

Proton-Conducting Polymers Based on Benzimidazoles and Sulfonated Benzimidazoles

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ABSTRACT: A sulfonated derivative of polybenzimidazole is reported, and its properties are analyzed in comparison with related polybenzimidazole proton-conducting materials. Poly(2,5-benzimidazole), poly(*m*-phenylenebenzobisimidazole), and poly[*m*-(5-sulfo)-phenylenebenzobisimidazole] were prepared by condensation of the corresponding monomers in polyphosphoric acid. Several adducts of these polymers with phosphoric acid were prepared. The resulting materials were characterized by chemical analysis, Fourier transform infrared spectroscopy, and thermogravimetric analysis; also, the dc conductivity of doped and undoped derivatives was measured. Similar to what has been observed for the commercial polybenzimidazole polymer (also examined here for comparison), the title polymers exhibit high thermal stability. Furthermore, their doping with phosphoric acid leads to a significant increase in conductivity from less than 10^{-11} Scm⁻¹ for the undoped polymers to 10^{-4} Scm⁻¹ (both at room temperature) for their acid-loaded derivatives. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 40: 3703–3710, 2002

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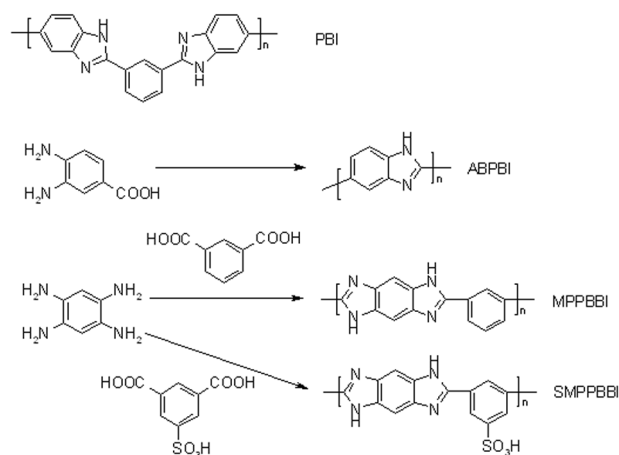
INTRODUCTION

The development of efficient proton-conducting membranes is of the greatest importance for the design and improvement of low-temperature fuel cells.^{1,2} Proton-exchange membrane fuel cells and direct methanol fuel cells in particular would benefit from the development of new solid proton conductors that could improve the properties of Nafion[®] membranes, especially concerning thermal stability, price, and reduction of fuel crossover.

Polybenzimidazoles have been considered as promising alternative materials for the fabrication of proton-exchange membranes, and a good number of very recent publications have appeared on this topic.^{3–15} These polymers present very good thermal stability¹⁶ and proton conductivity, especially when “doped” or loaded with acids.³ Among many possible polybenzimidazole derivatives, the polymer most extensively examined has been poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) (the only one commercially available) (Scheme 1). This material has been used for the fabrication of proton-exchange membranes and fuel cells making use of them, both with H₂^{15,17} and methanol¹⁸ as fuels. In addition to the commercial polymer, several laboratories have

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Scheme 1. Synthesis of polybenzimidazoles.

also centered on the synthesis and development of new materials; as a result, the polymer known as ABPBI [poly(2,5-benzimidazole)] has been reported as a proton-conducting membrane.^{11,12} Following these developments, we have been interested in pursuing the synthesis of other novel materials belonging to this very promising family of proton-conducting polybenzimidazoles. In particular, the introduction of sulfonate groups seems of interest and has been performed by direct sulfonation (on the nitrogen atom) of PBI polymers.^{8–10,20} The use of sulfonated monomers is a second possibility that must be considered and explored to widen the spectrum of materials available. This approach has been used for the synthesis of similar polymers for different applications (such as H^+ , Na^+ , and Li^+ conducting polymers).^{21,22}

Here we report two new acid-doped polybenzimidazoles and present their basic characterization and properties in comparison with the better known ABPBI. Both polymers present the same *m*-phenylenebenzobisimidazole backbone, but one has sulfonate groups added to investigate the effect of that group on the properties and hopefully get enhanced conductivity. Thus, we have carried out the syntheses and studied the properties of three different polymers on the basis of benzimidazole moieties, namely, ABPBI, poly(*m*-phenylenebenzobisimidazole) (MPPBBI), and poly[*m*-(5-sulfo)-phenylenebenzobisimidazole] (SMPPBBI) (Scheme 1) and present an analysis of the materials obtained, their Fourier transform infrared spectroscopic data (FTIR), conductivities, and thermal stability.

EXPERIMENTAL

PBI, isophthalic acid 99%, and 5-sulfoisophthalic acid mono-sodium salt 95% were purchased from Aldrich. Polyphosphoric acid (85% P_2O_5), 3,4-diaminobenzoic acid 95%, and 1,2,4,5-tetraaminobenzene tetrahydrochloride 90% were supplied by Fluka. All the reagents were used as received without further purification.

Methods

FTIR spectra were performed on a Shimadzu FTIR-8300 infrared spectrophotometer. Samples were prepared as KBr pressed pellets. Thermogravimetric analyses (TGAs) were recorded from a Mettler-Toledo CR50 thermobalance. Conductivity measurements were performed with a Hewlett-Packard HP 6114A power supply and an HP 3457A multimeter. Samples were prepared as pressed pellets. Both surfaces were covered with silver paint to ensure good contact, and the pellet was put between two copper electrode plates. All conductivity measurements were performed at room temperature.

Polymer Synthesis

ABPBI was obtained by condensation of 3,4-diaminobenzoic acid monomers in polyphosphoric acid (PPA). MPPBBI and SMPPBBI were prepared by condensation of tetraaminobenzene and sulfonated or non-sulfonated isophthalic acid (Scheme 1).

Synthesis of ABPBI (1)

This polymer was prepared by a modification of previously reported syntheses.^{23,24} Thus, the polymerization was carried out heating a solution of 3.040 g (20 mmol) of 3,4-diaminobenzoic acid in 50 g of PPA (85% P_2O_5) at 200 °C for 5 h under nitrogen. The polymer was isolated by precipitation in water, filtered, and washed repeatedly with water. To eliminate residual phosphoric acid, the polymer was washed with 10% NaOH stirring overnight. The dark purple polymer became brown after the NaOH addition. NaOH was eliminated by washing with water to neutrality and boiling the polymer in water for 6 h, three times. The purified polymer was dried at 100 °C for 24 h and 200 °C for another 24 h. A brown fibrous polymer was obtained.

Yield: 2.26 g. Calcd. for $C_7H_4N_2 \cdot 0.5 H_2O$: C, 67.20%; H, 4.00%; N, 22.40%. Experimental: C, 68.82%; H, 3.93%; N, 21.52%. The inherent viscosity of this polymer, $0.5 \text{ g} \cdot \text{dL}^{-1}$ measured in concentrated 96% sulfuric acid at 30°C was $1.4\text{--}1.8 \text{ dL} \cdot \text{g}^{-1}$.

Synthesis of MPPBBI (2)

For the synthesis of this material, we also followed a modified procedure on the basis of a previously reported synthesis.^{23,24} Thus, tetraaminobenzene tetrahydrochloride (TABH; 2.840 g, 10 mmol) was dissolved in 50 g of PPA and heated at 120°C for 25 min to eliminate the hydrochloric acid. When foaming finished, isophthalic acid (1.662 g, 10 mmol) was added, and the temperature was raised to 170°C for 6 h under nitrogen. The polymer was precipitated in water, washed with a large amount of water, stirred in 10% NaOH overnight, washed again with water to neutrality, and boiled with water for 6 h (three times). The brown powder obtained was dried at 100°C for 24 h and at 200°C for another 24 h.

Yield: 1.70 g. Calcd. for $C_{14}H_8N_4 \cdot 2 H_2O$: C, 62.68%; H, 4.51%; N, 20.88%. Experimental: C, 63.32%; H, 3.69%; N, 20.83%. The inherent viscosity of this polymer, $0.5 \text{ g} \cdot \text{dL}^{-1}$, measured in concentrated 96% sulfuric acid at 30°C was $0.25 \text{ dL} \cdot \text{g}^{-1}$.

Synthesis of SMPPBBI (3)

As far as we know, this is the first report for the synthesis of this polymer. TABH (2.840 g, 10 mmol) was dissolved in 50 g of PPA and heated at 120°C for 25 min to eliminate the hydrochloric acid. When foaming finished, 5-sulfoisophthalic acid (1.662 g, 10 mmol) was added, and the temperature was raised to 200°C for 5 h under nitrogen. The polymer was precipitated by addition into a large amount of water and washed with water to neutrality. In this case, we avoided washing with NaOH to prevent formation of a sodium sulfonate salt. To extract the remaining traces of acid, the polymer was stirred in water for 48 h, filtered, and dried at 100°C for 24 h. A brown powder was obtained.

Yield: 0.67 g. Calcd. for $C_{14}H_8N_4SO_3 \cdot 2.6 H_2O$: C, 46.82%; H, 3.70%; N, 15.60%; S, 8.93%. Experimental: C, 46.69%; H, 3.59%; N, 14.18%; S, 9.32%. Inherent viscosity was not measured, but it is expected to be as low as for MPPBBI because it was synthesized by the same tetraamine monomer.

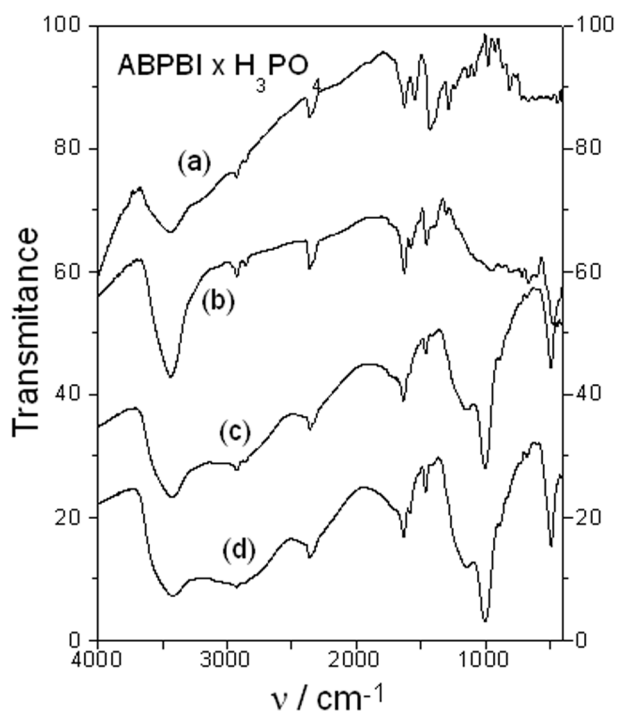


Figure 1. FTIR of phosphoric acid-doped ABPBI: (a) nondoped ABPBI, (b) $ABPBI \cdot 1.5 H_3PO_4$, (c) $ABPBI \cdot 2.9 H_3PO_4$, and (d) $ABPBI \cdot 5.0 H_3PO_4$.

Doping of Polybenzimidazoles

All previously described polymers were doped by immersion in phosphoric acid (85%). About 250 mg of polybenzimidazole (ABPBI, MPPBBI, or SMPPBBI) were dissolved in 10 mL of the acid. Each polybenzimidazole sample was precipitated from solution by addition of different amounts of water. The resulting doped polymers were filtered off under vacuum and dried at 100°C . The amount of phosphoric acid present in each sample was calculated by elemental analysis.

RESULTS AND DISCUSSION

FTIR Spectroscopy of Polybenzimidazoles

The FTIR spectra of pristine polybenzimidazoles are depicted in Figures 1–3. The assignments of bands for polybenzimidazole backbones (Table 1) have been made according to Musto et al.²⁵ and previous FTIR studies of phosphoric acid-doped PBI.^{5,10} The sharp bands from 3450 to 3400 cm^{-1} are attributed to the isolated N—H stretching of the imidazole, whereas the broad bands near $3250\text{--}2500 \text{ cm}^{-1}$ are assigned to the self-associ-

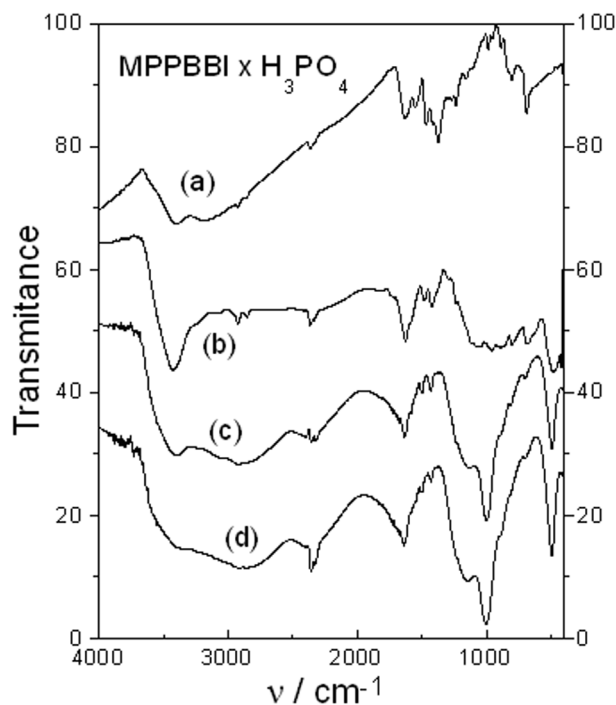


Figure 2. FTIR of phosphoric acid-doped MPPBBI: (a) undoped MPPBBI, (b) MPPBBI · 2.2 H₃PO₄, (c) MPPBBI · 4.4 H₃PO₄, and (d) MPPBBI · 5.4 H₃PO₄.

ated N—H bonds. This band is broader in the presence of moisture. In this range will appear the N⁺—H vibrations because of protonation of the imine in the doped samples. The C=C and C=N stretching appear in the region of 1630–1500 cm⁻¹. A strong band at 1495–1395 cm⁻¹ must be attributed to the inplane deformation of benzimidazole rings. Inplane C—H deformations appear at 1235–1225 cm⁻¹. Musto et al.²⁵ assigned the band at 1277 to the breathing mode of the imidazole ring in PBI.

The sulfonated polymer (**3**) presents bands characteristic of deprotonated —SO₃⁻. Thus, values shown in Table 1 agree adequately with the values of four characteristic bands at 1230, 1190, 1130, and 1040 cm⁻¹ reported for sulfonic acid salts. These bands can be assigned to three SO and one sharp and strong *S*-phenyl vibrations.²⁶ Therefore, in the pristine polymer (**3**) sulfonic acid groups are in their anionic form, compatible with the presence of basic imidazole groups.

FTIR Spectra of Phosphoric Acid-Doped Polybenzimidazoles

There are two regions of the IR spectrum that concentrate the information about the doping

level of the sample. Infrared spectra of acid-doped ABPBI, MPPBBI, and SMPPBBI are shown in Figures 1–3.

In the N—H stretching zone, an overview of the spectra reveals the evolution of nitrogen protonation by the acid. In the medium–high-doped samples, the broad band of the N⁺—H stretching becomes stronger, whereas the nonassociated N—H decreases, although never disappears. If there are protonated and nonprotonated rings, protons are able to jump from a protonated ring to a nonprotonated one through a phosphate molecule. Therefore, these spectra agree with the mechanism proposed by Bouchet and Siebert⁵ for acid-doped PBI. In MPPBBI, the wave number of the N—H stretching decreases slightly when the amount of acid is higher.

Chapman and Thirlwell²⁷ assign two bands to the O—H stretching modes in phosphoric acid. These same two bands can be detected in the infrared spectra of phosphoric acid-doped polybenzimidazoles. The first one at about 2700–3000 cm⁻¹ is overlapped by the N⁺—H stretching. The second band is centered at 2350 cm⁻¹ and is most apparent for the medium–high-doped samples.

Phosphoric acid also absorbs at 1250–850 and 495 cm⁻¹. This zone of the spectra also provides

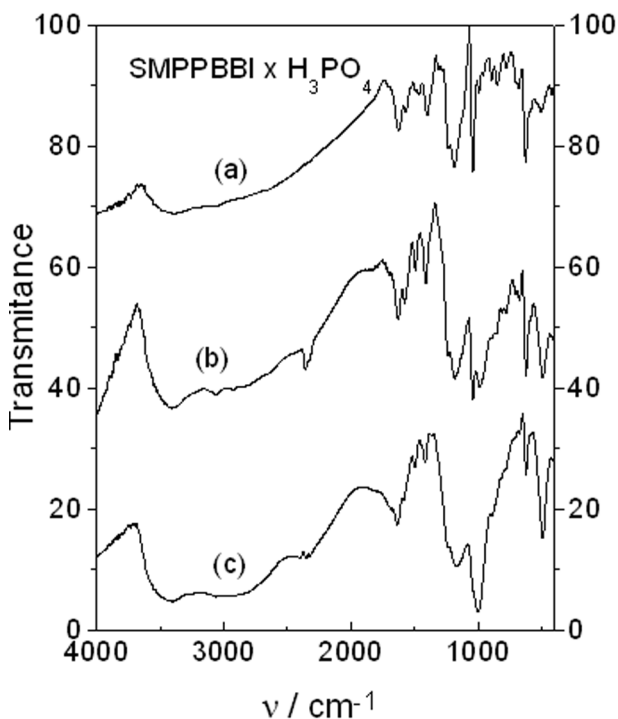


Figure 3. FTIR of phosphoric acid-doped SMPPBBI: (a) undoped SMPPBBI, (b) SMPPBBI · 2.0 H₃PO₄, and (c) SMPPBBI · 3.6 H₃PO₄.

Table 1. Infrared Spectra of Polybenzimidazoles

Wave Number (cm ⁻¹)				
PBI	ABPBI	MPPBBI	SMPPBBI	Assignment
3398	3434	3405	3400	Free non-hydrogen-bonded N—H stretching
		3185	3250–2500	Associated N—H stretching
1614	1626	1627	1628	C=C/C=N stretching
1527	1547	1547	1566	Ring-vibration characteristic of conjugation between benzene and imidazole rings
1431	1425	1464	1495	Inplane deformation of benzimidazole rings
1408	1395		1408	
1277	1281			Breathing mode of the imidazole ring
1225	1234	1234		Inplane C—H deformation
			1240	S—O stretching of aromatic sulfonic acid salts
			1187	
			1124	C—S stretching of aromatic sulfonic salts
			1038	
800	800	800		Out-of-plane C—H bending of the benzene rings
689	685		683	
			624	

rough information on the amount of acid present in the sample. Samples with a low doping level show a strong absorption not present in the polymer spectra at 495 cm⁻¹. This band is due to the PO₂ bending of H₂PO₄⁻. This is the strongest band at low doping levels (ABPBI: · 1.5 H₃PO₄, MPPBBI: · 2.2 H₃PO₄). As reported by Bouchet and Siebert,⁵ bands attributed to free phosphoric acid molecules appear in the spectra of the medium-high-doped samples at 1250–850 cm⁻¹.

Thermal Stability

TGAs were performed under dynamic N₂ atmosphere for ABPBI, MPPBBI, SMPPBBI, and commercial PBI for comparison.

Figure 4 displays TGA curves for the undoped polymers. An initial weight loss is observed in all cases between room temperature and about 150 °C (Fig. 4). This is assigned to the loss of variable amounts of loosely bound water. Although the figure shows obvious differences in thermal stability, it must be noted that all polymers are stable at least up to temperatures of about 400 °C (well above the temperature goal for application as proton-conducting membranes). PBI and ABPBI are the most stable of the polymers investigated, both reaching almost 600 °C without apparent weight loss. On the other hand, MPPBBI

exhibits a very small loss (almost imperceptible in the TGA trace but better detected in the derivative) at about 425 °C, after which it is as stable as PBI. Because of the small magnitude of this step, we tentatively assign it to the loss of end groups of the polymer. Finally, the TGA of the sulfonated polymer, SMPPBBI, shows a substantial weight loss centered at 470 °C (inflection point) not present in MPPBBI. This is assigned to the elimination of —SO₃H groups with the help of FTIR spectroscopy. Thus, after heating a sample of undoped SMPPBBI at 475 °C in air or N₂, the IR

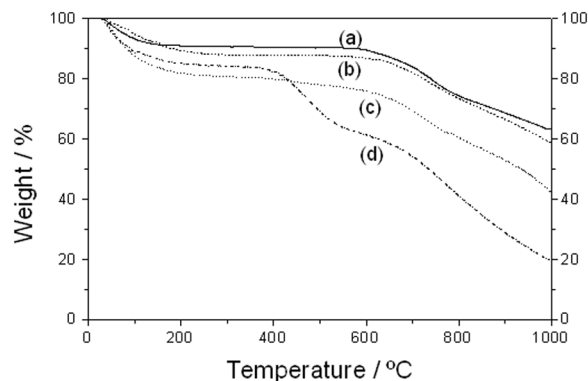


Figure 4. TGA of the nondoped polymers in nitrogen; heating rate 10 °C/min: (a) PBI, (b) ABPBI, (c) MPPBBI, and (d) SMPPBBI.

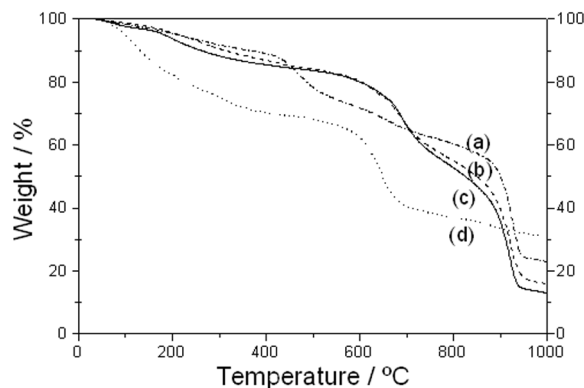


Figure 5. TGA of acid-doped polybenzimidazoles and 85% H_3PO_4 in nitrogen; heating rate $10\text{ }^\circ\text{C}/\text{min}$: (a) SMPPBBI $\cdot 3.6\text{ H}_3\text{PO}_4$, (b) MPPBBI $\cdot 5.4\text{ H}_3\text{PO}_4$, (c) ABPBI $\cdot 5.0\text{ H}_3\text{PO}_4$, and (d) 85% H_3PO_4 .

bands at 1250 , 1187 , 1124 , and 1038 cm^{-1} , characteristics of sulfonic acid, disappear. After losing the sulfonic groups, the weight of the polymer backbone stabilizes up to $600\text{ }^\circ\text{C}$ after which the final weight loss begins, similar to the non-sulfonated polybenzimidazoles.

Before discussing the thermal stability of acid-loaded polymers, we describe relevant data for phosphoric acid itself. Under our experimental conditions (under N_2 , $10\text{ }^\circ\text{C}/\text{min}$ heating rate), phosphoric acid presents the TGA curve portrayed in Figure 5(d). It shows a first loss, between 50 and $150\text{ }^\circ\text{C}$, corresponding to about a 15% water content of commercial 85% acid. After this and before $600\text{ }^\circ\text{C}$, continuing weight losses take place probably corresponding to successive dehydrations to pyrophosphoric and metaphosphoric acid, and finally a large weight loss is observed at $650\text{ }^\circ\text{C}$.

TGA of acid-doped polymers can be compared and related in part to that of phosphoric acid (Fig. 5) and the corresponding undoped polymers (Fig. 4). First, all doped derivatives exhibit an initial weight loss below $200\text{ }^\circ\text{C}$ most likely corresponding to water loss. The acid-doped sulfonated polymer shows (as its undoped counterpart) a significant loss at $450\text{ }^\circ\text{C}$ corresponding to the sulfonic acid group. On the other hand, and contrary to the stable weight featured by the undoped polymers, the TGA curves of all acid-doped derivatives indicate a slow and continuous weight loss that parallels that of phosphoric acid. Then, the most significant losses for acid-doped polymers take place at 690 and $920\text{ }^\circ\text{C}$. The former parallels that of phosphoric acid, whereas the second corresponds to decomposition of the polymer itself, in

good agreement with the study by Samms et al.¹⁶ on acid-doped commercial PBI, where a combination of TGA and MS allowed them to assign the onset of their polymer decomposition at about $650\text{ }^\circ\text{C}$ by detection of CO_2 .

Conductivity Measurements

Direct current (dc) conductivity of acid-doped polybenzimidazole pellets was measured by applying constant voltages of 1, 2, and 5 V to the sample and measuring the intensity produced. The pellets were covered with silver paint to improve contact with the two copper electrodes. Conductivity decreased as a function of time, very quickly at first, and stabilized after a few minutes. The fast drop of the conductivity, about one or two orders of magnitude, shows that the conduction of the acid-doped polybenzimidazoles is mainly ionic. After this sharp drop, the conductivity is almost stabilized at values directly proportional to the amount of acid in the materials. All the measurements were performed at room temperature. Figures 6 and 7. display the conductivity of acid-doped polybenzimidazoles as a function of the amount of phosphoric acid. We plotted the conductivity after the stabilization. The acid concentration was calculated from elemental analysis as the weight percentage of H_3PO_4 and as the number of acid molecules per repeating unit.

Undoped PBI is an electrical insulator (resistivity ca. $10^{12}\ \Omega \cdot \text{cm}$),⁶ and the conductivity of undoped MPPBBI was smaller than $10^{-11}\ \text{S} \cdot \text{cm}^{-1}$. The conductivity of the hydrated SMPPBBI $2.6\text{ H}_2\text{O}$ was about $10^{-9}\ \text{S} \cdot \text{cm}^{-1}$. Spry et al.^{21,22}

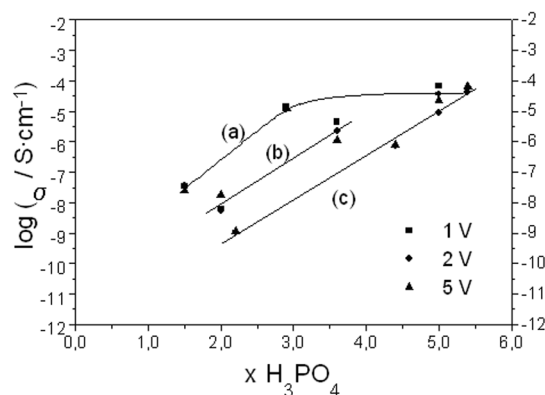


Figure 6. DC conductivity of polybenzimidazoles as a function of the number of acid molecules per polybenzimidazole repeating unit: (a) ABPBI $\cdot x\text{H}_3\text{PO}_4$, (b) SMPPBBI $\cdot x\text{H}_3\text{PO}_4$, and (c) MPPBBI $\cdot x\text{H}_3\text{PO}_4$.

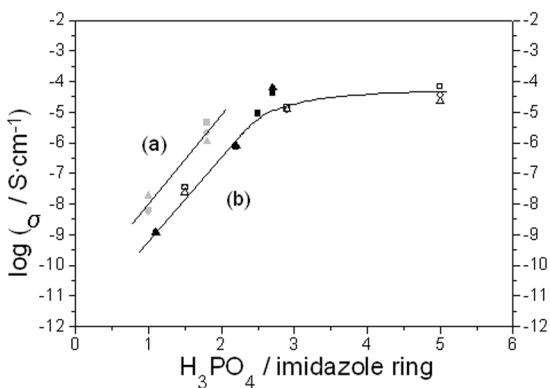


Figure 7. DC conductivity of polybenzimidazoles as a function of the number of acid molecules per imidazole ring: (a) SMPPBBI \cdot $x\text{H}_3\text{PO}_4$ and (b) ABPBI $x\text{H}_3\text{PO}_4$ (open symbols) and MPPBBI \cdot $x\text{H}_3\text{PO}_4$ (solid symbols).

reported a conductivity of $1.8 \cdot 10^{-10} \text{ S} \cdot \text{cm}^{-1}$ for poly[*p*-(2-sulfohenylene)benzobisimidazole].

Once loaded with acid, both ABPBI and MP-PBBI are good ionic conductors, and their conductivity depends on the amount of acid in the adducts formed. Because ABPBI and MPPBBI have a different number of imidazole rings per repeat unit, we compared the conductivities in three of the following ways: (1) as a function of weight percentage of acid, (2) as the number of acid molecules per repeating unit, and (3) as a function of the number of acid molecules per imidazole ring. A first glance to the data in Figure 6 (expressed as a function of x , the number of acid molecules per repeating unit) might suggest quite different behavior for ABPBI and MPPBBI acid-loaded materials. However, when the conductivity is considered as a function of acid molecules per imidazole ring, a common pattern emerges (Fig. 7). Thus, the conductivity of both polymers is comparable once normalized with respect to acid molecules per imidazole ring. Incidentally, their conductivity is also comparable when normalized per weight percentage of H_3PO_4 . In this particular case, both polymers have the same density of basic imidazole groups, that is, the same number of imidazole rings per unit weight. Maximum conductivity values of about $10^{-4} \text{ S} \cdot \text{cm}^{-1}$ are reached for materials with acid doping levels around 2.5–3 acid molecules per imidazole ring (Fig. 7). The addition of more acid up to 5 molecules per imidazole does not increase the conductivity. Thus, although ABPBI is able to absorb more acid than MPPBBI, the maximum conductivity is not higher.

The effect of sulfonation on polymer conductivity was investigated by Glipa et al.²⁰ and Kawahara and coworkers^{8,9} in both cases by direct sulfonation of the commercial PBI polymer on the N—H group of the imidazole ring. Glipa et al.²⁰ discovered an increase on the conductivity of about two orders of magnitude. In this study, MPPBBI reaches higher values of conductivity than the sulfonated SMPPBBI. Yet, comparing the conductivities of doped MPPBBI and SMPPBBI as a function of the acid percentage, the plot shows the same doping level (ca. 50%); the conductivity is more than one order of magnitude higher for the sulfonated polymer. The maximum conductivity for SMPPBBI \cdot $x\text{H}_3\text{PO}_4$ is $2 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ for the derivative with $x = 3.6$ (52% H_3PO_4). For comparison, the related MPPBBI \cdot $3.6 \text{ H}_3\text{PO}_4$ would show a conductivity of about $9 \cdot 10^{-8} \text{ S} \cdot \text{cm}^{-1}$ (as estimated by interpolation in Fig. 6).

As a referee has pointed out, sulfonic acid groups could be taken into account in considering a “normalized” plot of conductivity versus acid groups (whether phosphoric or sulfonic). Although this might be rigorously correct from a physical-chemical point of view, the covalent bonding of sulfonic (or other) groups to the polymer chain makes a great difference from a materials point of view. In other words, it would be great to have some of the phosphoric acid molecules “bonded” to the polymer chains. In a sense, that is what we have accomplished with our acid-doped novel sulfonated polymer reported here.

CONCLUSIONS

Below 400 °C acid-doped ABPBI, MPPBBI, and the new sulfonated SMPPBBI are all as stable as acid-doped PBI, and only some water is lost during heating. Thus, in principle all of them could be used as polymer electrolytes in enhanced-temperature PEM fuel cells.

Both polybenzimidazoles (ABPBI and MPPBBI) doped with phosphoric acid exhibit good proton conduction that agrees with previously reported results for commercial PBI and ABPBI. Their DC conductivities start at a maximum of $10^{-3} - 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ for the highest doping level, although because of the ionic nature of the process, those values drop sharply with time to $10^{-4} - 10^{-6} \text{ S} \cdot \text{cm}^{-1}$. The conductivity of the sulfonated polymer SMPPBBI is about two orders of magnitude higher than that of the related MPPBBI loaded

with the same percentage of acid. SMPPBBI has better conductivity for lower doping levels, but MPPBBI was doped with a higher amount of acid, achieving better proton conductivities. Thus, we are directing our efforts toward achieving higher doping levels for SMPPBBI, which should lead to the best proton-conducting polymer derivative of this family of materials.

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