Properties of polymer track membranes modified by grafting with poly(2-methyl-5-vinylpyridine) and poly(*N*-isopropylacrylamide)

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The properties of track membranes (TM) based on poly(ethylene terephthalate) (PETP) and polypropylene (PP) and modified by radiation-induced graft polymerization of 2-methyl-5-vinylpyridine (MVP) and *N*-isopropylacrylamide (NIPAA) were studied. The rate of grafting and the limiting degree of grafting increase linearly as the pore diameter of TM increases. The gasdynamic and hydrodynamic pore diameters of modified TM were determined. The dependence of water permeability of TM modified by grafting with poly(2-methyl-5-vinylpyridine) (PMVP) on the degree of grafting passes through a maximum, which, according to the data of wetting angle measurements, corresponds to the maximum hydrophilicity. The negative ζ-potential of TM changes sign after modification by grafting with PMVP. Thermosensitive TM based on PETP and PP were prepared by radiation-induced graft polymerization of NIPAA. The structure of modified TM was studied by electron microscopy and atomic force microscopy.

Key words: track membranes, grafting, modification, hydrophilicity, water flow rate, electrophysical properties of surface, γ-radiation, phase transitions, atomic force microscopy.

Recently, polymer track membranes (TM) have attracted considerable interest. These membranes are prepared by irradiation of polymer films with accelerated heavy ions followed by etching. By choosing appropriate conditions for irradiation and etching it is possible to prepare a rather wide assortment of polymer TM, which can be used in biotechnology, medicine, ecology, *etc.*[1,2] Modification of polymer TM by grafting with different polymers extends the possibilities of their use. Particularly topical is the development of methods for hydrophilization of polymer TM. In the case of TM based on poly(ethylene terephthalate) (PETP) it is important to prepare hydrophilic membranes with small pores (<0.1 μm), whereas hydrophobic membranes based on polypropylene (PP) require hydrophilization irrespective of the pore diameter. Preparation of polymer TM modified with so-called "smart" polymers, which respond to slight changes in the properties of the environment (temperature, pH, ionic strength, and electric field), is also topical. In this case, the modified TM can be considered controllable.

The aim of this work was to prepare hydrophilic and thermosensitive TM by grafting with the widely used hydrophilic polymer poly(2-methyl-5-vinylpyridine) (PMVP) and with a "smart" thermosensitive polymer poly(*N*-isopropylacrylamide) (poly-NIPAA). This problem was solved using radiation-induced graft polymerization (RIGP), which is a universal method for modification of polymers of virtually any chemical nature.[3,4] The effect of the pore size of TM on several RIGP parameters was also studied.

Information on the use of RIGP for modification of TM is rather scarce despite the fact that investigations in this area[5—8] have been rapidly progressing recently. Radiation-induced grafting of several monomers into PETP-based TM has been outlined[5] and permeability of choline chloride and insulin through modified TM has been studied. Modification of polyimide-based TM by radiation-induced grafting with styrene has been investigated.[6]

Data on RIGP in latent tracks formed in polymer films irradiated with accelerated heavy ions have been reviewed.[7] The formation of poly-NIPAA gels in the pores of PETP-based TM has been studied.[8]

Modified layers prepared using RIGP are tightly bound to the substrate, cannot be washed off by any solvents, and retain their properties for a rather long time.

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Experimental

Track membranes used in this work were prepared from Melinex biaxially oriented PETP-based film (ICI, USA) and Torayfan PP-based film (Toray, Japan). The parameters of the TM are listed in Table 1.

Radiation-induced graft polymerization was performed using pre-irradiation of TM either in air (the peroxide method) or *in vacuo*, as well as by direct method. γ-Radiation of the ^{60}Co and ^{137}Cs isotopes was used. The degree of grafting was determined with respect to the weight of the initial film after thorough washing of the homopolymer. Detailed description of the procedure for RIGP was reported earlier.[9,10]

The thickness of the initial and modified membranes was controlled by an IKV-3 telescope caliper and a TTd-20 thickness gauge (Tesa Tronik, Sweden); the error of measurements was ±0.2 μm.

Specific performance of the initial and modified TM with respect to gas and water were measured by conventional methods.[1] The effective gasodynamic pore diameter was calculated using a universal algorithm. In the case of small pores and low pressures, the results obtained using this algorithm coincide with those obtained from calculations using the Knudsen formula for the free-molecule gas flow. The hydrodynamic pore diameter was calculated using the Hagen—Poiseuille equation.

Hydrophilic properties of the surface of TM were assessed from the results of wetting angle measurements by the sessile drop method using an optical microscope. Swelling of grafted polymers was studied gravimetrically.

ζ-Potential and the density of electric charge of the surface and pore walls of TM were determined by measuring the potential (ΔE) produced by the electrolyte flow through the TM at a pressure drop (Δp). A 0.01 *M* KCl solution was used as electrolyte.

Table 1. Parameters of track membranes used for graft polymerization

TM	N^a /cm^{-2}	Pore diameter^b/μm			L/μm ^{c}
		d_g	d_{em}	d_p	
PETP-0.03 ^{d}	$3 \cdot 10^9$	0.031	0.042	—	11.9
PETP-0.03	$5.7 \cdot 10^9$	0.029	0.045	—	10.8
PETP-0.04	$3 \cdot 10^9$	0.042	0.055	—	11.9
PETP-0.2	$(4\pm2) \cdot 10^8$	0.18	0.23	—	9.7
PETP-0.05	$2 \cdot 10^9$	0.05	0.095	—	10.0
PETP-0.05	$2 \cdot 10^9$	0.044	—	—	9.8
PETP-0.06	$2 \cdot 10^9$	0.058	—	—	9.8
PETP-0.08	$2 \cdot 10^9$	0.078	—	—	9.7
PETP-1.0	$5 \cdot 10^6$	1.1	1.4	—	8.6
PETP-0.1	$3.2 \cdot 10^8$	0.12	0.18	—	10.1
PETP-1.0	$1.5 \cdot 10^7$	1.2	—	1.0	9.6
PETP-1.0	$4.6 \cdot 10^5$	1.2	—	—	20.0
PETP-1.0	$1.5 \cdot 10^6$	1.2	—	—	10.0
PP-0.3	10^8	—	0.3	0.32	9.7
PP-0.9	10^7	—	0.9	0.84	9.9

N is the number of pores per unit surface.

[b] d_g, d_{em}, and d_p are the pore diameters of TM determined by the gasdynamic method, using the electron microscope, and using a Porometer II porometer (Coulter Electronics Limited, UK), respectively.

[c] Measured on a TTd-20 thickness gauge (Tesa Tronik, Sweden); the error of measurements was ±0.2 μm.

Distribution of grafted polymer over the substrate volume was studied using a LINK System 860/500 (UK) X-ray spectral microanalyzer (an accessory to an SM-840 (JEOL, Japan) scanning electron microscope). The microanalyzer operated in a special Line Scan Profile (LSP) mode, which made it possible to study the distribution of a grafted layer over the cross-section (heavy iodine atoms were introduced by quaternizing the pyridine ring). Temperature sensitivity of TM grafted with poly-NIPAA was determined conductometrically; this method is based on registration of temperature changes in the electrical resistance of a membrane impregnated with the electrolyte (KCl) solution.

The surface of modified TM grafted with poly-NIPAA was studied using an atomic force microscope (Nanotechnology-MDT, Russian Federation). Three-dimensional images of the surface of the objects under study were obtained using a Solver P4-SPM-MDT scanning probe microscope (Nanotechnology-MDT, Russian Federation) at ~20 °C in air. In both the contact mode and the lateral force mode, the images were obtained using Si_3N_4-cantilevers (Park Scientific Instruments, USA) of length 85 μm with a resonance frequency of 120 kHz. In the case of Si_3N_4-cantilever, the probe was a quadratic pyramid of height 3 μm. The radius of curvature of the tip was 500 Å. To obtain precise metric data for the images of the surfaces under study, the atomic force microscope was calibrated against atomic-scale images of the surface of highly oriented pyrolytic graphite in the xy plane (the accuracy of measurements along the x and y axes was 1%) and against the test specimens along the z axis (the accuracy of measurements was 10%). The size of etched tracks (d) was determined using the surface profiles.

Results and Discussion

The kinetic curves of graft polymerization have a typical shape with "saturation" (Fig. 1). Such a behavior of the curves is explained by progressive conversion of the active centers of graft polymerization with time, especially in thin polymer films. It is noteworthy that the rate of graft polymerization of MVP is much higher than that of NIPAA. This can be explained both by higher diffusion rate and increased swelling of PETP in MVP compared to the analogous characteristics of the process in NIPAA which has larger molecules. Mention should also be made of higher MVP sorption on the surface of TM due to complexation between the nitrogen atoms of the pyridine rings of MVP and carboxylic groups formed in TM in the course of preparation. This results in activation of the monomer and in an increase in the polymerization rate.[11] Increased decomposition of peroxide groups, which are generated in TM exposed to irradiation in air, during their interaction with the pyridine bases of the MVP molecule also plays an important role.[12] Irradiation of PETP *in vacuo* is responsible for the higher initial rates and limiting degrees of grafting, which is explained by the fact that the graft polymerization proceeds involving free radicals generated immediately upon irradiation of PETP.[13] Noteworthy is also that, at nearly the same porosity values, the initial rate of graft polymerization and the limiting degree of grafting decrease linearly as the pore diameter

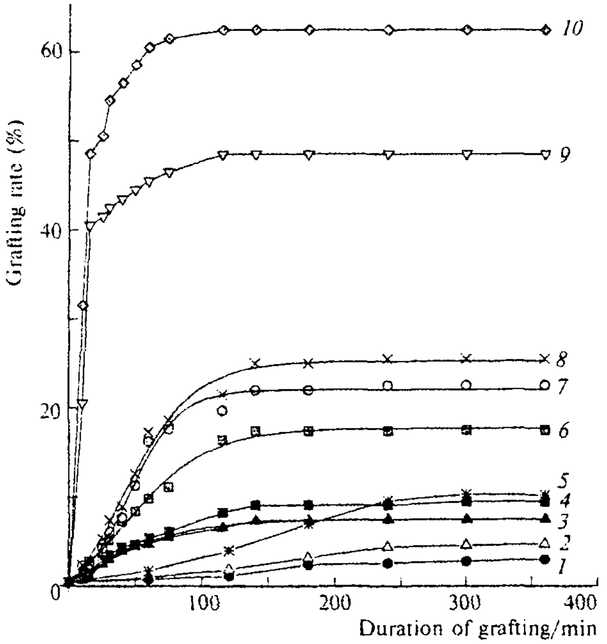

Fig. 1. Kinetic curves of post-graft polymerization of MVP and NIPAA onto the surface of PETP- and PP-based TM. Dependence of the yield of PMVP grafted at 70 °C onto the surface of PETP-based (*3, 4, 6, 7, 9, 10*) and PP-based (*8*) membranes and that of poly-NIPAA (*1, 2, 5*) grafted at 45 °C onto the surface of PETP-based TM (at a concentration of Mohr's salt of 0.025%; post-grafting on TM irradiated in air) on the duration of the process: the peroxide method (*1—8*), irradiation dose/kGy: 180 (*1—7*) and 10 (*8*); and the method of pre-irradiation *in vacuo* (*9, 10*) at an irradiation dose of 50 kGy and at a dose rate of 0.85 Gy s^{-1}. Pore diameter/µm: 0.03 (*1*); 0.05 (*2, 4*); 0.04 (*3*); 0.1 (*5, 6, 9*); 0.2 (*7*); 0.3 (*8*); and 1.0 (*10*).

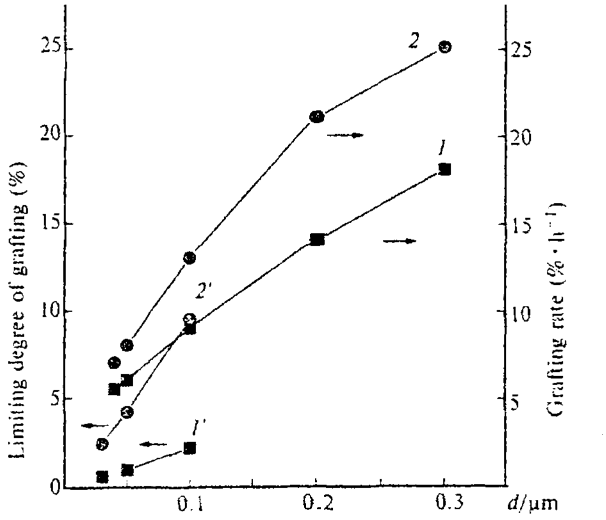

Fig. 2. Dependence of the rate of graft polymerization (*1, 2*) and limiting degree of grafting (*1', 2'*) of poly-NIPAA (*1, 1'*) and PMVP (*2, 2'*) onto the surface of TM by the peroxide method on the pore diameter (*d*) of TM.

decreases (Fig. 2). This can be explained by the fact that the effective surface of TM increases as both the pore diameter decreases and the number of pores increases and, hence, by the increase in defectiveness of the membrane material. Under these conditions, a radical recombination reaction is favored, thus decreasing the concentration of the active centers initiating the graft polymerization.[14]

Studies of gas permeability of the graft-modified membranes showed that it decreases as the degree of grafting increases (Fig. 3). A substantial decrease in the gas permeability and gasodynamic pore diameter is observed after the degree of grafting exceeds a particular threshold (Figs. 3, 4). In the former case, this is due to the characteristic features of RIGP. According to X-ray microanalysis data, initially grafting with PMVP proceeds rather uniformly over the membrane surface and the pore size remains unchanged; however, a decrease in the pore diameter as well as the formation of thin partition walls inside the pores is observed at particular degrees of grafting. These partition walls formed by the grafted polymer are clearly seen in the scanning electron microscopy image of a spalled TM (Fig. 5). All these factors take effect only at particular degrees of grafting which are dependent on the initial pore diameter. An increase in hydrophilicity of TM with increasing degree of grafting leads to a decrease in the wetting angle (Fig. 6). Hydrophilic properties are stabilized at a grafting value of 5—7% due to the coverage of the surface layer with grafted PMVP chains. Analogous physical effects have also been observed in studies of other grafted systems.[15]

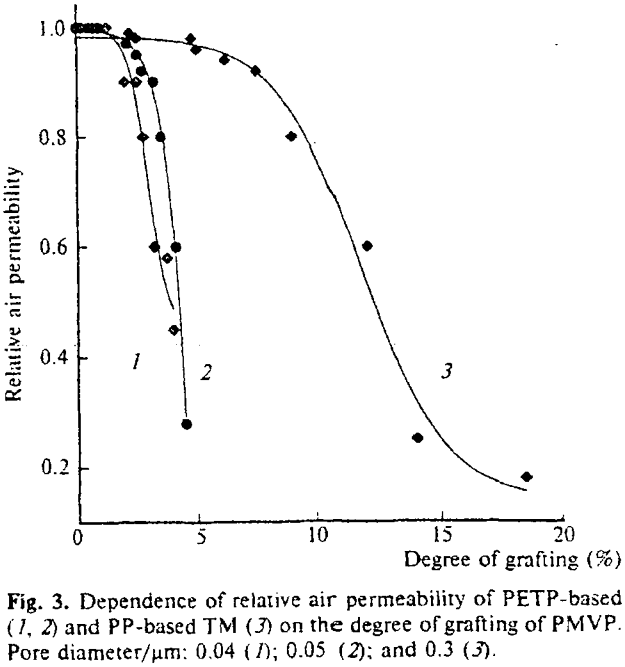

Fig. 3. Dependence of relative air permeability of PETP-based (*1, 2*) and PP-based TM (*3*) on the degree of grafting of PMVP. Pore diameter/µm: 0.04 (*1*); 0.05 (*2*); and 0.3 (*3*).

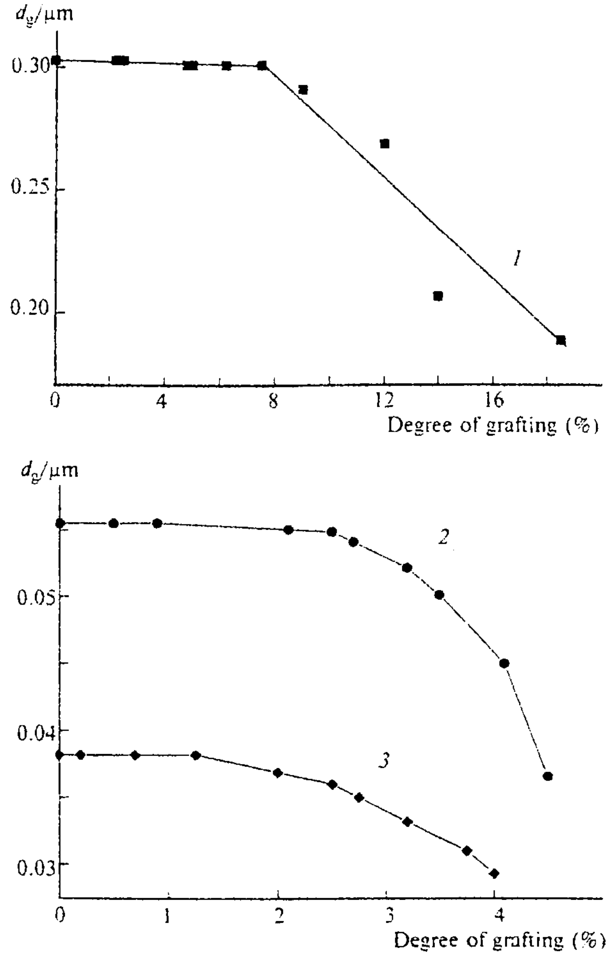

Fig. 4. Dependence of gasdynamic pore diameter (d_g) of PP-based (*1*) and PETP-based TM (*2*, *3*) on the degree of grafting of PMVP. Initial pore diameter/µm: 0.3 (*1*); 0.05 (*2*); and 0.04 (*3*). For clarity, the plots are shifted along the ordinate axis.

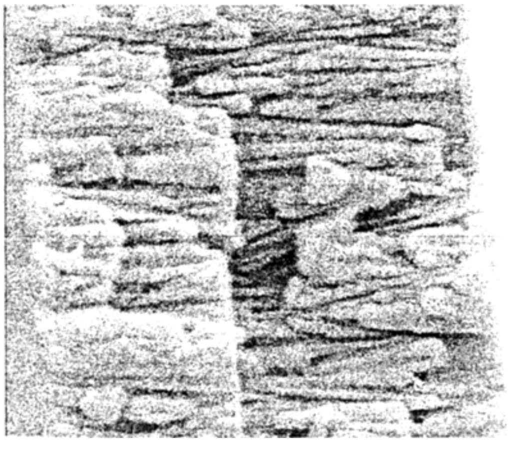

Fig. 5. Scanning electron microscopy image of a spalled PETP-based TM grafted with PMVP (degree of grafting 25%). Conditions: initial pore diameter, 0.1 µm; field of vision area, 14.4×12.2 µm^2.

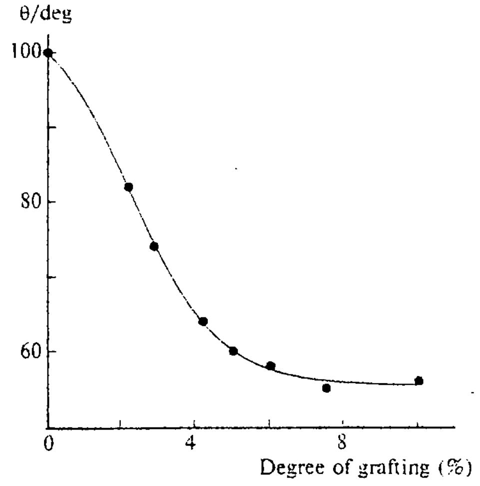

Fig. 6. Dependence of the wetting angle (θ) on the degree of grafting of PMVP for PP-based TM with a pore diameter of 0.3 µm.

Electrophysical characteristics of the surface of initial and modified TM were studied by the flow potential method. It is known that the surface of initial membranes carries a fixed negative charge due to the formation of carboxylic groups in the course of preparation of the membranes.[1] The data on the dependences of the flow potential and charge density on the degree of grafting onto the surface of initial and modified membranes grafted with PMVP are listed in Table 2. Initial membranes are characterized by a rather high negative ζ-potential. The charge density decreases and the potential changes its sign as the grafting value increases. This is due to the interaction of carboxylic groups with the pyridine rings of the molecules of the grafted polymer. This procedure was used for preparation of positively charged membranes.

The dependence of water permeability of the graft-modified membranes on the degree of grafting passes through a maximum (Fig. 7), whose position is shifted toward greater degrees of grafting as the pore size increases. We established that at the optimum content of grafted PMVP, the water permeability of hydrophilic small-pore PETP-based TM increases by a factor of 3—4 as compared to that of initial membranes (see

Table 2. Electrophysical properties of the surface of PETP-based TM modified by grafting with PMVP

Degree of grafting (%)	ζ-Potential /mV	Charge density /C m^{-2}
0	−14.2	$3.3 \cdot 10^{-3}$
1.32	−2.5	$5.8 \cdot 10^{-4}$
7.90	+5.0	$1.15 \cdot 10^{-3}$
8.60	+9.3	$2.1 \cdot 10^{-3}$

Note. Initial pore diameter was 0.05 µm.

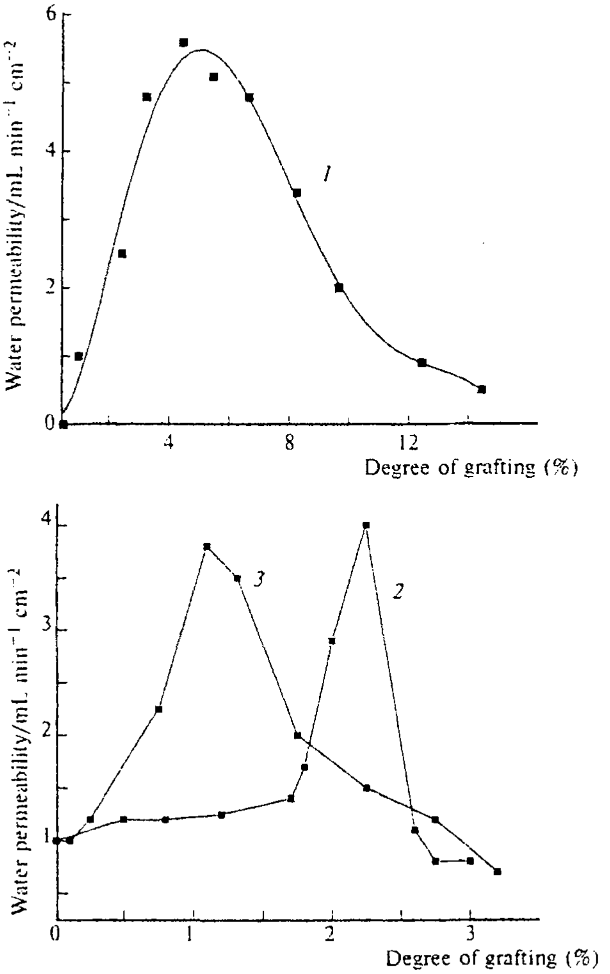

Fig. 7. Dependence of water permeability of PP-based (*1*) and PETP-based (*2*, *3*) TM on the degree of grafting of PMVP. Pore diameter/μm: *1*, 0.3; *2*, 0.05; and *3*, 0.04 (Δp = 0.07 MPa). For clarity, the plots are shifted along the ordinate axis.

Fig. 7). A clearly seen correlation is observed between the dependences of gasdynamic pore diameter and water permeability on the degree of grafting (*cf.* Figs. 4 and 7). The maximum value of water permeability is achieved at such degrees of grafting that correspond to virtually unchanged gasdynamic pore diameter. The range of grafting values at which the pore diameter decreases (see Fig. 4) corresponds to the region of drastic decrease in water permeability (see Fig. 7). Thus, modification of the properties of TM involves two stages. The characteristic of the first stage are insignificant changes in the geometric parameters of pores and pronounced changes in the surface properties (wetting). This imparts the desired hydrophilic properties and increased water permeability to the membrane. According to the data of wetting angle measurements (see Fig. 6), the maximum value of water permeability corresponds to the highest hydrophilicity. The second stage is characterized by marked changes in geometric parameters of the membrane and degradation of its service properties. It should be noted that the numerical values of the parameters characterizing transfer of liquid through modified membranes remain unchanged on storage of the TM under standard conditions over more than a year.

We also studied grafting of TM with poly-NIPAA. A characteristic of this polymer is the existence of a lower critical solution temperature in aqueous solution. At 32 °C, phase transition of the polymer occurs, caused by conformational transition of the macromolecule from a loose coil to a compact globule. This transformation is due to the increasing role of hydrophobic interaction with increase in temperature.[16] Hence it could be expected that the parameters of TM grafted with poly-NIPAA are temperature-dependent. In this connection, we carried out a conductometric study of temperature sensitivity of TM grafted with poly-NIPAA. The conductivity of initial PETP-based TM is a linear function of temperature both on heating and on cooling. The conductivity of PETP-based TM grafted with poly-NIPAA increases substantially in the temperature range 32—34 °C on heating and decreases drastically in the same temperature range on cooling (Fig. 8). This temperature range corresponds to the phase transition temperature of poly-NIPAA, at which the size of the macromolecules constituting the polymer decreases appreciably. The reverse is observed on cooling.

Investigation of water filtration through PETP-based TM grafted with poly-NIPAA in the temperature range 20—45 °C revealed a substantial increase in water permeability at temperatures between 30 and 34 °C (Fig. 9), which corresponds to the phase transition

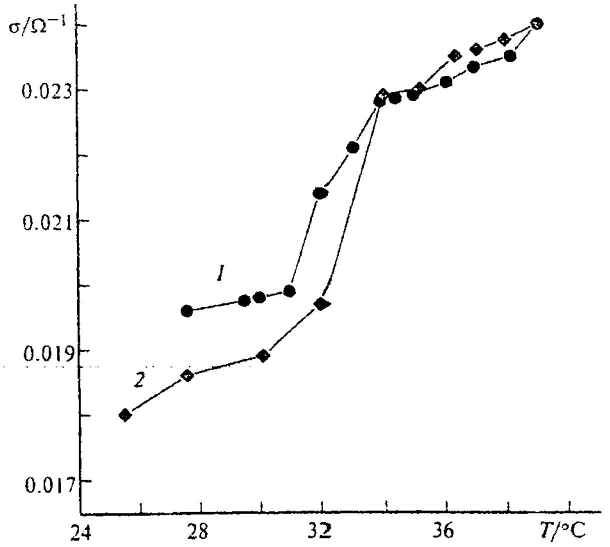

Fig. 8. Dependence of conductivity (σ) of PETP-based membrane grafted with poly-NIPAA on the temperature (*T*) of the medium: cooling (*1*) and heating (*2*). Conditions: degree of grafting, 5.6%; pore diameter, 1 μm; L = 20 μm; and $N = 4.6 \cdot 10^5$ cm^{-2}.

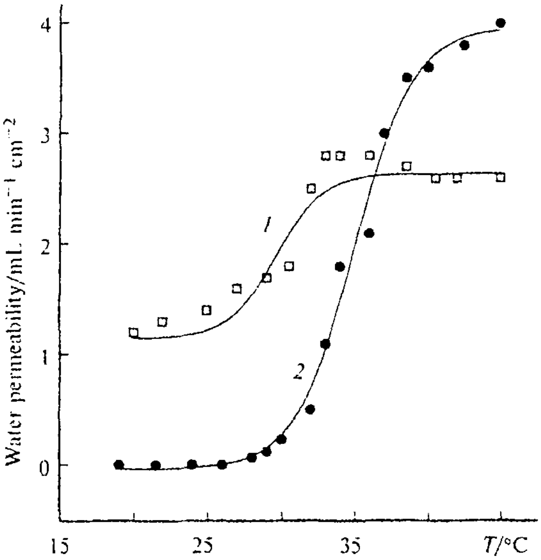

Fig. 9. Dependence of water permeability of TM grafted with poly-NIPAA on the temperature (*T*) of the medium. Conditions: Δp = 0.07 MPa, L = 10 μm, and N = $1.5 \cdot 10^6$ cm^{-2}. Degree of grafting (%): 3.4 (*1*) and 7.5 (*2*).

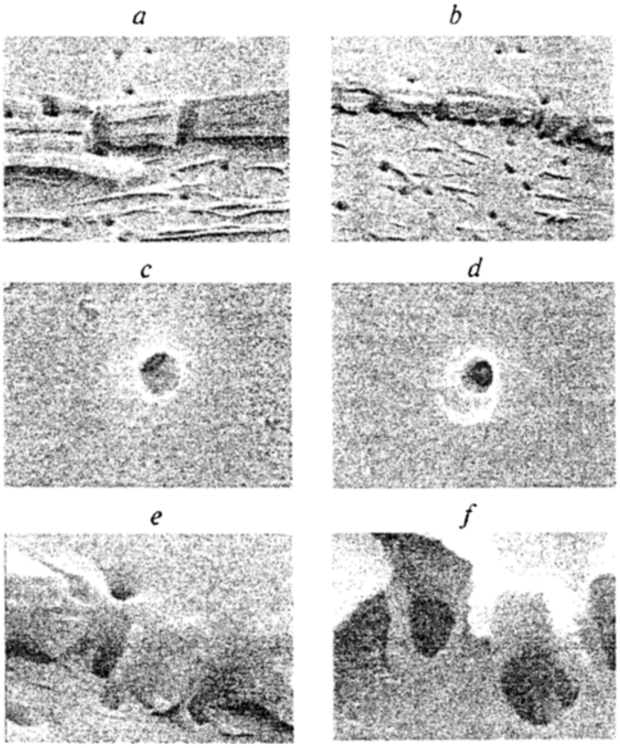

Fig. 10. Photomicrographs of PETP-based membranes obtained by scanning electron microscope: initial TM with a pore diameter of 1 μm (*a, c*) and TM grafted with poly-NIPAA (*b, d—f*). The degree of grafting was 12.7%. Field of vision area/μm^2: 15×11 (*a, b*); 5×3.8 (*c—e*); and 2.5×1.9 (*f*).

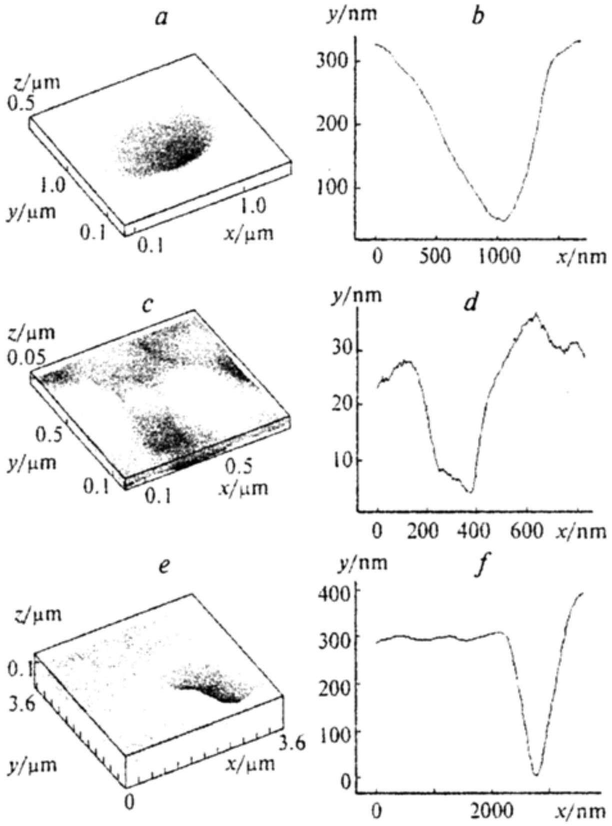

Fig. 11. Atomic force microscopy images of PP-based membranes (*a, c, e*) and profiles of the corresponding TM (*b, d, f*): surface of initial TM with a pore diameter of 0.9 μm (*a*); profile of the initial TM (*b*); surface of TM grafted with poly-NIPAA (degree of grafting 6.5%) swollen in water at room temperature (*c*); profile of a pore of TM grafted with PP (*d*); surface of TM grafted with poly-NIPAA (degree of grafting 6.5%) and kept in water at 50 °C for 30 min (*e*); and profile of a pore of TM grafted with PP (*f*).

temperature. Thus, the pore size of thermosensitive TM obtained in this work can be controlled by changing the temperature.

The structure of modified membranes was studied by scanning electron microscopy. Radiation-induced grafting with NIPAA leads to changes in the structure of the TM surface (Fig. 10), which becomes more regular (see Fig. 10, *b, d*). This is not observed for the initial PETP-based membrane. The pore size decreases due to the increase in the thickness of the grafted layer covering the walls of cylindrical openings (see Fig. 10, *d*). The near-surface layer of the graft modified membrane has a regular structure, which is different from the layered structure of the initial PETP-based membrane. At a grafting value of 12.7%, the thickness of the graft-modified membrane increases by approximately 2 μm. As can be clearly seen in the photomicrograph of an individual pore (see Fig. 10, *d*), the near-wall layer of grafted poly-NIPAA is partially destroyed on exposure to an electron beam, which is not observed for the initial PETP-based membrane (see Fig. 10, *c*). Not only does the grafted poly-NIPAA cover the membrane surface and the pore walls, but it also penetrates into them to some extent (see Fig. 10, *e*, *f*).

Atomic force microscopy images of the surface of TM and the corresponding profiles are shown in Fig. 11. On going from Fig. 11, *a* to Fig. 11, *e* it is possible to trace the changes in the pore size of the TM under study. Swelling of TM grafted with poly-NIPAA results in a decrease in the pore size (see Fig. 11, *c*). If TM grafted with poly-NIPAA is allowed to stay at elevated temperatures, phase transition occurs and the pores are opened (see Fig. 11, *e*).

Thus, our study revealed the possibility of preparation of new modified TM with a positively charged surface and thermosensitive TM with a temperature-dependent pore size.

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