Russian Chemical Reviews **71** (9) 761 – 774 (2002) © 2002 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2002v071n09ABEH000740

Proton-conducting electrolyte membranes based on aromatic condensation polymers

A L Rusanov, D Yu Likhatchev, K Müllen

Contents

I.	Introduction	761
II.	Sulfonated aromatic condensation polymers and membranes based on them	762
III.	Alkylsulfonated aromatic condensation polymers and proton-conducting electrolyte membranes based on them	767
IV.	Proton-conducting electrolyte membranes based on acid – base polymer complexes	771
V.	Fuel cell applications of proton-conducting membranes based on aromatic condensation polymers	772

Abstract. The results of investigations in the field of development and applications of proton-conducting electrolyte membranes based on aromatic condensation polymers are analysed and summarised. Primary attention is paid to the properties of the starting polymers, such as the thermal stability, water uptake and proton conductivity. General approaches to the preparation of aromatic condensation polymers with high proton conductivity are considered, including sulfonation, synthesis from monomers containing sulfonic acid groups, incorporation of alkylsulfonated substituents and formation of acid – basic polymer complexes. The bibliography includes 115 references.

I. Introduction

Advanced technologies of the 21st century are thought to be associated with wide use of fuel cells that allow fuels to be utilised in the fuel cell based engines with much higher efficiency compared to internal combustion engines.[1] Currently, fuel cells are used as power sources in both stationary and mobile (motor vehicles, buses, locomotives, *etc*.) engines. The most important components of fuel cells are proton-conducting, ion-containing membranes which can operate under severe conditions. The operating conditions include, first, high operating temperatures (sometimes, they exceed 100 °C) and, second, the medium that can be chemically active towards the material the membranes are made of due to the use of aggressive fuels (*e.g*., methanol and products of its partial oxidation), oxidants (*e.g*., oxygen) and catalysts, and due to the generation of active radicals at electrodes (especially, at cathode).[1]

Of particular interest are new proton-conducting ion-exchange membranes based on solid polymer electrolytes.[2, 3]

A L Rusanov A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation. Fax (7-095) 135 50 85. Tel. (7-095) 135 63 72.
E-mail: alrus@ineos.ac.ru
D Yu Likhatchev Materials Research Institute, UNAM, Cirquito Exterior s/n, CU, Apdo Postal 70-360 Coyoacan, 04510 Mexico City, Mexico.
Fax (52-555) 616 12 01. Tel. (52-555) 622 45 87.
E-mail: likhach@servidor.unam.mx
K Müllen Max-Planck-Institute of Polymer Research, Ackermanweg 10, 55128 Mainz, Germany. Fax (49-613) 137 91 00.
Tel. (49-613) 137 91 50. E-mail: muellen@mpip-mainz.mpg.de

Received 10 June 2002
Uspekhi Khimii **71** (9) 862 – 877 (2002); translated by A M Raevsky

The idea of using organic cation-exchange membranes as solid electrolytes in electrochemical cells was first materialised in 1959.[4] Currently, the solid polymer electrolyte fuel cells (SPEFCs) are considered to be the most promising candidate systems out of all types of fuel cells.[5–8] These devices are frequently called also as polymer electrolyte membrane or proton exchange membrane fuel cells (PEMFCs). The structure of a PEMFC is schematically shown in Fig. 1. A polymer electrolyte membrane is sandwiched between two noncorrosive porous electrodes. Electrochemical stacks can be fabricated by mechanically compressing individual assemblies across electrically conducting separators.

Generally, PEMFCs require humidified gases, *viz*., hydrogen and oxygen (or air) as fuels for their operation. The electrochemical reactions occurring at electrodes are as follows:

at anode: $H_2 \longrightarrow 2H^+ + 2e^-$;

at cathode: $0.5\,O_2 + 2H^+ + 2e^- \longrightarrow H_2O$;

overall: $H_2 + 0.5\,O_2 \longrightarrow H_2O + Q_1 + Q_2$,

where Q_1 is the electrical energy and Q_2 is the heat energy.

Membranes for PEMFCs [9] must possess some specific properties, such as:

– low permeability with respect to oxygen and hydrogen (to prevent membrane breakdown);

– high swelling (to provide efficient dissociation of acids and to form a hydrated ionic phase within the thickness of the membrane);

– good water uptakes at temperatures above 100 °C;

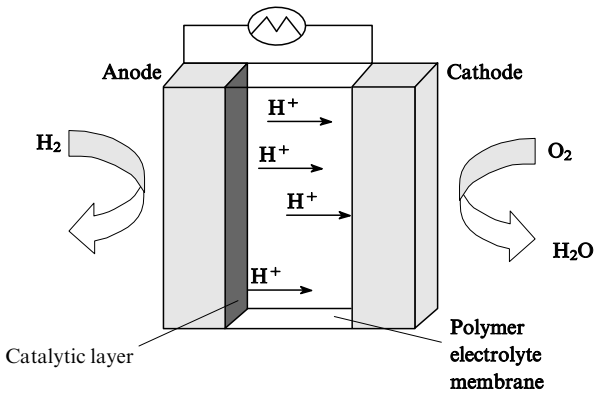


Figure 1. A scheme of a PEMFC.

– high ion-exchange capacity sufficient to provide a conductivity of the order of 10^{-1} S cm^{-1} at temperatures near 50 °C;

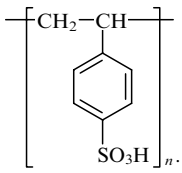
– high proton conductivity at temperatures above 100 and below 0 °C;

– high chemical and mechanical stability for long-term operation under severe conditions (over 2000 h for electric vehicle applications).†

In addition, ion-conducting films must be coated onto catalyst particles with ease. And of course, such membranes have to meet all requirements placed upon commercial products in the fuel cell market.

As a rule, proton-conducting polymers are prepared using polymer electrolytes containing negatively charged groups. The polymer electrolytes with sulfate and phosphate groups are most widely used. In dry state, they are rigid-chain, proton-conducting systems. As the content of water increases, the proton conductivity of hydrated polymer electrolytes substantially increases and can be as high as 10^{-2}–10^{-1} S cm^{-1}.

The first PEMFC (a 1 kW power plant) used in an operational system was built at General Electric Co. (USA).[10] The polymer membrane was made of poly(styrenesulfonic acid) (PSSA)



This type of PEMFC was used for primary power sources for the Gemini (USA) spacecrafts in the mid-1960s.

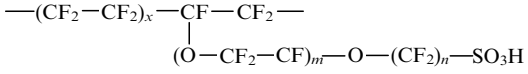
The lifetime of these PEMFCs was limited due to the degradation of the PSSA membrane under the action of $HO_2^{\bullet}$ radicals.

Research on fluorinated polymers[11–14] led to considerable advances in the development of polymer electrolytes. The most widely used fluorinated polymers are prepared by copolymerisation of tetrafluoroethylene and perfluorinated vinyl ethers of the type

$$F_2C{=}CF{-}O{-}CF_2{-}CF(CF_3){-}O{-}CF_2CF_2{-}SO_3{-}F,$$

accompanied by hydrolysis of fluorosulfonic acid groups. The basic perfluorinated chains of such polymers determine high chemical and thermal stability, while the side chains possess the properties of strong acids.

Perfluorinated electrolyte membranes with the general formula



are also widely used.

Membrane	x	m	n
Nafion	6–10	1	2
Flemion	3–10	0.1	1–5
Aciplex-S	1.5–14	0.3	2–5
Dow membrane	3–10	0	2

An improved PEMFC for the Gemini spacecrafts was based on a perfluorinated Nafion membrane. This membrane possesses substantially improved characteristics compared to the PSSA membranes; particular types of Nafion membranes are characterised by lifetimes of 50 000 h. Different types of Nafion membranes have different equivalent masses (grammes of polymer per mole H^+), namely, 1200 (Nafion 120), 1100 (Nafion 117 and Nafion 115) and 1000 (Nafion 105).

† Optimum durability is ten years.

Perfluorinated membranes (Dowmembrane) were developed at Dow Chemical Co. (USA). They have equivalent masses of 800–850 and a dry state thickness of ~5 μm.

The Flemion membranes with equivalent masses ~1000 were developed at Asahi Glass Co. (Japan).[5]

Aciplex-S membranes developed at Asahi Chemical Industry (Japan) are characterised by equivalent masses of 1000–1200.

All the membranes mentioned above, as well as the Neosepta-F (Tokuyama, Japan) and Gore-Select (W L Gore and Associates, Inc., USA) membranes possess high proton conductivity (10^{-2}–10^{-1} S cm^{-1}) at water uptakes up to 15 H_2O molecules per SO_3H group and are characterised by good thermal, chemical and mechanical properties. On the other hand, these membranes are poor ionic conductors at reduced humidity and/or elevated temperatures. For instance, the conductivity of fully hydrated Nafion membranes at room temperature reaches 10^{-2} S cm^{-1}; however, it dramatically decreases at 100 °C because of the loss of absorbed water in the membranes. In addition, such membranes tend to undergo chemical degradation at elevated temperatures. Finally, their fabrication is rather expensive. Therefore, the development of new solid polymer electrolytes, which combine sufficient electrochemical characteristics and low cost, is of current interest. A promising way of attacking this problem involves preparation of membranes based on aromatic condensation polymers (ACPs). The chemistry of ACPs was characterised by considerable progress in the 1960–1990s.[15–26]

ACPs have some advantages that make them practically attractive:

– ACPs are cheaper than perfluorinated polymers, and some of them are commercially available;

– ACPs containing polar groups have high water uptakes over a wide temperature range;

– decomposition of ACPs can be to a great extent suppressed by proper molecular design;

– ACPs are easily recycled by conventional methods.

A number of reviews concerning the development of proton-conducting membranes based on polymer electrolytes are available.[1,7,8,27–30] They contain information on the advanced materials, their electrochemical properties, water uptakes and thermal stabilities. However, rapid accumulation of newly obtained results gives an impetus to further generalisation of information in this field.

In the last decade, research into PEMFCs has been most intensively carried out in the following avenues:

– development of sulfonated aromatic condensation polymers (ACPs) and membranes based on them;

– development of alkylsulfonated ACPs and membranes based on them and

– development of acid–basic polymer complexes and membranes based on them.

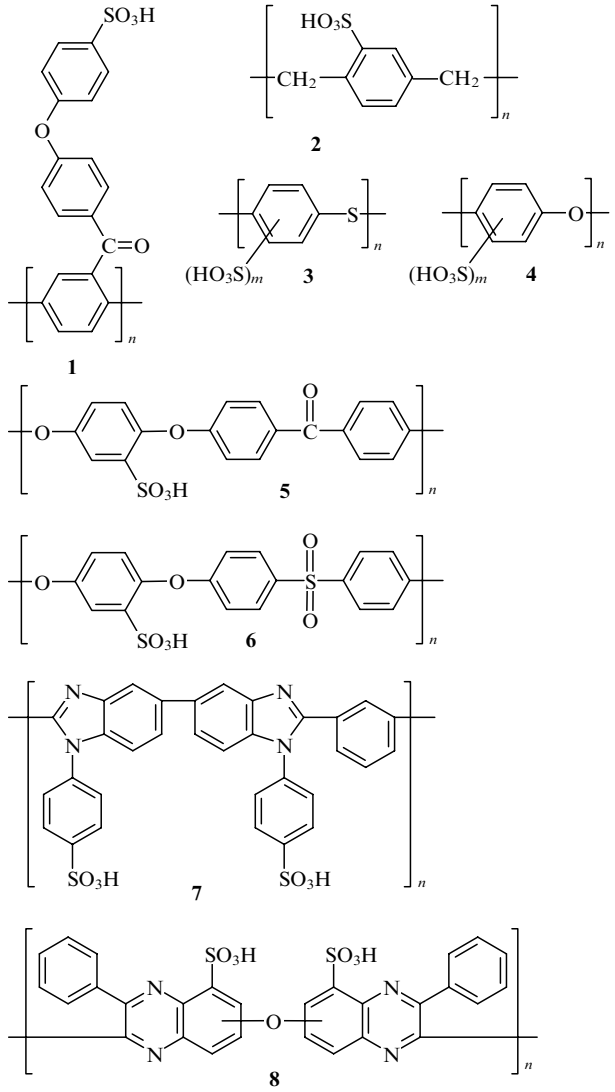
II. Sulfonated aromatic condensation polymers and membranes based on them

Aromatic polymers containing sulfonic acid groups can be prepared by sulfonation of high-molecular-mass ACPs or their fragments and by condensation of monomers containing sulfonic acid groups.

1. Sulfonation of high-molecular-mass aromatic condensation polymers

The simplest and most widely used method for the synthesis of sulfonated ACPs involves sulfonation of different classes of polymers, such as poly(1,4-phenylenes),[31–33] poly(*p*-xylylene),[34,35] poly(1,4-oxyphenylenes),[36] poly(ether ether ketones) (PEEK),[37–44] poly(arylene ether sulfones),[3,45–52] poly(phenylene sulfides),[53] poly(phenylquinoxalines),[54–56] poly(benzimidazoles)[57] and some other ACPs. The chemical structures of sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (S-PPBP) (**1**), poly(*p*-xylylene) (S-PPX) (**2**), poly(phenylene sulfide) (S-PPS) (**3**),

poly(phenylene oxide) (S-PPO) (**4**), poly(ether ether ketone) (S-PEEK) (**5**), poly(ether ether sulfone) (S-PEES) (**6**), arylsulfonated poly(benzimidazole) (S-PBI) (**7**) and sulfonated poly(phenylquinoxaline) (S-PPQ) (**8**) are shown below.



ACPs are sulfonated using known sulfonating agents.[58–60] In particular, PEEK can be sulfonated with concentrated sulfuric acid,[61] chlorosulfonic acid,[62] SO_3 (either pure or taken in a mixture),[42, 48, 62, 63] a mixture of methanesulfonic acid with concentrated sulfuric acid [64] and acetyl sulfate.[65, 66]

Sulfonation of ACPs was systematically studied taking a number of polymers (first of all, PEEK and PPBP) as examples.[7] It was shown that sulfonation with chlorosulfonic or fuming sulfuric acid is sometimes accompanied by degradation of these polymers. The sulfonation rate of ACPs in sulfuric acid can be controlled by varying the reaction time and the acid concentration.[67] This technique allows preparation of target ACPs with sulfonation degrees ranging from 30% to 100% without chemical degradation or cross-linking of the polymers.[68] However, it should be noted that direct sulfonation reactions cannot be used for preparation of random sulfonated copolymers and sulfonation levels of less than 30%, since sulfonation in sulfuric acid occurs under heterogeneous conditions due to high viscosity of the reaction solutions.[40, 61] For this reason, preparation of random copolymers requires the duration of the dissolution process to be shortened to 1 h. The dependences of the degree of sulfonation of PEEK and PPBP [23] on the reaction time at room temperature are shown in Fig. 2.

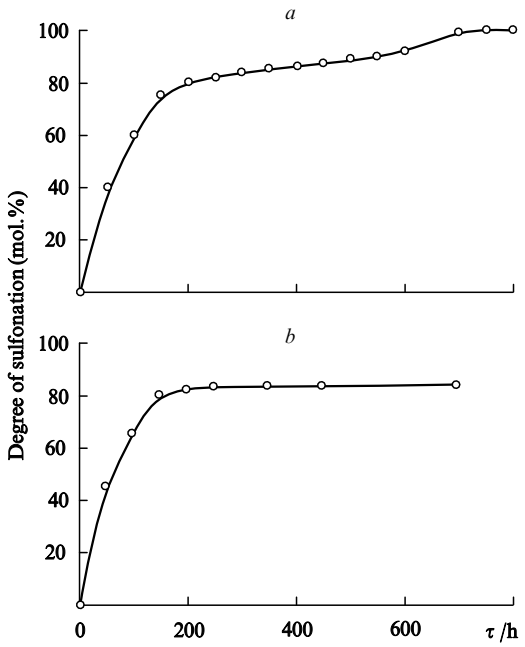


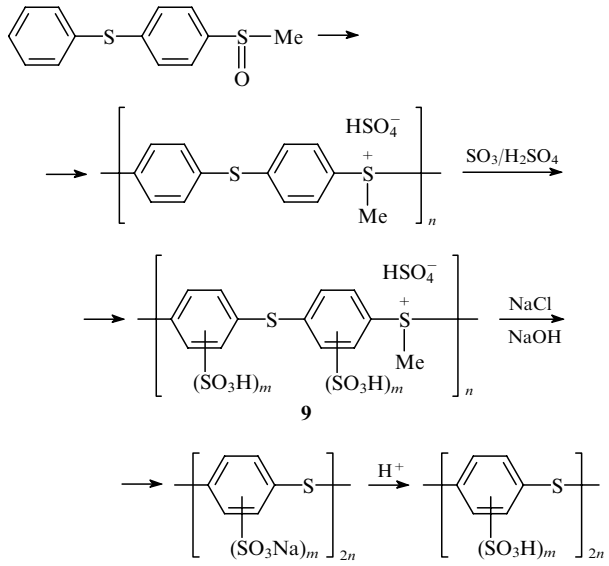
Figure 2. Degree of sulfonation of PEEK (*a*) and PPBP (*b*) as a function of reaction time at room temperature.[7]

Sulfonation is a kind of electrophilic substitution reaction; therefore, it strongly depends on the nature of substituents in the rings, namely, electron-donor substituents favour the reaction, whereas electron-acceptor substituents do not. For instance, in the case of PPBP the terminal phenyl ring of the side chain can be sulfonated under mild conditions that are comparable with the sulfonation conditions of PEEK. In contrast to this, the phenyl ring of the substituent in poly(4-benzoyl)-1,4-phenylene (PBP), which contains an electron-acceptor carbonyl group, cannot be sulfonated under these conditions.[7] The sulfonation level of PPBP and PEEK reaches nearly 80% within 100 h. The degree of sulfonation of PPBP is saturated at 85%, whereas that of PEEK can be as high as 100%. This is thought to be due to steric hindrances to further sulfonation of PPBP in a viscous sulfuric acid solution.

The solubility of polymers changes as the degree of sulfonation increases. For instance, S-PEEK containing 30 mol.% sulfonic acid groups can be dissolved in DMF, DMSO and *N*-methyl-2-pyrrolidone (*N*-MP); at 70% sulfonation, the polymer is soluble in methanol and at 100%, in water. Non-sulfonated PPBP is soluble in conventional chlorinated solvents (*e.g.*, chloroform and dichloromethane), whereas S-PPBP with 30% sulfonation is insoluble in these solvents; however, the polymer can be dissolved in DMF, DMSO and *N*-MP. At sulfonation levels above 65%, S-PPBP swells in methanol and water.

Sulfonation of PEEK in concentrated sulfuric acid at room temperature is accompanied by incorporation of no more than one sulfonic acid group into each repeating unit of the polymer.[62, 65, 69] From the results of FT-IR spectroscopy studies it follows that PEEK is sulfonated at the phenylene ring between the ether groups. Sulfonation of PPBP occurs at the *p*-position of the terminal phenoxy group.

Tsuchida *et al.*[70, 71] reported the synthesis of poly(thiophenylenesulfonic acid) containing up to two sulfonic acid groups per repeating unit. Polymerisation of 4-(methylsulfinyl)diphenyl sulfide in sulfuric acid upon heating or in the presence of SO_3 resulted in a sulfonated poly(sulfonium cation), which was then converted into the corresponding sulfonated poly(phenylene sulfide).



$m = 1-2$.

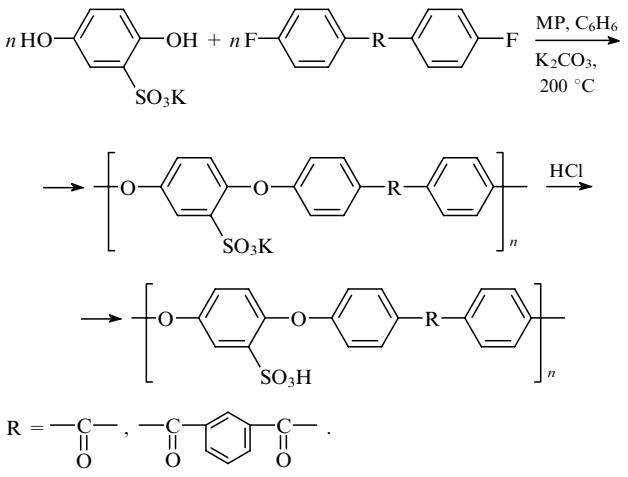
The course of sulfonation was controlled by varying the reaction time, the temperature and/or by adding SO_3. Polymer electrolytes thus obtained are soluble in water and methanol and can form transparent films.

Novel polymer electrolytes exhibiting high proton conductivity (higher than 10^{-2} S cm^{-1}) were prepared by sulfonation of poly(ether sulfone) (PES).[72,73] In these polymers the protons of the sulfonic acid groups are partially replaced by metal ions (Mg, Ti, Al, Ln), which leads to extension of the durability of the electrolytes.

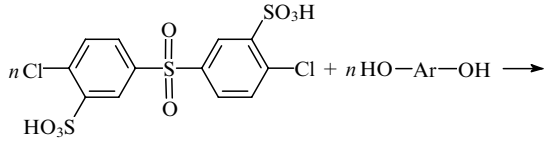
2. Synthesis of aromatic condensation polymers based on sulfonated monomers

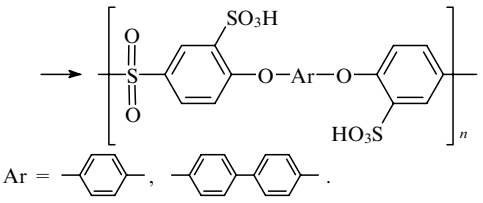
Sulfonated ACPs are prepared both by direct sulfonation and by the polycondensation and polycyclocondensation of sulfonated compounds.

In particular, sulfonated PEEK were prepared by the reactions of sulfonated hydroquinone with difluoro-substituted aromatic compounds containing carbonyl groups:[74]



An analogous procedure was employed in recent studies[75,76] on the synthesis of poly(arylene ether sulfones) in the reactions of sulfonated 4,4′-dichlorodiphenyl sulfone with various bisphenols.





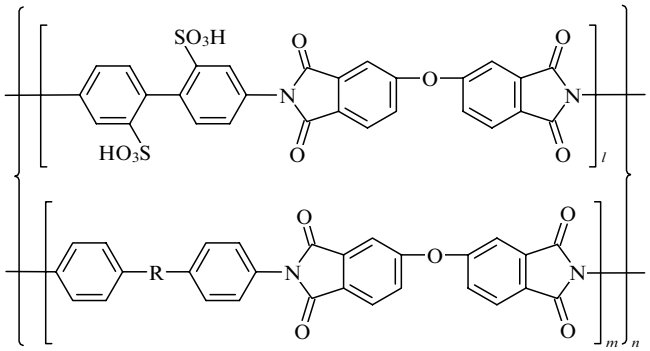
The use of *m*-aminophenol as an additive along with bisphenols allowed the preparation of poly(arylene ether sulfones) with terminal amino groups.[77]

Sulfonated poly(thiophenylene sulfones) were prepared by the interaction of sulfonated 4,4′-difluorodiphenyl sulfone with 4,4′-dimercaptobenzophenone.[78] Not only homopolymers, but also copolymers were obtained (in the latter case, a fraction of sulfonated 4,4′-difluorodiphenyl sulfone was replaced by non-sulfonated monomer) (Scheme 1).

Using this approach, one can not only prepare polymers with regular arrangement of sulfonic acid groups, but sometimes introduce a larger number of sulfonic acid groups into the ACP macromolecules compared to the sulfonation of ACPs in the last stage of the synthesis.

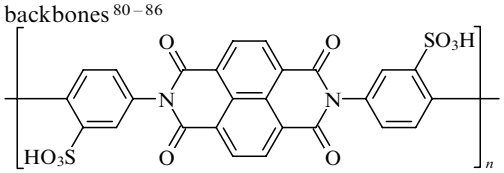
Sulfonated monomers were also used for the synthesis of sulfonated polyimides.[79,80] In particular, a sodium salt of sulfonated bis-4-[(3-aminophenoxy)phenyl]phenylphosphine oxide was used for the preparation of sulfonated polyimides (Scheme 2).[79]

Of considerable interest is the use of 4,4′-diamino-2,2′-diphenylsulfonic acid[80–82] produced on a semi-industrial scale as a sulfonated monomer for the preparation of polyimides. The reactions of a mixture of this monomer and 4,4′-diaminodiphenylmethane and 4,4′-diaminodiphenyloxide with diphenyloxido-3,3′,4,4′-tetracarboxylic acid dianhydride resulted in sulfonated polyimides[80] with the following formulae:



R = O, CH_2.

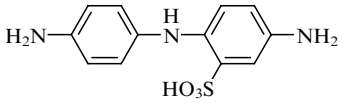
Poly(naphthylimides) containing six-membered imide rings in the backbones[80–86]



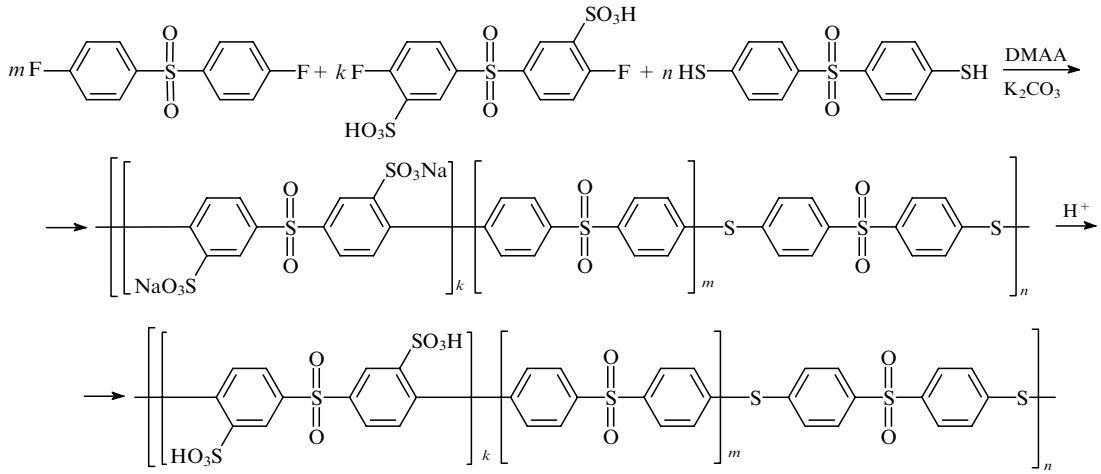
are characterised by substantially improved chemical resistance compared to analogous poly(phthalimides).[87–89]

Almost all studies on the synthesis of poly(naphthylimides) based on 4,4′-diamino-2,2′-diphenylenesulfonic acid were aimed at preparing copolymers with controlled properties that can be varied over a wide range.

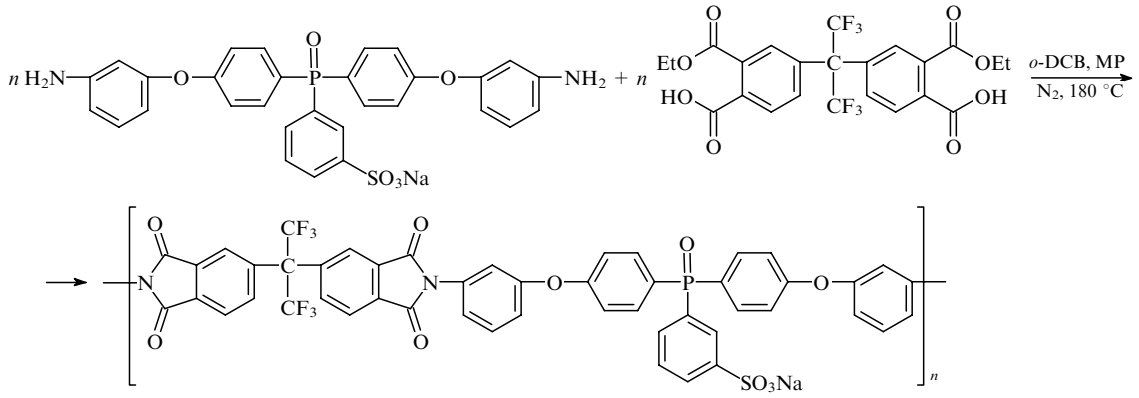
Poly(naphthylimides) can be synthesised from sulfonated diamines, *e.g.*, 4,4′-diaminodiphenylamino-2-sulfonic acid.[90]



Scheme 1



Scheme 2



3. Properties of sulfonated aromatic condensation polymers

The most important properties of sulfonated ACPs are their thermal stability, water uptake and proton conductivity.

PEMFCs and other electrochemical devices operating in the temperature range 100–200 °C require polymer electrolyte membranes characterised by fast proton transfer.

Operation of PEMFCs at elevated temperatures has a number of advantages. It causes an increase in the rates of the fuel cell reactions and reduces catalyst poisoning with absorbed carbon monoxide, thus reducing the demand for catalysts.

Thermal stability of proton-conducting polymer electrolyte membranes is an important characteristic, which determines the possibility of their use for fuel cell applications.

The thermal stability of polymer membranes based on S-PPBP was studied [7] by heating the samples followed by elemental analysis (thermogravimetric analysis, or TGA, at a heating rate of 10 deg min^{-1} in nitrogen atmosphere) (Fig. 3).

According to the results of TGA studies, S-PPBP showed a mass loss of nearly ~20% in the temperature range between 250 and 400 °C, which corresponds to the decomposition of sulfonic acid groups.

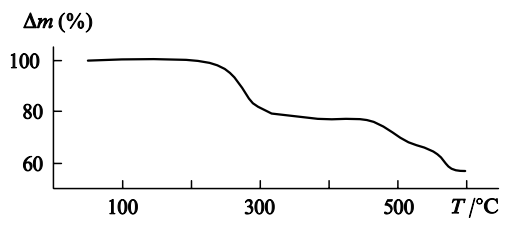


Figure 3. TGA curve of S-PPBP with 80 mol.% sulfonation level.[7]

The dependence of the degradation temperature, T_d, of S-PPBP and S-PEEK on the degree of sulfonation is presented in Fig. 4.

Degradation of sulfonated polymers was observed between 250 and 350 °C, *i.e.*, at temperatures that are much lower than the decomposition temperatures of non-sulfonated PPBP and PEEK.

As the degree of sulfonation increased, the degradation temperatures decreased from 500 down to 300 °C for S-PEEK and from 500 down to 250 °C for S-PPBP. The results of elemental analysis of the residues indicated a dramatic (nearly tenfold) decrease in the sulfur content in the polymers after heating at temperatures above 400 °C. These data confirm that thermal decomposition occurs by desulfonation mechanism.

No thermal decomposition of sulfonated polymers was observed at temperatures below 200 °C. This means that the thermal stabilities of the polymers are sufficient for fuel cell applications even at high sulfonation levels.[7]

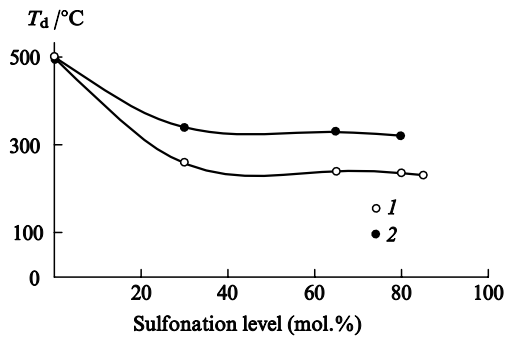


Figure 4. Degradation temperature of S-PPBP (*1*) and S-PEEK (*2*) as function of sulfonation level.[7]

Other proton-conducting polymer electrolytes based on sulfonated aromatic polymers also show the onset of thermal degradation at temperatures between 200 and 400 °C. Desulfonation of arylsulfonic acids occurs with ease on heating their aqueous solutions to 100–175 °C. Therefore, desulfonation imposes limitations on the thermal stability of sulfonated aromatic polymer electrolytes. Mention may be made that the presence of bulky substituents attached to the phenyl rings can to some extent favour an increase in the temperature of the onset of thermal degradation.

According to Tsuchida *et al.*,[70] highly sulfonated poly(phenylene sulfide) exhibits higher thermal stability compared to other sulfonated aromatic polymer electrolytes. This conclusion was based on the results of a TGA study of the thermal stability of poly(thiophenylenesulfonic acid) with different degrees of sulfonation. The degradation temperature of a highly sulfonated polymer (degree of sulfonation $m = 2.0$) is 265 °C, which is 125 °C higher than that of the low sulfonated polymer ($m = 0.6$). The C–S bond in the highly sulfonated polymer is stronger due to the presence of two electron-acceptor sulfonic acid substituents attached to each benzene ring. The initial mass loss of this polymer at 265–380 °C is only 13%, which corresponds to the loss of two water molecules per repeating unit. Therefore, the desulfonation reaction in this polymer slows down upon introduction of electron-acceptor.

Water is carried out in the fuel cells *via* humidified gas streams (H_2, O_2) and enters electrodes as a result of gas diffusion. A mixture of liquid water and water vapours passes through each electrode towards the electrode/electrolyte interface and crosses it, thus assisting the hydration of the electrolyte membranes. Oxygen reduction at the cathode provides an additional source of water in the electrolyte.

Water transport in the membrane occurs in two ways, *viz*., due to electro-osmotic drag of water by proton transfer from anode to cathode and due to diffusion of water molecules down concentration gradients that build up.

Optimum hydration level of electrolyte membranes is a key factor for normal fuel cell operation: if the electrolyte membrane is too dry, its conductivity decreases, whereas an excess of water in the membrane can lead to cathode flooding. In both cases the fuel cell performance reduces.

Absorption of water vapour by polymer films prepared from S-PEEK and S-PPBP was studied by placing the films in atmospheres with different humidities and measuring the equilibrium water content. The results obtained were found to be close to those reported in an analogous study of Nafion membranes.[10] The dependence of the water uptakes of the S-PEEK and S-PPBP films on the relative humidity at room temperature is shown in Fig. 5.

Assuming that water activity and water content in the membrane obey the Raoult law, the activity coefficient of water in the polymer is larger than unity at relative humidities exceeding a particular value. The equilibrium content of water in S-PEEK and S-PPBP increases as the sulfonation level increases. At relative humidities in the range from 0% to 50% (first region), a relatively small increase in the water uptake is observed, whereas an increase in the relative humidity from 50% to 100% (second region) leads to a much greater increase in the water uptake. The first region corresponds to water uptake due to solvation of the proton and sulfonate ions. During solvation, water is involved in the interaction with ionic components of the polymer. These interactions overcome the tendency of the polymer to exclude water due to its hydrophobic nature and resistance to swelling.[7] The second region corresponds to the uptake of water involved in polymer swelling.

The content of water in S-PPBP (65 mol.% sulfonation) is larger than in S-PEEK with the same sulfonation level. At a relative humidity of 100% and room temperature, the content of water in S-PPBP and S-PEEK is 8.7 and 2.5 molecules per sulfonic acid group, respectively.

Picnometric measurements showed that the densities of the polymers with a sulfonation level of 65 mol.% were 1.338 (S-PEEK) and 1.373 g cm^{-3} (S-PPBP). According to the results obtained by scanning electron microscopy, both polymers exhibited very close characteristics of their surfaces and fracture surfaces.

The difference in water uptake between S-PEEK and S-PPBP can be explained by the flexibility of the phenoxybenzoyl group in the side chain of S-PPBP, which favours water permeation into the polymer and water absorption in the terminal sulfonic acid groups. The water uptake of S-PPBP is comparable with that of Nafion membranes.

DTA studies revealed a rather strong interaction between the water molecules in sulfonated hydrocarbon polymers and their sulfonic acid groups, which leads to high proton conductivities at high temperatures and low humidities.

The proton conductivity of sulfonated poly(phenylene sulfide) is 10^{-5} S cm^{-1} at room temperature and a relative humidity of 30%. It exponentially increases as the relative humidity increases and reaches a value of 2×10^{-2} S cm^{-1} at 94% humidity (Fig. 6). In this case, the content of water in the polymer is 10.3 molecules per sulfonic acid group. The maximum conductivity of sulfonated poly(phenylene sulfide) ($m = 2.0$) at 80 °C was 4.5×10^{-2} S cm^{-1}.

Experiments[7] on water absorption in the S-PEEK and S-PPBP films showed that the proton conductivities of the films containing equilibrium amounts of absorbed water depend on the relative humidity. Figure 7 presents the plots of the proton conductivities of S-PPBP and S-PEEK with different sulfonation levels as a function of the relative humidity. As can be seen, the proton conductivities of the films increase with the relative

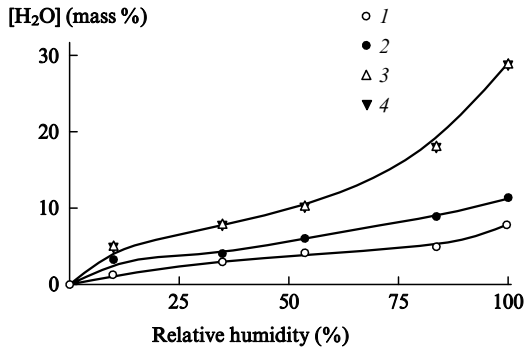


Figure 5. Water uptake of S-PPBP (*1*–*3*) and S-PEEK (*4*) at room temperature as function of relative humidity.[7]
Concentration of SO_3H groups in the polymer (mol.%): 30 (*1*), 65 (*2*), 80 (*3*) and 65 (*4*).

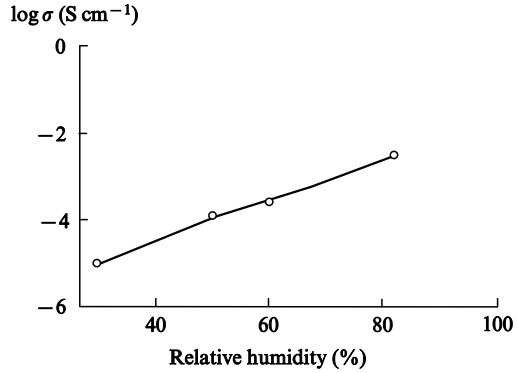


Figure 6. Proton conductivity of compound **9** ($m = 2.0$) at room temperature as function of relative humidity.[70]

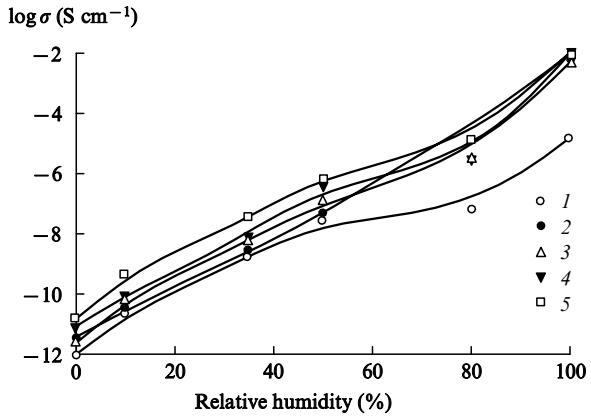


Figure 7. Proton conductivity of S-PEEK (*1*) and S-PPBP (*2*–*5*) with different sulfonation levels as a function of relative humidity at room temperature.[7]
Sulfonation level (mol.%): 65 (*1*), 30 (*2*), 65 (*3*), 80 (*4*) and 85 (*5*).

humidity and water uptake and can be as high as 10^{-5} S cm^{-1} (for S-PEEK).

The proton conductivities of S-PEEK and S-PPBP with equal degrees of sulfonation (65 mol.%) at a 100% relative humidity can be compared using the plots shown in Fig. 8. As can be seen, the proton conductivity and water uptake of S-PPBP are much higher than those of S-PEEK. Moreover, the proton conductivity of S-PEEK dramatically decreases at temperatures above 100 °C, whereas that of S-PPBP is much less temperature dependent.

Sulfonated poly(phenylene sulfide) and S-PPBP exhibit stable proton conductivities at elevated temperatures. For this reason, they are considered as promising polymers for creation of proton-conducting electrolyte membranes to be used at elevated temperatures and low humidities.

On the contrary, the conductivity of perfluorinated polymer electrolytes usually appreciably decreases with increasing temperature, that is, the conductivity of such electrolytes at 80 °C is by an order of magnitude lower than at 60 °C. Perfluorinated polymer membranes become less conducting at high temperatures, since the loss of water causes the channels to collapse, thus making proton transport more difficult.

In particular, the proton conductivity of Nafion membranes at temperatures above 100 °C dramatically decreases due to their dehydration.

In Fig. 9, we present the temperature dependences of the proton conductivity of S-PEEK with a sulfonation degree of 85 mol.% at different relative humidity values.

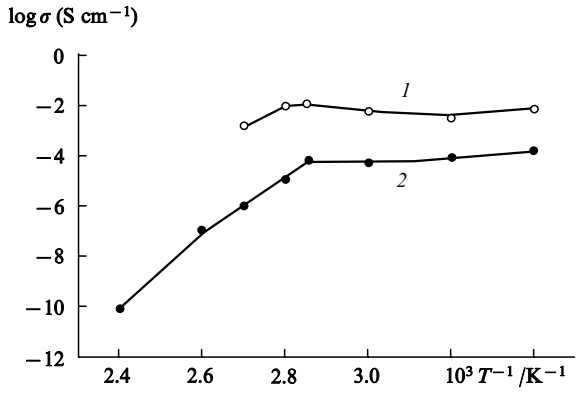


Figure 8. Temperature dependences of proton conductivity of S-PPBP (*1*) and S-PEEK (*2*) with the same degrees of sulfonation (65 mol.%) at a relative humidity of 100%.[7]

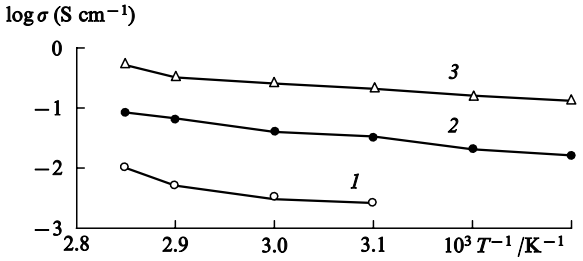


Figure 9. Temperature dependence of proton conductivity of an S-PEEK membrane with sulfonation level of 85% at a relative humidity of 50% (*1*), 70% (*2*) and 90% (*3*).[7]

Similarly to Nafion membranes, the proton conductivity of S-PEEK substantially decreases as the humidity decreases.[74] The dependence of proton conductivity on humidity reflects a tendency of S-PEEK to absorb water vapours. This can be attributed to the 'liquid' proton conductivity mechanism when protons are transported in the form of hydronium ions through water-filled pores in the membrane.[30]

S-PEEK samples exhibited a slight increase in conductivity with increasing temperature at all relative humidities (50%, 70% and 90%). This can be due to the strong interaction between the sulfonic acid groups and the absorbed water molecules.

Proton-conducting polymer electrolyte membranes based on ACPs such as S-PPBP and sulfonated poly(phenylene sulfide) contain rather large amounts of bound water. This seems to be the reason for such a salient feature of these membranes as an increased proton conductivity at high temperatures and/or low humidities. This conclusion was confirmed by the results of differential scanning calorimetry (DSC) studies of these systems.[7]

III. Alkylsulfonated aromatic condensation polymers and proton-conducting electrolyte membranes based on them

The major drawback of sulfonated proton-conducting polymer electrolytes is their degradation at 200–400 °C due to desulfonation.

By introducing alkylsulfonated substituents into the macromolecules of aromatic polymers one can prepare thermostable proton-conducting polymers. Their electrochemical properties can be controlled by varying the number of substituents and the length of alkyl chains. The water uptake and proton conductivity of alkylsulfonated polymers are close to those of sulfonated electrolytes that exhibit high thermal and chemical stability and mechanical strength.

Poly(*p*-phenyleneterephthalamido-*N*-propylsulfonate) and poly(*p*-phenyleneterephthalamido-*N*-benzylsulfonate) were synthesised based on related polyamides containing reactive NH groups.[91] The polyamides were modified by treating with NaH and DMSO[91,92] and the polyanion obtained was introduced in the reaction with 1,3-propane sultone (Scheme 3).

An analogous approach was employed in the modification of poly(benzimidazoles) (PBI).[93–100]

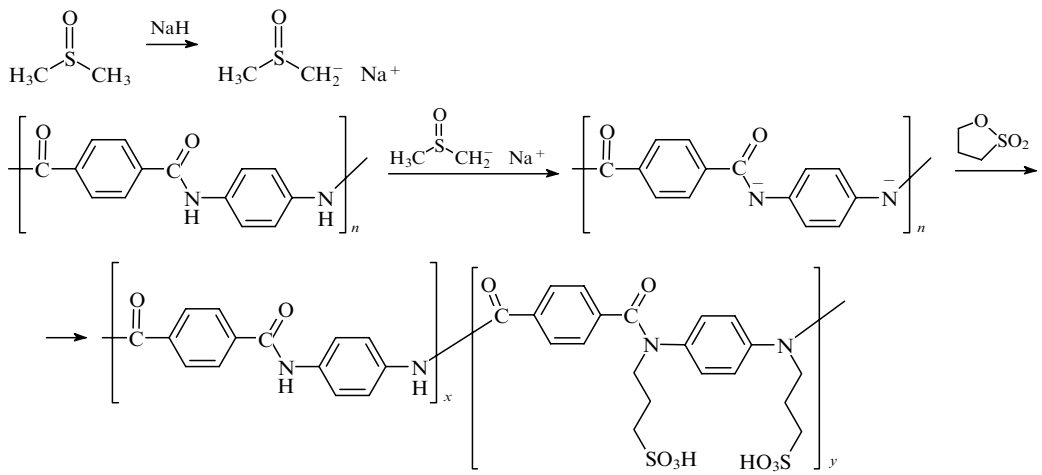
Yet another synthetic route to sulfonated PBI involves treatment of the above-mentioned polyanion with 4-bromobenzylsulfonate resulting in poly[2,2′-*m*-phenylene-bi(*N*-benzylsulfonato)benzoimidazolo-5,5′-diyl] (Scheme 4).

Compared to the starting polymers, alkylsulfonated PBI are more soluble in polar organic solvents (DMAA or DMSO). The solubility depends on the degree of alkylsulfonation.

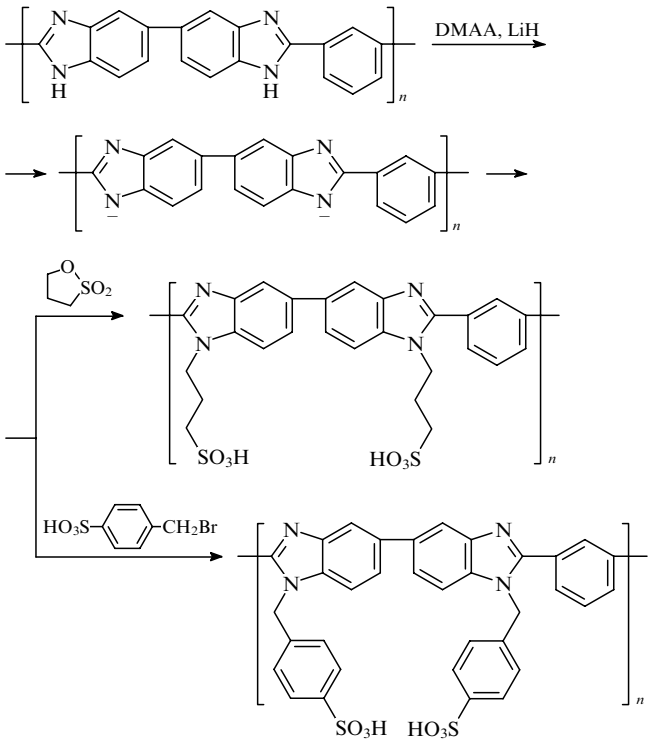
The degree of alkylsulfonation as a function of the 1,3-propane sultone : PBI ratio is plotted in Fig. 10.

The degree of alkylsulfonation of NH groups in PBI was estimated based on the results of ^{1}H NMR study and elemental analysis. This parameter can be controlled with ease by varying

Scheme 3



Scheme 4



the 1,3-propane sultone : PBI ratio. For instance, the alkylsulfonation level can be as high as 60 mol.% at a 1,3-propane sultone : PBI ratio of 5.0.

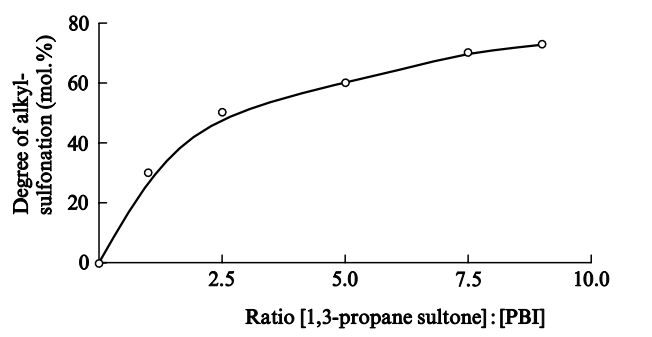


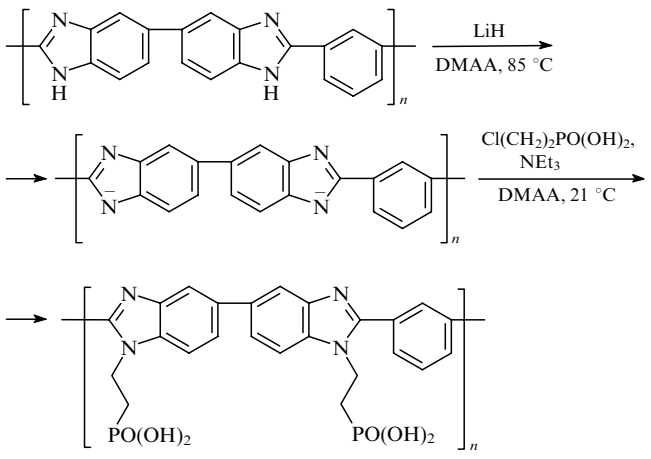
Figure 10. Degree of alkylsulfonation of PBI as function of 1,3-propane sultone : PBI ratio.[7]

An attempt to synthesise ethylphosphorylated PBI using the above-mentioned treatment of PBI at NH groups (Scheme 5) was reported.[7] The substitution reaction at the NH sites of benzimidazole rings was performed successfully, but the resulting polymer was insoluble in organic solvents. The reason can be aggregation of phosphoric acid groups during the substitution reaction. Ethylphosphorylated PBI exhibited high proton conductivity (10^{-3} S cm^{-1}) even in the pellet form. According to the results obtained, the presence of polar phosphoric acid groups enhances the proton conductivity of the polymer electrolytes.

Alkylsulfonation and arylsulfonation of the starting aromatic polymers was aimed at increasing their water uptakes and proton conductivities while retaining high thermal stabilities. The polymers obtained were studied by TGA in inert and oxidative atmospheres.[96] The parent PBI exhibits a very high thermal stability. In an inert atmosphere, the onset of its degradation occurs at 650 °C, a 5% mass loss is observed at 700 °C, while more than 80% of the initial mass is retained at 800 °C. Introduction of substituents that are not conjugated with the polymer backbones reduces the degradation temperature in an inert medium, which is consistent with the expectations. The degradation of poly[2,2′-*m*-phenylene-bi(*N*-benzylsulfonato)benzimidazolo-5,5′-diyl] with 22% substitution begins at 480 °C while the onset of mass loss process of poly-{2,2′-*m*-phenylene-bi[*N*-(3-propylsulfo)benzimidazolo-5,5′-diyl]} with a substitution level of 54% is observed at 450 °C. After removal of the substituents the degradation slows down so nearly 50% – 60% of the initial mass is retained at 800 °C.

The degradation of PBI in an oxidative atmosphere (dry air) begins at 520 °C, which is nearly 100 °C lower than the degradation temperature of this polymer in inert medium.

Scheme 5



The degradation temperatures of substituted PBI in oxidative media are close. For all polymers, the mass loss in air is much larger than in nitrogen and the amount of the residual char is much smaller. This is first of all due to the lower stability of the starting PBI in dry air and to some extent to the introduction of substituents.

In an inert atmosphere, poly(*p*-phenylene terephthalamide) (PPTA) is stable below 550 °C. Rapid mass loss of the polymer (up to 50% of the initial mass) begins at 600 °C. After modification with propylsulfonate side groups (a 66% substitution) the polymer is stable below 400 °C; only 40% of the initial mass is retained at 800 °C. The benzylsulfonated derivative of PPTA with 66% substitution level is more thermally stable compared to the propylsulfonated derivative; its degradation begins at 470 °C. A decrease in mass of the sample down to 50% of initial mass is observed at 800 °C. The degradation temperature of PPTA in a dry air atmosphere is 70 °C lower than in nitrogen atmosphere.[96] Comparison of degradation processes of benzylsulfonated PPTA with a 66% substitution in air and in nitrogen showed that the degradation in air begins at a lower temperature. The major difference in behaviour is that the mass loss is larger while after the initial mass loss it is much smaller at high temperatures, which is due to oxidative degradation of the polymer chains. Introduction of substituents into aromatic polymers reduces their thermal stability irrespective of the medium in which degradation occurs. This is the expected manner of changes in properties, since the side groups, especially sulfonic acid groups, are not stabilised by conjugation with the polymer backbones.

Gieselman and Reynolds concluded[96] that the benzylsulfonate side group is more stable than the propylsulfonate group irrespective of the structure of the polymer backbone. This suggests that the side group cleavage point is not only at the N–C bond. A TGA study of benzylsulfonated PBI with 75% degree of sulfonation in air at a heating rate of 1 deg min^{-1} showed[97] that introduction of benzylsulfonate groups into the polymer reduces its thermal stability. In this case, thermal degradation begins at 370 °C while the mass loss in the temperature range 370–420 °C is attributed to the degradation of the sulfonic acid groups. The degradation mechanism of these polymer electrolytes seems to be very complex, since the results of TGA studies are affected by the residual water, impurities, sulfonation level and measurement conditions.

In air, arylsulfonated PBI is stable up to 350 °C (see Ref. 97), while benzylsulfonated PBI is stable up to 500 °C (see Ref. 96). These results are hard to compare because of different degrees of sulfonation of the PBI samples under study. One can assume that benzylsulfonated PBI is less stable than propylsulfonated PBI due to the presence of weak aryl–S bond. In fact, the degradation temperature of benzylsulfonated PBI is comparable with those of polymer electrolytes obtained by sulfonation with sulfuric acid.

The thermal stability of anhydrous propylsulfonated PBI (PBI-PS) in a nitrogen atmosphere was studied[7] by TGA at a heating rate of 5 deg min^{-1}. Prior to analysis, all samples were vacuum oven dried at 60 °C for 48 h. However, this polymer is hygroscopic and again rapidly absorbs water after vacuum oven drying. Because of this, it was dried *in situ* and then differential thermal analysis was immediately performed.

In contrast to PBI, degradation of PBI-PS was observed in the temperature range 400–450 °C. The decomposition temperature of PBI-PS decreases as the degree of alkylsulfonation increases to 400 °C (Fig. 11); however, it is higher than the degradation temperature of perfluorinated polymer electrolytes (nearly 280 °C).

Degradation of PBI-PS was studied by elemental analysis and FT-IR spectroscopy. It was found that the intensities of SO stretching vibrations decreased after heating the PBI-PS samples above 400 °C for 1 h. These results are close to those reported by Gieselman and Reynolds[96] who found that the degradation of PBI-PS occurs due to desulfonation. Hence, alkylsulfonated PBI is more thermally stable than sulfonated aromatic polymer

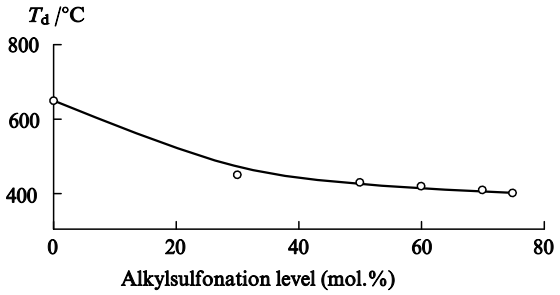


Figure 11. Decomposition temperature of PBI-PS as function of alkylsulfonation level.[7]

electrolytes characterised by degradation temperatures lying between 200 and 350 °C. The thermal stability of alkylsulfonated polymer electrolytes can be attributed to strong chemical bond between the alkyl and the sulfonic acid groups. The introduction of alkylsulfonic acid groups into thermostable polymers involving alkane sultone is one of the most important approaches to the preparation of thermostable proton-conducting polymer electrolytes.

Introduction of arylsulfonic and alkylsulfonic acid groups into aromatic polymers induces water absorption and makes them more hygroscopic. The water uptake of PBI-PS was determined[7] by measuring the mass of the polymer before and after hydration. In Fig. 12, we present the dependence of the water uptake of PBI-PS on the relative humidity. As can be seen, the water uptake changes with the relative humidity. The equilibrium water uptake of PBI-PS increases as the relative humidity and degree of alkylsulfonation increases. The water uptake of PBI-PS with an alkylsulfonation level of 73.1 mol.% is 11.3 H_2O molecules per SO_3H group at room temperature and a relative humidity of 90% (*cf.* 11.0 H_2O molecules per SO_3H group for Nafion 117 membranes under the same conditions).

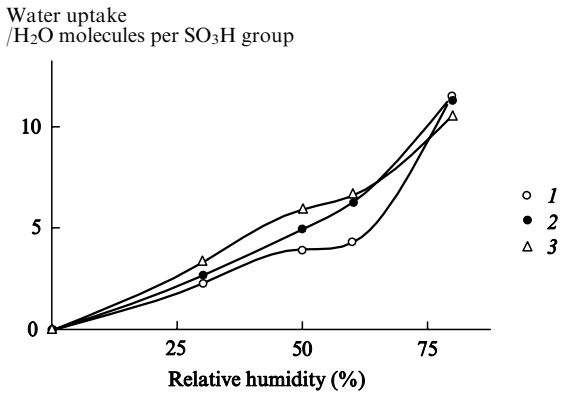


Figure 12. Water uptake of PBI-PS as a function of relative humidity at alkylsulfonation levels of 49.3 mol.% (*1*), 61.5 mol.% (*2*) and 73.1 mol.% (*3*).[7]

This procedure was also employed for the synthesis of butylsulfonated and (methyl)propylsulfonated PBI (PBI-BS and PBI-MPS, respectively) *via* butane sultone and methylpropane sultone. The water uptakes of these polymers differ from that of PBI-PS and are 19.5 (PBI-BS) and 27.5 (PBI-MPS) H_2O molecules per SO_3H group at a relative humidity of 90%. The water uptakes of alkylsulfonated PBI depend on the length of alkyl chains and on the degree of chain branching, that is, as the chain length and the degree of alkyl chain branching increase, the water uptake also increases. This is thought to be associated with the

greater flexibility of long alkyl chains and with larger amount of water absorbed in the cavities between the branched chains.

The specific role of the absorbed water in polymer electrolytes and the physical state of the water absorbed by polymer electrolytes were studied by IR [101] and ^{1}H NMR spectroscopy (low-temperature relaxation time measurements) [102] and DSC.[7] The DSC curve of a hydrated PBI-PS film (73.1 mol.%) containing 11.3 H_2O molecules per SO_3H group is shown in Fig. 13.

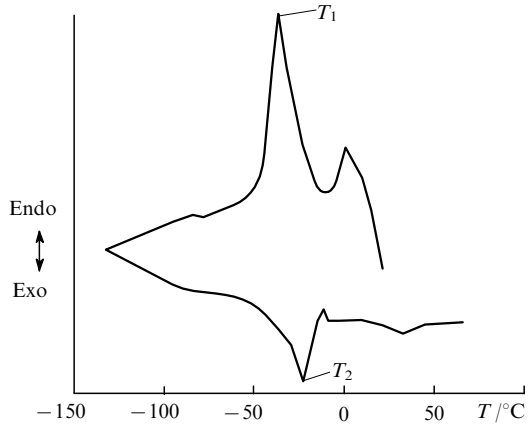


Figure 13. DSC curve of hydrous PBI-PS (73.1 mol.%) film containing 11.3 H_2O molecules per sulfonic acid group.[7]
T_1 is the freezing temperature (−36.6 °C) and T_2 is the melting temperature (−21.6 °C).

The DSC curve of anhydrous PBI-PS exhibited no peaks, whereas the DSC curve of hydrated PBI-PS exhibited two peaks corresponding to phase transitions of absorbed water at −36.6 and −21.6 °C that were attributed to the freezing and melting temperatures of the absorbed water, respectively.

A study of hydrated Nafion membranes under the same conditions revealed a phase transition at 0 °C. These results indicate that the adsorbed water in the Nafion membrane is bound to a lesser extent compared to PBI-PS which can exist in the hydrated state even at elevated temperatures.

Wet PBI-PS films possess no electron conduction despite the fact that the main polymer chains are conjugated. To elucidate the nature of charge carriers in PBI-PS, the conductivity of PBI-PS films containing H_2O and D_2O was measured.[7] The results of measurements are presented in Fig. 14. As can be seen, the conductivity of the films containing water increased with increasing water uptake and was higher than that of the PBI-PS films containing D_2O in the same temperature range. This points that the charge carrier in hydrated PBI-PS is a proton (hydronium ion).

The temperature dependence of proton conductivity of PBI-PS containing the equilibrium amount of water is shown in

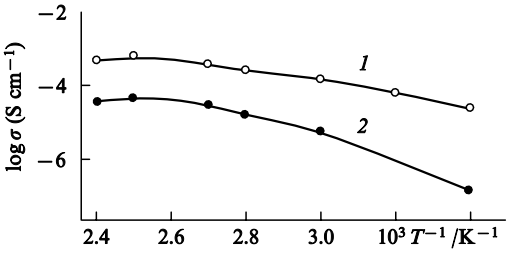


Figure 14. Temperature dependence of proton conductivity of PBI-PS (61.5 mol.%) films containing H_2O (*1*) and D_2O (*2*).[7]

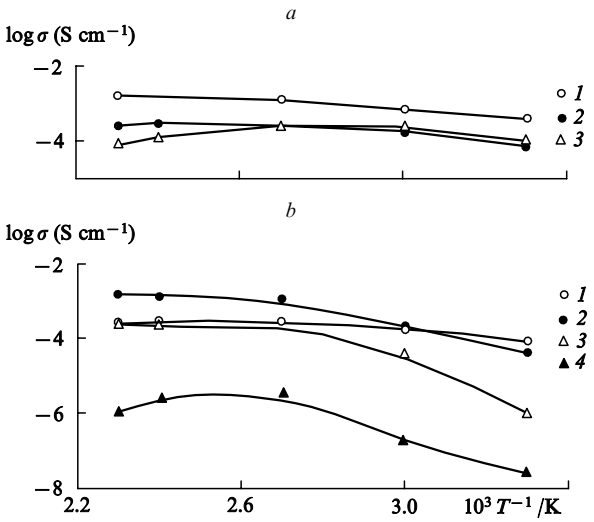


Figure 15. Temperature dependences of proton conductivity of PBI-PS films with the same water uptake (48%) and different degrees of sulfonation (*a*) and with the same degree of sulfonation (73.1%) and different water uptakes (*b*);[7]
(*a*): degree of sulfonation (mol.%): 49.3 (*1*), 61.5 (*2*) and 73.1 (*3*);
(*b*): water uptake: 11.2 (*1*), 25.0 (*2*), 29.0 (*3*) and 48.0 (*4*).

Fig. 15. Hydrated PBI-PS exhibits a high proton conductivity at room temperature. The conductivity of a PBI-PS sample containing 3.1 H_2O molecules per SO_3H group reached 10^{-5} S cm^{-1} at 80 °C and decreased slightly at higher temperatures due to a small loss of water (~10 mass %). The conductivity of a PBI-PS film containing more than 5.2 H_2O molecules per SO_3H group increased as the temperature increased and was as high as 10^{-3} S cm^{-1} at temperatures above 100 °C. The proton conductivity of a PBI-PS film containing 11.3 H_2O molecules per SO_3H group was $\sim 10^{-3}$ S cm^{-1}.

The water uptake of PBI-PS films placed in an atmosphere with a relative humidity of 90% was comparable with that of Nafion membranes. The proton conductivity of Nafion membranes was as high as 10^{-3} S cm^{-1} at room temperature; however, it decreased due to the loss of absorbed water at temperatures above 100 °C. In contrast to this, hydrated PBI-PS exhibited a high proton conductivity at temperatures above 100 °C.

The large water uptake and high proton conductivity of PBI-PS at temperatures above 100 °C are due to the specific properties of the polymer and the physical state of absorbed water.

The proton conductivity of benzylsulfonated PBI at different values of relative humidity has been studied.[102] It was found that the proton conductivity increases as the degree of substitution increases. The polymer with a 75% substitution level exhibited a conductivity of $\sim 10^{-2}$ S cm^{-1} at 40 °C and a relative humidity of 100%.

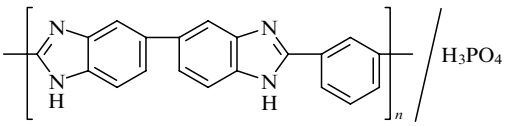
The results obtained in the above-mentioned studies suggest that alkylsulfonated aromatic polymer electrolytes exhibit sufficient thermal stabilities for fuel cell applications at 80 °C (a typical operating temperature for perfluorinated polymer electrolyte membranes). The water uptakes and proton conductivities of these polymers are close to the corresponding values for perfluorinated polymer electrolytes at temperatures below 80 °C but are larger than the latter at temperatures above 80 °C.

The absorbed water molecules are more strongly bound to alkylsulfonated rather than perfluorinated polymers. One can assume that this is related to the difference in the absorption mechanisms and to the physical state of the absorbed water in PBI-PS and perfluorinated polymer electrolytes.

IV. Proton-conducting electrolyte membranes based on acid – base polymer complexes

Proton-conducting membranes used in PEMFC operate under severe conditions (see above). Recently, complexes of basic polymers with strong acids have attracted a considerable interest. Such complexes are characterised by stable electrochemical properties and large water uptakes at high temperatures.

Recently, new proton-conducting polymer electrolyte membranes based on PBI – orthophosphoric acid complexes have been proposed for use in PEMFCs.[103–106]



10

The most important advantages of this polymer electrolyte over perfluorinated polymer electrolytes and other acid – basic polymer complexes are that PBI/H_3PO_4 possesses conductivity even at low activity of water and high thermal stability of these systems. The materials based on these complexes are expected to operate over a wide range from room to high temperature in both humid and dry gas. Such complexes are prepared by immersing PBI films into phosphoric acid solutions. In particular, the preparation of PBI – strong acid complexes by immersion of PBI films into solutions of strong acids in methanol was reported.[107,108] The absorption level of strong acid molecules increased with an increase in the concentration of the strong acid and reached up to 2.9 molecules per repeating unit for polymer complexes **10**. An IR spectroscopy study of the complexes revealed that the acid molecules, except for H_3PO_4, protonate the nitrogen atoms in the imidazole ring. Phosphoric acid (H_3PO_4) is incapable of protonating the imidazole groups in PBI but interacts with them *via* the formation of strong hydrogen bonds between NH and OH groups.

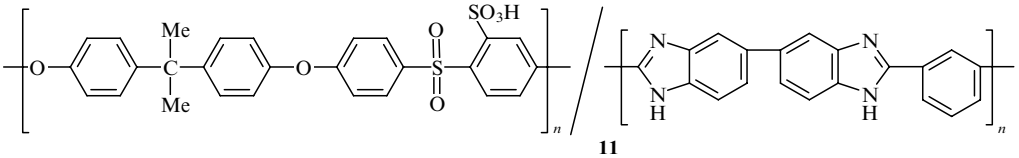
PBI films doped with phosphoric acid were prepared by immersion of PBI films in aqueous solutions of phosphoric acid for at least 16 h.[103–106] Upon equilibration in an 11 M H_3PO_4 solution a doping level of $\sim$5 phosphoric acid molecules per repeating unit of the polymer was achieved.

Anhydrous sulfonated aromatic polymers are highly brittle. Recently,[109] new materials with high mechanical strength were reported. They were prepared using polymer blending technique by combining PBI and sulfonated polymers (S-PEEK or *ortho*-sulfonated polysulfone **11**).

Such polymer blends exhibit high proton conductivities, moderate swelling values and high thermal stabilities. The specific interaction of SO_3H groups with basic nitrogen atoms was confirmed by FT-IR spectroscopy. The acid – base interaction between the sulfonated polymer and PBI provided a material with high mechanical strength and thermal stability.

The thermal stability of PBI – strong acid polymer complexes was studied by TGA and DTA. Figure 16 presents the TGA curves of polybenzimidazole and its complexes with strong acids. As can be seen, PBI exhibits an extremely high thermal stability over the entire temperature range. Small mass losses by all samples at temperatures below 200 °C are due to the loss of water and solvent present in the membranes.

Typical proton-conducting polymer electrolytes undergo considerable degradation in the temperature range under study.



11

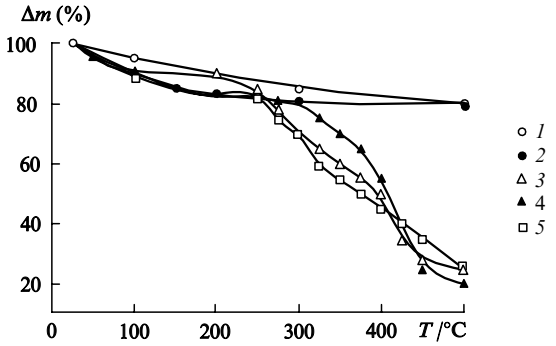


Figure 16. TGA curves of PBI (*1*) and its complexes with H_3PO_4 (*2*), H_2SO_4 (*3*), $MeSO_3H$ (*4*) and $EtSO_3H$ (*5*).[7]

A decrease in the degradation temperature of polymer complexes **10** was expected because of the complexation of acid molecules which easily corrode and oxidise the polymer macromolecules. However, no degradation was observed in nitrogen atmosphere. At the same time, thermal decomposition of PBI complexes with H_2SO_4, $MeSO_3H$ and $EtSO_3H$ begins at 330, 240 and 220 °C, respectively. After thermal decomposition of these polymer complexes in the temperature range 220 – 400 °C the residues were 50% of the initial masses of the samples. Therefore, complexation of PBI with H_2SO_4, $MeSO_3H$ and $EtSO_3H$ results in a loss of thermal stability. The decomposition of complexes is first of all due to elimination of acid molecules. This assumption was confirmed by the results of elemental analysis. At temperatures above 400 °C, the PBI chains gradually decompose under the action of high temperatures and strong acids.

Complexes **10** are thermally stable up to 500 °C. It was found that treatment of PBI with a phosphoric acid solution (27 mass %) improved the thermal stability of the polymer.[110] This was associated with the formation of benzimidazonium cations. Samms *et al.*[104] studied the thermal stability of polymer complexes **10** and showed that these complexes are promising for use as polymer electrolytes in the hydrogen – air and methanol fuel cells. To simulate the operating conditions in a high-temperature PEMFC, the polymer complexes **10** were coated with platinum black, doped with phosphoric acid (4.8 H_3PO_4 molecules per repeating unit of PBI) and heated in an atmosphere of nitrogen and 5% hydrogen or in air in a TGA analyser. The degradation products were identified by mass spectrometry. In all cases the mass loss below 400 °C was found to be due to the loss of water. In addition, it was found that polymer complexes **10** coated with platinum black are thermally stable up to 600 °C.

Variation of the conductivity of polymer complexes **10** as a function of water vapour activity, temperature and acid doping level was studied.[106] It was shown that the conductivity of heavily doped complexes (500 mol.%) is nearly twice as high as that of the film doped to 338 mol.% at the same temperature and humidity. For instance, the conductivity of PBI doped with 500 mol.% H_3PO_4 (5 H_3PO_4 molecules per repeating unit of PBI) is 3.5×10^{-2} S cm^{-1} at 190 °C and a water vapour activity of 0.1.

Raising the temperature and water vapour activity causes an increase in the conductivity of the polymers irrespective of the doping level of PBI with phosphoric acid. In addition, it was found that crossover of methanol molecules through the polymer complexes **10** is by an order of magnitude smaller than in the case of

perfluorinated polymer electrolytes and that the mechanical strength of such complexes is three orders of magnitude higher compared to that of Nafion membranes.

The proton conductivity of PBI polymer complexes prepared by the interaction of PBI with methanol solutions of strong acids was studied.[7] The temperature dependences of the conductivities of anhydrous PBI – strong acid polymer complexes are shown in Fig. 17 *a*.

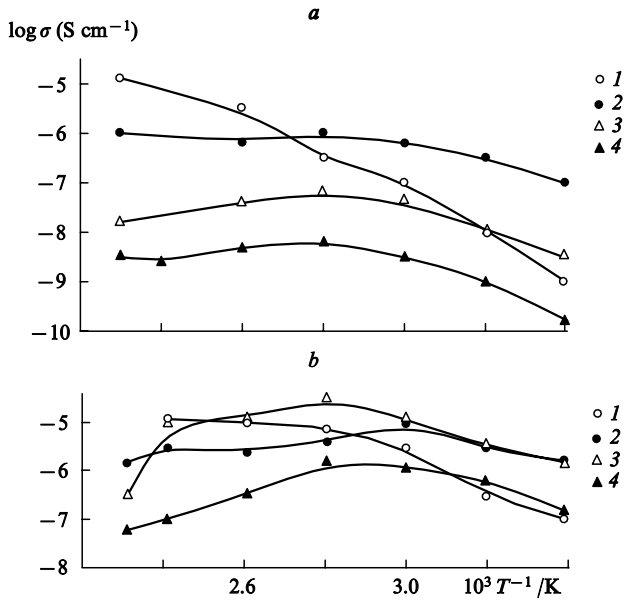


Figure 17. Temperature dependence of proton conductivity of anhydrous (*a*) and hydrous (*b*) PBI complexes with H_3PO_4 (*1*), H_2SO_4 (*2*), $EtSO_3H$ (*3*) and $MeSO_3H$ (*4*);[7]
(*a*): doping level, acid molecules per PBI unit: 2.0 (*1*), 1.8 (*2*), 2.0 (*3*), 1.9 (*4*); (*b*): water uptake (mass %): 13 (*1,4*), 19 (*2*) and 26 (*3*).

All anhydrous polymer complexes of PBI with strong acids possess a proton conductivity of the order of 10^{-6} – 10^{-9} S cm^{-1} at 100 °C. The conductivity of polymer complexes **10** can be as high as 10^{-5} S cm^{-1} at 160 °C, whereas other PBI – acid complexes showed a decrease in the conductivity at temperatures above 80 °C. These results point to high thermal stability of polymer complexes **10**.

To prepare hydrated systems, the films of PBI – strong acid polymer complexes were placed in a desiccator with a relative humidity of 90% for 72 h. The water uptakes of the complexes were 13 mass % –26 mass %. The proton conductivity of the hydrous PBI – strong acid polymer complexes was found to be nearly an order of magnitude higher than the conductivity of anhydrous polymer complexes (Fig. 17 *b*). This difference can be explained by the improvement of charge carrier generation in the absorbed water. Changes in the proton conductivity at room temperature are especially remarkable. Figure 18 presents the temperature dependences of the conductivity of anhydrous complexes **10** with different acid contents. As can be seen, the conductivity of polymer complexes **10** increases with the concentration of H_3PO_4.

The temperature dependence of the conductivity of polymer complexes **10** is quite different: in this temperature range the conductivity is low. This suggests that two H_3PO_4 molecules quantitatively react with the PBI units containing two imidazole groups. As a consequence, an excess of H_3PO_4 determines the necessary proton conductivity. A study of PBI/H_3PO_4 polymer complexes by FT-IR spectroscopy showed that the spectra exhibited three characteristic absorption maxima near 1090 cm^{-1} (HPO_4^{2-}), 1008 cm^{-1} (POH) and 970 cm^{-1} ($H_2PO_4^-$).[111–114] As

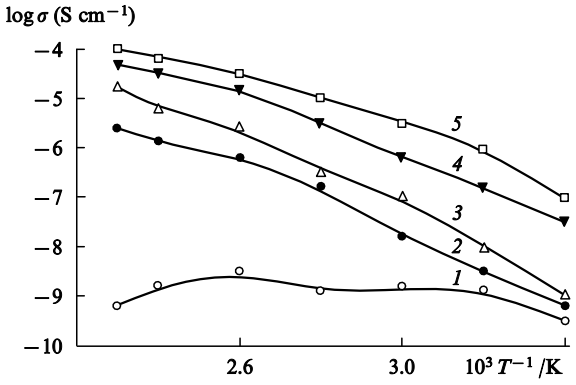


Figure 18. Temperature dependences of proton conductivity of anhydrous PBI/H_3PO_4 complexes containing 1.4 (*1*), 2.0 (*2*), 2.7 (*3*), 2.3 (*4*) and 2.9 (*5*) H_3PO_4 molecules per PBI unit.[7]

the concentration of H_3PO_4 increases, the intensity of the absorption maxima of HPO_4^{2-} and $H_2PO_4^-$ increases. This suggests that proton conductivity can occur by the Grotthus mechanism[115] involving an exchange of protons between H_3PO_4 and PO_4^{2-} or $H_2PO_4^-$.

V. Fuel cell applications of proton-conducting membranes based on aromatic condensation polymers

Two blend polymer electrolytes containing acid and basic functional groups (90 mass % PEEK and 10 mass % PBI or 95 mass % PES and 5 mass % PBI) were applied in H_2/O_2 fuel cells. The current-*vs*.-voltage curves of the membranes in the fuel cells were comparable with that of Nafion 112 membranes.[109]

Fuel cell tests of membranes based on sulfonated PES showed[7] a cell voltage of 550 mV at a current density of 700 mA cm^{-2} (atmospheric pressure, humidified gases, 70 °C). No significant loss of membrane performance was observed after long-term operation (1000 h) under fuel cell conditions.

The maximum power of fuel cells with S-PPBP membranes reaches 0.3 W cm^{-2} at a current density of 800 mA cm^{-2}. The conductivity of the electrolyte membranes was 3×10^{-3} S cm^{-1}; the membrane thickness and surface area were 0.01 cm and 3.15 cm^2, respectively.

The maximum power of fuel cells H_2/O_2 and CH_3OH/O_2 with membranes based on polymer complexes **10** (see Ref. 7) was as high as 0.25 W cm^{-2} at a current density of 700 mA cm^{-2}. The electrical resistance of electrolyte membranes was 0.4 Ω, the thickness and surface area of the membranes were 0.01 cm and 1 cm^2, respectively, and the doping level was 500 mol.%. The measured electrical resistance of the cell was equivalent to a conductivity of 0.025 S cm^{-1}. It was found that the electrical resistance of the fuel cell is independent of the water content in the gas (water produced at cathode is sufficient for maintaining the necessary conductivity of the electrolyte). This type of fuel cells was characterised by continuous operation at a current density of 200 mA cm^{-2} over a period of 200 h (and for longer times) without reduction of the membrane performance.

The power of CH_3OH/O_2 fuel cells at 200 °C and atmospheric pressure reached 0.1 W cm^{-2} at a current density of 250 – 500 mA cm^{-2}. The conductivity of membranes operating under these conditions remained constant in the temperature range 30 – 140 °C.

* * *

To summarise, the aforesaid shows that the aromatic condensation polymers can be thought to be candidates for fuel cell

applications: the structure of ACP-based polymer electrolytes can be modified with ease; these polymer electrolytes possess large water uptakes and high proton conductivities at high temperatures and low humidities, as well as sufficient thermal and chemical stability. Further investigations to design proton-conducting materials exhibiting long-term thermal stability and mechanical strength, capable of operating at high temperatures without humidification and further improvement of fuel cells are required.

References

1. J A Kerres *J. Membr. Sci.* **185** 3 (2001)
2. H Riedinger, W Faul *J. Membr. Sci.* **36** 5 (1988)
3. R Nolte, K Ledjeff, M Bauer, R Mulhaupt *J. Membr. Sci.* **83** 211 (1993)
4. K B Prater *J. Power Sources* **51** 129 (1994)
5. S Watkins, in *Fuel Cell Systems* (Eds L G Blumen, M N Mugerwa) (New York: Plenum, 1993) p. 493
6. J C Lasseques, in *Proton Conductors: Solids Membranes and Gels* (Ed. P Colombon) (Cambridge: Cambridge University Press, 1992) p. 311
7. M Rikukawa, K Sanui *Prog. Polym. Sci.* **25** 1463 (2000)
8. O Savadogo *J. New Matter. Electrochem. Syst.* **1** 66 (1998)
9. M Higuchi, N Minoura, T Kinoshita *Chem. Lett.* **2** 227 (1994)
10. T A Zawodzinski, C Derouin, S Radzinski, R J Sherman, U T Smith, T E Springer, S Gottesfeld *J. Electrochem. Soc.* **140** 1041 (1993)
11. M Yamabe, H Migake, in *Organofluorine Chemistry. Principles and Commercial Applications* (Eds R E Bomks, B E Smart, J C Tatlow) (New York: Plenum, 1994) p. 403
12. Yu E Kirsh, S A Smirnov, Yu M Popkov, S F Timashev *Usp. Khim.* **59** 970 (1990) [*Russ. Chem. Rev.* **59** 560 (1990)]
13. W G Grot *Macromol. Symp.* **82** 161 (1994)
14. A Steck, in *Proceedings of the 1st International Symposium on New Materials for Fuel Cell Systems, Membrane Materials in Fuel Cells* (Eds O Savadogo, P R Roberge, T N Vezirogly) (Canada: Montreal, 1995) p. 74
15. A S Hay *Adv. Polym. Sci.* **4** 496 (1967)
16. S Maiti, B Mandal *Prog. Polym. Sci.* **12** 111 (1986)
17. H Lee, D Stoffey, K Neville, in *New Linear Polymers* (New York: McGraw-Hill, 1967) p. 374
18. A H Frazer, in *High Temperature Resistant Polymers* (New York: Interscience, 1968) p. 338
19. V V Korshak *Termostoikie Polimery* (Thermally Stable Polymers) (Moscow: Khimiya, 1969)
20. P E Cassidy, in *Thermally Stable Polymers* (New York: Marcel Dekker, 1980) p. 163
21. J P Critchley, W W Wright, in *Heat-Resistant Polymers* (New York: Plenum, 1983) p. 259
22. K-U Bühler *Spezialplaste* (Berlin: Akademie-Verlag, 1978)
23. A L Rusanov, D S Tugushi, V V Korshak *Uspekhi Khimii Poligeteroarilenov* (Progress in the Chemistry of Heteroarylenes) (Tbilisi: Tbilisi State University, 1988)
24. V V Korshak, A L Rusanov *Vysokomol. Soedin., Ser. A* **26** 3 (1984) [a]
25. A L Rusanov *Vysokomol. Soedin., Ser. A* **28** 1571 (1986) [a]
26. A D Schluter *J. Polym. Sci., Polym. Chem.* **39** 1533 (2001)
27. E D Power, G A Serad *High Performance Polymers: Origin and Development* (New York: Elsevier, 1986)
28. R R Luise, in *Applications of High Temperature Polymers* (Boca Raton, FL: CRC Press, 1996) p. 272
29. K D Kreuer *J. Membr. Sci.* **185** 29 (2001)
30. K D Kreuer *Chem. Mater.* **8** 610 (1996)
31. Z Qi, P G Pickup *Chem. Commun.* **1** 15 (1998)
32. A D Child, J R Reynolds *Macromolecules* **27** 1975 (1994)
33. T Kobayashi, T Rikukawa, K Sanui, N Ogata *Solid State Ion.* **106** 219 (1998)
34. V A Sochilin, A V Pebalk, V I Semenov, I E Kardash *Vysokomol. Soedin., Ser. A* **33** 1536 (1991) [a]
35. V A Sochilin, A V Pebalk, V I Semenov, M A Sevast'yanov, I E Kardash *Vysokomol. Soedin., Ser. A* **35** 1480 (1993) [a]
36. A J Chalk, A S Hay *J. Polym. Sci. A* **7** 5843 (1982)
37. I L Bredas, R R Chomce, R Silbey *Phys. Rev. B* **26** 5843 (1982)
38. H Kobayashi, H Tomita, H Moriyama, A Kobayashi, T Watanabe *J. Am. Chem. Soc.* **116** 3153 (1994)
39. F Wong, J Roovers *Macromolecules* **26** 5295 (1993)
40. C Bailly, D J Williams, F F Karasz, W J McNight *Polymer* **28** 1009 (1987)
41. X Jin, M T Bishop, T S Ellis, F E Karazz *Br. Polym. J.* **17** 4 (1985)
42. M I Litter, C S Marvel *J. Polym. Sci., Polym. Chem. Ed.* **23** 2205 (1985)
43. J Devaux, D Delimoy, D Dauost, R Legras, J P Mercier, C Strazielle, E Nield *Polymer* **26** 322 (1985)
44. T Ogawa, C S Marwel *J. Polym. Sci., Polym. Chem. Ed.* **23** 1231 (1985)
45. US P. 4 625 000; *Chem Abstr.* **106** 85 292 (1987)
46. US P. 4 413 106; *Chem Abstr.* **100** 35 025 (1983)
47. A Noshay, L M Robeson *J. Appl. Polym. Sci.* **20** 1885 (1976)
48. B C Johnson, I Yilgor, C Tran, M Iqbal, J P Wightman, D R Lloyd, J E McGrath *J. Polym. Sci., Polym. Chem. Ed.* **22** 721 (1984)
49. C Mottet, A Revillon, P Le Perchec, M E Lauro, A Guyot *Polym. Bull.* **8** 511 (1982)
50. C Arnold Jr, R A Assinic *J. Membr. Sci.* **38** 71 (1988)
51. P Zschocke, D Guellmalz *J. Membr. Sci.* **22** 325 (1985)
52. P Genova-Dimitrova, B Baradie, D Foscallo, C Poisington, J Y Somchez *J. Membr. Sci.* **185** 59 (1976)
53. Z Qi, M C Lefebre, P G Pickup *J. Electrochem.* **459** 9 (1998)
54. Russ. P. 1 819 418; *Byull. Izobret.* (14) 61 (1992)
55. N M Belomoina, A L Rusanov, N A Yanul', Yu E Kirsh *Vysokomol. Soedin., Ser.B* **38** 355 (1996) [a]
56. Yu E Kirsh, N A Yanul', N M Belomoina, A L Rusanov *Elektrokhimiya* **32** 169 (1996) [b]
57. US P. 4 634 530; *Chem. Abstr.* **106** 157 701 (1987)
58. X L Wei, Y Z Wang, S M Long, C Bobeczko, A J Epstein *J. Am. Chem. Soc.* **118** 2545 (1996)
59. E E Gilbert, in *Sulfonation and Related Reactions* (New York: Wiley-Interscience, 1965) p. 78
60. E E Gilbert *Sul'firovanie Organicheskikh Soedinenii* (Sulfonation and Related Reactions) (Translated into Russian; Moscow: Khimiya, 1969)
61. X Jin, M T Bishop, T S Ellis, F E Karasz *Br. Polym. J.* **17** 4 (1985)
62. J Lee, C S Marvel *J. Polym. Sci., Polym. Chem. Ed.* **22** 295 (1984)
63. B C Johnson, I Ylgor, M Iqbal, J P Wrightman, D R Lloyd, J E McGrath *J. Polym. Sci., Polym. Chem. Ed.* **22** 72 (1984)
64. C Bially, D Williams, F E Karasz, W J MacKnight *Polymer* **28** 1009 (1987)
65. W A Thaler *J. Polym. Sci.* **20** 875 (1982)
66. W A Thaler *Macromolecules* **16** 623 (1983)
67. M T Bishop, F E Karasz, P S Russo, K H Langley *Macromolecules* **18** 86 (1985)
68. D Devaux, D Delimoy, D Daoust, R Legras, J P Mercier, C Strazielle, E Neild *Polymer* **26** 1994 (1985)
69. T Ogawa, C S Marvel *J. Polym. Sci., Polym. Chem. Ed.* **23** 1231 (1985)
70. K Miyatake, E Shouji, K Yamamoto, E Tsuchida *Macromolecules* **30** 2941 (1997)
71. K Miyatake, H Iyotani, K Yamamoto, E Tsuchida *Macromolecules* **29** 6969 (1996)
72. Jpn. P. 11-116 679; *Chem. Abstr.* **130** 325 763 (1999)
73. Jpn. P. 11-067 224; *Chem. Abstr.* **130** 239 961 (1999)
74. N Venkatasubramanion, D Deon, F E Arnold *Polym. Prepr.* **37** (1) 354 (1996)
75. M Ueda, H Toyota, T Ochi, J Sugiyama, K Yonetake, T Masuko, T Teremoto *J. Polym. Sci., Polym. Chem. Ed.* **31** 853 (1993)
76. J E McGrath, R Formato, R Covar, W Harrison, J B Mechant *Polym. Prepr.* **41** (1) (2000)
77. J Mecham, H K Shobha, F Wong, W Harrison, J E McGrath *Polym. Prepr.* **41** (2) 1388 (2000)
78. F Wong, J Mecham, W Harrison, J E McGrath *Polym. Prepr.* **41** (2) 1401 (2000)
79. N K Shobha, M Somkarapandion, T E Glass, J E McGrath *Polym. Prepr.* **41** (2) 1298 (2001)
80. S Faure, R Mercier, M Pineri, B Sillion, in *The 4th European Technical Symposium on Polyimides and Other High Performance Polymers* (France: Montpellier, 1996) p. 414
81. C Genies, R Mercier, B Sillion, R Petioud, N Cornet, G Gebel, M Pineri *Polymer* **42** 5097 (2001)
82. N Gunduz, J E McGrath *Polym. Prepr.* **41** (2) 1565 (2000)

83. C Genies, R Mercier, B Sillion, N Cornet, G Gebel, M Pineri *Polymer* **42** 359 (2001)
84. Y Zhang, M Litt, R F Savinell, J S Wainright, J Vendramun *Polym. Prepr.* **41** (2) 1561 (2000)
85. G I Timofeeva, I I Ponomarev, A R Khokhlov, R Mercier, B Sillion *Macromol. Symp.* **106** 345 (1996)
86. I I Ponomarev, O G Nikol'skii, Yu A Volkova, A V Zakharov *Vysokomol. Soedin., Ser. A* **36** 1185 (1994) [a]
87. A L Rusanov *Usp. Khim.* **61** 815 (1992) [*Russ. Chem. Rev.* **61** 449 (1992)]
88. A L Rusanov *Adv. Polym. Sci.* **111** 116 (1994)
89. A L Rusanov, L B Elshina, E G Bulycheva, K Myullen *Vysokomol. Soedin., Ser. A* **41** 2 (1999) [a]
90. V A Solomin, E N Lakh, B A Zhubanov *Vysokomol. Soedinen., Ser. A* **34** 274 (1992) [a]
91. M B Gieselman, J R Reynolds *Macromolecules* **23** 3188 (1990)
92. M Tarayanagi *Pure Appl. Chem.* **55** 819 (1983)
93. US P. 4 814 399; *Chem. Abstr.* **111** 1 956 601 (1989)
94. T D Domg, F E Arnold *Polym. Prepr.* **33** 912 (1992)
95. M B Gieselman, J R Reynolds *Macromolecules* **25** 4832 (1992)
96. M B Gieselman, J R Reynolds *Macromolecules* **26** 5633 (1993)
97. X Glipa, M E Haddad, D J Jones, J Roziere *Solid State Ion.* **97** 323 (1997)
98. K Tsuruhara, K Hara, M Kawahara, M Rikukawa, K Sanui, N Ogata *Electrochim. Acta* **45** 1223 (2000)
99. M Kawahara, M Rikukawa, K Sanui *Polym. Adv. Technol.* **11** 544 (2000)
100. M Kawahara, M Rikukawa, K Sanui, N Ogata, in *Proceedings of the 6th International Symposium on Polymer Electrolytes (Extended Abstracts), Hayawa, 1998* p. 98
101. H Yoshida, T Hatakeyama, H Hatakeyama *Polymer* **31** 693 (1990)
102. M Folk *Can. J. Chem.* **58** 1495 (1980)
103. J-T Wang, S Wasmus, R F Savinell *J. Electrochem. Soc.* **143** 1233 (1996)
104. S R Samms, S Wasmus, R F Savinell *J. Electrochem. Soc.* **143** 1225 (1996)
105. R F Savinell, E Yeager, D Tryk, U Landau, J S Wainright, D Weng, K Lux, M Litt, C Rogers *J. Electrochem. Soc.* **141** L46 (1994)
106. J S Wainright, J-T Wang, D Weng, R F Savinell, M Litt *J. Electrochem. Soc.* **142** L121 (1995)
107. M Kawahara, J Morita, M Rikukawa, K Sanui, N Ogata *Electrochim. Acta* **45** 1395 (2000)
108. M Kawahara, M Rikukawa, K Sanui, N Ogata *Solid State Ion.* **136** 1193 (2000)
109. J Kerres, A Ullrich, F Meier, T Haring *Solid State Ion.* **125** 243 (1999)
110. E D Powers, G A Serad, in *High Performance Polymers: Origin and Development* (New York: Elsevier, 1986) p. 355
111. J R Stevens, W Wieczorek, D Raducha, K R Jeffrey *Solid State Ion.* **97** 347 (1997)
112. W Wieczorek, J R Stevens *Polymer* **38** 2057 (1997)
113. R Tanaka, H Yamamoto, S Kawamura, T Iwase *Electrochim. Acta* **40** 2421 (1995)
114. M F Daniel, B Destbat, F Cruege, O Trinquet, J C Lassegues *Solid State Ion.* **28–30** 637 (1988)
115. N Agmon *Chem. Phys. Lett.* **244** 456 (1995)

[a] — *Polym. Sci. (Engl. Transl.)*
[b] — *Russ. J. Electrochem. (Engl. Transl.)*