Studies on surface structure of polymer membranes – biosensor carriers with dynamic force microscopy

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Abstract. Useful information about the surface pore structure of polymeric track and Millipore membranes chosen as biosensor carriers have been obtained using the easyScan dynamic force microscope.

1. Introduction
Biosensors are used in medical diagnostic nanoprocesses, environmental situation assessments and other processes based on the immobilization of bioobjects such as antibodies, antigens and their conjugates with collaurin nanoparticles in porous membranes. The design of biosensors suggests a thorough study of the formation of a contact of liquid media with porous carrier matrices, both at the stage of preparation of the biologically active composite material, and in the stage of its functioning [1]. Accordingly, it is essential that the polymer membrane’s surface structure be studied. The present study examined structures of polymer films having three types of pore structure: membranes having cylindrical pores, filters having pore reticular structure and these having a fibrous structure. The necessary information about the surface structure of these carriers was obtained with the dynamic force microscope [2, 3].

2. Examination procedures and materials
The images of surface topography of various polymer membrane biosensor carriers were obtained with the atomic force microscope easyScan Nanosurf (Switzerland) [3], operating in a dynamic force mode (DFM, Intermittent contact) under ambient conditions. The typical dynamic frequency of the cantilever is about 150 kHz, spring constant - 48 N m⁻¹, sensor type - NCLR (Nanoworld, Switzerland). In the given article, the DFM images contain 128×128 pixels and the time per line 0.5 s.

Polyethylenterephthalate track membranes obtained through matrix irradiation with massive high energy beams of ions Xe, following etching with alkaline solutions that resulted in pore effective diameters in nanometer range, were chosen to study the membranes having pore cylindrical structure (JINI, Dubna, Russia) [4].
The complex ether cellulose filters of Millipore Filter Corporation (USA) [5] were chosen as representatives of membranes with reticular structure of pores. The membranes with fibrous structure were based on nitrocellulose [6].

3. Experimental results and discussions

The images of the selected track membrane surface are shown in figure 1a and 1b. In all the figures, the left side (a) shows the topographical view 'Top View', while the right side (b) shows the space view '3D - View'.

The number of pores over the surface unit area was found to be about $2 \times 10^8$ cm$^{-2}$. The porosity amounted to 2%. It is readily apparent that the pore surface distribution shows some heterogeneity, such as several merged pores. Figure 2a and 2b show the individual pore of the same membrane.

The direct measurements of pore diameter on the images produced an effective value of 100 nm that fitted the estimates by other methods.

The surface images of the same membrane made on the opposite side revealed some asymmetry of the pore structure as compared to the front side. The presence of the hillocks is clearly recognized near
the pores, which is due to the passage of ions Xe through the original matrixes. These points can be of great value in interpreting the operation of sensors designed.

The surface images of the polymer membranes having reticular (nodular [6]) structure are shown in figures 3a and 3b, 4a and 4b (Millipore, 50 nm, type VM) from the front:

- **3a)** and **3b)**: Scan range $XY = 7740 \times 7740$ nm, $Z$ Range $= 1120$ nm.

- **4a)** and **4b)**: Scan range $XY = 1170 \times 1170$ nm, $Z$ Range $= 279$ nm.

Figures 3, 4. The DFM surface images of the membrane Millipore from the front side. Figures 5a and 5b, 6a and 6b show the images of the same membrane from the opposite side:

- **5a)** and **5b)**: Scan range $XY = 4240 \times 4240$ nm, $Z$ Range $= 559$ nm.
The complex asymmetric surface pore structure of these membranes is clearly seen and the pore diameter average value specified by the manufacture of these filters is apparent to be the first approximation in our case. The same appearance of surface topography images is characteristic of the membrane Millipore, 25 nm, type VS and Millipore, 100 nm, type VC.

We failed to receive surface topography images of the membranes having fibrous structure on the basis of nitrocellulose and pore diameter in the range of 8000 nm with the DFM because of substantial differences in height of the particles available on the surface. Meaningful information about their structure was obtained only with the scanning optical interference microscope New View – 5022 (Zygo, USA), having a vertical resolution as high as 1 nm and lateral one of less than 1000 nm. The images obtained are characteristic of substances having fibrous structure. In the design of biosensors, such membranes are used to immobilize collaurin conjugates with specific antibodies on fibres of the matrix of the test zone inlet area.

The obtained results on the surface topography of the polymeric membranes selected as promising biosensor carriers are essential in describing the interaction of biopolymers with these carriers, particularly in predicting normal and tangential movements of solutions involved in various reactions in the pore system of these materials.

4. Conclusion
The easyScan dynamic force microscope has been shown to produce useful information under ambient conditions about the structure of the surface, values of pore diameter, porosity and other properties of the surface of polymer membranes used in practical applications. The studies demonstrate ease and readiness of defining these important indicators with the DFM as compared to the other procedures.

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