

# High-Quality Ultrathin Polymer Films Obtained by Deposition from Supercritical Carbon Dioxide As Imaged by Atomic Force Microscopy

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Promising new technique of polymer deposition from solutions in supercritical carbon dioxide (sc CO<sub>2</sub>) has been applied to form ultrathin Teflon AF2400 copolymer films on substrates with different properties. Atomic force microscopy study of the coatings morphology has been performed for the first time and has revealed surprisingly high film uniformity, very low roughness, and good stability during the scanning procedure. Our findings have demonstrated the intriguing possibilities of the applied film-forming process allowing to deposit the thin-film coatings and also individual macromolecules in a controllable manner. This is because the variations of solution temperature and pressure influence significantly the dissolving power of sc CO<sub>2</sub>; therefore, the macromolecule precipitation depends strongly on the thermodynamic regime and can be easily controlled. The influence of substrate properties, exposure conditions, and deposition kinetics on the film morphology, thickness, and level of surface coverage has been shown.

## 1. Introduction

Atomic force microscopy (AFM) is routinely used in studies of different polymer structures deposited onto hard substrates: thin films, individual polymer molecules,<sup>1</sup> their complexes with surfactants,<sup>2</sup> proteins,<sup>3</sup> and so forth. Thin polymer films have considerable technological potential as a novel class of materials with special properties. The film stability and uniformity is of significant importance for possible applications. AFM data allowed to demonstrate that, in general, it is a nontrivial problem to form an ultrathin organic film with homogeneous and uniform morphology on a solid substrate.<sup>4,5</sup>

Various approaches to produce high-quality thin polymer films were tested by AFM. Luzinov et al.<sup>6</sup> have applied grafting to a chemically modified substrate surface (silicon) to ensure stability and uniformity of ultrathin elastomer poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] films with thickness of a few nanometers. The low values of surface roughness (0.2–0.3 nm) have been achieved. Maas et al.<sup>7</sup> succeeded in preparation of ultrathin (1–5 nm) polysty-

rene-poly(4-vinyl pyridine) films on flat silica surfaces by two approaches: (i) spin coating followed by annealing and rinsing and (ii) adsorption from dilute solution (dip coating). The degree of film inhomogeneity and roughness value (<0.5 nm for the best results) strongly depended on properties of a solvent used (as studied by AFM).

One of the promising approaches to formation of thin-film polymer coatings is based on self-assembly of polyanion–polycation layers from solutions.<sup>8,9</sup> Recently, AFM studies of self-assembled films of poly(diallyldimethylammonium chloride) + sulfonated polyaniline<sup>8</sup> and poly(*o*-ethoxyaniline) + sulfonated lignin<sup>9</sup> have been performed. However, prepared coatings (few bilayers) have exhibited grain structure with roughness of 5–7 nm<sup>8</sup> and 0.5–3.0 nm,<sup>9</sup> correspondingly (in the latter case the roughness strongly depends on the nature of the top bilayer). This inhomogeneity can be a consequence of the film-drying procedure. Indeed, it has been shown<sup>10</sup> using AFM and small-angle neutron scattering that the surface of ultrathin (3 nm) polystyrene film (prepared on silica substrate by spin coating method) becomes rougher and reveals cluster structure as a result of drying procedure.

The drying procedure results in nonequilibrium and uncontrollable increase of solution concentration. The strong hydrodynamic flows in dried droplets may arise, which are capable to move the deposited objects. It can essentially change the morphology of structures to be studied and complicate reproducibility of the results. Moreover, the presence of residual solvent (as well as an adsorbate layer<sup>11</sup>) on a substrate may also enhance the

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molecular mobility and induce unpredictable reorganization of deposited structures. Kumaki et al.<sup>12</sup> have investigated by AFM the conformation of polystyrene-poly(methyl methacrylate) diblock copolymer molecules deposited on a mica substrate. It has been revealed that the blocks of poly(methyl methacrylate) can be transferred into an extended conformation after keeping the specimen in 100% relative humidity air.

Summarizing, we can state that both the presence of solvent traces on a substrate with adsorbed polymer material and the drawbacks of the typical drying procedure are the factors to be eliminated to ensure the correct interpretation of the results and their good reproducibility. It would be desirable to design the sample preparation technique without any formation of a dried film or droplets of solvent during processes of polymer precipitation and solvent removing.

We believe that the use of sc CO<sub>2</sub> as a solvent is rather prospective for macromolecules deposition on a substrate. CO<sub>2</sub> has no liquid phase at atmospheric pressure, so it leaves a material completely and very rapidly after the end of an exposure with decompression of a reactor. Thus, application of sc CO<sub>2</sub> allows to exclude the drying procedure from sample preparation and also to eliminate the problem of a residual solvent.

The sc CO<sub>2</sub> is widely applied as a carrier in processes of impregnation<sup>13</sup> and polymer synthesis.<sup>14</sup> However, in the literature there are only a few works dealing with sc CO<sub>2</sub> usage as a carrier of macromolecules for their deposition on a substrate and for thin-film formation. At the same time, it is no doubt that the interest to this field will be increasing. This is stimulated by environment safety of CO<sub>2</sub> in comparison with organic solvents used in technological processes of polymer coatings. Henon et al.<sup>15</sup> have found that both supercritical and liquid carbon dioxide are good solvents for perfluoropolyethers, which are widely utilized for production of protective coatings, for example, in computer hard disks. Novick et al.<sup>16</sup> have reported results of liquid CO<sub>2</sub> usage as a solvent to deposit thin perfluoropolyethers films on solid substrates. It has been shown that even liquid CO<sub>2</sub> is a proper choice to be a solvent in a film-forming procedure because of its low viscosity and low surface tension. The typical thickness of the prepared coatings is in the range 3.5–35 nm (according to data of ellipsometry and AFM); however, results of AFM-examination of surface homogeneity and quality have not been presented.

Hoggan et al.<sup>17</sup> have deposited films from copolymers of 1H,1H-perfluorooctyl methacrylate and *tert*-butyl methacrylate on silicon substrates by the spin-coating method from solutions in liquid CO<sub>2</sub>. Coatings with a thickness of 0.1–3 μm have been prepared; however, films with a thickness less than 1 μm exhibit high degree of inhomogeneity. Conway et al.<sup>18</sup> have investigated the adsorption

of Teflon AF copolymer onto a glass substrate. Polymer has been deposited using the dip-coating method in sc CO<sub>2</sub> at temperature of 100 °C and pressure of 50–70 MPa. Deposition has been controlled by surface plasmon resonance technique, but the morphology of the films has not been studied.

A new method of rapid expansion of supercritical solution (RESS) is widely investigated now in applications related with coatings formation. This approach is based on deposition in a stream formed by nozzles of small diameter (50–100 μm). During rapid expansion after escaping from a nozzle, the supercritical polymer solution transfers into a supersaturated state. This gives rise to the creation of condensation centers around which small droplets are formed. If the substrate is placed into the flow of supersaturated solution, these droplets form a thin film being adsorbed on a substrate surface.

Wang et al.<sup>19</sup> have applied RESS method for deposition of thin paraffin coating from sc CO<sub>2</sub> solution onto SiO<sub>2</sub> spherical particles (diameter of 1 μm). The inhomogeneity of the prepared film is affected by the size of the droplets formed around condensation centers (about 40 nm). Schreiber et al.<sup>20</sup> have studied the same system and presented electron microscopy results, which have demonstrated that the prepared coatings are inhomogeneous and only partially coat microspheres surfaces. Shim et al.<sup>21</sup> have deposited poly(2-ethylhexyl acrylate) films from suspension in sc CO<sub>2</sub> stabilized by Monasil surfactant using RESS method. However, the prepared films have exhibited nonuniform surface according to the presented optical microscopy images.

The mentioned results lead us to conclude that RESS method is very convenient for technological application, but the prepared coatings are usually not uniform in thickness and morphology because of the peculiarities of the technique. More promising results seem to be obtained in experiments with polymer deposition directly in the sc reactor (for example, with Teflon AF copolymers);<sup>18</sup> however, there is still a lack of information concerning high-resolution studies of the coatings' morphology and uniformity.

In the present work, the extensive AFM study of structures created by polymer molecules deposition on a substrate from their solutions in sc CO<sub>2</sub> has been performed for the first time. The copolymer Teflon AF2400 (DuPont) has been selected as a film-forming polymer material because of its unique properties. These copolymers (i) are optically transparent materials in a wide spectral range (from IR to UV), (ii) have extremely low values of refractive index and dielectric constant (up to GHz range), (iii) are chemically resistant against the majority of solvents and aggressive mediums (have restricted solubility in some perfluorinated solvents), and (iv) have high thermal stability (up to 300 °C). The producer (DuPont) proposes these copolymers as appropriate materials for creation of homogeneous ultrathin coatings, which can find diverse applications in optics, electronics, and so forth.

The solubility of Teflon AF copolymers in sc CO<sub>2</sub> has been investigated by cloud point observation.<sup>22</sup> It has been revealed that these compounds have the best solubility in

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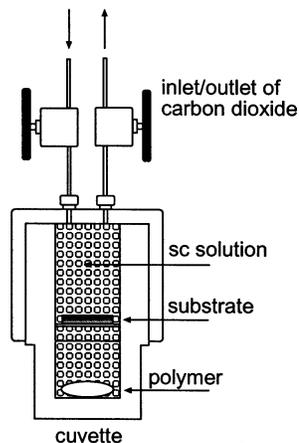
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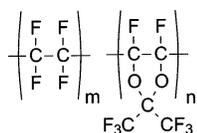
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**Figure 1.** The general scheme of the reaction chamber for polymer deposition from solution in sc CO<sub>2</sub>. The substrate is mounted on the grid holder above polymer material to be dissolved.

sc CO<sub>2</sub> in comparison with some other copolymers of poly-(tetrafluoroethylene). Authors have explained this by the influence of polar dioxole group interacting with CO<sub>2</sub> molecules and promoting the solubility, see chemical structure:



The thermodynamic solubility area of Teflon AF copolymers can be easily achieved in laboratory or industrial conditions. This solubility in sc CO<sub>2</sub> (at the same time, they are chemically resistant against the majority of solvents) does make this copolymer class an especially unique and prospective one for supercritical technologies.

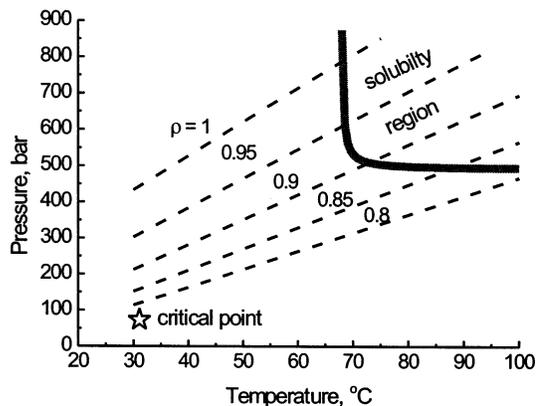
## 2. Materials and Methods

Teflon AF2400 copolymer (DuPont,  $M_n \sim 10^5$ ,  $\rho = 1.6 \text{ g/cm}^3$ ,  $T_g = 250 \text{ }^\circ\text{C}$ ) was used in experiments. The high purity CO<sub>2</sub> (>99.997%, GOST 8050-85 Russia, 0.0002% O<sub>2</sub>, 0.001% H<sub>2</sub>) was used as received. The mica (muscovite) and highly oriented pyrolytic graphite (pyrographite) were chosen as substrates for polymer molecules deposition. Both materials allow to obtain by cleaving the flat surface areas with angstrom- (mica) and nanometer- (graphite) level roughness. By the beginning of an exposure, the cleavage was performed to obtain clean substrate surface.

Film depositions have been carried out using experimental setup described earlier.<sup>23</sup> The system includes the hand-operated plunger pressure generator to create pressures up to 50 MPa. The pressure generator is connected to high-pressure chamber (cuvette), in which the exposure of samples is carried out. The 10-mL custom-made stainless steel cuvette (5-cm height) was used (Figure 1). The system is supplied with mechanical manometers for the monitoring of pressure. The temperature regime during an exposure was set either by temperature maintained in liquid thermostat or by specially designed computer-controlled temperature regulation system.

The polymer mass was determined using OhausAP250D (Ohaus Corp., U.S.) balance. Typically, the amount of polymer used in the experiments was 0.5–1.0 mg.

The sample preparation procedure used can be illustrated by Figure 1. At the first step, the polymer compound was placed on the bottom of the reaction chamber; the substrate was mounted



**Figure 2.** The typical solubility area of Teflon AF copolymers according to Rindfleisch et al.<sup>22</sup> In our case, one can expect even better solubility. The dashed lines in the CO<sub>2</sub> phase diagram show calculated isochores (for various density values), which define the relation between pressure and temperature in the closed cuvette.

above it on the grid holder. Further, the cuvette was intensely vented with CO<sub>2</sub> for removal of air and traces of water. After that, the cuvette was sealed and the desired density of CO<sub>2</sub> was generated at the given temperature and pressure. Then, the cuvette temperature was raised to the necessary value. This resulted in the increase of the pressure also which could be calculated knowing the density and the pressure (the polymer concentrations used were assumed to be negligible to affect the system thermodynamic properties). The equilibrium of the polymer solution was maintained during several hours. Then, the temperature (pressure) in the cuvette was reduced; it resulted in the decrease of the solvent quality and in the macromolecules' deposition on the substrate surface. After completing the precipitation process, the cuvette was decompressed. The substrate with deposited polymer molecules was extracted and its morphology was explored by AFM.

The AFM measurements were carried out in contact and tapping modes in air or in liquid using Nanoscope-IIIa probe microscope (Digital Instruments, U.S.). The device was equipped with D-scanner (dynamic range  $15 \times 15 \times 4 \text{ } \mu\text{m}^3$ ), which was calibrated using grate from the producer. AFM-images were collected with an information density of  $512 \times 512$  points at scanning frequencies: 1 Hz for tapping mode in air, 1–3 Hz for tapping or contact modes in liquid medium, and 5 Hz for contact mode in air. We used silicon nitride NP-S cantilevers (Nanoprobe, Digital Instruments, U.S.) with spring constant 0.32 N/m for studies in liquid and for contact mode in air and silicon TESP cantilevers (Nanoprobe, Digital Instruments, U.S.) with resonant frequency 200–400 kHz for studies of tapping mode in air. To build up the AFM-images and to analyze film structure parameters, we applied the Femtoscan Online software (Advanced Technology Center, Russia).

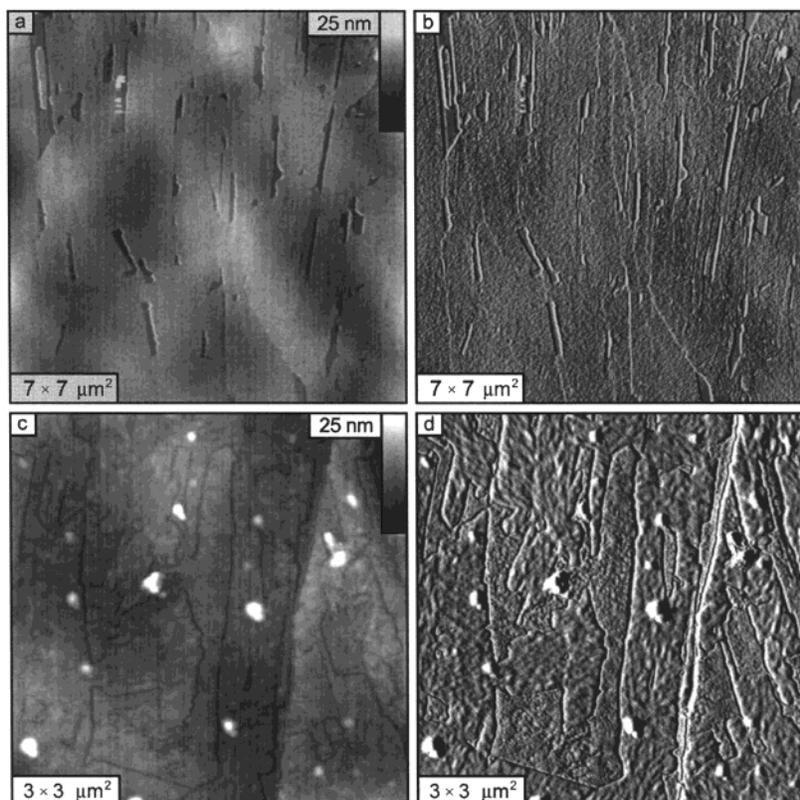
The calculations of thermodynamic parameters in the cuvette were performed using the NIST Thermophysical Properties of Pure Fluids software (National Institute of Standard and Technology, U.S.).

## 3. Results and Discussion

The typical solubility area of Teflon AF class copolymers is shown in Figure 2 according to results of Rindfleisch et al.<sup>22</sup> This area was detected for copolymer with 35:65 tetrafluoroethylene to dioxole unit ratio. In our case, the corresponding ratio is 10:90, which allows to expect even better solubility. Indeed, it is the interaction of the dioxole group with CO<sub>2</sub> that assumes to determine a solubility of this copolymers in sc CO<sub>2</sub>.

The dissolving power of supercritical media is highly sensitive to pressure and temperature (which define also solvent density). The prepared polymer solution can be moved out from solubility area in different manners, for example, (i) by lowering of temperature in closed cuvette,

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**Figure 3.** Polymer films deposited onto pyrographite substrate. Topography AFM images obtained in contact (a, b) and in tapping modes (c, d) in air. The images (b, d) were obtained by mathematical highlighting procedure of Femtoscan software to depict fine structure of images (a, c). Exposition at  $T = 65^\circ\text{C}$ ,  $P = 75\text{ MPa}$  for 3 h followed by temperature lowering to  $25^\circ\text{C}$  and decompression.

(ii) by lowering of pressure with  $\text{CO}_2$  outlet from cuvette or by cuvette volume increase.

The lowering of temperature at constant volume (closed cuvette) is an isochoric process, which is accompanied as well by pressure decrease. The typical isochores are shown as dashed lines in phase diagram of Figure 2 (calculated for various  $\text{CO}_2$  densities by means of the NIST software). The temperature monitoring gives us all information about pressure changes in the closed cuvette because at given density the corresponding isochore determines the relation between the temperature and pressure.

The pressure decrease by  $\text{CO}_2$  outlet gives rise to simultaneous cooling of the cuvette. The cuvette temperature is defined by interrelation of processes of cooling and heat exchange with surrounding medium and is hard to control at fast decompression. However, such manner of system moving out from the solubility area sometimes can be beneficial since the released  $\text{CO}_2$  also extracts an excess of the dissolved polymer material. Besides, in this case it is possible to control  $\text{CO}_2$  density decrease by regulation of the stream.

Figure 3 presents typical AFM images of copolymer Teflon AF2400 thin films deposited from sc  $\text{CO}_2$  on pyrographite substrate. The initial stage of copolymer dissolution was carried out during several hours at the temperature and pressure corresponding to the solubility area. The deposition procedure was performed by slow temperature decrease in the closed cuvette and was terminated by cuvette decompression when unused material was removed by  $\text{CO}_2$  stream coming out from the cuvette.

Figure 3 demonstrates that the applied procedure really allows to deposit ultrathin polymer coatings with high degree of uniformity on a pyrographite surface. The measurements of surface roughness on randomly selected

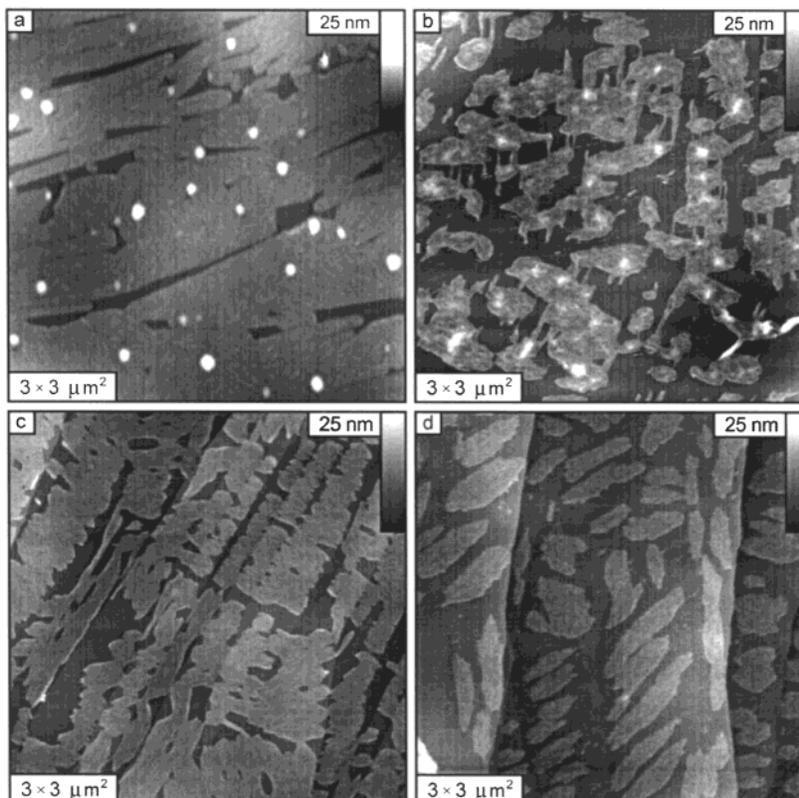
uniform  $0.5 \times 0.5\ \mu\text{m}^2$  surface areas give typical values in the interval of 0.4–0.6 nm (the film roughness is influenced by the roughness of the graphite substrate which usually contains many individual atomic steps). The low values of coating roughness allow to make a conclusion about close-packed arrangement of film-forming molecules. The uniformity of film structure and thickness is high in comparison with polymer coating usually prepared by other film-forming techniques described in Introduction: spin and dip coating,<sup>10</sup> self-assembly,<sup>8</sup> RESS,<sup>20,21</sup> and other methods. Besides the formed coatings are ultrathin ones having nanometer-level thickness.

We can state that the quality of our films is comparable to that of films prepared by Langmuir–Blodgett and similar methods. However, in our experience,<sup>4,5,24</sup> only a few organic compounds can be prepared as high-quality ultrathin LB films (few monolayers) on pyrographite substrate because of drawbacks due to reorganization during the transfer procedure and the subphase traces' removal. Moreover, such films on pyrographite substrate are usually not resistant to probe influence and can be locally destroyed during the scanning procedure.<sup>25,26</sup> At the same time, we found that Teflon AF2400 films prepared by deposition from sc  $\text{CO}_2$  are quite stable under the local probe influence and maintain their structure with time and during scanning procedure not only in air but also in ethanol, see Figure 4. To achieve partial destruction of film in the scanning area, it is necessary

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**Figure 4.** Polymer coatings deposited onto pyrographite substrate. Topography AFM image obtained in tapping mode in ethanol. Exposition at  $T = 70\text{ }^{\circ}\text{C}$ ,  $P = 80\text{ MPa}$  for 3 h followed by temperature lowering to  $25\text{ }^{\circ}\text{C}$  (a),  $60\text{ }^{\circ}\text{C}$  (b) and decompression; deposition in temperature gradient at  $T_{\text{bottom}} = 70\text{ }^{\circ}\text{C}$ ,  $T_{\text{top}} = 45\text{ }^{\circ}\text{C}$ ,  $P = 70\text{ MPa}$  (c), and  $T_{\text{bottom}} = 75\text{ }^{\circ}\text{C}$ ,  $T_{\text{top}} = 50\text{ }^{\circ}\text{C}$ ,  $P = 75\text{ MPa}$  (d) for 3 h followed by decompression.

to increase the probing force up to values exceeding 20 nN (in contact mode), which correspond to considerable contact pressures.<sup>27</sup>

It can be seen in the images of Figures 3a and 4 that the prepared coatings have lamellar structure and that the angle of mutual orientation of lamellae is close to  $30^{\circ}$  and  $60^{\circ}$ . The domain structure of the film is clearly seen in Figure 3c: coexistence of two types of domains (distinguished by surface morphology) with clear boundaries is observed. The formation of domains and lamellae in thin film from amorphous copolymer probably can be explained by the substrate influence; mechanism of their formation requires further examination.

Figure 4 demonstrates images (a, b) of films prepared in similar exposure conditions but with different subsequent temperature decrease (down to  $25\text{ }^{\circ}\text{C}$  (a) and  $60\text{ }^{\circ}\text{C}$  (b)). In the former case (a), we have obtained more homogeneous film with occasional defects; in the latter case (b), the coating islands only partially cover the substrate. Therefore, we can conclude that macromolecule precipitation is affected by regime of temperature decrease, which results in different levels of surface coverage.

The coatings visualized in Figure 4c and d were obtained using another technique: deposition in temperature gradient. The idea is to maintain the top and the bottom of the closed cuvette at different temperatures:  $T_{\text{bottom}} > T_{\text{top}}$ . In such geometry, the macromolecules being dissolved in the bottom region go up because of convection to the top region where they tend to precipitate and form the film. It can be concluded from comparison of images c and d that at smaller temperatures (sc  $\text{CO}_2$  densities are the same) the formed film is more completed. This may be

due to the decrease of solubility at the decrease of temperature, which may enhance macromolecule precipitation.

The AFM method provides real three-dimensional information about surface morphology allowing direct measurements of film thickness. It is difficult to measure film thickness when one has perfect coating without any defects, see Figure 3c (in such cases the artificial defects have to be created using local probe influence with increased force to have the information about substrate level<sup>25,26</sup>). However, the film thickness measurements can be easily performed for films visualized in Figure 3a and Figure 4. Indeed, the separate defects in the film structure are observed in the images of Figure 3a and Figure 4a. The coatings visualized in Figure 4b–d are not completed and consist of individual islands.

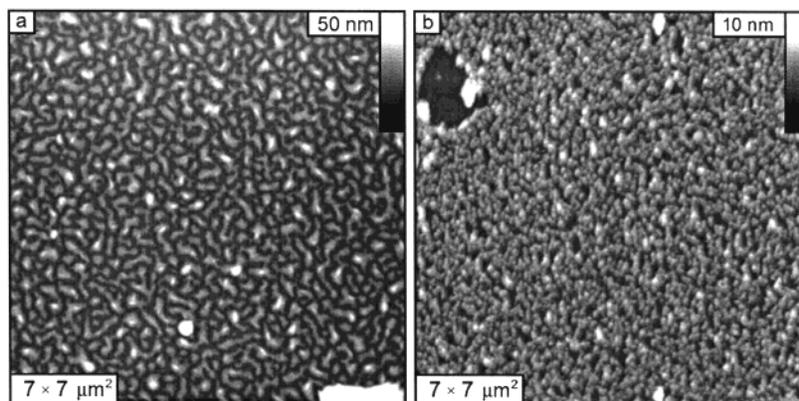
We found that the thickness of films deposited onto a pyrographite surface is equal to 4–8 nm almost independently of the exposure parameters and surface coverage degree. According to our observations, the material excess does not produce an increase of film thickness and seems to be spent for formation of aggregates, see Figure 3c and Figure 4a.

It is of interest to compare the film thickness with characteristic sizes of polymer molecule. One can estimate the diameter of compact globule containing one TeflonAF2400 copolymer molecule using the formula if the

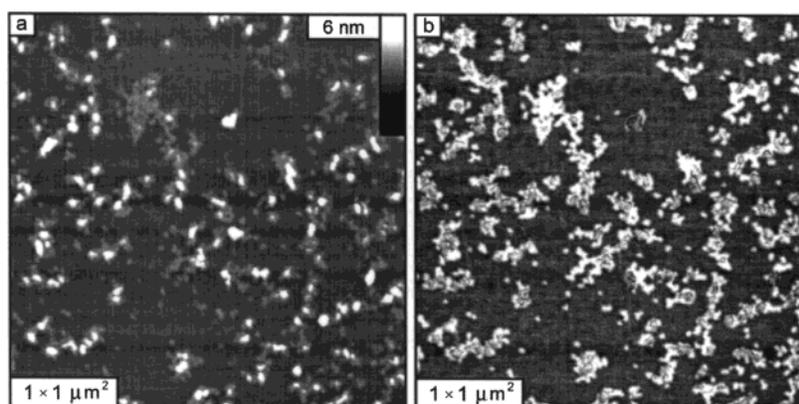
$$D = 2 \sqrt[3]{\frac{3m}{4\pi\rho}} \quad (1)$$

mass of molecule  $m$  and material density  $\rho$  are known. Applying estimation for molecular mass  $m \sim M_n/N_A$  and taking value for the copolymer density one can obtain

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**Figure 5.** Polymer coating deposited onto mica substrate. Topography AFM image obtained in contact mode in air (a) and in tapping mode in ethanol (b). Exposition at  $T = 65\text{ }^{\circ}\text{C}$ ,  $P = 80\text{ MPa}$  for 6 h followed by temperature lowering to  $25\text{ }^{\circ}\text{C}$  and decompression (a); at  $T = 40\text{ }^{\circ}\text{C}$ ,  $P = 50\text{ MPa}$  for 3 h followed by temperature lowering to  $25\text{ }^{\circ}\text{C}$  and decompression (b).



**Figure 6.** Polymer molecules deposited onto mica substrate. Topography (a) and phase (b) AFM images obtained in tapping mode in air. The phase image (b) shows better contrast. Exposition at  $T = 60\text{ }^{\circ}\text{C}$ ,  $P = 70\text{ MPa}$  for 4 h followed by temperature lowering to  $50\text{ }^{\circ}\text{C}$  and decompression.

diameter of compact globule  $D \approx 6\text{ nm}$ . The film thickness experimentally defined by AFM coincides well with the characteristic size of a single compact globule.

The AFM images in Figure 4 were obtained in liquid environment. Examination of a material surface in liquid medium (when both probe and sample are placed in liquid) allows to reduce the attractive forces between probe and sample, to thus reduce probe–sample contact area,<sup>27</sup> and to increase accordingly the spatial resolution.<sup>28</sup> The experimental setup in this case included AFM liquid cell, which was filled with ethanol. When using ethanol as an investigation medium, it was possible generally to achieve better spatial resolution (in tapping mode) in comparison with experiments in air, in water, or in aqueous salt solutions. It can be explained either by better dynamics of probe–sample force interaction in ethanol or by more effective removing of possible traces of contamination from film surface.

The structure of created films remained stable and unchangeable in ethanol during the scanning procedure. This result is to some extent expected when one takes into account the high resistance of Teflon AF2400 copolymer against mechanical and chemical influence. We found also that the films maintain their general morphology being placed in ethanol (by studying the same films in air and in ethanol).

When using mica as a substrate, the formed thin film revealed another type of morphology. The excess of polymer material in this case results in increase of coating

thickness. Also, the film-forming process was sometimes followed by structural reorganization of polymer molecules on a substrate. Such reorganization is seen in AFM image of the film (Figure 5a). The created film is not homogeneous in thickness (as on pyrographite substrate) but looks like a chevron texture. The measured surface roughness is in the range of 10–15 nm. Height of visualized structures is from 20 to 60 nm above a substrate surface according to AFM measurements.

At smaller temperatures and pressures of the exposure (at lower polymer solubility), it is possible to create on mica surface the film with 4–7-nm thickness (Figure 5b). The occasional defect presence (see upper left corner of the image in Figure 5b) allows to measure film thickness, which coincides with expected diameter of single globule. The roughness of the film is equal to about 2 nm, which is several times higher in comparison with results for graphite substrate. Thus, the films deposited on graphite (Figures 3 and 4) and film visualized in Figure 5b have the same thickness but different packing density. In Figure 5b, one can see individual globules forming the film. Films deposited on graphite seem to be significantly denser and show no evidence of structure consisting of individual globules (except for thickness coinciding with globule size). This finding is an indication that film morphology depends strongly on the substrate properties, which are dissimilar for mica and graphite.

We observed differences in adsorption of the copolymer molecules onto substrates used. The amount of material deposited onto pyrographite was usually bigger in comparison with mica at equal exposure condition and time

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(and even at the same exposure procedure). The observed effect may be an indication of the better Teflon AF2400 molecules' affinity to pyrographite surface in sc CO<sub>2</sub> environment. The better uniformity, smaller roughness, and higher packing density of the films prepared on pyrographite substrate in comparison with the ones on mica also may contribute to this conclusion.

The images of individual polymer molecules deposited on mica substrate are given in Figure 6. Two types of structures are seen. Higher objects have 2.5–5 nm of height. We suppose that they are either completely compacted individual globules or compacted regions of individual polymer molecules. At the same time, the objects with smaller height (0.5–1.0 nm) can be seen on the substrate which are most probably partially compacted strands of individual macromolecules. The morphology of these structures is clearly visualized in the phase image in Figure 6b (the corresponding topography image is shown in Figure 6a). The phase image is obtained in tapping mode and its contrast is determined by the difference of viscoelastic properties of substrate and adsorbed objects.

### Conclusion

We have studied by AFM the morphology of TeflonAF2400 copolymer thin film coatings deposited on different substrates from solutions in supercritical CO<sub>2</sub>

for the first time. Surprisingly, we have found that the ultrathin films deposited on pyrographite substrate have perfect homogeneity and low surface roughness (about 0.5 nm) in comparison with other types of polymer films. The coatings also reveal high resistance against mechanical influence of scanning probe and stability in air and in liquid during scanning procedure. The film thickness is as low as about 6 nm which coincides with the characteristic size of single compact globule of the macromolecule. The optimal conditions for the formation of films with the best quality (in the sense of uniformity, homogeneity, degree of surface coverage, etc.) have been determined. Films formed on mica substrate are rougher (may be due to lower affinity of the macromolecules to mica in sc CO<sub>2</sub>) and sometimes tend to reorganization. It was also possible to visualize partially compacted individual polymer molecules. Such examinations may contribute to a better understanding of macromolecules' conformational changes in supercritical solutions.<sup>29</sup>

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