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Template-dependent hydrophobicity in mesoporous organosilica films

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ABSTRACT

A template dependence of the degree of self-hydrophobization of methylene-bridged periodic mesoporous organosilica (PMO) films is reported. The film with the smallest pore size of 1.7 nm, templated by CTAC, results in higher hydrophilicity when compared to films with a pore size of 4.1 or 5.3 nm, templated by BrijL4 and BrijS10, respectively. Both the surface and the bulk hydrophilicity were evaluated by water contact angle measurements and water ellipsometric porosimetry and the same trends were observed. Additionally, we provide the first evidence for a steric hindrance of the self-hydrophobization process. We show that a partial template removal results in the methylene-to-methyl transformation being observed at a temperature as low as 200 °C, significantly lower than previously demonstrated. These results should be taken into account when PMO materials are considered for applications such as low-k dielectrics, membranes, catalyst and chromatographic supports, and drug carriers.

1. Introduction

Periodic mesoporous organosilica (PMO) materials possess organic groups as bridges between Si atoms, (R'O)$_3$-Si-R-Si-(OR')$_3$ where R is the organic bridging group [1–3]. These organic bridges allow for the tuning of the surface properties such as the hydrophobicity, the alteration of the surface reactivity and the protection from chemical attack [1,2,4,5]. Notably, the uniform distribution of the bridging organic groups in the bulk of the material means that their benefits extend beyond impacting only the surface properties. The uniform bulk distribution of functionalities is especially important in porous materials which are attractive due to their high surface-to-volume ratio. In this case, ideally all of the accessible surface possesses the desired functional groups. For instance, employing alkylene bridged organosilicates, the internal hydrophobicity of the PMO can be fine-tuned depending on the choice of the alkylene bridge, e.g. methylene or ethylene, and the annealing temperature [5]. The fine-tuning of the hydrophobicity enables the engineering of the host-guest interactions and benefits applications such as drug delivery, catalysis, protein refolding, and separation [1]. Furthermore, hydrophobic PMOs are stable in high humidity environment, giving them an advantage for applications in solar cells, nanoelectronics, and displays [3].

The hydrophobicity of the PMOs can be controlled by the annealing temperature due to a self-hydrophobization process, which has been shown to occur at a temperature of at least 350 °C [6]. The mechanism

of the self-hydrophobization of methylene-bridged PMO materials is reported in literature and involves the transformation of a methylene (Si-CH$_2$-Si) into a methyl group (Si-CH$_3$) in the presence of a silanol functionality (Si-OH) which is transformed into a siloxane (Si-O-Si) bridge [7]. The self-hydrophobization has also been observed in ethylene-bridged PMOs [5], but the mechanism has been asserted to be different than in the methylene-bridged PMO [7]. As a result, the hydrophobicity has been established to depend on the type of the alkylene bridge and the annealing temperature [5]. Nevertheless, in this work, we show that the PMOs' hydrophobicity depends also on the type of the templating molecules. The impact of the template on the hydrophobicity is discussed in light of its effect on the degree of polycondensation in as-deposited films [8] and on the pore size of the PMO materials.

2. Experimental section

Three methylene-bridged mesoporous organosilica films were prepared using the sol-gel method based on the evaporation-induced self-assembly mechanism. The films were templated by the cetyltrimethylamino chloride (CTAC), BrijL4 and BrijS10 and were labelled MPMOC, MPMOL4 and MPMOS10, respectively. The molar ratios of the reagents are given in Table 1. In a typical synthesis, 11.1 ml 1-methoxy-2-propanol were mixed with 0.81 ml 25% aqueous solution of CTAC and 1.05 ml 0.02 M HCl. After stirring for 10 min for homogenization,

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Table 1
Molar ratio of the reagents employed in the synthesis of the PMO films. MPMOC – CTAC; MPMOS10 – BrijS10; MPMOL4 – BrijL4.

Label	BTESM	1-methoxy-2-propanol	H_2O	Surfactant	$[H^+]$
MPMOC	1	31	25	0.17	0.0057
MPMOS10	1	31	16	0.1	0.0057
MPMOL4	1	31	16	0.27	0.0057

1.29 ml bis(triethoxysilyl)methane (BTESM) were added and further stirred for 15 min. After aging at ambient conditions for ≈ 24 h, the solutions were dispensed on a H_2O_2 cleaned Si substrate and spun at 1500 rpm for 60 s. Next, the films were annealed in an oven at 150 °C for 10 min in ambient atmosphere. Finally, the films were annealed at various temperatures between 200 and 500 °C in inert N_2 atmosphere for 2 h with a heating rate higher than 50°/min.

The film thicknesses and refractive indices (RIs) of the films were obtained by modelling the experimentally measured ellipsometric angles Ψ and Δ using the Cauchy dispersion relation. The measurements were carried out using a spectroscopic ellipsometer (SE) SENTECH801 (350–800 nm). The RI values are reported at 632.8 nm. Open (accessible) pore volume and pore size distribution (PSD) were calculated following toluene ellipsometric porosimetry (EP) measurements [9–11]. The chemical structure was determined by analysing FTIR (ThermoScientific, Nicolet 6700) spectra collected in the region 400–4000 cm^{-1} with a resolution of 2 cm^{-1} and averaged over 100 scans. The experimental spectra were treated by base-line correction. The surface hydrophilicity was characterized by surface water contact angle (WCA) measurements and the reported results are averaged over 5 droplets. The bulk hydrophilicity was evaluated by water EP measurements [12]. Finally, a grafting experiment, a vapour-phase silylation by dimethylamino trimethylsilane at 250 °C, was employed semi-quantitatively for evaluation of the Si-OH groups available for grafting in each porous film.

3. Results

The thermal self-hydrophobization process characteristic of PMO materials can occur at a temperature as low as 200 °C which is much lower than previously reported [6]. The self-hydrophobization was ascertained by difference FTIR spectra (Fig. 1) showing the appearance of a Si-CH$_3$ peak at 1275 cm^{-1}. The Si-CH$_3$ group is not present in the organosilica precursor and no IR absorption associated with its presence is observed in the as-deposited films (Fig. 1a). Nevertheless, upon a two hour anneal at 200 °C in N_2, a peak at 1275 cm^{-1} can be seen for the CTAC-templated film. The appearance of the peak is demonstrated by difference FTIR spectra (Fig. 1b) where the spectrum obtained before the anneal is subtracted from the spectrum after the anneal, as a result of which, the positive peaks (peaks above the baseline) are an indication of the formation of functionalities in the film. Notably, after the anneal at 200 °C, the Si-CH$_3$ peak is clearly present in the CTAC-

templated film. Nevertheless, in the BrijL4 and BrijS10-templated films, the peak is much less pronounced and close to noise level. The 1275 cm^{-1} peak becomes more prominent in the spectra associated with the films templated with the non-ionic surfactants after a two hours anneal at 250 °C (Fig. 1c). These observations seem to indicate that depending on the templating molecule, different activation energies are required in order to initiate the self-hydrophobization. However, this explanation seems unlikely given that the same organosilica precursor was employed for the synthesis of all of the films. Rather, the self-hydrophobization process is sterically hindered as long as the template is present in the films, i.e. when part of the template is decomposed and some pore volume is introduced, the Si-CH$_2$-Si to Si-CH$_3$ transformation occurs. The evidence for this explanation comes from SE measurements in which as a result of the anneal at 200 °C the RI of the MPMOC dropped by 0.12, from 1.49 down to 1.37, while the RI change of the MPMOL4 and MPMOS10 films were limited to 0.03 and 0.02, respectively. These changes in the RI values can be explained by a decrease in density associated to the thermal decomposition of the surfactant molecules of which CTAC shows the lowest stability. On the other hand, the anneal at 250 °C results in a ΔRI of 0.05 in the films templated with non-ionic surfactants, which reflects the presence of sufficient pore volume in order to initiate the self-hydrophobization, as evident from Fig. 1c. In order to test our hypothesis about the effect of the surfactant on the self-hydrophobizaiton, we deposited a BrijS10-templated film, annealed it at 150 °C for 10 min to crosslink the matrix, performed an hour long solvent extraction in acetone at room temperature and then annealed the film at 200 °C for 2 h in N_2. As a result of the solvent extraction of the template, the RI of the film dropped from 1.49 to 1.29 indicating that about 80% of the template was removed. The anneal at 200 °C caused further RI decrease of 0.01, which is smaller than the ΔRI of 0.02 observed when the film was annealed without the solvent extraction step which seems reasonable given that a majority of the template had been removed. Compared to the film on which no solvent extraction was performed, the film which was treated by both a solvent extraction and an anneal at 200 °C has two times larger concentration of Si-CH$_3$ groups, as inferred from the two times larger area associated with the FTIR peak located at 1275 cm^{-1} (Fig. S1). Therefore, the presence of a template in the pores has a strong contribution in deterring the self-hydrophobization reaction. Finally, no evidence of a self-hydrophobization was observed after a 2 h anneal at 150 °C.

As a result of the self-hydrophobization process, for all the investigated films, the temperature increase from 300 to 500 °C leads to an increase of the surface WCA by up to 30° (Fig. 2). However, systematically lower contact angles are observed for the CTAC-templated films. In an attempt of explaining this systematic difference, we consider the effect of the roughness, measured by AFM, on the WCA values. The lowest RMS roughness value of 0.3 nm was observed for the MPMOC films, while for MPMOL4 and MPMOS10 the RMS roughness was found to be 3.0 and 0.8 nm, respectively. Given the hydrophilicity of the layers, in a Wenzel regime, the higher roughness of the films
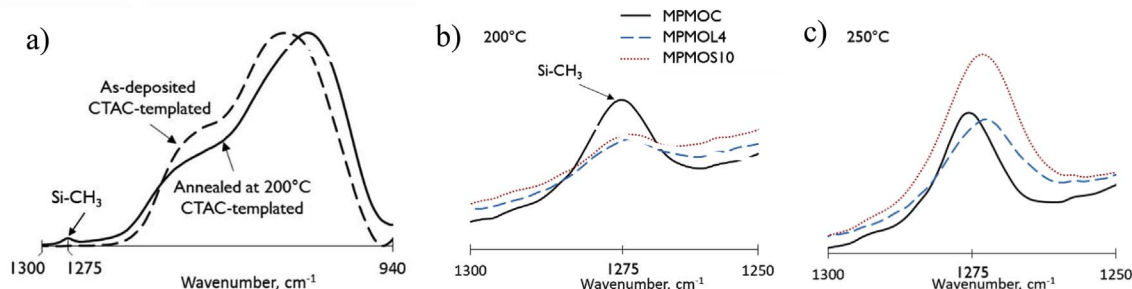

Fig. 1. Self-hydrophobization is evident from the difference FTIR spectra. a) FTIR spectra of as-deposited and annealed at 200 °C PMO. b) Difference spectra of the three PMO films after anneal at 200 °C. c) Difference spectra of the three PMO films after an anneal at 250 °C.
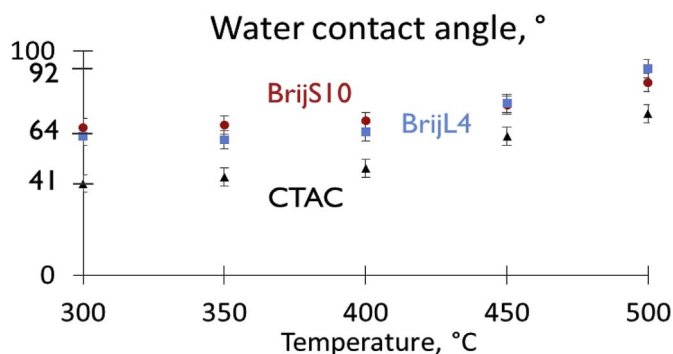
Fig. 2. Surface water contact angle as a function of the annealing temperature.

templated with non-ionic surfactants would result in lower effective contact angle [13], which does not explain why systematically lower contact angles are observed for MPMOC. However, the Wenzel description is probably unsuitable for the surface of a porous film since the pores under the droplet will be flooded by water which is better described by the Cassie equation [13]. In this scenario, for films obtained from the same matrix molecule, the effective WCA of films with higher porosity is expected to be lower than that of films with lower porosity. This expectation is not met by the results shown in Fig. 2 since, excluding the anneal at 300 °C, MPMOS10 is the film with the highest porosity, followed by MPMOL4, and the film with the lowest porosity is MPMOC (Fig. S2). Therefore, geometrical consideration cannot explain the observed differences in wetting. Notably, the WCA observed for all of the films are systematically lower than those reported in literature. This discrepancy can find an explanation in the low heating rate, e.g. 1°/min, which is usually reported [4,5] for the anneal of PMO films, in contrast to the anneal conditions applied in our work, where the heating rate was higher than 50°/min. Therefore, the effective anneal durations reported in literature are significantly longer than ours, leading to more effective self-hydrophobization reactions.

The hydrophobicity of the investigated PMO films decreases in the order MPMOS10 > MPMOL4 > MPMOC. An evidence for this conclusion is found in the FTIR spectra of the films (Fig. 3). An analysis of the region between the 3300 and 4000 cm^{-1}, where the absorption from O-H stretching vibrations is expected, reveals the bulk hydrophilicity of the films. The wide absorption centered around 3515 cm^{-1} is indicative of H-bonded -OH often attributed to the presence of moisture. On the other hand, the sharp peak at 3732 cm^{-1} is due to absorption from isolated, non-H-bonded, $\equiv$Si-OH groups. As it can be seen in Fig. 3, in agreement with the reported WCA values, the CTAC-templated films result in a stronger -OH absorption of both isolated $\equiv$Si-OH and H-bonded -OH groups. Given the high temperatures to which these films were subjected, the H-bonded -OH groups might be due to subsequently adsorbed moisture, as a consequence of the presence of the hygroscopic $\equiv$Si-OH groups. These results make it clear

that the hydrophilicity of the films is not limited to their surface but extends to the bulk since the transmission FTIR measurements are not surface sensitive and instead, they provide information about the bulk chemical composition. The hydrophilicity is observed in spite of the clear indication that the self-hydrophobization takes place. Therefore, the observed differences in the hydrophobicity seem to be due to a different extent to which the self-hydrophobization occurs in each film. Notably, in the temperature range between 350 and 500 °C, the CTAC-templated films result in the lowest SiCH$_3$-to-SiOSi ratio when compared with the films templated by the non-ioinic surfactants. The notation "SiOSi" refers to the peak centered at 1030 cm^{-1}, which is the result of matrix-related absorptions, such as the vibration of Si-O-Si and Si-C-Si groups (Fig. 4). The SiCH$_3$-to-SiOSi ratios are compared, rather than the absolute SiCH$_3$ intensities, in order to take into account the differences in density, which are nevertheless small and therefore do not affect the trends. As expected, the $\equiv$SiOH and $\equiv$SiCH$_3$ absorptions are inversely correlated, explaining the observed differences in hydrophilicity.

Nevertheless, deducing the hydrophilicity from the FTIR spectra is not completely reliable given the difference in the nature of the interactions between the organosilica oligomers and the ionic versus the non-ionic surfactants. The ionic surfactants interact with the organosilica oligomers and the organosilica walls through Coulomb forces, while the non-ionic surfactants interact through H-bonding. Therefore, the $\equiv$Si-OH groups present in the films templated by the non-ionic surfactants might be "disguised" due to the H-bonding with the remaining non-ionic surfactants and as a result the intensity of the –OH stretching absorption might be lowered and broadened. Furthermore, as shown earlier, the BrijL4 and the BrijS10 molecules are dissociated at a higher temperature than the CTAC molecules. Thus, compared to the film templated with the ionic surfactant, the larger amount of remaining template in the films templated with the non-ionic surfactants further reduces the reliability of the FTIR analysis.

An additional evidence for the template-dependent hydrophobicity comes from water EP measurements. Following an anneal at 400 °C, the MPMOC film adsorbs water at a relative pressure of 0.75 (Fig. 5a). In comparison, the MPMOL4 film starts adsorbing moisture at a relative humidity of 90%. The most hydrophobic film appears to be the MPMOS10 since no water adsorption is evident indicating a WCA higher than 90°. When the pore size is taken into account (Fig. S3) and the internal water contact angle is calculated using the Kelvin equation, the MPMOL4 and MPMOS10 show a contact angle close to or above 90° while the MPMOC film has a contact angle close to 80° (Fig. 5b). On the other hand, when all the annealing temperatures are considered, among the films being compared, the MPMOS10 requires the lowest activation energy in order to achieve a hydrophobic film. This conclusion is supported by the fact that an annealing temperature of 350 °C is sufficient to result in a MPMOS10 film which does not adsorb moisture, even at 100% relative humidity. The MPMOL4 becomes hydrophobic only at 400 °C, while the MPMOC must be annealed at a temperature higher than 450 °C before its internal WCA reaches 90°. Nevertheless, the
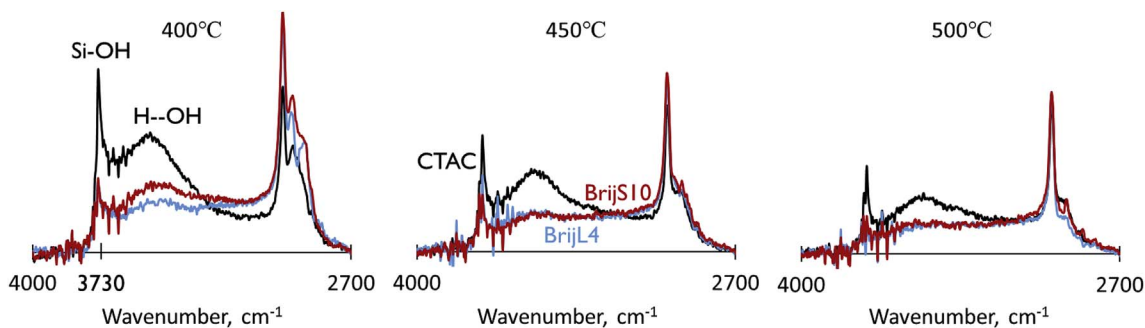

Fig. 3. FTIR spectra in the 2700-4000 cm^{-1} region where absorption from C-H and O-H stretch can be observed. The annealing temperatures after which the FTIR was measured is indicated.
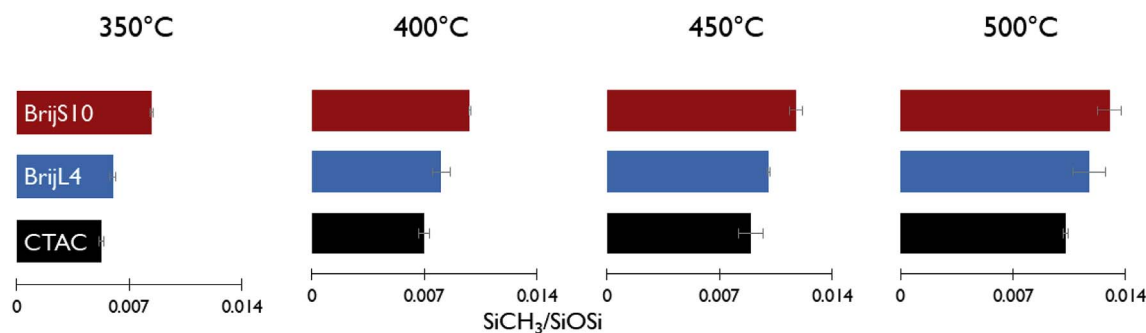
Fig. 4. Extent of self-hydrophobization, as revealed by the intensity ratio of the FTIR peaks at 1275 and 1030 cm^{-1} attributed to SiCH$_3$ and SiOSi, respectively.

values of the internal WCA calculated using the Kelvin equation might be questionable, since the Kelvin equation is not physically justified when approaching pore dimensions of ∼2 nm or smaller.

The final and most convincing evidence for the template-dependent hydrophobicity in PMOs comes from a grafting treatment, where the films were exposed to the silylation agent dimethylamino trimethylsilane from a vapour phase at 250 °C and the RI changes were observed. The ΔRI of the films follows similar trends independent of the annealing temperature (Fig. 6). Essentially, the ΔRI decreases in the order MPMOS10 > MPMOL4 > MPMOC. The RI of the films increases due to a decrease in the pore volume as a result of the grafting of the Si-OH groups with –Si(CH$_3$)$_3$ groups (Fig. S4). These results confirm that the largest concentration of Si-OH groups are associated with the MPMOC, while the smallest with the MPMOS10 film.

4. Discussion on the template-dependent hydrophobicity in PMO

In order to understand the observed template-dependence of the PMO hydrophobicity, we consider two main effects – the capillary condensation and the competition between the self-hydrophobization and the silanol condensation reactions. First, we consider the capillary condensation because of the clear trend observed between the pore size and the hydrophobicity, i.e. the smaller the pore size the more hydrophilic the film. This trend is similar to the higher hydrophilicity reported in silica films with smaller pore size as compared to films with larger pore size [14,15]. Nevertheless, compared to the PMO films, the porous silica films are hydrophilic and they readily adsorb ambient moisture. Therefore, the larger amount of water observed in the silica films with smaller pore size by Anedda et al. can be explained considering the Kelvin equation, which indicates that at a particular relative humidity the surface with a higher curvature, i.e. smaller pores, will adsorb more water. Additionally, in films with a small pore size, Anedda et al. report H-bonding interaction which ultimately "masks" the Raman signal from isolated Si-OH groups indicating that either H$_2$O molecules have adsorbed on these sites or due to their proximity the

silanols have formed H-bonds. Therefore, in their study, the signal from isolated silanols increases with pore size. Similarly, Eslava et al. [16], who investigated hydrophobic porous organosilica films, have suggested that in contrast to large pores, the silanols in small pores form H-bonds due to their proximity as a result of the high surface curvature of the small pores. This is contrary to what we observe (Fig. 3). The isolated silanols are present in the CTAC-templated films, while their presence is significantly reduced in the films with larger pore sizes. Therefore, the effect of the capillary condensation and the curvature of the pores seem insufficient to explain our observations.

Second, a silanol group can be consumed either by a condensation reaction or by a self-hydrophobization reaction. In contrast to the silanol condensation which occurs even at room temperature, the self-hydrophobization occurs only when a temperature of ca. 200 °C is reached. Therefore, any differences among the films in the Si-OH content upon reaching the temperature of 200 °C or higher will translate in varying potential number of self-hydrophobization reactions. Such differences are expected since a template-dependent polycondensation kinetics has been demonstrated in silica films [8], where the polycondensation in films templated by non-ionic surfactants was slowed down as compared to a film templated by an ionic surfactant. The effect of the template on the polycondensation has been attributed to the tendency of the hydrophilic poly(ethylene oxide) (PEO) chains of the non-ionic surfactants to penetrate into the silica walls which does not happen with the ionic surfactants. However, this effect influences the Si-OH condensation, not only during the drying of the film, but as long as the hydrophilic chains of the non-ionic template are present. Because of the small changes in RI at a temperature of ca. 200 °C for the films templated by non-ionic surfactants, the PEO chains seem to be unaffected up until at least 200 °C. As a result, we conclude that the silanol condensation during annealing is impeded in films templated by the non-ionic surfactants and therefore the Si-OH groups are available for self-hydrophobization reactions. At the same time, in the films templated by ionic surfactants, where no blocking of the silanol condensation occurs, the silanols are consumed in condensation reactions
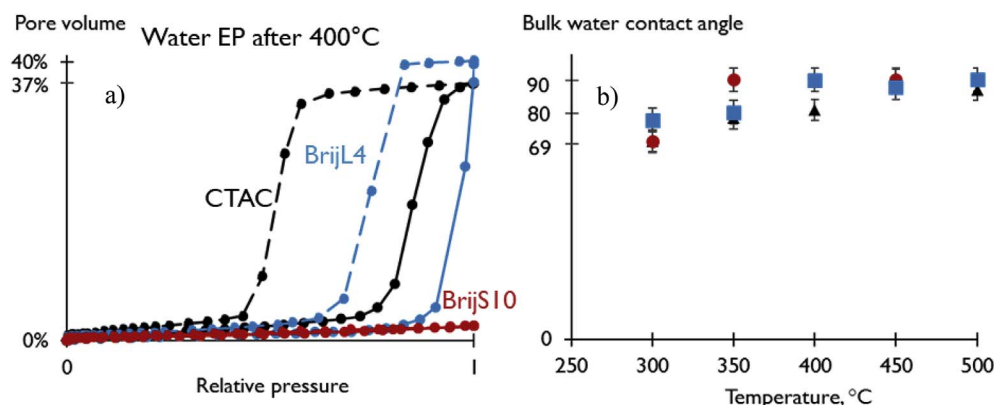

Fig. 5. Water EP results: a) Water adsorption isotherms after annealing the films at 400 °C; b) Internal (bulk) water contact angle calculated employing the Kelvin equation.
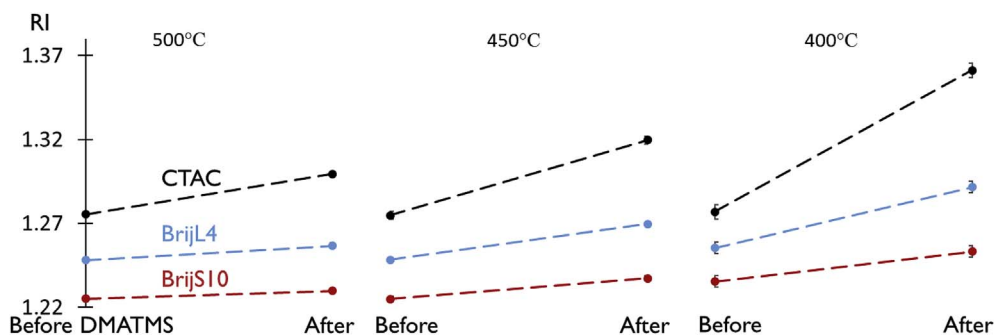
Fig. 6. Change of the refractive index (RI) as a result of a silylation with dimethylamino trimethylsilane of films annealed at a) 500 °C; b) 450 °C and c) 400 °C.

and therefore become unavailable for self-hydrophobization reactions. This hypothesis also explains the difference between the BrijL4 and BrijS10-templated films since BrijL4 has a shorter PEO chain than BrijS10.

5. Conclusions

We have demonstrated that the self-hydrophobization reaction characteristic of PMO materials can occur at a temperature as low as 200 °C, significantly lower than previously reported. Additionally, we have shown that the self-hydrophobization is affected by the presence of a template requiring a higher activation energy in low density materials. We have provided extensive experimental evidence for a template dependence of the degree of self-hydrophobization in methylene-bridged PMOs. The CTAC-templated film with a pore size of 1.7 nm results in a higher hydrophilicity when compared to films templated by BrijL4 and BrijS10 with a pore size of 4.1 or 5.3 nm, respectively. The template-dependent hydrophobicity has been tentatively attributed to the blocking of the silanol condensation by the poly(ethylene oxide) chains in the Brij-type surfactants leading to a higher concentration of Si-OH groups available for self-hydrophobization reactions. Our findings are important when PMO materials are expected to have both a small pore size and high hydrophobicity, such as for low-k dielectrics application. Similarly, the hydrophilic to hydrophobic balance is important for the diffusion of molecules in membranes, chromatographic supports and drug carriers.

Funding

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version. The following files are available: FTIR spectra showing the SiCH$_3$ peak of MPMOS10 after anneal at 200 °C with and without solvent extraction, pore size distribution of the films annealed at 400 °C, pore volume change as a result of the silylation.

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.micromeso.2017.10.005.

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