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Synthesis of polymers with protogenic groups by polymer-analogous transformations

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Abstract. The progress in the synthesis of polymers containing sulfonic and phosphonic acid groups by polymer-analogous transformations is analysed. Two key methods for the introduction of these groups are considered, namely, metallation of the original polymers followed by functionalisation and modification of reactive fragments of macromolecular chains. Special concern is focused on the properties of polymeric materials obtained. The bibliography includes 71 references.

I. Introduction

Permanently growing interest in fuel cells and their key components, proton-conducting membranes,[1–10] is the challenge for the search for new methods of the synthesis of polymeric electrolytes containing protogenic (sulfonic and phosphonic acid) groups. Despite significant progress in the creation of proton-conducting membranes based on basic polymer – acid complexes,[11] the membranes based on solid polymeric electrolytes in which the protogenic groups are linked to macromolecules by covalent bonds are the most interesting. These systems are usually prepared by functionalisation (for example, sulfonation or phosphorylation) of polymeric compounds or by polymerisation of monomers containing sulfonic and phosphonic acid groups.[1–10]

Each approach has its advantages and drawbacks. Thus, many aromatic polymers can readily be sulfonated at fragments with the highest electron density. However, sulfonic groups located at these positions can be substituted under the action of H^+, which decreases hydrolytic stability of sulfonated polymers in highly acidic media. The synthesis of polymers from monomers containing protogenic groups is complicated due to reduced reactivity and labourious procedure for purification of the starting compounds.

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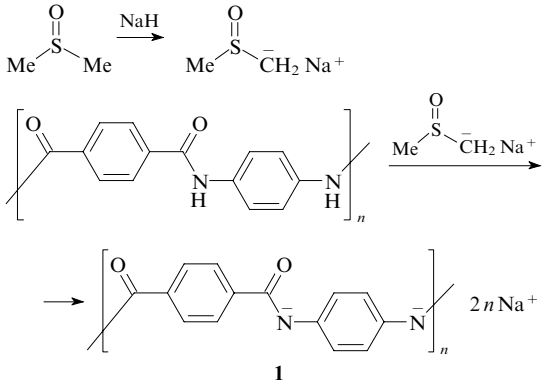
Currently, an alternative approach to the synthesis of polymers containing sulfonic and phosphonic acid groups is being developed, namely, polymer-analogous transformations of compounds containing protogenic groups in an explicit or latent form. In the present review, progress in development of this promising field of polymer chemistry is analysed.

II. Transformations of metallated polymers

Introduction of sulfonic acid groups into macromolecules usually includes preliminary metallation of polymers followed by the treatment of polyanions with compounds containing sulfonic acid groups in an explicit or latent form. Most researchers apply this method for the preparation of sulfonylated polyamides and polybenzimidazoles.

1. Polyamides and polybenzimidazoles containing sulfonic and phosphoric acid groups

Metallation of aromatic polyamides, primarily poly(*p*-phenyleneterephthalamide) (PPPTA), is discussed by Takayanagi *et. al.*[12–22] and by other researchers.[23–27] Treatment of PPPTA with sodium hydride in DMSO results in deprotonation of the amide groups of PPPTA to yield polyanion **1**.

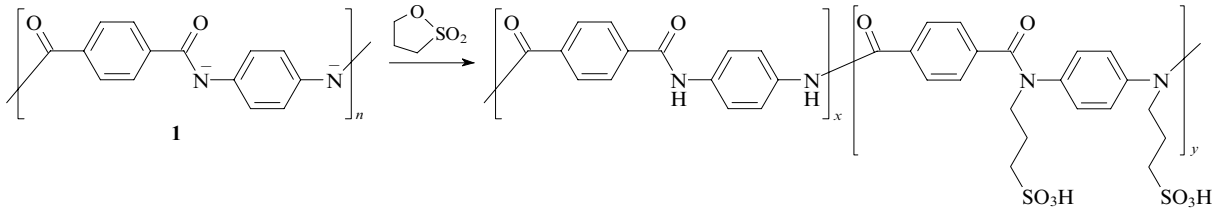


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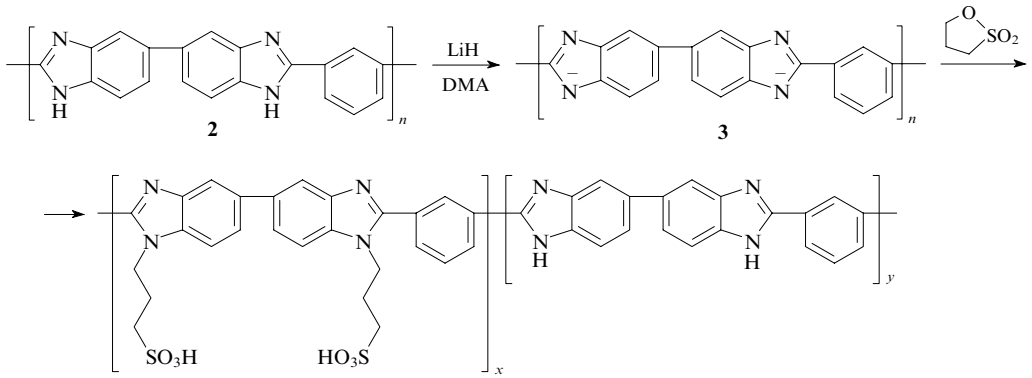
Subsequent reaction of polyanion **1** with propane 1,3-sultone gives a copolymer of *p*-phenyleneterephthalamide and 3-(*p*-phenyleneterephthalamido)propanesulfonic acid (Scheme 1).[28]

Transformation of poly(2,2′-*m*-phenylene-5,5′-dibenzimidazole) **2** was carried out in a similar way.[29–36] The corresponding polyanion **3** was prepared by the reaction of the initial polymer with lithium hydride in dimethylacetamide (DMA) (Scheme 2). The final reaction product is polybenz-

Scheme 1



Scheme 2



imidazole (PBI) containing propanesulfonic acid residues (PBI-PS).

Polymers with butanesulfonic acid (PBI-BS) and methylpropanesulfonic acid (PBI-MPS) residues were synthesised from polybenzimidazole and butane 1,4-sultone and butane 2,4-sultone, respectively, using the same procedure.

The degree of substitution (α) of sulfoalkyl groups for the hydrogen atoms at the nitrogen atom in polybenzamide was estimated from the ^{1}H NMR and elemental analysis data; α appeared to depend on the reactant ratio. For instance, α reaches 60% at a propane-1,3-sultone : PBI ratio equal to 5. PBI modified with these groups are better soluble in polar organic solvents (for example, in DMA or DMSO) than the initial polymers, solubility also depending on the α value.

Introduction of sulfoalkyl substituents into aromatic macromolecules gives heat-resistant proton conducting polymeric electrolytes having electrochemical characteristics that can be controlled by changing the amount of protogenic groups and the length of alkyl chains. These polymers exhibit good moisture absorption and proton conductivity, close to those observed for sulfonic groups, but they retain such important characteristics as heat resistance, chemical stability, and mechanical strength.

Heat resintance of PPPTA and PBI, as well as of their sulfoalkyl derivatives have been compared in a number of publications (see, for example, Ref. 32). It was found that no destruction of PPPTA occurs in a nitrogen atmosphere up to 550 °C, whereas fast mass loss (up to 50% of the initial mass) starts at 600 °C. Polymers modified with sulfopropyl side groups (α = 66%) are stable to 400 °C; at 800 °C 40% of the initial mass is retained.

Heat resistance of anhydrous copolymer PBI-PS was studied by thermogravimetric analysis (TGA) in a nitrogen atmosphere.[5] Destruction of PBI-PS occured in the temperature range of 400–450 °C, that is, at significantly lower temperatures than that of the initial PBI.

In spite of the fact that for copolymer PBI-PS, destruction temperature decreases to 400 °C with increasing α, it is nevertheless higher than destruction temperature for perfluorinated polymeric electrolytes (280 °C).

Elemental analysis and FTIR studies of destruction of copolymer PBI-PS showed that the sulfur content and the intensity of the S–O absorption band decrease following heating of the samples at the temperature above 400 °C for 1 h. This result is similar to that obtained by Gieselman and Reynolds,[32] who have found that destruction of PBI-PS was connected with desulfonation processes. Destruction temperatures for sulfonated aromatic polymeric electrolytes lie within the range of 200–350 °C. Thus, polybenzimidazoles containing sulfoalkyl groups are more heat resistant. Heat resistance of sulfoalkyl polymers is the result of strong chemical bond between alkyl and sulfonic acid groups. Introduction of sulfoalkyl groups into the polymer with the use of alkane sultones is one of the most common methods for the synthesis of heat-resistant proton-conducting polymeric electrolytes.

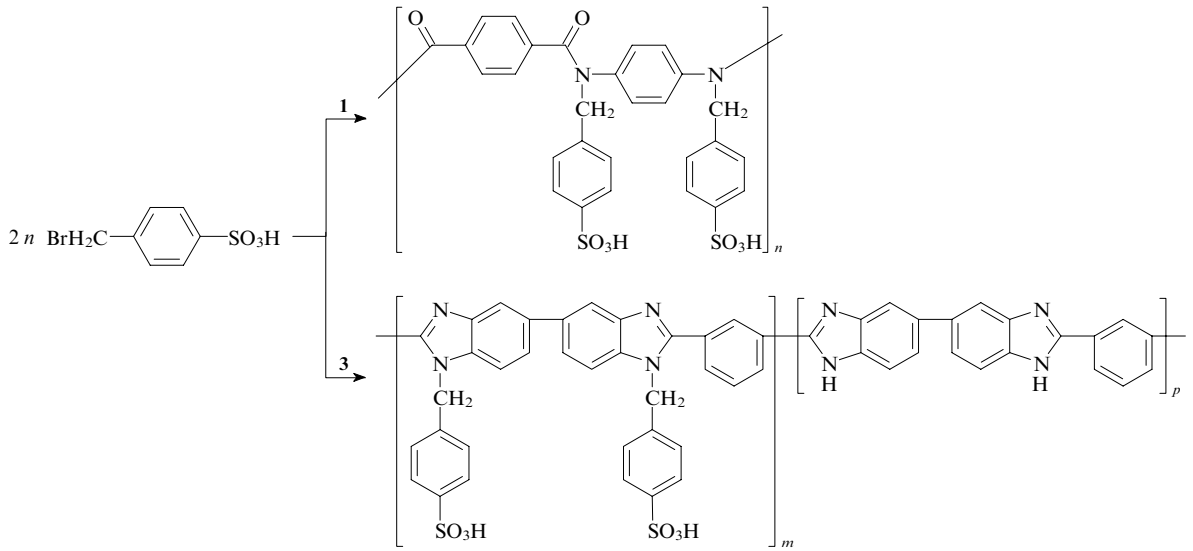
Arenesulfonic acid fragments can also be introduced into aromatic condensation polymers. Thus polyanions **1** and **3** prepared from PPPTA and poly(2,2′-*m*-phenylene-5,5′-dibenzimidazole), respectively, readily react with *p*-bromomethylbenzenesulfonic acid (Scheme 3).[28–36]

The peripheral sulfobenzyl substituent is detached from the polymeric chain under more drastic conditions than the sulfopropyl group, this being independent of the polymer type.

The above-considered polymers were studied by TGA in inert and oxidative (in the presence of oxygen) environments.[33] The initial PBI is a heat-resistant polymer: in an inert atmosphere, the mass loss begins at 650 °C, 5% mass loss is observed at 700 °C and at 800 °C, >80% of the initial mass is retained. Mass loss for substituted polymers in an inert environment starts at lower temperatures, as could be expected upon introduction of substituents non-conjugated with the polymer backbones. Destruction of poly (2,2′-*m*-phenylene-1,1′-(4-sulfobenzyl)-5,5′-dibenzimidazole) with α = 22% starts at 480 °C, while that with α = 54% starts at 450 °C. After elimination of all substituents from the polymer, the process slows down; at 800 °C, 50%–60% of the initial mass is retained.

In dry air, the mass loss of polybenzimidazole starts at 520 °C, whereas its destruction in an inert environment starts at a temperature about 100 °C lower. Substituted PBI demonstrate insignificant difference in destruction temperatures in oxidative environments. The main difference in the behaviour of polymers in air and in a nitrogen atmosphere is that in air the mass losses are markedly higher, but the amount of the residual

Scheme 3



coke at high temperatures is much less. This effect originates first from the lower stability of PBI in dry air and only then from the influence of substituents.

Introduction of sulfoaryl and sulfoalkyl groups into aromatic polymers increases moisture absorption, in other words, polymers become more hygroscopic. Moisture absorption of polymers is defined as a change in the polymer mass prior and after hydration and depends on the relative humidity of the medium. Equilibrium moisture absorption for the copolymer PBI-PS increases with an increase in relative air humidity and degree of sulfoalkylation. For example, moisture absorption of PBI-PS with $\alpha = 73.1\%$ is 11.3 mol H_2O (g-mol $SO_3H)^{-1}$ (see†) at a relative humidity of 90% and room temperature, whereas polymeric membrane Nafion 117 (perfluorinated polymer containing a small amount of sulfonate groups) has a moisture absorption of 11.0 mol H_2O (g-mol $SO_3H)^{-1}$ under the same conditions. Moisture absorption values for copolymers PBI-BS and PBI-MPS at a relative air humidity of 90% are 19.5 and 27.5 mol H_2O (g-mol $SO_3H)^{-1}$, respectively. These high dehumidification values for sulfoalkylated PBI result from a larger length and branching of alkyl chains. This seems to be associated with larger flexibility of long alkyl chains and larger water amount capable of being absorbed in cavities formed by branched substituents.

Studies of proton conductivity of polymers under consideration show that hydrated copolymers PBI-PS demonstrate high proton conductivity at room temperature. Conductivity of PBI-PS containing 3.1 mol H_2O (g-mol $SO_3H)^{-1}$ reaches 10^{-5} S cm^{-1} at 80 °C and somewhat decreases at higher temperatures due to moderate (about 10 mass %) loss of water. Conductivity of the PBI-PS film containing > 5.2 mol H_2O (g-mol $SO_3H)^{-1}$ increases with increase in temperature and reaches a value of 10^{-3} S cm^{-1} at temperatures above 100 °C. The PBI-PS film containing more water [moisture absorption 11.3 mol H_2O (g-mol $SO_3H)^{-1}$] also demonstrates high proton conductivity ($\sim 10^{-3}$ S cm^{-1}).

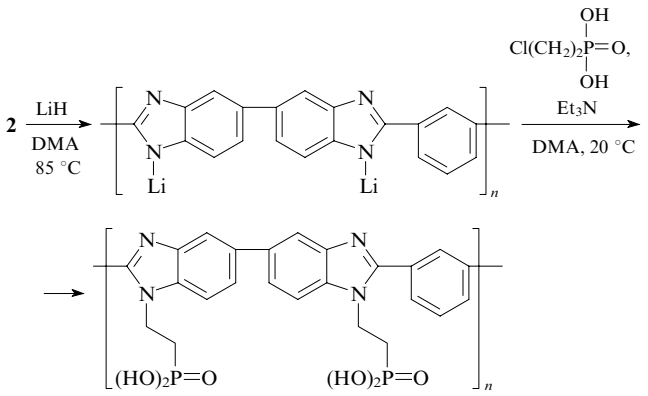
Moisture absorption values for membranes prepared from copolymers PBI-PS at a relative air humidity of 90% are comparable with that for Nafion.

Proton conductivity of the membrane Nafion reaches 10^{-3} S cm^{-1} at room temperature, but it decreases at temperatures > 100 °C due to a loss of absorbed moisture.[37] In contrast, high proton conductivity of hydrated PBI-PS is retained at temperatures above 100 °C. High values of moisture absorption and proton conductivity for copolymers PBI-PS at elevated temperatures are associated with peculiar behaviour and physical state of absorbed water.

The above results give reasons to conclude that sulfoalkyl aromatic polymeric electrolytes possess sufficient heat resistance to be used in fuel elements at 80 °C, that is, at the temperature that is optimal for the work of membranes based on perfluorinated polymeric electrolytes.

Study of proton conductivity of sulfobenzylated PBI at various relative humidity values showed[38] that conductivity increases with an increase in degree of substitution. Sulfobenzylated polybenzimidazole with $\alpha = 75\%$ demonstrates high conductivity (about 10^{-2} S cm^{-1}) at 40 °C and 100% relative humidity.

Phosphoalkylated polymer was obtained by metallation of PBI **2** followed by introduction of the phosphoethyl groups.[5]

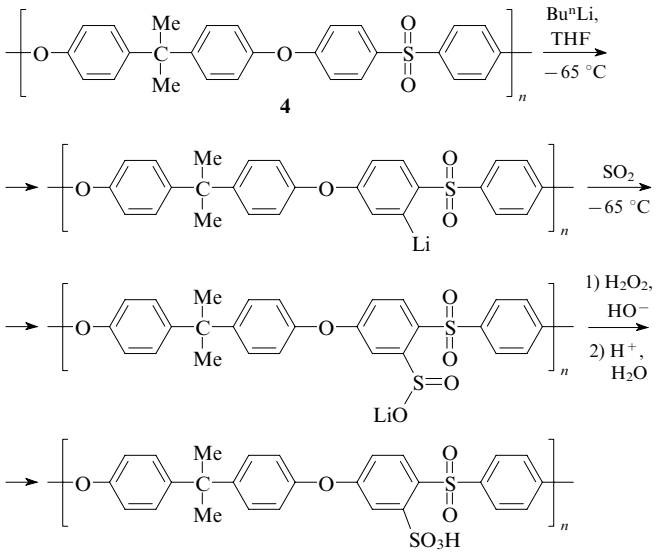


N-Substitution of the benzimidazole ring occurs readily. However, the polymer formed is insoluble in organic solvents, probably, due to self-aggregation of the phosphonate groups in the course of substitution. Phosphoethylated PBI demonstrates high proton conductivity (10^{-3} S cm^{-1}) even in the form of a pellet. Thus, it can be stated that introduction of polar phosphonic acid groups is an efficient method for the preparation of novel proton-conducting polymeric electrolytes.

† Hereinafter moisture absorption is expressed as moles of H_2O per 1 g-mol of SO_3H.

2. Poly(ether sulfones) containing sulfonic and phosphoric acid groups

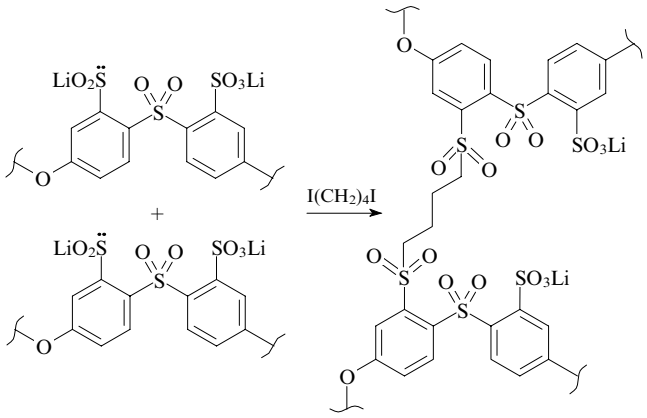
Metallation of polymers was also used for the introduction of protogenic groups into poly(ether sulfone)s (PES).[39–41] Synthesis of sulfonated PES based on commercially produced poly(ether sulfone) Udel (**4**) was reported.[39] The process includes lithiation of the polymer, treatment of the product with sulfur dioxide, oxidation of lithium sulfinate formed to lithium sulfonate, and transformation of the latter into corresponding polysulfonic acid under the action of HCl.



This approach allows the introduction of sulfonic acid groups into positions that determine high hydrolytic stability of the target polymers.[39]

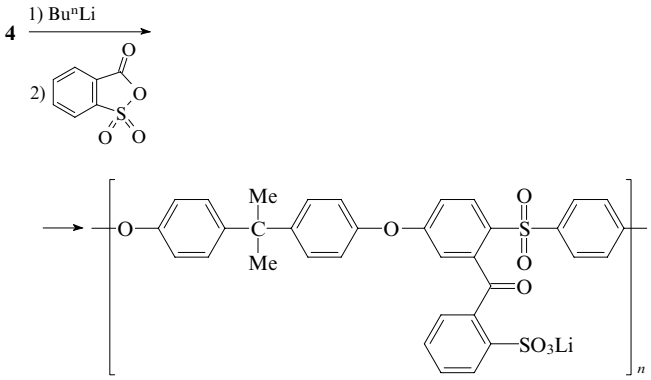
Sulfonated PES prepared in this way exhibit ion exchange capacity of $(0.5-3.2)\times10^{-3}$ g-mol SO_3H per 1 g of polymer. Membranes based on these polymers are characterised by high conductivity and hydrolytic stability in 1 N HCl and in water at temperatures up to 80 °C.

In continuation of this study, partial oxidation of lithium sulfinate groups of PES formed to lithium sulfonate groups was carried out,[40] and the residual lithium sulfinate groups were alkylated with α,ω-diiodoalkanes. This alkylation gave cross-linked polymers, which were transformed into the acidic form by the action of 1 N HCl.



Membranes from polymers obtained in this way with optimum degree of cross-linking and the length of alkylene cross-linking bridges demonstrate low ionic resistance and high heat resistance.

Lithiation of PES is also used for the preparation of sulfophenylated systems.[41] In this case, a metallated polymer reacts with cyclic anhydride of 2-sulfobenzoic acid, which followed by ion exchange under the action of 0.5 N HCl.

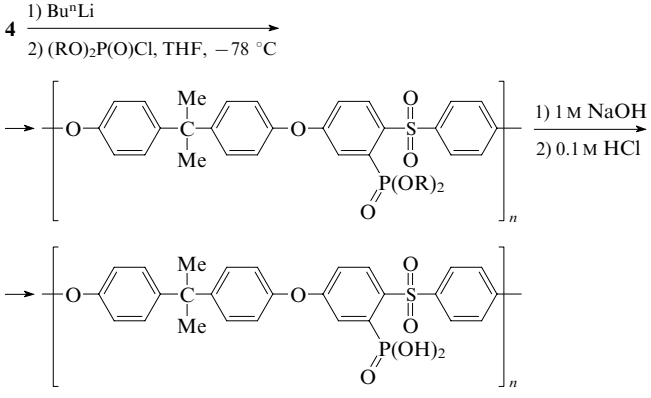


The values of proton conductivity for these polymeric membranes determined by impedance spectroscopy at 60 °C are $(14-32)\times10^{-3}$ S cm^{-1}, which, in principle, demonstrates a possibility to use them as promising proton-conducting materials. For a detailed description of electrochemical characteristics of membranes obtained, see Ref. 42.

PES with short alkyl chains in sulfoalkyl substituents have been synthesised.[43] In this case, the polymers containing lithium sulfinate groups reacted with sodium ω-bromoalkanesulfonates and butane-1,4-sultone (Scheme 4).

Thermogravimetric analysis of PES-based membranes containing sulfoethyl, -propyl, and -butyl groups showed that these materials are stable up to 300 °C in a nitrogen atmosphere. Calorimetry studies show that these modified polymers absorb more moisture [moisture absorption values are from 11 to 14 mol H_2O (g-mol $SO_3H)^{-1}$]. The proton conductivity value for membranes containing 0.9 sulfopropyl substituents per elementary unit of poly(ether sulfone) is 77 mS cm^{-1} at 70 °C.

Lithiated PES were used for the preparation of phosphorylated polymers. In particular, the synthesis of poly(ether sulfones) containing phosphonate groups in the *ortho*-positions relative to sulfo groups of the macromolecular backbone is reported [44] which is based on $S_nP(V)$ nucleophilic subsitution [45] The reaction of metallated PES **4** with dialkyl and diaryl phosphochloridates occurs without catalysts.

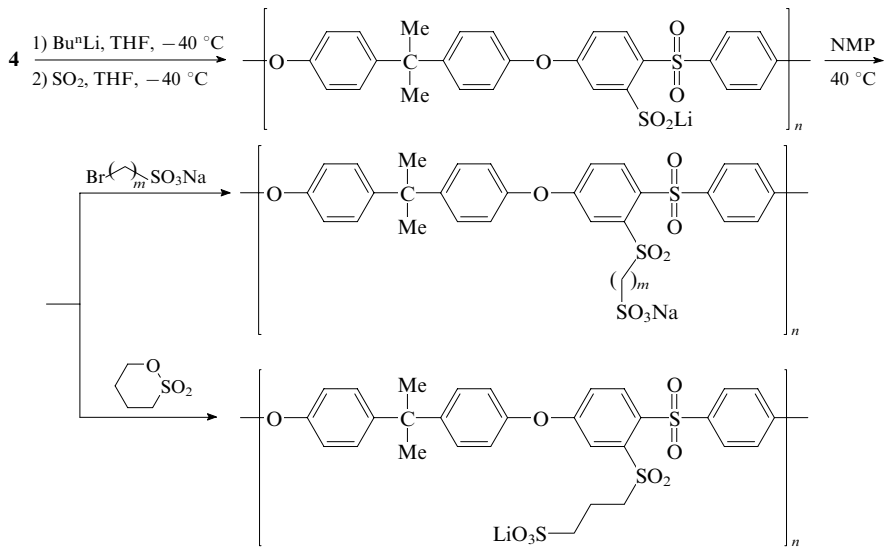


R = Et, Ph.

According to Guiver *et al.*,[46] lithiation and subsequent reaction of polyanions with electrophiles do not lead to destruction of macromolecules of poly(ether sulfones).

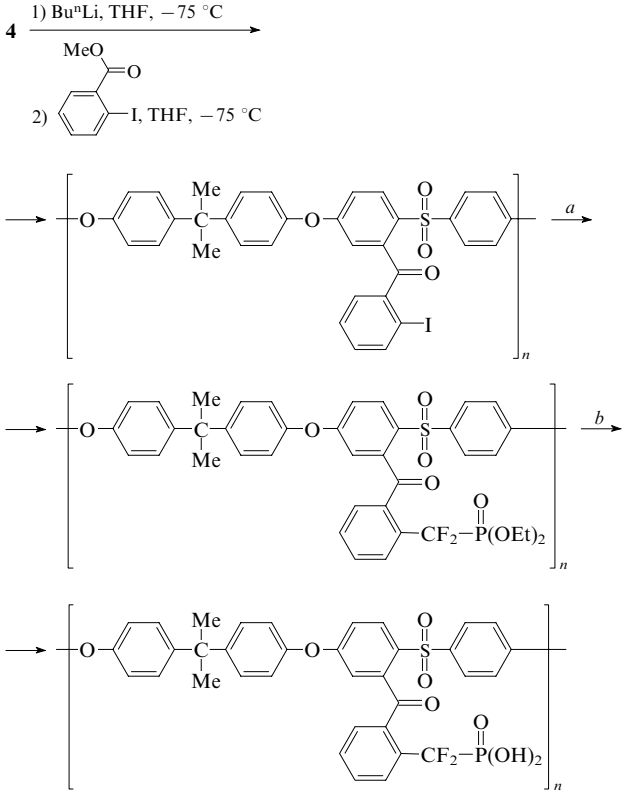
Polymer containing P(O)(OH) groups bound to the benzene ring through a difluoromethylene bridge was prepared by the following route: lithiation of PES **4**, its transformation into iodobenzoyl derivative, phosphorylation of the intermediate

Scheme 4



NMP is *N*-methylpyrrolidone.

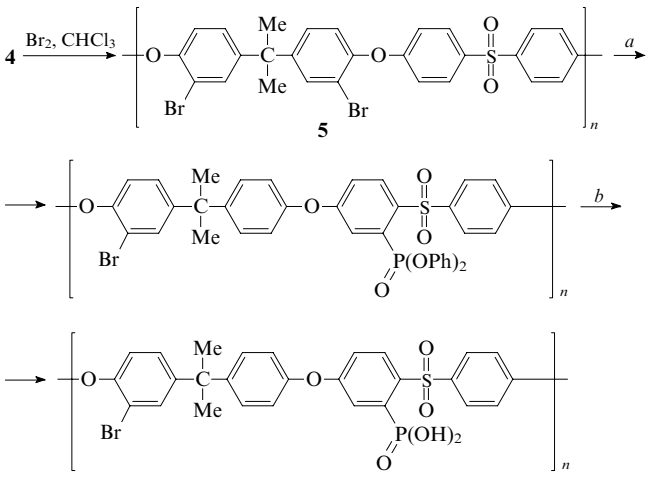
under the action of diethyl (bromodifluoromethyl)phosphonate in the presence of zinc and dealkylation of the polymer formed with bromotrimethylsilane.[47] This polymer exhibits enhanced acidity.



(*a*) Zn, $BrCF_2P(O)(OEt)_2$, CuBr, DMF, sonication, 25 °C;
(*b*) 1) $BrSiMe_3$, $CHCl_3$, 40 °C; 2) 5% 1 M HCl in MeOH.

Proton conductivity of membranes based on this polysulfone reached 5 mS cm^{-1} at 100 °C; according to TGA, destruction started at ~230 °C and was accompanied by the cleavage of the C–P bond.[47]

A more convenient approach to phosphorylated PES is based on lithiation of the brominated polymer **5**,[48] because substitution of lithium for the halogen atom occurs easier than for the hydrogen atom. The synthesis of phosphorylated PES after the stages of bromination and lithiation of the initial polymer **4** includes the reaction of the intermediate with diphenyl phosphochloridate followed by hydrolysis of the phenoxy groups.

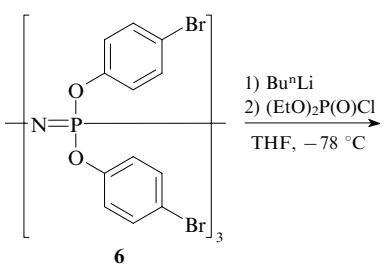


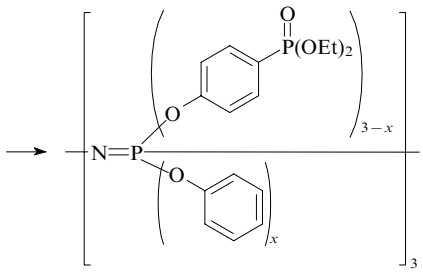
(*a*) 1) Bu^nLi, THF, −78 °C; 2) $(PhO)_2P(O)Cl$, THF, −78 °C;
(*b*) 1) 1 M NaOH, 2) 0.1 M HCl.

In this case, the degree of phosphorylation reached 50%.

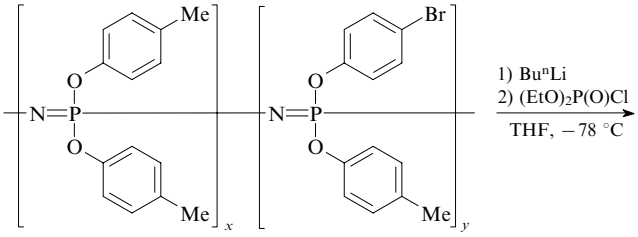
3. Poly(aryloxyphosphazenes) with phosphonic acid groups

Cyclic (**6**) and polymeric phosphazenes (**7**) containing *p*-bromophenoxy side groups are used for the synthesis of phosphorylated poly(aryloxyphosphazenes). Compounds **6** and **7** were treated with butyllithium and then with diethyl phosphochloridate.[49, 50]

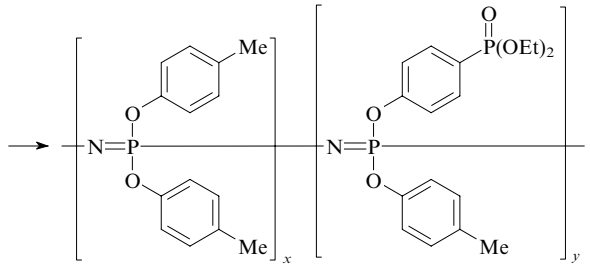




$x = 0-2$.



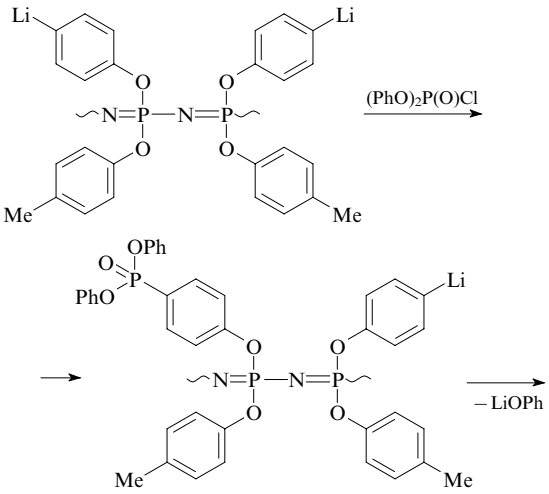
7



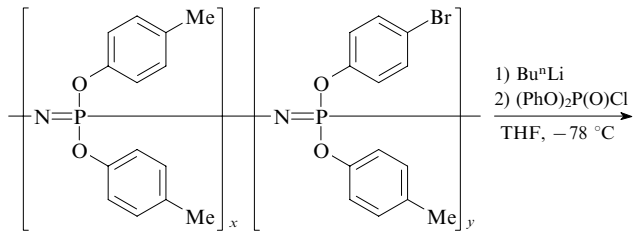
$x = 1.2\,m$, $y = 0.8\,m$.

Poly(aryloxyphosphazenes) functionalised by phenylphosphonic acid are formed [51] from the polymers **7** in accordance with Scheme 5. *tert*-Butyllithium is added to a solution of poly(aryloxyphosphazenes) **7** with different numbers of brominated benzene rings in THF at −75 °C, lithium phenoxide intermediates obtained are treated with diphenyl phosphochloridate. Subsequent alkaline hydrolysis and treatment with an acid give polymers with phenylphosphonate groups.

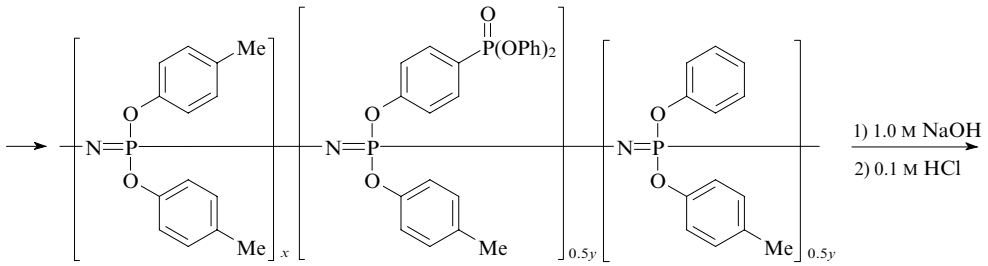
Attempts to phosphorylate lithiated polymers by gradual addition of diphenyl phosphochloridate to the reaction mixture resulted in precipitation of the polymer and formation of an insoluble product. If the reagent was added quickly, a soluble polymer was obtained. ^{31}P NMR studies showed that in the latter case, intramolecular reaction of diphenyl phosphonate groups with the lithium phenoxide fragments of the same polymeric chains takes place, thus promoting the formation of the phosphorus-containing 'bridge' between two aryloxide side groups.

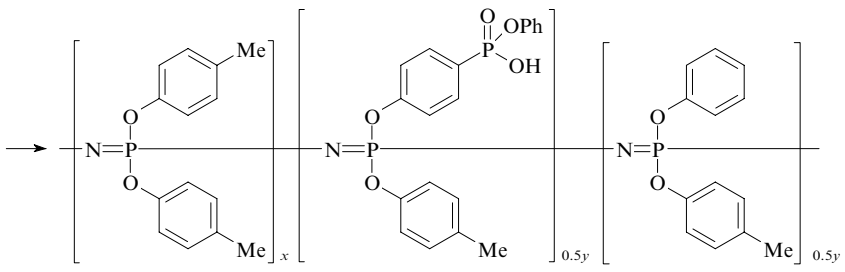


Scheme 5

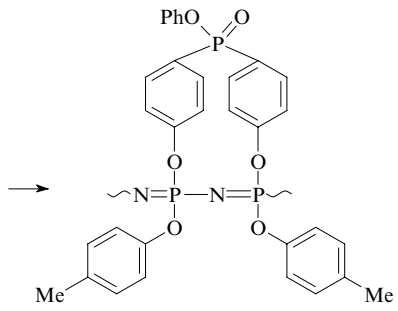


7





x/m	1.26	1.0	0.80
y/m	0.74	1.00	1.20



Phosphorylation of polymers *via* lithium phenoxide intermediates usually occurs with 50% conversion of bromophenoxy substituents into diphenyl phosphonates. The overall amount of lithium phenoxide intermediates that react with diphenyl phosphochloridate is about 70%; however, only half of the metallated groups is converted into the diphenyl phosphonate groups. According to elemental analysis, more than 90% of the bromine atoms of the initial polymer were lithiated. Thus, it is side reactions of reactive lithium phenoxide intermediates formed upon reaction with diphenyl phosphochloridate that is the limiting factor of the overall transformation rather than incomplete lithiation. These results are in accord with the data obtained for diethyl chlorophosphate.[50]

Hydrolysis of phenyl esters was performed by treatment of a polymer solution in THF with 1.0 N NaOH for 24 h. In the course of the reaction, the polymer precipitates from the solution, after that hydrolysis continues, but to an insignificant extent. No changes in the molecular mass of the polymer were observed, thus proving the known fact that polyphosphazene macromolecules are stable against basic hydrolysis.

The advantadge of this method for the synthesis consists of the possibility of varying the polymer composition by changing the ratio of the initial side aryloxide groups, degree of lithiation and the degree of hydrolysis of the ester groups.

The polymers obtained were tested as membranes for fuel elements.[52, 53] These membranes are characterised by a low coefficient of methanol diffusion. This coefficient for membranes based on phosphorylated polymers appeared to be 12 times smaller than that for membrane Nafion 117 and 6 times smaller than that for membrane made of cross-linked sulfonated polyphosphazenes.[52, 53] Ion-exchange capacity values for membranes from phosphorylated polymers are in the range of $(1.17-1.47)\times10^{-3}$ equiv g^{-1}, proton conductivity values lie in the range of $10^{-2}-10^{-1}$ S cm^{-1}. Thus, membranes under consideration exceed in some characteristics the analogues based on sulfonated polyphospazenes.[52, 53]

III. Transformations of polymers without preliminary metallation

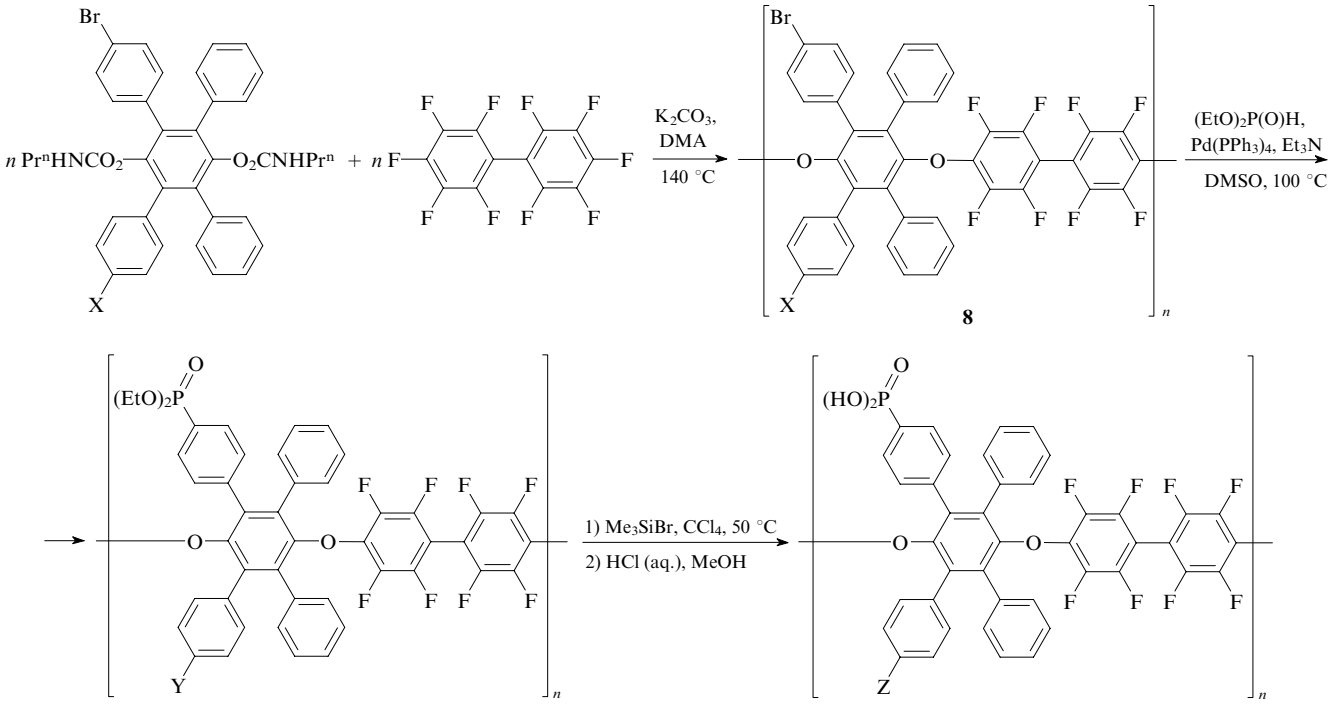
Along with the introduction of protogenic groups into metallated polymers, the method based on transformations of reactive groups of macromolecular chains without preliminary metallation is also widespread.[54–64] Bromine and fluorine atoms, NH fragment of the benzimidazole ring, and carboxy groups could be distinguished as reactive groups in polymers.

Bromination[54] of aromatic polyethers **8** obtained from bis(propylcarbamate) derivatives of mono- and dibromotetraphenylhydroquinone (Scheme 6) was among the first attempts to use substitution of bromine atoms in polymers for the introduction of phosphonic acid groups.

Treatment of polymers **8** with diethyl phosphite in the presence of triethylamine and tetrakis(triphenylphosphine)-palladium as a catalyst results in polymers containing diethyl phosphonate groups. Dealkylation of the latter is performed with an excess of bromotrimethylsilane in CCl_4. Bis(trimethylsilylated) intermediate is hydrolysed with HCl in methanol. The target polymers are well soluble in DMSO; flexible and strong films were cast from these solutions. Thermal, chemical and hydrophilic properties of the films suggest that they can be used as polymeric electrolyte membranes for fuel elements.[54]

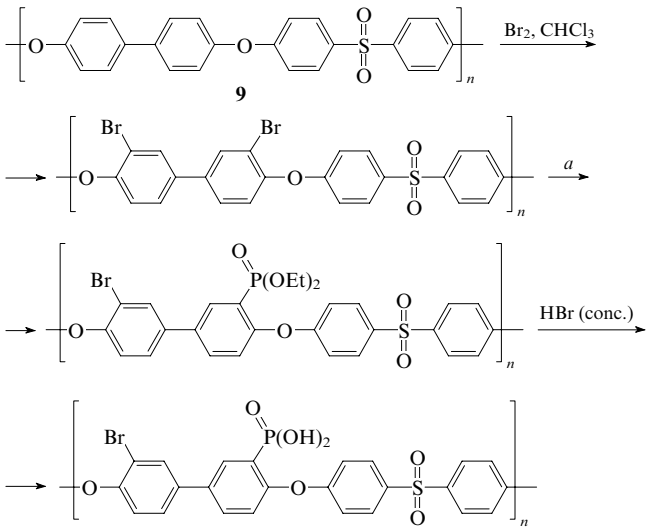
Brominated poly(ether sulfones) can be transformed into phosphorylated polymeric systems using Pd-catalysed formation of the P–C bond. Bromination of PES **9** followed by

Scheme 6



X = Y = Z = H; X = Br, Y = $(EtO)_2P(O)$, Z = $P(O)(OH)_2$.

phosphorylation of the bromine-containing product is described.[55]

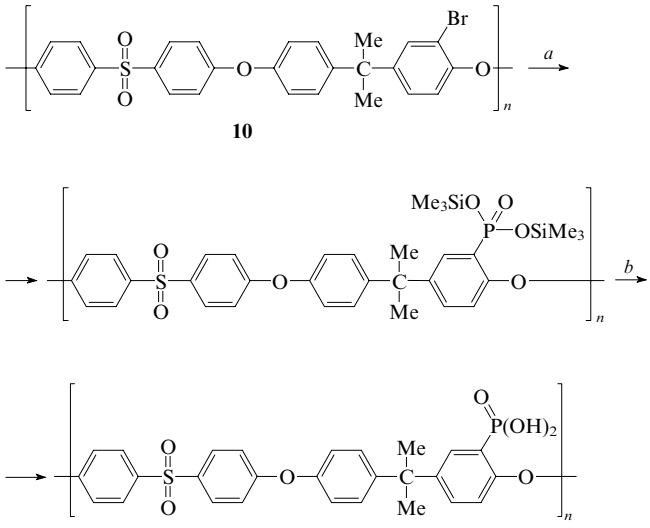


(*a*) $(EtO)_2P(O)H$, Et_3N, $Pd(Ph_3P)_4$ or $Pd(dba)_2$.

Complexes of Pd(0) with triphenylphosphine and dibenzylideneacetone (dba) were used as catalysts for phosphorylation. Triethylamine was added to the reaction mixture to bind the evolving the HBr. It is known [56, 57] that the molar ratio of the components and the reaction temperature markedly influence the yield, therefore, the effect of all these parameters on phosphorylation of polymers was comprehensively studied.

In particular, it was shown that an increase in temperature from 90 to 120 °C results in an increase in degree of phosphorylation, whereas further temperature increase to 140 °C causes destruction of the polymer. The Pd catalyst was found to be more active in the absence of triphenylphosphine ligands. The highest degree of phosphorylation ($\alpha = 88\%$) was achieved with diphenyl oxide as a solvent. The optimum aryl bromide : diethyl phosphite : triethylamine ratio was found to be 1 : 22 : 4, which is close to the values reported.[58]

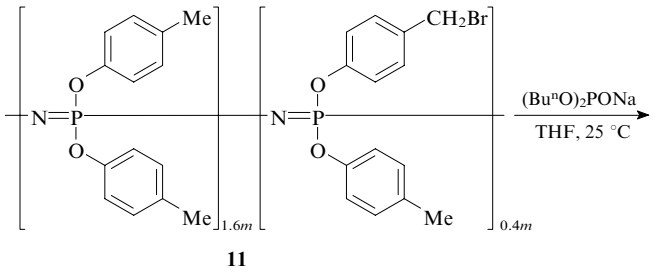
Transformation of brominated PES into phosphorylated PES also occurs in the presence of nickel catalysts. The reaction of brominated PES **10** with tris(trimethylsilyl) phosphite (TMSP) catalysed by $NiCl_2$ is reported.[59] Subsequent methanolysis results in removal of the trimethylsilyl groups to give phosphorylated product.

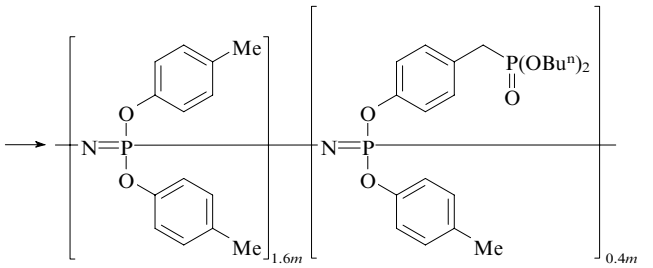


(*a*) $NiCl_2$, TMSP, PhOPh, 200 °C; (*b*) MeOH.

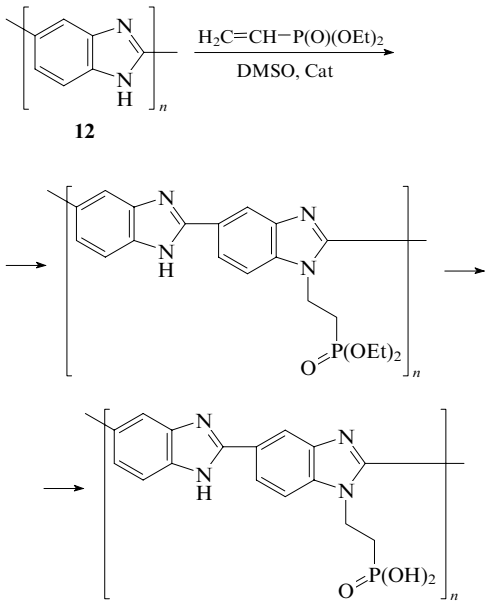
The polymers obtained are soluble in *N*-methylpyrrolidone as such or in the presence of 2 vol.% – 5 vol.% concentrated HCl. According to TGA, destruction of polymers with arylphosphonic groups starts at temperatures > 325 °C, whereas similar polymer with sulfonic acid groups decomposes at temperatures > 200 °C. Depending on the degree of acidic group substitution, proton conductivity values for PES with arylphosphonate groups at 25 °C are 1.2 – 8.7 mS cm^{-1}, which is less than proton conductivity of the polymer with sulfonic acid groups (20 mS cm^{-1}).

Polyaryloxyphosphazenes **11** containing bromomethyl groups are phosphorylated under the action of sodium organophosphites, in particular, sodium dibutyl phosphite.[50] The reaction proceeds in THF at 25 °C and results in the product in a quantitative yield. Studies of the routes for transformation of the ester fragments into phosphonic acid fragments are in progress.



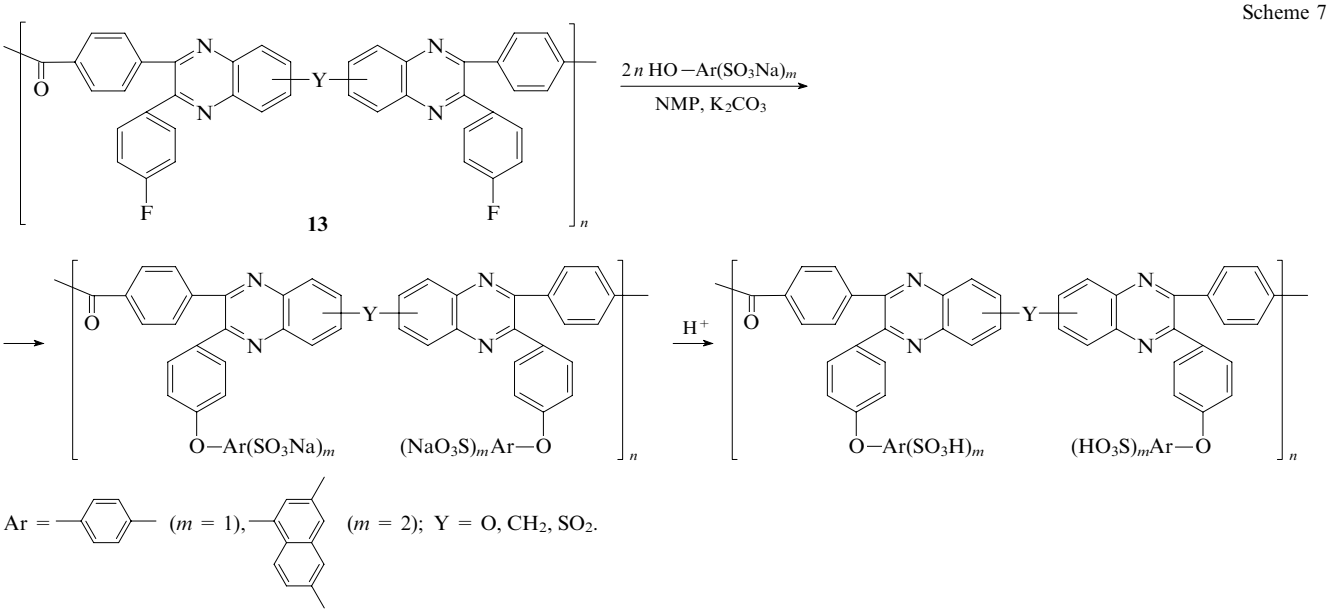


N-Substututed polybenzimidazoles containing the P(O)(OH) groups bound to the benzimidazole rings through the ethylene bridge were prepared by the reaction of polybenzimidazoles **12** with diethyl vinylphosphonate.[60]



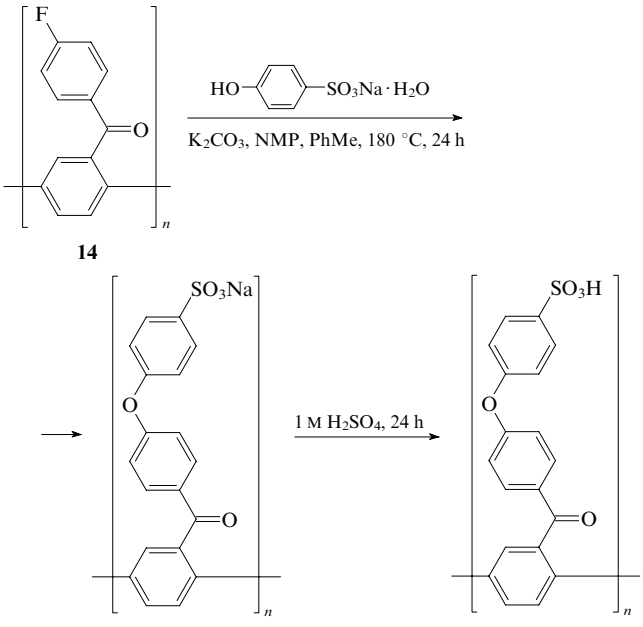
Currently, hetero- and carbocyclic polymers with activated fluorine atoms in aromatic rings have attracted significant

Scheme 7

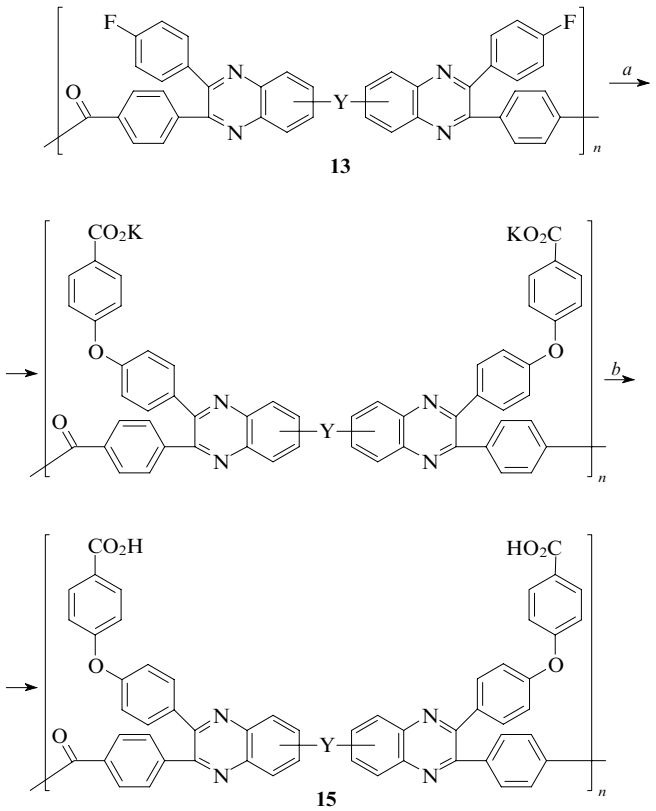


attention. These polymers can undergo aromatic nucleophilic substitution with various nucleophiles, for example, with phenols containing acidic groups.[59–62] In particular, *p*-fluorophenyl-substituted polyquinoxalines **13** were involved into the reactions with phenol- and naphtholsulfonic acids.[61–64] The reaction was carried out in NMP in the presence of potassium carbonate (Scheme 7). The polymers obtained in this way are well soluble in *m*-cresol, NMP, and possess film-forming properties.

Similar approach was used by Ghassemi and McGrath,[64] who performed the reaction of fluorinated polybenzophenone **14** with sodium *p*-phenolsulfonate. According to the ^{19}F and ^{13}C NMR data, about 50% of all fluorine atoms are substituted under these conditions. The authors believe that a relatively low degree of substitution is associated with deactivating effect of the sulfonate group on the phenoxide fragment. Another factor affecting the degree of transformation is partial precipitation of the sulfonated polymer.

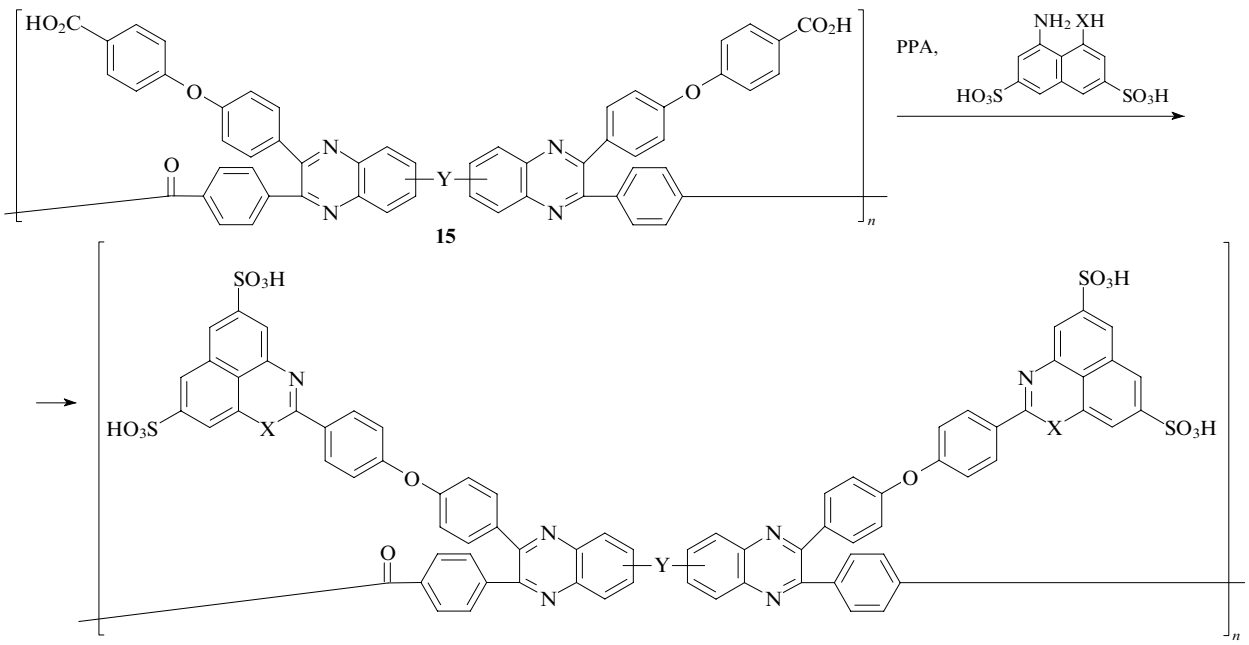


Poly[(4-carboxy)phenoxy]phenylquinoxalines **15** were synthesised by the treatment of *p*-fluorophenyl-substituted polyquinoxalines **13** by *p*-hydroxybenzoic acid under the conditions of aromatic nucleophilic substitution (NMP, K_2CO_3).[63]



Then poly[(4-carboxy)phenoxy]phenylquinoxalines **15** were involved into the reactions with 8-aminonaphth-1-ol-3,6-disulfonic acid and 1,8-diaminonaphthalene-3,6-disulfonic acid (Scheme 8)[62] in polyphosphoric acid. High-molecular-mass polymers containing naphthoxazine- and pyrimidinedisulfonic acid substituents were formed as products.

Scheme 8



X = O, NH.

This approach to the creation of polymers with sulfonic acid groups has a general character. Any polymers containing carboxy groups or their derivatives can be involved in the reaction. Moreover, introduction of two sulfonic acid groups into the same aromatic ring of the substituent leads not only to increasing proton conductivity of the membrane, but also to an increase in its heat resistance, because in this case sulfonic acid groups stabilise one another.

* * *

The method for the synthesis of polymers by polymer-analogous transformations, which has been recently developed, is a promising approach to polymers with protogenic, sulfonic and phosphonic acid groups. It is remarkable that this method is especially efficient for the preparation of polymers with phosphonic acid groups, because the latter show higher heat resistance and hydrolytic stability than sulfonic acid groups.[65] This method allows preparation of polymers containing protogenic groups not only in backbones the of macromolecules, but also in peripheral fragments, which, according to Refs 66–71, favours the increase in the resistance of these polymers against high temperatures, oxidation, and hydrolysis. Stability of polymers is a factor determining potentialities of this method for creation of novel proton-conducting membranes with valuable properties.

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