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The Use of Different Templates for the Synthesis of Reproducible Mesoporous Titania Thin Films and Small Pore Ultrafiltration Membranes**

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*The state of the art commercial membranes are made with the sol-gel method. But the pore size
of membranes and thin films synthesized via the sol-gel method is somewhat restricted to
control in a reproducible way. Furthermore, the synthesis of uniform pores via the sol-gel
method is a challenge, and therefore the resulting membranes often exhibit a limited selectivity.
In contrast, the template-assisted method (Evaporation Induced Self-Assembly) described in
the present paper is able to form defect free membranes and thin films with more narrow pore
size distributions and thus sharper cut-off curves in a more reproducible way. Moreover, the
effect of different templates (Brij 58, Brij 56, Brij 78 and Brij 76) and concentrations on the
porosity of the top layer and separation performance is thoroughly investigated. Our study also
discusses the pore formation mechanism of the template-assisted method. Under the here
described synthesis conditions, the Brij type templates act as a separator, whereby the final
pore size can be easily controlled by adjusting the amount of template used. Furthermore, the*

pores obtained with this template-assisted method are more uniform as compared to the sol-gel method. Such defect free, reproducible small pore ultrafiltration membranes with controllable pore size and narrow pore size distribution could open the path to further process intensification and more sustainable production by separating molecules with small difference in molecular weight.

1. Introduction

In addition to the successful application of membranes in the field of water treatment, the membrane market is more and more expanding towards more complex and process integrated separations. These membrane applications require mainly chemically stable nanoporous membranes. Nowadays, robust TiO₂ nanofiltration and tight ultrafiltration membranes are available on the market. Nevertheless, the development of high-selective membranes, fit to separate molecules with relative small size differences, can broaden the application field. Possible applications include e.g. product/reagent/catalyst separations, polymer/oligomer/monomer separations, and fractionations.

The state of the art ceramic membranes are made via the sol-gel process in which pores are formed as a result of cross-linking of inorganic precursor particles formed via condensation reactions (sol). Although some specific synthesis allow a narrow pore size distribution^[1, 2], generally the resulting membranes have a relative broad pore size distribution^[3] and thus exhibit a relative diffuse retention curve^[4]. Consequently, such membranes are classified as low selective, since they are incapable of separating molecules with a small difference in molecular weight. Moreover, the pore size of sol-gel membranes is somewhat limited to control and often multiple layers need to be deposited to end up with defect free membranes with the correct molecular weight cut-off (MWCO).^[5-7] In addition, there is no control over the organization and tortuosity of the pores in sol-gel membranes. Nevertheless, ceramic separation membranes with more controlled features (pore size, organization, ...) are desired in order to expand the

application range of this energy efficient separation technology.^[8] Finally, the robustness and reproducibility of the sol-gel process is restricted since the process is mainly under kinetic control due to the mild synthesis conditions.^[9] Therefore, minor changes in the experimental conditions can lead to considerable differences in the resulting material.

In order to improve the robustness, reproducibility, pore uniformity and pore size control of ceramic membranes, an alternative template-assisted method is applied in the present paper. Such defect free, reproducible small pore ultrafiltration membranes with controllable pore size could enable further process intensification and more sustainable production by separating molecules with small differences in molecular weight in applications where the current sol-gel membranes are inadequate. Originally, the template-assisted method was used for the formation of mesoporous silica materials.^[10-12] But nowadays, the template-assisted method is adjusted for the synthesis of more stable titania materials.^[13, 14] More details on the synthesis of template-assisted mesoporous titania powders^[15-17] and thin films^[14, 16, 18] made by the evaporation induced self-assembly (EISA) can be found in literature. Typically, an amphiphilic block copolymer (ABC) is applied as template around which precursor oligomers condensate. In EISA, it is critical to keep the inorganic precursor oligomers small prior to condensation around the template in order to obtain uniform pores (i.e. size precursor particle or clusters $\ll$ final pore diameter), which is recently described by a coarse-grained model based on promoting the template-cluster above the inorganic cluster-cluster interactions.^[19, 20] The precursor reactivity is controlled by limiting the water content and by working in strong acidic and diluted solvent environment so that condensation reactions are hindered. Upon solvent evaporation the ABC concentration increases and self-assembly is promoted. Then, the less volatile acid evaporates, leading to consolidation of the inorganic network around the template due to extended condensation as a result of the progressive increasing pH. Nevertheless, also the rate of evaporation of the acid, has been reported to play an important role that could drive the film towards a uniform or a non-uniform phase.^[19] The limited amount of water plays a crucial role

in the conformation process of the template and two different reaction pathways are known in literature based on the water-to-metal ratio.^[9, 21, 22] Keep in mind that the two reaction pathways described below are extremes and intermediate situations are possible. On the one hand, in media with relatively high water content ($[\text{H}_2\text{O}]/[\text{Ti}] \sim 10$), the pore size is determined by the size of the used ABC^[23, 24] like in typical mesoporous silica materials.^[25] Fast but controlled condensation reactions lead to the formation of hydrophilic oxo-oligomers that interact with the hydrophilic polyethylene oxide blocks of the template via hydrogen bonding (hydrophilic matching). Due to the relative weak interaction, a flexible hybrid interface is formed and upon solvent evaporation, phase segregation is enhanced leading to self-assembly of the template. The resulting materials exhibit well-ordered hexagonal or cubic mesostructures. The pore size can be further adjusted by a swelling agent.^[26] On the other hand, in media with low water content ($[\text{H}_2\text{O}]/[\text{Ti}] \sim 1-2$), the ABC acts as a separator and the pore size is dependent of the amount of the used ABC. Very slow hydrolysis and condensation occur and strong chelation reactions can take place between the metal centers of the inorganic source and the polar heads of the ABC or the ether groups of the polyethylene oxide chains of the ABC. Complexation is further enhanced upon solvent evaporation and the difference in solubility of the different blocks of the ABC decreases due to the reactions between the polar head of the ABC and the hydrophobic inorganic clusters. Therefore, template unfolding occurs, leading to wormlike mesophases. In either template-assisted pathway described above, prehydrolysis of the inorganic source (i.e. long aging of the solution, common in the sol-gel method) is avoided as it is harmful for the formation of uniform pores through EISA, because it typically leads to a drastic increase of the precursor particle size.^[27]

In our previous research we have determined optimal EISA conditions for mesostructured titania thin films, starting from optimal synthesis conditions for titania powder.^[28] Although synthesis conditions of mesoporous powders can be applied, some important differences have to be taken into account with respect to the underlying mechanisms, due to differences in

evaporation of thin coated layers versus powder synthesis. For instance, in contrast to the powder sample, no nanocrystal formation is observed during the thermal stabilization of the thin film, rendering the average pore size of the thin film independent of thermal stabilization (up to 140°C in casu) but at the same time also more sensitive to calcination in a later step. Nevertheless, the same calcination regime can be applied for the thin films and the powder without a structural collapse due to uncontrolled crystallization.^[28]

Even though this methodology is known for powders and thin films on dense supports, literature on template-assisted titania small pore ultrafiltration membranes (thin template-assisted layer on a porous support), with the purpose of controlling the porous properties of the top layer, is scarce. Some reports on template-assisted ultrafiltration membranes are available, but they consist of a silica top layer^[29, 30] or of titania top layers templated by Pluronic ABCs^[31, 32]. Note that in this paper we particularly aim at ultrafiltration membranes at the lower end, aiming for pores with controlled dimensions from 3 to 6 nm with a narrow pore size distribution. The main goal of the present research is to obtain a robust and reproducible template-assisted mesoporous titania membrane top layer in order to expand the membrane applications enabling an energy efficient separation technology. Furthermore, insight in the pore formation process is desired in order to be able to adjust the pore size of the titania top layer in an intuitive and easy way. Finally, a narrow pore size distribution is aimed at to obtain a membrane with a steep retention curve and thus high selectivity. Therefore, the use of different templates and different template concentrations on the properties of the membrane toplayer and the separation performance has been investigated.

2. Experimental details

2.1. Synthesis of mesoporous titania thin films and membranes

Initial solutions were prepared in a similar way as our previous research^[17, 28] based on the work of the Sanchez group.^[33-35] The final molar ratio of a typical solution was titanium tetra-

isopropoxide:1, surfactant:X, 2-propanol (IPA):40, water:10 and hydrogen chloride:2. After 30 minutes stirring, thin films were dip coated from the solution on a 500 μm thick <100> silicon wafer with a 10 cm diameter (purchased from Si-Mat) or on a 10 cm long tubular single channel asymmetric membrane support (outer diameter = 1 cm, channel diameter = 0.7 cm, mean pore size of the TiO_2 top layer is 5 nm, the macroporous support consists of $\alpha\text{-Al}_2\text{O}_3$, purchased from Inopor/IKTS). A contact time of 30 seconds with the solution was applied and afterwards the supports were withdrawn (dense support) or emptied (porous tubular support) at a constant rate of 2 mm/s and at a controlled relative humidity of 40-50 %. It is important to note that the silicon wafer is a dense support whereas the tubular membrane is a porous support, so capillary infiltration of the coating solution into the porous support can be expected. After the drying line visually reached the bottom of the film or in case of membranes the same time was applied after the dipping solution flowed out the membrane, the films or membranes were placed in a controlled atmosphere for 24 h (relative humidity (RH) = 75 % + IPA vapor). Subsequently, the thin films or membranes were transferred to an oven and heated at 1 $^\circ\text{C}/\text{min}$ to 120 $^\circ\text{C}$ to stabilize thermally for 24 h. Finally, the thin films or membranes were calcined at 360 $^\circ\text{C}$ (2 h, 30 $^\circ\text{C}/\text{h}$, ambient atmosphere), also a plateau at 300 $^\circ\text{C}$ for a duration of 12 h was executed.

Different Brij surfactants (Brij 58, Brij 56, Brij 78 and Brij 76, purchased from Aldrich) were used to synthesize titania thin films and membranes. Different amounts of Brij were investigated based on conditions mentioned in thin film literature and were applied in the alternative titania small pore ultrafiltration membrane synthesis. In literature, the following compositions can be found for thin films: Brij 58/Ti = 0.05 (41.3 wt % Brij 58 in the non calcined structure)^[33-35], Brij 58/Ti = 0.083 (53.9 wt % Brij 58 in the non calcined structure)^[36, 37], Brij 56/Ti = 0.125 (51.7 wt % Brij 56 in the non calcined structure)^[34]. Samples with the same surfactant/Ti ratio or same wt % surfactant in the non calcined structure but with different templates, altering in carbon chain length or polyethyleneglycol block length, were investigated. An overview of the performed synthesis and the surfactants used is given in Table

1. The sample names consist of a shortening of the surfactant name followed by the surfactant/Ti ratio, e.g. the sample B58 - 0.05 is made with the surfactant Brij 58 and a Brij 58/Ti ratio of 0.05. As a reference, the same synthesis condition was followed but without the addition of any surfactant (the sample is denoted as B58 – 0) and commercial membranes were purchased from Inopor/IKTS (single channel asymmetric membranes, ZrO₂ or TiO₂ top layer with an average pore size of 3 or 5 nm respectively, α -Al₂O₃ macroporous support, length = 10 cm, outer diameter = 1 cm, channel diameter = 0.7 cm).

2.2 Analysis of mesoporous titania thin films and membranes

The thin film porosity characteristics were determined by performing Kr adsorption measurements at 87 K using a Quantachrome Autosorb-iQ-C automated gas system as described by Thommes and coworkers.^[38-40] Kr-adsorption at 87 K is applied instead of conventional N₂-adsorption at 77 K since the latter is not suitable for the pore size analysis of thin films. This is due to the fact that the layer to be analyzed is only a few hundred nanometers thick and consequently, the total surface area and pore volume are extremely small. Therefore, the pressure changes resulting from adsorption cannot be determined with sufficient accuracy and precision with conventional N₂-adsorption at 77 K. This is the result of the presence of a large number of unadsorbed gas molecules in the void volume of the sample cell because of the high saturation pressure of N₂ (760 Torr). However, the phase transition pressure of Kr at 87 K is much lower (i.e. 13 Torr) and therefore, the number of unadsorbed gas molecules in the void volume is reduced, making Kr-adsorption a much more sensitive technique as compared to conventional N₂-sorption. Film-on-support sample pieces were transferred to a 12 mm diameter glass sample bulb. Prior to measurements, the samples were degassed at 120 °C for 16 h under vacuum. The krypton adsorption isotherms at 87 K were analyzed using the Quantachrome software (ASiQwin version 3.0). The “NLDFIT traceable” krypton calibration curve at 87 K developed by Quantachrome instruments was used to determine the PSD since

conventional methods for pore size analysis based on the Kelvin equation (BJH method) are not applicable for the pore size analysis with Kr-adsorption since drastic assumptions concerning the thermophysical properties have to be made, also methods like NLDFT or GCMC are not yet developed. Specific surface area and total pore volume are not reported since they are normalized with the sample mass, which is the mass of the entire sample (100 – 200 nm porous top layer and 500 micron dense support) and not only that of the porous top layer.

In general, an average error of 5 to 10% can be expected for sorption analysis results, even though the error for pore size distributions rather depend e.g. on the accuracy of the model for the particular pore geometry in relation to the materials properties.

Scanning electron microscopy (SEM) of thin films and membranes were performed with a Jeol JSM6340F microscope, which was operated at an acceleration voltage of 5 kV. Both top down and cross section images were acquired in order to assess the morphology and film thickness respectively. The obtained top down SEM images were further processed in Mipar image analysis software (version 2.2.4) to obtain Fourier diffractograms through Fast Fourier Transformation (FFT) analysis in order to assess the pore organization.

The pore size distributions of the membranes were determined by permoporometry. Permoporometry measures only the active pores that are responsible for the actual membrane performance, whereas sorption techniques measure the active as well as the passive (dead-end) pores. The pore size distributions (PSDs) were obtained using the Kelvin equation in combination with the average thickness of the t-layer as described by Cuperus and coworkers.^[41] Water was used as condensable vapor and the desorption curve was utilized to determine the PSD. The membranes were dried overnight at 120 °C prior to the measurements. Retention and MWCO of the membranes were determined by cross flow filtration experiments conducted on the membranes with an aqueous feed containing polyethylene glycols of different molecular weight (MW = 600, 1500, 3000, and 10000 Da). The retentate and permeate samples were analyzed by gel permeation chromatography. The applied unit consisted of a HPLC pump

(Waters 510, 1 mL / min), an auto sampler (Waters 717), two in series coupled columns (Ultrasphere 500 and 200) and a refractive index detector (Waters 2414). From the chromatography data the retention was calculated by the following equation.

$$R_i [\%] = \left(1 - \frac{C_{p,i}}{C_{r,i}}\right) \cdot 100$$

Where $C_{p,i}$ is the concentration of the permeate and $C_{r,i}$ is the concentration of the retentate for a given compound i . A retention or cut-off curve is obtained by plotting the retention against molecular weight. The molecular weight cut-off (MWCO) of a membrane is defined as the MW above which molecules are at least 90 % retained by the membrane.

3. Results and discussion

3.1 The use of different templates for the synthesis of titania thin films

3.1.1 Brij 58 as a template

Figure 1 displays the Kr adsorption isotherms and pore size distributions (inset) at 87 K of the titania thin films B58 – 0, B58 – 0.05 and B58 – 0.083. The porosity data is listed in Table 1. The isotherm of the sample B58 – 0 (without the template) exhibits a stepwise adsorption curve over the entire P/P_0 range indicating a wide diversity of adsorption environments and confinements. Consequently, the PSD of B58 – 0 shows multiple maxima as a result of pores with different sizes over the entire measured range instead of the desired single and uniform pore size. In contrast to the sample without the template (B58 – 0), the samples synthesized with the template show only one increase in adsorbed volume due to capillary condensation in the mesopores (Type IV isotherms according to the IUPAC classification^[42]). The sample B58 – 0.05 exhibits a steep capillary condensation step between $0 \leq P/P_0 \leq 0.4$ corresponding to uniform pores of 3.6 nm. Whereas the sample B58 – 0.083 exhibits a steep capillary condensation step between $0.3 \leq P/P_0 \leq 0.7$ corresponding to uniform pores of 4.8 nm. Both samples synthesized with the template (B58 – 0.05 and B58 – 0.083) have the same FWHM

(2.3 nm), corresponding to more uniform pores as compared to the sample synthesized without the template. SEM images (**Figure 2** (top) and supporting information **Figure S1**) of B58-0.05 before and after calcination at 360 °C show no observable cracks and a wormlike mesophase. The FFT diffractogram (supporting information Figure S1 bottom right) shows a diffuse signal without clear defined diffraction spots or rings, so no indication of a well-organized pores is observed. The film thickness was 175 nm before and 110 nm after calcination (shrinkage of 37 %).

The above results demonstrate the functioning of the template. By using the template, a single and uniform pore size is formed, instead of multiple pore sizes over a broad range, which are formed in the absence of the template. The uniform pore size is a necessity for the formation of high selective membranes. Furthermore, the pore size can be easily altered by adjusting the amount of template, that means that larger pores are obtained when more template is used while the FWHM and thus the uniformity of the pores remains the same. These results indicate that the template acts as separator since the pore size increases with the amount of template used. Typically, this behavior is observed in synthesis with much lower water content ($h = \text{H}_2\text{O}/\text{Ti} < 2$, whereas our synthesis has $h = \text{H}_2\text{O}/\text{Ti} = 10$). Furthermore, in a similar synthesis in literature by Crepaldi and coworkers (same surfactant and water content), different behavior is observed.^[34] Crepaldi and coworkers observe no significant increase in pore size when more Brij 58 is used although the organization of the template changes, which is expected in media with high water content. But Crepaldi and coworkers age their as-synthesized thin films at RH = 50 – 60 %, whereas our as-synthesized thin films are aged at RH = 75 % + IPA vapor. That means that in our synthesis no IPA evaporates during aging since the atmosphere is already saturated with IPA vapor. Thus, in our synthesis only water evaporates during aging of the thin film, lowering the water content in the as-synthesized thin film. Therefore, our synthesis shows the behavior of a low water content synthesis and consequently the template acts as a separator whereby the pore size increases with the amount of Brij 58 used in the synthesis.

3.1.2 Brij 56 as a template

Figure 3 displays the Kr adsorption isotherms and pore size distributions (inset) at 87 K of the titania thin films B56 – 0.05, B56 – 0.082 and B56 – 0.125. The porosity data is listed in Table 1. All samples exhibit a type IV isotherm (IUPAC classification^[42]), which is typical for a mesoporous material. The sample B56 – 0.05 shows an increase in adsorbed volume between $0 \leq P/P_0 \leq 0.4$ due to capillary condensation in the mesopores. Therefore B56 – 0.05 exhibits a mean pore size of 3.6 nm (FWHM = 3.1 nm). The sample B56 – 0.082 exhibits a capillary condensation step between $0 \leq P/P_0 \leq 0.5$, whereas B56 – 0.125 exhibits a steep capillary condensation step between $0.3 \leq P/P_0 \leq 0.7$. Consequently they have a mean pore size of 4.0 nm (FWHM = 2.5 nm) and 4.6 nm (FWHM = 1.9 nm) respectively. It is noteworthy to mention that the shoulder around 5.5 – 6 nm in B56 – 0.125 is probably due to lower sensitivity of the measurement at higher P/P_0 (since $P/P_0 \sim e^{(1/d)}$) rather than the existence of a bimodal pore size distribution.

The results obtained by using Brij 56 as a template are similar to those obtained by using Brij 58 as a template even though the length of the ethylene oxide chains are different. Moreover, in both cases the pore size of the final structure increases with the amount of template used. Therefore, as discussed at the end of section ‘3.1.1 Brij 58 as a template’, the template acts as a separator. Moreover, as the pore size of the Brij 56 templated structures increase, the FWHM of the PSD decreases and thus more uniform pores are formed.

3.1.3 Brij 78 as a template

Figure 4 displays the Kr adsorption isotherms and pore size distributions (inset) at 87 K of the titania thin films B78 – 0.05, B78 – 0.049 and B78 – 0.083. The porosity data is listed in Table 1. All samples exhibit a type IV isotherm (IUPAC classification^[42]) which is typical for a mesoporous material. B78 – 0.05 and B78 – 0.049 show a steep increase in adsorbed volume

between $0 \leq P/P_0 \leq 0.5$ and consequently the samples exhibit a similar PSD with a mean pore size of 4.3 nm (FWHM = 1.6 nm) and 4.1 nm (FWHM = 2.1 nm) respectively. The capillary condensation step of B78 – 0.083 shifts to higher relative pressures, between $0.3 \leq P/P_0 \leq 0.7$, and thus the sample exhibits an increased pore size of 4.7 nm (FWHM = 1.7 nm) as compared to the sample B78 – 0.05 and B78 – 0.049.

Obviously, the porosity characteristics of B78 – 0.05 and B78 – 0.049 are very similar since almost the same amount of Brij 78 was used. These synthesis were performed in order to have the same Brij/Ti ratio (B78 – 0.05) or weight percent Brij in the final structure (B78 – 0.049) as B58 – 0.05 (Table 1). Although the same ratio of Brij/Ti or weight percentage of Brij was used, the pores of B78-0.05 and B78-0.049 are larger than B58-0.05 effectuating an effect of the higher amount of carbons in the aliphatic chain (i.e. 18 instead of 16). Nevertheless, as with Brij 58 and Brij 56, increasing the amount of Brij 78 leads to an increased pore size. Similarly, also Brij 78 acts as a separator whereby the pore size is dependent of the amount of template instead of solely the type of template. Even though, compared to the same content in B58, the template size (i.e. the size of the alkyl chain) can also play a role at low Brij/Ti ratio.

3.1.4 Brij 76 as a template

Figure 5 displays the Kr adsorption isotherms and pore size distributions (inset) at 87 K of the titania thin films B76 – 0.05, B76 – 0.079 and B78 – 0.125. The porosity data is listed in Table 1. All samples exhibit a type IV isotherm (IUPAC classification^[42]), typical for a mesoporous material. The sample B76 – 0.05 shows a sudden increase in adsorbed volume due to capillary condensation in the mesopores between $0 \leq P/P_0 \leq 0.4$, whereas B76 – 0.079 shows a capillary condensation step between $0 \leq P/P_0 \leq 0.5$ and B76 – 0.125 between $0.3 \leq P/P_0 \leq 0.7$. Consequently the samples have a mean pore size of 3.8 nm (FWHM = 2.3), 4.1 nm (FWHM = 2.1 nm) and 4.6 nm (FWHM = 3.3 nm) respectively. The sample B76 – 0.125 has less uniform pores as visible in the broader PSD.

Similarly as with the thin films using Brij 58, Brij 56 and Brij 78 as template, the pore size of the thin films with Brij 76 as template increases with the amount of Brij 76 used. In the same way as with the other templates, the template acts as a separator and thus an increase in amount of template leads to a pore size increase instead of a change in template organization, as discussed in section ‘3.1.1 Brij 58 as a template’. Furthermore, B76 – 0.125 exhibits the broadest PSD of all deposited structures. This might be related to the high %wt of the synthesis in combination with the Brij 76 template, which has the largest hydrophobic fraction of all templates. This might impact the template behavior or the condensation of a stable inorganic framework around the template prior to template removal, leading to a partial collapse of the porous structure during calcination. This could be detrimental for the the performance of membranes made in a similar way.

3.1.5 Comparison of the different templates

All the templates used in the previous sections act as a separator whereby the pore size is mainly determined by the amount of surfactant used rather than the size of the applied surfactant molecule. Furthermore, the type of Brij surfactant utilized in the synthesis does not seem to have a strong influence on the final pore size. For example, synthesizing a titania thin film with 41.3 wt % surfactant in the non calcined structure leads to a pore size of 4.1 nm regardless of the fact that Brij 76 or Brij 78 is used. This confirms that, in our synthesis, the size of the surfactant has hardly influence since Brij 78 ($C_{18}H_{33}(OCH_2CH_2)_{20}OH$, $C_{18}EO_{20}$) is a much larger molecule as compared to Brij 76 ($C_{18}H_{33}(OCH_2CH_2)_{10}OH$, $C_{18}EO_{10}$). In a typical synthesis in water rich media the Brij/Ti ratio determines the organization of the mesostructure accompanied by small differences in pore size.^[34] **Figure 6** (top) illustrates that in our synthesis there is no linear correlation between the Brij/Ti ratio and the final pore size after calcination (correlation coefficient of 0.4751) and that different pore sizes are obtained with the same Brij/Ti ratio. The lack of correlation can of course be influenced by defects in the structural

uniformity introduced during calcination as exemplified in our previous research.^[17] However, figure 6 (bottom) illustrates that the correlation between the pore size of the calcined structure and the wt % Brij in the non calcined structure shows much better correlation (correlation coefficient of 0.8183). If B58 – 0.05 (41.3 % wt) is considered as an outlier (based on Dixon’s Q-test^[43] with confidence level of 90 %) the correlation coefficient becomes 0.951. This is a fairly good correlation considering the experimental and analytical errors. This confirms that the template acts as a separator whereby the pore size is mainly influenced by the amount of template (% wt Brij in the non calcined structure). Therefore, the template size (both aliphatic and EO part) has only a mild impact on the pore size. This conclusion is in contrast with the results of a typical synthesis in water rich media where the pore size is mainly determined by the size of the template.^[34] The section below explains the different behavior observed in our synthesis method.

As discussed in section ‘3.1.1 Brij 58 as template’, the differences of our synthesis with a typical synthesis in water rich media, being the dependence of the weight percentage of surfactant rather than its size, is most likely due to the presence of IPA vapor during aging of the thin film in our synthesis. Therefore, one can expect that only water can evaporate from the thin film leading to a decreased water content in the still wet thin film. Consequently, our synthesis acts like a low water content medium. Furthermore, the most narrow PSD and therefore most uniform pores are obtained with Brij 78 as a template. The FWHM of the PSDs are in the range of 1.6 – 2.1 nm whereas the FWHM of the other templates are in the range of 2.1 – 3.3 nm, except for B56 – 0.125 which has a FWHM of 1.9 nm (similar to the FWHM of the Brij 78 templated structures).

3.2 The use of Brij-58 templates for the synthesis of titania small pore ultrafiltration membranes

In this section, the alternative template-assisted approach is performed on a porous support instead of a dense support like in the previous section. But first of all, the reproducibility and pore size control of the state of the art commercial sol-gel membranes will be assessed. Secondly, the reproducibility and robustness of the template-assisted membranes will be investigated and compared to the commercial sol-gel membranes. Also the ability of the template-assisted approach to control the pore size of the deposited top layer of the membrane will be assessed and correlated to the results obtained on thin films. Finally, the selectivity of the template-assisted membranes will be discussed.

Retention curves and GPC chromatograms of two different batches 3 nm and 5 nm commercial sol-gel membranes can be found in the supporting information (**Figure S2** and **Figure S3**). The two different batches of the commercial 3 nm sol-gel membrane have a MWCO of 6104 Da and 2496 Da. Also the two different batches of the 5 nm sol-gel membranes have a great difference in MWCO, although less severe (5439 Da and 4596 Da), illustrating the limited reproducibility of the membranes made by the sol-gel method. The difficulty to control the pore size of the membranes made by the sol-gel method originates from the limits of control in the synthesis method itself and therefore will always result in a limited reproducibility/control of the pore size of these type of membranes. For example, the 3 nm sol-gel membrane has actually a higher MWCO than both 5 nm sol-gel membranes (6104 Da versus 5439 and 4596 Da).

Retention curves and GPC chromatograms of membranes synthesized with and without Brij 58 as template can be found in the supporting information (**Figure S4**). Remark that, to create better accuracy in the MWCO curve in between 3000 and 10000 Da, we added an extra polyethylene glycol molecule with a molecular weight of 8000 Da to the filtration mixture. The addition of the template to the synthesis leads to an increase in MWCO from 2242 Da (without the template, B58 – 0) to 2808 Da (with the template, B58 – 0.05). Furthermore, the retention curve of B58 – 0 shows a large plateau from approximately 2500 Da until 18000 Da, which is absent in the B58 – 0.05 membrane. Indeed, the GPC chromatogram of the permeate of B58-0

exhibits two additional peaks around 7000 and 12000 Da as compared to the GPC chromatogram of the permeate of B58 – 0.05. The additional peaks in the sample made without the template (B58 – 0) are a result of large defects in the deposited layer, which is detrimental for the selectivity of the final membrane. In case of the thin films, it was visually observed that the calcined thin film B58 – 0 was less homogeneous and contained uncoated parts which were absent when using a template. These large holes in the B58 – 0 thin film were not observed in the Kr adsorption PSD (Figure 1) since this analysis method cannot observe pores larger than 10 nm.^[38] The large defects are absent in the template-assisted membrane, which is necessary in order to maintain the selectivity of the membrane and reach 100% cut off. It is therefore clear, that the template has a vast impact on the uniformity of the pores and the quality of the deposited layer.

Figure 7 shows the permporometry desorption curves and pore size distributions of the B58 – 0 and B58 – 0.05 membranes. The membrane made without the template (B58 – 0) shows a more diffuse capillary evaporation step (between 30 % < RH < 65 %) as compared to the membrane made with the template (B58 – 0.05, capillary evaporation between 48 % < RH < 70 %). Furthermore, the capillary evaporation step of B58 – 0 occurs at lower RH. This indicates that the membrane top layer of B58 – 0 consists of smaller and less uniform pores ($\varnothing_{\text{pore}} = 3.9$ nm, FWHM = 1.7 nm, average thickness t-layer = 0.06 nm) as compared to B58 – 0.05 ($\varnothing_{\text{pore}} = 5.1$ nm, FWHM = 1.1 nm, average thickness t-layer = 0.03 nm). This is in agreement with the results of MWCO measurements (see supporting information, Figure S4) although a much larger difference in MWCO would be expected based on the difference in pore size as deduced from permporometry. This might indicate that mainly the largest pores in the PSD of B58-0 are responsible for the MWCO value and the performance of the membrane. Even though smaller pores exist that might cause some cut off of lower molecular weights as seen by the start-off point of the retention curve (see supporting information, Figure S4). The start-off point of the

retention curve is at much lower molecular weights for B58-0 than B58-0.05, while they coincide at higher molecular weights and percentage retention.

Furthermore, the relative permeation of the permoporometry desorption curve of B58 – 0 never reaches zero. This is the effect of large defects in the top layer, which is in good agreement with the retention curve of B58 – 0. This is in contrast to the relative permeation of the permoporometry desorption curve of B58 – 0.05 that reaches zero, which is in good agreement with the corresponding retention curve. Therefore, the membrane B58 – 0.05 can be regarded as defect free, a necessity for a high selective membrane in which the selectivity is only determined by the sieving/size exclusion effect of the pores. It has to be noted that top down SEM analysis of B58 – 0.05 (Figure 2 (bottom) and supporting information **Figure S5**) revealed a smooth wormlike nanoporous surface, although some cracks in top layer are present. Similar to the deposition on dense substrate, the FFT diffractogram of the film on a porous support (supporting information Figure S5 bottom right) shows a diffuse signal without clear defined diffraction spots or rings, so no indication of a well-organized pores is observed. The above MWCO and permoporometry analysis proof that the cracks are not large defects through the selective top layer since the retention towards high MW polymers is not affected. This shows the importance of performance tests like permoporometry and MWCO measurements above local techniques like SEM for defectivity assessment. It is difficult to distinguish the deposited template assisted layer from the porous support in the SEM cross section (supporting information Figure S5). Possibly (partial) infiltration of the coating solutions in the porous support is present, which might explain why the cracks do not affect the final performance of the membrane.

Retention curves and GPC chromatograms of 2 different batches of membranes made with the same amount of Brij 58 are shown in Figure 8. The retention curves and GPC chromatograms are almost identical. Also the MWCO of B58 – 0.05 and B58 – 0.05 bis are very similar (2808 Da and 2954 Da respectively, Δ MWCO = 146 Da), whereas the difference in MWCO of the

sol-gel membranes is much larger ($\Delta\text{MWCO} \geq 854 \text{ Da}$) and certainly for the commercial ones. Therefore, the template-assisted membrane synthesis is much more reproducible as compared to the sol-gel membrane synthesis. A highly reproducible synthesis method, like the template-assisted method, is necessary to obtain high selective membranes since the same MWCO is required to have reliable separation performance, independent of the batch. During this work, much more templated membranes were synthesized, confirming the good reproducibility of the method.

Retention curves and GPC chromatograms of membranes B58 – 0.05 – 80 °C and B58 – 0.05 – 120 °C, made with the same amount of Brij 58 (Brij 58/Ti = 0.05) but thermally stabilized at 80 °C or 120 °C (24 h) can be found in the supporting information (**Figure S6**). The MWCO of both membranes are almost identical regardless of the applied thermal stabilization at 80 or 120 °C, 2837 Da for B58 – 0.05 – 80 °C and 2808 Da for B58 – 0.05 – 120 °C. Again showing its robustness with respect to the MWCO. When looking more closely, the permeate chromatogram of B58 – 0.05 – 80 °C has 2 additional peaks around 7000 and 12000 Da as compared to the permeate chromatogram of B58 – 0.05 – 120 °C. Consequently, the retention curve of B58 – 0.05 – 80 °C has a large plateau from approximately 5000 until 15000 Da, which is absent in B58 – 0.05 – 120 °C. Thus thermal stabilization at 80 °C leads to large defects in the top layer of the membrane whereas thermal stabilization at 120 °C leads to a defect free membrane. This could be explained as follows: The thermal stabilization at 80 °C leads to a less condensed titania structure and therefore a structure with lower mechanical strength prior to calcination, as compared to the structure obtained with thermal stabilization at 120 °C. Upon template removal (calcination) the lower mechanical strength of B58- 0.05 – 80 °C could lead to a structural collapse due to larger impact of e.g. shrinking effects upon heating the coated toplayer and thus to large defects in the top layer. On repeating the same synthesis, similar results were obtained. Therefore, thermal stabilization at 120 °C is necessary in order to obtain a defect free membrane.

Retention curves and GPC chromatograms of B58 – 0.05 – 80 °C and B58 – 0.083 – 80 °C, made with different amounts of Brij 58 and thermally stabilized at 80 °C can be found in the supporting information (**Figure S7**). Increasing the amount of template from Brij 58/Ti = 0.05 to Brij 58/Ti = 0.083 leads to an increase in MWCO from 2837 Da to 3698 Da. This is in good agreement with the thin film results where the same increase in the amount of template leads to a pore enlargement from 3.6 to 4.8 nm (section ‘3.1.1 Brij 58 as template’, Figure 1). Therefore, keeping the good reproducibility of the template-assisted synthesis in mind, the template-assisted method and the choice in the amount of template is a successful approach in controlling the pore size and thus the MWCO of the membrane top layer. Different to depositions on dense supports, capillary infiltration of the coating liquid into the porous support during deposition is expected. It is known in literature that the capillary infiltration of the coating liquid can disturb the template self-assembly^[44]. However, no significant effect on the pore size of the membrane has been observed in the present research. The retention curves of B58 – 0.05 – 80 °C and B58 – 0.083 – 80 °C show a large plateau from 5000 until 15000 Da due to large defects in the top layer. As discussed above (see supporting information, Figure S6), this could most likely be prevented by thermal stabilization at 120 °C (24 h) instead of thermal stabilization at 80 °C (24 h).

Figure 9 shows the retention curve of a 3 nm commercial sol-gel membrane compared to the retention curves of membranes made with and without Brij 58 as a template (B58 – 0.05, B58-0.083 and B58 – 0 respectively). A steeper retention curve correlates to a membrane with a higher selectivity. This can be clarified when considering a feed mixture of 2 compounds with molecular weights of 600 resp. 3000 Da both in a concentration of 1 g/L. As can be deduced from the MWCO curves in figure 9, the small molecule will easily pass the B58 – 0.05 membrane (retention only about 10%) while the large molecule will be retained for about 90%. Or in other words, using the equation of section 2.2, the permeate of the B58 – 0.05 membrane will contain about 0.9 g/L of the small compound, and 0.1 g/L of the large compound. On the

contrary for the commercial 3 nm membrane, the same 2 molecules are more difficult to separate, as at 600 Da the retention is already >30%. In that case the permeate of the membrane will contain less than 0.7 g/L of the small compound and 0.1 g/L of the large one. The template-assisted membranes (B58 – 0.05 and B58-0.083) clearly have a steeper retention curve and thus more uniform MWCO as compared to the other membranes made without any template. Furthermore, the membranes made without any template (B58 – 0 and 3 nm sol-gel bis) have a large plateau from approximately 2500 until 18000 Da, caused by defects in the top layer.

4. Conclusions

The pore size of titania thin films and membranes can be successfully adjusted by using Brij type templates. Under the here described synthesis conditions, the Brij type templates act as a separator whereby the final pore size is mainly dependent of the amount of template. Thus using Brij templates with different size but with the same wt % in the non calcined thin film can give rise to thin films with similar pore sizes. Furthermore, the described template-assisted method provides an enhanced control of the pore size of the top layer of a membrane as compared to the sol-gel method. In addition, our results demonstrate that the pore size of the template-assisted thin films and membranes is more uniform than membranes synthesized without the template (as shown by Kr adsorption and permoporometry). Finally, it is shown that the template-assisted method is very reproducible for the synthesis of defect free membrane top layers, if a sufficiently high thermal stabilization temperature is applied, and results in sharp MWCO curves. Capillary infiltration of the coating solution into the porous support does not significantly impact the membrane pore size, as evaluated in the present study. However, future research on avoiding capillary infiltration by e.g. filling the porous support with a polymer ^[45-46] and studying the effect on the final membrane properties such as flux, would be interesting. Furthermore, evaluation of these membranes in real applications would be an interesting prospect to determine the impact of the sharper cut-off curves on separation performance.

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(Supporting Information is available online from Wiley InterScience or from the author).

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Fig. 1. Kr adsorption isotherms and pore size distributions (inset) at 87 K of titania thin films synthesized with different amounts of Brij 58 or without the template.

Fig. 2. Top down SEM images of B58-0.05 thin films after calcination at 360 °C on a dense (top) and porous support (bottom, membrane).

Fig. 3. Kr adsorption isotherms and pore size distributions (inset) at 87 K of titania thin films synthesized with different amounts of Brij 56.

Fig. 4. Kr adsorption isotherms and pore size distributions (inset) at 87 K of titania thin films synthesized with different amounts of Brij 78.

Fig. 5. Kr adsorption isotherm and pore size distributions (inset) at 87 K of titania thin films synthesized with different amounts of Brij 76.

Fig. 6. the pore diameter of the calcined structure obtained from Kr adsorption correlated to the Brij/Ti ratio (top) and correlated to the wt % Brij in the non calcined structure (bottom).

Fig. 7. permporometry desorption curves and pore size distributions (inset) of membranes synthesized with and without Brij 58 as a template.

Fig. 8. retention curves (solid lines, primary y-axis) and GPC chromatograms (dashed lines, secondary y-axis) of membranes synthesized with Brij 58 as a template showing the reproducibility of the synthesis.

Fig. 9. retention curves of a 3 nm commercial sol-gel membranes and membranes synthesized with and without Brij 58 as a template.

Table 1. Overview of the different synthesis and the chemical formulas of the surfactants used and porosity data obtained by Kr adsorption at 87 K of titania thin films synthesized with different amounts of Brij 58, Brij 56, Brij 78 or Brij 76.

Sample name	surfactant	Chemical formula	C_xEO_y ^[a]	Brij/Ti	wt % surfactant ^[b]	$\emptyset_{ads}$ ^[c] [nm]	FWHM ^[d] [nm]
B58 – 0	None	/	/	0	0	/	/
B58 – 0.05	Brij 58	$C_{16}H_{33}(OCH_2CH_2)_{20}OH$	$C_{16}EO_{20}$	0.05	41.3	3.6	2.3
B58 – 0.083	Brij 58	$C_{16}H_{33}(OCH_2CH_2)_{20}OH$	$C_{16}EO_{20}$	0.083	53.9	4.8	2.3
B56 – 0.05	Brij 56	$C_{16}H_{33}(OCH_2CH_2)_{10}OH$	$C_{16}EO_{10}$	0.05	29.9	3.6	3.1
B56 – 0.082	Brij 56	$C_{16}H_{33}(OCH_2CH_2)_{10}OH$	$C_{16}EO_{10}$	0.082	41.3	4.0	2.5
B56 – 0.125	Brij 56	$C_{16}H_{33}(OCH_2CH_2)_{10}OH$	$C_{16}EO_{10}$	0.125	51.7	4.6	1.9
B78 – 0.05	Brij 78	$C_{18}H_{33}(OCH_2CH_2)_{20}OH$	$C_{18}EO_{20}$	0.05	41.9	4.3	1.6
B78 – 0.049	Brij 78	$C_{18}H_{33}(OCH_2CH_2)_{20}OH$	$C_{18}EO_{20}$	0.049	41.3	4.1	2.1
B78 – 0.083	Brij 78	$C_{18}H_{33}(OCH_2CH_2)_{20}OH$	$C_{18}EO_{20}$	0.083	54.5	4.7	1.7
B76 – 0.05	Brij 76	$C_{18}H_{33}(OCH_2CH_2)_{10}OH$	$C_{18}EO_{10}$	0.05	30.8	3.8	2.3
B76 – 0.079	Brij 76	$C_{18}H_{33}(OCH_2CH_2)_{10}OH$	$C_{18}EO_{10}$	0.079	41.3	4.1	2.1
B76 – 0.125	Brij 76	$C_{18}H_{33}(OCH_2CH_2)_{10}OH$	$C_{18}EO_{10}$	0.125	52.7	4.6	3.3

^[a] abbreviation of the chemical formula of the surfactant in which C_x stands for the number (x) of carbon atoms in the carbon chain and EO_y stands for the number (y) of ethylene oxide blocks ^[b] wt % surfactant in the non calcined structure = $(m_{surfactant}/(m_{surfactant} + m_{titania})).100$

^[c] average pore diameter (NLDFT traceable method), based on the adsorption pore size distribution ^[d] FWHM = Full width at half maximum

Table of content:

Utilizing Brij templates leads to adequate control of the mesopore size of titania thin films and membranes in which the final pore size depends on the amount of template (separator mechanism). Furthermore, the template-assisted evaporation induced self-assembly method leads to more uniform pores (see figure 7) and enhances the reproducible synthesis of defect free template-assisted mesoporous titania top layers for selective membrane applications.

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The Use of Different Templates for the Synthesis of Reproducible Mesoporous Titania Thin Films and Small Pore Ultrafiltration Membranes