preconditions to formation of a superhydrophobic surface: (1) the surface should be rough with combined micro- and nanorelief features and (2) the surface material should be hydrophobic, i.e., the water contact angle for smooth surface of the material should exceed 90°.

Superhydrophobic coatings can be prepared by either of two techniques. One of them implies increaseing the roughness of initially smooth hydrophobic surface by such methods as, e.g., plasma, laser, or ion exposure, or deposition of a rough hydrophobic film. An alternative technique consists in imparting hydrophobizing properties to a rough surface.

It should be noted that, since recently, publications dedicated to superhydrophobicity have significantly increased in number (see reviews [46–53]).

The method for preparation of superhydrophobic coatings, implemented by us, implies deposition of a uniform film of a hydrophobizing agent, a fluorinated polymer, from a supercritical $CO_2$ solution. It is essential that the hydrophobic film covers the entire surface accessible for water droplets and vapor. If the walls of deep-lying pores will remain unmodified, they can become a site of vapor condensation, through which the surface will lose its superhydrophobic properties [54–56]. Also, when liquid solvents are used for hydrophobizing porous materials, capillary effect will prevent the hydrophobizing polymer solution from penetration into bottom pore areas, thereby reducing to zero the hydrophobization effect. With supercritical carbon dioxide this problem is eliminated because of the lacking surface tension. We used the above-described approach for deposition of thin Teflon AF 2400 and ultardispersed polytetrafluoroethylene coatings.

As substrates we tested various porous and rough materials: polymer track membranes, microporous and composite polymeric structures, porous woven and nonwoven materials, and nanostructured and crystalline surfaces.

We estimated the induced hydrophobicity degree for the modified surface from the water contact angle, as well as from the contact angle hysteresis. The results obtained for selected materials after fluoropolymer deposition from supercritical $CO_2$ on their surface are summarized in the table.

We successfully applied this method for hydrophobizing paper, fabrics, and carbon materials, as well as nanostructured graphite films [22]. In the case of paper, surface hydrophobizing is of much practical value for polygraphic applications, manufacture of photographic materials, etc.

Porous and rough carbon materials find extensive technological application as components of filters, sorbents, gas diffusion layers, electrodes. The deposited coating should not modify the structure and properties of the material (degree of porosity, pore size distribution, conductivity), and all this is provided by modification in supercritical $CO_2$.

Uniform hydrophobization of fabrics is topical for manufacture of separating filter systems in textile industry, as well as for preparation of functional elastic woven materials with controlled degree of permeability for biomedical applications. In the latter case, of much importance is biocompatibility of the fluoropolymers acting as hydrophobizing agents.

The method proposed is suitable for hydrophobizing inner surfaces of porous materials, as exemplified by deposition of a fluoropolymer coating onto an aluminum oxide-based ceramic sponge. Untreated sponge perfectly absorbs water due to capillary effects, and 15 s after it was brought into contact with water, the latter was spread in the bulk of a sponge sample (15 mm in height with 7×7-mm base), as suggested by $^1H$ NMR tomographic images. Deposition of an ultradispersed polytetrafluoroethylene fluoropolymer layer makes the sample hydrophobic and poorly absorbing water: Water is seen in the bottom part of the sample only after one hour. The hydrophobicity of the sponge with a fluorinated coating can be demonstrated by the following simple experiment: Untreated sample quickly sinks in a vessel filled with a large volume of water, while the treated sample remains on the water surface.

Providing higher stability and longer service life of superhydrophobic coatings is still a topical problem, whose solution can be found in the use of organofluorine compounds soluble in supercritical $CO_2$ and containing anchor groups through which they can form strong chemical bonds with the substrate surface [60]. Further development of this line will allow development of specific methods to impart superhydrophobic and superlyophobic properties to rough porous surfaces and items with intricate geometries.

In turn, preparation of superhydrophobic surfaces is promising for optimizing the parameters of gas

Water contact angle for the substrates and the deposited droplet–substrate contact area

| Substrate | Contact angle, deg | | Substrate contact area , $cm^2$ | | Water penetration into the porous structure of substrate |
|---|---|---|---|---|---|
| | after deposition | at droplet volume decreased by 50% | after deposition | at droplet volume decreased by 50% | |
| Paper | 84 | 50 | 0.075 | 0.075 | Observed |
| with ultradispesed polytetrafluoroethylene coating | 150 | 141 | 0.0095 | 0.0098 | Not observed |
| Nanostructured graphite substrate | 153 | 143 | 0.015 | 0.015 | Observed |
| with ultradispesed polytetrafluoroethylene coating | 158 | 154 | 0.009 | 0.007 | Not observed |
| Carbon fabric | 119 | 50 | 0.032 | 0.065 | Observed |
| with a Teflon AF 2400 coating | 133 | 116 | 0.022 | 0.024 | Not observed |

diffusion layers of membrane-electrode blocks for fuel rods, gas sensors, adsorbents, filters, sorbents in chromatographic columns, zeolites, microjet spray facilities, and typing elements of inkjet printers. Such modification of materials will provide better biocompatibility of transplants, catheters, and contact lenses and will allow creation of self-cleaning surfaces. The benefits provided by hydrophobization include: decreasing the resistance to water stream; protecting optical lenses, micro- or nanosystem facilities, and electron optical devices against contamination, and of dispersed particles of metals, gunpowders, and other porous combustible and explosive materials, against moisture condensation; imparting hydrophobic properties to fabrics, paper, and other materials; and safeguarding surfaces exposed to aggressive media. The method will allow preparation of thin antifriction coatings for units and mechanisms.

## Formation of Core-Shell Microparticles

Supercritical carbon dioxide is extensively used in formation of microcapsules, microparticles consisting of a core and a shell. This is a new type of materials with special physicochemical properties. They show promise for application in medicine and pharmacology (prolonged action medicines), food industry (encapsulation of flavonoids), and agriculture (new types of economical, prolonged action fertilizers and herbicides, whose application entails reduced amount of environmentally harmful materials).

The known experimental techniques for preparation of such materials are underlain by two approaches. The former is based on application of agents stabilizing the composite microparticles in a supercritical medium. In this connection, we will mention studies dedicated to water microemulsions in supercritical $CO_2$, whose stabilization is achieved with the use of fluorine-containing surfactants [58–60]. The water core of such capsules can serve as a microreactor for chemical synthesis [61, 62]. The latter approach to formation of composite particles is based on coprecipitation of the components of mixed solutions, when a precipitator is injected into the medium [63–66]. A solvent–precipitator pair can be represented by a supercritical medium combined with a gas phase [63] or with a liquid solvent [64–66]. This approach was applied for formation of, e.g., medicine particles coated with a polymer shell [63], as well as of composite protein [64], magnetic [65], and polymer microparticles with narrow size distribution [66]. An important benefit provided by supercritical $CO_2$ as the reaction medium consists in elimination of residual solvent problem, which is of special significance for pharmacological applications.

Below, we will discuss the method for formation of paraffin microparticles with a polymer shell comprised of ultradispersed polytetrafluoroethylene (model substances) in supercritical $CO_2$. This method implies paraffin emulsion stabilization in this medium by the fluoropolymer and, thus, takes advantage of the first of the two general approaches we described above. However, by contrast to the conventional technique of formation of composite particles in supercritical media [58–62], this method utilizes colloid particles of an ultradispersed material, rather than surfactants, as stabilization agents.

The microparticles were obtained in an autoclave at different ultradispersed polytetrafluoroethylene to paraffin ratios. The diameter of the resulting microparticles ranged from 50 to 300 μm, depending on the initial ratio of the mixture components. With paraffin material only (without fluoropolymer) the same technique did not allow formation of individual particles: When the autoclave was opened, it contained a homogeneous paraffin conglomerate.

Figure 4 shows the scanning electron microscopic images of the composite microparticles. They have a close to spherical shape. In the images with over ×2000 magnifications, a structure of the microcapsule surface and individual fluoropolymer particles forming a polymeric shell can be distinguished. The X-ray diffraction patterns of the microparticles contain, along with peaks characteristic for paraffin, those corresponding to polytetrafluoroethylene. Specifically, they belong both to the high-molecular-weight fraction and a low-molecular-weight fraction, with Bragg's angles of 4°.

The core-shell composite particles are formed by the following mechanism. In the temperature mode chosen, paraffin melts, and vigorous stirring of the mixture in supercritical $CO_2$ yields a paraffin emulsion stabilized with the fluoropolymer which precludes coagulation of the microparticles (this is a well-known effect of emulsions stabilization with solid colloid particles, the Pickering effect). Rapid cooling results in solidification of the paraffin emulsion microdroplets coated from outside with a layer of ultradispersed polytetrafluoroethylene particles, and the polymer coating prevents them from coagulation.

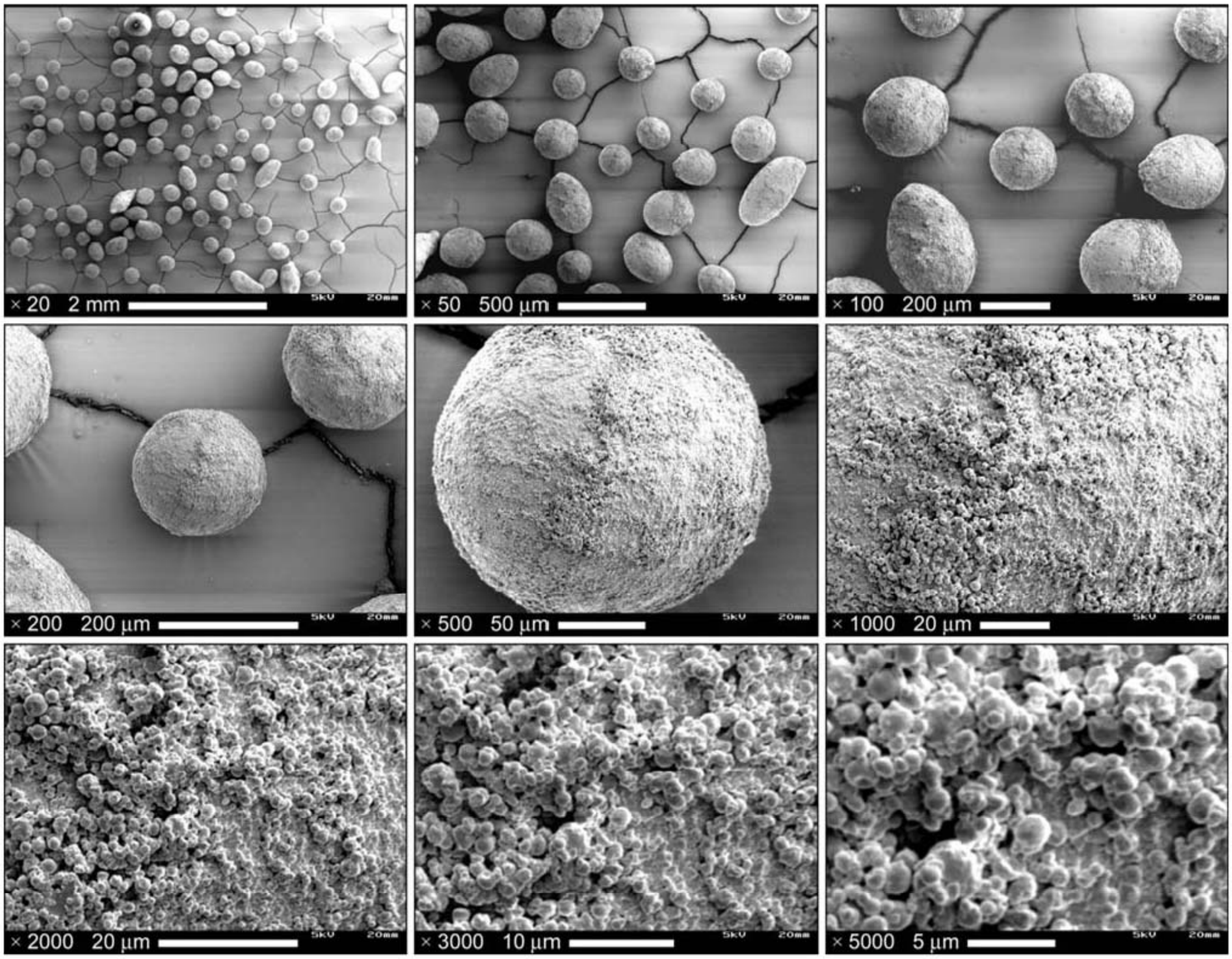

**Fig. 4.** Electron microscopic images of paraffin microparticles with ultradispersed polytetrafluoroethylene shell. This series of images was obtained at magnification successively increased from ×20 to ×5000.

The reason for emulsion stabilization by finely dispersed solid materials is that localization at the interface and stabilization of a certain type of emulsions (in our case, paraffin in supercritical $CO_2$ emulsion) is energetically more favorable for solid particles. The fluorine-containing polymer layer coats the paraffin particles from outside, thereby decreasing both the surface energy and the adhesion power of the particles. This versatile mechanism of emulsion stabilization does not impose rigid restrictions with respect to the triple system components, which makes ultradispersed polytetrafluoroethylene suitable for stabilization of emulsions of other materials in supercritical carbon dioxide.

Under presumption of complete segregation of the paraffin and fluoropolymer phases in the microparticles, the average thickness of the polymeric coating can be estimated from the mass ratio of the components, their density, and radius of the resulting composite particles. For an ultradispersed polytetrafluoroethylene layer this thickness was estimated at 1–1.5 μm. Figure 4 shows that this is a continuous coating, though some pores are also observed.

There exists an additional stabilizing factor for the polymer layer in the system of interest, namely, thermodynamic stability [71] of a thin fluoropolymer interlayer whose dielectric parameters are intermediate in the paraffin–fluoropolymer–solvent series. Indeed, supercritical carbon dioxide is characterized by lower dielectric permittivity and refraction index than solid materials, including fluoropolymers and paraffins. The fluoropolymers have poorer dielectric parameters than do paraffins and, hence, are intermediate in the series mentioned.

This stability condition will also be satisfied if paraffin will be replaced by any other nonpolar substance.

Thus, we implemented for the first time the technique of emulsion stabilization in a supercritical medium, in which the ultradispersed polymer material particles, rather than surfactants (a conventional approach), serve as stabilization agents.

The composite material obtained can find application as a new generation of ski ointments. The technique proposed can be fairly easily implemented on a commercial scale. Importantly, stirring in a melt in air or in an inert medium at atmospheric pressure, i.e. without supercritical $CO_2$, does not allow preparation of a sufficiently homogeneous paraffin–ultradispersed polytetrafluoroethylene mixture.

The developed technique implies a very general stabilization mechanism (especially the Pickering mechanism), which makes it suitable for a broad spectrum of encapsulation applications, in particular, in medicine, pharmacology, food industry, and agriculture.

## CONCLUSIONS

The recent decade has witnessed a growing interest in nonconventional, environmentally safe methods of polymer processing and modification. In this context, environmentally unfriendly processes and technologies utilizing harmful organic substances should be replaced by environmentally "acceptable" technologies. The latter can be underlain by the use of low-toxicity readily accessible inexpensive supercritical carbon dioxide as reactive medium in synthesis and modification of polymers and in other chemical processes. The physicochemical properties of supercritical $CO_2$ can be controlled by temperature and pressure, which makes it more flexible and versatile in application.

This approach found the technological applications discussed. Deposition of fluoropolymer coatings in supercritical $CO_2$ allows controlling the process and preparing nanometer-size layers via deteriorating the thermodynamic quality of this solvent by varying temperature and/or pressure. Nanometer-size fuoropolymer coatings deposited onto various materials impart superhydrophobic properties to their surface, thereby increasing the performance characteristics of the materials in many technological applications.

Finally, the new approach to formation of core-shell microparticles in supercritical $CO_2$, stabilized with fluoropolymers rather than with surfactants, will allow development of advanced "green" technologies.

## ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research (project nos. 07-03-91584, 08-03-00294, 08-03-90012_Bel_a), Russian Academy of Sciences (projects under complex programs of the Department of Chemistry and Materials Science, Russian Academy of Sciences "Development and Study of New Generations of Macromolecules and Macromolecular Structures" and "Development of New Metal, Ceramic, Polymer-Glass, and Composite Materials"), and Federal Agency for Science and Innovation of the Russian Federation (project no. 02.513.11.3230).

The authors are grateful to I. V. Koptyug (International Tomographic Center, Siberian Division, Russian Academy of Sciences) for recording the $^1H$ NMR tomograms.

## REFERENCES

1. Cooper, A.I., *J. Mater. Chem.*, 2000, vol. 10, p. 207.
2. Kazarian, S.G., *Polymer Science, C*, 2000, vol. 42, no. 1, p. 78.
3. Beckman, E.J., *J. Supercrit. Fluids*, 2004, vol. 28, p. 121.
4. McHugh, M.A. and Krukonis, V.J., *Supercritical Fluid Extraction: Principles and Practice*. Butterworth-Heinemann: Boston, MA, 1994.
5. Kendall, J.L., Canelas, D.A., Young, J.L., and DeSimone, J.M., *Chem. Rev.*, 1999, vol. 99, p. 543.
6. Said-Galiev, E.E., Pototskaya, I.V., and Vygodskii, Ya.S., *Vysokomol. Soed., Ser. C*, 2004, vol. 46, no. 12, p. 2124.
7. Said-Galiev, E.E., Vygodskii, Ya.S., Nikitin, L.N., Vinokur, R.A., Gallyamov, M.O., and Khohlov, A.R., *Vysokomol. Soed., Ser. B*, 2001, vol. 43, no. 8, p. 1434.
8. Nikitin, L.N., Said-Galiyev, E.E., Vinokur, R.A., Khokhlov, A.R., Gallyamov, M.O., and Schaumburg, K., *Macromolecules*, 2002, vol. 35, p. 934.
9. Gallyamov, M.O., Vinokur, R.A., Nikitin, L.N., Said-Galiev, E.E., Khohlov, A.R., and Schaumburg, K., *Vysokomol. Soed., Ser. A*, 2002, vol. 44, no. 6, p. 581.
10. Gallyamov, M.O., Vinokur, R.A., Nikitin, L.N., Said-Galiyev, E.E., Khokhlov, A.R., Yaminsky, I.V., and Schaumburg, K., *Langmuir*, 2002, vol. 18, p. 6928.

11. Said-Galiyev, E.E., Vygodskii, Y.S., Nikitin, L.N., Vinokur, R.A., Gallyamov, M.O., Pototskaya, I.V., Kireev, V.V., Khokhlov, A.R., and Schaumburg, K., *J. Supercrit. Fluids*, 2003, vol. 27, pp. 121, 130.
12. Nikitin, L.N., Gallyamov, M.O., Vinokur, R.A., Nikolaev, A.Yu., Said-Galiyev, E.E., Khokhlov, A.R., Jespersen, H.T., and Schaumburg, K., *J. Supercrit. Fluids*, 2003, vol. 26, p. 263.
13. Gallyamov, M.O., Buznik, V.M., Tsvetnikov, A.K., Vinokur, R.A., Nikitin, L.N., Said-Galiev, E.E., Lebedeva, O.V., Khokhlov, A.R., and Schaumburg, K., *Dokl. Ross. Akad. Nauk*, 2003, vol. 392, no. 1, p. 77.
14. Said-Galiev, E.E., Vygodskii, Ya.S., Nikitin, L.N., Vinokur, R.A., Khokhlov, A.R., Pototskaya, I.V., Kireev V.V., and Schaumburg, K., *Vysokomol. Soed., Ser. A*, 2004, vol. 46, no. 4, p. 634.
15. Gallyamov, M.O., Buznik, V.M., Tsvetnikov, A.K., Vinokur, R.A., Nikitin, L.N., Said-Galiev, E.E., Khokhlov, A.R., and Schaumburg, K., *Khim. Fiz*.., 2004, vol. 23, no. 6, p. 76.
16. Gallyamov, M.O., Bouznik, V.M., Tsvetnikov, A.K., Vinokur, R.A., Nikitin, L.N., Said-Galiev, E.E., Lebedeva, O.V., Khokhlov, A.R., and Schaumburg, K., *Polymer Preprints*, 2004, vol. 45(1), p. 504.
17. Said-Galiev, E.E., Leonov, Yu.N., Vasnev, V.A., Markova, G.D., Vinokur, R.A., Nikitin, L.N., and Khokhlov, A.R., *Vysokomol. Soed., Ser. A*, 2005, vol. 47, no. 1, p. 99.
18. Smirnov, M.A., Kuryndin, I.S., Nikitin, L.N., Sidorovich, A.V., Sazanov, Yu.N., Kudasheva, O.V., Bukoshek, V., Khokhlov, A.R., and El'yashevich, G.K., *Zh. Prikl. Khim*., 2005, vol. 78, no. 12, p. 2023.
19. Khrustalev, V.N., Nikitin, L.N., Vasil'kov, A.Yu., and Khokhlov, A.R., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2006, no. 3, p. 555.
20. Nikitin, L.N., Nikolaev, A.Yu., Said-Galiev, E.E., Gamzazade, A.I., and Khokhlov, A.R., *Sverkhkrit. Fluidy. Teor. Prakt*., 2006, vol. 1, no. 1, p. 77.
21. Gamzazade, A.I., Nasibov, S.M., Nikitin, L.N., Said-Galiev, E.E., and Khokhlov, A.R , *Sverkhkrit. Fluidy. Teor. Prakt*., 2006, vol. 1, no. 2, p. 60.
22. Gallyamov, M.O., Nikitin, L.N., Nikolaev, A.Yu., Obraztsov, A.N., Buznik, V.M., and Khokhlov, A.R., *Kolloidn. Zh*., 2007, vol. 69, no. 4, p. 448.
23. Kang, E.T. and Zhang, Y., Adv. Mater., 2000, vol. 12, no. 20, p. 1481.
24. Muidinov, M.R., *Doctorate (Chem.) Dissertation*, Inst. Probl. Khim. Fiz. Ross. Akad. Nauk, 2006.
25. Jessop, Ph.G. and Leitner, W., *Chemical Synthesis Using Supercritical Fluids*, Weinheim: Wiley VCH, 1999.
26. DeSimone, J.M., Guan, Z., and Elsbernd, C.S., *Science*, 1992, vol. 257, p. 945.
27. Consani, K.A. and Smith, R.D., *J. Supercrit. Fluids*, 1990, vol. 3, no. 2, p. 51.
28. Iezzi, A., Bendale, P., Enick, R.M., Turberg, M., and Brady, J*., Fluid Phase. Equil*., 1989, vol. 52, p. 307.
29. Hoefling, T.A., Enick, R.M., and Beckman, E.J., *J. Phys. Chem*., 1991, vol. 95, no. 19, p. 7127.
30. Hoefling, T.A., Newman, D.A., Enick, R.M., and Beckman, E.J., *J. Supercrit. Fluids*, 1993, vol. 6, no. 3, p. 165.
31. Hoefling, T.A., Stofesky, D., Reid, M., Beckman, E.J., and Enick, R.M., *J. Supercrit. Fluids*, 1992, vol. 5, no. 4, p. 237.
32. Henon, F.E., Camaiti, M., and Burke, A.L., *J. Supercrit. Fluids*, 1999, vol. 15, p. 173.
33. Kirby, C. and McHugh, M.A., *Chem. Rev*., 1999, vol. 99, no. 2, p. 565.
34. DiNoia, T.P., Conway, S.E., Lim, J.S., and McHugh, M.A., *J. Polym. Sci., Polym. Phys*., 2000, vol. 38, p. 2832.
35. Lora, M., Lim, J.S., and McHugh, M.A., *J. Phys. Chem. B*, 1999, vol. 103, no. 14, p. 2818.
36. Mertogan, C.A., McHugh, M.A., and Tuminello, W.H*., J. Appl. Polym. Sci*., 1999, vol. 74, no. 8, p. 2039.
37. Novick, B.J., DeSimone, J.M., and Carbonell, R.G., *Langmuir*, 2004, vol. 43, p. 515.
38. Wang, J., Khlobystov, A.N., Wang, W., Howdle, S.M., and Poliakoff, M., *Chem. Commun*., 2006, p. 1670.
39. Hoggan, E.N., Flowers, D., Wang, K., DeSimone, J.M., and Carbonell, R.G., *Ind. Eng. Chem. Res*., 2004, vol. 43, p. 2113.
40. Glebov, E.M., Yuan, L., Krishtopa, L.G., Usov, O.M., and Krasnoperov, L.N., *Ind. Eng. Chem. Res*., 2001, vol. 40, p. 4058.
41. Cho, D., Kim, Y.J., Erkey, C., and Koberstein, J.T., *Macromolecules*, 2005, vol. 38, p. 1829.
42. Puniredd, S.R. and Srinivasan, M.P., *J. Coll. Int. Sci*., 2007, vol. 306, p. 118.
43. Rindfleisch, F., DiNoia, T.P., and McHugh, M.A., *J. Phys. Chem*., 1996, vol. 100, p. 15581.
44. Zhavnerko, G.K., Agabekov, V.E., Gallyamov, M.O., et al., *Coll. Surf. A*, 2002, vol. 202, nos. 2–3, p. 233.
45. Zhavnerko, G.K., Zhavnerko, K.A., and Agabekov, V.E., et al., *Coll. Surf. A*, 2002, vols. 198–200, p. 231.
46. Nakajima, A., Hashimoto, K., and Watanabe, T., Monatshefte für Chemie, 2001, vol. 132, p. 31.
47. Feng, L., Li, S., Li, Y., Li, H., Zhang, L., Zhai, J., Song ,Y., Liu, B., Jiang, L., and Zhu, D., *Adv. Mater*., 2002, vol. 14, no. 24, p. 1857.
48. Quéré, D., *Nature Mater*., 2002, vol. 1, p. 14.
49. Blossey, R., *Nature Mater*., 2003, vol. 2, p. 301.
50. Gould, P., *Materials Today*, 2003, vol. 6, no. 11, p. 44.
51. Otten, A. and Herminghaus, S., *Langmuir*, 2004, vol. 20, no. 6, p. 2405.

52. Sun, T., Feng, L., Gao, X., and Jiang, L., *Acc. Chem. Res*., 2005, vol. 38, no. 8, p. 644.
53. Quéré, D., Rep. Prog. Phys., 2005, vol. 68, p. 2495.
54. Lafuma, A. and Quéré, D., *Nature Mater*., 2003, vol. 2, p. 457.
55. Cheng, Y.-T. and Rodak, D.E., *Appl. Phys. Lett*., 2005, vol. 86, p. 144101.
56. Wier, K.A. and McCarthy, T.J., *Langmuir*, 2006, vol. 22, no. 6, p. 2433.
57. Muidinov, M.R., *Ross. Khim. Zh. (Zh. Ross. Khim. O–va im. D.I. Mendeleeva)*, 2002, vol. 46, no. 3, p. 64.
58. Harrison, K., Goveas, J., Johnston, K.P., and O'Rear, E.A., *Langmuir*, 1994, vol. 10, no. 10, p. 3536.
59. Eastoe, J., Cazelles, B.M.H., Steytler, D.C., et al., *Langmuir*, 1997, vol. 13, no. 26, p. 6980.
60. Sagisaka, M., Yoda, S., Takebayashi, Y., et al., *Langmuir*, 2003, vol. 19, no. 2, p. 220.
61. Clarke, M.J., Harrison, K.L., Johnston, K.P., and Howdle, S.M., *J. Am. Chem. Soc*., 1997, vol. 119, no. 27, p. 6399.
62. Kane, M.A., Baker, G.A., Pandey, S., and Bright, F.V., *Langmuir*, 2000, vol. 16, no. 11, p. 4901.
63. Kim, J.-H., Paxton, T.E., and Tomasko, D.L., *Biotechnol. Prog*., 1996, vol. 12, no. 5, p. 650.
64. Elvassore, N., Bertucco, A., and Caliceti, P., *Ind. Eng. Chem. Res*., 2001, vol. 40, no. 3, p. 795.
65. Chattopadhyay, P. and Gupta, R.B., *Ind. Eng. Chem. Res*., 2002, vol. 41, no. 24, p. 6049.
66. Mawson, S., Johnston, K.P., Betts, D.E., et al, *Macromolecules*, 1997, vol. 30, no. 1, p. 71.
67. Chandler, K., Pouillot, F.L.L., and Eckert, C.A., *J. Chem. Eng. Data*, 1996, vol. 41, no. 1, p. 6.
68. Adamson, A.W., *Physical Chemistry of Surfaces*, New York: Wiley-Interscience, 1976, 3rd ed.
69. Dinsmore, A.D., Hsu, M.F, Nikolaides, M.G., et al., *Science*, 2002, vol. 298, p. 1006.
70. *CRC Handbook of Chemistry and Physics*, Lide, D.R., Ed., 72nd ed. Boca Raton: CRC, 1991–1992.
71. Deryagin, B.V., Churaev, N.V., and Muller, V.M., *Poverkhnostnye sily* (Surface Forces), Moscow: Nauka, 1985.