Solid State NMR Studies of Proton Conducting Polymer, Poly(vinyl phosphonic) acid

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Introduction
Various materials have been investigated in order to develop high temperature proton exchange membrane fuel cells. Polymers containing poly(vinyl phosphonic) acid segments are promising candidates to be used as proton conducting membranes. Knowledge concerning the chemical environment and proton motion is crucial to understanding the conduction mechanism in these materials. Solid state NMR spectroscopy is an ideal probe for investigating the molecular level because it allows us to selectively investigate the motion of interest. In this paper, we apply solid state NMR methods to study poly(vinyl phosphonic) acid (PVPA).

Experimental
Sample preparation. PVPA was synthesized in water by radical polymerization of vinyl phosphonic acid using 2,2-dimethoxypropane (DMP) as an initiator at 80°C. The product was analyzed and dried under vacuum. The weight averaged molecular weight Mw of PVPA was determined to be 74,280 g/mol by light scattering.

Solid State NMR. 1H and 31P magic angle spinning (MAS) NMR experiments were carried out at 700.13 MHz for 1H and 202.49 MHz for 31P on a Bruker Avance 700 and DRX 500 spectrometer, respectively. 1D and 2-dimensional DQ and DQ magic angle spinning (MAS) spectra were recorded with rotor synchronized back-to-back (BADB) pulse sequence. All spectra were acquired at spinning speeds of 20 kHz and 30 kHz pulse length was set to 3.5 μs.

Results and discussion
1H MAS NMR spectrum of PVPA shows two major resonances at 2.3 and 10.5 ppm which are assigned to the poly(vinyl backbone protons (CH2 and CH) and P=O protons, respectively (Figure 1a). A large shift in high frequency of P=O indicates that there is a strong hydrogen bonding between phosphonic acid groups. 31P MAS NMR spectrum of PVPA is dominated by a resonance at 33 ppm, resulting from phosphonic acid group (Figure 1b). A weak resonance is also observed at 25 ppm as a shoulder to the major resonance. The resonance at 25 ppm increases in intensity for material annealed at 150°C. Thus, we assign this resonance to condensed phosphonic acid groups. In 31P MAS NMR, a loss of signal intensity from P=O protons is observed for annealed samples. This is consistent with the loss of P=O proton due to hydrogen bond condensation.

In order to probe mobility of PVPA, 1H double quantum (DQ) experiment was performed. DQ signal is observed from backbone, while DQ signal is not observed from P=O proton. The absence of DQ signal is due to weak dipole-dipole coupling between protons. This indicates fast motion of P=O proton. Variable temperature NMR experiments also provide information on molecular dynamics. As the temperature increases, the resonance of P=O decreases in line width due to motional narrowing. Since the line width is related to the exchange rate, the activation energy can be deduced from line width at various temperature. An activation energy value of 25 kJ/mol is observed for P=O motion. A slightly higher activation energy is obtained from deuterated PVPA (selectively deuterated at P=O site). This is probably due to the isotope effect, resulting from Grothuss type hopping process.

31P 2D DQ spectroscopy reveals the information about the spatial proximity between different phosphonic acid groups (Figure 2). Autocorrelation signals among phosphonic acid pairs and condensed acid pairs, respectively, are observed along the diagonal, indicating each acid and proton is in close contact with each other among themselves. The DQ cross peak involving phosphonic acid and condensed acid is observed as well. This suggests that there is no phase segregation between regular phosphonic acids and condensed phosphonic acids. Below room temperature, an additional 1H signal at 15 ppm is observed. This high frequency signal appears to be related with condensation.

Figure 1. (a) 1H MAS NMR spectrum of PVPA (b) 31P MAS NMR spectrum of PVPA.

Figure 2. 31P 2D double quantum spectrum of PVPA.

Conclusions
Solid state NMR showed that poly(vinyl phosphonic) acid provides conductivity resulting from P=O proton through hydrogen bonding. However, PVPA suffers from the phosphonic acid condensation which reduces proton conductivity. This condensation occurs randomly throughout the material without phase separation.

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