

# Electron microscopy investigation of ion exchange membranes

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Transmission electron microscopy has been used for the recognition of the structural heterogeneity and the distribution of ionogenic groups in the cation exchange membranes. The investigations were performed on the fluorinated membranes (NAFION, MRF) and on the earlier known membranes containing poly(styrenesulphonic acid) (AMF C-322 and PE-PSSA membranes). The electron images of the ultra-thin sections revealed the homogeneous nature with the uniform distribution of small ionogenic group concentrations in the membranes NAFION and MRF-4MB, and the heterogeneous distribution of the groups in the poly(styrenesulphonic acid) membranes (AMF C-322, PE-PSSA membrane) and the membrane MRF-26, which is the consequence of the inhomogeneous nature of the polymer base of these membranes.

The homogeneity of ion exchange membranes is the main property determining their quality. It is known that the distribution of ionogenic groups has the greatest importance for the physicochemical, and especially for the electrochemical, properties of the membranes. Very often however even a homogeneous distribution of the base polymer and polymer carrying ionogenic groups in the membrane does not necessarily mean the homogeneous distribution of the ionogenic groups. This divergence may be the result of heterogeneous chemical attack, e.g. sulphonation processes carried out upon the membrane material.

Investigations of structural irregularities in membranes have been described previously by many authors. They have used methods such as light microscopy<sup>1</sup>; study of water permeability and electrical conductivity after treatment with H<sub>2</sub>O<sub>2</sub><sup>2</sup>; sorption and diffusion of ions<sup>3</sup>; local X-ray analysis<sup>4,5</sup>; autoradiography<sup>6</sup>; and electron microscopy<sup>1,7-10</sup>. From the above mentioned methods, transmission electron microscopy, local X-ray analysis and autoradiography give a direct indication of the distribution of ionogenic groups.

The quoted works<sup>1-9</sup>, have been conducted for membranes with poly(styrenesulphonic acid) (PSSA) dispersed in bonding material or grafted onto the polymeric backbone.

For the last few years, a new kind of cation exchange membranes with copolymeric fluoropolyelectrolytes has been known<sup>11-13</sup>. The membranes commercially available are those which contain  $\alpha,\beta,\beta'$ -trifluorostyrenesulphonic acid produced in the USSR and the so-called perfluorosulphonic acid membranes, NAFION, produced in the USA.

As far as we are aware, no work has been done on the microstructure of these last membranes. The purpose of this paper is to fill this gap with the aid of transmission electron microscopy. For comparison, results of the earlier known membranes containing poly(styrenesulphonic acid) have been given too.

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## EXPERIMENTAL

Two common approaches towards morphology investigations of polymers have been adopted:

(a) direct observation of ultra-thin sections of samples in the transmitting 'light'. The method very often requires, however, some suitable staining process, usually carried out by introducing electron dense atoms or ions.

(b) selective removal of one phase by etching the polymer surface followed by examination of its topography. For these purposes, two step replicas are usually prepared.

For our investigations the first method was chosen because it permits direct recognition of the distribution of ionogenic groups.

The membranes were converted into the lead form by immersion in a solution of 1 M Pb(NO<sub>3</sub>)<sub>2</sub> (60 h) and next, the unbonded Pb<sup>2+</sup> ions were carefully washed off. The stained membranes were dehydrated by passing strips through ethanol solutions (50, 70, 95% and absolute alcohol). Then they were swollen in 1,2-epoxypropane, and after 2 days embedded in the epoxy resin (at 60°C for 3 days).

Ultra-thin sections (60-80 nm) were cut with the Ultra-Microtom MT-2, Sorval, using a diamond knife. Micrographs were obtained using the electron microscope Elmiscop 101, Siemens, at the accelerating voltage 80 kV and at different magnifications.

The main characteristics of the investigated membranes are given in *Table 1*.

## RESULTS AND DISCUSSION

The micrograph of the NAFION 125 membrane is shown in *Figure 1*.

It is composed of very small and uniformly distributed dark points. The interpretation of such a micrograph must be carried out especially carefully as a similar image may be

Table 1 Characteristics of the investigated membranes

Type of membrane	Composition	Ion exchange capacity* (mval/g)	Specific conductivity† (ohm <sup>-1</sup> cm <sup>-1</sup> )
NAFION 125	Saponified copolymer of sulphonyl fluoride vinyl ether and tetrafluoroethylene	0.80	$1.1 \times 10^{-2}$
MRF-4MB	$\alpha, \beta, \beta'$ -Trifluorostyrene-sulphonic acid grafted onto tetrafluoroethylene-hexafluoropropylene copolymer. Radiation grafting	1.35	$7.7 \times 10^{-2}$
MRF-26	$\alpha, \beta, \beta'$ -Trifluorostyrene-sulphonic acid grafted onto vinylidene fluoride-hexafluoropropylene copolymer. Radiation grafting	0.60	$3.8 \times 10^{-2}$
AMF C-322	Poly(styrenesulphonic acid) grafted onto polytrifluorochloroethylene. Radiation grafting	0.93	$2.1 \times 10^{-2}$
PE-PSSA	Poly(styrenesulphonic acid) grafted onto polyethylene. 5% DVB. Chemical grafting	1.83	$1.8 \times 10^{-2}$

\* Ion exchange capacity was determined by the titration method  
 † Specific conductivity was measured for the leached membranes in the H<sup>+</sup> form after the method of Subrahmanyam<sup>14</sup>

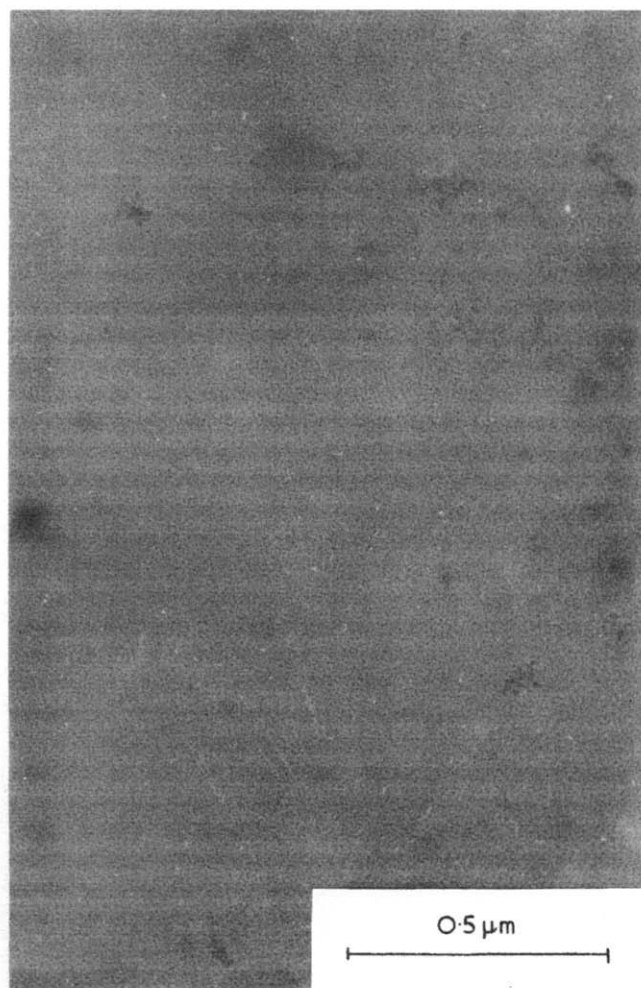


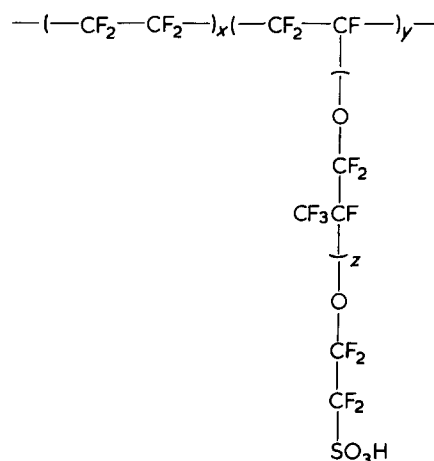
Figure 1 Electron micrograph of NAFION 125 membrane

the result of beam damage only. The best evidence of the correctness of the given micrograph is the observation of the same microsections after the exchange of the Pb<sup>2+</sup> ions into the H<sup>+</sup> ions. The micrograph after such a conversion is clear and does not exhibit any features visible in Figure 1.

The points observed in Figure 1 correspond to the areas of 3–6 nm in diameter in the membrane and are 'traces' of concentrations of a small number of ionogenic groups. Their uniform distribution shows the homogeneous distribution of such concentrations of the ionogenic groups.

The above observation corresponds very well to the statement of Yeo<sup>15</sup> about the presence of ionic clusters in the NAFION membranes.

According to the published data<sup>12</sup> NAFION membranes are prepared from perfluorinated copolymer which can be written as the formula:



It is known that the properties of this compound depend upon the proportions and distributions of the comonomers used, the length of the ether chain and molecular weight distribution. The values of  $x$ ,  $y$  and  $z$  are of decisive importance. The micrograph presented above permits us to suppose that at least the first two numbers have comparable and not high values.

Subsequent results deal with the MRF-4MB and MRF-26 membranes containing sulphonated  $\alpha, \beta, \beta'$ -trifluorostyrene grafted onto fluorocarbon backbones<sup>13</sup>.

The micrograph of the MRF-4MB membrane, the backbone of which is composed of so-called 'fluorinated ethylene propylene copolymer' (FEP), is almost identical with NAFION 125 membrane image. It shows clearly the absence of microphase separation and uniform distribution of the ionogenic groups. It can be expected then that the copolymer backbone of the membrane is homogeneous. The possible crystalline domains of FEP are very small or form loose systems allowing the penetration of fluorostyrene monomer.

Well selected conditions of grafting on FEP lead then to the formation of a homogeneous product. Similarly homogeneous products of radiation grafting were obtained e.g. by Chapiro<sup>16</sup> in the case of styrene grafted onto polytetrafluoroethylene.

The micrograph of the MRF-26 membrane (Figure 2) presents a different image although the membrane differs from the previous one only in the chemical composition of the copolymeric backbone.

The image in Figure 2 indicates that the MRF-26 membrane is of heterogeneous type. Some fragments of the image are typical for microphase separation occurring in

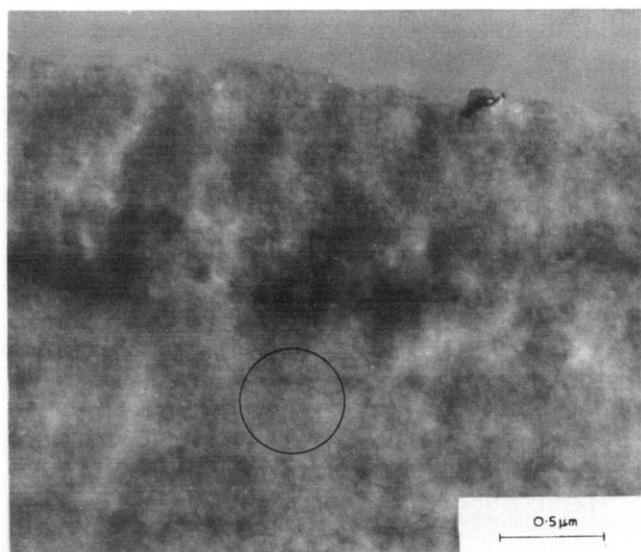


Figure 2 Electron micrograph of MRF-26 membrane

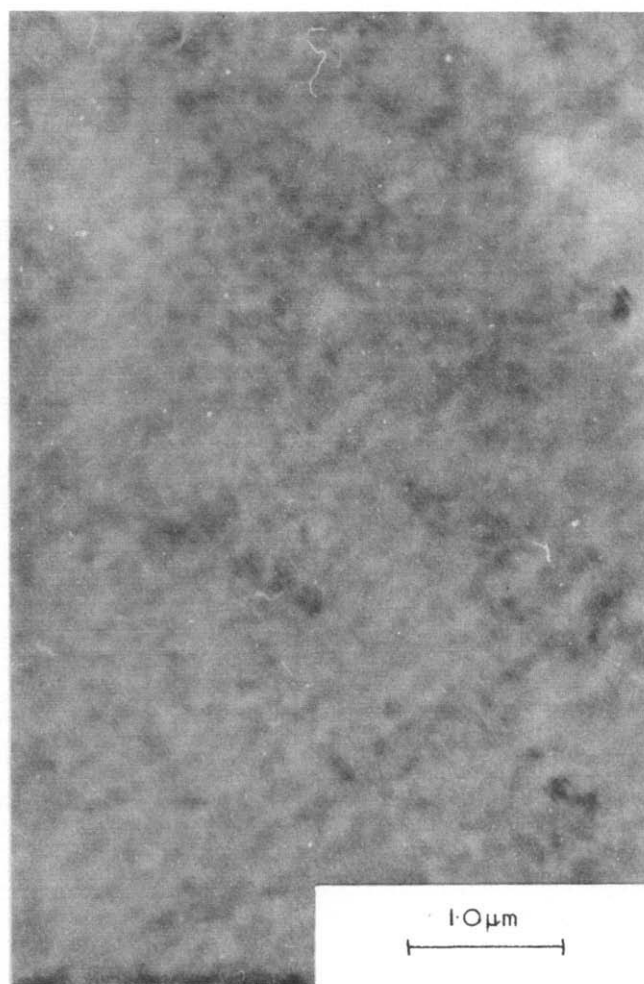


Figure 3 Electron micrograph of MRF-26 membrane; section cut perpendicular to that in Figure 2

block and graft copolymers<sup>17</sup> (see fragment marked by a circle). Round light stains visible in these regions represent the domains of 40 nm in diameter in the membrane. Such features confirm then the presence of blocks composed most probably of copolymeric arrangements:  $-\text{CF}_2-\text{CF}(\text{CF}_3)-\text{CH}_2-\text{CF}_2-$  with grafted  $\alpha,\beta,\beta'$ -trifluorostyrenesulphonic

acid as well as blocks of polyvinylidene. This conclusion is based on the known fact that about 93% of hexafluoropropylene (HFP) present in the  $\text{VF}_2$ -HFP copolymer occur in the form of the above mentioned arrangements and considerable excess of  $\text{VF}_2$  commonly used, forms separate blocks<sup>18</sup>.

Large dark regions of 0.5 to 0.7  $\mu\text{m}$  are probably due to the agglomeration of sulphonated fluorostyrene homopolymer in the membrane.

Additional information is given (Figure 3) by the micrograph of a section cut off in a direction parallel to the membrane surface i.e. perpendicularly to the direction of cutting of the section presented in Figure 2. This micrograph shows also the heterogeneous nature of the membrane and, moreover it indicates some striped rod arrangements.

The next two micrographs deal with ion exchange membranes containing poly(styrenesulphonic acid) as the carrier of the ionogenic groups.

Figures 4 and 5 present the micrograph of a membrane with a fluorocarbon backbone (AMF C-322) and a polyethylene backbone (so-called PE-PSSA membrane), respectively.

The micrograph of the AMF C-322 membrane looks like that of bipolymeric membranes where polyelectrolyte chains are interwoven among macromolecules of the polymeric backbone. Particular points have 20–30 nm in diameter. Careful observation of the micrograph allows us to recognize large regions with a different 'concentration' of dark points. The diameter of these regions comes up to 0.7–1.0  $\mu\text{m}$ . This indicates that there are some regions in the membrane backbone which differ in styrene penetration ability or in the number of places available for grafting. One can assume that this is due to the presence of different supermolecular structures in the membrane backbone. The presence of such structures in trifluorochloroethylene foil is described in the literature,<sup>18,19</sup>

In the AMF C-322 membrane the existence of heterogeneous supermolecular structure has been confirmed by observations of the light microscope images (magnification 320 $\times$ ) of 1  $\mu\text{m}$  thick sections of the membrane. The obser-

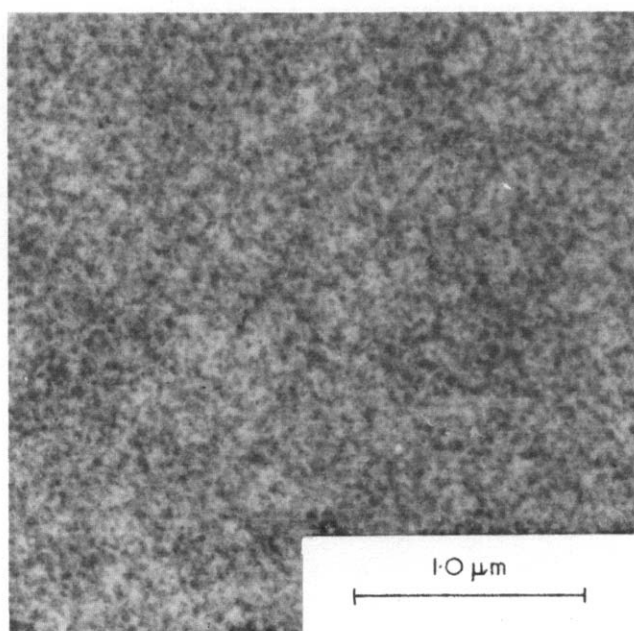


Figure 4 Electron micrograph of AMF C-322 membrane

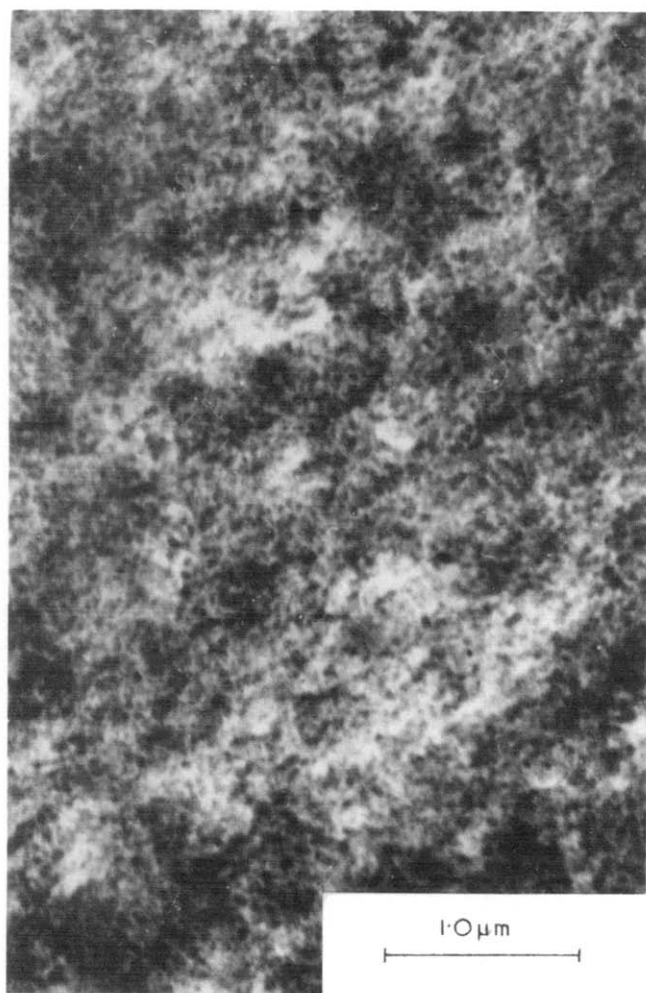


Figure 5 Electron micrograph of polyethylene-poly(styrenesulphonic acid) membrane

ved images in and without phase contrast, are grainy. The diameter of grains does not exceed  $1\ \mu\text{m}$ . This is in good agreement with the size of regions observed in the electron microscopy images.

Figure 5 presents the micrograph of polyethylene-poly(styrenesulphonic acid) membrane (PE-PSSA). It shows relatively large heterogeneity of the PSSA distribution. It is seen that PSSA macromolecules form larger irregular agglomerates of the size up to  $1-1.5\ \mu\text{m}$ . The constitution of the membrane corresponds then to the island structure, according to previous literature data<sup>8</sup>. The diameter of dark stains in the micrograph corresponds to  $40-60\ \text{nm}$  large regions in the membrane. So, the molecular weight of PSSA in that membrane is higher than that in the AMF C-322 membrane. However, it must be mentioned that the structure of such membranes depends also to some

extent on the amount of crosslinking agent used.

## CONCLUSIONS

The presented results proved the homogeneous nature of the perfluorinated membranes NAFION and MFR-4MB. The other membranes have miscellaneous heterogeneous nature. This depends on the microphase structure of the copolymer backbone in the case of the MRF-26 membrane, and/or on the different supermolecular structure of the backbone, which is particularly well seen in the AMF C-322 membrane. PE-PSSA membrane shows the greatest heterogeneity that results probably from a low degree of the PSSA grafting on the PE as well as from the heterogeneous supermolecular PE structure.

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