European Polymer Journal 45 (2009) 2391–2394

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Theoretical study on sulfonated and phosphonated poly[(aryloxy)phosphazenes] as proton-conducting membranes for fuel cell applications

Xiaobing Li [a], Shijun Liao [a,*], Jinhua Piao [a], Xueye Wang [b]

[a] *School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, China*
[b] *College of Chemistry, Xiangtan University, Xiangtan, Hunan 411105, China*

ARTICLE INFO

Article history:
Received 9 January 2009
Received in revised form 18 April 2009
Accepted 27 April 2009
Available online 8 May 2009

Keywords:
B3LYP/6-31G(d)
Poly[(aryloxy)phosphazenes]
Proton-conducting membrane
Proton conductivity
Water adsorption

ABSTRACT

Polyphosphazenes are considered to be more useful as proton-conducting membranes than Nafion due to their low methanol permeability, low water swelling ratios, satisfactory mechanical properties, and conductivities comparable to those of Nafion. In this work, compounds **1**–**6**, six polyphosphazenes with different side groups, were designed and calculated. Structural parameters, proton affinities and water adsorptions were obtained on the basis of the optimized geometrical structures. Our calculations were in agreement with experimental results. It was found that the proton conductivities of the sulfonated poly[(aryloxy)phosphazenes] ($R^1{=}SO_3H$) are higher than those of the phosphonated ones ($R^1{=}PO_3H_2$), while the phosphonated poly[(aryloxy)phosphazenes] will retain water better at higher temperature than the sulfonated ones. The electron-withdrawing substituent of R^2 is beneficial to proton conductivities and water adsorptions of both sulfonated and phosphonated poly[(aryloxy)phosphazenes].

1. Introduction

The proton-conducting membrane (PCM) is a key component in PCM-based fuel cells. Nafion, the most commonly used PFSA membrane, has some disadvantages such as high cost, strong dependence of proton conduction on the water content of the membrane, and a restricted operating temperature range (below 80 °C). A new class of polyphosphazenes membranes which has been developed recently holds promise for overcoming these problems. It has two side groups and an inorganic backbone consisting of alternating phosphorus and nitrogen atoms, which are particularly stable to free-radical skeletal cleavage reactions. The side groups can be organic, inorganic or organometallic. A very broad range of groups can be easily incorporated into the polyphosphazene chain, which creates unlimited possibilities for derivatization and fine tuning the properties of the resultant material. Some of the most thermally and chemically stable polyphosphazenes bear aryloxy side groups and these, in turn, can be functionalized to introduce acidic units such as sulfonic acids and phosphonic acids [1–4]. At present, there are rather many theoretical investigations on proton-conducting membranes such as Nafion membrane [5], SPEEK and PSU membranes [6], and other membranes [7,8], but no report on the theoretical investigation of sulfonated and phosphonated poly[(aryloxy)phosphazenes] membranes.

In this paper, compounds **1**–**6**, six polyphosphazenes with different side groups, were proposed and designed. The DFT B3LYP calculation with 6-31G(d) basis set was used to generate the geometrical structures for these compounds. Proton affinities and binding energies were obtained by using the total energies of these compounds. The useful information can be provided to design novel proton-conducting membranes for fuel cell applications.

---

* Corresponding author. Fax: +86 20 87113108.
E-mail address: chsjliao@scut.edu.cn (S. Liao).

0014-3057/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2009.04.032

2. Computational methods

It is impossible to calculate descriptors directly for entire molecule because all the polymers possess high molecular weights, but molecular descriptors calculated directly from polymeric repeating unit structure can be used on the study of polymers. Katritzky et al. [9,10] have chosen models consisting of repeating units end-capped by hydrogen, as small, yet representative structures, to calculate the descriptors. Therefore we focus on the following model (see Fig. 1) to calculate molecular quantum chemical descriptors. Geometry optimizations for all structures were carried out using Becke–Lee–Young–Parr composite exchange correlation functional (B3LYP) and 6-31G(d) basis set. Since the importance of including the basis set superposition error (BSSE) corrections in calculated binding energies has been well documented in literature, the full counterpoise (CP) procedure of Boys and Bernadi [11] was applied to eliminate BSSE. All the calculations were performed on Gaussian03W computational package [12].

3. Results and discussion

3.1. Geometries

The calculated bond distances and bond angles of compounds **1**–**6** are listed in Table 1. For compound **1**, the distances of N=P, P—O and P—O′ are 1.536, 1.668 and 1.643 Å, and the angles of NPO, NPO′ and OPO′ are 120.7°, 117.6° and 102.1°, respectively. The PO_3H_2 group of R^1 makes the N—P distance lengthened to be 1.541 Å, and the distances of P—O, P—O′ and the angle of OPO′ reduced to be 1.657, 1.630 Å and 97.2°, respectively. However, whether R^2 is electron-withdrawing or electron-donating substituent, all of the bond lengths and bond angles have only slight changes. It is clearly indicated that the distances of N=P, P—O and P—O′ and the angle of OPO′ are more influenced by R^1 substituent than by R^2 substituent. It should be noted that the experimental data are not available in the literature, thus we cannot make a comparison of our calculated results with experimental results.

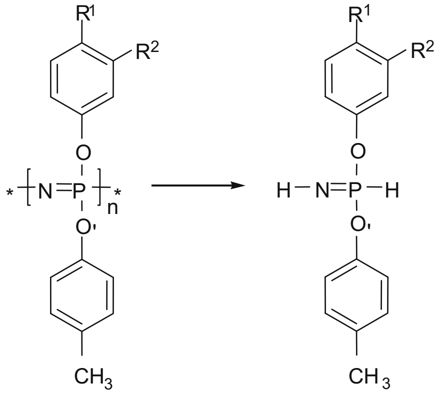

Fig. 1. Computational models of compounds **1**–**6** (**1**: R^1=SO_3H, R^2=H; **2**: R^1=SO_3H, R^2=CN; **3**: R^1=SO_3H, R^2=OCH_3; **4**: R^1=PO_3H_2, R^2=H; **5**: R^1=PO_3H_2, R^2=CN; **6**: R^1=PO_3H_2, R^2=OCH_3).

Table 1
Optimized geometries of compounds **1**–**6**.

	1	2	3	4	5	6
Bond lengths (Å)						
N=P	1.536	1.535	1.537	1.541	1.539	1.543
P—O	1.668	1.676	1.666	1.657	1.665	1.654
P—O′	1.643	1.640	1.643	1.630	1.626	1.629
Bond angles (°)						
NPO	120.7	120.2	121.4	121.8	121.3	121.7
NPO′	117.6	118.0	117.4	117.7	118.4	117.5
OPO′	102.2	102.0	102.1	97.2	96.9	97.4

3.2. Acidities

The calculated proton affinities of conjugate bases of compounds **1**–**6** are listed in Tables 2 and 3. As shown in Table 2, the order of their proton affinities is as follows: $\mathbf{3}^-$ (14.25) > $\mathbf{1}^-$ (14.09) > $\mathbf{2}^-$ (13.77). According to the proton theory of acids and bases, $RO^- + H^+ \rightarrow ROH$, the bigger the proton affinity is, the stronger the basicity of the compound is and, as a result, the stronger the acidity of its conjugate acid is. So the order of their acidities is as follows: **3** < **1** < **2**. From Table 3, the order of their acidities is as follows: **6** < **4** < **5**. It was found that the electron-withdrawing substituent of R^2 increases the acidities of sulfonated and phosphonated poly[(aryloxy)phosphazenes], while the electron-donating substituent of R^2 decreases the acidities of them. For proton-conducting materials, high acidity causes high proton conductivity. From this point of view, the electron-withdrawing substituent of R^2 is beneficial to the proton conductivities of both sulfonated and phosphonated poly[(aryloxy)phosphazenes] membranes. We also observed that, the acidities of sulfonated poly[(aryloxy)phosphazenes] (R^1=SO_3H) are stronger than phosphonated ones (R^1=PO_3H_2), indicating that the proton conductivities of the sulfonated poly[(aryloxy)phosphazenes] are higher than those of the phosphonated ones. These findings were in agreement with experimental results [3].

3.3. Water adsorptions

Minimum energy conformations were determined for each of compounds **1**–**6** with a single 'probe' water molecule to assess the relative binding of water to compounds **1**–**6** under nearly dry conditions. The minimum energy structures for compounds **1**–**6** each with a single water molecule are shown in Figs. 2 and 3. The corresponding energies are reported in Table 4. Double hydrogen bonds are formed between the water molecule and each of compounds **1**–**6**. As shown in Fig. 2a, the O—O distances in the hydrogen bonds are 2.802 and 2.663 Å. The electron-withdrawing substituent of R^2 makes the former lengthened to be 2.808 Å, and the latter shortened to be 2.641 Å (Fig. 2b). In contrast, the electron-donating substituent of R^2 makes the former shortened to be 2.758 Å, and the latter lengthened to be 2.666 Å (Fig. 2c). As shown in Fig. 3a, the PO_3H_2 group of R^1 makes the former shortened to be 2.744 Å, and the latter lengthened to be 2.675 Å. Similar results were found in Fig. 3b and c. The BSSE corrected bind-

Table 2
Proton affinities of conjugate bases of compounds **1**–**3**.

	1	**1**[a]	**2**	**2**[a]	**3**	**3**[a]
E (a.u.)	−1674.1614	−1673.6435	−1766.3927	−1765.8866	−1788.6817	−1788.1579
PA (eV)	–	14.09	–	13.77	–	14.25

$PA = E(\mathrm{RO}^-) - E(\mathrm{ROH})$.
[a] Conjugate bases of compounds **1**–**3**.

Table 3
Proton affinities of conjugate bases of compounds **4**–**6**.

	4	**4**[a]	**5**	**5**[a]	**6**	**6**[a]
E (a.u.)	−1618.0670	−1617.5286	−1710.3039	−1709.7767	−1732.5900	−1732.0443
PA (eV)	–	14.67	–	14.35	–	14.85

$PA = E(\mathrm{RO}^-) - E(\mathrm{ROH})$.
[a] Conjugate bases of compounds **4**–**6**.

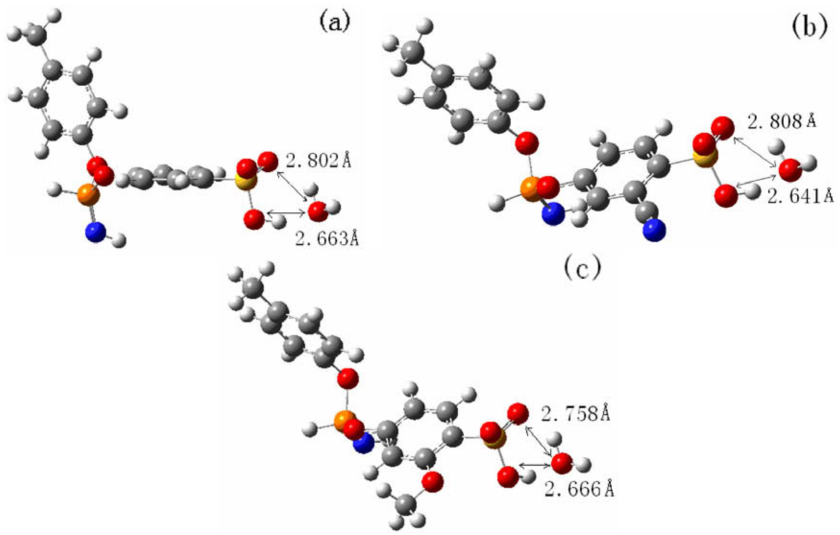

Fig. 2. B3LYP/6-31G(d) minimum energy conformations for (a) compound **1**; (b) compound **2**; (c) compound **3** each with a single water molecule.

ing energy is −51.5 and −53.9 kJ/mol for compounds **1** and **4**, respectively. Clearly, the water binds tighter to the phosphonated poly[(aryloxy)phosphazenes] than to the sulfonated ones, and does suggest that the phosphonated poly[(aryloxy)phosphazenes] will retain water better at higher temperature than the sulfonated ones. From Table 4, the BSSE corrected binding energy decreases to −52.3 kJ/mol for compound **2**, but increases to −50.2 kJ/mol for compound **3**, compared with that for compound **1**. Similarly, the BSSE corrected binding energy decreases to −57.5 kJ/mol for compound **5**, but increases to −53.6 kJ/mol for compound **6**, compared with that for compound **4**. Obviously, the electron-withdrawing substituent of R^2 is beneficial to the water adsorptions of both sulfonated and phosphonated poly[(aryloxy)phosphazenes]. These findings are needed to be proven by further experimental studies.

4. Conclusions

In this paper, compounds **1**–**6** were investigated at the B3LYP/6-31G(d) level of theory. Our results show that the substituents of R^1 and R^2 have different effect on molecular geometries, proton conductivities and water adsorptions of poly[(aryloxy)phosphazenes]. The distances of N=P, P—O and P—O′ and the angle of OPO′ are more influenced by R^1 substituent than by R^2 substituent. The proton conductivities of the sulfonated poly[(aryloxy)phosphazenes] are higher than those of the phosphonated ones, while the phosphonated poly[(aryloxy)phosphazenes] will retain water better at higher temperature than the sulfonated ones. It was also found that the electron-withdrawing substituent of R^2 is beneficial to proton conductivities and water adsorptions of both sulfonated and phosphonated poly [(aryloxy)phosphazenes].

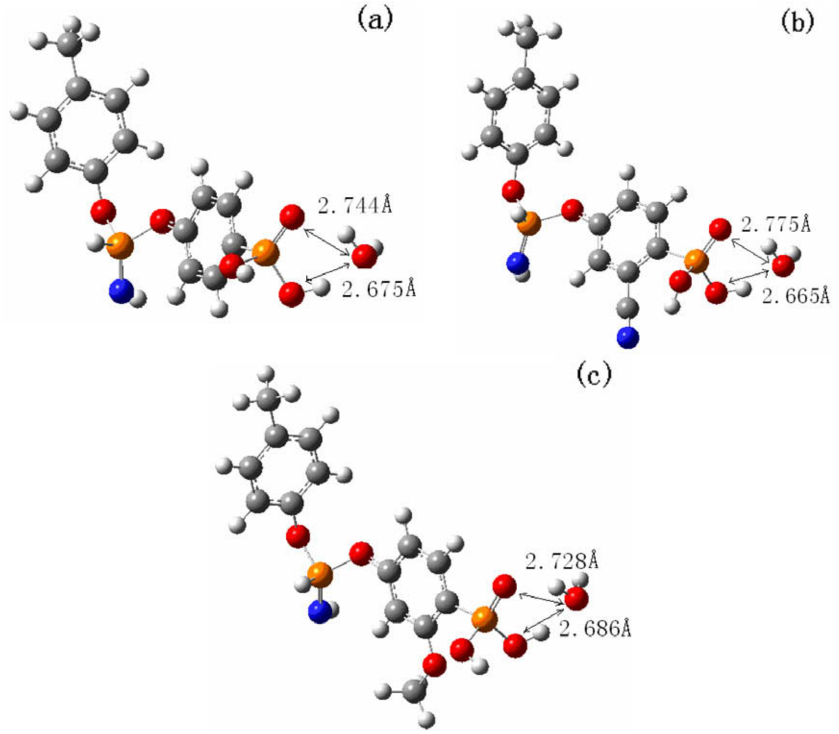

Fig. 3. B3LYP/6-31G(d) minimum energy conformations for (a) compound **4**; (b) compound **5**; (c) compound **6** each with a single water molecule.

Table 4
Calculated binding energies of compounds **1**–**6** each with a single water molecule.

	ΔE[a] (kJ/mol)	ΔE_{ZPE}[b] (kJ/mol)	ΔE_{BSSE}[c] (kJ/mol)
1 + H_2O	−68.8	−56.5	−51.5
2 + H_2O	−69.4	−57.8	−52.3
3 + H_2O	−67.3	−55.2	−50.2
4 + H_2O	−72.5	−60.2	−53.9
5 + H_2O	−75.4	−62.3	−57.5
6 + H_2O	−72.2	−59.9	−53.6

[a] Energy difference based on total electronic energy.

[b] Energy difference based on total electronic energy corrected for zero point energy (ZPE).

[c] Binding energy based on CP corrected energy.

Acknowledgements

The authors thank the State Natural Science Foundation of China and Guangdong Provincial Natural Science Foundation for financially supporting this work (Project Nos. 20476034, 20673040, 20876062, 03665).

References

[1] Fedkin MV, Zhou X, Hofmann MA, Chalkova E, Weston JA, Allcock HR, et al. Evaluation of methanol crossover in proton-conducting polyphosphazene membranes. Mater Lett 2002;52:192–6.

[2] Allcock HR, Hofmann MA, Ambler CM, Lvov SN, Zhou XY, Chalkova E, et al. Phenyl phosphonicacid functionalized poly[aryloxyphosphazenes]as proton-conducting membranes for direct methanol fuel cells. J Membr Sci 2002;201:47–54.

[3] Zhou XY, Weston J, Chalkova E, Hofmann MA, Ambler CM, Allcock HR, et al. High temperature transport properties of polyphosphazene membranes for direct methanol fuel cells. Electrochim Acta 2003;48:2173–80.

[4] Wycisk R, Pintauro PN. Polyphosphazene membranes for fuel cells. Adv Polym Sci 2008;216:157–83.

[5] Paddison SJ, Elliott JA. On the consequences of side chain flexibility and backbone conformation on hydration and proton dissociation in perfluorosulfonic acid membranes. Phys Chem Chem Phys 2006;8:2193–203.

[6] Panchenko A. DFT investigation of the polymer electrolyte membrane degradation caused by OH radicals in fuel cells. J Membr Sci 2006;278:269–78.

[7] Pereira RP, Felisberti MI, Rocco AM. Intermolecular interactions and formation of the hydration sphere in phosphonic acid model systems as an approach to the description of vinyl phosphonic acid based polymers. Polymer 2006;47(4):1414–22.

[8] Paddison SJ, Kreuer KD, Maier J. About the choice of the protogenic group in polymer electrolyte membranes: ab initio modelling of sulfonic acid, phosphonic acid, and imidazole functionalized alkanes. Phys Chem Chem Phys 2006;8:4530–42.

[9] Katritzky AR, Sild S, Lobanov V, Karlson M. Quantitative structure–property relationship (QSPR) correlation of glass transition temperatures of high molecular weight polymers. J Chem Inf Comput Sci 1998;38(2):300–4.

[10] Katritzky AR, Sild S, Karelson M. Correlation and prediction of the refractive indices of polymers by QSPR. J Chem Inf Comput Sci 1998;38:1171–6.

[11] Boys SF, Bernadi F. The calculation of small molecular interactions by the differences of separate total energies, some procedures with reduced errors. Mol Phys 1970;19:553–66.

[12] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 03, revision B.05; Gaussian. PA: Pittsburgh; 2003.