A study of the nitrogen-containing heterocycles on copolyimide properties for proton exchange membranes

Yuhan Li[a, b], Rui Lei [a, b], Lianxun Gao[a]

李玉邯[a, b]，雷瑞[a, b]，高连勋[a]

[a] State Key Laboratory of Polymer Physics and Chemistry,

Changchun Inst. of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

a 中国科学研究院长春应用化学研究所，高分子物理与化学重点实验室，中国，长春 130022

[b] Graduate School of Chinese Academy of Sciences, Beijing, 100049, China

b 中国科学研究生院，中国，北京 100049

Abstract:

Containing pyrimidine and pyridine monomers were incorporated respectively into the main chain of a sulfonated polyimide in order to investigate the effect of nitrogen-containing heterocycles on membrane properties such as water uptake and proton conductivity. With increasing content of the nitrogen-containing heterocycles, water uptake of membranes and dimensional changes remarkable decrease. Reduce the water uptake is primarily because of the reduction of IEC. On the other hand, the nitrogen groups in the heterocycles interact with sulfonic acid group and decrease the amount of free sulfonic acid group vailable to form hydrogen bond with water molecules. Hence, the amount of water molecules absorbed by the membranes remarkable decreased with increase in heterocyclic content. The copolymer showed higher thermal stability (desulfonation temperature up to 330 °C) and reasonable good mechanical properties. These membranes also showed higher proton conductivity, which was comparable or even higher than Nafion 117. Especially, The SPI-1 membrane with 60 mol % pyrimidine is found to have an increase in proton conductivity despite a decreased IEC value, which is contrary to typical behavior. However, the SPI-2 membrane with 60 mol % pyridine is not found this phenomenon. We think that pyrimidine (Py) is a heterocyclic molecule containing two N atoms, allowing it to pick a proton on one N and deliver the H from the other N site. When Py content to a certain value, it may promote the proton conduction. This may be one of the reasons for their different proton-conducting performance and the detailed studies are in progress. These results may be important in the design of proton conducting membranes from other polymer.

Keywords: Sulfonated polyimide; Nitrogen-containing heterocycles; pyrimidine group; pyridine.

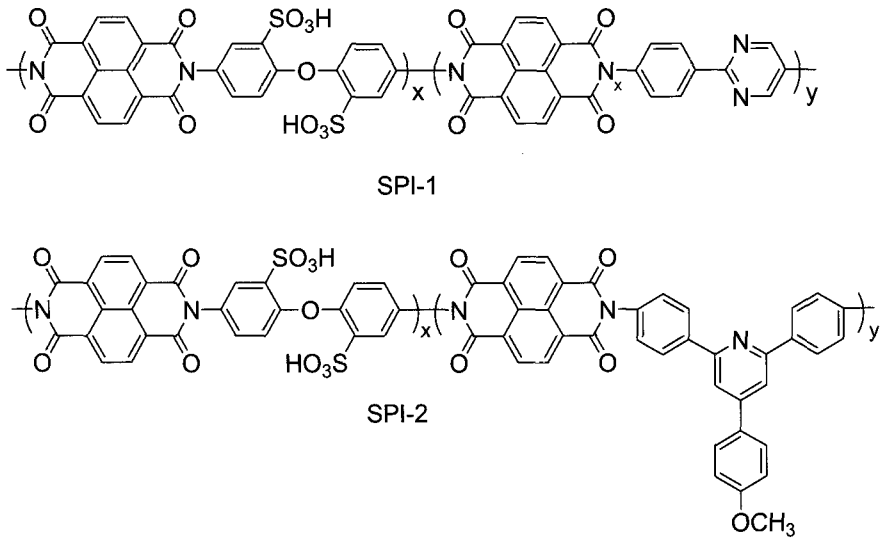

Fig. 1. Chemical structures of SPI-1 and SPI-2

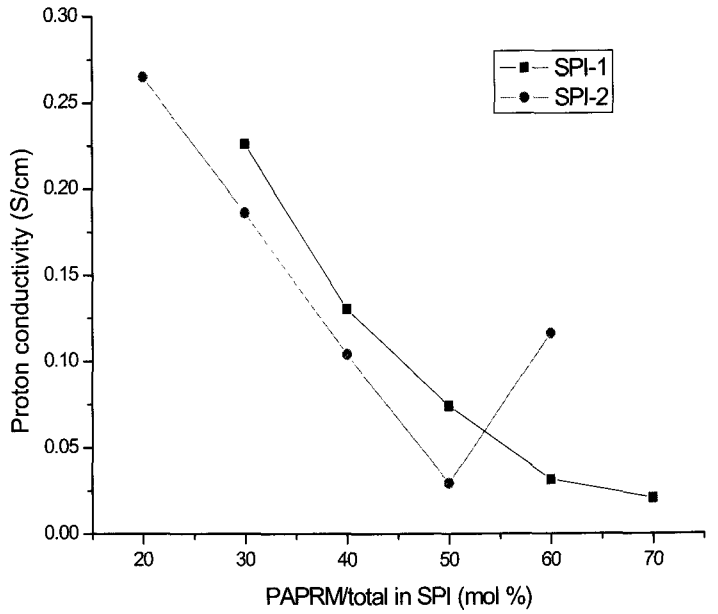

Fig. 2. Conductivity of the membranes with various mole percents of heterocycles