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Modification of the surface and pores of poly(ethylene terephthalate) track membranes using *N*-isopropylacrylamide for an improvement of membrane performances

Denis A. Trofimov,* Valery M. Shkinev and Boris Ya. Spivakov

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: da.trof@yandex.ru

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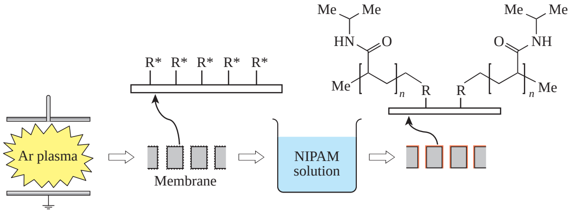
The track membranes based on poly(ethylene terephthalate) activated by low-temperature plasma were modified with the use of a solution of *N*-isopropylacrylamide in an organic solvent. The filtration efficiency of the modified membranes was higher by a factor of 2.5 than that of the original track membrane.



The distribution of radioactive and toxic metals and organic substances between micro- and nanoparticles in natural samples is of considerable current interest. Membrane filtration techniques are widely used in environmental analytical chemistry, biological and clinical assays and various technologies.[1,2] The membranes should not adsorb test components from the test solution and not release them into the solution; they should provide high filtration efficiency (high liquid flow) and sufficient selectivity for components to be separated.[2] Track membranes (TMs), also called track-etched membranes or nuclear filters, which are prepared by the bombardment of plastic films with heavy ions with the subsequent etching, meet most of these requirements.[3] They have a regular pore structure, high selectivity and a minimum emission of membrane components into the test solution; this is important in the analysis of micro and nanoquantities of substances. The main disadvantage of TMs is a highly hydrophobic surface and, hence, a low filtration efficiency of aqueous solutions under working pressures.

To overcome this disadvantage, the premodification of membranes, especially filters with small pores (< 0.2 μm), is required for TMs, including common poly(ethylene terephthalate)-based membranes (PET TMs). The preparation of conventional initial TMs or, in other words, providing working conditions for the filters takes a lot of time from several hours to a few days.[4] However, even after such a preparation, conventional TMs tend to reduce the filtration efficiency during the filtration process that increases the filtration time.

Therefore, the preparation of modified TMs with higher filtration rates is an important task. A primary requirement imposed on modification methods is a possibility of treating pore space because some methods, including plasma treatments, make it possible to modify only the polymer surface.[5] However, the modification should not significantly change the pore structure (the shape of pore channels, arising additional partitions inside the pore, *etc*.); otherwise, it may lead to a loss in membrane selectivity and filtration efficiency. The known methods for the modification of porous polymeric systems[6] can be divided into two groups: (1) the application of low- or high-molecular-weight compounds onto the membrane surface to form a layer with desired properties and (2) the alteration of the physicochemical properties of a thin surface layer of the polymer membrane.

The first group includes plasma- and radiation-chemical grafting and polymerization, modification by physical or chemical adsorption, or the chemical grafting of high-molecular-weight compounds. However, the applicability of developed procedures to TMs is limited.[7] Grafting occurs not only on the external membrane side but also, to a lesser extent, in the pores. This is due to significant changes in the pore structure of modified TMs (up to their healing) because of the formation of a significant thickness layer of the modifying substance that, in turn, leads to a significant change in the filtration efficiency and selectivity of the membrane.

In all cases, the grafting proceeds mostly on the external membrane side but not in the pores. The influence of modification on a change in the hydrophilicity rate of membrane surfaces is observed only at high degrees of grafting (7–10%), at which a significant decrease in pore diameters and in filtration efficiency (up to 100 times) occurs even in large-pore membranes. This is because the grafting takes place mainly around the pore mouths due to the energy and chemical heterogeneity of the surface.

The use of so-called smart polymers is interesting and promising for membrane modification.[8,9] Such polymers can change their size and other properties under the influence of environmental parameters. The application of the polymers to modification may allow one to obtain polymeric membranes with controlled properties, such as filtration efficiency, owing to changes in ambient temperature. *N*-Isopropylacrylamide (NIPAM) is such a polymer that can modify the surface and pore space of TMs.

In this work, TMs were modified by their treatment with a 1 м NIPAM solution. Activation using low-temperature plasma initiated the polymerization process. We used PET films with a pore diameter of 0.2 μm. The normal film thickness was 10 μm, and the pore density varied in a range of 108–109 cm^{-2}. The monomer NIPAM from Sigma-Aldrich (97% purity) was used for the surface modification.

A laboratory setup (Figure 1) was used for the activation of TMs by low-temperature plasma. An RF generator (13.56 MHz) was employed as a power source. The apparatus makes it possible

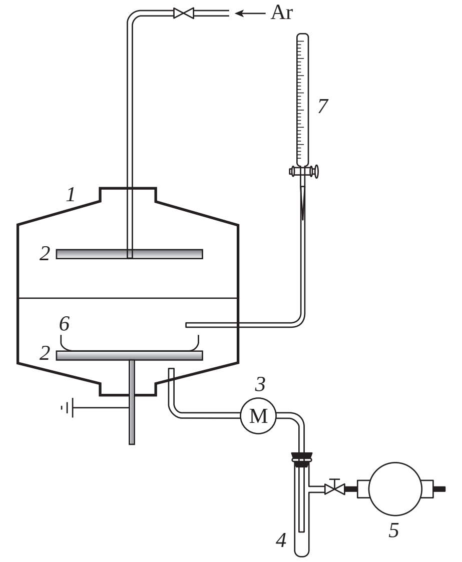


Figure 1 Plasma apparatus for applying a modifier from solution: (*1*) glass reactor, (*2*) aluminum electrodes, (*3*) pressure pump, (*4*) nitrogen trap, (*5*) vacuum pump, (*6*) Petri dish, (*7*) NIPAM solution.

Table 1 The membrane fluxes under different conditions.

Membrane	T/°C	Q/10^{-5} dm^3 min^{-1} m^{-2}				
		0.1 bar	0.4 bar	0.7 bar	0.9 bar	1.2 bar
Initial	25	0.7	1.3	1.5	1.5	1.6
Modified	25	0.6	1.3	2.2	3.0	3.9
	35	0.6	1.4	2.2	3.0	3.9
	40	0.6	1.4	2.2	3.0	3.9
	45	0.6	1.4	2.2	3.2	4.1

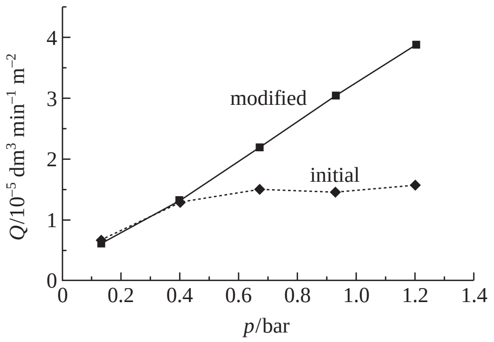


Figure 3 The pressure dependence of fluxes at 25 °C for the initial and modified membranes.

to perform the plasma treatment of TM surfaces by the ions of argon (used here), oxygen, nitrogen or their mixtures with the simultaneous or subsequent (after plasma treatment) grafting of various polymers or monomers.[10] In our experiment, a solution feed system was added to prevent a contact of the activated surface with air that could lead to a decrease in the number of active centers.

A membrane was placed in a Petri dish mounted on a metal electrode 12 cm in diameter, and the distance between the electrodes was 3 cm. The system was evacuated for 4–6 h to a pressure of 10^{-4} Pa. For the subsequent TM surface cleaning and activation, the membranes were pretreated with argon plasma for 4 min at a constant argon flow rate. During the argon pretreatment, the pressure and power were kept at 40 Pa and 35 W, respectively. When the activation process was over, the system was disconnected from the vacuum pump, and the pressure in the reactor was equalized to atmospheric one by feeding excess argon to the system.

After that, 50 ml of a 1 M modifier solution in acetone heated to 30–40 °C was fed to the system to cover the entire membrane surface. The feed solution was also heated. Then, the Petri dish containing the membrane and modifying solution was removed from the reactor and placed in a glass vessel bearing an excess of the modifying solution and heated at 50–55 °C for 2 h. The membrane was taken off and washed with distilled water to remove an excess modifier.

When a nonaqueous solution of the modifier is used, the deposition should occur not only on the surface but also in the pores, since the membranes are made of a hydrophobic polymer and a NIPAM solution in acetone should freely penetrate the pores.

Figure 2 illustrates a possible mechanism of the grafting of NIPAM onto the activated membrane surface. It is well known[11] that the action of plasma results in changing the chemical composition of the surface, increasing the number of polar functional groups (carbonyl and carboxylic) in the thin subsurface layer and increasing the surface energy. Hence, the most probable moieties for grafting are C(O)O and CO.[12]

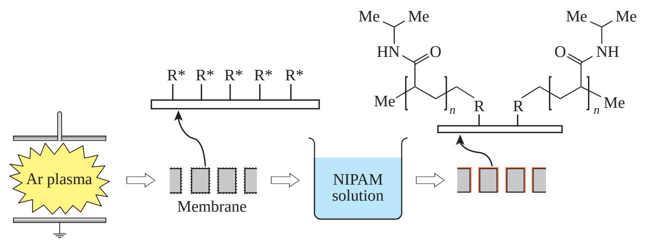


Figure 2 NIPAM grafting procedure.

The filtration efficiency (flux) Q (the volume of water passed through the membrane surface unit per unit time, dm^3 min^{-1} m^{-2}) was measured using a one-stage tangential flow filtration device of our own design[13] and a peristaltic pump (Minipulse 2, Gilson). The modified membrane was placed in the filtration device, and the whole system was thermostatted at 25 °C for 2–3 h. The pressure dependence of filtration efficiency (distilled water flux) was estimated at temperatures of 15, 35, 40 and 45 °C.

From the results (Figure 3, Table 1), it is evident that the flux through a modified membrane can increase dramatically. At low pressures, there is a slight difference between original and modified membranes. However, with increasing the pressure, the data on an initial membrane go up to a saturation dependence, while those on a modified filter exhibit an almost direct pressure dependence over a range of the pressures that corresponds to Darcy's law.[14] The deviation of a curve for the initial membrane from Darcy's law may be due to the fact that the pores are not completely filled with fluid at the working pressures.

Table 1 presents the results of the filtration efficiency measurements for the initial and modified membranes at different temperatures and pressures. Near a phase transition for the grafted polymer (35 °C), the efficiency values did not suffer a significant change; then, a change took place. This may suggest that the molecules of a linear structure can cover most of the hydrophobic parts of the pore structure, which could remain and decrease the flow.

Apparently the surface modification provides a significant increase in the filtering efficiency. The membrane selectivity (retention percentage) tests were made using the standard samples of dextranes with molecular weights from 9.5 to 2000 kDa. The selectivity of the modified membranes was 99.83% based on the original filter. Thus, with the use of filters modified by the method proposed in this work, the filtration performances can be improved without selectivity losses.

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