

High Resolution X-Ray Scattering of Ionic Clusters in Perfluorinated Ionomers

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ABSTRACT: Scattering maxima caused by ionic groups in perfluorinated ionomers such as XUS (from Dow) and Nafion[®] were obtained by finescan wide angle X-ray diffraction (WAXS), from which high resolution is achieved. Contrary to the conclusion that WAXS results of ionomers are similar for various cation forms, our diffraction results show systematic increase of scattering intensity near $2\theta = 9^\circ$ and 22° with increase of cation mass. Analysis of the spectra shows that cations must be separated by an average spacing of 11.9 Å and these ions compress the hydrophobic backbones of the ionomer so that the original peak at 17° associated with interchain distance is dispersed. In order to get a picture of the ionic cluster within ionomers consistent with current understanding, a new concept of sub ionic cluster is introduced. The results support bulk distribution of ions instead of ionic groups arranged as shell.

KEY WORDS Perfluorinated / Ionomers / X-Ray Diffraction / High Resolution / Ionic Clusters /

The structures and morphology of ionomers have long been an interesting subject.¹⁻⁷ For perfluorinated ionomers such as Nafion[®] (from du Pont) and XUS (recently from Dow), the study of structure is especially of interest because of application to electrochemical process as membrane separators or in fuel cell technology as cationic conductors. Both membranes contain polytetrafluoroethylene (PTFE)-like structures as hydrophobic backbones while cation-exchange capacity and ionic conduction are provided by terminal $-\text{SO}_3\text{H}$ groups in perfluorocarbon sulfonates ($-\text{OCF}_2-\text{CF}_2-\text{SO}_3\text{H}$) attached as pendant side-chains to the PTFE.²

Wide angle X-ray scattering (WAXS) results on Nafion[®] membrane and fibre present a broad maximum at $2\theta = 17^\circ$.^{3,4} At medium or high molecular weight ($\text{MW} > 1500$) a sharp peak developed on top of the broad maximum, having full width at half maximum (FWHM) $< 1.0^\circ$ attributed to the crystallites in PTFE. In

general, the WAXS spectra were found to be independent of the cationic form.³

In order to further investigate ionic distribution and its effect on host polymers, especially to reveal the structures of the so called "ion clusters" supported by small angle X-ray diffraction (SAXS) results,³⁻⁵ in the present report slow scan of WAXS was conducted to get high resolution scattering data on various cation forms of Nafion and XUS membranes. The same sample was used throughout the ion exchange route so that the scattering results of different ions may be compared. Analysis of the data was carried out to obtain scattering intensities attributed to cations to gain structural information.

EXPERIMENTAL

The Nafion[®] 117 (MW 1200) and XUS ionomer membranes (MW 800) were donated by du Pont and Dow Chemical, respectively.

Samples as received were about 0.1 mm thick and contained about 10 wt% water under 40% relative humidity (RH). To keep the X-ray diffraction intensities on the same relative scale so that the diffraction data of various cations would be comparable, single pieces of films of Nafion® and XUS were used throughout the experiment; that is, each film had to go through the ion exchange route of sodium, potassium and cesium by treatment in 5 M NaOH, 5 M KOH, and 5 M CsOH solutions consecutively. The cation concentrations are estimated to be *ca.* 3–5/SO₃.

A conventional wide angle X-ray diffractometer (Phillips Electronics) with a Cu-K_α target was computer interfaced and programmed for the scattering experiment. To achieve high resolution on the scattering intensity, a slow scan (up to 60 second per step, compared with usual 1 second per step) was employed so that fine, smooth data curves could be obtained.

RESULTS

The wide angle X-ray scattering intensities of Nafion® perfluorinated ionomer containing Na⁺, K⁺, and Cs⁺ were plotted against 2θ in Figure 1 with 2θ varying from 5° to 60° (up to 30° for Cs⁺ sample). Three broad maxima were observed on the curves. The peaks centered at $2\theta=9^\circ$ had a FWHM (full width at half maximum) of about 2.5°, while those positioned at $2\theta=17^\circ$ and 40° showed FWHMs of 5° and 8.5°, respectively. Contrary to the claim³ that WAXS results are similar in various cation forms of the membrane, the intensity of the lowest maxima at 9° increased with the ion mass, revealing a structural change in the presence of bigger cations. Peaks at $2\theta=17^\circ$ are lowered for heavy cations and even spread toward high 2θ values in the case of cesium, showing another effect of cation mass increase. At high scattering angles, intensities approach a common value, which can be understood by the fact that large 2θ values correspond to very small Bragg spacings to the cations. Similar

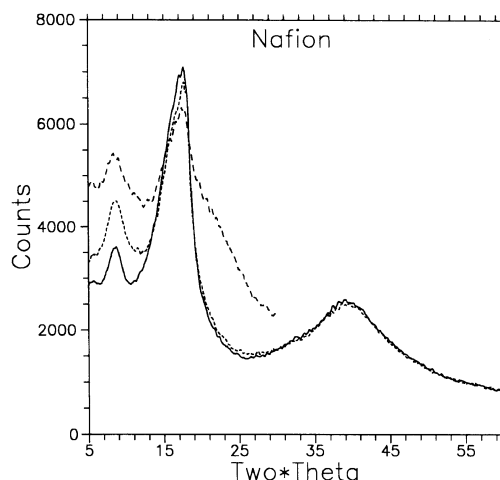


Figure 1. Wide angle X-ray scan of Nafion® containing: Na⁺ (solid curve), K⁺ (densely dashed), and Cs⁺ (sparsely dashed).

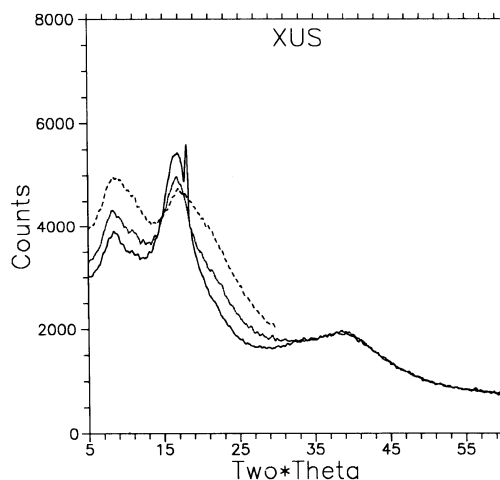


Figure 2. Wide angle X-ray scan of XUS containing: Na⁺ (solid curve), K⁺ (densely dashed), and Cs⁺ (sparsely dashed).

results were obtained from ion containing XUS membrane (Figure 2), where some spreading of 17° maximum was found for a K⁺ ion exchanged sample. A sharp crystalline peak was observed at $2\theta=18^\circ$ for Na⁺ containing sample, which was found in Nafion and well discussed in literature.³ It should be pointed out that the absence of a similar peak from Nafion membrane in the present report was

probably due to skip of the coarse steps in the X-ray scan. In all cases, the scattering pattern was confirmed to be isotropic at all sample orientations, as uniform concentric rings were observed by the photographic method of X-ray diffraction using a Flat-Film Camera (not shown).

According to the diffraction theory, X-ray scattering intensity of amorphous systems, $I(\theta)$, can be calculated and given by^{8,9}:

$$I(K) = N \langle f^2 \rangle \left\{ 1 + \int 4\pi r^2 dr P(r) \sin(Kr) / Kr \right\} \quad (1)$$

where N is total number of atoms, $\langle f^2 \rangle$ the mean square average atomic scattering factor of dissimilar atoms (ref 8, section 2.6), $P(r)$ the radial distribution function and $K \equiv 4\pi \sin \theta / \lambda$ (λ = wavelength). Fourier transformation gives:

$$4\pi r P(r) = (2/\pi) \int dK I'(K) K \sin(Kr) \quad (2)$$

with $I' \equiv I/N \langle f^2 \rangle - 1$. Since eq 1 and 2 are linear equations of $P(r)$, scattering intensity due to cations, $I_c(K)$, can be obtained by subtracting $I_p(K)$ of the polymer from total $I(K)$. This is understood by the fact that larger cations produce stronger scattering intensity related to $P_c(r)$ of cation distribution, because in these ionomer systems, very little crystallinity is involved. Hence intensities rather than amplitudes are summed. However, due to membrane hydration, it is very difficult to measure $I_p(K)$. Therefore $I(K)$ of sodium containing sample is used as a "baseline" so that I_c is studied via $I_{\text{total}} - I$ of the sodium form, as shown in Figures 3 and 4 where potassium- and cesium-containing sample scattering intensities are subtracted from those of sodium, for both Nafion and XUS, respectively.

According to eq 1 and 2, a peak in the radial distribution function $P(r)$ at r_m gives a maximum on $I(\theta)$ at certain θ_m . Higher order scattering maxima exist at larger θ but they decay much faster than those of crystalline

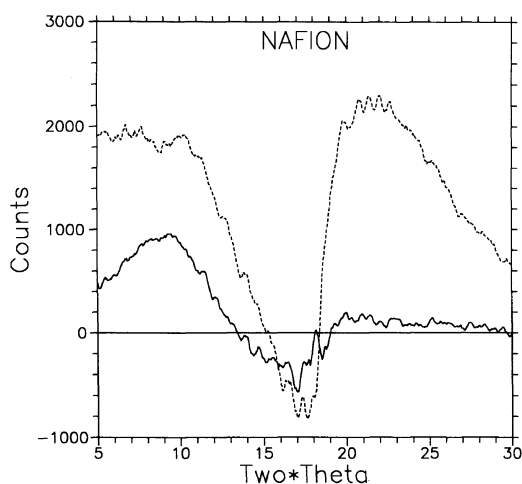


Figure 3. Wide angle X-ray scan of Nafion® of: $K^+ - Na^+$ (solid curve) and $Cs^+ - Na^+$ (dashed curve).

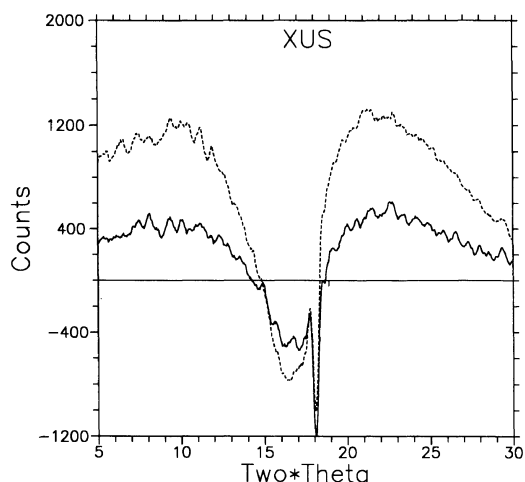


Figure 4. Wide angle X-ray scan of XUS of: $K^+ - Na^+$ (solid curve) and $Cs^+ - Na^+$ (dashed curve).

systems. Qualitative information on the radial atomic distribution function $P(r)$ can be estimated by⁸:

$$\lambda \approx (8/5) r_m \sin \theta_m \quad (3)$$

where λ is the X-ray wavelength. Therefore, the maximum at $2\theta = 9^\circ$ in Figures 3 and 4 would correspond to a peak in the radial distribution function $P(r)$ of cations at $r_m \approx 11.9 \text{ \AA}$. This peak is not likely to be higher

order scattering of the "ionic peak" found by SAXS (small angle X-ray scattering) at $2\theta = 1.6^\circ$ because it would then be at least 4th or 5th order and much weaker.

The maxima at 22° of Figures 3 and 4 are related to negative values of the intensity difference at 2θ around 17° . This major maximum at 17° ($r_m \approx 6.4 \text{ \AA}$) for Nafion and XUS was found to represent the intermolecular nearest neighbor distance for the $\text{CF}_2\text{-CF}_2$ backbones, judged by the interchain carbon distance observed in many X-ray diffraction experiments for organic liquids.⁷ The decrease of this maximum thus reveals that chain-chain distance is partially compressed by large cations such as Cs^+ or K^+ , as was found by sorption experiments.³ Dispersion of the radial distribution function $P(r)$ at r_m is reflected by increase in scattering intensity at higher 2θ values, according to eq 3. The maximum of $2\theta = 9^\circ$, however, can hardly be associated with the reduction of the major peak at 17° because expansion of hydrophobic area is not expected by introducing larger cations, since cations are always hydrated in these ionomers.¹⁻³

DISCUSSION

The results obtained by our slow-scan WAXS can be summarized as follows: 1, larger cations cause compression of the backbones (hydrophobic areas) and 2, cations are distributed with an average spacing of 11.9 \AA . While the former is not so difficult to accept, the latter poses a question when $r_m = 11.9 \text{ \AA}$ is compared with the Bragg spacing of ion clusters (d) and cation densities found for Nafion. In the literature³ the average spacing between the fixed charges (SO_3^- groups), given by $[\text{Volume of cluster/Fixed charges per cluster}]^{1/3}$, is about 6.1 \AA for K^+ and 5.6 \AA for Cs^+ (for Nafion) based on $d = 46\text{--}49 \text{ \AA}$ and d_c (cluster diameter) = $35\text{--}40 \text{ \AA}$. Obviously our r_m is too big and even bigger when more than one cation is accommodated by a sulphonic group. In fact, the cation concentration, ob-

tained by gravimetric analysis, may be 3—5 times that of the fixed charges (Donnan equilibrium). Therefore, one possible explanation for this r_m is that cations are sub-grouped within clusters and separated by an average distance of 11.9 \AA . Otherwise, if as many as a hundred cations are randomly distributed within each cluster of $45\text{--}50 \text{ \AA}$ $P(r)$ would have to peak at a spacing much smaller than the present r_m . Perhaps due to hydration shells, individual cations are not "visible" by X-ray scattering. Hence, no effect can be detected at higher 2θ values. Since higher order peaks of the same scattering spacing can only be found at larger 2θ , the proposed "sub-cluster" is probably an inevitable solution.

The present spacing is within the correct range given by $[\text{average fixed charge density}]^{-1/3}$. The present concept of cluster-sub-cluster supports the bulk distribution of cations, *i.e.*, cations are not arranged as "shells".

Our results show that the new ionomer XUS has a similar structure to that of Nafion except that the compression effect is enhanced when Na^+ is exchanged for K^+ .

CONCLUSION

Two scattering maxima caused by the ionic groups in perfluorinated ionomers such as XUS (from Dow) and Nafion[®] were obtained by fine WAXS. The lower angle peak located at $2\theta = 9^\circ$ was associated with cation groups separated by an average distance of 11.9 \AA and the other located at $2\theta = 22^\circ$ was attributed to compression effect on the hydrophobic backbones by the introduction of large cations. This compression effect also lowers the intensity of the major scattering maximum of polytetrafluoroethylene (PTFE) at $2\theta = 17^\circ$ as the main interchain distance is dispersed. The concept of cation sub-cluster is introduced to explain the new results and the present understanding of ionic cluster. The spacing is thus consistent with the calculation results from the literature

for ion cluster size and the number of ions included in cluster. Our results support the concept of bulk distribution of ions instead of ionic groups arranged in a shell.

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