Research Article

Plasma Modified Track-Etched Membranes for Separation of Alkaline Ions

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Abstract. Poly(acrylic acid) and copolymers of acrylic acid and di(ethylene glycol)methyl ether methacrylate were grafted onto polycarbonate and poly(ethylene terephthalate) membranes using dielectric barrier discharge plasma. The obtained membranes exhibited responses to pH change. When they were porous, they behaved as pH-sensitive valves. When pores were filled with gel, they were able to work in dialysis and separated LiCl, KCl, and NaCl salts. The best selectivity for alkaline ions was obtained for poly(ethylene terephthalate) membranes grafted onto copolymer of acrylic acid and di(ethylene glycol)methyl ether methacrylate with a grafting yield of 0.16 mg/cm^2. The separation should be conducted at pH $= 5.5$. It was noted that there is better membrane selectivity towards lithium and potassium than sodium ions.

Keywords: Dielectric barrier discharge plasma, pH-sensitive polymers, brush-like membranes, alkaline ions

1. Introduction

The alkali metals form an important group of elements. It is believed that increasing production in electronics and predicted change of the automobiles market should cause growing demand for lithium [1]. Potassium, the second important element of alkali metals, is critical for agriculture. The available amount of potassium in the soil is not sufficient for intensive farming and its supplementation by fertilizers is essential. Increasing demand for these elements and the possibility of their recovery from aqueous solutions promote the search for new separation techniques.

In our previous paper [2], we presented the possibility to separate alkaline ions by means of membranes showing the gating effect. As the membrane support, Celgard 2500 was used. At some temperatures, the grafted chains reorganized and were able to form some structures that facilitated ions transport. However, the used

Celgard 2500 membranes showed the substantial drawback: the membrane had irregularly shaped pores with pretty wide polydispersed size. To have narrow dispersity of pores, track-etched polyterephthalate and track-etched polycarbonate membranes were selected. Both of them had the same nominal pore diameter and comparable porosity.

Table 1: Properties of used membranes.

Membrane	PET	PC
Producer	SterliTech Corp.	GE Healthcare
Thickness [μm]	15–12	7–20
Pore size [μm]	0.2	0.2
Porosity [%]	24	20

Table 2: Plasma parameters for PET and PC membranes modification.

Plasma parameters	PET	PC
Voltage, kV	20	15
Current, mA	5	5
Argon flow, l/h	40	40
Modification time, sec	60	75

In this work, poly(acrylic acid), PAA, was used as the stimuli response polymer. It belongs to the group of polymers that is strongly sensitive to pH alteration and weakly to the temperature changes [3]. It was the authors' assumption that grafted brushes of acrylic acid, AA, copolymer with di(ethylene glycol) methyl ether methacrylate, DEGMEM, as ionophore can form membrane with controllable alkaline ions transport. In the literature some papers describing membranes with various ionophores can be found too [4–7].

The goal of presented studies was to prepare and evaluate separation effectiveness of ion-gating membranes obtained on track-etched polycarbonate, PC, and poly(ethylene terephthalate), PET, microfilters. When PC contained mostly aromatic structures, PET had aliphatic units too. That difference in chemistry of the polymers allowed us to compare the efficiency of plasma activated grafting and to verify the thesis on a chance to use prepared membranes for separation of alkaline ions.

2. Experimental part

2.1. Materials. Porous PET and PC membranes were used as the substrate. Their properties are shown in Table 1.

Before plasma treatment, both membranes were rinsed with ethanol and dried at room temperature. Di(ethyleneglycol)methyl ether methacrylate was purchased from Sigma Aldrich and used as delivered. Acrylic acid (Merck) was vacuum distilled before the use.

2.2. Plasma treatment. Membrane was modified in dielectric barrier discharge plasma in device supplied by Dora Power Syst., Poland. Plasma parameters (see Table 2) were kept constant during the whole studies.

2.3. Grafting procedure. Both membranes were placed into a plasma reactor and treated with dielectric discharge plasma

Table 3: Parameters for monomer(s) grafting process.

	PET		PC	
	AA in water	AA/ DEGMEM in ethanol	AA in water	AA/ DEGMEM in ethanol
Solution concentration, vol. %	25	25/50	25	25/50
UV illumination time, min	4	6	5	7

on both sides. After plasma treatment, the samples were kept in the air for 10 min. Next, they were immersed in 20% aqueous solution of acrylic acid or its mixture with di(ethyleneglycol) methyl ether methacrylate and irradiated with UV lamp (2 kW). Parameters of grafting protocol are given in Table 3. To remove unbound (co)polymers the samples were washed with a large volume of water and ethanol.

2.4. Characterization of modified membranes.

2.4.1. Grafting degree. The grafting yield (GY) was calculated gravimetrically and expressed in mg/cm^2:

$$GY = \frac{M_1 - M_2}{A}, \qquad (1)$$

where M_1 and M_2 are weights of membrane after and before grafting and A is membrane area.

2.4.2. Pores size. The pores size, r, were calculated according to the following formula:

$$r = \sqrt[2]{\frac{8J\,d\eta}{p\varepsilon}}, \qquad (2)$$

where J is water flux, d is membrane thickness, η is water viscosity, p is pressure, and ε is porosity.

2.4.3. IR spectroscopy. To characterize the obtained membranes, Perkin-Elmer IR System 2000 was used with ATR device equipped with Ge crystal of 45o. 64 scans with resolution of 4 cm^{-1} were collected.

2.4.4. Water permeability. Water permeability through evaluated membranes was tested at pH = 3.0 and pH = 5.5 at room temperature. For all measurements the pressure in Amicon 8200 cell was set at 0.002 MPa. Before filtration, membranes were hydrophilized by immersing them in 1:1 water:ethanol solution for 15 min and transferring them to pure water.

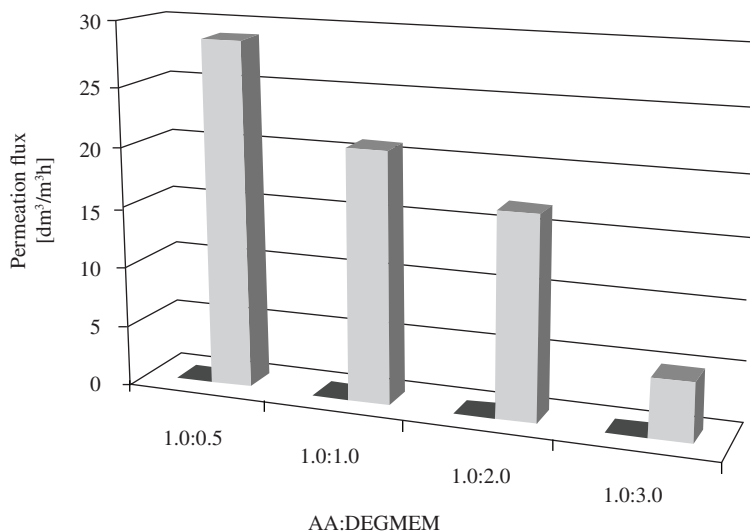*2.4.5. Dialysis process.* Ion separation properties of evaluated membranes were measured in the dialysis process.

Figure 1: Volumetric flux through PET membranes grafted with P(AA-co- DEGMEM) copolymers. Grey bar: pH = 3.0 and black bar: pH = 5.5.
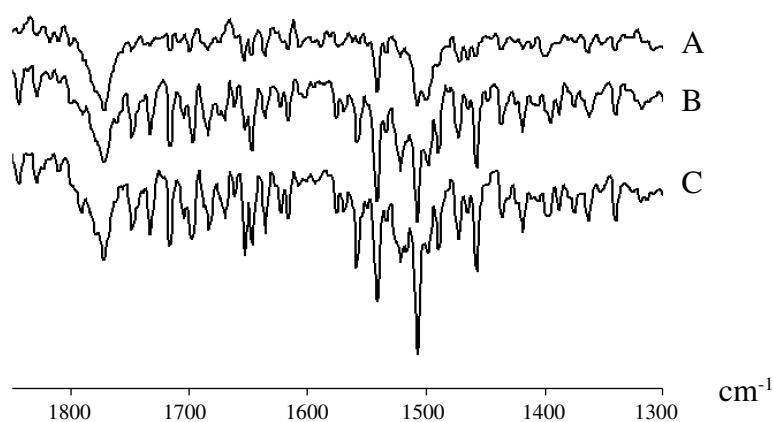

Figure 2: FTIR spectra: (A) no modified membrane PET, (B) membrane grafted with PAA, and (C) membrane grafted with P(AA-co-DEGMEM).

Solutions of KCl, NaCl, and LiCl with 0.1M concentration were used as feeding phase. HCl aqueous solutions of pH = 3.0 and 5.5 served as receiving phase. Both phases, of 35 mL volume mixed with a magnetic stirrer, were divided by membrane of 2.5 cm radius. Concentration of ions was monitored by atomic absorption spectroscopy (GBC SavantAA Sigma).

3. Results

Track-etched PET membranes were grafted with PAA or PAA-DEGMEM copolymers. Taking into account the different reactivity of acrylic monomers, the molar ratio of AA to DEGMEM was changed from 1:0.5 to 1:3 to obtain grafts with various compositions. The results are shown in Figure 1. It is visible that any increase of DEGMEM contents made the grafted membrane less permeable at pH = 3 when the carboxylic groups were neutral. At pH = 5.5, when the carboxylic groups dissociated, pores were completely plugged independently on the amount of used DEGMEM. On the basis of the presented studies, it was decided to use AA:DEGMEM 1:2 mixture to modify PET and PC membranes.

Chemical composition of modified membranes PET and PC was characterized by means of FTIR spectra (Figure 2). The peaks on spectra of grafted membranes demonstrated the presence of glycol derivatives. The differences of peak shapes in the area of 3300–3200 cm^{-1}, 1740–1720 cm^{-1}, and 1470-1410 cm^{-1} were attributed to hydroxyl and carbonyl groups introduced by DEGMEM.

Absorption peaks in the spectra of the modified PC membranes at 1558, 1457, and 1715 cm^{-1} were attributed to the carboxyl groups. Its widening proved presence of PAA and PAA-DEGMEM on the surface (Figure 3).
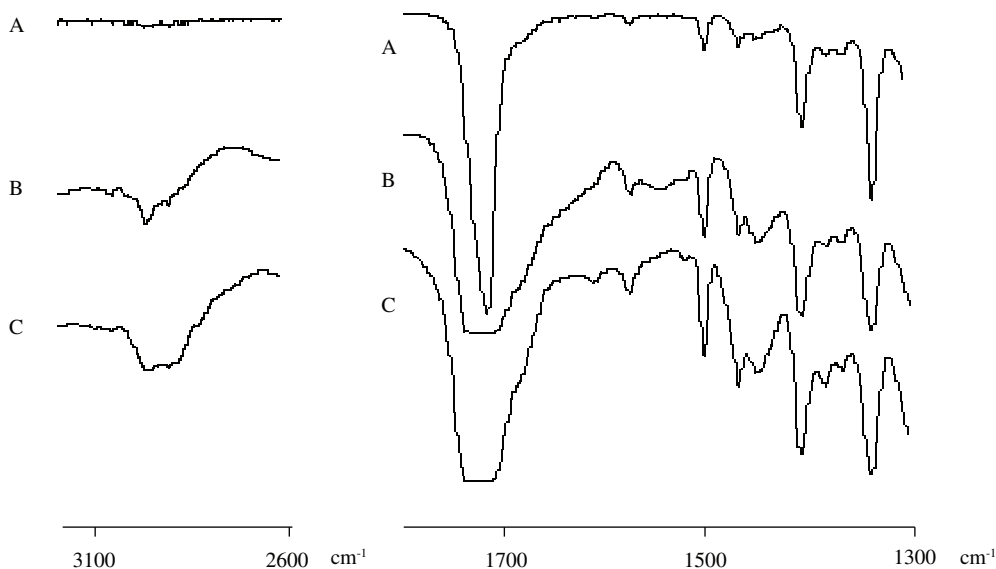
Figure 3: FTIR spectra: (A) no modified PC membrane, (B) PC membrane grafted with PAA, and (C) PC membrane grafted with P(AA-co-DEGMEM).

Table 4: Average pore size as function of grafting yield. Tested at pH = 3.

PC		PET	
GY, mg/cm^2	r, μm	GY, mg/cm^2	r, μm
0	0.200	0	0.200
0.0124	0.191	0.082	0.00935
0.0250	0.186	0.162	0.00126

3.1. Filtration membranes. Both membranes with low grafting yield showed similar phenomenon: they had volumetric flux at pH = 3.0 of order 52–59 dm^3/m^{2}h and were completely impermeable for solutions at pH = 5.5. When the grafting yield increased, the pores of the modified membranes got narrower (Table 4). In the case of PC support the average pore size did not reduce so fast as for PET support. It seemed it was the effect of small grafting yield for PC membranes resulted, probably, from the lower number of radicals formed on the plasma activated surface.

The obtained results on pH-sensitive membranes are in good agreement with data discussed in literature by Mika et al [8–10], Zhao et al [11], and Hu and Dickson [12].

3.2. Dialytic membranes. For studies on dialytic separation of alkaline ions, PC and PET membranes with the largest grafting yield were used. Hence, the following PET membranes with the grafting yield of 0.157 mg/cm^2 for PAA and 0.162 mg/cm^2 for PAA-DEGMEM were selected. Polycarbonate membranes had five times smaller grafting yield and reached values of 0.0210–0.0257 mg/cm^2.

Separation properties of PC and PET membranes were tested in relation to lithium, sodium, and potassium ions.

Dialysis was carried out with 0.1 M solutions of their chloride salts at pH 3.0 and 5.5. Figures 4–6 show changes in the concentration of LiCl, NaCl, and KCl during dialysis. It can be seen that the best transport properties showed PET membrane grafted by P(AA-DEGMEM).

The concentration of potassium ions after dialysis through PET/P(AA-DEGMEM) membrane was much higher than the concentration of potassium passing through PAA membranes. The differences between these concentrations were substantially higher when the process was carried out at pH = 5.5 than at pH = 3.0. It meant that DEGMEM units supported transport of alkali ions when grafted chains were swollen. Unfortunately PC membranes did not show such phenomenon. It seemed to be a result of a too low amount of polymer brushes grafted to the membrane.

Figure 7 summarized the kinetic studies on KCl, NaCl, and LiCl transport through PAA and P(AA-co-DEGMEM) grafted membranes. It is evident that potassium ions were transferred faster through membrane than sodium and lithium. Interesting data can be obtained by comparing fluxes for PAA and P(AA-co-DEGMEM) membranes. The value of flux improvement, caused by the presence of DEGMEM, can be expressed as follows:

$$Fi(X) = J_{P(AA-co-DEGMEM)} - J_{PAA}, \qquad (3)$$

where FI(X) is flux improvement and $J_{P(AA-co-DEGMEM)}$ and J_{PAA} are fluxes of X ion through P(AA-co-DEGMEM) and PAA membranes, respectively.

The calculated values of FI(X) are listed in Table 5. The data show that presence of DEGMEM, for single-component solution at pH = 5.5, improved fluxes of ions in the order: K > Li > Na. Dialyses at pH 3.0 were not sensitive to the presence of di(ethyleneglycol)methyl ether methacrylate.
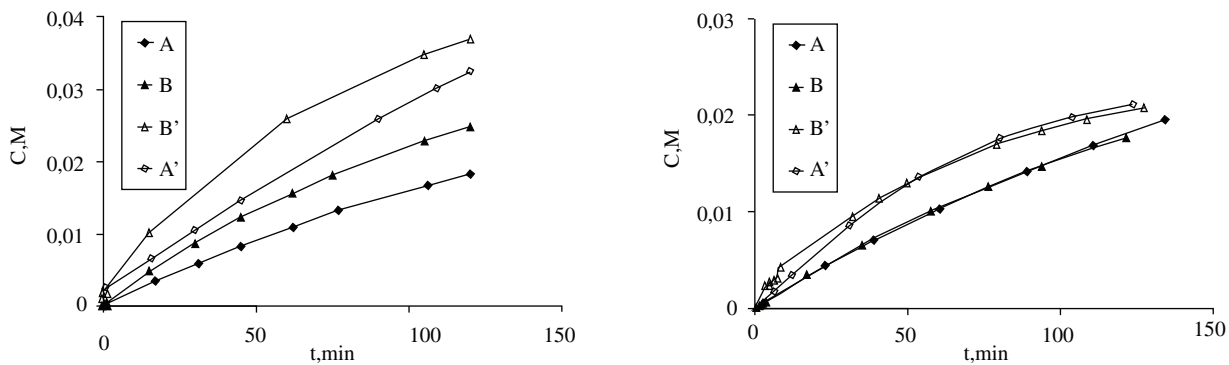
Figure 4: LiCl transport through membranes. Left: membrane PET: (A) PAA membrane at pH 5.5, (A') PAA membrane at pH 3.0, (B) P(AA-co-DEGMEM) membrane at pH 5.5, (B') P(AA-co-DEGMEM) membrane at pH 3.0; Right membrane PC (C) PAA membrane at pH 5.5, (C') PAA membrane at pH 3.0, (D) P(AA-co-DEGMEM) membrane at pH 5.5, (D') P(AA-co-DEGMEM) membrane at pH 3.0.
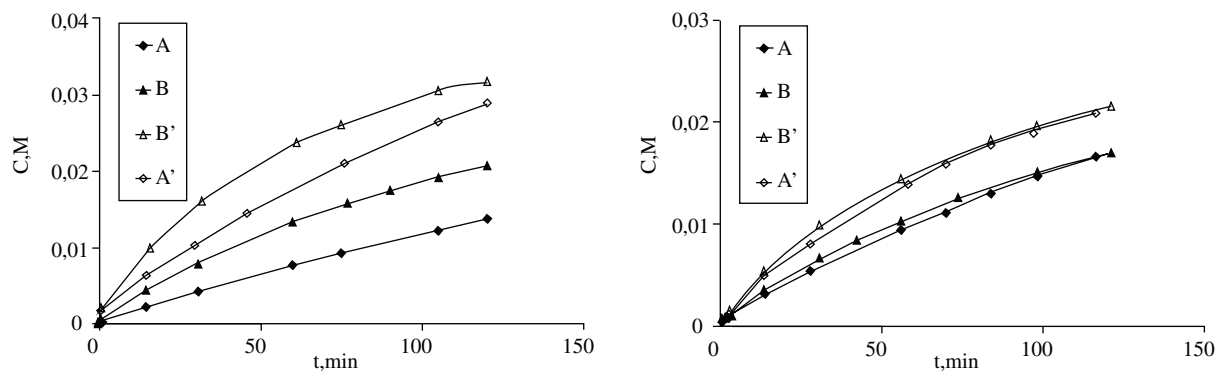

Figure 5: NaCl transport through membranes. Left: membrane PET: (A) PAA membrane at pH 5.5, (A') PAA membrane at pH 3.0, (B) P(AA-co-DEGMEM) membrane at pH 5.5, and (B') P(AA-co-DEGMEM) membrane at pH 3.0. Right: membrane PC: (C) PAA membrane at pH 5.5, (C') PAA membrane at pH 3.0, (D) P(AA-co-DEGMEM) membrane at pH 5.5, and (D') P(AA-co-DEGMEM) membrane at pH 3.0.

Table 5: Flux improvement for PET membranes grafted with PAA-DEGMEM brushes. Single salt tests.

Ion	pH	
	5.5	3.0
K	68%	9%
Na	13%	3%
Li	36%	9%

Table 6: Flux improvement for PET membranes grafted with PAA-DEGMEM brushes. Mixture of LiCl, NaCl and KCl. tests.

pH	FI(Li+)	FI(Na+)	FI(K+)
5,5	32%	19%	28%
3,0	3%	3%	4%

However, the most valuable results of membrane selectivity can be obtained when membrane is exposed to competitive transport of several ions. For that reason, membrane selectivity was evaluated for three-component solution (Table 6). At pH = 5.5, flux improvement for LiCl was comparable to that for KCl and higher than that for NaCl. It meant that the modified membranes transferred better lithium and potassium ions. At the lower pH, however, the separation selectivity of membranes disappeared almost completely. This observation confirmed the previous outcome: DEGMEM units were able to form complexes with alkaline ions and supported ions transport at pH =

5.5. That process took place when polymer brushes were expanded. It is hence possible that, at these conditions, the ion-transporting structures were formed.

4. Conclusion

Grafting of PAA and its copolymers with DEGMEM on PC and PET track-etched membranes allowed obtaining pH-sensitive nanovalves. However, any increase of ionophore content in the copolymer decreased the sensitivity of the membrane to pH changes.
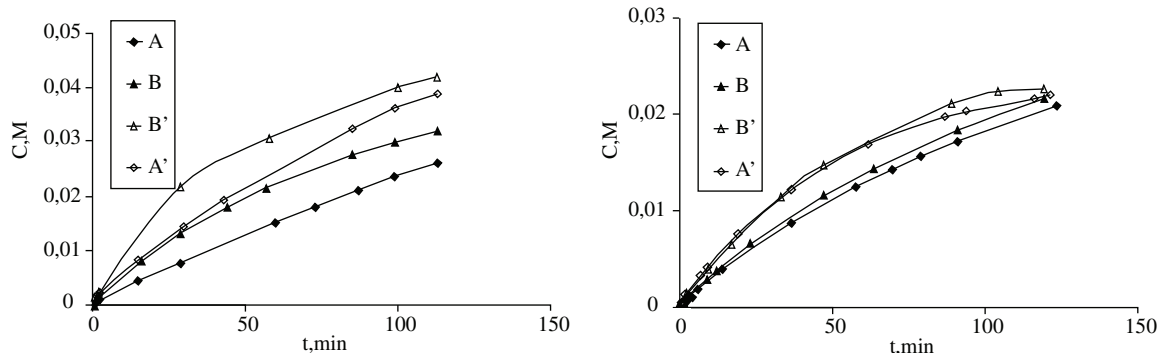
Figure 6: KCl transport through membranes. Left: membrane PET: (A) PAA membrane at pH 5.5, (A') PAA membrane at pH 3.0, (B) P(AA-co-DEGMEM) membrane at pH 5.5, and (B') P(AA-co-DEGMEM) membrane at pH 3.0. Right: membrane PC: (C) PAA membrane at pH 5.5, (C') PAA membrane at pH 3.0, (D) P(AA-co-DEGMEM) membrane at pH 5.5, and (D') P(AA-co-DEGMEM) membrane at pH 3.0.
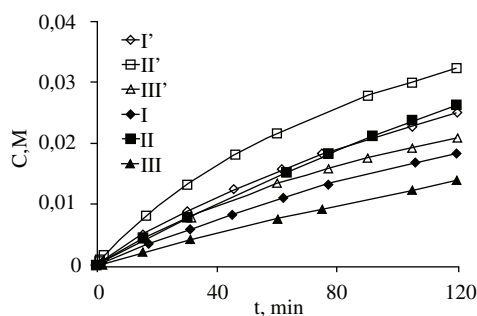

Figure 7: KCl, NaCl and LiCl transport through PET membranes at pH 5.5, (I) LiCl, PAA membrane, (I') LiCl, P(AA-co-DEGMEM) membrane, (II) KCl, PAA membrane, (II') KCl, P(AA-co-DEGMEM) membrane, (III) NaCl, PAA membrane, (III')NaCl, P(AA-co-DEGMEM) membrane.

PET membranes grafted with a large amount of P(AA-co-DEGMEM) copolymer allowed obtaining dialytic membranes that exhibited ions-transporting effect related to solution acidity. In the case of separation of ions from mixtures, the PET-modified membrane showed good selective properties for lithium and potassium. In the case of PC membranes a too small amount of grafted brushes did not allow using these membranes for dialysis.

Acknowledgement

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