IN-SITU SAXS ON A PERFLUOROSULFONATE IONOMER

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Title (PFS) ionomers are TFE co perfluorovinyl -ether (Nafion®) copolymers, with <15 mole % of comonomer terminated in sulphonic acid exchange sites. Sulfonate groups segregate forming ion rich clusters. Standing questions pertain to cluster shape and their behavior on swelling and deformation. Electron density contrast of clusters vs. matrix gives rise to a SAXS peak. A proposed network model of spherical clusters [1] has been challenged [2]. This network model invokes a non-reversible process to explain the reversible linear dependence of the SAXS d-spacing on swelling. In contrast, there is ample evidence for polar sulfonic acid domains that are locally planar and parallel [2]. Such morphology would explain naturally the linear swelling behavior. The high propensity for this material to orient has not been explained satisfactorily either. Anisotropic SAXS patterns obtained on uniaxial deformation have been explained in terms of spherical cluster elongation and orientation [3]. But, orientation of lamellar/cylindrical domains could instead be the responsible mechanism. We have performed swelling/stretching in-situ-SAXS of extruded PFS ionomer membranes. 1. Uniaxial deformation measurements confirmed the strong orientation propensity of this material. Measurements were performed along orthogonal orientations of the film (TD/SN, MD/SN, TD/MD) before and after uniaxial deformation. The results suggest that the morphology consists of oriented cylindrical domains, or oriented lamellar domains which are disordered in the plane normal to the deformation axis. 2. Dried membranes were allowed to hydrate under atmospheric humidity and SAXS data were collected in-situ. The specific surface was observed to increase and then to decrease with time. The ratio of the maximum to the stable value at high times is about what is expected for a spherical to lamellar domain transition. 3. A sample was saturated with water by boiling, quickly oriented in the beam, and data were collected as the sample equilibrated with atmospheric humidity. A sharp equatorial peak moved progressively to larger angles as drying progressed, as expected for oriented lamellar domains. 4. A simultaneous SAXS/WAXS/deformation experiment was performed in which the correlation of orientation of the ionic and crystalline domains was probed. The results indicate that the orientation of the two types of domain occur simultaneously, which is very likely the consequence of a close association between these.

[1] T. D. Gierke et al, J. Polymer. Sci. Polymer Physics Ed. 19, 1687 (1981).
[2] Litt, Morton H., Polym. Prepr, 38, 80-81 (1997.)
[3] K. M. Cable et al Polym. Prepr. (1994), 35, 421-2.