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Sulfonated polynaphthylimides as proton-conducting membranes for fuel cells †

A L Rusanov, E G Bulycheva, M G Bugaenko, V Yu Voytekunas, M J M Abadie

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Abstract. The main achievements in the field of synthesis of sulfonated polynaphthylimides and their precursors, namely, sulfonated aromatic diamines, are analysed. The relationship between the structure of sulfonated polynaphthylimides and their physicochemical characteristics such as chemical and thermal stability, moisture uptake, ion-exchange capacity and proton conductivity is studied. The prospects of using polynaphthylimides containing pendant sulfo groups for the development of proton-conducting polymeric electrolyte membranes for fuel cells are demonstrated. The bibliography includes 139 references.

I. Introduction

In the past decades, attention of scientists was focused on the development of fuel cells (FC) that utilise hydrogen and methanol because they represent environmentally safe power sources for stationary and portable power units.[1 – 20] Special attention was paid to the elaboration of cheap FC with high performance and long service life.

The key components of FC are the proton-conducting polymeric electrolyte membranes that are currently most often represented by Nafion membranes based on polyperfluoroalkanesulfonic acids.[4, 21, 22] These membranes are characterised by high proton conductivity (σ) and chemical stability. However, Nafion membranes are very expensive, exhibit a considerable methanol cross-over and can operate only at temperatures below 80 °C. Hence, the development of alternative polymeric electrolyte membranes, particularly, those based on sulfonated polyheteroarylenes, is of interest.[5, 9, 10, 13, 15 – 17, 23]

The synthesis of the first polyheteroarylenes dates back to the 1960s – 1970s.‡ In the series of polyheteroarylenes, the most noticeable place belongs to polyimides (PI), which possess good film-forming properties, high thermal and mechanical characteristics,[25 – 34] *i.e.*, the properties typical of polymers used as polymeric electrolyte membranes PI containing five-membered imide rings are the most abundant; however, they are characterised by low water resistance and chemical stability, which substantially limits the possibility of their use as polymeric electrolyte membranes.[35 – 40] That is why attention was focused on PI containing six-membered imide rings, particularly, polynaphthylimides (PNI).

Polynaphthylimides are characterised by the considerably higher resistance towards hydrolysis and different chemical reagents[40 – 45] as compared with PI containing five-membered imide rings.

Among polynaphthylimides, sulfonated polynaphthylimides (SPNI) are most interesting. The main method of their synthesis is polycondensation of naphthalenetetracarboxylic dianhydrides, first of all, naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTDA), with different aromatic diamines containing sulfo groups (sulfonated diamines SDA). The structure of the latter allows one to vary to a considerable extent the characteristics of the target SPNI, which explains the attention drawn to the development of new SDA.

II. Synthesis of aromatic sulfodiamines

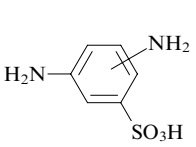
Certain SDA are commercial products, in particular, 2,5- (**1**) and 3,5-diaminobenzenesulfonic acids (**2**)[38, 46] and also benzidine- (**3**), 5,5′-dimethylbenzidine- (**4**) and 4,4′-diaminostilbene-2,2′-disulfonic acids (**5**).[36, 46 – 48]

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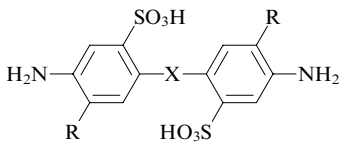
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† This review is dedicated to the 100th anniversary of Academician V V Korshak.

‡ The chemistry of polyheteroarylenes was considered in a monograph.[24]



1, 2



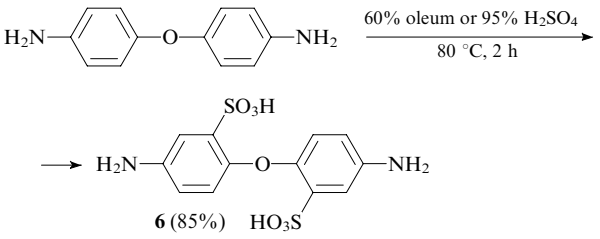
3–5

X = bond, R = H (**3**), Me (**4**);
X = −CH=CH−, R = H (**5**).

Among all these compounds, only benzidine-2,2′-disulfonic acid (**3**, BDSA)§ has found application in the SPNI synthesis, where as other compounds proved useless for this purpose, because SPNI based on them exhibited either poor solubility or low proton conductivity.[46]

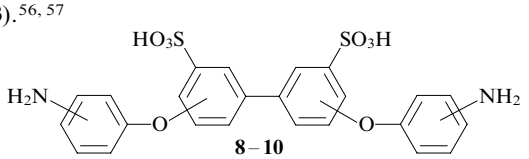
In addition to benzidine-2,2′-disulfonic acid, other aromatic diamines are employed in the synthesis of SPNI. These can be divided into two classes:[45] SDA with sulfo groups in the main chains of macromolecules and SDA that afford SPNI with pendant sulfo groups. Compounds of the former class are in turn divided into two types, namely, compounds with sulfo and amino groups in the same rings and compounds with sulfo and amino groups in different rings.

Among SDA of the first type, in addition to commercial products **1–5** discussed above, mention should be made of 4,4′-diamino-2,2′-disulfodiphenyl oxide (**6**)[49, 50] and 4,4′-bis(4-amino-2-sulfophenoxy)biphenyl (**7**),[45] which are obtained by sulfonation of the corresponding amines. For example,

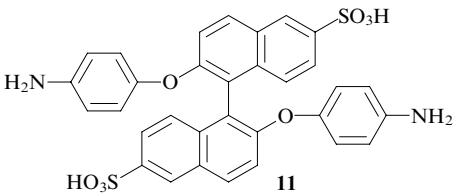


6 (85%)

SDA of the second type include 4,4′-bis(4-aminophenoxy)-3,3′-disulfobiphenyl (**8**),[50, 51] 4,4′-bis-(3-aminophenoxy)-3,3′-disulfobiphenyl (**9**),[45, 52] 2,2′-bis(4-aminophenoxy)-5,5′-disulfobiphenyl (**10**),[53] 2,2′-bis(4-aminophenoxy)-1,1′-binaphthyl-6,6′-disulfonic acid (**11**),[54] 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid (**12**)[50, 55] and bis[4-(3-aminophenoxy)-3-sulfophenyl] sulfone (**13**).[56, 57]

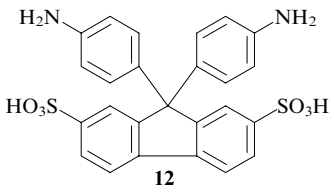


8–10

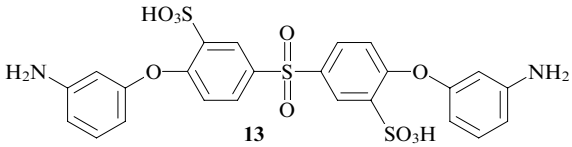


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§ Benzidine-2,2′-disulfonic acid (4,4′-diaminodiphenyl-2,2′-disulfonic acid) is a commercial product produced by Acros Organics, TCI and Tokyo Kasei Co.

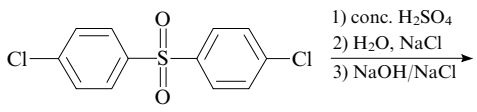


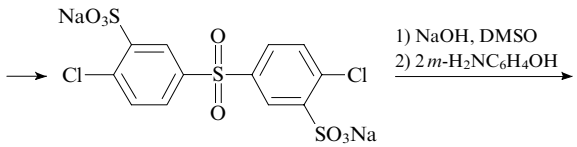
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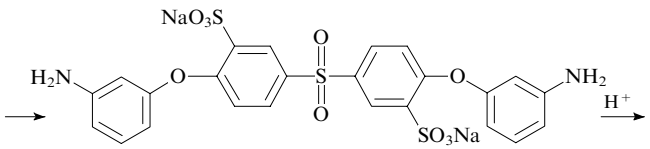


13

Compounds **8–12** were prepared by direct sulfonation of the corresponding diamines.[44, 50, 51] For these purposes, the following well-known sulfonating agents were used: concentrated sulfuric acid and sulfuric anhydride either pure or mixed with 95% H_2SO_4, *etc*. Reactions were carried out on heating (usually at 80 °C); the yields of products were 67%–93%. Bis[4-(3-aminophenoxy)-3-sulfophenyl]-sulfone (**13**) was synthesised as a result of several successive reactions including sulfonation of bis(4-chlorophenyl) sulfone, condensation of the resulting disodium salt with 3-aminophenol.[56, 57]

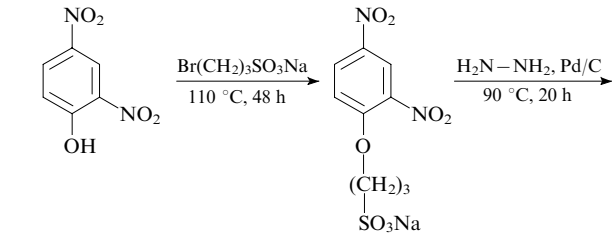


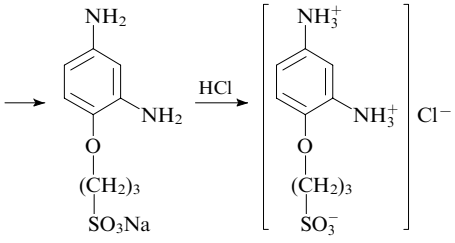




13 (92%)

Synthesis of a series of aromatic diamines containing sulfo groups in alkyl or alkoxy substituents was described.[58–65] One of the simplest compounds in this series, 3-(2,4-diaminophenoxy)propanesulfonic acid (**14**), was synthesised in the form of hydrochloride as a result of

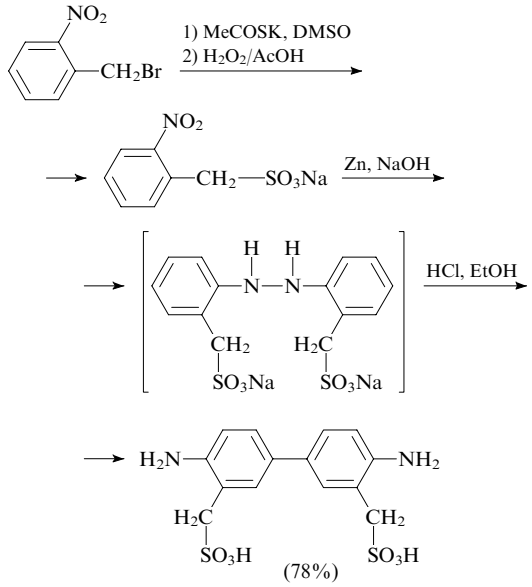




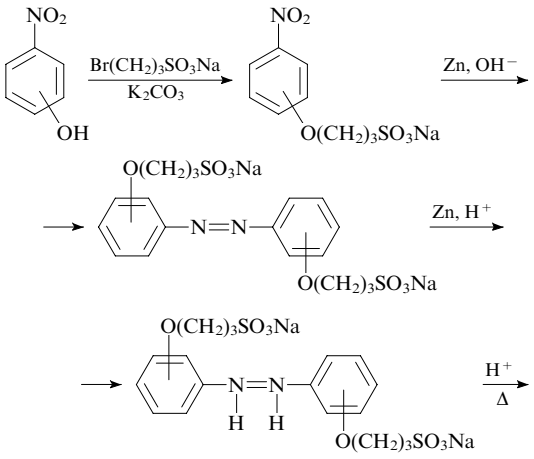
14 (92%)

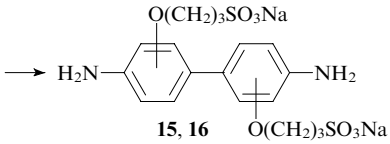
reaction of sodium 3-bromopropanesulfonate with 2,4-dinitrophenol followed by reduction of the nitro groups.[58]

Binuclear diamines with sulfo groups in alkyl side-substituents were synthesised by the following scheme:[59, 60]



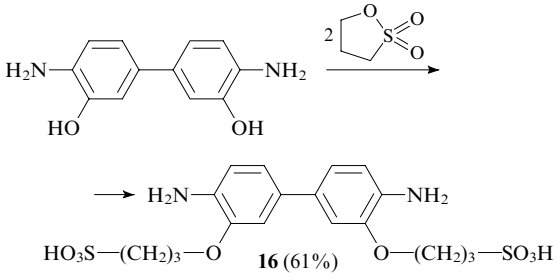
Benzidines with short ω-sulfoalkoxy substituents, for example, 2,2′- (**15**) and 3,3′-bis(3-sulfopropoxy)benzidines (**16**), were synthesised from the corresponding hydroxy derivatives.[61]





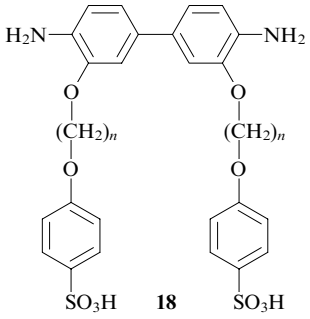
15: 2,2′-isomer, yield 60%; **16**: 3,3′-isomer, yield 30%.

Compound **16** was also obtained by the reaction of 3,3′-dihydroxybenzidine with sultone.[62]



Benzidines **17** with longer sulfoalkoxy groups¶ were synthesised by multistage transformations of 3,3′-dihydroxybenzidine (Scheme 1).[59, 63]

3,3′-Bis-[ω-(4-sulfophenoxy)alkoxy]benzidines (**18**) were synthesised analogously



n = 2, 12.

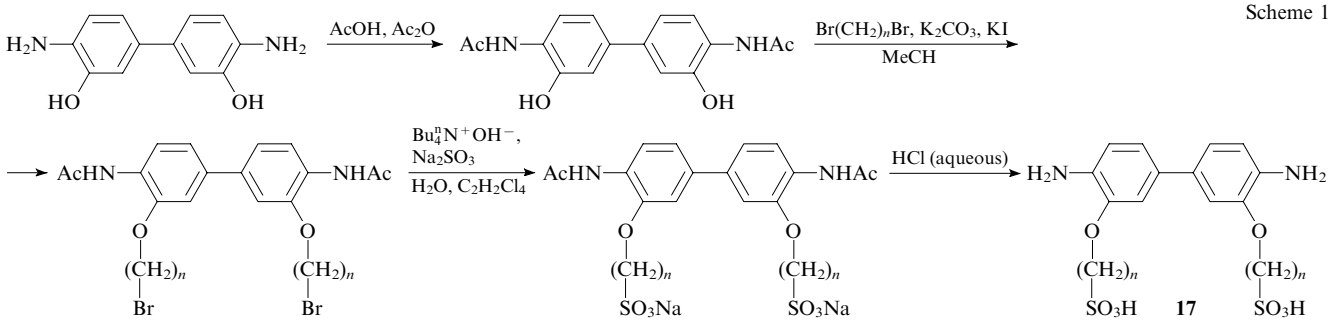
using sodium 4-hydroxybenzenesulfonate in place of Na_2SO_3.[59, 63–65]

A diamine containing a sulfoaryloxy group in the side chain, namely, 3,5-diamino-4′-sulfodiphenyl oxide (**19**), was synthesised from 2,4,6-trinitrotoluene† according to Scheme 2.[69, 70]

¶ This method can also produce derivatives with short sulfoalkoxy substituents.

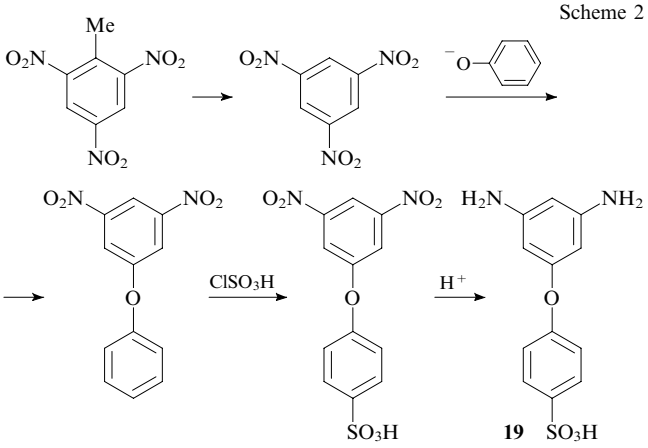
† The synthesis of condensation monomers based on 2,4,6-trinitrotoluene was decsribed.[66–68]

Scheme 1



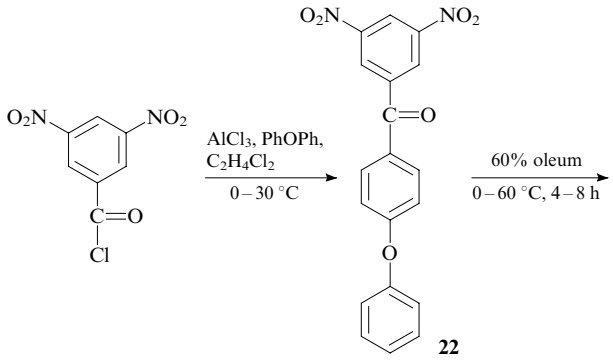
n = 2, 10 (90%), 12 (69%).

Scheme 2

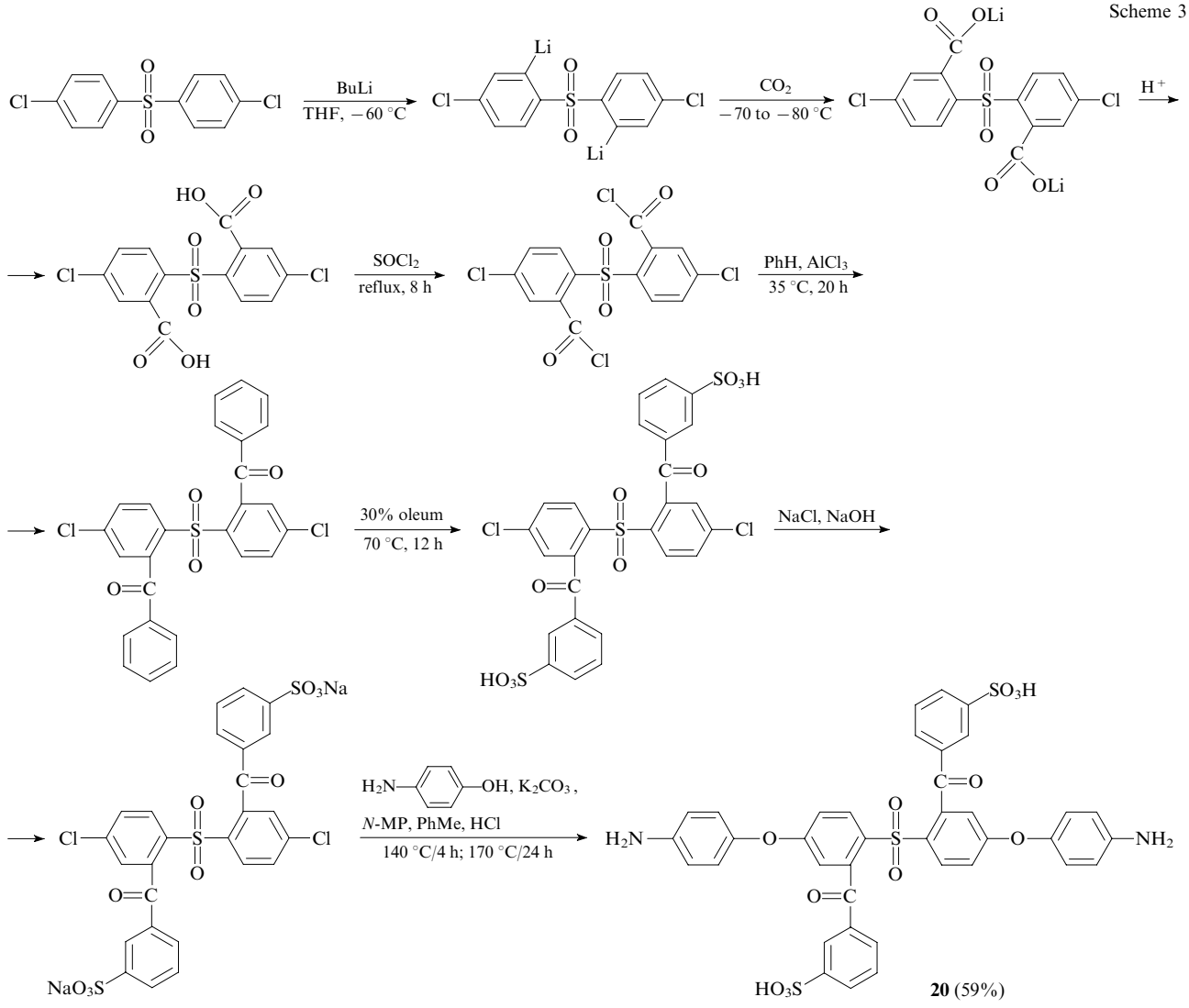


Bis[4-(4-aminophenoxy)-2-(3-sulfobenzoyl)phenyl] sulfone (**20**) was synthesised as a result of a multistage process starting from 4,4′-dichlorodiphenyl sulfone (Scheme 3).[64]

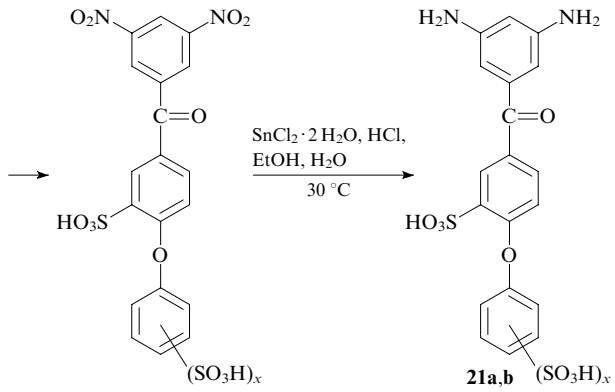
Diamines containing several sulfo groups in side chains [for example, 3,5-diamino-3′-sulfo-4′-(4-sulfophenoxy)- (**21a**) and 3,5-diamino-3′-sulfo-4′-(2,4-disulfophenoxy)benzophenones (**21b**)], were obtained by the Friedel–Crafts reaction of 3,5-dinitrobenzoyl chloride with diphenyl ether, followed by sulfonation of reaction product **22** and reduction of the nitro groups.[65]



Scheme 3



N-MP is *N*-methyl-2-pyrrolidone.



21a,**b**

x = 1 (**a**, 41%), 2 (**b**, 70%).

III. Sulfonated polynaphthylimides based of naphthalene-1,4,5,8-tetracarboxylic dianhydride and aromatic sulfodiamines

Polycyclocondensation of naphthalene-1,4,5,8-tetracarboxylic dianhydride with sulfonated diamines proceeded most efficiently in aromatic organic solvents (phenol, *m*-cresol, *p*-chlorophenol) in the presence of triethylamine, which allowed one to carry out the reactions under homogeneous conditions and avoid desulfonation.[35–37,71–76]

The synthesis of block and random SPNI was carried out using benzoic acid as the catalyst.[77–81] In some cases, to make the reaction more efficient, benzoic acid was used in combination with nitrogen heterocycles.

Studies by French scientists[35–37,71–76] demonstrated the advantages of synthesising co-polymeric SPNI by the reaction of NTDA with sulfonated and non-sulfonated aromatic diamines taken in different ratios as compared with the homopolymeric SPNT characterised by poor solubility in organic solvent and inferior mechanical properties.[49] Such an approach allowed varying the extent of sulfonation and certain other important characteristics of SPNI in a wide range.

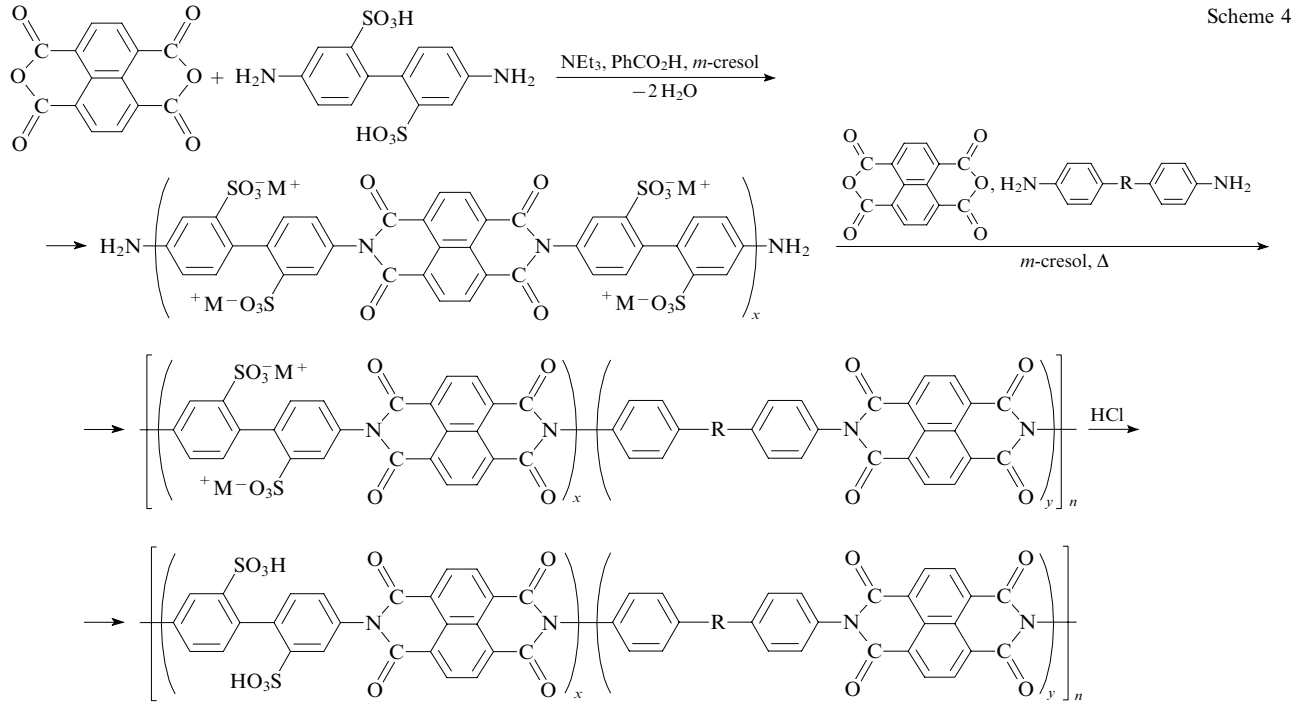
1. Polynaphthylimides containing sulfo groups in the main chains of macromolecules

The SPNI synthesis most often involved the use of NTDA and benzidine-2,2′-disulfonic acid (**3**) as the monomers containing sulfo groups in the main chains of macromolecules. Particularly, the reaction of BDSA and non-sulfonated diamines (4,4′-diaminodiphenyl oxide and 4,4′-diaminodiphenylmethane) with NTDA phenolic solvents afforded SPNI **23a**,**b** (Scheme 4).[36]

In the first stage of the synthesis, the reaction of NTDA with an excess of acid **3** produced sulfonated oligomers with terminal amino groups. The resulting oligomers were introduced into reaction with non-sulfonated diamines and NTDA. Membranes based on such SPNI were characterised by much higher stability under the FC operation conditions as compared with membranes based on sulfonated co-polyimides containing five-membered imide rings.

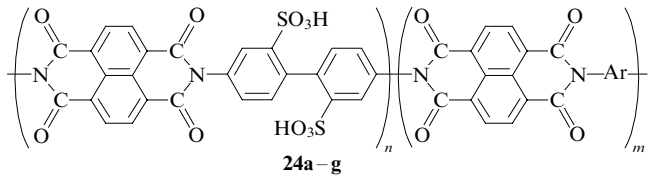
Pineri and co-workers[73] used an approach to the SPNI synthesis described in Ref. 36 to obtain new co-polymers **24** with the block structure based on BDSA, NTDA and tri- or tetranuclear non-sulfonated diamines.

Scheme 4

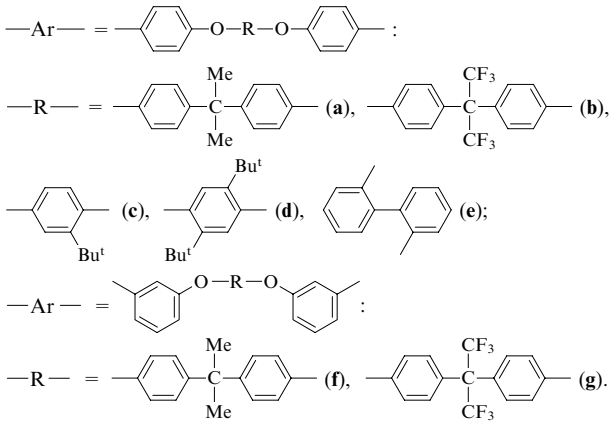


23a,**b**

$M^+ = \overset{+}{N}HEt_3$; R = O (**a**), CH_2 (**b**).



24a–g



In addition to SPNI with the block structure prepared according to Scheme 3, random co-polymers were synthesised; in the latter case, the reactions involving sulfonated and non-sulfonated diamines were not separated.

Depending on the structure, co-polynaphthylimides **24** (in the form of triethylammonium salts) were well soluble in cold or hot *N*-methyl-2-pyrrolidone (*N*-MP), less soluble in propylene carbonate and insoluble in diglyme. Their molecular masses could not be determined using size exclusion chromatography (SEC) and light scattering methods due to association of polymeric chains in solutions; however, the fact that fibrous materials were produced from the reaction solutions and also that strong films (membranes) could be prepared by casting methods pointed to the high molecular masses of polymers under consideration.

Membranes based on SPNI **24** were prepared by the casting method from solutions in *m*-cresol at 120 °C, followed by their drying on a hot plate at 50 °C/2 h, 100 °C/2 h and 150 °C/1 h. The membranes with the thicknesses of 25–40 μm were converted to the protonated form by the exposure to 0.1 M HCl solution followed by washing with water.

Studies of the thermal stability of membranes based on SPNI **24** carried out by the dynamic thermogravimetric analysis (DTGA) have shown the presence of several mass-loss regions, namely, in the range from 25 to 100 °C absorbed water was removed, in the range from 100 to 200 °C, residual *m*-cresol was removed, in the range from 200 to 400 °C, desulfonation occurred and at temperatures above 420 °C, destruction of the main chains of macromolecules took place.

As regards water stability at 80 °C, SPNI **24** occupy the intermediate position between the polyimide based on 4,4′-diaminodiphenyl oxide and 3,3′,4,4′-tetracarboxydiphenyl oxide dianhydride, which underwent hydrolysis and became brittle after several-minutes' exposure to water at this temperature, and SPNI **23a** considered earlier, which remained stable under these conditions for 1000 h.

The results obtained were well consistent with the data on the water stability of model compounds of the phthalimide and naphthylimide series.[82] Small-angle neutron scattering studies of the morphology of membranes based on SPNI **24** revealed the presence of broad scattering maxima (the so-called 'ionomeric peaks') typical of ionogenic block polymers, which was the result of phase separation of ionogenic domains and hydrophobic polymeric matrices.

Studies of the proton conductivity of membranes based on SPNI **24** (the data for SPNI **24f** and **24g** are listed in Table 1) have shown that as regards σ, these polymers were substantially inferior the conventional proton-conducting Nafion membranes[83] for which σ was $10^{-2}-10^{-1}$ S cm^{-1}. (However, it should be noted that for membranes based on the same co-polymers, the obtained σ values[49] were an order of magnitude higher than the values shown in Table 1 and virtually coincided with the values typical of Nafion-117 membranes.)

Table 1. Ion-exchange capacity (IEC), moisture uptake and proton conductivity (σ) of SPNI **24f** and **24g**.[73]

SPNI	*n*	*m*	IEC /mequiv g^{-1}	Moisture uptake[a]	σ /S cm^{-1}
24f	5	20.0	0.63	135.0	0.00032
	5	11.6	0.96	19.0	0.0013
	5	7.5	1.30	27.0	0.0065
	5	5.0	1.64	42.0	0.0059
24g	5	20.0	0.56	14.0	0.0004
	5	11.6	0.86	22.0	0.0017
	5	7.5	1.17	31.0	0.0046
	5	5.0	1.51	41.0	0.0071
	5	3.3	1.86	48.5	0.0083

[a] In % of dried polymer.

The synthesis of random SPNI **23a**, **23b**, **23c** (R = SO_2), **24a** and **24b** was described[84] (Scheme 5). In the latter study, the effect of the structure of non-sulfonated diamines on the characteristics of membranes based on these SPNI was considered. It was shown that all synthesised SPNI were soluble in *m*-cresol at room temperature. At the same time, their solubility in *N*-MP, dimethylacetamide (DNAA) and DMSO strongly depended on the structure of non-sulfonated diamines used. Thus SPNI **24b** was soluble in all solvents mentioned at room temperature, whereas SPNI **24a**, **23a** and especially **23b** were soluble in these solvents only partly or were insoluble at all.

Studies of the thermal stability of SPNI **23a–c**, **24a** and **24b** by the DTGA method (N_2, $\Delta T = 4.5$ deg min^{-1}) showed[84] that irrespective of the polymer structure, they decomposed in three steps in the same temperature ranges. At ~100 °C, the absorbed moisture was removed from SPNI; at ~300 °C, sulfo groups underwent degradation and at 470–525 °C, the destruction of the main chains of macromolecules took place. In this temperature range, SPNI **23a** had the highest thermal stability, while SPNI **24b** exhibited the lowest stability.

Studies of the ion-exchange capacity of SPNI **23a–c**, **24a** and **24b**, which is known to depend on the number of sulfo groups,[85–87] have shown that IEC decreased with the increase in the size of a bridge present in the non-sulfonated diamine residue and was within 1.28–2.01 mequiv g^{-1} (Table 2).[84]

Scheme 5

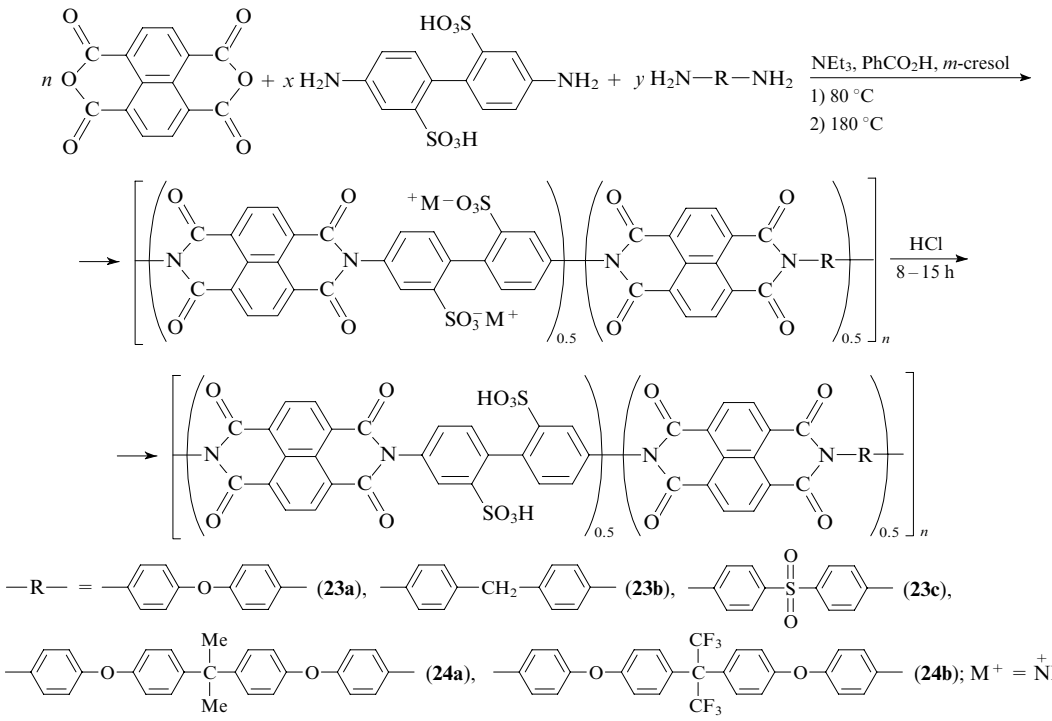


Table 2. Ion-exchange capacity and proton conductivity of co-polynaphthylimides **23a**–**c** and **24a**,**b**.

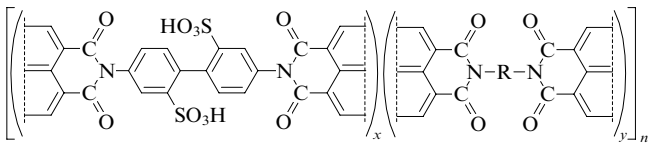
SPNI	IEC /mequiv g^{-1}	σ /S cm^{-1} at	
		50 °C	90 °C
23a	2.01	–	–
23b	1.76	0.0259	–
23c	1.66	0.0085	0.2218
24a	1.48	0.0758	0.1966
24b	1.28	0.0318	0.2828

Note. For comparison, the proton conductivity of Nafion-115 membranes was 0.1157 at 50 °C and 0.1759 at 90 °C.

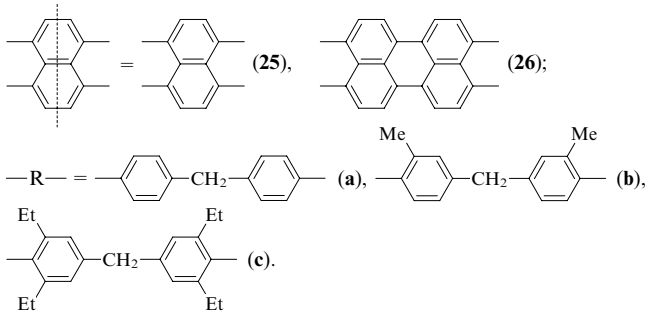
Studies of the proton conductivity of the discussed SPNI have not found any correlation between the IEC and σ (see Table 2). In the temperature range up to 50 °C, all the SPNI studied exhibited the lower proton conductivity as compared with Nafion-115; however, at 90 °C, all the SPNI demonstrated the conductivity higher than that of Nafion-115. The maximum σ value at 90 °C was observed for SPNI **24b**, which suggested that the proton conductivity preferentially depended on the fractional free volume, which determines the 'retention' of water molecules in the polymer pores.[88,89]

Considerable attention was paid to the water stability of SPNI.[84] In principle, a linear dependence between the ion-exchange capacity and hydrophilicity of polymers and, hence, the hydrolytic instability of membranes was observed. However, according to experimental data, the ion-exchange capacity was not the only factor determining the water stability of SPNI. A much more important factor was the flexibility of macromolecular chains, which determined the molecular relaxation and hence the water stability of membranes. The maximum flexibility was typical of SPNI **24a** and **24b**. This observation agrees with the data reported in Ref. 49.

The effect of structure of non-sulfonated diamines on the properties of random SPNI **25a**–**c** and **26a**–**c** was studied.[90] The solubility of polymers **25** and **26** increased in the sequences **25a** < **25b** < **25c** and **26a** < **26b** < **26c**, where SPNI **25** was better soluble than SPNI **26**. DTGA studies of the synthesised SPNI showed that the destruction of sulfo groups depended little on the polymer structure, whereas the destruction of the main chains accelerated with the increase in the number and the size of substituents in the bridge R.



25a–**c**, **26a**–**c**



At low (up to 70 °C) temperatures, SPNI **25** and **26** exhibited low proton conductivity as compared with Nafion-115; however, starting from 70 °C and higher, SPNI were characterised by the higher σ than Nafion-115. A comparson of the values of σ and IEC for polyimides **25a**, **25b** and **25c** has shown that at temperatures below 50 °C, a correlation was observed between the IEC and σ values, where the introduction of alkyl substituents favoured higher

proton conductivity (Table 3); for higher temperatures, no such correlation was observed.

Table 3. Ion-exchange capacities and proton conductivities of co-polynaphthylimides **25a**–**c** ($x = y = 0.5$) and Nafion-115.

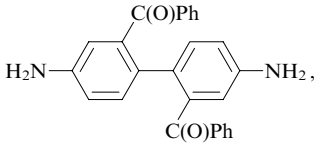
Polymer	IEC /mequiv g^{-1}	σ /S cm^{-1} at			
		50 °C	60 °C	80 °C	90 °C
25a	1.76	0.0259	0.0538	0.0790	–
25b	1.72	0.0173	0.1213	0.3137	0.3777
25c	1.12	0.0087	0.0195	0.3265	0.1403
Nafion-115	–	0.1157	0.1338	0.1606	0.1759

Several studies[91–95] were devoted to the synthesis of rigid-chain SPNI that formed solutions with high viscosity characteristics. The synthesis of such SPNI was based on the reaction of NTDA with BDSA and aromatic diamines free of 'hinge' groups [*e.g.*, with 9,9-bis(4-aminophenyl)-fluorene], taken in different proportions. If was carried out in *m*-cresol with isoquinoline as a catalyst (Scheme 6).

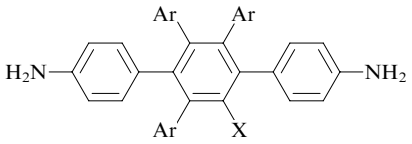
Membranes based on SPNI **27** exhibited high thermal and water stabilities and also attractive electrochemical characteristics comparable with those of Nafion membranes.[86,87] Thus the proton conductivity of membranes based on SPNI **27** containing 30 mol% BDSA was 0.67 S cm^{-1} at 120 °C and 100% relative humidity (RH).

Branched and cross-linked co-polynaphthylimides **28** were synthesised using 2 mol% of trifunctional melamine as the 'branching' monomer.[95] Branching and cross-linking of polymers favoured enhancement of their mechanical properties and enhanced the thermal and oxidative stability of membranes based on them with certain decrease in their proton conductivity.

In the syntheses of co-polymeric SPNI,[92,93] in addition to 9,9-bis(4-aminophenyl)fluorene, *p*-phenylenediamine and 4,4′-diaminodiphenyl oxide, diamines containing bulky substitients such as 2,2′-dibenzoylbenzidine

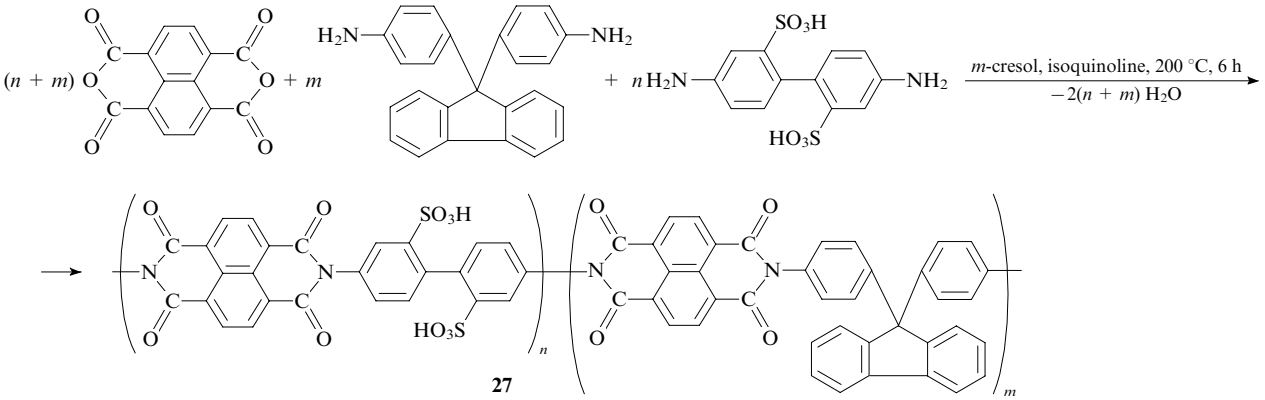


substituted 1,4-bis(4-aminophenyl)benzenes with the general structure

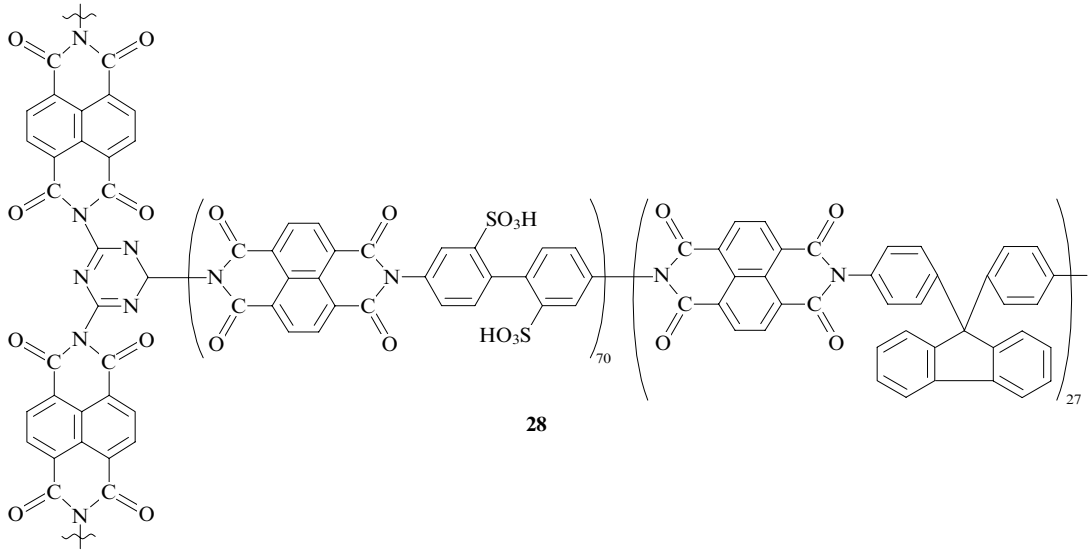


Ar = Ph: X = H, Ph; Ar = C_6H_4Ph-*p*, X = H; Ar = Naph, X = H,

Scheme 6

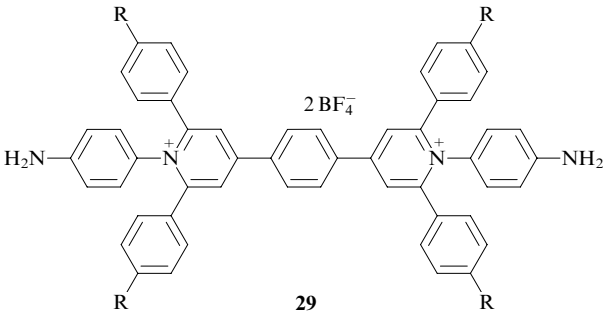


27



28

and also diazapentaphenylenediamines (**29**)‡



29

R = H, Me, OEt.

were used.

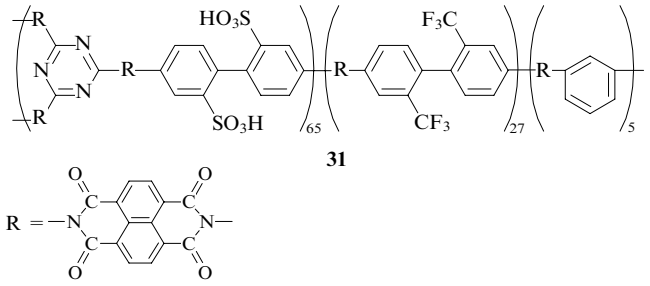
Due to the rigid-chain structure of synthesised co-polynaphthylimides, non-filled voids appear in the macromolecules, which favours water uptake. As a result, membranes based on such SPNI were characterised by the high proton conductivity even at low relative humidity.

In the quest for new SPNI with the high proton conductivity and water stability, two non-sulfonated diamines, namely, 2,2′-bis(trifluoromethyl)benzidine and *m*-phenylenediamine, were used simultaneously in a ratio of 3 : 1 as the BDSA co-monomers (Scheme 7).

Studies of membranes prepared on the basis of SPNI **30** have shown that the increase in the content of bis(trifluoromethyl)biphenylene fragments in macromolecules was accompanied by the increase in the thermooxidation stability of membranes. Membranes based of SPNI **30** possess the high proton conductivity (> 0.2 S cm^{-1}) at 30 – 140 °C (see Ref. 101) and are stable in water at 90 °C.[100]

‡ The synthesis of 2,2′-dibenzoylbenzidine was described in Refs 92, 93; the synthesis of 1,4-bis(4-aminophenyl)benzenes was described in Refs 96 – 98; for the synthesis of diazapentaphenylenediamines, see Ref. 99.

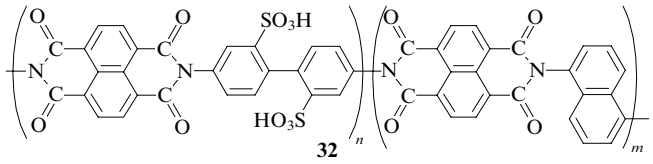
In addition to linear co-polymers **30**, branched co-polymer **31** was prepared.[101]



31

As the 'branching' co-monomer, a trifunctional monomer, melamine (2 mol %), was used.[95] It appeared that branched co-polymer **31** was more stable towards oxidants as compared with linear co-polymer **30**.[101]

The synthesis of co-polymeric SPNI **32** containing 1,5-naphthylene groups was described.[102]



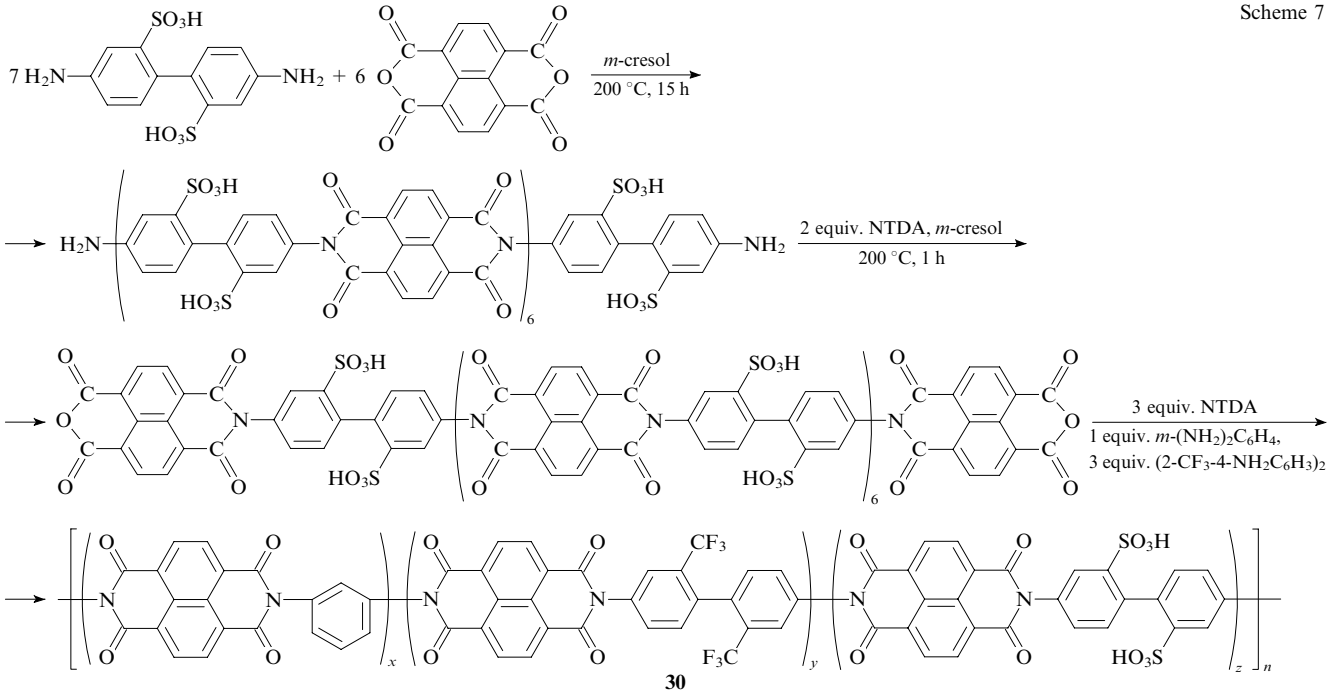
32

m = 10 mol % – 70 mol %.

Co-polymers **32** are soluble in DMSO, DMF and *N*-MP (their solubility decreased with the increase in *m*) and possess high molecular masses, which made it possible to manufacture strong membranes that, nonetheless, retained elasticity. Measurement of the proton conductivity of membranes based on SPNI **32** showed that, at 27 °C, a polymer containing 30% of 1,5-naphthylene groups had the conductivity of 0.06 S cm^{-1} comparable with that of Nafion-type membranes.

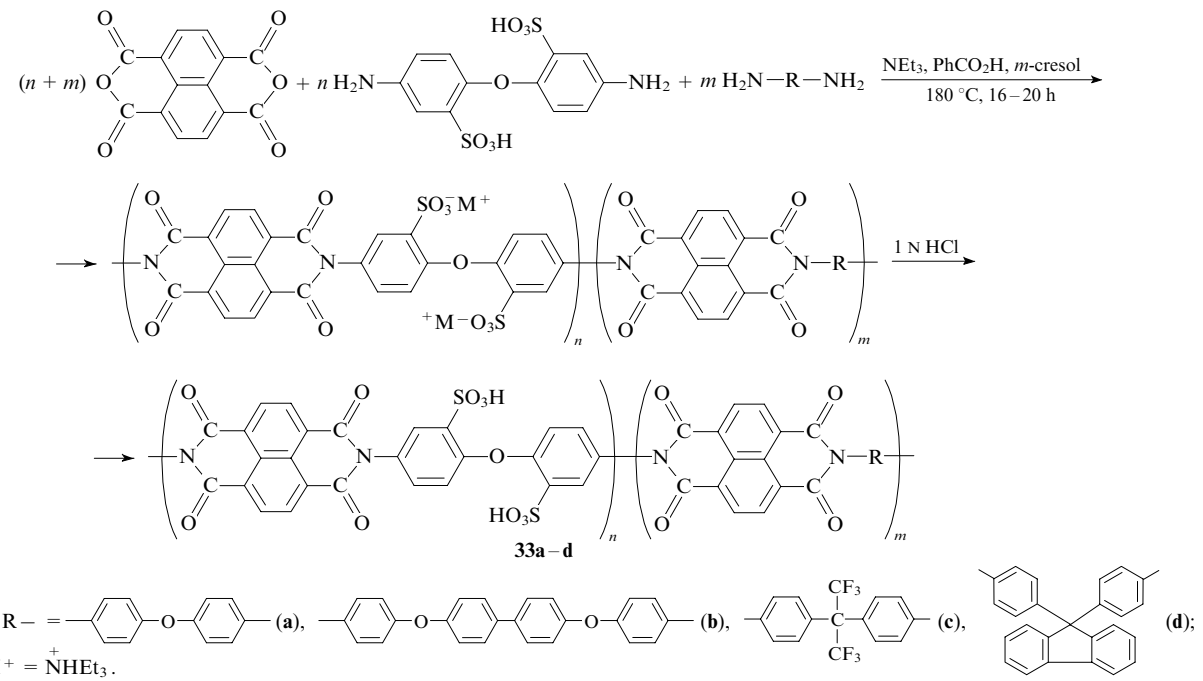
Analysis of different properties of SPNI based on BDSA has shown [73] that the main drawback of these polymers and membranes based on them was their low water stability.

Scheme 7



30

Scheme 8



In addition to BDSA, 4,4′-diamino-2,2′-disulfodiphenyl oxide (**6**, DADSO) or its mixtures with non-sulfonated diamines was used for the synthesis of SPNI. The synthesis of homo- and co-polymers based on acid **6** was carried out according to Scheme 8 by one-step high-temperature polycondensation in *m*-cresol in the presence of triethylamine and benzoic acid, the latter serving as a catalyst. In this way, different homo- and co-polynaphthylimides with the general formula **33** (see Scheme 8), the molecular mass $M_n = 16\,000-18\,000$, $M_w = 53\,000-72\,000$ (SEC) and the molecular-mass distribution equal to 2.9–4.5 were synthesised.[49, 50]

All the synthesised polymers (as the triethylammonium salts) are well soluble in *m*-cresol and some of them are soluble in DMSO. The transition from salts to neutral polymers had a substantial effect on their solubility, namely, many of them became soluble in *N*-MP on heating.

Studies of the thermostability of polymers carried out by DTGA in combination with mass spectrometry have related the initial mass loss observed up to 100 °C with the removal of absorbed moisture. Starting from 288 °C, the mass loss was due to the destruction of the sulfo groups with evolution of SO and SO_2; further mass loss at $T \sim 500$ °C was associated with the destruction of the main chains of macromolecules.

The ion-exchange capacity of membranes based on SPNI **33** was 1.71–3.37 mequiv g^{-1} (Table 4). Homopolyimide **33** ($n = 100\%$) was characterised by the highest IEC; for co-polyimides **33**, IEC values were below those of homopolyimide but above the IEC of Nafion-117. Considering the proton conductivity of homo- and co-polymers **33**, it should be mentioned that at 50 °C and 50%–100% RH, all co-polymers exhibited virtually the same conductivities, close to that of Nafion-117 membranes. All membranes demonstrated an increase in the proton conductivity with the increase in RH and temperature. By and large, the σ values of membranes under consideration were comparable with σ of SPNI based on BDSA.

The most substantial difference of membranes based on SPNI **33** from those based on SPNI synthesised from BDSA was their higher water stability. Whereas for a membrane based on homopolynaphthylimide **24** it took several seconds for complete dissolution in water at 50 °C, for a membrane prepared from SPNI **33** this took 2 h. In a series of co-polyimides, the membranes prepared from DADSO also demonstrated pronounced advantages. One of the reasons for the higher water stability of DADSO-based SPNI was the higher flexibility of macromolecules, which made their relaxation easier. A similar effect was observed earlier by the example of non-sulfonated polyphthalimides. The rigid-chain polyphthalimides were less stable towards hydrolysis as compared with those with flexible chains.[28]

The second reason was the higher basicity of DADSO as compared with BDSA. At the same time, it is well known that polyimides synthesised from more basic diamines are characterised by the higher water stability than those prepared from less basic diamines.[49, 50]

In addition to BDSA and DADSO, 4,4′-bis(4-aminophenoxy)biphenyl-3,3′-disulfonic acid (**8**) that contains amino and sulfo groups in different aromatic nuclei was also employed for the synthesis of co-polymeric SPNI.[50, 51, 103] The synthesis of SPNI **34** on the basis of

Table 4. Ion-exchange capacities and proton conductivities of membranes based on SPNI **33**.

SPNI	*n* (%)	*m* (%)	IEC /mequiv g^{-1}	σ /S cm^{-1}
Homopolymer	100	0	3.37	0.30
Co-polymers				
33a	50	50	1.95	0.12
33b	50	50	1.68	0.10
33c	50	50	1.73	0.11
33d	50	50	1.71	0.09

Note. For comparison, the proton conductivity and ion-exchange capacity of a Nafion-117 membrane were 0.10 S cm^{-1} and 0.91 mequiv g^{-1}, respectively.

acid **8** was also carried out in *m*-cresol in the presence of triethylamine and benzoic acid as the catalyst.

Of all synthesised polymers, homopolynaphthylimide **34** ($n = 100\%$) was studied in more detail. This polymer was soluble only in *m*-cresol, moreover, in both its salt and protonated forms. The ion-exchange capacity of 20 μm-thick membranes prepared on its basis was 2.63 mequiv g^{-1}, the moisture absorption at 80 °C was 107 mass % and the proton conductivity at 50 °C and 80% relative humidity was 0.020 S cm^{-1}. Membranes based on homopolymer **34** possessed high water stability, which is associated with high flexibility of macromolecules and high basicity of the sulfonated diamine used. Very close characteristics were observed for membranes based on a co-polymer prepared from NTDA and sulfodiamine **6** with addtion of 20% of 4,4′-bis(4-aminophenoxy)biphenyl.[51, 53]

Several high-molecular homo- and co-polymeric SPNI **35** were synthesised under the same conditions, but in place of acid **8**, isomeric 2,2′-bis(4-aminophenoxy)biphenyl-5,5′-disulfonic acid (**10**) was used.

Due to the non-linear configuration of their molecules, SPNI **35** are well soluble in *m*-cresol, DMSO, *N*-MP, DMF (in both salt and protonated forms). Membranes prepared from homopolynaphthylimide **35** ($n = 100\%$) were even water-soluble, whereas membranes based on co-polynaphthylimines were not; they retained mechanical strength after being soaked in water at 80 °C for 40 – 1000 h.

Studies of the proton conductivities of membranes based on SPNI **35** and Nafion-117 at 50 °C and RH 10% – 100% have shown that at low HR (30%), the conductivity of Nafion-117 membranes exceeded that of SPNI-based membranes tenfold. With the increase in the relative humidity, the proton conductivity of SPNI **35** increased faster than that of Nafion-117 so that at high RH, the conductivities of SPNI and Nafion-117 became comparable; moreover, due to its high ICE (Table 5), the homopolyimide exhibited higher conductivity than the co-polyimide.

Table 5. Certain characteristics of SPNI **35**.[53]

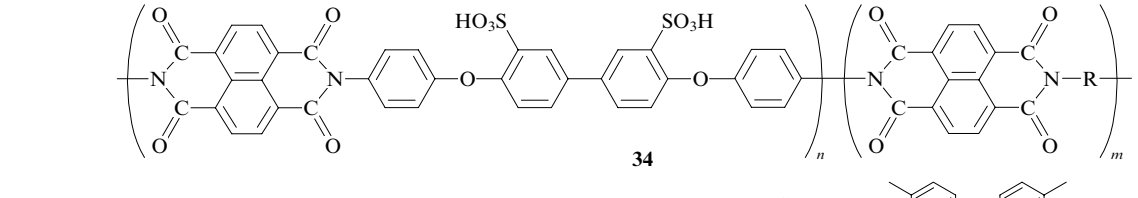
SPNI	*n* (%)	*m* (%)	η_{log} /dl g^{-1} (see [a])	IEC /mequiv g^{-1}
Homopolymer	100	0	–	2.63
Co-polymers				
35a	56	44	3.15	1.85
35b	66	34	1.51	1.89
35c	66	34	3.53	1.89
35d	66	34	3.24	1.83

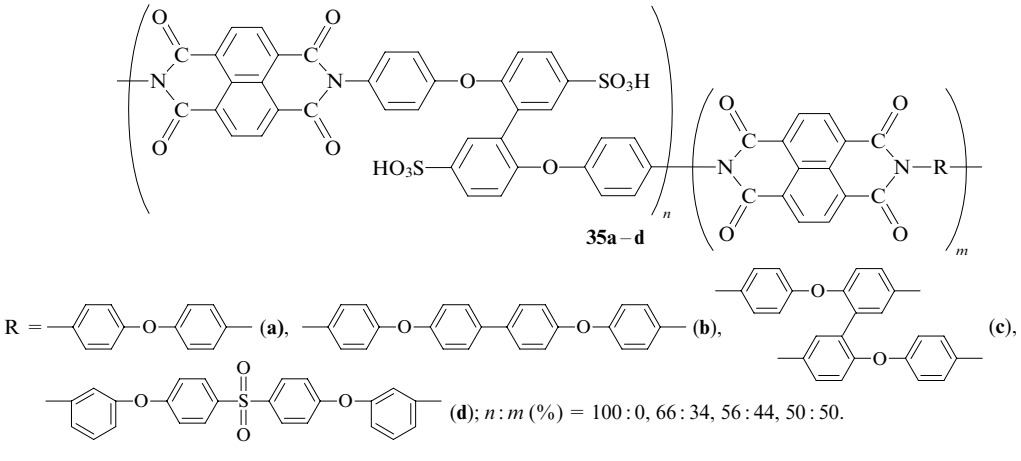
[a] Viscosities of SPNI salts were measured for their 0.5% solutions in DMSO at 35 °C.

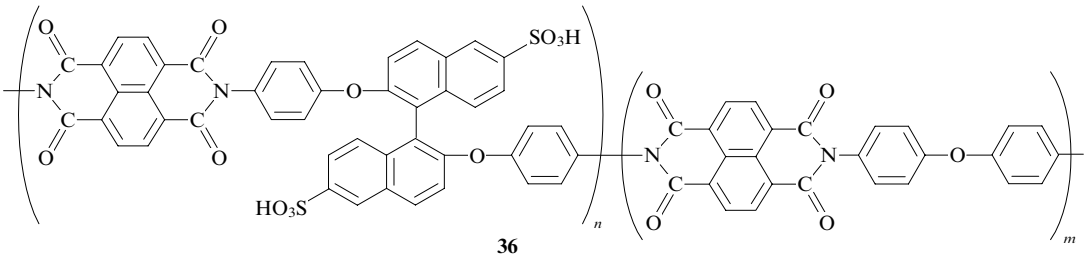
It should be noted that Nafion-117 possesses low ion-exchange capacity (0.91 mequiv g^{-1}) and low water absorption, but high proton conductivity. This was explained by the fact that Nafion-117 had a domain structure in which ion-enriched domains formed ionic channels, which favoured the proton transport.[104]

The non-linear configuration similar to that of SPNI **35** was typical of SPNI **36** synthesised from 2,2′-bis(4-aminophenoxy)-1,1′-binaphthyl-6,6′-disulfonic acid (**11**), 4,4′-diaminodiphenyl oxide and NTDA taken in different ratios.[54]

Like the overwhelming majority of the aforementioned SPNI, polymers **36** were synthesised by polycondensation in *m*-cresol in the presence of triethylamine and benzoic acid at the maximum temperature of 180 °C for 12 h. Initially, SPNI are formed as triethylammonium salts were well soluble in DMAA, *N*-MP and DMSO and formed solutions with high logarithmic viscosities (Table 6), which pointed to their high molecular masses. Good solubility and high







36

$n:m$ (%) = 30 : 70, 40 : 60, 50 : 50, 60 : 40, 70 : 30, 80 : 20.

Table 6. Certain characteristics of SPNI **36**.[54]

$n:m$	η_{log} /dl g^{-1} (see [a])	IEC, /mequiv g^{-1}	σ /S·cm^{-1} at		
			20 °C	60 °C	80 °C
30 : 70	1.32	1.00	0.0220	0.0356	0.0405
40 : 60	1.56	1.25	0.0496	0.0807	0.0933
50 : 50	1.45	1.50	0.0622	0.1010	0.1230
60 : 40	1.79	1.70	0.0945	0.1420	0.1610
70 : 30	1.74	1.81	0.0950	0.1280	0.1490
80 : 20	1.77	1.98	0.0875	–	–

Note. The values of σ for Nafion-117 were 0.0958, 0.1510 and 0.1720 S cm^{-1} at 20, 60 and 80 °C, respectively. [a] Measured for SPNI triethylammonium salts.

viscosity characteristics of SPNI made it possible to use them in the preparation of high-quality membranes that could be converted into their protonated forms by the exposure to 1 N H_2SO_4.

DTGA studies of the thermal stability of SPNI **36** have shown that, like other polymers of this type, the mass losses occurred in three temperature ranges, namely, below 100 °C (absorbed moisture loss), ~300 °C (destruction of sulfo groups) and ~500 °C (destruction of main macromolecular chains). All SPNI **36** were characterised by relatively high water stability associated with the flexibility of macromolecules and high basicity of the sulfonated diamine used in their synthesis.

As would be expected, the ion-exchange capacity of membranes based on SPNI **36** increased with the increase in the content of sulfonated diamine residues in SPNI (*i.e.*, with the increase in n, Table 6). The proton conductivity of each individual SPNI increased with the increase in the temperature (see Table 6). A co-polymer with the $n:m$ ratio 60 : 40 had the highest conductivity (comparable with that of Nafion-117).

Polymers with larger $n:m$ ratios exhibited lower conductivity, which was associated [54] with the peculiar microstructures of the polymers. The hydrogen permeation through membranes based on SPNI **36** at 20 °C was $9 \times 10^{-8} - 5 \times 10^{-7}$ cm^2 s^{-1} (depending on the degree of sulfonation), *i.e.*, an order of magnitude lower than the permeation through Nafion membranes (2×10^{-6} cm^2 s^{-1} at the same temperature).

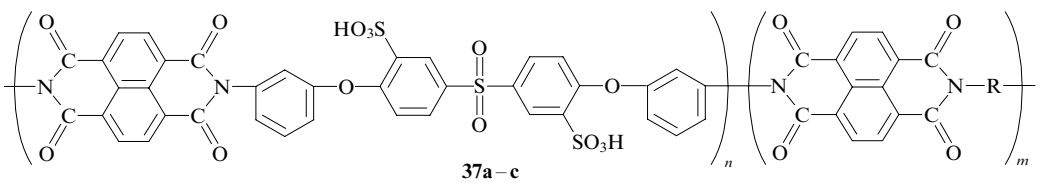
McGrath and co-workers [56, 57, 105, 106] synthesised SPNI **37a–c** based on NTDA, bis[4-(3-aminophenoxy)-3-sulfophenyl] sulfone (**13**) and *m*-phenylenediamine (SPNI **37a**), 4,4′-diaminodiphenyl oxide (SPNI **37b**) or bis[4-(3-aminophenoxy)phenyl] sulfone (SPNI **37c**).

Co-polymers **37a–c** were prepared in *m*-cresol in the presence of triethylamine, benzoic acid and isoquinoline as the catalysts. Acid **13** was first treated with triethylamine in *m*-cresol for 4 h at room temperature and thereafter other co-monomers were added. This procedure afforded high-molecular random co-polymers with the controllable degree of sulfonation. The properties of triethylammonium salts of SPNI **37a–c** with $n:m$ = 50 : 50 and 80 : 20 are listed in Table 7. Triethylammonium salts of SPNI **37a–c** were soluble in *N*-MP, DMSO and DMAA. Salts of polymers with high degrees of sulfonation were also soluble in hot methanol and water.

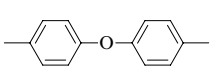
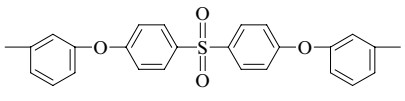
Table 7. Certain characteristics of triethylammonium salts of SPNI **37a–c**.

R	$n:m$	η_{log} /dl g^{-1} (*N*-MP, 30 °C)	M_n	Yield (%)
37a	50 : 50	2.01	30 600	99
	80 : 20	1.15	20 000	96
37b	50 : 50	1.54	28 400	95
	80 : 20	1.85	44 300	96
37c	50 : 50	2.40	28 400	97
	80 : 20	1.65	31 000	96

Strong elastic membranes were prepared by casting from solutions of SPNI **37a–c** in *N*-MP; attention was focused on the procedure of the transformation of synthesised membranes into the sulfonic acid form,[107] because this considerably affected the morphology and conductivity of the target membranes. ^{1}H NMR study demonstrated that



37a–c

R =  (**a**),  (**b**),  (**c**).

the high degree of ion exchange can be reached by the following methods:

— soaking of membranes in boiling 0.5 M H_2SO_4 for 2 h followed by their exposure to 1.5 M H_2SO_4 at 25 °C for 3 days and then to deionised water at 25 °C for 24 h;

— soaking in 1.5 M H_2SO_4 at 25 °C for 10 days.

Acid forms of SPNI **37a–c** and membranes on their basis were well soluble in polar aprotic solvents (*N*-MP, DMAA, DMF), whereas highly sulfonated co-polymers were soluble in aqueous acetone (6 : 1).

Studies of the thermostability of SPNI **37c** with different degrees of sulfonation carried out by the DTGA have shown that these SPNI exhibited higher thermostability in the sulfonic acid form as compared with their triethylammonium salts. The temperature corresponding to the 5% mass loss decreased with the increase in the degree of sulfonation (Table 8).

Table 8. Ion-exchange capacity and thermostability of SPNI **37c**.

n : *m*	IEC /mequiv g^{-1}	Temperature of 5% mass loss /°C
30 : 70	0.85	490
40 : 60	1.02	484
50 : 50	1.30	428
70 : 30	1.74	419
80 : 20	1.90	390

Insofar as cardo groups are the elements that may belong to both the main and the side chains of macromolecules of the corresponding polymers,[108, 109] SPNI based on sulfonated diamines containing cardo groups (*e.g.*, fluorene group) should be considered as the systems that occupy an intermediate position between SPNI containing sulfo groups in the main chains of macromolecules and SPNI with pendant sulfo groups.

Sulfonated polymers, namely, homopolynaphthylimide (**38**) based on NTDA and 9,9-bis-(4-aminophenyl)fluorene-2,7-disulfonic acid (**12**), and also co-polynaphthylimides (**39a–c**) with random structures based on NTDA, sulfonated diamine **12** and non-sulfonated aromatic diamines were synthesised by one-step polycyclocondensation. This was carried out in *m*-cresol in the presence of triethylamine and benzoic acid at 180 °C for 16–20 h. Block co-polymers **39** were prepared by a two-step procedure.

The synthesised random and block co-polymers **39** in the form of triethylammonium salts were well soluble in *m*-cresol and DMSO (with some exceptions); moreover, in the majority of cases, random SPNI were better soluble as compared with block SPNI. Films prepared from solution of both types of SPNI **39** exhibited high deformation and strength characteristics. Membranes were converted to the protonated form by treating them with 1 N HCl.

All synthesised SPNI were characterised by high molecular masses. Thus the weight-average mass was 32 000 for homopolymer **38** (in the protonated form) and 37 000 for random SPNI **39a**. TGA-MS studies of the thermostability of homopolyimide **38** have shown that its destruction began at ~270 °C with the evolution of SO and SO_2.

The results of measurements of the ion-exchange capacity and proton conductivity of SPNI **38** and **39a–c** showed (Table 9) that the highest IEC and σ values were typical of homopolymer **38** (n = 100%).[55] The IEC and σ values for random co-polymer **39a** decreased with an increase in the ratio of non-sulfonated diamine residues in SPNI. The proton conductivity of all membranes increased as the RH became higher, which was typical of almost all sulfonated polymers and Nafion.

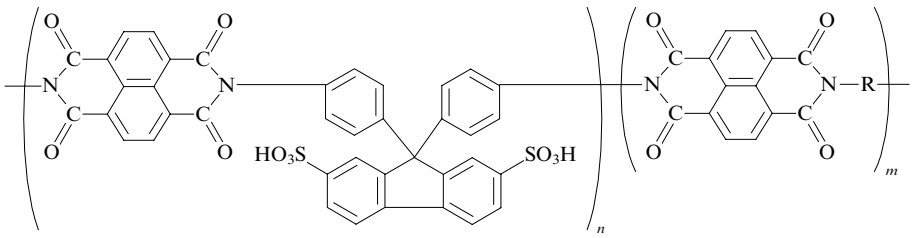
Table 9. Certain characteristics of membranes based on SPNI **38**, **39a–c**.

Co-polymer type	Polymer	*n* (%)	*m* (%)	IEC [a]	σ /S cm^{-1} (see [b]) at RH	
					50%	100%
Homopolymer	**38**	100	0	2.70	0.013	0.21
Random	**39a**	80	20	2.36	0.0065	0.20
		66	34	2.09	0.0038	0.17
		50	50	1.71	0.0035	0.12
	39b	56	44	1.68	–	0.10
	39c	66	34	1.87	–	0.11
Block	**39a**	66	34	2.09	0.0067	0.19
	39c	66	34	1.87	–	0.14

[a] From hereon, IEC values are given in mequiv g^{-1}; [b] conductivity was measured at 50 °C.

It should be noted that in some cases the polymer conductivity depended on its microstructure. Particularly, polymers with the same ICP values but different microstructures could substantially differ in their conductivities. By and large, the morphology of polymers also affected their proton conductivities. Thus at the same RH, block polymers **39a** and **39c** with $n : m = 64 : 34$ were characterised by higher conductivities than random co-polymers **39a** and **39c** with the same composition.

A comparison of the proton conductivities of membranes based on SPNI **38**, **39** and Nafion-117 showed that at 50 °C throughout the RH interval under consideration,



38 (m = 0), **39a–c** ($m \neq 0$)

R = —O— (**a**), —O—O— (**b**), —O—SO2—O— (**c**);

$n : m$ (%) = 100 : 0, 80 : 20, 66 : 34, 50 : 50, 56 : 44.

homopolyimide **38** had the conductivity comparable with that of Nafion-117, whereas conductivities of all co-polymers **39** were considerably lower than that of Nafion, although the former had considerably higher IEC values. Probably, this was associated with the fact that co-polyimides **39** were characterised by homogeneous structure, whereas 'Nafion' membranes had the domain structure with ionic channels, which favoured the higher σ.

Studies of the temperature dependence of the proton conductivities of SPNI **38** and **39** at 100% relative humidity have shown that the proton conductivity increased with temperature. Under these conditions, their conductivities are comparable with or higher than, that of Nafion-117.[55] This was probably associated with the fact that at 100% relative humidity, polyimide membranes were in fully hydrated state, which made easier the proton transport through them. Moreover, membranes based on block co-polyimides demonstrated the same or slightly higher conductivity as compared with membranes based on random co-polyimides. Under these conditions, the role of ionic channels in the increase in the conductivities of Nafion-117 membranes decreased.

Studies of the water stability of membranes based on SPNI **38** and **39** at 50 and 80 °C have shown that membrane based on homopolyimide was relatively stable only at low (50 °C) temperatures and completely dissolved in water at 80 °C due to the high ion-exchange capacity of this membrane. Membranes based on co-polyimides **39** dissolved in water neither at 50 °C nor at 80 °C and retained their shape after being soaked in water at 80 °C for 200 h. It should be noted that random co-polyimides had much higher water stability than block co-polyimides.

A comparison of the water stabilities of membranes prepared from different sulfonated diamines has shown that a membrane based of SPNI **39a** with $n:m = 2:1$ was much more stable in water than a membrane based on SPNI **23b** ($x:y = 2:1$), despite having higher ion-exchange capacity.

A comparison of the water stabilities of membranes based on SPNI with the same flexibility and ion-exchange capacity, *e.g.*, membranes based on random co-polymers **39a** ($n:m = 1:1$) and **33d** ($n:m = 1:1$), has shown that co-polymer **39a** exhibited the higher water stability. Presumably,[55] the basicity of BDSA and DADSO was substantially lower than that of diamine **12** because the former diamines contained strong electron-withdrawing sulfo groups in the same benzene rings as the amino groups, while in the latter diamine, sulfo groups were remote from the benzene rings containing amino groups.

As follows from the data discussed, the basicity of diamines and the flexibility of macromolecules are the main factors that determine the water stability of SPNI synthesised on their basis.

On the whole, studies of SPNI membranes based on 9,9-bis-(4-aminophenyl)fluorene-2,7-disulfonic acid (**12**) have shown that they could be used in FC operating at low temperatures (< 80 °C), while their stabilities may become insufficient at high (> 100 °C) temperatures.

2. Polynaphthylimides containing pendant sulfo groups

The concept of 'transferring' sulfo groups to the side chains of macromolecules relies not only on the trend to use more basic diamines, but also on the desire to break the homogeneous structure of SPNI in order to impart them the microphase-separated (domain) structure that would allow the formation of ionic channels.[104, 110, 111]

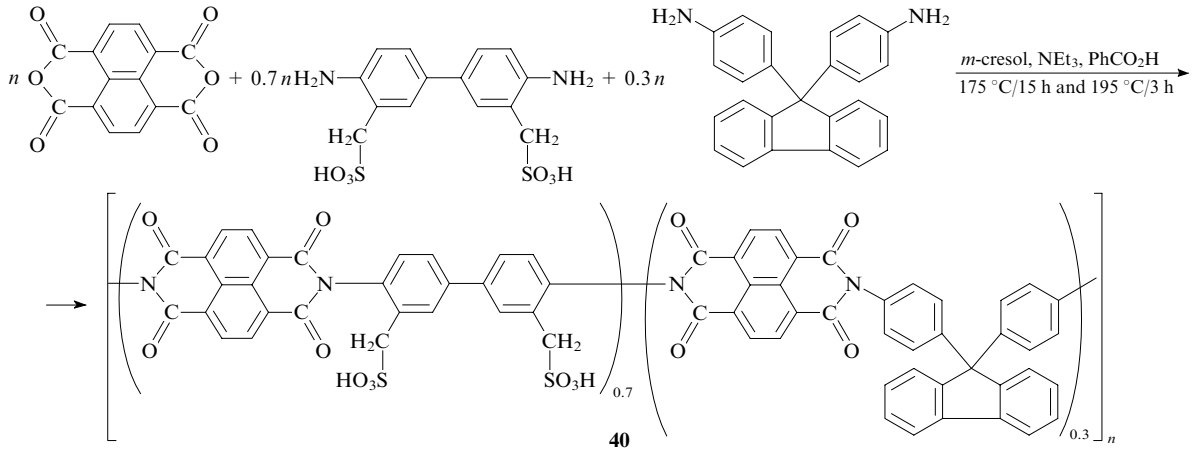
According to data from SEC, sulfonated polynaphthylimides **40** prepared upon polycondensation of NTDA with 3,3′-bis(sulfomethyl)benzidine and 9,9-bis(4-aminophenyl)-fluorene in *m*-cresol in the presence of triethylamine and benzoic acid had high molecular masses ($M_n = 1.14 \times 10^5$, $M_w = 1.75 \times 10^5$) (Scheme 9).[59]

Co-polymer **40** was completely soluble in *m*-cresol. From this solution strong cast membranes were prepared. Membranes based on SPNI **40** exhibited the ion-exchange capacity of 2.31 mequiv g^{-1} and the high proton conductivity (0.39 S cm^{-1} at 100 °C) comparable with that of Nafion-112.

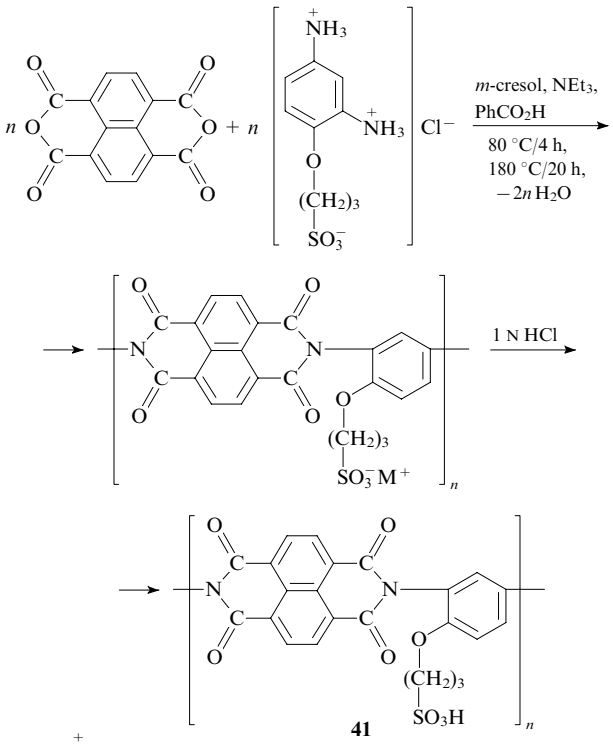
A drawback of membranes under consideration was their low stabilities towards oxidation and hydrolysis, which led to a substantial decrease in the molecular masses of polymers and deterioration of mechanical properties of membranes.

The synthesis of SPNI containing pendant sulfoalkoxy groups was described.[58, 59, 61, 112] The simplest SPNI **41** was prepared by the reaction of 3-(2,4-diaminophenoxy)propanesulfonic acid hydrochloride (**14**) with NTDA.[58]

Scheme 9



40



$M^+ = \overset{+}{N}HEt_3$.

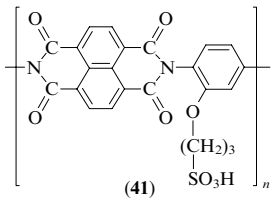
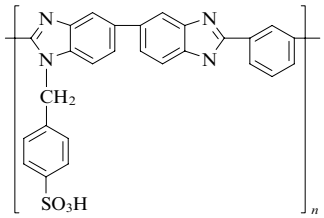
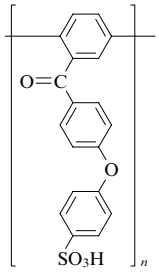
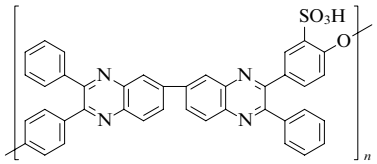
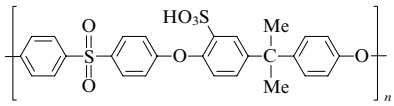
Polymer **41** was well soluble in *m*-cresol, DMSO and DMF both as the triethylammonium salt and in the protonated form. The weight-average molecular mass of SPNI **41** was 5.5×10^4 and the M_w/M_n ratio was 3.1. The thermostability of SPNI **41** was assessed by DTGA combined with mass spectrometry. As for the aforementioned SPNI, the mass loss of SPNI **41** in the vicinity of 100 °C was associated with the removal of water, while the mass loss in the vicinity of ~240 °C was due to the destruction of aliphatic side groups $-OCH_2CH_2CH_2-$ and sulfo groups to produce propene, allene and SO_2. Note that for SPNI **41**, the temperature of sulfo group destruction was somewhat lower as compared with the SPNI without alkyl side substituents.[37,49,55] Evolution of SO_2 was the most active at ~290 °C. The destruction of the main chains of SPNI **41** occurred at 450–700 °C.

Comparative studies of the water stability of SPNI-based membranes have shown that membranes based of SPNI **41** were more stable than those based on SPNI **33** and **39**, which was assumed[58] to be due to the high basicity of SPNI **41** caused by the electron-donating effect of alkoxy groups.

A comparison of the ion-exchange capacities, water uptake values and proton conductivities of different sulfonated polymers (Table 10)[58,87,112–117] deserves attention. The results obtained by different authors under different conditions are difficult to compare; nevertheless, it follows from the data in Table 10 that the proton conductivity of SPNI **41** is comparable with that of the best sulfonated polymers known.

Studies of the dependence of the proton conductivity of SPNI **41** on RH at 50 °C have shown that the σ values increased with RH. On the whole, throughout the relative humidity range under consideration, the conductivity of SPNI **41** was comparable or slightly lower than that of copolynaphthylimide **33a** (n = 75%, m = 25%).[112] (The higher σ values of SPNI **33a** were associated with the higher values of IEC and water uptake.)

Table 10. Certain characetristics of sulfonated polymers.

Polymer	IEC	RH (%)	σ [a]	Ref.
 (**41**)	1.98	90	0.035	58
	1.57	100	0.017	112
	1.85	100	0.01	87
	3.51	–	0.0098	113
	1.25	–	0.0043	114
PBI-BS [b]	–	90	0.17	115

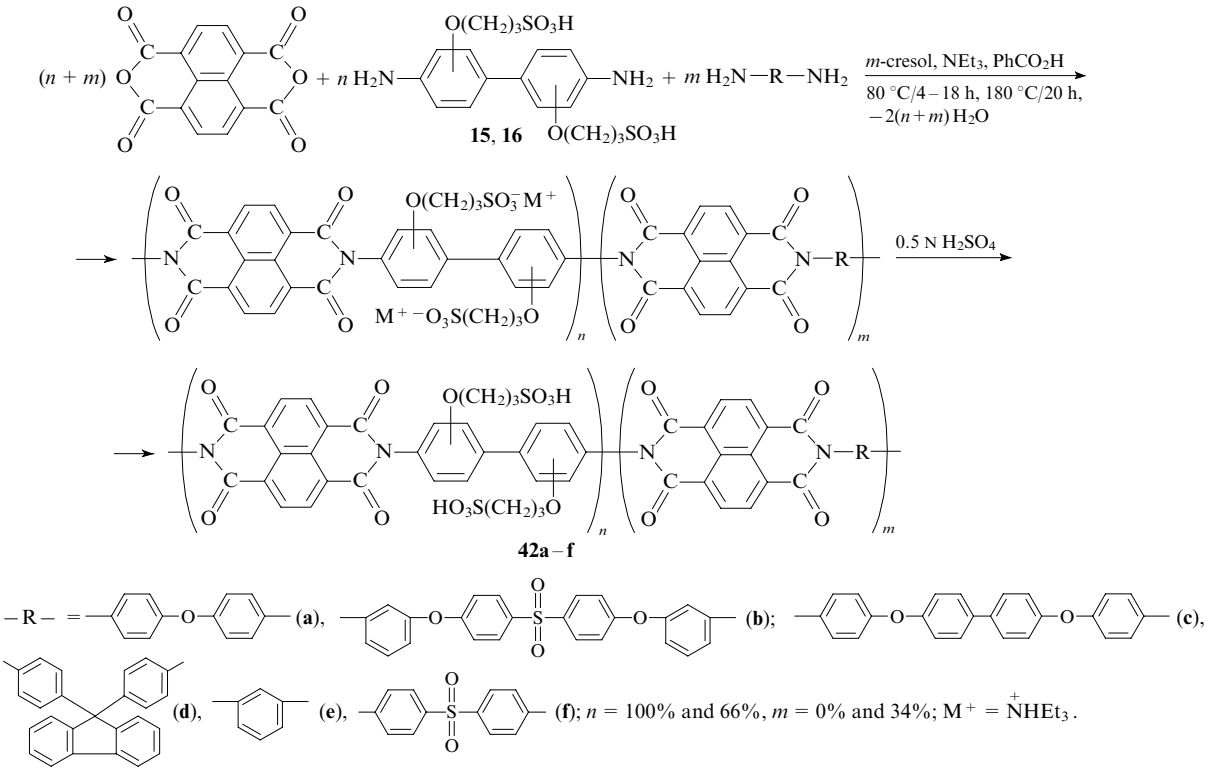
[a] In S cm^{-1}; PBI-BS is polybenzimidazole with sulfobutyl-substituents.

A comparison of the proton conductivities of membranes based on SPNI **41** with the conductivity of Nafion-117 showed that at RH < 100%, the conductivity of SPNI **41** was somewhat lower; however, in the completely hydrated form (in water), the conductivities of membranes based on SPNI **41** were comparable with that of Nafion-117 membranes and even exceeded it. Moreover, membranes based on SPNI **41** were characterised by the lower permeability towards methanol as compared with Nafion-117 membranes, which suggests that SPNI **41** is promising for use in FC.[116]

Studies of the temperature dependence of proton conductivity of SPNI **41** have shown that with an increase in the temperature, the conductivity increased to 0.35 S cm^{-1}.

The synthesis of more complicated SPNI with pendant propoxysulfonic acid substituents was decsribed.[61,109] Sulfonated homopolynaphthylimides **42** (n = 100%) were syn-

Scheme 10



thesised by the reaction of NTDA with sulfonated benzidines **15** and **16**. Synthesis of a series of co-polynaphthylimides **42** with random or block structures on the basis of NTDA, isomeric bis(sulfopropoxy)benzidines **15** or **16** and non-sulfonated diamines was undertaken to improve the membrane stability.[117] Co-polynaphthylimides with the random structure were prepared by a conventional method of high-temperature polycyclocondensation in *m*-cresol in the presence of triethylamine and benzoic acid (Scheme 10). The synthesis of block co-polymeric SPNI was carried by a two-step method, which afforded sulfonated oligomers with terminal anhydride groups in the first stage; in the second stage, these oligomers reacted with non-sulfonated aromatic diamines.

At room temperature all synthesised polymers were soluble in *m*-cresol and at elevated temperatures, in DMSO; some co-polymers were soluble completely or partly in *N*-MP and DMF. Co-polyimides were better soluble than the homopolyimide, while polymers based of diamine **16** were better soluble than the corresponding polymers based on diamine **15**.

Destruction of sulfonated aliphatic side chains in SPNI **42** began at 247 – 255 °C, as evidenced from the evolution of propene, allene, SO_2 and H_2O; the destruction of the main chains was observed at 490 – 540 °C.

The dynamic modulus of elasticity of membranes based on SPNI **42** decreased with the increase in RH, where co-polynaphthylimides demonstrated the smaller dynamic moduli of elasticity than homopolynaphthylimides.

According to the results of transmission electron microscopy, membranes based on homo- and co-polynaphthylimides **42** were built of hydrophilic and hydrophobic domains measuring 5 nm, *i.e.*, were characterised by microphase separation.

In homopolyimides, ionic domains are combined to form ionic channels. Such channels favoured the conservation of water molecules and made easier the proton transport. In membranes based on co-polynaphthylimides **42,** the formation of such channels was much less pronounced. Due to the underdeveloped structure of ionic channels, the lower ion-exchange capacity and the lower water uptake, the proton conductivity of co-polynaphthylimide membranes was much lower than that of homopolynaphthylimide membranes (especially at low RH).

Data on ion-exchange capacity, the moisture uptake and the proton conductivity of membranes based on SPNI **42** are listed in Table 11. It is evident that the membrane conductivity substantially increased with the increase in

Table 11. Certain characteristics of membranes based on homo- ($n:m = 1:0$) and co-polynaphthylimides **42** ($n:m = 2:1$).

Sulfonated diamine	Non-sulfonated diamine (R designations are in text)	IEC	Water uptake (%)	σ S cm^{-1} at RH		
				100%	90%	70%
16	–	2.89	250	0.23	0.110	0.0300
	a	2.23	73	0.15	0.041	0.0037
	a (see [a])	2.23	94	0.16	0.060	0.0056
	b	1.95	49	0.09	0.066	0.0076
	c (experiment 1)	2.02	62	0.11	0.031	0.0012
	c (experiment 2)	2.02	64	0.12	0.038	0.0068
	c (see [a])	2.02	78	0.13	0.050	0.0071
	d	2.04	58	0.11	0.040	0.0065
	f	2.17	68	0.15	0.042	0.0062
15	–	2.89	220	0.22	0.110	0.0350
	a (experiment 1)	2.02	44	0.06	0.018	0.0012
	a (experiment 2)	2.02	61	0.11	0.032	0.0038
	a (experiment 1)	2.02	76	0.14	0.078	0.0096
	b	1.95	39	0.05	0.018	0.0035
	e	2.32	55	0.15	0.045	0.0060

[a] Co-polymer with block structure.

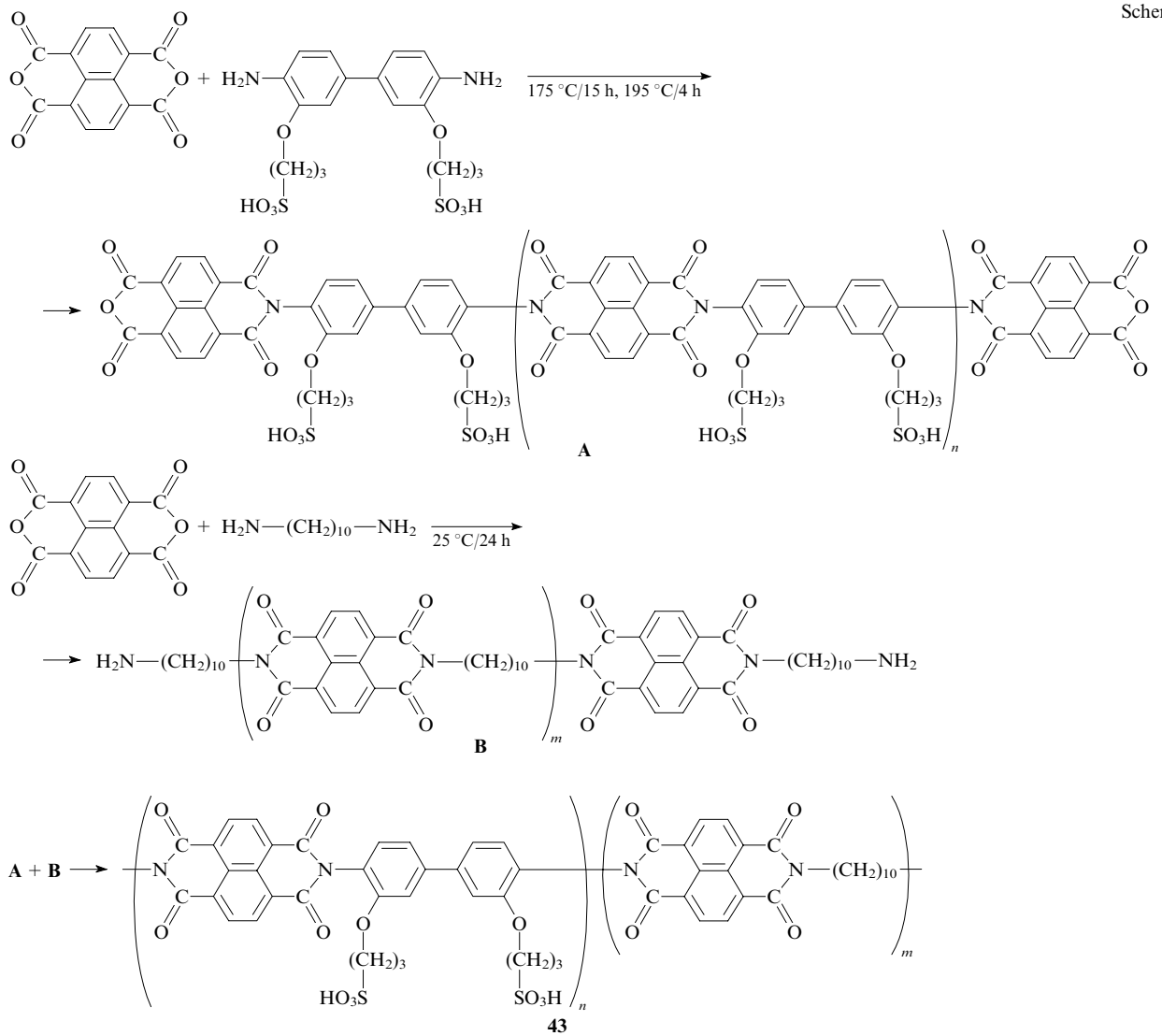
RH. At high RH (>90%), the proton conductivities of co-polyimide and homopolyimide membranes were comparable.

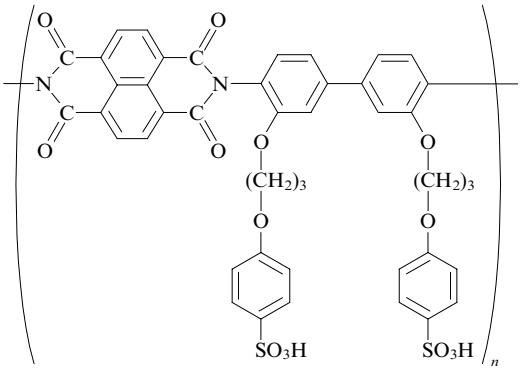
It is of note that the water uptake and the proton conductivities of membranes based on co-polymers **42** with the same chemical composition but synthesised in different experiments (see Table 11), were different, which is probably due to the differences in their morphologies. The proton conductivities of individual membranes based on co-polyimides **42** remained unchanged after their ageing in water (100 °C) for 300 h.

Insofar as according to the data by Kawakami and co-workers,[118] SPNI with the block structure exhibited the considerably higher proton conductivity as compared with random polymers of the same composition, an attempt was undertaken [119] to synthesise block co-polyimides using 3,3′-bis(sulfopropoxy)benzidine (**16**), 1,10-decamethylenediamine and NTDA. For this purpose, blocks with terminal anhydride (blocks **A**) and amino (blocks **B**) groups (Scheme 11) were synthesised followed by condensation to afford block polymer **43**. Block co-polymers **43** that contained blocks with different lengths (n and m) were well soluble in DMSO. From DMSO solutions of block co-polymers **43,** strong cast membranes were prepared. Among the synthesised block co-polymers, the 'long-block' system with $n = m = 150$ units deserves the keenest attention. The microstructure of such block co-polymers is built of domains with the size of several hundred of nanometres connected with one another. Such a structure of membranes based on SPNI **43** favoured the proton transport through them. The proton conductivity of SPNI **43** was 2×10^{-2} S cm^{-1} at 48% RH, which is comparable with the conductivity of Nafion membranes.

Synthesis of SPNI **44** containing sulfophenoxypropoxy groups was described.[63] Being isolated from the reaction solution, high-molecular-mass SPNI **44** (in the salt form) could not be dissolved in all tested solvents; hence, the membranes were cast directly from the reaction solutions. The membranes were converted to the protonated form by soaking in ethanol containing 1N HNO_3 for 12 h.

Scheme 11





44

TGA/DTGA – mass-spectrometric studies of the thermostability of SPNI **44** in the temperature range of 25 – 400 °C have shown that polymer lost its mass in the following two regions: below 130 °C (water removal) and above 200 °C (SO_2 evolution). These data are close to those obtained in the studies of different SPNI containing aliphatic substituents with terminal sulfo groups,[59, 120 – 122] *i.e.*, the presence of benzene rings in the side sulfoalkoxy substituents had virtually no effect on the thermostability of the polymers.

Studying the oxidation (Fenton's reagent, 80 °C/1 h) and hydrolytic (140 °C /24 h) stability of membranes based on SPNI **44** has shown that under these conditions, the polymer lost 16% and 19% of its mass, correspondingly. These results are comparable with those obtained for other SPNI containing sulfoalkoxy pendant groups.[120 – 122] Despite the considerable mass losses, membranes remained elastic on stretching but were brittle on bending.

According to certain studies,[123] SPNI with pendant sulfo groups undergo decomposition due to littler scission imide rings in the main chains of macromolecules or cleavage of the alkyl(aryl) ether bond in the substituents.

Under the conditions of FC operation, the degradation of the main chains of macromolecules that causes the membrane fragility seems more probable.[124]

The proton conductivity of SPNI **44** was studied in comparison with the conductivity of Nafion-112 and copolymeric SPNI **42d** ($n : m = 3 : 1$) with $HO_3S(CH_2)_3$ groups in the 3,3′-positions (the latter exhibited the same ion-exchange capacity as SPNI **44**). At low temperatures (40 °C) and 100% RH, the proton conductivity of membranes based on SPNI **44** and SPNI **42d** (0.76 : 0.24) was 0.2 S cm^{-1}, which twice exceeded the σ value of Nafion-112. With the increase in the temperature, the conductivity of SPNI **44** considerably increased and at 120 °C reached 1.0 S cm^{-1}, whereas the increase in the conductivities of Nafion-112 and SPNI **42d** was less pronounced. However, as the relative humidity decreased, the proton conductivity of SPNI-based membranes dramatically dropped. Studies of the microstructure of polymer **44** by small-angle X-ray scattering have shown that hydrophilic clusters in the SPNI under consideration were comparable in size with the clusters in Nafion-112, but the phase separation was far less pronounced.

The synthesis of SPNI **45a**,**b** with sulfo groups attached to long alkyl substituents was described.[59] Being isolated from the reaction solution, co-polyimide **45b** could not be dissolved in either of tested solvents; hence, the membranes were cast directly from the reaction solutions. Co-polyimide **45a** prepared under conventional conditions of SPNI synthesis (*m*-cresol – NEt_3 – $PhCO_2H$, heating at 80 °C for several hours), represented a gel-like mass. Changes in the polycyclocondensation conditions (40 °C/20 days and 60 °C/10 days) resultted in solutions of the co-polyimide that allowed the corresponding membranes to be cast. However, these membranes turned out to be very fragile; hence, later, the membranes were prepared by impregnating porous polyimide substrates with solutions of SPNI **45a**,**b**.

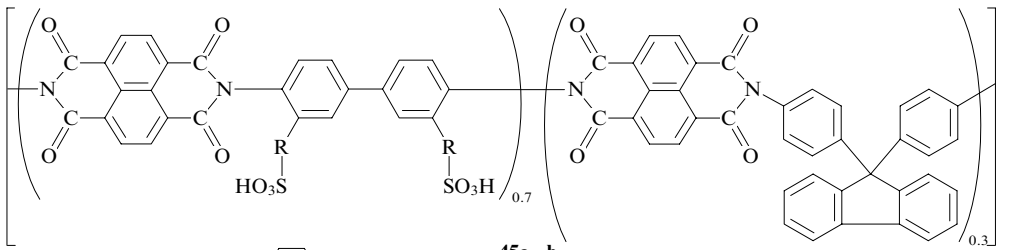
Termogravimetric and mass spectrometric analyses of SPNI **45** in the temperature range of 25 – 400 °C demonstrated the two-step mass loss: at 25 – 200 °C, water was removed and above 200 °C, the decomposition of the ionomeric groups began. The mass number of the main fragment formed as a result of decomposition was 64, which corresponds to SO_2.

The introduction of long side chains into SPNI did not reduce the glass-transition temperature of the polymers below the decomposition temperature. This suggests that thermal characteristics of SPNI depended stronger on the nature of the acidic group than on the side chain length.

Studies on the oxidation stabilities of membranes (Fenton's reagent, 80 °C) have shown that SPNI with pendant long sulfoalkoxy substituents were much more stable than SPNI containing sulfo groups in the main chains of the macromolecules or SPNI containing short sulfoalkoxy substituents. An analogous conclusion was drawn from studies of the water stability of SPNI (water, 140 °C).

Polymer **45b** was characterised by the highest oxidation and water stabilities in the series of all substituted SPNI. This was associated with the fact that the main chain of this co-polymer was remote from the hydrophilic acidic groups and hence less prone to the effect of moisture. Small ion-exchange capacity (IEC = 1.45 mequiv g^{-1}) of this SPNI is also favourable.

Small ion-exchange capacity of SPNI **45b** determined its relatively low proton conductivity at low temperatures ($\sigma = \sim 10^{-2}$ S cm^{-1}); however, at 120 °C, the σ value reached 0.1 S cm^{-1}. However, membranes prepared by impregnating porous polyimides with solutions of SPNI **45b** were characterised by far lower σ (10^{-4} S cm^{-1}).



45a – b

– R – = $-O(CH_2)_{10}-$ (**a**), $-O(CH_2)_{12}O-C_6H_4-$ (**b**).

Studies of the dependence of moisture uptake and the proton conductivity of membranes based on SPNI **45b** on RH at 80 °C have shown that as the RH increased from 40% to 80% σ increased by 2 orders of magnitude.

Most often, the dependence of the proton conductivity on RH was observed for hydrocarbon ionomeric membranes characterised by less pronounced hydrophobic and hydrophilic phases and hence protonic channels (this distinguished them from perfluoroalkylsulfonic acid polymers).[10]

A comparison of σ values for membranes based on SPNI with sulfo groups in the side chains has shown that a fragment with three or four CH_2 groups had the optimal length.[63]

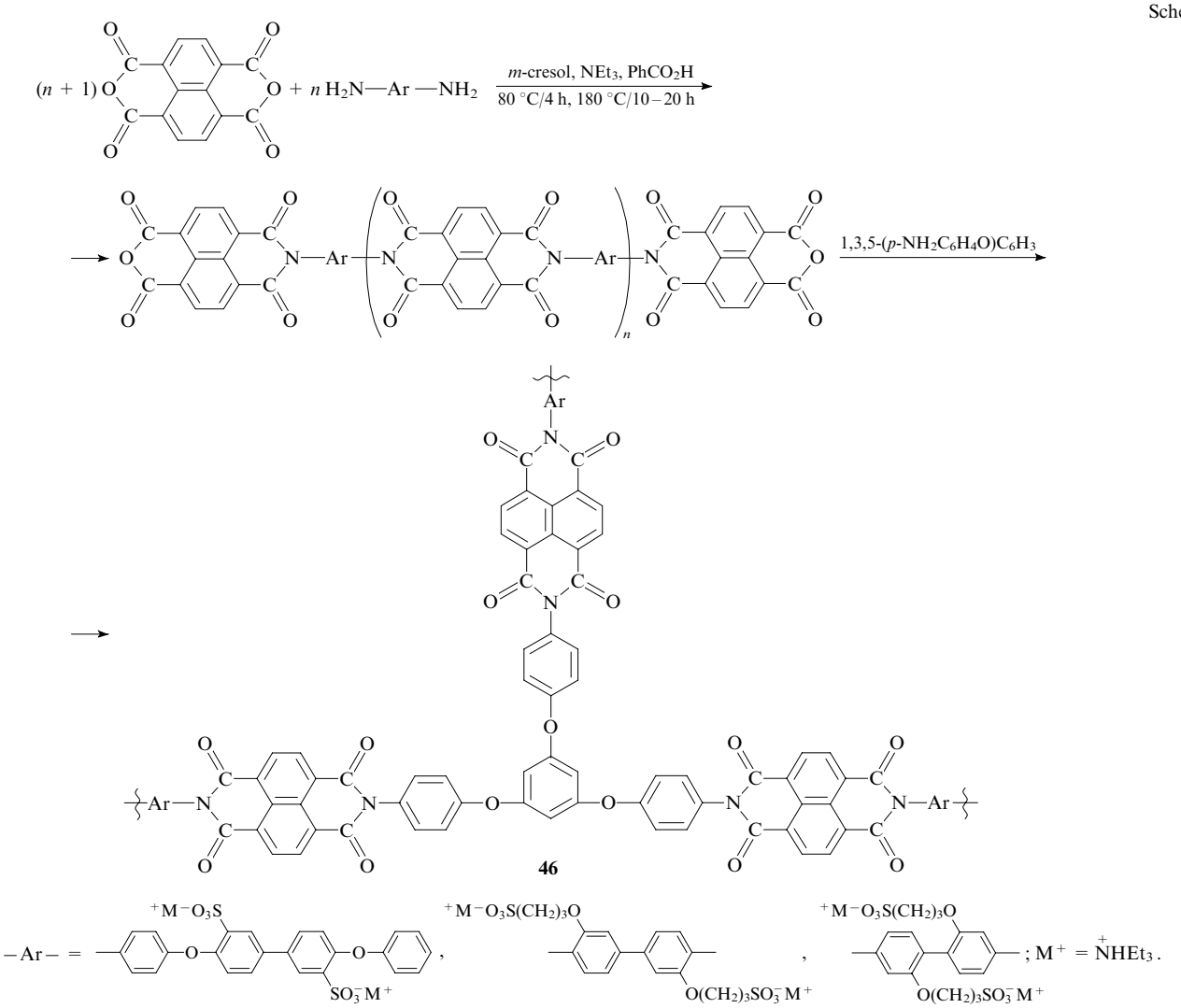
To improve the mechanical characteristics and stability of SPNI-based membranes, Okamoto and co-workers [123, 125, 126] synthesised polymers with the branched cross-linked structure. NTDA, sulfonated diamine [4,4′-bis-(4-aminophenoxy)-biphenyl-3,3′-disulfonic acid, 2,2′-bis(3-sulfopropoxy)-benzidine or 3,3′-bis(4-sulfopropoxy)benzidine]§ and 1,3,5-tris(4-aminophenoxy)benzene (5 mol %) were used as the starting compounds. The [NTDA] : [amine] ratios were 6 : 5, 5 : 4 and 4 : 3, respectively. Polycondensation was carried out in two steps. First, the reaction of NTDA with amines afforded oligomeric SPNIs containing terminal anhydride groups and then these oligomers reacted with 1,3,5-tris(4-aminophenoxy)-benzene (Scheme 12).

The branched products obtained as a result of this procedure, namely, polymers **46**, were used in the membrane preparation (casting). Membranes were subjected to thermal treatment in vacuum at the temperature gradually increasing to 200 °C with the aim of completing the imidisation. For the subsequent transformation of the salt forms of sulfo groups in polymer **46** into their protonated form, the membranes were soaked in methanol containing 0.5 N H_2SO_4 at 30 °C for 24 h.

Membranes based on SPNI **46** had high mechanical characteristics both before and after ageing in water at 130 °C for 96–196 h. They simultaneously exhibited both the high rigidity and elasticity. The proton conductivities of membranes based on SPNI **46** at 120 °C are sufficiently high (σ = 0.2–0.3 S cm^{-1} at 50% RH). Under real operation conditions of FC, the performance of membranes based on SPNI **46** was comparable with that of Nafion-112 membranes.

§ In certain cases, the reaction mixture also included non-sulfonated diamines such as 4,4′-bis(4-aminophenoxy)biphenyl, 4,4′-bis(4-aminophenoxy)diphenyl sulfone and 1,1,1,3,3,3-hexafluoro-2,2-bis(4-aminophenyl)propane.

Scheme 12



Summarising the above data on SPNI containing pendant sulfo alkoxy groups, it should be mentioned that the drawbacks of these systems include the low σ values at low RH and the low water stability at elevated temperatures (due to the destruction of alkoxy side groups).[123] Hence, in addition to SPNI containing sulfo groups in aliphatic side chains, attention was focused on SPNI containing sulfo groups in aromatic substituents.[64, 65, 69, 70] In such SPNI, aromatic substituents with sulfo groups are linked with the main chain through either an ether oxygen atom (compounds **47**) or a carbonyl group (compounds **48** and **49**).

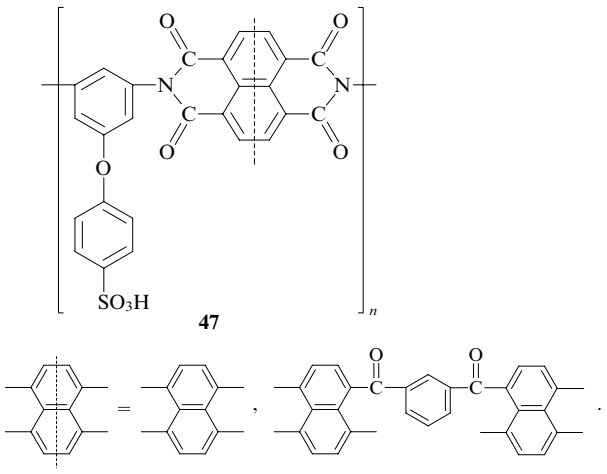
Polymers **47** had high molecular masses [69, 70] and were soluble in organic solvents. Unfortunately, no information on their electrochemical characteristics is available. Special attention was drawn to SPNI **48** and **49** that exhibited the high thermostability (the destruction onset temperature was 300 – 35 °C) due to the low electron density on sulfo groups, which was caused by the effect of an electron-withdrawing carbonyl group.

Both random and block SPNI **48** and **49** were synthesised.[64, 65] The synthesis of random co-polymers was carried out in a one-step process; block co-polymers were prepared in a two-step process, which included the formation of oligomers with terminal anhydride groups in the first stage and the reaction of these oligomers with NTDA and non-sulfonated diamines in the second stage.

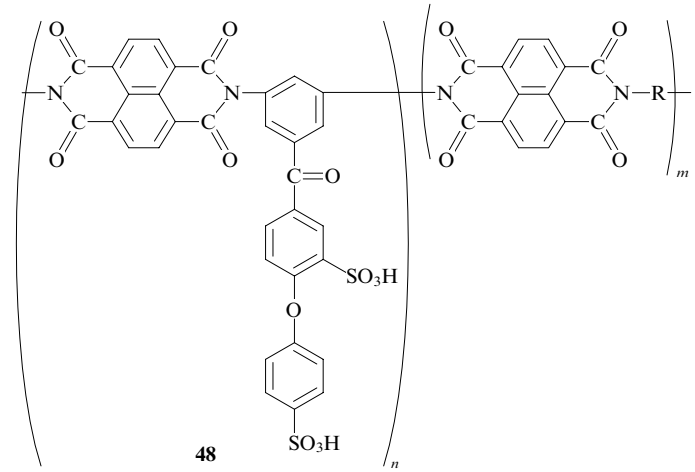
Random co-polymers **48** in the form of triethylammonium salts were well soluble in *m*-cresol, but insoluble in DMSO, *N*-MP, DMAA or DMF, whereas block co-polymers **48** were well soluble in all the solvents listed.

Co-polymers **49** in the form of triethylammonium salts were well soluble in DMSO, *N*-MP and DMAA; however, in the protonated form, their solubilities were much smaller (moreover, the solubility decreased with the increase in the content of the sulfonated diamines). The reduced viscosities (η_{red}) of solutions of polymer **49** in *m*-cresol were 0.43 – 1.80 dl g^{-1} (Table 12), which made it possible to prepare membranes with high strength characteristics.

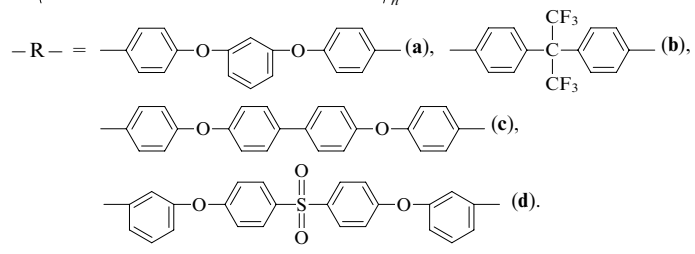
In the region of low RH, the σ values for homo- and co-polynaphthylimides **49** were lower than for Nafion-112, whereas in water these values were comparable. Particularly, for homopolymer **49** (n = 100%) characterised by the ion-exchange capacity of 1.94 mequiv g^{-1}, the σ value was 20 mS cm^{-1} at 60 °C and 70% RH and 135 mS cm^{-1} at

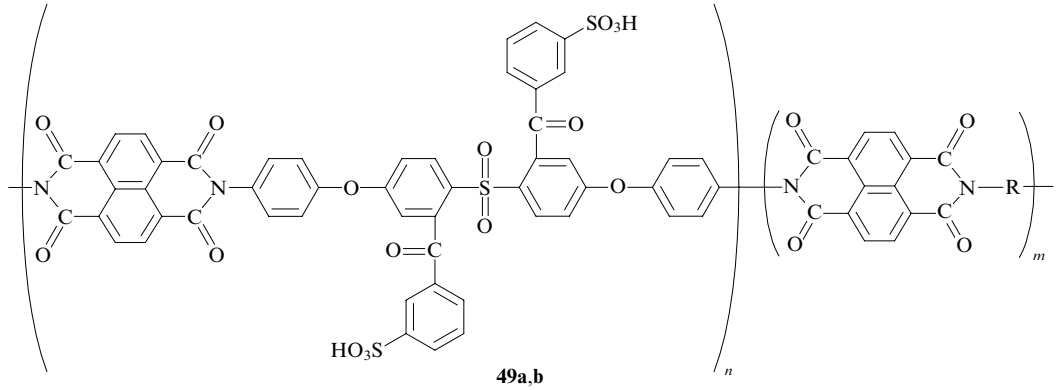


47



48





49a,b

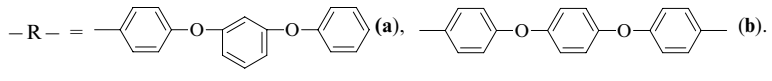


Table 12. Certain characteristics of SPNI **49**.

SPNI	$n:m$	η_{red} (see[a])	IEC	σ /mS cm^{-1} at 60 °C and RH	
				70%	100%
Homopolymer	1 : 0	0.43	1.94	20.0	135.0
Co-polymer **49a**					
random	3 : 1	0.60	1.66	7.7	7.8
	2 : 1	0.80	1.54	11.0	81.0
block	2 : 1	1.80	1.54	—	—
	3 : 2	0.94	1.45	5.8	69.0
Co-polymer **49b**					
block	3 : 1	1.04	1.66	—	—

[a] In dl g^{-1} (in *m*-cresol).

60 °C and 100% RH. The proton conductivities of co-polyimides were lower as compared with the homopolymer (see Table 12).

Membranes based on co-polymers **48** were cast from solutions of these co-polymers in *m*-cresol. To convert a membrane to the protonated form, it was treated with 1 N H_2SO_4 at 30 °C for 48 – 72 h.

Studies of the thermostability of SPNI **48** (DTGA in helium) have shown that by analogy with the other SPNI they are characterised by the three-step mass loss, namely, absorbed water was removed at 50 – 150 °C, sulfo groups decomposed at about 250 – 350 °C and the destruction of the main chains of macromolecules was observed at ~500 °C. Table 13 shows certain characteristics of membranes based on SPNI **48**.

Studies of the proton conductivities of membranes based on SPNI **48** have shown that at 100% RH their σ values were close or even higher than σ of Nafion-112, although

Table 13. Certain characteristics of SPNI **48**.

SPNI	$n:m$	η_{red} (see [a])	T_{destr}	IEC	σ /mS cm^{-1} at RH	
					70%	100%
48a						
block	1 : 1	—	310	1.64 (calc.)	17	87
	3 : 2	0.75	302	1.91 (calc.) 1.72 (titr.)	23	151
random	1 : 1	—	310	1.64 (calc.) 1.34 (titr.)	13	96
	5 : 4	0.92	—	1.79 (calc.) 1.47 (titr.)	14	113
48b						
block	2 : 1	—	—	1.99	27	109
random	1 : 1	0.36	—	2.24	35	159
48d (block)	1 : 1	0.62	—	2.08	39	163

[a] In dl g^{-1} (in DMSO).

the ion-exchange capacity of these SPNI considerably exceeded that of Nafion-112. The observed contradiction could be due to the specific morphology of Nafion-112. The structure of Nafion membranes was characterised by microphase separation and the presence of proton-conducting channels.

In the region of low RH, the membranes based on SPNI **48** and **49** exhibited higher proton conductivities than the membranes based on SPNI **41** – **45**, which could be due to the higher content of sulfo groups in SPNI **48**, **49**. In addition, they were characterised by the high water stability at elevated temperatures, which together with their other characteristics points to the possibility of their use in FC.

IV. Conclusion

In the past 10 – 15 years, substantial progress was achieved in the development of poly- and co-polynaphthylimides containing sulfo groups both in the main chains of macromolecules and in their side substituents. The general method of synthesis of such polymers was developed, namely, high-temperature polycyclocondensation in phenolic solvents in the presence of triethylamine and catalysts. A procedure of casting SPNI-based membranes was proposed, which made it possible to solve the problem of poor solubility of sulfonated polynaphthylimides. According to this scheme, polymers were synthesised in the form of organo-soluble triethylammonium salts, which were processed into membranes and then subjected to the action of dilute mineral acids to convert them to acid forms.

The relationship between the structure of synthesised polymers and their fundamental characteristics, namely, thermal and water stability, ion-exchange capacity and proton conductivity, was considered. The important role of the morphology of polymers and membranes on their basis was demonstrated, particularly, the presence of channels that favoured ionic transport. The main problem of using the considered materials in FC is to reach the balance between ICE, σ and mechanical stability of the membranes.

Summarising, it should be mentioned that the studies in the field of synthesis of both new sulfonated poly- and co-polynaphthylimides and their precursors, sulfonated aromatic diamines, continue to be actively developed, as is evident from the appearance of a large number of publications on this subject in the past year (see Refs 127 – 139).

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