ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 6, pp. 1056–1059. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © A.E. Solomyanskii, G.K. Zhavnerko, V.E. Agabekov, N.A. Marchik, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 6, pp. 886–889.

Tribotechnical Characteristics of the Langmuir–Blodgett Polyvinylpyridine Films

A. E. Solomyanskii, G. K. Zhavnerko, V. E. Agabekov, and N. A. Marchik

Institute of Chemistry of New Materials, National Academy of Sciences of Belarus, ul. F. Skoriny 36, Minsk, 220141 Belarus
e-mail: zhavn@ichnm.basnet.by

Received January 13, 2010

Abstract—The tribological properties of the Langmuir–Blodgett poly-4-vinylpyridine monomolecular films and cationic polyelectrolytes: polydiallyldimethylammonium chloride, polyallylamine, and polyethyleneimine monolayers were studied. The highest stability toward the mechanical impact of a steel ball (indenter) was observed in the poly-4-vinylpyridine film formed at the surface pressure 20 mN m^{-1}.

DOI: 10.1134/S1070363210060034

The development of nanostructured coatings based on amphiphilic polymers and the study of their wear resistance during friction is of interest for a wide range of technical applications like the manufacture of insulating and conducting ultrathin films, creation of passivating and protective coatings, and for the surface energy control [1, 2]. One way to obtain the nanostructured coatings on a solid surface is the method of Langmuir–Blodgett, which allows to create homogeneous highly ordered molecular layers with controlled nanometer thickness [3]. For studying the wear resistance of thin film coatings in the process of friction at the micro level, it was suggested to use a reciprocating microtribometer with the technical characteristics corresponding to the friction force in the microelectromechanical system. The sphere–plane scheme used in the instrument allows to eliminate the inevitable effects of inclination of the indenter and the plate on the geometry of the contact [4].

The purpose of this work is obtaining protective coatings based on poly-4-vinylpyridine promising for the use in microelectromechanical systems [4] and studying their tribological properties. Durability of the monomolecular films of polyvinylpyridine in the processes of friction is compared with the stability of coatings with the fullerene C_{60} nanoparticles in a polyvinylpyridine matrix and the monolayers of cationic polyelectrolytes: polydiallyldimethylammonium chloride, polyallylamine, and polyethyleneimine, formed by deposition onto a hard surface from a solution [5].

A specific feature of the compression isotherms of polyvinylpyridine is the existence of a liquid-condensed phase state with an extended plateau (Fig. 1a). Analysis of atomic force microscopy images of the

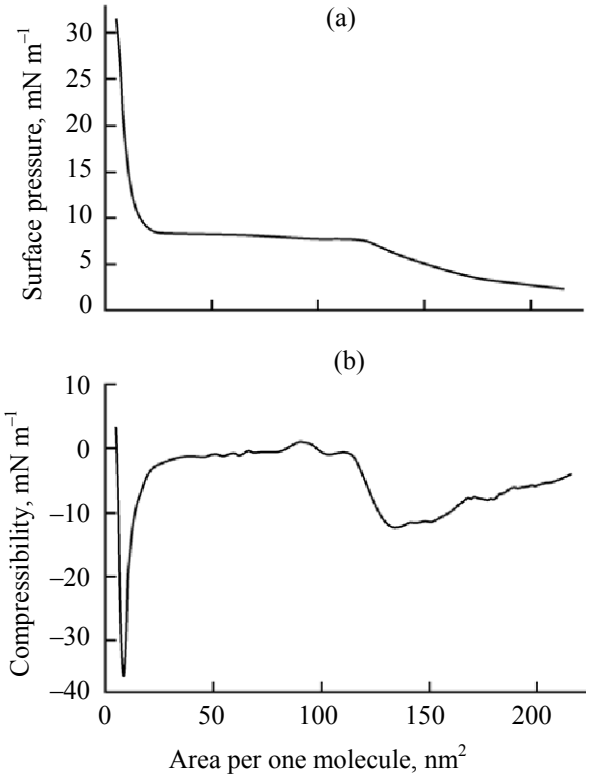

Fig. 1. Compression isotherms of polyvinilpyridine monolayer on water surface: the dependence of surface pressure (a) and compressibility (b) vs. the area per one molecule.

polyvinylpyridine films (Fig. 2) showed that the increase in surface pressure on the monolayer up to ~6 mN m^{-1} leads to the formation of folded structure and increase in the height of the folds (Fig. 2b). Note that the formation of the folds (collapse of the monolayer) at low surface pressure is characteristic for the investigated polymer. Perhaps some segments of the polyvinylpyridine macro-chain are squeezed out of the plane of the polymer monolayer. Upon reaching a high pressure on the monolayer (~20 mN m^{-1}) the folds converging occurs without further changes in their height and the formation of a homogeneous structure with the folds located close to each other (Fig. 2c).

The polyvinylpyridine film has two pronounced regions with different elasticity (Fig. 1b). Before the surface per molecule value becomes equal to 134 nm^2

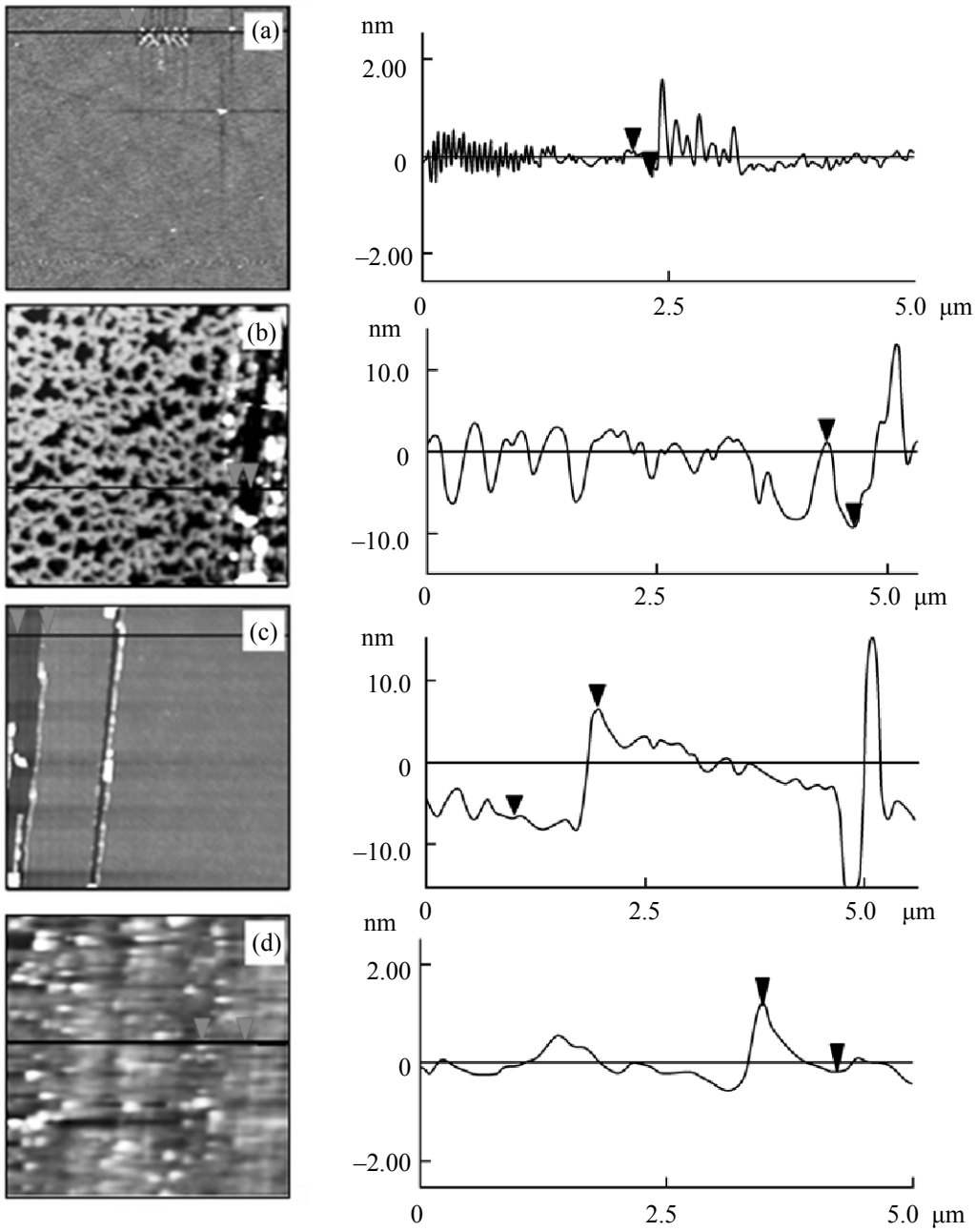

Fig. 2. Atomic force microscopy images and cross-sectional profile of polyvinylpyridine films with artificial defects in their structure obtained at different surface pressure, mN m^{-1}: (a) 3, (b) 6, (c) 20, and (d) aggregates of fullerene C_{60} in the polyvinylpyridine matrix.

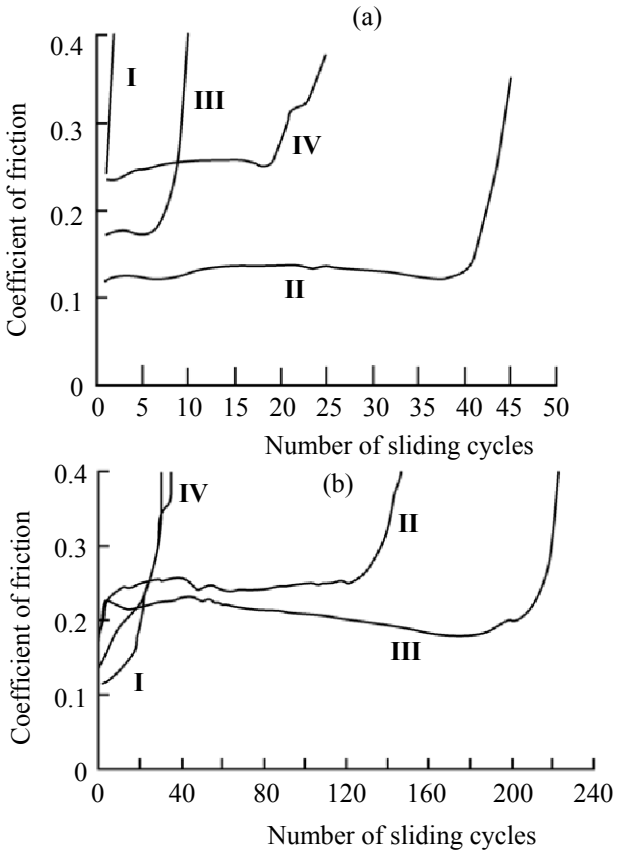

Fig. 3. The coefficient of friction vs. the number of sliding cycles for: (a) **I**, natural oxide layer, **II**, polyallylamine, **III**, polydiallyldimethylammonium chloride, **IV**, polyethyleneimine and (b) polyvinylpyridine films formed at different surface pressure, mN m^{-1}: (**I**) 3, (**II**) 6, (**III**) 20, and (**IV**) aggregates of fullerene C_{60} in the polyvinylpyridine matrix.

the elasticity modulus (C_s^{-1}) is ~12.4 mN m^{-1} and restructuring of the macro-chains occurs with the convergence of the segments. Further reduction of the surface per molecule leads to the formation of polymer folds. When the values of the surface per molecule reaches ~15 nm^2 the elasticity of the film decreased (C_s^{-1} ~37 mN m^{-1}) as a result of convergence of the folds.

The reciprocating type microtribometer registers changes in k_f of steel indenter on a silicon substrate with a sample as a dependence on the number of the sliding cycles [4]. In the experiment with a load 0.3 N the natural surface oxide layer was broken in the first cycle of sliding (Fig. 3). At testing the monolayers of cationic polyelectrolytes: polyallylamine, polyethyleneimine and polydiallyldimethylammonium chloride, the destruction of the SiO_2 and the displacement of the films from the contact zone between the surfaces was observed after ~43, 30, and 10 cycles of sliding, respectively (Fig. 3a). Displacement of the polyvinylpyridine layers formed at a surface pressure 3, 6, and 20 mN m^{-1} from the contact zone and the destruction of the SiO_2 surface occured after ~32, 146, and 220 cycles of sliding, respectively (Fig. 3b).

Polymer films have good adhesion to different materials, in particular, polyethyleneimine is characterized not only by the electrostatic interaction, but also by the formation of hydrogen bonds with the silicon surface [6]. On the other hand, we cannot exclude transfer of a part of layer on the indenter in the process of friction (lubrication effect), because of the mobility and flexibility of polymer chains. This effect is more evident for the Langmuir–Blodgett polyvinilpyridine films, as seen from the increase in durability of coatings. Perhaps in this case the factor influencing the film wear resistance is the coating thickness, which in the case of polyelectrolytes is ~1.5–2 nm [7], while the thickness of the polyvinylpyridine monolayer obtained at the surface pressure 3 mN m^{-1} is ~0.5 nm, and at the surface pressure 6 and 20 mN m^{-1} the thickness is ~8 and 11 nm respectively, which contributes to the "lubrication" of the rubbing surfaces.

It was found also that the introduction of fullerene into the film reduces wear resistance of the polyvinylpyridine coating. Ousting the cover from the contact zone of the rubbing surfaces was observed after ~34 sliding cycles, which may be due to defects in the monolayer because of the heterogeneity of the distribution of nanoparticles in the polyvinilpyridine matrix and their abrasive effect on the polymer in the process of friction. Therewith, the film thickness is 1 nm (Fig. 2d).

The value of k_f for the polyelectrolyte films during first run of indenter decreased compared to the unmodified surface from 0.15 to 0.09, while in the case of polyvinylpyridine it slightly increased, from 0.15 to 0.17, possibly due to the increased viscosity of the coating.

Thus, we found that the greatest wear resistance at the friction of monomolecular Langmuir–Blodgett films based on poly-4-vinylpyridine, formed by horizontal deposition on the silicon surface, is observed for the films obtained at the surface pressure 20 mN m^{-1}. The thin film coatings based on poly-4-vinylpyridine can be used as protective materials in

friction units of microelectromechanical systems of the appropriate type.

EXPERIMENTAL

Silicon rectangular wafers with ~2 cm^2 area, used as substrates for film formation, were pre-hydrophilized at 320 K for 15 min in a mixture of H_2O–NH_4OH–H_2O_2 in the ratio 5:1:1 by volume. The polyvinylpyridine films [molecular weight (M_w) ~73000} were formed on the surface of distilled water (pH 5.5) from 0.5 mM solution in chloroform. The surface pressure–area per molecule (π-A) isotherms were recorded at a compression rate of the monolayer 0.3 mm s^{-1} and subphase temperature 290 K, using a LT-103 installation coupled with a computer [8]. The polyvinylpyridine layers on the silicon substrates were formed by horizontal deposition at a surface pressures 3, 6, and 20 mN m^{-1} [9]. For obtaining the composite film of fullerene in the polyvinylpyridine matrix, to the polymer solution in chloroform was added 0.06% solution of fullerene in toluene and then the film was isolated by the same technique as for monolayers of polyvinylpyridine, at the surface pressure of 6 mN m^{-1}.

The monolayers of cationic polyelectrolyte: polyallylamine with M_w ~17000, polyethyleneimine with M_w ~750000 and polydiallyldimethylammonium chloride with M_w ~200000 were applied on a silicon substrate from their aqueous solutions of 1 mg ml^{-1} concentration (pH 5.5). The wafers were immersed in a solution of the polyelectrolyte for 15 min, then washed in distilled water at vigorous shaking the sample for 1 min to remove the polyelectrolyte excess [5].

Tribotechnical test of the samples in a steel (sphere)–silicon (plane) friction pair was carried out on microtribometer of reciprocating type (IMMS Institute of the Belarus National Academy of Sciences) [4]. As the indenter was used a steel ball of 3 mm diameter (steel 95X18, GOST 3722-81) with a roughness R_a ~0.1μm. Applied load was 0.3 N, the length of the indenter step 3 mm, linear speed 4 mm s^{-1}. The error in measuring the friction coefficients (k_f) is ±0.002. The destruction of the oxide layer of the silicon substrate is observed in the range of k_f sliding of steel on silicon from 0.2 to 0.4, most of the natural oxide layer of SiO_2 of thickness 2 nm is destroyed when the k_f reaches ~0.25 [4]. Consequently, at k_f ~ 0.4 the tribotechnical testing the samples terminated automatically.

The morphology of the formed coatings was studied using atomic force microscopy (AFM) on a scanning probe microscope Nanoscope IIID (Veeco, USA). The scanning conditions: contact mode, cantilever of silicon nitride with a constant stiffness 0.32 N m^{-1}, scanning rate 1–5 Hz, the reference value of the force of interaction 1–10 nN, the information density was 512×512 pixels. The thickness of the polyvinylpyridine coating was evaluated by measuring the depth of the worn film surface after tribological tests by the AFM method. In the case of polyvinylpyridine film formed at the surface pressure 3 mN m^{-1} the defect in the monolayer was formed by the microscope cantilever.

REFERENCES

1. Mittal, K.L., *Surfactants in Tribology*, London: CRC Press, 2008, p. 485.
2. Riess, G., *Prog. Polym. Sci*., 2003, vol. 28, p. 1107.
3. Blinov, L.M., *Usp. Fiz. Nauk*, 1988, vol. 155, no. 3, p. 443.
4. Myshkin, N.K., *Trenie, smazka, iznos* (Friction, Lubrication, and wear), Moscow: FIZMATLIT, 2007, p. 368
5. Paribok, I.V., Parfenova, M.S., Zhavnerko, G.K., and Agabekov, V.E., Abstract of Papers, *BelSZM-5 Conference*, 2002, p. 99.
6. Sukhorukov, G.B., Brumen, M., Donath, E., and Möhwald, H., *J. Phys. Chem., B*, 1999, vol. 103, no. 31, p. 6434.
7. Nalwa, H., *Handbook for Surfaces and Interfaces*, vol. 3, New York: Academic Press, 2001, p. 170.
8. Zhavnerko, G.K., Kuchuk, T.A., and Agabekov, V.E., *Zh. Fiz. Khim*., 1994, vol. 68, no. 8, p. 1505.
9. Agabekov, V.E., Zhavnerko, G.K., Staroverov, V.S., Bar, G., and Cantow, H.-J., *Acta Physica Polonica, A*, 1998, vol. 93, pp. 383–386.