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Communications

Morphology Effect of Sulfonated Triblock Copolymers for Water Retention and Proton Conductivity at High Temperature

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Introduction

Control of ion transfer paths in ion conducting polymers is an important factor in increasing efficiency in a variety of applications such as the use of ion exchange resins, sensors, secondary batteries, and fuel cells.¹ In particular, the fuel cell has recently gained attention as a promising candidate in generating environmental-friendly energy because of its direct energy conversion by electrochemical reactions.² For this application, many researchers have tried to increase efficiency by designing catalysts, electrodes, proton exchange

membranes (PEMs), etc. Among these components in the fuel cell, the PEM has a direct relationship with the increase of proton conductivity because the ionic channel formed in the PEM matrix creates a proton migration path from the anode to the cathode.³ The most famous PEM, Nafion[®], a perfluorosulfonic acid polymer, has been known to give sufficient proton conductivity, as well as good chemical and mechanical stability under 80 °C. However, it suffers from a decrease of proton conductivity and mechanical stability at high temperature, probably due to dehydration in the ionic channel.⁴ Among various alternative proton conducting polymers such as polyarylene, polyimide, polyphosphazene, polystyrene-based copolymer, etc., a block copolymer is an interesting candidate for use in overcoming such problems at high temperatures,⁵ because the hydrophilic domain (ionic channel) and hydrophobic domain (non ionic matrix) can be controlled by the self assembly of the block copolymer. This is achieved through the control of the molecular weights of the hydrophilic and hydrophobic block segments.⁶ Recent studies using these block copolymers, including sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) and sulfonated poly(styrene-*b*-[ethylene-*co*-butylene]-*b*-styrene poly(styrene-*isoprene*) etc., showed that the proton conductivity was strongly affected by morphology and ionic channel size.⁷ For example, the Balsara group recently reported that a cylinder structure with a narrow ionic domain size in sulfonated poly(styrene-*b*-methyl butylene) was important in keeping the water in the membrane at a high temperature.⁸ However, these polystyrene-based block copolymers may lack dimensional stability at high temperature (~120 °C) due to their lower glass transition temperature (~105 °C) and degradation via the elimination of the alpha-proton in the backbone due to radicals that are generated by the actual operation of the fuel cell.⁹

In this paper, poly(alpha-methyl styrene) was introduced to the block copolymer because of its high glass transition temperature (~170 °C) and the prevention of degradation by the alpha-methyl group in the backbone. Thus, the well-defined sulfonated poly(alpha-methyl styrene-*b*-isobutylene-*b*-alpha-methyl styrene) [poly(alphaMeSt-*b*-IB-*b*-alphaMeSt)] was used to examine the effect of the morphology, especially cylinder

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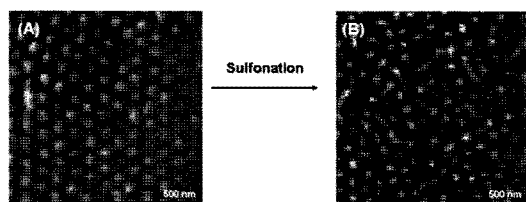


Figure 1. AFM images of poly(α MeSt-*b*-IB-*b*- α MeSt)s before sulfonation (A) and after sulfonation (B).

structure, for water retention and proton conductivity at high temperatures.

Results and Discussion

Well defined sulfonated poly(α MeSt-*b*-IB-*b*- α MeSt) was prepared by sequential living cationic polymerization followed by post sulfonation with acetyl sulfate.¹⁰ The triblock copolymer that was obtained showed an average molecular weight of 20,400 (M_n), with 1.12 of the molecular weight distribution (M_w/M_n) and 18% of the volume fraction of the α MeSt block segment. SAXS and AFM analyses determined that the morphology showed a cylindrical structure (Figures 1 and 2).

Control of sulfonation in the α MeSt block segment was achieved by changing the amount of acetyl sulfate, which gave almost 35% of the sulfonation efficiency, probably due to the mild sulfonation condition with acetyl sulfate and the precipitation in organic solvents during sulfonation. Water uptake with these sulfonated triblock copolymers increased as the sulfonation level and the swelling time increased. For example, 34% of the sulfonated triblock copolymer swelled to 90 wt% of water over 70 h.

Figure 1 shows AFM images of the triblock copolymers before and after sulfonation. The cylindrical structure remained after 18% of the sulfonation of the α MeSt block segment, although the hexagonal array was a little collapsed, which indicated that the ionic channel could be formed in the α MeSt block domain without any morphological change. SAXS profiles of the block copolymers, however, showed slightly unclear long range ordered peaks in the cylindrical structure; this was probably due to differences in the samples, which were film and bulk in AFM and SAXS analysis, respectively. Furthermore, the domain size of P α MeSt (18.6 nm) increased after sulfonation, which was probably due to the increase of the volume fraction by the introduction of the sulfonic acid groups into the α MeSt block segment (4.2 nm) (Figure 2(A)). The domain size of the sulfonated block copolymer with 34% of the sulfonation of P α MeSt was further increased after swelling with water (21%, w/w), from 22.8 to 25.6 nm. This indicated that the water was incorporated into the cylinder's ionic channel. This water-swollen sulfonated block copolymer was then examined for mor-

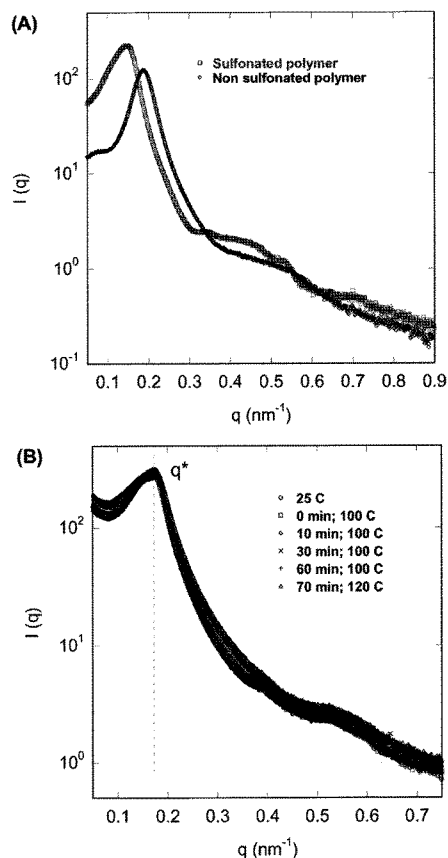


Figure 2. SAXS profiles of poly(α MeSt-*b*-IB-*b*- α MeSt) before and after sulfonation (A) and water-swollen sulfonated block copolymers as a function of time at different temperatures (B).

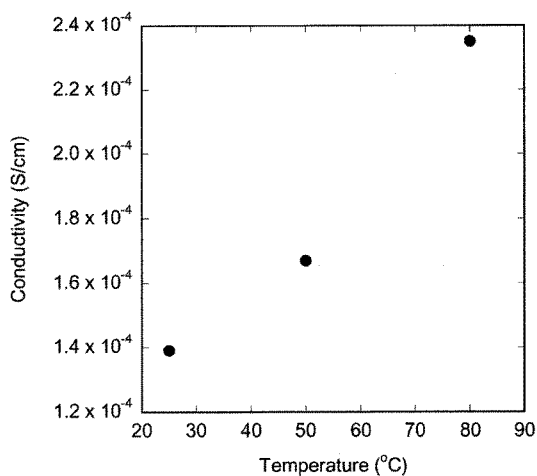


Figure 3. Proton conductivity results for sulfonated poly(α MeSt-*b*-IB-*b*- α MeSt) at different temperatures.

phological change at different temperatures by SAXS analysis (Figure 2(B)).

The q^* of the peak at 25 °C did not change, although the temperature was increased to 100 °C for 60 min and 120 °C for additional 10 min, which indicated that the water-swollen cylinder diameter did not change even above the boiling point of water. This result showed that the water was retained in the cylindrical ionic channel at such temperatures for at least 1 h without dehydration. This is probably due to the capillary condensation effect of the narrow ionic channel formed in the cylinder structure: water vapor is condensed into the narrow channel to form liquid water. Since water is indispensable for proton transfer in the membrane, it shows the possibility of operating fuel cells at high temperatures. Preliminary proton conductivity at different temperatures was determined using an AC impedance analyzer (frequency range: 1 Hz–8 MHz), which showed that there was a remarkable increase in proton conductivity for temperatures up to 80 °C, although the values of the proton conductivities as a whole were very low in comparison to Nafion® (Figure 3).

In summary, this study successfully demonstrated that morphology control in PEM is important for retaining the water as a liquid in the ionic channel and increasing proton conductivity at high temperatures with well defined cylindrical sulfonated poly(α MeSt-*b*-IB-*b*- α MeSt). More detailed examinations of proton conductivity, as well as the thermal, chemical, and mechanical stability of the α MeSt-based block copolymers with various volume fractions will be discussed in forthcoming papers.

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