

Characterization of Poly(styrene-*b*-vinylbenzylphosphonic acid) Copolymer by Titration and Thermal Analysis

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Abstract: Well defined amphiphilic diblock copolymers of poly(styrene-*b*-vinylbenzylphosphonic acid) (PS-*b*-PVBPA) were prepared by controlled radical polymerization technique, two-step hydrolysis reactions using trimethylsilyl bromide from the corresponding phosphonic ethyl ester. By indirect, backward pH titration of the block copolymer, a good titration curve of a dibasic acid was observed. The IEC values obtained from both backward pH titration and volumetric back titration were almost identical. Thermal gravimetric analysis (TGA) of the phosphonic acid containing block copolymer showed a high thermal stability up to 400 °C.

Keywords: ion exchange capacity, poly(vinylbenzylphosphonic acid), block copolymer, proton exchange membrane, thermal stability

Introduction

Polymers with phosphonic acid moiety have been studied for many applications such as chelation of metal ions,¹⁻⁵ templates for inorganic crystal growth,^{6,7} flame retardants by their esters,^{8,9} and recently as proton conducting polymers.¹⁰⁻¹³ Among them, applications for fuel cell membranes have attracted very special interest because of the fact that phosphonic acid containing polymeric membranes are known to have the possibility of operating at higher temperatures and at low humidity conditions by themselves¹⁰⁻¹² or as composite forms with bases.¹³

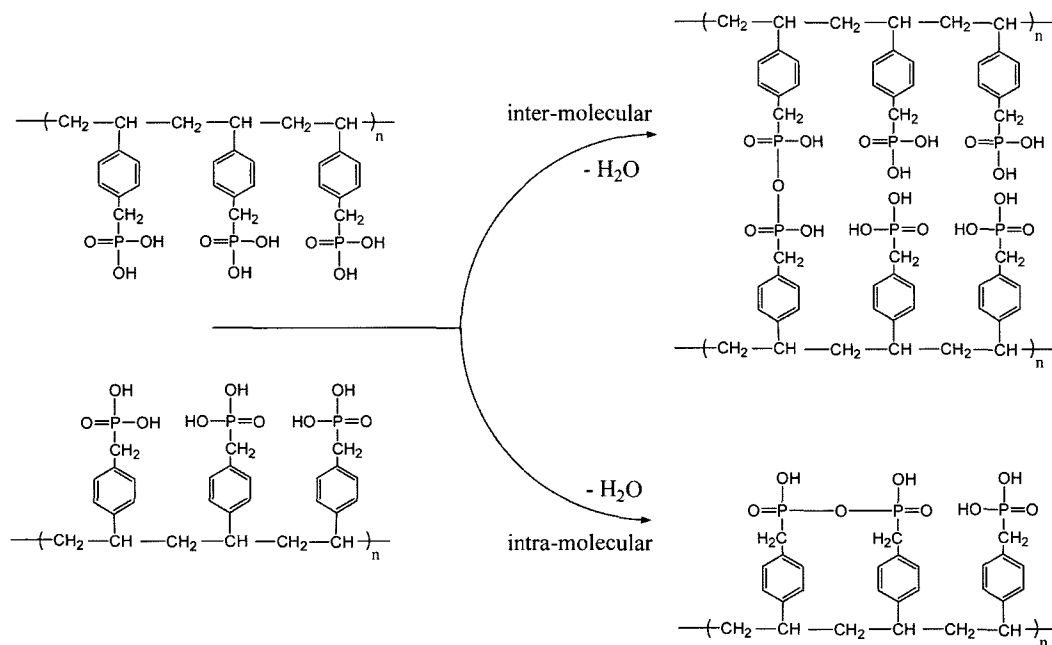
Polymers with phosphonic acid moiety are usually obtained by hydrolysis of the corresponding phosphonate polymers, and the precursors are prepared via many different synthetic procedures. Several representative examples include the reaction of triethyl phosphite with an alkyl or a benzyl halide (Arbuzov reaction),¹⁴ the reaction of an aryl bromide with diethyl phosphite in the presence of Pd catalyst,^{12,15-17} the reaction of an aryl bromide with alkyl lithium and subsequent reaction with diethyl chlorophosphate,¹⁸⁻²¹ the reaction of benzyl chloride with phosphorus trichloride in the presence of aluminum chloride,²² the polymerization of diethyl vinylbenzylphosphonate²³ or dimethyl vinylbenzylphosphonate,²⁴ the reaction of a carboxylic acid with phosphorus trichloride and phosphorus acid,²⁵ and the direct synthesis by Michael addition of vinylphosphonic acid to

amine group.⁶ Among them, Arbuzov reaction has been applied widely due to its flexibility in the choice of alkyl halide, and convenient reaction conditions for the preparations of dialkyl phosphonate.

Once the phosphonates are converted to phosphonic acids, obtained samples in dry state can have partially dehydrated anhydride structures by inter- or intra-crosslinking as shown in Scheme I. If the phosphonic acid containing block copolymer undergoes any drying procedure, the crosslinked portion of the sample will be increased, and this can make the sample insoluble in any solvent and make difficult the direct estimation of the acid content by titration. Similar problem was addressed in the block copolymers with similar structures.²⁶

Recently, syntheses of the block copolymers containing poly(vinylbenzylphosphonic acid) (PVBPA) were reported in literatures via nitroxide-mediated stable free radical polymerization (SFRP),^{27,28} but the detailed study on the determination of ion exchange capacity (IEC) or thermal stability was not reported. In this study, therefore, a similar synthetic procedure was re-examined in order to prepare well defined poly(styrene-*b*-vinylbenzylphosphonic acid) (PS-*b*-PVBPA) block copolymers, in an attempt to develop good proton exchange membranes via polymer blend approach.^{29,30} A couple of different synthetic routes for hydrolysis were investigated in order to generate block copolymers with better yield with lower extent of crosslinking. Determination of IEC was tried by back titration for a more reliable result, because it is essential to know the exact acid content and

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Scheme I. Intra-molecular and inter-molecular anhydride formation mechanism of PS-*b*-PVBPA.

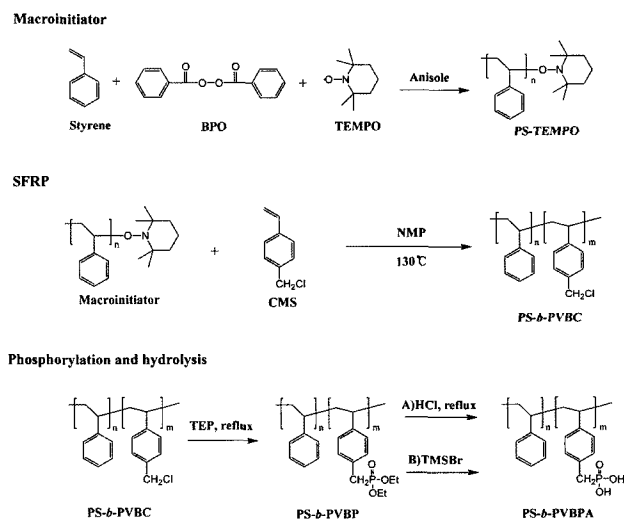
molecular structure of the block copolymer in order to study the structure-property relationship of the resultant materials for proton exchange membranes. Also thermal stability was measured to check the possibility of application of these polymers at high temperature.

Experimental

Materials. Styrene (St, Samchun pure chemical Co. Ltd, 99.0%) and *p*-vinylbenzyl chloride (VBC, Tokyo Kasei) were purified by passing through an alumina column to remove inhibitor. Benzoyl peroxide (BPO, Fluka) was recrystallized from methanol. Anisole (Samchun Pure Chemical Co. Ltd, 99.0%) and *N*-methyl-2-pyrrolidinone (NMP, Samchun Pure Chemical Co. Ltd, 99.0%) were distilled over calcium hydride before use. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO, Aldrich), triethyl phosphite (TEP, Aldrich, 98.0%), and trimethylsilyl bromide (Tokyo Kasei, 95%) were used as received. Other chemicals were reagent grade and used as received.

Preparation of Poly(styrene-*b*-vinylbenzylphosphonic acid) (PS-*b*-PVBPA) Block Copolymers. Poly(styrene-*b*-vinylbenzylphosphonic acid) (PS-*b*-PVBPA) block copolymer was synthesized by following the four step procedures as shown in Scheme II: (1) The preparation of PS-TEMPO, macroinitiators; (2) SFRP of vinyl benzyl chloride using the PS-TEMPO, macroinitiator; (3) Phosphonation of poly(styrene-*b*-vinylbenzyl chloride) by the Arbuzov reaction¹⁴ using triethyl phosphite (TEP); (4) Hydrolysis of poly(styrene-*b*-vinylbenzyl phosphonate).

PS-TEMPO Macroinitiator. PS-TEMPO macroinitiator



Scheme II. Synthetic scheme of poly(styrene-*b*-vinyl benzyl phosphonic acid).

was prepared as follows.³⁰ Styrene monomer (40 g, 0.385 mole), BPO (0.677 g, 2.8 mmole), TEMPO (0.567 g, 4.0 mmole) and anisole (40 mL) were added into one-neck round-bottom flask and degassed by flushing with nitrogen. Then, the flask was placed in an oil bath and stirred at 95 °C for 3.5 h, followed by heating at 130 °C for predetermined reaction time (15 h and 24 h). After reaction, product was precipitated into methanol, filtered, washed with methanol, and dried under vacuum.

Copolymer Synthesis. Poly(styrene-*b*-vinylbenzyl chloride) (PS-*b*-PVBC) block copolymers were prepared by

stable free radical polymerization (SFRP) of vinylbenzyl chloride (VBC) using PS-TEMPO as a macroinitiator. In a sealed round-bottom flask, 5 g (0.46 mmol and 0.84 mmol) of PS-TEMPO were dissolved in NMP, and VBC (17.1 mmol for 5 k and 34.2 mmol for 10 k) was gradually added dropwise, and then the reaction solution was stirred in a pre-heated oil bath at 130 °C for 15 h. The block copolymer was recovered by precipitation of the solution into methanol, filtered, and dried under vacuum at 80 °C overnight. The obtained block copolymer was dissolved in THF and precipitated again in methanol for purification.

Phosphonation. The Phosphonation reaction of PS-*b*-PVBC block copolymers was carried out using the conventional Arbuzov reaction. In a 250 mL round bottomed flask equipped with a reflux condenser, 5.0 g of PS-*b*-PVBC (14.3 mmol CH₂Cl₂ for 5 k-5 k) were dissolved in 80 mL of TEP (0.46 mol) and refluxed for 24 h at 120 °C. Then, unreacted TEP was rotary evaporated and remaining solution was precipitated into petroleum ether. The block copolymer of poly(styrene-*b*-vinylbenzylphosphonate) (PS-*b*-PVBP) was recovered, filtered, and dried under vacuum at 80 °C.

Hydrolysis. Poly(styrene-*b*-vinylbenzylphosphonic acid) (PS-*b*-PVBPA) copolymers were prepared by one of the following two methods. In the first method, PS-*b*-PVBP powder (5.0 g) was refluxed with concentrated hydrochloric acid (50 mL, 37%) at 90 °C for 24 h. Then, resulting suspension was gradually added into deionized water, filtered, washed with deionized water several times, and dried under vacuum at 60 °C. In the second method, PS-*b*-PVBP powder (5.0 g) was dissolved in 30 mL of methylene chloride, and trimethylsilyl bromide (5% excess) was added dropwise, then the reaction solution was stirred at ambient temperature for 24 h. Resulting solution was added slowly to 300 mL of methanol containing 30 mL of conc. HCl. Precipitated polymer mixture was stirred for 24 h, filtered, washed with deionized water several times, and dried under vacuum at 60 °C. The success of hydrolysis was confirmed by titration.

Characterization. The molecular weights and the molecular weight distribution of the PS-TEMPO and obtained block copolymer (PS-*b*-PVBC) were measured by gel permeation chromatography (GPC) equipped with a Waters 717 plus Autosampler, Waters 616 HPLC pump, Waters 2410 refractive index detector, and Waters styragel HR series columns (eluent: THF 35, flow rate: 0.3 mL/min). Polystyrene standards were used to calibrate the columns. The number-average degree of polymerization of obtained block copolymers was also determined using VARIAN 300 MHz Unitynova ¹H-NMR spectrometer with CDCl₃ as the solvent. Infrared spectra of the block copolymers were recorded as KBr pellets in the range of wave numbers 4000-400 cm⁻¹ using a MAGNa-IR760 spectrometer (Microfluidics, USA). Total amount of acid groups and form of dibasic acid were determined by pH titration using a Microproces-

sor pH Meter (pH 213, HANNA instruments). The sample was immersed and stirred in excess amount of 2.0 M NaCl solution for 24 h and titrated with 0.025 N NaOH aqueous solution³¹ to get a forward titration curve. Then the sample solution was back titrated with 0.05 N HCl aqueous solution to get a reverse titration curve. Additionally, IEC was determined by volumetric 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 h at room temperature.^{32,33} Subsequently, 15 mL of 0.10 N HCl solutions was added, and the excess amount of HCl was back titrated with 0.025 N NaOH aqueous solutions 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 solutions for the volumetric titration, V_B is volume of the NaOH aqueous solution for blank titration, and W_{dry} is dry weight of the samples. The degradation process and thermal stability of the block copolymers were investigated using a SDT 2960 thermogravimetric analyzer (TGA-DTA, Shin Do Scientific Corp., Japan). The TGA measurements were carried out under a nitrogen atmosphere at a heating rate of 10 °/min from room temperature to 800 °C.

Results and Discussion

Synthesis of Macroinitiators and PS-*b*-PVBC Copolymers by SFRP. Figure 1 shows ¹H-NMR spectrum of PS-TEMPO. The successful synthesis of PS-TEMPO was confirmed by styrenic aromatic signals at 7.2 and 6.2-6.8 ppm and tetramethyl signals at around 0.9 ppm originated from TEMPO. The tetramethyl signal was reported to occur at 0.1-1.3 ppm showing several peaks with variable intensities

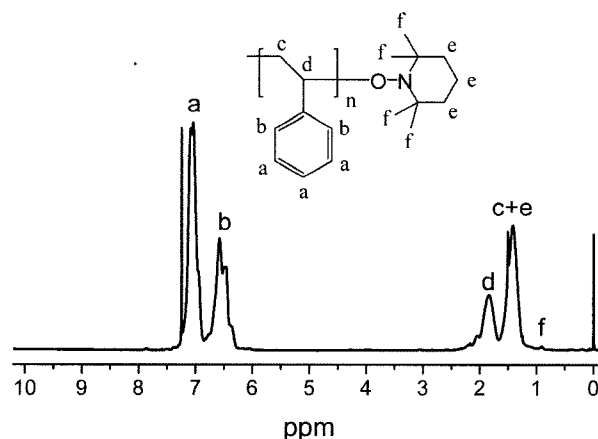


Figure 1. ¹H-NMR spectrum of PS-TEMPO macroinitiator in CDCl₃ ($M_{n,GPC} = 10,900$).

Table I. Synthetic Results of PS-*b*-PVBC Characterized by ¹H-NMR and GPC

Sample	PS Macroinitiator		PVBC		PS- <i>b</i> -PVBC		
	$M_{n,GPC}$	PDI	$M_{n,th}^a$	$M_{n,NMR}^b$	$M_{n,GPC}$	PDI	% Yield
PS- <i>b</i> -PVBC 5 k-5 k	5,980	1.14	4,620	4,700	10,890	1.28	79.0
PS- <i>b</i> -PVBC 10 k-5 k	10,900	1.17	4,880	4,750	15,500	1.42	78.7

^a $M_{n,th} = [VBC]/[PS - TEMPO] \times 152.6 \times \%Conversion$. ^bCalculated from integration ratio of the benzene ring and chloromethyl peak by ¹H-NMR with DP of PS-TEMPO.

due to the conformational inversion involving ring conversion. So the peak at 0.9 ppm was used only as an indication of the TEMPO attachment.³⁴⁻³⁶ Table I shows that the molecular weights of PS-TEMPO were well controlled via SFRP. The molecular weights observed by GPC were 5,980, 10,900 g/mol, and target M_n were 5,000, 10,000 g/mol, respectively. Also the observed polydispersity indices (PDI) were 1.14 and 1.17, respectively. PS-*b*-PVBC copolymers were prepared *via* SFRP of VBC with the PS-TEMPO macroinitiators. The molecular weight of the PVBC block was calculated by the % conversion of the VBC based on the weight of the isolated block copolymer. Also, the M_n of the PVBC block was calculated from ¹H-NMR spectra of PS-*b*-PVBC copolymer as shown in Figure 2, based on the peak integration ratio of the benzene ring and chloromethyl peaks at 4.5 ppm. The values in Table I show good agreements.

These block copolymers also contain TEMPO units at the chain ends, but the intensities of the NMR signal were very weak. The block copolymers show increased PDI values, and a similar result was reported on the homopolymerization of CMS.³⁶ Polymerization in a less polar solvent at a lower temperature with lower % yield will generate a block polymer with narrower PDI, because any possible side reactions involving benzyl chloride and termination by radical coupling will decrease, but no such attempt was made.

Phosphonation. The Arbuzov reaction takes place only at temperatures above 100 °C even for the low molecular weight compounds.¹⁴ At 100 °C, the yield of phosphonation reached only 60-70% for PS-*b*-PVBC, but at temperature above 120 °C most of the chlorines of PVBC block was phosphonated. The molecular structure of phosphonated copolymer was confirmed by ¹H-NMR by the disappearance of the signal derived from chloromethyl group at 4.5 ppm, and the appearance of three new signals at 3.8-4.1, 1.1-1.3, and 2.9-3.2 ppm, corresponding to the α -hydrocarbon ($-O-\underline{CH}_2-\text{CH}_3$), β -hydrocarbon ($-O-\text{CH}_2-\underline{CH}_3$) of phosphonic ethyl group, and methylene ($-\underline{CH}_2-\text{P}$) group adjacent to phosphorus atom, respectively (Figure 2). No trace of TEMPO was detectable by the NMR and this complies with the expectation that the TEMPO is replaced by phosphonate group. The ¹H-NMR was used to assess the M_n , based on the ratio of the integral of the twelve protons from the phosphonate group $-\text{CH}_2-\text{P}(\text{O})(\text{OCH}_2\text{CH}_3)_2$ and the benzene ring protons. The results were given Table II. Calculated DP of PVBC block were in good agreement with DP of the PVBC block of PS-*b*-PVBC. Simple comparison of GPC chromatograms, on the other hands, was not possible to give any molecular weight information, as shown in Figure 3, probably due to the change of solubility parameter and hydrodynamic volume of the block copolymer by the incorporation of diethyl phosphonate group. Phosphonation increases the molecular weight of the block copolymer, but the observed elution time was slightly shorter. PDI of the obtained PVBC block copolymer became broader compared to the PS macroinitiator as in Figure 3, but the major cause of the broadening is originated from the precursor PVBC, and the phosphonation caused very minor contribution to the broadening as in Tables I and II. It indicates that the phosphonation occurs selectively at the benzyl chloride functional group.

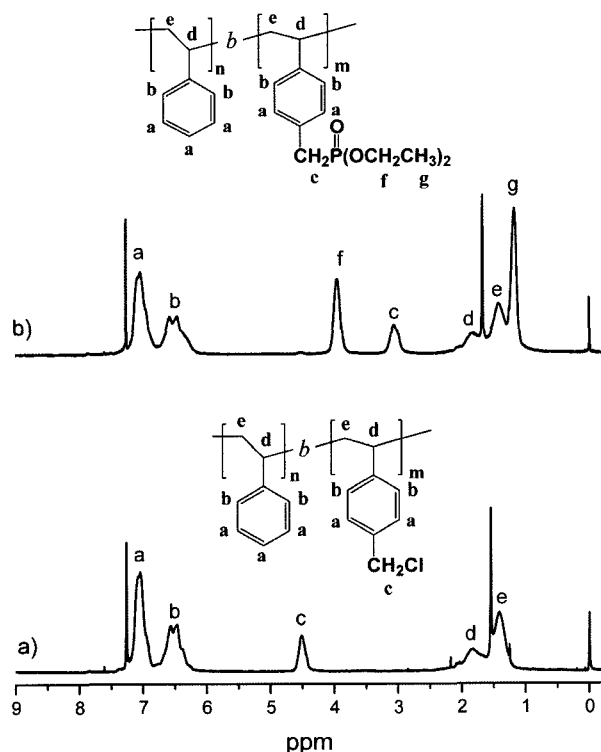


Figure 2. ¹H-NMR spectra of a) PS-*b*-PVBC 5 k-5 k and b) PS-*b*-PVBP 5 k-5 k in CDCl₃.

Table II. Synthetic Results of PS-*b*-PVBP Copolymers

Sample	PS	PVBP			PS- <i>b</i> -PVBP	
		$M_{n,th}^a$	$M_{n,NMR}$	DP	$M_{n,GPC}$	PDI
PS- <i>b</i> -PVBP 5 k-5 k	5 k	7,700	7,770	30.6	9,350	1.34
PS- <i>b</i> -PVBP 10 k-5 k	10 k	7,900	7,820	30.8	14,940	1.51

^aCalculated from DP of PVBC block determined by ¹H-NMR.

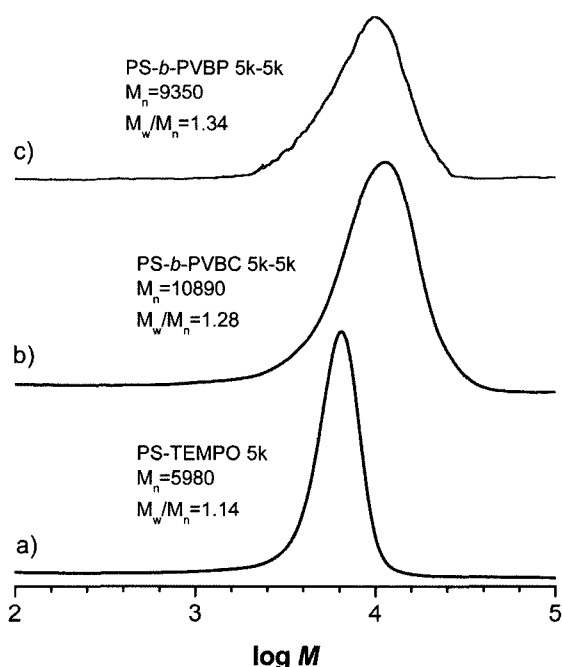


Figure 3. GPC traces of a) PS-TEMPO, b) PS-*b*-PVBC, and c) PS-*b*-PVBP copolymers.

Hydrolysis. Phosphonated copolymers could be hydrolyzed into the phosphonic acids by reaction with strong acid,^{12,15} strong base,^{1,20,21} or by reaction with trimethylsilyl halides as Scheme II.^{17,28,37,38} In this research hydrolyses by HCl and trimethylsilyl bromide were tried. In an attempt, a suspension of the polymeric phosphonate ester was heated under reflux in concentrated hydrochloric acid. Solution was heterogeneous throughout the reaction. In another attempt, trimethylsilyl bromide was used. Trimethylsilyl halides are

known to hydrolyze phosphonates selectively under mild reaction condition in two step hydrolysis reaction without attacking ester linkage.^{37,38} Homogeneous reaction solution of the block copolymer and trimethylsilyl bromide was observed in methylene chloride throughout the reaction. Subsequent reaction in methanol containing HCl yielded phosphonic acid containing block copolymer. The success of hydrolysis was checked by pH titration and volumetric back titration, and the resultant IEC values are listed in Table III. Hydrolysis with concentrated HCl showed difference in IEC values between theoretical and titrated, indicating incomplete conversion. The mismatch was probably caused by the heterogeneous nature of the reaction which makes insufficient contacts between hydrophobic phosphonate groups and aqueous HCl. Whereas, the two step hydrolysis reaction using trimethylsilyl bromide shows very good agreement between theoretical and titrated, indicating complete conversion. Change of trimethylsilyl bromide to trimethylsilyl iodide made the reaction solution with slightly red color, but the IEC value of the obtained acid block copolymer showed the same result.

Figure 4 shows the pH titration curves obtained from PS-*b*-PVBPA 10 k-5 k copolymer sample. The forward titration curve with NaOH does not give any information on the inflection point or equivalent point. This is probably due to the fact that the sample is the mixture of free phosphonic acid and anhydrides which are possible to be formed during sample drying step.³⁹ These anhydrides make intra-molecular as well as inter-molecular structures (Scheme I). And existence of anhydrides complicates the determination of the total amount of acid groups in two ways: 1) because the anhydrides acts as crosslinked structure, so the titrant can not penetrate quickly into the inside acid groups due to the steric hindrance, 2) also because the anhydrides are hydro-

Table III. Molecular Characteristics and Solubilities of PS-*b*-PVBPA Copolymers

Sample ^a	PVBPA $M_{n,th}^b$	Theoretical IEC ^b (mmol/g)	pH Titration (mmol/g)	IEC (mmol/g)	Solubility ^c			
					NMP	DMF	DMAc	DMSO
PS- <i>b</i> -PVBPA 5 k-5 k-H	6,060	5.08	-	4.64	+	+	+	-
PS- <i>b</i> -PVBPA 10 k-5 k-H	6,100	3.62	2.96	2.91	+	+	+	-
PS- <i>b</i> -PVBPA 10 k-5 k-T ^d	5,270	3.21	3.20	3.25	++	++	++	-

^aH denotes sample hydrolyzed by HCl, and T denotes sample hydrolyzed by TMSBr. ^bCalculated from DP of PVBP on the assumption that hydrolysis reaction is quantitative. ^c++, soluble at room temperature; +, soluble at elevated temperature; -, insoluble. ^d M_n of PS block is 11,320.

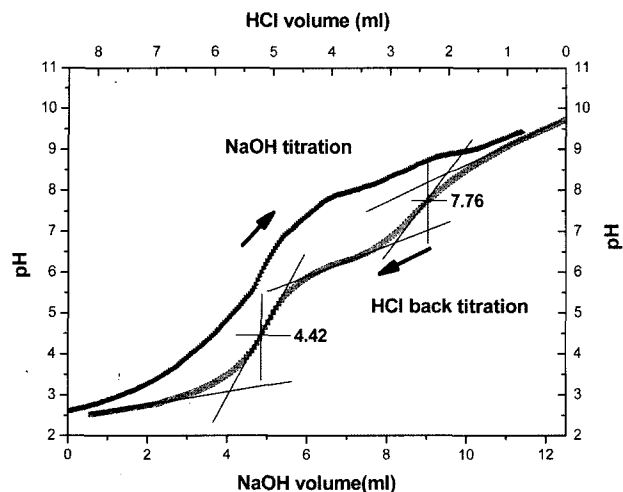


Figure 4. Titration curves PS-*b*-PVBPA (10 k-5 k-H) by direct titration with NaOH (0.025 M) and by backward titration with HCl (0.05 M).

lyzed slowly, the titration curve is not sensitive to the inflection points. Similar titration curves were observed in vinylphosphonic acid by direct titration.³ On the other hand, the backward titration curve with HCl shows a typical titration curve of a dibasic acid.^{26,31} The two different inflection points of the curve (pH 4.42 and pH 7.76) represent the equivalent points of first acid group and second acid group of the phosphonic acid, respectively. From the information of the inflection points and amount of added titrant, it was possible to calculate the total amount of acid content. As in Table III, the IEC values by pH titration and volumetric back titration show good agreement. In general, determination of acid contents by different methods should give the same value, and the result shows that this principle holds. If the time interval between the forward titration and the backward titration is more than enough (more than 10 h in this cases) all anhydrides are assumed to be hydrolyzed to the corresponding salt form, and this makes the backward titration curve nice. But if the degree of crosslinking is severe, the backward titration curve can not show the real IEC value even though the curve looks nice unless the time interval is sufficiently long. In a volumetric back titration procedure, the sample is reacted with excess NaOH for 12 h, and this duration may be considered enough to convert crosslinked anhydrides to the corresponding phosphonic acid salts. In the volumetric titrations, excess amount of HCl was added to the sample solution containing excess NaOH. Instead of using the excess amount of HCl, direct titration of the sample solution containing excess NaOH in the presence of a suitable indicator can give IEC value. But in this experiment, one additional step was added to titrate the sample solution by standard NaOH solution in the presence of phenolphthalein indicator. The sample prepared with trimethylsilyl bromide shows good agreement in IEC

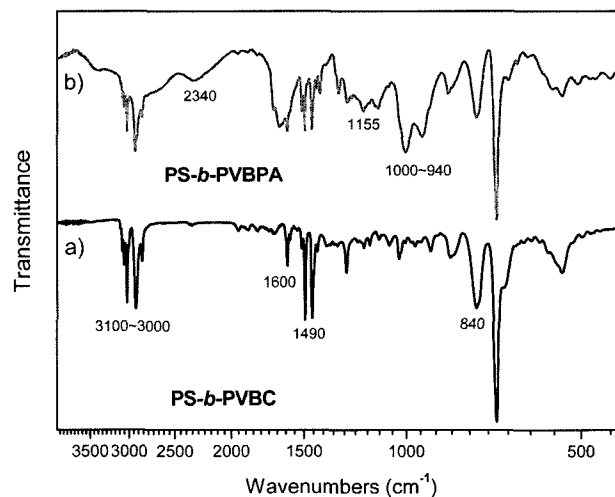


Figure 5. FT-IR spectra of two block copolymers; (a) PS-*b*-PVBC and (b) PS-*b*-PVBPA (10 k-5 k-H).

values among theoretical, pH titrated, and volumetric back titration. And this tells that the hydrolysis reaction is almost quantitative, and the resultant sample after drying is not highly crosslinked. Also the solubilities of the block copolymers in Table III show that these samples are not highly crosslinked, because a sample can not be soluble if it is highly crosslinked.

For the further identification of the structure of the synthesized block copolymers, IR spectra were analyzed. Figure 5 shows the IR spectra of two diblock copolymers. PS-*b*-PVBC spectrum a) shows C-H bending vibration of $-\text{CH}_2-\text{Cl}$ at 1265 cm^{-1} and $=\text{C}-\text{H}$ out-of-plane bending vibration of *p*-disubstituted benzene ring at 840 cm^{-1} . After phosphonation and hydrolysis, the spectrum b) shows P=O stretching vibration of the phosphonic acid at 1155 cm^{-1} , which is due to hydrogen bonding with the (P)OH groups in the acid derivative.⁴⁰ The (P)O-H bending vibration at $1000\text{--}940\text{ cm}^{-1}$ appeared for PS-*b*-PVBPA copolymer, and besides broad (P)O-H - - O=P hydrogen bonding via dimeric form showed broad absorption at around 2340 cm^{-1} , and free -OH groups and H₂O showed absorption band at 3400 cm^{-1} . Also, both spectra show the presence of PS block in the block copolymers: $=\text{C}-\text{H}$ out of plane bending vibration of monosubstituted benzene ring at 700 and 758 cm^{-1} , C-H stretching of benzene ring at 3100 cm^{-1} , skeletal vibrations of benzene ring at 1600 and 1490 cm^{-1} .

The degradation process and thermal stability of block copolymers were evaluated by TGA experiments and the results are shown in Figure 6. All samples showed slight weight loss of up to 100°C due to absorbed water. Two stages of degradation are evident in PS-*b*-PVBP copolymers, the first begins from about 300 to 370°C , and the second stage is from 400 to 500°C . According to the literature,^{11,41} a weight loss between 250 and 370°C is attributed to the

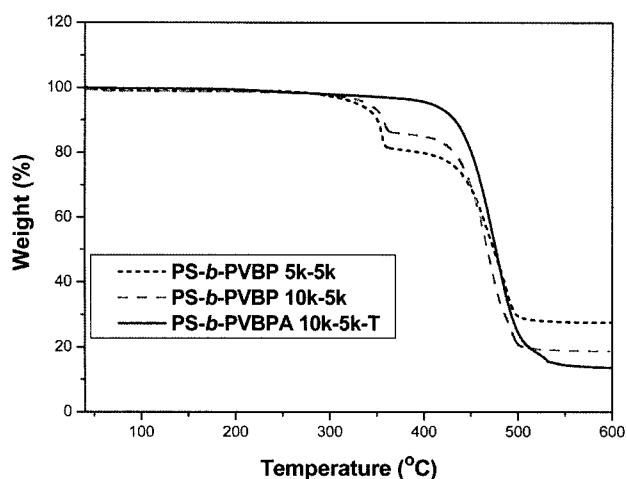


Figure 6. TGA thermograms of the PS-*b*-PVBP copolymers and PS-*b*-PVBPA copolymer.

fragmentation of the ethyl phosphate unit into the free acid and ethylene, and possibly a subsequent formation of anhydride groups from two phosphonic acids. Actually, the first weight losses were 13.2% for PS-*b*-PVBP 10 k-5 k and 18.3% for PS-*b*-PVBP 5 k-5 k, which corresponded nearly to the calculated values, i.e., 12.3% for PS-*b*-PVBP 10 k-5 k and 16.4% for PS-*b*-PVBP 5 k-5 k (16.4% accounts for 12.4% for de-ethylation and 4.0% for dehydration). The second stage is responsible for decomposition of anhydride form of polymeric phosphonic acid, which is in good agreement with that of PS-*b*-PVBPA copolymer. On the other hand, the first weight loss in PS-*b*-PVBPA copolymer occurred very slowly from room temperature to 400 °C, which corresponded to a weight loss due to absorbed water and the dehydration of phosphonic acids. Elimination of two water molecules from two phosphonic acid moieties will account for the theoretical maximum level of dehydration, and this corresponds to 2.8 wt% for PS-*b*-PVBPA 10 k-5 k-T. The observed weight loss of 3.0 wt% at 360 °C for this copolymer is, therefore, partially due to small amount of physically bound water. The anhydride form of poly(vinylphosphonic acid) is known to be stable up to 400 °C, and a poly(vinylphosphonic acid) sample with thermally aged above 400 °C under nitrogen was reported to be convertible into its acid form by hydrolysis in water.³⁹ Recently an aromatic polysulfone containing -CF₂-PO₃H₂ acid was reported to undergo thermal degradation from 230 to 320 °C corresponding to the elimination of the whole functional groups.⁴² But in this study the PS-*b*-PVBPA copolymer and its precursors exhibited better thermal stabilities by showing very similar thermal decomposition behaviors as in poly(vinylphosphonic acid) and its precursors. In Figure 6, the TGA thermogram of the PS-*b*-PVBPA shows very flat line from room temperature to 400 °C. When the copolymer was heated to 300 °C for 10 min under nitrogen, the recovered

sample showed almost identical IEC value as the original. So it may be stated that the PS-*b*-PVBPA copolymer sample is thermally stable up to 400 °C, at least under nitrogen atmosphere.

For a membrane with phosphonic acid containing polymer, proton conductivity of one or two orders lower is typically observed compared to that with sulfonic acid containing polymer for a given IEC value. The reason can be attributed to the low acidity of a phosphonic acid whose pK_a is 2-3.⁴³ Reported conductivity value of aromatic polysulfone containing difluoromethylenephosphonic acid was 5×10^{-3} S/cm at 100 °C in water when the IEC value was 1.79 meq/g,⁴² and that of poly(*p*-phenylene) containing phenylphosphonic acid was 1×10^{-4} S/cm at 60 °C and 90% relative humidity when the IEC value was 1.31.⁴⁴ These conductivity values are quite low when one compares them to the conductivity of Nafion (~0.1 S/cm at room temperature with IEC value of 0.91 meq/g). In this research, therefore, block copolymers with relatively high IEC values of 2.91-4.64 meq/g were prepared to obtain a membrane with reasonable proton conductivity value. But the block copolymers were very brittle that polymer blend membranes with an engineering plastic were tried as in the case with poly(vinylphosphonate-*b*-styrene),²⁹ and the results will be reported elsewhere.

Conclusions

Well-defined amphiphilic diblock copolymers with both hydrophilic segments (PVBPA) and hydrophobic segments (PS) were synthesized by consecutive preparation of TEMPO terminated PS, SFRP of VBC using PS-TEMPO, phosphonation via the Arbuzov reaction, and hydrolysis. The molecular structure of the obtained PS-*b*-PVBC copolymers was confirmed by ¹H-NMR, FT-IR, and GPC. The chain lengths of both blocks are easily controlled. In the phosphonation reaction of PS-*b*-PVBC, degree of phosphonation was quantitative at 120 °C, and the main chain of the diblock copolymers was stable as confirmed by ¹H-NMR. Quantitative conversion was observed in two step hydrolysis reaction using trimethylsilyl bromide. In the pH titration of the phosphonic acid containing block copolymer, a direct titration by NaOH solution was not possible to generate good titration curve of a dibasic acid probably due to anhydride formations between phosphonic acids, but back titration was good to generate a good titration curve. IEC values were calculated from both pH titration and volumetric back titration results. Both titration methods gave almost same IEC value, indicating that these two methods are good to titrate phosphonic acid containing polymers having some crosslinked phosphonic acid anhydride groups during their preparation steps, especially sample drying step. Thermal gravimetric analysis of the phosphonic acid containing block copolymers showed high thermal stability up to 400 °C, im-

plying that the diblock copolymers with well-defined structures are very good candidates for polymer electrolyte membranes in fuel cell applications at high temperature.

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