Structure Analysis of Sulfonated Block Copolymers by Contrast Variation Small-angle Scattering

Yamamoto, M. Inukai

Dept. of Life Sci. and Appl. Chem. Nagya Institute of Technolory Institute of Technology

Small-angle X-ray and Neutron Scattering (SAXS & SANS) has been used for structural analysis of block copolymers. Both enable the analysis of structures on a scale ranging from several nanometers to hundreds of nanometers, providing statistical structural information as opposed to the localized structural observation obtained by electron microscopy. However, while scattering methods have been widely utilized as one of the techniques for structural analysis of polymer materials, it is challenging to analyze complex structures such as multicomponent systems. For example, in the case of the 〈A-b-(B-co-C) type〉 shown in Figure 1, it is possible to analyze the phase separation between A and B, C components, but it is difficult to analyze how the C component is distributed within the B component. Therefore, for the structural analysis of multicomponent polymer materials, a method that measures while altering the scattering contrast of each component is used. In the case of X-rays, by utilizing the energy dependence of the atomic scattering factor through anomalous dispersion effects, structural information related to specific atoms can be extracted.

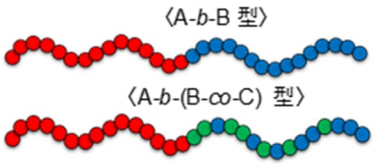

Figure1 Schematic diagram of block copolymer（Red: A, Blue: B, Green: C

In this study, sulfur was used for the C component in the 〈A-b-(B-co-C) type〉. Sulfur is included in many functional and important materials such as “Nafion,” essential for fuel cells. Furthermore, polymer materials like electrolyte membranes used in fuel cells are often in a hydrated state, and thus, analysis under conditions where water is incorporated is required. In this study, we aimed to extend the scattering experiments to include hydrated environments, targeting structural analysis under conditions similar to those used in real-world applications.

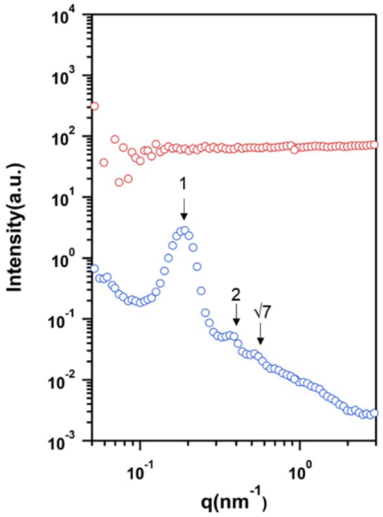

Figure 2. SANS profiles of SMA (red: dry state, Blue: in heavy water).

SANS measurements were conducted on the sample, poly(styrene-co-sulfonated styrene)-*b*-poly(methyl acrylate) (SMA), in both dry and hydrated (heavy water) states. SANS profiles are shown in Figure 2. Since the samples used were composed entirely of hydrogen, the microphase-separated structure, even if present in the dry state, was not observed with neutron scattering. However, in the neutron scattering measurement conducted in a heavy water environment, the use of heavy water created a difference in scattering ability, which provided scattering contrast and resulted in significant differences in the SANS profile. From these results, it is inferred that the water in the hydrated state is not uniformly distributed but is segregated at the locations of the styrene sulfonic acid. Moreover, the fact that the *q*-values of the peaks had a ratio of 1:2:√7 indicates the formation of a cylindrical structure, with an inter-lattice spacing of 33.03 nm. This result was consistent with the SAXS data.