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Ion exchange membranes derived from sulfonated polyaramides

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Abstract

Homo- and both random and block copolyaramides of high molecular weights, with sulfonated moieties in the backbone, were obtained by low temperature polycondensation technique in a dipolar aprotic solvent (NMP) using (a) free aromatic diamines in the presence of pyridine as acid acceptor and (b) N,N'-bis-trimethylsilyl derivatives of the diamines without additional acid acceptor. The addition of low molecular weight electrolytes (LiCl or CaCl$_2$) and in some cases trimesoyl chloride to the reaction mixture was found to be favorable for the synthesis of high molecular weight polyamides. The materials had a theoretical ion exchange capacity of up to 3.14 meq/g. The membranes were characterized in terms of morphology, thermal stability, water-uptake, and ion exchange capacities.
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1. Introduction

Coatings of sulfonated polymers are useful for different applications. For instance, polyamide textile materials are provided with stain blocking properties when coated with a sulfonated polymer. Sulfonated polyamide coatings with noble counterions are used as catalytic surfaces for electroless deposition of metals [1].

In the membrane field, sulfonated polymers bring advantages in a broad range of processes [2]. Ultrafiltration (UF) membranes are frequently prepared from hydrophobic materials with non-specific adsorption capacity. This phenomenon known as fouling usually leads to a rapid deterioration of the membrane permeability under operation. Hydrophilic materials are much less

susceptible to fouling. One effective way to turn UF membranes more hydrophilic is the use of a mixture of sulfonated and non-sulfonated polymers for their preparation [3,4], the sulfonation being carefully controlled to limit the water solubility. Although not completely disclosed in the literature, commercially successful membranes such as the G-series from Desal are coated with sulfonated polysulfones. The Desal-5 membrane for nanofiltration has a sulfonated overlay between the microporous polysulfone support and the top ultrathin polypiperazineamide layer [5]. The introduction of charged groups in nanofiltration membranes can considerably reduce the cut off of ionised molecules [6]. Sherman [7] has synthesized reverse osmosis membranes by using a sulfonated polyaramide obtained in a reaction of m-phenylene diamine and 2,4-diaminobenzene sulfonic acid (2,4-DABSA) with a molten mixture (70/30% w/w) of isophthaloyl chloride and terephthaloyl chloride. Sulfonated polyaramide membranes had an ion exchange capacity between 0.7 and 1.5 meq/g of polymer. Measurements of water permeability and salt rejection were reported. Recently, Konagaya et al. [8] have reported the polymerization of carboxylated or sulfonated copolyamides in order to achieve not only good reverse osmosis performance but also better chlorine resistance.

Polymer sulfonation gains importance in processes fundamentally based on the preferential transport of cations. Cation exchange membranes are required for electrodialysis and more recently sulfonated polymers are being intensively investigated for fuel cells. Due to their outstanding chemical properties and high proton conductivity, perfluorosulfonic acid polymer membranes such as Nafion® (DuPont), Flemion® (Asahi Glass), and DowMembrane® (Dow Chemical) are among the very few commercially available membranes for fuel cells. However the Nafion®-type membranes have the following disadvantages: (1) the costs of approx. 600 US $/m², which is by far to high for mass production in automotive application; proton conductivity reduction above 100 °C and (2) high water and methanol crossover, which is particularly disadvantageous for direct methanol fuel cells. World-wide research activities for

developing new materials for proton exchange membranes have been initiated, ranging from partially fluorinated to non-fluorinated fully aromatic materials in order to reduce costs. Overviews of recent developments in membrane research for fuel cells have been published by Savadogo [9], Rikukawa and Sanui [10], Costamagna and Srinivasan [11,12] or in a special issue of *J. Membr. Sci.* [13–20].

Research activities have been focused on sulfonated polyimides (PI), poly(ether ether ketone)s (PEEK), polysulfones (PSU) or poly(ether sulfone)s (PES) and others. One approach to obtain sulfonated samples of such polymers is the chemical modification of commercially available polymers by treatment with different types of sulfonation agents.

Less explored is the preparation of an alternative material via the introduction of ionic groups onto the polymer backbone, using a sulfonated monomer [21–27]. This method allows for a better control both of the sulfonation degree and the ionic group distribution. Wang and coworkers [21–23] have prepared both random and block copolymers from sulfonated 4,4′-dichlorodiphenylsulfone and 4,4′-dihydroxybiphenyl. Membranes with ion exchange capacities of up to 2.04 meq/g have been obtained. Faure et al. [24] have synthesized sulfonated polyimides, which were based on 4,4′-diamino-biphenyl-2,2′-disulfonic acid (BDSA), 4,4′-oxydianiline (ODA), and oxy-diphthalic dianhydride (ODPA). As second generation sulfonated polyimides based on 1,4,5, 8-naphthalenetetracarboxylic dianhydride (NTDA) instead of ODPA were investigated too. These sulfonated polyimides have a theoretical IEC from 0.8 to 2.5 meq/g. Cornet and co-workers [25,26] and Genies et al. [27] have reported the synthesis and properties of new naphthalene copolyimides obtained from BSDA and aryl ether diamine with an IEC ranging from 0.59 to 1.86 meq/g.

Here, we report on the synthesis of sulfonated polyamides including homopolymers, random and block copolymers. Aromatic polyamide AB multiblock copolymers having non-sulfonated blocks (A-blocks) and highly sulfonated blocks (B-blocks) were prepared with the aim of pro-

viding polymeric materials with a controlled phase-separated morphology. The phase of non-sulfonated blocks should enable good mechanical stability of the membrane material and reduce the swelling of the highly sulfonated B-blocks. On the other hand, the B-blocks can provide high hydrophilicity and enable high proton conductivity. The properties of multiblock copolymers are compared with those of random copolymers of same as well as different composition. All polymers are characterized in terms of water-uptake, ion exchange capacity, and thermal stability. In this report the degree of sulfonation (DS) is defined as number of sulfonic acid groups per total number of diamine units in the polymer backbone. For example, a polymer prepared from terephthaloyl chloride and 2,5-diaminobenzene sulfonic acid (2,5-DABSA) has a (theoretical) DS of 100%. On the other hand, a copolyamide prepared from an equimolar mixture of 2,5-DABSA and 1,4-phenylene diamine and isophthaloyl chloride has a DS of 50%.

2. Experimental

2.1. Materials

Isophthaloyl chloride (IPC), trimesoyl chloride (TMC), terephthaloyl chloride (TPC), 4,4′-oxydianiline (ODA), 1,4-phenylene diamine (1,4-PDA), and chlorotrimethylsilane were supplied by Aldrich. 2,5-Diaminobenzenesulfonic acid (2,5-DABSA) and triethylamine were purchased from Fluka. Calcium chloride and *N*-methyl-2-pyrrolidone (NMP) were obtained from Merck.

TPC was used as received, whereas IPC and TMC were purified by distillation in vacuum before use. CaCl$_2$ and LiCl were dried in vacuum

for 24 h at 150 and 120 °C, respectively. NMP was dried by distillation over P$_4$O$_{10}$ and K$_2$CO$_3$ under reduced pressure. It was stored over molecular sieves (4 Å). Pyridine (Py) and *N,N*-dimethylacetamide (DMAc) were dried over molecular sieves (4 Å).

1,4-PDA was purified by sublimation. 2,5-DABSA was recrystallized twice from pure water. The sodium salt of 2,5-DABSA (2,5-DABSA-Na) was prepared by the reaction of 2,5-DABSA with sodium hydroxide in water and was purified by recrystallization.

2.2. Silylation of amine monomers

A 2-l three-necked round-bottom flask, equipped with a reflux condenser with CaCl$_2$-tube, an overhead stirrer and a 100-ml dropping funnel was charged with 0.5 mol of the respective amine monomer and suspended in 1.5 l of dry toluene and 1.1 mol triethylamine. Under vigorous stirring 1.1 mol of chlorotrimethylsilane was added dropwise through the dropping funnel. In the case of 2,5-DABSA, 2 mol triethylamine and 1.8 mol chlorotrimethyl silane were used. After the addition of approximately 1 ml *N,N′*-dimethylformamide (DMF), the reaction mixture was refluxed for additional 8 h. After cooling to room temperature, the precipitated triethylamine hydrochloride was filtered off under exclusion of moisture and the solvent was removed to 1/3 with reduced pressure. To remove residual triethylamine hydrochloride, 300 ml of dry *n*-hexane was added to the reaction mixture and the precipitate was again filtered off. Finally, the solvent was removed completely under reduced pressure and the silylated product was isolated by vacuum distillation. Yields and boiling points are listed in Table 1.

Table 1
Yields and boiling points of silylated amine monomers

Diamine monomer	Yield (%)	b.p. (°C) (m.p., °C)	Lit. b.p. (°C) (m.p., °C)
N,N′-Bis-TMS-ODA	98	184[a,b] (0.01 mbar)	196–197 (1.8 mbar) (72–73) [28]
N,N′,O-Tris-TMS-2,5-DABSA	49	146 (0.01 mbar)	–

[a] An air-cooled short-path distillation assembly was used for distillation.
[b] Oil bath temperature.

2.3. Polymerization procedures using N,N′-bis-tri-methylsilyl diamines

2.3.1. Homopolymer synthesis

A 100-ml three-necked round-bottom flask equipped with a gas inlet tube, an overhead stirrer, and a CaCl$_2$-tube was charged with 50 ml of dry NMP/CaCl$_2$ ($c = 3$ g/l) and 20 mmol of the sily-lated diamine under a slight stream of dry nitro-gen. After complete dissolution of the diamine, the solution was cooled to −20 °C. Under vigorous stirring, 20 mmol of acid chloride was added as solid in one portion. The reaction was continued for 2 h at −20 °C and for additional 24 h at room temperature. During all operations the reaction vessel was purged with nitrogen.

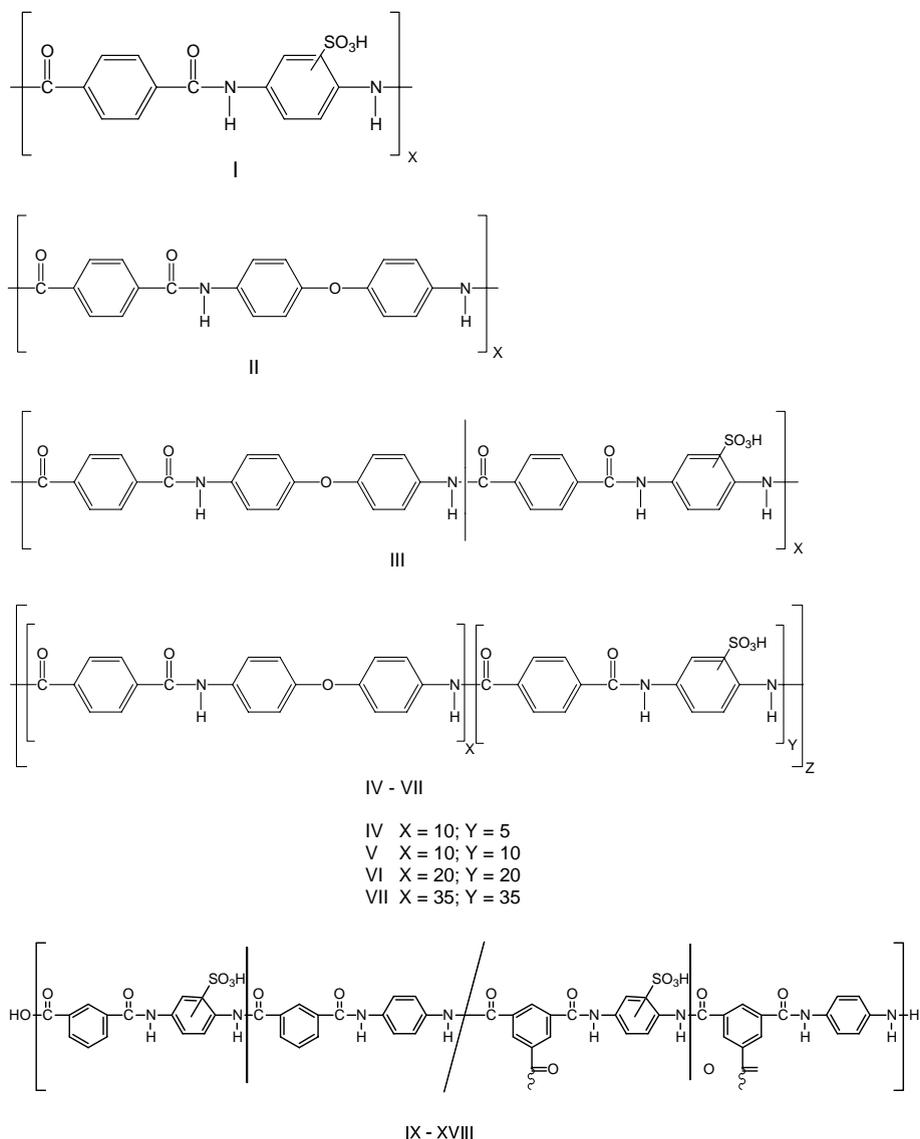The polymer was precipitated by pouring the reaction mixture into 500 ml cold ethanol. The

Fig. 1. Chemical structures of polyaramides prepared in this study.

Table 2
Yields and molecular weights of polyaramides prepared from terephthaloyl chloride and various silylated aromatic diamines

Sample	Silylated diamine	Yield (%)	$\eta_{inh.}$[a] (dl/g)	$M_w^{calc.\,b}$ (g/mol)	$M_w^{GPC\,c}$	$M_n^{GPC\,c}$
I	2,5-Diaminobenzene sulfonic acid	>99	1.57	11,400	157,800	74,600
II	4,4′-Oxydianiline	>99	1.49	10,800		
III	2,5-Diaminobenzene sulfonic acid 4,4′-Oxydianiline (random)	>99	2.66	18,700		
IV	2,5-Diaminobenzene sulfonic acid 4,4′-Oxydianiline (block 5/10)	>99	2.11	15,000	37,300	17,700
V	2,5-Diaminobenzene sulfonic acid 4,4′-Oxydianiline (block 10/10)	>99	2.14	15,200		
VI	2,5-Diaminobenzene sulfonic acid 4,4′-Oxydianiline (block 20/20)	>99	1.66	12,000		
VII	2,5-Diaminobenzene sulfonic acid 4,4′-Oxydianiline (block 35/35)	>99	2.19	15,500		
VIII	1:1 blend of samples I and II	–	–	–		

[a] Determined with $c = 2$ g/l in conc. sulfuric acid (96%) at 30 °C.
[b] Calculated by using the Mark–Houwink equation for Kevlar (given in Section 2).
[c] Measured in DMAc containing 2 vol% water and 3 g/l LiCl, poly(vinylpyrrolidone) standards were used for calibration.

precipitate was filtered off and washed thoroughly with hot ethanol. Finally, the polymer was dried at 80 °C in vacuum to constant weight (samples I and II in Fig. 1 and Table 2).

2.3.2. Synthesis of random block copolymer

A 100-ml three-necked round-bottom flask equipped with a gas inlet tube, an overhead stirrer, and a CaCl₂-tube was charged with 50 ml of dry NMP/CaCl₂ and 10 mmol of the silylated non-sulfonated diamine and silylated diaminobenzene sulfonic acid under a slight nitrogen stream. After complete dissolution of the diamines, the solution was cooled down to −20 °C. Under vigorous stirring, 20 mmol of acid chloride was added as solid in one portion. The reaction was continued for 2 h at −20 °C and for 24 h at room temperature. During all operations the reaction vessel was purged with nitrogen.

The polymer was precipitated by pouring the reaction mixture into 500 ml of cold ethanol. The precipitate was filtered off and washed thoroughly with hot ethanol. Finally, the polymer was dried at 80 °C in vacuum to constant weight (sample III in Fig. 1 and Table 2).

2.3.3. Synthesis of block copolymers

Preparation of the A-block. A 100-ml three-neck round-bottom flask equipped with a gas inlet tube, an overhead stirrer, and a CaCl₂-tube was charged with 25 ml of dry NMP/CaCl₂ and 9 mmol of the silylated non-sulfonated diamine under a slight nitrogen stream. After complete dissolution of the diamine, the solution was cooled down to −20 °C. Under vigorous stirring, 10 mmol of acid chloride was added as solid in one portion. The reaction was continued for 2 h at −20 °C and for 24 h at room temperature. During all operations, the reaction vessel was purged with nitrogen.

Preparation of the B-block. In a second 100 ml three-necked round-bottom flask equipped with a gas inlet tube, an overhead stirrer, and a CaCl₂-tube was charged with 25 ml of dry NMP/CaCl₂ and 10 mmol of the silylated diaminobenzene sulfonic acid under a slight nitrogen stream. After complete dissolution of the diamine, the solution was cooled down to −20 °C. Under vigorous stirring, 9 mmol of acid chloride was added as solid in one portion. The reaction was continued for 2 h at −20 °C and for 24 h at room temperature. During all operations, the reaction vessel was purged with nitrogen.

Preparation of block copolymers. For the preparation of the block copolymers, the reaction mixture with the B-block was added to the reaction mixture of the A-block. The mixed solutions are stirred at room temperature overnight to complete the reaction. The polymer was precipitated by

pouring the reaction mixture into 500 ml cold ethanol. The precipitate was filtered off and washed thoroughly with hot ethanol. The polymer was dried at 80 °C in vacuum to constant weight (samples IV–VII in Fig. 1 and Table 2).

2.4. Polymerization procedure using pyridine as HCl-acceptor

A flask equipped with a mechanical stirrer and purged with argon was filled with DMAc and 0.01 mmol of a diamine mixture: 2,5-DABSA, 1,4-PDA, and 0.02 mol of pyridine. The mixture was stirred at room temperature until complete dissolution of the diamines. The mixtures was then cooled to 0 °C and 0.01 mmol of acid chloride (IPC or IPC/TMC) was added. After stirring for 1 h at 0 °C, the mixture was heated to room temperature and was left overnight. The resulting polymer was poured into a large excess of meth-

anol. The precipitate was washed with methanol, redissolved in DMAc and precipitated again in methanol, washed three times with methanol, and then dried in vacuum at 70 °C for 24 h (samples IX–XVIII in Fig. 1 and Table 3).

2.5. Membrane preparation

2.5.1. Membranes from NMP-solutions

Membranes were prepared from prefiltered reaction mixtures containing approx. 10 wt% polymer in NMP/CaCl$_2$. From this solution a film was casted onto a glass plate. The film thickness was set to 700 μm. After removal of the solvent at 80 °C under normal pressure for 8 h, the membranes were immersed in water and peeled off. Finally the membranes were dried to constant weight at 80 °C in vacuum. The membranes had a thickness of approximately 70 μm.

Table 3
Yields and molecular weights of copolyaramides prepared from isophthaloyl chloride and trimesoyl chloride in the presence of pyridine as acid acceptor

Polymer	Composition	Yield (%)	M_w^{GPCa}	M_n^{GPCa}	% DS (EA)	% DS (NMR)
IX	2,5-DABSA 1,4-PDA 1:1	90	99,300		37	39
X	2,5-DABSA 1,4-PDA 1:1 + LiCl	92	79,000		45	44
XI	2,5-DABSA-Na 1,4-PDA 1:1	96	131,000		48	49
XII	2,5-DABSA-Na 1,4-PDA 1:3		227,100	103,300	–	24
XIII	2,5-DABSA-Na 1,4-PDA 1:1 TMC		225,300	101,000	–	49
XIV	2,5-DABSA-Na 1,4-PDA 6:4 TMC		172,600	98,200	–	55
XV	2,5-DABSA-Na 1,4-PDA 7:3		318,700	99,100	–	66
XVI	2,5-DABSA-Na 1,4-PDA 8:2 TMC		871,800	137,200	–	79
XVII	2,5-DABSA-Na 1,4-PDA 9:1 TMC		187,000	111,400	–	90
XVIII	2,5-DABSA-Na TMC		240,000	87,500	–	100

[a] Measured in DMF containing 50 mmol ammonium acetate, polystyrene standards were used for calibration.

2.5.2. Membranes from DMAc-solutions

Dense films were formed by dissolving the polyamide from reaction of IPC/TMC and 2,5-DABSA/1,4-PDA in DMAc (5% wt/wt) and casting the solution onto a glass plate. The solvent was evaporated from the casted membrane at 80 °C for 24 h.

2.6. Measurements

Prior to polymer characterization, all polymers were dried at 120 °C in vacuum to constant weight.

The viscosities were measured with an automated Ubbelohde viscometer thermostated at 30 °C. The polymer concentration was 2 g/l in conc. sulfuric acid (96%). Molecular weights were estimated from η_{inh} using the Mark–Houwink equation for Kevlar® [29].

$$[\eta] = 7.9 \times 10^{-5} M_{\text{w}}^{1.06}. \tag{1}$$

^{1}H and ^{13}C NMR spectroscopic investigations were carried out on a Bruker AMX 500 spectrometer operating at 500.13 MHz for ^{1}H and 125.74 MHz for ^{13}C. Deuterated trifluoromethane sulfonic acid was used as the solvent and sodium 3-(trimethylsilyl)-2,2,3,3-tetradeuteropropionate as the chemical shift reference. Further ^{1}H NMR spectra were recorded on a Bruker AMX 300 spectrometer (300.13 MHz for ^{1}H) using DMSO-d_6 as the solvent and internal standard. The degree a sulfonation was calculated from the proton signals of the 1,4-PDA unit ($\delta = 10.46$ ppm) and two signals of the 2,5-DABSA unit ($\delta = 10.52$ and 10.53 ppm).

GPC measurements were performed on a Knauer GPC equipped with two Zorbax PSM Trimodal S columns and a RI detector. A mixture of DMAc with 2 vol% water and 3 g/l LiCl was used as eluent. Polyvinylpyrrolidone samples were used as standards for molecular weight calibration. Further, GPC measurements were carried out with a JASCO GPC/HPLC chromatograph operated at 35 °C using an RI detector. DMF containing 50 mmol of ammonium acetate served as eluent. Polystyrene standards were used for molecular weight calibration.

Thermogravimetric measurements were performed on a TGA 7 (Perkin–Elmer) or a Netzsch thermobalance in inert gas atmosphere in the temperature range from 50 to 700 °C with a heating rate of 20 K/min.

Wide angle X-ray scattering (WAXS) experiments were performed on a P4 X-ray diffractometer (Siemens now Bruker axs, Karlsruhe) equipped with a HiStar detector. A graphite filtered Cu Kα-radiation was used.

2.6.1. Water-uptake

A piece of dry membrane was soaked in water for 24 h at 80 °C. The excess water is wiped off gently with a tissue and the membrane is weighed immediately. Subsequently, the membranes were dried at 80 °C in vacuum to constant weight. The water-uptake is calculated using Eq. (2) and is given in percentage increase in weight

$$W = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\%, \tag{2}$$

where m_{wet} and m_{dry} are the weights of the same water-swollen and dry membrane sample, respectively.

2.6.2. Ion-exchange capacity

The ion-exchange capacity (IEC, with units meq/g of dry polymer) of the sulfonated membranes was measured using the standard experimental method of immersing the membrane in 1 N HCl for 24 h, followed by soaking in distilled water to remove excess acid for another 24 h. Subsequently the membrane samples are soaked for 1 day in 2 M NaCl solution (exchange of H$^+$ by Na$^+$ within the film) and then titrating the solution with 0.01 N NaOH to determine the concentration of the exchanged protons.

3. Results and discussion

The silyl method has been applied for the preparation of various polymers in melt as well as in solution [30–32]. The application of the silyl method in polycondenzation reactions is advantageous for several reasons. First, no free hydrohalic acid is produced, thus acid catalyzed side reactions are avoided. Second, the condensation product chlorotrimethylsilane is highly volatile

and is easily removed from the reaction mixture. Third, silylation improves the solubility of the monomers in a given reaction medium or lowers the melting temperature or boiling point, due to elimination of hydrogen bonds, resulting in an effective purification of monomers by simple distillation. Fourth, by silylation, the low nucleophilicity of aromatic amines can be enhanced. Fifth, in this special case, side reactions in connection with the thermally labile sulfonic acid group is avoided due to the mild reaction conditions. In this study the silyl method has been successfully employed for the preparation of polyaramides from terephthaloyl chloride and 4,4′-oxydianiline (A-block) and terephthaloyl chloride and 2,5-diaminobenzene sulfonic acid (B-block) (Fig. 1). The multiblock copolymers of the A_nB_n-type, where n is in the range from 10 to 35 and having an overall theoretical DS of 50%, and a DS of 100% in the B-block were made from the respective oligomers with carboxylic and amino end groups. In addition, a random copolymer and a 1:1 blend from the homopolymers of A- and B-type (samples I and II) with a similar DS as A_nB_n-multiblock copolymers and finally a multiblock copolymer of different block length ($A_{10}B_5$) having an overall DS of 25% (100% in the B-block) were prepared for comparison. The average number of A and B blocks in the polymers, estimated from molecular weights of the polymer samples and the theoretical molecular weights of the oligomers, varies between 2 (sample VII) and 5 (sample V). Before preparing the block copolymers, NH_2- and COOH terminated oligomers with predetermined molecular weights were synthesized and characterized. The obtained molecular weights, as determined by end group titration, matched very well with the theoretical values with an uncertainty of 10%.

Yields and properties of the polyaramides are summarized in Table 2. Even though molecular weights, calculated from inherent viscosities by using the Mark–Houwink equation for Kevlar® [29], seemed to be low, they were high enough to prepare mechanically stable membranes. Since the solution behavior of the rigid Kevlar® in concentrated sulfuric acid is most probably different from the polymers prepared in this study, even from the ''sulfonated Kevlar'' (sample I), the true molecular

weights might be higher than the values determined by viscosity measurements. Unfortunately, other methods for molecular weight determination could not be used, since samples possessing long non-sulfonated blocks could not be redissolved in a dipolar aprotic solvent such as NMP or DMAc once precipitated. Only the samples I, III, and IV were soluble in DMAc and thus molecular weight determination by GPC was possible (results see Table 2). Obviously, the molecular weights determined by GPC are much higher than those determined by viscosity measurements. Similar results have been reported by Schaefgen et al. [29], who reported also much higher molecular weights for poly(*p*-phenylene terephthalic amide)s in DMAc determined by light scattering than by viscosity measurements in concentrated sulfuric acid. The differences in molecular weight were explained by the formation of aggregates in DMAc, whereas in sulfuric acid single chains are likely to be present.

Despite the advantages of the silyl method, a second series of copolyaramides were synthesized from isophthaloyl chloride using free diamines and pyridine as acid acceptor. In some cases up to 10 mol% trimesoyl chloride has been added to the reaction mixture to further increase the molecular weight (samples IX–XVIII). Yields and properties are summarized in Table 3. Three different routes were used to obtain polymers with 50% degree of sulfonation and high molecular weights.

Route A. IPC was reacted with equimolar quantities of 1,4-PDA and 2,5-DABSA using DMAc as solvent (sample IX, Table 3).

Route B. IPC was reacted with equimolar quantities of 1,4-PDA and 2,5-DABSA using DMAc as solvent in the presence of LiCl. LiCl in the initial reaction mixture increases the solubility of polyamides in DMAc (sample X, Table 3).

Route C. IPC was reacted with equimolar quantities of 1,4-PDA and 2,5-DABSA-Na using DMAc as solvent in the presence of LiCl. LiCl in the initial reaction mixture increases the solubility of polyamides in DMAc (sample XI, Table 3).

When the polymerization was carried out using route A, polyamides with degrees of sulfonation between 37% and 39% and of relatively low yields were obtained. These results are attributed to the low solubility of both the sulfonated monomer

(2,5-DABSA) and the resulting polymer in DMAc. The second procedure (route B) gave a slight increase in yield as well as in degree of sulfonation, which was close to the desired value of 50%. However, the molecular weight of this polymer was lower than that obtained by route A. The cause might be a possible hydration of the LiCl during addition to the reaction mixture, leading to the degradation of the IPC by hydrolysis and therefore to a decrease of the molar mass of the resulting polymer.

The polymerization by route C was conducted with the sodium salt of the sulfonated monomer (2,5-DABSA-Na). The high solubility of 2,5-DABSA-Na in DMAc improves the control of the degree of sulfonation and increases both, molecular weight and yield. Consequently, this procedure was used to prepare copolyaramides with different degrees of sulfonation with very good control.

Membranes prepared from copolyaramides having a DS of 70% or higher are very brittle. For this reason, TMC has been added as crosslinking agent in order to increase the mechanical properties of the polymers.

When up to 7.5×10^{-4} mol of TMC per 10 mmol IPC were added to the reaction mixture, the resulting copolyamides were found to be soluble in aprotic solvents at room temperature. Only co-polyamides with a DS of 25% or lower proved to be insoluble when the crosslinking agent was added to the reaction mixture. The molecular weights of polymers synthesized with different degrees of sulfonation and added crosslinking agent (samples XIII–XVIII) are summarized in Table 3. Obviously, considerably higher molecular weights were obtained by the addition of TMC to the reaction mixture as compared to the values for polymers prepared without the trifunctional monomer.

3.1. NMR spectroscopic investigations of multiblock copolyaramides

The composition of the copolyaramides were confirmed by ^{1}H and ^{13}C NMR spectroscopic investigations. Figs. 2 and 3 show the ^{1}H and ^{13}C NMR spectra of polymers II, III, IV, and V measured in deuterated trifluoromethane sulfonic acid. This solvent was chosen, because most of the precipitated samples could not be redissolved in dipolar aprotic solvents. The spectrum of sample II shows the expected peaks for the protons of the ODA-unit at 6.7 ppm (c) and 7.05 ppm (b), and for the TPC-protons at 7.75 ppm (a). However, the intensity of the signal of proton (c) in ortho-position
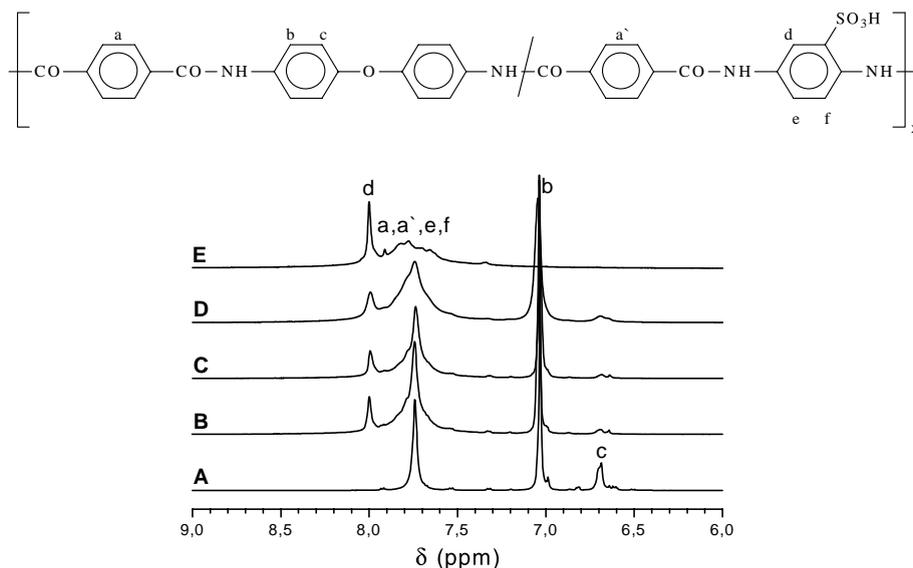

Fig. 2. ^{1}H NMR spectra of (A) sample II, (B) sample IV, (C) sample V, (D) sample III, and (E) sample I.
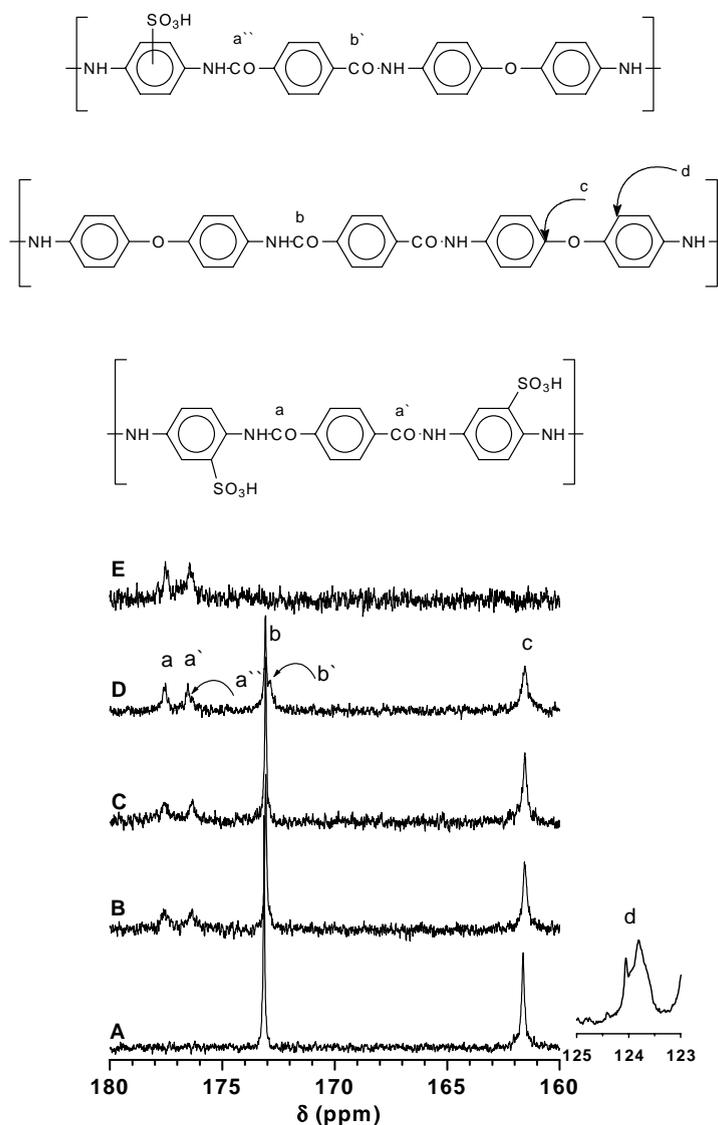
Fig. 3. ^{13}C NMR spectra (carbonyl region) of (A) sample II, (B) sample IV, (C) sample V, (D) sample III, and (E) sample I, and assignment of carbonyl carbons in different subunits of polyaramides.

to the ether linkage is much too low in this spectrum. This effect is attributed to the proton-deuterium exchange at this position with the SO_3D deuterium of the highly acidic solvent. On the other hand, spectra recorded from samples dissolved in DMSO (not displayed here) showed the correct intensity ratios of the signals (c) and (d). Further evidence for the H/D exchange is given by the ^{13}C NMR spectra shown in Fig. 3. Here, the

signal of carbon (d) in *ortho*-position to the ether linkage shows a triplett structure due to the C–D coupling (inserted part in spectrum 3A), whereas all other signals are singletts due to the applied broadband decoupling.

The peak appearing at approx. 8 ppm (d) in the ^{1}H NMR spectra of samples containing 2,5-DABSA units in the polymer backbone is attributed to the proton in *ortho*-position to the sulfonic

Table 4
Composition of copolyaramides detected by ^{1}H NMR spectra

Sample	ODA-TPC/2,5-DABSA-TPC ratio calculated	
	From monomer composition	From ^{1}H NMR data
III	1:1	1:0.67 (1:0.82[a])
IV	2:1	1:0.68
V	1:1	1:0.62 (1:1[a])

[a] Determined from NMR-spectra measured in DMSO-d$_6$.

acid group. Although the peaks of 2,5-DABSA and TPC are strongly superimposed, the content of the sulfonated blocks C(B1) in the copolymers can be estimated using Eq. (3) (content of non-sulfonated blocks = 1)

$$C(B1) = \frac{I(a, a', d, e, f) - I(b)}{7}. \tag{3}$$

Here, $I(a, a', d, e, f)$ and $I(b)$ (= 4) are the integrals of the respective peaks as assigned in the NMR spectra. Here, 7 is the number of protons related to the sulfonated repeating unit (for results see Table 4). Regardless of the theoretical composition, all copolymers have a nearly constant ratio (0.65) of sulfonated and non-sulfonated units. That means, the DS found in samples III and V is lower than the theoretical composition, while the DS in sample IV is higher than expected. DS of samples III and V, calculated from spectra measured in DMSO-d$_6$, showed nearly the expected ratio of sulfonated to non-sulfonated blocks.

There are several reasons to explain these findings. First, it is likely, that a proton–deuterium exchange has also occurred in the sulfonated repeating units, as observed for the ODA-unit, which lowers the intensity of the respective peaks in the NMR spectra. Second, polymer chains of relatively low molecular weight and high degree of sulfonation show good solubility in ethanol. This part of the prepared polymer is therefore not precipitated during isolation of the polymer. Although a proton–deuterium exchange at the sulfonated units seems to be most likely for the explanation of the NMR spectra, an unambiguous explanation cannot be given at the moment.

It has been shown, for example, by Kricheldorf and Mülhaupt [33], that ^{13}C NMR is a versatile tool to characterize copolymers concerning their composition and block length. Most often the carbonyl peak is used, because of its sensitivity to different chemical environments, e.g., in aliphatic copolyamides. In the ^{13}C NMR spectra of the copolyamides under investigation (Fig. 3), the carbonyl peaks of non-sulfonated units (b; 172.5 ppm) and sulfonated units (a, a'; 176, 177 ppm) are well separated. Noticeable is the splitting of the carbonyl signal of the sulfonated units, depending on the position of the sulfonic acid group of the 2,5-DABSA units relative to the amide linkage. According to work of Tirasirichai et al. [34] the peak at 176 ppm is assigned to the carbonyl carbon nearest to the sulfonic acid group (a). In the spectra of the copolyamides shoulders at the carbonyl peaks appear (a″, b′), which are most pronounced in the random copolyamide (sample III). These shoulders are attributed to the carbonyl carbons of heterogeneous diads. According to the work of Kricheldorf and Mülhaupt [33], the average length of sulfonated and non-sulfonated blocks $\bar{L}_{sulf}$ and $\bar{L}_{nonsulf}$, respectively, can be estimated using Eqs. (4a) and (4b). In random copolymers the number of sequences A–A and A–B should be equal and therefore the values of $\bar{L}$ should be 2. A $\bar{L}$-value higher than 2 indicates a more block-like structure of the copolymer, whereas a $\bar{L}$-value smaller than 2 indicates a more alternating copolymer.

$$\bar{L}_{sulf} = \frac{I_a + I_{a'}}{I_{a''}} + 1, \tag{4a}$$

$$\bar{L}_{nonsulf} = \frac{I_b}{I_{b'}} + 1. \tag{4b}$$

Due to the low S/N ratio and the broadness of the peaks a, a', and a″, only the length of the non-sulfonated blocks could be calculated. For the random copolymer we found a $\bar{L}_{nonsulf}$-value of 4, indicating a tendency to block formation for the non-sulfonated units, due to the higher reactivity of 4,4′-oxydianiline as compared to that of 2,5-diaminobenzene sulfonic acid and the higher content of non-sulfonated monomer in the polymer composition. For samples IV and V, we found $\bar{L}_{nonsulf}$-values of 8 and 11, respectively, which do agree quite well with the theoretical block length of 10.

Table 5
Ion exchange capacity and water-uptake of membrane samples

Sample	Ion exchange capacity (meq/g)		Water-uptake (%)
	Calculated	Measured	(H+-form)
I (DABSA)	3.144	2.025	79.0
II (ODA)	0	0.025	11.4
III (stat.)	1.543	1.080	27.5
IV (5/10)	1.022	1.146	45.4
V (10/10)	1.543	0.968	42.7
VI (20/20)	1.543	1.250	32.5
VII (35/35)	1.543	1.078	31.9
XII		0.94	
XIII		1.68	
XIV		1.87	
XV		2.25	
XVI		2.65	
XVII		2.95	
XVIII	3.144	3.09	
Nafion® 117	0.909[a]	0.769	28.9

[a] Ref. [35].

3.2. Water-uptake and ion exchange capacity

The experimentally determined ion exchange capacity of all samples except for the sample IV is approximately 30% lower than the calculated ones. Furthermore, the ''ion exchange capacity'' of sample II can be attributed to end group effects. The calculated molecular weight M_n calculated from this value is 40,000 g/mol, supposing that each polymer chain bears two carboxylic end groups which is substantially higher than $M_w = 10,050$ g/mol, calculated from viscosity measurements. All together, the ion exchange capacities determined by titration are in good accordance with the results from NMR spectroscopy, where also a 30% deviation from theoretical compositions was found. These observations can be explained by the same reasons given in the NMR part. Moreover, it is reasonable that not all sulfonic acid groups are accessible with the titration method. However, the ion exchange capacity of the prepared samples should be high enough for electrochemical applications. For the standard membrane material in fuel cell applications, i.e., Nafion®, an ion exchange capacity of 0.9 meq/g is reported [35].

The water-uptake of the membrane samples (I–VIII) depend strongly on the degree of sulfonation of the polymer (Table 5). The polymer with a degree of sulfonation of 100% (polymer I) shows a water-uptake as high as 79%, but does not dissolve even partially in water at 80 °C (or higher), as reported in earlier studies [36]. On the other hand the water-uptake of the non-sulfonated homopolymer is the lowest observed in this study (11%). All other polymers had a medium water-uptake in the range of 28% for sample III to 45% for sample IV, although the degree of sulfonation in the sulfonated block is always 100%. Obviously there is a correlation between block length and water-uptake. For the multiblock copolymers with equal block lengths (samples V–VII), the amount of sorbed water decreases with increasing block length. The dependence of water-uptake on the block length

$$(A)_{10}(B)_5 \sim (A)_{10}(B)_{10} > (A)_{20}(B)_{20} \sim (A)_{35}(B)_{35}$$

can be attributed to an increasing phase separation between the non-sulfonated and the sulfonated blocks with increasing block length. At an average block length <10 the phase separation is not well developed because the two types of blocks are partially miscible and is below the detection limit of, e.g., X-ray scattering techniques. The results of wide angle X-ray scattering experiments will be discussed in the following section. In this case both the sulfonated domains and the non-sulfonated domains, interpenetrated by sulfonated chains, swell in water. The increase of the average block length leads to systems in which the phase separation is more complete. In such materials the sulfonated domains mainly determine the water-uptake, but the surrounding non-sulfonated domains restrict the swelling.

The enhancement of hydrophilicity of sulfonated polyamides (samples IX–XVIII) can be followed by the swelling of membrane films or the water-uptake as a function of the degree of sulfonation, as shown in Fig. 4. As it was reported for several sulfonated polymers [35,37–39], the water-uptake by the sulfonated polyamides increases with the content of ionic groups in the polymer backbone. Fig. 4 also confirms this behavior both for films containing H+ and Na+ as counterions.
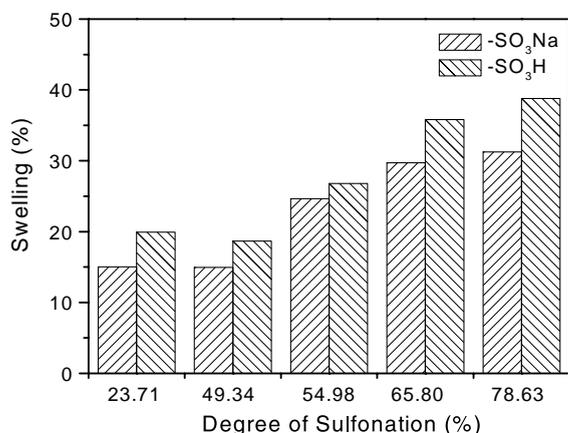
Fig. 4. Water-uptake of sulfonated polyamide membranes (samples IX–XVIII) after 24 h immersion in water at 25 °C (polymer films with H^+ and Na^+ as counterions).

The swelling of membranes with H^+ counterions was larger than those with Na^+, which agrees with other studies on sulfonated polysulfone and polyphosphazene [37,40]. Membranes with a DS of 90% and 100% are partially soluble in water.

Table 5 shows the values of ion-exchange capacity (IEC) of membranes with different sulfonation degrees evaluated by titration. A linear increase of IEC with values up to 3.09 meq/g was observed.

The formation of a phase-separated morphology has also a positive effect on the conducting properties of polyaramide ion-exchange membranes as confirmed by conductivity measurements at 100% r.h. (Fig. 5). The conductivity of membranes from multiblock copolymers is double that of a membrane from a corresponding random copolymer, having a comparable DS, but is by factor of three lower than that of a sulfonated homopolymer (sample I). These results show that a phase-separated morphology with sulfonated and non-sulfonated domains as occuring in multiblock copolymers is favorable in terms of conductivity over a randomly distributed sulfonation as it is present in random copolymers.

3.3. WAXS

The scattering diagrams of both the homo- and the block copolymers show a broad scattering maximum resulting from the amorphous structure of the samples (Fig. 6). The scattering angle at maximum intensity differs from non-sulfonated samples ($2\Theta = 20°$) to sulfonated samples ($2\Theta = 25°$). Moreover, there are no significant differences in the scattering curves of the random copolymer (III) (not shown in Fig. 6) and the block copolymers IV and V leading to the conclusion that no phase separation between the sulfonated and non-sulfonated blocks takes place in these samples. On the other hand, the scattering curves of a blend of the homopolymers I and II as well as those of the block copolymers VI and VII show two distinct intensity maxima in the scattering curves at

Fig. 5. Dependency of conductivity on temperature of sulfonated polyamide membranes at 100% r.h.
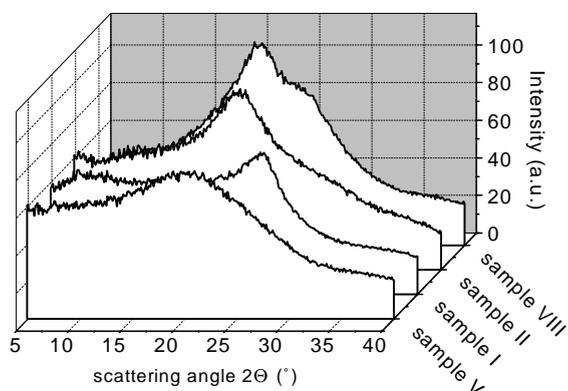

Fig. 6. Wide angle X-ray scattering curves of homopolymers I and II; the multiblock copolymer V and a 1:1 blend of the homopolymers I and II (sample VIII).
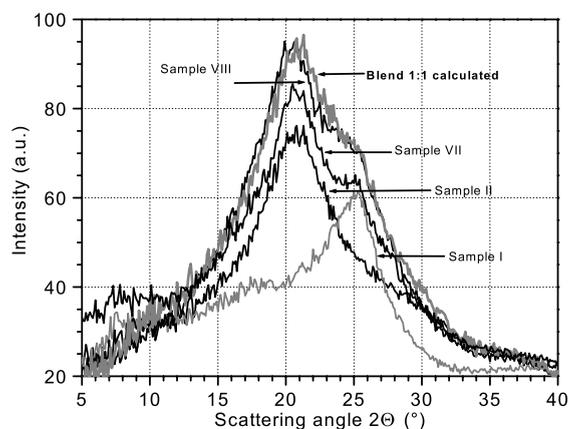
Fig. 7. Comparison of calculated and measured X-ray scattering curves of copolyaramides.

Fig. 9. *d*-Spacing of sulfonic acid groups in a sulfonated Kevlar-type polyaramide (polymer I), *d*-value depends on position of the sulfonic acid relative to the amide linkage.

at $2\Theta \sim 7$–$7.5°$ which corresponds with a *d*-spacing of approximately 12 Å. The intensity of this reflection depends on the degree of sulfonation of the sample. This reflection is also observed in the SAXS diagrams (not shown here). The intensity of the reflection was much higher after treatment of the samples with silver nitrate for 24 h, resulting from the formation of the silver salt of sulfonic acid groups (Fig. 8). The observed effect indicates, that the reflex at $2\Theta \sim 7$–$7.5°$ represents a structure in which sulfonic acid groups are incorporated. The exchange of protons by silver ions does enhance the electron density at the sulfonic acid sites leading to a higher scattering intensity. Assuming a stretched conformation of the rigid polyaramide chain, the calculated distance between neighboring sulfonic acid groups is between 9 and 15 Å (Fig. 9), which is in good agreement with the value calculated from the WAXS pattern.

3.4. Thermal stability

The thermal stability of sulfonated and non-sulfonated polyaramides was tested by thermogravimetric measurements in inert gas atmosphere. The TG-curves of the seven samples, displayed in Fig. 10, are representative of the general thermal behavior observed for all copolyaramides synthesized in this work. The weight loss between 25 and 200 °C corresponds to the elimination of water and residual solvent (DMAc, NMP). As expected, the non-sulfonated sample (sample II) shows the highest thermal stability. The onset of degradation for this sample is approximately at 450 °C and the maximum is at 560 °C. The introduction of sulfonic acid groups into the polymer backbone lowers the thermal stability of the polyamide

$2\Theta = 20°$ and $25°$. These maxima correspond very well with intensity maxima in the scattering curves of the respective homopolymers. Furthermore, the scattering curves of samples VI, VII, and VIII can be simulated by simple weighted addition of the scattering curves of the respective homopolymers I and II (Fig. 7). From these results a phase-separated morphology in membranes from multiblock copolymers with a block length higher than 10 is very likely.

The scattering diagrams of samples with sulfonated monomer units in the backbone exhibit an additional scattering maximum with low intensity
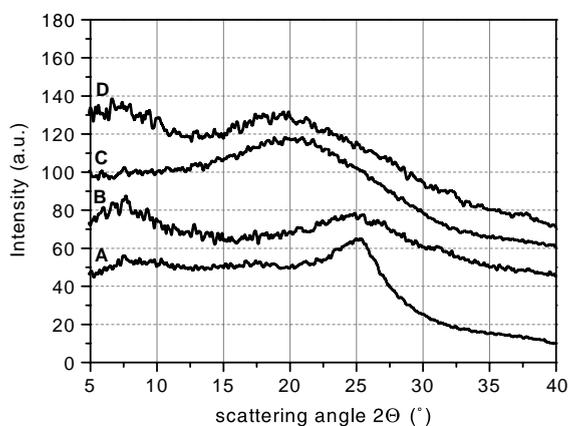

Fig. 8. WAXS curves of (A) polymer I, (B) polymer I after treatment with AgNO₃, (C) sample V, and (D) sample V after treatment with AgNO₃ (the curves have been shifted for better visualization).
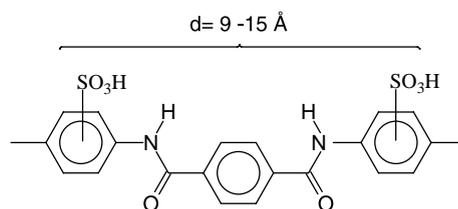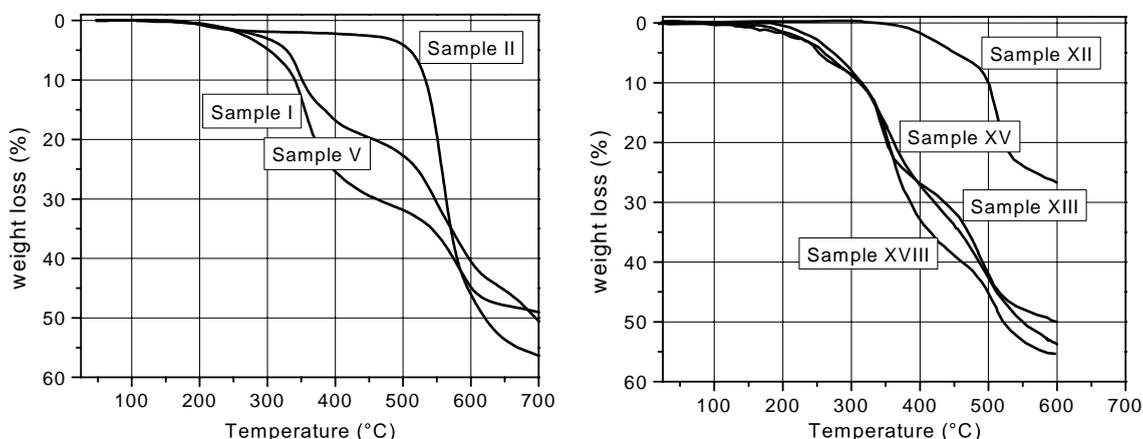
Fig. 10. TG-curves (weight loss vs. temperature) of samples I, II, and V (left) and samples XII, XIII, XV, and XVIII in the sodium form (right).

Table 6
Evaluation of the sulfonation degree by NMR and thermal analysis (TGA) and the residue remaining after heating up to 600 °C

Sample	DS (%) NMR	DS (%) TGA	Residue at 600 °C (%)
I	100	90	45
II	–	–	46
V	62	50	41
XII	24	13	79
XIII	49	51	49
XIV	55	66	45
XV	66	65	47
XVI	79	72	43
XVII	90	>100	45
XVIII	100	>100	45

sample substantially. A first degradation step of the polymers is observed at ca. 350 °C (maximum) due to the cleavage of C–S bond and the subsequent elimination of SO_x [41]. This temperature has been taken from the plot of the first derivative of the weight loss over temperature which is not shown here. Table 6 compares the values of DS estimated by NMR and by TGA, showing at least for medium DS a quite good agreement. The desulfonation of several polymers has been reported in the temperature range between 200 and 400 °C [27,37,42]. Recently, Kopitzke et al. [43] have assigned the weight loss not only to the loss of acid but also to the loss of organic fragments.

The weight loss observed for temperatures above 400 °C corresponds to the degradation of the polymer backbone.

4. Conclusions

Homo- and both random and multiblock co-polyaramides with sulfonated moieties in the backbone and of high molecular weights were synthesized by low temperature polycondensation technique in a dipolar aprotic solvent (NMP/ $CaCl_2$) using the N,N'-bis-trimethylsilyl derivatives of the diamines. Polyaramides with molecular weights up to 157,800 g/mol (GPC) were obtained with this method. A second route, using isophthaloyl chloride/trimesoyl chloride and free aromatic diamines, was investigated and optimized by the use of LiCl and the sodium salt of the sulfonated diamine. Polymers with molecular weight up to 240,000 g/mol were synthesized with the addition of less than 10 mol% trimesoyl chloride to the reaction mixture.

Ion-exchange polyamide membranes were obtained with IEC of up to 3.09 meq/g.

Mechanically stable membranes were prepared from these materials. Depending on the block length ($\geqslant 20$), a phase separation between sulfonated and non-sulfonated domains occurred, and was verified for the membranes by X-ray scattering

measurements. The water-uptake and the methanol crossover of the polyaramide membranes can be controlled by variation of block length. Especially, multiblock copolymers with block length ⩾ 20 showed enhanced properties with respect to methanol permeability and water-uptake (swelling) as compared to Nafion® due to the phase separation between sulfonated and non-sulfonated domains in such materials.

The sulfonated polyaramides may also find use as membranes in other applications where hydrophilic ion-exchange materials are required.

Acknowledgements

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