Polyethylene–Poly(Methacrylic Acid-co-Divinylbenzene) Interpolymer-Type Carboxylic Membranes

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SYNOPSIS

A short review of the methods of preparation of carboxylic membranes was presented. Details were given on the preparation procedure of polyethylene–poly(methacrylic acid-co-divinylbenzene) PE–poly(MA-co-DVB) interpolymer-type carboxylic membranes and on the optimization of the procedure. The membranes were synthesized by swelling PE in sheet form in a mixture of MA, DVB, and benzoyl peroxide (BP), with subsequent heating of the gel to interpolymerize the monomers. The dependence of ion exchange capacity, swelling, resistivity, and permeability on poly(MA-co-DVB) and DVB contents were investigated. With the use of an electron microscope a domain-type morphology was observed at low poly(MA-co-DVB) and DVB contents. Crystallinity of PE was not influenced by the presence of poly(MA-co-DVB).

INTRODUCTION

A separator from a polymer or polymeric composite containing carboxylic groups in free or salt form is called carboxylic ion exchange membrane or just carboxylic membrane. An additional condition is that the carboxylic groups content must exceed some critical (percolation) level, which is dependent on the spatial distribution of the carboxylic groups within the polymeric matrix and on the properties of the matrix itself.

Carboxylic membranes can be used in electrolysis, dialysis, pervaporation, reverse osmosis, and in electrochemical power sources.[1-11] The membranes can also be used as regulated chemical valves because of strong dependence of their transport characteristics on pH of the medium.[12-17]

There are various methods of preparation of carboxylic membranes.

Asahi Glass Co.,[2] produces carboxylic membranes, FLEMION, from a copolymer of tetrafluoroethylene and perfluorovinyl ether having a carboxylic ester group. After shaping the copolymer by extrusion, the ester groups are hydrolyzed to sodium salt. The membranes has been used in chlor-alkali production.

Gasperowicz et al.[18] prepared carboxylic membranes from copolymers of methyl acrylate and methyl methacrylate or butyl methacrylate. The presence of methacrylate mers ensured insolubility of the resulting polymer. Before shaping, the acrylate ester groups were hydrolyzed to potassium salt in a heterogeneous system.

Most of the literature on the preparation of carboxylic membranes concerns radiation-induced grafting of polyethylene (PE) or polypropylene (PP) in film form, with acrylic or methacrylic acid (AA, MA).[19-28] The process can be realized in two ways: by direct grafting or by preirradiation. The most important factors governing the structure of the membranes were the irradiation dose, concentration of AA or MA, and concentration of a homopolymerization inhibitor.

Narębska et al.[29,30] prepared membranes by volume grafting of ozone-activated PP with AA in the presence of $FeSO_4$. Because of the characteristic distribution of degree of grafting along the direction

perpendicular to the surface, the membranes were called gradient membranes.

Pegoraro et al.[31-34] grafted isotactic PP with AA in the presence of benzoyl peroxide (BP) in orthodichlorobenzene at 120°C. After evaporation of the solvent carboxylic membranes of thicknesses 1–50 μm and poly(AA) contents 20–60 wt % were obtained.

Habert et al.[35] developed a method of preparation of carboxylic membranes for dialysis and reverse osmosis. The method is based on ionic crosslinking of poly(AA) with polyvalent metal ions under controlled pH conditions. A dry technique was also described.[36]

Porous polymers were also used as matrices for carboxylic membranes. When the matrices were modified with monomers containing carboxylic groups in such a way that continuity of the pores was broken, the resulting membranes could be regarded as a gel type. Otherwise, porous carboxylic membranes were obtained.

Zdrahala and Karakelle[37] prepared carboxylic membranes with good dimensional stability by plasma deposition of a continuous coating of poly(AA) on all of the surface of CELGARD 2500 microporous PP film, including the inner surface of pores. The membranes had high hydrogen ion permeabilities.

Iwata and Matsuda[38] modified porous poly(vinylidene fluoride) by plasma pretreatment followed by exposure to air to introduce peroxide groups onto the surface. Then acrylamide was grafted onto the surface (from 5 wt % aqueous solution) at 60°C. Next, the amide groups were hydrolized to carboxylic in 1 N NaOH solution at 50°C.

Shataeva et al.[39,40] prepared carboxylic membranes by precipitation copolymerization of MA with a trivinyl crosslinking agent, within pores of porous phenylon (nominal pore size 0.22 μm).

In search for carboxylic membranes, many other polymers were also investigated and various monomers with carboxylic groups or precursors were grafted to them or copolymerized.[41-45]

There is an alternative method for the preparation of gel-type carboxylic membranes,[46,47] leading to so-called interpolymers, fitting in some cases the interpenetrating polymer network (IPN) formalism.[48] The membranes are synthesized by swelling PE in sheet form in a mixture of MA, divinylbenzene (DVB), and BP with subsequent heating of the gel to interpolymerize the monomers.

In this work details on preparation and characterization of PE/poly(MA-co-DVB) interpolymer-type carboxylic membranes are presented.

EXPERIMENTAL

Materials

Low-density PE having M_n = 19600 g/mol (by membrane osmometry) and 49 methyl groups per 1000 —CH_2— units (by IR[49]), MA (REACHIM) stabilized with hydroquinone and DVB (MERCK-Schuchardt) ca. 60% mixture of isomers, stabilized with 0.2% of 4-tert-butylpyrocatechol, were used without further purification. BP was recrystalized from acetone.

Kinetic Measurements

Kinetics of swelling of PE (hot pressed sheet, thickness 250 μm, 50 × 50 mm) in MA at a given temperature within a 60–90°C range was measured gravimetrically as a weight increase per unit gel weight at specified time intervals (0–3600 s). The values were corrected for extracted PE. To avoid a thermal polymerization of MA, small amount of CYANOX 425 inhibitor was added.

Induction time was measured in the following way. A mixture of MA, DVB (0, 1, 1.5, 2 wt %), and BP (0.5 wt %), was heated at a given temperature (60–90°C). The time that elapsed until opacity of the solution appeared was taken as the induction time.

Kinetics of interpolymerization of MA and DVB in PE was measured in the following way. Weighed samples of PE (hot pressed sheet, thickness 250 μm, 50 × 50 mm) were swollen in a mixture of MA, DVB (0, 1, 2, 5 wt %), and BP (0.5 wt %). Then the samples were taken out of the solution, their surfaces were blotted with a filter paper, placed between two poly(ethylene terephtalate) foils, and heated at 90°C. At specified time intervals, samples were successively taken out, cooled to room temperature, and placed under vacuum to remove unreacted monomers. Then the samples were weighed and percent weight increase, corrected for extracted PE, was plotted against heating (interpolymerization) time.

Preparation of the Samples

PE (hot pressed sheet, thickness 250 μm, 100 × 100 mm) was swollen in a mixture of MA, DVB (1, 1.5, 2 wt %), and BP (1.0 wt %), at 60–90°C, for 600–1800 s (depending on the kinetics of swelling and induction time). Then the gel was taken out of the mixture, wiped with a filter paper, placed between poly(ethylene terephtalate) foils, and heated for 2 h at 90°C.

By changing the swelling temperature and/or repeating the procedure, samples with different poly(MA-co-DVB) contents were prepared.

The samples were then treated by turns with 1 N KOH and 1 N HCl solutions, three times successively, and finally equilibrated with 0.1 N KOH solution.

Characterization of the Membranes

Equilibrium swelling of the membranes was measured gravimetrically, as weight increase per unit weight of the swollen membrane after 100 h immersion in 0.1 N KOH at 25°C.

Ion exchange capacity was measured in the following way. The membrane sample in COOH form was immersed in a known volume of 0.05 N KOH solution for 48 h at room temperature. The amount of COOH groups (in milimoles) was determined by back titration with a 0.05 N HCl solution. Then the sample was washed with distilled water, dried under vacuum, and weighed. Ion exchange capacity was calculated as the ratio of the amount of COOH groups to the weight of the dried membrane sample.

Resistivity of the membrane was measured in 0.1 N KOH solution using an AC resistivity bridge (1 kHz) and a two-compartment cell with platinum electrodes at 25°C.

Permeability coefficient was measured in a two-compartment cell at 25°C. The first compartment was filled with 35 cm^3 of 0.1 N KOH solution, and the second with the same volume of distilled water. From changes of KOH concentration in the second compartment, followed conductometrically, permeability coefficient, P, was calculated from the relationship

$$P = \frac{tg\beta \cdot V \cdot d}{2S}$$

where $tg\beta$ is the slope of the straight-line part of the plot $\log[c_0/(c_0 - 2c_t)]$ versus t, V is the volume of solution in a compartment (35 cm^3), d is thickness of the membrane and S is its active area, c_0 is the initial concentration of KOH in the first compartment (0.1 N), and c_t is the concentration of KOH in the second compartment after the time t.

Degree of crystallinity (X_{WAXS}) of PE in the samples was estimated according to the method of Hermans and Weindinger.[50] A three-phase structure [amorphous poly(MA-co-DVB), amorphous PE, and crystalline PE] was assumed. Diffractograms taken within $2\theta = 8$–$28°$ range, after the correction for air scattering and angular absorption, were deconvoluted numerically with the method of Marquardt[51] and Pearson VII[52] as a profile function. The quantity proportional to the crystalline PE fraction was the total area of the two crystalline bands at 2θ, ca. 21 and 23°. The quantity proportional to the amorphous PE fraction was the area of the halo at 2θ, ca. 20°. The average crystallite size was estimated according to the Sherrer's formula. The diffractometer used was HZG-4 (DDR) with CuK$_\alpha$ radiation and Ni filter.

Samples for transmission electron microscopy investigation were stained with uranyl acetate. Potassium concentration profiles in cross sections of samples in potassium salt forms were recorded on a scanning electron microscope, equipped with an X-ray microanalyzer. The transmission microscope used was Philips EM-301. The scanning microscope was Cambridge Stereoscan 180.

RESULTS AND DISCUSSION

The procedure of preparation of the membranes was a two-stage process. In the first stage PE was swollen with a mixture of MA, DVB, and BP. In the second stage the gel was isolated and heated to interpolymerize the comonomers. Both stages were investigated independently.

It was reported previously[47] that the equilibrium swelling values of PE in MA between 30 and 90°C were 7–26 wt %. The practical sense of this result was that after a sufficiently long period of swelling it was possible to introduce into 1 g of PE matrix from ca. 0.08–0.35 g of MA at 30 and 90°C, respectively.

In order to determine the time that had to elapse until the equilibrium was reached, kinetic measurements of swelling of PE in MA between 60 and 90°C were performed. Some resultant curves are shown in Figure 1. It follows from Figure 1 that the equilibrium was reached after ca. 25 min at 60°C and after ca. 11 min at 90°C. The time values are lower than the appropriate induction time limits, which ensured that polymerization would not start during the first stage of the membrane preparation process.

Kinetic measurements of the interpolymerization reaction at 90°C (Fig. 2) revealed that with the increase of DVB content in the comonomer mixture the time necessary for the termination of the polymerization reaction increased from ca. 55 min at 1 wt % to ca. 93 min at 5 wt % of DVB. This can be caused by an increased screening effect of growing macroradical by the just crosslinked MA chains. To
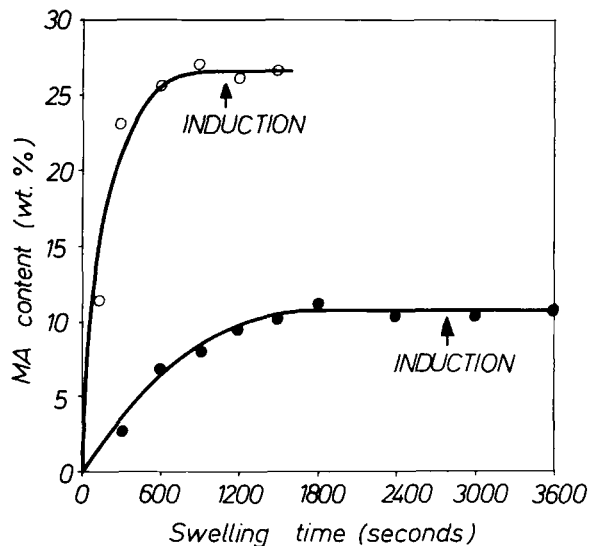
Figure 1 Kinetics of swelling of PE (foil, thickness 200 μm) in MA at 60°C (●) and 90°C (○).

allow for some safety margin, heating time of 120 min was assumed sufficient for the completion of the interpolymerization reaction at 90°C for DVB contents up to 5 wt %.

Three sets of membranes with poly(MA-co-DVB) contents ranging from 15 to 45 wt % were prepared (contents higher than 26 wt % were reached in two succeeding swelling/interpolymerization steps). Nominal DVB content was the same for each set and amounted to 1, 1.5, and 2 wt %.

It is advisable to recall the concept of the percolation theory at this stage. The theory was first proposed by Broadbent and Hammerslay[53] for mathematical description of transport processes in random media but proved very useful also in an ion exchange membrane area.[54-56] Some notions of the percolation theory will be utilized in the following discussion.

Measurements of equilibrium swelling (Fig. 3) and resistivity (Fig. 4) in 0.1 N KOH and measurements of ion exchange capacity (Fig. 5) of the membranes revealed the existence of three poly(MA-co-DVB) content regions.

The first region, from ca. 15 to 21 wt % can be called a prepercolation region. Samples of contents from this region had small equilibrium swelling values (4-5 wt %), low ion exchange capacities (0.2-0.3 mmol/g), and very high ionic resistivities (ca. 100 kΩ·m). It can be supposed that poly(MA-co-DVB) structure did not pervade (percolate) the whole PE matrix, and there were no internal ionic paths connecting both faces of the sample. The samples were then not permeable to ions. The measured ion exchange capacities and swelling values have to therefore be related to the carboxylic groups present at the surfaces of samples. Thus, according to the definition formulated in the introduction, the samples of contents from prepercolation region cannot be called carboxylic membranes.

The second region, from ca. 24 to 45 wt % can be called a percolation region. Equilibrium swelling
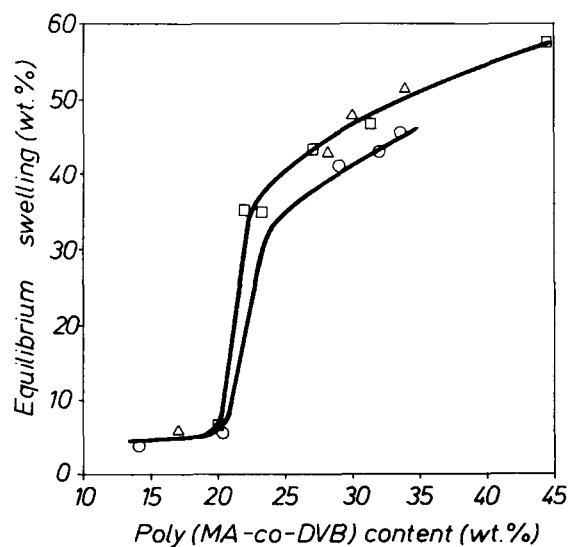

Figure 2 Kinetics of interpolymerization of MA and DVB in PE at 90°C. DVB content of 1 wt % (△) and 5 wt % (○).

Figure 3 Dependence of equilibrium swelling of the membranes in 0.1 N KOH on poly(MA-co-DVB) content. DVB contents of 1 wt % (△), 1.5 wt % (□) and 2 wt % (○).
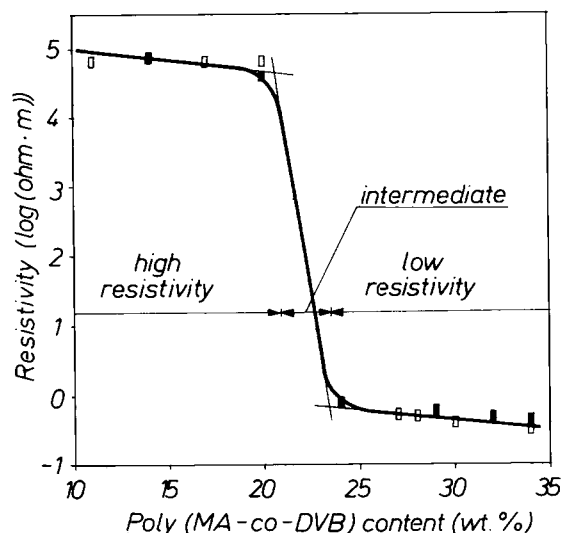
Figure 4   Dependence of resistivity of the membranes on poly(MA-co-DVB) content. DVB contents of 1 wt % (■) and 2 wt % (□).

According to the before-mentioned definition, the samples can be called carboxylic membranes.

The third region, from ca. 21 to 24 wt % can be called an intermediate or a threshold region. All the measured properties changed their values from those of prepercolation region to those of percolation region. The lower limit of the intermediate region can be attributed to formation of the first percolating cluster (infinite cluster) of hydrated potassium salt of poly(MA-co-DVB). The upper limit of the intermediate region, primarily called critical composition[47] can be attributed to stabilization of the membrane morphology.

As can be seen from Figure 3 membranes with DVB contents of 1 and 1.5 wt % swelled to the same extent, but membranes with DVB content of 2 wt % had smaller equilibrium swelling values. This means that there existed sufficiently large number of crosslinks, in the second case, to reduce the swelling of poly(MA-co-DVB) structure. Ion exchange capacities and resistivities did not depend on DVB content within the range tested. It should be noted also that, the measured ion exchange capacities were very close to the theoretically predicted values. It indicates that, in general, all the carboxylic groups within the membrane were potential ion exchanging sites and no significant steric hindrance effect was observed at this level of crosslinking.

Permeability measurements in the system,

values and ion exchange capacities of samples of contents from this region were greater than those of samples from the prepercolation region. Resistivities of the samples were very low and decreased from 0.8 to 0.3 $\Omega \cdot$ m with increasing poly(MA-co-DVB) content from 24 to 45 wt %. This indicates that poly(MA-co-DVB) structure pervaded (percolated) the PE matrix to form so-called infinite cluster and that there existed well-defined internal ionic paths connecting both faces of the samples.
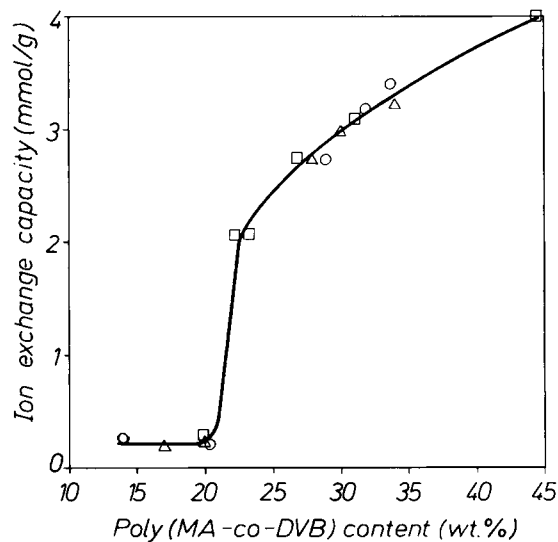
$$0.1 \ N \ \text{KOH-carboxylic membrane-H}_2\text{O}$$

Figure 5   Dependence of ion exchange capacity of the membranes on poly(MA-co-DVB) content. DVB contents of 1 wt % (△), 1.5 wt % (□) and 2 wt % (○).
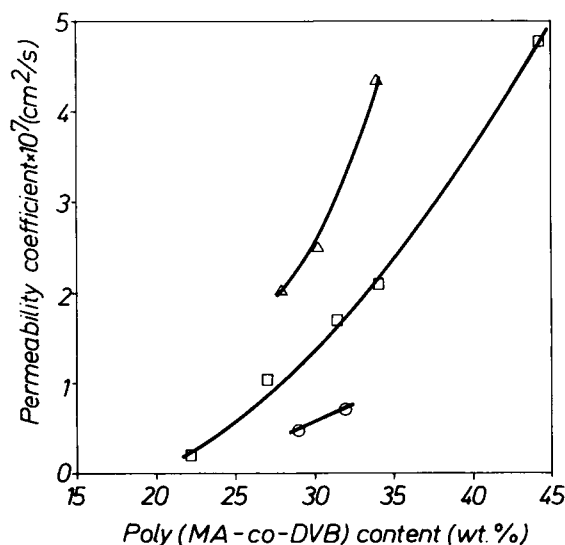

Figure 6   Dependence of permeability coefficient of the membranes in the system: 0.1 N KOH-carboxylic membrane-H₂O, on poly(MA-co-DVB) content. DVB contents of 1 wt % (△), 1.5 wt % (□), and 2 wt % (○).

revealed clear dependence of the transport properties of the membranes on poly(MA-co-DVB) and DVB contents (Fig. 6). It can be assumed that increase of poly(MA-co-DVB) content caused decrease of tortuosity of the ionic paths within the membranes, and thus increased permeability. When DVB content was increased, the ionic paths became more tight and tortuous. Also, some swelling reduction (increasing molality of carboxylic groups) was observed that intensified the Donnan effect of ion exclusion. These factors, in turn, can account for the flow reduction.

X-ray diffraction measurements (WAXS) of the samples in dry state showed (Fig. 7) that modification of PE did not influence its crystallinity. The degree of crystallinity of PE was the same for all the samples studied, equal to 51%. The average crystallite sizes were 10.1 and 16.7 nm along directions perpendicular to (200) and (110) planes, respectively.

Microscopic investigation of membranes stained with uranyl acetate showed that, in general, poly(MA-co-DVB) formed domains uniformly dispersed within the PE matrix (Figs. 8–10), the morphology typical to a system of two immiscible polymers.[57] The shape of the domains, their dimensions, and distances between them depend on composition of the membranes and on the preparation conditions. For DVB content of 1.5 wt %, isolated (in the dry state) domains ca. 20–25 nm could be observed at 24 wt % of poly(MA-co-DVB) [Fig. 8(a)], which at 45 wt % turned into continuous domain network spreading over the whole PE matrix [Fig. 8(b)]. The domains contacted each other, but it was not possible to deduce from the micrographs whether there were any covalent links between the domains.

The influence of DVB content was tested for membranes containing 34 wt % of poly(MA-co-DVB). For samples of 1 wt % of DVB, well-shaped domains of size 20–25 nm could be seen [Fig. 9(a)],
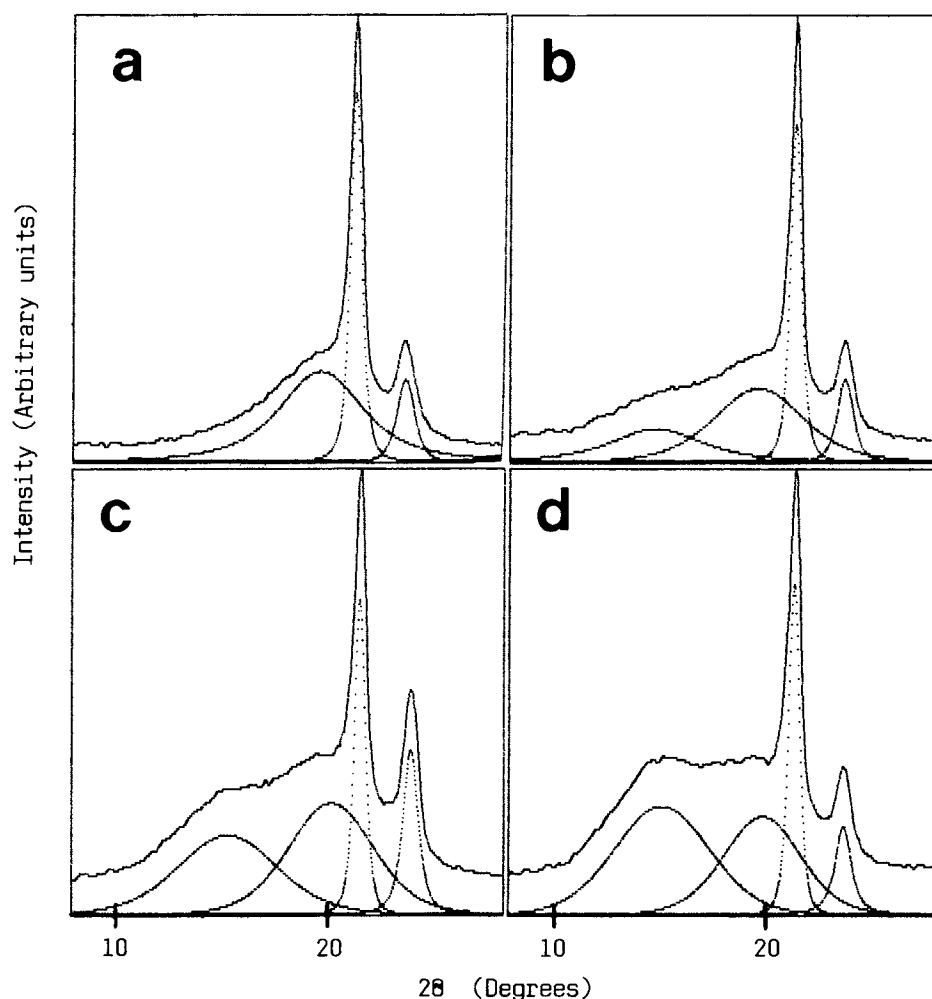

Figure 7 X-ray diffractograms recorded for the membranes with (a) 0 wt %, (b) 20 wt %, (c) 27 wt %, and (d) 44 wt % of poly(MA-co-DVB) containing 1.5 wt % of DVB.
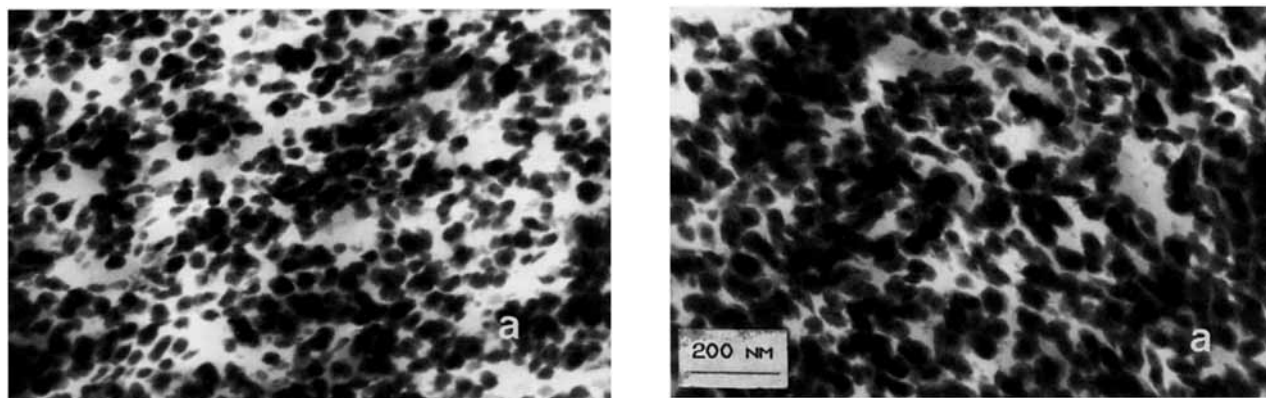
Figure 8 Electron micrographs of the membranes with (a) 24 wt % and (b) 45 wt % of poly(MA-co-DVB) containing 1.5 wt % of DVB.
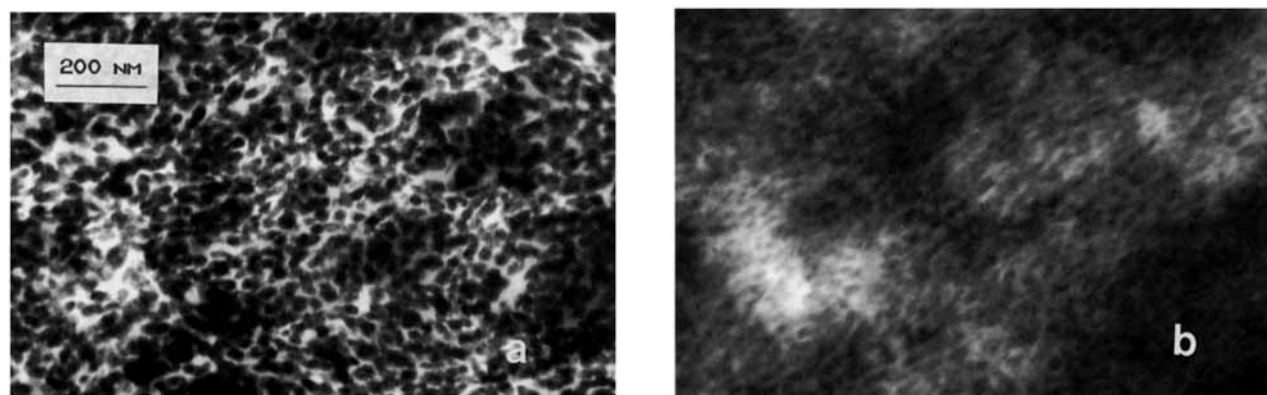

Figure 9 Electron micrographs of the membranes with 34 wt % of poly(MA-co-DVB) containing (a) 1 wt % and (b) 2 wt % of DVB.
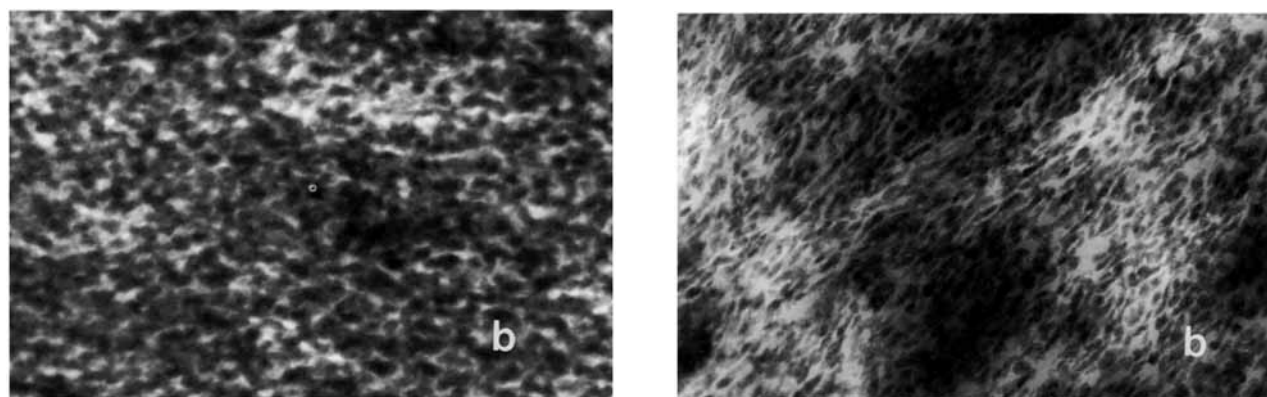

Figure 10 Electron micrographs of the membranes with 28 wt % of poly(MA-co-DVB) containing 1.5 wt % of DVB (a) prepared in one step and (b) prepared in two swelling-interpolymerization steps.

which turned into diffuse, continuous structure at 2 wt % of DVB [Fig. 9(b)]. The micrographs confirmed the morphology analysis based on permeability measurements.

The interpolymer morphology can be investigated in terms of the IPN formalism, because for temper-atures lower than T_m, PE can be treated as a polymer network with crystalites acting as physical crosslinks or nodes.[58] At low DVB content, adjoining spherical domains of poly(MA-co-DVB) dispersed within the PE network were observed. Packing density increased with increasing poly(MA-co-DVB) content.

Thus the system can be called semi-IPN. At DVB content of 2 wt %, formation of a continuous poly(MA-co-DVB) network was observed. The system consisted of the chemical network interpenetrating the physical network, and was called an IPN. In fact, because some amount of grafts between the two networks can be expected,[59] the name "graft-IPN" would be more appropriate in that case.

In Figure 10(a) and 10(b) there are micrographs of samples containing 28 wt % of poly(MA-co-DVB) and 1.5 wt % of DVB. The first sample was prepared in one step, after swelling in comonomer mixture at 91°C. The second sample was prepared in two successive swelling–interpolymerization steps (swelling at 60°C). In the first case, 30–35 nm spherical domains were observed, and 15–20 nm domains of not well-defined shapes and diffused edges could be observed in the second case. Various factors can account for this difference. Although nominal compositions of the swelling mixtures were the same in both cases, different concentrations of DVB and NB with respect to MA could develop in the PE gel phase because of different swelling temperatures. Also, PE network characteristics, i.e., number of nodes and their dimensions, changed with temperature and type of swelling agent. At low temperature, the number of crystallites (assumed to be impermeable to liquids) and their dimensions were relatively large, thus their influence on the spatial distribution of the swelling mixture was considerable. As the swelling temperature increased a fraction of the crystallites melted, decreasing in this way the number of nodes and their dimensions. The influence of PE network on the spacial distribution of the comonomer mixture was not so strong in this case.
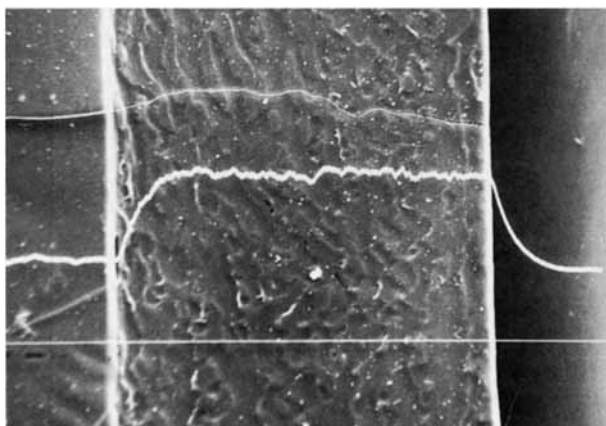
In order to test the macroscopic homogeneity of the samples, X-ray microanalysis recordings were made. They gave evidences that poly(MA-co-DVB) was uniformly dispersed within PE matrix. A sample recording for a membrane containing 34 wt % of poly(MA-co-DVB) and 1.5 wt % of DVB is shown in Figure 11. The edge effect at the left side of the membrane was caused by angular arrangement of the X-ray detector.

CONCLUSIONS

Samples of LDPE/poly(MA-co-DVB) interpolymers, containing 15–45 wt % of poly(MA-co-DVB) were obtained. Only the samples with more than ca. 24 wt % of poly(MA-co-DVB) had good ion exchange and transport properties and could be called carboxylic membranes.

Morphology of the interpolymers was investigated in terms of the IPN formalism because for temperatures lower than T_m, PE could be treated as a polymer network with crystallites acting as a physical crosslinks. At low DVB content, adjoining spherical domains of poly(MA-co-DVB) dispersed within the PE network were observed. Packing density increased with increasing poly(MA-co-DVB) content. The system could be called semi-IPN. At DVB content of 2 wt % formation of a continuous poly(MA-co-DVB) network was observed. The system consisted of the chemical network interpenetrating the physical network and was called an IPN.

Detailed analysis of the influence of DVB content on the morphology of the interpolymer membranes will be given in the next paper.[60]

Figure 11 Potassium concentration profile recorded for a cross section of a membrane with 34 wt % of poly(MA-co-DVB) containing 1.5 wt % of DVB.

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