

Effect of solvents of perfluorosulfonic acid dispersions on polymer nanostructure of their recasting membranes

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1 Introduction

In the solvent-swollen Nafion membrane, the resulting cluster structure is formed of water pools with the ionic groups located at the polymer-solvent interface, which is embedded in the perfluorinated sulfonic acid polymer matrix. These solvent-swollen clusters are closely related to the ionic conductivity. The modification of the proton exchange membranes (PEMs) with solvent effects has been recently reported. It is important to note that the ionic clusters are formed in the nano-size of the aggregates. Small-angle X-ray (SAXS) spectroscopy is one of the most efficient techniques to study the nanostructure of the phase-separated polymer materials with the unique advantages of a nondestructive way and easy sample preparation. [1] In this report, SAXS techniques are used to investigate the effect of solvents of dispersions on the nanostructure of perfluorinated sulfonic acid polymer based membranes, which is closely related to its proton conductivity. In addition, SAXS spectra are quantitatively analyzed to investigate the nanostructure of the phase separated clusters (or aggregates) with solvents, which are very important for developing high-performing and high-durable PEMs for fuel cells.

2 Experiment

SAXS was used to investigate micro-phase separation of cation conductive ionomer dispersed in various solvents. The SAXS measurements were performed at intervals during the drying stage of the film forming process at BL-6A in Photon Factory. The X-ray wavelength was 0.15 nm, the sample-to-detector distance was 2 m and the scattering intensity was measured using Pilatus 3. Nafion D521 dispersions were prepared by dispersing Nafion D521 in different solvent media such as N-methyl-2-pyrrolidone (NMP). Membrane recasting was carried out to completely evaporate the solvent at 80 °C for 24 hours under vacuum.

3 Results and Discussion

Figure 1 shows the SAXS spectra of cation-conductive recast membranes dispersed in various solvents at room temperature. We have confirmed the relationship of ion transport behavior, membrane fundamental characteristic,

and change of bulk-phase morphology of radiation-grafted membranes as represented in Figure 2. The Nafion D521 membrane prepared by Nafion D521 dispersion which is based on alcohol solvents show that its ion-domain distance was measured as 4.83 nm(wet) and 3.88 nm(dry). It results in an increase in distance between the ionic domains, compared to the NMP used membrane to 6.52 nm(wet) and 4.27 nm(dry). Ion-domain distance was calculated by Bragg's Law ($d = 2 \pi/q$). These results show that ion-domain distance is highly dependent on solvents used in dispersions.

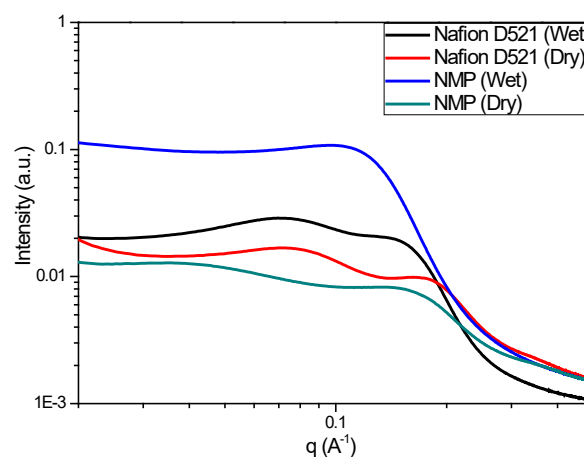


Fig. 1: SAXS profile of the wet and dry Nafion D521 membranes and the wet and dry recast Nafion membrane in NMP.

Table. 1: Summary of q maximum values and domain distance of the samples

Sample name	Nafion D521 (Wet)	Nafion D521 (Dry)	NMP (Wet)	NMP (Dry)
q max (\AA^{-1})	0.1302	0.16184	0.09644	0.1471
Domain distance (nm)	4.83	3.88	6.52	4.27

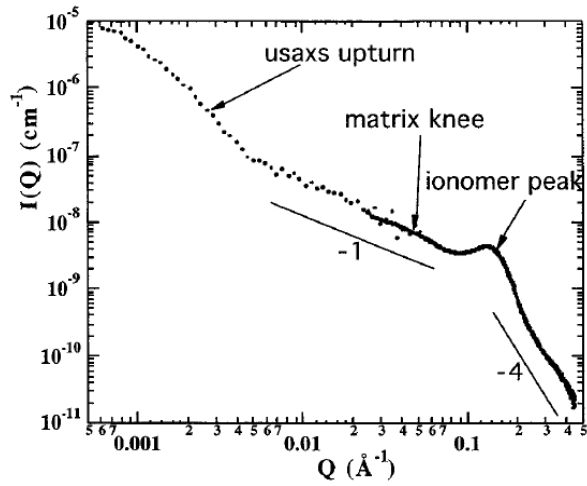


Fig. 2: A log-log representation of a typical SAXS spectrum from a swollen Nafion 117 film.

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References

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