Novel proton exchange membrane based on polyhedral oligomeric silsesquioxane(POSS)-poly(methyl methacrylate) (PMMA)-b-sulfonated polystyrene(PS)

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Proton exchange membrane（PEM） plays an important role in transportation of proton between anode and cathode and isolation of electrons and fuel, thus is regarded as the core component in proton exchange membrane fuel cells. Among the many types of matrix of PEM, Nafion still dominate the research and market in this field due to its higher conductivity below 90℃and excellent chemical stability[1]. However, a high cost and a sharp decline of proton conductivity due to loss of water content are the two main limitations for further development of Nafion. A kind of proton exchange membrane with higher tolerance of higher temperature and lower humidity will be a promising PEM material.

Block copolymer is becoming one of the most promising candidates for proton exchange membranes applications owing to two distinguish advantages. Microphase separation or well-defined nanostructures will be easily formed via self-assembly of block copolymers. For the block copolymer containing ionic groups, proton conductivity is guaranteed by ionic microdomains, and the mechanical strength of membranes is attributed to nonionic microdomains[2].

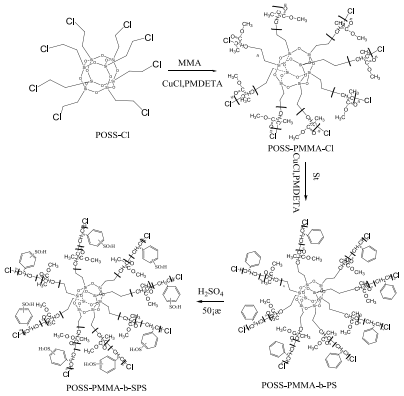

Figure 1. Synthesis scheme of polyhedral oligomeric silsesquioxane(POSS)-poly(methyl methacrylate(PMMA)-b-sulfonated polystyrene(PS)

Polyhedral oligomeric silsesquioxane is a class of well-defined and highly symmetric hybrid silsesquioxane with an excellent compatibility between organic and inorganic molecules and combing their advantages as well[3]. The hybrid organic-inorganic nanostructure of POSS show extremely high performance on thermal and chemical stability, and tethered reactive groups are proved to introduce determined molecules to perform functional properties such as self-assembly, biocompatible, photooxidative resistance materials and extreme rigid environment applications.

In this work, a serious of eight-arm POSS-poly(methyl methacrylate(PMMA)-b-sulfonated polystyrene(PS) block copolymer with different block length(1:1 ,1.5:1 and 2:1) were synthesized. In specific, PMMA grafting on a polyhedral oligomeric silsesquioxane worked as macroinitiator, and polystyrene was copolymerizaed on POSS-PMMA via Atom Transfer Radical polymerization (ATRP) and related proton exchange membrane were prepared through solution casting after post sulfonation of POSS-PMMA-b-SPS . The block copolymers with different block length of PMMA and PS were attained by controlling the molar ratio.

After the analysis of Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance(NMR), the desired structures of star-shaped block copolymers are obtained. The molecular weight and molecular weight distribution of the copolymer(block length ratio 1:1) was analyzed by GPC, and M_n and M_w are 61990 and 151536, respectively. A proper water uptake value could be tailored by SPS block length. Indeed, depending on different SPS block length, the membrane shown an excellent water preservation property under higher temperature and the maximum water uptake of copolymer could achieve to 150wt% under 100℃. Proton conductivity is measured by through plane conductivity measurement and reaches 1.8×10^{-2} S/cm at room temperature 100% relative humidity.

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