QUATERNIZED POLY(2-DIMETHYLAMINOETHYL METHACRYLATE)–PVC COMPOSITE MEMBRANES

Vlastimil KŮDELA, Stanislav ŠEVČÍK, Olen RYBA and Jiří VACÍK

Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic, 162 06 Prague 6, The Czech Republic

Received March 22, 1993
Accepted May 31, 1993

Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

A series of homogeneous and heterogeneous composite membranes consisting of PVC and crosslinked quaternized poly(2-dimethylaminoethyl methacrylate) was investigated electrochemically. Their electrolytic resistances ranged from nearly zero to insulator values at a permselectivity of 62 – 96.7%. Highly conductive and permselective membranes are promising for neutralization dialysis and dialysis of acids. Insulator-like membranes behave as bipolar ones (diode effect) and, in contact with KCl solutions of different concentrations, like electrets (persistent charge).

In a systematic search for hydrogels with improved properties, composite membranes were prepared[1] from PVC and crosslinked quaternized poly(2-dimethylaminoethyl methacrylate) (QPDMA):

– in the most *intimate* form as interpolymer systems (IS) arising in solution from both linear polymers by crosslinking quaternization (Fig. 1),

– in the most *hydrophilic* form as heterogeneous systems consisting of IS filled with QPDMA particles (HS–IS) (Fig. 2), and

– in the most *variable* form as heterogeneous systems prepared from PVC dissolved in DMF and filled with QPDMA particles (HS–PVC) (Fig. 3).

The membranes are evidently electrochemically active, therefore their electrolytic resistances and permselectivities were determined. A broad variety of differently usable membranes, as well as an unexpectedly behaving diode/electret membrane were found.

EXPERIMENTAL

Materials

Poly(2-dimethylaminoethyl methacrylate) (PDMA). An oxygen-free 30 wt.% solution of 2-dimethylaminomethyl methacrylate in benzene was subjected to a long-term radical polymerization[1] initiated by diffuse light. The polymer reprecipitated into an excess of hexane had M.w. 1.6 . 10^6.

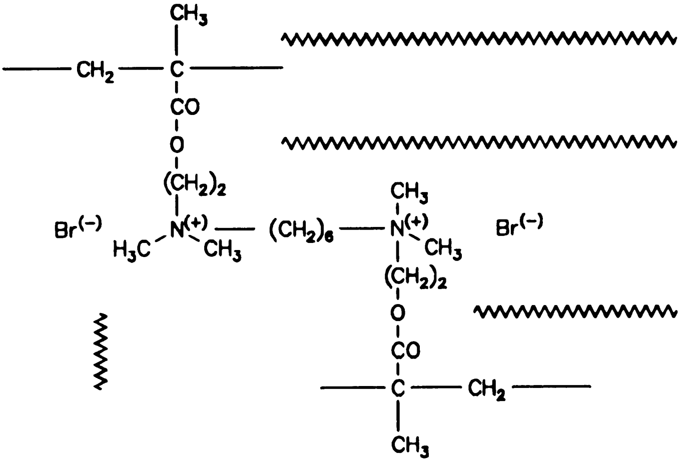

FIG. 1

Idealized scheme of interpolymer system (IS) membranes (∧∧∧∧∧∧∧ PVC chain)

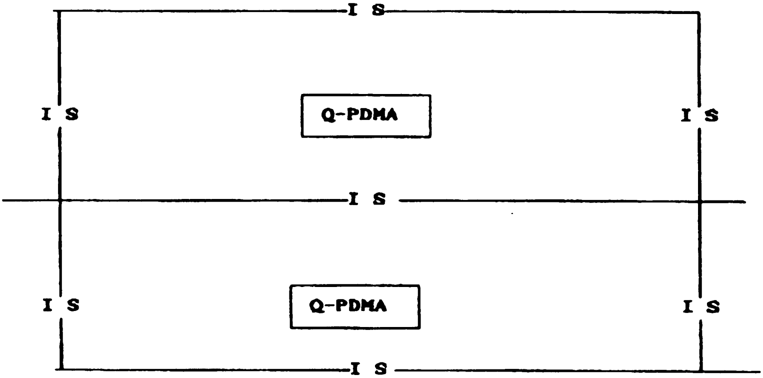

FIG. 2

Idealized scheme of the interpolymer system–hydrophilic filler composite (HS–IS)

Hydrophilic filler. Freeze-dried PDMA was dissolved in DMF and 1,6-dibromohexane was added under nitrogen. The mixture was thoroughly shaken and then kept at 55 °C for 64 h. The obtained gel was disintegrated, extracted with ether, ethanol, water and ethanol, ground, sifted through a 32 μm sieve and dried in vacuo.

IS membranes. A 10% solution of PDMA in dry DMF was thoroughly mixed in a special device[1] with equivalent amounts of 1,6-dibromohexane and of a 10% solution of PVC in dry DMF. The reaction mixture was cured on a Petri dish at 55 °C between two aluminium blocks for 24 h, the remaining liquid was then evaporated and the membrane was washed in distilled water until a constant weight was reached.

HS–IS membranes. To a reaction mixture for the IS membrane, containing 57% PVC in dry matter (Table I), a weighed amount of the hydrophilic filler was added. The same procedures followed as with IS membranes.

HS–PVC membranes. A weighed amount of the hydrophilic filler was dispersed in a 10% DMF solution of PVC. DMF was gradually evaporated and the obtained membrane was washed in distilled water.

Membranes contained no reinforcement tissue. Their characteristics are shown in Table I.

Methods

Ion-exchange capacities and weight swelling. Membrane samples were extracted in universal columns[2,3] with 0.1 M H_2SO_4, then with a 1 M solution in both Na_2CO_3 and $NaHCO_3$, regenerated with 1 M NaCl, and extracted with 1 M NH_4OH and 1 M Na_2SO_4. The halogen content in acidified extracts was determined potentiometrically with 0.1 M $AgNO_3$. Weight swelling was determined by drying equilibrium-swollen samples in vacuo at room temperature.

Electrochemical measurements. Electrolytic resistances of membranes were measured by means of a Philips PV Digital Conductivity Meter at 80 and 4 000 Hz in a 0.1 mol KCl/kg H_2O solution at 25 °C. DC resistances and concentration potentials of the membranes as well as the voltage–current characteristics of the insulator-like membrane were measured by means of the equipment described in ref.[4]. All membranes for electrochemical experiments were cut from membranes previously subjected to pervaporation tests.

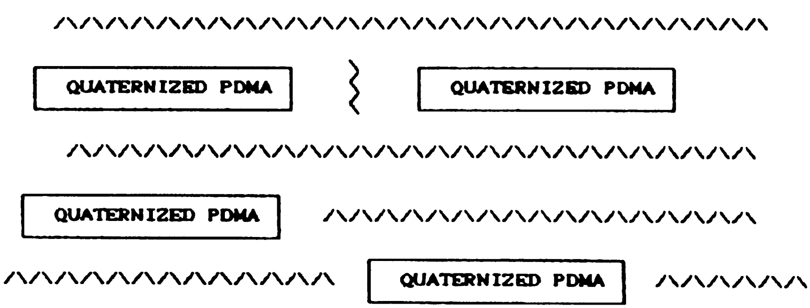

FIG. 3
Idealized scheme of the PVC–hydrophilic filler composite (HS–PVC) (^^^^^^^^^ PVC chain)

RESULTS AND DISCUSSION

Electrochemical properties of the membranes, their ion-exchange capacities and swelling are given in Table I. IS membranes equal good membranes for electrodialysis in resistance and approach them in permselectivity. Ideal values of concentration potentials are those calculated from the Nernst equation, i.e., for the 0.01 || 0.10, 0.20 || 0.10 and 0.50 || 0.10 mol KCl/kg H_2O cells E_0 are –55.0, 16.1 mV and 36.9 mV, respectively.

In spite of the variability in composition, the electrochemical variability of IS membranes is rather small. Their specific resistances are in the region of good membranes for electrodialysis (ED). The permselectivities P were calculated from concentration potentials E_c and anion transport numbers in solution, t_- and in the membrane, $\bar{t}_-$

$$P = 100\,(\bar{t}_- - t_-)/(1 - t_-) \qquad (1)$$

$$\bar{t}_- = (E_0 + E_c)/2\,E_0 \,. \qquad (2)$$

Permselectivities reach values as high as 97%, P of commercial ED membranes being 98 – 99%.

The extraordinarily hydrophilic HS–IS membranes keep surprisingly good permselectivities even with the samples whose resistance was “zero”, i.e. the same as that of the surrounding solution. This coincidence of a good permselectivity and an extra-high conductivity could be used in diffusive separation operations like neutralization dialysis and dialysis of acids into water because high conductivity is associated with a high diffusivity. From this point of view, the most promising is the membrane with 20.8% PVC.

Unexpected properties were found with HS–PVC membranes (Tables I and II). Their resistivities range from those typical of membranes for electrodialysis to nearly those of insulators (HS–PVC with 49.5% PVC). However, these insulator-like foils are not ion-exchange membranes any more, they behave like electrets. The potentials generated on them are not concentration potentials of the Donnan type but generally membrane potentials. They do not obey the Nernst equation being higher than the theory allows; they are irreproducible and show strong orientation effects. Typical results of this kind are summarized in Table II. Several potential values exceeded the theoretical ones. Moreover, both the signs and absolute values of the potential are dependent on the orientation of the membrane surface towards the two solutions which are in contact with it. The known membrane potential orientation effects arising from the anisotropy of the membrane are limited to the value of the potential without any influence on its sign[5]. In order to decide whether the negative potential on a membrane containing positively charged groups is virtual or not, the two sides of the membrane in contact with 0.1 || 0.2 mol KCl/kg H_2O were short-circuited, either with a Cu wire, or by an electro-

TABLE I
Properties of membranes

Membrane type	PVC content[a] %	Ion-exch. capacity[a] mval/g	Swelling[a] g H_2O/g	AC resistivity, Ω cm		DC resistivity, Ω cm		Concentration potentials[d], mV		
				80 Hz	4 kHz	25[b]	2.5[c]	0.10 ‖ 0.01	0.20 ‖ 0.10	0.50 ‖ 0.10
IS	64.3	0.766	0.260	515	516	498	494	52.0	15.2	34.4
	56.5	1.540	0.326	141	147	164	151	52.2	15.0	35.0
	45.6	1.606	0.315	54.5	69.3	46.3	49.6	52.1	15.1	31.9
	36.3	1.840	0.665	38.6	34.0	35.7	40.9	52.2	15.1	32.6
HS–IS	31.2	2.147	0.742	93.0	40.7	52.7	52.1	52.4	15.2	30.2
	25.6	2.320	0.907	0	0	0	0	44.4	15.1	29.4
	20.8	2.513	0.906	0	0	0	0	52.4	15.3	29.0
	13.3	2.655	1.284	0	0	0	0	43.8	13.3	20.8
HS–PVC	49.5	1.376	0.481	375 894	369 698	360 545	395 193	[e]	[e]	[e]
	39.6	1.650	0.519	4 649	4 639	4 795	4 744	52.4	15.2	37.5
	29.8	2.100	0.822	568	537	623	613	52.9	15.2	34.9
	20.2	2.422	1.230	157	159	171	166	47.8	14.6	31.7

[a] Related to dry matter; [b] μA/cm^2; [c] mA/cm^2; [d] mol KCl/kg H_2O; [e] see Table II.

lytical contact through the solution and immersed Pt electrodes. In both cases the membrane potential as measured by calomel electrodes changed abruptly, e.g., as follows:

$$-39.7\ \text{mV} \ldots |\text{voltage clamp}| \ldots +16.7\ \text{mV}\,.$$

At the opposite concentration gradient:

$$+52.9\ \text{mV} \ldots |\text{voltage clamp}| \ldots -54.0\ \text{mV}$$

$$+53.8\ \text{mV} \ldots |\text{voltage clamp}| \ldots -52.2\ \text{mV}\,.$$

This behaviour is similar, for instance, to that of polarized electrodes in the course of depolarization by a short circuit or to that of really existing concentration cells during a slow discharge. The two solution-containing compartments in contact with the membrane were well galvanically insulated from each other, so that only the membrane or voltage clamp was able to conduct electric current. pH of the solutions was still about 6.5. Similar persistent electrical polarization and capacity effects were observed in dry polyelectrolyte membranes charged in an electric field[6–8]. The membranes in question were charged merely by the contact with solutions differing in concentrations. To check the correctness of the obtained results and to avoid a systematic error, parallel measurements with the same solutions and using the same arrangement were carried out with a Nafion membrane. No deviations from the known behaviour were found in this case.

To know more about the high resistance-type membranes from our series the voltage–current characteristics were determined. They showed the shape typical of a diode (Fig. 4). The bipolar membranes, i.e. membranes composed of two adherent ion-exchange membranes one of them being anion- the other cation-active, behave in the same way. Thus, due to its high electrolytical resistance, one of the studied membranes exhibits the features both of an electret and a bipolar membrane which does not seem contradictory.

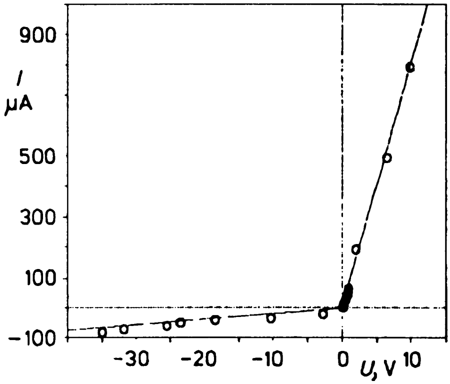

FIG. 4
Voltage–current characteristic of the insulator-like membrane (HS–PVC containing 49.5% PVC)

TABLE II
Potential differences between the sides of the HS–PVC membrane, containing 49.5% PVC, in KCl solutions of different concentrations

Concentration mol KCl/kg H_2O	Membrane	
	No. 1	No. 2
0.01 || 0.10	−18.4	−19.4
0.10 || 0.01	+41.2	+61.2
0.10 || 0.20	−49.9	−37.0
0.20 || 0.10	+10.1	+10.7

CONCLUSIONS

The membranes based on PVC–poly(2-dimethylaminoethyl methacrylate) composites exhibit an amazing variability in electrolytic resistance from “zero” to an insulator value. The extremely low resistance with a sufficient permselectivity makes some of them attractive for neutralization dialysis and simple dialysis of acids. The insulator-like type membranes behave in a similar way as electrets (persistent charge, orientation dependence of the membrane potential sign) and/or as bipolar membranes (diode effect).

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Translated by the author (V. K.).