Characterization of Poly(vinyl phosphate-*b*-styrene) by Solid-State ^{31}P NMR and Titration

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Abstract: Poly(vinyl phosphate-*b*-styrene) (PVPP-*b*-PS) block copolymers were synthesized successfully from poly(vinyl alcohol-*b*-styrene) (PVA-*b*-PS) by reaction with phosphorus oxychloride and subsequent hydrolysis. The obtained block copolymers were slightly crosslinked, and were characterized by various analytical techniques. The total phosphorus content and the ratio of the differently bound phosphorus were obtained by both solid-state ^{31}P NMR and pH titration, but the results differed slightly. Characterization by energy dispersion X-ray analysis (EDS) or Rutherford back scattering (RBS), on the other hand, determined the total phosphorus contents, but the results were quite different from those by solid-state ^{31}P NMR.

Keywords: poly(vinyl alcohol-*b*-styrene), poly(vinyl phosphate-*b*-styrene), ^{31}P solid-state NMR, Rutherford back scattering.

Introduction

For the characterization of acid group containing polymers, FTIR, NMR, GPC, and elemental analysis can generally be used in combination with pH titration. If a polymer makes a homogeneous solution in NMR solvent, then the characterization of the polymer will not be a difficult task. Characterization methods such as NMR, GPC, viscometry, FTIR, etc, can be easily applied. When the polymer is block copolymer or does not make homogeneous solution in NMR solvent, on the other hand, the characterization will be a challenging job. Even with a polymer which is soluble in a solvent, interpretation of the data is difficult because it is known that some amphiphilic block copolymers forms micelles in solution and this makes NMR resonance peaks different.[1-3]

In an attempt to develop direct methanol fuel cell (DMFC) membrane with low methanol permeability, we prepared poly(vinyl phosphate-*b*-styrene) (PVPP-*b*-PS) copolymers and their blend membranes with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO),[4] because poly(vinyl alcohol) based polymers are known to have low methanol permeability.[5-7] PVPP-*b*-PS copolymers were prepared from corresponding poly(vinyl alcohol-*b*-styrene) (PVA-*b*-PS)[8,9] by phosphoryl-

ation with phosphorus oxychloride.[10] The blend membranes showed improved thermal and hydrolytic stability. But the characterization of the PVPP-*b*-PS block copolymer was a challenge.

When PVA is phosphorylated with phosphorus oxychloride, the reaction can generate singly and doubly esterified phosphorus groups as shown in Scheme I. If the product contains solvent soluble product only, then the total amount of acid groups and the ratio of the singly and doubly esterified
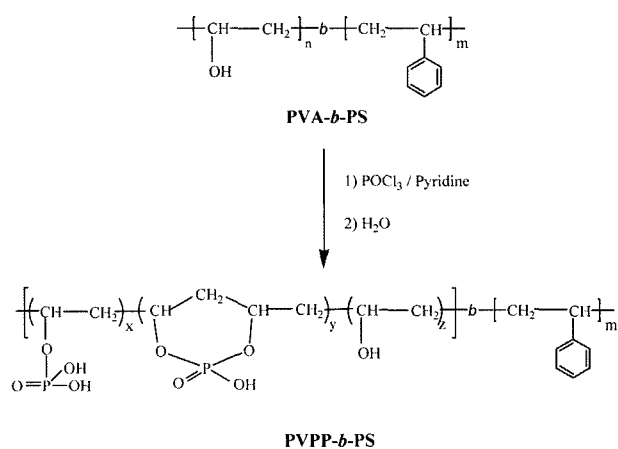
Scheme I. Synthetic scheme of PVPP-*b*-PS.

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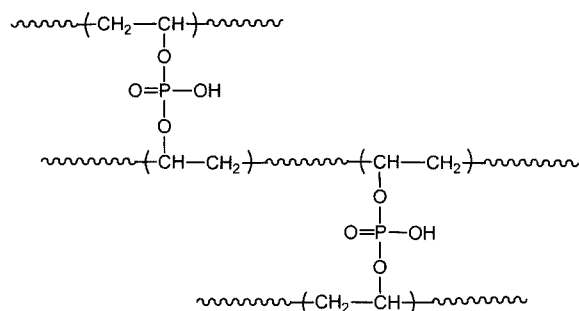
Scheme II. Crosslinked structure of PVPP-*b*-PS.

phosphorus groups can be determined by the total consumption of the base titrant and inflection points in the pH titration curve, respectively. But the doubly esterified groups can contain inter-chain reaction products (Scheme II) as well as intra-chain reaction products. Therefore, its characterization is not straightforward because the inter-chain reaction products can generate crosslinked structures. In this study, we characterized the PVPP-*b*-PS copolymers by solid-state ^{31}P NMR, pH titration, Rutherford backscattering spectrometer (RBS), and Energy disperse x-ray spectroscopy (EDS). Results from each characterization method were compared and discussed.

Experimental

Materials. Pyridine (Samchun Pure Chemical Co., Ltd, Extra Pure) and 1-methyl-2-pyrrolidone (NMP) (Samchun Pure Chemical Co., Ltd, 99%) were purified by drying over CaH$_2$ and distilled under atmospheric or reduced pressure, respectively. Acetone (Samchun Pure Chemical Co., Ltd, 99%), phosphorus oxychloride (POCl$_3$) (Aldrich Chemical Co., Inc, 99%), and calcium phosphate ((Junsei chemical, Japan, 98%) were used as received.

Preparation of PVPP-*b*-PS Copolymers. PVA-*b*-PS block copolymers were prepared first *via* consecutive telomerization of vinyl acetate (VAc), atom transfer radical polymerization with styrene, and saponification, as described in our previous papers.[8,9] Molecular characteristics of the block copolymer are shown in Table I. Syndiotacticity (diad %) of the PVA block is 53.2%.

In a sealed round-bottom flask, 2.0 g of PVA-*b*-PS copoly-

Table I. Molecular Characteristics of PVA-*b*-PS

Sample	PVA		PS		
	$M_{n,NMR}$[a]	DP	$M_{n,th}$[b]	$M_{n,NMR}$	DP
PVA-*b*-PS$_{10k}$	4,140	94	11,730	11,440	112.8
PVA-*b*-PS$_{5k}$	4,140	94	5,240	5,510	50.4

[a]Calculated from DP of PVAc-Cl determined by ^{1}H-NMR.
[b]$M_{n,th}$ = [St]/[PVAc-Cl] × 104 × Conversion (%).

mer was dissolved by stirring in purified NMP at 60 °C, and then the flask was cooled in an ice-cold water bath until the temperature was below 10 °C. Subsequently, excess phosphorus oxychloride (POCl$_3$), purified pyridine (-OH/pyridine= 1:1 mole/mole), and water (POCl$_3$/H$_2$O=1:2.8) were added dropwise one after another at such a rate that the reaction temperature does not exceed 10 °C. After the addition is completed, the solution was precipitated into acetone, filtered, washed with acetone, and dried under vacuum at 50 °C (brown powder).

Characterization. Infrared spectra of the block copolymers were recorded as KBr pellets in the range of wavenumbers 4000~400 cm^{-1} using a MAGNA-IR760 spectrometer (MICROFLUIDICS, USA). Total amount of acid groups and the ratio of the singly and doubly esterified phosphorus groups were determined by pH titration using a Microprocessor pH Meter (pH 213, HANNA Instruments). The samples were individually immersed and stirred in excess amount of 2.0 M NaCl solution for 3 days and titrated with 0.025 N NaOH aqueous solution.[10] The total amount of acid groups and the ratio of the singly and doubly esterified phosphorus groups were determined by the total consumption of the base titrant and inflection points in the pH titration curve, respectively.

The ion exchange capacity (IEC) of the membranes was determined by neutralization titration. A sample was immersed and stirred in 30 mL of 0.10 N NaOH/1.0 M NaCl mixed aqueous solution (1/4 by volume) for 12 hrs at room temperature.[11,12] Subsequently, 15 mL of 0.10 N HCl solution was added, and the excess amount of HCl was back titrated with 0.025 N NaOH aqueous solution in the presence of phenolphthalein indicator. The IEC value (mmol/g) of the samples was calculated using the following equation:

$$IEC = \frac{0.025 \times (V_{NaOH} - V_B)}{W_{dry}} \quad (1)$$

Where V_{NaOH} is volume of 0.025 N NaOH aqueous solution for the titration, V_B is volume of the NaOH aqueous solution for blank titration, and W_{dry} is dry weight of the membranes.

Phosphorus content of the block copolymers was determined by phosphorus solid-state nuclear magnetic resonance spectroscopy using 9.4 Tesla UNITYINOVA wide bore NMR spectrometer (VARIAN, USA) operating at ^{31}P NMR frequency of 161.89 MHz and ^{1}H NMR frequency of 399.92 MHz using (NH$_4$)H$_2$PO$_4$ 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 the 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 (20 to 24 °C). High-power decoupling (HPDEC) measurements[13-15] on PVPP-*b*-PS were carried out at magic angle spinning (MAS)[16] frequencies of 15 KHz. The magic

angle was set using the ^{79}Br resonance of KBr. HPDEC sequence was 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 hrs using a recycle delay of 20 s. The amount ratio of singly and doubly bound phosphorus and the total amount of phosphorus was calculated after deconvolution of the HPDEC spectra using WINNMR (BRUKER, Germany).

Energy disperse X-ray spectroscopy (EDS) was performed using JSM-6330F (JEOL, Japan) field emission scanning electron microscopy (FE-SEM) with accelerating voltage of 10 KV, take off angle of 35 degree, and live time of 120 sec. Powder samples were used. Rutherford backscattering spectrometer (RBS)/channeling was performed using 6 SDH-2 (NEC, Japan). He^{2+} ion beam with energy of 2 MeV and a total dose of approximately 10 μC was used.[17] Samples were prepared by casting from NMP solution (30 mg of block copolymer/2 mL of NMP) on slide glass at 80 °C, and drying overnight at 95 °C under vacuum.

Results and Discussion

Using the reactivity of hydroxyl groups, the PVPP-*b*-PS copolymers were prepared by means of the phosphorylation of the PVA-*b*-PS copolymers with phosphorus oxychloride in the presence of pyridine, and hydrolysis with water. Figure 1 shows the IR spectra of three diblock copolymers. Poly(vinyl acetate-*b*-styrene) (PVAc-*b*-PS) spectrum shows carbonyl peak at 1737 cm^{-1}, -C-O- and -O-CH- peaks in the ester groups at about 1025 and 1240 cm^{-1}, respectively, and methyl peak at 1374 cm^{-1}; PVA-*b*-PS spectrum shows -OH peak at 3360 cm^{-1}, and -C-OH peak at 1095 cm^{-1}, whereas carbonyl peak, -C-O- and -O-CH- peaks in the ester groups, and methyl peak disappeared; PVPP-*b*-PS spectrum shows -P=O peak at 1254 cm^{-1}, -P(O)OH peak at about 2810-2550 cm^{-1} and 2400-2030 cm^{-1}, -P-O-CH- peak at about 995 cm^{-1}, and H$_2$O peak at 3460 and 1674 cm^{-1}, whereas -C-OH peak mostly disappeared. Also, all spectra show the presence of polystyrene block (benzene ring -CH= at 3000-3100 cm^{-1}, skeletal vibrations at 1600 and 1490 cm^{-1}) in the block copolymers. From the IR spectra, it is not only con-
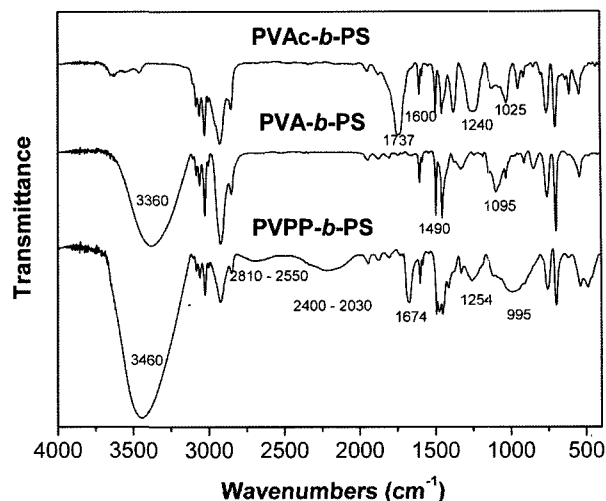

Figure 1. FTIR spectra of three block copolymers.

firmed that the PVAc-*b*-PS and PVA-*b*-PS copolymers were synthesized, but also confirmed that the PVPP-*b*-PS copolymer was successfully synthesized. But it is difficult to know whether the unreacted -OH group exists.

Synthetic results are summarized in Table II. If the reactants and the products are soluble in the solvent NMP, then the -OH group will react completely in the presence of excess POCl$_3$. If the product contains 100% of singly esterified phosphorus, then the weight increase will be 80.2% for PVPP-*b*-PS$_{5k}$ and 47.6% for PVPP-*b*-PS$_{10k}$. On the other hand, if the product contains doubly esterified phosphorus only, then the weight increase will be 31% for PVPP-*b*-PS$_{5k}$ and 18.4% for PVPP-*b*-PS$_{10k}$. Also the experimental weight increases were 32% for PVPP-*b*-PS$_{5k}$ and 19.4% for PVPP-*b*-PS$_{10k}$. Therefore, the experimental weight increase alone cannot tell the existence of unreacted -OH group for both cases.
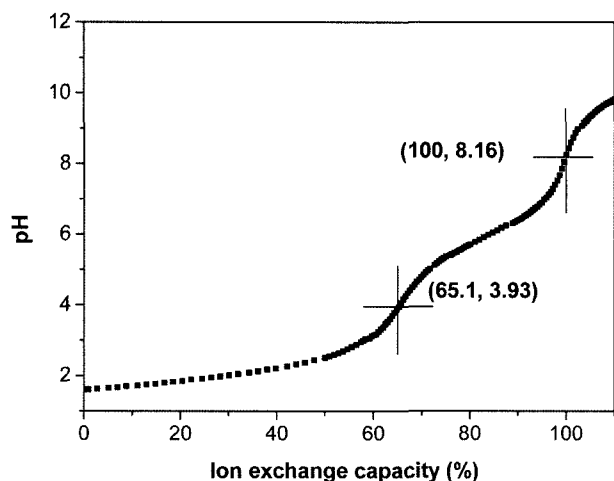
For further identification of the structure of the PVPP-*b*-PS copolymer, pH titration was carried out in the presence of excess NaCl aqueous solution.[10] Figure 2 shows the titration curve obtained from PVPP-*b*-PS$_{5k}$ copolymer sample. The curve is typical of that of a dibasic acid. This indicates that a certain amount of doubly bound phosphorus exists; the first portion of the curve represents the first acid group of the

Table II. Synthetic Results of PVPP-*b*-PS Characterized by ^{31}P NMR and Titration

Sample	^{31}P NMR		pH Titration		PVPP $M_{n,th}^{b}$	Theoretical IEC (mmol/g)*	pH Titration (mmol/g)	IEC (mmol/g)	Weight Increase (%)
	Mono/ Divalent	P wt%^{a}	the 1st eq. Point (mL)	End Point (mL)					
PVPP-*b*-PS$_{10k}$	39.8/60.2	5.94	4.95	7.80	6,600	2.77	2.42	-	19.4
PVPP-*b*-PS$_{5k}$	44.8/55.2	5.29	7.03	10.80	5,380	2.38	2.98	2.06	32.0

^{a}Calculated from the deconvoluted spectrum of the ^{31}P solid-state NMR. $^{b}M_{n,th}$ calculated from the values of ^{31}P solid-state NMR.
*Calculated from the value of x and y (x and y refer to Scheme I and ^{31}P solid-state NMR).

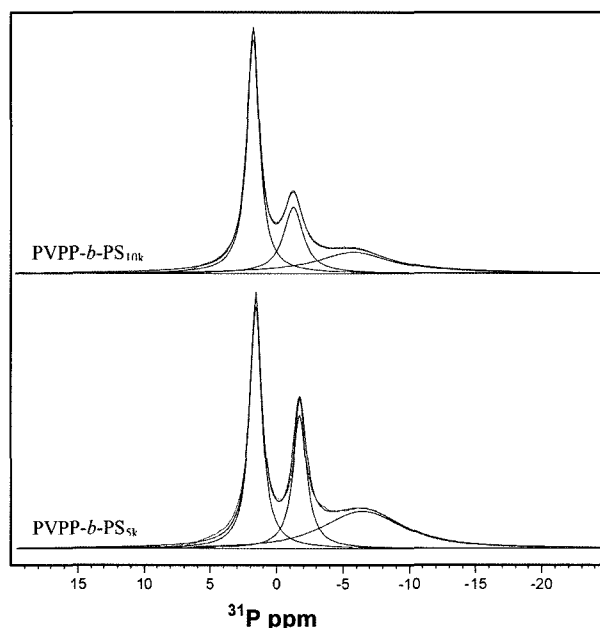**Figure 2.** pH versus ion exchange capacity of PVPP-b-PS$_{5k}$ copolymer.

Figure 3. Solid-state ^{31}P NMR spectra of PVPP-b-PS$_{5k}$ and PVPP-b-PS$_{10k}$ using Ca$_3$(PO$_4$)$_2$ as a internal standard for quantitative analysis. (NH$_4$)H$_2$PO$_4$ was used as an external chemical shift standard at 0 ppm.

singly esterified material and the single acid group of the doubly esterified material as shown in Scheme I.[9] In Table II, the total amount of acid content by titration was 2.98 and the amount of acid content by IEC measurement was 2.06 for PVPP-b-PS$_{5k}$. Determination of acid contents by different methods, in general, should give the same value, but they show some differences.

From the information of the inflection points and the total amount of added titrant, it is possible to calculate the ratio of singly and doubly bound phosphorus and the total content of phosphorus as in Table II. Also it is possible to calculate the values of x, y, and z in Scheme I as shown in Table III.

If any inter-chain phosphorylation takes place, it will generate crosslinked structure as shown in reaction Scheme II. Total amount of doubly bound phosphorus will be the sum of inter and intra-chain phosphorylation products, so the x, y, z values in Scheme I will have different meaning. Also the titration result will be different from its real value because the titrant cannot penetrate fully into the sample due to the sample's crosslinked nature.

Solid-state ^{31}P NMR was utilized to distinguish and obtain the amount of singly and doubly esterified groups. Figure 3 shows the spectrum which containing PVPP-b-PS$_{5k}$ and PVPP-b-PS$_{10k}$ with Ca$_3$(PO$_4$)$_2$ as the internal standard for a quantitative analysis. The signal at 1.6 ppm was assigned to the resonance of Ca$_3$(PO$_4$)$_2$, 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.[18] From the deconvoluted solid-state ^{31}P NMR spectra, it was possible to calculate the amount ratio of singly and doubly bound phosphorus and the total amount of phosphorus. The results are shown in Table II and represent true values irrespective of degree of crosslinking, from the analytical principle of solid state NMR.[15] Data in Table II and III shows that the titration and NMR experiments give very similar results, and this proves indirectly that the NMR chemical shifts are correctly assigned. The slight differences in the value of x, y, and z by titration and NMR experiments as in Table III, are probably due to the slightly crosslinked nature of the PVPP-b-PS copolymers.

For the analysis of a crosslinked polymer, a routine elemental analysis will give the information of elemental compositions of C, H, O, N, S, easily. But the existence of other

**Table III. Microstructure of Block Copolymer Calculated by ^{31}P NMR and Titration***

	PVPP-b-PS$_{5k}$			PVPP-b-PS$_{10k}$		
	x	y	z	x	y	z
^{31}P NMR	7.2	10.9	64.9	15.7	19.4	39.5
Titration	11.3	9.8	63.1	15.9	11.6	54.9

*Calculated from Table II and DP of PVPP.

elements needs special techniques. As an alternative method, surface analysis technique such as X-ray photoelectron spectroscopy (XPS), EDS, or RBS can be used, as reported in the analysis of sulfonated PPO by XPS.[19] Table IV shows the analysis results by EDS and RBS in atomic %, and this was converted into wt% in Table V. The results by EDS show quite higher phosphorus contents than that by NMR in Table V, probably because the phosphorylation reaction takes place at the surface of PVPP-*b*-PS particle or gel after the block copolymer makes crosslinked structure, and because the analyzed sample was in powder form. The results also show the presence of chlorine in Table IV, and this means that the hydrolysis reaction in Scheme I was not complete especially for the block copolymer with shorter PS block length, PVPP-*b*-PS$_{5k}$. The theoretical number of chlorine atoms of the precursor PVA-*b*-PS is 4,[8,9] but the calculated number of chlorine atoms from the results are 23.2 and 11.4 for, PVPP-*b*-PS$_{5k}$ and PVPP-*b*-PS$_{10k}$, respectively. This data shows that the hydrolysis reaction for both polymers is not complete. For RBS analysis each sample was made into film by casting from NMP solution. Both samples made homogeneous solution at 80 °C in their appearance when checked by naked eye. Figure 4 shows the RBS spectra for both block copolymers. Solid lines represent raw data and the dotted lines represent simulated data. Two show good agreement for both cases. Because the film was made from homogeneous solution, the composition at the surface is assumed to be the same as the bulk phase. Results in the Table V tell that RBS shows lower phosphorus content than EDS toward better agreement, but still higher compared to the result by solid-state ^{31}P NMR.

Conclusions

PVPP-*b*-PS block copolymers were synthesized success-
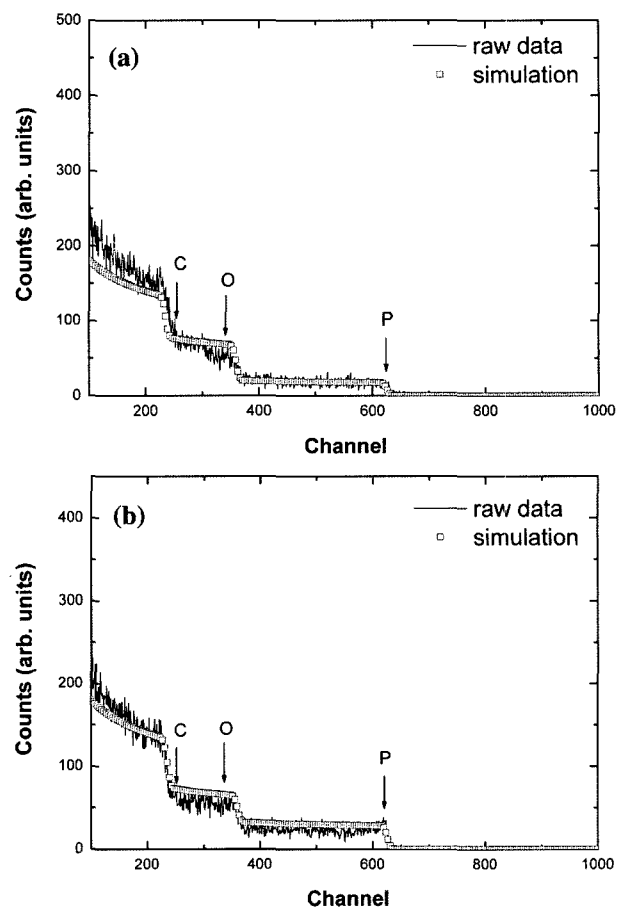
Figure 4. RBS spectra of (a) PVPP-*b*-PS$_{5k}$ and (b) PVPP-*b*-PS$_{10k}$ copolymers.

fully from PVA-*b*-PS by reaction with phosphorus oxychloride and subsequent hydrolysis. Obtained block copolymers were slightly crosslinked, but possible to be made into homoge-

Table IV. Elemental Compositions of Block Copolymer by EDS and RBS in Atomic %

	EDS(Atomic%)				RBS(Atomic%)		
	C	O	P	Cl	C	O	P
PVPP-*b*-PS$_{5k}$	59.48	32.31	5.85	2.35	65.9	31.0	3.1
PVPP-*b*-PS$_{10k}$	69.15	23.99	6.12	0.73	73.3	21.6	5.1

Table V. Calculated Weight Ratios of C, O, and P in PVPP-*b*-PS by Various Analytical Techniques

	PVPP-*b*-PS$_{5k}$			PVPP-*b*-PS$_{10k}$		
	C	O	P	C	O	P
EDS	50.6	36.6	12.8	59.2	27.3	13.5
RBS	57.2	35.9	6.9	63.5	24.9	11.6
^{31}P NMR[a]	72.0	22.3	5.7	76.7	16.9	6.4
Titration[a]	70.2	23.4	6.5	78.9	15.9	5.2

*The total sum of wt% of C, O, and P set to 100. [a]Calculated from the value of x , y and z (x , y and z refer to Scheme I and Table III).

neous NMP solution by dissolution at 80 °C. Obtained block copolymers were characterized by various analytical techniques. It was possible to distinguish singly and doubly bound phosphorus, and possible to obtain the total amount of phosphorus content as well as the ratio of the different phosphorus, by solid-state ^{31}P NMR as the most preferred analytical technique.

It was also possible to obtain the total amount of acid groups as well as the ratio of singly and doubly bound phosphorus by pH titration, but the result was slightly different from that by solid-state ^{31}P NMR due to the slightly cross-linked nature of the sample.

Characterization by EDS or RBS, on the other hand, was not possible to give information on the ratio of the singly and doubly bound phosphorus, but possible to give information on the total phosphorus contents. Analysis by EDS was performed with powdery samples, and showed quite higher phosphorus contents compared to those by solid-state ^{31}P NMR, and also showed the existence of unhydrolyzed oxychloride residue. Analysis by RBS was performed with thin films made from homogeneous solution, and showed better results than EDS, but still higher phosphorus contents than the solid-state ^{31}P NMR results.

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