NOTES

X-Ray Scattering Study of New Perfluorinated Ionomers

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XUS is a novel perfluorinated ionomer membrane developed by Dow Chemical. Besides its potential application as electrolytes in electrochemical industry, it is a promising candidate for fuel cell separators from which large current density (up to $4\,A\,cm^{-2}$) and energy density (up to $2.5\,Watt\,cm^{-2}$) were obtained.[1] While the exact method of preparation has been proprietary, the membrane involves polytetrafluoroethylene (PTFE) like backbones. Similar to Nafion,® its cation-exchange capacity and the ionic conduction are provided by the terminal $-SO_3H$ groups in perfluorocarbon sulfonates ($-OCF_2-CF_2-SO_3H$) attached as pendant side-chains to the PTFE.[2] However, its structural details and th ionic conducting mechanism remain to be explored.

The wide angle X-ray scattering (WAXS) studies on Nafion® membrane and fibre presented a broad maximum at $2\theta = 18°$.[3,4] At medium or high molecular weight (E.W. > 1500) a sharp peak developed on top of the broad maximum, having a full width at half maximum (FWHM) < 1.0°.[3] This was attributed to the crystallites in PTFE and related to the small angle X-ray scattering (SAXS) results, which served as a basis for the ionic cluster supposition.[5] The existence of the sharp line was found to be independent of the ionic form, and it diminishes in the low equivalent weight specimen.[3]

The pesent paper reports the initial WAXS study on XUS membrane. The results are compared with those of Nafion® and poly-tetrafluoro-ethylene to analyze its structure. Since the amount of crystallinity was found to be insensitive to the ionic form in Nafion® ionomer,[3-5] only H-form samples are investigated in this preliminary study.

EXPERIMENTAL

The XUS ionomer membranes (H-form) were donated by Dow Chemical. Samples as received were 0.1 mm thick and contain about 10 wt% water under 40% relative humidity (RH). The H_2O concentration variation can be achieved *via* the change of environmental RH. A conventional wide angle X-ray diffractometer (Phillips Electronics) with a $Cu(K_\alpha)$ target was employed for the scattering measurement.

To describe the three orthogonal sample orientations for the X-ray diffraction patterns, the plane normal to the scattering vector, $k_{out}-k_{in}$ (parallel to any reciprocal lattice vector), is defined as the reflection plane. The membrane was cut into $10 \times 10\,mm^2$ and was held by a special sample holder to yield three configurations on the diffractometer: one with the surface of the membrane lying in the reflection plane and the other two perpendicular positions with the scattering vector parallel

to the sample surface. In the latter cases the X-ray passes through the sample and gets diffracted.

RESULTS AND DISCUSSION

The wide angle X-ray scattering intensities of XUS perfluorinated ionomer were plotted against 2θ in Figure 1a with the surface of the membrane lying in the reflection plane. Two broad maxima were found. The one centred at $2\theta = 17°$ has a FWHM of 4.5°, while the other positioned at $2\theta = 40°$ shows a FWHM of 8.5°. Almost identical results were obtained for the cases of sample surface parallel to the scattering vector. Moreover, the scattering pattern was rather insensitive to the change of environmental humidity and was further confirmed to be isotropic in all sample orientations, as two uniform concentric rings were observed by photographic method of X-ray diffraction using a Flat-Film Camera (not shown).

These results were compared with that of Nafion® with a large molecular weight (> 1500 E.W.), where a sharp line at $2\theta = 18°$ with a FWHM $\leq 1°$ superimposed on a broad maximum was observed.[3-5] While the sharp peak was attributed to the crystallites in the PTFE backbones of Nafion,® the broad patterns of XUS membrane implies, however, that ordered structure is unlikely to exist. This is possibly caused by lower molecular weight in the new perfluorinated membrane. In fact, from data obtained the equivalent weight (E.W.) of this polymer is estimated to be less than 1000. The absence of crystallinity in XUS ionomer is further demonstrated by the discrepancy between its spectrum and the WAXS result of Teflon® composed of 100% PTFE (Figure 1b), whiere a series of sharp peaks are superimposed on a slow varying "background". These are found to be representative lines from the crystallite regions formed in PTFE. It is interesting to note that the "background" of the PTFE spectrum closely resembles the WAXS pattern of the

ionomer except that the small maximum at $2\theta = 10°$ was missing. This implies that the structure of XUS is similar to the amorphous part of PTFE.

To further investigate this similarity, X-ray diffraction was carried out for the XUS specimens subject to mechanical stretching. Without damaging the sample, a 30% of eleongation along its surface can be achieved by pulling the film in the 120°C environment. In the following, the direction of elongation will be designated as Y axis of the sample, the horizontal direction as X axis and the normal of the membrane as Z axis.

Using the same intensity scale, Figure 1c shows the X-ray scattering result of the Z axis parallel to the scattering vector, and with arbitrary X, Y orientations (because the X-ray only picks up the ordering information along the scattering vector). While the intensity of the $2\theta = 17°$ halo was reduced, the 40° halo has been diminished. Still larger changes were obtained in the X-ray diffraction pattern when the sample surface was aligned to the scattering vector. Along the Y or X axis of the stretched membrane, not only an upturn develops at low 2θ limit but also a third peak emerges from the amorphous background at $2\theta = 10°$ (Figure 1d and 1e). The latter is close in location to the missing maximum found in 100% tetrafluoroethylene spectrum (Figure 1b). Moreover, difference between Figure 1d and 1e was observed. While the information extracted by X-ray diffraction along the stretched direction (Y axis) presents reduced halo at 17° and almost zero at 40° (Figure 1d), X-ray diffraction results along X axis (Figure 1e) seems to show similar amorphous background to the unstretched sample superimposed with the additional 10° peak.

Contrary to some polymers such as stretched rubber,[6] these samples show no crystallinity peaks up to 40% of elongation, the verge of fracture.

The changes in amorphous background between Figure 1a and 1c—1e can be analyzed
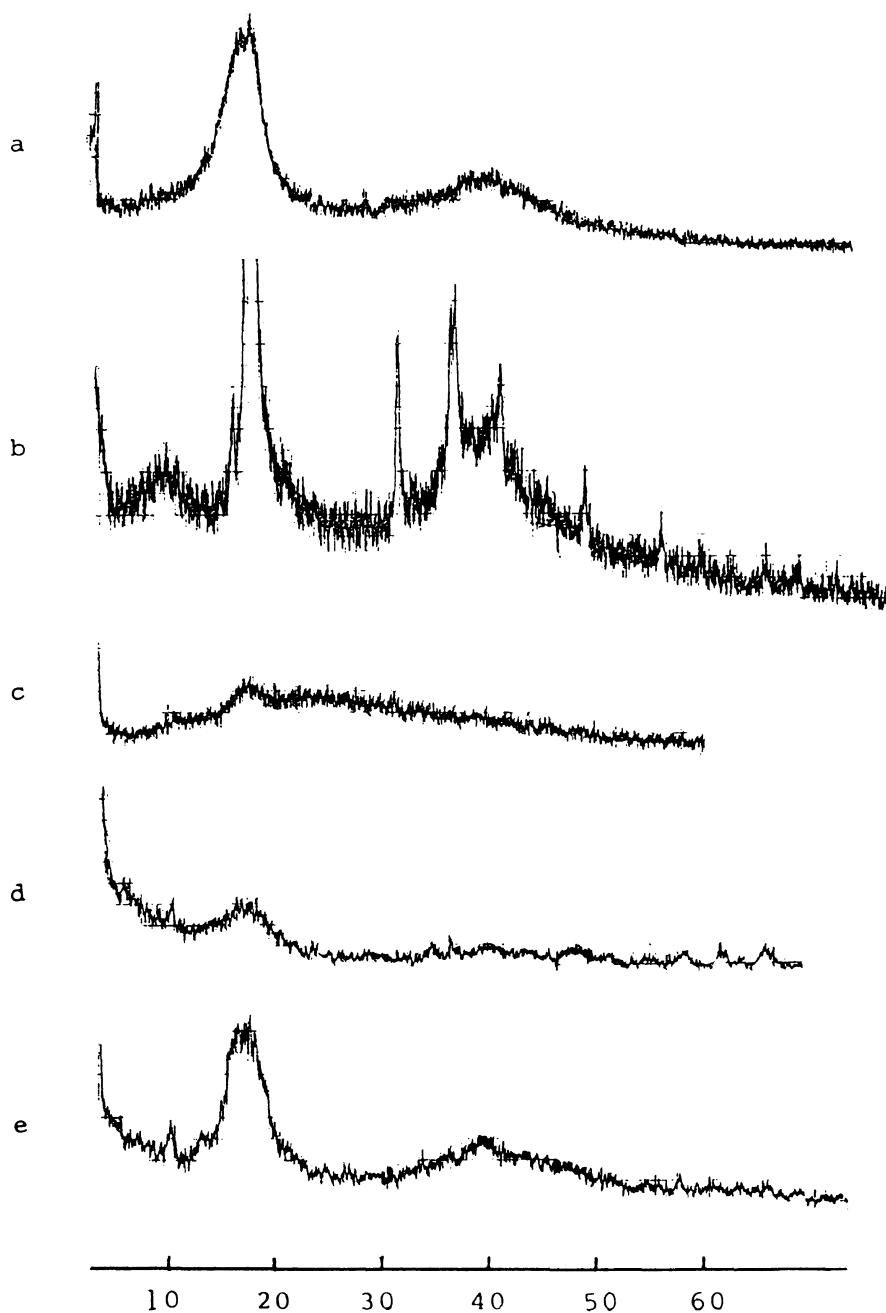
Figure 1. Wide angle X-ray scan of (with abscissa in 2θ unit): a, H-form XUS ionomer containing 10% water; b, Teflon® containing 100% PTFE; c, stretched XUS with its surface normal to the scattering vector; d, stretched XUS with its elongation (Y) direction parallel to the scattering vector; e, stretched XUS with its horizontal (X) direction parallel to the scattering vector.

in terms of redistribution of the coordination numbers between the three orthogonal directions after the sample was elongated. According to the diffraction theory, the qualitative information of the radial atomic distribution function $\rho(r)$, which presents the places where the neighboring atoms are concentrated, can be estimated by[7,8]:

$$\lambda \approx (8/5) r_m \sin \theta_m \tag{1}$$

Therefore, the maxima at $2\theta = 10°$, $17°$, and $40°$ correspond to the "peaks" in radial distribution function $\rho(r)$ at $r_m \approx 10.8$, 6.4, and 2.7Å. The major maximum at $17°$ ($r_m \approx 6.4 \text{Å}$) represents the intermolecular nearest neighbor distance, because it falls into the right order of magnitude for the interchain carbon distance that has been observed in many X-ray diffraction experiments for oeganic liquids. This is simply due to the fact that there is a fairly definite closest distance of approach of carbon atoms in different molecules.

Obviously, if certain anisotropy evolves during the elongation, the form of $\rho(r)$ will be changed accordingly and the equations given above must be modified to include the angular dependence. However, eq 1 can still be used to discuss qualitatively the corresponding changes found in different directions of scattering as it reflects the construction of the Bragg condition for the grouping of atoms the X-ray picks up. Thus the intensity difference of $17°$ maximum in Figure 1c—1e indicates that, as a result of elongation, the number of interchain atom pairs sensed by the X-ray along the scattering vector is kept constant in X direction (Figure 1e, compared with Figure 1a) and decreased both in Y (Figure 1d) and Z rection (Figure 1c). The appearance of $10°$ maximum in Figure 1d and 1e means the gathering of the atoms at 10.8Å intervals are developing along mostly the X axis. Similar structural changes apply to the upturn at lower angle where a still larger spacing is involved which is likely to be associated with the SAXS peak found near $0.9°$ for ionic cluster in Nafion®.[3] These results concerning change in coordination numbers can be related to the further exploration of the membrane structure.

It is therefore concluded that the new perfluorinated ionomer does not involve detectable crystalline states and has a similar structure to the amorphous PTFE. By 30% elongation a new maximum at $2\theta = 10°$ and an upturn at lower angle developed. These amorphous halos are analyzed by the Fourier transformation method and a qualitative picture resolved for the changes due to the stretching.

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