Macromol. Symp. **2004**, *210,* 175-184

Sulfonated Multiblock Copoly(ether sulfone)s as Membrane Materials for Fuel Cell Applications

Antje Taeger, Claus Vogel, Dieter Lehmann, Wolfgang Lenk,
*Kornelia Schlenstedt, Jochen Meier-Haack**

Institute of Polymer Research Dresden, P.O.Box 120411, 01005 Dresden, Germany
E-mail: mhaack@ipfdd.de

Summary: Arylene ether multiblock copolymers of the $(AB)_n$-type with various degrees of sulfonation have been prepared by a two-step polycondensation procedure. Multiblock copolymers in high yields and of high molecular weights were obtained. For comparison random copolymers with the same overall composition were synthesized. The theoretical ion-exchange capacities (IEC) of the materials were ranging from 0.50 mmol/g to 1.25 mmol/g. The water-uptake of the multiblock copolymers showed a linear dependency from the IEC and was increasing with increasing IEC. No differences were observed between random and block copolymers. Furthermore, the hydrolytic stability of aromatic sulfonic acid groups was investigated in this study. Aromatic sulfonic acids, having additional electron donating groups, especially in ortho- or para-position to the sulfonic acid group are sensitive to hydrolytic desulfonation. On the other hand electron-withdrawing groups in meta-position showed a stabilizing effect.

Keywords: ion-exchange membranes; multiblock copolymers; stability of aromatic sulfonic acids; sulfonated poly(ether sulfone)

Introduction

Recently, sulfonated polymers became of interest in processes requiring preferential transport of cations for example electrodialysis or in fuel cell applications. For the latter, perfluorosulfonic acid polymer membranes such as Nafion® (DuPont), Flemion® (Asahi Glass), DowMembrane® (Dow Chemical) are among the very few commercially available membranes for fuel cells due to their outstanding chemical properties and high proton conductivity. However, the Nafion®-type membranes have the disadvantages of (i) high costs of approx. 600 US\$/m^2, (ii) proton conductivity reduction above 100°C and (iii) high water and methanol crossover, which is particularly disadvantageous for direct methanol fuel cells. These drawbacks have initiated worldwide research activities for developing new materials for proton exchange membranes, ranging from partially fluorinated to non-fluorinated fully aromatic materials mainly in order to reduce costs.

DOI: 10.1002/masy.200450620

Overviews of recent developments in membrane research for fuel cells have been published for example by Savadogo [1], Rikukawa and Sanui [2], Costamagna and Srinivasan [3, 4] as well as in a special issue of *J. Membr. Sci.* [5 - 12].

Research activities have been focussed on sulfonated polyimides (PI), poly(ether ether ketone)s (PEEK), polysulfones (PSU), poly(ether sulfone)s (PES) and others. One approach to obtain sulfonated materials is the chemical modification of commercially available polymers by treatment with different types of sulfonation agents [13 - 17]. Less extensively explored is the preparation of an alternative material via the introduction of ionic groups onto the polymer backbone, using sulfonated monomers [18 - 24]. This method allows for a better control both of the sulfonation degree and the ionic group distribution. The synthesis of both random and block copoly(ether sulfone)s was reported by Wang et al.[18 - 20]. The preparation of polyimides using 4,4`-diamino-biphenyl-2,2`-disulfonic acid, 4,4`-oxydianiline and oxydiphthalic dianhydride or 1,4,5,8-naphthalene tetracarboxylic dianhydride was described for example by Faure et al. [21], Cornet et al. [22, 23] and Genies et al. [24].

Moreover, it is well known from organic chemistry textbooks [25] that the sulfonation of aromatic rings is a reversible process especially at low pH and at elevated temperature. However, this aspect has not been considered in the literature dealing with sulfonated polymers so far. Most often only the thermal stability is discussed.

Therefore, one aim of this study was to investigate the stability of sulfonated aromatic compounds. Model compounds, representing a repeating unit of the respective polymer chains were synthesized and treated at 135°C either in pure water or in 0.5N HCl. The samples were characterized by NMR spectroscopy before and after the treatment. The presence of sulfuric acid in the test samples was tested by titration with NaOH and precipitation of $BaSO_4$ by addition of $BaCl_2$ to the aqueous test solutions.

Secondly, $(AB)_n$ multiblock copolymers having non-sulfonated blocks (A-blocks) and highly sulfonated blocks (B-blocks) were prepared with the aim of providing polymeric materials with a phase-separated morphology. The phase of A-blocks should enable good mechanical stability and a reduction of the swelling of the highly sulfonated B-blocks whereas the B-blocks should provide a high proton conductivity. The properties of multiblock copolymers are compared with those of random copolymers of the same overall composition. All polymers are characterized in terms of water-uptake and ion exchange capacity.

Experimental

Materials

Bis-(4-fluorophenyl)sulfone (DFDPS) and chlorotrimethylsilane (TMSCl) were supplied by Aldrich. Hydroquinone sulfonic acid sodium salt (HQSA-Na) and 4,4`-dihydroxybiphenyl (DHBP) and N,N-dimethylacetamide (DMAc) were purchased from Acros. N-methyl-2-pyrrolidone (NMP) was purchased from Merck.

K_2CO_3 was dried in vacuum for 24 h at 150 °C. NMP was dried by subsequent distillation from P_4O_{10} and K_2CO_3 under reduced pressure. It was stored over molecular sieves (4 Å).

Silylation of Bisphenols

1 mol (186 g) of DHBP was suspended in a mixture of 500 ml dry toluene and 2.5 mol (244.5 g) of hexamethyl disilazane (HMDS). The reaction mixture was refluxed until the evolution of ammonia ceased (4 – 8 h). The toluene and excess of HMDS were removed using a rotary evaporator and the product was purified by distillation in vacuum (bis-TMS-DHBP: 140°C at $3\text{x}10^{-3}$ mbar, yield > 95%).

0.5 mol of HQSA-Na was suspended in 1.5 l dry THF. Per mol of functional groups 1.1 mol of an equimolar mixture of HMDS and chlorotrimethylsilane were added to the suspension. The mixture was refluxed for 96 h under exclusion of moisture. After cooling to room temperature precipitated ammonium hydrochloride and sodium chloride were filtered off and the THF was removed under reduced pressure using a rotary evaporator. The tris-silylated product was purified by distillation under reduced pressure (tris-TMS-HQSA: 146°C at $5.5\text{x}10^{-2}$ mbar). The yield was higher than 93%.

Synthesis of polymers

For the preparation of the poly(ether sulfone)s a three-necked round-bottom flask, equipped with a gas inlet tube, a magnetic stirrer, a still and a $CaCl_2$, was charged with equimolar amounts, typically 20 mmo,l of DFDPS and a mixture of silylated bisphenols with a predetermined ratio of tris-TMS-HQSA and bis-TMS-DHBP. The monomers were dissolved in dry NMP giving a 10 – 20 wt.-% polymer solution. After complete dissolution of the monomers, a double molar amout of K_2CO_3 was added to the solution and the temperature was raised to 150°C for 24 h. The reaction mixture was then filtered through a sintered-glass filter to remove unsoluble contents and the polymer was precipitated by pouring the reaction mixture into a 10-fold excess of cold ethanol. The precipitate was filtered off and washed thorougly with hot ethanol. The polymer was dried to constant weight at 80°C in vacuum.

In the case of block copolymers the A-block oligomers (hydroxy terminated) and B-block oligomers (fluoro terminated) were at first prepared separately. The multiblock copolymers were finally obtained by combining the reaction mixture of the A- and B-block and the reaction was completed by stirring the combined mixtures at 150°C overnight.

Membrane preparation

Membranes were prepared by casting a polymer solution containing approx. 20 wt.-% polymer in DMAc on 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 and 16 h at 80°C in vacuum, the membranes were peeled off by immersing the glass plate in water. Finally the membranes were dried to constant weight at 80°C in vacuum. The resulting membranes had a thickness of approximately 80 µm.

Measurements

Prior to characterization all polymers were dried at 120°C in vacuum to constant weight. The viscosities were measured with an automated Ubbelohde viscosimeter thermostated at 25°C. The polymer concentration was 2 g/l in DMAc. ^{1}H- and ^{13}C-NMR experiments were carried out on a Bruker AMX 500 spectrometer (500 MHz for ^{1}H) in 5 mm o.d. sample tubes using deuterated DMSO as solvent and chemical shift reference. 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. Poly(vinylpyrrolidone) samples were used as standards for molecular weight calibration.

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 equation (1) and is given in percentage increase in weight

$$W = \frac{m_{wet} - m_{dry}}{m_{dry}} x100\% \tag{1}$$

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

Ion-exchange capacity

The ion-exchange capacity (IEC, with units mmol/g of dry polymer) of the sulfonated membranes was measured using the standard experimental method of immersing the membrane in 1N HCl for 24 h, followed by soaking in distilled water to remove excess acid for another 24 h. Finally, 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 0.01N NaOH to determine the concentration of the exchanged protons.

Results and Discussion

Stability of aromatic sulfonic acids

Despite the fact, that the sulfonation of aromatic rings is reversible at elevated temperatures and at acidic conditions, most often only the thermal properties of proton-conducting membranes in an inert atmosphere are discussed in the literature. In this study sulfonated model compounds as well as polymer samples were used to test the hydrolytic stability in water and dilute acid (0.5N HCl) at 135°C for 168 h. The sulfuric acid formed during hydrolysis was determined quantitatively by titration of the test solution with NaOH and qualitatively by precipitation of $BaSO_4$ after the experiment.

As a result, nearly all compounds having electron-donating substituents at the sulfonic acid bearing ring are sensitive to desulfonation under the chosen test conditions. On the other hand, compounds having electron-withdrawing substituents were stable in most cases (Fig 1).

Furthermore, not only desulfonation was detected under test condition but also cleavage of imide and amide bonds leading to a reduction of the molecular weight of the polymers and the loss of mechanical stability. A more detailed discussion of the results will be published in a forthcoming paper.

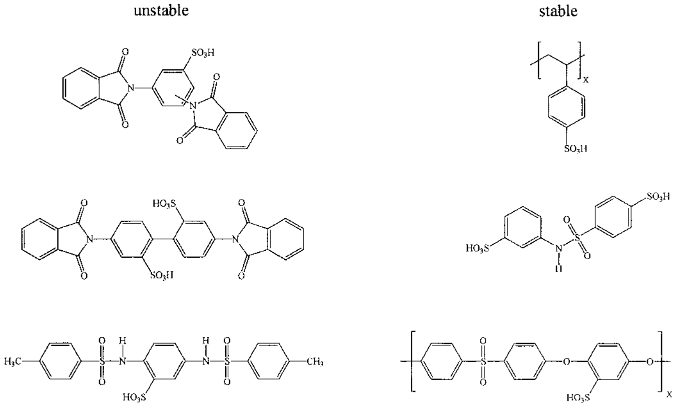


Figure 1. Examples for unstable and stable compounds under test conditions

Properties of sulfonated poly(ether sulfone)s

The so-called „silyl-method“ was employed to prepare poly(ether sulfone)s from difluoro compounds and trimethylsilyl derivatives of bisphenols. The general chemical structure of the synthesized poly(ether sulfone)s is given in Figure 2. The silyl-method has the advantage that the silylated bisphenols, especially hydroquinone sulfonic acid are much better soluble in dipolar aprotic solvents such as NMP than their non-silylated counterparts. Secondly, water and hydrohalic acid as reaction products are avoided, thus minimizing the risk of side reactions. Thirdly, the combination of silylation and distillation is an effective method for the purification of many monomers.

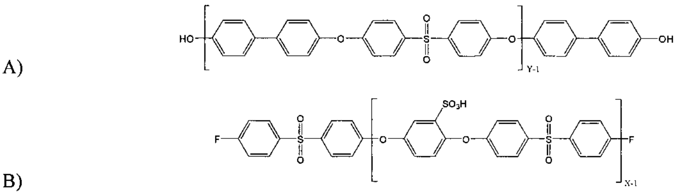


Figure 2. Chemical structure of A) A-block and B) B-block with X and Y ranging between 1 and 21 in the multiblock copolymers

As outlined in Table 1, the poly(ether sulfone)s were obtained in high yields and with molecular weights sufficient for the preparation of membranes. The number of blocks in the multiblock copolymers varies from 2 to 8 depending on the molecular weight of the individual block building oligomers. In general it can be said that the higher the molecular weight of the oligomers the lower the number of blocks in the final block copolymer.

Table 1. Yields and molecular weights of poly(ether sulfone)s.

Sample[1)]	Yield (%)	$\eta_{inh.}$[2)] (dl/g)	M_w[3)] (g/mol)	M_n (g/mol)	M_w/M_n	number of blocks
HPA	> 95	1.02	141850	36050	3.94	-
HPB	> 95	0.66	52750	14750	3.58	-
MBC 5/5	> 95	0.81	47450	12550	3.78	3/3
MBC 10/5	> 95	0.57	44000	20700	2.13	4/4
MBC 15/5	> 95	0.52	53700	24900	2.16	3/3
MBC 20/5	> 95	0.43	28650	9950	2.88	1/1
MBC 10/10	> 95	1.02	65360	18150	3.60	2/2
MBC 20/20	> 95	0.88	68250	16050	4.25	1/1
RC 1/1	> 95	1.18	63300	15900	3.98	-
RC 2/1	> 95	0.89	61300	18700	3.28	-
RC 3/1	> 95	0.46	35450	11550	3.07	-
RC 4/1	> 95	0.64	51350	16250	3.16	-

[1)] HPA = non-sulfonated homopolymer; HPB = sulfonated homopolymer; MBC = multiblock copolymer with numbers indicating the respective block length (A/B); RC = random copolymer with numbers indicating the ratio of non-sulfonated to sulfonated monomers
[2)] determined in DMAc at 25°C; c = 2g/l; capillary 0a
[3)] measured in DMAc containing 2 vol.-% water and 3 g/l LiCl, poly(vinylpyrrolidone) standards were used for calibration

Table 2 shows the water-uptake and ion-exchange capacities for poly(ether sulfone) membranes. The ion exchange capacities, determined by NMR spectroscopy are in good agreement with the values calculated from the initial monomer composition. However, using the titration method, the values are somewhat lower, which is explained by the fact that only a part of the sulfonic acids groups is accessible to the sodium ions.

On the other hand, with the NMR spectroscopy all sulfonic acid groups are detected, regardless of whether they play an active role in the ion exchange process or not. Therefore, the IEC determined by the titration method gives a more realistic value than the NMR spectroscopy concerning the behavior of the membrane in the fuel cells.

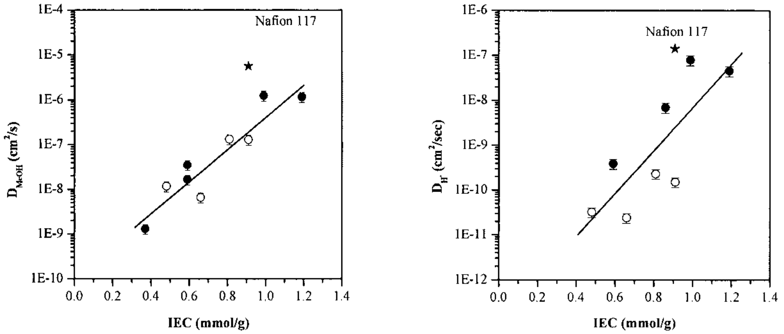
The water-uptake shows a linear dependency from the ion exchange capacity of the membranes. It is in the same range as observed for the Nafion membranes. Unexpectedly, no difference between the water-uptake of random and multiblock copolymers was observed in contrast to sulfonated polyaramide membranes [27]. From studies following the polymerization process of random sulfonated copoly(ether sulfone)s, it is known that during the preparation of random copolymers a block like structure is obtained due to differences in the reactivity of the monomers [28]. Therefore it is likely, that the morphology of the membranes prepared from random or block copolymers is very similar resulting in a similar behavior of the membranes.

Table 2. Ion exchange capacity and water uptake of poly(ether sulfone) membranes.

Sample[1)]	Water/uptake	H_2O/SO_3H	Ion exchange capacity (mmol/g)		
	(%)	mol/mol	calculated from monomer comp.	titration	NMR
HPA	1.4	-	0	-	-
HPB	n.d.[1)]	-	2.48	-	-
MBC 5/5	34.4	19	1.24	0.83	0.99
MBC 10/5	21.7	14	0.83	0.67	0.86
MBC 15/5	12.6	12	0.62	0.46	0.59
MBC 20/5	9.5	9	0.51	0.35	0.59
MBC 10/10	28.3	14	1.24	0.84	1.14
MBC 20/20	34.8	16	1.24	0.90	1.19
RC 1/1	33.2	16	1.24	1.15	1.14
RC 2/1	16.9	12	0.83	0.85	0.81
RC 3/1	11.8	11	0.62	0.45	0.61
RC 4/1	8.4	10	0.50	0.08	0.48
Nafion 117	28.9	21	0.91[2)]	0.77	-

[1)] not determined due to solubility in water
[2)] reference [26]

The diffusion coefficients for methanol and protons in sulfonated poly(ether sulfone) membranes together with the values for a Nafion membrane are displayed in Figure 3. The procedures for the measurement and the calculation of the diffusion coefficients were adopted from the literature [29]. As expected, the diffusion coefficients are increasing with increasing IEC, due to higher hydrophilicity resulting in an enhanced swelling of the membranes (Table 2).

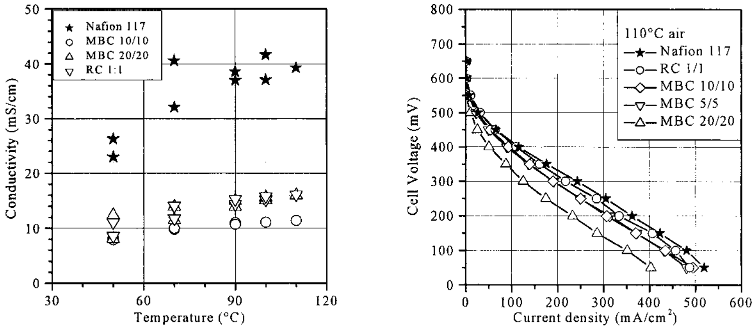


a) b)

Figure 3. Methanol (a) and proton (b) diffusion coefficients in sulfonated poly(ether sulfone) membranes; ● = MBC, O = RC; T = 50°C; c_{MeOH} = 20 wt.-%; c_{HCl} = 0,5 mol/l

At comparable IEC the methanol diffusion coefficients for poly(ether sulfone) membranes are one to two orders of magnitude lower than that of the Nafion membrane, indicating improved barrier properties for methanol (lower methanol crossover) of poly(ether sulfone) membranes. Still for most membranes the proton diffusion coefficients are also lower than that of the Nafion membrane.

The findings for the proton diffusion coefficients are reflecting in the results of conductivity measurements (Fig. 4a). The conductivities of sulfonated poly(ether sulfone) membranes are approximately by a factor of 2 lower than that of a Nafion membrane. However, the fuel cell performance of the introduced poly(ether sulfone) membranes is quite similar to that of Nafion, except for the BC 20/20 membrane (Fig. 4b). For this membrane a high methanol crossover was observed, which was in the same range as for the Nafion sample. All other membranes showed a lower methanol permeation during the fuel cell tests, as was expected from the diffusion coefficients measurements.



a) b)

Figure 4. Electrical properties of poly(ether sulfone) membranes compared to Nafion 117 membrane; a) conductivity at 100% relative humidity; b) polarization curves from DMFC tests at 110°C (1.5 mol/l MeOH; 2.5 bar air)

Conclusions

Aromatic sulfonic acid groups are susceptible to hydrolytic degradation, especially at elevated temperatures, acidic pH and with additional electron donating substituents on the ring. Such substituents facilitate the electrophilic attack of the proton, leading to desulfonation.

Sulfonated arylene ether sulfone block copolymers as well as random copolymers with predetermined IECs were successfully synthesized by the "silyl-method". Membranes with an IEC ≥ 1 mmol/g showed a fuel cell performance slightly less than Nafion but with lower methanol crossover.

Acknowledgements

The authors gratefully acknowledge the financial support of this work by the HGF Strategiefond project "Membranes and Electrodes for Direct Methanol Fuel Cells". Furthermore we like to thank S. P. Nunes (GKSS), R. Reißner and E. Gülzow (DLR) for performing the membrane tests.

[1] O. Savadogo, J. New Mat. Electrochem. Systems **1998**, *1*, 47.
[2] M. Rikukawa K. Sanui, Progr. Polym. Sci. **2000**, *25*, 1463.
[3] P. Costamagna, S. Srinivasan, J. Power Sources **2001**, *102*, 242.
[4] P. Costamagna, S. Srinivasan, J. Power Sources **2001**, *102*, 253.
[5] G. Alberti, M. Casciola, L. Massinelli, B. Bauer, J. Membr. Sci. **2001**, *185*, 73.
[6] P. Genova-Dimitrova, B. Baradie, D. Foscallo, C. Poinsignon, J. Y. Sanchez, J. Membr. Sci. **2001**, *185*, 59.
[7] S. Haufe, U. Stimming, J. Membr. Sci. **2001**, *185*, 95.
[8] I. Honma, S. Nomura, H. Nakajima, J. Membr. Sci. **2001**, *185*, 83.
[9] D.J. Jones, J. Rozière, J. Membr. Sci. **2001**, *185*, 41.
[10] J. Kerres, J. Membr. Sci. **2001**, *185*, 3.
[11] K.D. Kreuer, J. Membr. Sci. **2001**, *185*, 29.
[12] F. Finsterwalder, G. Hambitzer, J. Membr. Sci. **2001**, *185*, 105.
[13] H. Tang, P. N. Pintauro, Q. Guo, S. O'Connor, J. Appl. Polym. Sci. **1999**, *71*, 387.
[14] H. Tang, P. N. Pintauro, J. Appl. Polym. Sci. **2001**, *77*, 49.
[15] B. Lafitte, L. E. Karlsson, P. Jannasch, Macromol. Rapid Commun. **2002**, *23*, 896.
[16] A. Dyck, D. Fritsch, S. P. Nunes, J. Appl. Polym. Sci. **2002**, *86*, 2820.
[17] M.-S. Kang, Y.-J. Choi, I.-J. Choi, T.-H. Yoon, S.-H. Moon, J. Membr. Sci. **2003**, *216*, 39.
[18] F. Wang, Y. Kim, M. Hickner, T. A. Zawodzinski, J. E. McGrath, Polymeric Materials: Science & Engineering **2001**, *85*, 517.
[19] F. Wang, Q. Ji, W. Harrison, J. Mecham, R. Formato, R. Kovar, P. Osenar J. E. McGrath, Polymer Preprints **2000**, *41*, 237.
[20] W. Harrison, F. Wang, J. Mecham, T. E. Glass, M. Hickner, J. E. McGrath, Polymeric Materials: Science & Engineering **2001**, *84*, 688.
[21] French Patent 96/05707 (1996) S. Faure, P. Aldebert, R. Mercier, B. Sillion.
[22] N. Cornet, O. Diat, G. Gebel, F. Jousse, D. Marsacq, R. Mercier, M. Pineri, J. New Mat. Electrochem. Systems **2000**, *3*, 33.
[23] N. Cornet, G. Beaudoing, G. Gebel, Sep. Pur. Techn. **2001**, *22-23*, 681.
[24] C. Genies, R. Mercier, B. Sillion, N. Cornet, G. Gebel, M. Pineri, Polymer **2001**, *42*, 359.
[25] Organikum, 21st Edition, Wiley VCH, Weinheim 2001.
[26] F. Lufrano, G. Squadrito, A. Patti, E. Passalacqua, J. App. Polym. Sci. **2000**, *77*, 1250.
[27] A. Taeger, C. Vogel, D. Lehmann, D. Jehnichen, H. Komber, J. Meier-Haack, N.A. Ochoa, S.P. Nunes, K.-V. Peinemann, Reactive and Functional Polymers **2003**, *57*, 77.
[28] A. Taeger unpublished results
[29] M. V. Fedkin, X. Zhou, M. A. Hofmann, E. Chalkova, J. A. Weston, H. R. Allcock, S. N. Lvov, Mat. Lett. **2002**, *52*, 192.