Investigation on nanostructure in a block copolymer film having sulfonic acid groups

Kozo Matsumoto, Shuji Kage, and Hideki Matsuoka
Department of Polymer Chemsitry, Kyoto University

Nanostructure in a block copolymer film having sulfonic acid groups, which can be applicable for a proton conducting polymer electrolyte membrane for a fuel cell, was investigated by small angle neutron scattering (SANS).

A cross-linkable block copolymer, poly(styrene-co-4-(1-methylsilacyclobutyl)styrene)-b-poly(neopentyl styrenesulfonate) (poly(St-co-SBS)-b-polySSPen), was precisely synthesized by a nitroxy-mediated living radical polymerization. The degrees of polymerization for poly(St-co-SBS) and polySSPen were estimated to be 136 and 61, respectively. The molar ratio of St/SBS was determined to be 0.9/0.1. A cross-linked film with free sulfonic acid groups, poly(St-co-SBS)-b-polySSH, was obtained by casting a toluene solution of the block copolymer with a platinum catalyst and heating it at 230 degree C.

Neutron scattering experiments on the dry polymer film and wet polymer film in deuterium oxide were performed by SANS-U. Strong neutron scattering was observed in the small angle region in both samples, indicating that some kinds of nanostructure were formed in the block copolymer films. The SANS profile for the dry sample was reproduced well by applying a hard sphere model (Figure A), which suggested that spherical domains (12.5 nm in radius) were randomly distributed in the film. On the other hand, the profile for the wet sample was reproduced by adapting Fournet model (Figure B), which suggested that interaction between neighboring two spherical domains existed. The domain radius and the mean distance between the neighboring domains were evaluated as 14nm and 18nm, respectively. We can reasonably understand these results if we consider that the spherical polySSH domains existed in a matrix composed of poly(St-co-SBS) and that the polySSH domain was swollen by deuterium oxide in the wet sample.

The proton conductivity of the block copolymer film has been already examined and it was found that the film possesses high conductivity that is comparable to a well-known sulfonic acid containing membrane Nafion produced by Dupont.

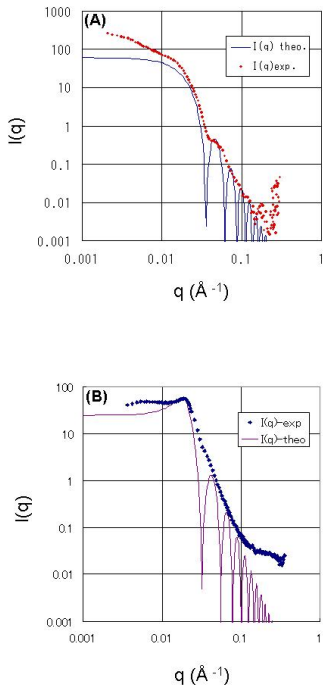

Fig. 1. Figure (A) SANS experimental and fitting profiles for dry block copolymer film; Figure (B) SANS experimental and fitting profiles for the wet block copolymer film in deuterium oxide.