

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

Young Joo Lee¹, Bahar Bingöl¹, Tatiana Murakhtina¹, Daniel Sebastiani², Jong Hwa Ok², Wolfgang H. Meyer¹, Gerhard Wegner¹, Hans Wolfgang Spiess^{1*}

¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

²Analytical Science Center, LG Chem Research Park, 104-1, Moonji-dong, Yuseong-gu, Daejeon, 305-380, Korea
leey@mpip-mainz.mpg.de
spiess@mpip-mainz.mpg.de*

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 of proton motion on the molecular level because it allows us to selectively investigate the nuclei 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'-Azobis(isobutyroic acid amide) dihydrochloride as an initiator at 80 °C. The product was dialyzed and then dried under vacuum. The weight averaged molecular weight M_w of PVPA was determined as 74280 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 202.45 MHz for ³¹P on a Bruker Avance700 and DSS500 spectrometer, respectively. 1-dimensional and 2-dimensional DQ ¹H and ³¹P MAS spectra were recorded with rotor-synchronized back-to-back (BABA) pulse sequence. All MAS NMR spectra were acquired at spinning speeds of 30 kHz and 90° pulse length was set to 2.5 μs.

Results and discussion

¹H MAS NMR spectrum of PVPA shows two major resonances at 2.3 and 10.6 ppm, which are assigned to the polyvinyl backbone protons (CH₂ and CH) and P-OH protons, respectively (Figure 1a). A large shift to high frequency of P-OH 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 the material annealed at 150 °C. Thus, we assign this resonance to condensed phosphonic acid groups. In ¹H MAS NMR, a loss of signal intensity from P-OH protons is observed for annealed sample. This is consistent with the loss of P-OH proton due to phosphonic acid 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 obtained from P-OH proton. The absence of DQ signal is due to weak dipole-dipole coupling between protons. This indicates fast motion of P-OH protons. Variable temperature NMR experiments also provide information about molecular dynamics. As the temperature increases, the resonance of P-OH decreases in line width due to the motional narrowing. Since the line width is related with exchange rate, the activation energy can be deduced from line width at various temperature. An activation energy value of 25 kJ/mol is obtained for P-OH motion. A slightly higher activation energy is obtained from deuterated PVPA (selectively deuterated at P-OH site). This is probably due to the isotope effects resulting from Grotthuss type hopping proton.

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 moiety is in close contact with each other among themselves. The DQ cross peak involving phosphonic acid and condensed acid is obtained 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.

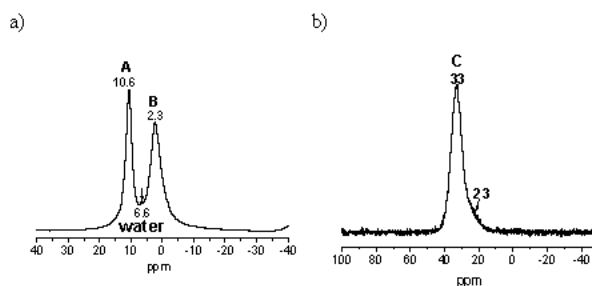


Figure 1. (a) ¹H MAS NMR spectrum of PVPA (b) ³¹P MAS NMR spectrum of PVPA.

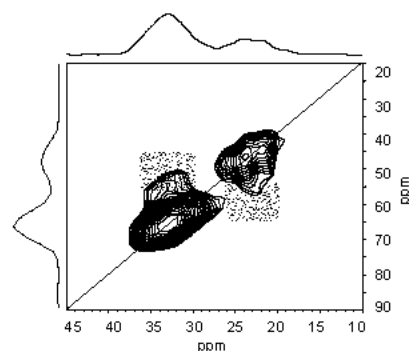


Figure 2. ³¹P 2d double quantum spectrum of PVPA.

Conclusions

Solid state NMR showed that poly(vinyl phosphonic acid) provide conductivity resulting from P-OH proton through hydrogen bonding. However, PVPA suffer from the phosphonic acid condensation which reduces proton conductivity. This condensation occurs randomly throughout the material without phase separation.

References

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