Synthesis and Characterization of New Ion-Exchange Membranes

A. ELMIDAOUI,[1] T. SARRAF,[2] C. GAVACH,[1] and B. BOUTEVIN[2]*

[1]Laboratoire de Physicochimie des Systèmes Polyphasés, C.N.R.S., Route de Mende, B.P. 5051, 34033 Montpellier, Cedex, France, and [2]URA D11930, Ecole Nationale Supérieure de Chimie de Montpellier 8, rue Ecole Normale, 34053 Montpellier Cedex 1, France

SYNOPSIS

The synthesis of grafted polymers of polyethylene (PE) with acrylic acid and N,N-dimethylamino-2 ethyl acrylate is performed in two steps. The first one needed the ozonization of powder of PE in well-defined conditions to obtain an expected activation. The second one consisted in bulk grafting the two monomers by thermal decomposition of the above hydroperoxides and peroxides of the activated PE. After elimination of homoacrylated by selective solubilization, we obtained films by pressing the copolymers either alone or the mixture of the two copolymers to prepare the anion (or cation) exchange membrane and the amphoteric ion-exchange membrane. The second part of the study deals with the physicochemical characterization of these membranes: thickness, exchange capacity, electrical resistance, transport number, and water content. These characteristics are given for various concentrations of equilibrating solutions and for various pH. The results show that we have perfectly corrected membranes that are competitive with the commercial ones.

INTRODUCTION

The ion-exchange membranes, which were conceived for the brackish water desalting, have nowadays many further applications in the industry. This success is the result of the improvement of the synthesis methods.

Ion-exchange membranes are synthesized according to several methods: chemical,[1,2] photochemical,[3,4] radiochemical,[5,6] and mechanical.[7,8] In our work, membranes were prepared by a chemical grafting of a weak acid and a weak base on the ozonized polyethylene (PE). This new method allowed us to obtain two selective membranes (cationic-exchange membrane [CEM] and anionic-exchange membrane [AEM]) and an amphoteric ion-exchange membrane that can exchange anions as cations. The composite structure of the amphoteric membrane exhibits a number of interesting properties, especially a higher permeability for electrolytes. This property makes possible the use of composite membranes for separating electrolytes from mixed aqueous solutions of electrolytes and nonelectrolytes by dialysis, electrodialysis, or piezodialysis.

The aim of this work consists of presenting a new chemical method for manufacturing ion-exchange membranes and in determining the physicochemical characteristics of the synthesized membranes.

EXPERIMENTAL

Ozonization

The ozonization was carried out with low-density powdered polyethylene having an index equal to 20 and an average molecular weight equal to 17,000 (Chemical C.D.F. Company). A predetermined amount of PE is introduced into a double-walled reactor, fluidized by a current of air, and heated at 50°C by circulation of a thermostatted oil in the

---

double-walled reactor. As soon as the temperature of the PE is stabilized, the ozone was generated using a standard ozone generator (Trailigaz type). The oxidation was started by bubbling the O_3/O_2 gas mixture through the PE. During oxidation, the production of ozone is maintained at its maximum. The reaction was stopped 1 h later.

Peroxides and Hydroperoxides Titration by the DPPH

The titration of the ozonized PE was carried out by introducing a predetermined amount (20–25 mg) of the ozonized PE into a container (round-bottom flask) connected with an argon entry and containing the DPPH solution in xylene at $17 \cdot 10^{-5}$ mol L^{-1}. The oxygen in the container was eliminated by passage of an argon flux for 5 min. The container was then heated at 110°C for about 15 min. At the end, the solution was cooled and the DPPH excess was titrated by colorimetry at 520 mn with a display of Varian type having an automatic compensation [Fig. 1(a)]. The titration was carried out with a standardized curve preliminary plotted [Fig. 2(b)] (absorbance D_0 as a function of the concentration). The amount of PE is chosen as to give a considerable decrease of the optical density. However, this decrease must not be very great so to avoid the absorbance of combination products remaining in the solution.
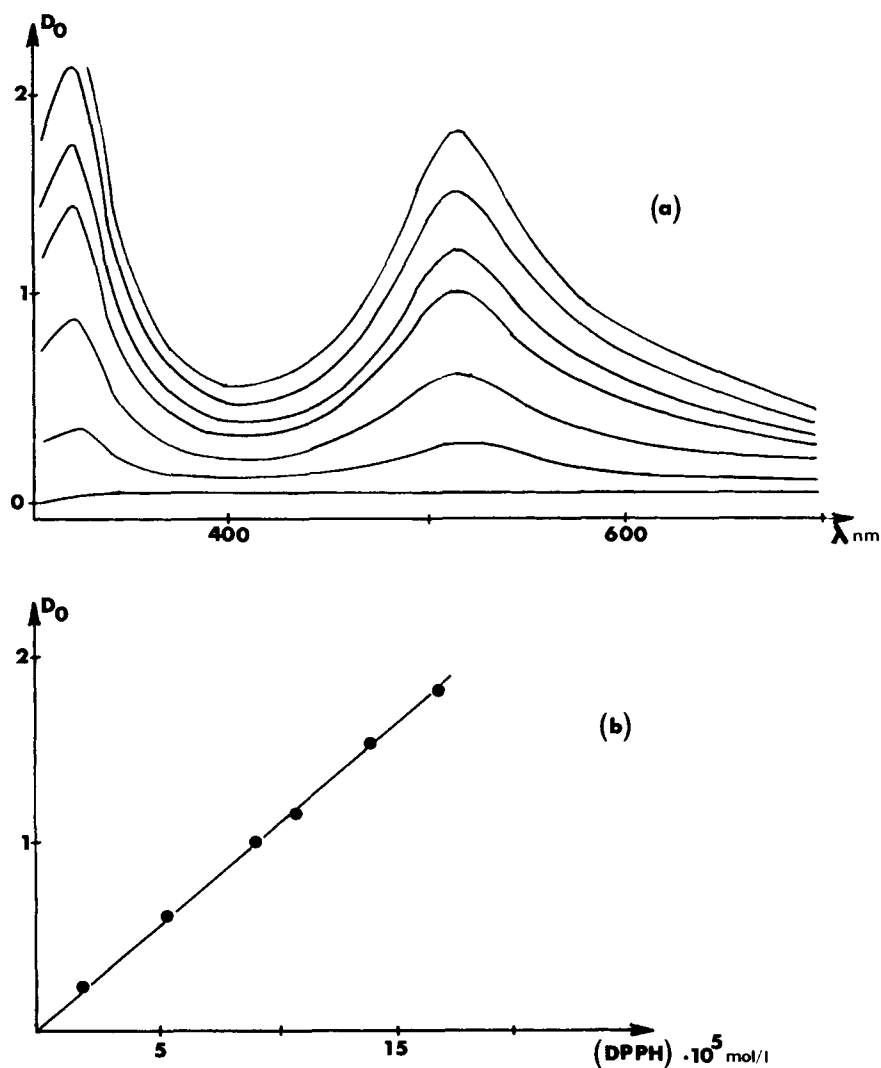

Figure 1   Standardized curves: (a) variation of the optical density (D_0) of the DPPH for various concentration as a function of the wavelength; (b) variation of the optical density (D_0) of the DPPH at 520 nm as a function of the concentration.
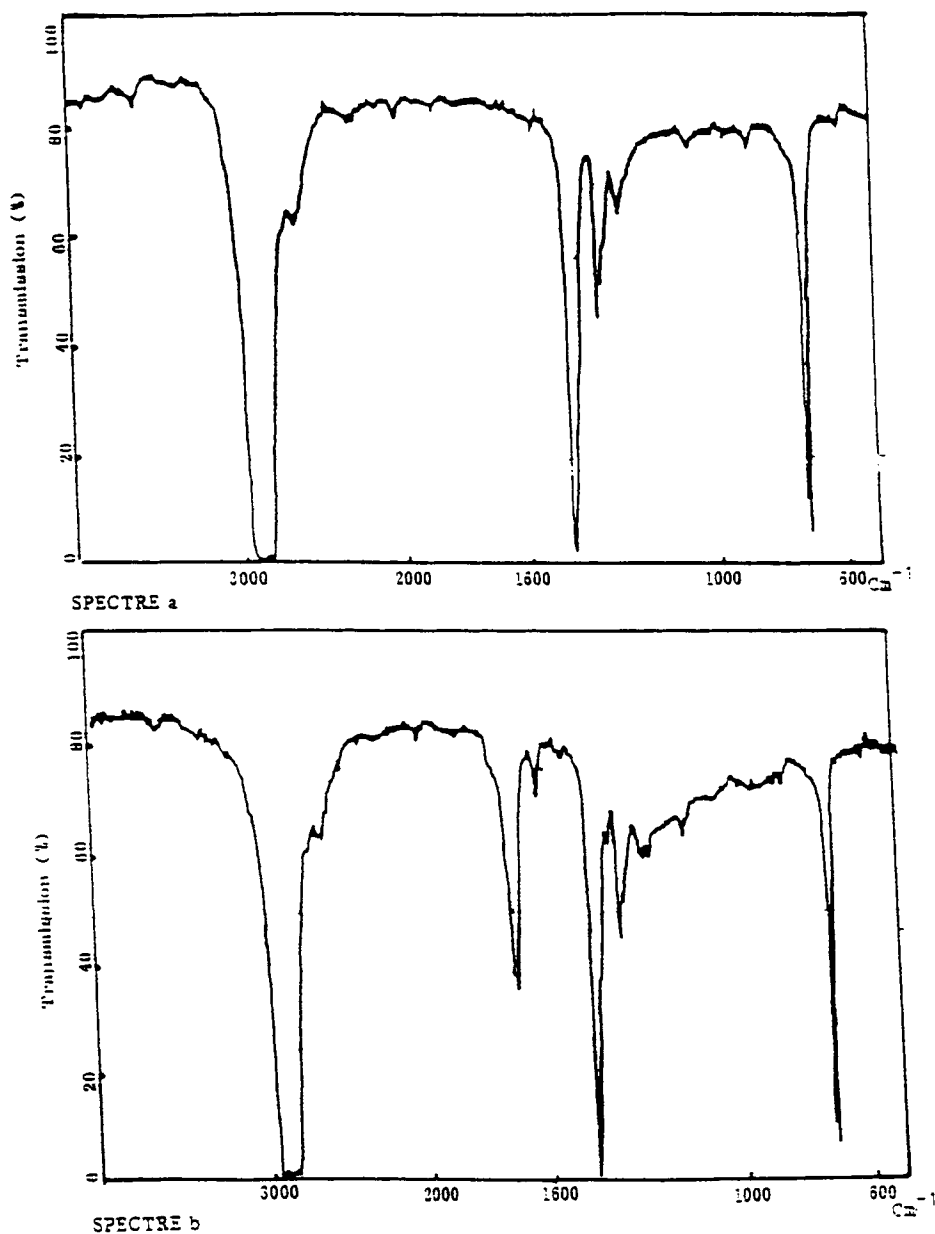
Figure 2 IR spectrum of ozonized and nonozonized PE: spectrum (a), nonozonized PE; spectrum (b), ozonized PE.

The amount of DPPH that reacted with the ozonized PE is given by the following formula:

$$N_0 = \frac{(Abs_0 - Abs_1)V}{m \cdot \epsilon \cdot 1000}$$

where $\epsilon = 1.06 \cdot 10^4$ mol^{-1} L cm^{-1} calculated from the standardized curve; m = weight (g) of ozonized PE added to the DPPH solution; V = volume of the DPPH solution; Abs_0 = absorbance of the DPPH solution without ozonized PE; Abs_1 = absorbance of

the DPPH solution with ozonized PE; and N_0 is given in mol equivalent per gram of the ozonized PE.

Selective Titration of Hydroperoxides

A predetermined amount of the ozonized PE (20–25 mg) is introduced in a flask containing about 15 mL of freshly distilled benzene and saturated with argon, and we let the PE enough time to swell. After 4 h, 1 mL of iron reactant is added and the mixture

is completed to 25 mL with distilled water. After the sedimentation of the PE (30 min), the resulting solution is titrated by colorimetry at 512 nm.

The hydroperoxide amount is given by

$$N_{\text{ROOH}} = \frac{V \cdot \Delta D}{2 \epsilon m 1000}$$

where $\epsilon = 1.68 \cdot 10^4$ mol L cm^{-1}; V = volume of the sample; m = weight (g) of ozonized PE; and ΔD = optical density of solution minus this of solvent.

Grafting

In the mixer cell, we introduced 20 g of ozonized PE and 30 g of monomer. The mixture was heated at 110°C with continuous stirring for 1 h. After the copolymerization, the product was recovered, founded, treated to eliminate the homopolymer, and dried at 50°C overnight.

Membrane Manufacturing

The method consists of melting the copolymer and pressing it in order to obtain a dense membrane after cooling and solidification.

Characterization

Before measurement, pretreatment is carried out in order to remove impurities from the membrane phase. Membranes are immersed in aqueous hydrochloric acid (1 h), distilled water (2 h), and aqueous sodium hydroxide (1 h) at room temperature.

Thickness

Thickness of the membranes was determined with a micrometer (PIGIMATIC) by measuring the thickness of membranes clasped between two glass plates. The thickness of the two glass plates is simultaneously determined by the same way.

Exchange Capacity

Exchange capacities of the CEM and of the AEM were determined by pH titration.[9]

Exchange capacities of the amphoteric membrane were determined by radioactive tracers. The general principle of the method has been already described by Gludeckauf and Watts.[10] It consists of following the kinetics of sorting out a labeled ion in the equi-librium solution of the electrolyte containing at least the ion, the labeled ion being its radioactive isotope.

Values of the exchange capacity for the ampho-teric membrane were deduced from curves repre-senting the variation of the ion content as a function of the NaCl concentrations in the equilibrium so-lutions. The exchange capacity corresponds to the extrapolated value at zero NaCl concentration in the equilibrium solutions.

Water Content

The water content of the membrane is determined after equilibrating a sample of the membrane with the studied solutions for 1 day at 25°C. The sample is then removed from solution, and both surfaces are wiped with filter paper. The water content is deduced from the difference in weight between the wet and dry membranes. The sample is dried for 4 days under vacuum at 30°C.

Electrical Resistance

The electrical resistance of the membrane equili-brated with a solution of NaCl at a given pH is mea-sured using the clamp cell technique already de-scribed.[11] The temperature is maintained at 25°C. The membrane resistance is measured at 250 Hz using a Dick and Jones bridge.

Membrane Potential and Transport Number

The membrane is placed inside a plexiglass cell be-tween two aqueous solutions at the same pH. So-lutions were circulated by means of two peristaltic pumps. The steady-state values of membrane po-tential are measured using two Ag/AgCl electrodes and a high-impedance millivoltmeter (Minisis 800 Tacussel). The measuring cell was thermostatted at 25°C. Values of transport numbers were calcu-lated from measurements of the membrane potential using the Teorell, Meyer, and Sievers theory.[12-14] For the AEM and the CEM, the membrane potential was measured for the following system: NaCl 0.1 M/membrane/NaCl 0.01 M. For the amphoteric mem-brane, the membrane potential was measured for the same system but at various pH's.
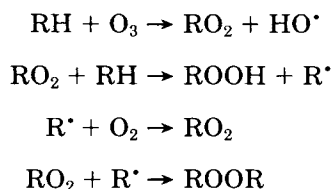
RESULTS AND DISCUSSION

Membrane Preparation

The membrane preparation is accomplished in three stages:

- ozonization of polyethylene
- grafting of monomers
- film preparation.

Ozonization

The ozonization of polymers is very well known and usually leads to a polymer blend that exhibits hydroperoxide and peroxides on the polymeric chain according to the reactions proposed by Kefeli et al.[15]:

$$RH + O_3 \rightarrow RO_2 + HO^\bullet$$

$$RO_2 + RH \rightarrow ROOH + R^\bullet$$

$$R^\bullet + O_2 \rightarrow RO_2$$

$$RO_2 + R^\bullet \rightarrow ROOR$$

The conditions of ozonization can be controlled, and so we obtain polymers with peroxide and hydroperoxide contents[16,17] known from analysis titration. The titration was carried out in two stages: (i) titration of both peroxides and hydroperoxides by the DPPH; (ii) then titration of hydroperoxides by iron salts. The DPPH is a stable radical that can react with radicals coming from the thermal decomposition of the ozonized PE at 110°C. The excess of DPPH was then titrated by colorimetry (Fig. 1). In this work, we noticed that after heating for 10 min at 110°C the decomposition of PE was completed. Zeppenfeld[18] showed that the hydroperoxides reacted only with the iron salts according to the following reactions:

$$ROOH + Fe^{2+} + H^+ \rightarrow RO^\bullet + Fe^{3+} + H_2O$$

$$RO^\bullet + Fe^{2+} + H^+ \rightarrow ROH + Fe^{3+}$$
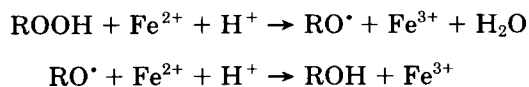
We observed that only one molecule of hydroperoxides (ROOH) reacted with two Fe^{2+}. The ROOH titration was performed by complexation of the ferric ions with ammonium thiocyanate. The red complex obtained was analyzed by colorimetry.

Table I gives the results of the titration of peroxides and hydroperoxides for various conditions of ozonization (temperature, time, flux, and ozone concentration). This table shows that the lower the temperature used, the higher the hydroperoxide content obtained. This was also observed by Boutevin et al.[17] in the synthesis of PE-g-MMA and PE-g-S, and by Michel and Monnet[19] in the case of PP. Actually, it is normal that by increasing the temperature the hydroperoxides ROOH decompose and give RO radicals that were stabilized in powder in peroxides ROOR by recombination.

Furthermore, the oxidized and nonoxidized PE were analyzed by IR spectroscopy. The spectrum of oxidized PE shows a large band at 1720 cm^{-1} ($C=O$) that does not exist in the IR spectrum of nonoxidized PE (Fig. 2).

The absorbance measurements at 1720 cm^{-1} ($\nu_{C=O}$) and 720 cm^{-1} (ν_{CH_2}) give an oxidation content that we compared with copolymers of ethylene and carbonyl oxide (for more details, see Ref. 10). Heating ozonized PE leads to ketone, as Nuchachenko showed[20]:
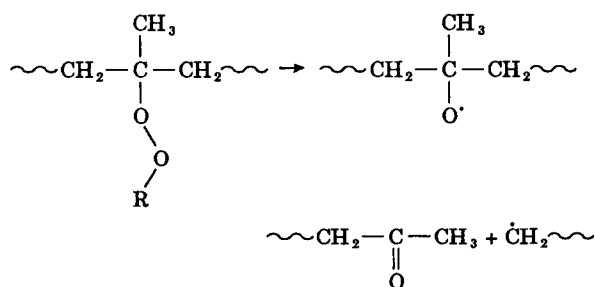
Grafting Reaction

Peroxides and hydroperoxides, resulting from the ozonization, are decomposed at high temperatures and produced $RO^\bullet$ and $HO^\bullet$ radicals. These initiate
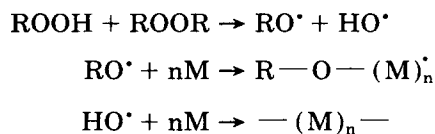
Table I   ROOR and ROOH Content of the Ozonized (PE) for Different Conditions of the Ozonization

T (°C)	t (min)	O_3 (g/L)	Flow (l h)	N_{ROOR}[a] (10^5 eq/g)	N_{ROOH}[b] (10^5 eq/g)	% ROOH
22	120	16	700	7.58	2.88	61
50	15	6	1200	2.30	0.62	37
50	120	16	700	3.60	0.90	35
50	120	6	700	7.51	1.86	34

[a] DPPH titration.
[b] Iron salts titration.

the polymerization of monomers that leads to graft copolymers (from RO$^\bullet$) and homopolymers (from HO$^\bullet$):

$$ROOH + ROOR \rightarrow RO^\bullet + HO^\bullet$$

$$RO^\bullet + nM \rightarrow R—O—(M)^\bullet_n$$

$$HO^\bullet + nM \rightarrow —(M)_n—$$

We used two monomers: acrylic acid (AA) and *N,N*-dimethylaminoethyl methacrylate (MADAME) to obtain polyanion and polycation.

The grafting reaction was performed in bulk in a mixer cell after introducing known quantities of ozonized PE and of monomer. During the polymerization, we measured the variation of the torque of the rotor in the cell. It was observed that this variation is greater for ozonized PE with monomer than for nonozonized PE (alone or with a usual free radicals initiations) (Fig. 3). This result clearly indicates that only in the first case did the reaction occur,

but we have also seen that after 1 h the torque decreased probably due to a cleavage of polymeric chain.

After copolymerization, the product was recovered and precipited by a solvent of the homopolymer and nonsolvant of the grafted copolymer in order to eliminate the homopolymer: Solvants used for polyacrylic acid and poly MADAME are, respectively, water and acetone.

The following step was the characterization of the copolymer and, specifically, the weight grafting content of the monomer on the PE. Because of the poor solubility of the copolymers, with the PE main chain, we used the centesimal analysis.

The elementary analysis of O and N in the products makes it possible to estimate rigorously the percentage of AA and MADAME in copolymers because O and N atoms are located only on the grafted chains. Therefore, the grafting content of the AA and MADAME can be determined from the following formulas:
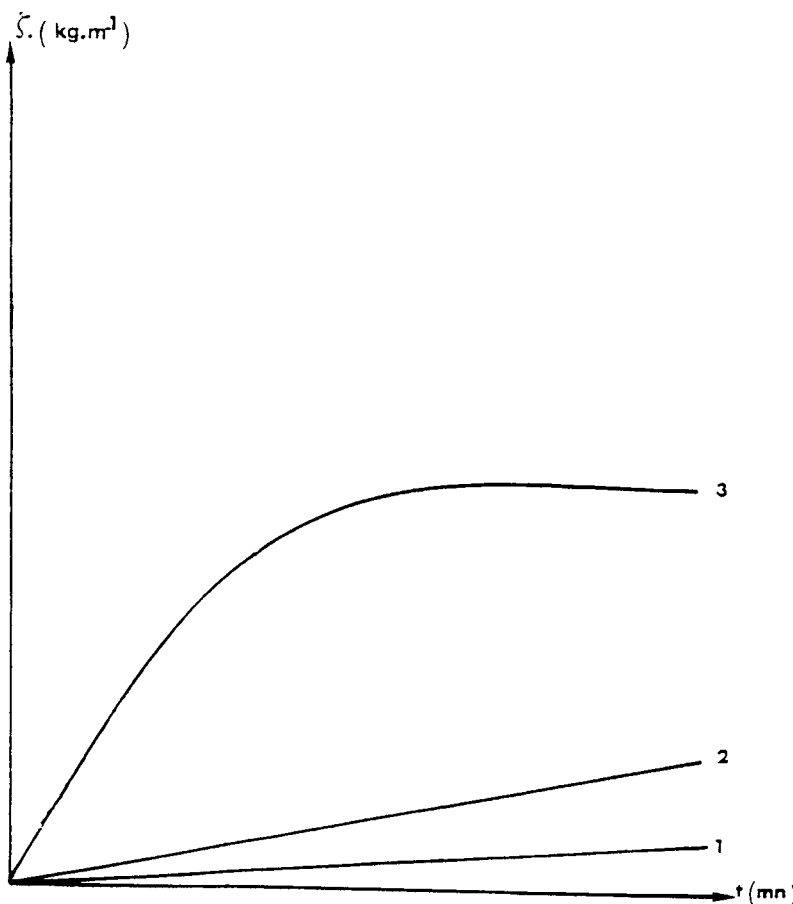

Figure 3 Variation of torsional couple that the mixture makes use of against the mixer: (1) nonozonized PE + monomer; (2) ozonized PE; (3) ozonized PE + monomer.

Table II   Weight Grafting Content and Number of Grafted Monomers (P) per Chain of PE

Product	% O	% N	% content of AA (weight)	% content of MADAME (weight)	P
P_{AA}	9.56	—	21.50	—	60
P_{MAD}	—	2.67	—	30	45

$$\% \; AA = 100 \; \frac{(O)\% \cdot M_{AA}}{32}$$

and

$$\% \; MADAME = 100 \; \frac{(N)\% \cdot M_{MADAME}}{14}$$

where M_{AA} and M_{MADAME} are the molecular weights of the AA and the MADAME monomers. From these percentages, we have calculated the number of monomers grafted by chain of PE. All the data are listed in Table II.

The molecular weight $\bar{M}_n$ of the PE was 17,000, i.e., 600 ethylene base units, and we obtained a weight grafting of 20%–30%, i.e., average molar grafting 10%, therefore, there are 60 units of acrylate per PE chain.

With reference to Michel and Verney's result,[21] we have calculated the average number of branching by PE chain α; these values depend on the $\bar{M}_n$ of polymers and peroxide and hydroperoxide contents. Under our conditions we obtained between 0.7 and 1.2 grafted, so we can consider that we have only one chain of acrylic monomer by chain of PE with a length of 100 units grafted.[22]

Membrane Manufacturing

The cation- and anion-exchange membranes have been prepared by pressing a known amount of copolymer between two metallic blocks of a press at 200°C. The amphoteric ion-exchange membrane was made by thoroughly mixing known amounts of copolymers PE-g-AA and PE-g-MADAME in the mixer at a sufficiently high temperature to obtain an homogeneous mixture.

Characterization

The characterization of the synthesized membranes consists of determining some physicochemical parameter in order to examine if they fit the requirement of the ion-exchange membrane: low electrical resistance, high selectivity, and good mechanical and chemical resistances. We determined the following parameters: thickness, exchange capacity, water content, membrane potential, and transport numbers.

Thickness

The measurements of thickness show a homogeneity of the thickness of the three membranes. The mean thickness is 200.0 ± 0.5 μm.

Exchange Capacity

The exchange capacity is the number of milliequivalent of ion that the membrane can exchange (in meq of ion per grams of membrane). They were determined by pH titration, and we obtained Ex(CEM) and Ex(AEM). From the AA and MADAME percent, we have calculated the exchanger groups n_s (AA) and n_s (MAD):

$$n_s \, (AA) = \frac{(AA)\%}{100 \cdot M_{AA}}$$

$$n_s \, (MAD) = \frac{(MADAME)\%}{100 \cdot M_{MADAME}}$$

From Table III where all the values are given, we can see that both these values are rather similar.

With the ionogenic groups of the amphoteric membrane being weakly acid and basic, their ionization depends on the pH in the membrane phase and, consequently, on the pH in the external solution. The exchange capacity of the amphoteric membrane was thus determined at different pH's

Table III   Exchange Capacity for the Membranes and for the Corresponding Resins (in meq/g)

	Membranes and Resins			
	Ex (CEM)	Ex (AEM)	n_s (AA)	n_s (MAD)
Exchange capacity	3.15	1.89	2.99	1.91

Table IV   Exchange Capacities of the Amphoteric Membrane (in meq/g)

	Labeled Ion			
	Cl⁺	Na⁺	Cl⁺	Na⁺
External pH	2	6	6	12
Exchange capacity	0.87	0.24	0.39	0.65

(pH 2, 12, and 6). The results are reported in Table IV. The difference of the exchange capacity between the amphoteric membrane and the *monofunctional* membranes (CEM and AEM) can be explained by the dilution of the concentration of the exchanger groups during the manufacturing of the amphoteric membrane (AIEM).

The lower values of the Na⁺ and Cl⁻ exchange capacities of the AIEM at pH 6 can be explained by a mutual neutralization of some acid groups and basic groups in the membrane phase.

Electrical Resistance

The relatively low values of electrical resistance for the CEM, the AEM, and the AIEM are plotted in Figure 4 as a function of the external pH. The NaCl concentration in the equilibrium solution was fixed at 0.1 M whatever the pH. Figure 4 shows that the behavior is similar for AIEM and AEM at low pH and for AIEM and CEM at high pH. These results are linked to the degree of the dissociation of the exchanger groups. With the ionogenic groups of the amphoteric membrane being weakly acid and basic, the degree of the ionization of these groups depends on their pK and pH values in the membrane phase and, hence, in the external solution. When the external solution is acid, the electrical resistance data show that the acrylic groups are not dissociated in the membrane, in contrast with the MADAME groups since the electrical resistance of the CEM is high at acid pH, while the AEM resistance is low. The amphoteric membrane thus behaves as an AEM. At basic pH's, the MADAME groups are not dissociated in membranes, since the electrical resis-
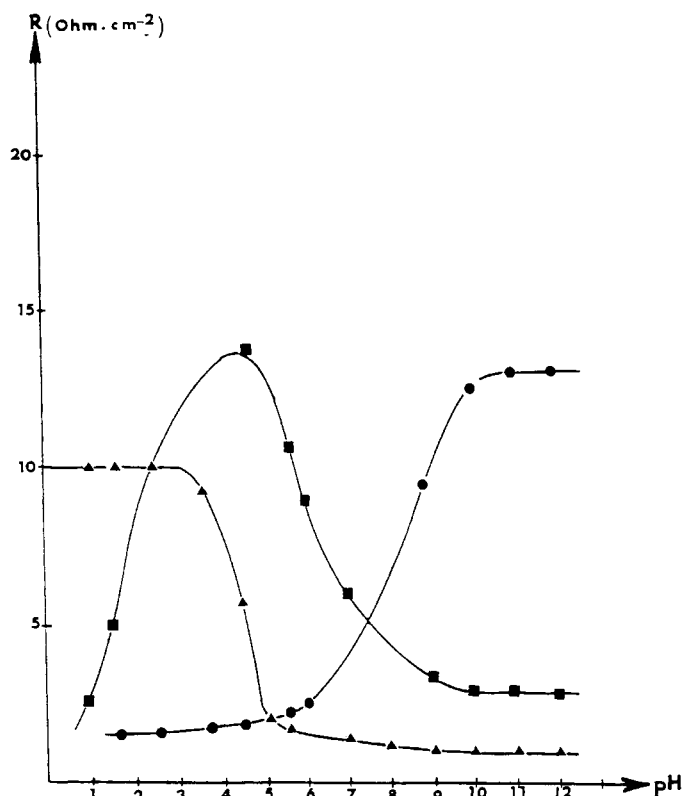

Figure 4   Variation of the electrical resistance of the amphoteric membrane as a function of the external pH: (▲) cationic-exchange membrane; (●) anionic-exchange membrane; (■) amphoteric membrane.

Table V   Transport Number of Na⁺ and of Cl⁻ in the (CEM) and in the (AEM)

	Membrane	
	CEM	AEM
t_{Na^+}	0.98	0.04
t_{Cl^-}	0.02	0.96

Table VII   Water Content in the CEM and in the AEM (in Percentage)

	External Solution		
	HCl 0.1M	NaCl 0.1M	NaOH 0.1M
CEM	53	280	210
AEM	125	158	70

tance of the AEM is high; nevertheless, the acrylic groups are dissociated since the electrical resistance of the CEM is low. The AIEM behavior is similar to that of the CEM. At neutral pH's, both acid and basic groups are assumed to be dissociated; nevertheless, the highest electrical resistance values of the AIEM at this pH reinforce the idea that a mutual neutralization of some acid groups and basic groups occurs in the membrane phase.

Membrane Potential and Transport Number

Measurement of membrane potential has become a routine procedure to characterize the membrane selectivity and to calculate the transport number. In Table V are listed the transport numbers of Na⁺ and Cl⁻ in the CEM and in the AEM. These values show a high selectivity of the two membranes. Values of the transport number in the AIEM are reported in Table VI. These values show a high selectivity of the AIEM at pH 2 and at pH 12; the amphoteric membrane behaves as an AEM at pH 2 and as a CEM at pH 12. At neutral pH, the AIEM is not permselective; it can exchange cations as well as anions.

Water Content

Ion-exchange membranes are able to sorb solvents in which they are dipped and, consequently, the

Table VI   Transport Number of Cations and Anions in the Amphoteric Membranes

	pH		
	2	6	12
t_+	0.01	0.41	0.83
t_-	0.99	0.59	0.17

membranes swell. The water content is the amount of water that the membrane absorbs. This water content depends on many parameters: external pH, electrolyte concentration, and chemical nature of the electrolyte in the equilibrium solution.

In Table VII are reported the values of water content in the AEM and in the CEM. The swelling is the highest for the CEM at equilibrium with a basic external solution, and for the AEM, at equilibrium with an acid external solution. These results are linked to the ionization degree of the exchanger groups, and they also can be explained by the fact that when the exchanger groups are substantially dissociated the solvating water of the electrolyte (which permeates into the membrane) adds to the free water in the membrane phase.

A systematic study of the swelling of the amphoteric membrane was carried out by varying both the NaCl concentration and the pH in the external solution (Table VIII). Figure 5 gives the variation of the water content in the amphoteric membrane as a function of the external NaCl concentration. These curves show that the water content decreases when the external NaCl concentration increases; this is in agreement with the models propounded for the study of the swelling of the ion-exchange polymers.[23,24] This decrease in the water content has been assigned to the osmotic pressure difference between

Table VIII   Water Content (in Percentage) in the Amphoteric Ion-Exchange Membrane

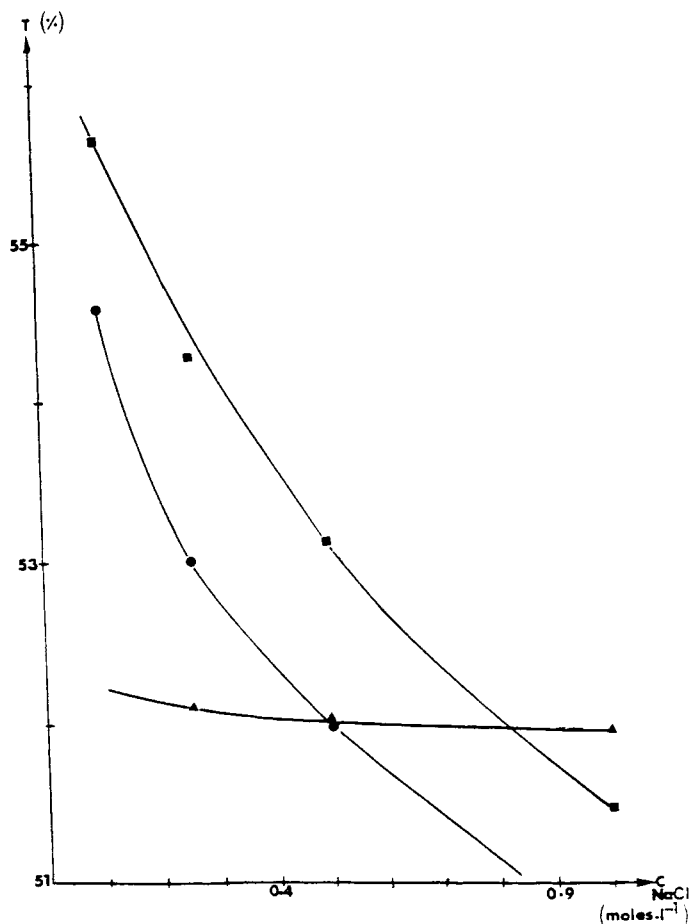| C_{NaCl} mol L⁻¹ in the external solution	0.01	0.1	0.25	0.5	1
Water content at pH 2	55.75	55.64	54.35	53.14	51.47
Water content at pH 6	52.33	52.21	52.09	52.05	51.94
Water content at pH 12	54.67	54.58	53	51.54	50.41

Figure 5 Water content of the amphoteric membrane (in percentage) as a function of the external NaCl concentration: (■) pH 2; (▲) pH 6; (●) pH 12.

the interior of the membrane and the external solution.

CONCLUSION

In this study, we presented a new procedure for manufacturing ion-exchange membranes. This procedure can be divided into three steps: ozonization of PE, mass grafting of monomers, and mixing and pressing for manufacturing the film with good mechanical properties (this last step is performed after washing the copolymers in order to eliminate the homopolymer). By this method, we prepared CEM, AEM, and AIEM. Some physicochemical parameters of these membranes have been determined (exchange capacity, electrical resistance, transport number, and water content). These properties are in agreement with the theoretical forecasting for

membranes having a weak acid and a weak base as ionogenic groups. These properties have been discussed as a function of the pH and the NaCl concentration of the equilibrium solution.

REFERENCES

1. Y. T. Tsumoda, T. Misumi, and K. Fujita, Japan Pat. 7054, *Chem. Abstr.*, **63**, 4481 (1965).
2. H. Zenftman, Ger. Pat. 1,082,412, *Chem. Abstr.*, **58**, 11529 (1963).
3. E. P. Cherneva, V. A. Kargin, E. G. Tokar, and N. N. Tunitski, USSR Pat. 185.052, *Chem. Abstr.*, **66**, 115253 (1967).
4. American Machine and Goundry, Brit. Pat. 988,526, *Chem. Abstr.*, **63**, 4481 (1965).
5. H. Hani and T. Uchino, Japan Pat. 17,637, *Chem. Abstr.*, **56**, 14488 (1962).

6. A. Chapiro, A. M. Jendrychoxska, and S. Mizrahi, *Eur. Polym. J.*, **12**, 773 (1976).

7. R. Bachmav, U. Krauss, H. Reurter, G. Shwachula, D. Warnecket, W. Wehlend, and F. Wolf, E. Ger. Pat. 3,42,616, *Chem. Abstr.*, **65**, 5628 (1966).

8. H. Ani, A. Nishihara, and Y. Soda, U.S. Pat. 3,276,991, *Chem. Abstr.*, **66**, 11558 (1967).

9. B. Auclair, Communication privé. Club Membrane, EDF (1983).

10. E. Glueckauf, J. Chem. Soc., 3280 (1949).

11. C. Gavach, A. Lindheimer, D. Cross, and B. Brun, *J. Electroanal. Chem.*, **33**, 190 (1985).

12. T. Teorell, *Z. Electrochem.*, **55**, 460 (1951).

13. K. H. Meyer and J. F. Sievers, *Helv. Chem. Acta*, **19**, 649,665,987 (1936).

14. T. Teorell, *Propr. Biophys. Biochem.*, **3**, 305 (1953).

15. A. A. Kefeli, S. D. Razumovskii, and G. E. Zaikov, *Vysokomol. Soed.*, **A13**, 803 (1971).

16. B. Boutevin, Y. Hervaud, J. Lafont, and Y. Pietrasanta, *Eur. Polym. J.*, **20**, 867 (1984).

17. B. Boutevin, Y. Pietrasanta, M. Taha, and T. Sarraf, *Eur. Polym. J.*, **20**, 875 (1984).

18. G. Zeppenfeld, *Makromol. Chem.*, **90**, 169 (1966).

19. A. Michel and C. Monnet, *Eur. Polym. J.*, **17**, 1149 (1981).

20. A. L. Nuchachenko, *J. Polym. Sci. Symp.*, **57**, 299 (1976).

21. A. Michel and V. Verney, *Rheol. Acta*, **24**, 627 (1985).

22. T. Sarraf, B. Boutevin, and Y. Pietrasanta, unpublished results.

23. H. P. Gregor, *J. Am. Chem. Soc.*, **73**, 642 (1951).

24. S. A. Rice and F. E. Harris, *Z. Physik. Chem.*, **8**, 207 (1956).