

Synthesis and Membrane Formation of Sulfonated Hyperbranched Polyimides for Fuel Cell Applications

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Introduction

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) have attracted much attention in the past decade because they provide cleaning, quiet and portable power for vehicular transportation and for other applications. One of the key components of a PEMFC is the polymer electrolyte membrane (PEM). From viewpoint of practical use, it is essential to develop PEMs with high proton conductivity and membrane durability. To achieve high proton conductivity, high ion exchange capacities (IECs) are generally needed. However, too high IEC often causes excessive swelling or even dissolution in water and thus lose mechanical strength. Cross-linking is a common and effective method to enhance the mechanical properties, to suppress membrane swelling ratio and to improve the membrane durability. On the other hand, the PEMs developed so far are almost limited to linear polymers. Quite few hyperbranched polymers have been reported to use as PEMs. Considering that hyperbranched polymers possesses many unique properties such as well-defined three dimensional architecture, a large number of terminal groups which may be used for further chemical modification such as covalent cross-linking, and many accessible cavities which absorb/accommodate guest molecules such as water, sulfonated hyperbranched polymers might be a novel type of PEMs with super performance to their linear analogues. In this presentation, a series of sulfonated hyperbranched polymers are synthesized and their membrane formation and properties are also reported.

Experimental

A novel dianhydride monomer, 9,9-fluorylidenebis(4,1-phenylene)bis(oxo)-4,4'-bis(1,8-naphthalenedicarboxylic anhydride) (FBPNA), was synthesized by reaction of 4-bromo-1,8-naphthalenedicarboxylic anhydride and 9,9-(4-hydroxyphenyl)fluorene in DMAc in the presence of potassium carbonate at 160 °C for 20 h. An amine-terminated six-membered ring type of hyperbranched polyimide (HBPI) was synthesized by polymerization of FBPNA (A_2 monomer) and tris(4-aminophenyl)amine (TAPA, B_3 monomer) in *m*-cresol in the presence of benzoic acid and isoquinoline at 180 °C for 20 h. The resulting HBPI was further chemically modified with an end-capping reagent, 4-phenoxy-1,8-naphthalic anhydride (PNA), to give PAN-end-capped polymers (HBPI-PANs). Post-sulfonation of the HBPI and the HBPI-PANs at 50 - 70 °C using sulfuric acid as the sulfonating reagent produced various sulfonated hyperbranched polyimides (SHBPI and SHBPI-PANs). Proton conductivity was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 100 Hz to 100 KHz (Hioki 3552) at 0% relative humidity at different temperatures.

Results and Discussion

Usually a hyperbranched polymer can be synthesized by polymerization of an AB_2 or A_2+B_3 type of monomers [1]. In this study, the amine-terminated HBPI was synthesized via the A_2+B_3 method at the monomer molar ratio of FBPNA/TAPA = 1:1 (**Fig. 1**). Here, the dianhydride FBPNA was used as the A_2 type of monomer, while the triamine TAPA was used as the B_3 type of monomer. It was found that

as the monomer (FBPNA + TAPA) concentration was controlled below 4 w/v% no gelation phenomenon was observed. The resulting HBPI is well soluble in *m*-cresol and 1-methylpyrrolidone (NMP) but insoluble dimethylsulfoxide (DMSO) or *N,N*-dimethylacetamide (DMAc). The HBPI was further chemically modified with the end-capping reagent PAN based on the reaction between the anhydride groups of the PAN and the terminal amino groups of the HBPI to give various hyperbranched polyimides (HBPI-PANs) with varied contents of the residual amino groups (75% and 50%). Post-sulfonation of the HBPI and the HBPI-PANs using concentrated sulfuric acid as the sulfonating reagent resulted in sulfonated hyperbranched polyimides (SHBPI and SHBPI-PANs, **Fig. 2**). Under the optimal sulfonation conditions (50 °C, 24 h), the sulfonation reactions underwent smoothly without significant polymer degradation. Sulfonation led to significant improvement in polymer solubility. The SHBPI and SHBPI-PANs could be dissolved in most aprotic solvents such as DMSO, DMAc, *N,N*-dimethylformamide (DMF) and NMP.

It is well known that hyperbranched polymers generally show poor film-forming ability due to lack of polymer chain entanglement. However,

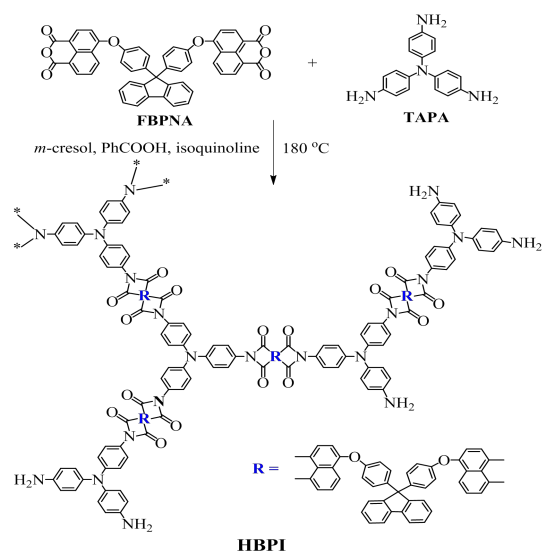


Fig. 1 Synthesis of the amine-terminated HBPI.

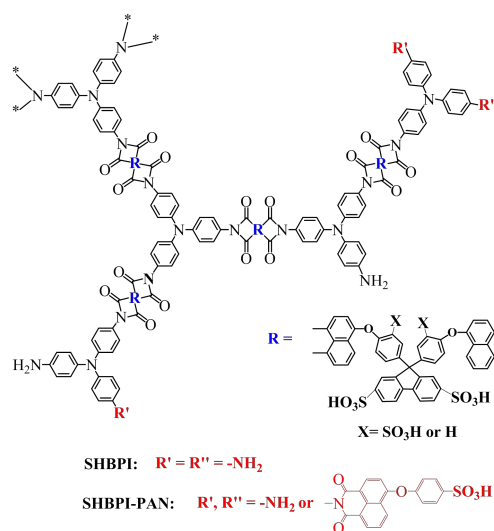


Fig. 2 Chemical structure of the SHBPI and SHBPI-PAN.

hyperbranched polymer membranes may be formed if cross-linking is properly conducted during the process of solution cast [2]. In the present study free-standing membranes (CSHBPI and CSHBPI-PANs) with reasonably good mechanical strength (25-50 MPa) have been successfully prepared by covalent cross-linking of the residual amino groups using bisphenol A epoxy resin (BADGE) as the cross-linker. The CSHBPI and CSHBPI-PAN membranes showed high heat resistance, good oxidative stability and high proton conductivity. The dependence of proton conductivity of the membranes on temperature in deionized water is shown in **Fig. 3**. It can be seen that for all the membranes the proton conductivity increases as the temperature increases. The CSHBPI-PAN50 membrane displayed the highest proton conductivity due to the highest IEC (2.21 meq/g). In the whole temperature range the proton conductivity of the CSHBPI-PAN50 membrane is higher than that of Nafion 112. The dependence of proton conductivity of the membranes on relative humidity (RH) is shown in **Fig. 4**. For all the membranes, the proton conductivity decreases rapidly as the RH decreases especially in low RH range. This is because at low RH there might be no enough

water molecules as carrier for proton transport. Such a phenomenon has been observed with many other sulfonated polymer membranes. However, it should be noted that The CSHBPI-PAN50 membrane still exhibited higher proton conductivities at low RHs than many linear sulfonated polyimide membranes with similar IEC values. This indicates that the hyperbranched architecture is likely favorable for improving the proton conductivity at low RHs. Fenton test (80 °C, 3% H₂O₂ + 3 ppm FeSO₄) results showed that the τ_1 values of CSHBPI and CSHBPI-PANs were about 60 min indicating relatively good radical oxidative stability of the membranes. Further studies on fuel cell performance of these membranes are in progress.

Conclusions

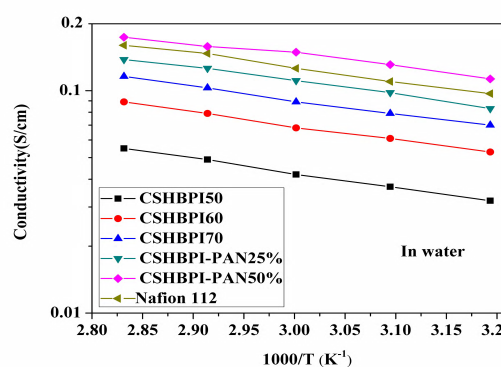


Fig. 3 Variation of proton conductivity of various series

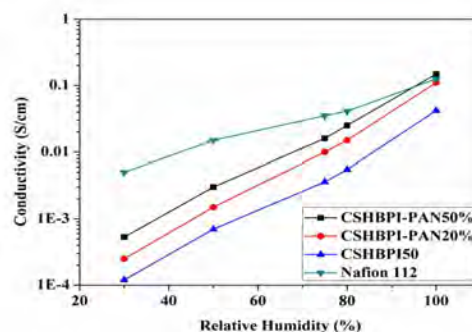


Fig. 4 Variation of proton conductivity of various membranes at 60 °C as a function of RH.

of novel sulfonated hyperbranched polyimides have been successfully synthesized by condensation polymerization of FBPNA (A₂) and TAPA (B₃) in *m*-cresol in the presence of benzoic acid and isoquinoline at 180 °C followed by chemical modification with PAN and post-sulfonation. The sulfonated hyperbranched polyimide membranes with reasonably good mechanical strength have been successfully prepared by covalent cross-linking of the residual amino groups using bisphenol A epoxy resin as the cross-linker. These membranes exhibited high proton conductivity and relatively good chemical stability.

Acknowledgement

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References

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