Adv Polym Sci (2008) 216: 125–155
DOI 10.1007/12_2008_131

Proton-Conducting Polymers and Membranes Carrying Phosphonic Acid Groups

Alexandre L. Rusanov[1] (✉) · Petr V. Kostoglodov[2] · Marc J. M. Abadie[3] · Vanda Yu. Voytekunas[3] · Dmitri Yu. Likhachev[4]

[1]A.N. Nesmeyanov Institute of Organoelement Compounds,
Russian Academy of Science, 28 Vavilova str., 119334 Moscow, Russia
alrus@ineos.ac.ru

[2]YRD Centre, Ltd., 55/1 b.2, Leninski pr., 119333 Moscow, Russia

[3]Laboratory of Polymer Science and Advanced Organic Materials – LEMP/MAO,
Universite Montpellier 2, Science et Techniques du Languedoc, 34095 Montpellier,
France

[4]Materials Research Institute, UNAM, Cirquito Exterioir s/n, CU,
Apdo Postal 70-360 Coyoacan, 04510 Mexico City, Mexico

Abstract The results of the research of novel proton-conducting membranes carrying phosphonic acid groups have been analyzed and summarized with respect to their application in fuel cells. General approaches to the preparation of heterochain and heterocyclic polymers carrying phosphonic acid groups have been considered, including polycondensation of phosphonic acid functionalized monomers and phosphorylation of existing polymers. The bibliography includes 85 references.

Keywords Condensation polymers · Fuel cells · Phosphorylation · Polyelectrolytes · Polyphosphazenes · Polysulfones · Proton exchanging membranes

Abbreviations

BPA	Bis-phenol A
NMR	Nuclear magnetic resonance
^{1}H NMR	Proton nuclear magnetic resonance
^{31}P-NMR	Phosphorus-31 nuclear magnetic resonance
DCB	*o*-dichlorobenzene
DEP	Diethyl phosphite
DMA	Dimethylacetamide
DMF	Dimethylformamide

DMSO	Dimethylsulfoxide
DCP	3,5-dicarboxylbenzenephosphonic acid
GPC	Gel permeation chromatography
IEC	Ion-exchange capacity
N-MP	*N*-methyl-2-pyrrolidone
PBI	Poly(Benzimidazole)
PEMFC	Proton-exchanging membrane fuel cells
PSU	Polysulfone
STA	2-sulfoterephthalic acid
TEA	Triethylamine
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran

1
Introduction

Proton-conducting ionomers for polymer electrolyte membrane fuel cell (PEMFC) is one area in which extensive research is ongoing to modify aromatic main chain polymers to tailor their properties as proton conductors [1–18]. When it comes to modifying these polymers with the aim of preparing ionomers, sulfonic acid units have been by far the acidic moiety of choice [1–19]. This is at least partly due to the wide range of reactants that are commercially available for sulfonation. Besides direct sulfonation by electrophilic substitution reactions with, for example, fuming sulfuric acid, sulfonated ionomers have been also accomplished by chemical grafting [20, 21] and by direct polymerization of sulfonated monomers [22–27].

Nowadays, research in the field of PEMFCs is mainly driven by the insufficiency of properties of Nafion membrane at temperatures above 100 °C [11, 13, 28]. Operating a fuel cell at these temperatures increases the kinetics of the electrode reactions, reduces the risk of catalyst poisoning, lowers the amount of catalyst needed, and reduces cathode flooding [7].

As a result, the overall performance and cost efficiency of the fuel cell system can be expected to be significantly improved. However, at high temperature, desulfonation, which is a loss of the sulfonic acid unit through hydrolysis, may become a critical issue [29]. This is currently motivating the search for ionomers with alternative acidic moieties, such as phosphonic acid [30, 31], which have higher chemical and thermal stabilities than sulfonic acid moieties [32–34].

Even though phosphonic acid units are less acidic than sulfonic acid units [35], they are known to have a greater ability to retain water than sulfonic acid unit [36]. This is crucial for maintaining high conductivities at elevated temperatures.

In spite of their potential usefulness, polymers containing phosphonic acid units have scarcely been studied for fuel cell applications, because the synthetic procedures available for phosphonation are limited and complex in comparison to sulfonation procedure. Furthermore, lower acidity of phosphonic acids, compared to sulfonic acids, requires higher degrees of substitution for sufficient proton exchange performance.

2
Proton-Conducting Polymers and Membranes Carrying Phosphonic Acid Groups

The first proton-conducting perfluorinated membrane carrying phosphonic acid units was prepared by Kotov et al. [34]. Several *co-* and *ter*-fluoropolymers based on tetrafluoroethylene and perfluorovinylenes, such as

$$CF_2 = CFO(CF_2)_2P(O)(OC_2H_5)_2 ,$$
$$CF_2 = CFO(CF_2)_3P(O)(OC_2H_5)_2 ,$$
$$CF_2 = CFOCF_2CF(CF_3)O(CF_2)_2P(O)(OC_2H_5)_2, \quad \text{and}$$
$$CF_2 = CFOC_3F_7 ,$$

were synthesized via redox-initiated emulsion polymerization. The polymers were subjected to acid hydrolysis and the corresponding fluorinated polymeric phosphonic acids were obtained. Both the polymeric phosphonated and phosphonic acids can be readily processed into films by compression molding. Perfluorinated phosphonic acid membranes with an ion-exchange capacity (IEC) within the range 2.5–3.5 milliequivalents per gram and a thermal stability of 300–350 °C were prepared. The characteristics of these acid membranes were explored, and these films show promising electrochemical properties, such as proton conductivity (0.006–0.076 S/cm) comparable with Nafion membranes.

Perfluorinated polymers with pendant phosphonic acid groups were also described in [37]. These polymers are analogues of Nafion and their synthesis requires demanding and expensive fluorine chemistry.

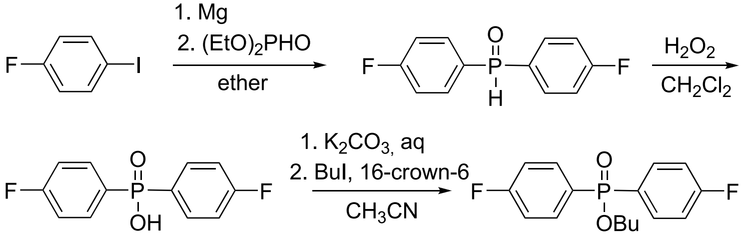
In addition, there are several investigations on proton exchange polymers, whose phosphonic acid sites are linked to aromatic ring directly or by means of alkylene spacers. These polymers can be prepared by polycondensation of phosphonic acid functionalized monomers or phosphorylation of existing aromatic condensation polymers. There are several methods reported for the preparation of arene phosphonates from aryl bromides [38–40]. The classical Arbuzow reaction [41, 42] is commonly used, in which triethylphosphite and nickel dichloride are employed as catalysts. The reaction often requires harsh conditions (160 °C) and suffers from low yields. Alternative palladium-catalyzed reaction [43–45] useful for phosphonation proceeds more smoothly.

2.1
Polycondensation of Phosphonic Acid Functionalized Monomers

Phosphonic and phosphinic acid moieties may be incorporated in the main chains of macromolecules or in the side groups.

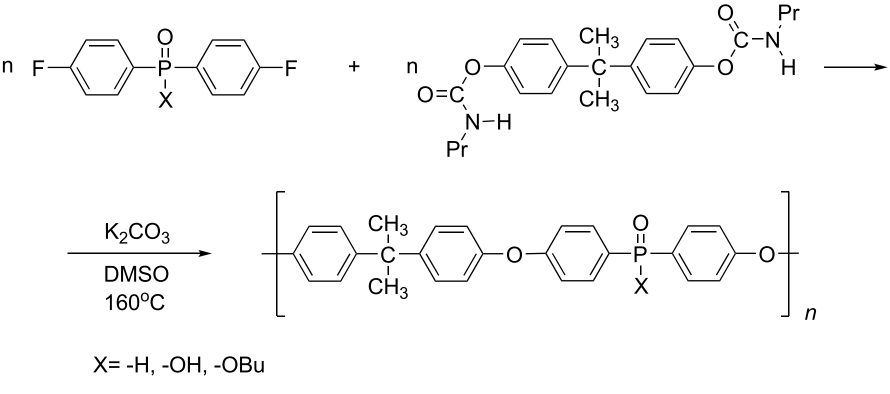
In general, few articles on the polycondensation of phosphonic acid functionalized monomers can be found.

Miyatake and Hay [46] reported the first phosphonic acid containing polymers and copolymers from three phosphine-containing aromatic difluorides, prepared in accordance with the following Scheme 1:



Scheme 1

The aforementioned difluoromonomers were polymerized with bisphenol A (BPA) bis-(propylcarbamate) under basic conditions at 160 °C in DMSO to produce the corresponding poly-(arylene ether)s (Scheme 2):



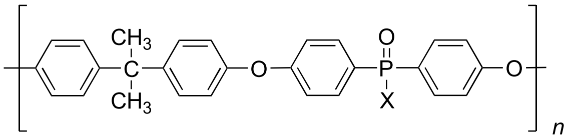
Scheme 2

Because the carbamoyl-masking groups improve these kinds of nucleophilic-substitution polymerization reactions [47], BPA bis-(propylcarbamate) was used.

Target polyethers were prepared with 25–78% yields [47].

Their general properties are given in Table 1.

Table 1 Properties of the polyethers of general formula

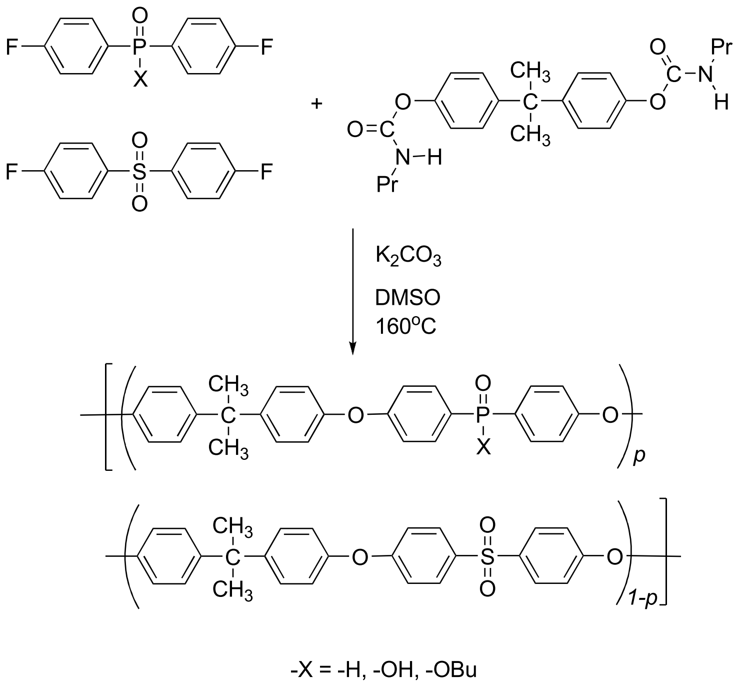


– X	Yield %	3_{inh} (dL g^{-1})[a]	*Tg* (°C)	$Td_{10\%}$[b] (°C)
– H	52	0.24	200	477
– OH	25	0.14	102	422
– OBu	78	0.30	125	325

[a] In NMP at 27 °C

[b] Temperature for 10% weight loss under nitrogen

Polyether with phosphonic acid groups in the main chain (– X = – OH) was very soluble in polar organic solvents (DMF, N-MP, DMSO), slightly soluble in chloroform, but insoluble in water. Polyether with *n*-butil phosphinate ester groups was soluble in many organic solvents like benzene, chloroform, THF, and DMF.



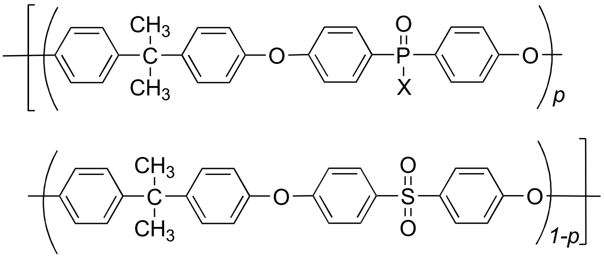
Scheme 3

Films obtained by casting from solution were brittle and self-supporting.

To produce higher molecular weight polymers, copolymerization with *bis*-(4-flourophenyl)sulfone was investigated (Scheme 3).

The copolymerization was successful and gave copolymers with a higher solution viscosities (up to 0.39 dL g^{-1} in N-MP) than that of corresponding homopolymers (Table 2).

Table 2 Properties of the copolyethers of general formula



– X	*p*	Yield %	3_{inh} (dL g^{-1})[a]	*Tg* (°C)	$Td_{10\%}$[b] (°C)
– H	0.5	78	0.32	202	432
– H[c]	0.5	65	0.39	225	454
– OH	0.1	85	0.33	191	490
– OH	0.2	67	0.37	183	452
– OH	0.3	59	0.14	184	465
– OH	0.5	31	0.14	157	428
– OBu	0.2	91	0.19	175	445
– OBu	0.4	81	0.11	183	401

[a] In NMP at 27 °C

[b] Temperature for 10% weight loss under nitrogen

[c] Polymerization run in *N*,*N*-dimethylacetamide

Because the copolymers were more soluble than the homopolymers and even somewhat soluble in methanol, the isolated yields were not quantitative.

From the stoichiometric investigations, it was found that trace amounts of water are crucial, and that they hydrolyze fluoride monomers. A 7 mol % excess of difluoride monomer was used to obtain the highest molecular weight copolymer (Table 3).

Copolymer with the highest viscosity was soluble in many organic solvents and gave a film by casting from solution. A high thermal stability ($Tg = 178$ °C, $T_{dec10\%} = 432$ °C) was observed.

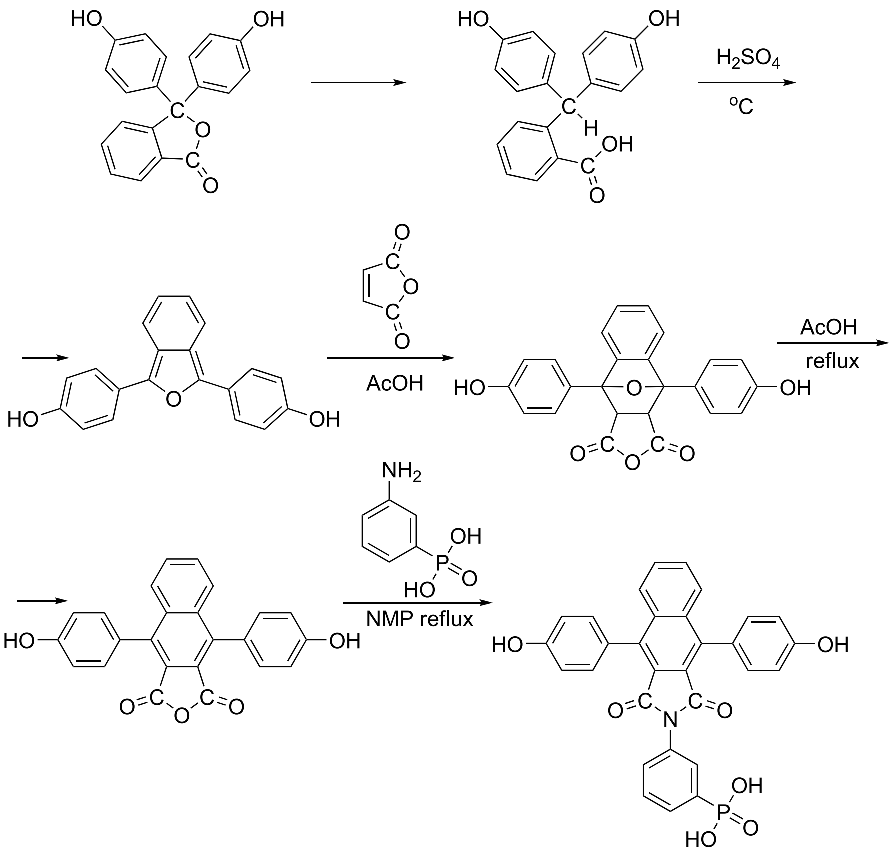
The polymers did not have high hydrophilicity; however, small amount of polar organic solvents helped them to swell in water.

Hay et al. [48, 49] have synthesized phosphonic acid containing *bis*-phenol by the interaction of 4,9-*bis*-(4-hydroxyphenyl)benzoisobenzofuran-1,3-

Table 3 Stoichiometric effect on the copolymerization of bis-(4-fluorophenyl)-phosphonic acid and bis-(4-fluorophenyl)-sulfone with BPA

Excess of bis-(4-fluoro-phenyl)-phosphinic acid	Yield %	3_{inh} (dL g^{-1})[a]	*Tg* (°C)	$Td_{10\%}$[b] (°C)
0	31	0.14	157	428
0.013	35	0.34	164	432
0.05	42	0.25	156	433
0.07	70	0.78	178	432
0.07[c]	45	0.16	171	422
0.1	48	0.29	169	439

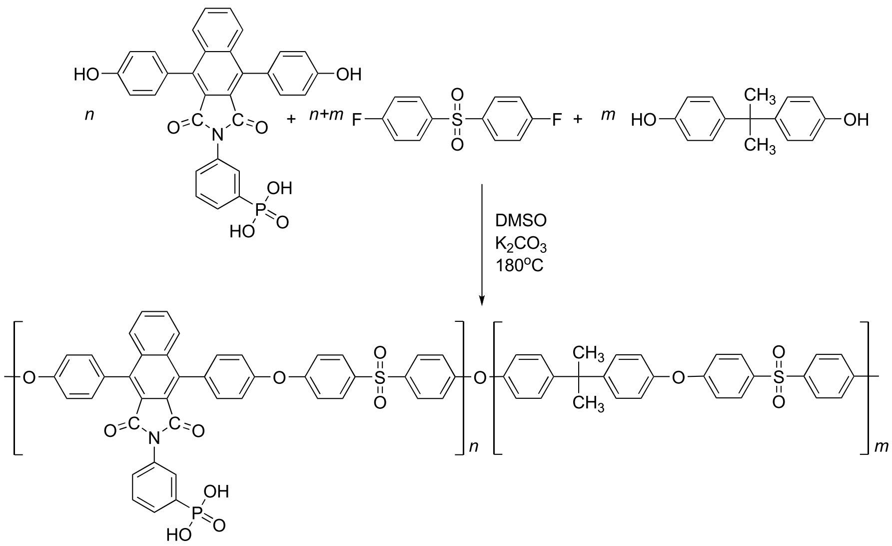
[a] In NMP at 27 °C
[b] Temperature for 10% weight loss under nitrogen
[c] Polymerization run at 200 °C in NMP



Scheme 4

dione – phenolphtaleine derivative [50, 51] – with *m*-aminophenylphosphonic acid (Scheme 4).

Poly(arylene ethers) containing phosphonic acid groups were prepared from the *bis*-phenol (mixed with *bis*-phenol A) and 4,4′-difluorodiphenyl sulfone [48, 49] in accordance with Scheme 5:



Scheme 5

The poly(arylene ethers) with various compositions were prepared.

Because of the very low nucleophilicity of phosphonic acid salts, high molecular weight polymers were obtained in a prolonged time of 5 hrs. The phosphorus-31 nuclear magnetic resonance (^{31}P-NMR) spectrum of polymers showed a single peak at 12.286 ppm indicating the presence of phosphonic acid group in the polymer chain.

Thus, general properties of the polymers were obtained, as given in Table 4.

As listed in Table 4, all the polymers have high molecular weights. Therefore, these polymers can easily be cast into tough clear and flexible films. Polymer based on 3-[4,9-*bis*(4-hydroxyphenyl)-1,3-dioxo-(1,3-dihydrobenzo[*f*]isoindolo-2-yl)-phenyl]-phosphonic acid only has the lowest molecular weight since the polymer precipitated during the polymerization reaction. Tg_s of the copolymers increase linearly with increasing phosphonic acid group content. The introduction of ionic moiety into the polymer generally leads to an increase of the interaction among the polymers chains; therefore, homopolymer (n_C = 10.0) has no detectable Tg. The thermogravimetric data indicates that the polymers listed in Table 4 are thermooxidatively stable, while the TGA_{onset} of these polymers decrease with the increase of phosphonic acid content. Nevertheless 5% weight loss temperature ($TGA_{5\%}$)

Table 4 Properties of polymers

n %	*m* %	3_{inh}	EM[a]	Water[b] Absorption %	*Tg* (°C)	$\text{TGA}_{\text{onset}}$ (°C)	$\text{TGA}_{5\%}$ (°C)	Proton Conductivity (S cm^{-1})
25	75	0.67	518	3.2	254	289.8	502.4	6.78×10^{-6}
50	50	0.60	596	4.7	277	245.7	498.0	2.96×10^{-5}
75	25	0.54	673	6.4	315	229.1	480.5	1.86×10^{-5}
100	0	0.43	750	7.5	ND	194.2	476.1	1.32×10^{-5}

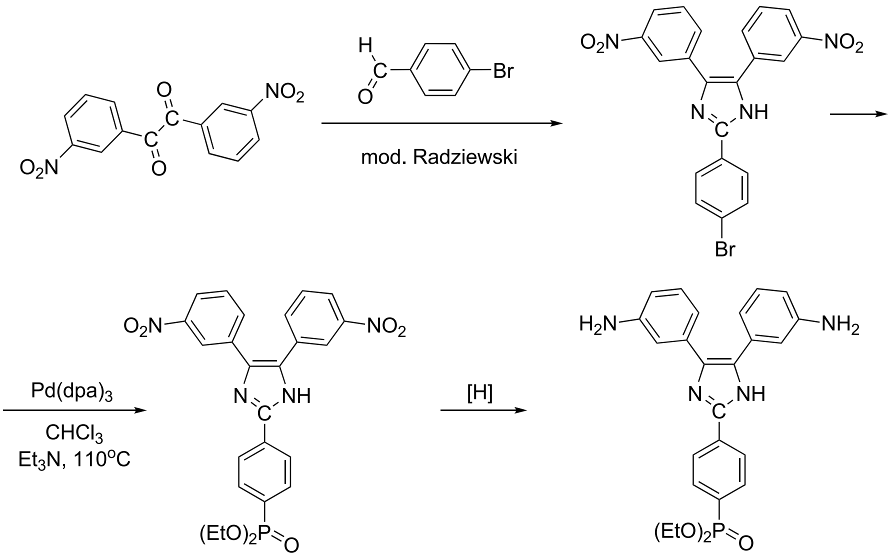
[a] EM-equivalent molecular weights that are defined as the equivalent weight per phosphonic acid group

[b] Water absorption in hot water (12 hrs)

is much higher than $\text{TGA}_{\text{onset}}$ for these polymers, demonstrating that these polymers are more stable than Nafion [52].

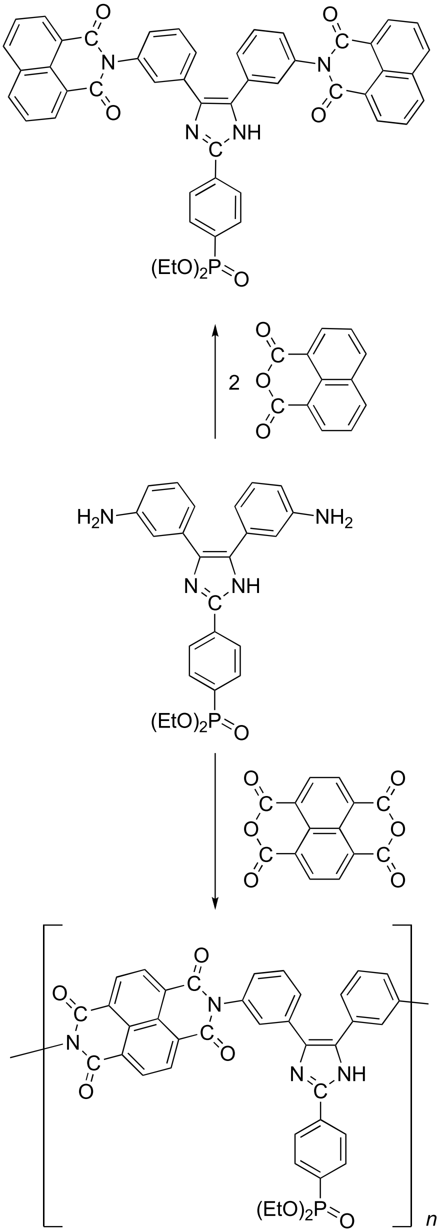
The proton conductivity of copolymer (50 : 50) was determined to be $2.96 \times 10^{-5}\ \text{S cm}^{-1}$. It is three orders of magnitude lower than that of Nafion ($10^{-2}\ \text{S cm}^{-1}$ under moisture). Surprisingly, there was no further increase in conductivity when the phosphonic acid moiety was larger than 50%. The conductivity decreased by a factor of two to $1.32 \times 10^{-5}\ \text{S cm}^{-1}$, because the increase in *Tg* values leads to the decrease in conductivity.

New diamine containing phosphonic acid groups – (4-[4,5-*bis*(3-aminophenyl)-1*H*-imidazol-2-yl]-phenyl)phosphonic acid diethyl ester – [53] was



Scheme 6

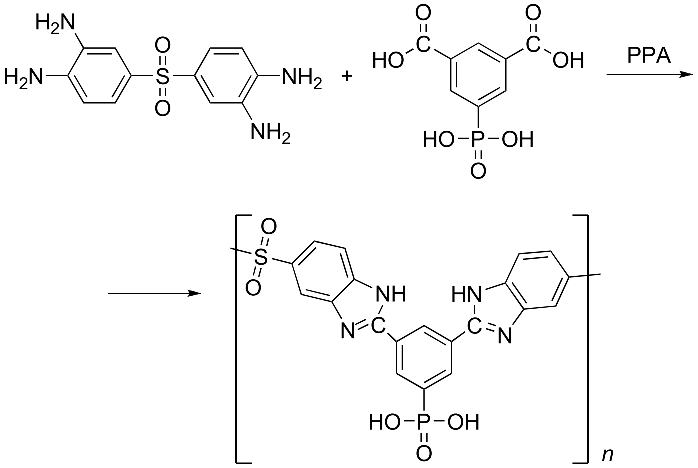
prepared in accordance with the scheme, including the interaction of 3,3′-dinitrobenzyl with *p*-bromobenzaldehyde [54] P – C coupling and reduction of the diethyl phosphonate (Scheme 6).



Scheme 7

Interaction of this diamine with two-fold molar amount of naphthalic anhydride and equimolar amount of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride led to the formation of *bis* (model) compound and polynaphthylimide-containing phosphonic acid groups, respectively (Scheme 7).

Phosphonated polybenzimidazoles were prepared by the interaction of 3,3′,4,4′-tetraaminodiphenylsulfone with 3,5-dicarboxylbenzenephosphonic acid (DCP) (Scheme 8) [55].

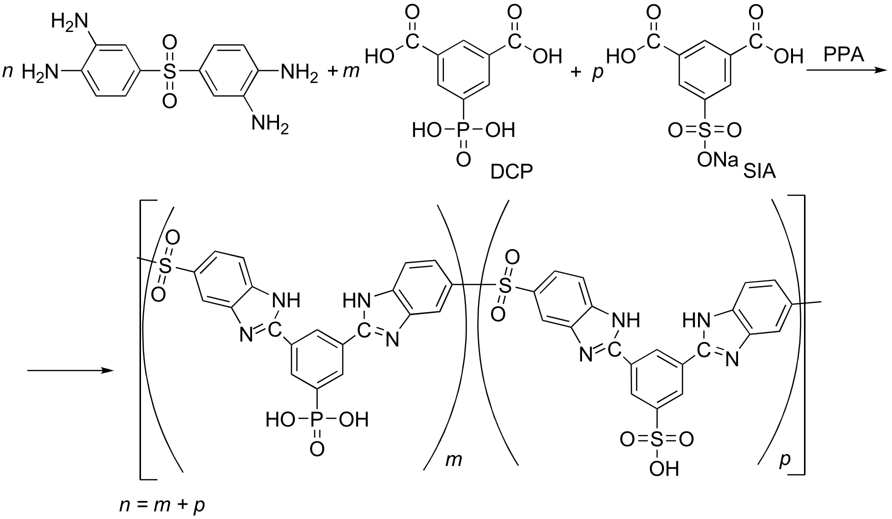


Scheme 8

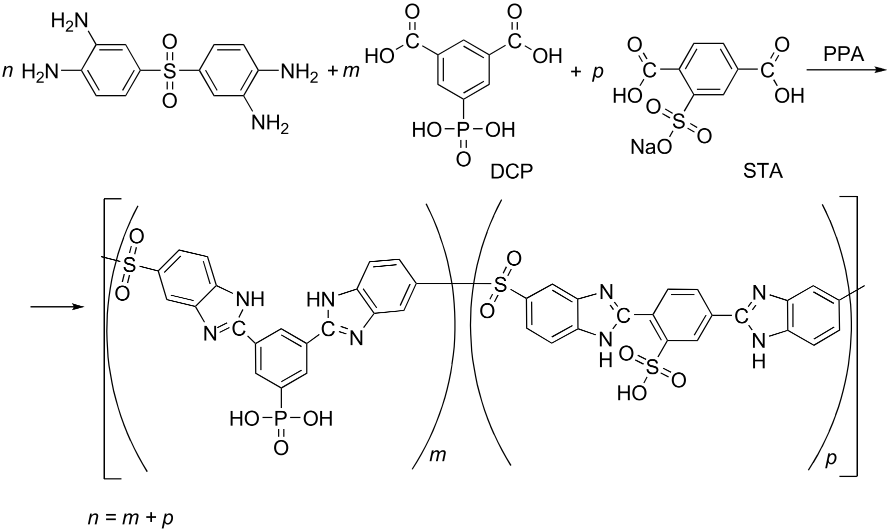
The proton conductivity of such polymers was close to 10^{-2} S cm^{-1}, and it was higher than that of sulfonated polymers. Although the phosphonated structure has advantage of increasing the proton conductivity in ion-containing polybenzimidazole, incorporation of DCP in these polymers decreases the solubility in *N*-methyl-2-pyrrolidone (N-MP).

In order to obtain the membrane in which both conductivity and solubility coexist, copolymers containing sulfonic and phosphonic acid groups at the same time were prepared (Schemes 9, 10) [55]. As dicarboxylic acids containing sulfonic acid groups 5-sulfoisophthalic acid monosodium salt (SIA) and 2-sulfoterephthalic acid monosodium salt (STA) were used.

The copolymer with STA : DCP = 50 : 50 showed good solubility in N-MP, but only similar level of conductivity to the sulfonated polymer. When the content of DCP was increased to STA/DCP = 30 : 70, the conductivity jumped to similar level of phosphonated polymer, while maintaining the solubility in N-MP. Further increase of DCP content to STA/DCP = 15 : 85 induced the decrease in solubility. There is a narrow region where good conductivity and solubility coexist in these copolymers. Ion-containing polybenzimidazoles showed excellent stability against hydrolysis, radical attack and dimensional change in wet/dry cycles.



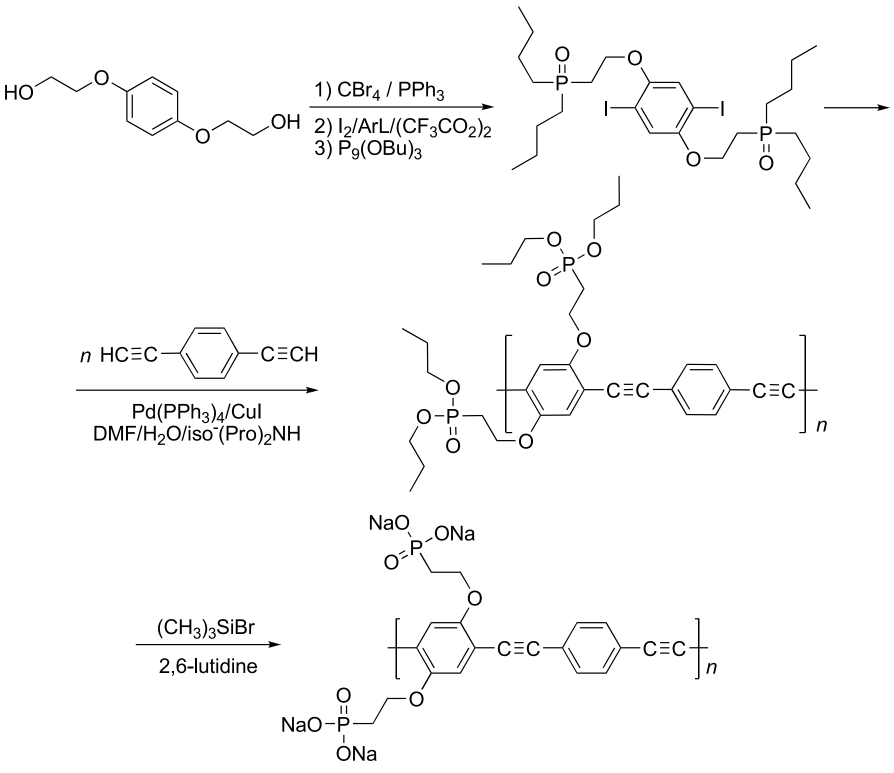
Scheme 9



Scheme 10

In a recent preliminary report [56], Shanze et al. described poly(phenylene ethynylene) which feature phosphonate groups appended to the polymer backbone (Scheme 11).

The phosphonated polymer was prepared via a neutral precursor polymer, which was soluble in organic solvents, enabling the material to be characterized by nuclear magnetic resonance (NMR) and gel permeation chromatog-



Scheme 11

raphy (GPC). Sonogashira polymerization of phosphonate monomer and 1,4-diethynylbenzene afforded neutral polymer in a 46% yield. Analysis of the neutral precursor polymer indicated $M_w = 18.3$ kD and polydispercity 2.9.

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

Generally, preparation of phosphonic acid functionalized monomers and their polymerization are problematic, because of the strong aggregation and condensation of phosphonic acid units which result in poor yields [7, 33, 56–58]. Consequently, a more attractive strategy is to phosphorylate existing polymers [59].

2.2
Phosphorylation of Existing Polymers

A number of procedures are well established for the preparation of aryl phosphonic acids by introducing phosphonic functional groups into aromatic compounds of low molecular weight [60], but some of them proved to be inappropriate for a polymeric starting material. The Friedel–Crafts reaction using phosphorus trichloride is, for example, a common efficient and low-cost procedure for direct phosphonation of aromatic rings. Systematic studies of this reaction on polystyrenes showed, however, that the trifunctionality of phosphorus trichloride leads to cross-linked products regardless of reaction conditions [61, 62].

Nevertheless, the possibility of modification of polysulfones main chains by Friedel–Crafts reaction with phosphorus trichloride and $SnCl_4$ as a catalyst was demonstrated by Ziaja et al. [63].

Recently, Jakoby et al. [64, 65] reported a synthesis of phosphonated polyphenylsulfone. This group has focused their efforts on two straightforward reactions for the synthesis of aryl phosphonic acids from brominated or iodinated aromatic starting materials.

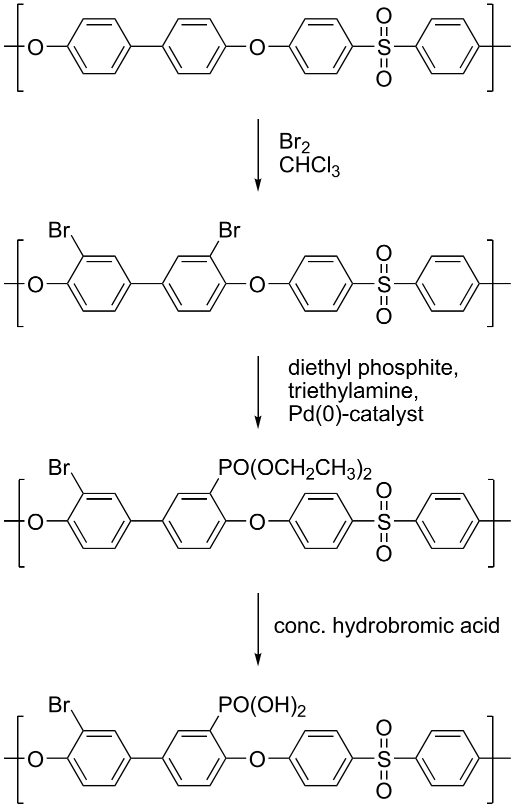
The bromination of different polysulfones, including polyphenylsulfone, was described in details by Guiver et al. [66]. The characterization of the product by elemental analysis gave a degree of substitution of 2 Br atoms per repeating unit of the polymeric structure.

The electron-donating effect of the ether linkages of the main chain activates the phenylene rings of the *bis*-phenol part towards nuclephilic attack, and they may, thus, be used as positions for halogenation, such as bromination [66].

After bromination, two different procedures were tested for a bromine-phosphorus exchange. The first one is the Michaelis-Arbuzow reaction in the presence of transition metal salt catalysts [41, 42]; the second one is a P – C coupling reaction catalyzed by Pd (0) complexes [43–45]. Both reactions are usually carried out without any solvent. It was found that the reaction conditions of the P – C coupling reaction could be adapted to the application of polymeric substrates [65].

The Michaelis-Arbuzow reaction was adapted to polymeric substrates using high-boiling solvents, such as dimethylacetamide (DMA) and N-MP. The application of these polar solvents was necessary, because triethyl phosphite is a very strong precipitation medium for polymeric substrate. It turned out that the Michaelis–Arbuzow reaction was very slow, either due to the dilution of the components in the mixture or due to the sterical hindrance of reaction sites on the polymer chain. As a consequence, the reduction of the metal catalyst by triethyl phosphite, which is a common and well-known side reaction for this procedure [41], was favored and became predominant. The rapid reductive deactivation process of the catalyst could be observed by color changes of the reaction mixture. After adding the first drops of triethyl phosphite to the mixture at 150 °C, the green active catalyst species were converted into colorless Ni(0) complexes or black Pd metal particles within 1 hour.

The Pd(O)-catalyzed P – C bond formation is another convenient modern method for the preparation of aryl phosphonic acids from aryl bromides or iodides and diethyl phosphite (DEP). The reaction conditions had to be modified again for polymeric substrates, because the conversion is usually carried out with liquid aryl halides at 90 °C in the absence of an additional solvent. The reaction for dibrominated polyphenylsulfone is depicted in Scheme 12:



Scheme 12

Diethyl phosphite turned out to be a less efficient precipitation medium for the dibrominated polyphenylsulfone than triethyl phosphite.

Systematic investigations showed that the polymer is soluble in mixtures of diethyl phosphite and *o*-dichlorobenzene (DEP : DCB = 1 : 2.5 v/v or 2 : 1 v/v), and insoluble in any of the pure components. Two different Pd(O) complexes with triphenyl phosphine or dibenzylideneacetone (dba) were used as ligands. Triethylamine (TEA) was required for the removal of the HBr side product. It is well known that the molar rations of the components, the choice of the catalyst, and the reaction temperature have a strong influence on the yield of the phosphonation product [67, 68]. Therefore, systematic variations of these parameters and their effect on the degree of phosphonation of the polymer material were investigated (Table 5).

Table 5 Influence of reaction conditions on the substitution (phosphonation) degree (DS – number of phosphoric groups per monomer unit)

Product no.	Temp. °C	Catalyst	Procedure	Solvent	DS [a]	Product weight [c] g
1	90	$Pd(PPh_3)_4$	2	DCB	0.40	8.5
2	120	$Pd(PPh_3)_4$	2	DCB	0.58	7.9
3	140	$Pd(PPh_3)_4$	2	DCB	decomposition	
4	120	$Pd_2(dba)_3 \cdot CHCl_3$	2	DCB	0.77	8.5
5	120	$Pd_2(dba)_3 \cdot CHCl_3$	3	DPE	0.88	9.2
6 [b]	120	$Pd_2(dba)_3 \cdot CHCl_3$	4	none	0.79	8.3
7	110	$Pd(PPh_3)_4$	2	pyridine	decomposition	

[a] Determined by ^{1}H NMR spectroscopy

[b] Post-phosphonation of product 4 in the absence of any additional solvent

[c] Starting from 10 g polymer

Due to solubility problems of the polymer, the reaction had to be started in presence of only 9–13 equivalents of diethyl phosphite and 1–2 equivalents of triethylamine, related to aryl bromide units. As the solubility of the polymer improved during phosphonation, the concentration of DEP and TEA could gradually be increased, until, finally, a molar ratio of ArBr : DEP : TEA = 1 : 22 : 4 resulted, which comes close to the reaction conditions described in [69].

An increase of the reaction temperature from 90 to 120 °C enhances the degree of phosphonation. If the temperature was further increased to 140 °C, the yellow color of the reaction mixture turned dark, and decomposition was observed. The Pd catalyst was obviously more active in the absence of triphenyl phosphine ligands. The highest degrees of phosphonation were achieved by using diphenyl ether as a solvent, instead of *o*-dichlorobenzene.

All phosphonated products could easily be converted into the free phosphonic acids by acid hydrolysis of the esters.

Concerning the polymer stability, the TGA curves show weight loss in the temperature range between 225 and 325 °C. According to the literature [34, 70], a weight loss between 250 and 350 °C is attributed to the fragmentation of the ethyl phosphonate units into the free acid and ethylene, and possibly a subsequent formation of anhydride groups from two phosphonic acids. This explains why the first weight loss in TGA curves was not found for free phosphonic acid samples.

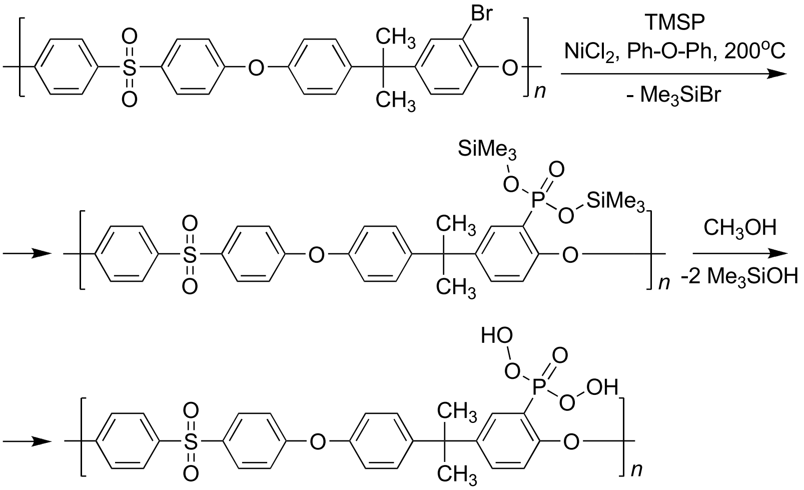
The decomposition of the polymeric free phosphonic acids only started above 350 °C. Unreacted bromine atoms are also believed to split above 250 °C [70].

All the polymers with free phosphonic acid pendant groups are insoluble in methanol and water. They are soluble in DMA or DMSO up to a DS of

0.58, whereas the highly phosphonated sample with a DS above 0.75 did not completely dissolve any longer. In DMA, these samples only formed a highly swollen polymer gel. It turned out, however, that the addition of 2 vol % of concentrated hydrobromic acid to the mixtures led to rapid dissolution. The gelation is supposed to be caused by strong ionic clusters in the highly functionalized material. These clusters are destroyed by the mineral acid.

For film casting, a solution with 8 wt % of polymer in DMA was prepared in the presence of 2 vol % of concentrated HBr. The resulting polymer films were mechanically stable and clear. These films are under investigation as solid electrolyte membranes for fuel cell applications.

Transformation of the brominated polyethersulfones to the phosphonated polyethersulfones was carried also using Ni catalysts. Mulhaupt et al. [71] have prepared phosphonated polyethersulfones via the treatment of the brominated polyethersulfone with tris-(trimethylsilyl)phosphate (TMSP) catalyzed with $NiCl_2$ and subsequent methanolysis of the reaction product (Scheme 13).



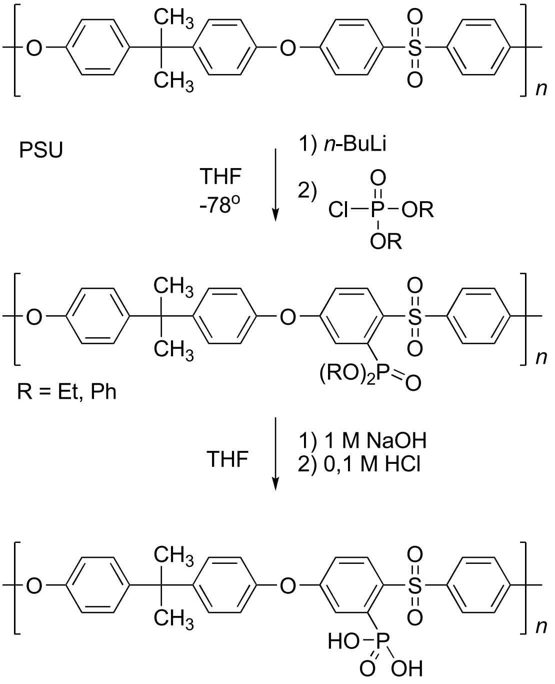
Scheme 13

Resulting polymers dissolve in N-MP or N-MP containing 2–5 vol % conc. HCl. In accordance with TGA data, degradation of polymers with arylphosphonic acids groups started at temperature >325 °C. Analog of this polymer containing sulfonic acid groups started to desulfonate at >200 °C. Depending on the conversion degree, protonic conductivity of the phosphonated polyethersulfone was ranged between 1.2–8.7 mSm cm^{-1}, which was lower than the conductivity of the polyethersulfone containing sulfonic acid groups (20 mSm cm^{-1}).

Another attractive way of functionalizing poly(arylene ether sulfone) is lithiation, followed by the reaction of the lithiated sites with an electrophile.

Savignac et al. [72] made an extensive study on the synthesis of phosphonates by nucleophilic substitution at phosphorus, a so-called $S_NP(V)$ reaction. They showed that organolithium compounds are the reagents of choice for the synthesis of phosphonates, because these compounds generally minimize the formation of side products.

In the frame of work [59],the feasibility of employing an $S_NP(V)$ reaction between lithiated polysulfones and either dialkylchlorophosphates or diarylchlorophosphates to phosphonate polysulfones without the use of a catalyst was investigated (Scheme 14):

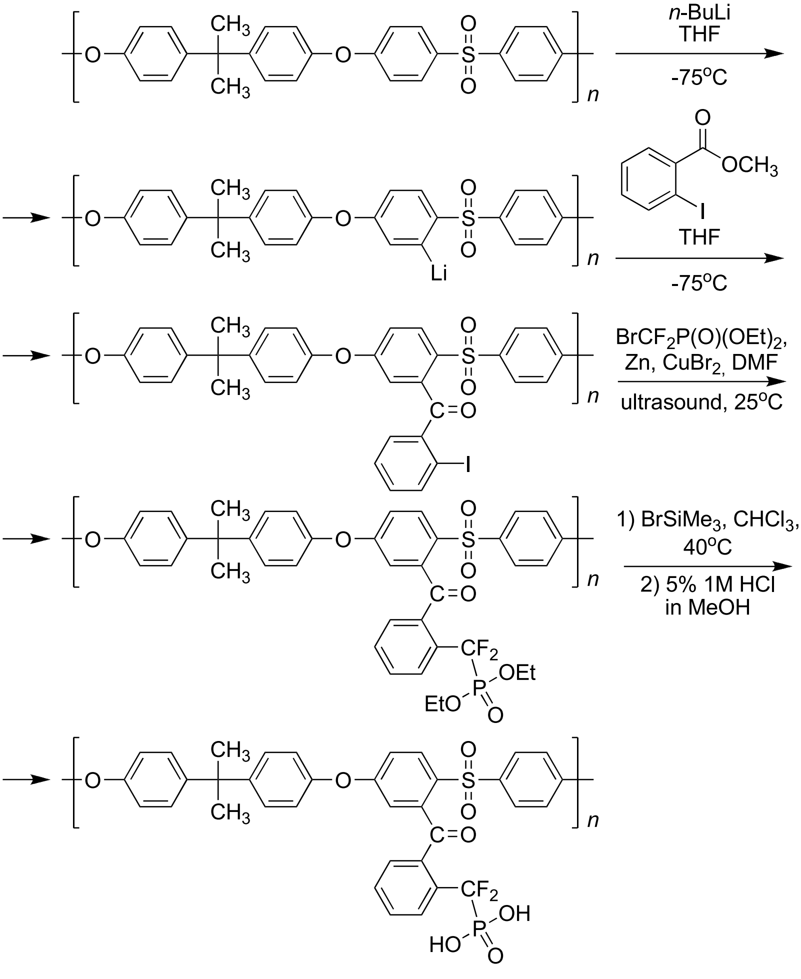


Scheme 14

Polysulfone, PSU, is an amorphous aromatic polymer that consists of alternating bisphenol A and biphenyl sulfone segments. The strong electron-withdrawing effect of the sulfone units gives a slight acidic character to the *ortho*-to-sulfone aromatic hydrogen. Thus, the carbon at these positions may be metalyzed by the use of a strong base, such as *n*-BuLi [73].

The use of lithium chemistry is a versatile and convenient way of modifying PSU. Moreover, lithiation and a subsequent reaction with an electrophile do not give rise to chain scission or any other degradation in the polysulfone main chain [74].

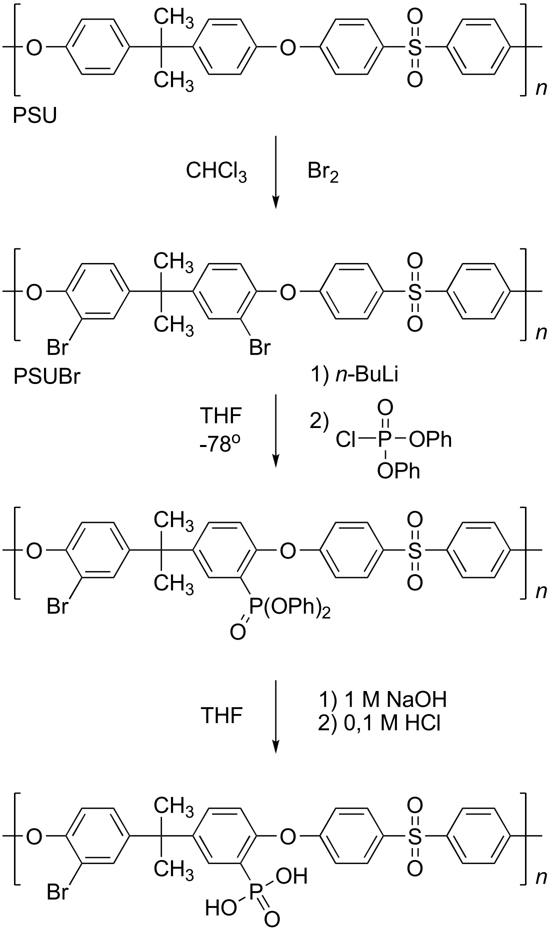
Polysulfones carrying benzoyl(difluoromethylenephosphonic) acid side groups [75] were prepared in accordance with (Scheme 15):



Scheme 15

In the first step, polysulfones were lithiated and reacted with methyl iodobenzoates to prepare *p*- and *o*-iodobenzoyl polysulfones. Next, the phosphonated polysulfones were prepared via CuBr – mediated cross-coupling reactions between the iodinated polymer and [(diethoxyphosphinyl)difluoromethyl]zinc bromide. Finally, dealkylation with bromotrimethylsilane afforded highly acidic $-CF_2-PO_3H_2$ derivatives. The replacement of the iodine atoms by $-CF_2-PO_3H_2$ units was almost quantitative in the case of *o*-iodobenzoul polysulfone. Membranes based on ionomers having 0.90 mmol of phosphonic acid units/g of dry polymer demonstrated protonic conductivities up to 5 mSm cm^{-1} at 100 °C. Thermogravimetry revealed that aryl-$CF_2-PO_3H_2$ arrangement decomposed at approximately 230 °C via cleavage of the C – P bond [75].

Alternative approach to the phosphonated PSU is based on lithiation of brominated PSU, because the halogen-lithium exchange is favored over the proton-lithium exchange at low temperatures [66] (Scheme 16):



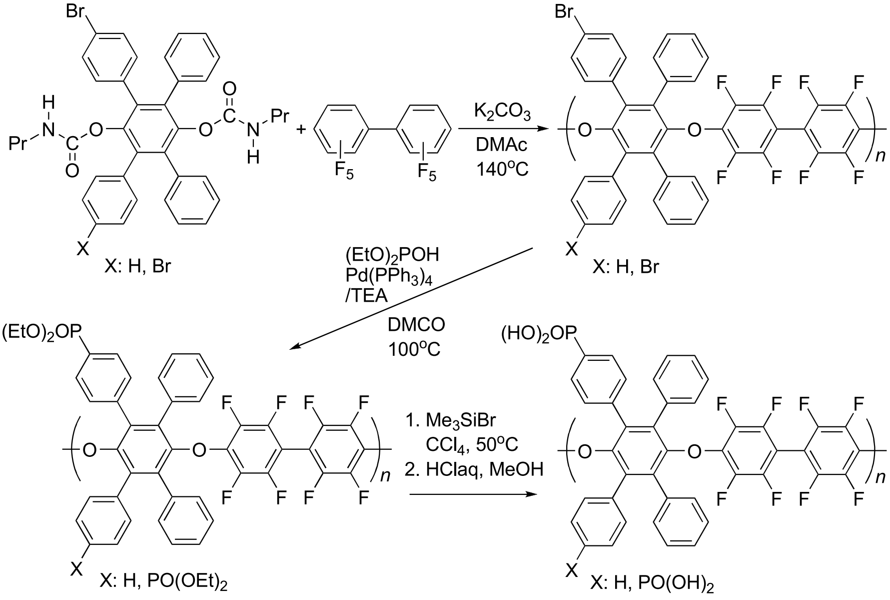
Scheme 16

Along with poly(arylene ether sulfones), some other polymers were phosphonated using above-mentioned procedures.

Hay and coworkers [76] reported on a catalyzed P – C coupling reaction to synthesize phosphonated poly(arylene ethers) (Scheme 17).

Starting *bis*-propylcarbomate-masked derivatives of mono- and dibromotetraphenylhydroquinone were prepared in accordance with the Scheme 18.

Highly fluorinated poly(aryl ether) with a phosphonic acid group was prepared by Guiver et al. [77] in accordance with the Scheme 19.



Scheme 17

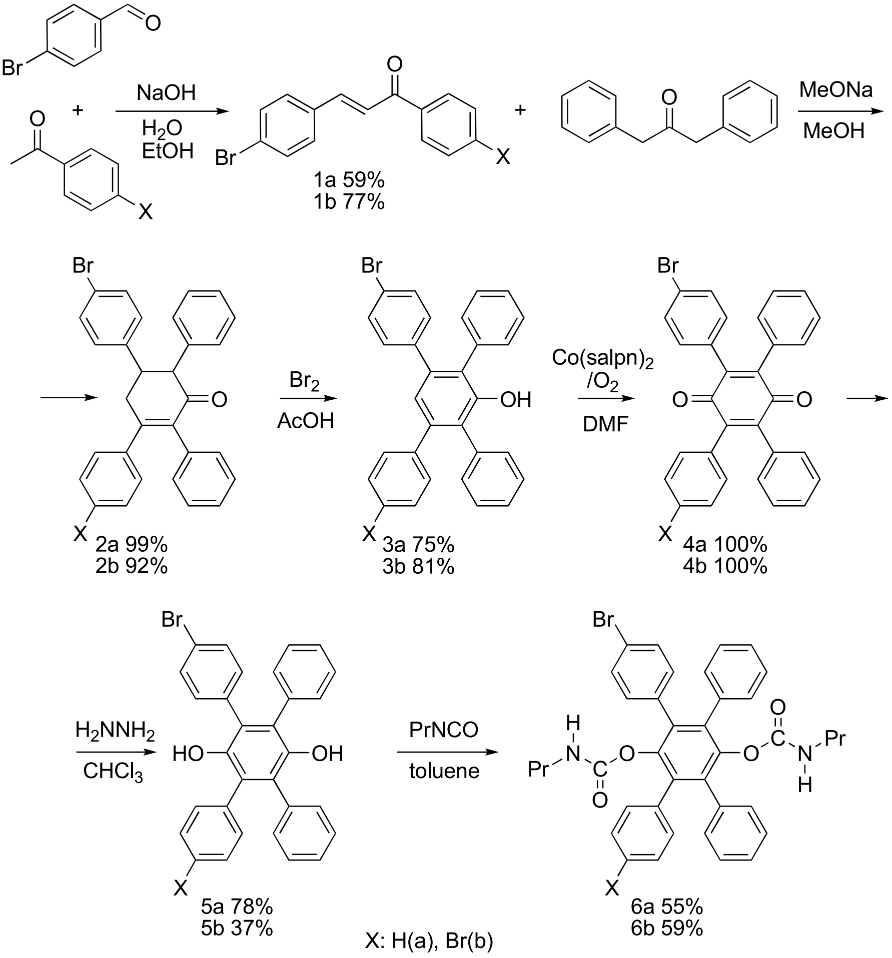
The polymer obtained has high thermal stability – no obvious decomposition is observed until the main chain decomposition at ~420 °C. Polymer is readily soluble in DMA, DMF, DMSO, and N-MP. The high solubility of the polymers enables thin films to readily be prepared.

Because of its higher temperature stability than its $-SO_3H$ analog and the possibility of conductivity at low humidity levels, polymer with phosphonic acid groups ($-PO_3H_2$) has been studied as potential candidate for use as PEM material. It showed promising conductivity up to 2.6×10^{-3} S cm^{-1} in water at room temperature, and 6.0×10^{-3} S cm^{-1} at 95% relative humidity at 80 °C. It also exhibits an extremely low methanol permeability value of 1.07×10^{-8} cm^2 S^{-1}.

An attempt to synthesize ethylphosphorylated polybenzimidazole was reported [2] using the Scheme 20.

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 could 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 polymer electrolytes.

Polybenzimidazole, whose phosphoric acid sites are linked to aromatic rings by means of alkylene spacers, were prepared by deprotonation of start-



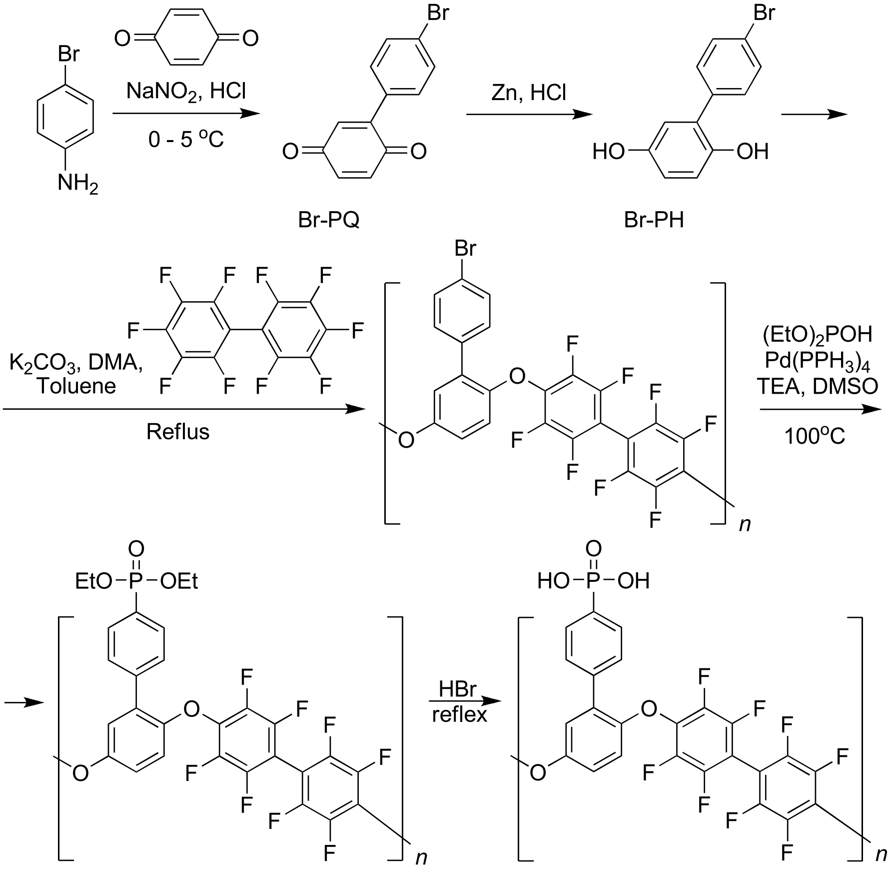
Scheme 18

ing polymers and subsequent conversion with chloro- or bromoalkylphosphonates [58].

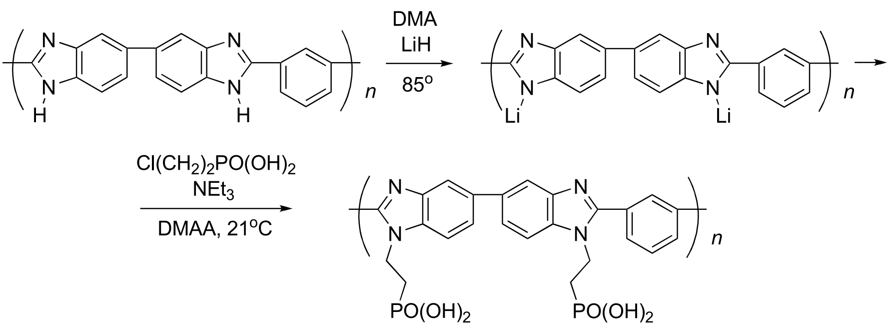
The instability of benzylic methylene groups in an oxidizing environment is, however, a severe shortcoming of these materials for fuel cell applications.

N-substituted polybenzimidazoles, containing phosphonic acid groups which are linked to benzimidazole cycles by means of ethylenic groups, were prepared by treatment of different polybenzimidazoles with diethylvinylphosphonate [78] in accordance with Scheme 21.

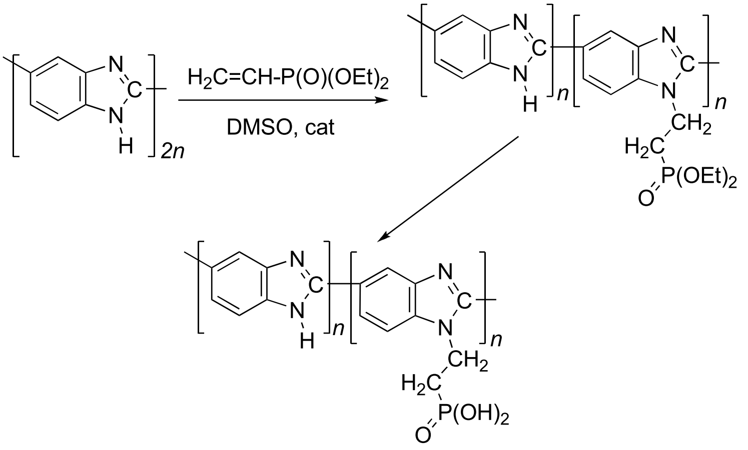
Allcock and coworkers [79–81] reported on phosphonation of polyphosphazenes. Incorporation of pendent phosphate groups into aryloxyphosphazenes through phosphorylation (phosphorus-oxygen-carbon linkages) led to the formation of polymers containing phosphate ester bonds.



Scheme 19



Scheme 20



Scheme 21

However, phosphate ester bounds are known to have limited thermal stability and are subject to chemical attack by hydroxide ions, which may result in hydrolysis of the phosphorous-oxygen-carbon linkage and cleavage of pendent phosphate group [82].

As a result, the incorporation of pendent phosphate groups into aryloxyphosphazenes attached through phosphonate (phosphorus-carbon) linkages was examined. The use of direct phosphorus-carbon bond ensures greater thermal and chemical stability [82, 83], which should provide materials with more versatile properties.

The linkage of pendent phosphate groups to aryloxyphosphazenes is of interest, because the conversion of pendent dialkyl phosphate groups to phosphoric acid groups could lead to interesting and useful proton conducting membranes.

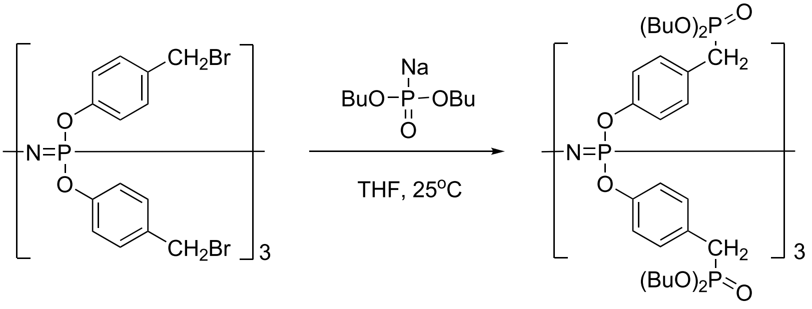
Two methods for the incorporation of dialkyl phosphonate units into the side groups of aryloxyphosphazenes were developed [80].

In the first approach, small molecule cyclic (Scheme 22) and high polymeric (Scheme 23) phosphazenes bearing bromomethylene – phenoxy side groups are treated with a sodium dialkyl phosphite, as shown in Scheme 22.

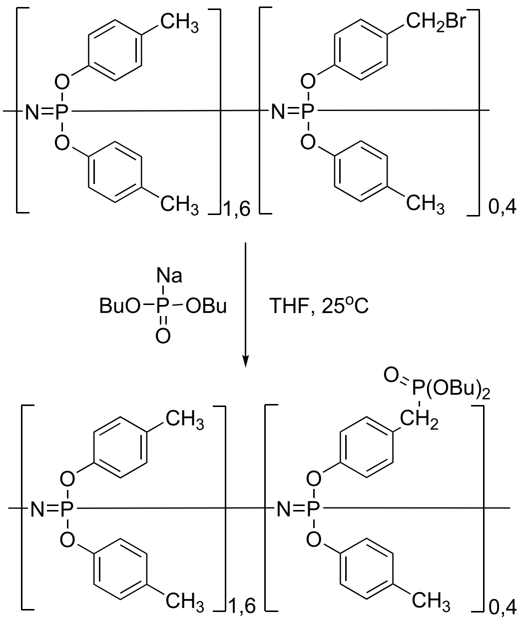
This method yields well-defined products at both the small-molecule and high polymeric level.

In the second route, a previously attempted procedure [64] was used, in which small-molecule cyclic (Scheme 24) and high polymeric (Scheme 25) phosphazenes bearing bromophenoxy side groups are treated with *n*-butyllithium, followed by a dialkyl chlorophosphonate, as shown in Scheme 24.

This method was improved for the synthesis of aryloxyphosphazenes with pendent dialkylphosphonate groups, and it led to well-defined products at both the small-molecule and polymeric level.



Scheme 22



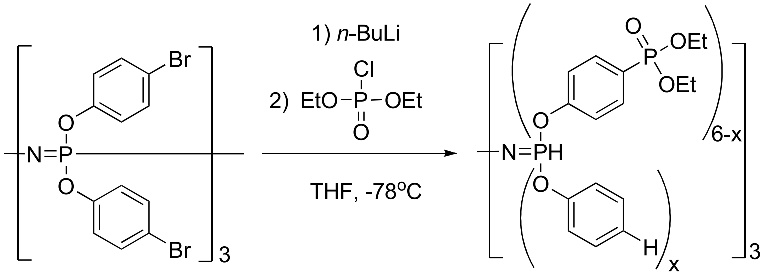
Scheme 23

Conversion of these pendent dialkyl phosphonate groups to phosphonic acid groups is a potential route to proton-conductive fuel cell membranes.

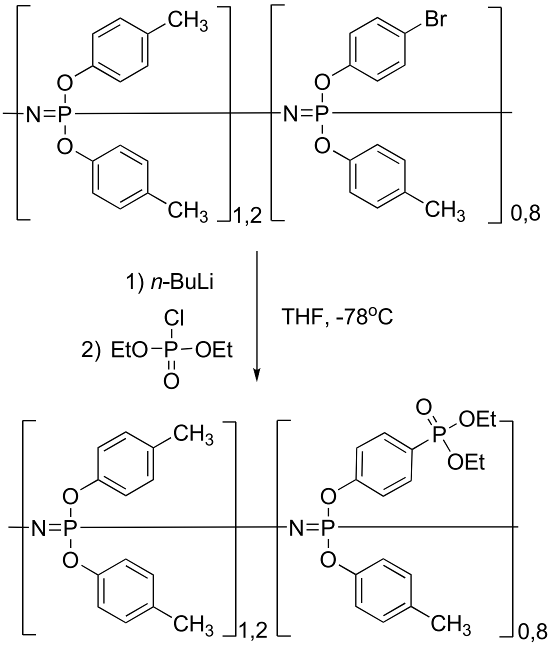
Phenylphosphonic acid functionalized poly-[aryloxyphosphazenes] were prepared [81] in accordance with the Scheme 26.

Phosphonation of poly(aryloxyphosphazenes) via lithiophenoxy intermediates was realized via addition of *tert*-butyllithium to a solution of the polymer in THF at −75 °C. The lithiated polymers were then treated with diphenyl chlorophosphate, and subsequent basic hydrolysis and acidification yielded phenylphosphonic groups, as shown in Scheme 26.

Initial attempts to phosphonate the lithiated polymers via the dropwise addition of diphenyl chlorophosphate resulted in precipitation of the polymer



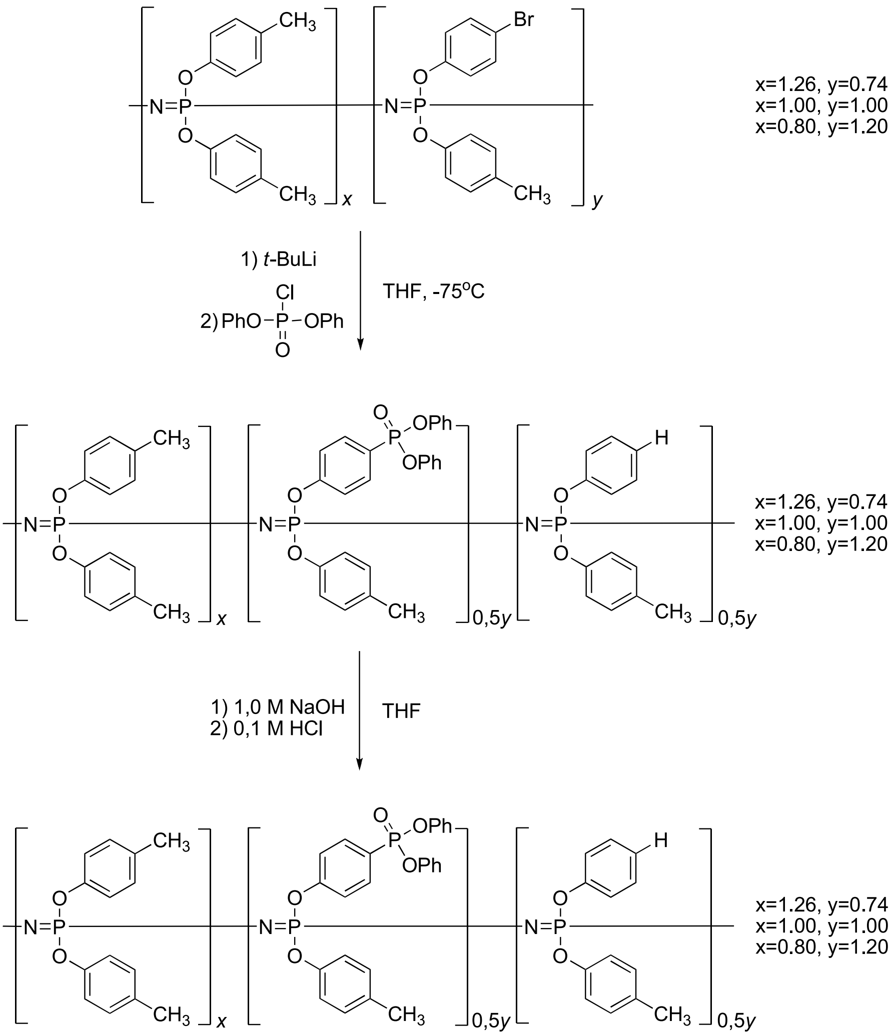
Scheme 24



Scheme 25

and formation of insoluble product. However, soluble product was obtained by the rapid addition of diphenyl chlorophosphate. On the basis of ^{31}P-NMR spectroscopy data, it was concluded that intramolecular coupling reaction takes place; in this reaction diphenyl phosphonate ester sites on the polymer react with a second lithio-phenoxy side groups on the same polymer backbone, resulting in a phosphorus bridge between two aryloxy side groups, as shown in Scheme 27.

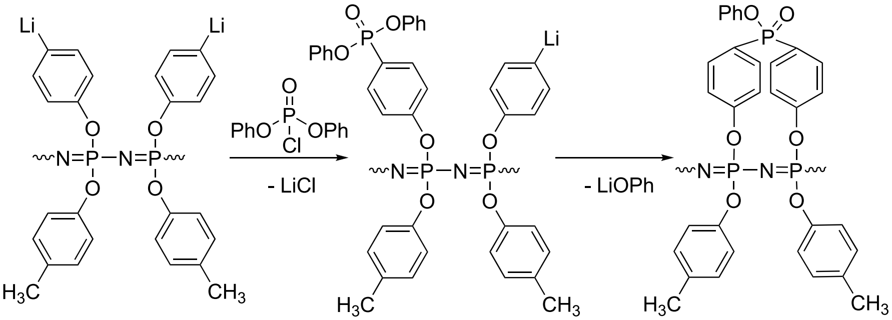
This was attributed to an intramolecular reaction rather than the analogous intermolecular cross-linking reaction, due to the high solubility of the polymers.



Scheme 26

The overall efficiency of the phosphonation method, with respect to percent conversion of the initial bromine atoms present, was determined by ^{31}P-NMR spectroscopy.

Phosphonation of polymers via lithiophenoxy intermediates proceeded with ~50% conversion of the bromophenoxy side groups to diphenyl phosphonate ester side groups. The total percentage of lithiophenoxy groups that had reacted with the diphenyl chlorophosphate was 70%. However, only ~50% of the lithiophenoxy groups resulted in formation of the diphenyl phosphonate ester.



Scheme 27

Elemental analysis revealed that >90% of the initial bromine atoms had been lithiated. Thus, rather than incomplete lithiation, the limiting factor in the overall reaction appears to be the side reaction of the highly reactive lithiophenoxy intermediate, which may occur during the addition of diphenyl chlorophosphate. This is also consistent with observations made using diethyl chlorophosphate [81].

Hydrolysis of the diphenyl phosphonate ester groups was accomplished by treatment of a THF solution of the phosphonated polymers with 1.0 M NaOH over 24 h. During this reaction, the polymer precipitates from solution, at which point little further hydrolysis take place. No change in the molecular weight of the polymers was detected, confirming the stability of the phosphazenes backbone to the basic hydrolysis conditions.

The advantage of this synthesis protocol is the freedom to tune the polymer composition and properties by varying the initial aryloxy side group ration, the degree of lithiation, and the amount of ester hydrolysis.

These polymers have been evaluated as membrane materials for fuel cell applications [84, 85]. They have low methanol diffusion characteristics; methanol diffusion coefficients for these membranes were found to be at least 12 times lower than that for Nafion 117 and 6 times lower than that for a cross-linked sulfonated polyphosphazene membrane [83, 84]. Membranes were found to have IEC values between 1.17 and 1.47 mequiv/g and proton conductivities between 10^{-2} and 10^{-1} S/cm. They appear to be superior to sulfonated polyphosphazene analogues [84, 85].

3
Conclusions

To summarize, the aforesaid shows that heterochain and heterocyclic polymers carrying phosphonic acid groups can be thought of as candidates for fuel cell applications. Of especially great interest are phosphorylated polyethers, polysulfones, polybenzimidazoles, and polyphosphazenes prepared on the basis of phosphonic acid functionalized monomers or by phosphorylation of existing polymers. Further investigations are required to design proton-conducting materials exhibiting long-term thermal stability and mechanical strength, capable of operating at high temperatures.

Acknowledgements This work was supported by the North Atlantic Treaty Organization (NATO) (Grant 981 672).

References

1. Watkins S (1993) Fuel Cell Systems. Plenum Press, New York
2. Zawodzinski TA, Deraum C, Rodzinski S, Sherman RT, Smith UT, Springer TE, Gottesfeld S (1993) J Elecrochem Soc 140:1041
3. Gottesfeld S, Zawodzinski TA (1997) In: Akire RC, Gerischer H, Kobb DM, Tobias CW (eds) Advances in electrochemical science and engineering, (5). Wiley, New York
4. Savadogo OJ (1998) J New Mater Electrochem Syst 1:47
5. Kordesch KV, Simader GR (1995) Chem Rev 95:191
6. Kreuer KD (1996) Chem Mater 8:610
7. Rikukawa M, Sanui K (2000) Prog Polym Sci 25:1463
8. Kerres JA (2001) J Membr Sci 185(1):3
9. Costamanga P, Srinivasan S (2001) J Power Sources 102:242
10. Steele BCH, Heinzel A (2001) Nature 414:345
11. Roziere J, Jones DJ (2003) Annu Rev Mater Res 33:503
12. Yang HC (2003) Nengyuan Jikan 33(2):127
13. Jannasch P (2003) Curr Opin Colloid Interface Sci 8:96
14. Hickner MA, Ghassemi H, Kim YS, Einsla BR, McGrath JE (2004) Chem Rev 104:4587
15. Rusanov AL, Likhachev DY, Mullen K (2002) Russ Chem Rev 71:761
16. Rusanov AL, Likhachev D, Kostoglodov PV, Mullen K, Klapper M (2005) Adv Polym Sci 179:83
17. Dobrovol'skiy YA, Volkov EV, Pisareva AV, Fedotov YA, Likhachev DY, Rusanov AL (2007) Russ J Gen Chem 77:766
18. Dobrovolskiy YA, Jannasch P, Lafitte B, Belomoina NM, Rusanov AL, Likhachev DY (2007) Russ J Electrochem 43(5):489
19. Javaid Zaidi SM (2003) Arab J Sci Eng 28(2B):183
20. Lafitte B, Karlsson LE, Jannasch P (2002) Macromol Rapid Commun 23:896
21. Karlsson LE, Jannasch P (2004) J Membr Sci 230:61
22. Wang F, Hickner M, Kim YS, Zawodzinski TA, McGrath JE (2002) J Membr Sci 197:231
23. Harrison WL, Wang F, Mecham JB, Bhanu VA, Hill M, Kim YS, McGrath JE (2003) J Polym Sci, Part A: Polym Chem 41:2264
24. Gao Y, Robertson GP, Guiver MD, Jian XG (2003) J Polym Sci, Part A: Polym Chem 41:497
25. Gao Y, Robertson GP, Guiver MD, Jian XG, Mikhailenko SD, Wang KP, Kaliaguine S (2003) J Polym Sci, Part A: Polym Chem 41:2731
26. Genies C, Mercier R, Sillion B, Cornet M, Gebel G, Pineri M (2001) Polymer 42:359
27. Wang F, Li J, Chen T, Xu J (1999) Polymer 40:795
28. Li Q-F, He R-H, Jensen JO, Bjerrum NJ (2003) Chem Mater 15:4896
29. Cerfontain H (1968) Mechanistic Aspects in Aromatic Sulfonation and Desulfonation; Interscience Monographs on Organic Chemistry. Interscience Publ New York

30. Lafitte B, Jannasch P (2007) Adv Fuel Cells 1(3):119
31. Rusanov AL, Solodova EA, Bulycheva EG, Abadie MJM, Voytekunas VY (2007) Russ Chem Rev 76:1073
32. Nolte R, Ledjeff K, Bauer M, Mulhaupt R (1993) BHR Group Conf Ser Publ 3:381
33. Xu X, Cabasso I (1993) Polym Mater Sci Eng 68:120
34. Kotov SV, Pedersen SD, Qui WM, Qui ZM, Burton DJ (1997) J Fluorine Chem 82(1):13
35. Jaffe HH, Fredman LD, Doak GO (1953) J Am Chem Soc 75:2209
36. Lassegues JC, Grondin J, Hernandes M, Maree B (2001) Solid State Ionics 145:37
37. Yamabe M, Akiyama K, Akatsuka Y, Kato M (2000) Eur Polym J 36:1035
38. Kosolapoff GM (1942) J Am Chem Soc 64:2982
39. Balthazor TM, Miles JA, Stults BR (1978) J Org Chem 43:4538
40. Foa M, Cassar L (1975) J Chem Soc, Dalton Trans, p 2753
41. Tavs P (1970) Chem Ber 103:2428
42. Balthazor TM, Grabiak RC (1980) J Org Chem 45:5425
43. Hirao T, Masunagawa T, Ohshiro Y, Agawa T (1981) Synthesis 1:56
44. Hirao T, Masunagawa T, Yamada N, Ohshira Y, Agawa T (1982) Bull Chem Soc Jpn 55:909
45. Yan YY, RajanBabu TV (2000) J Org Chem 65:900
46. Miyatake K, Hay AS (2001) J Polym Sci, Part A: Polym Chem 39:1854
47. Wang ZY, Carvalho NH, Hay AS (1991) J Chem Soc Chem Commun 17:1221
48. Meng YZ, Tjong SC, Hay AS, Wang SJ (2001) J Polym Sci, Part A: Polym Chem 39:3218
49. Meng YZ, Tjong SC, Hay AS, Wang SJ (2003) Eur Polym J 39(3):627
50. Meng YZ, Hill AR, Hay AS (2001) Polym Adv Technol 12:206
51. Meng YZ, Abu-Yousef IA, Hill AR, Hay AS (2000) Macromolecules 33(25):9185
52. Gierke TD, Munn GE, Wilson FC (1981) J Polym Sci, Part B: Polym Phys 19:1687
53. Alvares-Gallego Y, Lozano AE, Ferreiro JJ, Nunes SP, Abajo Jde (2002) In: Kricheldorf HR (ed) Polycondensation 2002. 25th Hamburger Macromolekulares Symposium, Hamburg 1:113
54. Akutsu F, Inoki M, Sawano M, Kasashima Y, Naruchi K, Miura M (1998) Polymer 39:6093
55. Sakaguchi Y, Kitamura K, Takase S (2005) In: Abstracts of Pacific Polymer. Conference IX, Mani Hawaii E-16
56. Pinto MR, Reynolds JR, Schanze KS (2002) Am Chem Soc Polym Prepr 43(1):139
57. Stone C, Daynard TS, Hu LQ, Mah C, Steck AE (2000) J New Mater Electrochem Syst 3(1):43
58. Samsone MJ, Onorato FJ, Ogata N, Hoechst Celanese Corp (1997) US Patent 5 599 639
59. Lafitte B, Jannasch P (2005) J Polym Sci, Part A: Polym Chem 43:273
60. Yasuda M, Yamashita T, Shima K (1990) Bull Chem Soc Jpn 63:938
61. Alexandratos SD, Strand MA, Quillen DR, Walder AJ (1985) Macromolecules 18:829
62. Popescu F (1969) Rev Roum Chim 14:1525
63. Ziaja J, Balogh L, Trochimczuk WW (1998) In: Prace Naukowe Inst Podstaw Eleck-trotech Electrotechnol Politech Wroclawskiej 34:153
64. Lehmann D, Meier-Haack J, Vogel C, Taeger A, Pereira Nunes S, Paul D, Peinemann K-V, Jakoby K (2003) Patent WO/2003/030289
65. Jakoby K, Peinemann KV, Nunes SP (2003) Macromol Chem Phys 204:61
66. Guiver MD, Kutowy O, ApSimon JW (1989) Polymer 30:1137
67. Park J, Lee JPH (1997) Bull Korean Chem Soc 18:1130
68. Skoda-Foldes R, Kollar L, Horvath J, Tuba Z (1995) Steroids 60(12):791
69. Hirao T, Kohno S, Ohchira Y, Agawa T (1983) Bull Chem Soc Jpn 56:1881
70. Cabasso I, Jagur-Grodzinski J, Vofsi D (1974) J Appl Polym Sci 18:1969

71. Bock T, Mülhaupt R, Möhwald H (2006) Macromol Rapid Commun 27:2065
72. Eymery F, Iorda B, Savignac P (1999) Tetrahedron 55:13109
73. Guiver MD, ApSimon JW, Kutowy O (1988) J Polym Sci, Part C: Polym Lett 26:123
74. Guiver MD, Robertson GP, Yoshikawa M, Tam CM (2000) ACS Symp Ser 744:137
75. Lafitte B, Jannasch P (2007) J Polym Sci, Part A: Polym Chem 45(2):269
76. Miyatake K, Hay AS (2001) J Polym Sci, Part A: Polym Chem 39:3770
77. Liu B, Robertson GP, Guiver MD, Shi Z, Navessin T, Holdcroft S (2006) Macromol Rapid Commun 27:1411
78. Rybkin YY (2005) In: PhD Thesis INEOS RAS Moscow
79. Allcock HR, Taylor JP (2000) Polym Eng Sci 40:1177
80. Allcock HR, Hofmann MA, Wood RM (2001) Macromolecules 34:6915
81. Allcock HR, Hofmann MA, Ambler CM, Morford RV (2002) Macromolecules 35:3484
82. Goldwhite H (1981) In: Introduction to Phosphorus Chemistry. Cambridge University Press Cambridge England
83. Hutchinson DW (1991) In: Townsen LB (ed) Chemistry of Nucleosides and Nucleotides. Plenum Press, New York
84. Allcock HR, Hofman MA, Ambler CM, Lvov SN, Zhou XY, Chalkova E, Weston J (2002) J Membr Sci 201:47
85. Fedkin MV, Zhou XY, Hofmann MA, Chalkova E, Weston JA, Allcock HR, Lvov SN (2002) Mater Lett 52:192