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Structure of Perfluorinated Ionomer Membranes Incorporating Organic Cations

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The structure of perfluorinated ionomer membranes (Nafion®) incorporating large organic cations, tetraethylammonium (TEA^+) and 1,1'-dialkyl-4,4'-bipyridinium cations (C_nV^{2+}, n = 3 and 8), is studied using small-angle X-ray scattering (SAXS). For TEA^+- and C_3V^{2+}-form membranes, the SAXS maxima show the presence of the ionic clusters as large as those for Na^+-form (ca. 4 nm in diameter). For C_8V^{2+}-form membranes, the inter-cluster distance expanded to a value larger than that for H^+-form after the ion-exchange reaction for 5 days. However, the water content and cluster size decreased significantly after the ion-exchange reaction for 50 days or boiling treatment.

"Nafion®" perfluorinated ionomer membranes are well known to be microscopically separated into two phases: an ionic cluster domain, which contains most of the sulfonate groups, cations and absorbed water, and a hydrophobic fluorocarbon backbone domain, which surrounds the ionic clusters.1,2) Electrodes coated with Nafion have been a subject of considerable recent interest.3-9) Several workers in this field have observed unusual behavior of organic cations incorporated into Nafion.6-9) For example, Nafion has strong affinity for large organic cations,6) the organic cations incorporated in Nafion have extremely small diffusion coefficients,7) etc. These unusual properties have been generally interpreted using the cluster-network model of Nafion, and attributed to the interactions between organic cations and Nafion. However, the presence of the ionic clusters has been confirmed only for the Nafion membranes incorporating inorganic cations, and few studies have been reported on the structure of Nafion incorporating organic cations. In this study, the structure of Nafion incorporating large organic cations, tetraethylammonium (TEA^+) and 1,1'-dialkyl-4,4'-bipyridinium cations (viologen), is studied using small-angle X-ray scattering (SAXS).

A perfluorinated sulfonate membrane, Nafion 117 (E. I. du Pont de Nemours and Co., equivalent weight = 1100), was used in this study. Nafion samples (2 cm x 2 cm x 170 μm) were immersed in aqueous 1 M (M = mol dm^{-3}) H_2SO_4 containing 3% H_2O_2 for 7 days to exchange the counter-ion from Na^+ to H^+ and to remove organic impurities, and were then treated in boiling water for 1 h. The samples were converted to various ionic forms by immersion in solutions containing the corresponding salts for 5 or 50 days at room temperature. Some of the samples were again boiled in the salt solutions for 1 h. These treatment conditions are summarized in Table 1.

SAXS measurements were performed using a 6-m SAXS system at the High Intensity X-ray Laboratory (HIXLAB) of Kyoto University. The sample was cut into a piece (ca. 5 x 5 mm^2), and was mounted in a cell for

Table 1. Treatment conditions of Nafion 117 membranes and the results of SAXS and water absorption measurements

Salt Solution		Immersion time	Boiling time	Bragg spacing	Water content	Polymer density	Cluster size
		day	h	nm	%-dry polymer	g cm^{-3}	nm
1 M	H_2SO_4	7	1[a]	5.3	31	1.9	4.9
1 M	KOH	5	-	5.3	19	1.9	4.5
1 M	KOH	5	1	5.1	18	2.0	4.3
100 mM	$TEAClO_4$[b]	5	-	5.2	21	1.7	4.4
10 mM	C_3VBr_2[c]	5	-	5.3	18	1.8	4.4
50 mM	C_3VBr_2	5	-	5.1	19	1.8	4.3
30 mM	C_3VBr_2	50	-	4.9	18	1.8	4.1
10 mM	C_8VBr_2[d]	5	-	6.1	19	1.8	5.1
50 mM	C_8VBr_2	5	-	5.8	18	1.7	4.7
50 mM	C_8VBr_2	50	-	3.5 + 4.9[e]	8	1.6	2.6 + 3.3[e]
50 mM	C_8VBr_2	5	1	3.3	7	1.6	2.2

a) The membrane was boiled in water. b) Tetraethylammonium perchlorate. c) 1,1'-dipropyl-4,4'-bipyridinium dibromide. d) 1,1'-dioctyl-4,4'-bipyridinium dibromide. e) Two maxima were observed on the Iq^2 *vs.* q plot.

liquid samples equipped with a mica windows (20 μm thick) to prevent from drying. The X-ray is CuK_α (λ = 1.54056 Å) from a fine-focus X-ray generator (Rigaku Co., RU-1000C3) operated at 40 kV and 50 mA. Isotropic two-dimensional intensity of X-ray scattering collected by a two dimensional position-sensitive proportional counter was corrected for the intensity of background and for the non-uniformity of detector sensitivity, and then circularly averaged to give the one-dimensional data.

The content of absorbed water in the membrane was determined as follows: The sample was quickly blotted between two sheets of filter paper and weighed. After it was dried under vacuum at 100°C for 72 h, the content of absorbed water was determined by subtracting the weight of the dry polymer from the total weight. The density of dry polymer was calculated from the weight and size of the sample after dried.

1,1'-dipropyl-4,4'-bipyridinium dibromide (C_3VBr_2) and 1,1'-dioctyl-4,4'-bipyridinium dibromide (C_8VBr_2) were prepared from 4,4'-dipyridyl and the corresponding alkyl bromides, and recrystallized from ethanol solutions. Other chemicals were of reagent grade, and were used without further purification.

Although details of the configuration of the ionic clusters cannot be obtained from SAXS results alone, we adopted Gierke's cluster-network model1) to calculate the inter-cluster distance and cluster size. In the cluster-network model, the counter-ion, ion-exchange sites and absorbed water are distributed in simple spherical domains, and the spherical clusters are connected by short narrow channels. In this model, the Bragg spacing (d), which is calculated from a SAXS maximum using scattering angle (2θ) and the Bragg equation ($\lambda = 2d \sin\theta$), is assigned to the average distance between clusters. The average size of the clusters is estimated using the amount of absorbed water assuming that the clusters would be distributed on a simple cubic lattice with an average lattice constant, i.e., the Bragg spacing.

Figures 1 to 3 show the Iq^2 vs. q plots for inorganic ion-, C_3V^{2+}- and C_8V^{2+}-form membranes, respectively. Here, I and q are scattering intensity and scattering vector, $q = (4\pi/\lambda)\sin\theta$, respectively. In Fig. 1, strong scattering maxima were observed at ca. q = 0.12 for swollen H^+- and Na^+-form membranes, while as-received dry Na^+-form membrane did not exhibit a maximum. Hence, these maxima are attributed to the formation of the ionic clusters by swelling treatments, which is in agreement with the results reported by Gierke *et al.*1)

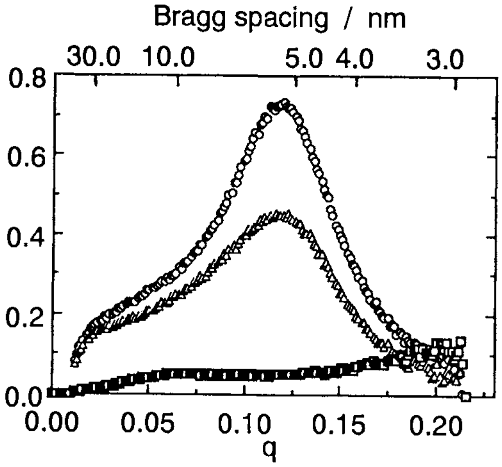

Fig. 1. Iq^2 vs. q plot of SAXS intensity for inorganic ion-form Nafion 117. (○) H^+-form, (△) K^+-form, and (□) as-received dry Na^+-form. $q = (4\pi/\lambda)\sin\theta$, where λ = wavelength in Å and 2θ = scattering angle.

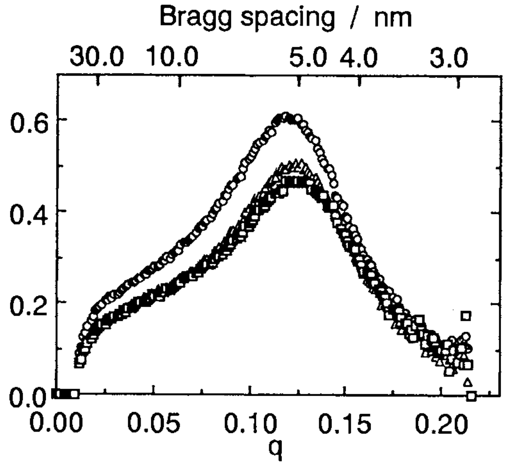

Fig. 2. Iq^2 vs. q plot of SAXS intensity for C_3V^{2+}-form Nafion 117. The counter-ion was exchanged to C_3V^{2+} immersing the H^+-form membranes in (○) 10 mM and (△) 50 mM C_3VBr_2 solutions for 5 days, and (□) in 30 mM solution for 50 days.

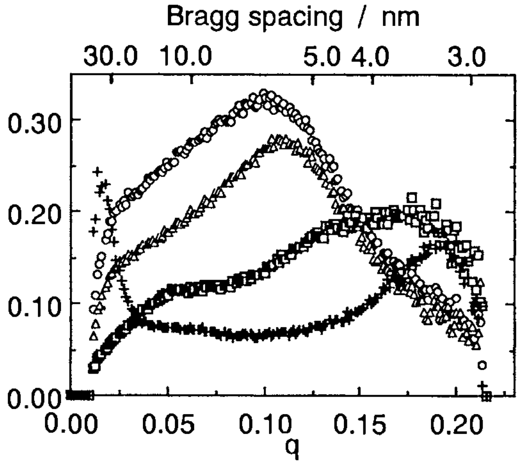

Fig. 3. Iq^2 vs. q plot of SAXS intensity for C_8V^{2+}-form Nafion 117. The counter-ion was exchanged to C_8V^{2+} immersing the H^+-form membranes in (○) 10 mM and (△) 50 mM C_3VBr_2 solutions form 5 days, (□) in 50 mM solution for 50 days, and (+) in 50 mM solution for 5 days followed by boiling for 1 h.

C_3V^{2+}- and C_8V^{2+}-form membranes also exhibited scattering maxima. This fact clearly shows the presence of the ionic clusters in these forms. For C_3V^{2+}-form membranes (Fig. 2), the Bragg spacing decreased with an increase in C_3V^{2+} concentration in the salt solution and with immersion time, although the decrease is not so significant. For C_8V^{2+}-form membranes (Fig. 3), the Bragg spacing decreased slightly with an increase in C_8V^{2+} concentration in the salt solution. On the other hand, it decreased significantly with immersion time, and after immersion for 50 days in a 50 mM salt solution a broad peak consisting of two maxima were observed, which showed that the inter-cluster distance was not uniform. The Bragg spacing further decreased after boiling for 1 h, and another sharp maximum was observed at q = 0.017 (d = ca. 37 nm) in addition to the maximum assigned to the ionic clusters. This membrane was opaque, and hence this sharp maximum is attributable to the partial crystallization of the backbone domain.[1]

The results for SAXS and water absorption measurements are summarized in Table 1 together with the treatment conditions. For the membranes incorporating inorganic cations, H^+ and Na^+, the cluster size was ranged from 4 to 5 nm, which is in agreement with the results reported by Gierke *et al.* When the counter-ion was exchanged to TEA^+, the amount of adsorbed water and the cluster size were still as large as those of Na^+-form (ca. 4 nm in diameter). The cluster size of the C_3V^{2+}-form membranes tended to decrease slightly with an increase in the concentration of C_3V^{2+} in the salt solution and with immersion time for C_3V^{2+}-form.

For C_8V^{2+}-form membranes after 5-day immersion, the Bragg spacing, i.e., the inter-cluster distance expanded to a value larger than that of H^+-form. The water content and cluster size were of the order of those of Na^+-form. After the membrane was immersed in the salt solution for 50 days or boiled for 1 h, the Bragg spacing and water content again decreased, resulting in a significant decrease in cluster size. The highly hydrophobic C_8V^{2+} cation would interact strongly with the fluorocarbon backbone domain of Nafion. Yeager and Steck[10)] have reported that a hydrophobic Cs^+ ion diffuses through the hydrophobic interfacial region located between the ionic cluster and fluorocarbon domains of Nafion. It is therefore considered that C_8V^{2+} cation resides in the hydrophobic domain of Nafion, which includes the interfacial region and even the fluorocarbon domain, as well as in the ionic clusters. This will cause structural changes of the fluorocarbon domain. Although the exact reason for the drastic change in the structure of the ionic cluster observed for C_8V^{2+}-form has not been clarified, it may be attributed to strong interactions between the highly hydrophobic C_8V^{2+} cation and the fluorocarbon backbone domain.

The above results clearly show the presence of the ionic clusters even when organic cations are incorporated in Nafion membranes. However, if strongly hydrophobic cations such as C_8V^{2+} are incorporated, the structure of the clusters will change significantly with immersion time or by boiling treatment. The model must be used carefully when highly hydrophobic cations are incorporated.

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