

트리블록 공중합체와 HPA를 도입하여 제조된 수소이온 전도성 복합전해질막

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Proton Conducting Composite Polymer Electrolyte Membranes Comprising Triblock Copolymer and Heteropolyacid

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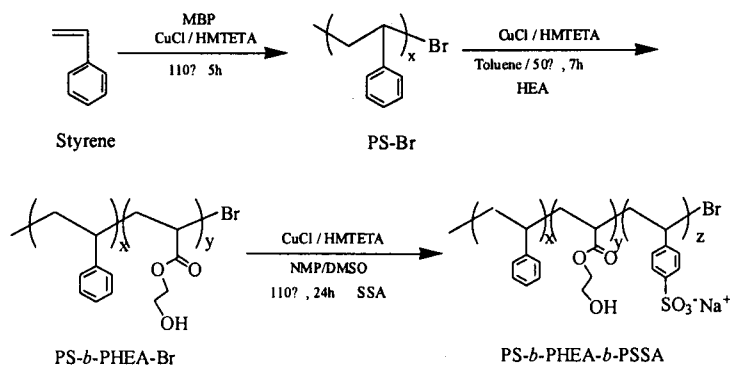
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1. Introduction

PS-*b*-PHEA-*b*-PSSA at 28:21:52 wt% was synthesized via atom transfer radical polymerization and solution-blended with a commercial HPA. Upon the incorporation of HPA to tBC, both the symmetric stretching bands of SO_3^- at 1187 cm^{-1} and the $-\text{OH}$ groups at 3440 cm^{-1} in pristine tBC shifted to lower wavenumbers at 1158 and 3370 cm^{-1} , respectively. These FT-IR band shifts suggest that the HPA particles strongly interact with both the sulfonic acid groups and the hydroxyl groups in PSSA and PHEA domains of the copolymer, respectively. The proton conductivity of the composite membranes increased from 0.048 to 0.065 S/cm at room temperature up to 0.2 weight fraction of HPA.

2. Experimental

The schematic diagram illustrating the synthesis triblock copolymer electrolyte is presented in Scheme 1. The synthesis was carried out in three steps: (1) synthesis of the PS-Br macroinitiator, (2) synthesis of the PS-*b*-PHEA-Br diblock copolymer, and (3) synthesis of the PS-*b*-PHEA-*b*-PSSA triblock copolymer.



Scheme 1. Synthetic procedure for the PS-*b*-PHEA-*b*-PSSA triblock copolymer.

The as-synthesized tBC soaked in 0.5N H₂SO₄ at room temperature for 15h. The proton-exchanged tBC was thoroughly washed with deionized water. It was then dried in a vacuum oven at room temperature for 24 h. The acidic tBC and the desired amount of HPA in weight ratios of 9:1, 8:2, 7:3, 6:4, 5:5, and 4:6 were dissolved in DMSO together. After complete dissolution, the polymer solutions were cast onto a glass dish.

3. Result and discussion

The FTIR spectra of the composite polymer electrolyte membranes are presented in Figure 1. The symmetric stretching of SO₃⁻ was observed at 1187 cm⁻¹ in the pristine tBC. Upon blending with HPA, the stretching band shifted to a lower wavenumber of 1158 cm⁻¹, indicating that the sulfonic acid moiety interacts with the HPA particles. Neat HPA exhibited absorption bands at 1075, 974, 904, and 804 cm⁻¹, attributed to the stretching vibrations of P-O, W=Ot (Ot is the terminal oxygen), W-Oc-W (corner-shared octahedral), and W-Oe-W (edge-shared octahedral), respectively[1]. When the tBC was combined with HPA, the stretching vibrations of P-O and W=Ot were hardly changed. On the other hand, the stretching vibrations of W-Oc-W and W-Oe-W shifted to 894 and 821 cm⁻¹, respectively. These results indicate that hydrogen bonding interaction takes place between the bridging oxygens in the HPA molecules and the sulfonic acid (SO₃H).

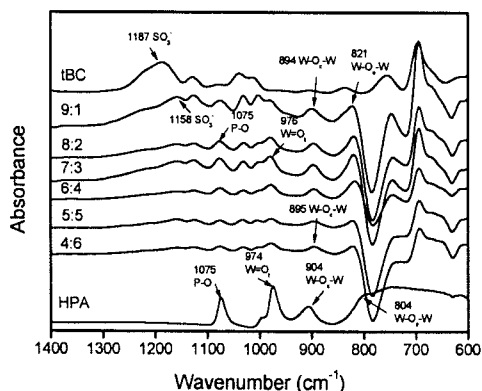


Figure 1. FTIR spectra of the composite polymer electrolyte membranes comprised of tBC and HPA in varying weight ratios.

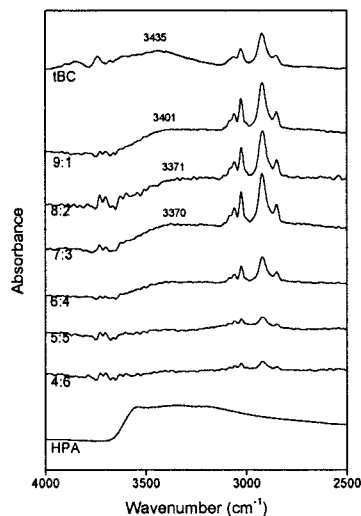
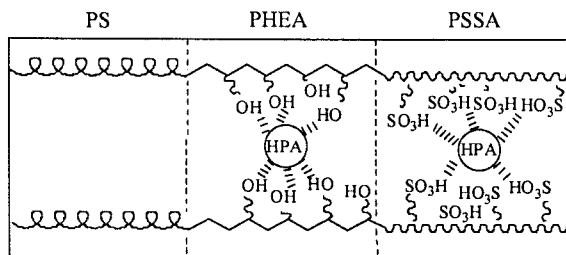


Figure 2. FTIR spectra of the hydroxyl regions.

The hydroxyl groups ($-OH$) of the PHEA domains may be involved in the hydrogen bonding interactions in the composite polymer electrolyte membranes. Figure 2 shows the FTIR spectra of the hydroxyl regions. The $-OH$ stretching band at 3435 cm^{-1} continuously shifted to a lower wavenumber, down to 3370 cm^{-1} , with increasing amounts of HPA. It is thus demonstrated that HPA molecules interact with hydroxyl groups ($-OH$), as well as the sulfonic acid (SO_3H) in the PSSA domains, through hydrogen bonding interactions. The resulting schematic structure of the tBC and HPA composite polymer electrolyte membranes is illustrated in Scheme 2.



Scheme 2. Schematic structure of the composite membranes.

The conductivity results were compared with those obtained from Nafion 117 in Figure 3. The proton conductivity increased with increasing amounts of HPA up to a weight fraction of 0.2, after which it continuously decreased. It is interesting to see that the proton conductivity increased with HPA content, even though the water uptake decreased. This behavior can presumably be attributed to two factors: (1) the intrinsic conductivity of the HPA particles and (2) the enhanced acidity of the sulfonic acid in the tBC matrix caused by HPA incorporation[1]. The continuous decrease of proton conductivity above 0.2 may result from the loss of ionic sites (SO_3). The loss of ionic sites is presumably because of the strong hydrogen bonding interaction between the sulfonic acid and the HPA particles[2].

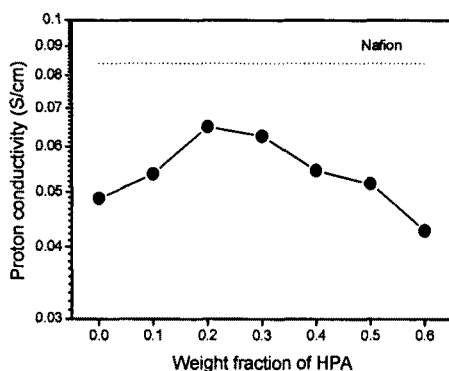


Figure 3. Proton conductivity of the composite polymer electrolyte membranes comprised of tBC and HPA in varying weight fractions of HPA.

4. References

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