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POROUS ION EXCHANGE MEMBRANES

This paper presents several methods allowing preparation of porous membranes with limited ability to be fouled. The methods are based on membrane surface modification by anchoring some ionogenic groups. Unique properties of these membranes enabled us to specify a peculiar class of membranes and call it Porous Ion Exchange Membranes (PIEMs). In the paper, the methods for PIEM preparation are described. They are based on our studies and some literature data. In the methods presented, the following techniques were applied: polymer blending, selective polymer etching, blend syneresis, and modification of membrane surface by chemical or plasma treatment.

1. INTRODUCTION

In the last decade, one could observe the growing interest in filtration processes in many branches of industrial applications. However, deposition of filtered solute on/in porous membrane causes the negative effect – permeate flux declines dramatically. As a consequence, the efficiency of a particular filtration unit decreases. The unit has to be turned off and some specific procedures of membrane cleaning should be applied which is time-consuming. Moreover, application of some chemicals (hopefully not harmful to solute or membrane) may vitally raise the total cost of production. Due to these drawbacks the filtration methods are considered less profitable and sometimes they may be located among another separation techniques. Deterioration of membrane efficiency is caused by deposited solutes that can significantly decrease the pore lumen or eventually plug it. The phenomenon of permeate flux reduction is called membrane fouling. In order to overcome the drawbacks of fouling, two approaches are being progressively applied. The first is connected with optimization of parameters of filtration media as well as designing a filtration unit. The second deals with the selection of membrane material that suppresses a solute deposition. Nevertheless the number of appropriate materials to be used in the production of porous membranes is mostly limited. To cope with this obstacle we try to modify some available membranes.

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There is a great number of papers published so far and each of them presents the main reasons of fouling [1], [2]. They can be itemized as follows: i) deposition of solute onto membrane surface and formation of poorly permeable layer – *filtration cake*, ii) deposition of solute into pores and reduction of a pore lumen which finally causes its plugging, iii) qualitative change of solutes in both regions – membrane surface and membrane pores. The great number of solute–solute and solute–membrane surface interactions result in formation of an insoluble deposit layer. It is also the fouling phenomenon mentioned by some authors [3], [4] – a decrease of driving force caused by osmotic pressure just in the region of polarization layer. However, for the simplicity of this presentation, the effect of osmotic pressure will not be considered herein.

Taking account of the above statements it is possible to put sorption as one of the most dangerous reasons, of the fouling phenomenon. It seems reasonable that any efforts to improve properties of the filtration membranes should be concentrated on a membrane sorbability feature [5]. In context of Ruckenstein's sorbability theory [6], some aspects of the fouling phenomenon seem to be relevant. In the case of both charged bodies, i.e. solute molecule and membrane, the solute molecule approaching the membrane surface is subjected to three potentials. They are as follows: double layer, van der Waals and short-range distance potentials. When both bodies bear the charge of the same sign the double-layer potential turns on repulsion forces – the membrane surface is not so extensively "contaminated" by deposited solutes. Of course, this effect may be reinforced by an increase in the charge of one or both interacting bodies. Hence, the observed alteration of membrane properties by changing the pH value of feed has been rationalized – at least the charge of solute has been varied. By the same token, the alteration of membrane charge, usually expressed as charge density, may also be highly profitable. The superposition of three potentials near the membrane surface may form not so deep potential well. In consequence, the solute molecule is not sorbed so strongly and may be released easily. The membrane appears as nonsorptive material. Our efforts to prepare such membranes are presented below.

2. PREPARATION AND PROPERTIES OF PIEMs

2.1. PIEM FROM POLYMER BLENDS AND COMPOSITES

Historically, this group of methods was the first procedure investigated in our laboratory to obtain PIEM. The idea arose from our attempts to prepare polymer blends and composites [7]–[9]. The mixtures of interpenetrating polymer network (IPN) of polyethylene and polystyrene crosslinked by divinylbenzene (PE//poly(St-co-DVB)), polypropylene and calcium carbonate were prepared in an extruder and extrudate was formed in sheets by mould pressing. The following reaction of the mixtures with chlorosulfonic acid resulted in formation of pores and sulfonation of aromatic

component, which occurred simultaneously. It was suggested a three-step formation of PIEM from the blends investigated:

Step 1. Diffusion of chlorosulfonic acid molecules towards calcium carbonate grains took place simultaneously with sulfonation of polystyrene chains.

Step 2. Release of the great quantities of carbon dioxide appeared as the result of reaction between acid molecules and chalk grains.

Step 3. Formation of cracks took place when the gas released was subjected to the critical pressure. The likely picture of this step can be described as some microshells' blasting, where accumulated CO_2 causes blowing up the multiphase matrix structure. The disruptions occur most frequently in the weakest places, i.e. in the interface regions.

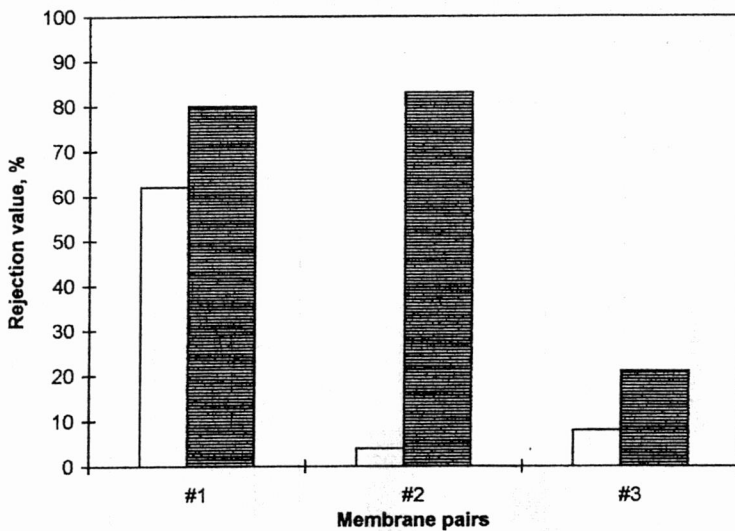


Fig. 1. Solute rejection coefficients for PIEM (ion-exchange capacity 1.2–1.4 mmol/g; hatched bars) and its off-charge analogue (ion-exchange capacity 0.1–0.12 mmol/g; empty bars).

Pair #1 – pore diameter 5 nm, solute RYD; pair #2 – pore diameter 2.5 nm, solute BSA; pair #3 – pore diameter 25 nm, solute BSA

The mechanism of pore formation by the microshells' blasting method was verified in some experiments with adhesion promoters [9]. Because of their specific localization, mostly between high-energy surfaces of chalk grains and low-energy polyolefins, the promoters reduced the effect of polyethylene transcrystallization. Diffusion of chlorosulfonic acid molecules was not so restricted as in the case of promoterless blank blends when a crystalline barrier at PE interface mostly reduced acid diffusivity. The microblasts formed larger pores. The difference was significant: after addition of stearic acid to the composite the pore diameters were 6–8-folds larger

compared to those in the promoterless sample. In both cases investigated, concentrations of ionogenic groups seemed to be comparable. The membranes obtained were tested for filtration of reactive yellow dye (RYD, 600 g/mol), bovine serum albumin (BSA, 69000 g/mol), skim milk and active sludge from a bioreactor. In all cases, the performance of PIEMs (ion-exchange capacity ranged from 1.0 to 1.4 mmol/g) was compared to the PIEMs off-charge analogues (ion-exchange capacity ranged from 0.1 to 0.12 mmol/g) that had the same pore diameters. Two parameters were evaluated: solute rejection (SR) and fouling index (FI); $FI = 1 - J_t/J_o$, where J_t and J_o were permeate fluxes during the process. Solute rejection expresses separation efficiency of membrane in ultrafiltration process, while fouling index represents, de facto, the relative measure of permeate flux decline. In all the systems investigated, the SR and FI parameters were much more profitable for PIEMs than their off-charge equivalents. Rejections were much higher if membranes were not fouled so intensively. These data are presented in figures 1 and 2.

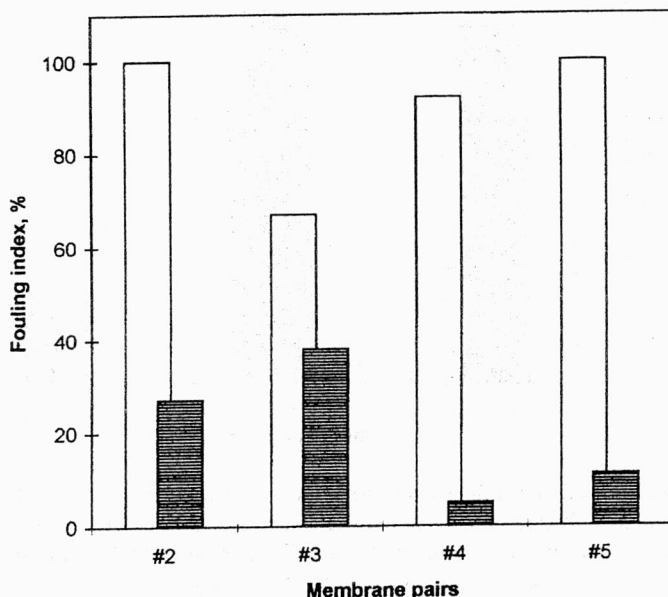


Fig. 2. Fouling indices for PIEM (ion-exchange capacity 1.2–1.4 mmol/g; hatched bars) and its off-charge analogue (ion-exchange capacity 0.1–0.12 mmol/g; empty bars). Pair #2 – pore diameter 2.5 nm, solute BSA; pair #3 – pore diameter 25 nm, solute BSA; pair #4 – pore diameter 30 nm, solute skim milk; pair #5 – pore diameter 5 nm, solute active sludge from a bioreactor

To check the properties of PIEMs in common filtration protocol, skim milk was subjected to filtration through the pair of #4 membranes. The process went on in 6 cycles. After 4 hours of filtration, the membrane was rinsed either with 0.1 M HCl or

with 0.1 M NaOH solutions and subsequently tested in the next filtration step. The fouling index for PIEM showed a narrow range of variation: from 2 up to 11% (see figure 3). The off-charge analogue was completely fouled just after the third cycle.

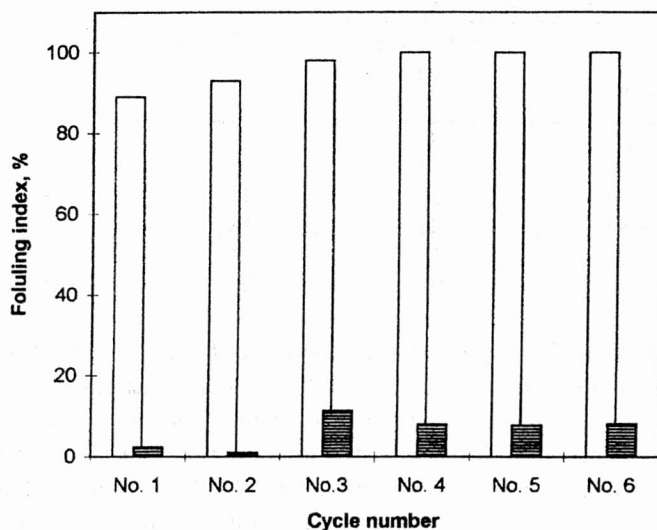


Fig. 3. Cyclic skim milk filtration through PIEM and its off-charge analogue of #4 membrane pair. Pore diameter 30 nm and ion-exchange capacity 1.2 and 0.1 mmol/g, respectively. Each run followed by acid-base cleaning procedure

The method presented above offered only flat membranes with rather poor mechanical properties. The search for new, stronger materials suitable for production of capillary or tubular membranes focused our attention on other ways of PIEM preparation. The most popular method of porous membrane preparation is phase inversion described in the following section. Preparation of such membranes is presented in detail in [10].

Generally speaking, the membranes were prepared from sulfonated polysulfone or its blends with neat polysulfone. Polymer/polymers were dissolved in *N,N*-dimethylformamide to obtain the solution of 20 wt.-% of solids. It was doctor-bladed on a glassy pane and immersed in water immediately.

Filtration of the buffered (pH = 7.0) solutions of BSA resulted in deposition of protein on membrane. Fouled membrane was regenerated by conventional method, i.e., rinsing either with 0.1 M solution of HCl or with 0.1 M solution of NaOH. The flux recovery parameter, being the ratio of the fluxes of the buffer passing through regenerated and fresh membranes, was used to evaluate the membrane performances. To evaluate the surface properties of the membranes obtained from blends, receding wetting angle of water was applied. Both measures are summarized in table 1.

Table 1

Receding wetting angle of water and flux recovery for membranes prepared from polysulfone//sulfonated polysulfone blends [10]

Blend composition		Contact angle [deg]	Flux recovery [%]
Polysulfone [wt.-%]	Sulfonated polysulfone [wt.-%]		
100	0	73	15
90	10	64	17
70	30	41	38
50	50	38	67
25	75	34	82
0	100	35	85

The data presented above proved once more that PIEMs behaved in a special way. When fouled, they can easily be regenerated by the conventional acid-base procedure. Their surface energy is shifted towards higher values and thus protects the membrane against damaging deposition. Moreover, the phase separation phenomenon can appear if we deal with the membranes obtained from blends. Similar behaviour of membranes obtained using 50:50, 75:25 and 100:0 compositions allows us to suggest that the use of less expensive blend instead of the pure modificate is possible. In all these cases, the irreversible sorption of BSA is mostly restricted. Similar conclusion may be withdrawn from the studies of membrane fouling caused by humic substances [11]. Membrane relative permeability for the blends containing 50% of sulfonated polysulfone is much higher than that for membranes with smaller amounts of modificate and is comparable to the permeability of membrane prepared from the sulfonated polymer.

2.2. PIEM FROM SELECTIVELY ETCHED POLYMER BLENDS

The idea of selective etching of one blend component is mostly attractive for the fact that polymer blend may be shaped in almost every required form. Hence there is not restriction of the final form of a membrane. One can obtain flat as well as capillary membrane taking the same starting material. The simplest method was described by MIZUTANI at al. [12], [13]. They removed sulfonated polystyrene from PVC blend by means of H_2O_2 :Fe(II) redox system. In our studies, we used the gel membrane of KESD-2 brand (supplier Galena, Wrocław, Poland) which is based on sulfonated interpolymer of PE//poly(St-co-DVB) [14]. This membrane was etched (ET) and then sulfonated (SU) or aminated (AM) to place some quantities of ionogenic groups on its surface [14]. Ion exchange capacity (in mmol of acidic or basic groups per 1 gram of dry membrane) shifted from 0.12 for ET membranes to 0.23 for sulfonated and to 0.22 for aminated modificates. Deposition of BSA on the membrane was investigated after

filtration of 0.1 wt.-% protein solution. The tests were carried out at three different values of pH, i.e. 3, 5 and 7. The data obtained are shown in table 2.

Table 2

Effect of the feed pH-value on BSA deposition (mg/cm^2) on etched (ET), sulfonated (SU) and aminated (AM) membranes.
Membranes obtained by selective etching of sulfonated poly(St-co-DVB) from interpolymer PE//poly(St-co-DVB) [14]

pH = 3			pH = 5			pH = 7		
ET	SU	AM	ET	SU	AM	ET	SU	AM
32	54	21	75	70	68	52	41	37

Evaluation of membrane performances was discussed based on the BSA net charge [14]. It was estimated to be +14, 0 and -18 for the respective value of pH equal to 3.0, 5.0 and 7.0 (VILKER et al. [15]). The studies allowed us to formulate the following statements: Oxidation of polyethylene matrix created some anchor-like sites on the pore surface. These sites were subjected to subsequent chemical modification. The localisation of the ionogenic groups placed just on the pore surface altered the membrane properties and caused it to behave as PIEM. It was also shown that solute deposition was not exclusively controlled by Coulomb's forces. The hydrophobic-hydrophilic interactions were the second effect that had to be considered.

2.3. PIEM OBTAINED BY CHEMICAL MODIFICATION OF MEMBRANE SURFACE

Capillary polysulfone membranes were the next material subjected to surface modification [16] by sulfonation. Concentration of BSA on the membrane surface was estimated by means of the following equation:

$$J = -k \ln(c_m/c_b),$$

Table 3

Surface concentration of BSA C_m (g/cm^3) for various transmembrane pressures.
Membranes: asymmetric tubular polysulfone and its sulfonated derivative [16]

Membrane	Transmembrane pressure [MPa]		
	0.03	0.06	0.09
Sulfonated polysulfone	0.114	0.174	0.249
Polysulfone	0.190	0.554	1.343

where J is the flux of permeate, k means the constant, and c_b and c_m are the concentrations of solute in bulk and on the membrane surface.

When bulk concentration reaches the concentration of solute on membrane surface a decline of permeate flux should be observed. This relationship allows us to estimate c_m . Numerical values of c_m for sulfonated and untreated polysulfone membranes are juxtaposed in table 3. These data once more confirmed the thesis that PIEM did not foul so intensively as their off-charge analogue.

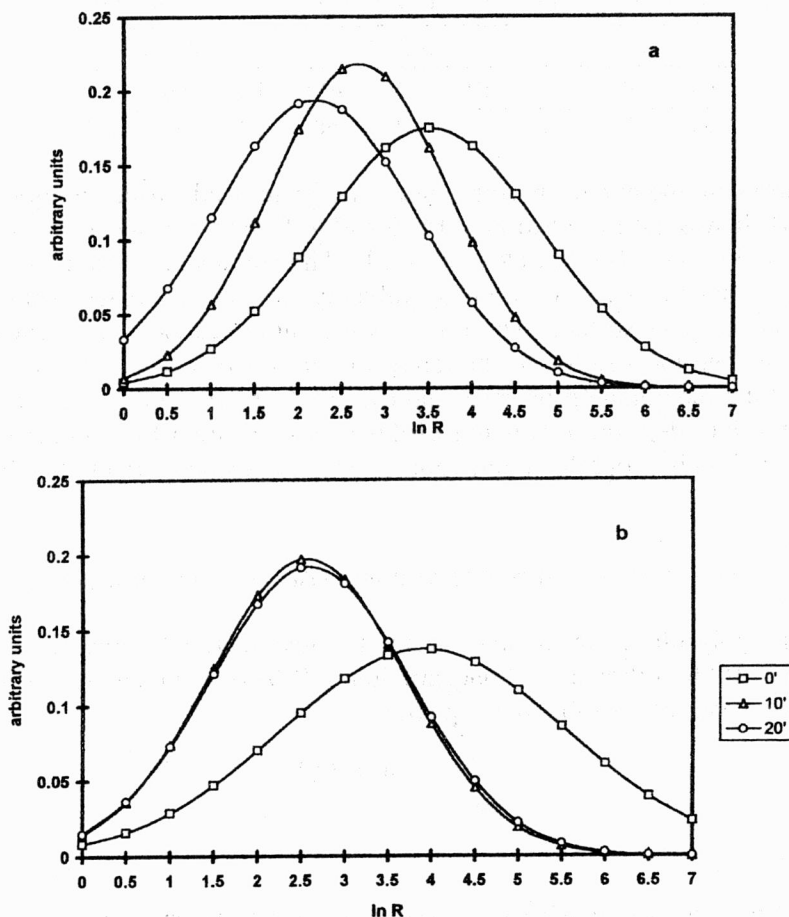


Fig. 4. Pore size distribution functions for modified (a) and unmodified (b) PAN1514 membranes. Membrane fouled after indicated time of service. Squares – unfouled membrane, triangle – 10 min fouling, dots – 20 min fouling

The next group of membranes, modified for the purpose of surface chemical treatment, was polyacrylonitrile membranes [17] manufactured by Deutsche Carbon

AG, Membran Trennverfahren GFT. The membrane with the PAN1514 symbol was used. The method of evaluating the pore size distribution function (PSDF) was presented elsewhere [18]. The PSDFs calculated for unmodified and NaOH-hydrolyzed membranes served as reference. The fouling process was monitored by filtration of BSA solution for particular time, washing out the excess of protein and successive evaluation of PSDF. The data obtained (see figure 4) allowed us to arrive at the extraordinary conclusion. When the membranes of unmodified PAN progressively reduced their own pore diameter during the process, PIEM did not produce such an effect. It attracted some amount of protein just at the beginning of the process but did not allow the subsequent layer of deposit to be formed when filtration was in progress.

2.4. PIEM FROM PLASMA-MODIFIED POROUS MEMBRANES

Some preliminary examinations dealing with membranes' modification by plasma deposition of polystyrene were conducted by means of 11.52 MHz plasma [16]. Chlorosulfonation of polystyrene according to common procedure [8] finished this modification. Porous polyethylene membrane was used as support. BSA solutions (pH = 7.8, concentrations from 0.01 to 0.5 wt.-%) were subjected to ultrafiltration in order to evaluate the surface concentration of protein. This concentration reached the value of 0.6 g/cm^3 for unmodified porous polyethylene membrane and was one order of magnitude smaller (0.05 g/cm^3) for surface-modified membranes. The results obtained stimulated us to more detailed study of some possibilities of using the plasma treatment in order to modify neutral membranes. Porous polyethylene membrane was selected and modified by high frequency (2.45 GHz) air plasma [19]. Contact angle measurements allowed us to estimate the surface energy of plasma-treated membranes. Hence, one was able to follow the modification progress. Flux recovery, i.e., the parameter that expresses the compactness and adhesion of the deposited protein layer, was used to evaluate the efficiency of the use of PIEMs. The properties of the membranes tested were juxtaposed in table 4.

Table 4

Surface properties and flux recovery for PIEM obtained by air plasma treatment.
Membrane from porous PE was fouled by BSA at various pH and then regenerated
by conventional acid-base cleaning procedure [19]

Membrane	Surface energy [mN/m]	Surface polarity [%]	Flux recovery [%]		
			pH = 3.0	pH = 5.0	pH = 7.0
PE	44	6.0	71	94	91
PIEM	57	60.0	90	99	97

In all cases, the flux recovery was higher for modified membranes, which meant that deposited layer of proteins was not sorbed so efficiently to the surface. It was relatively easy removable by means of a conventional (acid–base) cleaning protocol. However, the symmetric polyethylene membranes when treated by air plasma did not allow us to observe some other etching effects which might be explained by the fact that the layer subjected to destruction by plasma was too thick. Considering the tortuosity factor, this layer could be estimated as 250–300 μm . Some effects of plasma action can be observed, however, for thin membranes. Such membranes are known as asymmetric and have become very popular in the ultrafiltration business. The pore diameters of asymmetric membranes are estimated as less than 1–2 μm . Below we present a detailed discussion of polyacrylonitrile (PAN) membrane which may be considered as a typical asymmetric membrane.

Effect of action of 2.45 GHz air plasma on asymmetric membranes was investigated for polyacrylonitrile membrane, PAN1514, manufactured by Deutsche Carbon AG, Membrane Trennverfahren GFT. The membrane was subjected to various plasma powers regulated by time of the membrane exposition. Surface energies and pore size distribution functions were calculated. The data obtained are summarized in table 5.

Table 5

Effect of air plasma action on PAN1514 membranes [18]

Plasma power [W]	Surface energy [mN/m]	Surface polarity [%]	Average pore diameter [nm]
0	65.5	44.2	3.6
12	66.8	61.9	5.2
30	64.1	63.8	10.2
60	61.8	65.2	22.3
120	62.6	69.9	28.4
180	61.8	66.6	38.2

Having skipped the data presented one could draw a general conclusion that average pore diameter and surface polarity become greater for stronger plasma. However, more detailed inspection may reveal that pores become wider and wider when etching is in progress, but alteration of chemical groups on polymer surface is reached just at the beginning of the process. The slight drop in polarity observed for a sample prepared in 180 W plasma might result from redeposition of some species removed from PAN in earlier stages.

3. CONCLUDING REMARKS

This short review presents some aspects of membrane modification to make them less prone to deposition of solutes. The placement of some ionogenic groups on the

membrane surface makes the process less intensive. The modified membranes should keep working for a longer time than their off-charge analogue. Simple method like chemical or plasma modification allows us to obtain materials with properties which should match any requirements. We hope that the performances of porous ion-exchange membranes described here may actively supplement some activities of people involved in ultrafiltration business and help them in their battle with fouling phenomena.

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POROWATE MEMBRANY JONOWYMIENNE

Przedstawiono metody otrzymywania membran porowatych o przedłużonym czasie użytkowania. Omówiono metody modyfikacji materiału membranowego umożliwiającą otrzymanie membran odpornych na zatrucie. Przegląd metod modyfikacji oparto głównie na własnych opracowaniach. Ze względu na zdecydowanie różne zachowanie się modyfikowanych membran w procesie filtracji nazwano je Porowatymi Membranami Jonowymiennymi (PIEM). Przedstawiono metody otrzymywania PIEM oparte na takich technikach, jak: mieszanie polimerów, selektywne usuwanie jednego z polimerów z mieszaniny, inwersja faz czy separacja polimerów z ich mieszanin. Powierzchnie otrzymanych porowatych membran modyfikowano chemicznie lub plazmowo.

