Scanning Probe Microscopy Study of Polymer Molecules and Thin Films Deposited from Supercritical Carbon Dioxide

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We have shown that polymer solutions in supercritical carbon dioxide are convenient model systems to study the macromolecule-solvent interactions. One important advantage of such systems is that the macromolecule-macromolecule and macromolecule-solvent interactions depend strongly on the temperature and pressure of a supercritical medium, which can be easily varied during the experiment. Copolymer Teflon®AF2400 (material which is of much interest for technological applications) was chosen as an object to be studied. The controlled decrease of a solvent quality (by controllable change of temperature or pressure) was applied to deposit on solid substrate surfaces both individual compacted macromolecules and thin-film coatings. Morphology of these structures was explored by scanning probe microscopy.

1. Introduction

Scanning probe microscopy (SPM) is currently widely used in morphology examinations of thin films [1, 2], individual polymer molecules [3], their complexes with surfactants [4, 5], proteins [6, 7], and other ligands [8]. This is achieved due to high spatial resolution of the method in combination with the

absence of strong restrictions on the properties of the object and on medium of environment. While studying thin-film coatings SPM allows both to explore uniformity, homogeneity, defect density of a film and to determine local lattice parameters (for two-dimensionally arranged films) [1, 2]. Also it is possible to acquire the information about the thickness of a coating or to create artificial structures and defects by controlled local influence of a probe [9].

Various approaches to form homogeneous and defect-free thin polymer films were tested by SPM. The authors of Ref. [10] investigated by atomic-force microscopy (AFM) the polystyrene-poly(4-vinylpyridine) films prepared on a flat silica surface, deposited by spin-coating and dip-coating methods. In both cases the excess of material was removed by washing with a solvent at the final stage, after that the samples were dried. This procedure resulted in the changes of film surface morphology. It was found that the degree of film inhomogeneity depended on the properties of the solvent used.

Recently AFM studies [11, 12] were applied to self-assembled film with poly (diallyldimethylammonium chloride) + sulfonated polyaniline [11] and poly(o-ethoxyaniline) + sulfonated lignin [12] (polyanion-polycation layers deposited onto substrate). Created coatings were characterized by high degree of inhomogeneity and had grain structure. This inhomogeneity can be a consequence of the film drying procedure. It was shown [13] using AFM and small-angle neutron scattering that the polymer film surface becomes more rough and reveals cluster structure after it is dried.

The drying procedure results in nonequilibrium and uncontrollable increase of concentrations. The objects to be deposited can be removed from a substrate by the strong hydrodynamic flows which may arise when drying droplet. This complicates the reproducibility of results and essentially changes the morphology of adsorbed structures [14]. This problem can be solved when the macromolecules visualization is carried out directly in liquid medium [15, 16]. However, there are other problems, among which we can mention the problem of macromolecule fixation on a substrate surface during scanning procedure.

Therefore we believe that the use of supercritical (sc) media as solvents is rather promising for the deposition of macromolecules on a substrate. The carbon dioxide (CO_2) is a proper choice, because it can be easily converted to a supercritical state ($T > 31.1°C$, $P > 7.38$ MPa). This fluid is a solvent for some polymers and has unique properties: (i) the macromolecule-macromolecule and macromolecule-solvent interactions depend strongly on temperature and pressure, especially near the critical point [17]; (2) CO_2 has no liquid phase under atmospheric pressure, so it leaves a material completely and very rapidly after decompression. Thus, scCO$_2$ application as a solvent for macromolecules depos-

ition on a substrate allows to eliminate the drying procedure and to overcome the problem of a residual solvent. It is of no doubt, that the interest to this technique will increase. This is stimulated by environment safety of CO_2 in comparison with organic solvents used in technological processes of polymer coatings creation.

It was found [18] that both supercritical and liquid CO_2 are good solvents for perfluoropolyethers. These polymers are widely utilized for creation of protective coatings, for example in computer hard disks production.

Rapid expansion of supercritical solutions (RESS) was applied to the deposition of an ultrathin paraffin coating from $scCO_2$ solution on spherical SiO_2 particles [19]. During rapid expansion after escaping from a nozzle the supercritical polymer solution transfers into a supersaturated state. If the substrate is placed into the solution flow, a thin polymer film is adsorbed on a substrate surface from expanding supersaturated solution. The authors of the paper [20] have applied the RESS method to creation of sensor coating from polydimethylsiloxane microspheres. The RESS technique was applied for creation of films from a suspension of a polymeric compound in $scCO_2$ [21]. The suspension of poly (2-ethylhexyl acrylate) in $scCO_2$ was stabilized by the Monasil surfactant. However, prepared films were usually characterized as rather non-uniform surfaces.

The solubility of polymers in $scCO_2$ was investigated by cloud point observation for a number of compounds including Teflon®AF class copolymers [22]. The Teflon®AF copolymers are optically transparent materials in a wide spectral range (from IR to UV). They have extremely low values of refractive index and dielectric constant (up to GHz range) and are characterized by high thermal stability (up to 300°C). Due to unique optical properties and high stability the Teflon®AF thin films can find diverse applications in optics, electronics, optoelectronics, etc. These copolymers are chemically resistant against the majority of solvents and aggressive media, but, at the same time, they can be dissolved in $scCO_2$. This fact does make this class of copolymers especially unique and prospective one for supercritical technologies.

2. Materials and methods

Teflon®AF2400 copolymer (DuPont, $M_n \sim 10^5$, $\rho = 1.6 \text{g/cm}^3$, $T_g = 250$°C) was used in experiments. Chemical structure:

The high purity CO_2 (> 99.997%, GOST 8050-85 Russia, 0.0002% O_2, 0.001% H_2O) was used as received.

The mica (muscovite) and highly oriented pyrolytic graphite (pyrographite)

were chosen as substrates for deposition of polymer molecules. Exposure and deposition were carried out using experimental high-pressure setup described earlier in Ref. [23]. The system permits to create pressures up to 50 MPa and to transfer CO_2 into a supercritical state. The system temperature was regulated using a circulating water thermostat.

For the deposition process a polymer compound was placed at the bottom of the reaction chamber (10 ml volume); a substrate was mounted above it on the holder. At first, the cuvette with polymer and substrate inside was intensely vented by CO_2 to remove air and water. After that, the cuvette was sealed and the necessary density of CO_2 was produced at the given temperature and pressure. Then the cuvette temperature was raised up to necessary value. This resulted in the increase of the pressure also (the increase was calculated knowing the density and temperature). Primary equilibrium of a polymeric solution was reached during several hours. Then the pressure or temperature in the cuvette was gradually reduced which resulted in the decrease of the solvent quality and macromolecules deposition on a substrate surface. After completion of 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 a liquid using "Nanoscope-IIIa" probe microscope (Digital Instruments, USA). The device was equipped with "D"-scanner (dynamic range $15 \times 15 \times 4$ μm^3). AFM-images were collected with the information density of 512×512 points at scanning frequencies of 1 Hz in the tapping mode in air, 1–3 Hz in the tapping or contact modes in liquid medium, and 5 Hz in the contact mode in air. We used silicon nitride NP-S cantilevers and silicon TESP cantilevers (Nanoprobe, Digital Instruments, USA). To build-up the AFM-images we applied "Femtoscan Online v.1.2" software (Advanced Technology Center, Russia).

3. Results and Discussion

The typical solubility area of Teflon®AF copolymer with 35:65 composition, i.e. tetrafluoroethylene to dioxole monomer unit ratio, corresponds to: $T > 65°C$, $P > 50$ MPa according to Ref. [22]. In our case the corresponding ratio is 10:90, which allows to expect better solubility (it is the interaction of dioxole-group with CO_2 that determines the solubility of these fluorocontaining copolymers).

The dissolving capacity of supercritical media is highly sensitive to pressure and temperature (which define also solvent density). The prepared polymer solution can be moved out of the solubility area in different ways, for example:
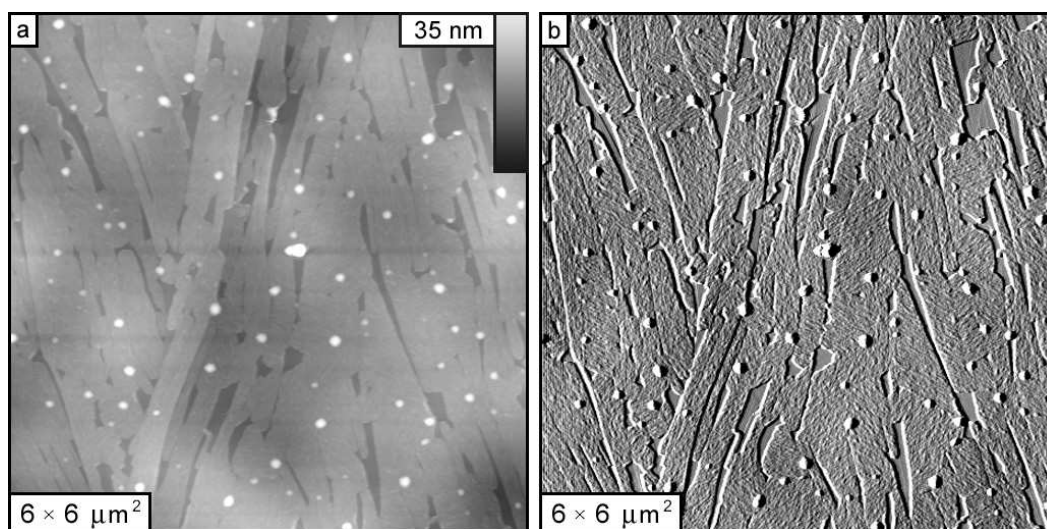
Figure 1. Polymer film deposited onto pyrographite substrate. Topography AFM image obtained in contact mode in air (a). The image (a) was modified by "highlighting" procedure to depict fine structure (b). Exposition at $T = 55°C$, $P = 75$ MPa for 3 h followed by temperature lowering down to $20°C$ and decompression.

(i) by reducing the temperature in the closed cuvette; (ii) by reducing the pressure with CO_2 outlet from the cuvette. The decrease of solubility results in macromolecules precipitation.

Figs. 1 and 2 present typical AFM images of copolymer Teflon®AF2400 thin film coatings deposited from sc CO_2 on pyrographite substrate. Initial stage of the copolymer dissolution and the stage of equilibration of the solution were carried out during several hours at thermodynamic parameters corresponding to the solubility area. The deposition procedure was performed by slow decrease of temperature in the closed cuvette. The deposition procedure was terminated by cuvette decompression, during which the unused material was removed by stream of CO_2 coming out from cuvette.

Figs. 1 and 2 demonstrate that the applied procedure really allows to create ultra thin polymer coatings characterized by high degree of uniformity and extremely small amount of impurities on the substrate surface. The surface of coatings has low roughness that allows to conclude about the close-packed arrangement of the film-forming molecules. The uniformity of the film structure is much higher compared with the coating usually prepared by traditional film-forming techniques (described in Introduction). Besides, the formed coatings are ultra thin ones characterized by nanometer-level thickness.
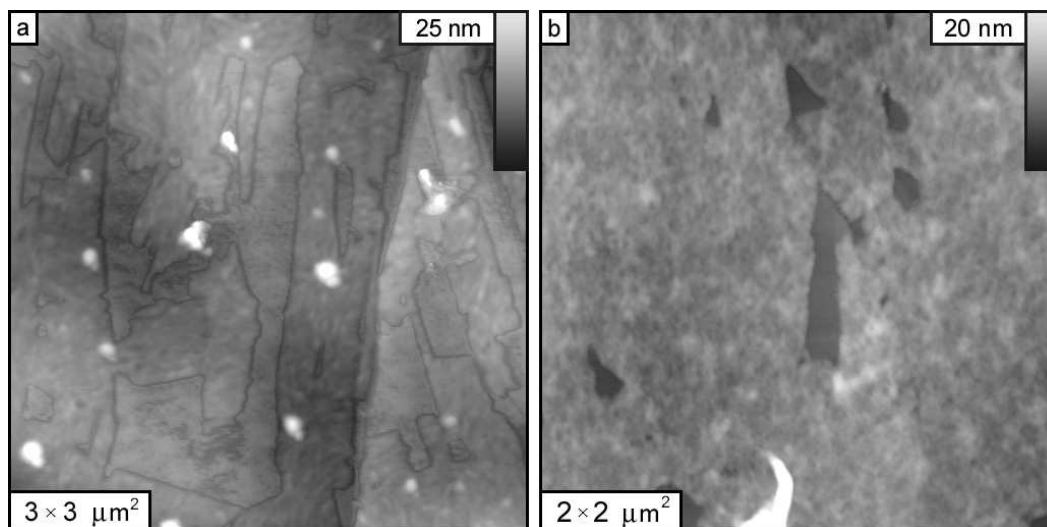
Figure 2. Polymer film deposited onto pyrographite substrate. Topography AFM image obtained in tapping mode in air (a), and in ethanol (b). Exposition at $T = 55°C$, $P = 80$ MPa for 3 h followed by temperature lowering down to 20°C and decompression.

We can state that these films are characterized by quality which is comparable with the quality of films prepared by Langmuir-Blodgett method. However, thin LB films (few monolayers) often appear to be unstable and inclined to reorganization [9]. Ours coatings maintain their structure with time and during scanning procedure not only on air, but also in liquid medium, see Fig. 2b.

It can be seen in the images of Fig. 1 that the prepared coating has lamellar structure, and the angle of mutual orientation of lamella is close to 30°. The domain structure of the film is clearly seen in Fig. 2a: 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 can be explained probably by the substrate influence; mechanism of their creation requires further examination.

The isolated defects in the film structure are observed in the images of Fig. 1 and Fig. 2b which allows to measure the film thickness. We found that the thickness of our thin film coatings is equal to 5–8 nm on graphite surface for different parameters of the exposure. According to our observation the material excess does not produce an increase of the film thickness and is spent to formation of aggregates, see Fig. 1 and Fig. 2a.

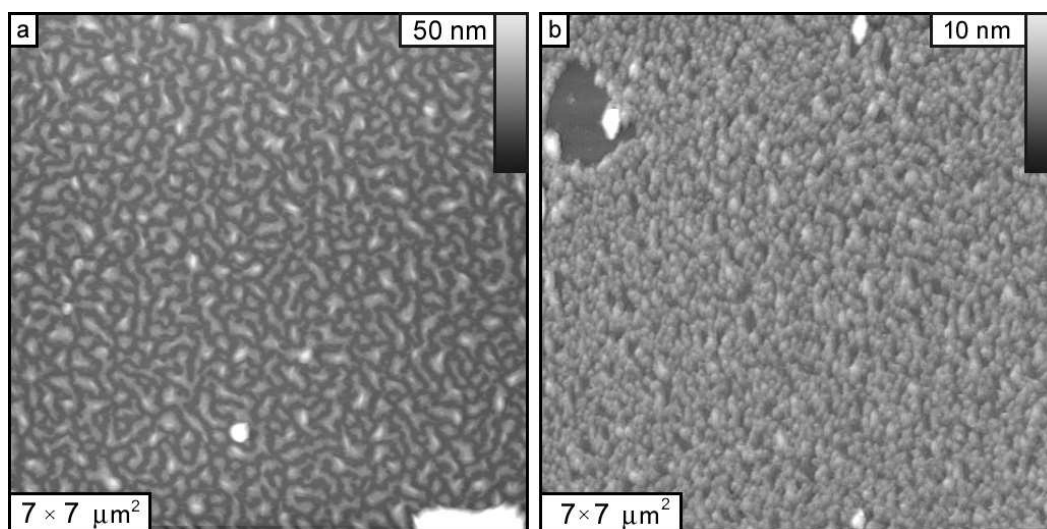One can estimate the size of compact globule containing one Teflon®AF2400

Figure 3. Polymer film deposited onto mica substrate. Topography AFM image obtained in contact mode in air. Exposition at: $T = 65°$C, $P = 79$ MPa for 6 h (a), and $T = 35°$C, $P = 40$ MPa for 3 h (b) followed by temperature lowering down to $20°$C and decompression.

copolymer molecule using the formula:

$$D = 2\sqrt[3]{\frac{3M}{4\pi\rho}}, \tag{1}$$

where M is the molecular mass and ρ is the material density. Applying the estimation for the molecular mass $M \sim M_n/N_A$ we estimate the diameter of the compact globule as $D \sim 6$ nm. The film thickness experimentally determined by AFM approximately coincides with the estimation of compact globular size.

The AFM image in Fig. 2b is obtained in a liquid cell. When using ethanol as an investigation medium, it was possible to achieve better spatial resolution (in tapping mode) in comparison with the experiments in air or in water. It can be explained either by better dynamics of the probe-sample force interaction in ethanol [24] or by more effective removal of possible traces of contamination from the film surface.

When using mica as a substrate, the formed thin film revealed other type of morphology. The excess of a polymer material in this case results in increase of coating thickness. However, the film formation process was followed by structural reorganization of polymer molecules on the substrate. This reorganization is seen in the AFM image of the film (Fig. 3a). The created film is not homogeneous in thickness (as on pyrographite substrate) but consists of a set of
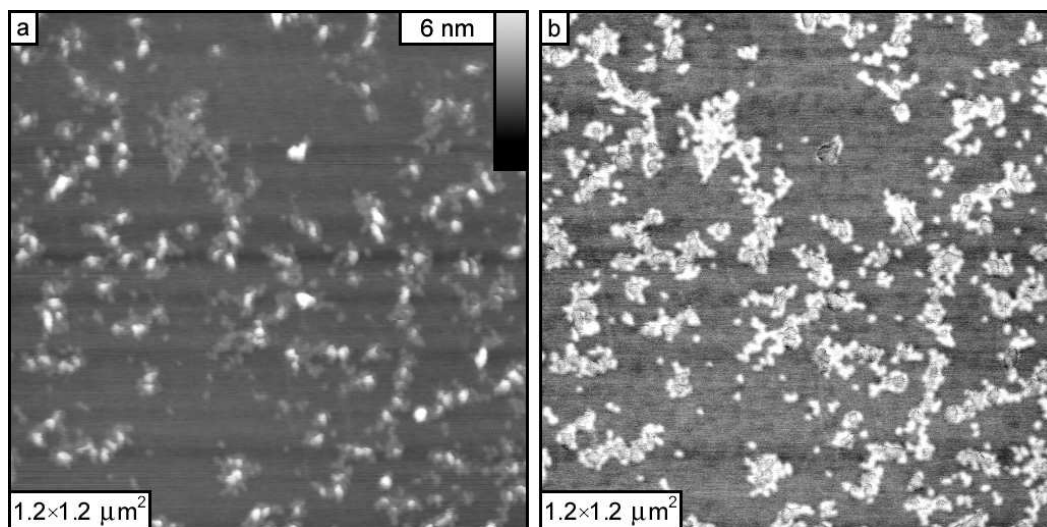
Figure 4. Polymer molecules deposited onto mica substrate. Topography (a) and phase (b) AFM images obtained in tapping mode in air. The phase image (b) is characterized by better contrast. Exposition at $T = 60°$C, $P = 70$ MPa for 4 h followed by temperature lowering down to $50°$C and decompression.

structures with complex morphology. 20 to 60 nm above the substrate surface.

In more mild exposure conditions (at lower polymer solubility) it is possible to form the film 4–7 nm in thickness (Fig. 3b) on a mica surface. The deposited film is not closely packed, that allows to see individual globules.

The images of individual polymer molecules deposited on a mica substrate are given in Fig. 4. Two types of structures are seen. Higher objects have 2.5–5 nm 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 (0.5–1nm) can be seen which are most probably the partially compacted macromolecules. The morphology of these structures is clearly visualized in the phase image (Fig. 4b). The corresponding topography image is shown in Fig. 4a. The phase image is obtained in tapping mode and its contrast is determined by the difference of viscoelastic properties of the substrate and adsorbed object which usually allows to achieve the better contrast in comparison with the topographical image.

4. Conclusion

We have explored the structure of thin-film coatings and individual molecules of Teflon®AF2400 copolymer deposited on different substrates from solutions in

supercritical CO_2. Using AFM we have shown that the thin Teflon®AF2400 films deposited on pyrographite substrate are characterized by perfect homogeneity (in comparison with other types of polymers films), they reveal high resistance against mechanical influence of the scanning probe, and stability in air and in liquid medium. At the same time the coatings are about 6 nm in thickness (this corresponds to thickness of one monolayer of closely packed compact globules). Films formed on a mica substrate are less homogeneous and tend to reorganization. It was also possible to visualize both completely and partially compacted individual polymer molecules. Such examinations may contribute to better understanding of macromolecule conformational changes in supercritical solutions.

Acknowledgements

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