DOI: 10.1002/masy.200750421

^{31}P Solid-State NMR Characterization of Poly(vinylphosphate-*black*-styrene) for DMFC Membrane

Tae-Joon Park,[1] Sang Hun Kim,[2] Guang Hua Li,[2] Chang Gi Cho,[2] Yongae Kim[1]*

Summary: In an attempt to develop direct methanol fuel cell (DMFC) membrane with low methanol permeability, we synthesized successfully poly(vinyl phosphate-b-styrene) copolymers from poly(vinyl alcohol-b-styrene) by reaction with phosphorus oxychloride and subsequent hydrolysis. We obtained the ratio of the differently bound phosphorus by ^{31}P Solid-state NMR Spectroscopy because the majority of block copolymer is not soluble or does not make homogeneous solution in a NMR solvent. The total amount of acid groups as well as the ratio of singly and doubly bound phosphorus by ^{31}P Solid-state NMR and pH titration was slightly different due to the cross-linked nature of the sample. Therefore, solid-state NMR spectroscopy is the most powerful technique to characterize cross-linked polymers like DMFC membrane.

Keywords: block copolymers; NMR; solid-state NMR spectroscopy; structure

Introduction

We synthesized successfully poly(vinyl phosphate-b-styrene) (PVPP-b-PS) copolymers from poly(vinyl alcohol-b-styrene) (PVA-b-PS) by reaction with phosphorus oxychloride and subsequent hydrolysis.[1–3] Poly(vinyl phosphate-b-styrene) copolymers and their blend membrane with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were used to develop direct methanol fuel cell (DMFC) membrane with low methanol permeability.[4] ^{1}H and ^{31}P solid-state NMR spectroscopy were used to obtain the ratio of the singly and doubly esterified phosphorus because the inter- and intra-chain cross-linked block copolymers are not soluble in NMR solvents. As in Figure 1-A, an intra-chain reaction generate a divalent 6-membered ring which can be considered to be more stable than singly esterified phosphoric acid, and the polymer with this structure can be soluble in a solvent. But inter-chain reactions will generate a crosslinked structure which is insoluble in a solvent as in Figure 1-B. In a reaction for a high content of phosphate group containing polymer, inter-chain reaction is unavoidable, and this makes difficult the characterization of the resultant polymer by simple pH titration. We analyzed the PVPP-b-PS copolymers qualitatively and quantitatively by ^{1}H and ^{31}P Solid-state NMR spectroscopy.

Experimental Part

PVPP-b-PS block copolymers were prepared from the corresponding PVA-b-PS block copolymers as we described before.[1–3] First, PVAc-Cl was prepared by telomerization of vinyl acetate by using CCl_4 as a telogen. The PVAc-Cl was used as a macro-initiator in the living radical polymerization of styrene, and the obtained block copolymer was converted into PVA-b-PS by saponification. Figure 2 shows the ^{1}H solution NMR spectra of a) PVA-b-PS-10k in DMSO-d_6 and b) PVAc-Cl in $CDCl_3$. The molecular characteristics of

---

[1] Department of Chemistry, Hankuk University of Foreign Studies, Yongin, Korea
E-mail: yakim@hufs.ac.kr
[2] Department of Fiber & Polymer Engineering, Hanyang University, Seoul, Korea

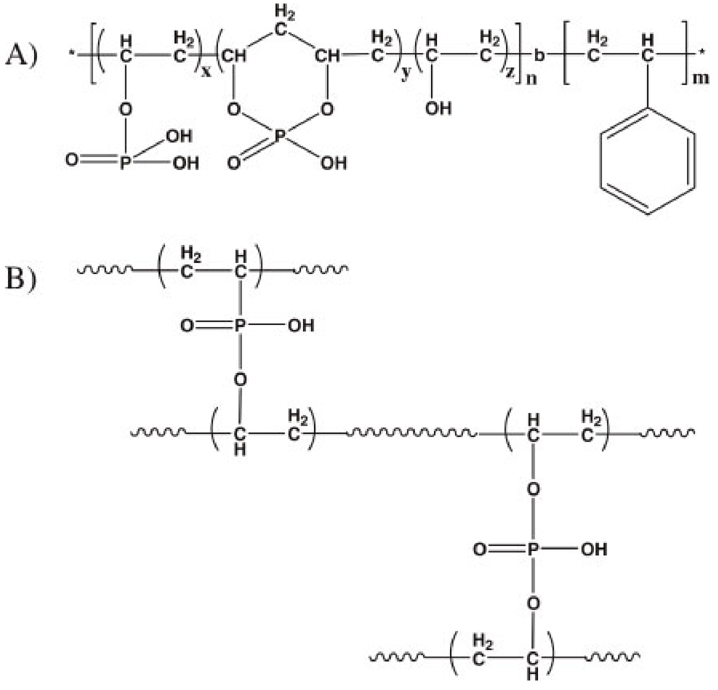

Figure 1.
Structures of PVPP-b-PS of A) singly bound phosphorous and doubly bound phosphorous in intrachain, and B) doubly bound phosphorous in interchain are shown.

PVA-b-PS are shown in Table 1. It shows the molecular weights of the PVA block and PS blocks. The molecular weights of PS blocks were determined by ^{1}H NMR in DMSO-d_6 solvent by comparing the integral ratio of aromatic and aliphatic resonance peaks. And that of PVA block was determined by ^{1}H NMR in $CDCl_3$ solvent from its precursor, PVAc-Cl, of which degree of polymerization (DP) is 94. The data shows that PS molecular weight by NMR matches very well with theoretical one based on monomer conversion.

NMR Characterization

Phosphorus content of the block copolymers was determined by phosphorus solid-state nuclear magnetic resonance spectroscopy using 9.4 Tesla unity INOVA wide bore NMR spectrometer (VARIAN, USA) operating at a ^{31}P NMR frequency of 161.89 MHz and a ^{1}H NMR frequency of 399.92 MHz using $(NH_4)H_2PO_4$ as an external chemical shift standard at 0 ppm. PVPP- b-PS samples were ground with a mortar and pestle, and then were packed with $Ca_3(PO_4)_2$ as an internal standard for quantitative analysis in a 4 mm ZrO_2 rotor. A double-resonance 4 mm CPMAS probe (VARIAN, USA) was used. All of the measurements were taken at room temperature. High-Power Decoupling (HPDEC)[5–7] measurements on PVPP-b-PS were carried out at Magic Angle Spinning (MAS)[8–11] frequencies of 15 KHz. The magic angle was set using the ^{79}Br resonance of KBr. HPDEC sequence were used to generate ^{31}P magnetization at a field of 71.4 KHz with a proton radio frequency irradiation of 55.6 KHz. Proton decoupling was accomplished with continuous-wave decoupling. The total signal averaging times were approximately 3 hours using a recycle delay of 20 s. The amount ratio of singly and doubly bound phosphorus shown in Figure 1 and the total amount of

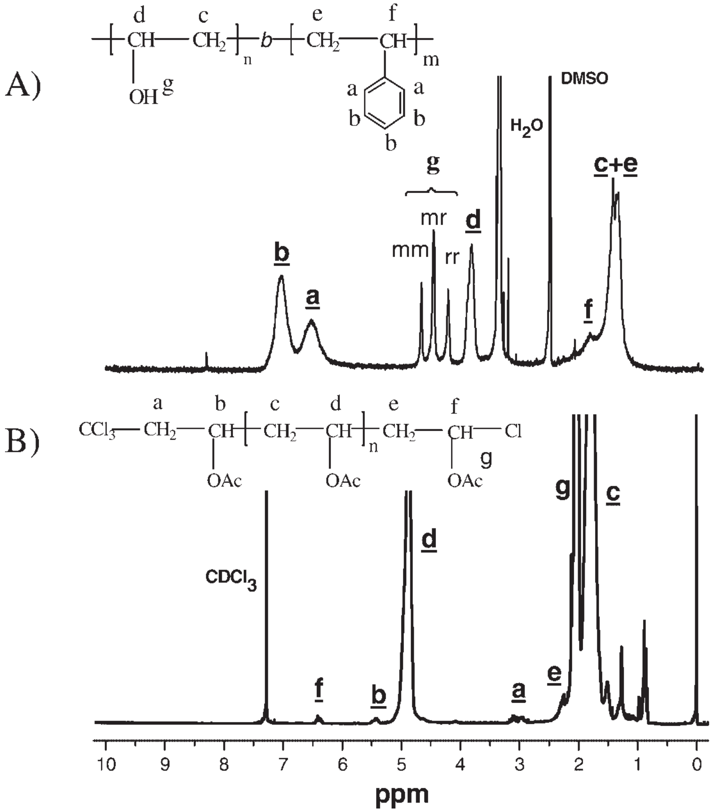

Figure 2.
^1H solution NMR spectra of a) PVA-b-PS in DMSO-d_6, and b) PVAc-Cl in $CDCl_3$.

phosphorus were calculated after a deconvolution of the HPDEC spectra using WINNMR (BRUKER, Germany).

Results and Discussion

Figure 3 shows the ^1H solid-state NMR spectra of PVPP-*b*-PS-10k and PVPP-b-PS-5k with $Ca_3(PO4)_2$ as an internal standard for a quantitative analysis. PVPP-*b*-PS-5k was a dark-brown crystalline state and PVPP-b-PS-10k was a reddish brown powder form by external appearance. ^1H solid-state NMR spectrum of PVPP-*b*-PS-5k shows sharp alkyl and acidic proton resonances near 1–3 ppm and sharp benzyl resonance near 7–9 ppm. ^1H solid-state NMR spectrum of PVPP-*b*-PS-10k also shows alkyl proton resonance and acidic

Table 1.
Characterization results of PVA-b-PS and PVPP-b-PS.

PVA	PS		PVPP				Sample
$M_{n,\ NMR}$[a]	$M_{n,\ th}$[b]	$M_{n,\ NMR}$	^{31}P NMR		pH titration		
			Mono/divalent	P wt%[c]	1st eq.point (ml)	End point(ml)	
4140	11730	11440	44.8/55.2	5.94	4.95	7.80	PVPP-*b*-PS-10k
	5240	5510	39.8/60.2	5.29	7.03	10.80	PVPP-*b*-PS-5k

[a] Calculated from DP of PVAc-Cl determined by ^1H-NMR;
[b] $M_{n\ ,th} = [St]/[PVAc\text{-}Cl] \times 104 \times$ Conversion (%);
[c] Calculated from the deconvoluted spectrum of the ^{31}P solid-state NMR.

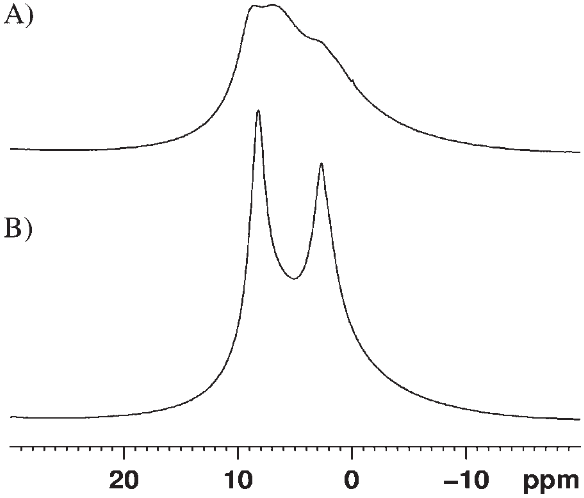

Figure 3.
^{1}H solid-state NMR spectra of A) PVPP-b-PS-10k and B) PVPP-b-PS-5k using $Ca_3(PO4)_2$ as an internal standard are shown. Magic angle spinning speed is 15 kHz.

proton resonances and benzyl proton resonance but they are broad. Amorphous solids are randomly oriented to magnetic field so that they showed very broad lines for solid-state NMR spectroscopy. However, rigid crystalline solids are well ordered and have remarkably narrow lines for solid-state NMR spectroscopy. From the ^{1}H solid-state NMR spectra, we found out the crystallinity of the block copolymers which is a distinctive feature of solid-state NMR spectroscopy. That is, PVPP-b-PS-5k has relatively higher order of crystallinity than PVPP-b-PS-10k.

^{31}P Solid-state NMR was utilized to distinguish and obtain the amount of singly and doubly esterified groups. Figure 4 shows the ^{31}P solid-state NMR spectra which containing PVPP-b-PS-10k and PVPP-b-PS-5k with $Ca_3(PO4)_2$ as an internal standard for a quantitative analysis. The signal at 1.6 ppm was assigned to the resonance of $Ca_3(PO4)_2$, and the signal at -1.7 ppm to that of singly bound phosphorus, finally the signal at -6.4 ppm to that of doubly bound phosphorus. The assignment was based on the chemical shift sequences of structural units of polyphosphoric acid in polybenzimidazole fuel cell membrane.[12] From the deconvoluted ^{31}P solid-state NMR spectra, it was possible to calculate the amount ratio of singly and doubly bound phosphorus and the total amount of phosphorus. Phosphorous content and the ratio of the monovalent to divalent phosphorous of PVPP-b-PS-10k are 5.94 wt% and 44.8/55.2. And phosphorous content and the ratio of the monovalent to divalent phosphorous of PVPP-b-PS-5k are 5.29 wt% and 39.8/60.2.

Table 1 shows the summary of the characterization results of PVPP-*b*-PS block copolymers by ^{31}P Solid-state NMR as well as by titration. For the conversion of singly esterified to doubly esterified phosphate by either intra- or inter-molecular reaction one water molecule is eliminated for each case. Based on the assumption that the intra-molecular 6-membered ring is the major structure, and the inter-molecular reaction is very minor, one can calculate the value of x, y, and z in Figure 1a) by using the total weight % of the P and the relative ratio of mono/divalent P. Degree of polymerization of PVPP block is needed for this calculation. Calculated values are listed in Table 2. Also from the listed values, it is possible to calculate theoretical weight

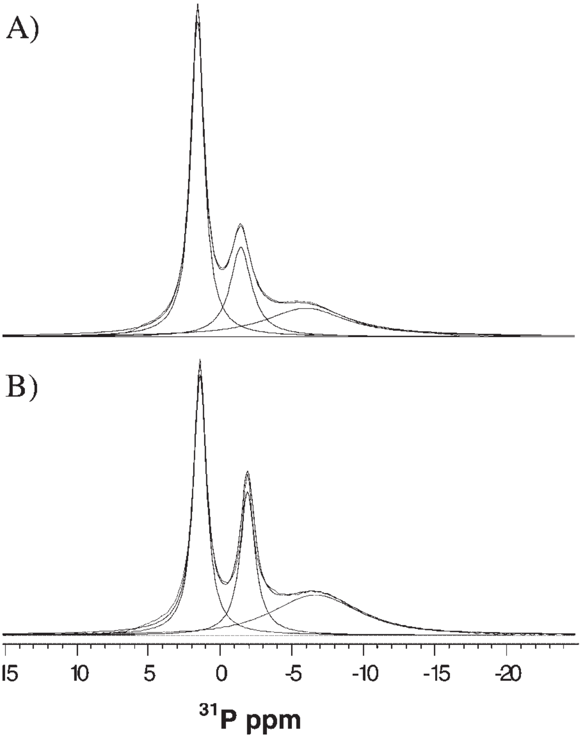

Figure 4.
^{31}P Solid-state NMR spectra of A) PVPP-b-PS-10k and B) PVPP-b-PS-5k using $Ca_3(PO4)_2$ as an internal standard.

increase by phosphorylation. The value is 15.5%, 13.3%, and the experimental values were 19.4%, and 32.0%, respectively, as in the Table. The values do not show good matches, due to incomplete hydrolysis of the phosphoryl chloride.[1]

Similar calculations can be made by using the titration results. Titration can give the information on the total amount of acid groups and the ratio of the singly and doubly esterified phosphorus groups, by the total consumption of the base titrant and inflection points in the pH titration curve, respectively, as in the titration curve of PVPP-b-PS-10k as in Figure 5. The curve is typical of that of a dibasic acid. The first portion of the curve represents the first acid group of the singly esterified material and the single acid group of the doubly esterified material as shown in Figure 1.[13] The result is shown in Table 1, and the calculated x, y, z values are listed in Table 2. The differences of weight % increase in the theoretical and the observed in Table 2 can

Table 2.
Microstructure of block copolymers calculated by ^{31}P NMR and Titration[a].

Sample	^{31}P NMR				Titration				Exp. wt% Increase
	x	y	z	Theo. wt% Increase[b]	x	y	z	Theo. wt% increase[b]	
PVPP-*b*-PS-10k	15.7	19.4	39.5	15.5	15.9	11.6	54.9	12.5	19.4
PVPP-*b*-PS-5k	7.2	10.9	64.9	13.3	11.3	9.8	63.1	16.1	32.0

[a] Calculated from Table 1 and DP of PVPP;
[b] Calculated from x, y, z values.

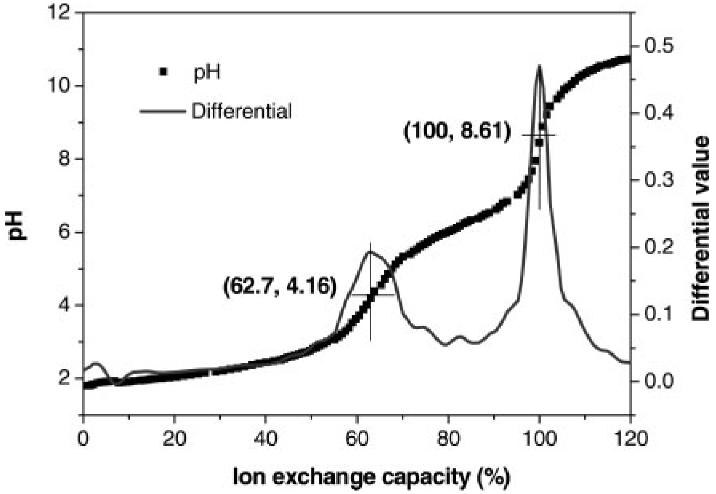

Figure 5.
pH titration curve and its differential curve for PVPP-b-PS-10k.

be attributed to the same reason as in the above. Both block copolymer samples are only slightly crosslinked, so the x, y, z values by two different characterization methods do not show big differences. As the degree of inter-chain crosslinking reaction increases, however, the differences will increase, and remains only the solid state NMR as the valuable characterization method.

Conclusions

The resonances and morphology of the PVPP-b-PS-5k and PVPP-b-PS-10k are measured by using ^{1}H solid-state NMR spectroscopy. The ratio of the differently bound phosphorus was obtained by ^{31}P Solid-state NMR Spectroscopy because the majority of block copolymer is not soluble or does not make homogeneous solution in a NMR solvent. The total amount of acid groups as well as the ratio of singly and doubly bound phosphorus by ^{31}P Solid-state NMR and pH titration was slightly different due to the slightly cross-linked nature of the sample. Therefore, solid-state NMR spectroscopy is the most powerful technique to characterize cross-linked polymers like DMFC membrane.

Acknowledgements: This research was supported by the HUFS Research Fund of 2006 and Center for Advanced Functional Polymers.

[1] G. H. Li, S. H. Kim, C. G. Cho, T. J. Park, Y. Kim, *Macromolecular Research* **2006**, *14*, 504.
[2] G. H. Li, C. G. Cho, *Macromolecular Research* **2002**, *10*, 339.
[3] G. H. Li, C. G. Cho, *Colloid & Polymer Science* **2005**, *283*, 946.
[4] G. H. Li, C. H. Lee, Y. M. Lee, C. G. Cho, *Solid State Ionics* **2006**, *177*, 1083.
[5] M. Mehring, A. Pines, W. K. Rhim, J. S. Waugh, *J. Chem. Phys.* **1971**, *54*, 3239.
[6] J. A. Pople, H. B. Schneider, H. Bernstein, "*High-Resolution NMR Spectroscopy*", McGraw-Hill, New York, USA **1959**.
[7] E. D. Becker, "*High Resolution NMR. Theory and Chemical Applications*", 2nd ed., Academic Press, New York 1980.
[8] E. R. Andrew, A. Bradbury, R. G. Eades, *Nature* **1958**, *182*, 1659.
[9] I. J. Lowe, *Phys. Rev. Lett.* **1959**, *2*, 285.
[10] A. Samoson, E. Kundla, E. Lippmaa, *J. Magn. Reson.* **1982**, *49*, 350.
[11] S. Schramm, E. Oldfield, *J. Am. Chem. Soc.* **1984**, *106*, 2502.
[12] L. Xiao, H. Zhang, E. Scanlon, L. S. Ramanathan, E.-W. Choe, D. Rogers, T. Apple, B. C. Benicewicz, *Chem. Mater.* **2005**, *17*, 5328.
[13] G. C. Daul, J. D. Reid, R. M. Reinhardt, *Ind. Eng. Chem.* **1954**, *46*, 1042.