

## ELECTRICALLY INDUCED STRUCTURAL CHANGES IN QUATERNIZED METHYL METHACRYLATE-*N*-[2-METHYL-5-(DIMETHYLAMINO)-PHENYL]MALEIMIDE COPOLYMER MEMBRANES\*

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*Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.*

Homogeneous membranes were prepared by casting chloroform solutions of methyl methacrylate-*N*-[2-methyl-5-(dimethylamino)phenyl]maleimide copolymers containing 2.3–8.7 mole % of the imide. After quaternization with methyl iodide, diffusive permeabilities and electric resistances (both with alternating and direct current) of the membranes were determined. During the passage of electric current a substantial decrease (2–10 fold) in the membrane resistance was observed; the lower the imide content was, the greater was the effect. The decrease suggests structural changes in the membranes due to electrohydrodynamic convection of unstable polymer chains caused by electric force. Significant correlations between the imide content and the resistance, both before and after the treatment with electric current, were found. According to oriented concentration potentials, the internal symmetry of the membranes was also affected by electric current.

Membranes based on quaternized methyl methacrylate-*N*-[2-methyl-5-(dimethylamino)phenyl]maleimide copolymers were prepared for the study of their pervaporation ability, but they were not sufficiently mechanically resistant to the conditions in the pervaporation cell. Nevertheless, their hydrophilicity made them potentially useful for dialysis and their ionisable groups content for electromembrane operations. Diffusion of NaCl from its 0.5 M aqueous solution through the membranes into pure water was measured without difficulties. But the measurement of their AC and DC electrical resistances in 0.5 M NaCl solutions brought about a surprise: The resistance decreased during the measurement, evidently under the influence of electric current passed through the membrane. The aim of this study is to explain the phenomenon.

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## EXPERIMENTAL

## Materials

Methyl methacrylate (MMA) was a commercial product (Fluka). The other monomer, *N*-[2-methyl-5-(dimethylamino)phenyl]maleimide (*I*) was synthesized by the reaction of 2-methyl-5-(dimethylamino)aniline with maleic anhydride and subsequent cyclodehydration of the maleamic acid (MA) obtained<sup>1,2</sup>. Copolymers of MMA and *I* were prepared by heating a solution of *I* (0.45, 0.90 or 1.20 g), MMA (4.05, 3.60 or 3.30 g) and 2,2'-azobisisobutyronitrile in benzene (12 ml) at 50 °C for 20 h; they were precipitated with a sevenfold volume of ethanol<sup>2</sup>. Their composition was determined by elemental analysis. Conversions of monomers (approx. 20%) were calculated from the composition and mass of the copolymers.

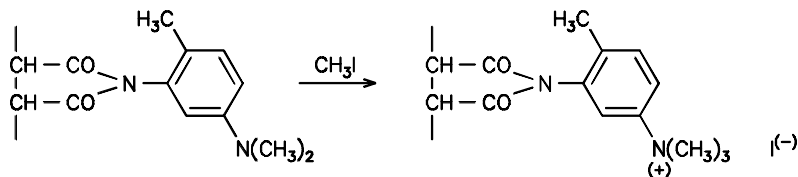
Primary, uncharged membranes were obtained by casting 10 wt.% chloroform solutions of copolymers on a glass plate to form a 0.35-mm thick layer. After evaporation of the solvent at room temperature, membranes with a thickness of approximately 30 μm were released from the glass plate by immersing in water. Then, the membranes were quaternized (Scheme 1) by placing them at room temperature for 20 h in a solution of 1 g CH<sub>3</sub>I in 20 ml of ethanol<sup>3</sup>. The degree of quaternization of the incorporated imide units was determined from the N and I contents. The membranes were conditioned by alternating immersion into 1.0 M NaOH and 1.0 M HCl for 4 × 2 h, washed and equilibrated with 0.5 M NaCl.

## Measurements

Membrane permeabilities to NaCl (from 0.5 M NaCl solution into pure water) were determined by the method described elsewhere<sup>4</sup>. In principle, permeabilities were measured in a two-compartment thermostatted cell with one compartment filled with 0.5 M NaCl solution and the other one with water. Both liquids were vigorously stirred by magnetically driven stirrers made of stainless steel. Concentration changes in both compartments were measured as changes in electric conductivity and calculated by means of a calibration formula. Permeability coefficients were calculated from the slope of the *t* vs *c* plot in steady state according to the equation

$$Q = cV = PA \left( \frac{c_0}{d} \right) \left( t - \frac{d^2}{6D} \right),$$

where *Q* is the total amount of the salt transported through the membrane during time *t*; *c* is the concentration in the downstream compartment in time *t*, *c*<sub>0</sub> is the initial concentration in the upstream



SCHEME 1

compartment,  $V$  is the volume of the downstream compartment (50 ml),  $A$  is the membrane area ( $3.14 \text{ cm}^2$ ),  $d$  the membrane thickness, and  $D$  the diffusion coefficient of NaCl in the membrane.

Electric conductances of the membranes were measured first in an alternating field (80 Hz) and then by means of the voltage drop on the membrane in 0.5 M NaCl solution when stabilized constant direct current ( $0.25 \text{ mA cm}^{-2}$ ) passed through the membrane. For all electrochemical measurements, a two-compartment thermostatted cell with conical inner chambers served<sup>5</sup>. AC resistance was measured with a Philips PW 9527 digital conductivity meter and with slightly platinized platinum electrodes inserted into each cell compartment. Membrane resistance was calculated from the difference between the values measured with and without the membrane. DC conductance was calculated from the voltage drop in the vicinity of the membrane (or of the orifice for the membrane) surrounded with the solution. The voltage drop was measured by means of a pair of saturated calomel electrodes and a Meratronik digital multimeter V553, the current value was determined from the voltage drop on a calibrated resistor displayed by an other multimeter of the same type. Before each experiment, the whole measuring equipment was calibrated by means of standard resistors. Concentration potentials of membranes in contact with  $0.010 \parallel 0.001 \text{ M}$  KCl were measured with saturated calomel electrodes and the electrometer mentioned above. Oriented concentration potentials are the values obtained with the denser side (i.e., evaporation side in the case of cast membranes) in contact with the more and less concentrated solution. The comparison of the two so obtained potential values makes it possible to reveal inner asymmetry (anisotropy) of the membrane<sup>6</sup>. Symmetrical (isotropic) membranes manifest identical oriented concentration potentials.

## RESULTS AND DISCUSSION

Table I shows the composition of the copolymer and the extent of quaternization of imide units in the membranes. With increasing content of quaternized imide groups, the permeability of the membrane to NaCl increases and its resistivity decreases. In the right-hand side of the Table electric resistances before and after the measurement can

TABLE I  
Characteristics of quaternized methyl methacrylate-*N*-[2-methyl-5-(dimethylamino)phenyl]maleimide copolymer membranes

Membrane	Quaternary units <sup>a</sup> mole %	Permeability $P_{\text{NaCl}} \cdot 10^{11}$ $\text{cm}^2 \text{ s}^{-1}$	Electric charge passed $\text{C cm}^{-2}$	Resistivity $R \cdot 10^{-4}, \Omega \text{ cm}$ before/after charge passing	
				AC	DC
A	1.6 (2.3)	2.5	72	346/55.4	330/55.2
B	2.8 (5.1)	6.8	23	34.8/20.4	35.7/21.3
C	4.5 (7.4)	99.0	105	2.58/1.53	2.69/1.82
D	5.1 (8.7)	155.0	91	0.822/0.371	0.896/0.466

<sup>a</sup> In parentheses, mole % of maleimide units in the starting copolymer are given.

be seen. From the data it follows to which extent membrane resistivities decreased by the influence of the electric force during the measurement. The decrease was deeper for less charged (quaternized) copolymers. This decrease could not be caused by a mere conditioning of membranes by electric current, because they were conditioned in 1.0 M HCl and 1.0 M NaOH before the measurements, and because the decrease in resistance was inversely proportional to the logarithm of the maleimide and its quaternary ammonium salt contents in the swollen membrane. The probable reason for this phenomenon consists in the influence of the electric force on mobile polymer chains in non-stable positions after evaporation of the solvent. In particular, polymer A has a very low electric conductivity and behaves to some extent like a dielectric fluid. A non-uniform distribution of dielectric permittivity values in the polymer causes an intrinsic convection under the influence of the electric force until an equilibrium as well as more permeable state of the polymer is reached, in which the dielectric permittivity loses its importance. The condition for an intrinsic electrohydrodynamic convection in a fluid is  $\nabla \bar{X} \neq 0$  or  $\nabla \kappa \neq 0$  ( $\bar{X}$  being the free charge density,  $\kappa$  the dielectric permittivity)<sup>7</sup>. This condition is probably fulfilled in non-quaternized membranes. It should be emphasized that the polymer is linear, not crosslinked. The less conductive the original polymer is, the more significant improvement of the electric conductivity can be achieved. The loosening and ordering of the internal structure of the membrane became manifest in the asymmetry (Table II) originating in the conditions of membrane formation (casting, evaporation). The minimum electric quantity necessary to evoke the described phenomenon was not investigated. Electric charge values in Table I serve for informative orientation and should be taken as excess electric quantities.

Oriented concentration potentials (Table II) prove the change in the internal structure of the membrane by the electric force: Before the treatment with electric current the membrane seemed to be or really was isotropic. The inner anisotropy caused by the conditions during casting the membrane (partial evaporation of the solvent and densification of a thin skin on the upper side of the membrane) was not revealed until the electric force rearranged mobile polymer chains.

TABLE II  
Oriented concentration potentials (mV) of membrane A in 0.010||0.001 M KCl

Membrane A	- Orientation	+ Orientation <sup>a</sup>
Before current passing	+4.50	+4.55
After current passing	+8.40	+0.74

<sup>a</sup> The denser (evaporation) side in contact with the more concentrated solution.

## CONCLUSIONS

Slightly charged non-crosslinked cast polymer membranes swollen in aqueous electrolyte solutions can behave like a dielectric fluid under influence of electric force, e.g., during electrical resistance measurement. The influence of electric force exerted on partly loose polymer chains results in their more conductive ordering caused by intrinsic electrohydrodynamic convection and reveals internal asymmetry typical of membranes formed by casting polymer solutions and subsequent evaporation of the solvent. The electrically induced decrease in polymer resistivity can be intentionally used, e.g., in preparation of membranes from non-crosslinked polymers.

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