Real-time analysis of small-angle X-ray scattering from perfluorocarboxylic ionomer membranes during electrodialysis*

A. Okawara, H. Horie, H. Miyake and H. Nishimura
Research Center, Asahi Glass Co. Ltd, Yokohama 221, Japan

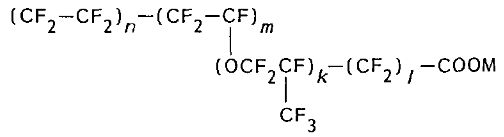
K. Saijo and T. Hashimoto†
Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan
(Received 4 February 1991; revised 11 March 1991; accepted 29 March 1991)

The effects of electrodialysis on the structures of ionic clusters in a perfluorocarboxylic membrane were studied by means of small-angle X-ray scattering (SAXS). Specially made cells for the electrodialysis were used for measuring SAXS profiles *in situ* and in real time during the electrodialysis. It was found that the electric field did not reshape the structure of ionic clusters during the electrodialysis within our experimental conditions.

(Keywords: small-angle X-ray scattering; ionomers; membranes; electrodialysis; ionic clusters; perfluorocarboxylates)

INTRODUCTION

A perfluorocarboxylic ionomer membrane used for chlor-alkali dialysis has the following general chemical structure:



$$(CF_2-CF_2)_n-(CF_2-\underset{\underset{(OCF_2\underset{\underset{CF_3}{|}}{C}F)_k-(CF_2)_l-COOM}{|}}{C}F)_m$$

$M = H, CH_3$ or metal
$k = 0,1 \quad l = 1-5$

The electrochemical behaviour, such as current efficiency, and the mechanical properties of perfluorinated ionomers as ion exchange membranes are closely related to their internal structure. It is known that the metal salt forms or the acid form of ionomers consist of ionic clusters, especially in the state absorbing water. There are many studies on structure in perfluorosulphonic ionomer membranes[1–6].

Ionic clusters have been found to exist in hydrocarbon-based ionomers, such as polyethylene, polystyrene and so on, by using the small-angle X-ray scattering (SAXS) technique. For perfluorinated ionomers, clustering of ionic groups was found in perfluorosulphonic acid by Yeo *et al.*[2] using SAXS and thermo-rheological measurements. Three models have been proposed to explain the existence of SAXS maxima: (1) core–shell models, as proposed by MacKnight *et al.*[7], (2) two-phase models by Marx *et al.*[8] and (3) lamellae models by Roche *et al.*[9]. Fujimura *et al.* supported the core–shell models, by studying the deformation and swelling behaviour of ionic clusters by means of SAXS[6,10,11].

However, these studies have been conducted in the absence of external electric fields. In practice, the perfluorinated ionomer membranes are used under an electric field contacting one side with sodium chloride and the other side with caustic soda solution in order to produce caustic soda solution in the chlor-alkali industry. It is conceivable that the electrochemical and mechanical properties of ionomer membranes depend on the structure of ionic clusters under the electric field. The purpose of this work is to investigate the influence of electric field during electrodialysis on the structure of the ionic clusters, which governs the electrical properties of the membrane. Two special SAXS cells were designed to measure the effect of electric field on the structure of the ionic clusters. We studied the change of SAXS profiles during electrodialysis under the electric field.

EXPERIMENTAL

SAXS cells

The two types of SAXS cells displayed in *Figures 1* and *2* were made for measuring SAXS profiles on site under the electric field. In *Figures 1* and *2* X-ray beams are applied parallel and perpendicular to the electric field, respectively. These cells were devised so that it is possible to study the time-resolved transient change of the structure of the ionic clusters *in situ* and in real time by SAXS measurement after starting up the electrodialysis. The chambers of these cells are made of an acrylic resin and the electrodes consisted of a platinum wire. The dimensions of a specimen are minimized to equalize the distribution of intensity of the electric current. The electrolyte of 2% caustic soda solution is continuously

---

*This work was presented at the Annual Meeting of the Society of Polymer Science, Japan, May 1987

†To whom correspondence should be addressed

0032-3861/92/081579-04

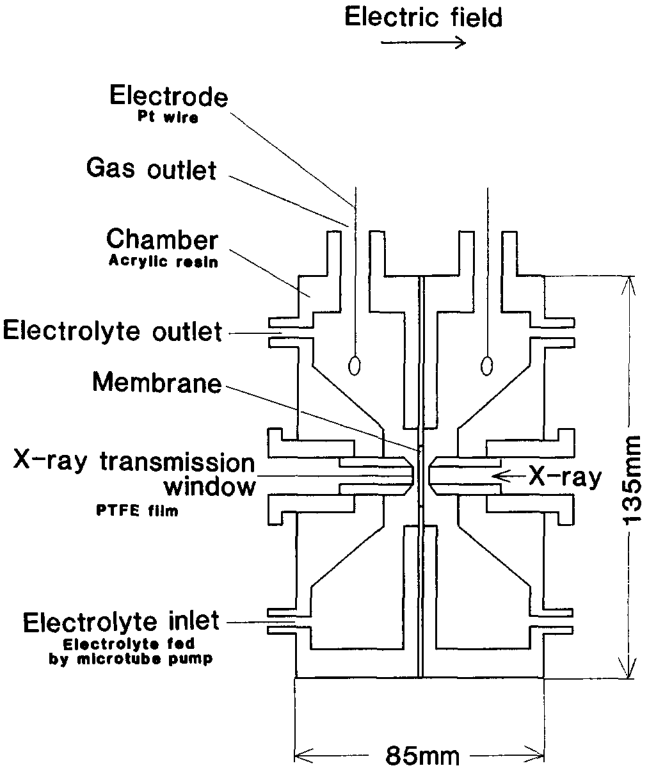


Figure 1 Cross-sectional view of the cell for SAXS measurements (X-rays parallel to electric field)

supplied by the microtube pump in order to keep its concentration constant.

Test specimens

The salt form of perfluorocarboxylic ionomers having ion exchange capacity of 1.12 milli-equivalents per gram (17 mol%) and 400 μm in thickness was used. Test specimens were neutralized by sodium hydroxide or potassium hydroxide solutions to obtain the sodium or potassium salt form, respectively. *Table 1* shows treatment conditions and the water content of specimens.

Electrodialysis

When SAXS was measured parallel to the electric field (in *Figure 1*), the electrodialysis was imposed under a current density of 10 A dm^{-2} and a cell voltage of 5.5–6.3 V. In the case of SAXS measurement perpendicular to the electric field, it was conducted under the conditions of a current density of 20 A dm^{-2} and a cell voltage of 14–28 V. (This high voltage was due to the long electric path of the specimen of about 20 mm, as shown in *Figure 2*.) The duration of the electrodialysis was more than one and a half hours at room temperature, while a slight increase of the temperature of the membrane was seen because of heat generated by electric current in the membrane.

The uniformity of electric current intensity over the area of the SAXS measurement was examined by mapping of deposited Ni metal in the test membrane after 5 h electrodialysis by energy dispersive X-ray fluorescence analysis, by using the SAXS cell of *Figure 1* and 2% caustic soda solution containing 5 ppm of nickel chloride as electrolyte. Ni ion was found to be uniformly distributed on the surface of the test specimen, confirming that the electric current was uniformly distributed on the membrane. The current efficiency of this cell in this condition was found to be about 85%, almost equal to the real production condition (90–95%).

X-ray measurements

The SAXS profiles were taken with a one-dimensional position-sensitive proportional counter. Cu Kα radiation monochromatized by a graphite crystal ($\lambda = 1.54$ Å) was used as the incident X-ray beam. The X-ray beam was generated by a rotating-anode X-ray generator under a power of 12 kW (Rigaku Denki, Ru-a). A series of time-sliced SAXS profiles were taken with a measuring time of 10 min, at an interval of every 20 min after onset or cessation of the electrodialysis. The scattering curves were corrected for absorption and background scattering. The gas bubbles (H_2, Cl_2 or O_2) effect was corrected by monitoring the Ni-filtered transmitted X-ray beam.

The details of the SAXS apparatus and the position-sensitive proportional counter were described elsewhere[12–14].

RESULTS AND DISCUSSION

Effect of treatment conditions on size of ionic cluster

Figure 3 shows a comparison of SAXS profiles of ionomer membranes obtained by varying the treatment

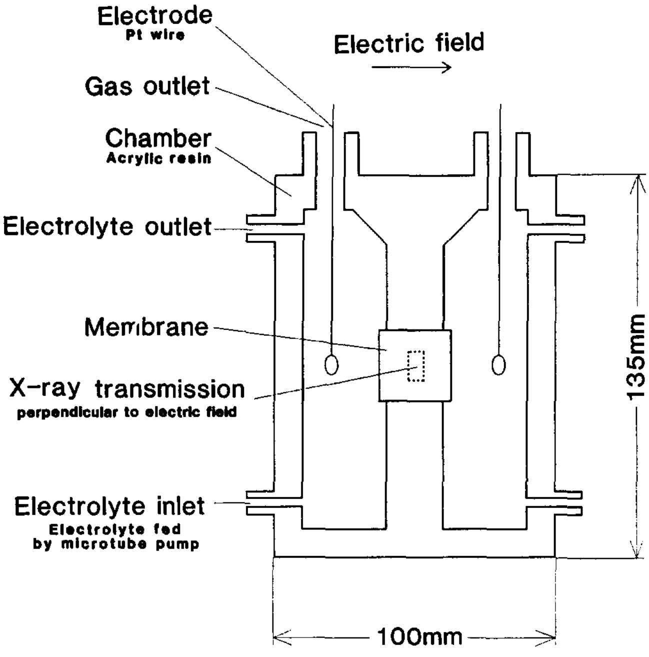


Figure 2 Cross-sectional view of the cell for SAXS measurements (X-rays perpendicular to electric field)

Table 1 Test specimens

Specimen number	Condition	Salt form	Water content (%)
1	Soaked in 11% KOH/30% DMSO[a] at 90°C for 20 min	K	39
2	Soaked in 12% NaOH at 90°C for 16 h	Na	16
3	Soaked in 12% NaOH at 90°C for 16 h and boiled in water for 1 h	Na	38

[a] DMSO, dimethylsulphoxide

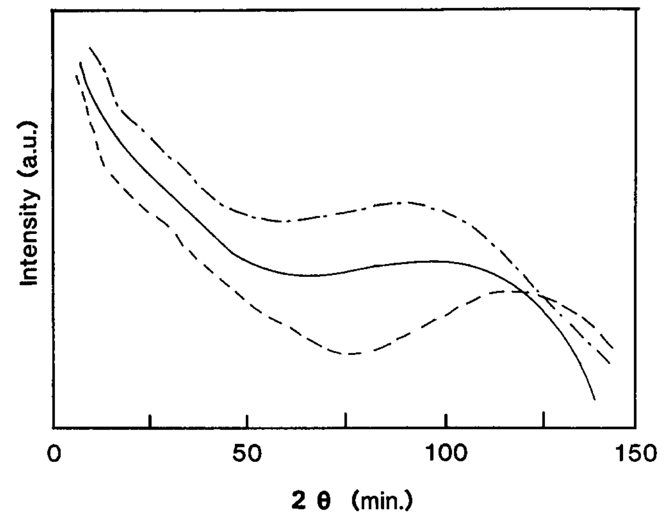


Figure 3 Influence of membrane pretreatment on SAXS patterns of the salt form of perfluorocarboxylic membranes after soaking in 2% NaOH: (——) hydration by 11% KOH solution and 30% DMSO solution; (– – –) hydration by 12% NaOH solution; (–·–) hydration by 12% NaOH solution and boiled in water

Table 2 Results of SAXS. Effect of membrane treatment on characteristic cluster size and water content

Specimen number	Angle of SAXS maximum (minute)	Characteristic cluster size (Å)	Water content (%)
1	100	53	39
2	115	46	16
3	92	58	38

conditions. In this figure, the vertical axis is represented on a logarithmic scale and the level of each profile was shifted arbitrarily to avoid overlapping. A scattering maximum originating from the ionic clusters exists at scattering angle 2θ of about 100′ (minutes) in each membrane. Obviously this maximum ('ionic scattering maximum') depends on the membrane treatment conditions, that is, on the water content of the membranes. *Table 2* displays the effect of the water content of each specimen on 2θ of the scattering maximum and the characteristic cluster size calculated by Bragg's equation, $2d \sin\theta = \lambda$.

The characteristic cluster size of specimen 1 is smaller than that of specimen 3, despite their similar water contents, which will be ascribed to the difference of salt form. With membranes of a given ion exchange capacity and the same salt form, the angle of the SAXS maximum shifts to lower angle by increasing the water content in the membrane as seen by comparing specimens number 2 and 3. This tendency coincides with that in other reports[8,10,11]. The details of the ionic cluster structure were described previously[6,10,11]. In this paper we aimed to study effects of electrodialysis on the ionic cluster structure.

Effect of electric field on size of ionic cluster

Figure 4 shows the time variation of SAXS profiles of ionomer membranes of specimen 2 during electrodialysis, when the X-ray beam was imposed parallel to the electric field by using apparatus as in *Figure 1*. The full curve is the SAXS profile measured before electrodialysis, the broken curve is measured from 0 to 10 min after start-up of electrodialysis, the dash-dot chain curve is measured from 80 to 90 min after start-up and the dash-dot-dot chain curve is measured from 0 to 10 min after cessation of the electrodialysis. There is a SAXS maximum at about 2θ of 115′. There was little change in SAXS profiles during the electrodialysis in terms of both the scattered intensity and the scattering angle for the 'ionic scattering maximum'. This result gives a very important conclusion that there is no significant change in the structure of the ionic cluster, at least in the plane perpendicular to electric field.

In order to detect a possible structural change of the ionic clusters in the direction parallel to the electric field, it is necessary to observe the cluster in the plane containing the electric field. This can be achieved by undertaking SAXS measurements in the direction perpendicular to the electric field using another type of SAXS cell as in *Figure 2*. *Figure 5* shows the time variation of SAXS profiles of the ionomer membranes of specimen 3 during and after cessation of the electrodialysis. It was found again that there is no change in SAXS profiles during the electrodialysis, again in terms of both the scattered intensity and the scattering angle for the ionic scattering maximum. The SAXS maximum appearing at 2θ of 90′, different from that for the membrane of specimen 2, simply reflects the difference of conditioning between specimens 2 and 3. From these results it was unequivocally concluded that the size and the shape of ionic clusters in ionomer membranes does not change at least in the range of applied electric field strength covered in this experiment.

Discussion

This study clearly revealed that the structure of ionic clusters in the perfluorocarboxylic membrane undergoes no significant change by applying electrodialysis in either parallel or perpendicular direction to the electric current. The structure of the ionic cluster depends rather deeply

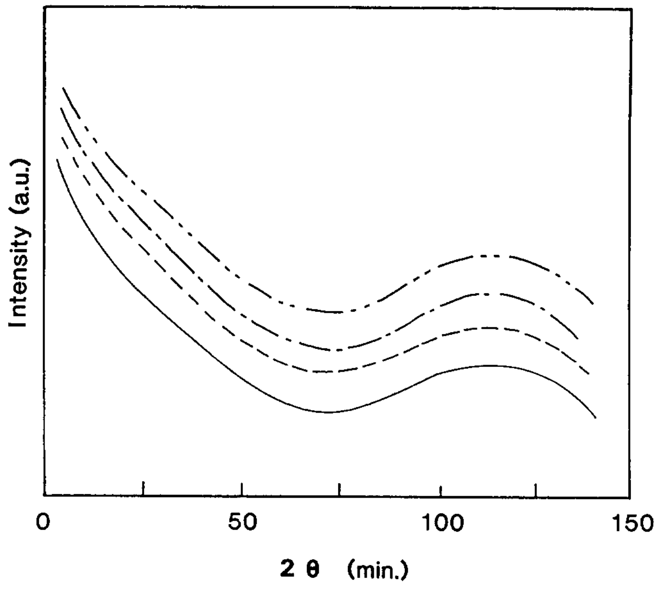


Figure 4 Influence of electrodialysis on SAXS patterns of the sodium form of perfluorocarboxylic membranes: (——) measured before electrodialysis; (– – –) measured from 0 to 10 min after start-up of electrodialysis; (–·–) measured from 80 to 90 min after start-up; (–··–) measured from 0 to 10 min after cessation of electrodialysis (in the direction parallel to electric field)

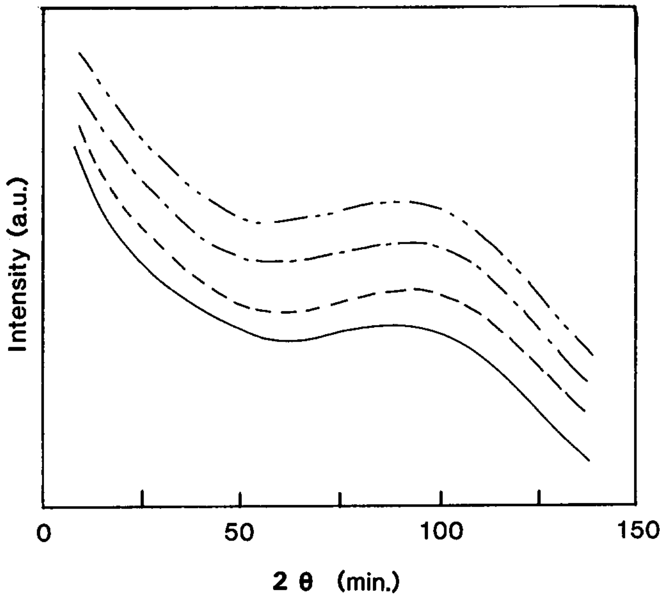


Figure 5 Influence of electrodialysis on SAXS patterns of the sodium form of perfluorocarboxylic membranes: (——) measured before electrodialysis; (- -) measured from 0 to 10 min after start-up of electrodialysis; (— - —) measured from 80 to 90 min after start-up; (— · · —) measured from 0 to 10 min after cessation of electrodialysis (in the direction perpendicular to electric field)

on the hydrolysis condition and subsequent neutralization of the membrane. Ionic clusters in the membrane are formed by hydrolysing them into acid form from methyl ester form and subsequent neutralizing to sodium or potassium salt form. These phenomena are based on electrostatic interaction between the fixed carboxylate ions and the metallic ions or H^+ ions including water molecules. The cluster size is controlled essentially by both the thermodynamic work required for polymer coil deformation in order to form the clusters and the electrostatic energy released upon cluster collapse through ion–dipole interactions[15]. The water in the membrane will be concentrated in ionic clusters, and therefore water uptake in a membrane is considered to change the distance between clusters and size of clusters.

Gierke *et al.*[1] discussed the electrochemical behaviour during electrodialysis based on the structure of ionic clusters in the absence of an external electric field. The structure of an ionic cluster was expected to change owing to a change of water content by a rise in temperature[10] during electrodialysis. Judging from the result that the cluster size did not change clearly, it was estimated that the change of water content was very small in this condition of electrodialysis. Therefore, it turns out that the examination in the absence of the electric field is sufficient to discuss the relation between the current efficiency and the structure of the ionic clusters.

SUMMARY

We devised special SAXS cells for measuring SAXS *in situ* and in real time during electrodialysis and studied the structure of the ionic cluster in perfluorocarboxylic membranes under an electric field in both transient and steady states. It was found that the ionic cluster size and morphology did not change at all under application of an electric field during electrodialysis.

REFERENCES

1 Gierke, T. D., paper presented at 152nd National Meeting, The Electrochemical Society, Atlanta, Georgia, October 1977
2 Yeo, R. S. and Eisenberg, A. *Polym. Prepr., ACS Div. Polym. Chem.* 1975, **11**, 104; *J. Appl. Polym. Sci.* 1977, **21**, 875
3 Yeo, R. S. *J. Electrochem. Soc.* 1983, **130**, 533
4 Hsu, W. Y. and Gierke, T. D. *J. Membr. Sci.* 1983, **13**, 307
5 Volino, F., Pineri, M., Dianoux, A. J. and DeGeyer, A. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 481
6 Hashimoto, T., Fujimura, M. and Kawai, H. *ACS Symp. Ser.* 1982, **180**, 217
7 MacKnight, W. J., Taggart, W. P. and Stein, R. S. *J. Polym. Sci., Polym. Symp.* 1974, **45**, 113
8 Marx, C. L., Caufield, D. F. and Cooper, S. L. *Macromolecules* 1973, **6**, 344
9 Roche, E. J., Stein, R. S., Russell, T. P. and MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 1497
10 Fujimura, M., Hashimoto, T. and Kawai, H. *Macromolecules* 1981, **14**, 1309
11 Fujimura, M., Hashimoto, T. and Kawai, H. *Macromolecules* 1982, **15**, 136
12 Todo, A., Hashimoto, T. and Kawai, H. *J. Appl. Crystallogr.* 1978, **11**, 558
13 Hashimoto, T., Suehiro, S., Shibayama, M., Saijo, K. and Kawai, H. *Polym. J.* 1981, **13**, 501
14 Fujimura, M., Hashimoto, T. and Kawai, H. *Mem. Fac. Eng., Kyoto Univ.* 1981, **43** (2), 224
15 Eisenberg, A. *Macromolecules* 1970, **3**, 147