Surface modification of polymers using cationic polyelectrolyte solutions*

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Surface modification of polystyrene and Nafion™ films with a cationic polyelectrolyte poly(diallyldimethylammonium chloride), or PDADMAC, through adsorption of the polyelectrolyte from its aqueous solutions was studied. It was established that the PDADMAC adsorption layers strongly adhere to the polystyrene films, thus hydrophilizing their surface. Attempts to modify the surface of Nafion™ films revealed that PDADMAC is localized in channels of the swollen polymer film without any noticeable effect on the characteristics of the film surface.

Key words: Nafion™, polystyrene, wetting, adsorption, modification, polyelectrolyte, surface energy.

Modification of solid surfaces with surfactant adsorption layers is widely used to control wetting and adhesion in many technological processes. One of the most important colloid chemistry methods for changing these properties is based on adsorption of surfactants from solutions on the surface solids. The adsorption layers change the surface properties of materials by imparting them a necessary degree of surface hydrophilization or hydrophobization.[1] Measurements of the contact angles of various liquids on the modified surfaces allow one to calculate various physicochemical characteristics, *e.g.*, the roughness factor, the surface coverage, the specific free surface energy, the interfacial energy at the solid—solution interface, and to compare the results obtained with the corresponding parameters of untreated surfaces.[2]

Modification of high-energy solid surfaces involves strong immobilization of surfactant molecules on substrates. This can be done by either chemical bonding of surfactants with the surface[3] or physisorption. In the latter case the adsorbate—adsorbent bond can be comparable in strength with chemical bonding depending on the type of intermolecular interactions.[4] Monolayer coverage of the surface with an adsorption layer causes hydrophobization of the initially hydrophilic substrate. An increase in the surfactant concentration can be followed by the formation of a bilayer which is not strongly bound to the monolayer and can be removed with ease from the surface by, *e.g.*, washing the sample. A particular position is occupied by the modification of high-energy surfaces (metals, quartz, glasses) with self-assembling monolayers (SAMs) of thiols and disulfides[5] as well as organosilicon compounds.[6] Chemisorbed (covalently bonded) modifier molecules form ordered structures that are strongly adhered to the surface. Adsorption is performed from solutions or from the vapor phase and can involve variation of the modifier concentration and the time of its contact with the surface. The surface properties of substrates can be finely tuned depending on the nature of the terminal functional groups in the modifier molecules. For instance, by coating the surface of gold with thiol and disulfide SAMs one can go from the high-energy surface of the untreated substrate (*e.g.*, gold with the surface energy σ_{SV} = 1650 mJ m^{-2}) to the SAM-covered surfaces that simulate low-energy surfaces, *e.g.*, Teflon™, paraffin, polyimides, and polycarbonates with the surface energy σ_{SV} = 18—40 mJ m^{-2}.[5]

Modification of low-energy (hydrophobic) surfaces with adsorption layers of low-molecular-weight surfactants affords hydrophilized substrates; however, the adsorption layers are loosely bound to the surface

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and can be completely removed upon washing in water. This also holds for nonionic high-molecular-weight surfactants, *e.g.*, Pluronics®; however, their adsorption layers stabilize polymer suspensions under the conditions of heterophase polymerization.[7]

Adsorption layers of high-molecular-weight surfactants, *e.g.*, natural polyelectrolytes (proteins), strongly adhere to both high- and low-energy surfaces, thus being universal modifiers of solid surfaces. Specific features of their modifying action are due to the presence of hydrophilic and hydrophobic fragments in the protein macromolecule. It was demonstrated that hydrophilic substrates covered with protein adsorption layers become water-resistant while hydrophobic substrates are hydrophilized.[8] The modifying action of gelatin, α-chymotrypsin, and bovine serum albumin has been best studied. Gelatin was shown to be the best modifier of solid surfaces of different nature, especially, when its macromolecules adopt a coil conformation.

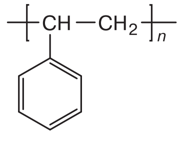
Synthetic polyelectrolytes have been less studied as modifiers of solid surfaces. It was reported that modification of Teflon™ with solutions of polyacrylic and polymethacrylic acids[9] was followed by irreversible adsorption of the modifiers and by weak hydrophilization of the polymer surface. The modifying action of polyelectrolytes in regard to polymeric materials is of undoubtful interest because these substances are widely used in various practical applications (*e.g.*, biomedicine and membrane technologies) and seem to be rather promising for solving particular problems. Indeed, polymers are used as biocompatible materials for, *e.g.*, manufacturing of implants and auxiliary medical facilities.[10] Such materials must meet severe requirements, *viz.*, they should be stable, bioinert, and nontoxic, as well as possess stable mechanical properties under operating conditions. All these factors are traditionally referred to as "biocompatibility of polymeric materials", *i.e.*, the ability of a material to exist in contact with a biological medium without being harmful or toxic.

To a first approximation, a material is suitable for medical purposes if the contact angle of water on its surface is nearly 60°.[10] Most polymers are hydrophobic compounds, therefore, various methods are used for hydrophilization of their surface. These include grafting of hydrophilic monomers, partial oxidation of the surface, modification with lipids, poly(ethylene glycol), *etc.*[11] Surface modification of polymers with polyelectrolytes aimed at solving the problem of biocompatibility of materials was not carried out so far.

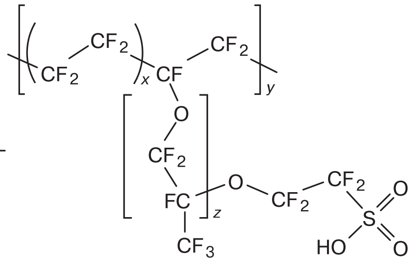
In the development of criteria for biocompatibility[12] it was revealed that the behavior of the polymer in the biological medium is governed by the equilibrium interfacial energy at the polymer—water interface ($\sigma_{\mathrm{SW(W)}}$) which should be close to the cell—blood plasma interfacial energy (1—3 mJ m^{-2}).[12] This approach takes into account (i) structural rearrangement of the surface of the material due to conformational lability of polymer chains in the surface layer in the case of long-term contact with the biological medium, (ii) the fact that no proteins are adsorbed, and (iii) retention of the mechanical properties of the polymer. However, polymeric materials used in medicine are characterized by a wider range of $\sigma_{\mathrm{SW(W)}}$ values. Namely, a polymer can be treated as biocompatible one even at $\sigma_{\mathrm{SW(W)}} \approx 1$ mJ m^{-2} provided that its mechanical properties deteriorate only slightly and the material in not dispersed in the biological medium.

Currently utilized surface modifiers (proteins, phospholipids, Pluronics®) responsible for the thromboresistant properties of biomaterials[11] are efficient for certain polymers only. The range of such agents can be extended using synthetic polyelectrolytes.

In this work we studied the modifying action of poly(diallyldimethylammonium chloride) (PDADMAC) in regard to the surfaces of two polymeric materials, *viz.*, polystyrene (PS) and Nafion™ using an original procedure developed earlier[13] as part or research into modification of various solid surfaces with adsorption layers of classical low-molecular-weight surfactants.



Polystyrene



Nafion™

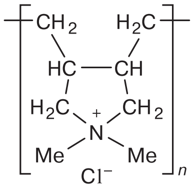
Although PS is a widely used component of materials for biomedical applications, it is characterized by the interfacial surface tension values: $\sigma_{\mathrm{SW(W)}} > 1$—3 mJ m^{-2}. Note that modification of the PS surface with natural polyelectrolyte bovine serum albumin does not cause these $\sigma_{\mathrm{SW(W)}}$ values to decrease.[10] Therefore, it was of interest to answer the question whether or not can this problem be solved using a synthetic polyelectrolyte.

At present, Nafion™ is the most in-demand membrane material which is widely used in various modern technologies (separation of liquids and gases, catalysis, fabrication of ion-selective membranes). Unique chemical structure of Nafion™ provides not only high chemical stability and mechanical properties of the polymer, but also high proton conductivity and high water uptake.[14] The transport properties of Nafion™ membranes are modified using different types of surfactants both during and after the fabrication step;[15] in the latter case, the finished membranes are immersed into surfactant solutions.[16] Although numerous experimental data are available, the effect of the nature of surfactants on the water uptake and proton conductivity of Nafion™ membranes still remains debatable; however, it was established that modification of Nafion™ membranes with cation-active surfactants can change their transport properties.[17] The use of just a cationic polyelectrolyte for these purposes is of specific interest.

Experimental

Fabrication of polymer films. Polystyrene (Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences) and Nafion™117 (Sigma—Aldrich) were used. The characteristics of PS were as follows: the weight-average molecular weight $M_w = 4.3 \cdot 10^4$, the weight-average-to-number-average molecular weight ratio $M_w/M_n = 2.1$, and the residual amount of monomer was 0.2—0.3%. The characteristics of Nafion™ 117 are as follows: the equivalent weight EW = 1100 g mol^{-1} and the density $\rho = 1.5$ g cm^{-3}. Polystyrene films were cast from a 0.5% solution of PS in toluene onto a solid substrate. Nafion™ films were fabricated using a 5% solution of the polymer in aqueous solutions of aliphatic alcohols with the density $\rho = 0.874$ g cm^{-3}. The advancing and receding contact angles of water on the surface of the PS films measured after evaporation of the solvent were $\theta_a = 86°$ and $\theta_r = 84°$, respectively. A small contact angle hysteresis ($\Delta\theta = \theta_a - \theta_r$) of 2° suggests that the PS film surfaces are rather uniform. The Nafion™ films were also characterized by a small contact angle hysteresis ($\Delta\theta = \theta_a - \theta_r = 83° - 80° = 3°$). The thickness of the PS and Nafion™ films determined by the piezoelectric microbalance (PM) method[13] was 200 nm and 1.5 μm, respectively.

Surface modification of polymer films. The surface of polymer films was modified with poly(diallyldimethylammonium chloride) (PDADMAC, Wako Chemicals) with $M = 10^5$, EW = 161.7 g mol^{-1}, and $\rho = 1.22$ g cm^{-3}. Solutions (pH 6.5) containing from 0.1 to 1.0% of the cationic polyelectrolyte were prepared by diluting the starting 20% aqueous PDADMAC solution.



PDADMAC

The surface modification of the PS films was performed as follows. The films were kept in the PDADMAC solutions for 30 min, dried, and the amount of the polyelectrolyte adsorbed on the surface of the films was measured. Then, the films were washed with water, dried, and the amount of adsorbed PDADMAC was measured again. The advancing and receding contact angles of water on the surface of the PS films were measured in all stages of the experiment.

Nafion™ membranes are characterized by high water uptake.[18] Therefore, the surface modification of the polymer films was preceded by measurements of their water absorption (W (%)), that is, the ratio of the weight of water in the swollen membrane (m_{wet}) to the weight of the dry film (m_{dry})

$$W = [(m_{wet} - m_{dry})/m_{dry}] \cdot 100. \qquad (1)$$

as function of the duration of film contact with water.

The Nafion™ films were kept in water for 2—48 h, dried, and the water absorption was calculated. Based on the results obtained, samples fully saturated with water were selected for further experiments. The selected Nafion™ films were modified by keeping them in a PDADMAC solution with $C = 3.5 \cdot 10^{-5}$ mol L^{-1} for a certain time. Then, the films were washed in water, dried, and the residual amount of adsorbed cationic polyelectrolyte was determined. We also carried out experiments with the films which were not preliminarily brought in contact with water.

The quartz crystal microbalance (QCM) method. The amount of PDADMAC adsorbed on the polymer surface was determined following a procedure we have developed earlier.[13] It involves measurements of (i) the amount of substance adsorbed on the polymer surface using the same samples film by the highly sensitive QCM method and (ii) the contact angles of various fluids in order to control the formation of adsorption layer on the solid surface (determination of the preferred orientation of molecules in the adsorption layer and the specific free surface energy of the modifier layers). The QCM method is a direct gravimetric method based on the dependence of the eigenfrequency

(f) of the quartz resonator (sensor) of a microbalance on the amount of substance (m) supported on the resonator surface[19]:

$$\Delta f = -c_f \cdot \Delta m, \qquad (2)$$

where Δf is the frequency shift (Hz), c_f is the weight sensitivity coefficient, which depends on the properties of the quartz crystal and on the resonator eigenfrequency (f_0), and Δm is the change in the weight per unit area (g cm^{-2}) of the electrode surface.[19] High sensitivity of the QCM method (to 10^{-12} g) allows one to measure the adsorption values at low solution concentrations. This method was used to measure the adsorption of surfactants on solid surfaces and its correctness was confirmed by other relevant techniques.[4]

The sensor of the microbalance is a thin disk-shaped quartz crystal (d = 5—16 mm) coated by thermally sprayed metal (gold, silver, aluminum, chromium, and platinum) electrodes on both sides. The weight-sensitive region of the quartz disk matches the surface of the electrode. In this work we used AT-cut quartz crystals with an eigenfrequency, f_0 of 5 MHz and silver electrodes 200 nm thick. The weight sensitivity coefficient of the quartz crystal was $c_f = 56.75 \cdot 10^6$ Hz cm^2 g^{-1}.[13]

To determine the adsorption, the eigenfrequency (f_0) of the quartz crystals was first measured. Next, the resonator surface was coated with the polymer film, dried to remove the solvent, and the oscillation frequency (f_1) was measured. The film thickness was calculated using the frequency shift $\Delta f = f_1 - f_0$ and the known values of the polymer density. Then, the quartz crystals coated with the films were kept in PDADMAC solutions, washed in water (3×50 mL), dried in air for 24 h, and the oscillation frequency (f_2) of the quartz crystals coated with the polycation adsorption layer was measured. The amount adsorbed (Γ, g cm^{-2}) was calculated by the equation:

$$\Gamma = -1.76\Delta f \cdot 10^{-8}, \qquad (3)$$

where $\Delta f = f_2 - f_1$.

The quartz crystal oscillation frequency was measured using a Ch3-54 electronic frequency meter (Electropribor, Russia) in a thermostatted chamber at 20 °C with an accuracy of ±1 Hz. The error in the determination of adsorption was $\pm 10^{-8}$ g cm^{-2}.

Determination of the surface characteristics of polymer films. Rather large surface area of the quartz crystal electrodes (~0.5 cm^2) allows one to measure the contact angles which provide information on the state of the solid surface (degree of surface coverage with the adsorption layer, preferred orientation of molecules in the adsorption layer, specific free surface energy of the modifier layers)[20] using the same samples.

The contact angles were measured under the advancing (θ_a) and receding (θ_r) conditions. In the former case, a water drop was released from a microsyringe onto the surface. In the latter case, an air bubble approached the surface immersed in water. The measurements were carried out in closed cells at room temperature for 2—3 drops (bubbles). The volume of the drop (bubble) was 2 μL.

The specific free surface energies (σ_{SV}) of the starting polymer films and those of the films modified with the polycation adsorption layers were calculated with inclusion of the contributions of the dispersion ($\sigma^d{}_{SV}$) and non-dispersion ($\sigma^p{}_{SV}$) components $\sigma_{SV} = \sigma^d{}_{SV} + \sigma^p{}_{SV}$ (see Ref. 21) using the molecular theory of wetting in the Owens—Wendt—Calbley approximation.[22] The calculations were performed using the advancing contact angles θ_1 and θ_2 of the test fluids (water (θ_1), hexadecane, or methylene iodide (θ_2)), the known values of the surface tension $\sigma_{LV(1)}$ and $\sigma_{LV(2)}$ (subscripts "1" and "2" stand for water and organic fluid, respectively), and the values of the dispersion $\sigma^d{}_{LV}$ and polar $\sigma^p{}_{LV}$ components[23] (Table 1). The accuracy in determination of the surface energy (σ_{SV}) was ±0.8 mJ m^{-2}. Calculations for pairs of fluids, H_2O/CH_2I_2 or H_2O/hexadecane, were carried out by solving the system of equations (4):

$$\begin{cases} \sigma_{LV}(1 + \cos\theta_1) = 2(\sigma^d{}_{LV(1)}\sigma^d{}_{SV})^{1/2} + 2(\sigma^p{}_{LV(1)}\sigma^p{}_{SV})^{1/2} \\ \sigma_{LV}(1 + \cos\theta_2) = 2(\sigma^d{}_{LV(2)}\sigma^d{}_{SV})^{1/2} + 2(\sigma^p{}_{LV(2)}\sigma^p{}_{SV})^{1/2} \end{cases} \qquad (4)$$

This approach is widely used to determine the surface energy of solids, surfactant adsorption layers on solid substrates, SAMs of organic molecules on solid surfaces,[20] and organic films.[24]

The equilibrium polymer—water interfacial energy was calculated following E.Ruckenstein using the results of measurements of the advancing and receding contact angles and selective wetting.[12,25] The receding contact angles of water were measured under water using an air bubble (θ_{VW}) and an octane drop (θ_{OW}) brought to the surface of a sample which was preliminarily equilibrated in water for 24 h.[12]

Table 1. Surface tension of test fluids (σ) determined with inclusion of the contributions of dispersion ($\sigma^d{}_{LV}$) and polar ($\sigma^p{}_{LV}$) components

Fluid	σ_{LV}	$\sigma^d{}_{LV}$	$\sigma^p{}_{LV}$
		mJ m^{-2}	
H_2O	72.6	21.8	50.8
CH_2I_2	50.8	48.5	2.3
Hexadecane	27.6	27.6	~0

Table 2. Adsorption of PDADMAC (Γ) on the surface of polystyrene films and the contact angles (θ_a) of water on the modified surface

C (%)	$-\Delta f$/Hz	$\Gamma \cdot 10^6$/mol m^{-2}	θ_a/deg	$-\Delta f$/Hz	$\Gamma \cdot 10^6$/mol m^{-2}	θ_a/deg
	before washing			after washing		
0.1	149	0.26	80	69	0.12	80
0.2	244	0.43	70	95	0.17	75
0.4	265	0.47	65	99	0.18	72
0.5	306	0.54	61	110	0.19	70
0.8	354	0.62	55	120	0.21	68
1.0	400	0.71	56	133	0.23	68

Results and Discussion

Large differences between the amounts of PDADMAC adsorbed on the PS films before and after washing in water (Table 2, Fig. 1) suggest that a considerable proportion of the polycation modifier layer is removed from the polymer surface upon washing.

A comparison of the contact angles of water on the untreated and on the modified surfaces of the PS films also showed that a firmly adhered polycation adsorption layer is present on the surface even after washing in water. These results agree with the published data,[8] according to which macromolecules of the first polyelectrolyte layer are strongly and irreversibly adsorbed on the solid surface with retention of the ability to change their conformations. The bonding of macromolecules with the polymer surfaces is driven by hydrophobic interaction, being essentially entropic in nature.[26]

At $C > 0.1\%$, the amount of adsorbed substance depends only slightly on the concentration of the modifier solution, being on the average equal to $\Gamma = 0.2 \cdot 10^{-6}$ mol m^{-2}, which corresponds to a PDADMAC adsorption layer thickness of 19.3 nm. This value is close to the size of the PDADMAC coil in 0.5 *M* NaCl solution ($R_h = 11$ nm),[27] being consistent with the assumption that the size of polyelectrolyte coils in the adsorption layers at different interfaces and in solutions decreases as the ionic strength increases.

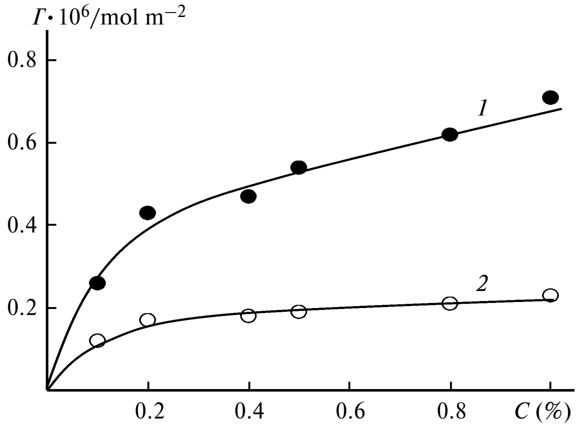


Fig. 1. Adsorption isotherms of PDADMAC on polystyrene surface: no washing (*1*) and after washing (*2*) of samples in water.

Surface modification of PS films with the PDADMAC adsorption layers is accompanied by hydrophilization of the starting film (Table 3). The surface energy of PS calculated using the experimental contact angle values of the test fluids (H_2O and CH_2I_2) is in good agreement with the published data.[23] Surface modification with the PDADMAC adsorption layer causes the σ_{SV} value to increase owing to an increase in the polar component of the surface energy. It follows that the outer part of the modifier layer is enriched with polar groups.

The surface area ratio of the polar and nonpolar regions on the surface of the PDADMAC modifier layer can be calculates using the theory of wetting of heterogeneous surfaces.[2] Since the surface is made

Table 3. Contact angles (θ) of test fluids (H_2O and CH_2I_2) and the energy characteristics of polystyrene (σ) after 24 h of contact with water and with PDADMAC solutions

Surface	θ_a[a]	θ_r	θ[b]	σ_{SV}	σ^d_{SV}	σ^p_{SV}
		deg			mJ m^{-2}	
PS	86	84	32	43.6	42.2	1.4
PS[c]	83	80	30	44.2	42.1	2.1
PS + PDADMAC	68	65	25	48.2	40.1	8.1
PS + PDADMAC[c]	65	56	20	50.5	41.2	9.3

[a] H_2O.
[b] CH_2I_2.
[c] After equilibration in water for 24 h.

up of regions with different wettability, the equilibrium contact angle θ is determined by the Rebinder—Cassie—Baxter equation:

$$\cos\theta = x\cos\theta_1 + (1 - x)\cos\theta_2, \qquad (5)$$

where x and $(1 - x)$ are the fractions of the surface area occupied by the Type-1 and Type-2 regions, respectively, while θ_1 and θ_2 are the contact angles of water on the uniform Type-1 and Type-2 regions, respectively.

The adsorption layer which completely screens the surface of PS films contains both polar (hydrophilic) and nonpolar (hydrophobic) groups. Assume that the polar regions are completely wetted with water, *i.e.*, $\theta_1 = 0$ and $\cos\theta_1 = 1$. The contact angle of water on the nonpolar regions formed by hydrocarbon radicals is the same as that on paraffin, *i.e.*, $\theta_2 = 105°$ and $\cos\theta_2 = -0.26$. The contact angle of water on the modified surface $\theta = 68°$ and $\cos\theta = 0.37$ (see Table 2). From Eq. (5) one gets $x = 0.58$, *i.e.*, 58% of polar groups of the polycation are arranged in the outer part of the modifier layer.

Note that equilibration of the PS films in water for 24 h has little effect on the energy characteristics of the film surface (see Table 3). It follows that the conformational lability of PS macromolecules brought in long-term contact with water is low and no structural rearrangements occur in the near-surface layer of the polymer.

The surface tension of the water-equilibrated polymer surface at the interface with the aqueous phase, $\sigma_{SW(W)}$, was calculated using the experimental values of the contact angles, namely, $\theta_{VW} = 80°$ and $\theta_{OW} = 145°$ for the untreated surface of PS films and $\theta_{VW} = 56°$ and $\theta_{OW} = 135°$ for the PDADMAC-modified surface of PS films. Surface modification of the PS films with the polycation causes the $\sigma_{SW(W)}$ value to decrease from 18.3 mJ m^{-2} (PS) to 3.4 mJ m^{-2} (PDADMAC-modified PS). Thus, the PDADMAC-modified PS can be recommended for further studies as a material for biomedical applications.

Table 4. Kinetics of water and PDADMAC absorption by the Nafion™ film

t/h	Amount in Nafion™ film/• 10^{-6} mol	
	H_2O	PDADMAC*
0.5	—	
1.0	—	
2.0	0.37	0.020
4.0	1.10	0.035
6.0	1.40	0.040
12.0	1.80	0.038
18.0	2.10	
24.0	2.40	0.120
40.0	2.50	
48.0	2.40	0.120

* Nafion™ films were preliminarily equilibrated in water for 24 h.

The content of water in the Nafion™ membrane reaches a constant value at equilibration times (t) longer than 24 h (Table 4, Fig. 2). The water uptake W calculated from Eq. (1) is 44%, which agrees with the published data.[28] A study on the kinetics of PDADMAC sorption by water-saturated Nafion™ membranes showed that the amount of the polycation increases with increasing time of membrane contact with the PDADMAC solution and reaches a constant value after 12 h (Table 5).

The Nafion™ films modified with the PDADMAC solution for 24 h were not preliminarily kept in water. It was established that the amount of the polycation in the bulk of such films is six times lower than in the films preliminarily brought in contact with water, being equal to $0.02 \cdot 10^{-6}$ mol after 24 h; note that one had $W = 19\%$ at that time. One can assume that PDADMAC is sorbed in the near-boundary Nafion™ layers and blocks the sulfonic groups in the perfluorinated matrix of the polymer, thus reducing the water uptake and, therefore, the proton conductivity. This follows from a comparison of the size of the "squeezed" PDADMAC coil with the pore size in the Nafion™ film brought in contact with aqueous solution, namely, from 20 nm (see Ref. 29) to 100 nm

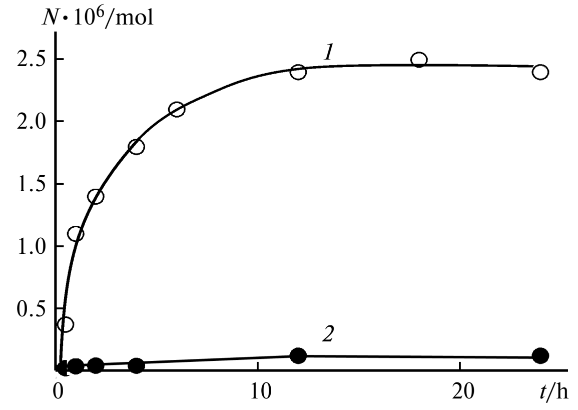


Fig. 2. Amount of water (*1*) and PDADMAC (*2*) absorbed by the Nafion™ film as function of modification time (t).

Table 5. Contact angles of the test fluids H_2O (θ_1) and hexadecane (θ_2) as functions of the duration of contact of the Nafion™ films with water and the calculated values of the polar ($\sigma_{SV}{}^p$) and dispersion ($\sigma_{SV}{}^d$) components of the surface energy (σ_{SV}) of these films

t/h	θ_1	θ_2	$\sigma^d{}_{SV}$	$\sigma^p{}_{SV}$	σ_{SV}
	deg		mJ m^{-2}		
0	83	35	22.8	6.7	29.5
0.5	82	35	22.8	7.1	29.9
1.0	82	35	22.8	7.1	29.9
2.0	80	35	22.8	8.1	30.9
4.0	58	18	26.8	19.7	46.5
6.0	52	18	23.3	23.7	50.0
12.0	53	18	23.3	23.0	49.3
24.0	53	18	26.3	23.0	49.3
40.0	52	16	26.5	23.6	50.1
48.0	53	16	26.5	22.9	49.4

(see Ref. 30) depending on the degree of swelling of the film. Nevertheless, localization of PDADMAC in the bulk of the film cannot be excluded too, especially, in the case of long-tern contact with aqueous polyelectrolyte solutions. A comparison of the size of the "squeezed" PDADMAC coil with the size of channels in the swollen Nafion™ film suggests an anchoring mechanism of the polyelectrolyte coil immobilization in the bulk of the film. Thus, preliminary swelling of the Nafion™ membranes in water provides a higher sorption of PDADMAC.

Bringing Nafion™ films in contact with water leads to saturation of the polymer and the surface layer of the membrane with water. The specific free energy increases owing to an increase in the polar component $\sigma_{SV}{}^p$ (Table 6).

A comparison of the contact angles of the test fluids on the Nafion™ films kept in water and in the PDADMAC solutions and the specific free surface energies (σ_{SV}) calculated from Eq. (4) with inclusion of the contributions of the dispersion ($\sigma_{SV}{}^d$) and non-dispersion ($\sigma_{SV}{}^p$) components allows one to assume that the surface of the films is free from the polycation (see Tables 5 and 6). This assumption is qualitatively confirmed by the fact that the modified Nafion™ film did not turn blue under the action of the Bradford reagent.[31]

Table 6. Contact angles of the test fluids H_2O (θ_1) and hexadecane (θ_2) and the energy characteristics of the surface of the PDADMAC-modified Nafion™ film preliminarily equilibrated in water for 24 h

t^a/h	θ_1	θ_2	$\sigma^d{}_{SV}$	$\sigma^p{}_{SV}$	σ_{SV}
	deg		mJ m^{-2}		
2	52	18	23.3	23.7	50.0
6	52	18	23.3	23.7	50.0
12	52	15	26.7	23.5	50.2
24	53	15	26.7	22,8	49.5
24^b	55	18	26.3	21.7	48.0

^{a} Modification time.

^{b} No preliminary equilibration in water.

Probably, such a different behavior of PDADMAC in regard to modification of PS and Nafion™ films is due to different character of the interaction between the polycation with the surface polymers and, as a consequence, to the influence of some other factors on the localization of the adsorbed PDADMAC.

It was reported that at pH 7 and at concentrations $C > 0.01\%$, the polyelectrolyte macromolecules represent coils (aggregates) and are adsorbed on solid surfaces in just the same state as their state in solution.[8] A convenient model for aggregates is provided by a "brush heap" type branched structure where macromolecules contact at random points.[32] Strong immobilization of the cationic polyelectrolyte on the surface of a PS film is due to hydrophobic interactions. However, the PS macromolecules can contain carboxyl terminal groups that are formed upon oxidation by the initiator and can contribute to the surface charge.[33] Indeed, the ζ-potential of the PS surface in the range of neutral pH values is $\zeta \approx -(40-60)$ mV.[34]

The surface of Nafion™ films is characterized by $\zeta \approx -5$ mV (isoelectric point pH 8).[35] In this case, the low ζ-potential does not promote the interaction between PDADMAC and the membrane surface. If the contacting phases have different polarities, one deals with physisorption of the polycation on the surface of the Nafion™ film, but the modifier layers are not tightly bound to the surface and can be removed with ease by washing in water. Swelling in water improves the transport properties of the Nafion™ membranes and increases the affinity to water owing to reorientation of sulfonic groups toward the aqueous phase. Joint action of the concentration gradient and capillary forces promotes diffusion of PDADMAC in the Nafion™ membrane. An increase in the ζ-potential in the film microchannels compared to the macroscopic surface of the film due to an increase in the concentration of sulfonic groups per unit area cannot also be ruled out.

The results obtained showed that PDADMAC is an efficient surface modifier of PS films. The polyelectrolyte adsorption layers are strongly immobilized on the surface of the PS films and equilibration of the modified surface with water allows one to reach a $\sigma_{SW(W)}$ value of nearly 3 mJ m^{-2}, which suggests a potential biocompatibility of this surface.

In the case of Nafion™ membranes, PDADMAC does not modify the surface, being incorporated into the bulk of the polymer. The conditions were determined under which PDADMAC influences the water uptake of the Nafion™ membranes, which allows one to control the mass transfer across the membranes to the aqueous medium.**[31]** It should be noted that modification with PDADMAC can be a promising route to membranes for separation of gas mixtures containing CO_2 using specific interaction between the carbon dioxide molecules and the polyionic complex.**[36]** At present, data on the permeability and separation of gases by polyionic membranes are scarce; therefore, information on localization of the modifier in the polymer film obtained in this work is topical for modern membrane materials science.

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References

1. P. A. Rebinder, *Poverkhnostnye yavleniya v dispersnykh sistemakh. Kolloidnaya khimiya. Izbrannye trudy* [*Surface Phenomena in Dispersed Systems. Colloid Chemistry. Selected Works*], Vol. 1, Nauka, Moscow, 1978, 368 pp. (in Russian).
2. B. D. Summ, Yu. V. Goryunov, *Fiziko-khimicheskie osnovy smachivaniya i rastekaniya* [*Physicochemical Foundations of Wetting and Spreading*], Khimiya, Moscow, 1976, 232 pp. (in Russian).
3. A. Ulman, *Chem. Rev.*, 1996, **96**, 1533; DOI: 10.1021/cr9502357.
4. M. G. Krekhova, V. D. Dolzhikova, B. D. Summ, Yu. G. Bogdanova, *Moscow Univ. Chem. Bull.*, 1995, **36**, 578 (in Russian).
5. V. D. Dolzhikova, Y. G. Bogdanova, A. G. Majouga, E. K. Beloglazkina, A. A. Kudrinsky, *Russ. J. Phys. Chem. A*, 2017, **91**, 240; DOI: 10.1134/S003602441702008X.
6. *Khimiya privitykh poverkhnostnykh soedineniy* [*Chemistry of Grafted Surface Compounds*], Ed. G. V. Lisichkin, FIZMATLIT, Moscow, 2003, 592 pp. (in Russian).
7. I. D. Kovtun, N. A. Lobanova, A. V. Andreeva, V. I. Gomzyak, S. M. Levachev, S. A. Gusev, S. N. Chvalun, I. A. Gritskova, *Russ. Chem. Bull.*, 2021, **70**, 1784; DOI: 10.1007/s11172-021-3283-3.
8. V. N. Izmaylova, G. P. Yampol´skaya, B. D. Summ, *Poverkhnostnye yavleniya v dispersnykh sistemakh* [*Surface Phenomena in Dispersed Systems*], Khimiya, Moscow, 1988, 238 pp. (in Russian).
9. K. B. Musabekov, B. A. Zhubanov, V. N. Izmaylova, B. D. Summ, *Mezhfaznye sloi polielektrolitov* [*Interfacial Polyelectrolyte Layers*], Nauka, Alma-Ata, 1987, 110 pp. (in Russian).
10. G. P. Yampol´skaya, V. D. Dolzhikova, *Moscow Univ. Chem. Bull.*, 2007, **62**, 27; DOI: 10.3103/S0027131407010075.
11. Yu. G. Bogdanova, V. D. Dolzhikova, *Sbornik statey XVI Vseross. konf. "Struktura i dinamika molekulyarnykh sistem"* [*Coll. XVIth All-Russia Conf. "Structure and Dynamics of Molecular Systems"*], Vol. 3, MarGTU, Yoshkar-Ola, 2009, 4 (in Russian).
12. E. Ruckenstein, S. V. Gourisankar, *Biomaterials*, 1986, **7**, 403; DOI: 10.1016/0142-9612(86)90028-1.
13. Yu. G. Bogdanova, V. D. Dolzhikova, G. A. Badun, B. D. Summ, *Russ. Chem. Bull.*, 2003, **52**, 2352; DOI: 10.1023/B:RUCB.0000012355.12717.86.
14. C. M. Moor, S. Hackman, T. Brennen, S. D. Minteer, *J. Membr. Sci.*, 2005, **255**, 233; DOI: 10.1016/j.memsci.2004.11.027.
15. T. Xiangguo, D. Jicui, S. Jing, *J. Solid State Electrochem.*, 2014, **19**, 1091; DOI: 10.1007/s10008-014-2713-7.
16. V. D. Dolzhikova, Yu. G. Bogdanova, *J. Colloid Polym. Sci.*, 2019, **297**, 469; DOI: 10.1007/s00396-018-4446-0.
17. E. N. Gribov, I. M. Krivobokov, E. V. Parkhomchuk, A. G. Okunev, G. Spoto, V. N. Parmon, *Russ. J. Electrochem.*, 2009, **45**, 199; DOI: 10.1134/S1023193509020116.
18. K. A. Mauritz, R. B. Moor, *Chem Rev.*, 2004, **104**, 4535; DOI:10.1021/cr0207123.
19. G. Sauerbrey, *Z. Physik*, 1959, **155**, 206; DOI: 10.1007/BF01337937.
20. J. Genzer, K. Efimenko, *Biofouling*, 2006, **22**, 339; DOI: 10.1080/08927010600980223.
21. F. M. Fowkes, *J. Colloid Interface Sci.*, 1968, **28**, 493; DOI: 10.1016/0021-9797(68)90082-9.
22. J. Vojtechovska, L. Kvitek, *Acta Univ. Palacky. Olomouc. Chemica*, 2005, **44**, 25.
23. A. Carre, *J. Adhesion Sci. Technol.*, 2007, **21**, 961; DOI: 10.1163/156856107781393875.
24. H. Wang, S. Chen, L. Li, S. Jiang, *Langmuir*, 2005, **21**, 2633; DOI: 10.1021/la046810w.
25. E. Ruckenstein, S. H. Lee, *J. Colloid Interface Sci.*, 1987, **120**, 153; DOI: 10.1016/0021-9797(87)90334-1.

26. M. E. Soderquist, A. G. Walton, *J. Colloid Interface Sci.*, 1980, **75**, 386; DOI: 10.1016/0021-9797(80)90463-4.
27. J. Xia, P. L. Dubin, S. Edvards, H. Havel, *J. Polym. Sci.*, *Part B*, 1995, **33**, 1117; DOI: 10.1002/polb.1995.090330715.
28. A. K. Philips, R. B. Moor, *J. Polym. Sci.*, *B: Polym. Phys.*, 2006, **44**, 2267; DOI: 10.1002/polb.20866.
29. V. V. Volkov, B. V. Mchedlishvili, V. I. Roldugin, S. S. Ivanchev, A. B. Yaroslavtsev, *Nanotechnol. in Russia*, 2008, **3**, 656; DOI: 10.1134/S1995078008110025.
30. V. I. Zabolotskiy, V. V. Nikonenko, *Perenos ionov v membranakh* [*Ion Transport in Membranes*], Nauka, Moscow, 1996, 392 pp. (in Russian).
31. J. A. Zakharova, M. F. Zansokhova, E. A. Karpushkin, V. G. Sergeyev, *Mendeleev Commun.*, 2021, **31**, 839; DOI: 10.1016/j.mencom.2021.11.023.
32. H. Boedtker, P. Doty, *J. Phys. Chem.*, 1954, **58**, 968; DOI: 10.1021/j150521a010.
33. P. Connor, R. H. Ottewill, *J. Colloid Interface. Sci.*, 1971, **37**, 642; DOI: 10.1016/0021-9797(71)90342-0.
34. Z. Kolska, Z. Makajova, K. Kolarova, N. Kasalkova, S. Trostova, A. Reznickova, V. Svorcik, *Polymer Sci.*, 2013, 203; DOI: 10.5772/46144.
35. Z. Haining, P. Jingjing, He Xiuchong, P. Mu, *J. Appl. Polymer Sci.*, 2008, **107**, 3306; DOI: 10.1002/app.27473.
36. A. Yu. Alentiev, V. E. Ryzhikh, N. A. Belov, *Polymer Sci. Ser. C*, 2021, **63**, 181; DOI: 10.1134/S1811238221020016.

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