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The effects of water on the morphology and the swelling behavior of sulfonated poly(ether ether ketone) films

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Abstract Thin sulfonated poly(ether ether ketone) films swell excessively in water. The extent of water-induced swelling is shown to be correlated with the optical anisotropy of the films, due to two distinct phenomena. Firstly, the optical anisotropy is directly related to the amount of water taken up from the surrounding ambient atmosphere, and thus to amount of water present in the material just prior to swelling. Secondly, the optical anisotropy corresponds to internal stresses in the film that affect the free energy of the film, and thus the potential of the film to swell. The anisotropy vanishes upon sorption of liquid water and returns when the water is desorbed. When the water is completely removed, the film changes from more or less colorless to an intense yellow color that can be attributed to molecular assembly of the aromatic rings in the polymer backbone. The color change is reversible and occurs immediately upon exposure to low humidity. For films prepared in the absence of water, the lack of hydration of the sulfonic acid groups affects the microphase separation behavior of the polymer. This is manifested by an apparent lower propensity to water-induced swelling. The possibility to affect the properties of sulfonated polymer films by varying the hydration state of the polymer during preparation can have important implications for applications of such films.

Introduction

Membranes from highly sulfonated poly(ether ether ketone) (SPEEK) strongly swell upon contact with water. This is due to the high affinity that water has for the sulfonic acid groups in SPEEK. For some applications, a high concentration of water in the polymer can be beneficial, for instance, to facilitate proton transport in fuel cells [1] or for the dehydration performance [2–4]. A drawback of too excessive swelling is the reduced mechanical strength that may lead to ruptures, in particular in the case of thin films that are constrained on a substrate. Constrained films can only swell in a single direction, and at a similar degree of swelling, the elastic deformation of their network is thus more pronounced as compared to free-standing films [5]. Excessive swelling is also known to have an impact on the performance of membranes in molecular separation. In general, swelling leads to larger fluxes of all species present, and causes drastic reductions in selectivity. Much effort has been devoted to the reinforcement of SPEEK films. Approaches include chemical modifications, such as covalent and ionic cross-linking [6], doping with inorganic particles [7, 8] and creating structures with integrated skin layers [9].

The relations between swelling, proton transport, and the chemical and intermolecular structure of SPEEK and

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other sulfonated polyelectrolyte films have been studied extensively [10–12]. The performance of membranes made from these polymers is reported to be affected by molecular orientations and chain assembly. Zhang et al. reported that SPEEK films with the same chemical structure (i.e., with a degree of sulfonation of 40 %) but formed at various relative humidity degrees, exhibit distinct molecular arrangement, and orientation of the sulfonic acid groups [13]. The proton conductivity performance of those membranes is dissimilar. This implies that the proton transport characteristics of SPEEK are not only dictated by the amount of sulfonic acid groups, but also by their molecular arrangement. It can be anticipated that the molecular structural arrangements of SPEEK will also affect the swelling behavior upon contact with water.

In a previous study, we reported that thin SPEEK films exhibit certain structural arrangements, in particular, inherent orientations in the in-plane direction [14]. In short, SPEEK films, independently on the preparation route and formation procedure, are preferentially oriented in the xy direction as compared to the z direction [14]. This is manifested by optical anisotropy Δn, i.e., $\Delta n = n_{xy} - n_z > 0$. In this expression, n_{xy} is the in-plane refractive index and n_z is the out-of plane refractive index. In the present paper, we study the relations between those structural arrangements of supported thin SPEEK films and (the dynamics of) their water-induced swelling, to assess if swelling can be significantly affected without chemical modification of the polymer.

The paper comprises two parts. In the first part, the focus is on the correlation between optical anisotropy and swelling. In the second part, the focus is on presence of water on the molecular assembly of the aromatic rings in the polymer backbone, and on the microphase behavior during film formation in the absence of water.

Materials and methods

Materials

Two batches of SPEEK polymer were used: SPEEK with a degree of sulfonation (DS) 84 %—homemade, obtained by sulfonation of PEEK (Victrex) using sulfuric acid according to the procedure described elsewhere [15], and SPEEK DS 68 %—fumion® ELM-505 obtained from Fumatech (Germany) as 5 wt% solution of methanol. Methanol (Emsure® grade of purity) was obtained from Merck (The Netherlands). Rhodamine 6G was obtained from Sigma-Aldrich (The Netherlands). ⟨100⟩-oriented silicon wafers P/Boron were obtained from Okmetic (Finland). Quartz glass slides Nr. 1.5 were obtained from Menzel Gläser (Germany). Nylon Membrane 25 mm syringe filters

0.45 μm were obtained from VWR International. Porous α-alumina disks were purchased from Pervatech (The Netherlands). Nitrogen gas (4.5) was supplied by Linde (Germany). Deionized water (18.2 MΩ·cm) was obtained using a Milli-Q Advantage A10 system (Millipore).

Film preparation

For spectroscopic ellipsometry

Films were spin-coated from SPEEK 5 wt% dissolved in methanol on pre-cut pieces of silicon wafers. Prior to spin-coating, the solutions were filtered using a syringe filter in order to remove residual contaminations. SPEEK in the 5 wt% methanol solution from Fumatech has a relatively high molecular weight and correspondingly high viscosity. The solution was diluted with methanol (SPEEK solution to fresh methanol volume ratio was 3.5:1) prior to spin-coating to decrease the viscosity, such that all films for swelling experiments are ~300 nm thick. Spin-coating was conducted under two distinct humidity conditions:

Humid atmosphere Spin-coating was conducted in air, at ambient relative humidity. The spin speed was set at 2000 or 3000 rpm.

Dry atmosphere Spin-coating was conducted under a large stream of dry nitrogen ($RH = 0$ %). The spin speed was always set at 2000 rpm.

The spinning time was set to 50 s. Directly after spin-coating, the films were conditioned under vacuum at 140 °C for 48 h. This procedure is implemented to induce non-covalent attachment of the film to the substrate and to prevent detachment of the film upon swelling.

Before water swelling experiments, all films were equilibrated directly after removal from a vacuum oven, at the ambient relative humidity degree, and characterized subsequently ex situ using spectroscopic ellipsometry (SE). The equilibration time was about 30 min for single experiments, in case of multiple experiments (several samples measured in a row) this time had to extend. The following nomenclature is used to describe the samples: degree of sulfonation-spin speed_formation atmosphere-RH of equilibration atmosphere; example: 84-2000_humid-40 denotes a SPEEK film with a DS of 84 %, formed at 2000 rpm in a humid atmosphere and equilibrated before swelling experiment in surrounding ambient atmosphere of $RH = 40$ %.

The details of ex situ characterization of thin SPEEK films using SE have been described in our previous paper [14]. That paper shows that SPEEK films always exhibit optical anisotropy which is a result of the internal stresses present in the films, due to preferential orientations of the

polymer chains [14]. The internal stresses and consequently, optical anisotropy in SPEEK films, decrease upon sorption of plasticizers, such as water or organic solvents [14, 16]. Consequently, the increase of the relative humidity degree (RH %) of the surrounding ambient atmosphere, to which films are exposed after the formation procedure, results in an increased water vapor sorption and therefore, in depression of optical anisotropy. On the contrary, sample drying/water desorption causes increase of optical anisotropy. Table 1 shows the approximate values of optical anisotropy of the SPEEK films investigated in this paper for swelling experiments that are affected by, as mentioned, RH of the surrounding ambient atmosphere during sample equilibration, and additionally, by the spin speed used in spin-coating [14]. Moreover, no variations of optical anisotropy and refractive indices as a function of the substrate radius/position were found for thin SPEEK films, only the shear thinning behavior was observed [14]. Therefore, it is not of importance which sample spot is measured for swelling experiments, as long as the thickness of this spot is recorded.

The initial thickness of the films used for swelling experiments was in the range 280–350 nm. We assumed no impact of the film thickness in this range on swelling behavior.

For fluorescence microscopy

Two methods were applied to prepare SPEEK films with the protons of the negatively charged sulfonic acid groups being exchanged with the cationic fluorescent dye. (1) Films were spin-coated from a mixture of 3 wt% SPEEK in methanol and Rhodamine 6G on quartz glass slides at 2000 rpm. The molar ratio of Rhodamine 6G/sulfonic acid groups was 6×10^{-9}. Alternatively, (2) films were spin-coated from 3 wt% SPEEK in methanol at 2000 rpm, without Rhodamine 6G in the solution. Subsequently, 0.1 ml of the Rhodamine 6G water solution was deposited, with the similar molar ratio as in the first method, on the film surface and left for 2 h.

Table 1 The approximate dependency of optical anisotropy in thin SPEEK films on the RH of the ambient atmosphere during sample equilibration at room temperature and on the spin speed during spin-coating

Optical anisotropy Δn (–)	RH of the ambient atmosphere during sample equilibration (%)	Spin speed during spin-coating (rpm)
0.043–0.041	20–40	3000
0.028–0.025	20–40	2000
0.023–0.014	50–90	2000

Spin-coating was done in humid and dry atmosphere, as described above for the film formation for spectroscopic ellipsometry. The thicknesses of the films for fluorescence microscopy were ~150 nm.

Films on porous alumina supports

Films were spin-coated on porous α-alumina supports, which were coated with a single layer of γ-alumina (according to the procedure described by Luiten et al. [17]), from 10 wt% SPEEK dissolved in methanol, under humid ambient (RH = 60 %) and dry atmosphere (RH = 0 %) at 2000 rpm. The thicknesses of the films were ~800 nm.

Measurements

Spectroscopic ellipsometry (SE)

SE experiments were performed on two devices: alfa-SE and M-2000 (J.A. Woollam Co., Inc.). The size spot of the light beam was 2 mm and a 70° angle of incidence was applied for ex situ and in situ measurements. In situ measurements were conducted in demineralized liquid water at a temperature of either 20 or 40 °C using a custom-made temperature-controlled 70 mL-volume glass cell [18]. A photo of the experimental set-up is shown in Fig. 1. The temperature-controlled glass cell (here filled with water) is located between the light source (left arm) and the detector (right arm) of the ellipsometer. A SPEEK film is placed in the glass cell and the set-up is aligned in such a way that the incident polarized light hits, and is reflected from the sample at 70°, and hits the detector. For more details about SE technique, the interested reader is referred to Tompkins et al. [19] or Fujiwara [20].

For water experiments in the glass cell, the delta offset was determined prior to measurements using a calibration wafer. The recording of the swelling data started in the first half minute after immersion in water. Modeling of the data obtained from SPEEK film measurements using CompleteEase 4.64 software (J.A. Woollam Co., Inc.) is described in detail in our previous paper [14]. The ambient refractive index of water at 20 and 40 °C was taken from the H_2O Pribil Temperature Library from the CompleteEase software.

The time-dependent swelling factor $S_{F(t)} = d(t)/d_{initial}$ is defined as the thickness d at time t normalized with respect to the initial thickness. The initial film thickness is measured by ex situ ellipsometry prior to the swelling experiment. After immersion of the sample in liquid water, the ellipsometer has to be aligned prior to recording of the data. Therefore, the data at the time $t = 0$–0.5 min are lost. Consequently, the initial values of swelling factors shown in the graphs are always >1 because these correspond to $t > 0.5$ min.
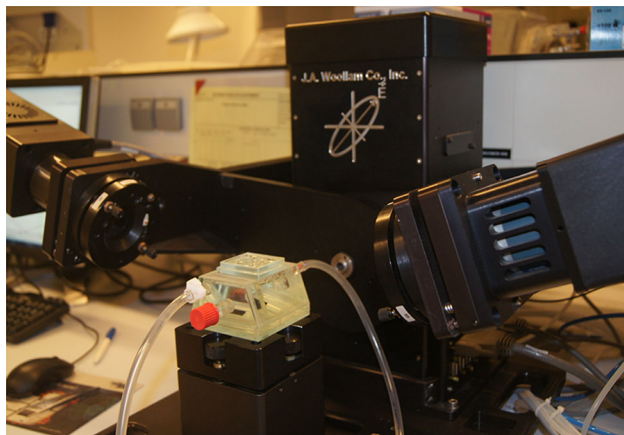
Fig. 1 Photo of the experimental set-up: J. A. Woollam Co., Inc. M-2000 ellipsometer with the custom-made temperature-controlled glass cell [18]

Total internal reflection fluorescence microscopy (TIRF)

TIRF microscopy was performed using a Nikon Eclipse Ti microscope equipped with a $100 \times$ Oil, Plan Apo objective (numerical aperture 1.45, Olympus) and an Andor DU-885 camera in TIRF mode. The Rhodamine 6G was excited using a 488 nm laser with a readout speed of 35 MHz. The emission signal from the green dye was collected at 520 nm.

Results and discussion

The effect of anisotropy on swelling of thin films formed at $RH \geq 20\%$

Figure 2 shows the swelling dynamics for two distinct SPEEK films, prepared from the same polymer batch, *DS* 84 % and formed under humid conditions at 2000 rpm, upon exposure to liquid water at 40 °C. Prior to the exposure to water, the extent of optical anisotropy of the films is different. The differences in optical properties are due to dissimilarities in the relative humidity of the surrounding ambient atmosphere during sample equilibration (see Table 2). Despite the equal degree of sulfonation, the swelling dynamics and the final degree of swelling are extremely distinct for the two films. The film that has the higher initial anisotropy, $\Delta n = 0.028$, swells slower and its swelling factor shows a maximum value of ~ 3.5 followed by a continuous relaxation-induced decrease in film thickness. Such overshoot swelling dynamics have been observed for SPEEK and other charged polymers [21–23]. For the film with the lower initial optical anisotropy, $\Delta n = 0.023$, the swelling dynamics are much faster. Most of the swelling occurs immediately, upon contact with
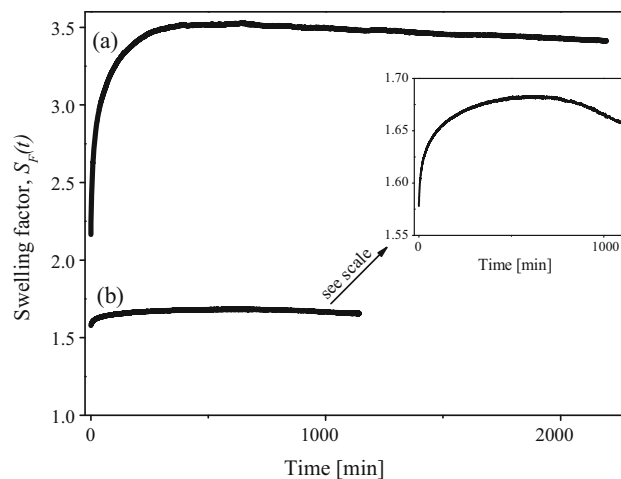

Fig. 2 Time-dependent water-induced swelling at 40 °C of ~ 300 nm SPEEK films with a *DS* of 84 % and *a* relatively high optical anisotropy ($\Delta n = 0.028$) and *b* relatively low optical anisotropy ($\Delta n = 0.023$)

water. Closer inspection of the shape of the curve reveals that this film also exhibits overshoot dynamics, albeit far less pronounced, with the maximum swelling factor of only ~ 1.7.

In the last years, we have measured the swelling of several dozens of thin SPEEK films and found a positive correlation between the value of Δn and the extent of swelling. The observed differences in the swelling behavior can be related to two superimposed phenomena.

Firstly, the distinct swelling behavior can be associated with a different initial concentration of water in the film. Due to the sulfonic acid groups, SPEEK has a high affinity for water. A SPEEK film that is exposed to higher *RH* of the surrounding ambient atmosphere will have a higher concentration of sorbed water. It is known that a higher water concentration in a SPEEK film results in a reduction of density and anisotropy [14]. The higher initial concentration of water in the film is manifested by a lower value of Δn and less apparent swelling during exposure to liquid water. Secondly, the distinct swelling behavior can be due to an inherent relation between optical anisotropy in a film and the swelling of this film. The theoretical prediction of penetrant-induced swelling of polymers is generally based on free energy considerations [24]. Within such a context, the contributions to the free energy that ultimately determine the extent of swelling, are related to the changes in enthalpy and entropy upon mixing of polymer and penetrant, and an elastic contribution due to deformation of the network. The optical anisotropy in the thin films is associated with internal stresses, and consequently constitutes a distinct free energy status prior to swelling. After swelling with water at a high activity (~ 1, or liquid water), the internal stresses, and hence anisotropy, either vanish or are

Table 2 Properties of the SPEEK films from Fig. 2

Sample	Nomenclature	Δn (–)	n_{xy} (–)	d_{initial} (nm)	Max. S_F (–)	Corresponding $d(t)$ (nm)
(a)	84-2000_humid-20	0.028	1.648	316	3.5	1106
(b)	84-2000_humid-50	0.023	1.659	346	1.7	588
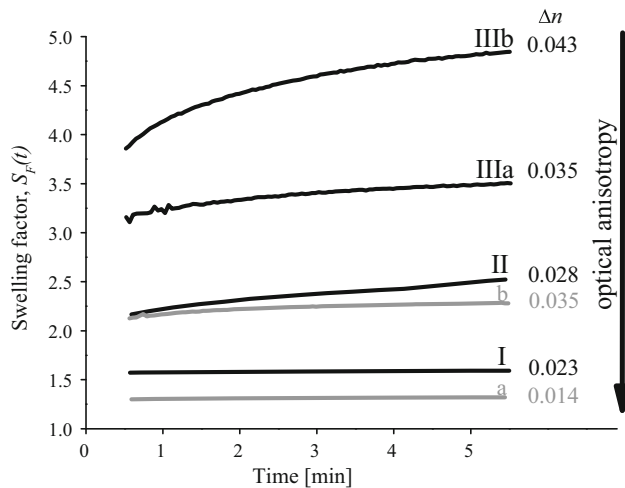
Fig. 3 Water-induced swelling, recorded for 5 min, of SPEEK films with a *DS* of 84 % and with various initial optical anisotropy, at 20 °C (*gray lines a* and *b*) and 40 °C (*black lines I, II, IIIa,* and *IIIb*)

very minor. This implies that the distinct initial free energy must result in a distinct extent of swelling.

For both phenomena, a larger extent of optical anisotropy will correspond to a larger extent of swelling, which complicates deconvolution of the two phenomena. This is illustrated by the swelling of a selection of four films at 40 °C and 2 films at 20 °C, in Fig. 3 (properties of the films are listed in Table 3).

All films have been prepared from the batch with a *DS* of 84 % and have been formed under humid conditions. The four samples swollen at 40 °C have been obtained from three different sets, I, II, and III, and the swelling of the films has been studied at different times under various

relative humidity conditions. Only samples IIIa and IIIb are from the same set and their swelling is studied on the same day, i.e., under the same relative humidity conditions. IIIa and IIIb differ in the extent of optical anisotropy, which has been induced by differences in the spinning conditions [14], 2000 and 3000 rpm for IIIa and IIIb, respectively. The two samples swollen at 20 °C have been obtained from two different sets, 'a' and 'b.' Sample 'a' with very low optical anisotropy, $\Delta n = 0.014$, was exposed prior to swelling to a surrounding ambient atmosphere with $RH \gg 80$ % (Table 3).

As we have generally found, the film with the lowest initial optical anisotropy shows the lowest degree of swelling. Because the humidity conditions during the swelling studies of these films are not well defined, it is not possible to quantify the relative contributions of the effect of initial relative humidity and the contribution of the initial stresses and density in the film, to the overall extent of swelling. When comparing samples I, IIIa, and IIIb, the refractive indices of the materials are similar ($n_{xy} = 1.659$, 1.658 and 1.661, respectively). This implies a comparable initial density of the samples. Hence, the higher degree of swelling must be predominantly due to initially higher internal stresses in this film. Such an observation is further supported when comparing samples IIIa and IIIb; for these samples, the synthesis and sample equilibration have been identical, except for the spin speed. The consequent difference in optical isotropy of the two films is accompanied by a significant difference in swelling. In this case, this divergent extent of swelling can be attributed to the difference in initial stresses in the two films. Considering Fig. 2, sample 'a' has lower refractive index than sample

Table 3 Properties of the SPEEK films from Fig. 3

Sample	Nomenclature	Δn (–)	n_{xy} (–)	d_{initial} (nm)	S_F after 5 min. (–)	Corresponding $d(t)$ (nm)
Swelling at 40 °C						
I	84-2000_humid-50	0.023	1.659	346	1.6	554
II	84-2000_humid-20	0.028	1.648	316	2.5	790
IIIa[a]	84-2000_humid	0.035	1.658	336	3.5	1176
IIIb	84-3000_humid	0.043	1.661	287	4.8	1378
Swelling at 20 °C						
a	84-2000_humid-90	0.014	1.644	340	1.3	442
b	84-2000_humid	0.035	1.658	339	2.2	746

[a] Samples IIIa, IIIb, and b have been studied under very low *RH* conditions

'b' (n_{xy} = 1.648 and 1.659, respectively—Table 2), but the extent of swelling is greater for sample 'a'.

Thus, the swelling factor in water of thin SPEEK films is dependent not only on the degree of sulfonation and water temperature, but also on the initial film properties that are strongly responsive to relative humidity degree of the ambient atmosphere to which they are exposed to.

The effect of $RH = 0$ % during, and after, film formation on film swelling

In the above section, a correlation is discussed between the optical anisotropy and swelling of thin SPEEK films, prepared via spin-coating in a humid atmosphere. In a previous paper, we have found that a spin-coating with a relatively concentrated (5 wt%) SPEEK alcohol solution at relatively low spin speed (2000 rpm), can result in SPEEK films with lower anisotropy as compared to films spun at 3000 rpm [14]. For less concentrated solutions and higher spin speeds, the extent of optical anisotropy of thin SPEEK films is more or less insensitive to variations in the spinning conditions [14]. The anisotropy of the formed films has been also found to increase with a decrease in relative humidity of the surrounding ambient atmosphere [14]. In this paper, a particular swelling behavior is observed when films are prepared by spin-coating in the absence of water ($RH = 0$ % due to flushing with nitrogen). The thickness and optical anisotropy of these films are comparable with those of films formed in the presence of water. However, the swelling of the films upon exposure to liquid water is very different. This is illustrated in Fig. 4, by the dynamic swelling of two films with a DS of 84 %, of which the optical anisotropy is comparable, $\Delta n \sim 0.028$ (Table 4). Film 'a' is prepared under relatively humid conditions ($RH \sim 30$ %) and film 'b' under dry nitrogen ($RH = 0$ %). The film formed under dry conditions shows
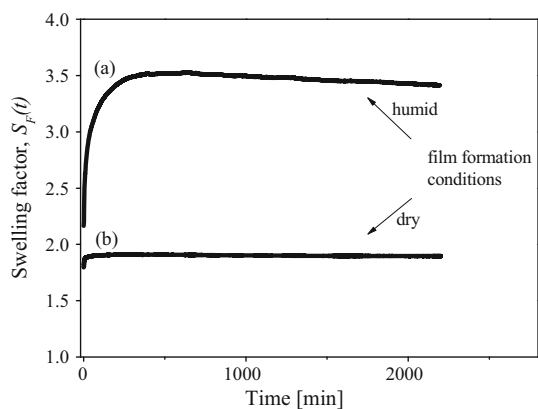

Fig. 4 Water-induced swelling dynamics at 40 °C of ∼300 nm SPEEK films with a DS of 84 %, formed under *a* humid, $RH \sim 30$ % and *b* dry, $RH = 0$ % atmosphere. For both films, the extent of optical anisotropy is comparable, $\Delta n = 0.028$

significantly less swelling. The different swelling indicates that the hydration state of the polymer, during film formation, affects the final polymer morphology.

It is known that hydration of the negatively charged sulfonic acid groups causes the structural separation of the polymer into hydrophilic domains that are formed from ionic clusters, and hydrophobic domains that are formed from the polymer backbone [25, 26]. The hydrophilic domains are responsible for the transport of water and ions, such as protons, and the hydrophobic domains give the polymer morphological stability [13, 27]. Additionally, Jarumaneeroj et al. recently reported that the absence of water alters reversibly the molecular arrangements in SPEEK [28]. They reported a color change of the material: initially SPEEK is transparent to light in the visible range, upon heating to 190 °C a yellow color develops. The reduced hydration of the sulfonic acid groups allows them to come closer to each other. This facilitates more pronounced attractive non-covalent interactions between the aromatic rings that are present in the polymer backbone. These attractive interactions are considered to result in an ordered arrangement of the aromatic rings that is referred to as π–π stacking, which has been further supported with UV–Vis spectroscopy [28]. The reported color change is reversible; upon cooling in ambient or exposure to water, the material becomes transparent again [28].

In Fig. 5, the reversible color change, induced by the removal of water, is shown for a thin (∼800 nm) SPEEK film on top of a porous ceramic γ/α-alumina support. The usage of ceramic support allows observing the actual colors of coated SPEEK films upon water sorption/desorption. Thin SPEEK films coated on a silicon wafer possess thickness-dependent varieties of colors, caused by light interference between thin layers and the silicon substrate. Those colors also appear to change as the angle of view changes. The color changes of thin SPEEK films coated on a silicon wafer are indicative for the thickness changes upon water sorption/desorption. The film in Fig. 5 was spin-coated on γ/α-alumina support under humid conditions and initially it is colorless to the human eye (only the white substrate is visible). Figure 5a shows the film directly after incubation at 60 °C in a vacuum oven. The yellow color is indicative for the changed hydration state and corresponds to the color change reported by Jarumaneeroj et al. at high temperature [28]. The occurrence of the color change at relatively low temperature, in vacuum, implies that it is actually the removal of the water that causes the change in color, rather than an inherent thermochromic characteristic of SPEEK.

Upon the removal of water, an ordered arrangement of the aromatic rings due to non-polar interactions is induced that is destroyed when water molecules are introduced again [28]. Upon exposure to the surrounding humid
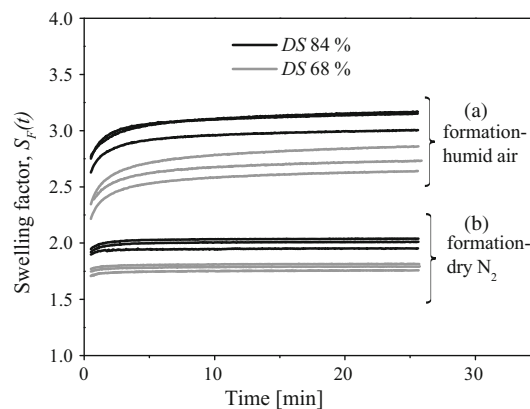
Table 4 Properties of the SPEEK films from Fig. 4

Sample	Nomenclature	Δn (–)	n_{xy} (–)	d_{initial} (nm)	Max. S_F (–)	Corresponding $d(t)$ (nm)
(a)	84-2000_humid	0.028	1.648	316	3.5	1106
(b)	84-2000_dry	0.028	1.655	291	1.9	553
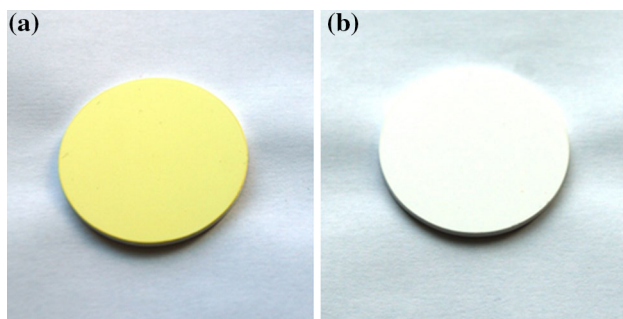
Fig. 5 Photos of a SPEEK film ~ 800 nm with a *DS* of 84 % coated on a γ/α-alumina support **a** directly after incubation in a 60 °C vacuum oven and **b** after few minutes in a humid atmosphere

Fig. 6 Time-dependent water-induced swelling (each experiment conducted in triplo) at 40 °C of ~ 300 nm SPEEK films, with a *DS* of 84 % (*black lines*) and 68 % (*gray lines*), formed *a* in a humid *RH* ~ 30 % and *b* dry *RH* = 0 % atmosphere. Films are formed simultaneously, in an identical manner from the two methanol solutions of SPEEK *DS* 68 and 84 %, except for a difference in humidity during spinning. All films are measured at the same time, under very low *RH* conditions

ambient atmosphere, the sorption of water causes the film to become colorless again (Fig. 5b). We have observed that SPEEK membranes with a thickness >20 μm also start to appear yellowish to the human eye, which is caused by slight absorption in the visible range. This yellowish color becomes more apparent with increasing film thickness (the thicker the films, the higher the light absorption) and transforms to intense yellow, which is induced, as reported by Jarumaneeroj et al. [28], by benzene stacking, and is visible in Fig. 5a.

An identical color transformation was observed also for a SPEEK film on top of a porous ceramic γ/α-alumina support formed under dry nitrogen. Yet the distinct swelling of films prepared under dry conditions (Fig. 4) implies that in that case the morphology of the polymer film is irreversibly affected by the absence of the water during film formation. This is possibly caused by altered microphase separation and the interactions between aromatic rings. Figure 6 shows the dynamic swelling of 12 films, 6 with *DS* 68 % and 6 with *DS* 84 %. The films have been prepared in an identical manner from the same solutions of SPEEK with particular *DS*, except for a difference in relative humidity during spinning (for each *DS*, 3 films have been formed in dry N$_2$, and 3 films in the surrounding humid ambient atmosphere). To some extent, the sample properties slightly deviate. The Δn of 84-2000_dry is lower than of 84-2000_humid, but Δn of 68-2000_dry is higher than of 68-2000_humid (Table 5). Yet the swelling of films formed without the presence of water is reduced in all cases, and the extent of overshoot swelling and polymer reorganization is minor. The SPEEK films with a lower *DS* swell also less than those with a higher *DS*, which is

consistent with literature [29]. The swelling experiments confirm the lower propensity to water-induced swelling of films formed under dry conditions. Distinct swelling can have impact on membrane selectivity and stability. In the paper of Zhang et al., SPEEK membranes formed from solvent casting under high relative humidity exhibited the highest proton conductivity, whereas the lowest conductivity was obtained in films formed in dry atmosphere [13]. In general, the lack of water during membrane formation prevents the formation of the ionic clusters of sulfonic acid groups and water, while a percolative network of such clusters is responsible for a high proton conductivity and a high degree of swelling [13, 27, 30]. As such, the properties of thin SPEEK films can be altered without chemical modification, just by varying the humidity during their preparation process.

Table 5 Properties of the SPEEK films from Fig. 6

Sample nomenclature	Δn (–)	n_{xy} (–)	d_{initial} (nm)
84-2000_humid	0.033 ± 0.001	1.652 ± 0.001	332 ± 2
84-2000_dry	0.029 ± 0.001	1.648 ± 0.001	344 ± 3
68-2000_humid	0.033 ± 0.000	1.656 ± 0.001	346 ± 6
68-2000_dry	0.036 ± 0.001	1.655 ± 0.001	349 ± 7

The average values are taken based on 3 samples for each experiment

To support the differences between SPEEK films formed under humid and dry conditions, negatively charged sulfonic acid groups are labeled with the positively charged fluorescent dye (Rhodamine 6G), and the TIRF microscopy is used to monitor the SPEEK films through the emission of the dye at 520 nm.

The relative humidity during film formation affects the distribution of sulfonic acid groups in SPEEK, as is evident from the TIRF images in Fig. 7. The fluorescent images represent the SPEEK films obtained by using the first experimental method described in the experimental section (film preparation). For the second film formation method, comparable images have been obtained. This confirms that the presence of the dye molecules does not interfere or alter the structural arrangements of SPEEK in a substantial manner. Figure 7a is representative for samples prepared under humid conditions. Such films show a homogenous distribution of the fluorescent cations, and thus of the sulfonic acid groups. When the film is formed in dry conditions, a manifestly different distribution of sulfonic acid groups is observed (Fig. 7b), indicating an altered morphology of the film. This altered film morphology is irreversible upon the exposure of the film to moisture, in contrary to reversible π–π stacking, and results in lower propensity to water-induced swelling.

For relatively thick films, the effect of water on microphase-separated morphology can be studied using SAXS, as has been reported by Swier et al. for sulfonated poly (ether ketone ketone) (SPEKK) [31]. They confirmed that the water-swollen membrane exhibit a microphase-separated morphology, consisting of water-swollen ionic domains and a non-polar phase. For the dry sample, no phase separation was observed, but this is possibly due to insufficient electron density contrast between the acidic domains and the PEKK matrix [31]. It has to be noted that our investigation compares the swelling behavior and TIRF
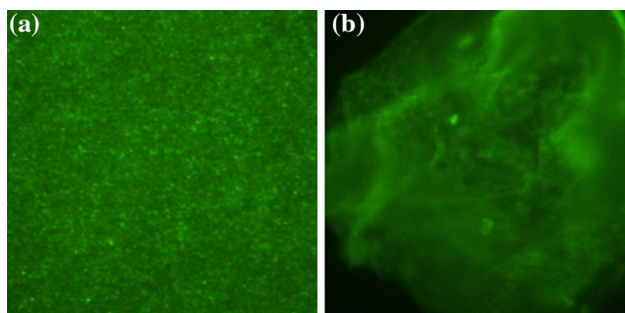
images (Figs. 6, 7, respectively) of the two different thin films that are both in a hydrated state (films are measured in identical *RH* conditions); the thin film formation is executed either under humid or dry conditions. This is in contrast to the research of Swier et al., who studied films in a dry state. Hence, their results cannot be directly compared with our results. The possible interactions and ordered arrangement of the aromatic rings (π–π stacking) in the films formed without the presence of water, could be investigated on thicker films, for instance, using XRD [32, 33]. Our films are too thin for a conclusive X-Ray scattering study, we have encountered the problems presented in the review [34], and could not detect the structural differences between the SPEEK films formed under dry and humid conditions. Yet the distinct distribution of hydrophilic and hydrophobic domains in those SPEEK films is conclusively shown with TIRF and the altered propensity to water-induced swelling is proven using SE. This is in line with the research of Zhang et al. who also inferred based on the SEM and XPS analysis that water in the environment during formation not only leads to the phase separation in SPEEK, but also induces the orientation arrangement of sulfonic acid groups [13].

Conclusions

Water-induced swelling in thin oriented sulfonated poly (ether ether ketone) films has been studied using in situ spectroscopic ellipsometry. For films with a comparable degree of sulfonation, the swelling behavior is significantly correlated with the extent of optical anisotropy. Films with high optical anisotropy swell considerably more than less anisotropic films. The correlation is attributed to two superimposed phenomena; a higher anisotropy can imply a lower initial water concentration at the start of the experiments, and a higher anisotropy is associated with higher internal stresses that imply a distinct free energy status. At very low water concentration, assembly of the aromatic rings in the backbone of the polymer can occur, which is manifested by a color change from clear to intense yellow. When the polymer is deprived of water during film formation, the film morphology is affected. This results in a lower propensity of the films to swell in water, signifying that control of the humidity during film formation allows changing the final film properties, without chemical modification.

Fig. 7 Fluorescence microscopy images of SPEEK films (*DS* of 84 %) labeled with Rhodamine 6G, formed under **a** humid ambient and **b** dry conditions. The Rhodamine 6G was excited using 488 nm laser and the emission signal from the green dye was collected at 520 nm. Image size corresponds to a region of $28 \times 28 \ \mu m^2$ for both images

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