Adv Polym Sci (2005) 179: 83–134
DOI 10.1007/b104480

Proton-Exchanging Electrolyte Membranes Based on Aromatic Condensation Polymers

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Abstract The results of the research and development of novel proton-exchanging membranes based on aromatic condensation polymers have been analysed and summarized with respect to their application in fuel cells. Primary attention has been paid to the basic properties of the starting polymers, such as thermal stability, water uptake and proton conductivity. General approaches to the preparation of aromatic condensation polymers with high proton conductivity have been considered, including direct suffocation, synthesis from monomers containing sulfonic acid groups, incorporation of alkylsulfonated substituents and formation of acid-basic polymer complexes. The bibliography includes 200 references.

Keywords Proton exchanging membranes · Fuel cells · Condensation polymers · Polyelectrolytes

Abbreviations

^{13}C-NMR	Carbon-13 nuclear magnetic resonance
^{1}H-NMR	Proton nuclear magnetic resonance
ACPs	Aromatic condensation polymers
DMAA	N,N-Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DNTA	Naphthalene-1,4,5,8-tetracarboxylic acid dianhydride
DSC	Differential scanning calorimetry
FT-IR	Fourier transform infrared spectroscopy
IR	Infrared spectroscopy
m-disulfo PBT	Poly[(benzo[1,2-*d*:4,5-*d′*]bisthiazole-2,6-diyl)-4,6-disulfo-1,3-phenylene]
m-sulfo PBT	Poly[(benzo[1,2-*d*:4,5-*d′*]bisthiazole-2,6-diyl)-5-sulfo-1,3-phenylene]
N-MP	N-Methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
PBI-MPS	(Methyl)propylsulfonated poly(benzimidazole)
PBI-PS	Propylsulfonated poly(benzimidazole)
PBP	Poly(4-benzoyl)-1,4-phenylene
PBTs	Poly(benzobisthiazoles)
PEEK	Poly(ether ether ketones)
PEMFS	Proton-exchanging membrane fuel cells
PES	Poly(ether sulfone)
PMFC	Polymer membrane fuel cell
PPA	Polyphosphoric acid
PPBP	Poly(4-phenoxybenzoyl-1,4-phenylene)
PPTA	Poly(*p*-phenylene terephthalamide)
PSPPI	Phenoxy substituted polyperyleneimide
PSSA	Poly(styrenesulfonic acid)
p-sulfo PBT	Poly[(benzo[1,2-*d*:4,5-*d′*]bisthiazole-2,6-diyl)-2-sulfo-1,4-phenylene]
S-PBI	Arylsulfonated poly(benzimidazole)
S-PEEK	Sulfonated poly(ether ether ketone)
S-PEES	Sulfonated poly(ether ether sulfone)
SPEFC	Solid polymer electrolytes fuel cells
S-PPBP	Sulfonated poly(4-phenoxybenzoyl-1,4-phenylene)
S-PPO	Sulfonated poly(phenylene oxide)
S-PPQ	Sulfonated polyphenylquinoxaline
S-PPS	Sulfonated poly(phenylene sulfide)
S-PPX	Sulfonated poly(p-xylylene)
TGA	Thermogravimetric analysis

1
Introduction

Proton-exchanging membrane fuel cells (PEMFC) are considered to be one of the most promising types of electrochemical device for power generation [1–10]. Low operation temperatures and the wide range of power make them attractive for portable, automotive, and stationary applications. However, advances made in these markets require further cost reduction and improved reliability. These can be achieved through development and implementation of novel proton-exchange membranes with higher performance and lower cost as compared to the state of the art polymeric electrolytes.

The basic design of a mono PEMFC cell is shown schematically in Fig. 1. The polyelectrolyte membrane is sandwiched between two noncorrosive porous electrodes. The electrochemical reactions occurring at the electrodes are the following:

$$\begin{array}{ll} \text{on the anode:} & H_2 \rightarrow 2H^+ + 2e^- \,; \\ \text{on the cathode:} & 0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O \,; \\ \text{net reaction:} & H_2 + 0.5O_2 \rightarrow H_2O + Q_1 + Q_2 \,, \end{array}$$

where Q_1 is the electrical energy and Q_2 is the heat energy. Individual membrane electrode assemblies can be arranged into stacks to give the power range desired.

The proton-exchanging membrane is the most important component of the PEMFC. It must possess some specific properties [9], such as:

- a high ion-exchange capacity sufficient to provide a conductivity of the magnitude of $0.1\ \mathrm{S\,cm^{-1}}$ at operational temperatures;

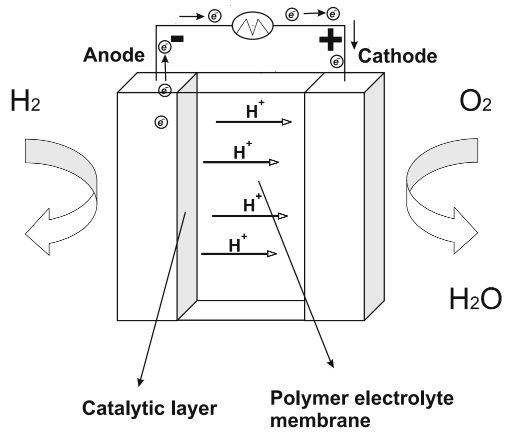


Fig. 1 A scheme of a PEMFC

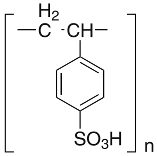


Fig. 2

- low permeability to the fuel (hydrogen or methanol) and oxidant (oxygen) to prevent crossover of the membrane;
- substantial water uptake and good swelling to provide efficient dissociation of acids and to form a hydrated ionic phase within the entire volume of the membrane;
- sufficient chemical and mechanical stability for long-term operation under severe conditions (over 5000 h for electric vehicle applications).

The polymer membrane made of poly(styrenesulfonic acid) (PSSA) (Fig. 2) was used in the first PEMFC power plant built by General Electric in the mid-sixties for the Gemini space mission. The lifetime of these PMFCs was limited due to the degradation of the PSSA membrane under the impact of hydrogen peroxide radicals.

Further development and implementation of perfluorinated polymers [11–16] led to considerable advances in polymer electrolytes. The most widely-used fluorinated polymers are prepared by copolymerisation of tetrafluoroethylene with perfluorinated vinyl ethers of the following type

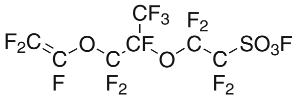
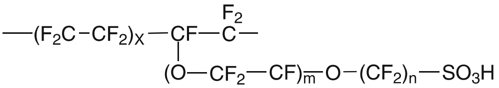


Fig. 3

accompanied by hydrolysis of fluorosulfonic acid groups. Basic perfluorinated chains of such polymers determine high chemical and thermal stability, while side chains possess the properties of strong acids. Perfluorinated electrolyte membranes with the general formula shown below are also widely used.



$$-(F_2C-CF_2)_x-\underset{\displaystyle (O-CF_2-CF)_{m}-O-(CF_2)_n-SO_3H}{CF}-\overset{F_2}{C}-$$

Fig. 4

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

The improved PMFC for the Gemini spacecraft 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 a lifetime 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).

Perfluorinated membranes (Dow membrane) were developed by Dow Chemical Co. (USA). Their equivalent masses are equal to 800–850 g, while dry state thickness is of $\sim 5\ \mu m$. Flemion membranes with equivalent masses of ~ 1000 were developed by Asahi Glass Co. (Japan) [5]. Aciplex-S membranes were developed by Asahi Chemical Industry (Japan) and possess equivalent masses of 1000–1200 g.

All the membranes mentioned above, as well as Neosepta-F (Tokuyama, Japan) and Gore-Select (W L Gore and Associates Inc., USA) membranes possess a high proton conductivity (10^{-2}–10^{-1} S cm^{-1}) at water uptake 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 the 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 solving 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 [17–30].

ACPs have some advantages that make them particularly attractive:

- ACPs are cheaper than perfluorinated polymers and some of them are commercially available;
- ACPs containing polar groups have high water uptake 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, 31–33]. They contain information on the advanced materials, their electrochemical properties, water uptake and thermal stabilities. However, rapid accumulation of newly-obtained results gives an impetus to further generalisation of information in this field.

During the last decade, research on PEMFCs has been most intensively carried out in the following directions:

- development of sulfonated aromatic condensation polymers (ACPs) and membranes on their basis;
- development of alkylsulfonated ACPs and membranes on their basis;
- development of acid-basic polymer complexes and membranes on their basis.

2
Sulfonated Aromatic Condensation Polymers and Membranes On Their Basis

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

2.1
Sulfonation of High Molecular Mass Aromatic Condensation Polymers

The simplest and the most widely-used method for the synthesis of sulfonated ACPs involves sulfonation of different classes of polymers, such as substituted poly-(1,4-phenylenes) [34, 35], poly-(p-xylylene [36, 37]), poly-(1,4-oxyphenylenes) [38–44], poly(ether ether ketones) (PEEK) [46–59], polyarylene(ether sulfones) [3, 60–74], poly(phenylene sulfides) [75], polyphenylquinoxalines [76–79], polybenzimidazoles [80], polyperyleneimides [81] 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) sulfonated polyphenylquinoxaline (S-PPQ) (8) and sulfonated phenoxy polyperyleneimide (PSPPI) (9) are shown below. ACPs are sulfonated using common sulfonating agents [82–85]. In particular, PEEK can be sulfonated in concentrated sulfuric acid [50], chlorosulfonic acid [86], SO_3 (either pure or as a mixture) [53, 65, 86, 87], a mixture of methanesulfonic acid with concentrated sulfuric acid [88] and acetyl sulfate [89, 90].

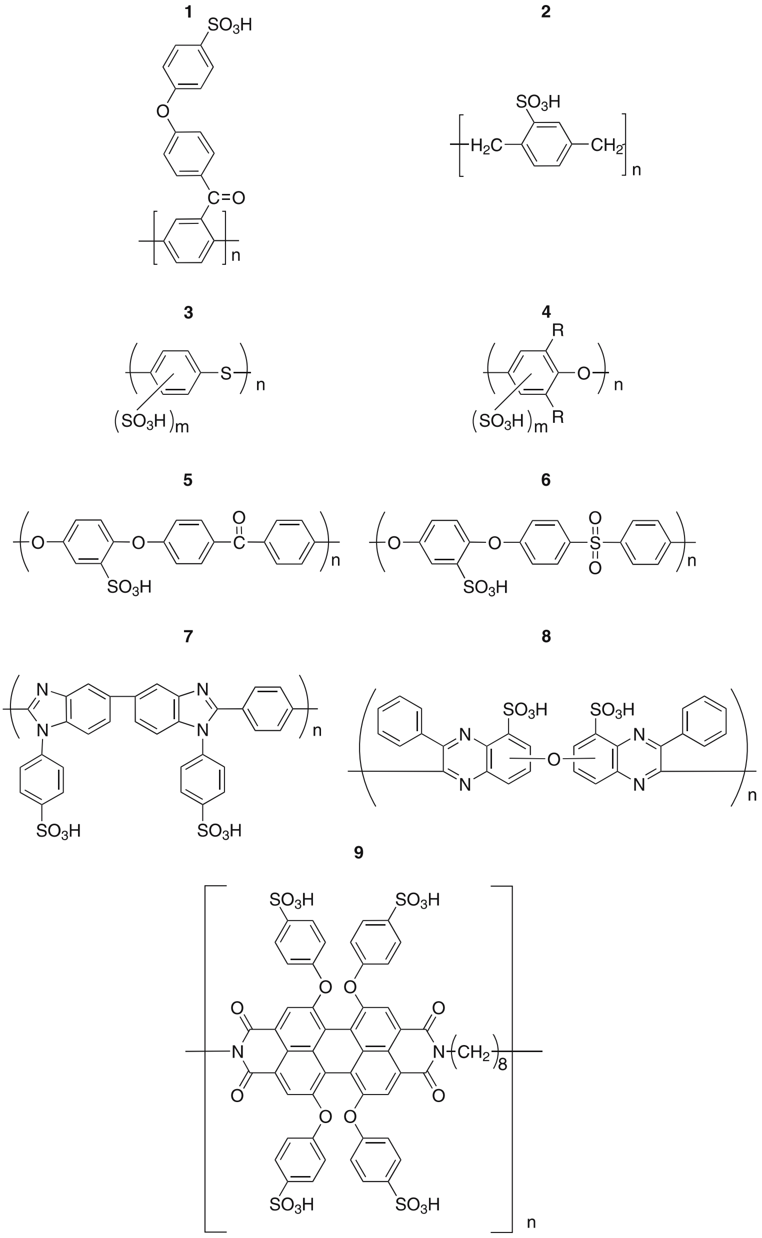


Fig. 5

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 [91]. This technique allows preparation of target ACPs with sulfonation degrees ranging from 30% to 100% without chemical degradation or crosslinking of the polymer [92]. However, it should be noted that a direct sulfonation reaction cannot be used for preparation of random sulfonated copolymers and a sulfonation level of less than 30%, since sulfonation in sulfuric acid occurs under heterogeneous conditions due to high viscosity of the reaction solutions [49, 50]. For this reason, preparation of random copolymers requires the duration of the dissolution process to

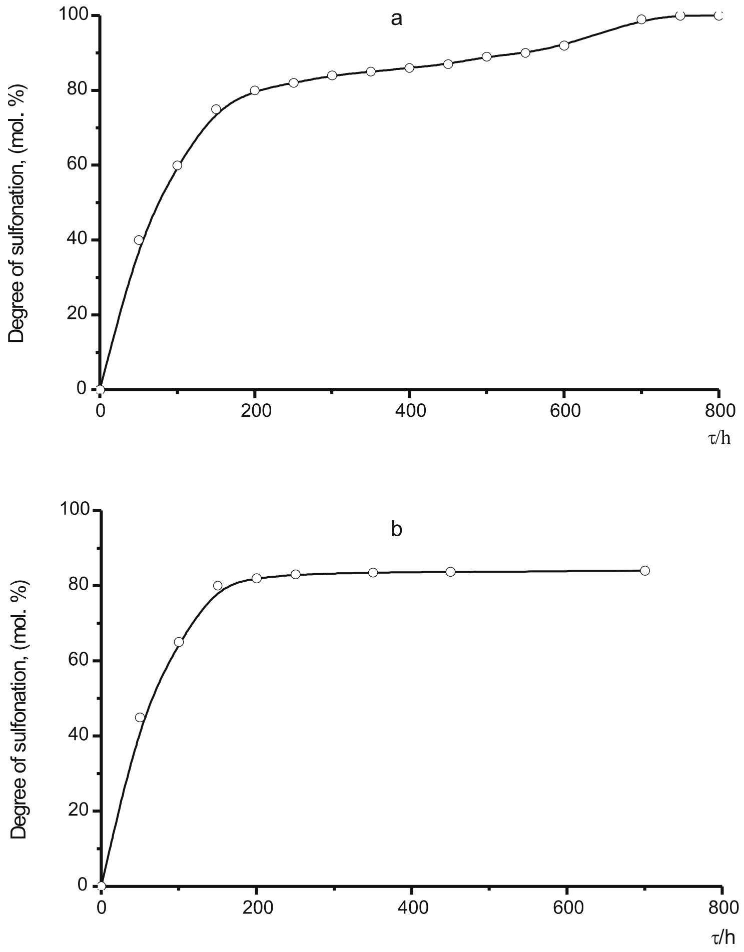


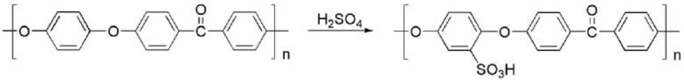
Fig. 6 Degree of sulfonation of PEEK (**a**) and PPBP (**b**) as a function of reaction time at room temperature [7, 35]

be shortened to 1 h. The dependences of the degree of sulfonation of PEEK and PPBP [35] on the reaction time at room temperature are shown in Fig. 6.

Sulfonation belongs to electrophilic substitution reactions, therefore, it strongly depends on the nature of substituents in the aromatic ring. Namely, electron-donating substituents favour the reaction whereas electron-withdrawing substituents slow it down significantly. For instance, in the case of PPBP, terminal phenyl rings in the side chain can be sulfonated under mild conditions similar to the sulfonation conditions for PEEK. In contrast to this, the phenyl ring substituent in poly(4-benzoyl)-1,4-phenylene (PBP), which contains an electron-withdrawing carbonyl group, cannot be sulfonated under these conditions [7]. The sulfonation level of PPBP and PEEK reaches nearly 80% within 100 h. The highest sulfonation degree for PPBP is 85%, whereas that of PEEK can be as high as 100%. This phenomenon can be attributed to steric hindrances to further sulfonation of PPBP in a viscous sulfuric acid solution.

The solubility of polymers changes while the degree of sulfonation increases. For instance, S-PEEK containing 30 mol% sulfonic acid groups dissolves 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 the sulfonation levels above 65%, S-PPBP swells in methanol and water.

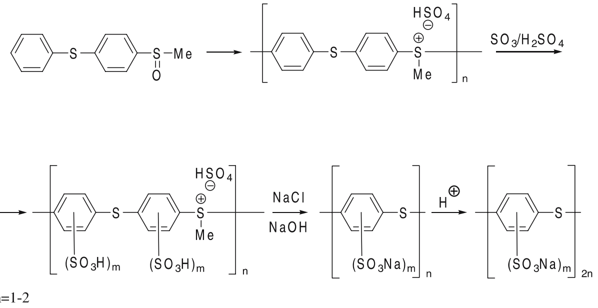
Sulfonation of PEEK in concentrated sulfuric acid at room temperature is accompanied by incorporation of not more than one sulfonic acid group into each repeating unit of the polymer [86, 90, 93, 94]. FT-IR spectroscopy studies show that PEEK is sulfonated at the phenylene ring between the ether groups.



Scheme 1

Sulfonation of PPBP occurs at the *p*-position of the terminal phenoxy group.

Tsuchida et al. [95, 96] reported the synthesis of poly(thiophenylene sulfonic 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 sulfonated poly(sulfonium cation), which was then converted into the corresponding sulfonated poly(phenylene sulfide).

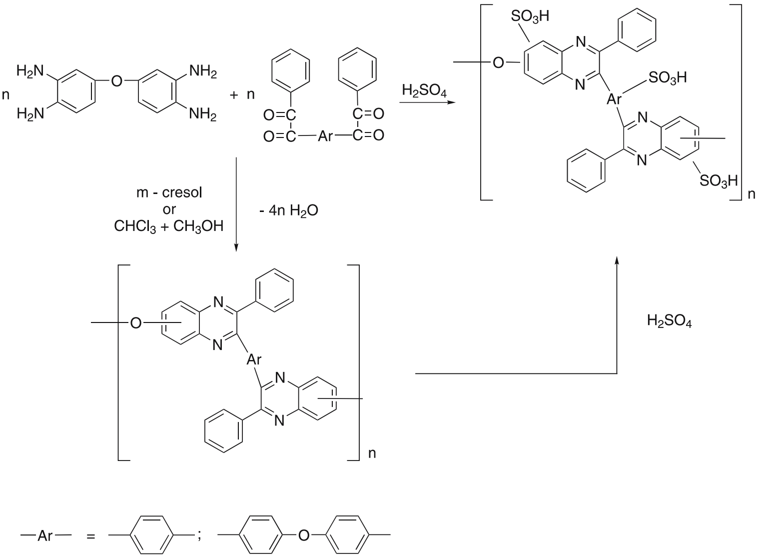


Scheme 2

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

Novel polymer electrolytes exhibiting high proton conductivity (higher than $10^{-2}\,S\,cm^{-1}$) were prepared by sulfonation of poly(ether sulfone) (PES) [97, 98]. 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.

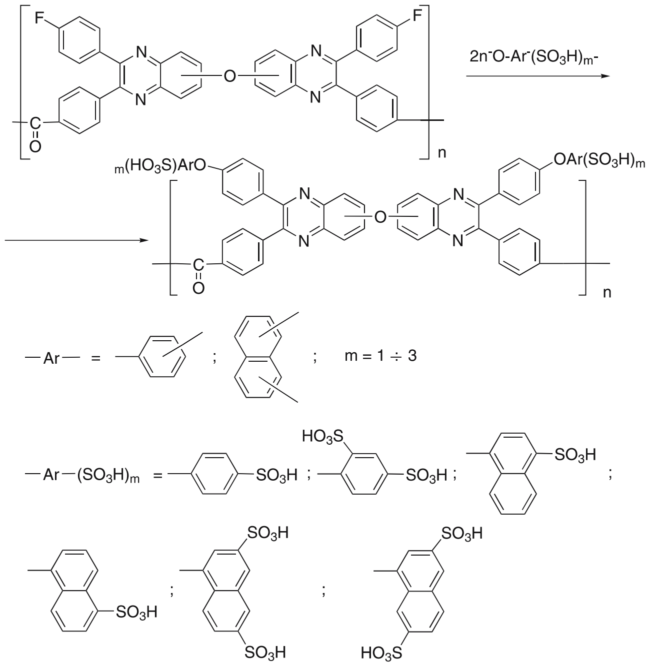
Sulfonated polyphenylquinoxalines were prepared using two approaches: sulfonation of polyphenylquinoxalines prepared by the conventional technique [76–79, 99], or synthesis of polyphenylquinoxalines directly in the sulfonating medium [76–79, 99]:



Scheme 3

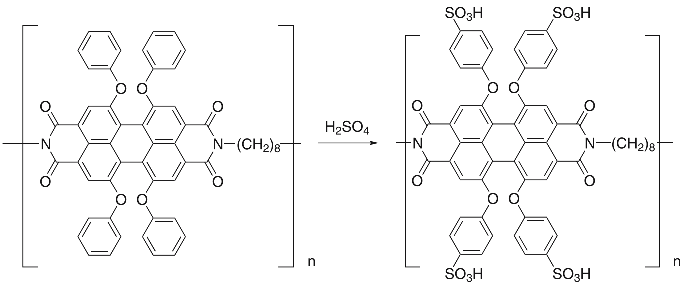
In both cases, sulfonation was performed in sulfuric acid: oleum mixture (4 : 1) at 125 °C. High-strength thermally stable films showing high hydrolytic stability were cast from the solution of sulfonated polyphenylquinoxalines in DMF.

Another approach to the preparation of sulfonated polyphenylquinoxalines is based on the treatment of polyphenylquinoxalines containing activated fluorine atoms [100, 101] with hydroxyarylsulfonic acids [99, 102]:



Scheme 4

Sulfonated polyperyleneimide was obtained by sulfonation of the corresponding polyimide in concentrated H_2SO_4 at room temperature [81].



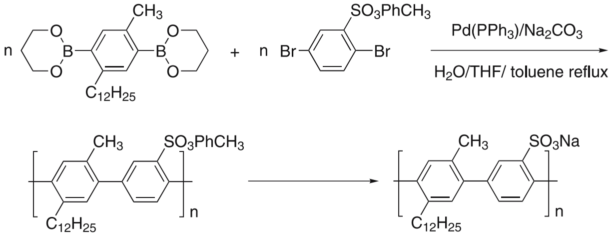
Scheme 5

No evidence for side reactions, e.g. three-fold sulfonation or cleavage of phenoxy substituents was detected by ^{1}H-NMR spectroscopy.

The organic solvent solubility of the starting polyimide can be modified by sulfonation to give water-soluble polyimide possessing film-forming properties.

2.2
Synthesis of Aromatic Condensation Polymers Based On Sulfonated Monomers

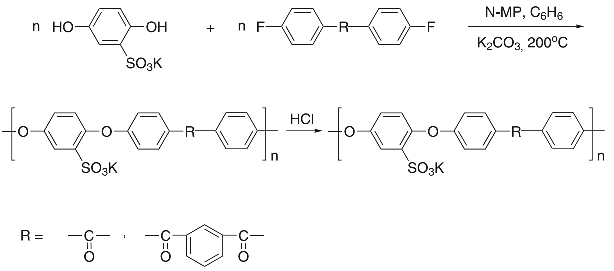
Sulfonated ACPs are prepared both by direct sulfonation and by polycondensation and polycyclocondensation of sulfonated compounds. Synthesis of the first sulfonated poly(*p*-phenylene) was reported by Wegner and co-workers [103]. The Suzuki coupling of diboronic ethers with dibromoaromatic monomers furnished poly(*p*-phenylene) with 95% yield.



Scheme 6

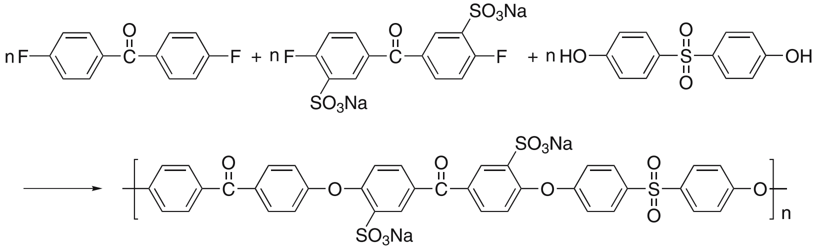
Absolute molecular weight of 36 kD was determined by membrane osmometry in toluene. Surprisingly, the final polymer was not soluble in a basic aqueous solution, but it was soluble in DMSO. In a subsequent report from the same research group [104, 105] this synthetic approach was extended to produce other isomeric structures.

Sulfonated PEEKs were prepared by the reactions of sulfonated hydroquinone with difluoro-substituted aromatic compounds containing carbonyl groups [106, 107]:



Scheme 7

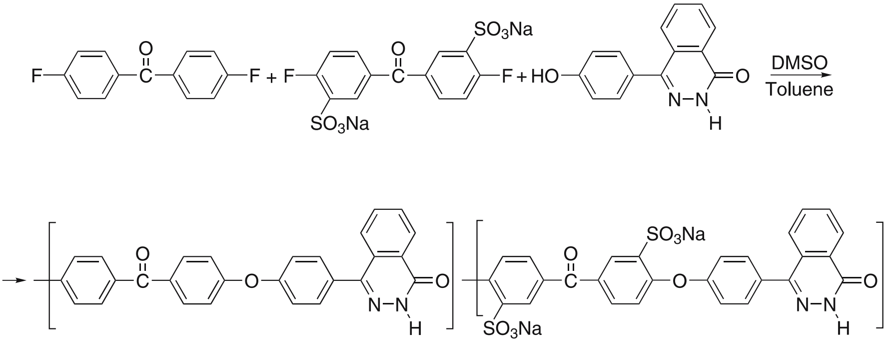
Novel sulfonated PEKs were prepared directly by nucleophilic polycondensation of 4,4′-sulfonyldiphenol with various ratios of 4,4′-difluorobenzophenone to 5,5′-carbonyl-bis-(2-fluorobenzenesulfonate) in DMSO [108].



Scheme 8

The resulting polyelectrolytes have been characterised by IR, NMR, TGA and DSC. The 10% weight loss temperature is higher than 510 °C, which indicates that the introduction of 4,4′-sulfonyldiphenol with the powerful electron-withdrawing group – SO_2 – into the main chain of sulfonated PEK improves the thermal stability against desulfonation.

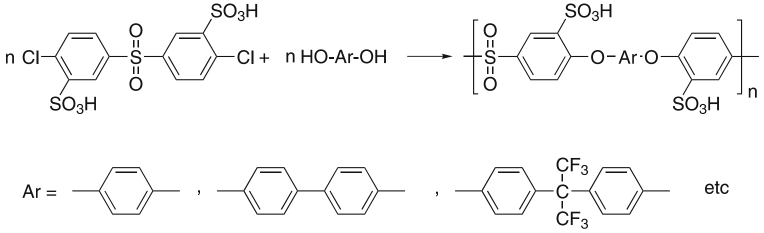
Sulfonated poly(phthalazinone ether ketones) were synthesized directly by aromatic nucleophilic polycondensation of 4-(4-hydroxyphenyl)phthalazinone with various ratios of 5,5′-carbonylbis-(2-fluorobenzenesulfonate) or 4,4′-difluorobenzophenone [109].



Scheme 9

The 10% weight loss temperature of the product is higher than 500 °C.

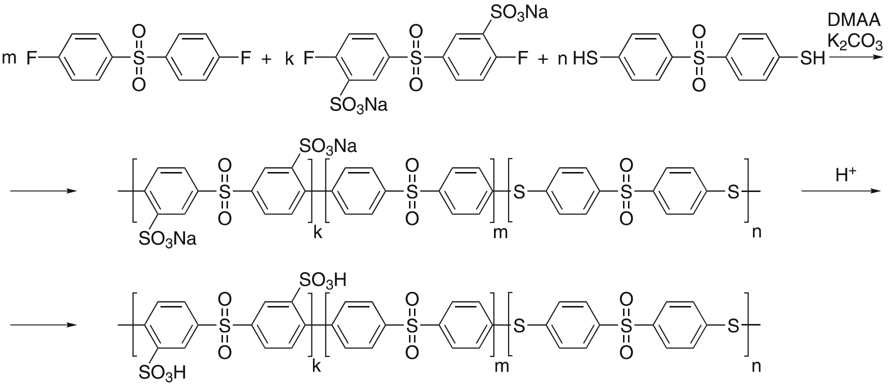
An analogous procedure was employed in recent studies [110–114] on the synthesis of poly(arylene ether sulfones) using reactions of sulfonated 4,4-dichlorodiphenyl sulfone with various bisphenols.



Scheme 10

The use of *m*-aminophenol as an additive along with bis-phenols allowed the preparation of poly(arylene ether sulfones) with terminal amino groups [115].

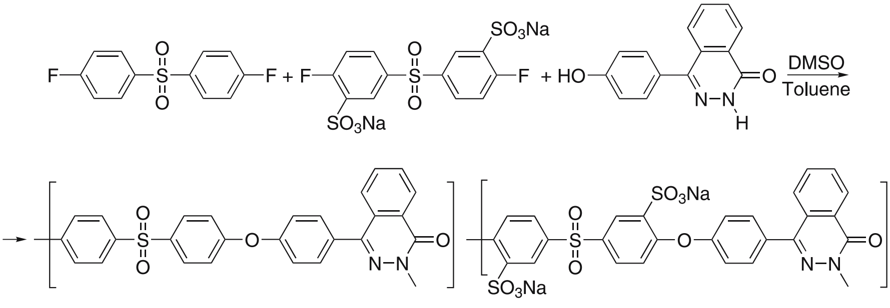
Sulfonated poly(thiophenylene sulfones) were prepared by the interaction of sulfonated 4,4′-difluorodiphenyl sulfone with 4,4′-dimercaptobenzophenone [116]. Not only homopolymers, but also copolymers were obtained. In the latter case, the fraction of sulfonated 4,4′-difluorodiphenyl sulfone was replaced with nonsulfonated monomers.



Scheme 11

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

Sulfonated poly(phthalazinone ether sulfones) were directly prepared by polycondensation of 4-(4-hydroxyphenyl)phthalazinone with various rations of disodium salt of 5,5′-sulfonylbis-(2-fluorobenzenesulfonate) to 4-fluorophenylsulfone [117].



Scheme 12

The resulting ionomers demonstrated high molecular weight, high ion-exchange capacity and low swelling. Low swelling originates from the hydrogen bonding between hydrogen atoms of sulfonic acid and carbonyl groups, which has been validated by variable temperature IR spectra.

High molecular weight water soluble sulfonated polyamides were prepared by the interaction of sulfonated diamines with terephthalic and isophthalic acid dichlorides [118–122].

For this purpose the following diamines were used:

1. 4,4′-diaminobiphenyl-2,2′-disulfonic acid (10)
2. 4,4′-diaminostilbene-2,2′-disulfonic acid (11)
3. para or metadiaminobenzene sulfonic acid (12)
4. 2,5-diaminobenzene-1,4-disulfonic acid (13)

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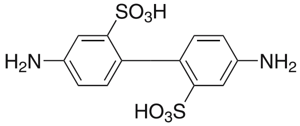

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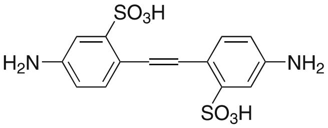

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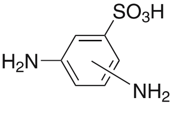

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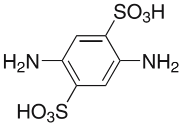
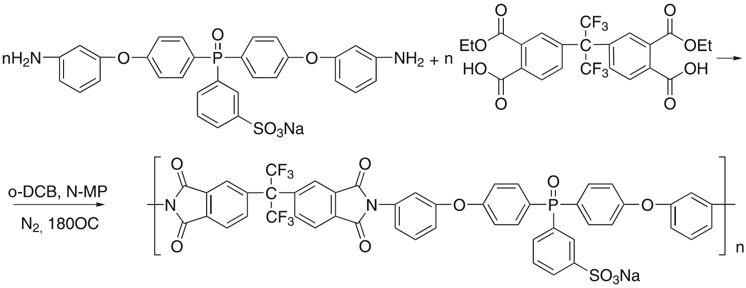


Fig. 7

Some polymers had a sufficiently high molecular weight (more than 200 000), extremely high intrinsic viscosity (~ 65 dl/g), and appeared to transform into a helical coil in saline solution.

Sulfonated monomers were also used for the synthesis of sulfonated polyimides [123, 124]. In particular, sodium salt of the sulfonated bis-4-[(3-aminophenoxy)phenyl]phenylphosphine oxide was used for the preparation of sulfonated polyimides [123].



Scheme 13

Of particular interest is the use of 4,4′-diamino-2,2′-diphenylsulfonic acid [124–126] produced on a semi-industrial scale as a sulfonated monomer for preparation of polyimides. The reactions of a mixture of this monomer and 4,4′-diaminodiphenylmethane and 4,4′-diaminodiphenyloxide with diphenyloxide-3,3′,4,4′-tetracarboxylic acid dianhydride resulted in sulfonated polyimides [124] with the following structure:

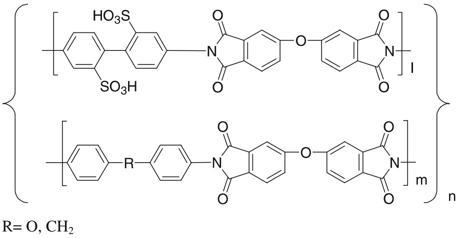


Fig. 8

Great attention has been paid to the polynaphthalenecarboximides (polynaphthylimides) containing sulfonic acid groups [126]. Such polymers are usually prepared by the reaction of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (DNTA) with 4,4′-diamino-2,2′-diphenylsulfonic acid

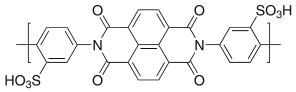
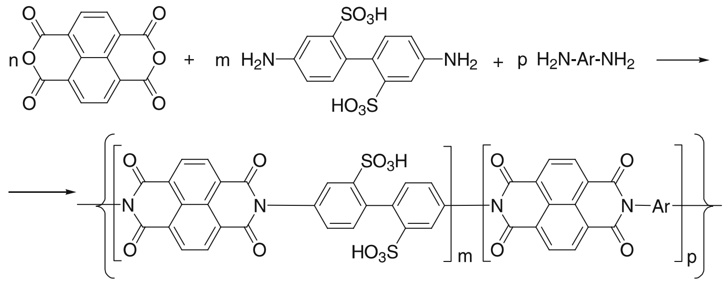


Fig. 9

or a mixture of this sulfonated monomer with other aromatic diamines.



n=m+p

Scheme 14

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

Other diamines were used for a similar purpose and these were the following:

1. 4,4′-diaminodiphenylamino-2-sulfonic acid (14) [138];
2. sulfonated bis-(3-aminophenyl)phenyl phosphine oxide (15) [136];
3. 3,3-disulfonate-bis[4-(3-aminophenoxy)phenyl]sulfone (16) [137];
4. 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid (17) [139–142];
5. 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (18) [142, 143];
6. 4,4′-bis-(4-aminophenoxy)biphenyl-3,3′-disulfonic acid (19) [142, 143].

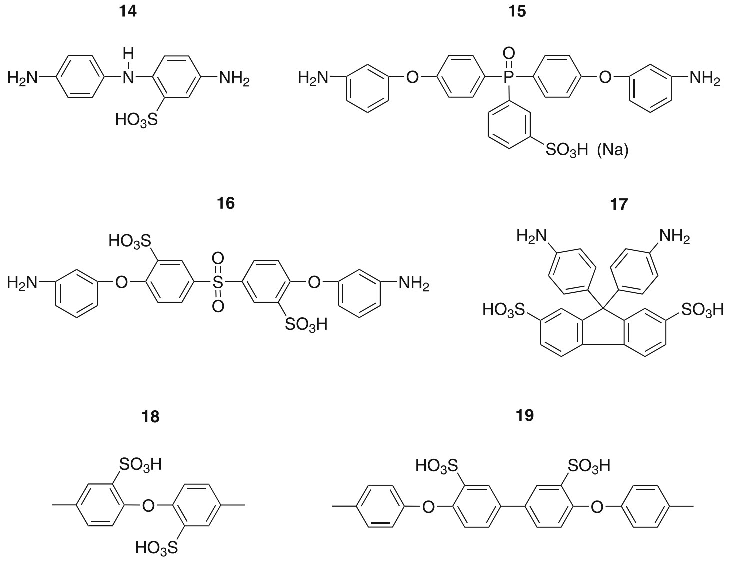
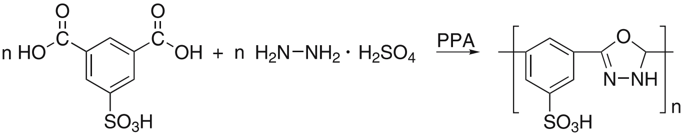


Fig. 10

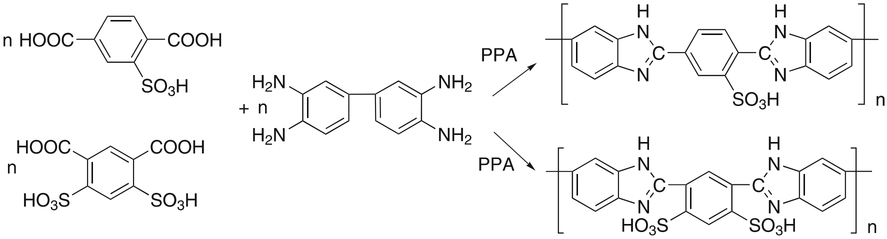
In general, poly(naphthylimides) containing six-membered imide rings in backbones are characterised by significantly improved chemical resistance compared to analogous poly(phthalimides) [144–147]. A similar conclusion was made comparing the chemical resistance of sulfonated polyimides and poly(naphthylimides) [124, 125].

Several attempts have been made to develop sulfonated polyazoles [148, 149] and polybenzazoles [150–160]. Sulfonated poly-1,3,4-oxadiazoles have been prepared by the interaction of 5-sulfoisophthalic acid with hydrazine sulfate in polyphosphoric acid (PPA) [148, 149]



Scheme 15

Sulfonated polybenzimidazoles have been prepared by polycondensation of sulfoterephthalic acid and disulfoisophthalic acid with 3,3′-diaminobenzidine using high temperature solution polycondensation in PPA [150–153].

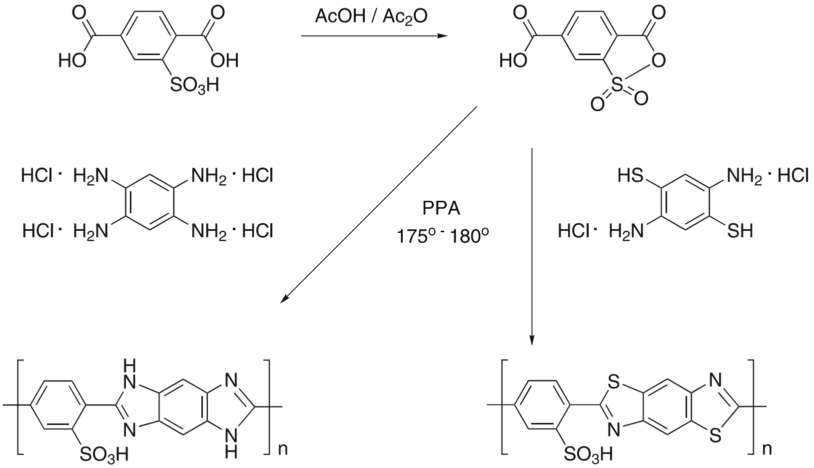


Scheme 16

The polymers obtained were soluble in sulfuric acid, some organic solvents, and aqueous strong alkaline solutions. The polymers were stable up to 400 °C, but they yielded polybenzimidazoles by eliminating sulfonic acid groups, instead of ring closure.

Sulfonated polybenzobisimidazoles were prepared by the interaction of 1,2,4,5-tetraaminobenzene tetrahydrochloride with sulfoterephthalic acid [154, 155] and 5-sulfoisophthalic acid [156] using high temperature solution polycondensation in PPA.

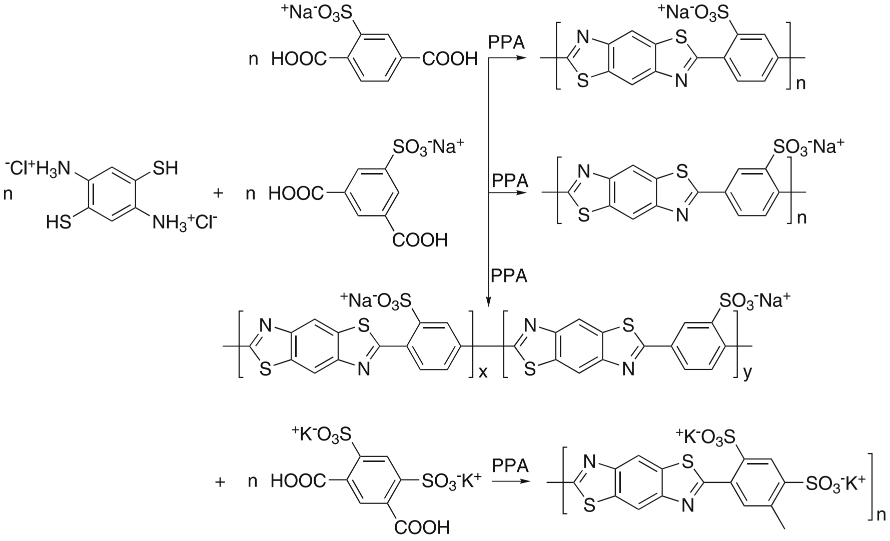
Alternatively polybenzobisimidazoles were prepared by the interaction of 1,2,4,5-tetraaminobenzene tetrahydrochloride with 4-carboxy-2-sulfobenzoic anhydride [157]:



Scheme 17

The same synthetic approach was used for the preparation of sulfonated polybenzobisthiazoles [157] (Scheme 17).

Aromatic polyelectrolytes based on sulfonated poly(benzobisthiazoles) (PBTs) have been synthesized also by polycondensation of sulfo-containing aromatic dicarboxylic acids with 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) in freshly prepared PPA [158].

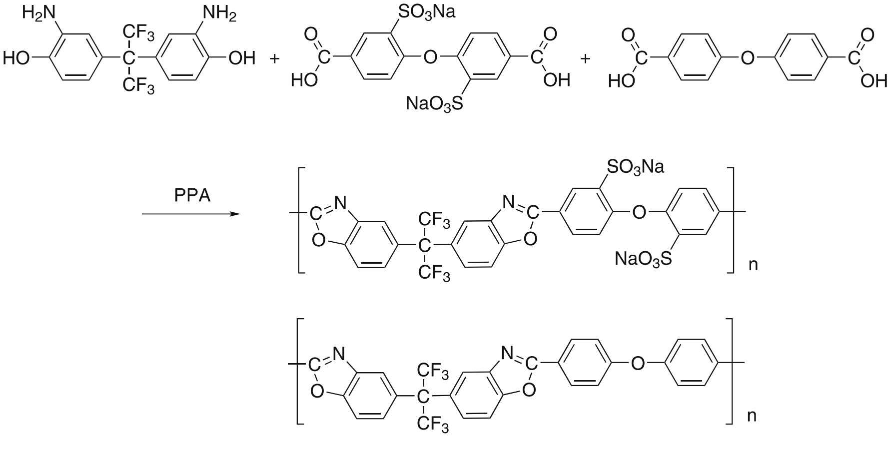


Scheme 18

Several sulfonated PBTs, poly[(benzo[1,2-*d*:4,5-*d*′]bisthiazole-2,6-diyl)-2-sulfo-1,4-phenylene] sodium salt (p-sulfo PBT), poly[(benzo[1,2-*d*:4,5-*d*′]-bisthiazole-2,6-diyl)-5-sulfo-1,3-phenylene] sodium salt (m-sulfo PBT), their copolymers, and poly[(benzo[1,2-*d*:4,5-*d*′]bisthiazole-2,6-diyl)-4,6-disulfo-1,3-phenylene] potassium salt (m-disulfo PBT), have been targeted and the polymers obtained characterised by ^{13}C-NMR, FT-IR, elemental analysis, thermal analysis and solution viscosity measurements. Structural analysis confirms the structure of p-sulfo PBT and m-disulfo PBT, but suggests that the sulfonate is cleaved from the chain during synthesis of m-disulfo PBT. The polymer m-disulfo PBT dissolves in water as well as strong acids, while p-sulfo PBT dissolves well in strong acids, certain solvent mixtures containing strong acids, and hot DMSO. TGA indicates that these sulfonated PBTs are thermally stable up to over 500 °C. Free-standing films of p-sulfo PBT, cast from dilute neutral DMSO solutions, are transparent, tough, and orange in colour. Films cast from basic DMSO are also free standing, while being opaque yellow-green.

Sulfonated polybenzoxazoles were prepared from 5-sulfoisophthalic or 2-sulfoterephthalic acids and different bis-(o-aminophenols) [159].

Disulfonated polybenzoxazoles were prepared by the interaction of 2,2′-bis-(3-amino-4-hydroxy-phenyl)hexafluoropropane with disodium-2,2′-disulfonate-4,4′-oxydibenzoic acid and 4,4′-oxydibenzoic acid using PPA as the polymerisation media [160].



Scheme 19

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 electrochemical devices on their basis operating in a temperature range of 100–200 °C require polymer electrolyte membranes characterised by fast proton transfer. The operation of PEMFCs at elevated temperature has a number of advantages. It causes an increase in the rates of fuel cell reactions and reduces catalyst poisoning with absorbed carbon monoxide, thus reducing the demand for catalysts.

Thermal stability of polymer membranes based on S-PPBP has been studied [7, 35] by sample heating followed by elemental analysis (thermogravimetric analysis, or TGA, at a heating rate of 10 °C min^{-1} under nitrogen) (Fig. 11).

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.

The dependence of the degradation temperature, (T_d), of S-PPBP and S-PEEK on the degree of sulfonation is presented in Fig. 12.

Degradation of sulfonated polymers was observed between 250 °C and 350 °C, i.e., at temperatures that are much lower then those for 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 residues indicate a dramatic (nearly ten-fold) decrease in sulfur content of the polymers after heating at temperature above 400 °C. These data confirm that thermal stabilities of polymers are sufficient for fuel cell application even at high sulfonation levels [7, 35].

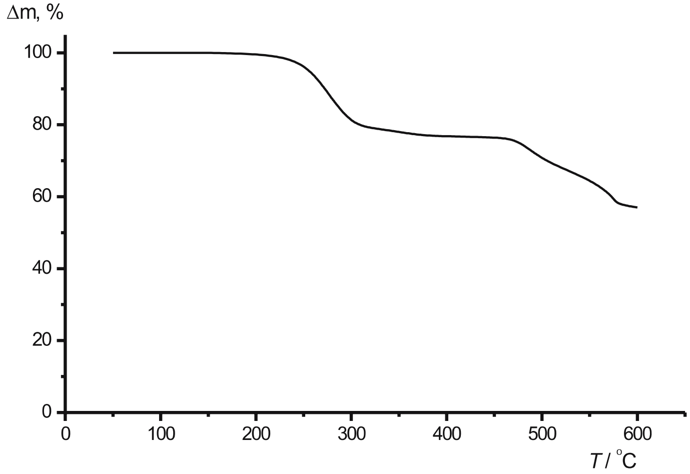


Fig. 11 TGA curve of S-PPBP with 80 mol% sulfonation level [7, 35]

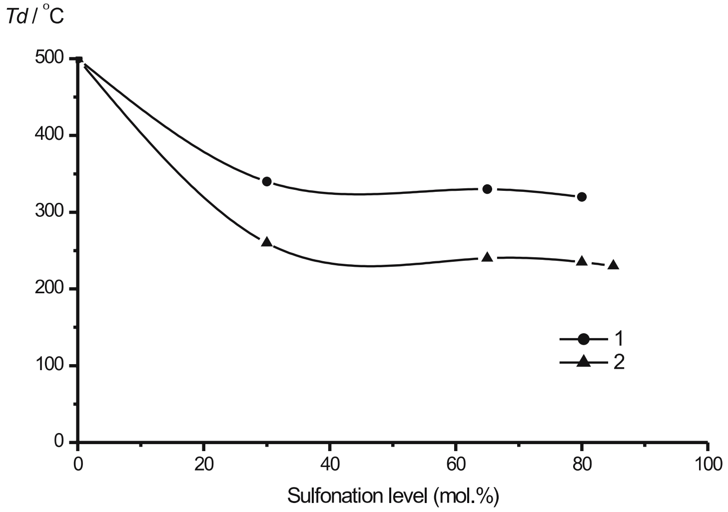


Fig. 12 Degradation temperature of S-PEEK (1) and S-PPBP(2) as a function of sulfonation level [7, 35]

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

According to Tsuchida et al. [96], 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 thermal stability of poly(thiophenylenesulfonic acid) with different degrees of sulfonation. The degradation temperature of 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 highly sulfonated polymer is stronger due to the presence of two electron-withdrawing sulfonic acid substituents in each benzene ring. The initial mass loss of this polymer at 265–380 °C is only 13%, which correspond to the loss of two H_2O molecules per repeating unit. Therefore, the desulfonation reaction in this polymer slows down upon introduction of the electron-acceptor.

Water is carried into the fuel cell with humidified gas (H_2, O_2) steams 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 electrolyte membranes. Oxygen reduction at the cathode provides an additional source of water.

Water transport through the membrane occurs due to electro-osmotic drag of water by proton transfer from anode to cathode and due to diffusion of water molecules across concentration gradients.

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 fuel cell performance drops.

Absorbtion of water vapour by polymer films prepared from S-PEEK and S-PPBP was studied by placing films into the atmosphere with different humidities and subsequent measuring of the equilibrium water content. The results obtained were found to be close to those reported in similar studies for Nafion membranes [10]. The dependence of water uptake for S-PEEK and S-PPBP films on relative humidity at room temperature is shown in Fig. 13.

Assuming the water activity and water content in the membrane obey Raoult's 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

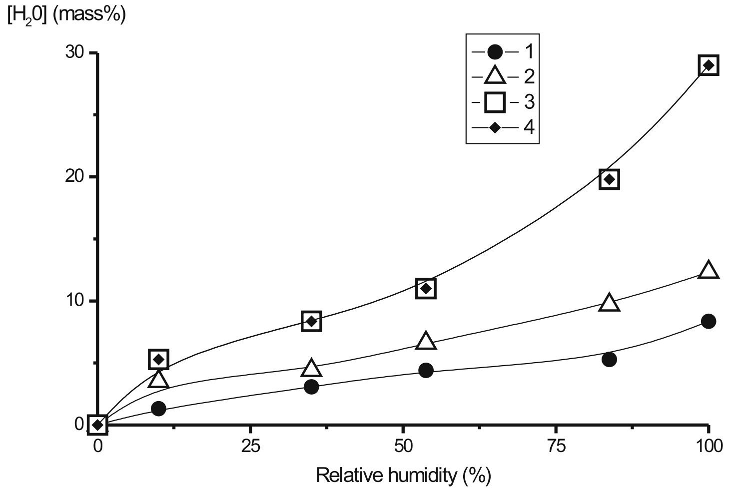


Fig. 13 Water uptake of S-PPBP (1–3) and S-PEEK (4) at room temperature as a function of relative humidity [7]. Concentration of SO_3H groups in the polymer (mol %): 30 (**1**), 65 (**2**), 80 (**3**) and 65 (**4**)

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 at 65 mol % sulfonation is higher than for 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 surface and fracture surface.

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

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

Proton conductivity of sulfonated poly(phenylene sulfide) is 10^{-5} S cm^{-12} at room temperature and relative humidity of 30%. The conductivity exponentially grows with the increase in relative humidity and reaches a value of 2×10^{-2} cm^{-1} at 94% humidity (Fig. 14).

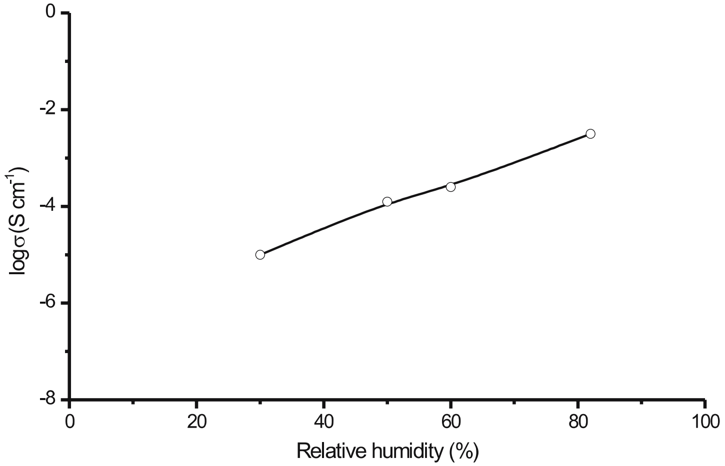


Fig. 14 Proton conductivity of the sulfonated polyphenylene sulfide (Scheme 2) ($m = 2$) at room temperature as a function of relative humidity [95]

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 by S-PEEK and S-PPBP films showed that proton conductivities of the films containing equilibrium amounts of absorbed water depend on the relative humidity. Fig. 15 represents the dependency of the proton conductivities of S-PEEK and S-PPBP with different sulfonation levels as a function of relative humidity.

It becomes clear that proton conductivities of the films increase with the relative humidity and water uptake and can become as high as 10^{-5} S cm^{-1} (for S-PEEK).

The proton conductivities for S-PEEK and S-PPBP with equal degrees of sulfonation (65 mol %) at a 100% relative humidity can be compared using the graphs shown in Fig. 16.

It is obvious that the proton conductivities and water uptake for S-PPBP are much higher than those for S-PEEK. Moreover, the proton conductivity for S-PEEK dramatically decreases at temperature above 100 °C, whereas that of S-PPBP appears to be 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 prospective polymers for manufacture of proton-conducting electrolyte membranes operating at elevated temperatures and low humidity.

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

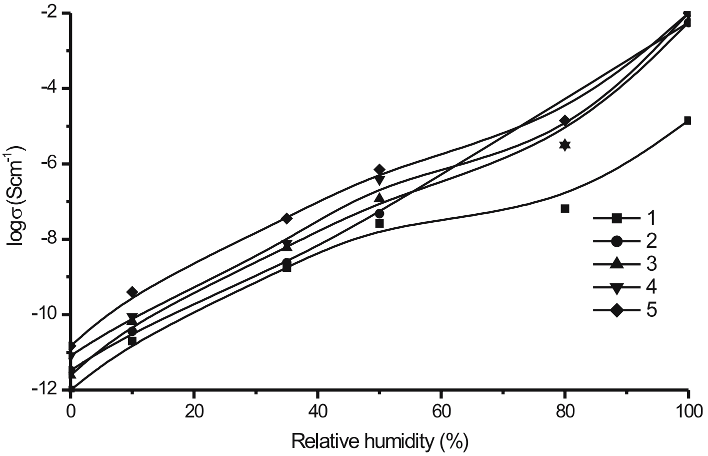


Fig. 15 Proton conductivity of S-PEEK (1) and S-PPBP (2–5) with different sulfonation levels as a function of relative humidity at room temperature [7]. Sulfonation level (mol %): 65 (1), 30 (2), 65 (3), 80 (4) and 85 (5)

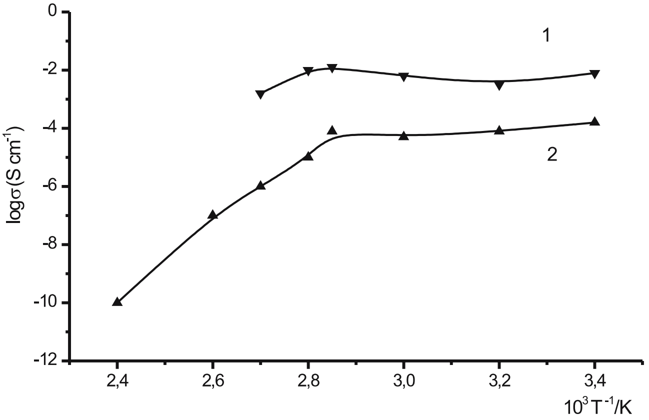


Fig. 16 Temperature dependences of proton conductivity as S-PPBP (1) and S-PEEK (2) with the same degrees of sulfonation (65 mol %) at a relative humidity of 120% [7]

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

Figure 17 represents temperature dependences of the proton conductivity of S-PEEK with a sulfonation degree of 85 mol % at different relative humidity values.

Similarly to Nafion, the proton conductivity of S-PEEK substantially drops as the humidity decreases [86]. The dependence of proton conductivity on

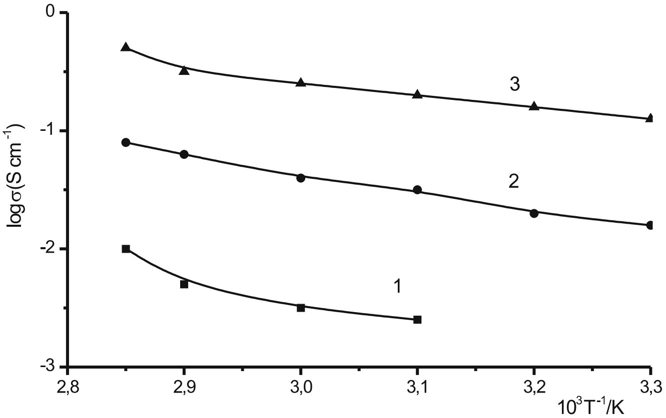


Fig. 17 Temperature dependence of proton conductivity of an S-PEEK membrane with sulfonation level of 85% at relative humidity of 50% (1), 70% (2) and 90% (3) [7]

humidity reflects a tendency of S-PEEK to absorb water vapours. This can be attributed to a "liquid" proton conductivity mechanism when protons are transported in the form of hydronium ions through water-filled pores of the membrane [32].

S-PEEK samples exhibit a slight increase in conductivity with 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].

3

Alkylsulfonated Aromatic Condensation Polymers and Proton-Conducting Electrolyte Membranes on their Basis

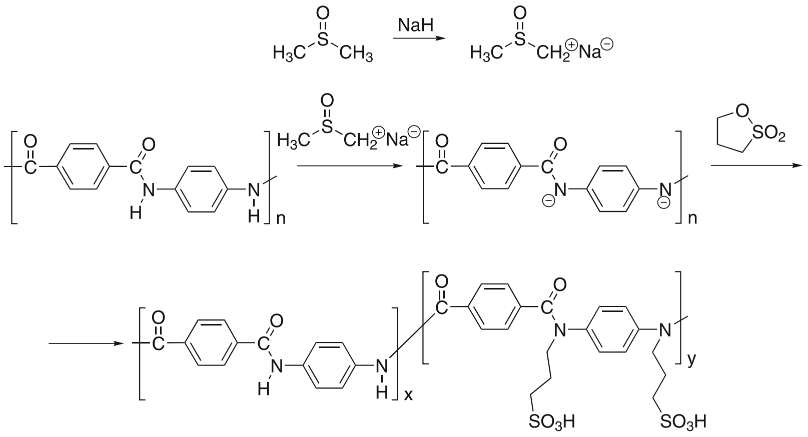
The major drawback of sulfonated proton-conducting polymer electrolytes is their degradation at 200–400 °C occurring due to desulfonation. By introducing alkylsulfonated substituents into the macromolecules of aromatic polymers one can prepare thermostable proton-conducting polymers. Their electrochemical properties can be controlled by varying the number of substituents and the length of alkyl chains. 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 using correspondent polyamides containing reactive NH groups [161]. The polyamides were modified by treatment with NaH in DMSO [161, 162], and the resulting polyanion obtained was introduced into the reaction with 1,3-propane sultone (Scheme 20).

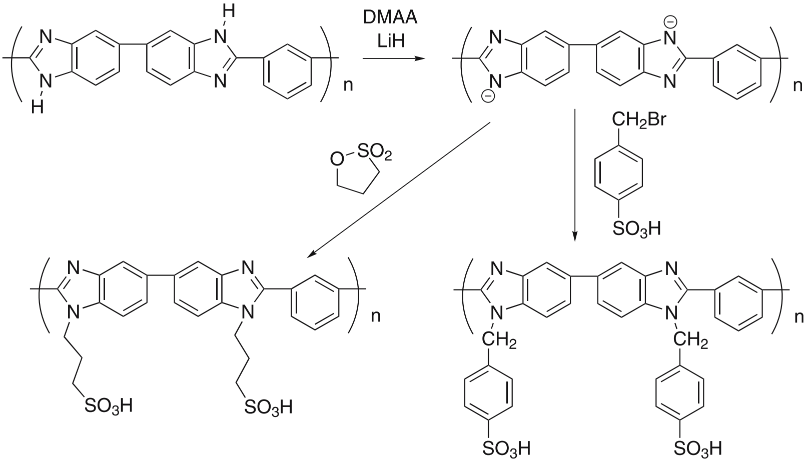
A similar approach was employed for the modification of poly(benzimidazoles) (PBI) [163–171].

Yet another synthetic route to obtaining sulfonated PBI involves treatment of the above mentioned polyanion with 4-bromobenzyl sulfonate resulting in poly[2,2′-m-phenylene-bi(N-benzylsulfonate)benzimidazolo-5,5′-diyl] (Scheme 21).

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



Scheme 20



Scheme 21

The degree of alkylsulfonation as a function of the ratio of 1,3-propane sultone to PBI is represented in Fig. 18.

The degree of alkylsulfonation of NH groups in PBI was estimated considering the results of ^{1}H NMR study and elemental analysis. This parameter can be controlled easily by varying the ratio of 1,3-propane sultone to PBI. For instance, the alkylsulfonation level can be as high as 60 mol % at 1,3-propane sultone: PBI ratio of 5.0.

An attempt to synthesise ethylphosphorylated PBI using the abovementioned treatment of PBI (Scheme 22) was reported [7].

The substitution reaction at the NH sites of benzimidazole rings was performed successfully, but the resulting polymer appeared to be insoluble in organic solvents. The reason for this can be aggregation of phosphoric acid

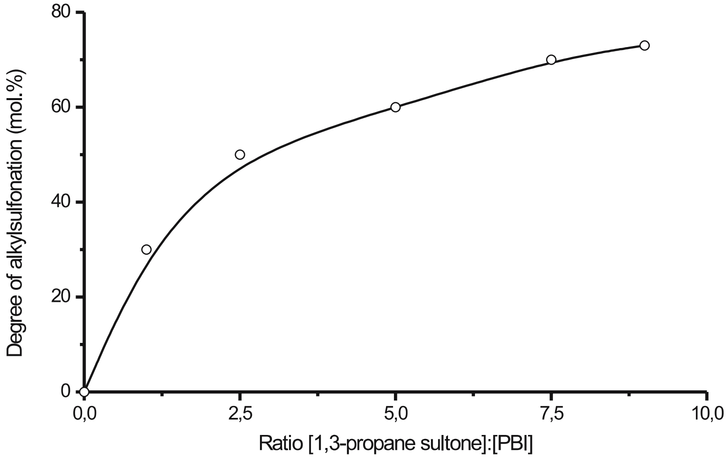
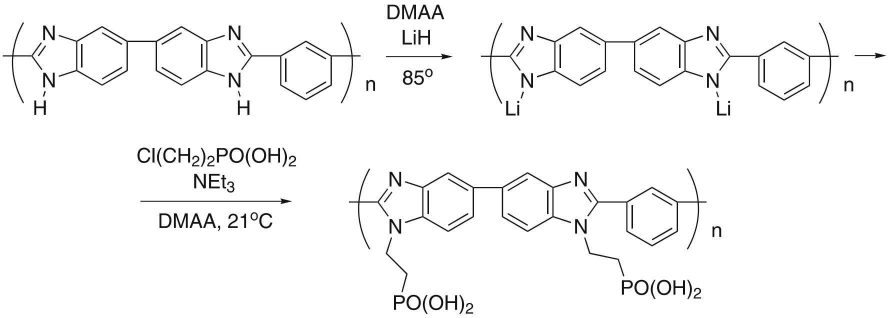


Fig. 18 Degree of alkylsulfonation of PBI as a function of 1,3-propane sultone: PBI ratio [7]

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 polymer electrolytes.

Alkylsulfonation and arylsulfonation of the starting aromatic polymers was aimed at increasing their water uptake and proton conductivity while retaining high thermal stability. The polymers obtained were studied by TGA in inert and oxidative atmospheres [166]. Parent PBI exhibits very high thermal stability. In the inert atmosphere, the onset of its degradation occurs at 650 °C. The 5% mass loss is observed at 700 °C, and more than 80% of the polymer's initial mass is retained at 800 °C. Introduction of substituents that are not conjugated with the polymer backbones reduces the degradation temperatures in the inert medium, which is consistent with the expectations. The



Scheme 22

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 the 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 the removal of the substituting group the degradation slows down thus 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 about 100 °C lower than the degradation temperature for this polymer in an inert medium. Degradation temperatures of substituted PBI in oxidative media are close to those of the unsubstituted ones. For all polymers, the mass loss in air is much higher than in nitrogen and the amount of residual char is much smaller. This happens primarily due to the lower stability of starting PBI in dry air and to some extent due 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 initial mass) begins at 600 °C. After modification with propylsulfonate side groups (66% substitution) the polymer is stable below 400 °C; only 40% of its initial mass is retained at 800 °C. The benzylsulfonated derivative of PPTA with a 66% substitution level is more thermally stable compared to the propylsulfonated derivative. Degradation of the latter begins at 470 °C. The decrease in mass of a sample down to 50% of its initial mass is observed at 800 °C. The degradation temperature of PPTA in a dry air atmosphere is 70 °C lower than in nitrogen [166]. Comparison of degradation processes of benzylsulfonated PPTA with 66% substitution in air and in nitrogen showed that the degradation in air begins at a lower temperature. The major difference is that the initial mass loss is higher, while the initial degradation is much smaller at high temperature, 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 [166] 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 occurs not only at the N – C bond. The TGA study of benzylsulfonated PBI with 75% degree of sulfonation in air at a heating rate of 1 °C min^{-1} showed that introduction of benzylsulfonated 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 sulfonic acid groups. The degradation mechanism for 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, while benzylsulfonated PBI is stable up to 500 °C. These results are hard to compare because of different degrees of sulfonation of the PBI samples undergoing investigation. One can assume that benzylsulfonated PBI is less stable than propansulfonated PBI due to the presence of the weak Aryl–S bond. In fact, the degradation temperature of benzylsulfonated PBI is comparable with the degradation temperatures of polymeric electrolytes prepared via sulfonation with sulfuric acid.

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

In contrast to PBI, the 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. 19); 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 similar to those reported by Gieselman and Reynolds [166] who found that the degradation of PBI-PS occurs due to desulfonation. Hence, alkylsulfonated PBI is more thermally stable than sulfonated aromatic polymer electrolytes characterised by a degradation temperature between

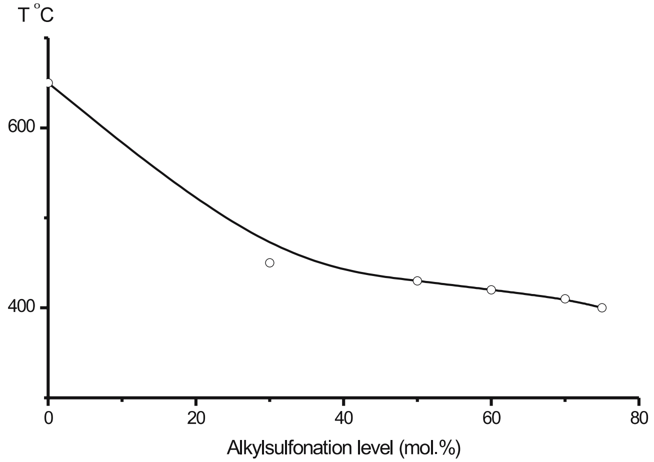


Fig. 19 Degree of alkylsulfonation of PBI-PS as a function of alkylsulfonation level [7]

200–350 °C. The thermal stability of alkylsulfonated polymer electrolytes can be attributed to the 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 polymer induces water absorption and makes them more hydroscopic. The water uptake of PBI-PS was determined by measuring the mass of the polymer before and after hydration. The dependence of the water uptake of PBI-PS on the relative humidity is presented in Fig. 20.

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 molecules per SO_3H group for Nafion 117 membranes under the same conditions). This procedure was also employed for the synthesis of buthylsulfonated and (methyl)propylsulfonated PBI (PBI-BS and PBI-MPS, respectively) via butane sultone and methylpropane sultone. The water uptake 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 uptakes also increases. This is thought to be associated

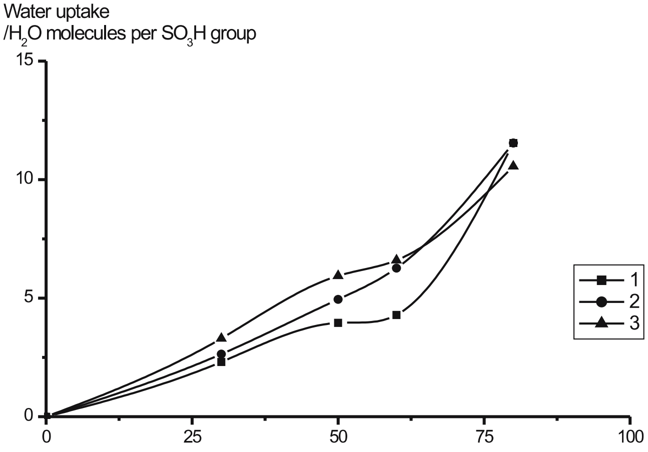


Fig. 20 Water uptake of PBI-PS as function of relative humidity at alkylsulfonation levels of 49.3 mol % (1), 61.5 mol % (2) and 73.1 mol % (3) [7]

with the greater flexibility of long alkyl chains and the 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 [172] and ^{1}H NMR spectroscopy (low temperature relaxation time measurements) [173] 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. 21.

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 membranes 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. 22.

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

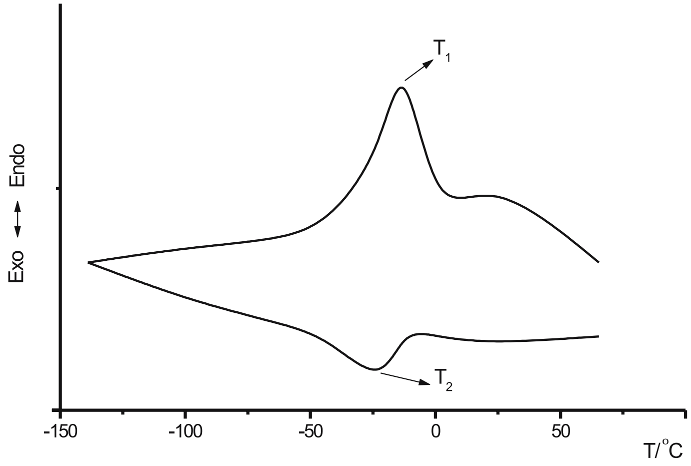


Fig. 21 DSC curve of hydrated PBI-PS (73.1%) film containing 11.3 H_2O molecules per sulfonic acid group [7]

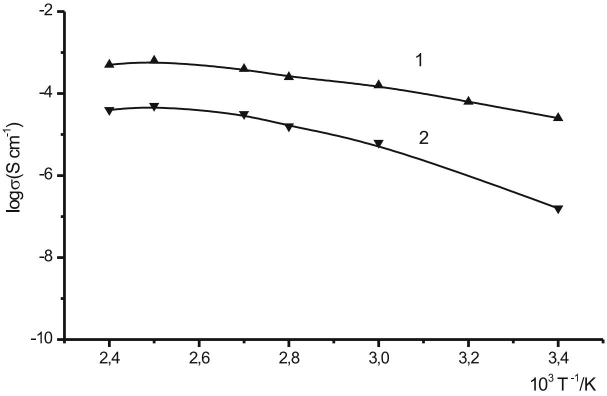


Fig. 22

containing D_2O in the same temperature range. This suggests 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 Fig. 23.

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 sm^{-1} at 80 °C and decreased slightly at higher temperatures due to a small loss of water ($\sim$ 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 a temperature above 100 °C. The proton conductivity of a PBI-PS film containing 11.3 H_2O molecules per SO_3H group was 10^{-3} S cm^{-1}.

The water uptake of a PBI-PS film placed in an atmosphere with a relative humidity of 90% was compared with that of Nafion membranes. The proton conductivity of Nafion membranes was as high as 10^{-3} S cm^{-1} at 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 a temperature above 100 °C.

The large water uptake and proton conductivity of PBI-PS at a temperature 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 [173]. It was found that the proton conductivity increases as the degree of the substitution increases. The polymer with a 75% substitution level exhibited a conductivity of 10^{-2} S cm^{-1} at 40 °C and a relative humidity of 100%.

The results obtained in the above mentioned studies suggest that the alkyl sulfonated aromatic polymer electrolyte exhibit sufficient thermal stabilities for fuel cell applications at 80 °C (a typical operating temperature for per-

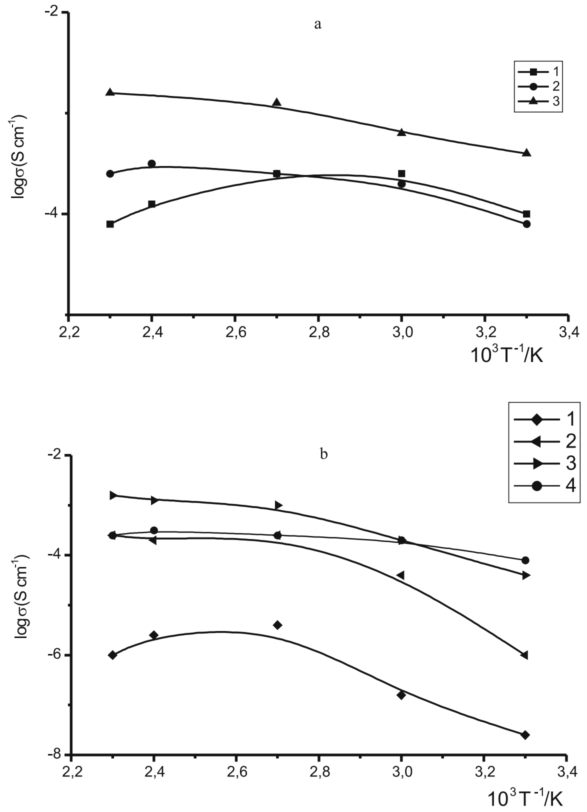
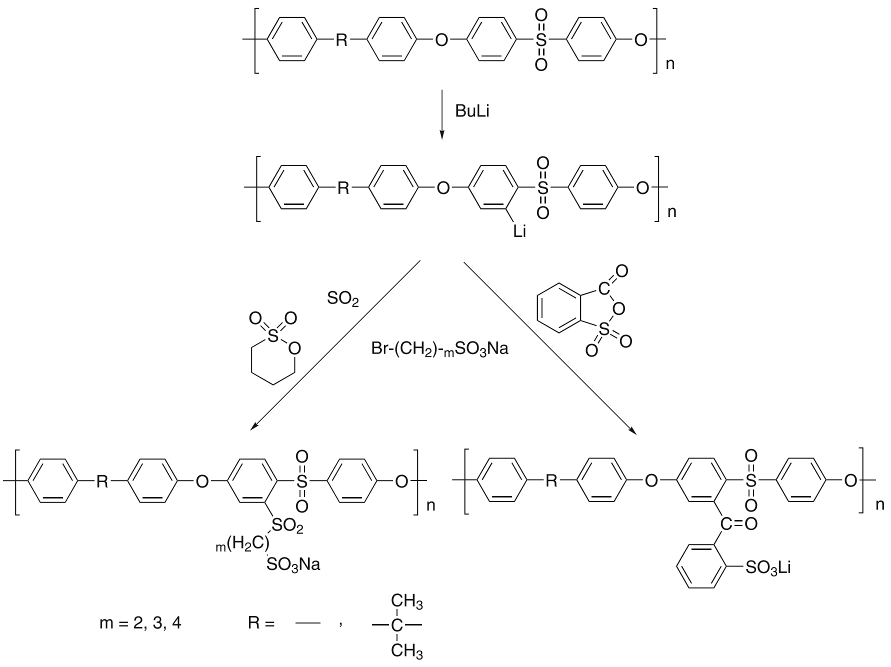


Fig. 23 Temperature dependences of proton conductivity of PBI-PS films with the same water uptake (48%) and different degrees of sulfonation (**a**) and with the same degree of sulfonation (73.1%) and different water uptakes (**b**) [7]; (**a**): degree of sulfonation (mol %): 49.3 (1), 61.5 (2), and 73.1 (3) (**b**): water uptake : 11.2 (1), 25.0 (2), 29.0 (3) and 48 (4)

fluorinated polymer electrolyte membranes). The water uptake and proton conductivity of this polymer 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.

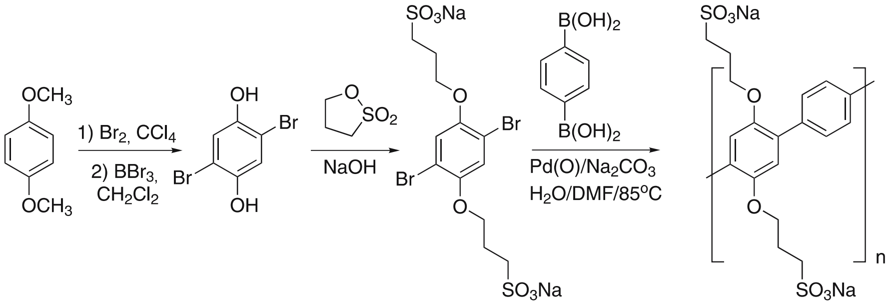
The absorbed water molecules are more strongly bound to alkylsulfonated rather than perfluorinated polymers. One can assume that this is related to the difference in the absorbtion mechanisms and to the physical state of absorbed water in PBI-PS and perfluorinated polymer electrolytes.

A series of new sulfonated polymers where the sulfonic acid units are separated from the polymer main chains via short molecular spacers were developed [174, 175] using treatment of polyethersulfones with BuLi leading to the formation of lithiated polymers and subsequent transformations under the action of bromoalkanesulfonates, butansultone or 2-sulfobenzoic acid cyclic anhydride.



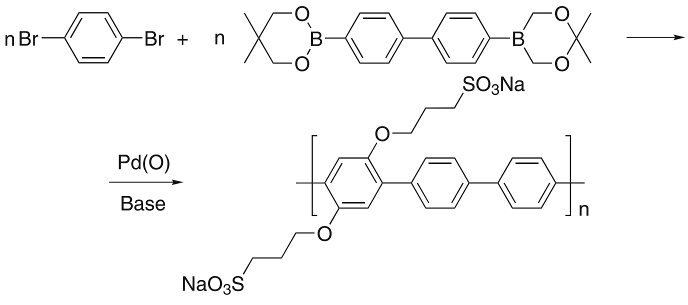
Scheme 23

Recently conjugated polyelectrolytes containing alkylsulphonic and alkylphosphonic groups have received considerable interest [176–180]. Sulfonate-substituted poly(*p*-phenylene) was prepared [176] using Suzuki co-polymerisation of 1,4-benzenediboronic acid with sulfonate monomer in three steps starting from 1,4-dimethoxybenzene:



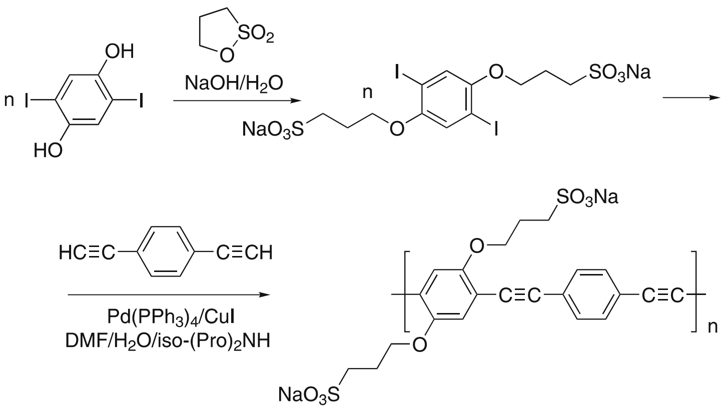
Scheme 24

Several years later, Reynolds and co-workers [179] extended this work to prepare another sulfonated poly(*p*-phenylene) using the same approach by replacing 1,4-diboronic acid with 4,4′-biphenyl diboronic ester:



Scheme 25

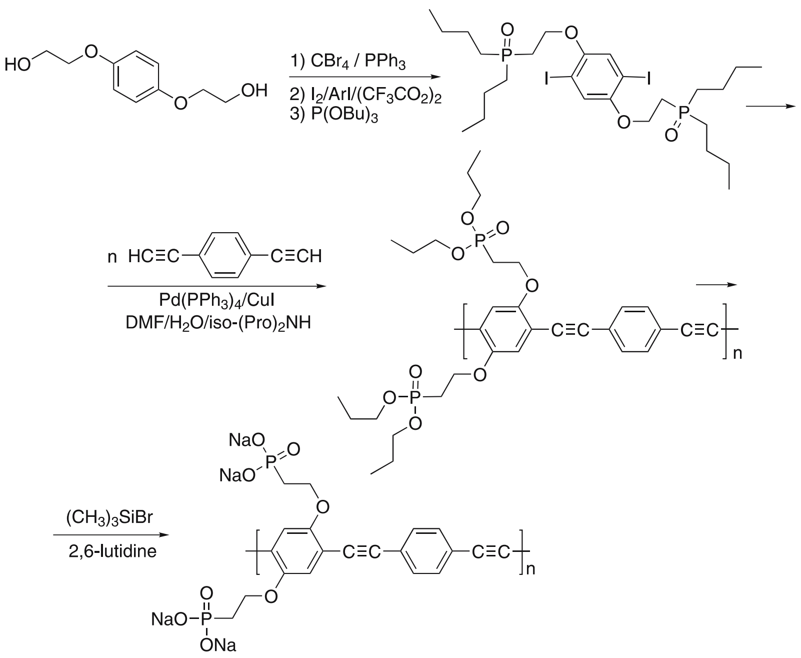
In a recent paper Shanze and co-workers [177] reported the synthesis of poly(*p*-phenylene ethynylene) which was obtained by Sonogashira coupling in accordance with the following scheme:



Scheme 26

The resulting polymer was obtained in a 68% yield, and it was soluble in water and low molecular weight alcohols. A molecular weight of 100 kD was estimated by the polymer's ultrafiltration properties and by iodine end-group analysis.

In a recent preliminary report [178] Shanze et al. described poly(phenylene ethynylene) which features phosphonate groups appended to the polymer backbone:



Scheme 27

The phosphonate polymer was prepared via a neutral precursor polymer, which was soluble in organic solvents, enabling the material to be characterised by NMR and GPC. Sonogashira polymerisation of phosphonate monomer and 1,4-diethynylbenzene afforded neutral polymer in a 46% yield. Analysis of the neutral precursor polymer indicated Mw = 18.3 Kd and polydispersity 2,9.

The target polymer was prepared by bromotrimethylsilane-induced cleavage of the *n*-butyl phosphonate ester groups in neutral precursor polymer. After neutralisation of the reaction mixture with aqueous sodium hydroxide, the target polymer has exhibited good solubility in water.

4

Proton-Exchanging Electrolyte Membranes Based On Polymer Complexes

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

Recently, new proton-conducting polymer electrolyte membranes based on PBI – orthophosphoric and other strong acid complexes have been proposed for use in PEMFCs [181–188].

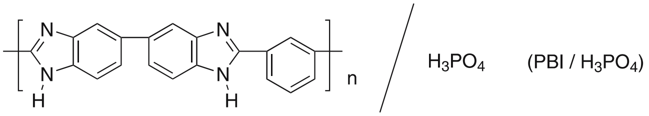


Fig. 24

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 at 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 PBI films into solutions of strong acids in methanol was reported [187, 189]. 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 PBI/H_3PO_4. 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 [181–185]. Upon equilibration in a 11 M H_3PO_4 solution a doping level of $\sim$ 5 phosphoric acid molecules per repeating unit of the polymer was achieved.

PBI membranes loaded with high levels of phosphoric acid were prepared using a new sol-gel process [190]. This process, termed the PPA process, uses PPA as the condensing agent for the polycyclocondensation and the membrane casting solvent. After casting, absorption of water from the atmosphere causes hydrolysis of the PPA to phosphoric acid.

The thermal stability of PBI-strong acid polymer complexes was studied by TGA and DTA. Fig. 25 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.

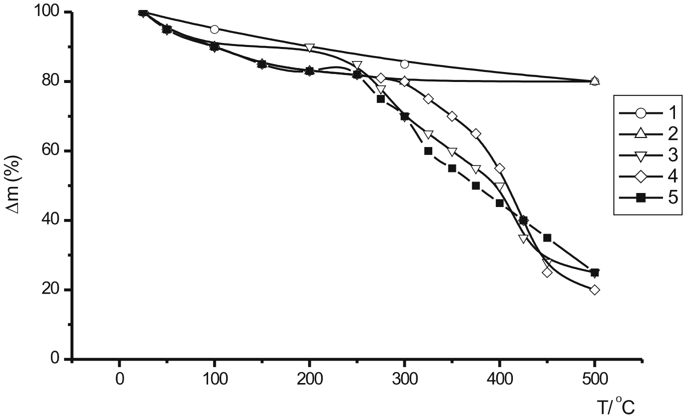


Fig. 25 TGA curves of PBI (1) and its complexes with H_3PO_4 (2), H_2SO_4 (3), $MeSO_3H$ (4) and $EtSO_3H$ (5) [7].

A decrease in the degradation temperature of polymer complexes PBI/H_3PO_4 was expected because of the complexation of acid molecules which easily corrodize and oxidise the polymer macromolecules. However, no degradation was observed under the nitrogen atmosphere. At the same time, thermal decomposition of PBI complexes with H_2SO_4, $MeSO_3H$, $EtSO_3H$ 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, $MeSO_3H$, $EtSO_3H$ 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 temperature and strong acids.

Complexes PBI/H_3PO_4 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 [191]. This was associated with the formation of benzimidazonium cations. Samms et al. [185] studied the thermal stability of polymer complexes 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 PBI/H_3PO_4 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 the 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 PBI/H_3PO_4 coated with platinum black are thermally stable up to 600 °C.

Variation of the conductivity of polymer complexes PBI/H_3PO_4 as a function of water vapour activity, temperature and acid doping level was studied [183]. 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 ($5H_3PO_4$ molecules per repeating unit of PBI) is 3.5×10^{-2} S cm^{-1} at 190 °C and 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 (Fig. 24) is by an order of mag-

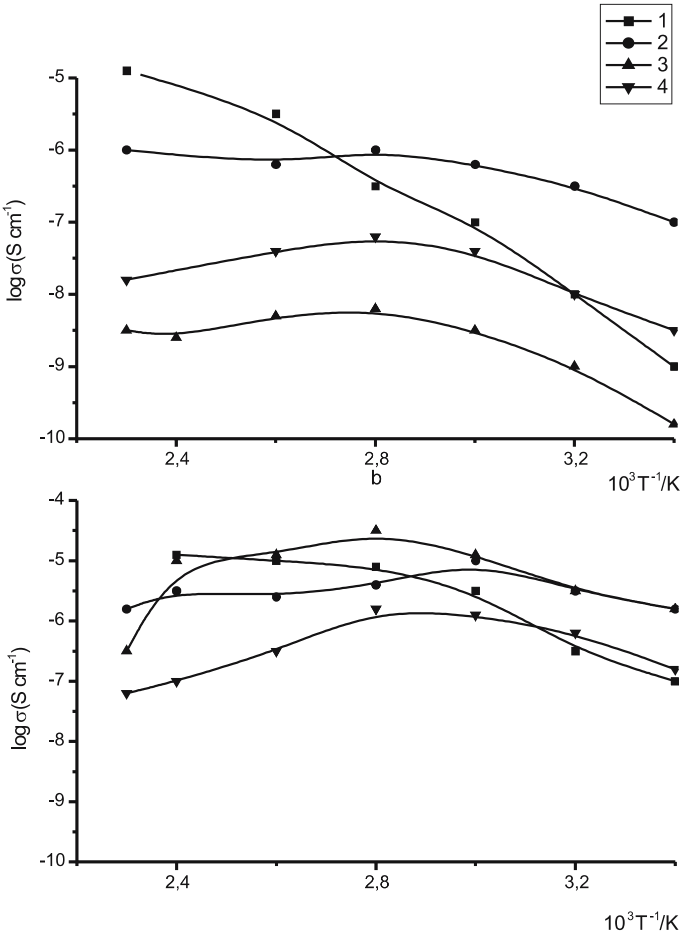


Fig. 26 Temperature dependence of proton conductivity of anhydrous (**a**) and hydrated (**b**) PBI complexes with H_3PO_4 (1), H_2SO_4 (2), $EtSO_3H$ (3), $MeSO_3H$ (4) [7]

nitude 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. 26a.

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 PBI/H_3PO_4 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 temperature above 80 °C. These results point to high thermal stability of polymer complexes PBI/H_3PO_4.

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 uptake of the complexes were 13–26 mass %. The proton conductivity of the hydrated PBI-strong acid polymer complexes was found to be nearly an order of magnitude higher than the conductivity of anhydrous polymer complexes (Fig. 26b). 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. Fig. 27 presents the temperature dependences of the conductivities of anhydrous complexes PBI/H_3PO_4 with different acid contents. As can be seen, the conductivity of polymer complexes PBI/H_3PO_4 increases with the concentration of H_3PO_4.

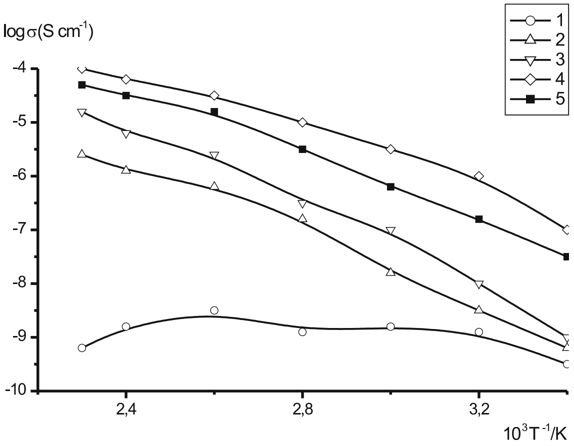


Fig. 27 Temperature dependence of proton conductivity of anhydrous PBI/H_3PO_4 complexes containing 1.4 (1), 2.0 (2), 2.7 (3), 2.3 (4), 2.9 (5) H_3PO_4 molecules per PBI units [7]

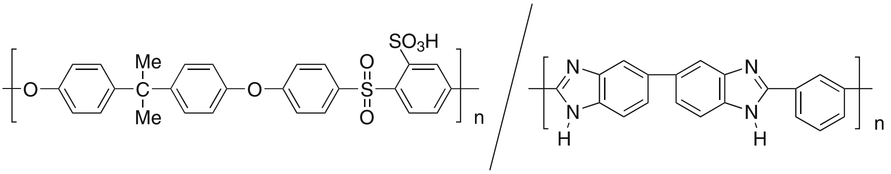


Fig. 28

The temperature dependences of the conductivities of polymer complexes PBI/H_3PO_4 are 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} (P-OH) and 970 cm^{-1} $H_2PO_4{}^{-1}$ [192–195]. As the concentration of H_3PO_4, 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 [196] involving an exchange of protons between H_3PO_4 and $PO_4{}^{-2}$ or $H_2PO_4{}^{-}$.

Anhydrous sulfonated aromatic polymers are highly brittle. Recently [197], new materials with high mechanical strength were reported. They were prepared using a polymer blending technique by combining PBI and sulfonated polymers (S-PEEK or *ortho*-sulfonated polysulfone) (Fig. 28).

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.

Along with PBIs for the preparation of basic polymer strong acid complexes polyphenylquinoxaline [198],

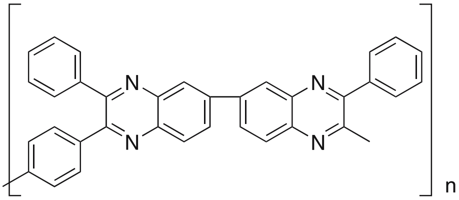


Fig. 29

poly-1,3,4-oxadiazole [199]

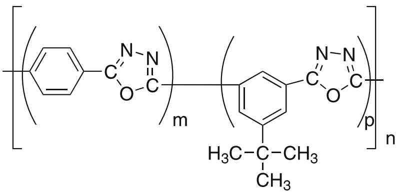
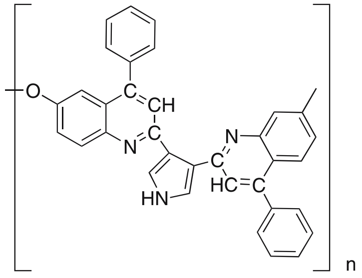


Fig. 30

and pyrrole-containing polyquinoline [200] were used:



PCPQ

Fig. 31 Temperature dependence of conductivity for PCPQ/H_3PO_4 and PBI/H_3PO_4 complexes at 3.8 and 1.5 mol unit^{-1}

The last polymer with good solubility in DMAC was chosen to prepare a membrane and to examine the proton conductivity. For comparison, the PBI was also measured under the same experimental conditions.

Temperature dependences of conductivity for PCPQ/H_3PO_4 and PBI/H_3PO_4 complexes at 3.8 and 1.5 mol unit^{-1}, respectively, are shown in Fig. 32:

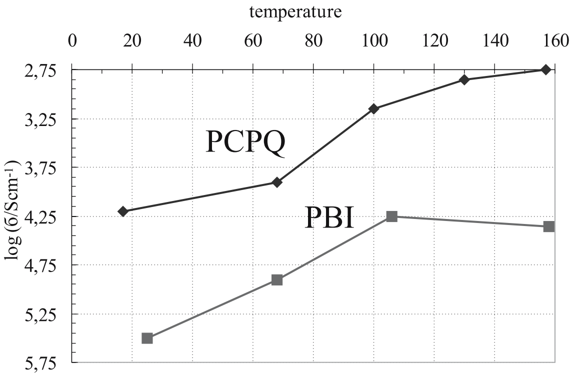


Fig. 32

As can be seen from Fig. 32, the conductivities of PCPQ/H_3PO_4 and PBI/H_3PO_4 complexes increased with temperature, and the PCPQ/H_3PO_4 complex exhibited a higher conductivity compared with that of the PBI/H_3PO_4 complex, reaching 1.5×10^{-3} S cm^{-1} at 157 °C, while the conductivity of PBI/H_3PO_4 complex was 7×10^{-5} S cm^{-1} at 150 °C. In addition, under the same experimental conditions PCPQ could complex more H_3PO_4 (3.8 mol $unit^{-1}$ than PBI (1.5 mol $unit^{-1}$. That may be the main reason for PCPQ/H_3PO_4 having a higher conductivity.

5
Fuel Cell Applications of Proton-Exchanging 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 [197].

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 a membrane based on polymer complexes PBI/H_3PO_4 [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, 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 the cathode is sufficient for maintaining the necessary conductivity of the electrolyte). This type of fuel cell was characterised by continuous operation at a current density of 200 mA cm^{-2} over a period of 200 h (and for longer time periods) 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.

6
Conclusions

To summarise, the aforesaid shows that aromatic condensation polymers can be thought of as candidates for fuel cell applications; the structure of ACP-based polymer electrolytes can be modified with ease; these polymer electrolytes possess a large water uptake and high proton conductivity at high temperature 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.

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Editor: Manfred Schmidt