Bio-inspired ion selective crown-ether polymer membranes

Sinem Taş

***BIO-INSPIRED ION SELECTIVE CROWN-
ETHER POLYMER MEMBRANES***

Sinem Taş

This thesis is part of the Industrial Partnership Program (IPP) "Spectroscopic analysis of particles in water" of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). This IPP is co-financed by Wetsus, Centre of Excellence for Sustainable Water Technology, as part of Wetsus' TTI program. Wetsus is co-funded by the Dutch ministry of economics, agriculture and innovation.

Promotion committee:

Prof. Dr. Ir. W.G van der Wiel (chairman)	University of Twente
Prof. Dr. Ir. D.C. Nijmeijer (supervisor)	University of Twente
Prof. Dr. Ir. K. Seshan	University of Twente
Dr. Mark A. Hempenius	University of Twente
Prof. Dr. M. Ulbricht	Universität Duisburg-Essen
Prof. Dr. E. J. R. Sudhölter	Technische Universiteit Delft
Prof. Dr. A. P. H. J. Schenning	Technische Universiteit Eindhoven

Cover design:

Goffe-Jan Mellema

Printed by:

Ipskamp, Enschede

© 2016 S.Tas

ISBN: 978-90-365-4074-2

DOI: 10.3990/1.9789036540742

BIO-INSPIRED ION SELECTIVE CROWN- ETHER POLYMER MEMBRANES

DISSERTATION

to obtain

the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
prof. dr. H. Brinksma,
on account of the decision of the graduation committee
to be publicly defended
on Friday 11 March 2016 at 16:45

by

Sinem Taş
born on 25 May 1986
in Tunceli, Turkey

This thesis has been approved by:

Prof. Dr. Ir. D.C. Nijmeijer (promotor)

Contents

Chapter 1

Introduction	1
--------------	---

Chapter 2

Synthesis of poly(arylene ether ketone)s bearing skeletal crown ether units for cation exchange membranes	15
---	----

Chapter 3

Monovalent cation separation with crown ether containing poly(arylene ether ketone)/SPEEK blend membranes	43
---	----

Chapter 4

PAN/crown ether composite nanofibers for the selective adsorption of cations	65
--	----

Chapter 5

Electromechanical performance of a crown ether containing ionic polymer metal composite actuator	87
--	----

Chapter 6

General discussion and outlook	113
--------------------------------	-----

Summary	120
---------	-----

Samenvatting	122
--------------	-----

Acknowledgement	124
-----------------	-----

1

Introduction

1.1. Mining metals from seawater

Oceans cover 71% of the surface of planet Earth¹ and they contain essential metals and elements such as uranium, lithium, copper, cobalt, silver and gold.² To date, mostly concentrated minerals like sodium, magnesium, calcium and potassium have been commercially recovered from seawater.² Due to the gradual depletion of conventional mineral ores, seawater has been considered as a promising alternative source as well and is targeted to meet future metal demands of the process, manufacturing and energy industries.³

To highlight the potential of seawater, the amounts of critical metals and valuable element reserves in seawater are listed in Table 1. Moreover, Table 1 also compares the amounts in seawater with land reserves, as listed in the United States Geological Survey (USGS).²

Table 1: Concentrations, estimated amounts of metal ions in seawater and their estimated land resources.

Element	Seawater concentration (ppm)	Total oceanic abundance ($\times 10^6$ tons)	Land reserves ($\times 10^6$ tons)
Na	10800	1.40×10^{10}	-
K	392	5.10×10^8	8.30×10^3
Li	0.178	2.31×10^5	4.10×10^3
Ca	411	5.34×10^8	-
Mg	1290	1.68×10^9	2.20×10^3
Ba	0.21	2.73×10^4	1.9×10^2
Ni	0.0066	8.58×10^3	67
Zn	0.005	6.50×10^3	1.9×10^2
Fe	0.034	4.42×10^3	1.5×10^5
U	0.0033	4.29×10^3	2.6-5.47
Cu	0.0009	1.17×10^3	4.9×10^2
Co	0.00039	5.08×10^2	7.0×10^2
Au	0.000011	14.3	0.0042

Although the chemistry of the seawater is dominated by sodium, potassium, magnesium and calcium ions, there is a great interest in the extraction of uranium and lithium from seawater. Uranium, in the form of the 235 isotope, is fuel for the present nuclear reactors whereas lithium can be transformed to tritium which could be used as a fuel for the next generation nuclear reactors. Currently, lithium is also used for ceramics, glass, multipurpose greases, catalysts, pharmaceuticals and lithium-ion batteries.⁴ The rapid growth in e.g. lithium-ion battery production makes a forecast of the future lithium demand difficult. Therefore, questions regarding to short- and long term availability of lithium sources have been raised.

The two most important lithium reserves are terrestrial pegmatite ores and brine.^{5,6} The current lithium supply mostly comes from lithium brines in Argentina, Chile and Bolivia because production of lithium from brine is less expensive compared to production from pegmatite,⁵ as the production of lithium from pegmatite includes energy intensive steps of extraction and beneficiation.⁵

Since the market is expected to remain driven by consumer products that require lithium-ion batteries, the lithium potential of the seawater has been taken into consideration. Although there is a debate on the feasibility of the extraction of uranium and lithium from seawater due to the relatively low concentrations of these metals in seawater, there has been continuous research carried out in order to meet the growing energy related demand of those elements in the future.^{2,3,7}

It is also worth mentioning the potassium potential of the seawater. Potassium is essential to plant growth and potassium consumption is expected to increase due to the demand for fertilizer production. Owing to its high concentration in seawater (392 ppm), potassium recovery from seawater as a by-product is economically feasible.⁶

In regards to this need for additional sources of valuable metals/elements, adsorption,⁸ ion exchange⁹ and electrodialysis⁷ have been proposed for the separation of metals and elements from seawater. The concept of adsorption and ion exchange has been used for the extraction of lithium from seawater. For example, manganese oxide and aluminum hydroxide are commonly used adsorbents for lithium recovery.^{10,11} Lithium separation with tin(IV) antimonate cation exchanger¹² and Dowex 50-X16 consisting of beads of

polystyrene crosslinked with 16 % divinylbenzene⁷ have been studied in literature. Although there is a huge metal potential in seawater, the critical question is how to process a large amount of water having relatively low concentrations of the target ions for the metal recovery. Membrane technology has been used for this kind of large-scale applications as well. Reverse osmosis (RO) and electrodialysis, the latter using so-called ion exchange membranes (IEMs), are extensive and well-proven large scale applications of membrane technology. However, the current problem is that commercially available membranes lack specific ion selectivity. Therefore, development of a membrane that contains functional groups that selectively bind to specific ionic species is necessary for the selective recovery of target metals from seawater.

1.2. Ion exchange membranes

Ion exchange membranes (IEMs) are made from ionic polymers that have either negatively or positively charged moieties bound covalently to the polymer backbone. Ion exchange membranes are classified into cation exchange membranes (CEM) and anion exchange (AEM) membranes, depending on the charge of the ionic groups attached to the polymer backbone. CEMs carry negatively charged groups (Figure 1) that make them selectively permeable to positively charged species, yet almost impermeable to anions.^{13,14} AEMs carry positively charged groups (Figure 1) in the polymer backbone and allow the transport of negatively charged species.¹³ Generally, IEMs have been widely used in electrodialysis,^{15,16} reverse electrodialysis^{17,18} and diffusion dialysis.^{19,20}

Figure 1: Schematic illustration of cation and anion exchange membranes.

Although CEMs can separate cations from anions, such membranes are not capable of selectively recognizing and transporting specific ions (e.g. K^+ , Li^+ , Na^+) from multicomponent systems. However, the membrane properties are crucial for electrodialysis, reverse electrodialysis and diffusion dialysis performances. Especially in electrodialysis, selective transport of specific ions from multicomponent mixtures is important for e.g. the separation of specific cations in industrial waste water treatment,²¹ removing harmful anions (e.g. F^-) from groundwater,²² the production of table salt from seawater,^{14,23} the electrochemical acidification of milk and water softening to produce drinking water.²⁴ In the case of reverse electrodialysis,²⁵ the membrane permselectivity has a strong effect on the power production. The natural presence of multivalent ions such as Mg^{2+} and Ca^{2+} in river and seawater increase the membrane electrical resistance, resulting in lower power outputs.^{26,27} Therefore, the development of monovalent ion selective membranes, capable of selectively transporting monovalent ions from multivalent ions, is vital for reverse electrodialysis performance. In order to meet those electromembrane process requirements, CEMs have been modified in order to achieve monovalent over divalent ion selectivity.²⁸⁻³¹ Despite this, the development of membranes that allow the selective transport of one specific ion from a mixture of other ions, including ions of the same valence, remains a major challenge.

1.3. Modification of cation exchange membranes

As mentioned above, both from an industrial and academic point of view, achieving preferential selectivity for a specific ion is crucial. Numerous methods have been reported in the literature for the development of cation exchange membranes with specific ion selectivity.

CEMs with a thin layer of a conducting polymer, such as polypyrrole or polyaniline, were developed to improve monovalent/divalent ion selectivity. Formation of a tight and rigid conducting polymer layer on the CEM decreased the permeation of divalent cations due to the difference in electrostatic repulsion forces between the divalent (Ca^{2+}) and monovalent (Na^+) cations.^{31,32} Formation of a polypyrrole or polyaniline layer on CEM resulted in a 4 times lower Ca^{2+}/Na^+ ion permeability compared to that of the native CEM.

The synergistic effects from using polymer blends has fuelled the development of new CEMs with enhanced ion selectivity as well. For instance, sulfonated poly ether sulfone (SPES) was blended with sulfonated poly(ether ether ketone) (SPEEK). This composite membrane exhibited four times higher monovalent ion (Na^+) permeability with respect to the bivalent ions (Ca^{2+} , Mg^{2+} , Cu^{2+}).³³ Another example is the blending of poly(ether sulfone) (PES) with the cation exchange polymer SPEEK. This resulted in lower divalent cation transport.^{25,28}

Another example of membrane modification is the formation of a thin cationic polyelectrolyte layer on the surface of a cation exchange membrane.³⁴⁻³⁶ Cations with a higher valence and a smaller hydrated radius experience strong electrostatic repulsion forces due to the presence of a thin cationic polyelectrolyte layer. In this way, effective separation of ions with the same charge but different valence is possible. However, the major drawback is the stability of the thin polyelectrolyte layer, as this layer is easily detached from the surface during long-term electrodialysis.²³ In recent studies, layer-by-layer (LbL) deposition of polyelectrolytes onto CEMs was employed to control the polyelectrolyte layer thickness and to increase membrane selectivity.^{29,30,37} For instance, standard cation exchange membranes (CMX) consisting of a layer-by-layer (LbL) assembly of poly(ethyleneimine) (PEI)/poly(styrenesulfonate) (PSS) polyelectrolyte multilayers were prepared.³⁷ Due to the synergistic effect of Donnan exclusion for divalent ions and the hydrophobization of the surface, membranes exhibited Na^+ over Ca^{2+} ion permselectivity. Another example is the coating Nafion membranes with poly(allylamine hydrochloride) (PAH)/poly(styrenesulfonate) (PSS) multilayers. In this case, $\text{K}^+/\text{Mg}^{2+}$ ion selectivity was investigated under electrodialysis conditions. At high source-phase concentrations or at low current densities, membranes exhibited significant selectivity increase ($\text{K}^+/\text{Mg}^{2+}$ selectivity > 1000) with multilayer coatings.²⁹

Due to these developments, to date, the separation of monovalent and multivalent ions from each other is possible with the modification of CEMs. However, the separation of ions with the same valence from aqueous environments (e.g. K^+ from Li^+) with high separation efficiency has not been achieved yet.

1.4. Crown ethers and the incorporation of crown ethers in polymer backbone

The picture developed in the previous section for CEM modification is often inspired by the selective transport exhibited in biological membranes. Transmembrane ion channels can control the flow of specific ions in and out of biological cells by changing the membrane potential or binding to a ligand.³⁸⁻⁴⁰ This makes mimicking these types of ion channels attractive for achieving ion selectivity for different sized monovalent ions, such as sodium and potassium. Inspired by these biological host-guest interactions between membrane proteins and ions, crown ethers have been proposed as guest molecules for ions and attracted great interest regarding mimicking the biological ion transport mechanism.⁴¹⁻⁴⁴

Crown ethers are macrocyclic compounds and are able to selectively bind specific cationic species due to the ion-dipole interaction of the positively charged metal ion with the negatively polarized oxygen atoms in the crown ether ring.⁴⁵ Generally, the complexation itself is not selective for specific ions but crown ethers can form the most stable complexes with ions having diameters comparable to that of the open cavity of the crown ether. Complexes with larger ions are nevertheless also possible to some extent.⁴⁶ Crown ether cavity sizes and cation sizes of a selected series are listed in Table 2.⁴⁷

Table 2: Size of selected crown ether cavities and ionic diameter of alkali metal ions.⁴⁷

Crown ether	Cation	Cavity diameter (Å)	Ionic diameter (Å)
12-crown-4	Li ⁺	1.2	1.46
14-crown-4	Li ⁺	1.54	1.46
15-crown-5	Na ⁺	1.80	2.04
18-crown-6	K ⁺	2.80	2.76
21-crown-7	Rb ⁺	3.80	2.98

When the diameter of the cation is relatively equal to the size of the crown ether cavity, crown ether-ion, 1:1 complexes are formed (Figure 2a). As can be seen in Table 2, for

example, the cavity size of the crown ether 18-crown-6 (cavity diameter: 2.8 Å) and the potassium ion are relatively similar (ionic diameter: 2.76 Å) and the same is true for e.g. 12-crown-4 and the lithium ion. Therefore 18-crown-6 has a high affinity to form a 1:1 complex with potassium ions⁴⁸ and 12-crown-4 preferentially associates could associate with lithium ions.⁴⁷ When the size of the cation gets larger than the cavity of the crown ether, the crown ethers sandwich and form a 2:1 complex (Figure 2b), with the metal ion between adjacent crown ether units.⁴⁹ Although the ionic size of K^+ (2.8 Å, Table 2) is bigger than the cavity size of the 15-crown-5 (1.8 Å, Table 2), the formation of a 2:1 sandwich complex between 15-crown-5 and the K^+ ion is well-known.⁵⁰

Figure 2: Schematic illustration of the crown ether-metal binding a) 1:1 and b) 2:1 complex.

From an application point of view, incorporation of crown ethers in polymer structures used for membrane preparation allows the application of crown ethers for in continuous processes. Moreover, stability, handling and recyclability problems could be eliminated by incorporation of crown ethers in the polymer backbone. For this reason, crown ether containing polymers have been synthesized by chain-growth addition polymerization of vinyl derivatives of crown ethers, step-growth condensation polymerization of bifunctional derivatives of crown ethers, graft polymerization of crown ethers onto polymer matrices and cyclopolymerization of bifunctional derivatives of crown ethers.

Owing to their high selectivities, considerable research interest has been devoted to the design of crown ether-polymer adsorbents. For example a crown ether incorporated thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel was synthesized for Pb^{2+} adsorption. The Pb^{2+} adsorption capacity of the PNIPAM hydrogel at 23 °C increased from 120 mg/g to 142 mg/g after crown ether incorporation.⁵¹ Crown ether incorporated ion imprinted polymers were successfully employed for the selective recovery of Li^+ , K^+ and Pb^{2+} ions.⁵²⁻⁵⁴ Additionally, crown ether polymers have been used

as an adsorbent, finding a broad range of applications as stationary phase in capillary chromatography,⁵⁵ chemical sensor devices^{42,56} and ion transport membranes.⁵⁷

1.5. Scope of the thesis

This thesis focuses on the development of new membrane materials for the efficient and effective separation of ions with the same valence from aqueous environments.

Chapter 2 describes the synthesis and characterization of sulfonated poly (arylene ether ketone) (SPAEEK) and non-sulfonated (PAEK) containing crown ether units in the main chain, which can be used in sensing applications and ion-selective membranes. Combining the ionic polymer (SPAEEK) with a crown ether, a strong and flexible polymer film is developed that alters the specific ionic selectivity due to the complexation ability of the crown ether with the specific ion. The influence of the crown ether moieties in the SPAEEK main chain is assessed by diffusion dialysis using potassium ions.

Chapter 3 focuses on the preparation of crown ether-containing PAEK (CPAEK) and sulfonated poly(ether ether ketone) (SPEEK) blend membranes. The membranes are prepared by mixing the two polymers in different weight ratios, polymer miscibility and membrane properties are investigated. By blending CPAEK with SPEEK, the aim is to tailor the transport properties of the membranes by getting an advantage of the presence of the crown ether in the polymer backbone. Ion transport of the membranes is investigated by diffusion dialysis for the monovalent ions Li^+ and K^+ .

Electrospinning is a versatile method for producing nanofibers from various polymers. Due to their unique properties, such as high surface area-to-volume, pore size within the nano range, high porosity, and flexibility for chemical/physical functionalization, nanofibers have potential for applications such as membranes, adsorbents, catalysis and biosensors. In **Chapter 4**, crown ether functionalized electrospun polyacrylonitrile (PAN) nanofiber membranes are prepared that have adsorption selectivity towards specific cations depending on the choice of crown ether.

Ionic polymer metal actuators (IPMCs) have a “sandwich” structure that comprises an ion exchange membrane between two noble metal electrodes. SPAEEK is an ionic polymer and has fixed negatively charged sulfonate groups in the main chains. The sulfonate groups can form bonds with cations such as Li^+ , Na^+ and K^+ . Under an electric field the ions move through the material resulting in bending of the IPMC actuator. However, this

is not very selective for specific ions. **Chapter 5** focuses on the incorporation of ion selective crown ether moieties in the main SPEAK polymer chain to tailor the actuation performance of SPAEK and make it selective for a specific ion (e.g. Na^+ or K^+).

Chapter 6 summarizes the main conclusions of the present work and elaborates on future research perspectives.

References

1. Pidwirny, M. Introduction to the oceans. In fundamentals of physical geography, **2006**, <http://www.physicalgeography.net/fundamentals/8o.html>.
2. Bardi, U. Extracting minerals from seawater: an energy analysis. *Sustainability* **2010**, *2* (4), 980-992.
3. Diallo, M. S.; Kotte, M. R.; Chot, M. Mining critical metals and elements from seawater: opportunities and challenges. *Environ Sci Technol* **2015**, *49* (16), 9390-9399.
4. Ebensperger, A.; Maxwell, P.; Moscoso, C. The lithium industry: Its recent evolution and future prospects. *Resour. Policy* **2005**, *30* (3), 218-231.
5. Goonan, T. G. U.S. Geological Survey, lithium use in batteries **2012**, Virginia USA
6. Shahmansouri, A.; Min, J.; Jin, L. Y.; Bellona, C. Feasibility of extracting valuable minerals from desalination concentrate: a comprehensive literature review. *J Clean Prod* **2015**, *100*, 4-16.
7. Schwochau, K. Extraction of Metals from Sea-Water. *Top Curr Chem* **1984**, *124*, 91-133.
8. Ooi, K.; Miyai, Y.; Katoh, S. Recovery of lithium from seawater by manganese oxide adsorbent. *Separ Sci Technol* **1986**, *21* (8), 755-766.
9. Gibert, O.; Valderrama, C.; Peterkova, M.; Cortina, J. L. Evaluation of selective sorbents for the extraction of valuable metal ions (Cs, Rb, Li, U) from reverse osmosis rejected brine. *Solvent Extr Ion Exc* **2010**, *28* (4), 543-562.
10. Tian, L. Y.; Ma, W.; Han, M. Adsorption behavior of Li⁺ onto nano-lithium ion sieve from hybrid magnesium/lithium manganese oxide. *Chem Eng J* **2010**, *156* (1), 134-140.
11. Hamzaoui, A. H.; Jamoussi, B.; M'nif, A. Lithium recovery from highly concentrated *Membr Sci* **2009**, *330* (1-2), 65-72.
12. Abe, M.; Hayashi, K. synthetic inorganic ion-exchange materials .34. selective separation of lithium from seawater by tin(IV) antimonate cation exchanger. *Hydrometallurgy* **1984**, *12* (1), 83-93.
13. Xu, T. W. Ion exchange membranes: State of their development and perspective. *J Membr Sci* **2005**, *263* (1-2), 1-29.
14. Strathmann, H. *Ion exchange membrane separation processes*; Elsevier: Amsterdam, The Netherlands, **2004**.
15. Dlugolecki, P.; Anet, B.; Metz, S. J.; Nijmeijer, K.; Wessling, M. Transport limitations in ion exchange membranes at low salt concentrations. *J Membr Sci* **2010**, *346* (1), 163-171.
16. Krol, J. J.; Wessling, M.; Strathmann, H. Concentration polarization with monopolar ion exchange membranes: current-voltage curves and water dissociation. *J Membr Sci* **1999**, *162* (1-2), 145-154.
17. Guler, E.; Elizen, R.; Vermaas, D. A.; Saakes, M.; Nijmeijer, K. Performance-determining membrane properties in reverse electrodialysis. *J Membr Sci* **2013**, *446*, 266-276.
18. Guler, E.; Zhang, Y. L.; Saakes, M.; Nijmeijer, K. Tailor-made anion-exchange membranes for salinity gradient power generation using reverse electrodialysis. *Chemsuschem* **2012**, *5* (11), 2262-2270.

19. Agarwal, C.; Mhatre, A.; Goswami, A. Transport studies of divalent ions through nafion-117 ion exchange membrane in the presence of polyacrylate. *Ind Eng Chem Res* **2015**, *54* (13), 3445-3450.
20. Miyoshi, H. Diffusion coefficients of ions through ion-exchange membranes for Donnan dialysis using ions of the same valence. *Chem Eng Sci* **1997**, *52* (7), 1087-1096.
21. Saracco, G.; Zanetti, M. C.; Onofrio, M. Novel application of monovalent-ion-permselective membranes to the recovery treatment of an industrial waste-water by electrodialysis. *Ind Eng Chem Res* **1993**, *32* (4), 657-662.
22. Amor, Z.; Malki, S.; Taky, M.; Bariou, B.; Mameri, N.; Elmidaoui, A. Optimization of fluoride removal from brackish water by electrodialysis. *Desalination* **1998**, *120* (3), 263-271.
23. Sata, T. Ion exchange membranes: preparation, characterization, modification and application; RSC: Cambridge, United Kingdom, **2004**.
24. Van der Bruggen, B.; Koninckx, A.; Vandecasteele, C. Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration. *Water Res* **2004**, *38* (5), 1347-1353.
25. Balster, J.; Krupenko, O.; Punt, I.; Stamatialis, D. F.; Wessling, M. Preparation and characterisation of monovalent ion selective cation exchange membranes based on sulphonated poly(ether ether ketone). *J Membr Sci* **2005**, *263* (1-2), 137-145.
26. Guler, E.; van Baak, W.; Saakes, M.; Nijmeijer, K. Monovalent-ion-selective membranes for reverse electrodialysis. *J Membr Sci* **2014**, *455*, 254-270.
27. Post, J. W.; Hamelers, H. V. M.; Buisman, C. J. N. Influence of multivalent ions on power production from mixing salt and fresh water with a reverse electrodialysis system. *J membranes composed of cation exchange membranes and polypyrrole. Macromolecules* **1996**, *29* (11), 4029-4035.
28. Wilhelm, F. G.; Punt, I. G. M.; van der Vegt, N. F. A.; Strathmann, H.; Wessling, M. Cation permeable membranes from blends of sulfonated poly(ether ether ketone) and poly(ether sulfone). *J Membr Sci* **2002**, *199* (1-2), 167-176.
29. White, N.; Misovich, M.; Yaroshchuk, A.; Bruening, M. L. Coating of Nafion membranes with polyelectrolyte multilayers to achieve high monovalent/divalent cation electrodialysis selectivities. *ACS Appl Mater Inter* **2015**, *7* (12), 6620-6628.
30. Deng, H. N.; Wang, Z. X.; Zhang, W.; Hu, B. S.; Zhang, S. F. Preparation and monovalent selective properties of multilayer polyelectrolyte modified cation-exchange membranes. *J Appl Polym Sci* **2015**, *132* (8).
31. Sata, T.; Funakoshi, T.; Akai, K. Preparation and transport properties of composite solutions: Response surface methodology (RSM) process parameters optimization. *Hydrometallurgy* **2008**, *90* (1), 1-7.
32. Sata, T.; Ishii, Y.; Kawamura, K.; Matsusaki, K. Composite membranes prepared from cation exchange membranes and polyaniline and their transport properties in electrodialysis. *J Electrochem Soc* **1999**, *146* (2), 585-591.
33. Gohil, G. S.; Nagarale, R. K.; Binsu, V. V.; Shahi, V. K. Preparation and characterization of monovalent cation selective sulfonated poly(ether ether ketone) and poly(ether sulfone) composite membranes. *J Colloid Interf Sci* **2006**, *298* (2), 845-853.

34. Sata, T.; Mizutani, Y. Modification of properties of ion-exchange membranes .6. electro-dialytic transport properties of cation-exchange membranes with a electrodeposition layer of cationic polyelectrolytes. *J. Polym. Sci., Part A: Polym. Chem.* **1979**, *17* (4), 1199-1213.
35. Takata, K.; Yamamoto, Y.; Sata, T. Modification of transport properties of ion exchange membranes - XIV. Effect of molecular weight of polyethyleneimine bonded to the surface of cation exchange membranes by acid-amide bonding on electrochemical properties of the membranes. *J Membr Sci* **2000**, *179* (1-2), 101-107.
36. Amara, M.; Kerdjoudj, H. Modification of cation-exchange membrane properties by electro-adsorption of polyethyleneimine. *Desalination* **2003**, *155* (1), 79-87.
37. Abdu, S.; Marti-Caatayud, M. C.; Wong, J. E.; Garcia-Gabaldon, M.; Wessling, M. Layer-by-layer modification of cation exchange membranes controls ion selectivity and water splitting. *ACS Appl Mater Inter* **2014**, *6* (3), 1843-1854.
38. Jentsch, T. J.; Hubner, C. A.; Fuhrmann, J. C. Ion channels: Function unravelled by dysfunction. *Nat Cell Biol* **2004**, *6* (11), 1039-1047.
39. Fertig, N.; Klau, M.; George, M.; Blick, R. H.; Behrends, J. C. Activity of single ion channel proteins detected with a planar microstructure. *Appl Phys Lett* **2002**, *81* (25), 4865-4867.
40. Liu, H. M.; Jameson, C. J.; Murad, S. Molecular dynamics simulation of ion selectivity process in nanopores. *Mol Simulat* **2008**, *34* (2), 169-175.
41. Liu, T.; Bao, C. Y.; Wang, H. Y.; Fei, L. B.; Yang, R. Y.; Long, Y. T.; Zhu, L. Y. Self-assembly of crown ether-based amphiphiles for constructing synthetic ion channels: the relationship between structure and transport activity. *New J Chem* **2014**, *38* (8), 3507-3513.
42. Gokel, G. W.; Leevy, W. M.; Weber, M. E. Crown ethers: Sensors for ions and molecular scaffolds for materials and biological models. *Chem Rev* **2004**, *104* (5), 2723-2750.
43. Cazacu, A.; Tong, C.; van der Lee, A.; Fyles, T. M.; Barboiu, M. Columnar self-assembled ureido crown ethers: An example of ion-channel organization in lipid bilayers. *J. Am. Chem. Soc.* **2006**, *128* (29), 9541-9548.
44. Sakai, N.; Matile, S. Synthetic ion channels. *Langmuir* **2013**, *29* (29), 9031-9040.
45. Nogami, M.; Haratani, T.; Tachibana, Y.; Kaneshiki, T.; Nomura, M.; Suzuki, T. Adsorptivity of various metal ions onto benzo-18-crown-6 and dibenzo-18-crown-6 resins. *J Radioanal Nucl Ch* **2015**, *303* (2), 1549-1553.
46. Fabre, B.; Simonet, J. Electroactive polymers containing crown ether or polyether ligands as cation-responsive materials. *Coordin Chem Rev* **1998**, *178*, 1211-1250.
47. Collie, L. E. Lithium transport in crown ether polymers. PhD thesis, Durham University, 1995.
48. Rounaghi, G.; Eshaghi, Z.; Ghiamati, E. Thermodynamic study of complex formation between 18-crown-6 and potassium ion in some binary non-aqueous solvents using a conductometric method. *Talanta* **1997**, *44* (2), 275-282.
49. Alexandratos, S. D.; Stine, C. L. Synthesis of ion-selective polymer-supported crown ethers: a review. *React Funct Polym* **2004**, *60*, 3-16.
50. Lin, S. Y.; Liu, S. W.; Lin, C. M.; Chen, C. H. Recognition of potassium ion in water by 15-crown-5 functionalized gold nanoparticles. *Anal Chem* **2002**, *74* (2), 330-335.

51. Ju, X. J.; Zhang, S. B.; Zhou, M. Y.; Xie, R.; Yang, L.; Chu, L. Y. Novel heavy-metal adsorption material: ion-recognition P(NIPAM-co-BCAm) hydrogels for removal of lead(II) ions. *J Hazard Mater* **2009**, *167* (1-3), 114-118.
52. Luo, X. B.; Guo, B.; Luo, J. M.; Deng, F.; Zhang, S. Y.; Luo, S. L.; Crittenden, J. Recovery of Lithium from Wastewater Using Development of Li Ion-Imprinted Polymers. *Acc Sustain Chem Eng* **2015**, *3* (3), 460-467.
53. Rajabi, H. R.; Shamsipur, M.; Pourmortazavi, S. M. Preparation of a novel potassium ion imprinted polymeric nanoparticles based on dicyclohexyl 18C6 for selective determination of K⁺ ion in different water samples. *Mat Sci Eng C-Mater* **2013**, *33* (6), 3374-3381.
54. Luo, X. B.; Liu, L. L.; Deng, F.; Luo, S. L. Novel ion-imprinted polymer using crown ether as a functional monomer for selective removal of Pb(II) ions in real environmental water samples. *J Mater Chem A* **2013**, *1* (28), 8280-8286.
55. Zhang, A.; Ge, J.; Guan, Z. X.; Deng, J. H.; Liu, H. W.; Zhu, J.; Fu, R.; Huang, Z.; Zhang, B. Poly(crown ether) stationary phase for open-tubular capillary column chromatography. *J Chromatogr* **1990**, *521* (1), 128-133.
56. Schuwer, N.; Klok, H. A. A potassium-selective quartz crystal microbalance sensor based on crown-ether functionalized polymer brushes. *Adv Mater* **2010**, *22* (30), 3251-3255.
57. Kimura, K.; Yoshinaga, M.; Kitazawa, S.; Shono, T. Synthesis of polyvinyl alcohol)-based poly(crown ether)s and permeability of their polymeric membranes. *J Polym Sci Pol Chem* **1983**, *21* (9), 2777-2785.

2

Synthesis of poly(arylene ether ketone)s bearing skeletal crown ether units for cation exchange membranes

This chapter has been published as:

Bram Zoetebier, Sinem Tas, G. Julius Vancso, Kitty Nijmeijer and Mark A. Hempenius
Synthesis of poly(arylene ether ketone)s bearing skeletal crown ether units for cation exchange membranes
Journal of Polymer Science: Part A Polymer Chemistry, 53 (2015), 2786-2793

Abstract

Poly(arylene ether ketone)s (PAEKs) are the most commonly known high performance materials used for ion exchange and fuel cell membranes. Described here is the design of novel sulfonated and non-sulfonated PAEKs (SPAEEKs) containing crown ether units in the main chain, which can be used in sensing applications and ion-selective membranes. To this end, 4,4'(5')-di(hydroxybenzo)-18-crown-6 is synthesized and used as monomer in a step growth polymerization to form crown ether containing PAEKs and SPAEEKs. The successful synthesis of PAEKs containing 18-crown-6 and sulfonate groups is confirmed by gel permeation chromatography, FTIR and NMR spectroscopy. Membranes are fabricated from the sulfonated polymers. Potassium ion transport properties of the SPAEEK and crown ether containing SPAEEK membranes are assessed by diffusion dialysis. Potassium ion diffusion in the crown ether containing SPAEEK membranes is almost four times lower than K^+ diffusion in the native polymer membranes, without crown ether.

2.1 Introduction

Integral membrane proteins such as ion channels can gate the flow of ions in and out of cells by adopting closed and open states. Controlled by different mechanisms such as membrane potential or binding of a ligand, ion channels are of central importance for many biological functions (e.g. cell-cell communications, muscle contraction) by allowing the movement of particular ionic species across the membrane.¹⁻³ In view of the central role played by ion channels in biology, synthesis and development of artificial ion channels are of great importance for creating new functional materials. A combination of the biological ion transport mechanism with polymer chemistry has opened many avenues in materials science, particularly in sensing applications and in the area of ion selective membranes.⁴⁻⁶

Crown ethers are widely used as guest molecules for ions and attract great interest in terms of mimicking the biological ion transport mechanism. These structures are able to selectively bind specific cationic species due to the ion-dipole interaction of the positively charged metal ion with the negatively polarized oxygen atoms.⁷ Besides their specific binding with cations, crown ethers can also function as ion carriers.⁸ Moreover, the stacking ability of the crown ether moieties makes them a potential candidate for the design of one-dimensional ion channels.⁹ Therefore, several interesting molecular architectures including crown ether polymers have been designed in the context of synthetic ion channels and responsive materials.^{10,11}

Polymers containing crown ethers are widely used in polymer chemistry and have been around for a long time.¹² The first example of such a polymer, bearing crown ethers in the main chain, was published by Feigenbaum and Michel.¹³ These authors reported a polyamide that extracted alkali cations from aqueous metal chlorides. Other polymer configurations followed soon, including end-functionalized polymers¹⁴⁻¹⁶ or polymers with pendant crown ether groups.¹⁷ Nowadays, these crown ether containing polymers are still intensively studied, due to their potential use in ion recognition,^{18,19} supramolecular assemblies²⁰⁻²³ and self-healing gels.²⁴⁻²⁷ Recent work on main chain crown ether containing supramolecular polymers includes processing by electrospinning to form nanofibers,²¹ polymers responsive to heat, pH, potassium cations or competitive ligands^{22,23} and interesting cases where linear supramolecular polymers constructed of

AB-type monomers formed supramolecular fibrils which subsequently self-organized into cross-linked networks.²⁴ The thermo- and pH-responsive sol-gel transition of similar gels was successfully employed for the controlled release of rhodamine B.²⁵ Other gels were prepared with multifunctional supramolecular monomers,²⁶ results including self-healing gels, showing 100% recovery even under 10,000% strain in less than ten seconds.²⁷ Recently, fluorescent supramolecular polymers were prepared for sensing applications.^{28,29}

Poly(arylene ether ketone)s (PAEKs) are the most commonly known high performance materials that have been extensively studied as actuators, and as ion exchange and fuel cell membranes.³⁰⁻³⁴ PAEKs belong to the class of aromatic polyethers³⁵ and possess outstanding thermal stability, chemical resistance, processability and mechanical properties.³⁶ To date, incorporation of various chemical moieties and post modification reactions of PAEKs have been investigated.³⁷⁻⁴⁰ However, the major current challenge in ion exchange membrane development is how to improve the selective transport of a specific ion with a very high degree of specificity. To our knowledge, there are no examples of PAEKs or even of aromatic polyethers such as poly(sulfone)s or poly(ether sulfone)s with crown ether moieties incorporated in their main chain. However, copoly(ether sulfones) of moderate molar mass containing azo linkages and crown ether units in the main chain have recently been reported.⁴¹ Crown ether containing PAEKs would alter the specific ionic selectivity and are valuable for the development of ion selective membranes and electrodes.

In this chapter we report the design of novel sulfonated poly(arylene ether ketone)s containing crown ether moieties in the main chain. The synthesized polymers were characterized by gel permeation chromatography, NMR and FTIR spectroscopy and their thermal and film forming properties were investigated. Diffusion dialysis experiments for potassium ions were performed as a proof of concept for the use of these membranes as ion selective materials and to elucidate the influence of crown ether moieties in the PAEK main chain on ion transport.

2.2 Experimental

Materials

Dibenzo-18-crown-6 (98%), Eaton's reagent, 4,4'-difluorobenzophenone (DFBP, 99%), bisphenol A (BPA, $\geq 99\%$), 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%), DMSO- d_6 (99.9 atom % D), NaOH ($> 98\%$), Na_2HPO_4 ($> 99\%$), Na_2SO_3 ($> 98\%$), Na_2SO_4 (anhydrous, $> 99\%$), NaHCO_3 ($> 99.7\%$) and NaCl ($> 99\%$) were obtained from Aldrich and used as received. K_2CO_3 (99.9%) and *m*-chloroperbenzoic acid (*m*-CPBA, 77%) were obtained from Aldrich and dried before use. CDCl_3 (99.8 atom %D) was purchased from Cambridge Isotope Laboratories. Methanol, DMSO, THF and dichloromethane were obtained from Biosolve, The Netherlands. Milli-Q water (Millipore) was used in all experiments. Acetone, hydrochloric acid (37%) and DMF (extra dry, 99.8%) were purchased from Acros Organics, Belgium. Glacial acetic acid was obtained from Merck, USA.

Techniques

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz instrument at 400.1 and 100.6 MHz, respectively, in CDCl_3 or DMSO- d_6 . ^1H and ^{13}C chemical shifts were based on the solvent residual signals. Peak assignments were based on ^1H - ^{13}C correlated 2D NMR (HSQC) spectra. FTIR spectra were measured with a Bruker ALPHA. Gel permeation chromatography (GPC) measurements were performed using a Shimadzu GPC LC-20AD equipped with a Shodex LF-801 column and a refractive index detector, using NMP containing 0.5 mM LiBr as the eluent. GPC measurements for sulfonated polymers were carried out in NMP containing 5 mM LiBr, using PSS GRAM analytical 30Å and 1000Å GPC columns and a dual detection system consisting of a differential refractometer (Waters model 410) and a differential viscometer (Viscotek model H502). Molar masses were determined relative to narrow polystyrene standards. All sample solutions were prepared at a concentration of 1 mg mL $^{-1}$ and filtered through a 0.45 μm PTFE filter prior to a GPC run. Thermal gravimetric analysis (TGA) measurements were performed on a Perkin Elmer TGA 4000 under N_2 atmosphere at a linear heating rate 20 $^\circ\text{C min}^{-1}$. Samples (10 mg) were heated over a 30-900 $^\circ\text{C}$ temperature range. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC 8000. Each sample (10 mg) was subsequently cooled

and heated at a rate of 20 °C min⁻¹ between 30 °C and 350 °C under N₂ atmosphere. This cycle was repeated four times. Glass transition temperatures (T_g's) were determined from the second heating cycle. X-ray diffraction measurements were performed using an XRD D2 Phaser Bruker instrument employing Cu K α radiation. The generator was set to 30 kV and 10 mA. Data was collected in the 2 θ range of 10-40° with an interval of 0.02°. The potassium concentration during the diffusion experiments was measured by BWB-XP flame photometer. In case of sulfonated polymers, FTIR, GPC, TGA, DSC and XRD measurements were performed in the H-SPAEEK form.

4,4'(5')-Di(acetylbenzo)-18-crown-6 1.^{43,44}

Dibenzo-18-crown-6 (20.0 g, 55.5 mmol), 1.5 equivalent glacial acetic acid (10.0 g, 166.5 mmol) and Eaton's reagent (145 mL) were mixed under argon. The mixture was heated to 50 °C under argon and stirred overnight. About 250 g of ice was added to the cherry red mixture. The solid was filtered with a POR 3 glass filter and dissolved in 500 mL of CH₂Cl₂. The organic layer was washed with 5 % aqueous NaOH solution (3 x 150 mL) and brine (150 mL). The CH₂Cl₂ layer was dried over Na₂SO₄, and evaporated in vacuo to yield 24.71 g (99 %) of product as a light yellow solid with mp 192 °C. ¹H NMR (400 MHz, CDCl₃, δ): 2.55 (s, 6H, CH₃), 4.01-4.07 + 4.22-4.24 (m, 16H, 18C6), 6.86 (d, *J* = 8.5 Hz, 2H, Ar *o*-CH₂), 7.49-7.58 (m, 4H, Ar *m*-CH₂). ¹³C NMR (100 MHz, CDCl₃, δ): 26.26 (CH₃), 68.29, 69.48 (18C6), 111.02 (Ar C), 123.40 (Ar C), 130.45 (Ar C), 148.50 (Ar C-O), 152.82 (Ar C-O), 196.90 (C=O); IR: ν = 1666 (s, C=O), 1266 (s, C-O) and 1129 (s, C-O) cm⁻¹.

4,4'(5')-Di(acetatobenzo)-18-crown-6 2.^{43,44}

To a solution of 4,4'(5')-di(acetylbenzo)-18-crown-6 (24.64 g, 55.4 mmol) in CH₂Cl₂ (1.5 L), dried *m*-chloroperbenzoic acid (47.35 g, 274.4 mmol) and Na₂HPO₄ (20.7 g, 145.8 mmol) were added. After the mixture was stirred for 2 days under argon atmosphere, the solution was concentrated in vacuo and the organic layer was subsequently washed with 5 % aqueous Na₂SO₃ (500 mL), a saturated solution of NaHCO₃ (3 x 500 mL) and brine (300 mL). Then, the organic layer was dried over Na₂SO₄, and evaporated in vacuo to yield 23.16 g of product (86 %) with mp 112 °C. ¹H NMR (400 MHz, CDCl₃, δ): 2.25 (s, 6H, CH₃), 3.96-4.06 + 4.10-4.20 (m, 16H, 18C6), 6.60 (m, 4H, Ar *o*-CH₂), 6.81 (m, 2H, Ar *m*-CH₂). ¹³C NMR (100 MHz, CDCl₃, δ): 21.18 (CH₃), 68.70-69.91 (18C6), 107.36 (Ar C),

113.31 (Ar C), 113.42 (Ar C), 144.65 (Ar C-O), 146.47 (Ar C-O), 149.11 (Ar C-O), 169.83 (C=O); IR: ν = 1747 (s, C=O), 1202 (s, C-O) and 1123 (s, C-O) cm^{-1} .

4,4'(5')-Di(hydroxybenzo)-18-crown-6 3.^{43,44}

4,4'(5')-Di(acetatobenzo)-18-crown-6 (18.9 g, 39.7 mmol) was dissolved in a mixture of CH_2Cl_2 (725 mL) and MeOH (900 mL). The mixture was purged with argon for 1 h, before adding an argon-purged solution of NaOH (6.1 g, 154 mmol) in MeOH (100 mL). The mixture was neutralized with concentrated HCl after stirring under argon for 24 h and dried in vacuo. The crude product was dissolved in MeOH (200 mL) and CH_2Cl_2 (800 mL) was added. Solids were filtered off and the filtrate was dried in vacuo. The product was redissolved in MeOH (100 mL) and crystallized by adding Milli-Q water (750 mL), yielding 12.8 g of pure product (82 %), mp 212 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ): 3.74-3.87 + 3.91-4.04 (m, 16H, 18C6), 6.24 (dd, J = 2.5 and 8.5 Hz, 2H, Ar *o*-CH₂), 6.39 (d, J = 2.5 Hz, 2H, Ar *o*-CH₂), 6.72 (d, J = 8.5 Hz, 2H, Ar *m*-CH₂), 8.97 (s, 2H, OH). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, δ): 67.5-69.4 (18C6), 101.1 (Ar *o*-C), 105.76 (Ar *o*-C), 114.15 (Ar *m*-C), 140.87 (Ar C-O), 148.94 (Ar C-O), 151.80 (C-OH); IR: ν = 3583 (w, OH), 1219 (s, C-O) and 1123 (s, C-O) cm^{-1} .

Sulfonated 4,4'-difluorobenzophenone.⁴²

4,4'-Difluorobenzophenone (30 g, 0.137 mol) was dissolved in 65% fuming sulfuric acid (60 mL) in a 100 mL, three necked flask equipped with a stirrer bar and a nitrogen inlet/outlet. The solution was heated to 150 °C for 6 hours to produce a homogeneous solution. Then it was cooled to room temperature, and poured into 450 mL of ice-water. Next, NaCl (180.0 g, 3.08 mol) was added which produced a white solid. This was filtered and re-dissolved in 300 mL of Milli-Q water. The solution was neutralized with 2M NaOH and NaCl (110.0 g, 1.88 mol) was added to salt out the sodium form of the sulfonated monomer. The crude product was recrystallized from a 3:1 mixture of isopropanol and Milli-Q water (3/1 in volume). The product was obtained as white crystals with a yield of 87%.

Poly(arylene ether ketone)s (PAEKs) 4.

A typical polycondensation was conducted as follows: A mixture of DFBP (2.18 g, 10 mmol), BPA (2.28 g, 10 mmol) and K_2CO_3 (1.57 g, 15 mmol) was dissolved in dry NMP (16 mL) and toluene (8 mL) in a three necked round-bottomed flask equipped with a

magnetic stirring bar, Dean-Stark trap and thermometer. The content was heated to 150 °C for 4 h while removing water by azeotropic distillation. Heating was then continued at 175 °C for 20 h. The viscous solution was diluted with NMP and the polymer was precipitated in a 10-fold excess of cold ethanol. The solid was filtered off and dried in vacuo at 60 °C. For the C-PAEKs (featuring crown ether units), part of the BPA was substituted by 4,4'(5')-di(hydroxybenzo)-18-crown-6. For the S-PAEKs (featuring sulfonate units), 25 mol% of the DFBP was substituted by SDFBP. The copolymers were designated as S(x)-C(y)-PAEK where x and y represent the mol percentages of SDFBP and di(hydroxybenzo)-18-crown-6.

Membrane fabrication

20 wt% solutions of S(25)-PAEK and S(25)-C(75)-PAEK were prepared in NMP at 60 °C. The viscous solutions were cast on a glass plate with a 0.5 mm casting knife. After casting, the solvent was evaporated under N₂ atmosphere for 5 days at room temperature, followed by 5 days at 60 °C and 2 days at 110 °C under vacuum. Next, the membranes were peeled off from glass plate by immersing into water and then transferred into 1.0 M HCl to convert the Na-SPAEEK into H-SPAEEK. Afterwards, the membranes were rinsed several times with Milli-Q water.

Water swelling

The fabricated membranes were immersed in Milli-Q water for 24 hours to measure the wet weight of the membranes. Then the wet membranes were subsequently dried at 60 °C for 24 hours. Membrane swelling was calculated by the following equation:

$$\text{Swelling} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \% \quad (1)$$

Here, m_{wet} and m_{dry} are the mass (g) of the wet and the dry membranes.

Permselectivity

The permselectivity of the membranes was determined by the Nernst potential method. In a two-compartment cell, KCl solutions of 0.5 M and 0.1 M are recirculated on each side of the test membrane. The membrane potential is measured by two reference electrodes. The permselectivity of the membranes was calculated by the following equation:

$$\text{permselectivity } (\%) = \frac{\Delta V_{\text{measured}}}{\Delta V_{\text{theoretical}}} \times 100 \quad (2)$$

$$\Delta V_{\text{theoretical}} = \frac{RT}{zF} \ln \frac{C_2 \gamma_2}{C_1 \gamma_1} \quad (3)$$

Here, R is the gas constant (J mol⁻¹ K⁻¹), T the temperature (K), z the electrochemical valence, F the Faraday constant (A·s mol⁻¹), C₁ and C₂ the concentrations of the two solutions (mol L⁻¹) and γ₁ and γ₂ the activity coefficients of the two solutions.

Diffusion dialysis

The two compartments of a glass diffusion cell (35 mL) were separated by the membrane under investigation with an effective area of 12 cm². The receiver solution had a concentration of 10 mM HCl for each experiment, while 10 mM KCl was prepared as feed solution. Each side was constantly mixed during the diffusion experiments and 0.1 mL samples were taken in time and analyzed using a flame photometer.

The ion flux through the membrane was calculated from the concentration change in the receiving compartment.

$$J = \frac{V}{A} \frac{dc}{dt} \quad (4)$$

where V is the volume of the receiving compartment, A the membrane area and dc/dt the concentration change in time.

2.3 Results and discussion

In the present work, we describe the direct incorporation of dibenzo-18-crown-6 units into a poly(arylene ether ketone) main chain as repeating unit. In the employed step-growth polymerization, a hydroxyaryl-containing crown ether was required. Accordingly, 4,4'(5')-di(hydroxybenzo)-18-crown-6^{43,44} **3** was synthesized (Appendix, Scheme A1). Copolymers were synthesized by polycondensation of 4,4'-difluorobenzophenone with bisphenol A (BPA) and 4,4'(5')-di(hydroxybenzo)-18-crown-6 at 175 °C in NMP (Scheme 1). The molar masses of the polymers were measured by GPC and the results are summarized in Table A1 and Figure A1 (Appendix). The obtained polymers possessed molar masses in the range of $M_n = 16000\text{--}33000$ g/mol and polydispersities ranging from 1.6–2.9. The molar masses reached were sufficiently high to provide these polymers with useful mechanical properties, allowing the fabrication of stable membranes. The polydispersity values measured by GPC are typical of polymers prepared by step growth

polymerization methods. One exception is polymer S(25)-C(75)-PAEK ($M_n = 29000$ g/mol) which has a typical molar mass but a relatively high polydispersity value ($M_w/M_n = 5.9$). This polymer features both crown ether units and sulfonate pendant groups which likely interact and may influence its interactions with the stationary phase of the GPC column.

Scheme 1: Polycondensation procedure for PAEKs bearing crown ether units in their main chain.

NMR studies confirmed the chemical structure of PAEK (Appendix, Figure A2) and C-PAEK (Figure 1 and Appendix Figure A3). The characteristic peak of the methyl groups present in the BPA units of PAEK is clearly visible in the ^1H NMR spectra at $\delta = 1.74$ ppm and in the ^{13}C NMR spectra at $\delta = 31.1$ ppm. Also, the carbonyl carbon of the DFBP units was present in the ^{13}C NMR spectra at $\delta = 194.3$ ppm (Appendix, Figure A2c). Furthermore, the signal associated with the hydroxy groups of BPA is missing in the spectrum of PAEK, confirming successful polymerization.

When 4,4'(5')-di(hydroxybenzo)-18-crown-6 was included in the step growth polymerization, signals of the incorporated crown ether became clearly visible. Peaks O and P (Figure 1), ^1H NMR at $\delta = 4.06\text{--}4.19$ ppm belong to the protons present in the oxyethylene groups of the crown ether, while peaks M and Q in the ^1H NMR spectrum originate from the phenyl rings of the crown ether units (Figure 1). Corresponding peaks in the ^{13}C NMR spectrum are shown in Figure A3 (Appendix).

Figure 1: 400 MHz ^1H NMR spectrum of C-PAEK, recorded in CDCl_3 .

When increasing the crown ether feed ratio in the reaction mixture, the crown ether content in the polymer increased correspondingly (Appendix, Table A1). When introducing SDFBP in the polymerization, the polymer became soluble in DMSO. In the ^1H NMR spectra, measured in $\text{DMSO}-d_6$, new peaks emerged. Most evident is the signal associated with protons located between the sulfonate and carbonyl groups (Appendix, Figure A4a, peak N and Figure A5a, peak B). The signal of these protons is shifted downfield and can be used to calculate the mol percentage of sulfonated monomer introduced in the polymer chain. Combining all monomers, bisphenol A, 4,4'(5')-di(hydroxybenzo)-18-crown-6, DFBP and SDFBP, the NMR spectra became complex. The molar percentages were calculated with the non-overlapping ^1H NMR signals ($\text{DMSO}-d_6$, δ) 3.87+4.10 (16H), 8.33 (2H) and 1.66 (6H) corresponding to protons from the crown ether, the SDFBP and the bisphenol A units (Appendix, Figure A5).

The chemical structure of the synthesized polymers was also confirmed by FTIR. Figure A6 (Appendix) shows the FTIR spectra of PAEK, C(75)-PAEK, S(25)-PAEK and S(25)-C(75)-PAEK. In the spectra, all polymers showed an absorbance at 1650 cm^{-1} , which is related to the carbonyl stretching of $\text{Ar}-\text{C}(=\text{O})-\text{Ar}$ moieties. The typical $\text{C}=\text{C}$ aromatic stretching bands were observed at 1590 cm^{-1} and 1495 cm^{-1} . The crown ether containing polymers showed, next to the characteristic absorption bands of PAEK, also the characteristic $\text{C}-\text{O}-\text{C}$ stretching signals of the crown ether at 1058 and 988 cm^{-1} .⁴⁵ Furthermore, the absorbance values at these frequencies increased with increasing crown ether content in the polymer. This confirms the successful incorporation of dibenzo-18-

crown-6 units into the polymer. Also the stretching vibration absorption of phenyl ether (C=C–O) groups at 1120 cm⁻¹ became stronger. In addition, absorption bands of the aromatic ether (Ar–O–Ar) linkages formed during polycondensation, around 1229 cm⁻¹, were observed for all polymers synthesized. The presence of a characteristic band at 1030 cm⁻¹, assigned to the symmetric stretching vibration of sulfonate groups, confirmed the successful introduction of these moieties in the polymer chains.⁴⁶

Table 1: Thermal properties of PAEKs and C-PAEKs.

Polymer	T _g ^a (°C)	T ₅ ^b (°C)	Char yield ^c (%)
PAEK	162	488	43
C(25)-PAEK	144	430	42
C(50)-PAEK	143	407	42
C(75)-PAEK	143	390	45
S(25)-PAEK	180	454	47
S(25)-C(75)-PAEK	158	285	31

^a Glass transition temperature. ^b Temperature corresponding to 5% weight loss. ^c Residual mass percentage after heating to 900 °C.

Thermal characteristics of the synthesized polymers were determined by TGA and DSC under N₂ atmosphere. The results of thermogravimetric analysis, summarized in Table 1, shows that crown ether incorporation influenced the thermal stability of the polymers. PAEK exhibits a high thermal stability and showed only 5% weight loss at 488 °C, while C(25)-PAEK, C(50)-PAEK, and C(75)-PAEK copolymers began to decompose at 430 °C, 407 °C, and 390 °C, respectively. C-PAEKs display a lower thermal stability due to the fact that the crown ether units are more sensitive to thermal degradation than the thermally stable bisphenol A moieties of PAEK.

TGA curves of the polymers are shown in Figure 2. PAEK exhibited a one-stage degradation profile and the weight loss around 500–600 °C was assigned to intramolecular thermal cleavage of benzophenone units.^{47,48} C(75)-PAEK copolymer also

Figure 2: TGA curves of PAEK, C(75)-PAEK and sulfonated copolymers.

showed one weight loss step with a maximum at 414 °C, indicating that thermal decomposition was mainly due to crown ether degradation.^{41,49} S(25)-PAEK copolymer displayed high thermal stability (5% weight loss at 454 °C), comparable to PAEK. A three-step degradation profile was observed for S(25)-C(75)-PAEK. The first weight loss at around 250 °C, typically assigned to desulfonation processes,⁵⁰ is followed by loss of crown ether units and decomposition of the polymer main chain. The char yield for PAEK and the C-PAEK and sulfonated copolymers remained in the 31–47 % range. The somewhat lower thermal stability of S(25)-C(75)-PAEK compared to the other CPAEKs presented in this work, as expressed by its T_5 temperature corresponding to 5% weight loss (285 °C), cannot be explained by the presence of the crown ether units, nor by the presence of the sulfonic acid pendant groups, but likely results from their combined presence in this PAEK.

The glass transition temperatures (T_g 's) were measured by differential scanning calorimetry (DSC). As shown in Table 1, PAEK has a T_g of 162 °C which is in good agreement with literature values.^{51,52} PAEK has rigid arylene linkages that allow limited segmental motion and consequently this polymer has a relatively high T_g . However, crown ether incorporation in the polymer backbone lowered the T_g by around 20 °C for all compositions synthesized. Similar trends have been observed for crown ether containing polyamides and polyimides.⁵³ This implies that crown ether moieties enhance chain flexibility, which may be attributed to the aliphatic ether bonds present in these macrocycles. In addition, the crown ether units likely increase free volume, which also

contributes to a decrease in T_g . The introduction of sulfonate groups into PAEK and C(75)-PAEK increased the T_g by around 15 °C. Here, intermolecular ion-dipole interactions hinder the chain mobility.⁵⁴ No crystallization or melting peaks were observed in the DSC traces, indicating an amorphous polymer structure.

The amorphous structure of the polymers synthesized was further confirmed by X-ray diffraction measurements. In all cases broad amorphous scattering was observed and crystalline reflections were completely missing.^{55,56}

The solubility of the synthesized polymers in common organic solvents is summarized in Table A2 (Appendix). The solubility of the polymers was tested by dissolving 20 mg of polymer in 1 mL of solvent. PAEK, C(25)-PAEK, and C(50)-PAEK showed a high solubility in polar aprotic solvents, such as NMP, DMF and DMAc, at room temperature. These polymers also dissolved in moderately polar solvents like THF, dichloromethane and chloroform. However, both PAEK and C(25)-PAEK were not soluble in DMSO at room temperature. PAEK, C(25)-PAEK, and C(50)-PAEK exhibited solubility in common organic solvents due to their amorphous structure. In contrast, C(75)-PAEK showed partial solubility in polar aprotic solvents as well as in moderately polar solvents. Although C(75)-PAEK also has an amorphous structure, its increased crown ether content apparently lowers the solubility of this polymer. The solubility change can be explained by stacking of crown ether units in the main chain.^{57,58} The phenyl rings in dibenzo-18-crown-6 may favor π -stacking interactions.^{57,59} The sulfonated PAEK and C-PAEK were only soluble in the aforementioned polar aprotic solvents.

The fabricated membranes were characterized in terms of permselectivity and swelling. Membrane permselectivity is a measure of how well the membrane permits the transport of cationic species while restricting the passage of anionic ones. Membrane permselectivities are listed in Table 2.

Table 2: *S(25)-PAEK and S(25)-C(75)-PAEK membrane properties.*

Membrane	d_{wet} (μm)	Swelling (%)	Permselectivity (%)
S(25)-PAEK	50 ± 3	17 ± 1	82 ± 1
S(25)-C(75)-PAEK	40 ± 5	22 ± 3	77 ± 2

S(25)-PAEK and S(25)-C(75)-PAEK have permselectivities of around 80 %. Membranes with a sulfonation degree of 65 % have permselectivities of around 90 %.⁶⁰ Membranes with low fixed charge densities (low degrees of sulfonation) exhibit low permselectivities, likely due to less effective anion exclusion.⁶¹ S(25)-C(75)-PAEK had a slightly lower permselectivity compared to S(25)-PAEK. The presence of crown ether in the polymer backbone increases the counter-ion (K^+) sorption in the membrane, which may reduce the effective fixed charge density. For this reason, the membrane is probably slightly less able to exclude co-ions (Cl^-).

Water plays a critical role in ion transport within membranes. The measured water content for a S(25)-PAEK membrane was 17 %. Introduction of crown ether units into the SPAEK backbone slightly increased the water content in the membrane due to the hydrophilic ether groups of the crown ether. This also contributes to a decrease in fixed charge density of the membrane.

Donnan dialysis is an ion exchange membrane process, in which a concentration gradient over the membrane is the driving force for the transport of ions from the concentrated side of the membrane to the lower concentration side.⁶² Potassium ion transport properties of S(25)-PAEK and S(25)-C(75)-PAEK membranes were evaluated using a two compartment Donnan dialysis set up with the membrane under investigation positioned between the two compartments. Figure 3a shows the change in K^+ concentration of the feed and receiving side with time for S(25)-PAEK and S(25)-C(75)-PAEK membranes. At the initial stages of the operation, K^+ diffusion in the S(25)-C(75)-PAEK membrane was almost four times lower than that of the native polymer without crown ether (Figure 3b). PVA-based poly(crown ether) showed similar effects for potassium picrate, with a two-fold decrease in permeability due to strong crown ether-cation interactions.⁶³

These results confirmed the potassium selective nature of the dibenzo-18-crown-6 in the synthesized polymer.⁶⁴ For non-porous membranes, diffusion of the ionic species in the membrane is the rate limiting step and transport of ions within the membrane is controlled by the exchange rate of ions. For the S(25)-PAEK membranes, where only sulfonate groups are present and which does not contain crown ether moieties, potassium ion transport is facilitated by a vehicle mechanism from sulfonate group to sulfonate group.⁶⁵

Figure 3: a) Change in K⁺ concentration in the feed and receiving compartments for the membranes at 25 °C and b) K⁺ flux through the membranes in time.

The mobility of the ions depends on the exchange kinetics between H⁺ and K⁺ ions at the sulfonate group, the swelling state of the polymer matrix and the diffusional jump distance between the carrier (sulfonate) groups.⁶⁶ In addition to sulfonate-cation interactions, crown ether-cation complexation also influences the overall potassium ion transport in the S(25)-C(75)-PAEK membrane. In the synthesized crown ether polymers, the relative amount of crown ether in the membrane was kept higher than that of the SO₃⁻ groups, to be able to investigate the contribution of the crown ether moieties to cation transport.

Figure 4: Schematic illustration of potassium ion and S(25)-C(75)-PAEK interactions.

The dialysis results show that the presence of the crown ether units hinders the transport of K⁺ ions by introducing additional interactions (Figure 4), as the crown ether is selective for

K^+ . The crown ether polymer can bind a K^+ ion by sandwiching it between two crown ether units.⁶³ Moreover, dibenzo-18-crown-6 can form a 1:1 crown ether ring-to-cation complex with potassium ion.⁶⁴ Finally, SO_3^- and the crown ether can accommodate the cation together.⁶⁷ These interactions significantly affect the diffusion behavior of potassium ions in the S(25)-C(75)-PAEK membranes, resulting a decrease in the transport of these ions through the membrane.

2.4 Conclusion

A series of novel crown ether containing poly(arylene ether ketone)s (C-PAEK)s and sulfonated C-PAEKs were successfully synthesized with reasonably high molecular weights. For this study, dihydroxy-functionalized crown ethers were employed as monomer. Structural and thermal properties of the synthesized polymers were investigated. DSC and X-ray diffraction analysis confirmed that the polymers are amorphous. Membranes were fabricated from crown ether containing sulfonated PAEKs. In Donnan dialysis, the crown ether containing SPAEK membranes formed complexes with potassium ions which resulted in a lower K^+ diffusion compared to native sulfonated PAEK polymer films.

The idea of incorporating crown ether moieties into the SPAEK backbone could potentially be used for monovalent ion separation. Moreover, this new membrane material could inspire innovations in ion selective electrodes and ion sensors.

Acknowledgement

Sinem Tas would like to acknowledge the Industrial Partnership Program (IPP) "Spectroscopic analysis of particles in water" of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). This IPP is co-financed by Wetsus, Centre of Excellence for Sustainable Water Technology, as part of Wetsus' TTI program. Wetsus is co-funded by the Dutch ministry of economics, agriculture and innovation. Bram Zoetebier acknowledges NanoNextNL, a micro and nanotechnology consortium of the Government of the Netherlands and 130 partners.

We especially thank Dr. Maruti Hedge (TU Delft) and Clemens Padberg (University of Twente) for GPC measurements and fruitful discussions

Appendix

Table A1: Molecular characteristic of PAEK and C-PAEKs.

Polymer	Mn ^a (Dalton)	PDI ^b	Yield ^d (%)	x ^c (%)	y ^d (%)
PAEK	16000	1.6	88	-	-
C(25)-PAEK	18000	1.8	87	-	21
C(50)-PAEK	14000	2.9	88	-	43
C(75)-PAEK	21000	1.8	88	-	66
S(25)-PAEK	33000	2.0	91	21	-
S(25)-C(75)-PAEK	29000	5.9	82	26	68

^a M_n : number average molar mass by GPC, relative to polystyrene standards. ^b PDI: (M_w/M_n), polydispersity index. ^c x corresponds to the incorporated mol% SDFBP by ¹H NMR. ^d y corresponds to the incorporated mol% 18C6 by ¹H NMR.

Table A2: Solubility characteristics of PAEK and C-PAEKs.

Polymer	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	CH ₂ Cl ₂
PAEK	+	+	+	-	+	+	+
C(25)-PAEK	+	+	+	-	+	+	+
C(50)-PAEK	+	+	+	+/-	+	+	+
C(75)-PAEK	+/-	+/-	+/-	+/-	-	+/-	+/-
S(25)-PAEK	+	+	+	+	-	-	-
S(25)-C(75)-PAEK	+/-	+/-	+/-	+	-	-	-

Solubility at room temperature: + fully soluble; +/- partially soluble; - insoluble. Sulfonated polymers are in the sulfonic acid form.

Scheme A1: Synthesis of 4,4'(5')-di(hydroxybenzo)-18-crown-6 (**3**).⁴⁴

Figure A1: GPC traces of a) S(25)-PAEK and S(25)-C(75)-PAEK, b) PAEK and C-PAEKs.

Figure A3: a) Structure and b) ^{13}C NMR spectrum of C(25)-PAEK.

Figure A4: a) ^1H NMR spectrum, b) structure and c) ^{13}C NMR spectrum of SPAEK.

Figure A5: a) Structure and b) ^1H NMR spectrum of SCPAEK.

Figure A6: FTIR spectra of PAEK, C(75)-PAEK and sulfonated copolymers. The central dotted red line indicates the symmetric stretching vibration peak of sulfonate groups at 1030 cm^{-1} .

References

1. Jentsch, T. J.; Hubner, C. A.; Fuhrmann, J. C. Ion channels: Function unravelled by dysfunction. *Nat. Cell Biol.* **2004**, *6* (11), 1039-1047.
2. Fertig, N.; Klau, M.; George, M.; Blick, R. H.; Behrends, J. C. Activity of single ion channel proteins detected with a planar microstructure. *Appl. Phys. Lett.* **2002**, *81* (25), 4865-4867.
3. Hille, B. Ionic channels of excitable membranes. *Sinauer, Verlag* **1992**.
4. Kim, J.; McQuade, D. T.; McHugh, S. K.; Swager, T. M. Ion-specific aggregation in conjugated polymers: Highly sensitive and selective fluorescent ion chemosensors. *Angew. Chem. Int. Ed.* **2000**, *39* (21), 4026-4030..
5. Schuwer, N.; Klok, H. A. A potassium-selective quartz crystal microbalance sensor based on crown-ether functionalized polymer brushes. *Adv. Mater.* **2010**, *22* (30), 3251-3255.
6. Yin, J.; Li, C. H.; Wang, D.; Liu, S. Y. FRET-derived ratiometric fluorescent K⁺ sensors fabricated from thermoresponsive poly(N-isopropylacrylamide) microgels labeled with crown ether moieties. *J. Phys. Chem. B* **2010**, *114* (38), 12213-12220.
7. Marrone, T. J.; Hartsough, D. S.; Merz, K. M. Determination of atomic charges including solvation and conformational effects. *J. Phys. Chem.* **1994**, *98* (4), 1341-1343.
8. Kimura, K.; Sunagawa, T.; Yajima, S.; Miyake, S.; Yokoyama, M. Neutral carrier-type ion sensors based on sol-gel-derived membranes incorporating a bis(crown ether) derivative by covalent bonding. *Anal. Chem.* **1998**, *70* (20), 4309-4313.
9. Zhang, B.; Wang, J.; Yu, Z. Q.; Yang, S.; Shi, A. C.; Chen, E. Q. Novel optical anisotropy of a liquid crystalline "cubic" phase in a discotic crown ether derivative. *J. Mater. Chem. C* **2014**, *2* (26), 5168-5175.
10. Voyer, N.; Robitaille, M. A Novel functional artificial ion-channel. *J. Am. Chem. Soc.* **1995**, *117* (24), 6599-6600.
11. Liu, T.; Bao, C. Y.; Wang, H. Y.; Fei, L. B.; Yang, R. Y.; Long, Y. T.; Zhu, L. Y. Self-assembly of crown ether-based amphiphiles for constructing synthetic ion channels: the relationship between structure and transport activity. *New J. Chem.* **2014**, *38* (8), 3507-3513.
12. Tunca, U.; Yagci, Y. Crown ether-containing polymers. *Prog. Polym. Sci.* **1994**, *19* (2), 233-286.
13. Feigenbaum, W. M.; Michel, R. H. Novel polyamides from macrocyclic ethers. *J. Pol. Sci., Part A: Polym. Chem.* **1971**, *9* (3), 817-820.
14. Rasmussen, J. K.; Smith, H. K. Chemistry of naked persulfate, .3. phase-transfer free-radical reactions - polymerization of acrylic-monomers in organic solution using potassium peroxydisulfate in the presence of quaternary ammonium-salts. *Macromol. Chem. Phys.* **1981**, *182* (2), 701-703.
15. Walba, D. M.; Richards, R. M.; Sherwood, S. P.; Haltiwanger, R. C. A strategy for the synthesis of cylindrical macropolycyclic hosts with hydrophilic interior surfaces - crown ether rings fused by the tetrahydroxymethylethylene (thyme) unit. *J. Am. Chem. Soc.* **1981**, *103* (20), 6213-6215.

16. Akashi, R.; Nagasaki, Y.; Tsuruta, T. Synthesis of monoazacrown ether containing styrene derivatives and monoazacrown ether end-capped 3 or 4-vinyl substituted styrene oligomers and polymers. *Macromol. Chem. Phys.* **1987**, *188* (4), 719-730.
17. Hogen-Esch, T. E.; Smid, J. Evidence for stepwise solvation of strontium carbanion salts in ethereal solvents. *J. Am. Chem. Soc.* **1972**, *94* (26), 9240-9241.
18. Ju, X. J.; Chu, L. Y.; Mi, P.; Song, H.; Lee, Y. M. Synthesis and characterization of a novel thermo-sensitive copolymer of N-isopropylacrylamide and dibenzo-18-crown-6-diacrylamide. *Macromol. Rapid Commun.* **2006**, *27* (24), 2072-2077.
19. Aydogan, A.; Coady, D. J.; Kim, S. K.; Akar, A.; Bielawski, C. W.; Marquez, M.; Sessler, J. L. Poly(methyl methacrylate)s with pendant calixpyrroles and crown ethers: polymeric extractants for potassium halides. *Angew. Chem. Int. Ed.* **2008**, *47* (50), 9648-9652.
20. Zheng, B.; Wang, F.; Dong, S. Y.; Huang, F. H. Supramolecular polymers constructed by crown ether-based molecular recognition. *Chem. Soc. Rev.* **2012**, *41* (5), 1621-1636.
21. Dong, S. Y.; Gao, L. Y.; Chen, J. Z.; Yu, G. C.; Zheng, B.; Huang, F. H. A supramolecular polymer formed by the combination of crown ether-based and charge-transfer molecular recognition. *Polym. Chem.* **2013**, *4* (4), 882-886.
22. Tian, Y. K.; Wang, F. Main-chain supramolecular polymers based on orthogonal benzo-21-crown-7/secondary ammonium salt and terpyridine/metal ion recognition motifs. *Macromol. Rapid Commun.* **2014**, *35* (3), 337-343.
23. Ding, Y.; Wang, P.; Tian, Y. K.; Tian, Y. J.; Wang, F. Formation of stimuli-responsive supramolecular polymeric assemblies via orthogonal metal-ligand and host-guest interactions. *Chem. Commun.* **2013**, *49* (53), 5951-5953..
24. Xia, D.; Xue, M. A supramolecular polymer gel with dual-responsiveness constructed by crown ether based molecular recognition *Polym. Chem.* **2014**, *5*, 5591-5597.
25. Dong, S. Y.; Luo, Y.; Yan, X. Z.; Zheng, B.; Ding, X.; Yu, Y. H.; Ma, Z.; Zhao, Q. L.; Huang, F. H. A dual-responsive supramolecular polymer gel formed by crown ether based molecular recognition. *Angew. Chem. Int. Ed.* **2011**, *50* (8), 1905-1909.
26. Ge, Z. S.; Hu, J. M.; Huang, F. H.; Liu, S. Y. Responsive supramolecular gels constructed by crown ether based molecular recognition. *Angew. Chem. Int. Ed.* **2009**, *48* (10), 1798-1802.
27. Zhang, M. M.; Xu, D. H.; Yan, X. Z.; Chen, J. Z.; Dong, S. Y.; Zheng, B.; Huang, F. H. Self-healing supramolecular gels formed by crown ether based host-guest interactions. *Angew. Chem. Int. Ed.* **2012**, *51* (28), 7011-7015.
28. He, L. P.; Liang, J. J.; Cong, Y.; Chen, X.; Bu, W. F. Concentration and acid-base controllable fluorescence of a metallosupramolecular polymer. *Chem. Commun.* **2014**, *50* (74), 10841-10844.
29. Chen, D.; Zhan, J. Y.; Zhang, M. M.; Zhang, J.; Tao, J. J.; Tang, D. T.; Shen, A. L.; Qiu, H. Y.; Yin, S. C. A fluorescent supramolecular polymer with aggregation induced emission (AIE) properties formed by crown ether-based host-guest interactions. *Polym. Chem.* **2015**, *6* (1), 25-29.

30. Gil, M.; Ji, X. L.; Li, X. F.; Na, H.; Hampsey, J. E.; Lu, Y. F. Direct synthesis of sulfonated aromatic poly(ether ether ketone) proton exchange membranes for fuel cell applications. *J. Membr. Sci.* **2004**, *234* (1-2), 75-81.
31. Shang, X. Y.; Tian, S. H.; Kong, L. H.; Meng, Y. Z. Synthesis and characterization of sulfonated fluorene-containing poly(arylene ether ketone) for proton exchange membrane. *J. Membr. Sci.* **2005**, *266* (1-2), 94-101.
32. Balster, J.; Krupenko, O.; Punt, I.; Stamatialis, D. F.; Wessling, M. Preparation and characterisation of monovalent ion selective cation exchange membranes based on sulphonated poly(ether ether ketone). *J. Membr. Sci.* **2005**, *263* (1-2), 137-145.
33. Tanaka, M.; Fukasawa, K.; Nishino, E.; Yamaguchi, S.; Yamada, K.; Tanaka, H.; Bae, B.; Miyatake, K.; Watanabe, M. Anion conductive block poly(arylene ether)s: synthesis, properties, and application in alkaline fuel cells. *J. Am. Chem. Soc.* **2011**, *133* (27), 10646-10654.
34. Jeon, J. H.; Kang, S. P.; Lee, S.; Oh, I. K. Novel biomimetic actuator based on SPEEK and PVDF. *Sens. Actuators, B: Chem.* **2009**, *143* (1), 357-364.
35. Kricheldorf, H. R.; Nuyken, O.; Swift, G. *Handbook of polymer synthesis*; second edition ed.; Marcel Dekker, New York 2005.
36. Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. Alternative polymer systems for proton exchange membranes (PEMs). *Chem. Rev.* **2004**, *104* (10), 4587-4611.
37. Liu, Z.; Li, X. B.; Shen, K. Z.; Feng, P. J.; Zhang, Y. N.; Xu, X.; Hu, W.; Jiang, Z. H.; Liu, B. J.; Guiver, M. D. Naphthalene-based poly(arylene ether ketone) anion exchange membranes. *J. Mater. Chem. A* **2013**, *1* (21), 6481-6488.
38. Miyake, J.; Watanabe, M.; Miyatake, K. Sulfonated Poly(arylene ether phosphine oxide ketone) block copolymers as oxidatively stable proton conductive membranes. *ACS Appl. Mater. Interfaces* **2013**, *5* (13), 5903-5907.
39. Henneuse, C.; Goret, B.; Marchand-Brynaert, J. Sulfonated poly(arylene ether phosphine oxide ketone) block copolymers as oxidatively stable proton conductive membranes *Polymer* **1998**, *39* (4), 835-844.
40. Dhara, M. G.; Banerjee, S. Fluorinated high-performance polymers: Poly(arylene ether)s and aromatic polyimides containing trifluoromethyl groups. *Prog. Polym. Sci.* **2010**, *35* (8), 1022-1077.
41. Iftime, M.; Ardeleanu, R.; Fifere, N.; Airinei, A.; Cozan, V.; Bruma, M. New copoly(ether sulfone)s containing azobenzene crown-ether and fluorene moieties. *Dyes and Pigments* **2014**, *106*, 111-120.
42. Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J. I.; Yonetake, K.; Masuko, T.; Teramoto, T. Synthesis and characterization of aromatic poly(ether sulfone)s containing pendant sodium-sulfonate groups. *J. Polym. Sci. Pol. Chem.* **1993**, *31* (4), 853-858.
43. Wada, F.; Arata, T.; Goto, T.; Kikukawa, K.; Matsuda, T. New application of crown ethers. iii. synthesis of 4'-hydroxybenzocrown ethers and their bis(benzocrown ether)s linked by poly(oxyethylene) chain. *Bull. Chem. Soc. Jpn.* **1980**, *53* (7), 2061-2063.

45. Diwan, P.; Dollinger, S.; Raetzke, K.; Chandra, A. Conductivity modification in polymer electrolyte-crown ether complexes. *Solid State Ionics* **2013**, *247*, 71-75.
46. Xing, P.; Robertson, G.P.; Guiver, M.D.; Mikhailenko S.D.; Wang K.; Kaliaguine, S. Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes. *J. Membr. Sci.* **2004**, *229* (1-2), 95-106.
47. Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. Direct polymerization of sulfonated poly(arylene ether sulfone) random (statistical) copolymers: candidates for new proton exchange membranes. *J. Membr. Sci.* **2002**, *197* (1-2), 231-242.
48. Montaudo, G.; Puglisi, C.; Samperi, F. Primary thermal-degradation processes of poly(ether ketone) and poly(ether ketone) poly(ether-sulfone) copolymers investigated by direct pyrolysis mass-spectrometry. *Macromol. Chem. Phys.* **1994**, *195* (4), 1241-1256.
49. Gomes, A. S.; Oliveira, C.M.F. Formation of complexes of crown ethers in the absence of solvent observed by differential thermal analysis. *Thermochim. Acta* **1976**, *17* (1), 107-111
50. Harrison, W. L.; Wang, F.; Mecham, J. B.; Bhanu, V. A.; Hill, M.; Kim, Y. S.; McGrath, J. E. Influence of the bisphenol structure on the direct synthesis of sulfonated poly(arylene ether) copolymers. I. *J. Polym. Sci. Part A: Pol. Chem.* **2003**, *41* (14), 2264-2276.
51. Parthiban, A.; LeGuen, A.; Yansheng, Y.; Hoffmann, U.; Klapper, M.; Mullen, K. Amino-functionalized poly(arylene ether ketone)s. *Macromolecules* **1997**, *30* (8), 2238-2243.
52. Goodwin, A. A.; Mercer, F. W.; McKenzie, M. T. Thermal behavior of fluorinated aromatic polyethers and poly(ether ketone)s. *Macromolecules* **1997**, *30* (9), 2767-2774.
53. Maya, E. M.; Lozano, A. E.; de la Campa, J. G.; de Abajo, J. Soluble polyamides and polyimides functionalized with benzo-15-crown-5-pendant groups. *Macromol. Rapid Commun.* **2004**, *25* (4), 592-597.
54. Harrison, W. L.; Hickner, M. A.; Kim, Y. S.; McGrath, J. E. Poly(arylene ether sulfone) copolymers and related systems from disulfonated monomer building blocks: Synthesis, characterization, and performance - A topical review. *Fuel Cells* **2005**, *5* (2), 201-212.
55. Krishnaswamy, R. K.; Kalika, D. S. Glass transition characteristics of poly(aryl ether ketone ketone) and its copolymers. *Polymer* **1996**, *37* (10), 1915-1923.
56. Blundell, D. J. On the interpretation of multiple melting peaks in poly(ether ether ketone). *Polymer* **1987**, *28* (13), 2248-2251.
57. Ganin, E. V.; Basok, S. S.; Yavolovskii, A. A.; Botoshansky, M. M.; Fonari, M. S. From chains to ladders in co-crystals with 2,3-thiophene-15-crown-5, 2,3-naphtho-15-crown-5, and bis-(18-crown-6)-stilbene constructed by weak hydrogen bonding. *CrystEngComm* **2011**, *13* (2), 674-683.
58. Rueda, D. R.; Nogales, A.; Hernandez, J. J.; Garcia-Gutierrez, M. C.; Ezquerro, T. A.; Roth, S. V.; Zolotukhin, M. G.; Serna, R. Stacking of main chain-crown ether polymers in thin films. *Langmuir* **2007**, *23* (25), 12677-12681.
59. Assouma, C. D.; Crochet, A.; Cheremond, Y.; Giese, B.; Fromm, K. M. Kinetics of ion transport through supramolecular channels in single crystals. *Angew. Chem. Int. Ed.* **2013**, *52* (17), 4682-4685.

60. Guler, E.; Elizen, R.; Vermaas, D. A.; Saakes, M.; Nijmeijer, K. Performance-determining membrane properties in reverse electrodialysis. *J. Membr. Sci.* **2013** (1-2), 446, 266-276.
61. Dlugolecki, P.; Nymeyjer, K.; Metz, S.; Wessling, M. Current status of ion exchange membranes for power generation from salinity gradients. *J. Membr. Sci.* **2008**, 319 (1-2), 214-222.
62. Strathmann, H. *Ion-Exchange Membrane Separation Processes*; Elsevier Science 2004.
63. Kimura, K.; Yoshinaga, M.; Kitazawa, S.; Shono, T. Synthesis of poly(vinyl alcohol)-based poly(crown ether)s and permeability of their polymeric membranes. *J. Polym. Sci. Pol. Chem.* **1983**, 21 (9), 2777-2785.
64. Grootenhuys, P. D. J.; Kollman, P. A. Molecular mechanics and dynamics studies of crown ether cation interactions - free-energy calculations on the cation selectivity of dibenzo-18-crown-6 and dibenzo-30-crown-10. *J. Am. Chem. Soc.* **1989**, 111 (6), 2152-2158.
65. Saito, M.; Arimura, N.; Hayamizu, K.; Okada, T. Mechanisms of ion and water transport in perfluorosulfonated ionomer membranes for fuel cells. *J. Phys. Chem. B* **2004**, 108 (41), 16064-16070.
66. Li, Y. F.; Wang, S. F.; He, G. W.; Wu, H.; Pan, F. S.; Jiang, Z. Y. Facilitated transport of small molecules and ions for energy-efficient membranes. *Chem. Soc. Rev.* **2015**, 44 (1), 103-118.
67. Okada, T. Complexation of polyethers in cation exchange resin and application to chromatographic determination of complexation constants in solution. *J. Phys. Chem. B* **1998**, 102 (16), 3053-3059.

Monovalent cation separation with crown ether containing poly(arylene ether ketone)/SPEEK blend membranes

Abstract

Blend membranes of sulfonated poly(ether ether ketone) (SPEEK) and poly(arylene ether ketone) (PAEK) derivatives containing crown ether units in the main chain (CPAEK) were prepared and characterized in terms of water swelling and ion exchange capacity (IEC). The miscibility of the polymers was verified by DSC and HR-SEM. Ion transport characteristics of the membranes were established for the monovalent ions Li^+ and K^+ and the separation of these ions by the cation exchange membranes was investigated. Diffusion experiments for aqueous KCl, LiCl and their mixtures were carried out with pure SPEEK membranes as well as with the CPAEK/SPEEK membranes. Blending significantly decreased the ion permeability due to cation-crown ether complexation and increased the hydrophobicity of the matrix. The K^+ over Li^+ selectivity of the SPEEK membrane was enhanced by blending SPEEK with CPAEK by a factor of nearly 4, indicating that the presence of a crown ether polymer changes the relative mobility of the ions in the membrane.

3.1 Introduction

Cation exchange membranes (CEMs) have been widely used in electrodialysis,^{1,2} fuel cells^{3,4} and diffusion dialysis.^{5,6} CEMs are made from ionic polymers that have negatively charged moieties bound covalently to the polymer backbone. This makes CEMs selectively permeable to positively charged species, yet almost impermeable to anions. Therefore oppositely charged ions can be separated with such membranes. However, the major current challenge in ion exchange membrane development is how to improve the selective transport of a specific ion with a very high degree of specificity.

To date, most of the research on cation exchange membranes has focused on monovalent/divalent ion selectivity improvements (e.g. separation of $\text{Na}^+/\text{Mg}^{2+}$). CEMs with a thin layer of a conducting polymer, such as polypyrrole or polyaniline, were developed for that purpose. The presence of a conducting polymer on the surface of cation exchange membranes decreased the permeation of divalent ions, therefore an improved monovalent over divalent ion selectivity was observed.^{7,8} In recent studies, layer-by-layer deposition of polyelectrolytes onto CEMs was employed to enhance monovalent over divalent ion selectivity.⁹⁻¹¹

Crown ethers, widely used as host molecules, are able to selectively bind specific cationic species due to the ion-dipole interaction of the positively charged metal ion with the negatively polarized oxygen atoms.¹² The host-guest interactions between crown ethers and various guests (e.g. cations) generated interest in the development of various well-defined, crown ether containing polymers. For example, Tunca et al. and Alexandratos et al. have reviewed crown ether polymer synthesis and the functionalization of pre-formed polymers with crown ether moieties.^{13,14} These authors showed that the choice of the polymer matrix for crown ether incorporation greatly influences the complexation ability of crown ethers; for example, it is important to use a hydrophilic polymer matrix to achieve a high degree of ion complexation.¹⁴ Van de Water et al. synthesized a polar azathia crown ether-functionalized poly(glycidyl methacrylate) resin for membrane applications. This hydrophilic resin exhibited selectivity towards Ag^+ ions in the presence of Cu^{2+} , Zn^{2+} and Cd^{2+} ions.¹⁵

Various researchers have prepared self-standing membranes with crown ether polymers.²¹⁻²⁴ For instance, to a polymer consisting of alternating co-monomers of ethylene and maleic

anhydride, crown ethers were attached as side groups. Simultaneous to the attachment of the crown ethers, carboxylic acid groups were formed which enable active ion transport.²⁴ Another example for self-standing membranes with crown ether polymers consists of a polymer that contains pendant crown ether moieties, synthesized by the reaction of poly(vinyl alcohol) (PVA) with formyl derivatives of crown ethers. This polymer was capable of forming mechanically strong films, and had different permeabilities for metal picrates compared with PVA films.²² In addition, Nafion membranes impregnated with crown ethers²⁵⁻²⁷ were also investigated, but a major drawback of crown ether impregnation for these membranes was that the crown ethers leached out under the applied electric potentials.²⁵

Sulfonated poly(ether ether ketone) (SPEEK) has been used as cation exchange membrane material owing to its excellent chemical and mechanical stability.²⁸⁻³⁰ Unfortunately, SPEEK membranes lack specific ion selectivity and the need for specificity has driven efforts aimed at their modification.^{31,32} Polymer blending is a versatile and cost-effective method for creating new functional materials,³³ but obtaining homogenous blends is limited by the degree of miscibility of the polymers.^{32,34-36} Although the use of SPEEK membranes for monovalent-divalent ion separation has been reported,^{31,37} there are only few reports in the literature on the use of ion exchange membranes for the separation of two monovalent ionic species^{25,26}.

We recently reported on the synthesis of a novel main-chain crown-ether-containing poly(arylene ether) ketone (CPAEK) and its sulfonated derivatives applicable for membrane applications.²³ In this chapter, we blended PAEK and CPAEK polymers with a hydrophilic polymer, SPEEK, to prepare hydrophilic thin films. Our aim was to tailor the monovalent ion transport properties of the SPEEK membranes by exploiting the presence of crown ethers in the polymer backbone. Membranes with different blending ratios of PAEK/SPEEK and CPAEK/SPEEK were prepared. The miscibility of these polymers was investigated by DSC and HR-SEM. Single and mixed ion transport properties of the SPEEK and CPAEK/SPEEK membranes for K^+ and Li^+ ions were assessed by diffusion dialysis.

3.2 Experimental

Materials

For poly(arylene ether ketone) (PAEK) and crown ether poly(arylene ether ketone) (CPAEK) synthesis, 4,4'-difluorobenzophenone (DFBP, 99%), bisphenol A (BPA, $\geq 99\%$), 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%), and K_2CO_3 (99.9%) were obtained from Sigma-Aldrich and used as received. Sulfonated poly(ether ether ketone) (SPEEK) with a sulfonation degree of 40% (SD 40) was obtained from FumaTech GmbH. For the diffusion experiments, LiCl (99%) and KCl (99%) were obtained from Sigma-Aldrich and used without further purification. 4,4'(5')-Di(hydroxybenzo)-18-crown-6 was prepared as described in previous work.²³

Blend membrane preparation

The blend membranes were defined as CPAEK/SPEEK (x/y) and PAEK/SPEEK (x/y), where x and y represent the weight percentages of the different polymers. A 20 wt% polymer solution was prepared with the desired ratio of CPAEK and SPEEK (SD 40) or PAEK and SPEEK (SD 40) in NMP. The viscous solution was cast onto a glass plate with a 0.5 mm casting knife. After casting, the solvent was evaporated under a nitrogen atmosphere for 5 days at room temperature, followed by 5 days at 60 °C under a nitrogen atmosphere and 2 days at 110 °C under vacuum (9 mbar).

The membranes were peeled off the glass plate after immersion into water. Prior to diffusion experiments they were converted into their sulfonic acid (H^+) form with 1.0 M HCl; the excess HCl was removed by washing in Milli-Q water.

Blend membrane characterization

The membranes obtained were characterized by DSC, TGA, and HR-SEM. The miscibility of the polymers in the blend was verified by DSC and HR-SEM. The membranes obtained were also characterized in terms of water swelling and ion exchange capacity (IEC). Thermogravimetric analysis (TGA) measurements were carried out with a Perkin Elmer TGA 4000 instrument. Samples of 10 mg were heated under a nitrogen atmosphere at 20 °C min⁻¹ over a 50–900 °C temperature range. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC 8000 (Perkin-Elmer, Waltham, MA, USA). Specimens with a mass of 10 mg were cooled and heated at

a rate of 20 °C min⁻¹ from 30 °C to 220 °C under a nitrogen atmosphere. The T_g of the membranes was determined from the second heating cycle at 20 °C min⁻¹.

The microstructure of the membranes was analyzed with high-resolution scanning electron microscopy (HR-SEM) (Zeiss Merlin, GeminiSEM, Oberkochen, Germany). Sample cross sections were prepared by freezing the films in liquid nitrogen and subsequently breaking them. After drying under vacuum, the samples were coated with gold.

Swelling measurements were performed by immersing the prepared membranes in Milli-Q water for 24 hours to measure the wet weight of the membranes. The wet membranes were subsequently dried at 60 °C for 12 hours. Membrane swelling was calculated using the following equation:

$$\text{Swelling} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\% \quad (1)$$

Here, m_{wet} and m_{dry} are the mass (g) of the wet and the dry membranes, respectively.

A titration method was used to determine the membrane ion exchange capacity (IEC)³⁸. First, the membranes were converted into the sulfonic acid (H⁺) form by stirring the membrane in a 1.0 M HCl solution for at least 15 hours. Subsequently the membranes were converted back into the sodium form by immersing them in a 2.0 M NaCl solution for 3 hours. The released amount of H⁺ in the solution was then determined by titration with 0.1 M NaOH. The IEC (mmol g⁻¹_{dry membrane}) values were calculated with the following equation:

$$\text{IEC} = \frac{V_{\text{NaOH}}}{m_{\text{dry}}} \times C_{\text{NaOH}} \quad (2)$$

Here, V_{NaOH} is the added volume of NaOH solution (mL), m_{dry} is the mass of the dry membrane (g), and C_{NaOH} is the concentration of the NaOH solution (mmol mL⁻¹).

Diffusion dialysis

Diffusion experiments were performed with a glass diffusion cell (70 mL) in which the two compartments were separated by the membrane under investigation, with an effective area of 12 cm². For the single-ion diffusion experiments (Figure 1a), the receiving

chamber contained an aqueous 10 mM HCl solution, while the feed chamber contained aqueous solutions of 10 mM KCl or LiCl. For the mixed-ion diffusion experiments (Figure. 1b), an aqueous solution of 10 mM KCl and 10 mM LiCl was added to the feed chamber, while the receiving chamber contained an aqueous solution of 20 mM HCl.

The two compartments were stirred vigorously throughout the experiments. Every 15 min, a 0.1 mL sample was taken and analyzed. The potassium and lithium ion concentrations were measured with a BWB-XP flame photometer (BWB Technologies, Newbury, UK).

Figure 1: Schematic illustration of the glass diffusion cell for a) single-ion and b) mixed-ion diffusion experiments.

The specific ion flux through the membrane was calculated from the concentration change of the specific ion in the receiving compartment, as follows:

$$J_i = \frac{V}{A} \frac{dc_i}{dt} \quad (3)$$

where V (cm^3) is the volume of the receiving compartment, A (cm^2) is the membrane area and dc_i/dt ($\text{mol cm}^{-3} \cdot \text{s}^{-1}$) is the concentration change in time. Membrane selectivity can be defined as:

$$\text{Selectivity} = \frac{J_i \Delta C_j}{J_j \Delta C_i} \quad (4)$$

where J_i ($\text{cm}^2 \cdot \text{s}^{-1}$) is the flux and ΔC (mol cm^{-3}) is the concentration difference between the feed compartment and the receiving compartment.

3.3 Results and discussion

Polymer blend and membrane characterization

PAEK and CPAEK were synthesized according to a literature procedure.²³ The molecular structures of the polymers are shown in Figure 2. Polymer blend membranes of PAEK/SPEEK and CPAEK/SPEEK were prepared by solution-casting.

Figure 2: Molecular structure of PAEK, CPAEK, and SPEEK polymers used for the preparation of the CPAEK/SPEEK and PAEK/SPEEK blend membranes.

The thermal characteristics of the membranes were determined with DSC and TGA under a nitrogen atmosphere. A detailed understanding of the thermal properties is needed to be able to correlate these properties with the miscibility of the polymers. Thermodynamically, miscible polymer blends can be achieved when the free energy of mixing has a negative value, a condition induced by specific interactions such as hydrogen bonding, dipole-dipole interactions or acid-base interactions between the polymers in the mixture.³⁹⁻⁴¹ DSC is often employed to study the miscibility of the polymers of interest by analyzing the glass transition temperature (T_g) of the blend.⁴⁰ A single T_g , intermediate to the T_g values of the individual components, is often taken as an evidence of polymer/polymer miscibility.⁴¹ However, the glass transition temperature is not an ideal indicator for the thermodynamic miscibility of the polymers. T_g is rather a measure of the state of dispersion.⁴² Moreover, a single T_g indicates that the domain size of the homogenous polymer/polymer dispersion is at least smaller than the proposed resolution limit of DSC for domains.^{39,42,43} Generally, a minimum

detectable domain size for DSC is in the range of 10-50 nm.^{40,43,44} Partially miscible blends exhibit two T_g values, however in such cases, T_g values differ slightly from those of the pure polymers.^{43,45} In case of completely immiscible blends, two T_g values can be observed and they are similar to those of the individual components.⁴³

Table 1 lists the T_g values of the starting materials and the blend membranes prepared in this study. SPEEK exhibits a glass transition temperature around 205 °C, which is in good agreement with literature values.⁴⁶ The pure CPAEK and PAEK polymers show a glass transition temperature of 144 °C and 162 °C, respectively. The CPAEK/SPEEK (40/60) blend exhibits two T_g values. The lower T_g is similar to that of CPAEK. The higher T_g is decreased by 26 °C compared with the T_g of pure SPEEK. For CPAEK/SPEEK (60/40), also two T_g values are observed, although the depression of the higher T_g in this case is about 20 °C.

Table 1: T_g values of the pure and the blend membranes.

	$T_{g,1}$ (°C)	$T_{g,2}$ (°C)
PAEK	162	-
CPAEK	144	-
SPEEK	-	205
CPAEK/SPEEK (40/60)	145	179
CPAEK/SPEEK (60/40)	144	185
PAEK/SPEEK (40/60)	159	202

The shifts in glass transition temperature provide indication for the partial miscibility of CPAEK and SPEEK. In the CPAEK/SPEEK blend systems, the first T_g indicates the presence of a CPAEK phase. The shifts of the second, higher glass transitions towards lower temperatures indicate partial miscibility of CPAEK in the SPEEK rich phase.⁴⁷ The PAEK/SPEEK blend exhibits immiscible characteristics. In this case, the blend clearly demonstrates the two T_g values that correspond to the respective pure components.

Figure 3a shows thermogravimetric curves for SPEEK, CPAEK and PAEK. The first thermal decomposition of SPEEK around 290 °C is associated with the degradation of sulfonic acid groups and the second decomposition stage at 527 °C is related to thermal

degradation of aromatic moieties.^{48,49} PAEK exhibits a one-stage degradation with a maximum weight loss around 550 °C indicating the degradation of aromatics.^{49,50} CPAEK is more sensitive to thermal degradation as compared with PAEK and shows two main degradation steps. The first weight loss step around 400–450 °C is due to the loss of crown ether units from the polymer.^{23,51} This is followed by decomposition of thermally stable aromatic moieties.^{49,50}

Figure 3: TGA curves of a) SPEEK, PAEK, and CPAEK; b) blend membranes.

Figure 3b shows the thermal decomposition behavior of the blend membranes. A three-stage thermal degradation profile was observed for the CPAEK/SPEEK (40/60) membrane. In contrast to the SPEEK membranes, desulfonation started at a slightly higher temperature (310 °C) and occurred over a more narrow temperature range. This was probably caused by an interaction between the crown ether units of the CPAEK and the sulfonic acid groups of SPEEK. When the CPAEK weight ratio in the blend was increased, the CPAEK/SPEEK (60/40) membrane showed no weight loss around 310 °C. Instead, the thermal degradation started at 454 °C, which is possibly associated with the loss of sulfonic acid and crown ether groups. The PAEK/SPEEK (40/60) membrane exhibited a three stage thermal degradation profile. The first weight loss around 250 °C is ascribed to the loss of residual NMP in the membrane that continues with desulfonation and finally with decomposition of the thermally stable aromatic groups.

The microstructure of the blend membranes was investigated using HR-SEM. Photographs of sample cross sections are displayed in Figure 4. In Figure 4a, images of a PAEK/SPEEK (40/60) blend are shown at different magnifications, revealing the presence of micrometer-

Figure 4: HR-SEM of PAEK/SPEEK, SPEEK, and CPAEK/SPEEK (40/60 and 60/40) membranes.

size, droplet-shaped PAEK domains (dotted line), surrounded by SPEEK. For comparison, the morphology of pure SPEEK is displayed in Figure 4b. Clearly, the PAEK/SPEEK (40/60) membrane exhibited macroscopic phase separation. PAEK and SPEEK apparently lack the specific interactions necessary to form miscible blends of these polymers.^{33,52}

In contrast, CPAEK/SPEEK (40/60) and (60/40) membranes did not exhibit any signs of macroscopic phase separation. HR-SEM images of these membranes showed smooth morphologies where micrometer-size, droplet-like features were completely absent (Figure. 4c, 4d).

These results are in agreement with the DSC observations and indicate that favorable intermolecular interactions exist between CPAEK and SPEEK. The SPEEK polymer in the CPAEK/SPEEK membranes was in the sulfonic acid (H^+) form. In an aqueous environment, protonation of water results in formation of hydronium ions (H_3O^+) which can form proton bridges with the six oxygen atoms present in the 18-crown-6 cavity, creating a stable complex.^{53,54} In our case, the ionic groups of SPEEK and the dibenzo-18-crown-6 moieties of CPAEK can interact with H_3O^+ simultaneously, which may favor miscibility of the two polymers (Figure. 5).

In CPAEK/SPEEK systems, the crown ether and the sulfonic acid groups together can accommodate H_3O^+ ions or metal cations. Such ion-dipole interactions are known to play a role in forming compatible blends.⁵⁵ Ion-dipole interactions have also been reported for poly(ethylene oxide)/ polystyrene sulfonate (PEO/PSS) blends in the presence of a lithium salt.³⁶ PEO is able to bind alkali metals just as crown ethers do; the lithium ion is situated in the electron-rich environment of the ethers' oxygen atoms of the PEO chain and also interacts with the ionic groups of PSS.³⁶ Another study showed that disulfonated poly(arylene ether sulfone) and poly(ethylene glycol) (PEG) form compatible blends due to strong ion-dipole interactions between potassium ions located between the sulfonate groups of poly(arylene ether sulfone) and PEG.^{56, 57}

Figure 5: Schematic illustration of ion-dipole interaction between SPEEK and CPAEK polymer chains.

Water swelling, ion exchange capacity and ion transport properties of the blend membranes

Figure 6 shows the water swelling, indicated by blue squares, and the ion exchange capacity (IEC), represented by red dots, of the SPEEK and CPAEK/SPEEK membranes as a function of the CPAEK mass ratio. In agreement with the literature, the SPEEK membranes exhibit 20 wt% swelling in water.^{3,49} CPAEK is a hydrophobic polymer and the CPAEK film shows only 3 wt% swelling in water. Blending SPEEK with CPAEK increases the hydrophobicity of the membranes and the water content of the membranes linearly decreases with increasing CPAEK mass ratio.

Figure 6: Water swelling and IEC of SPEEK and SPEEK/CPAEK membranes.

The IEC of the blend membranes decreases with increasing CPAEK content. As the ionic groups (sulfonate groups) become increasingly surrounded by hydrophobic domains, relatively less sulfonate groups are available for ion exchange.³²

The Li^+ and K^+ transport properties of the SPEEK and CPAEK/SPEEK blend membranes were evaluated with a Donnan dialysis setup, with the membrane under investigation positioned between the feed compartment and the receiving compartment. The ion concentration difference between the feed compartment and the receiving compartment causes a transport of potassium (or lithium) ions from the feed side to the receiving side. Table 2 shows the Li^+ and K^+ fluxes at the initial stage of the operation for the single-ion and mixed-ion diffusion experiments.

Table 2: Ion fluxes of the membranes for single-ion and mixed-ion diffusion.

Membrane	$J_{\text{Li}^+, \text{single 15min}}$ ($\text{mol cm}^{-2} \text{s}^{-1}$) 10^{10}	$J_{\text{K}^+, \text{single 15min}}$ ($\text{mol cm}^{-2} \text{s}^{-1}$) 10^{10}	$J_{\text{Li}^+, \text{mixed 15min}}$ ($\text{mol cm}^{-2} \text{s}^{-1}$) 10^{10}	$J_{\text{K}^+, \text{mixed 15min}}$ ($\text{mol cm}^{-2} \text{s}^{-1}$) 10^{10}
SPEEK	47 ± 5	113 ± 8	24 ± 4	65.8 ± 1.0
CPAEK/SPEEK(40/60)	7.8 ± 1	31 ± 13	2.7 ± 0.5	37.6 ± 0.1
CPAEK/SPEEK(60/40)	5.1 ± 0.4	7.1 ± 1	~ 0	3.9 ± 0.1

The Li^+ ion has a larger hydrated radius (0.34 nm) than the K^+ ion (0.23 nm).^{58,59} The mobility of Li^+ ions in Nafion membranes is greater than that of K^+ ions.^{60,61} However, for single ion diffusion, SPEEK and blend membranes exhibit lower ion fluxes for Li^+ ions than for K^+ ions.

As a general trend, it is observed that blending CPAEK with SPEEK reduces the ion flux of both ions, compared with pure SPEEK membranes. This is partially caused by the dependence of the ion flux on the membrane water content, since ion mobility is closely related to the extent of water swelling of the matrix and diffusion rate of water molecules in the membrane.⁶² The water molecules facilitate the transport of cationic species (K^+ and Li^+) from one sulfonate group to the next.⁶³ Increasing the CPAEK content in the membrane significantly reduces the water uptake of the membranes; therefore ion fluxes decrease.

Another reason for the reduced ion flux is the cation complexation by the crown ether moieties in the CPAEK polymer backbone. In previous research, we reported that the K^+ flux for sulfonated poly(arylene ether ketone) (SPAEEK) membranes is almost 4 times higher than for SPAEEK membranes with crown ether moieties incorporated in the main chain.²³ Kimura et al. obtained similar results for PVA-based poly(crown ether)s, which were ascribed to the strong interactions between crown ethers and cations.²² Bhattacharyya et al. investigated the mobility of alkali metal ions in dibenzo-18-crown-6-loaded Nafion-117 membranes. In these membranes, the mobility of Li^+ and Cs^+ ions was found to be extremely low relative to their mobility in pure Nafion-117 membranes.²⁶ These results indicate that the cation complexing ability of crown ethers changes the mobility of these ions in the membranes.

Dibenzo-18-crown-6 can selectively bind K^+ ions,^{64,65} therefore increasing the CPAEK content influences the K^+ ion flux more significantly than the Li^+ ion flux. For the CPAEK/SPEEK (60/40) membrane, the K^+ ion flux decreased 16 times compared to that of the pure SPEEK membranes, against only 9 times for Li^+ ions. Therefore, single ion diffusion experiments confirm the potassium selective nature of the CPAEK polymer.

Ion fluxes in mixed-ion experiments with Li^+ and K^+ ions are lower than in the single-ion transport experiments. This may be related to a competition between Li^+ and K^+ ions for the available ion exchange sites (SO_3^- groups) in the membrane.^{60,66} Since ion fluxes are related to the gradient of fractional occupancy of the SO_3^- sites by a specific ion, one can speculate that in the competition between Li^+ and K^+ ions for the available ion exchange sites, the increased hydrophobicity of the membrane and the crown ether-ion complexation⁶⁶ lead to lower ion fluxes.

Figure 7 shows the K^+/Li^+ selectivity change in time for the single-ion and mixed-ion diffusion experiments. For single-ion diffusion, SPEEK and CPAEK/SPEEK membranes show almost similar selectivities. The SPEEK membrane exhibits the same K^+/Li^+ selectivity in the mixed-ion experiment as in the single-ion experiment.

Figure 7: Membrane potassium over lithium ion selectivity change in time during single-ion diffusion and mixed-ion diffusion.

In the mixed-ion experiment, the K^+/Li^+ selectivity of the CPAEK/SPEEK (40/60) membrane is 3.8 times greater than for SPEEK membranes in the initial stage of the diffusion. The CPAEK/SPEEK (60/40) membrane is only permeable to K^+ ions during the first 15 minutes of the operation. As mentioned before, Li^+ and K^+ ions compete for the available SO_3^- sites in the SPEEK membrane.⁶⁷ This applies to CPAEK/SPEEK membranes as well, but in this case, transport is also affected by complex formation between Li^+ and K^+ ions and dibenzo-18-crown-6. These interactions combined determine the selectivity of the membranes.

The blend membranes only show the higher selectivity in the initial stage of operation. This can be most probably explained by the decreasing availability of crown ether sites for complex formation with the ions during Donnan dialysis, diminishing the complexation rate due to the lack of available crown ether binding sites at longer operation times. The CPAEK/SPEEK membrane's selectivity decreases to values comparable to those of the pure SPEEK membrane from 45 minutes on. The results of the mixed-ion experiments suggest that not only the presence of crown ether moieties in the membrane matrix, but also the increased hydrophobicity of the membrane, influences the relative mobility of K^+ and Li^+ ions in the initial stage of the operation. Overall, the CPAEK/SPEEK blend membranes have demonstrated their utility in the separation of monovalent ions. Regeneration of these mechanically robust membranes by acid treatment allows one to restore their selectivity, which implies that their arrangement in series could lead to an effective, continuous ion separation process.

3.4 Conclusions

This study explored the selective permeability of crown-ether-containing PAEK blend membranes for monovalent ions (K^+/Li^+). CPAEK/SPEEK and PAEK/SPEEK membranes were prepared by solution blending the two polymers of interest in different weight ratios, and their morphology and thermal characteristics were investigated. Membranes made from PAEK and SPEEK exhibited macroscopic phase separation, as was established by DSC and HR-SEM. CPAEK and SPEEK, however, were found to be partially miscible. The IEC and water content of the membranes decreased with increasing CPAEK content in the membrane. Single and mixed ion transport characteristics of SPEEK and CPAEK/SPEEK membranes for K^+ and Li^+ ions were assessed by Donnan dialysis. The presence of the hydrophobic crown ether polymer in the matrix resulted in a lower ion transport for both single and mixed ion diffusion cases. However, in the initial stage of mixed-ion diffusion experiments, CPAEK/SPEEK membranes exhibited selectivity towards K^+ ions over Li^+ ions.

Acknowledgments

Sinem Tas acknowledges the Industrial Partnership Program (IPP) "Spectroscopic analysis of particles in water" of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). This IPP is co-financed by Wetsus, Centre of Excellence for Sustainable Water Technology, as part of Wetsus' TTI program. Wetsus is co-funded by the Dutch ministry of economics, agriculture, and innovation. Bram Zoetebier acknowledges NanoNextNL, a micro and nanotechnology consortium of the government of the Netherlands and 130 partners. We especially thank Mark Smithers for HR-SEM analysis.

References

1. Dlugolecki, P.; Anet, B.; Metz, S. J.; Nijmeijer, K.; Wessling, M. Transport limitations in ion exchange membranes at low salt concentrations. *J Membr Sci* **2010**, *346* (1), 163-171.
2. Krol, J. J.; Wessling, M.; Strathmann, H. Concentration polarization with monopolar ion exchange membranes: current-voltage curves and water dissociation. *J Membr Sci* **1999**, *162* (1-2), 145-154.
3. Gil, M.; Ji, X. L.; Li, X. F.; Na, H.; Hampsey, J. E.; Lu, Y. F. Direct synthesis of sulfonated aromatic poly(ether ether ketone) proton exchange membranes for fuel cell applications. *J Membr Sci* **2004**, *234* (1-2), 75-81.
4. Wang, C.; Shin, D. W.; Lee, S. Y.; Kang, N. R.; Robertson, G. P.; Lee, Y. M.; Guiver, M. D. A clustered sulfonated poly(ether sulfone) based on a new fluorene-based bisphenol monomer. *J Mater Chem* **2012**, *22* (48), 25093-25101.
5. Miyoshi, H. Diffusion coefficients of ions through ion-exchange membranes for Donnan dialysis using ions of the same valence. *Chem Eng Sci* **1997**, *52* (7), 1087-1096.
6. Agarwal, C.; Mhatre, A.; Goswami, A. Transport studies of divalent ions through nafion-117 ion exchange membrane in the presence of polyacrylate. *Ind Eng Chem Res* **2015**, *54* (13), 3445-3450.
7. Sata, T.; Funakoshi, T.; Akai, K. Preparation and transport properties of composite membranes composed of cation exchange membranes and polypyrrole. *Macromolecules* **1996**, *29* (11), 4029-4035.
8. Sata, T.; Ishii, Y.; Kawamura, K.; Matsusaki, K. Composite membranes prepared from cation exchange membranes and polyaniline and their transport properties in electrodialysis. *J Electrochem Soc* **1999**, *146* (2), 585-591.
9. White, N.; Misovich, M.; Yaroshchuk, A.; Bruening, M. L. Coating of nafion membranes with polyelectrolyte multilayers to achieve high monovalent/divalent cation electrodialysis selectivities. *ACS Appl Mater Inter* **2015**, *7* (12), 6620-6628.
10. Abdu, S.; Marti-Caatayud, M. C.; Wong, J. E.; Garcia-Gabaldon, M.; Wessling, M. layer-by-layer modification of cation exchange membranes controls ion selectivity and water splitting. *ACS Appl Mater Inter* **2014**, *6* (3), 1843-1854.
11. Deng, H. N.; Wang, Z. X.; Zhang, W.; Hu, B. S.; Zhang, S. F. preparation and monovalent selective properties of multilayer polyelectrolyte modified cation-exchange membranes. *J Appl Polym Sci* **2015**, *132* (8), 41488-41495.
12. Marrone, T. J.; Hartsough, D. S.; Merz, K. M. Determination of atomic charges including solvation and conformational effects. *J Phys Chem-Us* **1994**, *98* (4), 1341-1343.
13. Tunca, U.; Yagci, Y. Crown ether-containing polymers. *Prog Polym Sci* **1994**, *19* (2), 233-286.
14. Alexandratos, S. D.; Stine, C. L. Synthesis of ion-selective polymer-supported crown ethers: a review. *React Funct Polym* **2004**, *60*, 3-16.
15. Van de Water, L. G. A.; ten Hoonte, F.; Driessen, W. L.; Reedijk, J.; Sherrington, D. C. Selective extraction of metal ions by azathiacycrown ether-modified polar polymers. *Inorg Chim Acta* **2000**, *303* (1), 77-85.

16. Roman, M. F. S.; Bringas, E.; Ibanez, R.; Ortiz, I. Liquid membrane technology: fundamentals and review of its applications. *J Chem Technol Biot* **2010**, *85* (1), 2-10.
17. Behr, J. P.; Kirch, M.; Lehn, J. M. Carrier-mediated transport through bulk liquid membranes - dependence of transport rates and selectivity on carrier properties in a diffusion-limited process. *J Am Chem Soc* **1985**, *107* (1), 241-246.
18. Wong, K. H.; Yagi, K.; Smid, J. Ion-transport through liquid membranes facilitated by crown ethers and their polymers. *J Membr Biol* **1974**, *18* (3-4), 379-397.
19. Stolwijk, T. B.; Sudholter, E. J. R.; Reinhoudt, D. N. Crown-ether mediated transport - a kinetic-study of potassium perchlorate transport through a supported liquid membrane containing dibenzo-18-crown-6. *J Am Chem Soc* **1987**, *109* (23), 7042-7047.
20. Skelland, A. H. P.; Meng, X. Q. A new solution to emulsion liquid membrane problems by non-Newtonian conversion. *Aiche J* **1996**, *42* (2), 547-561.
21. Thunhorst, K. L.; Noble, R. D.; Bowman, C. N. Properties of the transport of alkali metal salts through polymeric membranes containing benzo-18-crown-6 crown ether functional groups. *J Membr Sci* **1999**, *156* (2), 293-302.
22. Kimura, K.; Yoshinaga, M.; Kitazawa, S.; Shono, T. Synthesis of poly(vinyl alcohol)-based poly(crown ether)s and permeability of their polymeric membranes. *J Polym Sci Pol Chem* **1983**, *21* (9), 2777-2785.
23. Zoetebier B., Tas. S., Vancso G. J., Nijmeijer K., Hempenius M. A. Synthesis of poly(arylene ether ketone)s bearing skeletal crown ether units for cation exchange membranes. *J. Polym. Sci. A Polym. Chem.* **2015**, *53* (23), 2786-2793.
24. Kimura, K.; Sakamoto, H.; Yoshinaga, M.; Shono, T. Membranes of Novel Crown Ether Polymers for Proton-Driven Cation-Transport. *J Chem Soc Chem Comm* **1983**, *24* (17), 978-979.
25. Chaudhury, S.; Bhattacharyya, A.; Goswami, A. Electrodriven ion transport through crown ether-Nafion composite membrane: enhanced selectivity of Cs⁺ over Na⁺ by ion gating at the surface. *Ind Eng Chem Res* **2014**, *53* (21), 8804-8809.
26. Bhattacharyya, A.; Goswami, A. effect of cation driven loading of dibenzo-18-crown-6 in nafion-117 membrane on the diffusion and transport behavior of alkali metal ions. *J Phys Chem B* **2009**, *113* (39), 12958-12963.
27. Hayashita, T.; Lee, J. C.; Bartsch, R. A. Transport of alkali metal cations through monoazacrown ether-modified Nafion(TM) 117 membrane. *J Membr Sci* **1996**, *116* (2), 243-251.
28. Reyna-Valencia, A.; Kaliaguine, S.; Bousmina, M. Tensile mechanical properties of sulfonated poly(ether ether ketone) (SPEEK) and BPO₄/SPEEK membranes. *J Appl Polym Sci* **2005**, *98* (6), 2380-2393.
29. Dang, H. S.; Kim, D. Cross-linked poly(arylene ether ketone) membranes sulfonated on both backbone and pendant position for high proton conduction and low water uptake. *J Power Sources* **2013**, *222*, 103-111.
30. Zhang, Y.; Zhang, G.; Wan, Y.; Zhao, C. J.; Shao, K.; Li, H. T.; Han, M. M.; Zhu, J.; Xu, S. A.; Liu, Z. G.; Na, H. synthesis and characterization of poly(arylene ether ketone)s

bearing pendant sulfonic acid groups for proton exchange membrane materials. *J Polym Sci Pol Chem* **2010**, *48* (24), 5824-5832.

31. Balster, J.; Krupenko, O.; Punt, I.; Stamatialis, D. F.; Wessling, M. Preparation and characterisation of monovalent ion selective cation exchange membranes based on sulphonated poly(ether ether ketone). *J Membr Sci* **2005**, *263* (1-2), 137-145.
32. Wilhelm, F. G.; Punt, I. G. M.; van der Vegt, N. F. A.; Strathmann, H.; Wessling, M. Cation permeable membranes from blends of sulfonated poly(ether ether ketone) and poly(ether sulfone). *J Membr Sci* **2002**, *199* (1-2), 167-176.
33. Kerres, J. Blend concepts for fuel cell membranes; Springer, 2009, 185-221.
34. Sabzi, F.; Boushehri, A. Compatibility of polymer blends. I. Copolymers with organic solvents. *J Appl Polym Sci* **2006**, *101* (1), 492-498.
35. Nandan, B.; Kandpal, L. D.; Mathur, G. N. Glass transition behaviour of poly(ether ether ketone)/poly(aryl ether sulphone) blends: dynamic mechanical and dielectric relaxation studies. *Polymer* **2003**, *44* (4), 1267-1279.
36. Eisenberg, A.; Hara, M. A Review of miscibility enhancement via ion-dipole interactions. *Polym Eng Sci* **1984**, *24* (17), 1306-1311.
37. Gohil, G. S.; Nagarale, R. K.; Binsu, V. V.; Shahi, V. K. Preparation and characterization of monovalent cation selective sulfonated poly(ether ether ketone) and poly(ether sulfone) composite membranes. *J Colloid Interf Sci* **2006**, *298* (2), 845-853.
38. Heiner S., Preparation and characterization of ion exchange membranes, Elsevier, 2004, 89-146.
39. Gedde, W. U. Polymer Physics; Springer-Science Business Media, 1999 70-73.
40. Kulshreshtha A.K., Handbook of Polymer Blends and Composites Volume 3. Smithers Rapra Technology, 2002, 1-13.
41. Lu, X.; Weiss, R. A. Relationship between the Glass-Transition Temperature and the Interaction Parameter of Miscible Binary Polymer Blends. *Macromolecules* **1992**, *25* (12), 3242-3246.
42. Utracki, L. A. Glass transition temperature in polymer blends. *Adv Polym Tech* **1985**, *5* (1), 33-39.
43. Newman, A.; Engers, D.; Bates, S.; Ivanisevic, I.; Kelly, R. C.; Zograf, G. characterization of amorphous API:Polymer mixtures using x-ray powder diffraction. *J Pharm Sci* **2008**, *97* (11), 4840-4856.
44. Van Eerdenbrugh, B.; Lo, M.; Kjoller, K.; Marcott, C.; Taylor, L. S. Nanoscale mid-infrared evaluation of the miscibility behavior of blends of dextran or maltodextrin with poly(vinylpyrrolidone). *Mol Pharmaceut* **2012**, *9* (5), 1459-1469.
45. Bikiaris, D.; Prinos, J.; Botev, M.; Betchev, C.; Panayiotou, C. Blends of polymers with similar glass transition temperatures: A DMTA and DSC study. *J Appl Polym Sci* **2004**, *93* (2), 726-735.
46. Zaidi, S. M. J.; Mikhailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. Proton conducting composite membranes from polyether ether ketone and heteropolyacids for fuel cell applications. *J Membr Sci* **2000**, *173* (1), 17-34.

47. Marin, N.; Favis, B. D. Co-continuous morphology development in partially miscible PMMA/PC blends. *Polymer* **2002**, *43* (17), 4723-4731.
48. Harrison, W. L.; Wang, F.; Mecham, J. B.; Bhanu, V. A.; Hill, M.; Kim, Y. S.; McGrath, J. E. Influence of the bisphenol structure on the direct synthesis of sulfonated poly(arylene ether) copolymers. I. *J Polym Sci Pol Chem* **2003**, *41* (14), 2264-2276.
49. Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. Direct polymerization of sulfonated poly(arylene ether sulfone) random (statistical) copolymers: candidates for new proton exchange membranes. *J Membr Sci* **2002**, *197* (1-2), 231-242.
50. Montaudo, G.; Puglisi, C.; Samperi, F. Primary Thermal-degradation processes of poly(ether ketone) and poly(ether ketone) poly(ether-sulfone) copolymers investigated by direct pyrolysis mass-spectrometry. *Macromol Chem Phys* **1994**, *195* (4), 1241-1256.
51. Maya, E. M.; Lozano, A. E.; de la Campa, J. G.; de Abajo, J. Soluble polyamides and polyimides functionalized with benzo-15-crown-5-pendant groups. *Macromol Rapid Comm* **2004**, *25* (4), 592-597.
52. Zhang, W.; Tang, C. M.; Kerres, J. Development and characterization of sulfonated-unmodified and sulfonated-aminated PSU Udel (R) blend membranes. *Sep Purif Technol* **2001**, *22-3* (1-3), 209-221.
53. Buhl, M.; Ludwig, R.; Schurhammer, R.; Wipff, G. Hydronium ion complex of 18-crown-6: Theory confirms three "normal" linear hydrogen bonds. *J Phys Chem A* **2004**, *108* (51), 11463-11468.
54. Hurtado, P.; Gamez, F.; Hamad, S.; Martinez-Haya, B.; Steill, J. D.; Oomens, J. Crown ether complexes with H_3O^+ and NH_4^+ : proton localization and proton bridge formation. *J Phys Chem A* **2011**, *115* (25), 7275-7282.
55. Okada, T. Complexation of polyethers in cation exchange resin and application to chromatographic determination of complexation constants in solution. *J Phys Chem B* **1998**, *102* (16), 3053-3059.
56. Lee, C. H.; VanHouten, D.; Lane, O.; McGrath, J. E.; Hou, J. B.; Madsen, L. A.; Spano, J.; Wi, S.; Cook, J.; Xie, W.; Oh, H. J.; Geise, G. M.; Freeman, B. D. Disulfonated poly(arylene ether sulfone) random copolymer blends tuned for rapid water permeation via cation complexation with poly(ethylene glycol) oligomers. *Chem Mater* **2011**, *23* (4), 1039-1049.
57. Lee, C. H.; Spano, J.; McGrath, J. E.; Cook, J.; Freeman, B. D.; Wi, S. Solid-state NMR molecular dynamics characterization of a highly chlorine-resistant disulfonated poly(arylene ether sulfone) random copolymer blended with poly(ethylene glycol) oligomers for reverse osmosis applications. *J Phys Chem B* **2011**, *115* (21), 6876-6884.
58. Marcus, Y. A Simple Empirical-Model Describing the Thermodynamics of hydration of ions of widely varying charges, sizes, and shapes. *Biophys Chem* **1994**, *51* (2-3), 111-127.
59. Izquierdo-Gil, M. A.; Barragan, V. M.; Villaluenga, J. P. G.; Godino, M. P. Water uptake and salt transport through Nafion cation-exchange membranes with different thicknesses. *Chem Eng Sci* **2012**, *72*, 1-9.
60. Stenina, I. A.; Sistat, P.; Rebrov, A. I.; Pourcelly, G.; Yaroslavl'tsev, A. B. Ion mobility in Nafion-117 membranes. *Desalination* **2004**, *170* (1), 49-57.

61. Okada, T. Satou.; Sistat, H.; Okuno, M. Yuasa, M, Ion and water transport characteristics of perfluorosulfonated ionomer membranes with H⁺ and alkali metal cations *J.Phys Chem B* **2002**, *106* (6), 1267-1273
62. Yeager, H. L.; Steck, A. Cation and water diffusion in nafion ion-exchange membranes - influence of polymer structure. *J Electrochem Soc* **1981**, *128* (9), 1880-1884.
63. Saito, M.; Arimura, N.; Hayamizu, K.; Okada, T. Mechanisms of ion and water transport in perfluorosulfonated ionomer membranes for fuel cells. *J Phys Chem B* **2004**, *108* (41), 16064-16070.
64. Grootenhuys, P. D. J.; Kollman, P. A. Molecular mechanics and dynamics studies of crown ether cation interactions-free-energy calculations on the cation selectivity of dibenzo-18-crown-6 and dibenzo-30-crown-10. *J Am Chem Soc* **1989**, *111* (6), 2152-2158.
65. Nakajima, M.; Kimura, K.; Shono, T. Ion-chromatographic behavior of silica-gels modified by poly(crown ether)s and bis(crown ether)s of benzo-18-crown-6. *B Chem Soc Jpn* **1983**, *56* (10), 3052-3056.
66. Sodaye, S.; Agarwal, C.; Goswami, A. Study on multicomponent diffusion of ions in poly (perfluorosulfonated) ion-exchange membrane using radiotracers. *J Membr Sci* **2008**, *314* (1-2), 221-225.
67. Li, Y. F.; Wang, S. F.; He, G. W.; Wu, H.; Pan, F. S.; Jiang, Z. Y. Facilitated transport of small molecules and ions for energy-efficient membranes. *Chem Soc Rev* **2015**, *44* (1), 103-118.

PAN/crown ether composite nanofibers for the selective adsorption of cations

Abstract

In this chapter, we prepared electrospun polyacrylonitrile (PAN) nanofibers functionalized with dibenzo-18-crown-6 (DB18C6) crown ether and showed the potential of these fibers for the selective recovery of K^+ from other both mono- and divalent ions in aqueous solutions. The nanofibers were formed using 8 wt% PAN/dimethylformamide (DMF) polymer solutions with varying crown ether amount. Nanofibers were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and thermal gravimetric analysis (TGA). SEM results showed that the crown ether addition resulted in thicker nanofibers and higher mean fiber diameters, in a range of 138 to 270 nm. Batch adsorption experiments were conducted in order to evaluate the potential of the crown ether modified nanofibers as an adsorbent for ion removal. The maximum adsorption capacity of the crown ether modified nanofibers for K^+ was 0.37 mmol g^{-1} and the nanofibers followed the selectivity sequence of $K^+ > Ba^{2+} > Na^+ \sim Li^+$ for single ion experiments. Adsorption of Ba^{2+} ions onto crown ether-modified nanofiber was examined by X-ray photoelectron spectroscopy (XPS) and the results confirmed the adsorption of the ion. Mixed ion adsorption experiments revealed competitive adsorption between K^+ and Ba^{2+} ions for the available binding sites. This effect was not observed for the other monovalent ions present in the solution and exceptionally high selectivities for K^+ over Li^+ and Na^+ were obtained. This makes the developed fibers good candidates for the selective recovery of K^+ from an aqueous mixture with also Li^+ and Na^+ present in the solution. Also the crown ether modified nanofibers exhibited good regeneration properties and a good reusability over multiple consecutive adsorption-desorption cycles. Electrospinning thus shows to be a very versatile tool to prepare crown ether functional polymer adsorbents for the selective recovery of ions.

4.1 Introduction

Electrospinning is a versatile and powerful technique for nanofiber formation from a wide variety of polymers such as water soluble polymers, biopolymers and liquid crystalline polymers.¹⁻⁴ In this technique, electrical forces are applied to produce polymer fibers with diameters ranging from a few nanometers to several micrometers.⁵ Electrospun nanofibers feature a high surface area-to-volume, high porosity and flexibility for chemical/physical functionalization.^{1,5} Moreover, consistent production of nanofibers allows their application in various filtration applications⁶⁻⁸ as fuel cell membranes^{9,10}, for drug delivery¹¹ and as protective textiles.^{12,13}

The high surface area to volume ratio, porosity, and mechanical integrity of electrospun fibrous materials make them attractive alternatives to conventional adsorbents. A potentially attractive functionalization to increase the selectivity of the nanofibers includes their macrocycle functionalization. A macrocycle is a cyclic macromolecule or a macromolecular cyclic portion of a molecule. Such macrocycle functionalized fibers can serve as an adsorbent in water treatment owing to the selective binding ability of macrocycles with specific ions or organic molecules. Therefore, significant work on this topic has been performed and many researchers particularly focused on nanofiber modification with calixarenes and cyclodextrin. For example, nanofibers functionalized with calixarenes and cyclodextrins allow the removal of organic contaminants (e.g. Congo red, phenanthrene) from water.¹⁴⁻¹⁶ Another possible application of calixarene modified nanofibers is the selective adsorption of ions such as La^{3+} and $\text{Cr}_2\text{O}_7^{2-}$ ions onto the nanofibers.^{17,18} Electrospun PAN nanofibers modified with *p*-sulfonatocalix[8]arene showed a maximum adsorption capacity of 155.1 mg g⁻¹ and a selectivity for La^{3+} ion in the presence of Fe^{3+} , Al^{3+} , Cu^{2+} , Ca^{2+} , Mg^{2+} and K^{+} ions.¹⁷

Following this line of reasoning, also electrospun nanofibers coupled with crown ethers could in principle also provide efficient platforms for selective metal ion removal. Crown ethers are well-known host molecules and have attracted increasing interest owing to their ability to form stable complexes with metal ions.¹⁹ Crown ethers possess negatively polarized oxygen atoms with variable cavity size. Therefore they can selectively bind various ions.²⁰ This led to the design and synthesis of new crown ethers and various well-defined crown ether polymers.^{21,22} Owing to their high selectivities, considerable research interest

has been devoted to the design of crown ether adsorbents as well. Duman et al. modified activated carbon cloth with mono and dibenzo derivatives of crown ethers. They investigated the adsorption behavior of Cr^{3+} , Co^{2+} and Ni^{2+} ions onto crown ether modified activated carbon cloth. In this case, activated carbon cloth modified with benzo-18 crown-6 exhibited the highest adsorption capacity of 0.22 mmol g⁻¹ for the Co^{3+} ion.²³ Eliseo et al. prepared crown ether immobilized carbon nanotubes as adsorbent for Li^+ ions.²⁴ The dibenzo-14-crown-4 modified carbon nanotube adsorbent showed a preference for cation uptake and followed the sequence of $\text{Li}^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} \sim \text{K}^+ \sim \text{Sr}^{2+}$. Jie et. al. synthesized a crown ether incorporated thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel. This hydrogel exhibits Pb^{2+} ion recognition and adsorption characteristics. The Pb^{2+} adsorption capacity of the hydrogel decreased from 142 mg g⁻¹ to 112 mg g⁻¹ when the temperature increased from 23 °C to 50 °C.²⁵ Crown ether incorporated ion-imprinted polymers were synthesized by many researchers as well. Those adsorbents have promising prospects in the selective recovery of Li^+ , K^+ and Pb^{2+} ions.²⁶⁻²⁸

In this chapter, we use the high selectivity of crown ethers towards specific ions and the versatility for functionalization and the high surface area to volume ratio of electrospun nanofibers. To the best our knowledge, for the first time, we introduce the concept of crown ether/polyacrylonitrile (PAN) nanofibers for the selective binding of monovalent ions from aqueous solutions. PAN was chosen as polymer for the electrospinning process because of two reasons. Firstly, PAN membranes have been widely used in aqueous filtration applications.^{29,30} Secondly, PAN is a well-known carbon fiber precursor due its easy conversion into carbon fibers, its high carbon yields and its cost effective processing.^{31,32} In this regard, we prepared PAN nanofiber mats with different loading ratios of crown ether. We investigated the effect of crown ether loading and contact time on the adsorption capacity of functionalized nanofiber mats for both single and mixed ion solutions of Li^+ , K^+ , Na^+ and Ba^{2+} ions. We believe that the introduction of crown ethers enhances the operating window of electrospun nanofibers and will introduce specific ion selectivity, making them promising and more effective for adsorption and filtration applications.

4.2 Experimental

Materials

Dibenzo-18-crown-6 (DB18C6) (98%), polyacrylonitrile (PAN, 99% Mw 150 000) and *N,N*-dimethylformamide (DMF, 99.8%) were obtained from Aldrich.

Electrospinning

8 wt. % PAN (Figure 1a) powder was dissolved in DMF and mechanically stirred at room temperature for 24 h. DB18C6 (Figure 1b) was washed 3 times with 1.0 M HCl in deionized water at least 3 times and the purified crown ether was dried before use.

Figure 1: Chemical structures of a) PAN and b) dibenzo-18-crown-6 (DB18C6).

Five DB18C6 concentrations (0, 5, 10, 15 and 20 wt. %) were selected. Homogeneous, stable suspensions were prepared and used for electrospinning. During spinning, the processing and ambient conditions were held constant during fiber formation. The electrospinning set up was positioned in a horizontal configuration, as shown in Figure 2. The homogenous solutions were put in a 2 mL glass syringe kept with an 18 gauge metal needle. The syringe was placed horizontally positioned in a syringe pump. A high voltage power supply was connected to the needle tip. As ground electrode, a rotating drum covered with aluminum foil was used. The working distance between the needle tip and the rotating cylinder was 15 cm. The cylinder rotated at 120 rpm. The flow rate of the solution was varied from $250 \mu\text{L h}^{-1}$ to $400 \mu\text{L h}^{-1}$. The electrospinning voltage was set to 15 kV. All electrospinning experiments were carried out at standard room temperature and relative humidity. Nanofibers were coded as PAN-x where x represents the weight percentage of DB18C6 with respect to PAN.

Figure 2: Schematic representation of the electrospinning set-up.

Characterization

The morphologies and mean diameters of the nanofibers were investigated by scanning electron microscopy (JEOL SEM JSM 5600 LV). Around 50 fibers were analyzed per sample and the mean fiber diameter (MFD) was determined from the scanning electron microscopy (SEM) images. Fourier transform infrared (FTIR) spectra were measured with a Bruker ALPHA. Thermogravimetric analysis (TGA) measurements were carried out using a Perkin Elmer TGA 4000. 10 mg of sample was heated under N₂ atmosphere with a 20 °C min⁻¹ heating rate over a 50 to 800 °C temperature range. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Quantera SXM with monochromatic Al K α as the excitation and an X-ray power of 50 W.

Adsorption experiments

Single ion adsorption

Batch single ion adsorption experiments were performed by adding 10 mg of nanofibers in 10 ml of 10 mM solutions of KCl, BaCl₂, LiCl and NaCl in ultrapure water. All adsorption tests were carried out at room temperature. For analysis, 0.1 mL samples were taken at different time intervals. The samples were diluted and filtered with a 0.20 μ m filter (LLG, cellulose acetate (CA) syringe filter). The residual metal ions in the solution were analyzed using a BWB-XP flame photometer. The amount of metal ions adsorbed by the nanofibers was calculated from:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where q_e is the adsorbed amount of metal ions per gram of nanofibers (mmol/g), C_0 and C_e are the initial and the equilibrium concentration (mM) of the specific cation in the solution, respectively. V is the volume of the salt solution (mL) and m is the mass of the dry nanofibers (g).

Mixed ion adsorption

In the case of the mixed ion adsorption experiments, the 10 mg of nanofibers were left in contact with 10 mL of a mixture of 10 mM KCl, 10 mM BaCl₂, 10 mM LiCl and 10 mM NaCl in ultrapure water for 24 h. For analysis, 0.1 mL samples were taken after 24 h. The samples were filtered over a 0.20 µm filter (LLG, cellulose acetate (CA) syringe filter). The adsorption capacity for each ion was calculated using the equation 1

Adsorbent regeneration

Desorption experiments were carried out using a 1.0 M HCl solution in ultrapure water. The used PAN-10 nanofibers were placed in the 1.0 M HCl solution and magnetically stirred at 300 rpm at 25 °C for 48 h. Then the nanofibers were washed with distilled water several times and dried at 60 °C overnight. In order to assess the regeneration and reusability of the PAN-10 nanofibers, consecutive adsorption–desorption cycles were repeated four times. The adsorption tests were carried out with a 10 mM KCl solution at 25 °C for 24 h. The selectivity coefficient was calculated using equation (2):

$$S_{K^+/C^+} = \frac{q_{K^+,24}}{q_{C^+,24}} \quad (2)$$

where $q_{K^+,24}$ and $q_{C^+,24}$ are the adsorption capacities (mmol g⁻¹) of K⁺ and other cations (Li⁺, Na⁺ or Ba²⁺) after 24 h, respectively.

4.3 Results and discussion

Morphology of composite electrospun fibers and mats

The properties of the electrospun nanofiber formed, in particular the fiber diameter and morphology, depend on various parameters that can be divided into three groups: polymer solution properties, processing conditions and ambient conditions. In this study, processing

(applied voltage, volume flow rate) and ambient conditions (temperature, humidity) were held constant in order to systematically investigate the effect of polymer solution properties (crown ether concentration) on the mean fiber diameter. Suspending the DB18C6 in the polymer solution and ensuring the formation of homogenous stable suspensions prior to electrospinning are the frontline challenges in the electrospinning process. Completely transparent solutions that are stable over a long term were achieved without using any surfactants. Morphologies of the neat and crown ether modified PAN nanofiber mats were characterized by SEM and the micrographs are shown in Figure 3. The diameter distribution of the nanofibers is also presented in Figure 3. In these pictures, the DB18C6 concentration was varied while the voltage was kept constant at 15 kV at a constant collector distance of 15 cm. Without the addition of DB18C6, neat PAN nanofibers have a diameter of 102 ± 41 nm, which is comparable with the values reported in literature³³. PAN-5, PAN-10, PAN-15, and PAN-20 nanofibers have mean diameters of 138 ± 24 nm, 224 ± 56 nm, 248 ± 77 nm, and 270 ± 124 nm, respectively. The mean fiber diameter increased with DB18C6 concentration, while variance in the fiber diameter was also elevated. The effect on the fiber radii upon addition of crown ether is attributed to two factors: electrical conductivity and rheological changes in the polymer solution. These two contributions have opposing effects on the mean fiber diameter. For instance, the increase of electrical conductivity of a polymer solution leads to thinner fibers, while the fiber diameter tends to increase with shear viscosity^{34, 35}. As anticipated, the addition of nonconductive DB18C6 will not increase the electrical conductivity of the solutions ($\sigma_{\text{ethanol}} = 1.5 \pm 0.1 \mu\text{S/cm}$ and $\sigma_{0.1 \text{ wt\% crown ether/ethanol}} = 1.8 \pm 0.2 \mu\text{S/cm}$), while the shear viscosity of PAN-5, PAN-10, PAN-15, and PAN-20 solutions increased with the crown ether concentration. Figure 3 shows that the mean fiber diameter tends to increase with the crown ether/PAN stochastic ratio. Also, increasing crown ether concentrations lead to the formation of bead-like structures (red arrow in Figure 3, (PAN-15)) and a higher variance in the fiber diameter. The mean fiber diameter distribution of PAN and PAN-5 is rather uniform. However, PAN-10, PAN-15 and PAN-20 nanofibers have a broader fiber diameter distribution and comparatively high diameter range from 120 to 650 nm. We assume that the increased viscosity due to the higher crown ether fractions³³ and the reduced solution conductivity are the primary reason of fiber thickening.

Figure 3: The morphology and fiber diameter distribution of PAN and PAN/crown ether electrospun nanofibers.

FTIR

Figure 4 shows the FTIR spectra of PAN, PAN-10, and PAN-20 nanofibers. In the spectra, all nanofibers exhibited an absorbance at 2921 cm^{-1} that can be assigned to the stretching vibration of the -CH and -CH_2 groups.¹⁴ The peaks at 2242 cm^{-1} and 1451 cm^{-1} belong to $\text{C}\equiv\text{N}$ stretching and CH vibration of PAN.^{14,36} The presence of crown ether at the PAN surface is confirmed by an absorption peak at 1505 cm^{-1} that is ascribed to the C-H stretching vibrations of the alkanes in the aromatic ring of the crown ether.³⁷ Moreover, the characteristic C-O-C stretching signals of the crown ethers are observed at around 1060 cm^{-1} and 1129 cm^{-1} ^{37, 8} for all PAN/crown ether fibers, while these are absent for neat PAN fibers.

Figure 4: FTIR spectra of PAN and PAN/crown ether nanofibers.

Thermogravimetric analysis (TGA)

TGA was conducted in order to determine the thermal stability of the nanofibers. Figure 5 shows the thermogravimetric curves of PAN and PAN/crown ether nanofibers. The removal of residual DMF from the PAN-5 nanofibers causes a slight weight loss around $\sim 150\text{ }^{\circ}\text{C}$. PAN decomposition starts around $335\text{ }^{\circ}\text{C}$ with the cyclization of the nitrile groups and the decomposition reaction of PAN.^{39,40}

PAN-5, PAN-10, PAN-15, and PAN-20 nanofibers exhibit a two-stage thermal degradation profile. The first weight loss results from the removal of the crown ether around $250\text{ }^{\circ}\text{C}$.^{41,42} The crown ether is more sensitive to thermal degradation and starts to decompose at around $250\text{ }^{\circ}\text{C}$.⁴²

Figure 5: Thermogravimetric curves of PAN and PAN/crown ether nanofibers

The decomposition of crown ether is followed by thermal cleavage of PAN at around 350 °C. Films made from block copolymers often have perpendicular orientated block copolymers at the top, initiated by fast evaporation, but still have cylinders with a different orientation deeper inside the film.^{28,29,48} Thus, a thicker film fabricated by using a higher polymer.

Single ion adsorption

The ion adsorption potential of the developed fibers was investigated for both single and mixed aqueous ion solutions. First, the effect of the adsorption time on the static adsorption capacity of single ions on neat PAN and PAN/crown ether nanofibers was investigated. Figure 6 shows the results of the adsorption of Li^+ , Na^+ , K^+ and Ba^{2+} ions. Neat PAN nanofibers have almost no adsorption capacity for Li^+ , Na^+ , K^+ and Ba^{2+} ions, whereas PAN/crown ether fibers have a tendency to Li^+ , Na^+ , K^+ and Ba^{2+} ion uptake. This leads to the conclusion that the crown ether moieties, which are known to be able to form a complex with the ions, are responsible for the adsorption capacity of the prepared PAN/crown ether nanofibers.^{21,43,44} The adsorption capacity increases over time and levels off after 8 h, indicating that the adsorption equilibrium is achieved.

Figure 6 indicates that the adsorption capacity for K^+ ions is higher than that for Li^+ , Na^+ , and Ba^{2+} ions due to the selective complexation ability of the crown ether with K^+ ions.^{45,46} PAN-10 and PAN-20 nanofibers exhibit a K^+ adsorption capacity of 0.37 mmol/g, which is slightly higher than that of PAN-15 nanofibers (0.34 mmol/g). The K^+ uptake increases

with crown ether concentration, up to 10 wt.%, and remains nearly constant with a further increase in crown ether addition. This is expected because higher crown ether loading results in a higher number of available binding sites for the ions. However, this only accounts till a maximum of approximately 10 wt.% crown ether. Beyond this point, a further increase of the crown ether concentration does not have a significant effect on the ion adsorption capacity. Presumably, some of the binding sites are not accessible due to crown ether aggregation. Another reason might be that a fraction of the crown ether is embedded in or covered by the PAN polymer, preventing the binding sites from being freely accessible to the K^+ ions.

Figure 6: Adsorption kinetics of Li^+ , Na^+ , K^+ and Ba^{2+} onto PAN and PAN/crown ether nanofibers.

The Ba^{2+} adsorption capacities obtained with PAN-5, PAN-10, PAN-15, and PAN-20 nanofibers are 0.10 mmol g^{-1} , 0.17 mmol g^{-1} , 0.15 mmol g^{-1} , and 0.15 mmol g^{-1} , respectively

and the capacities are in all cases lower than the K^+ ion adsorption capacity. Takeda et al. investigated benzo-18-crown-6-metal complex formation constants in water by conductometry or potentiometry and spectrophotometry, respectively. They found a selectivity sequence of $Ba^{2+} > K^+ > Na^+$.⁴⁷ Shchori et al. determined the aqueous stability constants for complex formation of DB18C6 with Li^+ , Na^+ , K^+ and Ba^{2+} . In this case, K^+ and monodissociated ion pairs $[BaCl]^+$ complex more strongly with DB18C6 compared to Li^+ and Na^+ .⁴⁸ Although the previous researches demonstrate a strong affinity between DB18C6 and Ba^{2+} , we observe higher K^+ ion uptakes by the PAN/crown ether nanofibers. We will come back to this issue while discussing the mixed ion adsorption results.

The Na^+ and Li^+ ion adsorption capacities are the lowest of all ions investigated. In both cases, the adsorbed amount is almost the same and hardly changes with an increase of the crown ether mass fraction. We reason that, due to weak interactions between Na^+ and Li^+ ions and DB18C6, the adsorption capacity of the crown ether for these ions is lower and less stable complexes are formed in which the ions can easily dissociate from the crown ether.⁴⁹

XPS spectra

Elemental analyses of PAN and PAN-10 nanofibers were conducted by XPS in order to investigate the presence and effectiveness of the crown ether upon ion adsorption. The atomic ratios of C/O and C/N are shown in Table 1. As expected, we observe a slight C/N ratio increase as a result of an increase in the percentage of carbon relative to nitrogen due to the addition of the crown ether.

Table 1: Atomic ratios of C/O and C/N for neat PAN and PAN-10 nanofibers.

	C/O	C/N
PAN	21.0	3.6
PAN-10	16.3	4.0

Figure 7 exhibits the survey spectrum and the high resolution C 1s, O 1s spectra of PAN, PAN-10 before and PAN-10 nanofibers after Ba^{2+} adsorption. The survey XPS spectrum of PAN nanofibers shown in Figure 7 exhibits two intense peaks at 286.4 and 339.5 eV corresponding to C 1s and N 1s core levels, respectively. In addition to those peaks, we also observe a water induced O 1s peak centered at 533.03 eV.⁵⁰ The C 1s core spectra of PAN

can be curve-fitted to three peaks. The peaks at 286.74, 285.84 and 284.94 eV belong to the $-CH_2$, $-CH-CN$ and $-C\equiv N$ groups, respectively. The peak areas of the functional groups of $-CH_2$, $-CH-CN$ and $-C\equiv N$ are equal to each other.^{51,52} The survey spectrum of PAN-10 shown in Figure 7 also shows the peaks of the C 1s, N 1s, and O 1s core levels. Comparison of the PAN-10 C 1s spectra with those of PAN shows a peak shift. The relative peak intensities of the peaks change upon crown ether addition, and the peak at 286.34 eV becomes more intense compared to the other two peaks. The peak at 286.34 eV reflects the presence of ether carbon.^{53, 54} The O 1s spectrum of PAN-10 has one peak, similar to that of PAN. However, the peak shifts to a slightly lower binding energy, which is in good agreement with the previously reported O 1s spectra of the native crown ether.⁵⁵

Figure 7: XPS survey and high resolution XPS spectra of C_{1s}, O_{1s} of PAN, PAN-10 and PAN-10-Ba²⁺.

Finally, the spectra for PAN-10 nanofibers after barium adsorption clearly show the oxidation states of the barium ions. The O 1s peak appears again at 532.79 eV, and no

significant chemical shift in O 1s peak is observed after complexation of the crown ether with Ba^{2+} ions. The two peaks at 795.3 and 780.5 eV correspond to the Ba $3d_{3/2}$ and Ba $3d_{5/2}$ binding energies respectively^{56, 57} and confirm the adsorption of the Ba^{2+} ions on the PAN/crown ether nanofiber.

Mixed ion adsorption

Competitive adsorption experiments are carried out in order to assess the selective and competitive recognition of the crown ether modified PAN nanofibers for specific ions. Figure 8 shows the adsorption capacities of PAN, PAN-5, PAN-10, PAN-15, and PAN-20 nanofibers for a mixture of Li^+ , Na^+ , K^+ and Ba^{2+} ions.

Figure 8: Adsorption capacities of neat PAN and PAN/crown ether nanofibers for mixed ion systems.

Neat PAN nanofibers exhibit no adsorption capacity for Na^+ and Li^+ ions and only very small capacities for K^+ and Ba^{2+} ions. Single ion experiments showed that the PAN/crown ether nanofibers exhibited the highest adsorption capacities for K^+ ions compared to the other ions. The same behavior is observed for K^+ over Li^+ and Na^+ . The developed nanofibers can be used to separate selectively K^+ from Li^+ and Na^+ ions. The presence of Ba^{2+} ions in the mixture, however, shows a different behavior. Ba^{2+} and K^+ ion adsorption capacities are fairly equal in mixed ion adsorption measurements. Moreover, as Figure 8 reveals, the Ba^{2+} ion adsorption capacities are more or less equal to their single ion equivalents, while the K^+ adsorption is significantly reduced when Ba^{2+} is present in the solution. As we mentioned before, DB18C6 can form stable complexes with K^+ and Ba^{2+} ions, and therefore competition exists between K^+ and Ba^{2+} ions for the available binding

sites.^{47,48} Among the metal ions, Na^+ and Li^+ have the weakest ability to bind to the PAN-10 nanofibers.

Table 2 presents the adsorption selectivities of the different cationic species for the different crown ether concentrations in the PAN fibers. Selectivities calculated based on both single and mixed ion adsorptions are shown.

Table 2: Adsorption selectivities of PAN/crown ether nanofibers.

	$S_{\text{K}^+/\text{Li}^+}$		$S_{\text{K}^+/\text{Na}^+}$		$S_{\text{K}^+/\text{Ba}^{2+}}$	
	Single	Mixed	Single	Mixed	Single	Mixed
PAN	1.6 ± 0.2	n.a.	1.6 ± 0.2	n.a.	0.8 ± 0.1	2.0 ± 0.1
PAN-5	2.7 ± 0.6	7.6 ± 3.2	3.6 ± 0.7	5.0 ± 1.5	2.9 ± 0.9	0.8 ± 0.1
PAN-10	2.6 ± 0.1	10.6 ± 6.2	4.7 ± 0.7	21 ± 16.3	2.2 ± 0.2	0.6 ± 0.6
PAN-15	2.9 ± 0.5	12.4 ± 5.8	4.2 ± 0.6	6.0 ± 1.8	2.4 ± 0.6	1.2 ± 0.1
PAN-20	3.2 ± 0.9	14.2 ± 6.5	4.7 ± 0.7	28 ± 12.9	2.6 ± 0.7	1.0 ± 0.1

Table 2 shows the K^+/Li^+ , K^+/Na^+ and $\text{K}^+/\text{Ba}^{2+}$ adsorption selectivity coefficients of PAN/crown ether nanofibers for single ion and mixed ion adsorption experiments. For single ion experiments, increasing the crown ether mass fraction does not significantly affect the K^+/Li^+ , K^+/Na^+ , and $\text{K}^+/\text{Ba}^{2+}$ adsorption selectivities. The crown ether fibers seem to exhibit a slightly higher selectivity for K^+ over Na^+ than for the other ions, but still selectivities are low.

When mixtures are considered, the behavior changes drastically. Selectivities for K^+ over especially Li^+ but also Na^+ significantly increase, while the selectivity for K^+ over Ba^{2+} decreases due to competition for the binding sites. So in the case of Li^+ and Na^+ , competition is for the benefit of K^+ , while this switches when Ba^{2+} is present. In that case, Ba^{2+} is preferentially adsorbed. This is due to the preference of the crown ether for Ba^{2+} over K^+ , as also observed in literature^{47,48}. These results clearly show exceptionally high K^+ over Li^+ and Na^+ selectivities, making the developed fibers very attractive for the selective recovery of K^+ from mixtures with other monovalent ions.

Reusability of nanofibers

Effective regeneration of the nanofibers is essential for their potential application as an adsorbent for the selective recovery of ions from aqueous solutions. Therefore, we investigated the K^+ adsorption onto PAN-10 nanofibers, and the subsequent regeneration of the K^+ loaded PAN-10 nanofibers. Desorption tests were performed with 1.0 M HCl, and the regenerated fibers were used for in total 4 adsorption-desorption cycles. The results are shown in Figure 9. Figure 9 shows a slight capacity loss of only 10 % after the first 2 adsorption-desorption cycles, but overall, the adsorption capacity remains rather constant after that. This small loss is most probably due to the fact that not all K^+ ions could be desorbed with 1.0 M HCl and some small amounts remain adsorbed.

Figure 9: K^+ adsorption capacity of PAN/crown ether (PAN-10) nanofibers as a function of the number of adsorption-desorption cycles.

4.4 Conclusions

PAN/crown ether nanofiber mats containing different weight fractions of the crown ether DB18C6 were prepared by electrospinning. FTIR confirmed the presence of the crown ether in the PAN nanofiber matrix. SEM microscopy images showed that the addition of crown ether resulted in thicker nanofibers. The average diameter of the PAN nanofibers increased from 102 nm to 270 nm with the addition of 20 wt. % crown ether with respect to PAN. Single ion adsorption results revealed a selectivity sequence of $K^+ > Ba^{2+} > Na^+ \sim Li^+$ for DB18C6 modified PAN nanofibers. In mixed salt solutions the adsorption capacity of K^+ ion declined in the presence of especially Ba^{2+} ions suggesting competition between the

ions for the available binding sites. The PAN/crown ether nanofibers exhibit exceptionally high selectivities for K^+ over Li^+ and Na^+ . Considering reusability, PAN/crown ether nanofibers only lose 10% of the K^+ adsorption capacity after four consecutive adsorption and desorption cycles. Electrospinning thus shows to be a very versatile tool to prepare crown ether functional polymer adsorbents.

Acknowledgments

Sinem Tas acknowledges the Industrial Partnership Program (IPP) "Spectroscopic analysis of particles in water" of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). This IPP is co-financed by Wetsus, Centre of Excellence for Sustainable Water Technology, as part of Wetsus' TTI program. Wetsus is co-funded by the Dutch ministry of economics, agriculture and innovation. Elif Ozden-Yenigun acknowledges İTÜ-BAP (Grant number: 38227).

References

1. Bhardwaj, N.; Kundu, S. C. Electrospinning: A fascinating fiber fabrication technique. *Biotechnol Adv* **2010**, *28* (3), 325-347.
2. Zhang, C. X.; Yuan, X. Y.; Wu, L. L.; Han, Y.; Sheng, J. Study on morphology of electrospun poly(vinyl alcohol) mats. *Eur Polym J* **2005**, *41* (3), 423-432.
3. Schiffman, J. D.; Schauer, C. L. A review: Electrospinning of biopolymer nanofibers and their applications. *Polym Rev* **2008**, *48* (2), 317-352.
4. Canejo, J. P.; Borges, J. P.; Godinho, M. H.; Brogueira, P.; Teixeira, P. I. C.; Terentjev, E. M. Helical twisting of electrospun liquid crystalline cellulose micro- and nanofibers. *Adv Mater* **2008**, *20* (24), 4821-4825.
5. Bajj, A.; Mai, Y. W.; Wong, S. C.; Abtahi, M.; Chen, P. Electrospinning of polymer nanofibers: Effects on oriented morphology, structures and tensile properties. *Compos Sci Technol* **2010**, *70* (5), 703-718.
6. Yun, K. M.; Hogan, C. J.; Mastubayashi, Y.; Kawabe, M.; Iskandar, F.; Okuyama, K. Nanoparticle filtration by electrospun polymer fibers. *Chem Eng Sci* **2007**, *62* (17), 4751-4759.
7. Gopal, R.; Kaur, S.; Ma, Z. W.; Chan, C.; Ramakrishna, S.; Matsuura, T. Electrospun nanofibrous filtration membrane. *J Membrane Sci* **2006**, *281* (1-2), 581-586.
8. Homaeigohar, S. S.; Buhr, K.; Ebert, K. Polyethersulfone electrospun nanofibrous composite membrane for liquid filtration. *J Membrane Sci* **2010**, *365* (1-2), 68-77.
9. Tamura, T.; Kawakami, H. Aligned Electrospun Nanofiber Composite Membranes for Fuel Cell Electrolytes. *Nano Lett* **2010**, *10* (4), 1324-1328.
10. Shabani, I.; Hasani-Sadrabadi, M. M.; Haddadi-Asl, V.; Soleimani, M. Nanofiber-based polyelectrolytes as novel membranes for fuel cell applications. *J Membrane Sci* **2011**, *368* (1-2), 233-240.
11. Sill, T. J.; von Recum, H. A. Electrospinning: Applications in drug delivery and tissue engineering. *Biomaterials* **2008**, *29* (13), 1989-2006.
12. Gorji, M.; Jeddi, A. A. A.; Gharehaghaji, A. A. Fabrication and characterization of polyurethane electrospun nanofiber membranes for protective clothing applications. *J Appl Polym Sci* **2012**, *125* (5), 4135-4141.
13. Lee, S. Developing UV-protective textiles based on electrospun zinc oxide nanocomposite fibers. *Fiber Polym* **2009**, *10* (3), 295-301.
14. Chen, M.; Wang, C. J.; Fang, W.; Wang, J.; Zhang, W.; Jin, G.; Diao, G. W. Electrospinning of calixarene-functionalized polyacrylonitrile nanofiber membranes and application as an adsorbent and catalyst support. *Langmuir* **2013**, *29* (38), 11858-11867.
15. Celebioglu, A.; Demirci, S.; Uyar, T. Cyclodextrin-grafted electrospun cellulose acetate nanofibers via "Click" reaction for removal of phenanthrene. *Appl Surf Sci* **2014**, *305*, 581-588.
16. Kayaci, F.; Aytac, Z.; Uyar, T. Surface modification of electrospun polyester nanofibers with cyclodextrin polymer for the removal of phenanthrene from aqueous solution. *J Hazard Mater* **2013**, *261*, 286-294.

17. Hong, G. S.; Wang, M.; Li, X.; Shen, L. D.; Wang, X. F.; Zhu, M. F.; Hsiao, B. S. Micro-nano structure nanofibrous p-sulfonatocalix[8]arene complex membranes for highly efficient and selective adsorption of lanthanum(III) ions in aqueous solution. *Rsc Adv* **2015**, 5 (27), 21178-21188.
18. Bayrakci, M.; Özcan, F.; Ertul, Ş. Synthesis of calixamide nanofibers by electrospinning and toxic anion binding to the fiber structures. *Tetrahedron* **2015**, 71 (21), 3404-3410.
19. Nogami, M.; Haratani, T.; Tachibana, Y.; Kaneshiki, T.; Nomura, M.; Suzuki, T. Adsorptivity of various metal ions onto benzo-18-crown-6 and dibenzo-18-crown-6 resins. *J Radioanal Nucl Ch* **2015**, 303 (2), 1549-1553.
20. Hintze, K. J.; Lutzen, A.; Bredow, T. Structure and stability of supramolecular crown ether complexes. *J Comput Chem* **2015**, 36 (19), 1467-1472.
21. Tunca, U.; Yagci, Y. Crown ether-containing polymers. *Prog Polym Sci* **1994**, 19 (2), 233-286.
22. Alexandratos, S. D.; Stine, C. L. Synthesis of ion-selective polymer-supported crown ethers: a review. *React Funct Polym* **2004**, 60, 3-16.
23. Duman, O.; Ayranci, E. Attachment of benzo-crown ethers onto activated carbon cloth to enhance the removal of chromium, cobalt and nickel ions from aqueous solutions by adsorption. *J Hazard Mater* **2010**, 176 (1-3), 231-238.
24. Torrejos, R. E. C.; Nisola, G. M.; Park, M. J.; Shon, H. K.; Seo, J. G.; Koo, S.; Chung, W. J. Synthesis and characterization of multi-walled carbon nanotubes-supported dibenzo-14-crown-4 ether with proton ionizable carboxyl sidearm as Li⁺ adsorbents. *Chem Eng J* **2015**, 264, 89-98.
25. Ju, X. J.; Zhang, S. B.; Zhou, M. Y.; Xie, R.; Yang, L.; Chu, L. Y. Novel heavy-metal adsorption material: ion-recognition P(NIPAM-co-BCAm) hydrogels for removal of lead(II) ions. *J Hazard Mater* **2009**, 167 (1-3), 114-118.
26. Luo, X. B.; Guo, B.; Luo, J. M.; Deng, F.; Zhang, S. Y.; Luo, S. L.; Crittenden, J. Recovery of lithium from wastewater using development of Li ion-imprinted polymers. *Acc Sustain Chem Eng* **2015**, 3 (3), 460-467.
27. Rajabi, H. R.; Shamsipur, M.; Pourmortazavi, S. M. Preparation of a novel potassium ion imprinted polymeric nanoparticles based on dicyclohexyl 18C6 for selective determination of K⁺ ion in different water samples. *Mat Sci Eng C-Mater* **2013**, 33 (6), 3374-3381.
28. Luo, X. B.; Liu, L. L.; Deng, F.; Luo, S. L. Novel ion-imprinted polymer using crown ether as a functional monomer for selective removal of Pb(II) ions in real environmental water samples. *J Mater Chem A* **2013**, 1 (28), 8280-8286.
29. Musale, D. A.; Kumar, A.; Pleizier, G. Formation and characterization of poly(acrylonitrile)/Chitosan composite ultrafiltration membranes. *J Membrane Sci* **1999**, 154 (2), 163-173.
30. Musale, D. A.; Kumar, A. Solvent and pH resistance of surface crosslinked chitosan/poly(acrylonitrile) composite nanofiltration membranes. *J Appl Polym Sci* **2000**, 77 (8), 1782-1793.

31. Wang, T.; Kumar, S. Electrospinning of polyacrylonitrile nanofibers. *J Appl Polym Sci* **2006**, *102* (2), 1023-1029.
32. Soo Jin Park, G. Y. H. Precursors and Manufacturing of Carbon Fibers. In *Carbon Fibers*; Springer: The Netherlands, 2015; Vol. 210, pp 31-66.
33. Yördem, O. S.; Papila, M.; Menceloğlu, Y. Z. Effects of electrospinning parameters on polyacrylonitrile nanofiber diameter: An investigation by response surface methodology. *Mater Design* **2008**, *29* (1), 34-44.
34. Deitzel, J. M.; Kleinmeyer, J.; Harris, D.; Tan, N. C. B. The effect of processing variables on the morphology of electrospun nanofibers and textiles. *Polymer* **2001**, *42* (1), 261-272.
35. Ozden-Yenigun, E.; Mencelolu, Y. Z.; Papila, M. MWCNTs/P(St-co-GMA) Composite Nanofibers of Engineered Interface Chemistry for Epoxy Matrix Nanocomposites. *ACS Appl Mater Inter* **2012**, *4* (2), 777-784.
36. Zhang, C. Q.; Yang, Q. B.; Zhan, N. Q.; Sun, L.; Wang, H. G.; Song, Y.; Li, Y. X. Silver nanoparticles grown on the surface of PAN nanofiber: Preparation, characterization and catalytic performance. *Colloid Surface A* **2010**, *362* (1-3), 58-64.
37. Zhu, H.; Du, M. L.; Zou, M. L.; Xu, C. S.; Li, N.; Fu, Y. Q. Facile and green synthesis of well-dispersed Au nanoparticles in PAN nanofibers by tea polyphenols. *J Mater Chem* **2012**, *22* (18), 9301-9307.
38. Dulak, M.; Bergougnant, R.; Fromm, K. M.; Hagemann, H. R.; Robin, A. Y.; Wesolowski, T. A. Water trapped in dibenzo-18-crown-6: Theoretical and spectroscopic (IR, Raman) studies. *Spectrochim Acta A* **2006**, *64* (2), 532-548.
39. Shi, Y. Z.; Li, Y. J.; Zhang, J. F.; Yu, Z. Z.; Yang, D. Z. Electrospun polyacrylonitrile nanofibers loaded with silver nanoparticles by silver mirror reaction. *Mat Sci Eng C-Mater* **2015**, *51*, 346-355.
40. Abeykoon, N. C.; Bonso, J. S.; Ferraris, J. P. Supercapacitor performance of carbon nanofiber electrodes derived from immiscible PAN/PMMA polymer blends. *Rsc Adv* **2015**, *5* (26), 19865-19873.
41. Gurrieri, S.; Seminara, A.; Siracusa, G.; Cassol, A. Thermal-decomposition of metal-complexes .4. lanthanide(iii) complexes with dibenzo-18-crown-6. *Thermochim Acta* **1975**, *11* (4), 433-439.
42. Bhattacharyya, A.; Goswami, A. Effect of cation driven loading of dibenzo-18-crown-6 in nafion-117 membrane on the diffusion and transport behavior of alkali metal ions. *J Phys Chem B* **2009**, *113* (39), 12958-12963.
43. Tzeng, D. L.; Shih, J. S.; Yeh, Y. C. Adsorption of heavy-metal ions on crown-ether adsorbents. *Analyst* **1987**, *112* (10), 1413-1416.
44. Bond, A. H.; Dietz, M. L.; Chiarizia, R. Incorporating size selectivity into synergistic solvent extraction: A review of crown ether-containing systems. *Ind Eng Chem Res* **2000**, *39* (10), 3442-3464.
45. Grootenhuis, P. D. J.; Kollman, P. A. Molecular mechanics and dynamics studies of crown ether cation interactions - free-energy calculations on the cation selectivity of dibenzo-18-crown-6 and dibenzo-30-crown-10. *J Am Chem Soc* **1989**, *111* (6), 2152-2158.

46. Nakajima, M.; Kimura, K.; Shono, T. Ion-chromatographic behavior of silica-gels modified by poly(crown ether)s and bis(crown ether)s of benzo-18-crown-6. *B Chem Soc Jpn* **1983**, *56* (10), 3052-3056.
47. Takeda, Y.; Kohno, R.; Kudo, Y.; Fukada, N. Stabilities in water and transfer activity-coefficients from water to nonaqueous solvents of benzo-18-crown-6-metal ion complexes. *B Chem Soc Jpn* **1989**, *62* (4), 999-1003.
48. Shchori, E.; Nae, N.; Jagurgrodzinski, J. Stability-constants of complexes of a series of metal cations with 6,7,9,10,17,18,20,21-octahydrodibenzo[b,k][1,4,7,10,13,16]hexa-oxa-cyclo-octadecin (dibenzo-18-crown-6) in aqueous-solutions. *J Chem Soc Dalton* **1975**, (22), 2381-2386.
49. Maleknia, S.; Brodbelt, J. Cavity-size-dependent dissociation of crown-ether ammonium ion complexes in the gas-phase. *J Am Chem Soc* **1993**, *115* (7), 2837-2843.
50. Abu Hajja, M.; Guimond, S.; Uhl, A.; Kuhlenbeck, H.; Freund, H. J. Adsorption of water on thin $V_2O_3(0001)$ films. *Surf Sci* **2006**, *600* (5), 1040-1047.
51. Li, L.; Chan, C. M.; Weng, L. T. Effects of the sequence distribution of poly(acrylonitrile-butadiene) copolymers on the surface chemical composition as determined by XPS and dynamic contact angle measurements. *Macromolecules* **1997**, *30* (12), 3698-3700.
52. Beamson G., B. D. High Resolution XPS of Organic Polymers: *The Scienta ESCA 300 Database*, John Wiley and Sons: Chichester, England, New York 1992.
53. Johnston, E. E.; Bryers, J. D.; Ratner, B. D. Plasma deposition and surface characterization of oligoglyme, dioxane, and crown ether nonfouling films. *Langmuir* **2005**, *21* (3), 870-881.
54. Vance, A. L.; Willey, T. M.; van Buuren, T.; Nelson, A. J.; Bostedt, C.; Fox, G. A.; Terminello, L. J. XAS and XPS characterization of a surface-attached rotaxane. *Nano Lett* **2003**, *3* (1), 81-84.
55. Tran, T. K.; Smaali, K.; Hardouin, M.; Bricaud, Q.; Ocafrain, M.; Blanchard, P.; Lenfant, S.; Godey, S.; Roncali, J.; Vuillaume, D. A Crown-ether loop-derivatized oligothiophene doubly attached on gold surface as cation-binding switchable molecular junction. *Adv Mater* **2013**, *25* (3), 427-431.
56. Liu, B. W.; Zhang, Y.; Tang, L. D. X-ray photoelectron spectroscopic studies of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode for solid oxide fuel cells. *Int J Hydrogen Energ* **2009**, *34* (1), 435-439.
57. Vandoveren, H.; Verhoeven, J. A. T. XPS spectra of Ca, Sr, Ba and their oxides. *J Electron Spectrosc* **1980**, *21* (3), 265-273.

Electromechanical performance of a crown ether containing ionic polymer metal composite actuator

This chapter has been submitted for publication, authored by:
Sinem Tas, Bram Zoetebier, Ozlem Sardan Sukas, Muharrem, Bayraktar, Mark A. Hempenius, G.
Julius Vancso and Kitty Nijmeijer

Abstract

The development of new ionic polymer composite actuators (IPMCs) enables breakthroughs in biomimetic technologies. In the present work a new ion selective polymer actuator concept is developed that could mimic natural muscle-like motion. For this purpose, sulfonated PAEKs (SPAEEKs) and crown ether containing SPAEEKs were synthesized. The successful synthesis of SPAEEK and di(4-fluorobenzophenone)-18-crown-6 containing SPAEEK was confirmed by gel permeation chromatography, FTIR and NMR. Membranes were fabricated by a solution-casting method. The crown ether containing SPAEEK actuator displayed improved actuation performance compared to the SPAEEK actuator without crown ether. Also, the incorporation of crown ether units in the polymer backbone resulted in an ion-related bending displacement. The Na^+ form of the actuators showed larger bending displacement than the K^+ form. In its Na^+ form, the crown ether containing SPAEEK actuator exhibited an improvement of the maximum bending displacement of up to 25 %. The performance of this actuator could be improved further by varying the amount and type of crown ether incorporated, the sulfonation degree of the polymer, and the thickness of the membrane and the electrode layers.

5.1 Introduction

A variety of polymers have emerged to imitate natural motions. In particular, some types of polymers exhibit deformations in response to applied voltages,¹ which makes them promising candidates for use in biomedical devices,² biomimetic robots,³ artificial muscles⁴ and biomimetic sensors.⁵ Specifically, conducting polymers^{6,7} and ionic polymer-metal composites (IPMCs)⁸ have been employed in the development of new muscle-like actuators. IPMCs undergo a large bending displacement under a low applied voltage (1-5 V)^{9,10} and are currently considered as suitable candidates for mimicking of biological muscle motion.

IPMCs consist of a hydrated ionic polymer membrane and metal electrodes, typically Pt and/or Au plated on both surfaces of the membrane.^{4,5} The ionic polymer membrane has covalently bond negative or positive charges that are neutralized by oppositely charged mobile counter ions. Under an applied voltage, for a membrane with fixed negative charges, the solvated mobile cations move towards to the oppositely charged electrode. Redistribution of the cations and water molecules, as shown in Figure 1, results in swelling near the negative electrode and shrinkage near the positive electrode. Accordingly, IPMCs experience bending.⁴

Figure 1: Schematic illustration of an actuator without (left) and with (right) applied voltage.

Nafion is set as a benchmark membrane for IPMC technology^{11,12} and many current studies focus on the improvement of the Nafion actuator performance.¹² As an alternative to Nafion, to further improve the performance of the IPMC in terms of bending response, researchers work on designing new membrane materials with controlled levels of polar functionality. Sulfonated polymers such as poly(arylene ether sulfone)s,¹³ poly(vinyl alcohol)s,^{14,15} poly(styrene)s,¹⁶ poly(phenyl sulfone)s¹⁷ and a poly(ether ether ketone)-poly(vinylidene fluoride)¹⁸ blend have been investigated within this context.

In muscles, membrane proteins are ion selective and gate the flow of K^+ and Na^+ ions in and out of cells by adopting closed and open states.¹⁹⁻²¹ The selective transport of these ions is of central importance for muscle contraction and expansion. Inspired by these membrane ion channels, we hypothesize that crown ether containing polymers can potentially yield ion selective actuation, as natural muscles do. Crown ethers can selectively bind specific cationic species due to the ion-dipole interaction of the positively charged metal ion with the negatively polarized oxygen atoms of the crown ether.²² Therefore, crown ethers and crown ether polymers are often employed to develop artificial ion channels.^{23,24}

Up to date, sulfonated polymers have been prepared for IPMC applications^{13,16,17} but to the best of our knowledge, there are no examples of sulfonated PAEKs (SPAEEK) containing crown ether moieties reported as IPMCs. We believe that incorporation of crown ether functionality in SPAEEK will alter the specific ion selectivity and has potential in terms of mimicking natural muscle-like motions. For this reason, crown ether containing SPAEEK was synthesized by step growth polymerization including di(4-fluorobenzophenone)-18-crown-6. The synthesized sulfonated polymer with crown ether moieties in the main chain of the polymer is used for membrane preparation. The prepared SPAEEK and crown ether containing SPAEEK membranes are characterized in terms of water swelling and ion exchange capacity. The actuation performance of the SPAEEK and crown ether containing SPAEEK membranes is determined for both the Na^+ and K^+ forms.

5.2 Experimental

Materials

4,4'-difluorobenzophenone (DFBP, 99%), bisphenol A (BPA, $\geq 99\%$), 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%), $NaHCO_3$ ($> 99.7\%$), dibenzo-18-crown-6 (98%), 4-fluorobenzoic acid (98%), Eaton's reagent, $CDCl_3$ (99.8 atom%D), $DMSO-d_6$ (99.9 atom%D), tetraammineplatinum chloride hydrate ($[Pt(NH_3)_4]Cl_2 \cdot xH_2O$, 98%), sodium borohydride ($NaBH_4$, $\geq 99\%$), ammonium hydroxide (NH_4OH , 28.0-30.0%), hydrazine monohydrate ($NH_2NH_2 \cdot H_2O$, 98%) hydroxylammonium chloride ($NH_2OH \cdot HCl$, 99%), lithium chloride $LiCl$ (99%) and potassium chloride KCl (99%) were obtained from Sigma-Aldrich (the Netherlands) and used as received. K_2CO_3 (99.9%) was obtained from Sigma-Aldrich (the Netherlands) and dried before use. Dichloromethane (99.9%) was obtained from Biosolve (the Netherlands). Ethyl acetate (99.5%) was purchased from Merck (the Netherlands). Milli-Q water (Millipore) was used in all experiments. Sulfonated 4,4'-

difluorobenzophenone (SDFBP) was prepared according to an established literature procedure.²⁵

Synthesis of di(4-fluorobenzophenone)-18-crown-6.

Dibenzo-18-crown-6 (19.97 g, 55.4 mmol), 1.01 equivalent 4-fluorobenzoic acid (15.65 g, 111.8 mmol) and Eaton's reagent (102.7 mL) were mixed under argon and stirred for 50 hours (scheme 1). Approximately 250 g of water and ice were added to the mixture. The mixture turned green and the solid was filtered with a POR3 glass filter and dissolved in 250 mL of CH₂Cl₂. The organic layer was neutralized with a concentrated NaHCO₃ solution and evaporated *in vacuo* to yield the crude product as a light orange solid. Recrystallization from boiling ethyl acetate yielded di(4-fluorobenzophenone)-18-crown-6 (DFBP18C6) with a yield of 9.7 g (29.0%) of pure product with a melting point of 189 °C. ¹H NMR (CDCl₃, δ , ppm): 4.04 + 4.23 (18C6, m, 16H); 6.86 (ar *o*-CH, d, *J* = 8.3 Hz, 2H); 7.14 (F-ar *o*-CH, m, 4H); 7.32 (ar *m*-CH, dd, *J* = 8.3 Hz; *J* = 1.9 Hz, 2H); 7.41 (ar *o*-CH, m, *J* = 1.9 Hz, 2H); 7.77 (F-ar *m*-CH, m, 4H). ¹³C NMR (CDCl₃, δ , ppm): 68.60, 69.69 (18C6); 110.93 + 110.99 (ar *o*-C); 113.44 (ar *o*-C); 115.25 + 115.47 (F-ar *o*-C); 125.31 + 125.43 (ar *m*-C); 130.10 + 130.17 (ar C-C=O); 132.28 + 132.37 (F-ar *m*-C); 134.47 + 134.50 (F-ar C-C=O); 148.48 (ar-crown C); 152.64 + 152.71 (ar-crown C); 163.83 + 166.34 (C-F); 194.18 (C=O). FTIR (cm⁻¹): 1740 and 1638 (C=O); 1245 and 1129 (C-O).

Scheme 1: Reaction route to synthesize di(4-fluorobenzophenone)-18-crown-6 (DFBP18C6).

A mixture of DFBP (0.273 g, 1.25 mmol), SDFBP (0.528 g, 1.25 mmol), DFBP18C6 (1.661 g, 2.5 mmol), BPA (1.141 g, 5 mmol) and K₂CO₃ (1.57 g, 5.75 mmol) (Scheme 2) was dissolved in dry NMP (18 mL) and toluene (9 mL) in a three-necked round-bottomed flask equipped with a magnetic stirring bar, Dean-Stark trap and thermometer. The content was heated to 150 °C for 4 h while removing water by azeotropic distillation. Heating was then continued to 175 °C and kept at that temperature for 20 h. The viscous solution was diluted with NMP and the polymer was precipitated in a 10-fold excess of cold ethanol. The solid was filtered off and dried *in vacuo* at 60 °C. The crown ether containing copolymer was

designated as S(y)-C(z)-PAEK where y and z represent the mole percentages of SDFBP and di(4-fluorobenzophenone)-18-crown-6.

Scheme 2: Polycondensation procedure for sulfonated-crown ether containing poly(arylene ether ketone) S(y)-C(z)-PAEK.

Polymer characterization

1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz instrument at 400.1 and 100.6 MHz, respectively, in $CDCl_3$ or $DMSO-d_6$. 1H and ^{13}C chemical shifts were based on the residual solvent signals. FTIR spectra were measured with a Bruker ALPHA. Gel permeation chromatography (GPC) measurements were performed using a Shimadzu GPC LC-20AD equipped with a Shodex LF-801 column and a refractive index detector using NMP containing 0.5 mmol L^{-1} LiBr as the eluent; polystyrene standards were used to calibrate the instrument. All sample solutions were prepared at a concentration of 1 mg/mL and filtered through a 0.45 μm PTFE filter prior to the GPC run. Thermal gravimetric analysis (TGA) measurements were performed on a Perkin Elmer TGA 4000 under a N_2 atmosphere at a linear heating rate of 20 $^{\circ}C min^{-1}$. 10 mg sample was heated over a 30 - 900 $^{\circ}C$ temperature range. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC 8000 with 10 mg of each sample cooled and heated at a rate of 20 $^{\circ}C min^{-1}$ between 30 $^{\circ}C$ and 350 $^{\circ}C$ under N_2 . This cycle was repeated three times. Glass transition temperatures (T_g) were determined from the second heating cycle. The morphology of the IPMC actuator was analyzed with high-resolution scanning electron microscopy (HR-SEM)

(Zeiss Merlin, GeminiSEM). Sample cross sections were prepared by freezing the films in liquid nitrogen and subsequent breakage.

Membrane fabrication

20 wt% solutions of sulfonated poly(arylene ether ketone) (S(25)-PAEK) and crown ether containing sulfonated poly(arylene ether ketone) S(25)-C(50)-PAEK were prepared in NMP at 80 °C. The viscous solutions were cast on a glass plate with a 0.5 mm casting knife. After casting, the solvent was evaporated under N₂ atmosphere for 5 days at room temperature, followed by 5 days at 60 °C and 2 days at 110 °C under vacuum. Next, the membranes were peeled off from glass plate by immersing them into water.

Membrane characterization

Swelling measurements were performed by immersing the prepared membranes in Milli-Q water for 24 hours to measure the wet weight of the membranes vs. the dry weight. The wet membranes were subsequently dried at 60 °C for 12 hours. Membrane swelling was calculated using the following equation:

$$\text{Swelling} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\% \quad (1)$$

Here, m_{wet} and m_{dry} are the mass (g) of the wet and the dry membranes, respectively.

A titration method was used to determine the membrane ion exchange capacity (IEC).²⁶ First, the membranes were converted into the H⁺ form by stirring the membrane in a 1.0 M HCl solution for at least 15 hours. Then, the membranes were converted back into the sodium form by immersing them in a 2.0 M NaCl solution for 3 hours. The NaCl solution was refreshed every hour and all used solutions were combined to obtain the titration solution. The released amount of H⁺ in the solution was then determined by titration with 0.1 M NaOH. The IEC (mmol g⁻¹_{dry membrane}) values were calculated with the following equation:

$$\text{IEC} = \frac{V_{\text{NaOH}}}{m_{\text{dry}}} \times C_{\text{NaOH}} \quad (2)$$

Here, V_{NaOH} is the added volume of the NaOH solution (mL), m_{dry} is the mass of the dry membrane (g), and C_{NaOH} is the concentration of the NaOH solution (mmol mL⁻¹).

Membrane fabrication

Following the characterization of the membranes in terms of swelling and ion exchange capacity, the membranes were used to prepare the IPMC actuators. To facilitate application of voltage across the membrane, both surfaces of the membranes were covered with platinum using an electroless plating method with two reduction steps.^{27,28} In order to improve the bending performance of the actuators, a pre-treatment step was applied to the membranes. In this pretreatment step, the membranes were first roughened with sand paper to increase the surface area, followed by boiling in 1.0 M HCl for 30 min and subsequent rinsing in deionized water. For the first reduction step, the membranes were then immersed in 100 mL of a 5 wt.% aqueous solution of $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ overnight to induce ion exchange between H^+ to Pt^{2+} . The membranes were rinsed with deionized water again and stirred in 200 ml of deionized water at 40 °C. 3 ml of 5 wt.% aqueous NaBH_4 solution was added every 30 min during 6 hours. During the addition of reducing agent, the temperature was gradually increased to 60 °C. After completion of the first plating series, the membranes were again washed with deionized water and boiled in 1.0 M HCl for 5h, followed by the second reduction step. The membranes were rinsed once again with deionized water and then stirred in 240 mL $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ (0.5 mg Pt mL^{-1}) solution at 40 °C for 5h. Meanwhile, 5 mL of 5 wt.% aqueous solution of NH_4OH was slowly added, followed by the addition of 6 mL of 20 wt.% hydrazine hydrate solution and 3 mL of 5 wt.% hydroxylammonium chloride at 60 °C over 4h. The resulting Pt covered membranes were boiled in 1.0 M HCl for 30 min and rinsed with Milli-Q water.

Characterization of the actuation performance

The electromechanical actuation response of the membranes in both Na^+ and K^+ forms was measured in deionized water. To do so, the resulting IPMC actuators were soaked in 2.0 M NaCl or KCl solution overnight for complete ion exchange between H^+ and Na^+ or K^+ .^{27,28} Finally, the actuators were cut into 0.7 cm x 3 cm pieces to prepare test cantilevers, rinsed with deionized water to remove excess salt (NaCl or KCl) and stored in deionized water. The actuator performance was measured using a laser Doppler vibrometer (Polytec GmbH, MSA-400 micro system analyzer). An AC voltage with a peak-to-peak amplitude of 1.5V Vp-p was applied across the electrodes at frequencies of 10 Hz, 15 Hz and 20 Hz.

5.3 Results and discussion

Chemical structure of S(25)-PAEK and S(25)-C(50)-PAEK

NMR studies confirmed the chemical structure of S(25)PAEK (Appendix, Figure A1) and S(25)-C(50)-PAEK (Figure 2 and Appendix, Figure A2). The characteristic peak of the methyl groups present in the BPA units of PAEK is clearly visible in the ^1H NMR spectra at $\delta = 1.66$ ppm (Figure 2, peak denoted with A) and in the ^{13}C NMR spectra at $\delta = 30.5$ ppm. Also, the carbonyl carbon of the DFBP units is present in the ^{13}C NMR spectra at $\delta = 193.1$ ppm (Appendix, Figure A1c and A2b). Furthermore, the signal associated with the hydroxy groups of BPA is absent in the spectrum of PAEK, confirming successful polymerization. Most evident for the introduction of SDFBP is the peak related to protons in between the sulfonate and carbonyl groups at 8.21 ppm (Figure 2 peak B and Appendix, Figure A1a, peak N). The signal of these protons is shifted downfield and this can be related to the molar percentage of sulfonated monomer introduced in the reaction mixture.

Figure 2: ^1H NMR spectrum and structure of S(25)-C(50)-PAEK, recorded in $\text{DMSO}-d_6$.

When di(4-fluorobenzophenone)-18-crown-6 is included in the step growth polymerization, the signals of the incorporated crown ether become clearly visible. The peaks, C in Figure 2, ^1H NMR at $\delta = 3.9 + 4.2$ ppm represent the protons present in the oxyethylene groups of the crown ether. Corresponding peaks in the ^{13}C NMR spectrum are shown in Figure A2 (Appendix).

The molar percentages are calculated (Table 1) from the non-overlapping ^1H NMR signals (DMSO- d_6 , δ) 3.9 + 4.2 (16H), 8.21 (2H) and 1.66 (6H) corresponding to protons from the crown ether, the SDFBP and the bisphenol A units, respectively (Figure 2, Table 1).

S(25)-PAEK and S(25)-C(50)-PAEK possess molar masses (M_n) of 33 and 19 kDa respectively, which are sufficient for preparing membranes. The polydispersity index of S(25)-PAEK measured by GPC ($M_w/M_n = 2.0$) is typical of polymers prepared by step growth polymerization methods. However S(25)-C(50)-PAEK has a relatively high polydispersity value ($M_w/M_n = 4.0$). We think that this high PDI index stems to a certain extent from the measurement method. This polymer features both crown ether units and sulfonate pendant groups, which likely interact with Li^+ due to presence of LiBr in the eluent and may influence the interactions with the stationary phase of the GPC column.²⁹

Table 1: Molecular characteristics of S(25)-PAEK and S(25)-C(50)-PAEK.

Polymer	M_n ^a (kDa)	PDI ^b -	Yield (%)	y ^c (%)	z ^d (%)
S(25)-PAEK	33	2.0	91	21	-
S(25)-C(50)-PAEK	19	4.0	88	25	43

^a M_n : number average molar mass by GPC, relative to polystyrene standards. ^b PDI: (M_w/M_n), polydispersity index. ^c y corresponds to the incorporated mol% SDFBP as determined by ^1H NMR. ^d z corresponds to the incorporated mol% 18C6 as determined by ^1H NMR.

FTIR was performed to confirm the chemical structure of the synthesized polymers. Figure 3 shows the FTIR spectra of S(25)-PAEK and S(25)-C(50)-PAEK. The absorbance at 1650 cm^{-1} indicates the carbonyl stretching of Ar-C(=O)-Ar moieties while the absorbance bands appearing at 1590 cm^{-1} and 1497 cm^{-1} are due to C=C stretching of aromatics. S(25)-PAEK and S(25)-C(50)-PAEK exhibit an absorbance at 1236 cm^{-1} attributed to the formation of (Ar-O-Ar) linkages during polycondensation. The characteristic asymmetric and symmetric stretching vibrations of sodium sulfonate are visible at 1080 cm^{-1} and 1013 cm^{-1} .²⁵ Furthermore, S(25)-C(50)-PAEK shows the C-O-C stretching signals of the crown ether at 1128 cm^{-1} .^{30,31} This absorbance band confirms the presence of crown ether moieties in the polymer chain.

Figure 3: FTIR spectra of *S*(25)-PAEK and *S*(25)-C(50)-PAEK.

Thermal analysis

The thermal properties of the synthesized polymers were characterized by TGA and DSC under N₂ atmosphere; these results are provided in Figure 4 and Table 2. As shown in Figure 4, *S*-(25)-PAEK exhibits a two-stage degradation profile.

Figure 4: TGA curves of *S*(25)-PAEK and *S*(25)-C(50)-PAEK copolymers.

The first weight loss between 200 °C and 250 °C is due to desulfonation of the polymer chains.³² The second weight loss step, with a maximum at 490 °C, indicates decomposition of the aromatic units.^{33, 34} *S*(25)-C(50)-PAEK undergoes the first weight loss around 180 °C, which can be ascribed to the loss of residual NMP. The thermal degradation of *S*(25)-C(50)-PAEK starts around 400 °C, probably linked to loss of sulfonic acid and crown ether groups, and continued with the decomposition of the thermally stable aromatic groups of *S*(25)-CF(50)-PAEK.²⁹

Table 2: Thermal properties of S(25)-PAEK and S(25)-C(50)-PAEK copolymers.

Polymer	T _g ^{a)} (°C)	T ₅ ^{b)} (°C)	Char yield ^{c)} (%)
S(25)-PAEK	180	454	47
S(25)-C(50)-PAEK	167	404	45

a) Glass transition temperature; b) Temperature corresponding to 5% weight loss; c) Residual mass percentage after heating to 900 °C.

As shown in Table 2, crown ether incorporation influences the thermal stability of the polymer. S(25)-PAEK displays high thermal stability with a weight loss of only 5% at 454 °C. Crown ether moieties on the other hand are relatively sensitive to thermal degradation.²⁹ Therefore, S(25)-C(50)-PAEK displays a lower thermal stability (5% weight loss at 404 °C already). The char yields for S(25)-PAEK and the S(25)-C(50)-PAEK are 47% and 45%, respectively.

DSC was employed in order to study the glass transition temperatures (T_g) of S(25)-PAEK and S(25)-C(50)-PAEK. S(25)-PAEK shows a T_g of 180 °C, which is in good agreement with literature values.^{35,36} S(25)-C(50)-PAEK has a T_g of 167 °C, so the T_g of the crown ether polymer is lowered by around 13 °C by the introduction of the crown ether in the polymer backbone. Such behavior can be attributed to the aliphatic ether bonds present in these macrocycles. The aliphatic bonds enhance chain flexibility; as a consequence the T_g of the polymer decreases. In addition, the presence of the crown ether increases the free volume of the polymer and contributes to a decrease in T_g. Previously, we observed similar behavior for synthesized SPAEK with 4,4'(5')-di(hydroxybenzo)-18-crown-6.²⁹ Moreover, T_g decreases have also been observed for polyamides and polyimides after incorporation of crown ether units.³⁷

Properties of S(25)-PAEK and S(25)-C(50)-PAEK membranes

Table 3 summarizes the membrane thickness, water swelling, and ion exchange capacity (IEC) of the S(25)-PAEK and S(25)-C(50)-PAEK membranes. Both membranes have comparable thicknesses. Water content is an important parameter affecting ion transport in membranes, as well as the actuation performance of IPMCs.¹ The mobile cations move through the water swollen polymer and water facilitates cation transport from sulfonate group to sulfonate group.^{38,39} Therefore, the mobility of the ions depend on the swelling

state of the matrix.³⁸ The water swelling of S(25)-PAEK and S(25)-C(50)-PAEK membranes is 17 % and 19 %, respectively, which is comparable to values reported for Nafion membranes, which are in the range of 16% to 24%.^{1,9,10,13,40} The S(25)-C(50)-PAEK membrane seems to exhibit slightly higher water swelling compared with the S(25)-PAEK membrane. This can be due to the hydrophilic ether groups of the crown ether,⁴¹ differences are however marginal.

Table 3 S(25)-PAEK and S(25)-C(50)-PAEK membrane properties.

Membrane	d _{wet} (μm)	Swelling (%)	IEC (mol kg ⁻¹)
S(25)-PAEK	50 ± 5	17 ± 1	0.71 ± 0.01
S(25)-C(50)-PAEK	45 ± 3	19 ± 2	0.86 ± 0.01

The IEC is an important parameter for the performance of IPMC actuators. The IEC expresses the amount of available fixed (ionic) sites available for interaction with the mobile cations. So IPMCs with high IEC values have better actuation performance.¹⁷ The S(25)-PAEK and S(25)-C(50)-PAEK membranes have an IEC of 0.71 mol kg⁻¹ and 0.86 mol kg⁻¹, respectively. Incorporation of crown ether in the SPAEK backbone increases the IEC. Next to the sulfonate moieties of the sulfonated polymer, also dibenzo-18-crown-6 (DB18C6) can form a complex with Na⁺ and K⁺ ions due to ion–dipole interactions between the Na⁺ and K⁺ ion in the membrane and the negatively polarized oxygen of DB18C6.⁴² This adds up to the amount of sulfonate moieties present in the polymer and thus contributes to the observed IEC increase.

Morphology of the IPMC actuators

Figure 5 shows the surface and morphology of the S(25)-PAEK IPMC actuator. Figure 5 clearly shows the presence of a densely deposited Pt layer on the S(25)-PAEK membrane after one deposition cycle. Surfaces and cross sections of the corresponding membranes from the crown ether containing polymer are comparable.

The bending performance of IPMCs is strongly dependent upon the electrode properties.⁴³ The Pt coating plays an important role in terms of eliminating the voltage drop away from the contact electrode by decreasing the surface resistance of IPMCs.⁴⁴ The lower surface resistance enhances the current movement through the membrane, resulting in improved actuation performance.^{44,45}

Figure 5: HR-SEM images of a *S(25)-PAEK* membrane cross section without Pt coating, and b *S(25)-PAEK* IPMC actuator cross section, and c the surface of the actuator. Surfaces and cross sections of the corresponding membranes from the polymer containing also the crown ethers are comparable.

Repetitive reduction of the Pt layer during application of the electrode increases the hardness of the electrode and ensures a defect-free electrode layer.⁴⁵ An electrode layer with cracks on the surface has high electrical resistance, resulting in lower actuation performance.^{28,45} Moreover, such cracks are responsible for the formation of a porous layer that allows water evaporation from the membrane.²⁸ This combined effect of higher electrical resistance and water removal from the membrane lowers the actuation performance.^{28,45} Consequently, the actuator performance is sensitive to the electrode layer properties and thickness.⁴³

The SEM analysis shows that the Pt particles are homogeneously distributed over the electrode layer with a layer thickness of around 120 nm (0.120 μm). Typically, the Pt layer thickness ranges between 1 and 20 μm in order to produce large bending performances.^{17,28,40} The obtained electrode thicknesses in our work are rather thin compared to those reported in literature. Despite this, it still provides a uniform current distribution through the IPMC, albeit at a lower bending performance. Vargantwar et al. studied the effect of the Pt layer thickness on the actuation efficiency. The Pt electrode layer in their study was extremely thin after a single coating cycle, although the actual thickness is not specified in the paper. However, it allowed an uninterrupted current flow to obtain actuation.⁴³ Another example is a microvalve system based on a Nafion IPMC actuator coated with a 177 nm thin Pt electrode layer, in spite of the thinness of the layer, the actuator performed effectively.⁴⁶

Bending performance of S(25)-PAEK and S(25)-C(50)-PAEK actuators

The electromechanical bending of the membrane cantilevers was quantified by measuring the tip displacement with respect to time. Figure 6 shows the responses of the K^+ saturated S(25)-PAEK and S(25)-C(50)-PAEK actuators to a sinusoidal voltage applied at a frequency of 10 Hz. A similar bending response was also observed for the actuators in their Na^+ form. This bending was repeatedly observed and is due to the migration of hydrated cations (K^+ or Na^+ ions) and free water molecules under the sinusoidal voltage applied. The cations and water molecules migrate through the ionic channels, resulting in an asymmetric swelling of the IPMC matrix.^{47,48} The cathode side expands due to the accumulation of hydrated cations and free water molecules, whereas the anode side contracts. The effective transport of mobile ions and water to the cathode side drives the bending towards the anode side.^{28, 49}

Figure 6: The displacement of S(25)-PAEK and S(25)-C(50)-PAEK actuators under a 1.5 V sinusoidal voltage at 10 Hz.

As our focus was to develop a fast ion selective-responsive actuator, the bending performance of the S(25)-PAEK and S(25)-C(50)-PAEK IPMC actuators for both K^+ and Na^+ ions was compared at 1.5V at frequencies of 10 Hz, 15 Hz and 20 Hz.

As Figure 7 illustrates the incorporation of crown ether units in the polymer backbone improves the actuation performance. An increase of respectively 127 ± 26.5 nm and 88 ± 15.0 nm as maximum displacement is observed for the Na^+ saturated S(25)-C(50)-PAEK and the K^+ saturated S(25)-C(50)-PAEK actuator, at a voltage frequency of 10 Hz. Figure 7 shows that the maximum tip displacement of Na^+ saturated and K^+ saturated actuators decreases with increasing frequency from 10 Hz to 20 Hz.

Figure 7: Frequency dependent maximum displacement of S(25)-PAEK and S(25)-C(50)-PAEK actuators in Na⁺ and K⁺ form. Δd is the maximum displacement difference between S(25)-C(50)-PAEK and S(25)-PAEK actuators.

The reason for that is that the speed of the voltage polarity change at a certain point becomes faster relative to the migration speed of K⁺ and Na⁺ ions and water molecules, leading to less bending.¹⁷

Also, the Na⁺ saturated S(25)-PAEK and S(25)-C(50)-PAEK actuators exhibited slightly larger bending displacements than the K⁺ saturated S(25)-PAEK and S(25)-C(50)-PAEK actuators.⁵⁰ Na⁺ ions have an ionic radius of 1.02 Å, and are smaller than K⁺ ions (1.38 Å).⁵¹ However, Na⁺ has a bigger hydrated radius (2.80 Å) than K⁺ (2.30 Å).⁵² Electrochemical motion in the actuator is facilitated by migration of the hydrated ions towards the oppositely charged electrode. For this reason, the hydration state of the counterion plays an important role in determining the bending performance of the actuator. Guzman et al. formulated a model for the bending deformation of a Nafion IPMC actuator and compared the bending performance of the actuator for five different types of counter-ion systems. In agreement

with our result, their computational and experimental results also showed that the actuator saturated with Na^+ ions displayed larger bending deformation compared to the one saturated with K^+ ions.⁵³

For the S(25)-PAEK actuator, actuation is controlled by the sulfonate-cation interactions. In case of the S(25)-C(50)-PAEK actuator, in addition to sulfonate-cation interactions (Figure 8a), crown ether-cation complexation also plays a role in the bending performance. The crown ether polymer can bind the cation by sandwiching it between two crown ether units, forming a 2:1 complex (Figure 8b), but it can also accommodate the cation directly in the ring structure of the crown ether, leading to a 1:1 (Figure 8c) crown ether-to-cation complex.^{54,55} Moreover, also a SO_3^- unit and a crown ether can accommodate a cation together (Figure 8d).⁵⁶ Combined, these interactions increase the concentration of cations in the crown ether containing sulfonated polymer membrane relative to that in the sulfonated polymer without crown ethers, and consequently, also the bending performance is improved.

The difference in the maximum displacement of the S(25)-PAEK ($\text{IEC}=0.71 \text{ kg mol}^{-1}$) and the S(25)-C(50)-PAEK ($\text{IEC}=0.86 \text{ kg mol}^{-1}$) actuators may originate from the difference in their IEC and water swelling properties. The IEC determines the amount of available fixed positions for cation capturing. Incorporation of crown ether in the SPAEK backbone increases the IEC owing to the crown ether-cation interactions mentioned above. The higher IEC indicates that more mobile cations can migrate to the anode side, resulting in a larger bending displacement. Moreover, also the water swelling slightly increases after incorporation of crown ether. This also contributes to some extent to the larger bending displacement. However, the contribution of the different effects cannot be quantified.

The Na^+ saturated S(25)-C(50)-PAEK actuator exhibited larger bending displacement relative to the native S(25)-PAEK actuator. On the other hand, the K^+ saturated S(25)-C(50)-PAEK actuator displayed a bending displacement comparable to that of the K^+ saturated S(25)-PAEK actuator at a frequency of 15 Hz and 20 Hz. This behavior may be due to the interactions between the crown ether and the K^+ ion. Dibenzo-18-crown-6 binds selectively to K^+ ions and complexes more strongly with K^+ ions compared to Na^+ ions.^{42,55,57}

Figure 8: Schematic illustration of S(25)-C(50)-PAEK IPMC actuator; a) sulfonate-cation interaction, b) 2:1 crown ether-cation complexation, c) 1:1 crown ether-cation complexation, and d) accommodation of cation between SO_3^- unit and a crown ether.

The weaker interaction between the crown ethers and Na^+ ions means that the Na^+ ions can easily dissociate from the crown ethers under an applied potential. Especially at a frequency of 20 Hz, there was hardly any improvement in performance of the K^+ saturated S(25)-C(50)-PAEK actuator relative to the S(25)-PAEK actuator. We hypothesize that at this rapid polarity change, there is not sufficient time for K^+ ions to dissociate from the crown ether moieties. Consequently, only K^+ ions interacting with the sulfonate groups (SO_3^-) contribute to the bending response at a frequency of 20 Hz.

The bending performance of the S(25)-C(50)-PAEK actuator is compared with previously reported results. The displacement was normalized for different-sized IPMCs and the strain was calculated according to a formula proposed in literature.^{17,58} The maximum strain values for the Na^+ and K^+ forms of the S(25)-C(50)-PAEK actuator at a frequency of 10 Hz are $(0.53 \pm 0.03) \times 10^{-6}$ and $(0.47 \pm 0.01) \times 10^{-6}$, respectively. This is almost 400 times lower than the reported value for the Li^+ form of a sulfonated polyphenylsulfone based IPMC actuator under 1.5V at a frequency of 10 Hz.¹⁷ The Li^+ form of a sulfonated poly(ether ether ketone) (SPEEK) IPMC actuator also exhibited a higher bending strain than reported in the present work, but that was only 9 times higher under 1.5V at a frequency of 7 Hz.¹⁸

Although the bending performance of the S(25)-C(50)-PAEK actuator was without any doubt significantly lower than the reported values for other sulfonated polymers, crown ether incorporation increased the bending displacement by 28 % and 20 % for the Na^+ and

K⁺ ionic forms of the S(25)-C(50)-PAEK actuator relative to the native S(25)-PAEK actuator. Also, owing to the binding ability of crown ethers with specific ions, the S(25)-C(50)-PAEK actuator exhibited an ion selective actuation performance, which is not observed for the other sulfonated materials without crown ethers. That brings us to the conclusion that the idea of incorporating crown ether moieties into the sulfonated polymer backbone can have an important contribution to the development of ion selective biomimetic actuators. Moreover, the performance of this actuator can potentially be tuned further by varying the amount and type of crown ether incorporation, the sulfonation degree of the polymer, and the thickness of the membrane and the electrode layers.

5.4 Conclusions

Sulfonated PAEK (SPAEEK) and crown ether containing SPAEEK were synthesized with reasonably high molecular weights. Structural and thermal properties of the synthesized polymers were characterized using NMR, FTIR, TGA, and DSC. IPMC actuators were fabricated by electroless chemical deposition of a Pt layer on both sides of membranes, resulting in an electrode layer thickness of around 120 nm. The actuation experiments demonstrated that the electromechanical response and bending degree is counter-ion specific. For the actuators based on S(25)-PAEK and S(25)-C(50)-PAEK, the Na⁺ form of the actuators showed larger bending displacement than the K⁺ form. The incorporation of crown ether units in the polymer backbone resulted in an improved and ion-related bending displacement. This performance improvement can be attributed to the higher ion exchange capacity and increased water swelling properties of the membrane as well as to the ion-selective binding ability of the crown ether. Although current bending performance is significantly lower than what is reported in literature, the performance of this actuator can be further improved by varying the amount and type of crown ether incorporated, the sulfonation degree of the polymer, and the thickness of the membrane and the electrode layers.

Acknowledgments

Sinem Tas acknowledges the Industrial Partnership Program (IPP) “Spectroscopic analysis of particles in water” of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). This IPP is co-financed by Wetsus, Centre of Excellence for Sustainable Water Technology, as part of Wetsus’ TTI program. Wetsus is co-funded by the Dutch Ministry of Economics, Agriculture and Innovation. Bram Zoetebier acknowledges NanoNextNL, a micro and nanotechnology consortium of the government of the Netherlands and 130 partners. We especially thank Dr. Sertan Sukas for fruitful discussions and Remco Sanders for his help during laser Doppler vibrometer measurements.

Appendix

Figure A1: a) ^1H NMR spectrum, b) structure and c) ^{13}C NMR spectrum of SPAEK.

References

1. Jung, J.-H.; Jeon, J.-H.; Sridhar, V.; Oh, I.-K. Electro-active graphene–Nafion actuators. *Carbon* **2011**, *49* (4), 1279-1289.
2. Smela, E. Conjugated polymer actuators for biomedical applications. *Adv Mater* **2003**, *15* (6), 481-494.
3. Yeom, S. W.; Oh, I. K. A biomimetic jellyfish robot based on ionic polymer metal composite actuators. *Smart Mater. Struct.* **2009**, *18* (8), 1-10.
4. Mirfakhrai, T.; Madden, J. D. W.; Baughman, R. H. Polymer artificial muscles. *Mater Today* **2007**, *10* (4), 30-38.
5. Shahinpoor, M.; Bar-Cohen, Y.; Simpson, J. O.; Smith, J. Ionic polymer-metal composites (IPMCs) as biomimetic sensors, actuators and artificial muscles - a review. *Smart Mater. Struct.* **1998**, *7* (6), 15-30.
6. Ismail, Y. A.; Martinez, J. G.; Al Harrasi, A. S.; Kim, S. J.; Otero, T. F. Sensing characteristics of a conducting polymer/hydrogel hybrid microfiber artificial muscle. *Sensor Actuat B-Chem* **2011**, *160* (1), 1180-1190.
7. Bay, L.; West, K.; Sommer-Larsen, P.; Skaarup, S.; Benslimane, M. A conducting polymer artificial muscle with 12% linear strain. *Adv Mater* **2003**, *15* (4), 310-313.
8. Chung, C. K.; Fung, P. K.; Hong, Y. Z.; Ju, M. S.; Lin, C. C. K.; Wu, T. C. A novel fabrication of ionic polymer-metal composites (IPMC) actuator with silver nano-powders. *Sensors and Actuators B: Chemical* **2006**, *117* (2), 367-375.
9. Han, M. J.; Park, J. H.; Lee, J. Y.; Jho, J. Y. Ionic polymer-metal composite actuators employing radiation-grafted fluoropolymers as ion-exchange membranes. *Macromol Rapid Comm* **2006**, *27* (3), 219-222.
10. Lee, J.-W.; Hong, S. M.; Kim, J.; Koo, C. M. Novel sulfonated styrenic pentablock copolymer/silicate nanocomposite membranes with controlled ion channels and their IPMC transducers. *Sens. Actuator B-Chem* **2012**, *162* (1), 369-376.
11. Nemat-Nasser, S.; Wu, Y. X. Tailoring the actuation of ionic polymer-metal composites. *Smart Mater. Struct.* **2006**, *15* (4), 909-923.
12. Duncan, A. J.; Leo, D. J.; Long, T. E. Beyond Nafion: Charged macromolecules tailored for performance as ionic polymer transducers. *Macromolecules* **2008**, *41* (21), 7765-7775.
13. Tang, Y.; Xue, Z.; Zhou, X.; Xie, X.; Tang, C.-Y. Novel sulfonated polysulfone ion exchange membranes for ionic polymer-metal composite actuators. *Sens. Actuator B-Chem* **2014**, *202* (4), 1164-1174.
14. Lee, J.-W.; Kim, J.-H.; Goo, N. S.; Lee, J. Y.; Yoo, Y.-T. Ion-conductive poly(vinyl alcohol)-based IPMCs. *Journal of Bionic Engineering* **2010**, *7* (1), 19-28.
15. Inamuddin; Khan, A.; Jain, R. K.; Naushad, M. Development of sulfonated poly(vinyl alcohol)/polypyrrole based ionic polymer metal composite (IPMC) actuator and its characterization. *Smart Mater Struct* **2015**, *24* (9) 1-14.
16. Luqman, M.; Lee, J.-W.; Moon, K.-K.; Yoo, Y.-T. Sulfonated polystyrene-based ionic polymer-metal composite (IPMC) actuator. *J Ind Eng Chem* **2011**, *17* (1), 49-55.

17. Tang, Y. J.; Chen, C.; Ye, Y. S.; Xue, Z. G.; Zhou, X. P.; Xie, X. L. The enhanced actuation response of an ionic polymer-metal composite actuator based on sulfonated polyphenylsulfone. *Polym Chem* **2014**, *5* (20), 6097-6107.
18. Jeon, J.-H.; Kang, S.-P.; Lee, S.; Oh, I.-K. Novel biomimetic actuator based on SPEEK and PVDF. *Sens. Actuator B-Chem* **2009**, *143* (1), 357-364.
19. Jentsch, T. J.; Hubner, C. A.; Fuhrmann, J. C. Ion channels: Function unravelled by dysfunction. *Nat Cell Biol* **2004**, *6* (11), 1039-1047.
20. Fertig, N.; Klau, M.; George, M.; Blick, R. H.; Behrends, J. C. Activity of single ion channel proteins detected with a planar microstructure. *Appl Phys Lett* **2002**, *81* (25), 4865-4867.
21. Liu, H. M.; Jameson, C. J.; Murad, S. Molecular dynamics simulation of ion selectivity process in nanopores. *Mol Simulat* **2008**, *34* (2), 169-175.
22. Marrone, T. J.; Hartsough, D. S.; Merz, K. M. Determination of atomic charges including solvation and conformational effects. *J Phys Chem-Us* **1994**, *98* (4), 1341-1343.
23. Roks, M. F. M.; Nolte, R. J. M. Biomimetic macromolecular chemistry - design and synthesis of an artificial ion channel based on a polymer containing cofacially stacked crown-ether rings - incorporation in dihexadecyl phosphate vesicles and study of cobalt ion-transport. *Macromolecules* **1992**, *25* (20), 5398-5407.
24. Savoie, J. D.; Otis, F.; Burck, J.; Ulrich, A. S.; Voyer, N. Crown ether helical peptides are preferentially inserted in lipid bilayers as a transmembrane ion channels. *Biopolymers* **2015**, *104* (4), 427-433.
25. Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J. I.; Yonetake, K.; Masuko, T.; Teramoto, T. Synthesis and characterization of aromatic poly(ether sulfone)s containing pendant sodium-sulfonate groups. *J Polym Sci Pol Chem* **1993**, *31* (4), 853-858.
26. Heiner S., Preparation and characterization of ion exchange membranes, Elsevier, 2004, 89-146.
27. Takenaka, H.; Torikai, E.; Kawami, Y.; Wakabayashi, N. Solid polymer electrolyte water electrolysis. *Int J Hydrogen Energy* **1982**, *7* (5), 397-403.
28. Shahinpoor, M.; Kim, K. J. Ionic polymer-metal composites: I. Fundamentals. *Smart Mater. Struct.* **2001**, *10* (4), 819-833.
29. Zoetebier B., Tas. S., Vancso G. J., Nijmeijer K., Hempenius M. A. Synthesis of poly(arylene ether ketone)s bearing skeletal crown ether units for cation exchange membranes. *J. Polym. Sci. A Polym. Chem.* 2015, *53* (23), 2786-2793. 30.
30. Zhu, H.; Du, M. L.; Zou, M. L.; Xu, C. S.; Li, N.; Fu, Y. Q. Facile and green synthesis of well-dispersed Au nanoparticles in PAN nanofibers by tea polyphenols. *J Mater Chem* **2012**, *22* (18), 9301-9307.
31. Dulak, M.; Bergougnant, R.; Fromm, K. M.; Hagemann, H. R.; Robin, A. Y.; Wesolowski, T. A. Water trapped in dibenzo-18-crown-6: Theoretical and spectroscopic (IR, Raman) studies. *Spectrochim Acta A* **2006**, *64* (2), 532-548.
32. Harrison, W. L.; Wang, F.; Mecham, J. B.; Bhanu, V. A.; Hill, M.; Kim, Y. S.; McGrath, J. E. Influence of the bisphenol structure on the direct synthesis of

- sulfonated poly(arylene ether) copolymers. I. *J Polym Sci Pol Chem* **2003**, *41* (14), 2264-2276.
33. Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. Direct polymerization of sulfonated poly(arylene ether sulfone) random (statistical) copolymers: candidates for new proton exchange membranes. *J Membrane Sci* **2002**, *197* (1-2), 231-242.
 34. Montaudo, G.; Puglisi, C.; Samperi, F. Primary thermal-degradation processes of poly(ether ketone) and poly(ether ketone) poly(ether-sulfone) copolymers investigated by direct pyrolysis mass-spectrometry. *Macromol Chem Phys* **1994**, *195* (4), 1241-1256.
 35. Swier, S.; Chun, Y. S.; Gasa, J.; Shaw, M. T.; Weiss, R. A. Sulfonated poly(ether ketone ketone) ionomers as proton exchange membranes. *Polym Eng Sci* **2005**, *45* (8), 1081-1091.
 36. Liu, B. J.; Robertson, G. P.; Kim, D. S.; Guiver, M. D.; Hu, W.; Jiang, Z. H. Aromatic poly(ether ketone)s with pendant sulfonic acid phenyl groups prepared by a mild sulfonation method for proton exchange membranes. *Macromolecules* **2007**, *40* (6), 1934-1944.
 37. Maya, E. M.; Lozano, A. E.; de la Campa, J. G.; de Abajo, J. Soluble polyamides and polyimides functionalized with benzo-15-crown-5-pendant groups. *Macromol Rapid Comm* **2004**, *25* (4), 592-597.
 38. Saito, M.; Arimura, N.; Hayamizu, K.; Okada, T. Mechanisms of ion and water transport in perfluorosulfonated ionomer membranes for fuel cells. *J Phys Chem B* **2004**, *108* (41), 16064-16070.
 39. Chen, C.-Y.; Garnica-Rodriguez, J. I.; Duke, M. C.; Costa, R. F. D.; Dicks, A. L.; da Costa, J. C. D. Nafion/polyaniline/silica composite membranes for direct methanol fuel cell application. *J Power Sources* **2007**, *166* (2), 324-330.
 40. Lee, J. W.; Yoo, Y. T.; Lee, J. Y. Ionic polymer-metal composite actuators based on triple-layered polyelectrolytes composed of individually functionalized layers. *Acs Appl Mater Inter* **2014**, *6* (2), 1266-1271.
 41. Bartsch, R. A.; Yang, I. W.; Jeon, E. G.; Walkowiak, W.; Charewicz, W. A. selective transport of alkali-metal cations in solvent-extraction by proton-ionizable dibenzocrown ethers. *J Coord Chem* **1992**, *27* (1-3), 75-85.
 42. Maleknia, S.; Brodbelt, J. Cavity-size-dependent dissociation of crown-ether ammonium ion complexes in the gas-phase. *J Am Chem Soc* **1993**, *115* (7), 2837-2843.
 43. Vargantwar, P. H.; Roskov, K. E.; Ghosh, T. K.; Spontak, R. J. Enhanced biomimetic performance of ionic polymer-metal composite actuators prepared with nanostructured block ionomers. *Macromol Rapid Comm* **2012**, *33* (1), 61-68.
 44. Shahinpoor, M.; Kim, K. J. The effect of surface-electrode resistance on the performance of ionic polymer-metal composite (IPMIC) artificial muscles. *Smart Mater. Struct.* **2000**, *9* (4), 543-551.
 45. Kim, S. M.; Kim, K. J. Palladium buffer-layered high performance ionic polymer-metal composites. *Smart Mater. Struct.* **2008**, *17* (3).

46. Yun, J. S.; Yang, K. S.; Choi, N. J.; Lee, H. K.; Moon, S. E.; Kim, D. H. Microvalves based on ionic polymer-metal composites for microfluidic application. *J Nanosci Nanotechnol* **2011**, *11* (7), 5975-5979.
47. Nemat-Nasser, S.; Li, J. Y. Electromechanical response of ionic polymer-metal composites. *J Appl Phys* **2000**, *87* (7), 3321-3331.
48. Lee, J. Y.; Wang, H. S.; Han, M. J.; Cha, G. C.; Jung, S. H.; Lee, S.; Jho, J. Y. Performance enhancement of ionic polymer-metal composite actuators based on radiation-grafted Poly(ethylene-co-tetrafluoroethylene). *Macromol Res* **2011**, *19* (10), 1014-1021.
49. Park, J. K.; Jones, P. J.; Sahagun, C.; Page, K. A.; Hussey, D. S.; Jacobson, D. L.; Morgan, S. E.; Moore, R. B. Electrically stimulated gradients in water and counterion concentrations within electroactive polymer actuators. *Soft Matter* **2010**, *6* (7), 1444-1452.
50. Nemat-Nasser, S.; Wu, Y. X. Comparative experimental study of ionic polymer-metal composites with different backbone ionomers and in various cation forms. *J Appl Phys* **2003**, *93* (9), 5255-5267.
51. Marcus, Y. A simple empirical model describing the thermodynamics of hydration of ions of widely varying charges, sizes, and shapes. *Biophys Chem* **1994**, *51* (2), 111-127.
52. Izquierdo-Gil, M. A.; Barragán, V. M.; Villaluenga, J. P. G.; Godino, M. P. Water uptake and salt transport through Nafion cation-exchange membranes with different thicknesses. *Chem Eng Sci* **2012**, *72*, 1-9.
53. Guzman, J. F.; Cortes, J. A.; Fuentes, A.; Kobayashi, T.; Hoshina, Y. Modeling the displacement in three-layer electroactive polymers using different counter-ions by a phase transformation approach. *J Appl Polym Sci* **2009**, *112* (6), 3284-3293.
54. Kimura, K.; Yoshinaga, M.; Kitazawa, S.; Shono, T. Synthesis of poly(vinyl alcohol)-based poly(crown ether)s and permeability of their polymeric membranes. *J Polym Sci Pol Chem* **1983**, *21* (9), 2777-2785.
55. Grootenhuys, P. D. J.; Kollman, P. A. Molecular mechanics and dynamics studies of crown ether cation interactions - free-energy calculations on the cation selectivity of dibenzo-18-crown-6 and dibenzo-30-crown-10. *J Am Chem Soc* **1989**, *111* (6), 2152-2158.
56. Okada, T. Complexation of polyethers in cation exchange resin and application to chromatographic determination of complexation constants in solution. *J Phys Chem B* **1998**, *102* (16), 3053-3059.
57. Nakajima, M.; Kimura, K.; Shono, T. Ion-Chromatographic Behavior of Silica-Gels Modified by Poly(Crown Ether)s and Bis(Crown Ether)s of Benzo-18-Crown-6. *B Chem Soc Jpn* **1983**, *56* (10), 3052-3056.
58. Kim, O.; Shin, T. J.; Park, M. J. Fast low-voltage electroactive actuators using nanostructured polymer electrolytes. *Nat Commun* **2013**, *4*, 2208-2217

6

General discussion and outlook

Seawater has been considered as the largest lithium repository. Although there are many drawbacks associated with seawater mining (e.g. operating cost, complexity of the seawater, energy intensive process) that might limit its application, a great deal of interest has been devoted to the development of new materials to extract metals from seawater and brines rejected by desalination plants.¹ Development of a membrane containing functional groups that can bind the specific ion of interest is crucial for the extraction of low concentration ions. Within this context, in this thesis, the synthesis of crown ether polymers, their possible applications as an ion exchange membrane (IEM) and as an ionic polymer metal composite actuator (IPMC) are investigated and discussed. In addition to those applications, the monovalent ion adsorption potential of crown ether functionalized electrospun nanofibers is also studied.

The key aspect in the recovery of lithium from seawater is the development of selective, stable membranes. Crown ethers are well known for the highly selective capturing of specific ions, a mechanism based on crown ether-metal ion host-guest interactions. To prevent leaching out (which occurs when polymer and crown ether are blended), the direct incorporation of crown ether units into the polymer main chain, as repeating units, is investigated. Crown ether (4,4'(5')-di(hydroxybenzo)-18-crown-6) containing sulfonated poly(arylene ether ketone) (SPAEEK) was synthesized and diffusion experiments proved that the crown ether selectively captures the targeted ion. To further improve the properties of the material, it was blended with sulfonated poly(ether ether ketone) (SPEEK), which improved the K^+ over Li^+ selectivity by a factor of nearly 4 compared to the native polymer blend without crown ether.

A different approach was also followed to prepare a selective lithium adsorbent. For that, crown ether dibenzo-18-crown-6 (DB18C6) was incorporated during the electrospinning of polyacrylonitrile (PAN) nanofibers. The developed nanofiber adsorbents showed selectivity for K^+ ions over Li^+ and Na^+ ions.

Finally, crown ether containing polymer sulfonated poly(arylene ether ketone) (SPAEEK) was synthesized by step growth polymerization of di(4-fluorobenzophenone)-18-crown-6 in the presence of Bisphenol A, 4,4'-difluorobenzophenone and sulfonated 4,4'-difluorobenzophenone and its actuation performance was evaluated as a way to mimic muscle contraction. The actuator showed ion sensitive bending displacement and the

bending displacement improved by nearly 30% compared to that of SPAEK without the crown ether.

Crown ether polymer-ion exchange membranes

It is known that an enormous amount of lithium is present in the seawater.¹ Extraction of lithium from seawater and brine, rejected by desalination plants, is technically viable. However, the most difficult problem is the complexity of the system. Seawater is dominated by Na^+ ions and many others (e.g K^+ , Ca^{2+} , Mg^{2+}) are present in the seawater¹. Therefore, development of efficient and cost effective membrane materials and separation systems is crucial to extract Li^+ from seawater and brine with high recovery.

Crown ethers have excellent binding properties with specific metals. In addition crown ethers show high selectivities for the specific ion. However, their industrial scale applications are restricted due to their high price. Attempts have been made to impregnate crown ethers into ion exchange membrane matrices for use in electrodialysis applications but a major drawback of crown ether impregnation for these membranes was that the crown ethers leached out under the applied electric potentials.²⁻⁴ From economic and environmental point of view recovery of crown ethers is very important. To overcome the leaching out problem, in Chapter 2 and Chapter 3, the synthesis and preparation of thermally and hydrolytically stable membranes of poly(arylene ether ketone) with crown ether units in the main chain are described. Although the presence of the crown ether in the polymer main chain changes the relative mobility of the ions (Li^+ and K^+) in the membrane, the large-scale applications of those membranes may not be commercially viable. First of all, functionalization of crown ethers is time consuming and includes many purification steps, which adds considerably to the cost of membrane. Secondly, at longer operation times, the complexation rate diminishes due to the lack of available crown ether binding sites. Therefore, continuous regeneration of membranes is required to overcome this decreasing availability of the crown ether adsorption sites.

The idea of incorporating crown ether moieties into the SPAEK polymer backbone is potentially more attractive for smaller scale applications, such as in ionic polymer metal composite (IPMC)s actuators. The most important challenges for the IPMC actuator design are the achievement of large electromechanical bending, fast switching response, and low operating voltages.⁵ With respect to this, crown ether incorporated ionic polymers exhibits a

potential to improve the electromechanical bending performance. The actuation performance increased by 28 % and 20 % for Na⁺ and K⁺ ionic forms compared to the ionic polymer (SPAEC) without crown ether.

Membrane adsorbents

There are two possible strategies to extract lithium from seawater with membranes. The first one is to pump the seawater through an ion selective membrane that separates the lithium ions from the water and the other ions. This, however, is relatively costly in terms of energy requirements. The second strategy is the use of membrane adsorbents. In this way, when in contact with seawater, lithium can be selectively adsorbed on the active membrane sites.¹ This approach is relatively simple, but requires periodic regeneration of the adsorbent.

Owing to the high binding selectivities of crown ethers, considerable research interest has been devoted to the design of crown ether adsorbents for the selective recovery of specific ions.⁶⁻⁸ To enable cost-effective membrane adsorbent production, researchers have developed membranes with containing inorganic ion exchange materials that show high selectivity for lithium ions only.⁹⁻¹¹ Lithium manganese oxide is a widely used adsorbent for lithium and its lithium adsorption capacity changes between 30 mg/g_{adsorbent} and 40 mg/g_{adsorbent}.¹²

As an alternative to lithium manganese oxide, titanium oxide nanotubes have been studied as anode material for rechargeable batteries and it possesses a large lithium intercalation capacity.^{13,14} Recently, Moazeni et. al. reported the synthesis of titanium dioxide nanotubes as lithium adsorbent. Titanium dioxide nanotubes exhibited an adsorption capacity of 39.4 mg/g_{adsorbent}, which is quite comparable with the adsorption capacity of lithium manganese oxide.¹⁵ Therefore, preparation of titanium oxide nanotube impregnated membranes could allow the selective adsorption of lithium ions from a mixture of ions and those membranes could be potentially used in filtration applications. Moreover, electrochemical recovery of lithium ions from aqueous mixed ion systems could be possible using titanium oxide nanotube based electrodes.

Although lithium selective membrane adsorbents may be more promising and efficient compared to lithium selective ion exchange membranes, huge amounts of water are still required to be processed in order to meet the current lithium demand. For this reason, a

larger mass of membranes are needed for the recovery and the cost for regeneration of the adsorbent still remains an obstacle to overcome.¹

Final remarks

Owing to the growing interest in seawater mining, there has been much research carried out to assess the feasibility of extracting valuable metals from seawater and brine.^{1, 16} According to those studies, the most viable approach to recover metals from seawater is the implementation of metal extraction systems into desalination plants. Although, the processing of desalination waste streams has technical, cost and energy considerations, the feasibility of recovering lithium also depends on the future lithium demand and its price fluctuations in the market. Until now, those assessments show that it is unlikely that lithium recovery from seawater and desalination brines will become economically feasible in the near future.¹ It is a well-known fact that lithium has a great economic importance. The rapid growth of the lithium ion and lithium polymer batteries market and the potential applications of lithium in the nuclear fusion process seem likely to increase the dependency on lithium.¹⁷ Therefore, development of a cost effective and highly selective membrane may increase the efficiency and reduce the cost of seawater and desalination brine mining.

At present, there is the amount of lithium deposits is sufficient and most of them are concentrated in Argentina, Chile and Bolivia. However, government regulations greatly affect the lithium supply and its market price.¹⁷ In order to minimize the risk of accessibility of the raw material, current research interests have shifted towards to development of effective and feasible lithium battery recycling technologies to fulfill the lithium demand in the future and also ensure its sustainable use.¹⁸

References

1. Bardi, U. Extracting Minerals from Seawater: An Energy Analysis. *Sustainability* **2010**, *2* (4), 980.
2. Chaudhury, S.; Bhattacharyya, A.; Goswami, A. electrodriven ion transport through crown ether-Nafion composite membrane: enhanced selectivity of Cs^+ over Na^+ by ion gating at the surface. *Ind Eng Chem Res* **2014**, *53* (21), 8804-8809.
3. Chaudhury, S.; Bhattacharyya, A.; Agarwal, C.; Goswami, A. Temperature dependence of ion and water diffusion in crown ether loaded Nafion matrix. *J Phys Chem B* **2011**, *115* (30), 9395-9400.
4. Bhattacharyya, A.; Goswami, A. Effect of cation driven loading of dibenzo-18-crown-6 in nafion-117 membrane on the diffusion and transport behavior of alkali metal ions. *J Phys Chem B* **2009**, *113* (39), 12958-12963.
5. Kim, O.; Shin, T. J.; Park, M. J. Fast low-voltage electroactive actuators using nanostructured polymer electrolytes. *Nat Commun* **2013**, *4*.
6. Torrejos, R. E. C.; Nisola, G. M.; Park, M. J.; Shon, H. K.; Seo, J. G.; Koo, S.; Chung, W. J. Synthesis and characterization of multi-walled carbon nanotubes-supported dibenzo-14-crown-4 ether with proton ionizable carboxyl sidearm as Li^+ adsorbents. *Chem Eng J* **2015**, *264*, 89-98.
7. Duman, O.; Ayranci, E. Attachment of benzo-crown ethers onto activated carbon cloth to enhance the removal of chromium, cobalt and nickel ions from aqueous solutions by adsorption. *J Hazard Mater* **2010**, *176* (1-3), 231-238.
8. Luo, X. B.; Guo, B.; Luo, J. M.; Deng, F.; Zhang, S. Y.; Luo, S. L.; Crittenden, J. Recovery of lithium from wastewater using development of Li ion-imprinted polymers. *Acc Sustain Chem Eng* **2015**, *3* (3), 460-467.
9. Umeno, A.; Miyai, Y.; Takagi, N.; Chitrakar, R.; Sakane, K.; Ooi, K. Preparation and adsorptive properties of membrane-type adsorbents for lithium recovery from seawater. *Ind Eng Chem Res* **2002**, *41* (17), 4281-4287.
10. Chung, K.-S.; Lee, J.-C.; Kim, W.-K.; Kim, S. B.; Cho, K. Y. Inorganic adsorbent containing polymeric membrane reservoir for the recovery of lithium from seawater. *J Membrane Sci* **2008**, *325* (2), 503-508.
11. Hoshino, T. Innovative lithium recovery technique from seawater by using world-first dialysis with a lithium ionic superconductor. *Desalination* **2015**, *359*, 59-63.
12. Chitrakar, R.; Kanoh, H.; Miyai, Y.; Ooi, K. Recovery of lithium from seawater using manganese oxide adsorbent ($\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$) derived from $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$. *Ind Eng Chem Res* **2001**, *40* (9), 2054-2058.
13. Li, J. R.; Tang, Z. L.; Zhang, Z. T. Preparation and novel lithium intercalation properties of titanium oxide nanotubes. *Electrochem Solid St* **2005**, *8* (6), A316-A319.
14. Lo, W.-C.; Chu, H.-J.; He, J.-L. Micro- and nanomorphology coexisting in titanium dioxide coating for application as anode material in secondary lithium-ion batteries. *Thin Solid Films* **2015**, *579*, 14-20.

15. Moazeni, M.; Hajipour, H.; Askari, M.; Nusheh, M. Hydrothermal synthesis and characterization of titanium dioxide nanotubes as novel lithium adsorbents. *Mater Res Bull* **2015**, *61*, 70-75.
16. Shahmansouri, A.; Min, J.; Jin, L. Y.; Bellona, C. Feasibility of extracting valuable minerals from desalination concentrate: a comprehensive literature review. *J Clean Prod* **2015**, *100*, 4-16.
17. Ebensperger, A.; Maxwell, P.; Moscoso, C. The lithium industry: Its recent evolution and future prospects. *Resources Policy* **2005**, *30* (3), 218-231.
18. Xu, J.; Thomas, H. R.; Francis, R. W.; Lum, K. R.; Wang, J.; Liang, B. A review of processes and technologies for the recycling of lithium-ion secondary batteries. *J Power Sources* **2008**, *177* (2), 512-527.

Summary

Development of functional membranes that are capable of selectively recognizing and transporting ions have key importance for the recovery and separation of specific ions (e.g. K^+ , Li^+ , Na^+) from multicomponent mixtures. In this thesis, new membrane materials based on crown ether-metal ion host-guest interactions are developed. Crown ethers are widely used as guest molecules for ions and are able to bind selectively specific cationic species. The main focus of this thesis is the direct incorporation of crown ether units into the polymer main chain, as repeating units, in contrast to the blending of crown ethers with polymers or postfunctionalization of linear polymers. A major disadvantage of the two last options is the lower effectiveness or washing out of the selective crown ether. With the in-chain crown ether units, crown ether polymers show unique membrane functions, i.e. the selective binding of a specific ion to a very high degree of specificity.

Chapter 2 describes the synthesis of a sulfonated poly(arylene ether ketone) (SPAEEK) containing crown ether unit in the main chain. At present, there are no examples in the literature describing high performance membrane polymers with crown ether units in the main chain, that are also thermally and hydrolytically stable. The polymer is based on 4,4'(5')-di(hydroxybenzo)-18-crown-6. Next to the commonly used Bisphenol A, 4,4'-difluorobenzophenone and sulfonated 4,4'-difluorobenzophenone, were synthesized. Diffusion dialysis experiments with potassium ions proved the influence of crown ether moieties in the SPAEEK main chain and confirmed the selective capturing of the target ion by the crown ethers, visible as an almost four times decrease in ion transport compared to that of native SPAEEK.

As a next step, in **Chapter 3**, blend membranes of poly(arylene ether ketone) (PAEK)/sulfonated poly(ether ether ketone) (SPEEK) and crown ether containing poly(arylene ether ketone) (CPAEK)/SPEEK were prepared. Macroscopic phase separation between PAEK and SPEEK was observed by DSC and HR-SEM. The presence of the crown ether in the polymer backbone did enhance the miscibility of PAEK with SPEEK. The synergistic effect of CPAEK and SPEEK blending on the ion transport was proved by diffusion experiments. Blending improved the K^+ over Li^+ selectivity by a factor of nearly 4.

The selective recovery of a specific monovalent ion from a mixture of other mono- and divalent ions is difficult. Owing to the selective binding ability of crown ethers, they are

often used as adsorbents. **Chapter 4** describes the incorporation of the crown ether dibenzo-18-crown-6 (DB18C6) into electrospun polyacrylonitrile (PAN) fibers for the selective recovery of the monovalent ion K^+ from a mixture of both mono- and divalent ions in aqueous solutions. Electrospinning is a flexible and versatile technique to prepare an adsorbent due to its flexibility for chemical/physical functionalization. The developed nanofiber adsorbents selectively recover K^+ ions from an aqueous mixture with also Li^+ and Na^+ ions present in the solution.

In **Chapter 5**, the concept of crown ether containing SPAEK for the use as ionic polymer metal composite (IPMC) applications is introduced as a way to enable breakthroughs in the design of artificial muscles. For this purpose the crown ether containing polymer sulfonated poly(arylene ether ketone) (SPAEK) was synthesized by step growth polymerization of di(4-fluorobenzophenone)-18-crown-6 in the presence of Bisphenol A, 4,4'-difluorobenzophenone and sulfonated 4,4'-difluorobenzophenone. To validate the concept, the actuation performance of SPAEK and the crown ether containing SPAEK were tested in Na^+ and K^+ ionic form. The incorporation of the crown ether in the polymer backbone enabled to achieve improved and ion sensitive bending displacement. Moreover, the presence of crown ethers in the polymer backbone increased the bending displacement by nearly 30% compared to that of native SPAEK.

In **Chapter 6**, the large-scale application of crown ether containing membranes and adsorbent is briefly discussed and an outlook of the future on membrane development for lithium recovery from seawater is provided. Moreover, the feasibility and challenges of mining lithium from seawater and desalination brines are highlighted. According to current feasibility assessments lithium mining from seawater is an expensive process due to the low lithium concentrations and currently the potential for application is limited. However development of cost effective and highly selective membranes can increase the lithium recovery efficiency and reduce the cost of seawater mining, potentially improving the commercial viability.

Samenvatting

Ontwikkeling van functionele membranen die in staat zijn om selectief ionen te herkennen en transporteren. Deze membranen zijn van belang voor de scheiding van specifieke ionen (bijvoorbeeld K^+ , Li^+ , Na^+) uit multicomponente mengsels. In dit proefschrift worden nieuwe membraan materialen ontwikkeld op basis van kroonether-metaalion complexatie. Kroonethers worden veel gebruikt als gastmoleculen voor ionen, en kunnen selectief bepaalde kationen binden. De nadruk van dit onderzoek is de directe inbouw van kroonether als repeterende eenheden in de polymere hoofdketen. Dit in tegenstelling tot het mengen van kroonethers met polymeren of functionalisatie achteraf van lineaire polymeren. Een groot nadeel van de laatste twee opties is de lagere effectiviteit of het uitwassen van de selectieve kroon ether. De geïntegreerde kroonether eenheden in de polymeerketen vertonen unieke membraanfuncties, namelijk het selectief binden van een specifiek ion met een zeer hoge mate van specificiteit.

Hoofdstuk 2 beschrijft de synthese van een gesulfoneerd poly (aryleenether keton) (SPAEK) dat kroonether eenheden in de hoofdketen bevat. Momenteel zijn er geen voorbeelden in de literatuur beschreven van hoogwaardige membranen met polymere kroonether eenheden in de hoofdketen, die ook thermisch en hydrolytisch stabiel zijn. Het polymeer is gebaseerd op 4,4'-(5') - di (hydroxybenzo) -18-crown-6. Naast de gebruikelijke bisfenol A, werden 4,4'-difluorbenzofenon en gesulfoneerd 4,4'-difluorbenzofenon gesynthetiseerd. Diffusie dialyse experimenten met kaliumionen tonen de invloed van kroonether delen in de SPAEK hoofdketen aan, en bevestigen het selectief afvangen van het specifieke ion door de kroonethers. Dit resulteert in een bijna viervoudige afname van de ionentransport vergeleken met die van onbehandelde SPAEK.

Als volgende stap in **hoofdstuk 3**, zijn er blend membranen van poly (aryleenether keton) (PAEK) / gesulfoneerd poly (ether ether keton) (SPEEK) en kroonether bevattend poly (aryleenether keton) (CPAEK) / SPEEK gemaakt. Macroscopische fasescheiding tussen PAEK en SPEEK werd waargenomen met DSC en HR-SEM. De aanwezigheid van de kroonether in het polymeerskelet verbeterde de mengbaarheid van PAEK met SPEEK. Het synergistische effect van CPAEK en SPEEK mengen op de ionentransport werd bewezen doormiddel van diffusie experimenten. Mengen verbeterde de K^+ Li^+ selectiviteit met een factor van bijna 4.

De selectieve terugwinning van bepaalde eenwaardige ionen uit een mengsel van mono- en divalente ionen is moeilijk. Door het selectief bindend vermogen van kroonethers, worden ze vaak gebruikt als adsorbens. **Hoofdstuk 4** beschrijft de samenwerking van de kroonether dibenzo-18-kroon-6 (DB18C6) in electrogesponnen polyacrylonitril (PAN) vezels voor het selectief terugwinnen van de monovalente K^+ ionen uit een mengsel van zowel mono- en tweewaardige ionen in waterige oplossingen. Electrospinning is een flexibele en veelzijdige techniek om een adsorbens te produceren vanwege zijn veelzijdigheid in chemische/fysische functionalisering. De ontwikkelde nanovezels adsorbens herwinnen K^+ -ionen selectief uit een waterig mengsel die ook opgeloste Li^+ en Na^+ ionen bevat.

In **hoofdstuk 5**, wordt het concept van de kroonether bevattende SPAEK als ionische polymeer metaal composiet (IPMC) applicaties geïntroduceerd, als een manier om een doorbraak in het ontwerp van kunstmatige spieren mogelijk te maken. Hiervoor is een kroonether bevattend gesulfoneerd poly (aryleenether keton) (SPAEC) polymeer gesynthetiseerd doormiddel van een stapsgewijze polymerisatie van di (4-fluorobenzophenone)-18-kroon-6 in de aanwezigheid van bisfenol A, 4,4'-difluorbenzofenon en gesulfoneerd 4,4'-difluorbenzofenon. Om het concept te valideren, is de mechanische respons van SPAEC en de kroonether bevattend SPAEC getest in Na^+ en K^+ ionvorm. De opname van de kroonether in het polymeerskelet is nodig om verbeterde en iongevoelige buiging te bereiken. Bovendien verhoogd de aanwezigheid van kroonethers in het polymeerskelet de buiging met bijna 30% vergeleken met die van onbehandelde SPAEC.

In **hoofdstuk 6**, wordt de grootschalige toepassing van kroonether bevattende membranen en adsorbens kort besproken. Ook wordt er een blik geworpen op de toekomst van de membranen die lithium uit zeewater kunnen herwinnen. Bovendien wordt de haalbaarheid en de uitdagingen van het winnen van lithium uit zeewater en pekels uit ontzoutingsprocessen besproken. Volgens de huidige haalbaarheidsstudies is het winnen van lithium uit zeewater een kostbaar proces vanwege de lage lithium concentraties.

Acknowledgement

The completion of my PhD has been a long journey with lots of frustration. During my PhD, I have become a true believer of the Murphy's law. I had miserable days when nothing worked and all the experiments failed. I have doubted whether I would finish my PhD. I have questioned myself and lost my confidence so many times. Although I thought that I could confront with failures, the Murphy's law always caught me unprepared. Whatever happened during those four years, finishing my thesis always stayed one of my first priorities. I could not have completed my thesis without the invaluable support. Therefore, I owe gratitude to many people who have contributed inspiration, advice, and support.

First of all, I would like to express my appreciation and thanks to my supervisor and promotor Prof. **Dr. Ir Kitty Nijmeijer**. Kitty, thank you very much for your help, guidance, support, and encouraging words. You have fought with my worries, concerns to keep me on track and handled my stressful nature. Thanks for believing in me. I wish to thank **Prof. Dr Ir. Julius G. Vansco** for welcoming me to his group. Thank you for all scientific discussions and valuable corrections for my papers. I would like to extend great thanks to **Dr. Mark Hempenius**, without your help and support this thesis would not have been possible. You generously shared your passion and expert knowledge of polymer chemistry, which were a great benefit to this thesis I always felt lucky to work with you and I have learned a lot from you. I would like to thank to **Dr. Elif Ozden Yenigun** for her research collaboration and friendship.

I would like to thank my promotion committee, **Prof. Dr. Ir. Kulathuier Seshan**, **Dr. Mark Hempenius**, **Prof. Dr. Mathias Ulbricht**, **Prof. Dr. Ernst Sudhölter** and **Prof. Dr. Albert Schenning** for evaluating my thesis and giving the approval to defend it publicly. I would also like to thank **Prof. Dr. Ir. Wilfred van der Wiel** for chairing my defense. Furthermore, I would like to thank my **project partners** Wetsus, FOM, Fujifilm and FrieslandCampina for their collaboration and financial support. I also would like to thank all the members of the Wetsus Biomimetic research team for their feedback on my work.

I thank **Antoine Kemperman**, **Zandrie Borneman**, **Wiebe de Vos** and **Erik Roesink** for the scientific discussions after Monday morning presentations. I owe my gratitude to **Matthias Wessling** for making time whenever I wanted to discuss things with him and also for inspiring suggestions.

I would like to make a special thanks to **Bram Zoetebier**. It was a pleasure for me to collaborate with you. We both suffered in this crown ether project, your contribution is definitely very valuable to this research. I also thank to the members of Material Science and Technology of Polymers Group (MTP). I would like thank to my friends **Ozlem Sardan Sukas** and **Muharrem Bayraktar**, without your help, the actuator idea cannot be turned into a chapter and hopefully a paper soon. Many thanks to **Clemens Padberg**, **Herman Teunis**, **Harmen Zwijnenberg**, **Gerard Kip**, **Remco Sanders** and **Mark Smithers** for making time to help me with all kind of experiments and measurements. I should especially thank to **Patrick Goossens**, your small trick for the polymerization made my project work. I also would like to thank **Audrey Haarnack** for helping us with all of the paper work (and there was a lot).

Greet, you were one of friendly faces of MST. It was difficult for me to imagine MST without you. No matter how busy you were, you always had time for us whenever we asked for help. I was impressed by your memory, managing skill and kind approach to everybody. Like a mother, you always supported us, kept our secrets and solved our difficulties. Thanks a lot for everything. Luckily, we can still meet with you at the PhD defences. **John**, you will always be remembered as a smiling face, a warm and friendly heart Thank you John, I keep you in my sweet memories.

I would like to thank **Goffe-Jan** for the beautiful cover design. You were very generous to offer me to design my thesis cover. You really saved me....

I had a lot of ups and downs during my PhD, but the peaceful and friendly environment of MST inspired me to continue. I am absolutely sure that it was my great chance to work in such a nice environment and I would like to thank everyone who made those years very special.

First of all I would like to thank my officemates, **Erik**, **Szymon**, **Irdham**, **Harro**, **Kah-Pheng**, **Dennis**, **Bob**, **Ozlem** and **Shazia** for making ME 322 is a special office and giving me many precious memories. **Erik**, my dear friend, we shared struggles; we laughed and complained a lot. You have been supportive, caring, and very trustworthy. Thank you for being my paranymp together with **Olga** and sharing this special day with me. **Olga**, thanks for taking care of stukjes, joining me for tequila shots, Rico Latino parties, "Friends" episodes that I watched while waiting you to get ready **Yali**, thanks for being my part-time

housemate, all the nice conversations in the evenings, being my sister in Enschede and thanks to you & **Jie** for all the delicious Chinese dinners and Chinese wine which burned everything inside me. **Krzysztof**, we started together, saved a lot of memories but the one in China I will always remember... since the bill that I paid for my mobile was unforgettable .. **Damon**, you are such a special character and make me smile always. Thanks to **Saghar** and you for Disco Damon and great company for friday borels/parties. **Jeroen**, thank you for seeing me as the secretary of Erik, calling my mobile phone but asking to speak with him without asking how I am doing. **Izabella**, thanks for being a very lovely couple with Erik and being calm and helpful. **Harmen**, you are very good at making me lost in your stories and thank you for keeping all the secrets of the group and sharing with everyone when you are drunk, helping me when I moved and carrying my washing machine alone. **Zandrie**, thanks for your great sense of humour but it is always difficult to understand your jokes. **Antoine**, you are the one of the friendly faces of MST, you have a very big heart and you care a lot. Thanks for asking me whether I am happy. **Can&Laura**, thanks turning borrels and PhD parties to legendary ones. **Enver**, thanks helping me to understand how things were running in MST and tips & tricks about people. Thanks to **Harro& Imre** taking me out when I had a terrible nervous breakdown cause of IND and trying to cheer me up. **Beata**, thanks teaching us Polish words, sharing difficulties that you faced with during your PhD. **Wojtek** thanks for all the encouragement when I was so disappointed about my project. **Jeff**, thanks for proof reading almost half of my thesis, bringing me tea from Munster, you are very talented, you quickly learnt my office dance choreography. **Timon**, for being helpful, of course calling me Tasje and very good pronunciation of Turkish words of "merhaba" and "gunaydin". **Joris**, thanks for all scientific discussions and of course for the Sinterklaas poem. **Ozlem**, for being very much caring officemate, joining my singing and dancing sessions in the office and beautiful Firat t-shirt, it is the best gift ever. **Pelin**, thanks for being a great listener when I need and keeping me company on weekends and evenings while I was writing my thesis. **Valentina**, thanks for delicious Italian dinner, joining Saturday tea routine and Sunday beer. **Charu**, thanks for all the nice conversions, you and **Indranil** introduced me to mediation. **Bob**, you are the one of the talkative person I know, thanks for being funny Bob. Thanks for **Kah-Pheng, Violetta, Mette, Aylin, Sooi Lee, Ramato** and **Alessio** bringing joy when the energy of the group was down.

Thank you core party group: **Erik, Krzysztof, Jeroen, Olga, Antoine, Can, Laura** and **Harmen** for making all Friday borrels, conferences and study tour evenings very special. For Luxemburg trip too, Erik, Izabella, Krzysztof, Marzena, Olga, Estavão, Yali, Jie, Damon, Saghar, Jeroen and Beata.

I would like to thank all other MST, SFI and IM members: Andrew , Janneke, Kanwal, Roberto, Björn, Terica, Renaud, Dafne, Parshu, David, Vic, Yusuf, Slywin, Namik, Salman, Al-Hadidi, Shazia, Miriam, Christina , Marcel, Ivonne, Jordi, Jumeng, Joanna, Mayur, Sander, Aura, Ineke, Jan, Hani, Khalid, Rob, Michiel, Bas, Patrick, Emiel, Kristianne, Cheryl, Anne, Amy, Joeri, Rian, Frank, Arian, Louis, Mieke, Cindy, Susanne for all coffee breaks, monthly lunches and nice conversations.

Kafiye abla, you are the nicest and most generous person that I have ever met. Thank you for all the wonderful food that you provided me during my PhD.

Next, I would like to thank my students, **Nungky, Ying, Mahbub** and **Yasar**. It was a pleasure to work with you, especially **Nungky** were very brave and determined enough to work in this challenging project.

Kaisa, I was thinking that the crazy neighbour incident was the worst thing happened in Enschede. But I met with you since you accepted to come together with me to real estate agency as a witness. Since then I have a very good friend. Thanks for everything my friend.

Corina, thank you for the sweet gypsy birthday party, we are sweet gypsies and we will be always 29. **Maurizo** canim, you are the best Italian ever, thank you being Maurizo, making me smile. **Ozlem, Pelin, Valentina** and **Jeff**, thanks for joining Saturday tea routine and **Jonny** for baking delicious cakes for sure Germans know how to bake cake.

I would like to thank Turkish community with whom I had great time during lunch, coffee breaks, BBQs and other events: Ece, Elif, Burcu, Mustafa Akin, Seckin, Berk, Pinar, Cem, Alim, Bedile, Muharrem, Nurcan, Fehmi, Nese, Didem, Semih, Hayrettin, Umut, Kardelen, Oguzcan, Eda, Emre, Yakup, Ozlem, Sertan, Ertug, Oguzhan, Aysegul, Aysun Yusuf, Gulistan, Bade, Guner, Pelin, Ozlem, Hasan, Recep, Engin, Duygu, Imran, Buket, Hande, Devrim. Plus, the cutest kids: Tunc, Gokce, Aylin, Ayca....

Since I live far away from my family, some of friends become family. I'd also like to give a heartfelt thanks to **Elif, Burcu, Hayrettin, Ertug, Didem & Semih** for being my family

here. I shared a lot with you, I was not worried to show my feelings, I cried, laughed in front of you. I don't know what else to say or what else needs to be said. Thank you for being you, thank you for being there and supporting me whenever I need.

I must mention **Elif, Yeliz, Deniz Ali, Mahir**. You made a place in my heart. I feel lucky to be blessed with your friendships. I know how much you care about me. Thank you for sending supportive whatsapp messages, and phoning me to ask about me. Yeliz, Burak, Mahir, Gulnur and Deniz Ali, your visits during these years have been invaluable. Elif, I enjoyed our trips to Poland and Denmark.

Guluzar ablacim, my lovely sister, I know you are going through a difficult time and that is the reason why you can not be together with us. I admire your strength and happiness. You stay positive and keep fighting and I am sure you will stay positive as well. Thank you for being "my little mom" and sister

Last, but certainly not least, I would like to thank my parents and my sister. The words are just not enough to express my feelings. Mom and Dad, you have taught me about hard work, self respect, honesty, and fairness. I am proud to be your daughter and I know how proud you are of me and how much you love me. Thank you always being there for me, your endless love and support.

All the best,

Sinem

ISBN 978-90-365-4074-2