

CHROM. 7718

INVESTIGATION OF STRUCTURE HETEROGENEITY IN ION-EXCHANGE MEMBRANES

MIKHAIL S. GORODNEV, GRIGORI K. SALDADZE, VALERI K. VARENTSOV and IRINA M. ABRAMOVA

Scientific Research Institute for Plastics, 35 Perovsky Proyezd, Moscow E-112 (U.S.S.R.)

SUMMARY

Electron microscopy and local X-ray spectral analysis (utilizing an electron probe) have been used to evaluate structural heterogeneity in ion-exchange membranes. X-ray patterns, reflecting radiation intensity changes along the test sample proportional to the fixed charge density, can be obtained through X-ray microanalysis. Electron microscopic studies of ultra-thin sections of ion-exchange membranes indicated that the structural heterogeneity expressed by alternating zones with various electron densities associated with the presence of pores in the membranes is the basic feature of these membranes.

INTRODUCTION

Homogeneity of polymeric ion-exchange membranes is of prime importance for the interpretation of almost all of the physico-chemical properties of the membranes. This question is of particular importance in understanding the ion transfer mechanism and the electrochemistry of the membrane processes.

The existing division of the membranes into homogeneous and heterogeneous types is very arbitrary, and is not based on data reflecting the micro-structure of the membranes. The explanation of membrane properties is more often based on the assumption of their homogeneity. However, graft and block polymerization processes used for the manufacture of the membranes are mostly heterogeneous reactions proceeding with the formation of various supermolecular structures.

In previous work¹⁻³, the inevitability of the formation of a heterogeneous structure of ion-exchange materials at the expense of different concentrations of a cross-linking agent, the presence of micro-cavities, differences in the distribution of ionogenic groups, etc., was shown.

Morphological features of the structure of "homogeneous" membranes obtained by chemical grafting of 2,5-methylvinylpyridine-*ftorlon* copolymer in the shape of a film (membrane I) and in the shape of granules (membrane II) were studied in the present work by electron microscopy and local X-ray spectral analysis with an electron probe. The relationship between micro-structure of the membranes and certain properties was also studied.

EXPERIMENTAL

X-ray microanalysis utilizing an electron probe

The samples of anion-exchange membranes investigated by local X-ray spectral analysis were pre-saturated with PO_4^{3-} and thoroughly washed free from the non-exchange absorbed electrolyte; they were then dried and fixed in an air-dry state in a specially made mould with an epoxy resin. As the sample-making method affects the accuracy of the results, all of the membrane samples were fixed in one mould coated with a thin layer of graphite before making measurements. This mould was placed in the working chamber of an MS-46 microanalyzer (Cameca, Courbevoir, France), in which 10^{-5} -mmHg vacuum was maintained. The voltage on the probe was 20 kV and the current was $3 \cdot 10^{-8}$ A. X-ray patterns were taken from the sample areas free from mechanical defects observed with a $500\times$ power microscope.

Electron microscopy

An electron microscopic method utilizing ultra-thin sections prepared with ChMTP-2 ultramicrotome was used for the investigation of a thin structure of homogeneous ion-exchange membranes. The membrane samples, in the shape of a thin strip, were placed in a foil holder and filled with an epoxy resin. After polymerization, $0.2 \times 2 \times 0.2$ -mm samples were cut from the block obtained, and a section up to 1000 Å in thickness was made from the latter. Ethanol was used for making the above sections. The sections were observed with a $20,000\times$ magnification IEM-5V electron microscope with 10 Å resolution.

RESULTS AND DISCUSSION

Basic physico-chemical characteristics of the membranes under study are listed in Table I. Attention is drawn to the high resistivity of homogeneous membrane II. It is clear from Table I that the q for this membrane is considerably in excess of an electric resistivity value even for heterogeneous membrane III.

We decided to look for an explanation of this phenomenon by considering the distribution of active groups in a polymeric matrix. Information relating to the structure of the membranes obtained by using an X-ray microanalyzer with an electron probe is very convenient for this purpose. Fig. 1 shows the photographs obtained using characteristic PK_α radiation and shows the distribution of PO_4^{3-} ions in the membranes. These photographs make possible a qualitative estimation of the distribution

TABLE I
PHYSICO-CHEMICAL CHARACTERISTICS OF MEMBRANES

No.	Type of membrane	Static exchange capacity (mequiv./g dry membrane)	Degree of swelling, K (%)	Transfer number	Resistivity in 1 N HCl (ohm·cm)	$H_{m,30}$ (%)
1	Homogeneous	2.0	109	0.95	17	36.7
2	Homogeneous	2.1	118	0.94	198	47.5
3	Heterogeneous	1.45	108	0.97	29.5	78.6

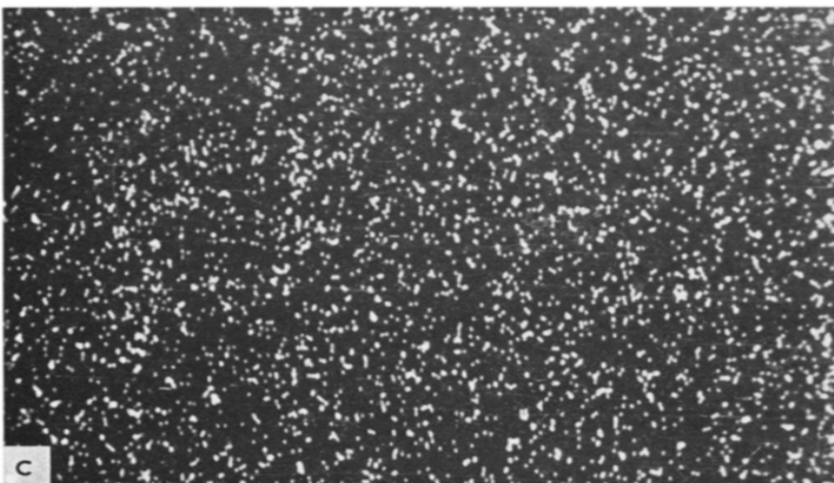
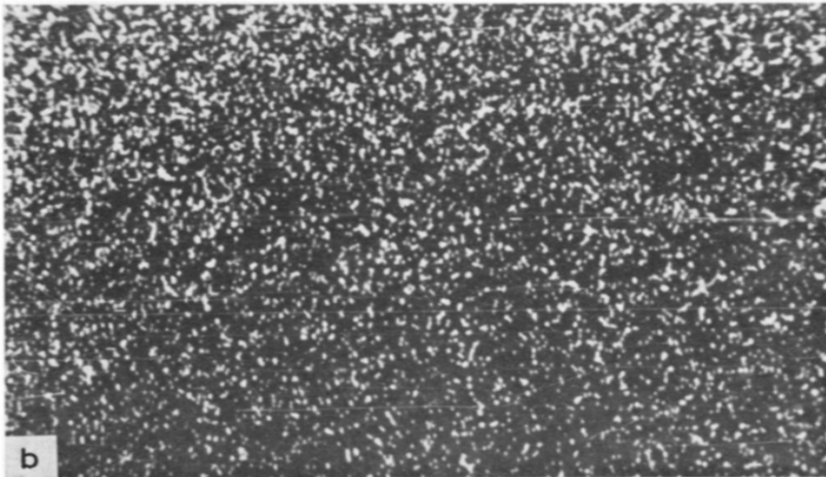
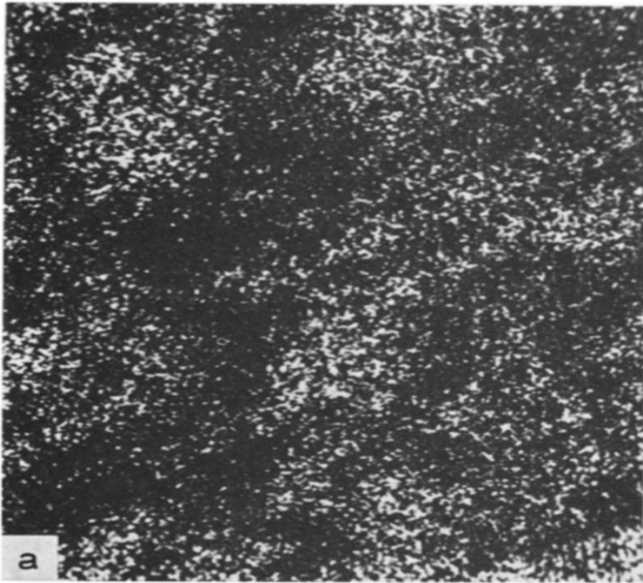


Fig. 1. Microphotographs obtained in characteristic PK_{α} radiation: (a) for heterogeneous membranes ; (b) and (c) for homogeneous membranes.

of counter ions in homogeneous and heterogeneous membranes. Although the distribution of counter ions is of a discrete character in all instances, in homogeneous membranes, however, it is characterized by a sufficiently high degree of uniformity.

The quantitative estimation of the distribution of the ionogenic groups in the membrane was obtained through processing X-ray patterns (obtained with a microanalyzer) reflecting the changes in radiation intensity proportional to the fixed charge density.

When processing X-ray patterns by the method described earlier⁴, we calcul-

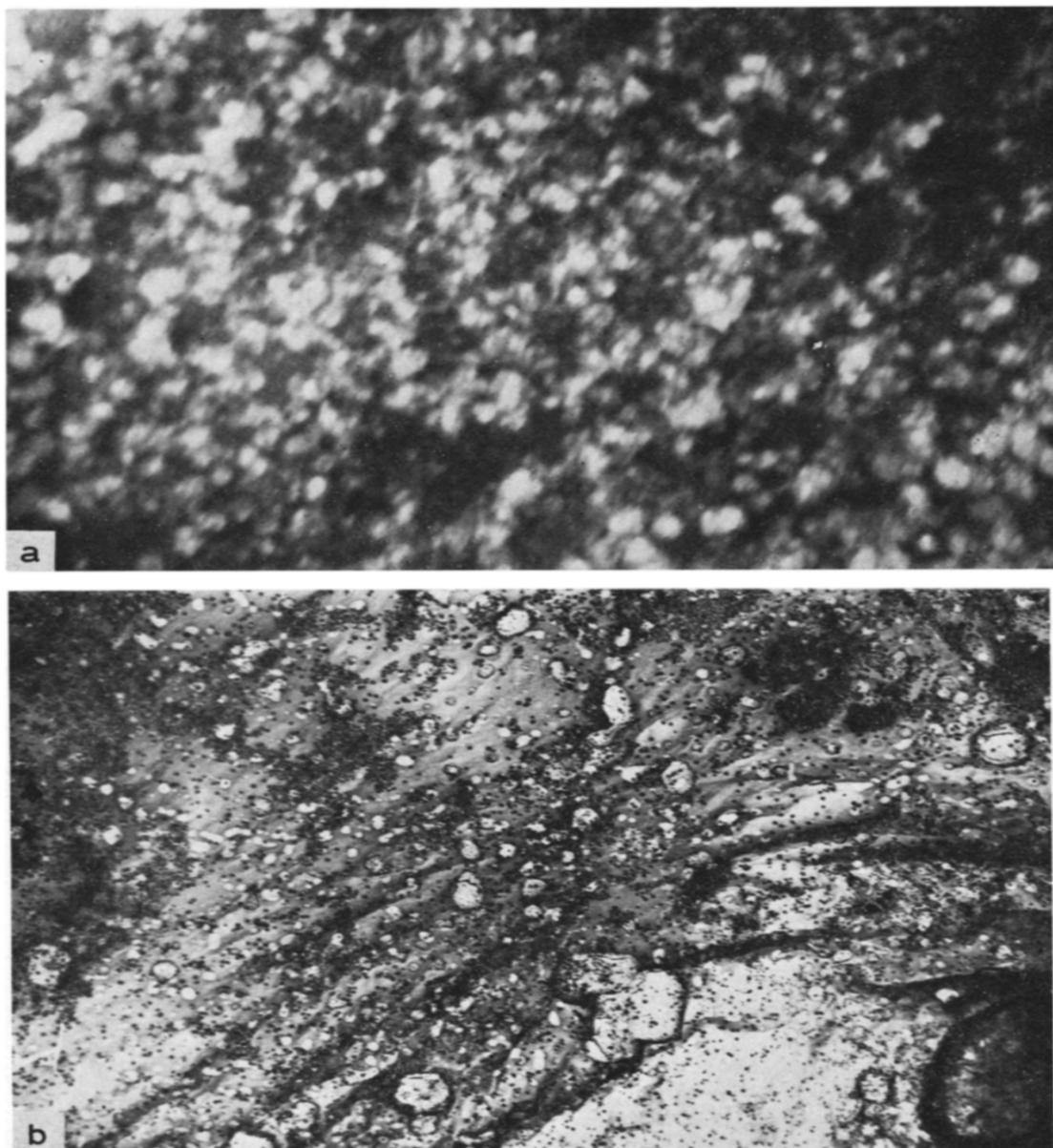


Fig. 2. Electron structure microphotograph of (a) membrane I and (b) membrane II.

ated the $H_{m.sq.}$ parameter, which shows the distribution non-uniformity of ionogenic groups in the membrane. The $H_{m.sq.}$ value for a heterogeneous membrane, given in Table I, substantially exceeds $H_{m.sq.}$ values for both homogeneous membranes. The $H_{m.sq.}$ value for membrane II is much higher than that for membrane I, which corresponds to a higher distribution non-uniformity of the active groups in membrane II, although the static exchange capacities are almost identical for both homogeneous membranes, thus indicating an equal amount of active groups in a macro-volume.

2,5-Methylvinylpyridine-*ftorlon* copolymerization processes differ depending upon the nature of the *ftorlon* (film or granules). It can be assumed that active groups are distributed in the surface layer of the granules when being chemically grafted on *ftorlon* granules. This is even more evident when taking into account the fact that the diffusion of 2,5-methylvinylpyridine molecules into *ftorlon* granules is difficult owing to steric effects.

A higher distribution non-uniformity of active groups in membrane II affects its electrochemical properties. Ion transfer in the ion-exchange membrane takes place, however, not only at the expense of available fixed active groups, but also at the expense of the electrolyte found in the membrane pores.

Using electron microscopy, we investigated the structural heterogeneity of homogeneous membranes represented by micro-cavities. Fig. 2 presents structural microphotographs of homogeneous membranes. It is clear from Table II that the structure of membrane I is more homogeneous at a supermolecular level compared with the structure of membrane II.

TABLE II
RESULTS FOR HOMOGENEOUS AND HETEROGENEOUS MEMBRANES

No.	Type of membrane	Size of micro-cavities (\AA)		Gas permeability $\left(\frac{\text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{sec} \cdot \text{atm}} \right)$
		Electron microscopy	Low-angular X-ray scattering	
1	Homogeneous	150-250	230	$3.2 \cdot 10^{-8}$
2	Homogeneous	250-800 2000-4000	350	$4.5 \cdot 10^{-8}$
3	Heterogeneous	—	—	$9.6 \cdot 10^{-8}$

The presence of hydrophobic areas is possible in membrane II material owing to the non-uniform distribution of ionogenic groups. In this case, hydrophobic pores are not filled with the electrolyte, which leads to a disturbance of the ion contact between the active groups of the membrane and the electrolyte solution, and therefore to an abnormal decrease in electrical conductivity.

The combination of the two methods of investigation permits one to evaluate structural features of ion-exchange membranes; this structure makes a substantial contribution to the migration of ions in an electric field.

REFERENCES

- 1 F. Körösy and E. Zeigerson, *J. Appl. Polym. Sci.*, 11 (1967) 909.
- 2 J. Klinowski and M. Leszko, *Rocz. Chem.*, 42 (1968) 123.
- 3 V. K. Varentsov, K. H. Urusov, Yu. G. Lavrentiev and M. V. Pevnitskaya, *Dokl. Akad. Nauk SSSR*, 186, No. 2 (1969).
- 4 V. K. Varentsov and M. V. Pevnitskaya, *Izv. Sib. Akad. Nauk SSSR*, No. 2 (1972) 139.