

Styrene/Phosphonic Acid Copolymers: Synthesis and Thermal, Mechanical, and Electrochemical Characterization

L. E. P. Santos,¹ L. S. Hanamoto,¹ R. P. Pereira,² A. M. Rocco,³ M. I. Felisberti¹

¹Instituto de Química, Universidade Estadual de Campinas, Campinas 13083-970, SP, Brazil

²Instituto de Ciências Exatas, Universidade Federal Fluminense, Volta Redonda, RJ, Brazil

³Grupo de Materiais Condutores e Energia, Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro 21945-970, RJ, Brazil

Received 11 May 2009; accepted 14 April 2010

DOI 10.1002/app.32641

Published online 27 July 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this study, a series of poly(styrene-co-vinyl phosphonic acid) [P(S-co-VPA)] copolymers were synthesized by the free-radical copolymerization of styrene and vinyl dimethyl phosphonate followed by alkaline hydrolysis. The P(S-co-VPA) copolymers were characterized by size exclusion chromatography (gel permeation chromatography), Fourier transform infrared vibrational spectroscopy, proton nuclear magnetic resonance, thermogravimetric analysis, differential scanning calorimetry, dynamic mechanical analysis, and electrochemical impedance spectroscopy. Despite the difference between the copolymerization ratios of styrene and vinyl dimethyl phosphonate, the resulting copolymers presented single glass transitions at temperatures that depended on the acidic group amount. The glass transition shifted to a

higher temperature and became broader as the amount of phosphonic acid increased. The storage modulus at temperatures higher than the glass transition also increased with increasing acidic groups because of intramolecular and intermolecular interactions. All of the acid copolymers were thermally stable to at least 300°C. A high oxidative stability was found for 3 : 1 P(S-co-VPA), which also presented conductivity values on the order of $10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at room temperature. The 1 : 1 P(S-co-VPA) membrane presented Arrhenius-type behavior at temperatures from 30 to 80°C and conductivity on the order of $10^{-5} \Omega^{-1} \text{ cm}^{-1}$. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 460–471, 2011

Key words: copolymerization; functionalization of polymers; membranes

INTRODUCTION

Fuel cells (FCs) are devices in which the chemical energy stored in a fuel (e.g., H₂) is converted into electrical energy; they represent a step toward a hydrogen-based economy.¹ FCs are considered one of the best alternatives so far for both mobile and stationary sources of energy because of their numerous features, including their high conversion efficiency, lower pollutant emissions, and scalability.² FC-powered vehicles present a higher conversion efficiency than conventional (internal combustion) engines under identical test conditions.³ Additionally, gas emissions from internal combustion engines, especially CO and NO_x, are known to be largely responsible for increasing air pollution,

whereas FCs provide water vapor as the product of the process. However, even with the high investments in FC technology in many countries, prototypes for FC-based vehicles still require optimizations, especially to decrease the size and weight of the devices and to increase their power density.

Among the different FCs developed, the proton-exchange membrane fuel cell (PEMFC) is one of the most promising devices.⁴ It has been mostly designed for small-power density applications, such as vehicles and electronic devices.⁵ Most of the PEMFCs described in the literature use commercial proton-exchange membranes, such as Dow (Dow Chemicals), Flemion (Asahi Glass), and Nafion (DuPont) membranes.⁶ However, the characteristics of these materials restrict the temperature range of PEMFC operation from 50 to 125°C.⁷ Different studies have shown the ability of styrene copolymers and styrene-modified polymers (e.g., sulfonated or phosphonated styrene) in the prevention of fuel crossover.⁸ The absence or decrease of crossover in FC membranes can reduce current at the cathode and, hence, the efficiency of the device.

Nafion is among the most used membranes in PEMFCs and possesses good properties, such as good conductivity and chemical stability.⁹ However,

Correspondence to: M. I. Felisberti (misabel@iqm.unicamp.br).

Contract grant sponsors: Conselho Nacional de Desenvolvimento Científico e Tecnológico, Fundação de Amparo à Pesquisa do Estado de São Paulo, Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro, Rede de Células a Combustível/Ministério da Ciência e Tecnologia.

its proton mobility decreases strongly with dehydration at high temperatures because of the chemical structure of the chain backbone.¹⁰ The relation between the proton-conduction mechanisms and the nanostructure of Nafion is important for guiding the molecular architecture and nanostructure of new polymer electrolytes.¹¹

In proton-conductive membranes, the conductivity is usually attributed to hydronium ion (H_3O^+) transport through the hydrated solid. In some examples, a highly hydrated channel-like structure is responsible for the ion path during the process. Considering specific features of fluorinated and nonfluorinated membranes, many studies have been developed to obtain new proton-conductive membranes,¹² especially for use in electric vehicles.¹³

Among the numerous applications of vinylphosphonic acid copolymers described thus far, some have focused on dental and orthopedic biomaterials,^{14,15} cation-exchange membranes, specific cation binding and removal,¹⁶ separation membranes,¹⁷ conductive blends,¹⁸ FC membranes,^{19,20} and other applications.²¹ Particularly, much attention has been devoted to the synthesis, characterization, and proton conduction of phosphonic acid-based membranes, with their application aimed in FCs.²² For phosphonated polymer membranes, the proton-conductivity dependence on the number of phosphonic acid groups has been studied, as high values can be achieved for sufficiently high phosphonic acid group concentrations.²³ Thus, the relevance of studying the synthesis and characterization of phosphonated polymers is not only based on the fundamental issues to be addressed but also on their potential applications.

Aslan and Bozkurt²⁴ developed and characterized polymer electrolyte membranes based on ironical crosslinked poly(1-vinyl-1,2,3-triazole) and poly(vinyl phosphonic acid). The membrane materials produced by the complexation of both polymers were homogeneous and showed a proton conductivity of 2.5×10^{-5} S/cm at 180°C in the anhydrous state. After humidification, the observed proton conductivities were close to that of Nafion 117 at the same humidity level.

Thermoresponsive hydrogels based on poly(*N*-isopropylacrylamide-*co*-vinylphosphonic acid) have been studied. These hydrogels presented lower critical solution temperature behavior at temperatures that were dependent on the copolymer composition. The water content in these hydrogels also depended on the copolymer composition. After biomineralization by urea, the potential of the resulting membranes as deliverers of bovine serum albumin used as a model drug were tested.²⁵

Poly(styrene-*co*-vinyl phosphonic acid) [P(*S-co*-VPA)] ionomers were synthesized by free-radical polymerization and characterized by Wu and Weiss.²⁶ These authors observed a lower glass-transition tem-

perature for the phosphonate ester and a higher glass-transition temperature for the phosphonic acid derivative in comparison with polystyrene. Moreover, the ionomers absorbed relatively little water, and this behavior was due to the nature and effectiveness of the hydrogen bonding between the phosphonic acid groups, which were unavailable for hydrogen bonding with water.

More recently, the synthesis of poly(styrene-*b*-vinylphosphonic acid) diblock copolymers via sequential anionic polymerization was studied, and the nanostructure of these polymer electrolytes was reported. First, poly(styrene-*b*-diethyl vinylphosphonate) copolymers were synthesized, and the poly-(diethyl vinylphosphonate) block was subsequently completely hydrolyzed. The copolymers presented two distinct glass transitions; this indicated phase separation between the two blocks. Atomic force microscopy studies revealed nanophase-separated morphologies with continuous phosphonated domains. After humidification, the copolymers reached proton conductivities on the order of 30 mS/cm at 130°C.²⁷

The main goal of this study was the synthesis of random P(*S-co*-VPA) copolymers and the evaluation of their thermal, spectroscopic, and electrochemical characteristics. For this purpose, copolymers of styrene and vinyl dimethyl phosphonate (VDMP) obtained by free-radical polymerization were hydrolyzed with a sodium hydroxide solution followed by neutralization to give P(*S-co*-VPA). This route differed from that reported by Wu and Weiss²⁶ by the polymerization time and temperature and by the hydrolysis step: the copolymers were obtained from the acid hydrolysis of poly(styrene-*co*-vinyl dimethyl phosphonate) [P(*S-co*-VDMP)]. The acid hydrolysis produced an insoluble polymer in the reaction medium, which made the complete hydrolysis difficult. As we demonstrate, the alkaline hydrolysis of the copolymer was also not complete; however, the steps of separation and purification were easier because no emulsion was formed. Because of the parameters used in the synthesis, thermal, spectroscopic, and mechanical characterizations were performed to compare our results with those previously reported. To establish a wider characterization of the obtained copolymers, part of our attention was dedicated to electrochemical characterizations of the membranes. The copolymerization of vinylphosphonic acid and styrene may have resulted in polymers that combined the characteristics of proton conductivity, associated with the presence of phosphonic acid protogenic groups, with a lower methanol crossover, characteristic of styrene-based copolymers.²⁸ The study of membranes based on this polymer for FC applications, however, will be the goal of a future study. Methanol crossover characterizations and FC tests with the obtained membranes, thus, were out of the scope of this study.

EXPERIMENTAL

Materials and synthesis procedures

P(S-co-VDMP)

Styrene monomer (Rhodia, Paulinia, Brazil) was washed with a 5% NaOH solution to remove the hydroquinone present as a polymerization inhibitor; this was followed by vacuum distillation. The distillate was stored at 5°C in amber flasks. VDMP from Fluka (Munich, Germany) was distilled and also stored at 5°C in amber flasks. Benzoyl peroxide, used as an initiator, was previously dried *in vacuo* for 3 h. The polymerization was carried out in bulk. Styrene and VDMP monomers and benzoyl peroxide at a concentration of 0.1 mol % with respect to the monomer content were placed in a glass vessel; this was followed by degassing for O₂ removal. After this procedure, the ampule was sealed *in vacuo* and put into a silicone oil bath at 80°C for 1 week. After polymerization, P(S-co-VDMP) was dissolved in chloroform and precipitated by ethyl ether to remove residual monomers. This procedure was repeated twice, and then, the product was dried *in vacuo*. Different molar ratios of styrene/VDMP were used in the synthesis: 1 : 1, 3 : 1, 4 : 1, and 5 : 1.

Poly(styrene-co-vinyl phosphonic acid) produced via the alkaline hydrolysis of P(S-co-VDMP)

P(S-co-VDMP) was dissolved in a 9 : 1 solution of benzyl alcohol and methanol containing 5 wt % NaOH. This medium was kept under stirring at 110°C for 3 days and was then cooled to 50°C, and concentrated HCl was added until the pH was equal to 1. The precipitated salt (NaCl) was removed by filtration, and the solution containing the polymer was slowly added to ethanol to precipitate the P(S-co-VPA) copolymer. The copolymer was separated by filtration, washed with water to pH 7, dried *in vacuo* at 80°C, and stored in a desiccator to avoid humidity.

P(S-co-VPA) was dissolved (ca. 10 wt %) in benzyl alcohol at 90°C, and the solution was stirred for 2 h. Membranes were obtained by casting from these solutions onto Petri dishes; this was followed by drying at 90°C *in vacuo* until a constant weight was reached.

Copolymer characterization

The molar masses of the copolymers and the molar mass distributions were determined by size exclusion chromatography (gel permeation chromatography) with a Waters chromatograph equipped with polystyrene columns (Ultrastaygel) (Montgomeryville, PA) and calibrated with polystyrene standards. Dimethylformamide was used as an eluent, and the runs were performed at 70°C.

The infrared spectra of the membranes obtained by casting were collected with a Bohmer Hartman Braun MB series Fourier transform infrared spectrometer (Varian Gemini Spectrometer, Canton, MA) with a resolution of 2 cm⁻¹ and 32 scans.

Proton nuclear magnetic resonance (¹H-NMR) spectra of the copolymers were obtained with 5-mm quartz tubes at 22°C in a Gemini spectrometer. Chloroform-*d* and dimethyl sulfoxide-*d*₆ were used as solvents for the ester copolymers and acid copolymers, respectively. The copolymer composition, expressed as the molar ratio of styrene units to VDMP units, was determined from the ¹H-NMR spectra by the integration of the peaks corresponding to hydrogen atoms of the aromatic ring of the styrene segments (*A*_{5H}) and those of the methyl groups of the VDMP segments (*A*_{6H}) as follows:

$$\text{Styrene/VDMP molar ratio} = \frac{(A_{5H}/5)}{(A_{6H}/6)}$$

Differential scanning calorimetry was performed with a TA Instruments DSC 2910 (New Castle, DE) under an N₂ atmosphere with around 8 mg of sample and the following program: (1) heating from 25 to 250°C at 20°C/min, (2) isotherm of 5 min, (3) cooling to 25°C at 20°C/min, (4) isotherm of 5 min, and (5) heating to 200°C at 20°C/min. The differential scanning calorimetry curves shown in this article correspond to the second heating scan (step 5), and they were normalized with respect to each sample mass.

Dynamic mechanical analysis of the acid copolymer membranes was performed on a Rheometric Scientific DMTA V (Piscataway, NJ) with a tensile fixture in the temperature range between -80 and 240°C at a heating rate of 2°C/min with a fixed frequency of 1 Hz and a strain amplitude of 0.01%.

The thermal stability was evaluated in a TGA 2950 (TA Instruments) at a heating rate of 10°C/min under an argon atmosphere. The initial mass of the samples was kept around 5 mg.

Swelling, oxidative behavior, and electrochemical characterization of the P(S-co-VPA) membranes

Membranes of the acid copolymers were immersed in water or methanol at 25°C for 168 h and were then dried with paper (to remove only excess water or methanol), weighed (*W*_S), dried *in vacuo* at 80°C, and weighed again (*W*₀). The swelling quotient (*Q*) was calculated as follows:

$$Q = \frac{(W_S - W_0)}{W_0}$$

Membranes (3 cm × 0.7 cm × 70 μm) were also immersed in an aqueous solution containing 3% H₂O₂ and 4 ppm FeCl₃ at 80°C for 5 days. The sample weight was measured every 24 h; then, the sample was dried *in vacuo* at 80°C until a constant

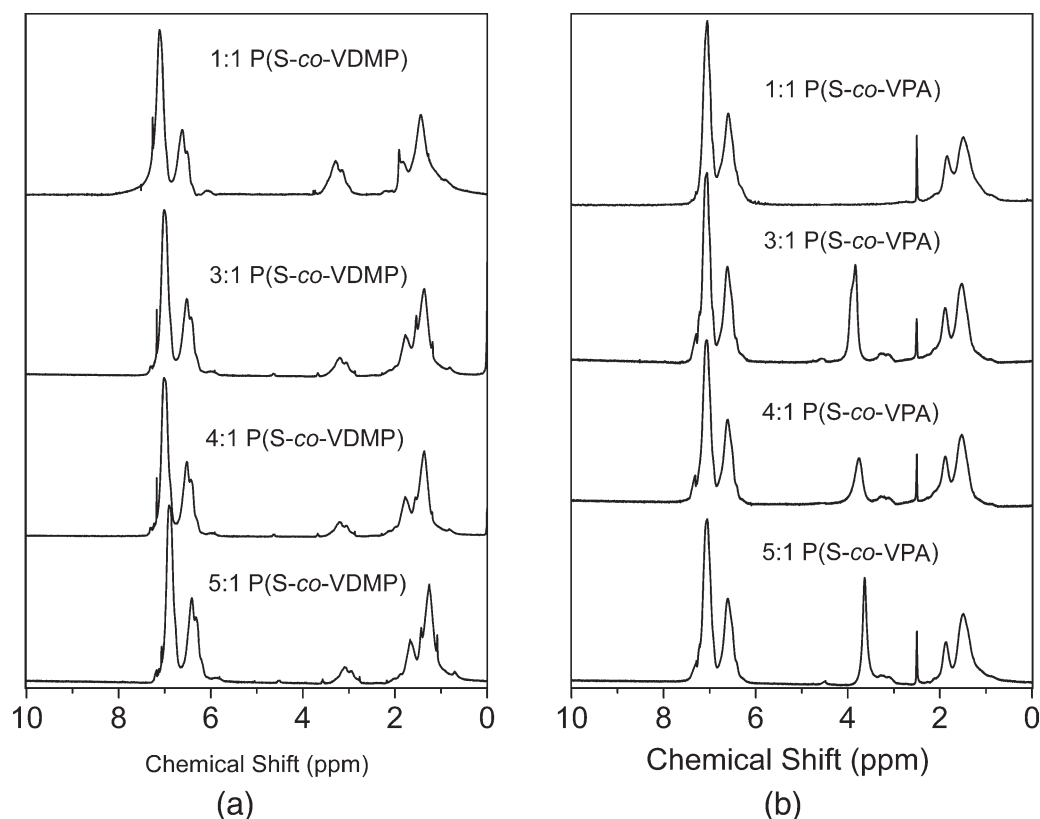


Figure 1 $^1\text{H-NMR}$ spectra of the copolymers: (a) P(S-co-VDMP) and (b) P(S-co-VPA).

weight was reached. To compare the behavior of the synthesized polymers, a Nafion 117 sample was used as a control in the measurements.

Electrochemical impedance spectra were obtained for the dry membranes and for membranes previously immersed in water or 10% H_3PO_4 at room temperature with two electrode (stainless steel) cells of 1 cm^2 under ambient pressure. The spectra were obtained in the frequency range from 1 MHz to 10 mHz in a Autolab EcoChemie PGSTAT30/FRA (Utrecht, Netherlands). The conductivity was calculated with the following equation on the basis of the resistance values obtained from each electrochemical impedance spectrum:

$$\text{Conductivity} = \frac{L}{AR}$$

where L is the thickness of the film, A is the area (1 cm^2), and R is the resistance obtained through simulation of the impedance spectra in the high-frequency region. All samples were analyzed in triplicate, and the data presented in this article reflect the mean values accompanied by their respective deviations.

RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization of the copolymers

The ester copolymers obtained were soluble in chloroform, tetrahydrofuran, dioxane, benzene, and tol-

uene, whereas the corresponding acid copolymers were soluble in dimethylformamide and benzyl alcohol at temperatures above 80°C . Below this temperature, the solutions produced a thermoreversible gel, probably because of interactions among acid groups. As a result, some properties, such as molar mass, were determined for the ester copolymers.

The $^1\text{H-NMR}$ spectra of the ester and acid copolymers are shown in Figure 1. The signals at 7.25 ppm [Fig. 1(a)] and 3.25 ppm [Fig. 1(b)] were attributed to CDCl_3 and dimethyl sulfoxide- d_6 , respectively. The spectra of the ester copolymers exhibited signals at 6.5 and 7 ppm (hydrogen of the aromatic ring), 3.3 ppm (hydrogen of methyl group of VDMP), and 1.44 and 1.88 ppm (hydrogen of the CH and CH_2 groups of the main chain). Hydrogen atoms of methyl groups were also observed in the spectra of the P(S-co-VPA) copolymers, except for the 1 : 1 copolymer; this indicated that the acid hydrolysis was not complete. The copolymer solutions in the 9 : 1 solution of benzyl alcohol/methanol containing 5 wt % NaOH were transparent before the reaction. However, some of these solutions became turbid as the hydrolysis proceeded as consequence of phase segregation. This meant the hydrolysis occurred in a heterogeneous medium and should have been diffusion-controlled, except for the 1 : 1 copolymer solution, which was homogeneous (transparent) during the reaction. The copolymer compositions determined

TABLE I
Compositions, Molar Masses, and Molar Mass Distributions of the Copolymers

Copolymer	Styrene/VDMP molar ratio		M_n (g/mol)	M_n/M_w
	Reaction medium	Copolymer		
1 : 1 P(S-co-VDMP)	1 : 1	6 : 1	112,000	1.5
3 : 1 P(S-co-VDMP)	3 : 1	12.2 : 1	108,000	1.8
4 : 1 P(S-co-VDMP)	4 : 1	12 : 8 : 1	104,000	1.8
5 : 1 P(S-co-VDMP)	5 : 1	13.0 : 1	108,000	1.8
Styrene/VPA molar ratio				
1 : 1 P(S-co-VPA)	0	6 : 1	112,000	1.5
3 : 1 P(S-co-VPA)	33 : 1	~ 19 : 1	108,000	1.8
4 : 1 P(S-co-VPA)	32 : 1	~ 19 : 1	104,000	1.8
5 : 1 P(S-co-VPA)	18 : 1	~ 47 : 1	108,000	1.8

M_n = number-average molecular weight; M_w = weight-average molecular weight.

from the $^1\text{H-NMR}$ spectra are shown in Table I. The molar ratios of styrene to vinyl phosphonic acid (VPA) in the P(S-co-VPA) copolymers were determined as the differences between the concentrations before and after the hydrolysis of VDMP. The pronounced difference in the monomer composition from the reaction medium compared to the synthesized copolymers was due to the different copolymerization ratios of each monomer. In an earlier study, Santos²⁹ found reactivity parameters of 3.6 for styrene and 0.15 for vinyl dimethylphosphonate using the method of Kellen and Tüdos.³⁰ The copolymers obtained from the monomer solution with molar ratios of styrene to vinyl dimethylphosphonate equal to 3 : 1, 4 : 1, and 5 : 1 presented similar compositions ($\sim 13 : 1$), whereas the copolymer obtained from monomer solutions having a molar ratio of 1 : 1 was richer in vinyl dimethylphosphonate (6 : 1). These results differed from those reported by Wu and Weiss.²⁶ These authors synthesized copolymers with different compositions from monomer solutions with comparable compositions with those used in this study. The main differences between the methods used by these authors and by us were the time, temperature, and medium where the polymerization was conducted. Wu and Weiss²⁶ performed their polymerization at 100°C for 24 h in toluene. In this study, the bulk polymerization was conducted at 80°C for 1 week. As reported earlier, the reactivity parameters of styrene and vinyl dimethylphosphonate were 3.6 and 0.25, respectively.²⁹ Thus, the relative concentration of styrene and vinyl dimethylphosphonate decreased as the reaction conversion increased. As consequence, the reaction rate and the reaction conversion decreased with the polymerization time. After a long polymerization time, it is possible that the global composition of copolymers tends to be very close, as

observed in this study. However, the monomer distribution in the polymer chains should not have been the same because of the large difference between the reactivity parameters.

Table I also shows the average molar mass and its distribution for P(S-co-VDMP). The molar masses of the copolymers obtained in this study were higher than those reported by Wu and Weiss²⁶ for copolymers with similar compositions, perhaps because the polymerization temperature used in this study was lower. Because the amount of vinyl dimethylphosphonate in the copolymers was relatively low, the same molar mass and distribution for the acid copolymers was assumed.

Figure 2 shows the vibrational spectra of 3 : 1 P(S-co-VDMP) and its corresponding acid copolymer 3 : 1 P(S-co-VPA) obtained by alkaline hydrolysis. The spectrum of the ester copolymer showed bands corresponding to aromatic C—H stretching (between 3125 and 3000 cm^{-1}),³¹ C=C aromatic stretching (1493 and 1452 cm^{-1}),^{17,31} P=O stretching (between 1240 cm^{-1}),²⁶ and P—O—C stretching (1059, 1033, and 820 cm^{-1}).²⁶ The spectra of the acid copolymers exhibited bands corresponding to O—H stretching of the acid group (a broad band between 3300 and 2500 cm^{-1})¹⁷ and P—OH stretching (980 and 930 cm^{-1}).²⁶ The spectrum of the 3 : 1 P(S-co-VPA) also presented bands at 1059, 1033, and 820 cm^{-1} ; this indicated the incompleteness of the hydrolysis. Because the electrochemical characterization and FC application of the P(S-co-VPA) membranes were conducted in acid media, these residual ester groups might have been hydrolyzed, and their presence did not interfere with the final properties.²⁶

Figure 3 shows the differential scanning calorimetry curves of the copolymers. The glass transitions of the ester copolymers were lower than those for the corresponding acid copolymers. In general, the glass-transition temperature of the acid copolymers

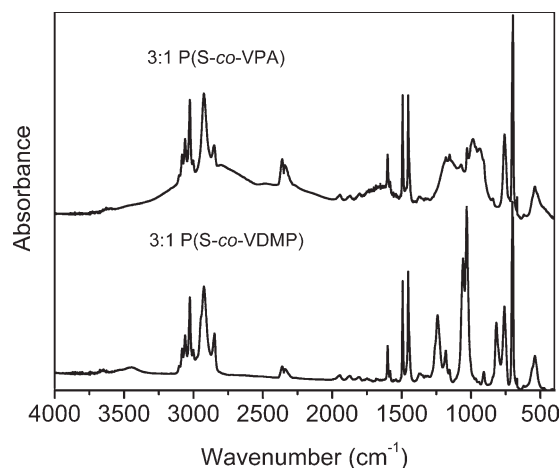


Figure 2 Infrared vibrational spectra of the copolymers.

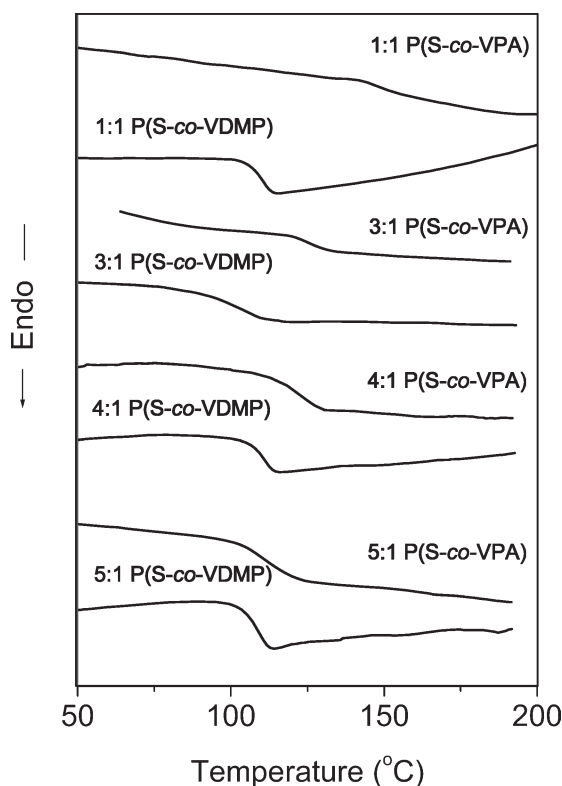


Figure 3 Differential scanning calorimetry curves of the copolymers (second heating scan at 20°C/min).

TABLE II
Thermal Properties of the Copolymers

Copolymer	T_g (°C)	$T_{5\%}$ (°C)	Residue at 600°C (%)
1 : 1 P(S-co-VDMP)	108	366	3,6
3 : 1 P(S-co-VDMP)	100	360	~ 0
4 : 1 P(S-co-VDMP)	109	384	~ 0
5 : 1 P(S-co-VDMP)	106	371	~ 0
1 : 1 P(S-co-VPA)	158	346	10
3 : 1 P(S-co-VPA)	125	360	5.5
4 : 1 P(S-co-VPA)	122	384	4.3
5 : 1 P(S-co-VPA)	113	371	3.5

$T_{5\%}$ = temperature corresponding to a 5 wt % mass loss;
 T_g = glass-transition temperature.

increased as the amount of phosphonic acid increased (Table II). This was mainly attributed to hydrogen-bond interactions between the acid groups of the copolymers. The same interaction was responsible for the dynamic mechanical behavior shown in Figure 4. The storage modulus presented an intense drop in the glass-transition region, whereas the loss modulus presented a peak whose width increased as the number of acid groups increased; this indicated the broadness of the relaxation time distribution. For acid copolymers obtained from 3 : 1, 4 : 1, and 5 : 1 P(S-co-VDMP), in addition to the hydrogen bond interaction that contributed to the broadening of the relaxation spectra, the hydrolysis was not complete,

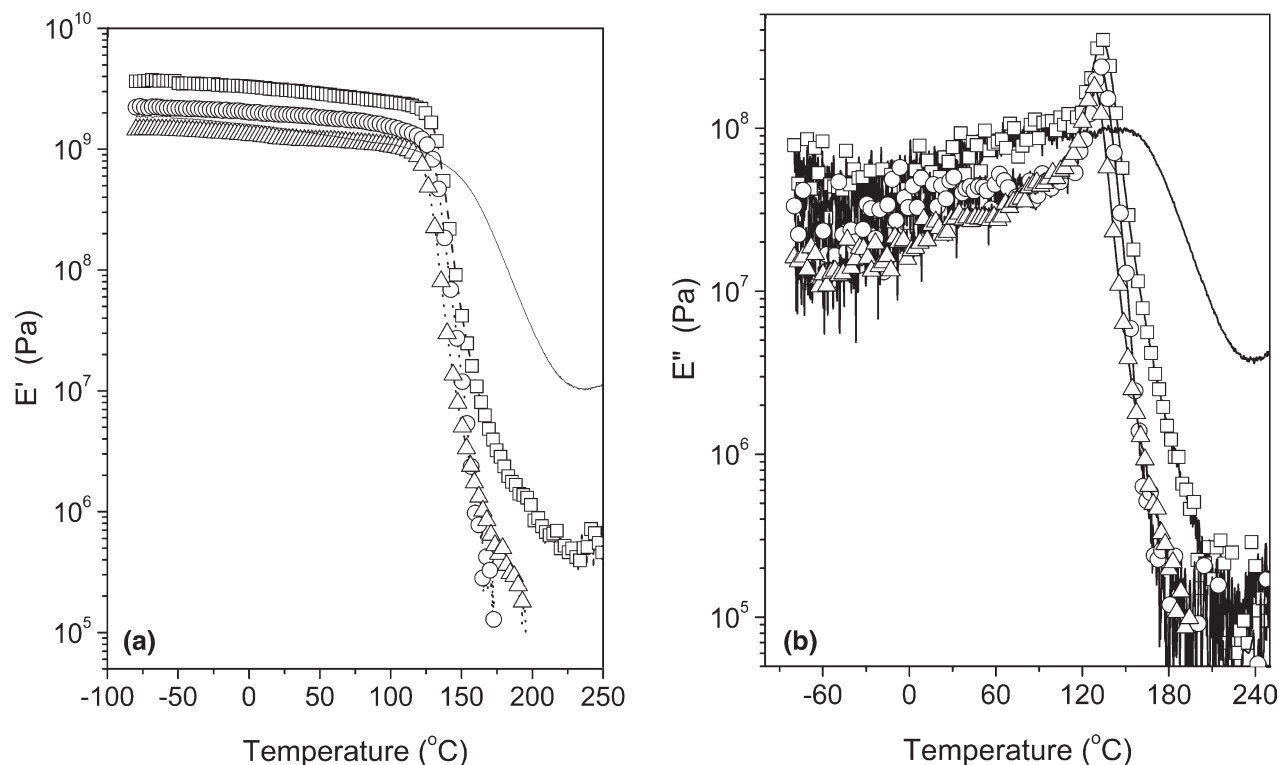


Figure 4 Dynamic mechanical curves of P(S-co-VPA) copolymers as a function of temperature with styrene/VPA ratios of (○) 5 : 1, (△) 4 : 1, (□) 3 : 1, and (—) 1 : 1 : (a) storage modulus (E') and (b) loss modulus (E'').

TABLE III
Water and Methanol Swelling for the P(S-co-VPA) and Nafion 117 Membranes

Membrane	Water swelling (%)	Methanol swelling (%)
1 : 1 P(S-co-VPA)	44.0 ± 12	58 ± 2
3 : 1 P(S-co-VPA)	6.7 ± 1	16.3 ± 1
Nafion 117	21.2 ± 4	51.7 ± 3

and therefore, these spectra should have presented additional relaxations of the ester segments. Despite these characteristics, the 1 : 1 P(S-co-VPA) copolymer presented the broadest loss modulus curves; this indicated that the hydrogen-bond interactions were more effective in the creation of microheterogeneities through the material. Another consequence of the hydrogen-bond interactions was the high modulus value for 1 : 1 P(S-co-VPA) at temperatures higher than the glass-transition temperature [Fig. 4(a)].

The thermal stabilities of the copolymers under an inert atmosphere were studied by thermogravimetric analyses. In this study, the thermal stability was examined with respect to the temperature corresponding to a 5 wt % mass loss. The temperatures corresponding to a 5 wt % mass loss and the residual masses at 600°C are listed in Table II. The ester copolymers exhibited a higher thermal stability than the corresponding acid copolymers, as shown in Table II. Polymers containing carboxylic and sulfonic groups exhibited a very distinct thermal decomposition behavior when compared to the phosphonic acid based polymers. Although carboxylic and sulfonic acid polymers usually undergo thermal decomposition by decarboxylation³² and desulfonation,^{33,34} respectively, phosphonic acid polymers tend to dehydrate, forming phosphonic anhydrides with strong P—O—P bonds²⁰ and crosslinking. These anhydrides and crosslinked structures, which resulted from the dehydration of phosphonic acid containing membranes, exhibited higher decomposition temperatures than the corresponding acid polymers. Despite the dehydration process of the acid copolymers, their thermal stability was higher than 300°C. The residue at 600°C was higher for the acid copolymers and increased as the amount of vinyl acid groups in the copolymer increased as a consequence of the P—O—P crosslinking.

Swelling and electrochemical characterization of the P(S-co-VPA) membranes

Table III lists the water and methanol swelling values for the 1 : 1 and 3 : 1 P(S-co-VPA) membranes. The membranes (70 μm thick) presented water swellings of 44.0 ± 12 and 6.7 ± 1%, respectively. Nafion 117 membranes 200 μm thick absorbed 21.2 ± 4% water

under similar experimental conditions. With the total number of hydrophilic groups in each polymer [sulfonic groups for Nafion 117 and phosphonic groups for P(S-co-VPA)] considered, the water absorption by the functional groups was higher in P(S-co-VPA), even for the 3 : 1 copolymer, than in Nafion 117. Methanol absorption for the 1 : 1 and 3 : 1 P(S-co-VPA) and Nafion 117 were, respectively, 58 ± 2, 16.3 ± 1, and 51.7 ± 3%. These results point to a strong dependence of the methanol absorption on the number and type of hydrophilic groups in the polymer chain.

Several proton-conductive polymeric membranes have been described in the literature, both acid and basic, doped with inorganic acids, for example, sulfonated polysulfone and polybenzimidazole doped with phosphoric acid.³⁵ The addition of an inorganic acid to these membranes is performed, mainly, to increase the charge carriers (proton/hydronium ions) in the system, which can lead to higher conductivity values. Specifically, for phosphonic acid membranes with a small number of phosphonic groups inserted in the chain, the presence of an inorganic acid can guarantee a minimum number of protogenic groups in the system (which contributes, thus, to the proton conductivity) and, simultaneously, inhibits phosphonic anhydride formation. Additionally, theoretical calculations³⁶ on phosphonic acid hydration spheres indicated that a proton excess (the inorganic acid added to the membrane) played an important role in the charge transport of such systems. These calculations also showed the formation of hydration spheres around the phosphonic acid group, the first (h¹) formed by four water molecules, whereas theoretical calculations indicated seven water molecules forming a complete inner hydration sphere. Hydrogels and hydrophilic polymers usually present high swelling behavior, which corresponds to higher [H₂O]/[Acid] ratios than that of the hydration sphere. In P(S-co-VPA) membranes, as the styrene-acid ratio decreased (with an increase in acid content), the number of water molecules absorbed by the membrane increased because of a larger number of acid sites in the system. Additionally, the styrene units acted only as a hydrophobic barrier to water molecules, and thus, there was a higher concentration of bulk water for the acid-rich P(S-co-VPA) membranes.

Figure 5 shows the accelerated oxidation test for 3 : 1 P(S-co-VPA) and Nafion 117. During FC operation, the formation of radicals takes place, which can induce the degradation of the membrane and other cell components.³⁷ Degradation leads, usually, to the hardening of the membrane, which culminates in the destruction of the material. A mass loss of about 2% was observed for Nafion 117 after 5 days, whereas the 3 : 1 P(S-co-VPA) did not exhibit any mass loss over the same period. The high resistance

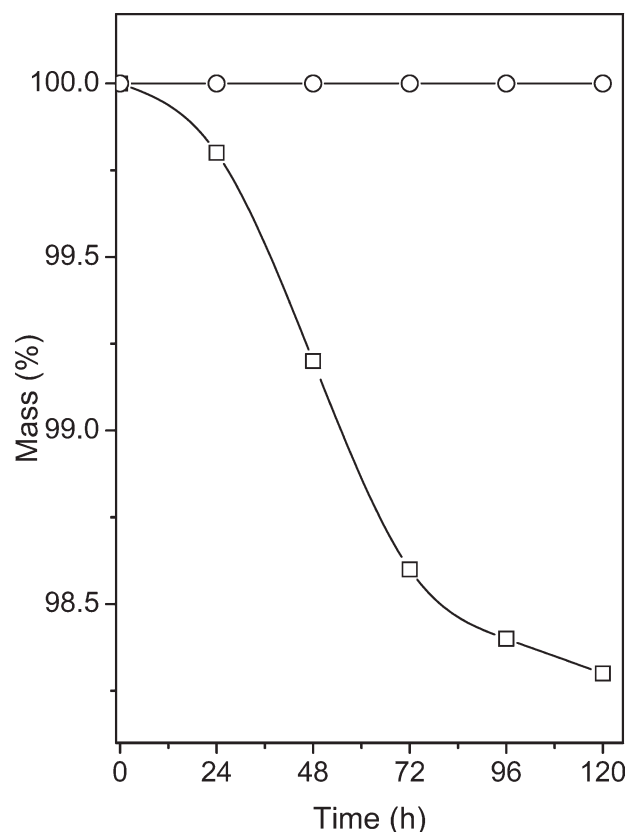


Figure 5 Oxidative stability curves for (○) 3 : 1 P(S-co-VPA) and (□) Nafion 117.

to oxidation determined for the P(S-co-VPA) samples could have been associated with the presence of a large styrene portion in the chains, which presented a low reactivity.

The electrochemical, structural, thermal, and spectroscopic characteristics of several polymer/H₃PO₄ electrolyte membranes have been studied and reported in the literature, and among the studied systems were PEO/H₃PO₄,³⁸ PVA/H₃PO₄, three-dimensional interpenetrating networks,³⁹ poly(ethylene oxide)/poly(methyl methacrylate) (PEO/PMMA)/H₃PO₄,⁴⁰ and polyacrylamide hydrogels with H₃PO₄.⁴¹ Polymer electrolyte membranes based on polymer/acid systems were reviewed by Lassegues,⁴² who identified the thermal stability of such systems as usually limited to 100°C.

The electrochemical impedance spectra of the P(S-co-VPA) samples are shown in Figure 6 for the dry membranes and for membranes immersed in 10% aqueous H₃PO₄ solutions. The spectra were characteristic of ion-conductive materials, presenting a semicircle in the high-frequency region associated with the ion-transport resistance and a straight line in the region of low frequencies. The dry samples presented a purely capacitive behavior, except for the 5 : 1 P(S-co-VPA) membrane, which presented proton conductivity on the order of 10⁻¹⁰ Ω⁻¹ cm⁻¹. In the absence

of water, even protogenic-group-containing polymers presented low or no conductivity because the charge-transport mechanisms included water molecules as carriers or as media for proton migration. The conductivity values calculated for the P(S-co-VPA) membranes are listed in Table IV. A progressively more resistive behavior is shown in Table IV and Figure 6(b-d). For each monomer ratio (styrene/VPA), the proton-transfer resistance decreased as the membranes absorbed H₂O or H₂O/H₃PO₄.

The spectra of the P(S-co-VPA)/H₃PO₄ membranes presented one or more semicircles in the high-frequency region associated with ion-transport resistance in different domains in the polymer bulk. Samples with ratios of 4 : 1 and 5 : 1 immersed for 4 h in 10% aqueous H₃PO₄ solutions presented two consecutive semicircles in the regions of intermediate frequencies. The number of resistive responses varied with the immersion time in acid solution, with one semicircle lasting for 2 h and two more lasting for 4 h. Each of these resistive responses was associated with the formation of isolated hydrated structures, which probably possessed different resistance values for intrastructure and interstructure ion transport. Because of the number of styrene units between the phosphonic acid groups acting as separators and because of the hydration shell around the phosphonic acid groups, these hydrated domains should have presented a smaller resistance to ion transport compared to the transport between adjacent dry domains.

These results suggest that the 4 : 1 and 5 : 1 copolymers presented different structures, despite their similar global composition, as discussed earlier.

As shown in Table IV, the effects of both water and acid on the conductivity of the membranes were observed. The 3 : 1 P(S-co-VPA) sample immersed in water for 72 h at room temperature presented a conductivity of 10⁻⁷ Ω⁻¹ cm⁻¹, whereas the 5 : 1 P(S-co-VPA) sample immersed in water for 24 h presented a conductivity of 10⁻⁹ Ω⁻¹ cm⁻¹.

The maximum conductivities achieved for the membranes immersed in 10% aqueous H₃PO₄ solutions were about 10⁻⁵ Ω⁻¹ cm⁻¹ for 1 : 1 P(S-co-VPA) after 4 h of immersion. Compared to other proton-exchange membranes, 1 : 1 P(S-co-VPA) exhibited a maximum conductivity similar to that of the material reported by Meng et al.,⁴³ which was based on poly(arylene ether) functionalized with phosphonic acid. In their study, membranes containing up to 50 mol % phosphonic acid and 50% humidity presented conductivity values on the order of 10⁻⁵ to 10⁻⁶ Ω⁻¹ cm⁻¹.

Hybrid membranes based on organosiloxanes and phosphonic acid presented conductivity values with a strong dependence on the number of phosphonic acid groups; these values reached 10⁻² Ω⁻¹ cm⁻¹ at

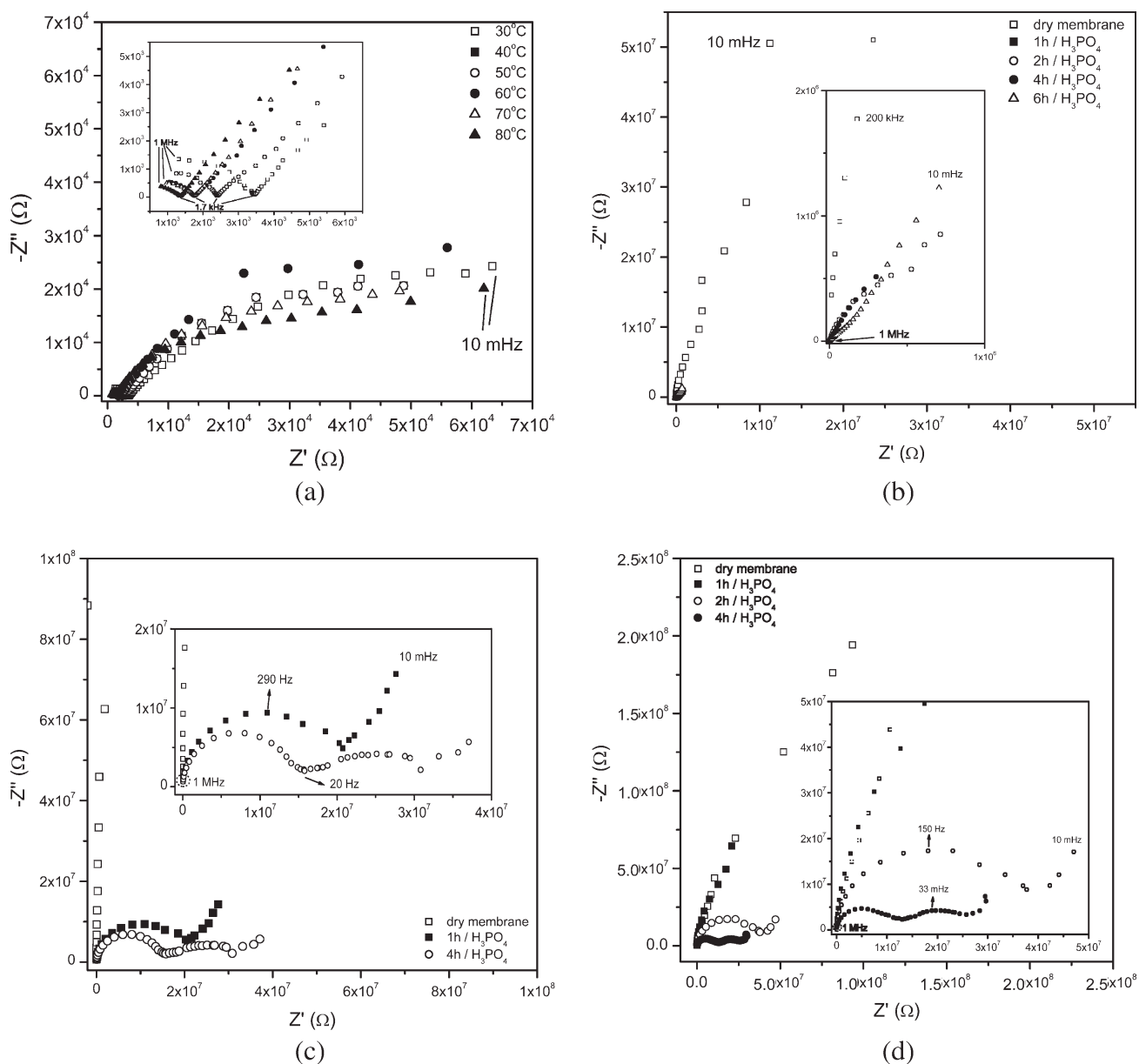


Figure 6 Electrochemical impedance spectra of dry P(S-co-VPA) membranes and the membranes after immersion in aqueous 10% H_3PO_4 solutions: (a) 1 : 1 P(S-co-VPA) at different temperatures and (b) 3 : 1 P(S-co-VPA), (c) 4 : 1 P(S-co-VPA), and (d) 5 : 1 P(S-co-VPA) at room temperature (25°C).

TABLE IV
Conductivity of the Dry Membranes, Membranes Immersed in Water, and Membranes Immersed in 10% Aqueous H_3PO_4 Solutions at Ambient Temperature

Time (h)	Conductivity ($\Omega^{-1} \text{cm}^{-1}$)			
	1 : 1 P(S-co-VPA)	3 : 1 P(S-co-VPA)	4 : 1 P(S-co-VPA)	5 : 1 P(S-co-VPA)
0 (dry)	C	C	C	$7.16 \pm 0.23 \times 10^{-11}$
24/ H_2O	C	C	C	$4.00 \pm 0.43 \times 10^{-9}$
48/ H_2O	C	C	C	C
72/ H_2O	$5.58 \pm 0.64 \times 10^{-8}$	$3.32 \pm 0.38 \times 10^{-7}$	C	C
1/ H_3PO_4	$2.42 \pm 0.12 \times 10^{-7}$	$8.02 \pm 0.20 \times 10^{-7}$	$1.51 \pm 0.08 \times 10^{-9}$	$4.20 \pm 0.47 \times 10^{-11}$
2/ H_3PO_4	$8.32 \pm 0.28 \times 10^{-7}$	$2.64 \pm 0.13 \times 10^{-6}$	$2.99 \pm 0.10 \times 10^{-10}$	$1.50 \pm 0.06 \times 10^{-10}$
4/ H_3PO_4	$9.79 \pm 0.29 \times 10^{-6}$	$5.41 \pm 0.16 \times 10^{-6}$	$1.11 \pm 0.03 \times 10^{-9}$	$5.92 \pm 0.34 \times 10^{-10}$
6/ H_3PO_4	$4.86 \pm 0.31 \times 10^{-6}$	$5.42 \pm 0.24 \times 10^{-7}$	$3.44 \pm 0.06 \times 10^{-9}$	$1.33 \pm 0.08 \times 10^{-8}$

C = capacity behavior.

130°C for the system with a 1 : 1.05 ratio at 100% relative humidity.⁴⁴ VPA homopolymer membranes, studied by Kaltbeitzel et al.,²⁰ presented highly hygroscopic behavior and proton-conductivity values reaching $10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 150°C and 1 bar H_2O atmosphere. In this study, styrene units inhibited water absorption by the membrane, and the maximum conductivity reached $10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 25°C.

The VPA homopolymers were also characterized by NMR spectra and conductivity measurements,⁴⁵ which showed the formation of anhydride units by the condensation of phosphonic acid groups, which greatly inhibited long-range proton transport in the membranes. In the styrene/VPA membranes examined in this study, phosphonic acid groups were separated by styrene units; this resulted in two principal consequences: (1) the mechanical properties of the membranes were strongly influenced by the styrene comonomer content, and (2) the swelling and conductivity were lower than those of the poly(vinyl phosphonic acid) homopolymer. Additionally, the condensation of neighboring phosphonic acid units should have affected the conductivity values only peripherally because the $-\text{PO}_3\text{H}_2$ units possessed a hydration sphere, which allowed their separation in principle and inhibited anhydride formation, despite chain folding.

The 1 : 1 P(S-co-VPA) membranes were immersed for 24 h in 10% H_3PO_4 before the electrochemical analyses. The electrochemical spectra of the 1 : 1 P(S-co-VPA) membranes recorded at different temperatures, as shown in Figure 6(a), exhibited different intercepts at the real component of the electrochemical impedance (Z') axis; this indicated different resistance values, whereas the inclined lines in the low-frequency region did not tend to vary with temperature. Under the conditions of these experiments, the semicircles represented the resistance of the electrolyte, and the inclined lines indicated the resistance against ion passage at the membrane/electrode interfaces. The use of blocking electrodes resulted in a polarization phenomenon in the polymer bulk because there was no proton source or sink. The electrical double layer at each interface possessed infinite resistance against ion transfer, which in the Nyquist plot of the impedance spectra, was represented by a straight line, parallel to the ordinate, associated with a limiting capacitance.^{46,47} In a PEMFC device, however, there is a constant proton supply because of the electrocatalyzed fuel oxidation reaction.

The conductivity of the 1 : 1 P(S-co-VPA) membranes after immersion in 10% H_3PO_4 for 24 h was $10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 25°C. Because a higher acid ratio in the polymer chain is usually associated with the highest proton conduction,⁴⁸ the conductivity of the membrane with a higher ratio of protogenic groups [1 : 1 P(S-co-VPA)] was studied as a function of tem-

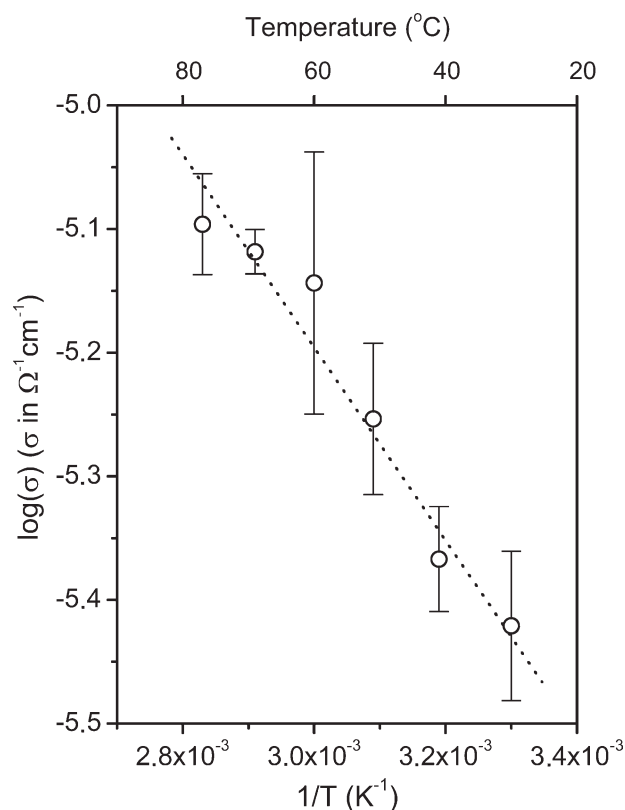


Figure 7 Dependence of the logarithm of the conductivity (σ) on the reciprocal of the temperature ($1/T$) for 1 : 1 P(S-co-VPA) (Arrhenius plot).

perature. Figure 7 shows a plot of the logarithm of the conductivity versus the reciprocal of the temperature (Arrhenius plot) for the 1 : 1 P(S-co-VPA) membrane. The conductivity values reached $10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 80°C, for the 1 : 1 P(S-co-VPA) acid-doped membranes at 100% relative humidity, and linear behavior was observed in the temperature range studied; these findings were compatible with the findings of Kato et al.⁴⁹ for phenylvinylphosphonic acid membranes. The Arrhenius behavior detected for P(S-co-VPA), associated with the conductivity dependence on water and acid immersion, indicated that the proton (H_3O^+) dissociation contribution to conductivity increased with humidity, H_3PO_4 concentration, and temperature.

Yamada and Honma⁵⁰ reported the synthesis and tests in a FC prototype of a poly(vinyl phosphonic acid)/heterocycle composite materials. In their study, membranes achieved a conductivity of $10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 150°C under anhydrous conditions. A nonvehicular mechanism was proposed by the authors to explain the diffusive proton behavior on the basis of the activation energy for charge transport. The transport mechanisms proposed in the literature included a vehicular description, where the proton was complexed by a diffusive molecule, which acted as a carrier.⁵¹ Thus, without water

molecules acting as carriers, conventional polymer membranes do not exhibit sufficient proton conductivity.⁵² Proton transport in polymer membranes in the absence of water is usually described with a nonvehicular mechanism, such as hopping, where the proton moves between adjacent immobile coordination sites, as in poly(imidazole) and poly(benzimidazole).⁵³ The proton transport in a commercial membrane, such as Nafion or poly(ether ether ketone) membrane,^{54,55} and in some composite membranes⁵⁶ is promoted by the presence of water in the system. In this study, the presence of phosphonic acid sites in the polymeric membrane led to a higher proton conductivity in the presence of water and dissolved acids.

CONCLUSIONS

Copolymers of styrene and VPA were synthesized by the copolymerization of styrene and vinyl dimethylphosphonate followed by alkaline hydrolysis. The amount of phosphonic acid in the copolymer influenced the glass-transition temperature and the storage modulus at temperatures higher than the glass-transition temperature. Increases in both properties were observed as the amount of phosphonic acid increased as a consequence of intramolecular and intermolecular hydrogen interactions among the acid groups.

The thermal stability achieved by the products was considerably higher than other matrices used in the assembly of PEMFC. This high thermal stability was accompanied by a high chemical (oxidative) stability, whereas water swelling was coherent with the number of phosphonic acid groups in the chain, as indicated by the theoretical calculations and other results. The conductivity values of the P(S-co-VPA) membranes presented a strong variation with the hydration of the system and with the phosphoric acid content, achieving $10^{-5} \Omega^{-1} \text{ cm}^{-1}$ at ambient temperature. The 1 : 1 P(S-co-VPA) membranes exhibited an Arrhenius-type conductivity dependence from 25 to 80°C. In the P(S-co-VPA) membranes, the conductivity was thermally activated and was limited by the water content in the system. The conductivity dependence on the temperature, water, and H₃PO₄ confirmed the theoretical results,³⁶ which indicated a contribution of externally generated H₃O⁺ ions to proton transport.

The authors are grateful to C. H. Collins for revising the article.

References

- Andújar, J. M.; Segura, F. *Renew Sust Energy Rev* 2009, 13, 2309.
- Wee, J.-H. *Renew Sust Energy Rev* 2007, 11, 1720.
- Carrete, L.; Friedrich, K. A.; Stimming, U. *Fuel Cells* 2002, 1, 5.
- Acres, G. J. K.; Frost, J. C.; Hards, G. A.; Potter, R. J.; Ralph, T. R.; Thompsett, D.; Burtein, G. T.; Hutchings, G. J. *Catal Today* 1997, 38, 393.
- Kobayashi, T.; Rikukawa, M.; Sanui, K.; Ogata, N. *Solid State Ionics* 1998, 106, 219.
- Poltarzewski, Z.; Wieczorek, W.; Przulski, J.; Antonucci, V. *Solid State Ionics* 1999, 119, 301.
- Kordesch, K. V.; Simader, G. R. *Chem Rev* 1995, 95, 191.
- Won, J.; Choi, S. W.; Kang, Y. S.; Ha, H. Y.; Oh, I.-H.; Kim, H. S.; Kim, K. T.; Jo, W. H. *J Membr Sci* 2003, 214, 245.
- Randin, J.-P. *J Electroanal Chem* 1982, 129, 1215.
- Savinell, R. F.; Yeager, E.; Tryk, D.; Landau, U.; Wainright, J.; Weng, D.; Lux, K.; Litt, M.; Rogers, C. *J Electrochem Soc* 1994, 141, L46.
- Haubold, H. G.; Vad, T.; Jungbluth, H.; Hiller, P. *Electrochim Acta* 2001, 46, 1559.
- Poltarzewski, Z.; Wieczorek, W.; Przulski, J.; Antonucci, V. *Solid State Ionics* 1999, 119, 301.
- Fontela, P.; Soria, A.; Mielgo, J.; Sierra, J. F.; Blas, J.; Gauchia, L.; Martinez, J. M. *J Power Sources* 2007, 169, 184.
- Adusei, G. O.; Deb, S.; Nicholson, J. W. *Dent Mater* 2005, 21, 491.
- Rzaev, Z. M. O.; Dinçer, S.; Pişkin, E. *Prog Polym Sci* 2007, 32, 534.
- Rivas, B. L.; Pereira, E.; Gallegos, P.; Homper, D.; Geckeler, K. E. *J Appl Polym Sci* 2004, 92, 2917.
- Park, C. H.; Nam, S. Y.; Lee, Y. M. *J Appl Polym Sci* 1999, 74, 83.
- Sahoo, S. K.; Nagarajan, R.; Samuelson, L. A.; Kuma, J.; Cholli, A. L. *Macromolecules* 2004, 37, 4130.
- Smitha, B.; Shridhar, S.; Khan, A. A. *J Membr Sci* 2005, 259, 10.
- Kaltbeitzel, A.; Schauff, S.; Steininger, H.; Bingöl, B.; Brunklaus, G.; Meyer, W. H.; Spiess, H. W. *Solid State Ionics* 2007, 178, 469.
- Schull, T. L.; Knight, D. A. *Coord Chem Rev* 2005, 249, 1269.
- Souzy, R.; Ameduri, B. *Prog Polym Sci* 2005, 30, 644.
- Schuster, M.; Rager, T.; Noda, A.; Kreuer, K. D.; Maier, J. *Fuel Cells* 2005, 5, 355.
- Aslan, A.; Bozkurt, A. *J Power Sources* 2009, 191, 442.
- Kim, S. Y.; Lee, S. C. *J Appl Polym Sci* 2009, 113, 3460.
- Wu, Q.; Weiss, R. A. *J Polym Sci Part B: Polym Phys* 2004, 42, 3628.
- Perrin, R.; Elomaa, M.; Jannasch, P. *Macromolecules* 2009, 42, 5146.
- Neburchilov, V.; Martin, J.; Wang, H.; Zhang, J. *J Power Sources* 2007, 169, 221.
- Santos, L. E. P. Ph.D. Thesis, Universidade Estadual de Campinas, 2010.
- Tüdos, T. K.; Földes-Bereznich, T.; Turcsányi, B. *J Macromol Sci Chem* 1976, 10, 1513.
- Smitha, B.; Sridhar, S.; Khan, A. A. *J Membr Sci* 2003, 225, 63.
- Żeliazkowiak, M. S. *Polym Degrad Stab* 2006, 91, 1233.
- Sun, L.; Thrasher, J. S. *Polym Degrad Stab* 2005, 89, 43.
- Silva, A. L. A.; Takase, I.; Pereira, R. P.; Rocco, A. M. *Eur Polym J* 2008, 44, 1462.
- Hasiotis, C.; Qingfeng, L.; Deimede, V.; Kallitsis, J. K.; Kontoyannis, C. G.; Bjerrum, N. J. *J Electrochem Soc A* 2001, 148, 513.
- Pereira, R. P.; Felisberti, M. I.; Rocco, A. M. *Polymer* 2006, 47, 1414.
- Mattsson, B.; Ericson, H.; Torell, L. M.; Sundholm, F. *Electrochim Acta* 2000, 45, 1405.
- Donoso, P.; Gorecki, W.; Berthier, C.; Defendini, F.; Poin-signon, C.; Armand, M. B. *Solid State Ionics* 1988, 28, 969.
- Pettyweeks, S.; Zupancic, J. J.; Swedo, J. R. *Solid State Ionics* 1988, 31, 117.
- Przulski, J.; Wioczerek, W.; Potarzewski, Z.; Staiti, P.; Giordano, N.; Chovdari, B. V. R.; Liu, Q.; Chen, L. *Recent Advances in Fast Ion Conducting Materials and Devices*; World Scientific: Singapore, 1990.

41. Stevens, J. R.; Wiczorek, W.; Raducha, D.; Jeffrey, K. R. *Solid State Ionics* 1997, 97, 347.
42. Lasseques, J. C. In *Materials and Devices*; Colombari, P., Ed.; Cambridge University Press: Cambridge, United Kingdom, 1992; p 311.
43. Meng, Y. Z.; Tjong, S. C.; Hay, A. S.; Wang, S. J. *Eur Polym J* 2003, 39, 627.
44. Kato, M.; Katayama, S.; Sakamoto, W.; Yogo, T. *Electrochim Acta* 2007, 52, 5924.
45. Lee, Y. J.; Bingöl, B.; Murakhtina, T.; Sebastiani, D.; Meyer, W. H.; Wegner, G.; Spiess, H. W. *J Phys Chem B* 2007, 111, 9711.
46. Li, X.; Hsu, S. L. *J Polym Sci Polym Phys Ed* 1984, 22, 1331.
47. Rocco, A. M.; Fonseca, C. P.; Loureiro, F. A. M.; Pereira, R. P. *Solid State Ionics* 2004, 166, 115.
48. Kato, M.; Sakamoto, W.; Yogo, T. *J Membr Sci* 2008, 311, 182.
49. Kato, M.; Sakamoto, W.; Yogo, T. *J Membr Sci* 2007, 303, 43.
50. Yamada, M.; Honma, I. *Polymer* 2005, 46, 2986.
51. Yamada, M.; Honma, I. *Electrochim Acta* 2003, 48, 2411.
52. Sumner, J. J.; Creager, S. E.; Ma, J. J.; DesMarteau, D. D. *J Electrochem Soc* 1998, 145, 107.
53. Münch, W.; Kreuer, K.-D.; Silvestri, W.; Maier, J.; Seifert, G. *Solid State Ionics* 2001, 145, 437.
54. Rikukawa, M.; Sanui, K. *Prog Polym Sci* 2000, 25, 1463.
55. Kreuer, K. D. *J Membr Sci* 2001, 185, 29.
56. Nakajima, H.; Honma, I. *Solid State Ionics* 2002, 148, 607.