2015 winter

Membrane News Twente

News magazine of the Membrane Science and Technology Group

Membrane Science & Technology

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Welcome

Times are a changing, something that is especially true this year for MST. In November, our group leader Professor Kitty Nijmeijer announced that she is leaving the group to take up a full professorship at Eindhoven University of Technology (TU/e) to start a new group there, Membrane Materials and Processes. Of course, we wish our colleague all the best in her new position and we are very thankful for all the great work that Kitty has done for our group over the years. Strong ties will remain between MST and the new membrane group and we look forward to many fruitful collaborations between the groups.

One might wonder what this means for MST, and on this we can be very clear: research on (polymeric) membranes, and on membrane applications related to clean water, energy and life sciences will remain a key focus area of the University of Twente. For this we a have strong support from the Board of the University, as will also be clear from the contribution to this newsletter of the Dean of our Faculty, Prof. Hans Hilgenkamp. This strong support is both for the academic part of the group as well as for the part dedicated to the valorization of our research, the European Membrane Institute. Both groups will continue.

With its strong infrastructure, the experience of our technicians and the expertise of our staff members, MST will thus remain a key European knowledge center for membrane science and technology. We are currently working very hard on possibilities to strengthen the group, including looking in detail at the possibilities to attract new talents and expertise. More information will follow in the coming newsletters.

We invite you to read this newsletter and hope you will enjoy it. In case you have additional questions or you would like to receive further information or publications, please feel free to contact us at MSTtnw@utwente.nl or +31 53 489 2950.
On behalf of all members of the Membrane Science and Technology group of the University of Twente, we would like to wish you pleasant Christmas holidays and a prosperous and happy 2016!

Dr. Wiebe de Vos
On behalf of the MST and EMI staff members: Dr. Antoine Kemperman, Prof. Erik Roesink, Dr. Zandrie Borneman

Some group members during the Euromembrane 2015.

Follow MST on Facebook!

Interested in the latest news of our Membrane Science and Technology group? Follow us and like us on Facebook (www.facebook.com/membranetechnology). There you will find all our most recent publications, PhD defenses, and MSC colloquia, as well as the more social aspects of our group. Enjoy!

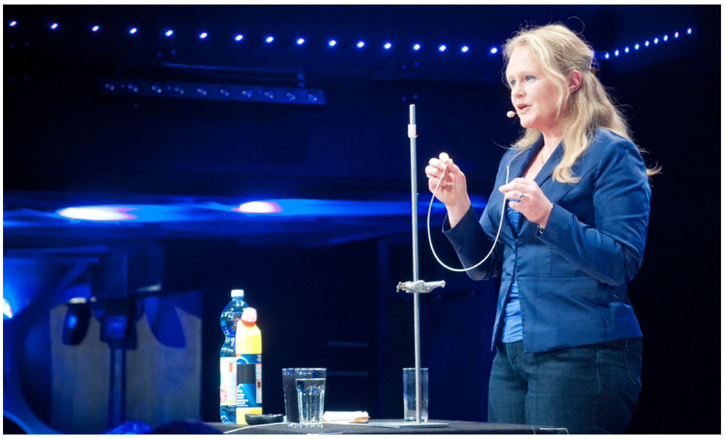
New position for Prof. Kitty Nijmeijer at Eindhoven University of Technology

Kitty Nijmeijer

After more than 15 years of being a member of the Membrane Science and Technology group of the University of Twente, I decided that it is time for the next step. From the 1st of February 2016 on, I accepted a position at Eindhoven University of Technology (TU/e) in Eindhoven (NL). I will be professor Membrane Materials and Processes in the faculty of Chemical Engineering and Chemistry, where I will work on the development of new polymer materials and membranes for technological applications in the field of sustainable energy and clean water.

I worked for more than 15 years in the membrane group at UTwente. It is the place where I first learned about membranes, where I got my education and did my PhD. It is also the place where I could develop myself professionally and where I got the chance to build my own research line. The education and experiences I gained in Twente provide me with a very strong base, such that I can now take the next step in my scientific career.

Over the past 15 years I had the great pleasure to work with many Ph.D. students, researchers, technicians, staff members and students in the group. Together we tried to bring the membrane research and education a step forward. I appreciated the close connection between on one side the fundamental, academic research performed by the Ph.D., Master and Bachelor students and on the other side the more applied research executed by the highly skilled people of the European Membrane Institute Twente. The natural connection and collaboration between these two entities offers extensive flexibility in terms of education, knowledge transfer, academic and industrial collaborations, thus providing a strong base for high quality membrane research and application. Next to science, I also enjoyed the fun, multiple discussions and jokes during e.g. coffee breaks, monthly group lunches, Sinterklaas parties, bicycle tours and Friday afternoon drinks. I will never forget all this. Thank you very much for everything! I will definitely miss you.



I had a great time in Twente and I have always worked with a lot of pleasure at UTwente. I enjoyed the collegiality within the faculty and the university. I am looking forward to a close and intensive collaboration with the University of Twente and in particular with the Membrane Science and Technology group.

Being at this point in my career, the transition to the TU/e allows me to further extend my research expertise developed in Twente, i.e. molecular membrane design to control mass transport for energy and water applications. The TU/e offers a platform to bridge and strengthen the connection between materials science and process technology, the two strong core disciplines of the faculty of Chemical Engineering and Chemistry at the TU/e. I will focus on the role of membranes in the concept of the circular economy, focusing on closing cycles, reuse and recycling of water and resources, reducing CO_2 emissions and energy consumption and minimizing waste. This is, among others, also reflected in the collaboration with e.g. the Dutch research institutes Wetsus (Centre of Excellence for Sustainable Water Technology) and ISPT (Institute for Sustainable Process Technology).

I will remain a member of the membrane community, so I am sure that I will meet many of you in the future. For now I wish you all the best and I hope to see you soon again.

Best regards,
Prof. Dr. D.C. (Kitty) Nijmeijer

Membrane science research in Twente

Since 2011, Prof. Kitty Nijmeijer has been leading the Membrane Science and Technology group in Twente. She has done this with great success; in this period the MST group has been the environment for many Bachelor, Master and PhD students to carry out their research as a basis for their graduations. The MST group has been involved in many high level scientific and commercialization efforts. In addition, Kitty Nijmeijer has devoted tremendous time and energy to outreach activities. At this place, I like to express my great gratitude to Kitty for all her work for the Membrane Science and Technology group and for the University of Twente.

Kitty Nijmeijer will continue her career at Eindhoven University of Technology, our sister university in the Dutch 3-TU federation. Our faculty wishes her all the best with this new position and we look forward to a continued collaboration.

Naturally, with this departure questions come up about the future of Membrane Science and Technology in Twente. To answer this question, it will be good to note first that membrane research has a long and successful history within our university. This already started under the leadership of Prof. Kees Smolders in the early seventies, followed by Prof. Heiner Strathmann and Prof. Matthias Wessling. In this time, the MST-group has become a very fertile breading ground for new professors within our Faculty, as besides Kitty Nijmeijer, also Profs. Rob Lammertink, Dimitrios Stamatialis and Nieck Benes have followed in the footsteps of Prof. Wessling. Further principal investigators in the area of Membrane Science are tenure track Assistant-Professor Wiebe de Vos and part-time Profs. Arian Nijmeijer and Erik Roesink. With this excellent team of PI's we will continue to set out our strategy for the coming time. This will also include considerations on the follow up of Kitty Nijmeijer as the group leader of the MST group.


Hans Hilgenkamp

It is without any doubt that Membrane Science and Technology still fits perfectly within the current focus areas of the university such as "High Tech Engineering" and "Nano Technology", while the applications of membranes such as clean water, reduced waste streams, and saving or even generating energy gives membrane technology a high relevance to society. Also the European Membrane Institute (EMI), a key part of the MST group and a very valuable entity for our University, is very well aligned with the profile of the University of Twente as being The Most Entrepreneurial University

In conclusion, in continuation up of its successful past, Membrane Science and Technology will have a very strong future in Twente. Stay tuned!

Prof. Hans Hilgenkamp
Dean of the Faculty of Science and Technology, University of Twente

Upcoming Ph.D. defenses

Erik Vriezekolk
All the Same, Isoporous Membranes for Water Purification
February 5, 2016; 12.45 h, University of Twente

Sinem Tas
Bio-inspired Ion Selective Crown Ether-Polymer Membranes
March 11, 2016; 16.45 h, University of Twente

Krzysztof Trzaskus
Filtration of Engineered Nanoparticles using Porous Membranes. February 5, 2016; 16.45 h, University of Twente

Filtration of engineered nanoparticles using porous membranes

Krzysztof Trzaskus

The rapid growth of nanotechnology in the past decades has resulted in many products containing engineered nanoparticles. This inevitably leads to the discharge of engineered nanoparticles into aquatic systems after usage, with associated health and environmental consequences. To make nanotechnology more sustainable, it therefore is essential to develop technologies that can remove these engineered nanoparticles from aquatic environments. Membrane technology is an obvious solution for nanoparticle removal from water sources since already since a long time, porous membranes are frequently employed to retain colloidal particles. However, being a new and unexplored cause of water contamination, not much is known about membrane filtration of engineered nanoparticles. Therefore, the research described in my thesis aims at providing a better understanding of the fundamental aspects responsible for nanoparticle removal and fouling development during membrane filtration of engineered nanoparticles. The emphasis was put on the role of interparticle interactions in the feed solution, nanoparticle stability, and aggregation in relation to the filtration mechanisms.

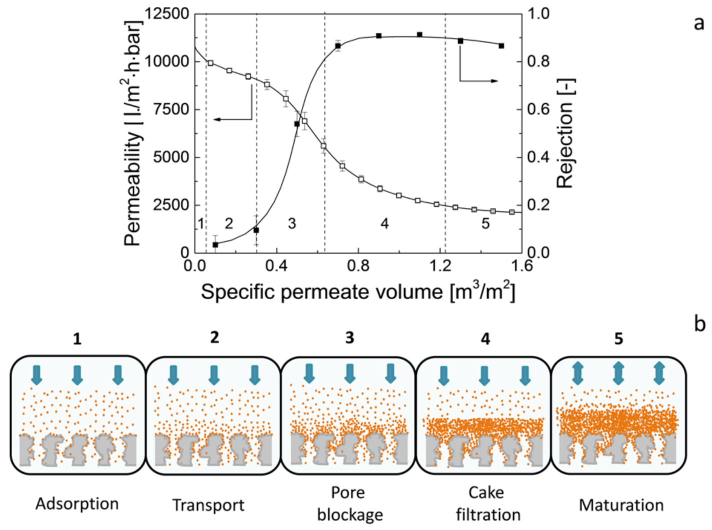


Figure 1: (a) Permeability decay and rejection development during filtration of a suspension containing 2 mg/L of monodisperse 25 nm silica nanoparticles using a microfiltration membrane, (b) proposed nanoparticle filtration mechanism.

In order to investigate the role of electrostatic interactions during membrane filtration of nanoparticles, a microfiltration hollow fiber membrane was used in constant pressure dead-end mode for the filtration of monodisperse silica nanoparticles [2]. A low concentration of nanoparticles in the feed solution and a large difference between the membrane pore size (~200 nm) and the nanoparticle size (~25 nm) allow determination of the fouling mechanisms by a detailed analysis of the course of permeability decline and nanoparticle rejection (Fig. 1a). We postulate that for a stable suspension of electrostatically stabilized nanoparticles fouling occurs in five subsequent stages: adsorption, unrestricted transport through pores, pore blocking, cake filtration, and finally cake maturation (Fig. 1b). After the pore blockage stage, nanoparticle rejection is enhanced from approx. 10% to 90-95%.

It was observed that an increase of the nanoparticle concentration does not change the filtration behavior but only accelerates fouling. Due to the high sensitivity of the stability of electrostatically stabilized nanoparticles, the solution chemistry, the presence of salts, the solution pH and the valence of the cation strongly influence the duration and severity of the fouling stages. In general, lower repulsive interactions between the nanoparticles accelerate fouling by faster pore blockage and aggregation on the membrane surface. Moreover, porosity and permeability of the formed filtration cake are strongly dependent on the repulsive interactions between the nanoparticles. Bigger monodisperse silica nanoparticles block membrane pores easily, accelerating pore blockage and cake layer formation.

In the case of polydisperse silica nanoparticles (obtained by mixing monodisperse suspensions in various ratios), an increasing concentration of smaller nanoparticles in the suspension causes delayed pore blockage, and cake filtration occurs at a later stage (Fig. 2a). Moreover, due to the surface charge of the nanoparticles and a less ordered structure of the filtration cake formed as a result of the nanoparticle polydispersity, the filtration cake has a more porous, open structure. This allows transport of smaller nanoparticles through the filtration cake and the polymeric membrane (Fig. 2c). As a result, nanoparticle rejection is reduced proportionally to the fraction of the smaller nanoparticles present in the feed solution (Fig. 2b). An increase in the applied transmembrane pressure during filtration of the polydisperse suspension causes densification of the filtration cake with only a slight improvement in nanoparticle rejection.

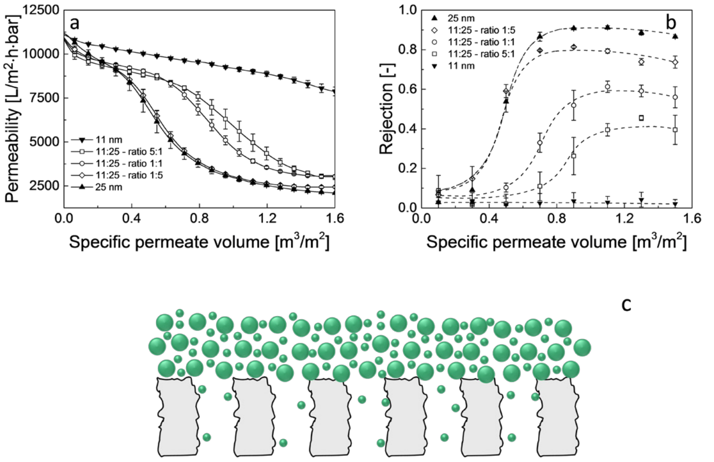


Figure 2: (a) Permeability decay and (b) rejection development during silica nanoparticle filtration as a function of specific permeate volume for mixtures of 11 nm and 25 nm silica nanoparticles during dead-end microfiltration of 2 mg/L silica nanoparticle suspensions. (c) Proposed mechanism for the transport of smaller nanoparticles through a filtration cake and a porous membrane.

Stabilizers or surface-active compounds added to a feed solution containing nanoparticles change both membrane-nanoparticle and nanoparticle-nanoparticle interactions. An improved stability due to enhanced steric repulsions (introduced by polymers) or stronger surface charges (introduced by low-molecular weight compounds, e.g. surfactants), reduces aggregation of nanoparticles. This facilitates their transport through the porous membrane and increases porosity of the filtration cake formed. On the other hand, stabilizers can also act as foulants, and as such can increase the thickness of the filtration cake and occupy the voids between the nanoparticles in the filtration cake.

The influence of molecular mass, concentration of the steric stabilizer (i.e. PVP, polyvinylpyrrolidone) and the transmembrane pressure applied was investigated as well. The results show that the addition of a steric stabilizer significantly influences the pore blockage and the cake filtration stage during filtration of model silica nanoparticles (Table 1).

In general, PVP with a lower molecular mass is a better stabilizer for nanoparticles and contributes less to fouling by delaying the occurrence of pore blockage. On the other hand, at a higher PVP concentration, PVP contributes to the fouling due to an increase of the total solute load. Moreover, stabilizers with a higher molecular mass block the pores more easily, leading to faster fouling- and rejection development. The nanoparticle rejection drops with increasing PVP concentration and this effect is more pronounced for low-molecular weight PVP. Use of a higher transmembrane pressure results in compression of the filtration cake and improved nanoparticle rejection at the expense of permeability.

Table 1. Blocking point, which indicates the transition from the pore blocking stage to the cake filtration stage during membrane filtration of a suspension containing 2 mg/L of 25 nm silica nanoparticlse and various concentrations of PVP in various molecular masses (na = not available due to instantaneous pore blockage).

PVP Concentration [mg/L]		0	1	2	4
V_{block} [m^3/m^2]	10 kDa	0.23±0.03	0.31±0.01	0.35±0.02	0.23±0.02
	40 kDa		0.21±0.01	0.31±0.02	0.25±0.04
	360 kDa		na	na	na

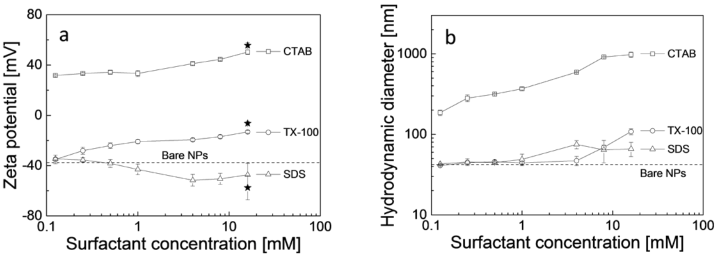


Figure 3: Zeta potential (a) and hydrodynamic diameter (b) of silica nanoparticles as a function of the CTAB, TX-100 or SDS surfactant concentration at pH 8 at 30°C. The stars represent pure surfactant suspensions at 16 mM.

Also low-molecular weight compounds such as surfactants are often added to nanoparticle suspensions in order to influence their surface properties and stability. The work demonstrated that the type of surfactant used (anionic, cationic or non-ionic) and its concentration influence nanoparticle stability as reflected in the particle zeta potential and hydrodynamic diameter (Fig. 3), which directly affects fouling behavior and rejection of the nanoparticles during dead-end constant flux membrane filtration. Reduced repulsive interactions between nanoparticles due to the addition of non-ionic surfactant (Triton X-100) caused the most severe fouling and the highest nanoparticle rejection. We hypothesize that the difference in nanoparticle rejection in the presence of the investigated surfactants has its origin in the homogeneity and density of the cake layer formed.

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Finally the effect of the position in the membrane fiber on rejection of the nanoparticles was investigated. Non-homogeneous hydrodynamic conditions over the length of a membrane fiber during inside-out dead-end filtration can result in differences in fouling development depending on the axial position inside the fiber (Fig. 4).

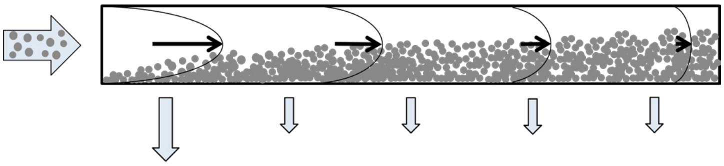

Figure 4: Schematic representation of nanoparticle deposition inside a hollow fiber membrane during dead-end operation (adapted from van de Ven et al.[1]). Horizontal arrows indicate cross-flow velocity inside the fiber, whereas the parabolas show the laminar flow profile; the vertical arrows are the local permeate fluxes along the length of the fiber.

Fouling along the fiber length develops irregularly during filtration of model silica nanoparticles. Moreover, the exact fouling behavior along the hollow fiber membrane is strongly influenced by the applied feed flow rate. However, after the occurrence of pore blockage and the formation of nanoparticle deposit on the membrane surface, rejection of the nanoparticles is no longer determined by the position inside the hollow fiber. Extensive concentration polarization as occurs at some parts of the fiber does not influence significantly the rejection of silica nanoparticles.

Acknowledgement

This work is supported by NanoNextNL, a micro- and nanotechnology consortium of the Government of The Netherlands and 130 partners.

For more information about this work, please contact
Dr. Antoine Kemperman (a.j.b.kemperman@utwente.nl)
phone: +31 (0)53 489 2956.

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Awards

Membrane awards during Euromembrane for Jordi Moreno and David Vermaas

Jordi Moreno (left), Prof. Dr. Kitty Nijmeijer (middle) and Dr. David Vermaas (right).

During Euromembrane 2015, the largest membrane conference of Europe, two members of our group were awarded for their work.

Jordi Moreno, PhD student in our group received one of the three oral presentation awards of the conference for his presentation entitled ‘The Breathing Cell: Smart stack design for reverse electrodialysis. The award involves a grant of 500 euro and a one-year free membership of the European Membrane Society.

Dr. David Vermaas, a former PhD student of our group, received the Excellence award in Membrane Engineering of the European Federation of Chemical Engineers. This award is granted once in three years for the most outstanding PhD thesis in membrane engineering in the area of process technology during that period. David’s PhD thesis was also in the field of reverse electrodialysis and entitled ‘Energy generation from mixing salt water and fresh water: Smart flow strategies for reverse electrodialysis’ (http://www.utwente.nl/tnw/mtg/publications/mstpublications/pdf/2014-vermaas.pdf).

If you wish to receive more information about reverse electrodialysis or about the specific work of Jordi Moreno or David Vermaas, please contact Prof. Dr. Kitty Nijmeijer (e-mail: d.c.nijmeijer@utwente.nl or phone: +31 53 489 4185).

Membrane lecture and demonstrations at Mañana Mañana festival

On August 29, 2015, Prof. Dr. Kitty Nijmeijer gave a membrane lecture and showed a series of experimental demonstrations at the Mañana Mañana music festival in Hummelo (NL). The 3-day festival is a combination of music and performances, and since this year it also provides a podium for science and technology. Several professors of the University of Twente presented their recent research progress and innovations in the field of sustainable energy to a broad audience aged from 5 till 80 years. Kitty explained the principles of membrane separations, showed how to make a polymer membrane and elucidated the magic of Blue Energy. This was completed with a series of on-site experiments on membranes for drinking water production.

We wish you Merry Christmas
and Happy 2016!

Membrane Science and Technology Group
University of Twente
The Netherlands

All the same:
Isoporous membranes for water purification

Erik Vriezekolk

In my PhD project, the focus is on three approaches that allow fabrication of films and membranes that contain ordered and uniform pores with pore sizes in the ultrafiltration range. Special attention is given to the tuning of pore sizes by varying simple parameters during the fabrication process.

For the first approach, solvent exposure is studied as a simple method to decrease the dimensions of polymeric microsieves. Microsieves, having very uniform and straight-through pores, can be fabricated via phase separation micromolding (PSμM), which is a technique that combines the principle of polymer phase inversion to fabricate membranes with the use of microstructured molds to fabricate replicates. Pore sizes of microsieves are usually in the range of micrometers due to limitations in the size of the molds, but need to be reduced to below 1 μm to make the microsieve attractive for other aqueous filtration applications such as ultrafiltration (UF). Polyethersulfone (PES)/polyvinylpyrrolidone (PVP) microsieves were fabricated with (perforated) pores of 2-8 μm in diameter and a very open internal structure. The pore sizes of the microsieves were then further reduced by solvent-shrinkage, where the microsieves were immersed in mixtures of acetone and N-methylpyrrolidone (NMP) (Figure 1).

Microsieves shrink because of swelling and weakening of the polymers, and subsequent collapse of the open internal structure. Size reduction in terms of pore size and porosity of the perforated pores was monitored over time. The pore size of microsieves was reduced from an initial pore diameter of 2.6 μm to only 0.2 μm. A higher NMP concentration leads to a higher shrinking rate. Shrinking typically occurs in two stages: first, a stage where both the perforated pores and periodicity shrink, and second, a stage where the perforated pores continue to shrink while the periodicity remains constant. For the microsieve to retain a high porosity, it is desired that both the perforated pores and periodicity shrink at similar rates, a process called isotropic shrinkage. The shrinking rate of the periodicity depends on the geometry of the microsieve and the structure of the polymer matrix.

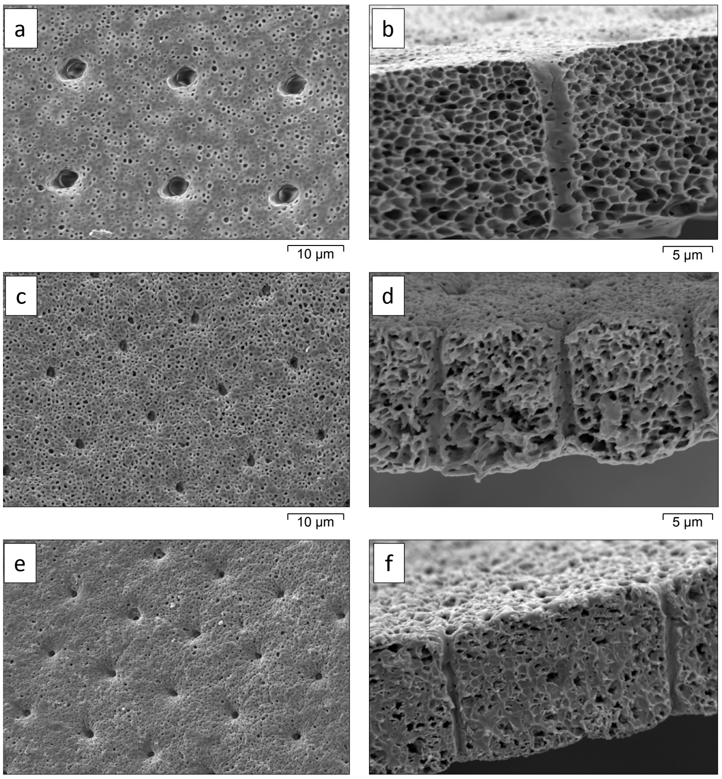

Figure 1: Surfaces (left, magnification 2000x) and cross-sections (right, magnification 3500x) of microsieves after immersion in a 5 wt% NMP in acetone mixture for 0 minutes (a and b), 20 minutes (c and d) and 70 minutes (e and f).

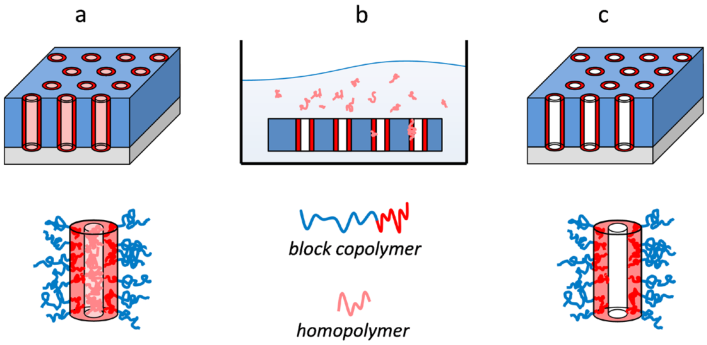

Figure 2: Schematic overview of the fabrication of nanoporous layers. (a) A PS-b-P4VP block copolymer/P4VPHP homopolymer film is made by spin coating a PS-b-P4VP/P4VPHP solution on a silicon substrate. The block copolymers self-assemble in a hexagonal cylindrical structure perpendicular to the surface, where the homopolymers reside in the cylinders. Subsequent removal of the homopolymer with a solvent rinse (b) leads to a film with uniform and straight-through nanopores (c).

The maximum obtained isotropic shrinkage is ~35%, which is determined by the amount of voids in the polymer matrix.

The second approach focuses on the fabrication of composite membranes with a thin top layer based on self-assembling diblock copolymers (dBCPs) and homopolymers. The block copolymers self-assemble into a morphology of hexagonally packed cylinders perpendicular to the surface, while the homopolymers reside in the core of the cylinders because of favorable interactions. Subsequent selective removal of the homopolymers leads to the formation of ordered, nanoporous layers (Figure 2).

First, fundamentals of this approach are investigated, where layers are fabricated on model surfaces. A system of polystyrene-block-poly(4-vinyl pyridine) (PS-b-P4VP) block copolymer, poly(4-vinyl pyridine) homopolymer and chloroform was used. The pore size and porosity can be tuned by varying the homopolymer content and molecular weight of the block copolymer. In this way, pore sizes were obtained between 10 and 50 nm. Uniformity of the pore size, however, is lost when the average pore size exceeded 30 nm because of macrophase separation (Figure 3).

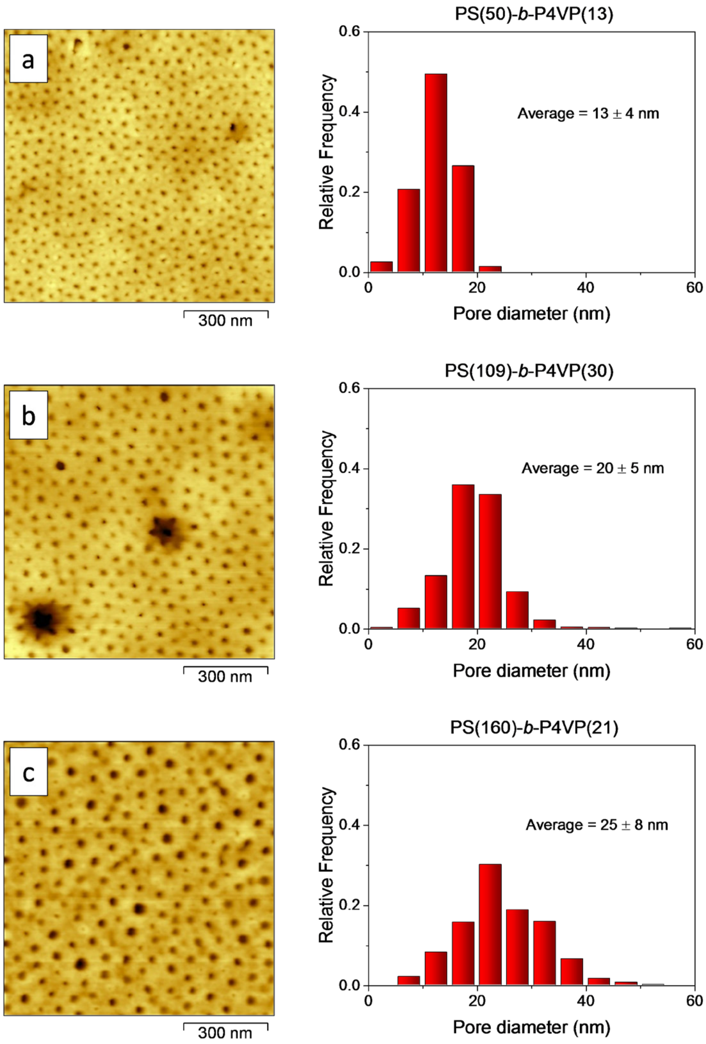

Figure 3: AFM height images and relative pore diameter frequencies of films made of PS-b-P4VP/P4VPHP blends using the same P4VP(22) content (fP4VP-HP = 0.1) but different BCPs: (a) PS(50)-b-P4VP(13), (b) PS(109)-b-P4VP(30) and (c) PS(160)-b-P4VP(21).

In a continued investigation, composite ultrafiltration membranes were fabricated by coating a thin nanoporous BCP layer on top of a support membrane. A system of polystyrene-block-poly(ethylene oxide) (PS-b-PEO) block copolymer, poly(acrylic acid) (PAA) homopolymer dissolved in tetrahydrofuran (THF) was used. The pore size and morphology of the polymer layer could be controlled by varying the content of homopolymers, as in agreement with the results discussed before. The polymer concentration of the coating solution influenced both the morphology and the thickness of the layer. The different pore sizes and morphologies lead to membranes with different molecular weight cut-offs (MWCO) (Figure 4) and permeabilities. The work thus demonstrates clearly that membranes with different performances can be fabricated using just a single type of BCP by simply varying the homopolymer content.

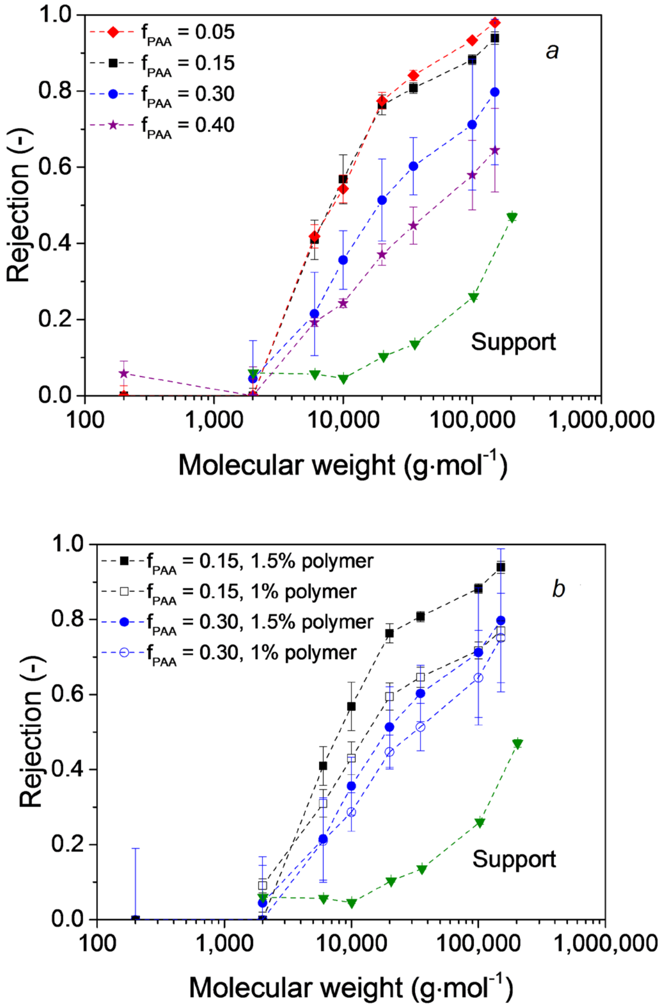

Figure 4: Rejection of PEG mean molar masses using different composite membranes. a) Block copolymer top film made from 1.5 wt% polymer solutions with homopolymer weight fractions of 0.05, 0.15, 0.30 and 0.40. b) Block copolymer top film made from 1.0 and 1.5 wt% polymer solutions with homopolymer weight fractions of 0.15 and 0.30. Dotted lines are shown to guide the eye.

In the third approach, freestanding, asymmetric BCP membranes having a selective top layer were fabricated via dry-wet phase separation. A mixture of PS-b-P4VP, volatile THF and non-volatile NMP was used as polymer solution. After casting a film, THF was allowed to evaporate for a very short duration (1 second). The still liquid film was then immersed in a coagulation bath where the polymer solidifies. The evaporation step increases the polymer concentration locally at the top of the film, which results in a very thin top layer. It also gives the BCP time to form cylindrical micelles that can lead to an ordered honeycomb structure formed by threadlike cylinders. Changing the ratio of THF/NMP and polymer concentration leads to membranes with different structures (Figure 5), hence, different performances. The best ordered honeycomb structures were obtained using a 18 wt% polymer solution with a THF/NMP ratio of 70/30 and a 21 wt% polymer solution with a THF/NMP ratio of 60/40. The THF/NMP ratio also influences the morphology of the support layer, which determines the permeability of the membrane (349-1320 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$). Filtration experiments with 30 and 10 nm silver nanoparticles and BSA showed that a sharper size cutoff is obtained when the pores are more ordered (Figure 6). This indicates that the ordered honeycomb-like pores indeed have a more narrow pore size distribution that allows for more selective filtration.

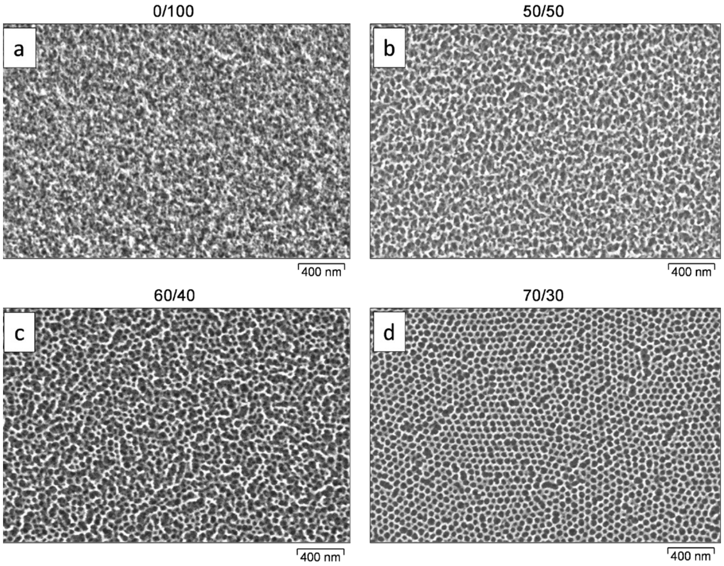

Figure 5: SEM surface images (magnification 100,000x) of PS-b-P4VP membranes made of 18 wt% polymer solutions with different THF/NMP ratios. a) 0/100, b) 50/50, c) 60/40 and d) 70/30.

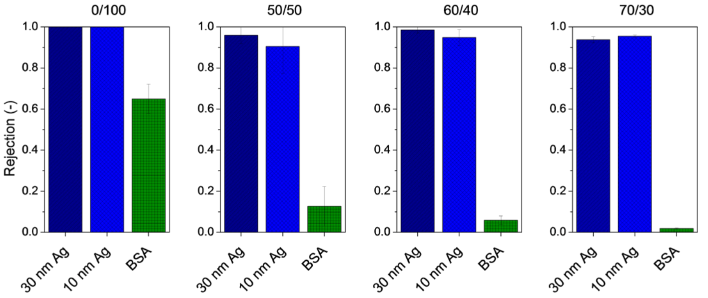

Figure 6: Rejection of 30 and 10 nm silver nanoparticles and BSA using membranes fabricated with polymer solutions with THF/NMP ratios of 0/100, 50/50, 60/40 and 70/30. Filtrations were performed in a dead-end setup at 1.0 bar.

For more information about this work, please contact
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Acknowledgement

This work is supported by NanoNextNL, a micro and nanotechnology consortium of the Government of The Netherlands and 130 partners. We would like to thank our project partners from 04A.01 (Biomimetic Membranes): Pentair X-flow, KWR and Wageningen University, Organic Chemistry, for the good cooperation and the constructive discussions.

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PhD defenses

Membrane reactors for the direct conversion of CO_2 to dimethyl carbonate

On Thursday October 22, 2015 Harro Mengers defended his PhD thesis entitled 'Membrane reactors for the direct conversion of CO_2 to dimethyl carbonate'. In his thesis, Harro investigated the potential of CO_2 as feedstock for the production of dimethyl carbonate. He investigated the most critical operational parameters of a membrane reactor process based on model calculation. Based on the outcomes of this, he worked on the development of polymer membranes for application in a membrane reactor for the conversion of CO_2 and finally he performed an economic analysis of the CO_2 conversion process in a membrane reactor.

Due to the increasing oil prices the chemical industry searches for alternative feedstock for the production of chemicals. CO_2 is considered as an interesting alternative for environmental and economic reasons. This work investigated the direct conversion of CO_2 in dimethyl carbonate using membrane reactors. DMC is a frequently used chemical for the production of polycarbonates, as methylation agent, in the use as solvent for lithium ion batteries and potentially as fuel additive.

Model calculations were performed to compare the performance of a catalytic membrane reactor (CMR) in which locations of reaction and separation coincide, with an inert membrane reactor (IMR) in which locations of reaction and separation do not overlap. The results indicate that the performance of both membrane reactor configurations can be divided in three different regimes, based on the value of the equilibrium constant (Keq).

Based on these calculations, highly water vapor permeable membranes, meanwhile retaining the reactant CO_2 were developed using sulfonated poly(ether ether ketone) (SPEEK)/chitosan membranes. The results show that the addition of a chitosan layer on top of SPEEK enhances the water vapor permeation and simultaneously improves the H_2O/CO_2 selectivity.


Harro Mengers

Subsequently, the effect of the counter ion in the polymer membrane SPEEK on water vapor permeability and water vapor/CO_2 selectivity was investigated. Mono- (H^+, Li^+, Na^+, K^+), di- (Ca^{2+}) and trivalent (Al^{3+}) counter ions were considered. In general it can be concluded that replacing the H^+ cation in SPEEK for another cation results in an improved thermal stability up to 450-500 °C. Further, the results indicate that the water vapor sorption increases with an increasing cation hydration enthalpy, but the water vapor and the CO_2 permeability decrease with increasing cation hydration enthalpy.

Finally a techno-economic evaluation was performed using water vapor selective catalytic membrane reactors for the direct conversion of CO_2 and methanol into DMC. The Aspen simulations show that even at an excess of methanol, the removal of water vapor is insufficient to stimulate the conversion and therefore only a maximum of 1.5 mol% DMC in the reactor effluent is obtained. To purify this to the required specifications, large size equipment and a substantial amount of energy (13.61 kWh/kg DMC) is required, which results in high investment and utility costs.

For more information, please contact Prof. Dr. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl; phone: +31 (0)53 489 4185).

Thin sulfonated poly(ether ether ketone) films for the dehydration of compressed carbon dioxide

On Friday October 9, 2016 Beata Koziara defended her PhD thesis entitled 'Thin sulfonated poly(ether ether ketone) films for the dehydration of compressed carbon dioxide'. In her thesis, Beata Koziara investigated the intrinsic properties of thin SPEEK films that can potentially be used in composite follow fiber membranes, to assess their applicability (in terms of stability) in high water activity systems. In addition, the design of processes for dehydration of compressed carbon dioxide were evaluated and the added value of a membrane unit in such processes was assessed.

The dehydration of compressed carbon dioxide is needed to recover this fluid after its use to extract water from food products. The removal of water from food aids to extend the shelf life of food. Currently, the dehydration of compressed carbon dioxide is performed via adsorption of the water on zeolite adsorbents. Membrane technology has been considered a competitive alternative for the zeolites. The need to replace zeolites with another technology comes from the fact that the full recovery of the adsorption capacity of zeolites requires heating to 600 °C, which causes high operating costs. Membrane technology is known to be energy efficient.

The properties of thin SPEEK films are investigated using spectroscopic ellipsometry. The measurements showed that the SPEEK films are always anisotropic, and the refractive index n_{xy} is always higher than n_z. This is independent on formation procedures or solvent used. The results indicate that internal stresses are inherent to membranes from this polymer. The stresses can be reversible relieved via plasticization by sorbents such as water vapor from the ambient or residual organic solvents. The relief of stresses is manifested by a reduction in value of the optical anisotropy. Upon removal of the plasticizer the anisotropy increases. The work revealed that the water-induced swelling of SPEEK films with an equal DS (coated in a humid atmosphere) at the particular temperature can be dissimilar. This discrepancy was found to be dependent on the anisotropy in the material. Films with higher initial optical anisotropy prior to swelling swell more than films with lower initial anisotropy. We observed a particular swelling behaviour for films that were formed without access of water (RH= 0 %). Hydration of the polymer during membrane formation affects the internal molecular structure of SPEEK membranes and their morphology, which in turn has impact on swelling. The swelling of the 'dry' film is significantly reduced as compared to the 'humid' film, despite the equal degree of sulfonation, anisotropy and water temperature. Finally, Aspen Plus® simulations of the dehydration of supercritical carbon dioxide using a hollow fiber membrane module, and an economic evaluation based on these simulations are performed. The process is assessed in terms of the duration of the dehydration process and the size of the feed. For a design with multiple membrane separation steps, the recirculation and regeneration of the permeate requires high investment and operating costs for compressors. On the other hand, a simple design with only one membrane separation step can be considered environmentally unfriendly and has high operating costs caused by the high CO_2 emissions.


Beata Koziara

This research was performed in the cooperation framework of Wetsus, centre of excellence for sustainable water technology (www.wetsus.nl). Wetsus is co-funded by the Dutch Ministry of Economic Affairs and Ministry of Infrastructure and Environment, the European Union Regional Development Fund, the Province of Fryslân, and the Northern Netherlands Provinces. The authors would like to thank the participants of the research theme "Dehydration" for the fruitful discussions and their financial support.

For more information, please contact Prof. Dr. Nieck Benes (n.e.benes@utwente.nl) or Prof. Dr. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl).

University of Twente hands out Innovation Vouchers to SME's

The University of Twente has eight SME's awarded an innovation voucher worth 10,000 euros. The companies will use the voucher for the use of facilities, coaching, training or research in one of seven Expertise Centers of the University. The University of Twente has 50 innovation vouchers for SMEs available with a total value of 500,000 euros. They are intended to further stimulate collaboration between the knowledge-intensive SMEs and the Centers of Expertise. "It's interesting to see that the international and regional SMEs are interested in starting up the collaboration with the University of Twente," says Miriam Luizink, Director of Strategic Business Development.

First vouchers

On December 3, the first vouchers awarded were handed over in the Thermoplastic Composite Research Center to eight companies: WhiteFox Technologies, BLUE-tec, Sound Energy, Van Wees UD and Crossply Technology BioVolt, Info Topics, DiaBox and EyemergE. WhiteFox and Blue-tec received UT Vouchers for the European membrane institute. BLUE-tec, which is developing a new type of membrane technology, is pleased with the award of the innovation voucher. The company will do this research at the European Membrane Institute (EMI) of the UT. "We are investigating whether we are able to produce Forward Osmosis membranes and modules based on existing membranes. This allows us to develop an optimal membrane concept at an acceptable price," says director / founder Lex van Dijk of BLUE-tec.

New opening round

The University of Twente has opened the application for the next round of innovation vouchers. SME's have until March 31, 2016 the time to submit their Voucher application. To qualify for a voucher of € 10,000, a requirement is that they are a new client of the relevant Center of Expertise. Next to this there is a own contribution of at least 2,500, - Euro required.

Centers of expertise

The vouchers can be used by any of the Centers of Expertise of the University of Twente: e.g. the European Membrane Institute (EMI).

Innovation vouchers are part of the program, Strategic Business Development at the University of Twente, to strengthen the relationship with the business.

Handing over of the UT Voucher to Blue-tec's Lex van Dijk (left) and WhiteFox (not present; right) by Dr. Zandrie Borneman from the European Membrane Institute (EMI) Twente.

Follow MST on Twitter!

The Membrane Science and Technology group has its own Twitter account!
Follow @MST_UTwente for the latest news of the MST group in a nutshell!

It all started in Twente

What is your name?

Wilbert van de Ven

What are your date of birth and your place of birth?

14 May 1977 in Beesd, The Netherlands.

What is your marital status and do you have children?

Married with Astrid since 2002 and we have two kids, Cedric who is 4 and Elvira who will turn 3 just before this Christmas.

Where are you currently employed and what is your position?

I currently work at Grundfos as research manager. Grundfos is the largest, in units, pump company in the world, producing pumps for heating and cooling in domestic and commercial buildings, as well as for water transport and treatment for utilities and industries. My team consists of the key material specialists of Grundfos and the team that works on developing products in a new area for Grundfos, water quality monitoring and treatment.

Where is your company located and where do you live?

Grundfos' headquarter is located in Bjerringbro in Jutland, Denmark. I live about 20 minutes away from Grundfos in Viborg, a historic town of about 35,000 people (which is quite a city from a Danish perspective).

When did you start your PhD and when did you receive your PhD degree?

I started in September 2003 and had my defense in April 2008.

On which topic did you do your PhD?

I looked into optimal control of membrane operation, and specifically looked at how we could improve ways to monitor water quality in relation to membrane system performance. It was a large project together with the process control department in Twente, where another two PhD students (Bastiaan Blankert and Edwin Zondervan) worked on control and optimization algorithms.

Do you still have contacts with your former PhD students from that time?

Some have become my best friends and we still see each other regularly! But I also would like to add that it would be nice to meet and talk to many of the others I have not seen in a while.

What was your first job after your PhD?

After my PhD, I took a job at Vitens as Water Treatment expert, working together with Walter van der Meer.

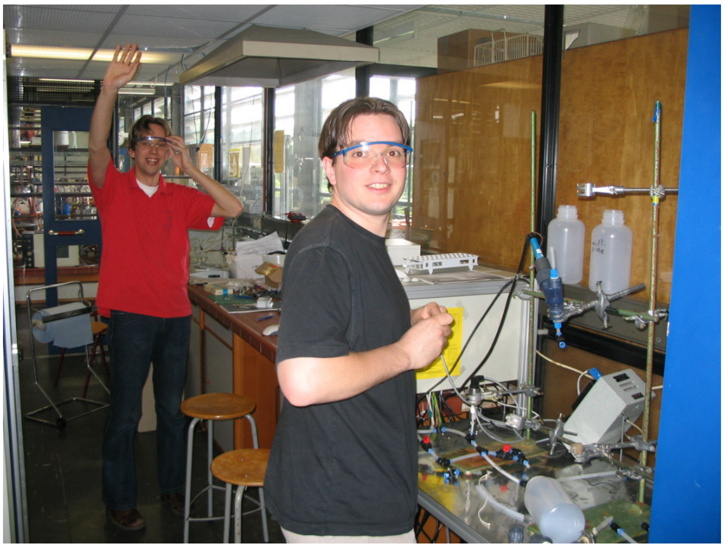
How did your career develop?

I quickly found out that I aspired a leadership role and had the luck that I could become manager of the group I was working in after about 2 years. That was probably the steepest learning curve I encountered, suddenly being responsible for a group of 20+ people. After a total of four and a half year in Vitens I decided I needed a new challenge and joined the startup company BiAqua in Delft (NL). In BiAqua we developed

enzyme-based adsorbents for water treatment. I started as the technology manager and became Managing Director and CTO after a year where I had the pleasure to work closely together with Lute Broens. At some point though, I came to the conclusion that I did not believe enough in BiAqua's proposition to continue in that role. Astrid and I decided to pursue a dream of us to work abroad and within 3 months I had signed the contract with Grundfos.

How do you relate your career to the experience you gained during your PhD?

It took Matthias Wessling some time to convince me that I should do a PhD, but I am very glad I did it at the end. It definitely helped me through my career, as the technical and academic experience comes hand in hand with the jobs I had. I worked and work extensively with universities. On the content side, Grundfos started working on concepts that we studied during my PhD and I intend to build on that even more in the near future.



How did you experience your time in Twente?

Overall, I have lived 12 years in Twente. Still the longest period I have lived anywhere during my life. The chemical engineering education in Twente was very good and experimenting with new educational concepts, e.g. the focus on project education in the first years, has been very useful to me later.

I really enjoyed working in the membrane technology group. A lot of things were possible and there were always many experts around to help me out with new ideas. The most important factor that influenced my experience was the great people in the group.

What important things did you learn during your PhD?

Apart from the obvious things, like scientific writing and doing structured (well, at least a bit structured in my case) research, I learned a lot about membranes and membrane processes, skills that I use often today. I also learned to put electronics together and develop software in Labview. Perhaps not something I use a lot today, but something that I really enjoyed. I also learned that I have a lot of interest in entrepreneurship and the area between science and business due to courses I took. And finally, I think I found out that I am happier to be involved in research rather than actually doing it myself :).

What was the biggest challenge during your PhD?

Getting through the last year, I felt that the learning curve was flattening a bit and that made the task less engaging for me :). Oh yeah, and my first paper, that took ages to get accepted by JMS.

Do you maybe remember an anecdote or a specific moment of that time?

Jorrit de Jong (PhD colleague at that time) and I had the idea to spin SPEEK UF fibers from 98% sulphuric acid. This was a brilliant idea and after some initial tests, we decided to test the idea in the small spinning setup. We got off to a good start but after some time the set up started to act up, we stopped the pumps and went for one of our regular lunch walks over the campus. When we came back, we were stopped by two angry men (Geert-Henk Koops and Herman Teunis) and told in very straight terms we completely screwed up the setup. Luckily it wasn't that bad, but we spent the rest of the day and some of the day after to remove semi-phase-separated polymer from pumps, spinnerets, and tubing. The experience, and my hole-covered clothing, quenched my enthusiasm for membrane production a bit :).

Less collected memories I have of the parties involving German Muttis, it appears that they were usually part of the best parties. I also remember we could spend weeks on making movies and show pieces for graduating colleagues. This may not have helped much to write papers, but it formed strong bonds and group feeling.

What was the best moment of your PhD (except the graduation)?

I think the first moment that I could leave my self-built filtration equipment, go home to leave it running in the weekend and come back on Monday to find my first high quality data.

What would you have done differently if you could do your PhD again?

I should have done much more work together with our project partners, bringing my equipment to the field and working with them to come up with even smarter solutions.

Which advice do you have for the current generation PhD students?

Make the best of your time. The freedom that you have during your PhD will probably never come back. Engage with the outside world as much as you can and do crazy experiments with your colleagues. And, take any opportunity to learn some business skills in a course, you will need them later!

What is your precious memory of the group?

A strange one maybe, but the lunch walks I have made with Bernke Papenburg, Jorrit de Jong, Tymen Visser, Hylke Sijbesma (all former PhD colleagues) and with Matthias Wessling from time to time linger most. We discussed both science and frustrations but also shared difficult and beautiful moments from our private lives.

What could be different in our research group?

Probably what I wish would be different in many research groups; reduce the amount of time spent on administration, money hunting etc. and spend even more time in the nice facilities you have.

What did you miss while working in the group?

Nothing :)

Bio-inspired ion selective crown-ether polymer membranes


Sinem Tas

On March 11, 2016 at 16.45 h Sinem Tas will defend her thesis entitled 'Bio-inpsired ion selective crown-ether polymer membranes. The 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, 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 high degree of specificity.

For more information of this work, please contact Prof. Dr. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl; phone: +31 53 489 4185).

Interview with Kitty Nijmeijer in 'Chemie Magazine'

In the October edition of 'Chemie Magazine' of the Association of the Dutch Chemical Industry (VNCI), Kitty Nijmeijer was interviewed about her role as VNCI Ambassador of the Dutch Chemical Industry and her work on membranes at the University of Twente. The article is in Dutch and can be found at: https://www.vnci.nl/nieuws/chemie-magazine/. The main message Kitty wants to communicate is: 'Chemistry is Fun'.

The VNCI promotes the collective interests of the chemical industry in the Netherlands by means of consultations, information meetings and recommendations. The VNCI acts on behalf of the entire sector as a central contact point and undertakes activities that have a positive impact on the image of the chemical industry. 'Chemie Magazine' is the monthly chemistry magazine of the VNCI.

New people

Membrane development for fuel feedstock production by a combined approach of controlled plasma conversion and membrane separation

Name: Özlem Haval Demirel

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Özlem Haval Demirel obtained her Bachelor degree in Chemical Engineering at Yildiz Technical University, in Istanbul, Turkey. After her graduation, her first experience with membrane technologies was during the IAESTE (International Association for the Exchange of Students for Technical Experience) internship in Evonik Industries, Germany. During that period she worked for three months on the modelling of organic solvent nanofiltration (OSN) processes using Aspen Plus and Aspen Custom Modeler. After this internship, she started her master education in the Membrane Materials & Separation Technologies (MeMaSep) research group at Istanbul Technical University (ITU). During her master, she also collaborated with the Institute of Chemical Technology (ICT), Prague, where she synthesized titanium-silicalite-1 (TS-1) fillers for mixed matrix membrane applications. At ITU she explored the gas separation performance of modified TS-1 fillers in a polymer matrix and completed her master thesis. At that time, she was also working as a teaching assistant in the Chemical Engineering department of ITU.

In September 2015 she joined the Membrane Science and Technology Group at the University of Twente as a PhD candidate. In her project, mixed matrix membranes based on polymer-MOF membranes will be developed for the separation of a mixture of O_2/CO_2/CO. The effect of different MOFs on the membrane performance will be explored in terms of mechanical properties, thermal properties and gas separation performance.

New membranes for the removal of sodium & micropollutants from wastewater

Name: Valentina Balloi

Origin: Italy

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Valentina Balloi studied chemistry at the University of Cagliari, in Italy. She obtained her Bachelor degree in 2012 presenting a project about the synthesis of mesoporous materials for the sequestration of carbon dioxide. In the same year she started her Master in chemical sciences in the same University and she decided to extent her knowledge and experience and joined an international Erasmus project for six months. During that period, she worked in the Material Science Institute of Seville, where she developed materials with photocatalytic properties for the removal of organic pollutants from aqueous solutions. The mayor interest of Valentina is research concerning the development of new functional materials for environmental applications. For this reason, in November 2015, she started her PhD at the Membrane Science and Technology group. Valentina is participates in the Water Nexus project, which is dedicated to developing water treatment solutions focusing on industry and agriculture, sectors that both use large volumes of water. In this project the possibility of using salt water as a resource is investigated, aiming at the use of salt water where possible, and the use of fresh water only where really necessary. The aim of Valentina’s research is the buildup of new membranes for the removal of sodium and micropollutants from wastewater.

Membrane Science and Technology

Vision

The research group Membrane Science and Technology of the University of Twente, headed by Prof. Kitty Nijmeijer, focuses on the multidisciplinary topic of polymer membranes to control mass transfer through interfaces.

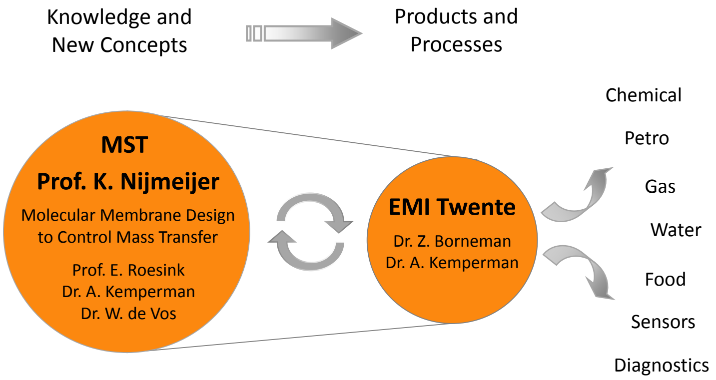

Figure 1: Organizational structure research group.

The group consists of two separate entities (Figure 1): the academic research group Membrane Science and Technology (MST) and the European Membrane Institute Twente (EMI), which performs confidential research directly with the industry.

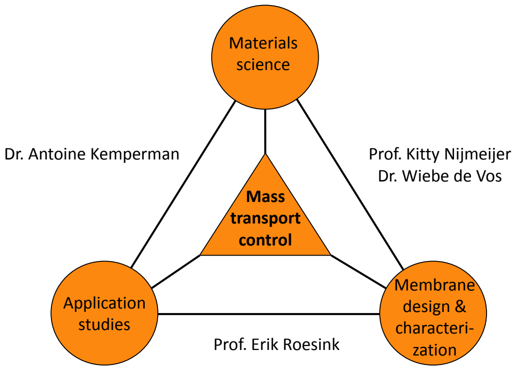

Figure 2: Membrane Science & Technology.

Research within the group is dedicated to the design, development, characterization and application of polymer membranes for Energy, Water and Life Sciences. We aim at tailoring membrane design, morphology and characteristics on a molecular level to control mass transport in applications (Figure 2). More specifically, our research focuses on the separation of molecular mixtures and achieving selective mass transport. We consider our expertise as a multidisciplinary knowledge chain ranging from molecular design towards process applications.

Most of our research is dedicated towards specific applications. We distinguish three main application clusters, i.e. Energy, Water and Life Sciences (Figure 3).

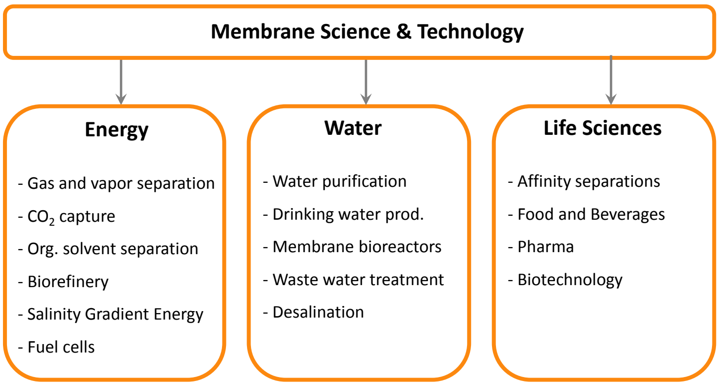

Figure 3: Major application clusters Membrane Science & Technology.

Energy

The research cluster Energy is dedicated to the molecular design and synthesis of polymer membranes for e.g. gas and vapor separations (CO_2 capture, olefin/paraffin separation, water vapor removal), biorefinery applications, fuel cells and the generation of energy from the mixing of salt and fresh water (‘salinity gradient energy’ or Blue Energy). Relevant research aspects are control of structure-properties relationships, ultimate selectivity, molecular recognition, and separation of complex, multi-component mixtures.

Water

Within the application cluster Water, research addresses the development of membranes and the application of membrane technology for water treatment, e.g. water purification, desalination, membrane bioreactors and waste water treatment. In particular it investigates the relation between membrane design, morphology and membrane properties in relation to performance, selectivity and causes, consequences and control of fouling.

Life sciences

The cluster Life Sciences focuses on the design of porous membranes to separate complex multicomponent mixtures in pharmaceutical, food, beverage and biotech applications. Important subjects are the tuning of the material properties and structure (e.g. pore morphology and porosity), the development of functional materials (e.g. affinity separations of biomolecules) and the creation of improved processes. In addition, aspects related to process design and industrial implementation, such as scale-up of novel membrane fabrication methods, are investigated. The research group consists of 30-35 people among which approximately 15-20 Ph.D. students, three permanent researchers, five B.Sc. and M.Sc. students and five academic staff members. Next to the head of the group, Prof. Kitty Nijmeijer, the staff consists of Prof. Erik Roesink, Dr. Wiebe de Vos, Dr. Antoine Kemperman and Dr. Zandrie Borneman, who is responsible for the EMI Twente. Next to extensive, general knowledge on polymer membrane science and technology, each of the staff members has his/her own specific field of dedicated expertise (Table 1).

Table 1: Specific expertise of the staff members of MST.

Name	**Specific expertise**
Prof. Kitty Nijmeijer	Membrane design and characterization, molecular selectivity, molecular recognition, dense membranes, Energy and Water
Prof. Erik Roesink	Membrane formation, porous systems, phase inversion, solvent-free membranes, biomimetic membranes, Water and Life Sciences
Dr. Antoine Kemperman	Causes, consequences, cleaning and control of membrane fouling, interactions at the interface, Water European Membrane Institute (EMI) Twente: Confidential contract research directly with the industry
Dr. Wiebe de Vos	Membrane surface science, surface modification, multilayers, polymer brushes, Water and Energy.
Dr. Zandrie Borneman	European Membrane Institute (EMI) Twente: Confidential contract research directly with the industry

Knowledge valorization

Our group has decided to establish a significant effort in the valorization of its knowledge. The European Membrane Institute Twente (EMI Twente) was established in 1995 and performs confidential contract research directly with the industry and public organizations. Research is governed by questions from stakeholders. To guarantee confidentially, we work with highly skilled researchers with long standing experience in membrane technology in our group. Students are not involved. EMI Twente creates, transfers and translates (fundamental) scientific knowledge into products, processes and applications. Projects can last from only a few days up to three years and can involve membrane development and synthesis, membrane characterization, and/or membrane application studies. The EMI Twente acts as the interface between the academic research and the industrial needs.

Services

The EMI Twente provides the following services:

- Membrane development
- Membrane characterization
- Membrane application studies
- Desktop studies
- Consultancy
- Selling of equipment (e.g. cells for gas separation, UF and MF, casting knives, cloud point meters, hollow fiber spinning lines, spinnerets

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MNT- Information

Membrane News Twente is published two times per year and aims to inform the membrane community about the activities of the Membrane Technology Group of the University of Twente (membrane@utwente.nl www.utwente.nl/tnw/mtg).

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